SORPTION BEHAVIOUR OF RADIOCAESIUM IN SOILS

CHEUNG YIN PING IRENE

FOR THE DEGREE OF

MASTER OF PHILOSOPHY

AT

DEPARTMENT OF APPLIED PHYSICS

THE HONG KONG POLYTECHNIC UNIVERSITY

2002

ABSTRACT

The general purpose of this study is to investigate the sorption behaviour of ^{137}Cs in soils in Hong Kong reservoir. This provides information about the long-term mobility of radiocaesium for remedial decisions and effective response to any accidental releases from the nearby nuclear power plants. Three sets of soils were collected from a local reservoir and characterized for their physical and chemical properties.

The time variations of ^{137}Cs concentration in water were monitored using five different isotherms until equilibrium had been established. The conductivity and the pH of the water-soil mixture were also monitored. The first isotherm was defined by varying the mass of soils added while maintaining a constant initial ^{137}Cs activity concentration. The mass of soils ranged from 0.05 g to 5 g. The second isotherm was defined by varying the initial water activity concentration with constant mass of random sizes. The initial water activity concentrations varied from 29 kBq l^{-1} to 120 kBq l^{-1}. The third isotherm was defined by varying the sizes of soil particles while keeping constant initial activity concentration and mass of soil. The diameters of soils ranged from 0.15 mm to 2 mm. The fourth isotherm was defined by varying the mass of soil added in one specific pH value while maintaining constant initial activity concentration. The mass varied from 2 g to 7 g and three different pH values of 2.6, 3.0 and 3.6 were used. The fifth isotherm was defined by varying the pH values of water but maintaining constant mass of soils. It was found that the high density polyethylene (HDPE) container also played a part in the sorption process and ways had to be devised to minimize its effect.

The sorption behavior of ^{137}Cs to soils has generally been described by the distribution coefficient K_d, a quantity commonly used by other researchers to the understanding and determination of the eventual fate of metal and radionuclides released in aquatic environments. It was found in this project that K_d depended on initial activity concentration, slurry ratio and sorption time.

A logistic theory was devised to explain the experimental results. It was based on irreversible exchange of ^{137}Cs to soil. However, the model could only explain certain trends but failed to describe some of the quantitative aspects of the findings. Agreement between theory and experiment was good only for small masses. The theory also failed to fit theoretical values with experimental data to consistently deduce the sorption coefficient, which should be unique for a particular type of soils. Experiments also showed that the fraction of activity concentration remaining in water was never zero, showing that there might be some reversible exchange mechanism taking place.

A revised logistic theory was devised based on the simultaneous occurrence of the sorption and desorption processes, quantified by the sorption coefficients and desorption coefficients, respectively. By fitting theoretical with experimental data, reasonably constant sorption and desorption coefficients have been obtained for a particular type of soils, independent of mass of soils added. The number of sorption sites available could also be estimated and was found to vary almost linearly with the mass of a particular type of soils. Our model provides coefficients that are time independent, unlike the conventional distribution coefficients K_d, with more information on the sorption sites and sorption-desorption process.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Dr. C. K. Man, for his patient guidance and support. Not only did he enlighten me with ideas, but he also provided tireless encouragement throughout the course of research study.

My gratitude also goes to Dr. F. G. Shin. He is knowledgeable and experienced. He provided me with some advice that was very useful for my experimental analysis. His comments and suggestions helped me solve many problems.

I am indebted to Dr. F. T. Cheng for his support. He shared his experiences with me and I have learnt much from him.

I wish to thank Mr. C. S. Lo in the SEM laboratory for his technical support.

Finally, my thankfulness goes to my family members and my friend, Mr. Keith Kwok, for their continual encouragement and unfailing support.

Table of Contents

CHAPTER 2 FACTORS AFFECTING BEHAVIOUR OF RADIOCAESIUM IN SOILS

CHAPTER 3 EXPERIMENTAL

CHAPTER 7 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

The Guangdong Nuclear Power Station (GNPS), located northeast of Hong Kong at Da Keng, Daya Bay (22° 35.8'N, 114° 32.5'E), has been in operation since 1995. Additional units are scheduled to be built at the same site. More units are being planned at Linguo, about 4 km northeast of the GNP station. The risk as assessed by the United Kingdom Atomic Energy Authority has thus increased (HKSAR, 1999).

If major accidents were to occur at the GNPS, radioactive materials would be released into the atmosphere. Some of the gaseous and volatile radioactive isotopes could be transported by wind to Hong Kong. The invisible radioactive substances would behave in a way similar to a plume of smoke dispersing into the atmosphere and depositing some of its contents on the ground. The concentration of radioactive materials in the plume decreases with distance from the site. Through the plume exposure, pathway could be contaminated from

- External irradiation from radionuclides in the plume;
- External irradiation from deposited radionuclides;

- Internal irradiation due to radionuclides inhaled during passage of the plume;
- Internal irradiation due to inhalation of radionuclides resuspended from surface deposits;
- Internal irradiation due to ingestion of radionuclides in contaminated food and drinking water.

Models commonly used in other countries for the assessment of consequences after accidents have been focused on terrestrial food pathways. However, this pathway is rather insignificant in the situation of Hong Kong because most of the food consumed by the local people is imported from inland China and other countries. On the other hand, drinking water is heavily dependent on local supply and cannot be sufficiently imported for a population of more than 6.5 million.

Since Hong Kong has no natural lakes or rivers the main water sources are from China. Dongjang (the East River) is the major source of water supply for Hong Kong from Guangdong. Water, extracted from the river at a point some 83 kilometers north of Hong Kong, is pumped over a series of dams built across the Shima River. It is eventually discharged into the Shenzhen Reservior before being fed by pipelines to the Shenzhen Special Econonmic Zone and across the border at Muk Wu to Hong Kong. When a major release of radioactivity occurs at Daya Bay, the wind could carry the plume to the rivers, reservoirs and catchment area. This would contaminate the water supplies and increase the radiation dose of the population, as we have no choice but to consume the contaminated water. This hypothetical situation may not be unfounded as something similar (the Chernobyl accident) had happened before.

Following the accident at the Chernobyl power station, large quantities of radioactive substances were emitted into the atmosphere. Radionuclides were then transported and dispersed by air plumes to European soils (Müller, 1986; Persson et al., 1987; Antononpoulos-Domis et al., 1988; Duvernet, 1989; Gudiksen et al., 1989) and European lakes (Smith et al., 1999).

As a result of the Chernobyl accident soils in Europe had become a focus of much investigation, since radiocaesium was found to be persistently available in these soils for uptake by grazing sheep (Howard et al., 1987). This persistence has been attributed to the retention of radiocaesium on organic sorption sites where it remained readily exchangeable. Soil contamination with radionuclide is causing a long term burden on the food chain as soil-transfer is the first step by which radionuclide enters the food chain. The process is highly variable between types of soils.

Radionuclides deposited onto a lake may be removed through the outflow, by sedimentation of suspended particles (Carlsson, 1978; Robbins et al., 1992; Robbins and Jasinski, 1995) and by direct uptake by the bottom sediments as a result of diffusional transport across the sediment/water interface (Santschi et al., 1986;

Hesslein, 1987). Once in the water, radionuclides reach the bottom sediments by direct sorption or by sorption on suspended solids that later deposit on the bottom. Studies have shown that radionuclides may also be remobilized from contaminated bottom sediments by diffusion (Evans et al., 1983; Comans et al., 1989; Smith and Comans, 1996), and re-suspension of contaminated particles. Additional inputs may also result from transport of activity from contaminated catchment soils. In general, sediment plays a leading role in aquatic radioecology by functioning either as a sink or as a temporary repository for radionuclides.

One of the more hazardous radionuclides is radiocaesium because of its long half-life, large transfer factor by inhalation and ingestion (WHO, 1987). It has long residence in biological systems and it is an artificial radionuclide dispersed worldwide. It was deposited in our environment in the 1960's as a result of global fallout from nuclear weapon tests and again in 1986 after the Chernobyl reactor accident (Rosner et al., 1990; Bunzl and Kracke, 1987; Bunzl et al., 1994). It is chemically similar to potassium. The common chemical forms of caesium are soluble in water and, if inhaled or ingested, are rapidly and completely absorbed in the lungs and across the gastrointestinal tract. It is localized intracellular and since muscle represents the largest portion of body intracellular space, muscle also represents the largest portion of the cesium content of the body (Clough, 1990). Radiocaesium has been found to be strongly adsorbed on organic materials and clay in the soil. Studies on the behavior and distribution of radiocaesium in the environment are important for assessing radiation doses received by man through various environmental pathways.

Studies on radiocaesium transfer in sediments have been investigated in the past (Ijuin et al., 1973; Hakonson and Whicker, 1975; Linsalata, 1984; Brobberg, 1989; Maubet et al., 1990). The main conclusion of these investigations is that radiocaesium is trapped in specific fixation sites provided by clays, in particular illite and micaceous clays and confined to a region of 2-3 cm deep. (Sawhney, B. L., 1972)

There are processes to remove portion of the deposited radiocaesium from reservoirs, including:

- Settlement and sorption by soil
- Direct diffusion across sediment – water interface
- Water treatment

Removal of radiocesium from water by settlement and sorption has been found to have more influence than by diffusion across sediment-water interface. (Nishita, et al., 1956; 1962; Frysinger et al., 1960; Schulz et al., 1960; Fredriksson et al., 1966; Fredriksson, 1970). Radiocaesium is strongly adsorbed on clay minerals (Sawhney, 1972; Maes & Cremers, 1986; Cornell, 1993). This adsorption is highly specific, particularly on illitic materials which are thought to contain a small proportion of sites, and frayed edges sites (FES) which have a very strong affinity for caesium (Brouwer et al., 1983). In soils, specific retention of radiocaesium occurs in a very small number of sorbing sites, which are the frayed edges sites (FES) born out of weathered micaceous minerals (Nathalie and Bruno, 2002). Sorption behavior is thus strongly dependent on chemical properties of the soils. Sorption study of radioactive nuclides is important in connection with the soils characteristics such as pH level, clay content, conductivity, organic matter content, cation exchange capacity and potassium content and this has not been extensively investigated in Hong Kong.

The general purpose of this study is to investigate the sorption behavior of ^{137}Cs in soils in Hong Kong reservoirs. This is important as the sorption of radiocaesium to soil constituents is one of the factors which determines the availability of radiocaesium to biological systems. Such information provides the long-term mobility of radiocaesium for remedial decisions and effective response to any accidental releases from the nearby Daya Bay nuclear power plants.

CHAPTER 2

FACTORS AFFECTING BEHAVIOUR OF RADIOCAESIUM IN SOILS

2.1 Behaviour of Radiocaesium in Soils

Sorption behaviour of radiocaesium in soils is generally described by the distribution coefficient K_d, defined as the ratio of the dry sediment concentration q (Bq g^{-1}) to the water activity concentration C_w (Bq ml^{-1}), (Shenber and Eriksson, 1993; Dumat and Staunton, 1999; De Koning et al., 2000). Distribution coefficients are widely used as a first approach to the understanding and determination of the eventual fate of metal and radionuclides released in aquatic environments.

Reported K_d values, measured in different environments, can vary within a range of more than two orders of magnitude (IAEA, 1985). Even in the same scenario, large variations from one location to another and variations in time at the same location can be observed (Periañez et al., 1994). A constant K_d has been obtained only for low activity concentrations (< 20 Bq ml^{-1}) for profundal sediments of a Savannah River site reservoir (Stephens et al., 1998). Non-linear relation between dry sediment concentration and water concentration has been observed for calcareous soil (Du et al., 1998) and for sediments of Lake Pamvotis of Ioannina (Kirikopoulos et al., 1996).

It is generally believed that soil properties, such as pH level, soil structure, soil texture, organic matter, cation exchange capacity and the potassium content determined the capacity for radiocaesium sorption by soils as well as the level of plant uptake (Nishita et al., 1956, 1962; Frysinger et al., 1960; Schulz et al., 1960; Fredrikkson et al., 1966; Fredriksson, 1970). A brief description of soil properties is given in the following sections (Henry, 1990; Winegardner, 1995; Brady, 1996).

2.2 Soil Separates

Soil separates are the size groups of mineral particles less than 2 millimeters (mm) in diameter or the size groups that are smaller than gravel. The diameters of the separates are given in Table 2.1.

Table 2.1 Characteristics of soil separates. (Henry, 1990)

Separate	*Diameter*[1] *(mm)*	*Diameter*[2] *(mm)*
Very coarse sand	2.00-1.00	-
Coarse sand	1.00-0.50	2.00-0.2
Medium sand	0.50-0.25	-
Fine sand	0.25-0.10	0.20-0.02
Very fine sand	0.10-0.05	-
Silt	0.05-0.0002	0.02-0.002
Clay	Below 0.002	Below 0.002

[1] United States Department of Agriculture System.
[2] International Soil Science Society System.

Sand is the 2.0 - 0.05 mm fraction and, according to the United States Department of Agriculture (USDA) system, the sand fraction is subdivided into very fine, medium, coarse, and very coarse sand separates. Silt is the 0.05 to 0.002 millimeter (2 microns) fraction. The sand and silt separates of many soils are dominated by quartz. There is usually a significant amount of weatherable minerals, such as feldspar and mica, that weather slowly and release ions that supply plant needs and recombine to form secondary minerals, such as clay. Clay particles have an effective diameter less than 0.002 millimeters (less than 2 microns). They tend to be plate-shaped, rather than specific surface of clay, is many times greater than that of sand or silt. Clay adsorbs much more water than silt or sand, because water adsorption is a function of surface area.

2.2.1 Soil Texture Classes

Once the percentages of sand, silt and clay have been determined, the soil can be placed in one of 12 major textural classes. The texture of a soil is expressed with the use of class names, as shown in Fig. 2.1. The sum of the percentage of sand, silt, and clay at any point in the triangle is 100. A soil containing equal amounts of sand, silt, and clay is a clay loam. Soils in the loam class are influenced almost equally by all three separates: sand, silt, and clay. For sandy soils (sand and loamy sand), the properties and use of the soil are influenced mainly by the sand content of the soil. For clays (sandy clay, clay, silt clay), the properties and use of the soil are influenced mainly by the high clay content. There is an appropriate key for a normal assessment, as shown in Table 2.2.

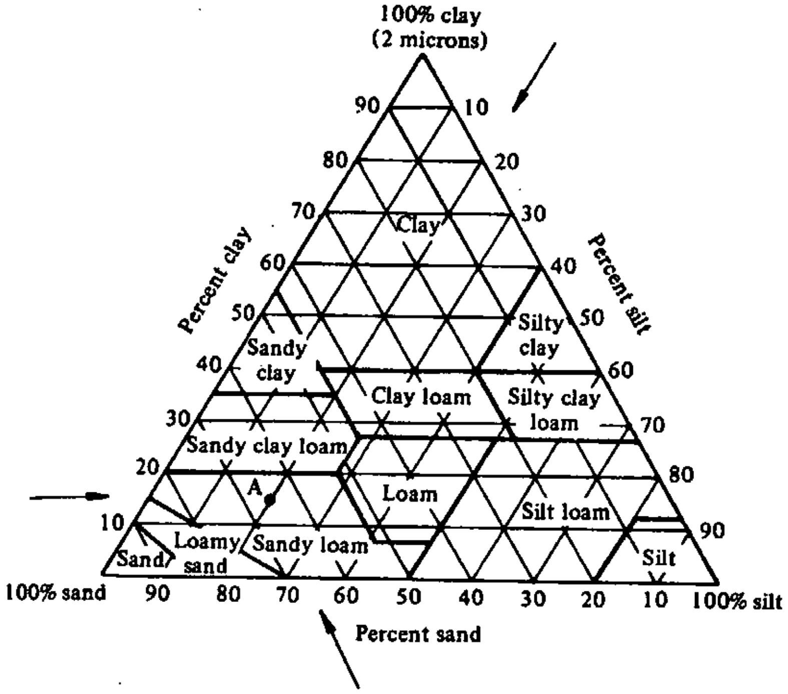


Fig. 2.1 Textural triangle showing the limits of sand, silt, and clay contents of the various texture classes. (Winegardner, 1996)

Table 2.2 Key for the assessment of soil texture. (Gerrard, 2000)

Grittiness	Smoothness	Stickiness and plasticity	Ball and thread formation	Texture
Non-gritty to slightly gritty	Not smooth	Extremely sticky and plastic	Extremely cohesive balls and long threads, which bend into rings easily	Clay
	Moderately smooth	Very sticky and plastic	Very cohesive balls and long threads, which bend into rings	Silty clay
	Moderately smooth	Moderately sticky and plastic	Moderately cohesive balls from threads, that will not bend into ring.	Silty clay loam
	Extremely smooth	Very sticky and plastic	Moderately cohesive balls from threads with difficulty that have broken appearance	Silt
	Very smooth	Slightly sticky and plastic	Moderately cohesive balls from threads with difficulty that have broken appearance	Silt loam
Slight to moderately gritty	Slightly smooth	Moderately sticky and plastic	Very cohesive balls, forms threads that will bend into rings.	Clay loam
Moderately gritty	Not smooth	Very sticky and plastic	Very cohesive balls, forms threads that bend into rings with difficulty.	Sandy clay
	Not smooth	Moderately sticky and plastic	Moderately cohesive balls, forms threads that bend into rings with difficulty.	
	Slightly smooth	Slightly sticky and plastic	Moderately cohesive balls, forms threads with great difficulty.	Loam
Very gritty	Not smooth	Not sticky or plastic	Slightly cohesive balls, does not form threads	Sandy loam
Extremely gritty	Not smooth	Not sticky or plastic	Slightly cohesive balls, does not form threads	Loamy sand

2.3 Particle Shape

The shape of individual particles has important influence on the physical properties of soil. Round particles tend to be more easily separated than flat particles. Soils that are predominately silt are plate-like. The low permeability of clay soils is partly due to plate-like shape of clay mineral grains. The following shapes are the most common:

(1) Bulky or equidimensional grains

These shapes may include rounded, sub-rounded angular, and subangular, as shown in Fig. 2.2. Coarse-grained soil components tend to be included in this category, which usually consists of quantz and fledspar.

(2) Flaky or plate-like grains.

These are common shapes in the finer grain size fraction. Most clay minerals and mica occur as flat plate-shape grains.

(3) Elongated grains and fibers.

These shapes are encountered in soil containing the clay mineral hallow site, asbestos, volcanic ash or organic soils (peat).

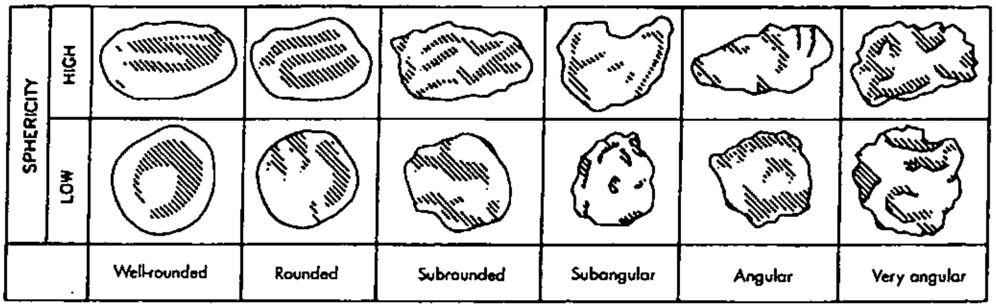


Fig 2.2 Soil grain shapes. (Winegardner, 1996)

2.4 Soil Structure

Soil structure describes the geometric orientation of the soil grains with respect to each other. Factors influencing structure include: grain shape, size, mineralogical content, and water content. Different structures develop in cohesive and non-cohesive soils.

The basic structures which develop in cohesive (clay and silt) soils and dependent on the attractive forces acting between clay particles and water. Most clay particles have a predominantly negative charge on their flat surface and some positive charges on the edges of the plate-like crystals. Negatively charged area attracts cations, and positive charges attract anions (Henry, 1990).

Soil structures existing in cohesionless (sand and gravel) soils are based on both single-grained and "honeycombed" organizations. Single-grained structures are the result of the orientation of particles into intimate contact with the surface and size distribution of the particles, in addition to the packing pattern. Honeycombed structures sometimes occur in soils that contain large percentages of fine sand and silt.

Texture is used in reference to the size of soil particles, and used in reference to the arrangement of the soil particles. Sand, silt and clay particles are typically arranged into secondary particles called peds, or aggregates. The shape and size of the peds determine the soil's structure.

2.5 Soil Organic Matter

The addition and decomposition of plant and animal residues in soils produced labile and stable fraction of organic matter. The labile and stable organic matter fractions correspond, in general, to the organic residues and humus fractions, respectively.

2.5.1 Labile Soil Organic Matter

Labile organic matter is an important reservoir of nutrients because the nutrients, especially nitrogen, are rapidly recycled in the soil ecosystem. The labile organic matter is rapidly degraded when conditions are favorable. The decomposers are frequently quite inactive, owing to the rapidly disappearance of readily decomposable substrates or labile organic matter.

2.5.2 Stable Soil Organic Matter

The stable soil organic matter fraction consists of resistant compounds: decomposing residues, microbial products and products formed as a result of interaction of organic compounds with each other and with the mineral components of the soil, especially clay. The stable organic matter is equivalent to humus. The nutrients within it are recycled very slowly. Radioactive studies have shown that certain stable organic matter fractions are commonly more than thousands of years old. The stable organic matter has a long residence time in the soil and plays important roles in structure formation stability, water adsorption, and adsorption of nutrient cations. Scientists believe that the organic matter is protected from decomposition; this protection helps to increase the stability of both readily decomposable and resistant organic matter.

2.6 Ion Exchange

Ion exchange is of great importance in soils. Ion exchange involves cations and anions that are adsorbed from solution onto negatively and positively charged surfaces, respectively. Such ions are readily replaced or exchanged by other ions in the soil solution of similar charge.

2.6.1 Nature of Cation Exchange

Cation Exchange is the interchange between a cation in solution and another cation on the surface of any negatively charged material, such as clay colloid or organic colloid. The negative charge or cation exchange capacity of most soils is dominated by the secondary clay minerals and organic matter. Cation exchange reactions in soils occur mainly near the surface of clay and humus particles, called micelles. Each micelles have thousands of negative charges that are neutralized by the adsorbed or exchangeable cations. For the purpose of illustration, if X represents a negatively charged exchanger that has adsorbed a sodium ion (Na^+), this will produce NaX. When placed in a KCl solution, it will follow a reaction as:

$$K^+ + Cl^- + NaX = Na^+ + Cl^- + KX$$

In the reaction, K^+ in solution replaces or exchanges for adsorbed Na^+, resulting adsorbed Na^+ in solution and leaving K^+ adsorbed as KX. Cations area adsorbed and exchanged on a chemically equivalent basis, one K^+ replaces one Na^+, and two K^+ are required to replace or exchange for Ca^{2+}.

2.6.2 Cation Exchange Capacity of Soils

The cation exchange capacity of soils (CEC) is defined as the sum of positive (+) charges of the adsorbed cations that a soil can adsorb at a specific pH. The CEC of a soil is equal to the CEC of both the mineral and organic fractions. The major source of CEC in the mineral fraction comes from the clay. The negative charge of organic matter is due mainly to dissociation of H^+ from the –OH of carboxyl and phenolic groups. The clays have great variation in CEC, while sand and silt fractions contribute little to the CEC of soils. CEC of soils is thus affected mainly by the amount and type of clay and the amount and degree of decomposition of the organic matter.

2.6.3 Relation Between Cation Exchange Capacity and Soil pH

The CEC is positively correlated with pH. Most CEC of 2:1 clays are non-pH dependent. However, the CEC of soil organic matter (SOM) is entirely pH dependent. Soil high in organic matter content, kaolinite and oxidic clays have relatively large changes in CEC with changes in pH due to the dominance of pH dependent.

2.6.4 Kinds and Amounts of Exchangeable Cations

The amount and kinds of cations adsorbed are the result of the interaction of the concentration of cations in solution and the energy of adsorption of the cations for the exchange surfaces. The cations compete for adsorption. When the concentration in the soil solution increases, there is an increased chance for adsorption. The more strongly a cation is attracted to the exchange surface, the greater is the chance for adsorption. The energy of adsorption of specific ions is related to valence and degree of hydration. The energy of adsorption of divalent cations is about twice that of monovalent cations. For cations of equal valence, the cation with the smallest hydrated radius is most strongly adsorbed because it can move close to the site of charge. The dehydrated and hydrated radii of four monovalent cations are shown in Table 2.3. The hydrated radius is inversely related to the non-hydrated radius. It is because the water molecules can move closer to the charge that is located at the center of a small ion. Small ions are more strongly attracted to the water molecules. The more strongly that water molecules are attracted to ions, the greater is the number of hydrated molecules and the hydrated radius of the ions.

Table 2.3 The dehydrated and hydrated radii of four monovalent cations. (Henry, 1990)

Ion	Radii of Ions, nanometers		Order of Energy of Adsorption
	Dehydrated	Hydrated	
Li	0.078	1.003	4th
Na	0.098	0.790	3rd
K	0.133	0.532	2nd
Rb	0.149	0.509	1st

The difference in the hydrated radius and valence of Ca^{2+} and Na^{+} are shown in Fig 2.3. Calcium is adsorbed more strongly than sodium because it is divalent and it has the smallest hydrated radius. As a result of the strong energy of adsorption, calcium is typically more abundant as an exchangeable cation than magnesium, potassium, or sodium. The energy of adsorption sequence is: Ca > Mg > K > Na.

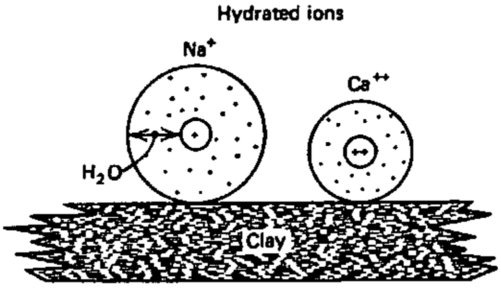


Fig. 2.3 The difference in the hydrated radius and valence of Ca^{2+} and Na^{+}. Calcium ions are more strongly adsorbed by clay than are sodium ions. (Henry, 1990)

2.7 Soil pH

The pH is the negative logarithm of the hydrogen ion activity and is related to ion exchange capacity. Soil pH is normally determined by mixing one part of soil with two parts of distilled water.

2.8 Effects of Soil Properties on Sorption Behaviour

Many researchers attempted to predict the factors affecting the sorption behavior of radiocaesium to soils. Among the various factors, it was found that organic matter could trap Cs^{+} and made a great contribution to the sorption of Cs^{+} to soil (Du et al., 1998; Lee and Lee, 2000; Wang et al., 2000). Organic matter contents could affect the retention and migration of the fallout radionuclides in the environment.

Besides the organic matter, the clay content also played an influential part in the sorption behavior of radiocaesium to soils (Boggs et al., 1985; Buckau et al., 1986; Kim, 1986). The activity concentrations of radionuclides in soils tended to increase with increasing clay content, probably due to the greater adsorption capacity of clay. The reduction in distribution coefficient K_d was observed to decrease with decreasing pH. It was largest on soils with low clay contents resulting in lower sorption capacity for caesium. As the CEC values depend on the clay content, it was also found that the K_d value increased with CEC (Shenber and Eriksson, 1993).

Particle size may also have some effects on the sorption behavior. It was found that the amount of ^{137}Cs sorbed to soils apparently increased with a decrease in the size of soil particle, probably related to the increased specific surface area as well as organic matter contents in those fractions (Boggs et al., 1985; Buckau et al., 1986; Kim, 1986). However, the opposite effect had sometimes been observed (Muller and Sprugel, 1977; Matkar et al., 1992) for cases when soils contained more organic matter. This is probably due to that the heavily carbonated and hydrated Cs ion was too large to be adsorbed easily on a clay particle.

The role of pH on sorption behavior is quite controversial. Schimmack et al. (1991) did not observe the pH effects on the distribution of ^{137}Cs in the soil profile by adding water with different pH value and Baeza et al. (1995) did not observe the pH effects on ^{90}Sr in the soil. On the other hand, some researchers (Muller and Sprugel, 1977; Matkar et al., 1992) claimed that pH value may affect the adsorption process and solubilization of radionuclides in soil.

Sorption behavior of radiocaesium is influenced by the presence of cation. Shenber and Eriksson (1993) found that K_d value was strongly reduced after small additions of stable caesium. However, at increasing concentrations of stable caesium Cs^+, the effect became much less. Other ions such as potassium K^+ and ammonium NH_4^+ also reduced the cesium sorption capacity of the soils. They concluded that the ability to block cesium sorption sites decreased in the order of $Cs^+ >> NH_4^+ > K^+$. It was because the smaller ammonium ions can penetrate more than potassium into the clay minerals, therefore they were competing more for the selective sorption sites of the caesium ions.

Another factor affecting the sorption capacity is frayed edge sites (FES). When Cs^+ is bound to the FES, it will lose its hydration shell and form bonds with surface oxygen groups in the ditrigonal cavities of siloxane surface of illite. Cs^+ was bound to illite in the same way as the interlayer K^+ ions (Sposito, 1984). The Cs^+ ion can be displaced from the FES by other univalent cations of similar size and low hydration such as K^+, NH_4^+ and Rb^+. In anoxic fresh water sediments the NH_4^+ ion was the major competing ion which can displace the Cs^+ ion from the FES (Evans et al., 1983; Comans et al., 1989). Apart those competing ion, ammonium was more important than potassium because NH_4^+ reaches higher concentration in anoxic sediments and is five times more selectively bound by the FES than K^+ (De Peter, 1990).

2.9 General Findings on Sorption Behaviour

Sorption characteristics of radiocaesium on various soils and sediments have been the subject of many recent investigations (Sawhney, 1966; Erten et al., 1998; Lieser and Steinkopff, 1989; Hsu and Chang, 1994; Ohnuki, 1994; Champbell and Davies, 1995; Hse and Chang, 1995; Du et al., 1998).

K_d for given soil was found to depend on the initial water concentration, sorption time and slurry ratio. K_d reported by researchers had been using different initial water concentrations, time of sorption and slurry ratios (Dumat and Staunton, 1999; Du et al., 1998; Wang et al., 2000; De Koning et al., 2000; Elejalde et al., 2000; Shenber and Eriksson, 1993; Stephen et al., 1998) and it is hard to intercompare K_d values. It is thus not surprising that the reported K_d values, measured in different environments, can vary within a range of more than two orders of magnitude (IAEA, 1985). Even in the same scenario, large variations from one location to another, and variations in time at the same location can be observed (Periañez et al., 1994). Some factors have been found to affect the distribution coefficient K_d. Lieser and Steinkopff (1989) concluded that the sorption of Cs^+ in sediments was mainly determined by the presence of clay minerals and that the values of K_d at low salinity was roughly proportional to the clay content in the sediments. Furthermore, they described the sorption of Cs^+ ions on clay minerals by an ion exchange mechanism, and found that the organic matter can take up radiocaesium in competition with clay minerals, or may react with clay minerals and block the Cs^+ uptake metal ions such as K^+, Rb^+ and Cs are fixed in the clay lattices. It was because of the very high selectivity and the change in geometry of the lattices (Bolt et al., 1976). It is thus imperative that some guidelines, as to the initial water concentration, time of sorption and slurry ratio, be set up to standardize the procedures.

CHAPTER 3

EXPERIMENTAL

3.1 Study Site and Sampling

Three sets of soils had been collected from the Shek Lei Pui reservoir. Location A refers to soil collected next to the water level, location B refers to soils at ground–level and location C refers to soils in the catchment area. These locations were fenced-off areas and would remain undistributed for some times.

3.2 Sample Treatment

Samples collected required treatment including cleaning, homogenization and drying. Soils were first cleaned with de-ionized water, oven dried at 120°C for 24 h and then crushed to loosen up the soil particles. Care has be taken not to break the individual soils minerals during the process. Sub-samples of soils were analyzed for selected physical and chemical properties by using standard methods of soil analyses.

3.2.1 Particle Size Analysis

The procedures for determining the particle-size distribution of soils were dispersion followed by both sieving and sedimentation methods, based on British Standard 1377. Combined sieving and sedimentation procedures enabled a continuous particle size distribution curve of a soil to be determined from the size of the coarsest particles down to the clay size.

3.2.2 Dispersion

100 ml of a dispersant solution (sodium hexametaphosphate) was added in a conical flask, and shaken in a mechanical shaking device for at least 4 h, until all the soils were in suspension. The suspension was then transferred to a 63 μm test sieve and placed on the receiver using a jet of distilled water from a wash bottle to wash the soil into the sieve. The amount of water used should not exceed 500 ml. The sieved soils were collected in a measuring cylinder and filled to make 1 liter with distilled water. The suspension was to be used for the sedimentation analysis.

3.2.3 Sedimentation by the Hydrometer Method

This method covered the quantitative determination of soils from the coarse silt size to the clay size (about 2 μm). The procedure enabled the percentages of coarse, medium and fine slit, and clay to be determined. These percentages can be linked to the curve obtained by dry sieving to provide a single curve for the whole soil sample.

At least 1 h after dispersion, the suspension was shaken vigorously end-over-end about 60 times in 2 min. At the instant when the cylinder with the soil suspension was placed upright, a timer was started. A hydrometer was placed in the suspension, as shown in Fig. 3.1. Reading was taken after periods of 0.5 min, 1 min, 2 min, 4 min, 8 min, 30 min, 1 h, 2 h, 4h, 8 h, and 24 h from the start of sedimentation. This procedure was repeated twice during the following day. The soil particles settled in the water at a speed directly related to the square of their diameter and inversely related to the viscosity of the water.

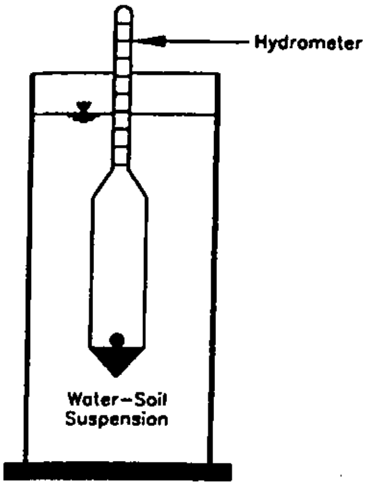


Fig. 3.1 Hydrometer test in progress. (Winegardner, 1996)

3.2.4 Dry Sieving Method

Soils retained from the 63 μm test sieve was transferred to an evaporating dish and dried in an oven maintained at 105°C to 110°C overnight. When cool, these materials were sieved using different mesh-size from 10 mm to the 63 μm. Mass of soils retained on each test sieve was weighed to an accuracy of 0.01g. This method provided a quantitative determination of the particle size distribution in cohesionless soil.

3.3 Soil Characterization

Soil pH was measured with a Bragg pH combination electrode in a 1:5 suspension of soil and water. The cation exchange capacity (CEC) was determined by the method of Polemio and Rhodes (1977). Metal ions were determined by the method of digestion. The total organic carbon (TOC) was determined by inductively coupled plasma (ICP). Conductivity of water-soil mixture was measured using a WPA model CMD 8000E conductivity meter. Soils were analyzed by using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) to obtain the morphology and composition of soils.

3.4 Measuring System

A 3-inch NaI (Tl) well-type detector was used to assay the ^{137}Cs contents. The detector was housed inside a lead shield of 5 cm thick and 20 cm diameter which was connected to an EG&G ORTEC NOMAD Portable Spectroscopy System, Model 92X-P. The efficiency of the well of the NaI(Tl) detector was obtained by measuring 10 ml of known activity of ^{137}Cs inside a polypropylene (PP) test-tube. Samples were counted for about 2 min and the relative uncertainties were estimated to be within ±5%.

3.5 Experimental Procedures

Five sorption isotherms were measured using ^{137}Cs tracer. The first isotherm was defined by varying the mass of soils added and maintaining a constant spike activity. About 0.14 MBq of ^{137}Cs were added to make 1 liter of solution in a 1.25-ℓ high density Polyethylene (HDPE) container. Soils of random sizes, ranging from 0.05 g to 5 g, were added to the Cs solution and the conductivity and pH of the water-soil mixture were measured. The mixture was constantly stirred with a magnetic stirrer. At prescribed intervals, 30 ml of the mixture was withdrawn and centrifuged at 3000 RPM for 2 min to separate the solution from soils. 10 ml of the solution was then inserted into a PP test tube for measurement of the Cs-content in the well of the NaI(Tl) system. Solution and soils were then poured back to the container. This procedure was repeated until equilibrium had been established when the concentration of the solution had reached a steady value. Soils collected from different locations had been measured.

The second isotherm was defined by varying the initial water concentration with constant mass of random sizes. A constant mass of soils was added to spike concentrations varying from 29 kBq ℓ^{-1} to 120 kBq ℓ^{-1}. Six sets of data had been obtained using procedures similar to those for the first isotherm to determine the time variations of the amount of radiocaesium in solution.

The third isotherm was defined by varying the sizes of soil particles while keeping constant initial water concentration and constant mass of soils. Two sets of data had been obtained. The first set involved 1 g of soils of diameters ranging from 0.15 mm to 2 mm, which had been sieved using a mechanical sieve shaker. The second set was for 20 g of similar diameters as the first set. Samples were added to 1 liter of 0.13 MBq of ^{137}Cs solution. Similar procedures as for the first isotherm were used.

The fourth isotherm was defined by varying the masses of soils added, while maintaining a specific pH value of water and constant initial water concentration. pH values of radiocaesium solution was varied by adding a few drops of concentrated hydrochloric acid (HCl). Three sets of data had been obtained using pH values of 2.6, 3.0 and 3.6. The initial water concentration of ^{137}Cs solution was about 0.13 MBq ℓ^{-1} and the mass of soils varied from 2g to 7g. Similar procedures as for the first isotherm were used.

The fifth isotherm was defined by varying the pH value of water concentration with constant mass of random sizes. Eight sets of data had been obtained. Each set involved a constant mass (e.g., 1 g of soils) at pH values of 2.6, 3.0 and 3.6. Similar procedures as for the first isotherm were used.

CHAPTER 4

EXPERIMENTAL RESULTS

The physical and chemical properties of soils in the three locations are shown in Table 4.1. Soils from some other countries are also included for comparison. The variations in soils in the three locations within the vicinity of a reservoir were quite large. In general, soils in Hong Kong were relatively low in organic matter and consistently more acidic than those in other countries.

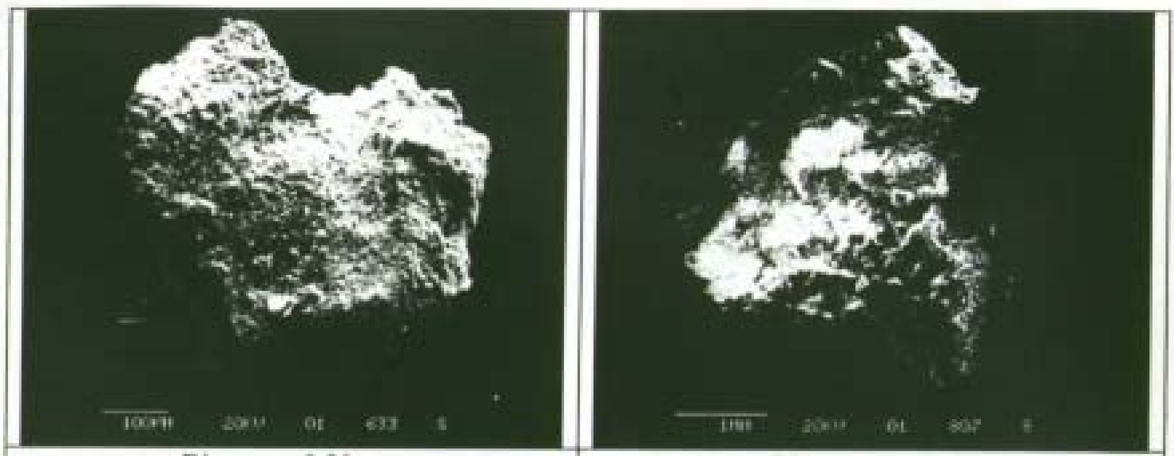
Using criteria as described in Chapter 2, soils in location A, B and C can be classified as loam soil, clay loam and sandy loam, respectively. Soil in location A has the largest percentage of silt and the lowest K-content. It also contained the largest percentage of sodium. Soil in location B was the most acidic and contained the highest value of aluminum. Soil in location C has the largest percentage of sand, the smallest percentage of clay, the highest pH and the highest CEC value.

Table 4.1 Properties of soils in Hong Kong reservoir and in other countries.

Location	**A (HK)**	**B (HK)**	**C (HK)**	**U.S.A.[5]**	**Sweden [6]**	**Sweden [6]**	**Italy[7]**
Soil Location	water-level soil	ground-level soil	Catch-ment soil	Profundal sediments	Libya	Sweden	Marche
Soil Type	Loam	Clay loam	Sandy loam	Sandy clay loamy	Loamy sand	Loamy sand	Clay loam
Depth (cm)	0-5	0-5	0-5	1	-	-	0-5
Clay[1] (%)	21.9	22.2	7.9	53	18	14	21-26
Silt[2] (%)	59.6	25.4	12.1	45	18	12	25-37
Sand[3] (%)	20.97	26.3	63.53	2	64	71	37-54
Gravel[4] (%)	7.53	26.1	16.47	-	-	-	-
Organic Matter (%)	1.75	1.84	1.70	28	1.26	4.3	9.76-44.6
pH (in water)	4.37	3.9	5.13	5.8	7.7	5.6	6.72-6.85
CEC(meq/100g dry soil)	16.1	15.3	30.4	32	8.7	6	10.5-16.6
Al ($\mu g\ g^{-1}$)	1518	2096	149.4	-	-	-	-
Ca ($\mu g\ g^{-1}$)	7.9	7.1	12	-	-	-	-
K ($\mu g\ g^{-1}$)	14.65	23.5	44.35	1.4	-	-	-
Na ($\mu g\ g^{-1}$)	27.9	22.7	18.95	4.5	-	-	-

1— Particle size ranging from 0 to 0.002mm
2— Particle size ranging from 0.002 to 0.06mm
3— Particle size ranging from 0.06 to 2mm
4— Particle size ranging from 2 to 60mm
5— Ref: Stephens et al., 1998
6— Ref: Shenber and Eriksson, 1993
7— Ref: Jia et al., 1999

Typical results of scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis are shown in Fig. 4.1. From the SEM images, the shapes and surfaces of soil particles were observed to be highly irregular. Result of the EDX analysis showed that the main compositions in soils were Aluminum (Al), Silicon (Si), Iron (Fe) and Potassium (K).



Diameter= 0.56 mm					Diameter=3.8 mm				
Elements	Al	Si	Fe	K	Elements	Al	Si	Fe	K
Atom %	41.671	53.756	4.025	0.548	Atom %	46.591	50.87	2.27	0.27

Fig. 4.1 SEM images and composition of soils from EDX.

4.1 Sorption on Walls of Containers

It was found that high density polyethylene (HDPE) container also played a part in the sorption process. It was observed that the Cs-concentration dropped by 5 to 10 % within 1 h, and then became steady about 1 day. To minimize the effects of the container walls on the sorption behavior, radiocaesium solution were to remain in the container for at least 2 day prior to the introduction of the soils.

4.2 Distribution Coefficient K_d of Soils

K_d values at t=24 h of soils from the 3 locations are shown in Table 4.2. 24-h was chosen as this had been the time used by some researchers in determining the K_d values of soils in other countries (Stephen et al., 1998; Shenber and Eriksson, 1993) and intercomparisons can be made. It can be seen that the values of K_d and % sorption were quite different for the 3 locations, probably due to the different physical and chemical properties of soils. For equal mass, K_d of soils in location A was consistently larger than those in other locations. This may be related to the higher percentage of silt and Na^+ concentrations in location A soils. Higher slit content provided more surface area and higher Na^+-content provided more ion exchange with the Cs^+ ions in water.

Table 4.2 The 24-h K_d values (ml g^{-1}) and sorption percentages of different soil samples in Hong Kong reservoir.

Mass (g)	*Slurry Ratio (g ml^{-1})*	*% Sorption*			*K_d (10^3) (ml g^{-1})*		
		Location A	Location B	Location C	Location A	Location B	Location C
0.1	1:10000	49.24	16.38	6.83	9.70	1.96	0.73
0.2	1:5000	60.60	34.7	11.31	7.52	2.66	0.64
0.6	1:1667	85.94	66.86	42.07	10.2	3.36	1.21
0.8	1:1250	91.80	73.19	47.35	14.0	3.41	1.12
2.0	1:500	93.93	90.28	80.17	5.01	4.64	2.30

Comparisons of K_d values of soils in different countries are shown in Table 4.3. As K_d depends on sorption time and slurry ratio, the data shown are all of 24-h sorption time and 1:20 slurry ratio. It can be seen that K_d of soils in Hong Kong is comparable to that in U.S.A., but is less than those in Libya and Sweden.

Table 4.3 Comparisons of K_d values of soils in different countries. Data are for slurry ratio of 1:20 and sorption time of 24 h.

Sampling site and country	**K_d (ml g^{-1})**
Shek Lei Pui Reservoir (location B), Hong Kong	780
Savannah River Site Reservoir, U.S.A[1].	630
Loamy sand, Libya[2]	2448-5515
Clay soil, Libya[2]	5860-5996
Loamy sand, Sweden[2]	1507-3512
Clay soil, Sweden[2]	4348-6189

1—Ref: Stephens et al., 1998
2—Ref: Shenber and Eriksson, 1993

Variations of K_d at t=24 h and conductivity with slurry ratio R for soils in location A, B and C are shown in Fig. 4.2 and Fig. 4.3, respectively. Data shown are of uncertainty within ± 5%. It was observed that the K_d values in location A were larger than those in location B, which in turn were larger than those in location C. In general, K_d and conductivities increased as the slurry ratio increased. As the slurry ratio increased % sorption increased and the concentration of radiocaesium in water decreased. Furthermore, as the slurry ratio increased more ions incorporated in the soils were released to water, thus increasing the conductivity. The conductivity is proportional to the total dissolved ion concentration.

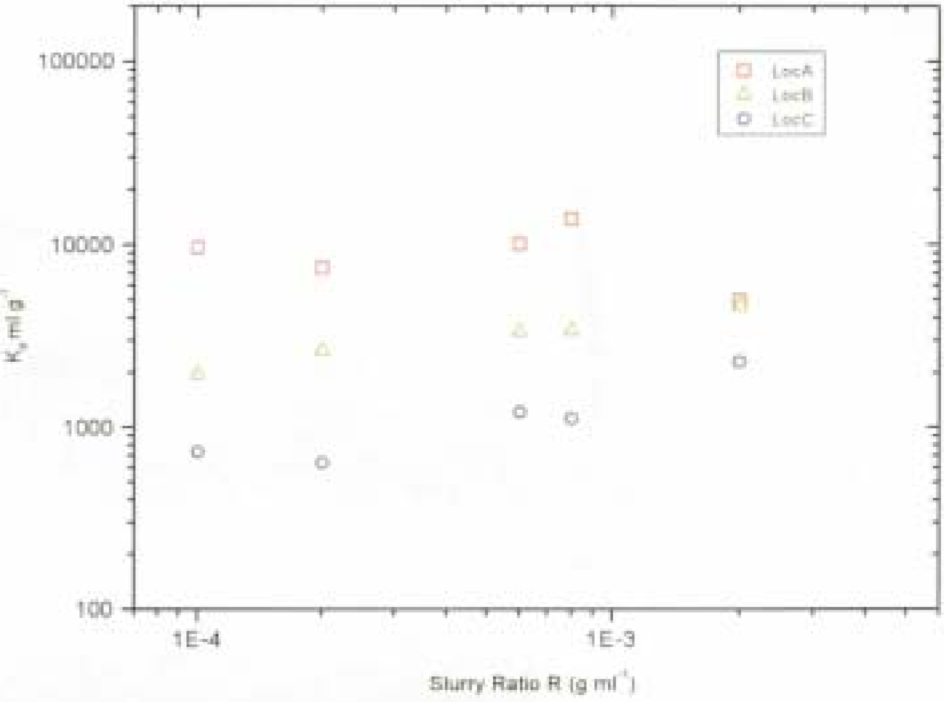


Fig. 4.2 24-h K_d values as a function of the slurry ratio R in location A, B and C.

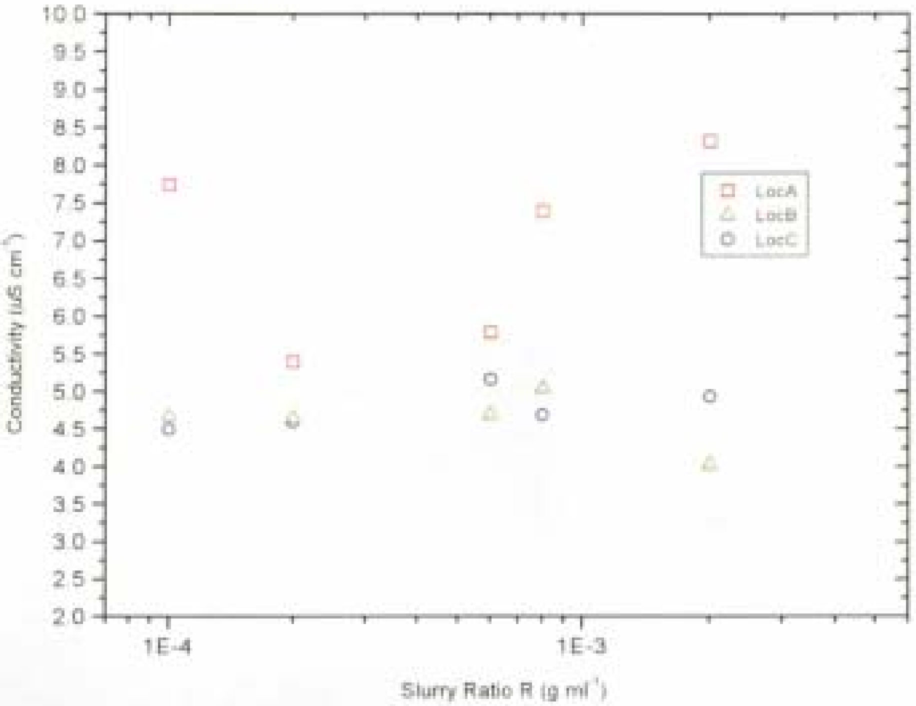


Fig. 4.3 Conductivity as a function of the slurry ratio R in location A, B and C.

Results of the first isotherm for soils from location A, B and C are shown in Fig. 4.4, 4.5 and 4.6, respectively. N_o stands for the initial number of radiocaesium in water, N(t) stands for the number of radiocaesium at time t and N_∞ stands for the number of radiocaesium at equilibrium ($t \rightarrow \infty$). The rates of decrease in water concentration were initially very high, higher for larger mass, and then slowed down after about 10 h. The larger the mass, the shorter was the time for equilibrium. Equilibrium values, N_o/N_∞ were found to decrease with increasing masses. The equilibrium values were about the same and approached zero for masses larger than or equal to 5 g.

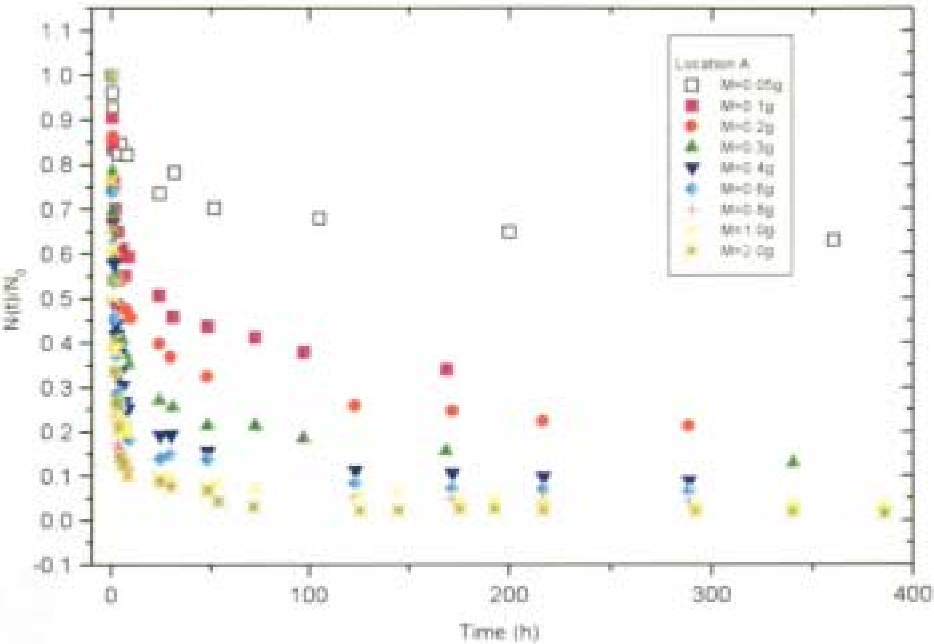


Fig. 4.4 Time variations of fraction of radiocaesium remaining in water for different masses of soils of random sizes for soils from location A.

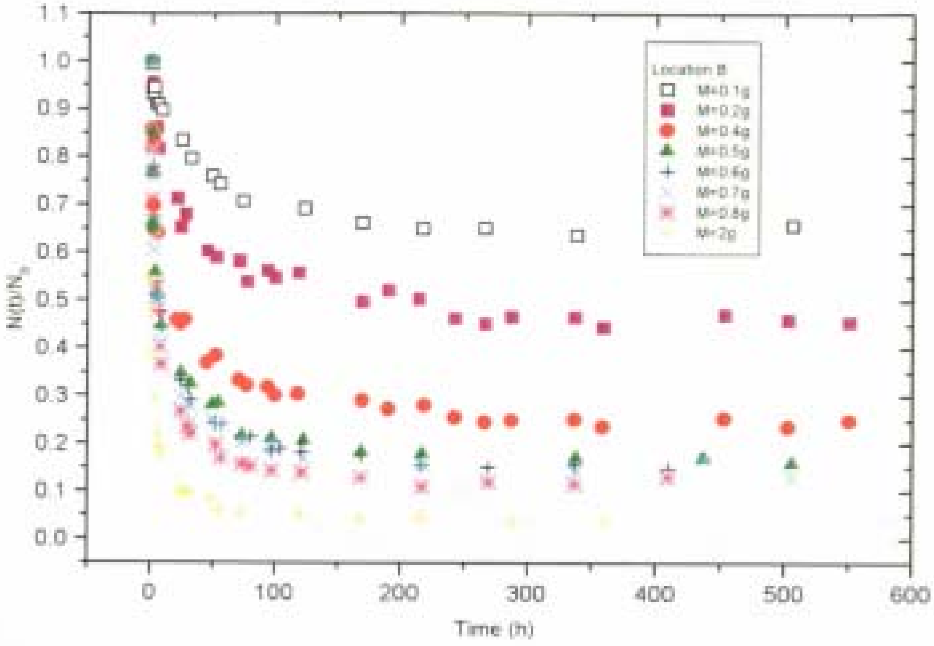


Fig. 4.5 Time variations of fraction of radiocaesium remaining in water for different masses of soils of random sizes for soils from location B.

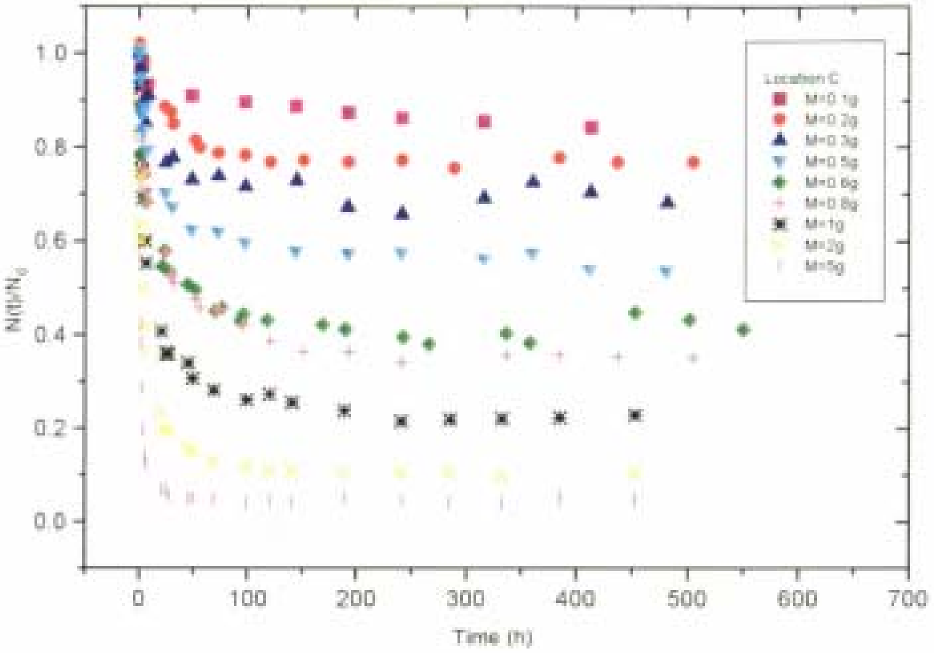


Fig. 4.6 Time variations of fraction of radiocaesium remaining in water for different masses of soils of random sizes for soils from location C.

Results of the second isotherm, effects of initial water concentration on the sorption behavior of soils of constant mass, are shown in Table 4.4. Six different slurry ratios, ranging from R = 1: 1,000 to R = 1: 10,000, have been used. It can be seen that K_d and % sorption at equilibrium increased with decreasing initial water concentration and also with increasing mass of soils added (smaller slurry ratio).

Table 4.4 Equilibrium K_d and % sorption at different initial water concentrations.

Mass (g)	Slurry Ratio (g ml^{-1})	Initial water activity (kBq ℓ^{-1})	% sorption	K_d 10^3(ml g^{-1})
0.1	1:10000	110	65.9	19.3
		45.6	78.2	38.0
		26.2	85.6	59.6
0.2	1:5000	57	74.8	14.8
		34	84.3	26.9
0.4	1:2500	58.8	88.8	19.8
		35.1	90.4	23.5
0.6	1:1667	58.8	91.8	18.7
		33.0	93.8	19.0
0.8	1:1250	61.0	91.4	13.2
		28.0	92.7	21.1
1.0	1:1000	95.0	91.5	10.8
		67.0	93.5	14.4
		16.0	96.1	24.6

Time variations of the fraction of radiocaesum remaining in solution at different initial water concentrations for various slurry ratios are shown in Fig. 4.7 to Fig. 4.12. The rates of decrease in water concentration were very high, higher for larger mass, and gradually slow down after 10 h. We also observed that the larger the mass, the shorter the time for equilibrium. It can be seen that the initial rates of decrease of $N(t)/N_0$ were about constant for the different initial water concentrations (more apparent from the insert of Fig. 4.7). The values of N_∞/N_0 at equilibrium increased (decrease in % sorption) with increasing initial water concentration for mass less than 0.8 g and were about the same for larger masses.

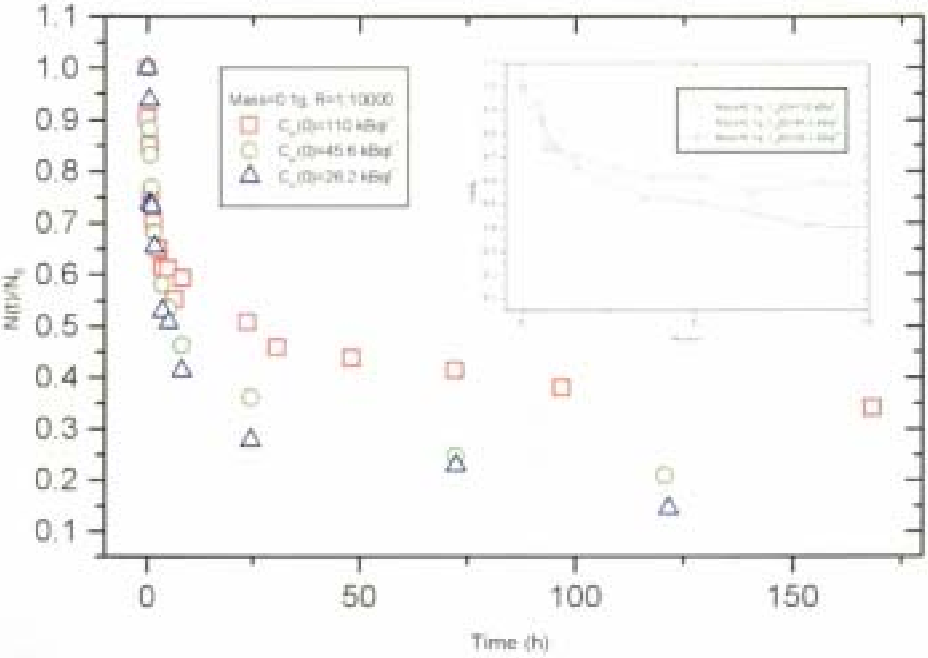


Fig. 4.7 Time variation of fraction of radiocaesium remaining in water at different initial water concentrations. Mass of soils used was 0.1g (R=1:10000) of random sizes. (Insert shows enlarged portion of initial values).

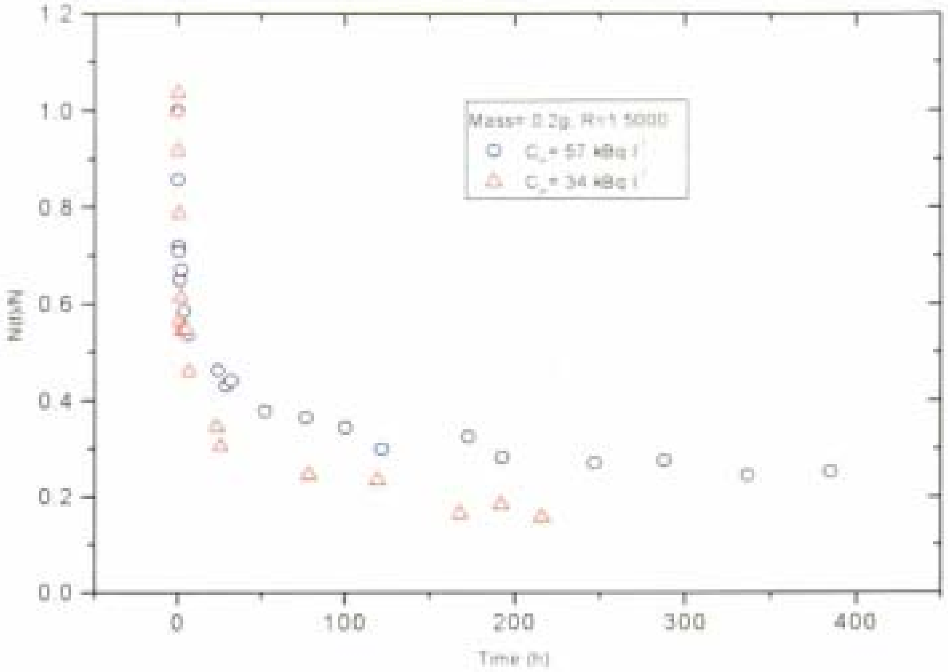


Fig. 4.8 Time variation of fraction of radiocaesium remaining in water at different initial water concentrations. Mass of soils used was 0.2 g (R=1:5000) of random sizes.

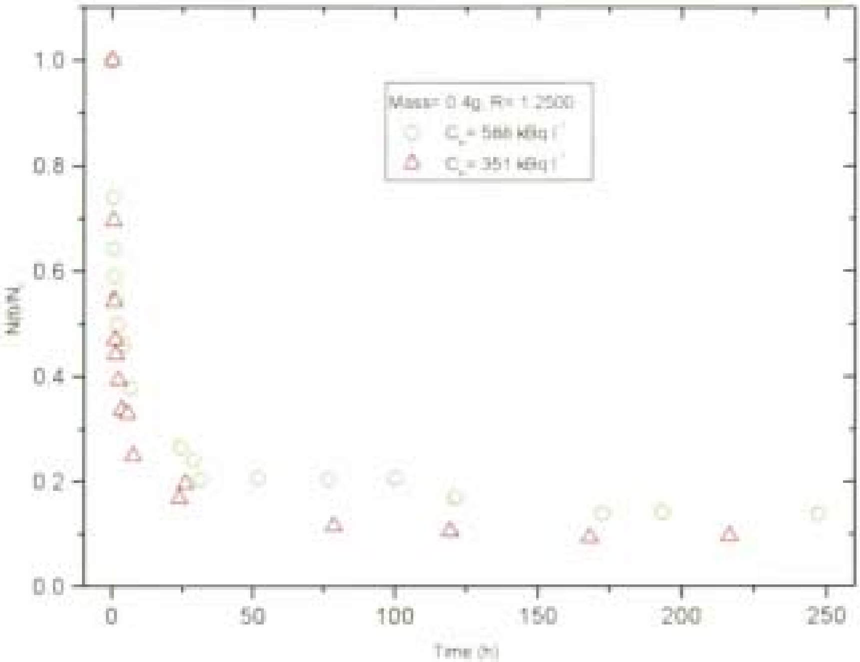


Fig. 4.9 Time variation of fraction of radiocaesium remaining in water at different initial water concentrations. Mass of soils used was 0.4 g (R=1:2500) of random sizes.

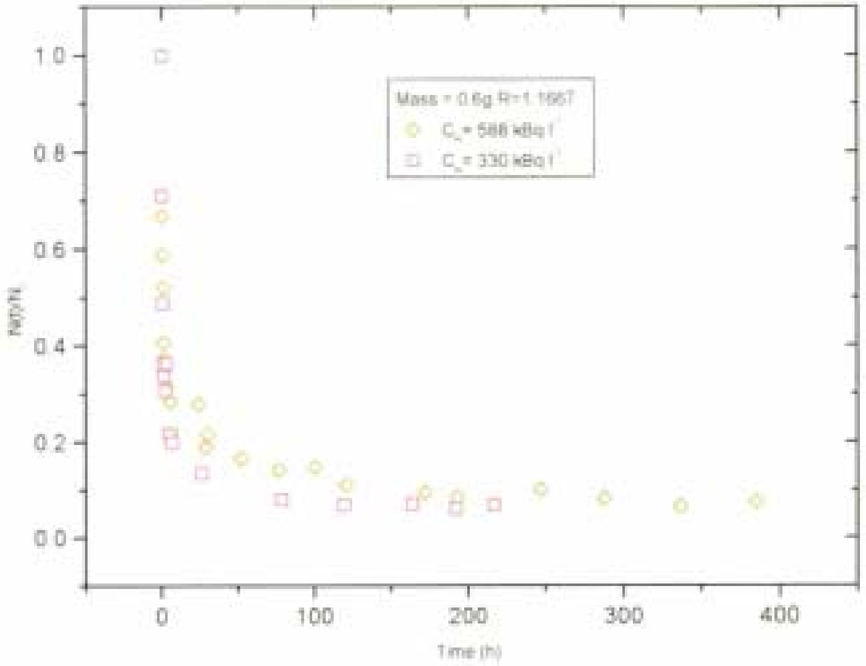


Fig. 4.10 Time variation of fraction of radiocaesium remaining in water at different initial water concentrations. Mass of soils used was 0.6 g (R=1:1667) of random sizes.

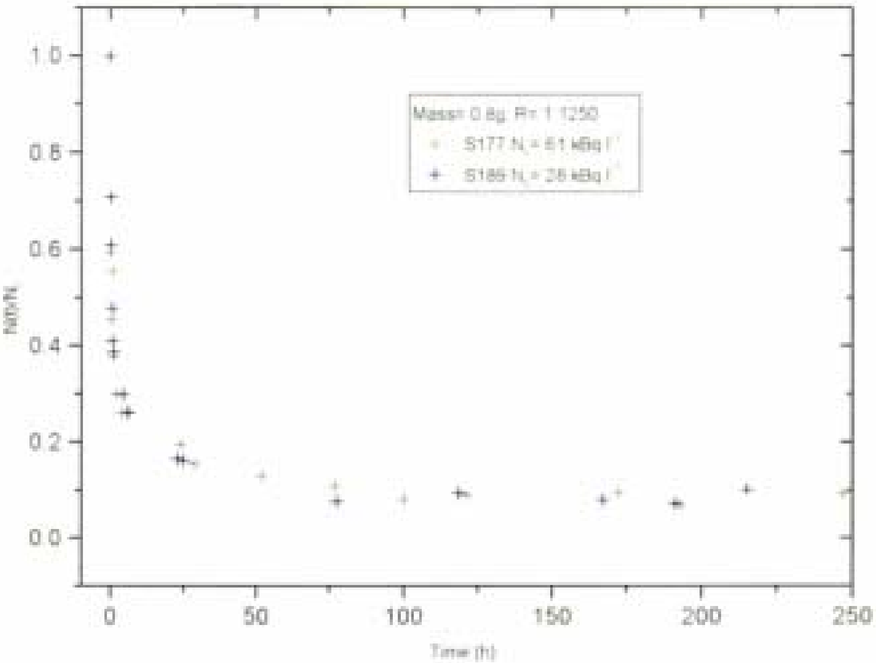


Fig.4.11 Time variation of fraction of radiocaesium remaining in water at different initial water concentrations. Mass of soils used was 0.8 g (R=1:1250) of random sizes.

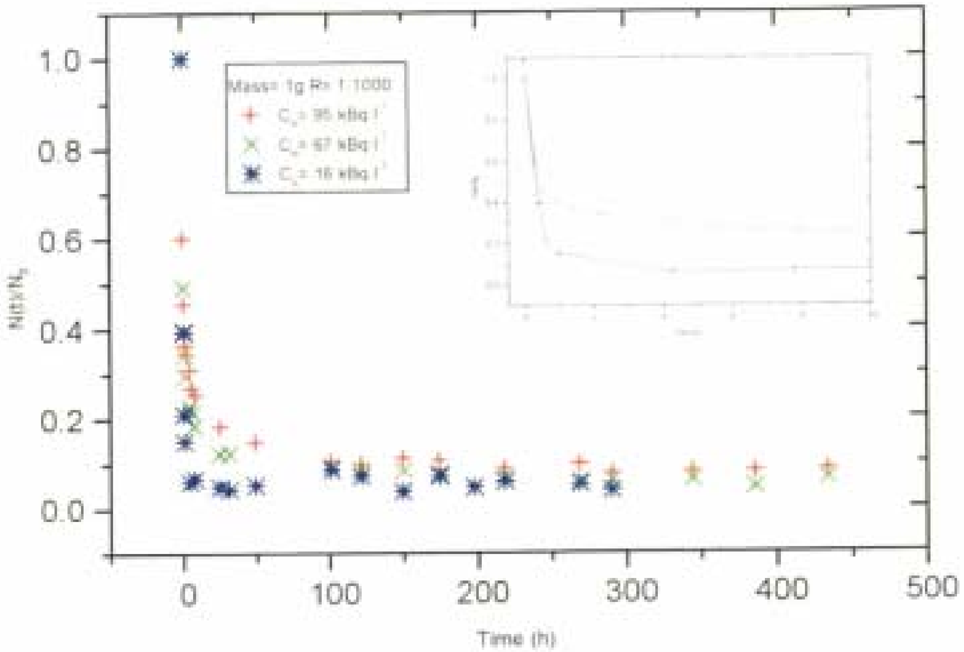


Fig. 4.12 Time variation of fraction of radiocaesium remaining in water at different initial water concentrations. Mass of soils used was 1 g (R=1:1000) of random sizes. (Insert shows enlarged portion of initial values).

Results of the third isotherm, effects of size of particles on the sorption behavior at constant initial water concentration and constant mass, are shown in Table 4.5, Fig. 4.13 and Fig. 4.14. For 1 g of different sizes, as the diameter decreased, N_t/N_o decreased and the rate of initial decrease was higher. The values of N_t/N_o did not approach zero at equilibrium. For constant mass, smaller diameter particles have larger total surface area and thus have large number of sites for sorption.

For the case of 20 g, the initial rates of decrease of water concentration were also observed to increase for smaller particles size (more apparent from the insert of Fig. 4.14). However, N_∞/N_0 approached zero at equilibrium for all sizes. This is probably due to that all the sorption sites were eventually filled for large mass, independent of the sizes.

The data in Table 4.5 are those at t= 24 h and at t= 350 h, the latter can be taken effectively as $t \to \infty$ as equilibrium has long been attained. The % sorption and K_d increased as the size of the soil particles decreased. It can be seen that K_d values were different for different sorption time, indicating that K_d was time dependent and the use of 24-h K_d values by some researchers (Stephens et al, 1998, Shenber and Eriksson, 1993) may create some ambiguity.

Table 4.5 Percentage sorption and K_d of different sizes of soil at constant initial water concentration at different sorption time.

		t=24 h		**t=350 h**	
Diameter (mm)	**Mass (g)**	**% sorption**	**K_d (10^3) (mℓ g^{-1})**	**% sorption**	**K_d (10^3) (mℓ g^{-1})**
≥2.00	1	66.9	2.0	84.2	5.3
≥0.43	1	76.3	3.2	90.1	9.1
≥0.30	1	84.1	5.3	93.7	15.0
≥0.15	1	87.5	7.0	95.0	18.8
≥2.00	20	96.4	1.4	99.2	6.2
≥0.43	20	98.1	2.6	99.4	8.3
≥0.30	20	98.7	3.8	99.5	10.0
≥0.15	20	98.8	4.1	99.9	50.0

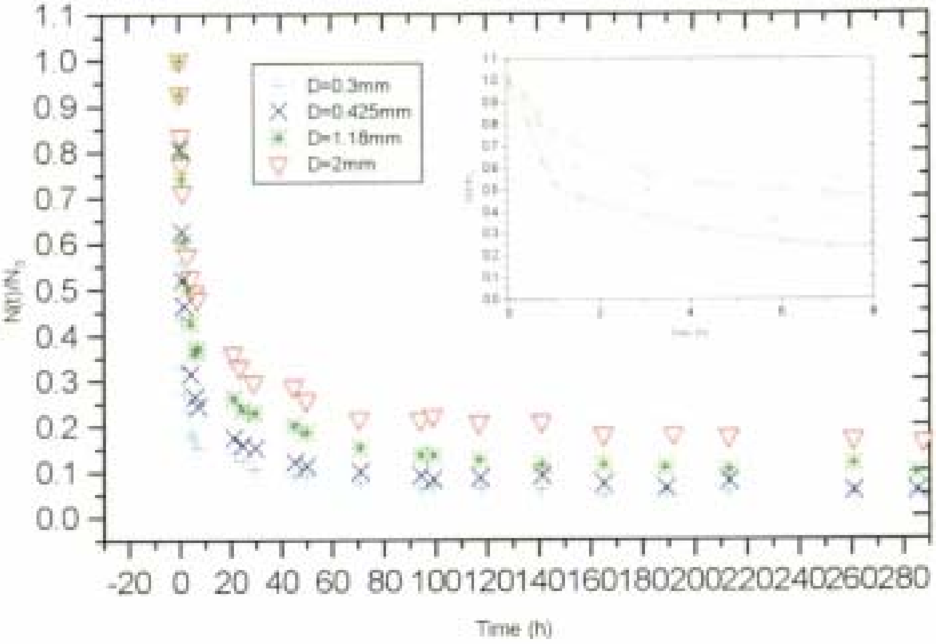


Fig. 4.13 Time variations of fraction of radiocaesium remaining in water for different sizes of soil particles at constant initial water activity and slurry ratio. Mass of soils used was 1 g. (Insert shows enlarged portion of initial values).

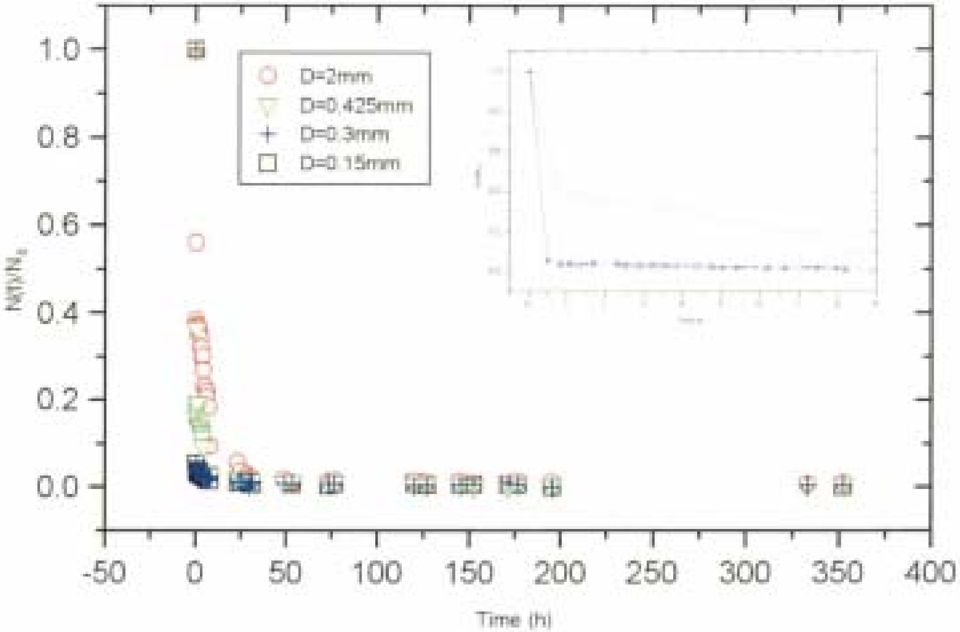


Fig. 4.14 Time variations of fraction of radiocaesium remaining in water for different sizes of soil particles at constant initial water activity and slurry ratio. Mass of soils used was 20 g. (Insert shows enlarged portion of initial values).

Results of the fourth isotherm, effects of pH on sorption behavior at constant initial water concentration, are shown in Fig.4.15 to Fig. 4.17 and Table 4.6 and 4.7. Three pH values of 2.6, 3.0 and 3.6 had been used at an initial water concentration of about 0.13 MBq ℓ^{-1}. Soils from location C were used and diameter of soils particles was 1.8 mm, with the mass varied from 2 g to 7 g. The rates of decrease in water concentration were initially very high, higher for higher pH value, and slowed down after about 10 h. The larger was the mass, the shorter was the time for equilibrium.

From Table 4.6 and 4.7, the % sorption and the K_d values increased with time, indicating that 24-h measuring time used by some researchers may not reflect the actual values. In general, % sorption and K_d values decreased with decreasing pH values. These phenomena occurred because the addition of bulk acids affects the soil properties. Firstly, addition of bulk acids may increase the quantity of free Fe, Al, and other metal cations in the soil water. H^+ is a very small ion which can easily replace Ca^{2+} and Mg^{2+}. It may also dissolve crystalline minerals. If the pH drops below 5, the soil loses its capacity to retain cations. However, if the pH buffering capacity is sufficient, the soil may neutralize the acid. Secondly, it may cause dissolution of clay minerals. In some clay soil, addition of acid can dissolve significant amount of SiO_2. The activity of free SiO_2, K, and H^+ favor the formation of kaolinite. Thirdly, it may alter soil permeability. Acids (e.g. HCl) favor formation of sparingly soluble soil mineral permeability changes (Winegardner, 1996).

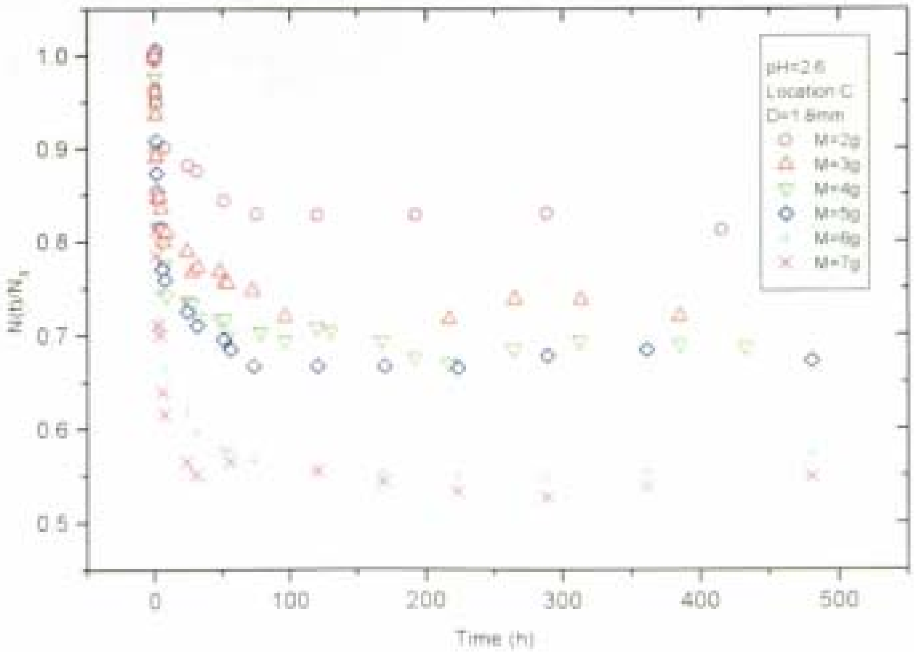


Fig. 4.15 Time variations of fraction of radiocaesium remaining in water of pH= 2.6 for different masses of soils.

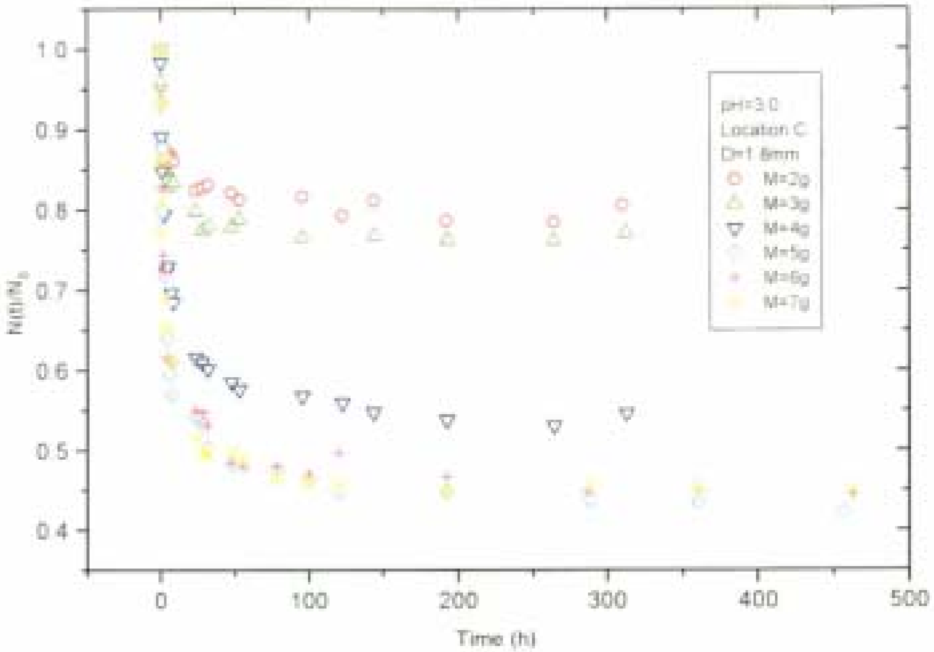


Fig. 4.16 Time variations of fraction of radiocaesium remaining in water of pH= 3.0 for different masses of soils.

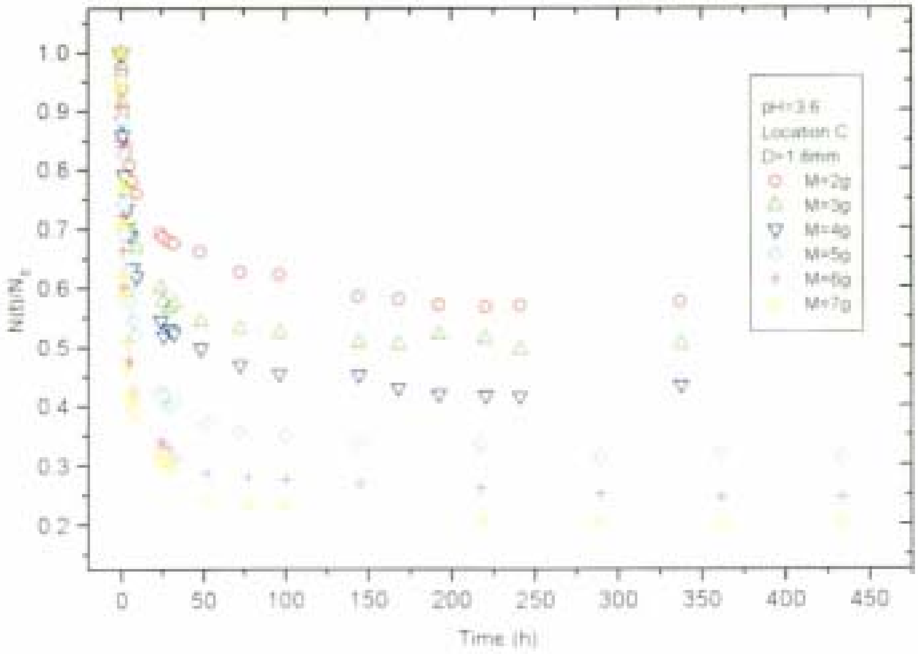


Fig. 4.17 Time variations of fraction of radiocaesium remaining in water of pH= 3.6 for different masses of soils.

Table 4.6 Percent sorption (24 h) and K_d (24 h) at different pH values of soils of constant size (D= 1.8mm) and at constant initial water concentration (0.13 MBq l^{-1}).

	pH= 2.6		pH=3.0		pH=3.6	
Mass (g)	% sorption	K_d ($m\ell\ g^{-1}$)	% sorption	K_d ($m\ell\ g^{-1}$)	% sorption	K_d ($m\ell\ g^{-1}$)
2	11.78	66.8	17.57	107.0	30.69	221.0
3	20.94	88.3	22.56	97.1	39.87	221.0
4	26.33	89.4	38.39	150.0	48.06	231.0
5	27.41	75.5	45.71	168.0	57.53	271.0
6	38.22	103.0	46.79	147.0	65.73	320.0
7	43.50	110.0	48.27	133.0	67.88	302.0

Table 4.7 Percent sorption (t = 350 h) and K_d (t = 350 h) at different pH values of soils of constant size (D= 1.8mm) and at constant initial water concentration (0.13 MBq l^{-1}).

	pH= 2.6		pH=3.0		pH=3.6	
Mass (g)	% sorption	K_d ($m\ell\ g^{-1}$)	% sorption	K_d ($m\ell\ g^{-1}$)	% sorption	K_d ($m\ell\ g^{-1}$)
2	18.72	115.0	19.38	120.0	42.31	367.0
3	27.20	125.0	23.80	104.0	49.58	328.0
4	31.27	114.0	45.34	207.0	58.47	352.0
5	33.52	101.0	53.20	227.0	67.93	424.0
6	44.50	134.0	55.10	205.0	75.28	507.0
7	46.10	122.0	56.28	184.0	80.12	576.0

Results of the fifth isotherm, effects of pH value on sorption behavior at constant initial water concentration, are shown in Fig. 4.18 to Fig. 4.23 for constant mass of 2 g, 3 g, 4 g, 5 g, 6 g and 7 g, respectively. The pH values of 2.6, 3.0 and 3.6 have been used for each mass of diameter D = 1.8 mm. It can be found that the rates of decrease in water concentration were slower for lower pH value and the % sorption at equilibrium increased with higher pH value. Equilibrium values were reached after shorter time interval for lower pH value. Lower pH value indicated that there were more H^+ ions in the solution. These cations may take up some of the available sites in soils, leaving more unattached Cs^+ ions in the solution. Our findings agreed with those of some researchers (Muller & Sprugel, 1977; Matkar et al., 1992) who claimed that pH might affect the adsorption process and solubilization of radiocaesium in soils, influence the retention of radiocaesium in soils and affect its mobility.

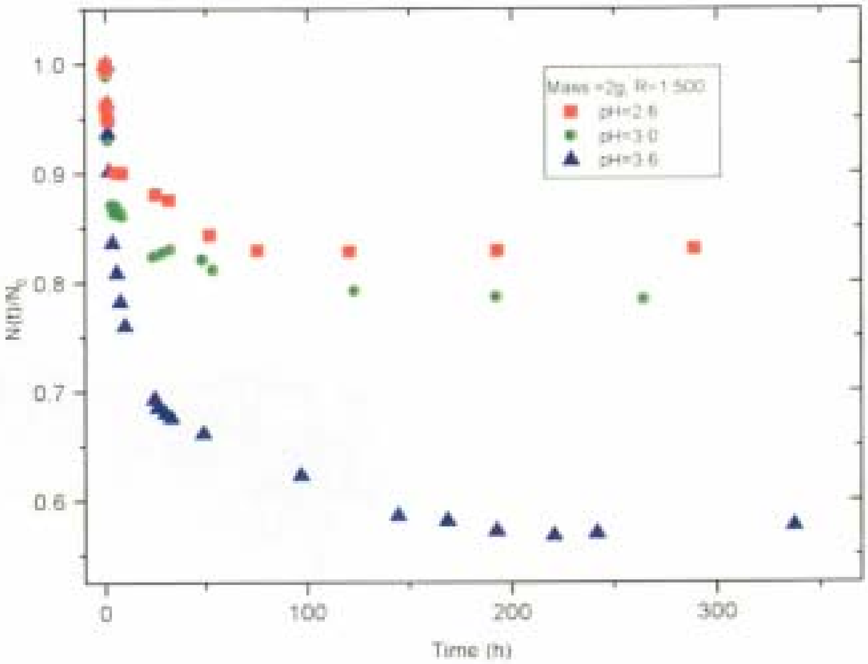


Fig. 4.18 Time variations of fraction of radiocaesium remaining in water of pH= 2.6, 3.0 and 3.6 for 2 g of soils.

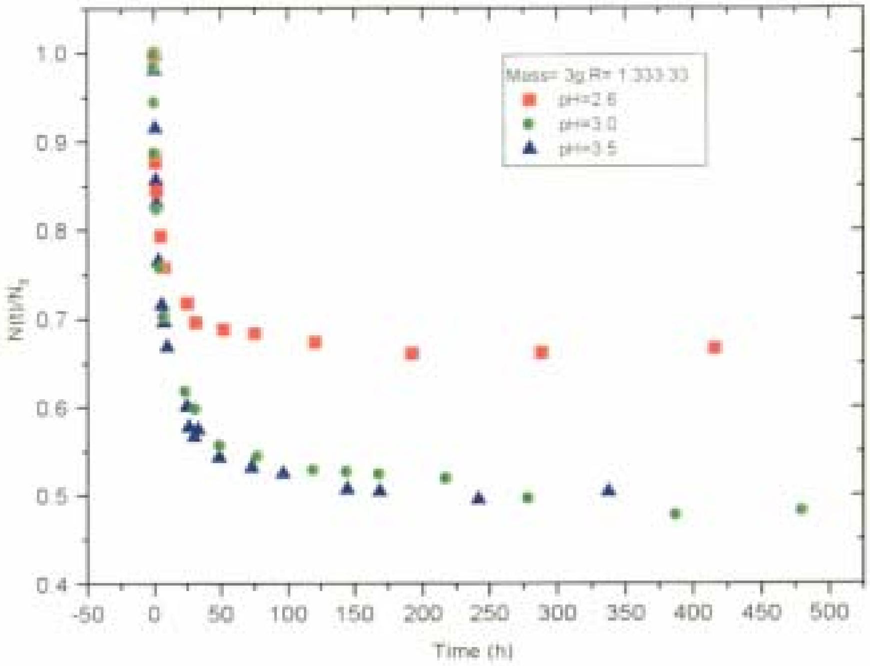


Fig. 4.19 Time variations of fraction of radiocaesium remaining in water of pH= 2.6, 3.0 and 3.6 for 3 g of soils.

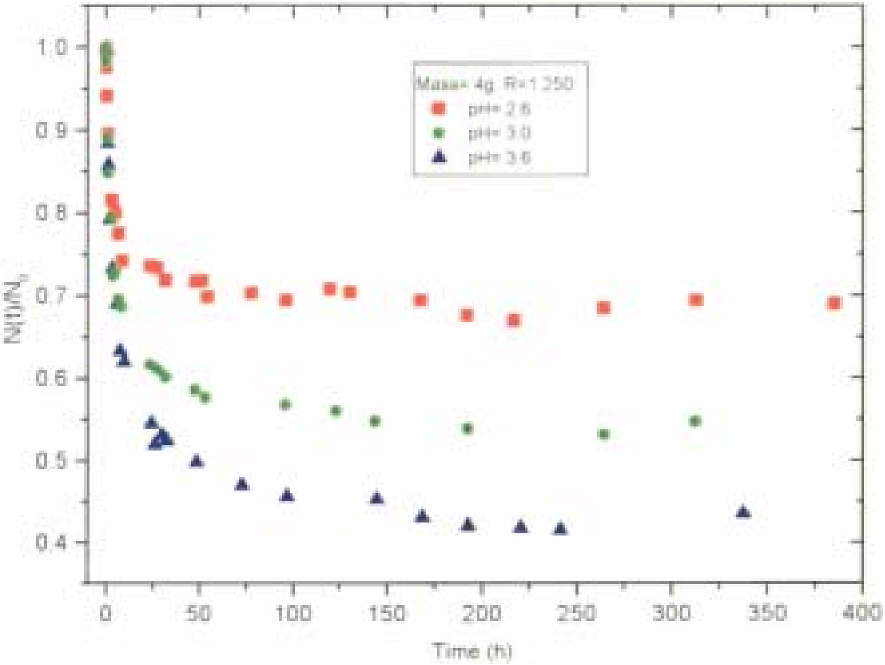


Fig. 4.20 Time variations of fraction of radiocaesium remaining in water of pH= 2.6, 3.0 and 3.6 for 4 g of soils.

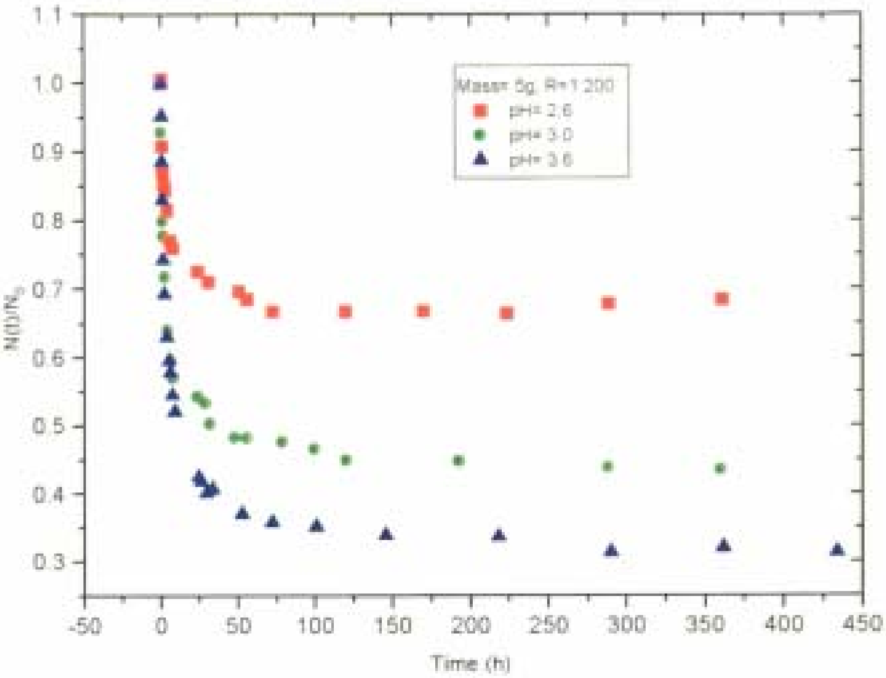


Fig. 4.21 Time variations of fraction of radiocaesium remaining in water of pH= 2.6, 3.0 and 3.6 for 5 g of soils.

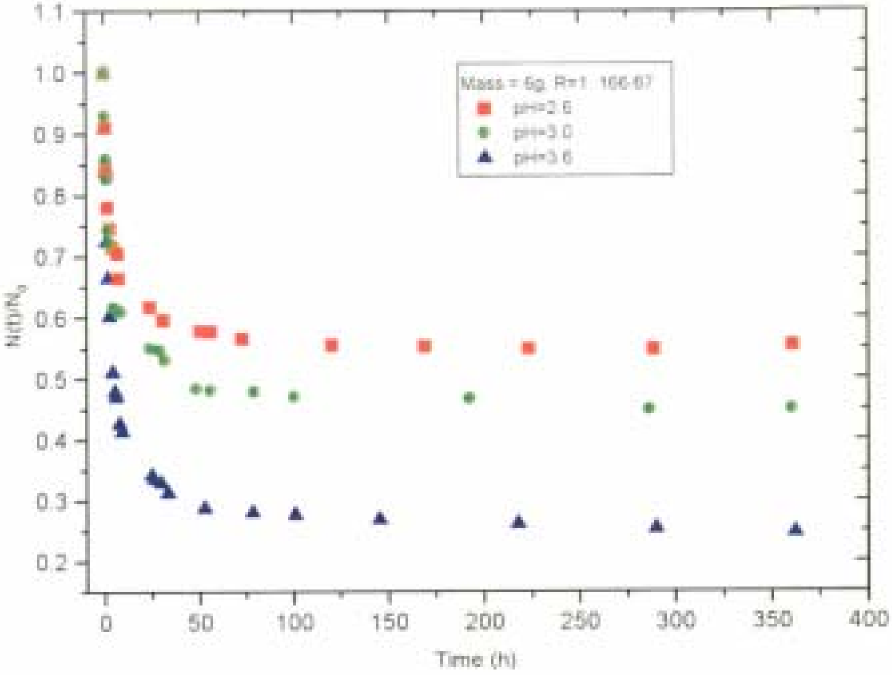


Fig. 4.22 Time variations of fraction of radiocaesium remaining in water of pH= 2.6, 3.0 and 3.6 for 6 g of soils.

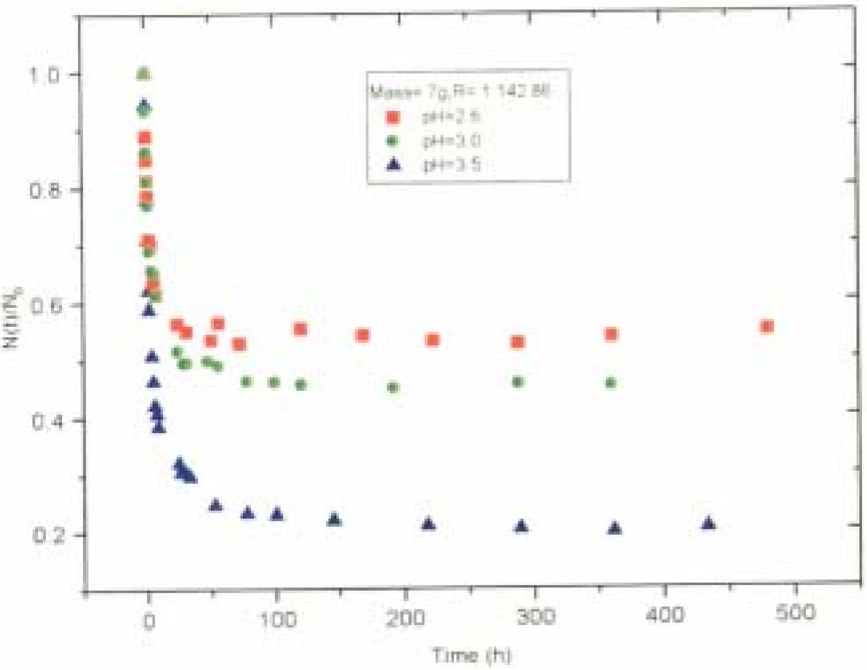


Fig. 4.23 Time variations of fraction of radiocaesium remaining in water of pH= 2.6, 3.0 and 3.6 for 7 g of soils.

This study provides data on the sorption behavior of radiocaesium to soils in Hong Kong reservoir. Some findings are summarized as follows:

- Soils examined were generally more acidic than those in other countries.
- K_d of soils in Hong Kong were lower than those in Libya and Sweden.
- The rates of decrease in water concentration were initially very high, higher for larger mass of soils added, and then slowed down.
- The larger the mass, the shorter was the time for equilibrium.
- Increased slurry ratio led to increased conductivity in soil-water mixture.
- K_d values at 24 h were found to increase with slurry ratios.

- The initial decrease in water concentration increased with larger slurry ratio and smaller size of particles and was independent of initial water concentration.
- The equilibrium fraction sorbed to soils increased with larger slurry ratio of soils of random sizes at constant initial water concentration.
- For constant mass of soils of random sizes, increased initial water concentration decreased fraction sorbed to soils and decreased values of K_d.
- At constant slurry ratio and initial water concentration, K_d and % sorption increased as the size of the soil particles decreased.

CHAPTER 5

MODEL

In Chapter 4, soils from a local reservoir had been analyzed for physical and chemical properties and the sorption behavior under different environments investigated. In this Chapter, we try to develop a model to explain some of the findings from our experimental results.

5.1 Theory

We propose a simple conceptual model consisting of an irreversible exchange between radiocaesium in water and sites of finite capacity in soils. The rate of sorption of radiocaesium to soils is postulated to be proportional to the number of radiocaesium per unit volume in water and the number of unoccupied sites in the soil materials according to the following equation

$$\frac{dn(t)}{dt} = S\frac{N(t)}{V}(n_0 - n(t)) \qquad (5\text{-}1)$$

where $n(t)$ = number of radiocaesium sorbed to solids at time t,

$N(t)$ = number of radiocaesium in water at time t,

V = volume of water,

n_0 = total number of sites in soils available for sorption,

S= proportionality constant relating to the sorption process.

If negligible physical loss from e.g. sorption to the container wall and mass loss of water or sediment can be assumed, then

$$N(t) + n(t) = N_0 \tag{5-2}$$

where N_0 = initial number of radiocaesium in water.

Using Eq. (5-2), Eq. (5-1) can be written as

$$\frac{dn(t)}{dt} = \alpha(N_0 - n(t))(n_0 - n(t)) \tag{5-3}$$

where α = S/V and is here defined as the sorption coefficient.

The solution of Eq. (5-3) with initial condition $n(0) = 0$ gives

$$N(t) = \frac{N_0 - n_0}{1 - \frac{n_0}{N_0} e^{-(1-\frac{n_0}{N_0})N_0 \alpha t}} \tag{5-4}$$

Defining $C = n_0/N_0$ as the receptor-to-donor ratio, Eq. (5-4) can be rewritten as

$$\frac{N(t)}{N_0} = \frac{1 - C}{1 - Ce^{-(1-C)N_0 \alpha t}} \tag{5-5}$$

$N(t)/N_0$ represents the fraction of radiocaesium remaining in water at time t and this fraction falls off as a functions of the receptor-to-donate ratio C, the sorption coefficient α and time t. Note that at time t = 0 (initial condition), the fraction equals 1.

It is interesting to note that for C< 1, that is, the number of available sites n_o is smaller than the number of radiocaesium N_o initially in water, then at equilibrium when $t \to \infty$ and $N(t) = N_\infty$, Eq. (5-5) gives

$$\frac{N_\infty}{N_0} \approx 1 - \frac{n_0}{N_0} \tag{5-6}$$

When C> 1, that is, the number of available sites n_o is larger than the number of radiocaesium initially in water N_o, then at equilibrium when $t \to \infty$ and $N(t) = N_\infty$

$$\frac{N_\infty}{N_0} \approx (C-1)Ce^{-(C-1)N_0\alpha t} \to 0 \tag{5-7}$$

The distribution coefficient K_d is defined as the ratio of the dry sediment concentration C_s (Bq g^{-1}) to the water concentration C_w (Bq ml^{-1}):

$$K_d = \frac{C_s}{C_w} \tag{5-8}$$

The amount of radiocaesium sorbed to the sediment from water is

$$[C_w(0) - C_w(t)]V$$

where $C_w(0)$ is the initial water concentration, $C_w(t)$ is the water concentration at time t and V is the volume of water. Eq. (5-8) can be rewritten as

$$K_d(t) = \frac{1}{R}\left[\frac{C_w(0)}{C_w(t)} - 1\right] \tag{5-9}$$

where R is the slurry ratio, defined as the ratio of the dry mass m_s of sediment to the volume of water

$$R = \frac{m_s}{V} \tag{5-10}$$

Using Eq. (5-5) and Eq. (5-9), it can be shown that

$$K_d(t) = \frac{C\left[1 - e^{-(1-C)N_0\alpha\, t}\right]}{(1-C)R} \tag{5-11}$$

For the case C< 1, that is, the number of available sites n_o is smaller than the initial radiocaesium N_o in water, then at equilibrium when $t \rightarrow \infty$

$$K_d \approx \frac{C}{(1-C)R} = \frac{n_0}{(N_0 - n_0)R} \tag{5-12}$$

For the case C>1, that is, the number of available sites n_o is larger than the initial radiocaesium N_o in water, then at large t,

$$K_d \approx \frac{Ce^{(C-1)N_0\alpha\, t}}{(C-1)R} = \frac{n_0}{(n_0 - N_0)R} e^{(C-1)N_0\alpha\, t} \tag{5-13}$$

K_d increases exponentially with t and can be quite large.

Results of the first isotherm for soils from location A, B and C are shown in Fig. 4.4, 4.5 and 4.6, respectively. In general, for larger masses the rates of decrease in water concentration were higher and the time for equilibrium was shorter. For masses smaller than 5 g, the equilibrium values of N_∞/N_o decreased with increasing mass. The equilibrium values were about the same and approached zero for masses larger than or equal to 5 g.

To explain the experimental results, we can differentiate Eq. (5-5) with respect to time and evaluate at t = 0, this gives

$$\frac{d[N(t)/N_0]}{dt} = -CN_0\alpha \qquad \text{at } t = 0 \tag{5-14}$$

If we can assume that the number of sites available for sorption is related to the mass according to the following equation

$$n_0 = km^y \qquad (5\text{-}15)$$

where k and y are positive constants depending on the characteristics and geometric factors of soils, then Eq. (5-14) can be rewritten as

$$\frac{d[N(t)/N_0]}{dt} = -km^y\alpha \qquad \text{at } t = 0 \qquad (5\text{-}16)$$

Eq. (5-16) shows that the initial rate of decrease is higher for larger mass m, and this has been observed in the experiment.

Using Eq. (5-15), Eq. (5-16) becomes

$$\frac{N_\infty}{N_0} \approx 1 - \frac{km^y}{N_0} \qquad \text{for } C < 1 \qquad (5\text{-}17)$$

According to Eq. (5-17), at constant initial water concentration increasing mass m decreases N_∞/N_0, and this has been observed in the experiment for small masses (less than 5 g).

For large masses (more than or equal to 5 g), experiment showed that N_∞/N_0 approaches zero at equilibrium, as predicted by Eq. (5-7) for the case $C > 1$.

Results of the second isotherm are shown in Fig. 4.7 - Fig. 4.12. These particular slurry ratios were chosen as it was initially observed that N_∞/N_0 did not approach zero at equilibrium at an arbitrary initial water activity concentration of 0.13 MBq ℓ^{-1} and thus fulfill the requirement that $C=n_0/N_0<1$, according to Eq. (5-6).

K_d values and % sorption at equilibrium at different initial water concentrations and slurry ratio are shown in Table 4.4. As seen from Fig. 4.7 – Fig. 4.12, N_∞/N_0 at equilibrium increased (decrease in % sorption) with increasing initial water concentration, in agreement with Eq. (5-6) for constant n_0 (implying constant mass m according to Eq. (5-15)). The initial rates of decrease of N/N_0 were about constant for the different initial water concentrations. This is predicted in Eq. (5-16) which indicates that the initial decrease is independent of the initial water concentration. From Table 4.4, it can also be seen that K_d at equilibrium increases with decreasing initial water concentration. This is predicted by Eq. (5-12) ($C< 1$ and $t\rightarrow\infty$) for constant mass and volume (implying constant n_0 and R).

Results of the first set of the third isotherm, the effects of sizes of particles on sorption behavior at constant initial water concentration and constant mass of 1 g, are shown in Fig. 4.13 and Table 4.5. This is apparently the case for $C<1$ as the values of N_∞/N_0 did not approach zero at equilibrium. As the diameter decreases, N_∞/N_0 decreases and the rate of initial decrease is higher.

For constant mass, particles with smaller diameter have larger surface area and thus have larger number of sorption sites. We assume that, for constant mass of soils, the number of sites for sorption is related to the size d of the soil particles according to the following equation

$$n_0 = \frac{z}{d^{\gamma}} \qquad (5\text{-}18)$$

where z and γ are positive constants depending on the characteristics and geometry of soils.

Using Eq. (5-18), Eq. (5-14) can be rewritten as

$$\frac{d[N(t)/N_0]}{dt} = -\frac{z}{d^\gamma}\alpha \qquad \text{at } t = 0 \qquad (5\text{-}19)$$

Using Eq. (5-18) and for C<1, Eq. (5-6) can be rewritten as

$$\frac{N_\infty}{N_0} \approx 1 - \frac{z}{N_0 d^\gamma} \qquad \text{as } t \to \infty \qquad (5\text{-}20)$$

Eq. (5-19) and Eq. (5-20) state that at constant initial water concentration, decreasing particle size d leads to increasing initial decrease of water concentration and decreasing N_∞/N_0. These trends have been demonstrated in Fig. 4.13.

Results of the second set (20 g of different sizes) of the third isotherm are shown in Fig. 4.14 and Table 4.5. Since N_∞/N_0 approaches zero as time increases, this set of data is for the case C>1, according to Eq. (5-7). From Fig. 4.15, the initial rate of decrease of water concentration can be observed to increase for smaller particle size, again confirming Eq. (5-19).

The data in Table 4.5 are those at t=24 h and at t=350 h, the latter can be taken effectively as t→∞ as equilibrium has long been attained. The % sorption and K_d increased as the size of the soil particles decreased.

Using Eq. (5-18) and for C>1, Eq. (5-7) and Eq. (5-13) can be rewritten as

$$\frac{N_\infty}{N_0} \approx \left(\frac{z}{N_0 d^\gamma} - 1\right)\frac{z}{N_0 d^\gamma} e^{-(\frac{z}{d^\gamma} - N_0)\alpha t} \qquad \text{for large t} \qquad (5\text{-}21)$$

$$K_d \approx \frac{z}{(z - N_0 d^{\gamma})R} e^{(\frac{z}{d^{\gamma}} - N_0)\alpha t} \qquad \text{for large t} \qquad (5\text{-}22)$$

At large enough t, the decrease in N_{∞}/N_0 and the increase in K_d are dictated by the exponential terms (C>1 implies $(z/d^{\gamma})>N_0$) in Eq. (5-21) and Eq. (5-22). Smaller size (smaller d) gave faster decrease in N_{∞}/N_0 and faster increase in K_d, and these had been observed in the experiment.

5.2 Conclusions

A simple model had been proposed and was able to explain some of the experimental results, namely:

- ☐ The initial decrease in water concentration increased with larger slurry ratio and smaller size of particles and was independent of initial water concentration.
- ☐ The equilibrium fraction sorbed to soils increased with larger slurry ratio of soils of random sizes at constant initial water concentration.
- ☐ For constant mass of soils of random sizes, increased initial water concentration decreased fraction sorbed to soils and decreased values of K_d.
- ☐ At constant slurry ratio and initial water concentration, K_d and % sorption increased as the size of the soil particles decreased.

However, the model can only describe certain trends but failed to describe the quantitative aspects of the findings. According to Eq. (5-6), spacing between equilibrium values for different masses should be proportional to the mass difference. Agreement between theory and experiment was good only for small masses. The theory also fails to fit theoretical values with experimental data to consistently deduce the sorption coefficient, which should be unique for a particular type of soils. Experiment also showed that N_∞/N_0 was never zero, showing that there may be some reversible exchange mechanism going on in the process.

CHAPTER 6

REVISED MODEL

In Chapter 5, a simple logistic model with a single parameter, the sorption coefficient, has been proposed to explain the rate of ^{137}Cs sorption to soils. The model was able to describe many observed experimental phenomena, but failed to give some quantitative results, e.g. a consistent sorption coefficient for a given type of soils.

This chapter aims at developing a revised logistic model to better describe the experimental results. Many studies (e.g. Cremers et al., 1988; Valcke and Cremers, 1994) have shown that radiocaesium interacts mainly with two types of sorption sites on soils: cation exchange sites, such as those on organic matter and planar sites of clays, and frayed edges of illitic clay minerals (Sanchez et al., 2000). The former interactions are reversible, whereas uptake on illitic minerals can be irreversible (Wauters et al., 1996). Results of our experiments showed that the activity concentration of ^{137}Cs was never zero, indicating that there may be some reversible exchange mechanism going on in the sorption process. Our revised model is thus based on simultaneous occurrence of the sorption and desorption processes.

6.1 Theory

The rate of sorption of radiocaesium to soils is postulated to depend on the number of radiocaesium in solution, the number of unoccupied sites available in soils, a sorption coefficient and a desorption coefficient, according to the following equation

$$\frac{dn(t)}{dt} = \alpha N(t)[n_o - n(t)] - \beta n(t) \qquad (6\text{-}1)$$

where n(t) = number of ^{137}Cs sorbed to soils at time t

n_o = number of available sorption sites in soils

N(t) = number of ^{137}Cs in water solution at time t

N_o = initial number of ^{137}Cs in water solution

α = proportionality constant relating to the sorption of ^{137}Cs to soil particles and is defined here as the sorption coefficient

β = proportionality constant relating to the desorption of ^{137}Cs back to the water solution and is defined here as the desorption coefficient

If negligible physical loss from e.g. sorption to the container wall and mass loss of water or sediment can be assumed, then

$$N(t) + n(t) = N_0 \qquad (6\text{-}2)$$

Using Eq. (6-2), Eq. (6-1) becomes

$$\frac{dn(t)}{dt} = \alpha(N_0 - n(t))(n_0 - n(t)) - \beta n(t) \qquad (6\text{-}3)$$

Eq. (6-3) is similar to Eq. (5-3) of the previous model, except that a desorption term βn(t) has been incorporated to describe the reversible process. Eq. (6-3) can be rewritten as

$$-\frac{dN(t)}{dt} = \alpha N(t)(n_0 - N_0 + N(t)) - \beta(N_0 - N(t)) \qquad (6\text{-}4)$$

or

$$\frac{dN(t)}{aN(t)^2 + bN(t) + c} = -dt \qquad (6\text{-}5)$$

where $a = \alpha$ (6-6)

$$b = \alpha(n_0 - N_0) + \beta \qquad (6\text{-}7)$$

$$c = -\beta N_0 \qquad (6\text{-}8)$$

Using integral table, Eq. (6-5) becomes

$$\frac{1}{\sqrt{b^2 - 4ac}} \ln \frac{2aN(t) + b - \sqrt{b^2 - 4ac}}{2aN(t) + b + \sqrt{b^2 - 4ac}} = \delta - t$$

where δ is the constant of integration. Alternatively,

$$\frac{1}{h} \ln \frac{2aN(t) + b - h}{2aN(t) + b + h} = \delta - t \qquad (6\text{-}9)$$

where $h = \sqrt{b^2 - 4ac}$ (6-10)

At t = 0, N(t) = N_0, Eq. (6-9) becomes

$$\frac{1}{h} \ln \frac{2aN_0 + b - h}{2aN_0 + b + h} = \delta$$

or,

$$\frac{1}{h} \ln g = \delta \qquad (6\text{-}11)$$

where $$g = \frac{2aN_0 + b - h}{2aN_0 + b + h} \tag{6-12}$$

Using Eq. (6-11), (6-9), becomes

$$\frac{1}{h}\ln\frac{2aN(t) + b - h}{2aN(t) + b + h} = \frac{1}{h}\ln g - t$$

or,

$$N(t) = \frac{h}{a}\left(\frac{1}{1 - ge^{-ht}}\right) - \left(\frac{b + h}{2a}\right) \tag{6-13}$$

At t = 0, N(t)= N_0, Eq. (6-13) becomes

$$N_0 = \frac{h}{a}\left(\frac{1}{1 - g}\right) - \left(\frac{b + h}{2a}\right)$$

or,

$$-\left(\frac{b + h}{2a}\right) = N_0 - \frac{h}{a}\left(\frac{1}{1 - g}\right) \tag{6-14}$$

Using Eq. (6-14), (6-13) becomes

$$N(t) = \frac{h}{a}\left(\frac{1}{1 - ge^{-ht}}\right) + N_0 - \frac{h}{a}\left(\frac{1}{1 - g}\right)$$

or,

$$\frac{N(t)}{N_0} = 1 - \frac{hg}{aN_0(1 - g)}\left[\frac{1 - e^{-ht}}{1 - ge^{-ht}}\right] \tag{6-15}$$

At t = 0, N(t)=N_0. As t → ∞, N(t→∞)= N_{eq} (number of ^{137}Cs in water solution at equilibrium) and the last term in bracket of Eq. (6-15) approaches 1, so that

$$F = N_0 - N_{eq} = n_{eq} = \frac{hg}{a(1 - g)} \tag{6-16}$$

$$f = \frac{N_0 - N_{eq}}{N_0} = \frac{n_{eq}}{N_0} = \frac{hg}{aN_o(1 - g)} \tag{6-17}$$

These are just the number and fraction of ^{137}Cs sorbed to soils at equilibrium, respectively, the values of which can readily be read off from the experimental data. Furthermore, as $t \to \infty$, the sorption process has reached equilibrium and the left-hand-side of Eq. (6-1) is zero, making

$$\alpha N_{eq}(n_0 - n_{eq}) = \beta n_{eq} \tag{6-18}$$

or,

$$\alpha N_{eq}(n_0 - N_0 + N_{eq}) = \beta(N_0 - N_{eq}) \tag{6-19}$$

If we assume that the number of available sites n_o is proportional to the mass of soils m, then

$$n_0 = km \tag{6-20}$$

where k, defined here as the mass constant, is a proportionality constant depending on the physical and chemical properties of the soil.

Using Eq. (6-20), Eq. (6-19) can be rearranged to become

$$\frac{km}{N_0 - N_{eq}} = 1 + \frac{\beta}{\alpha N_{eq}} \tag{6-21}$$

If we plot

$$\frac{m}{N_0 - N_{eq}} \text{ against } \frac{1}{N_{eq}}$$

a straight line should be obtained, with

$$\text{intercept} = \frac{1}{k}\text{, and}$$
$$\text{slope} = \frac{\beta}{k\alpha}$$

The ratio of the slope and intercept is

$$z = \frac{\beta}{\alpha} \qquad (6\text{-}22)$$

and is the ratio of the desorption coefficient to the sorption coefficient. We define z as the distribution ratio.

Using Eq. (6-7) and (6-22), it can be shown that

$$b = \alpha(n_0 - N_0 + z) \qquad (6\text{-}23)$$

Alternatively, using Eq. (6-8) and (6-22), it can be shown that

$$c = -\alpha z N_0 \qquad (6\text{-}24)$$

Using Eqs. (6-6), (6-10), (6-12) and (6-23), Eq. (6-15) becomes (with the help of Mathematica® 4)

$$\begin{aligned}\frac{N(t)}{N_o} = {} & (a(-1+e^{t\sqrt{a^2(4N_0z+(n_0-N_0+z)^2)}})\ (-n_0+N_0+z)+(1+e^{t\sqrt{a^2(4N_0z+(n_0-N_0+z)^2)}}) \\ & \sqrt{a^2(4N_0z+(n_0-N_0+z)^2)})/\ (a(-1+e^{t\sqrt{a^2(4N_0z+(n_0-N_0+z)^2)}})\ (n_0+N_0+z)+ \\ & (1+e^{t\sqrt{a^2(4N_0z+(n_0-N_0+z)^2)}})\ \sqrt{a^2(4N_0z+(n_0-N_0+z)^2)})\end{aligned} \qquad (6\text{-}25)$$

Eq. (6-25) can be simplified to become

$$\frac{N(t)}{N_0} = \frac{-q+\sqrt{o+p^2}+e^{a\sqrt{o+p^2}t}(\sqrt{o+p^2}+q)}{-r+\sqrt{o+p^2}+e^{a\sqrt{o+p^2}t}(\sqrt{o+p^2}+r)} \qquad (6\text{-}26)$$

where $o = 4N_0 z$ (6-27)

$$p = n_0 - N_0 + z \qquad (6\text{-}28)$$

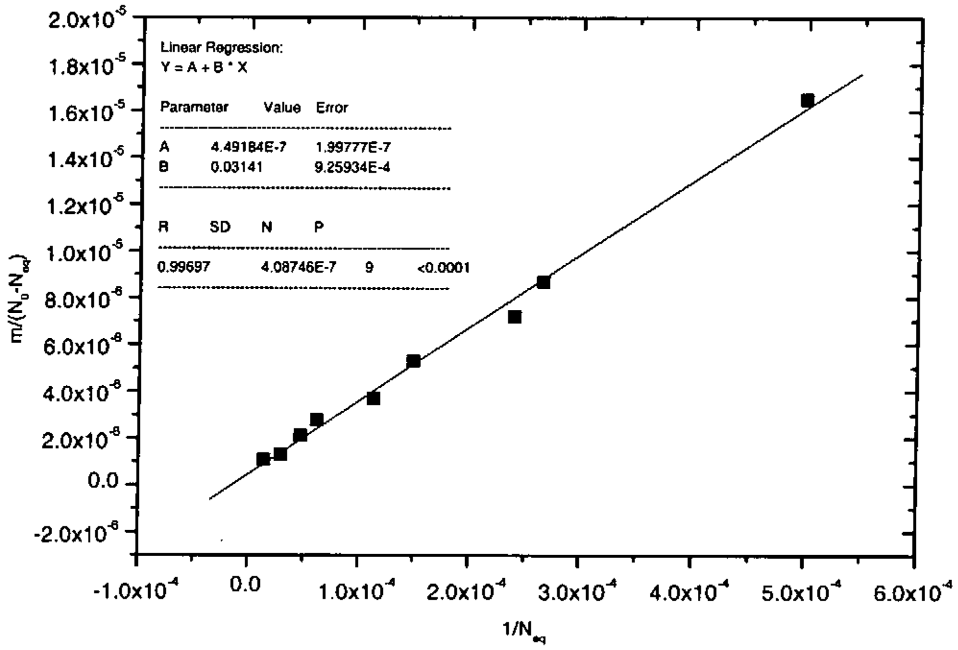
$$q = -n_0 + N_0 + z \qquad (6\text{-}29)$$

$$r = n_0 + N_0 + z \qquad (6\text{-}30)$$

N_o is the initial number of radiocaesium in solution and is a known value. The ratio of the intercept to slope of plot ($m/[N_o-N_{eq}]$) against ($1/N_{eq}$) gives the value of z. n_o can be found known using Eq. (6-20). The values of o, p, q and r can then be calculated using known values of n_o, z and N_o. The only unknown in Eq. (6-26) is the sorption coefficient α which can be obtained by fitting with experimental data. Once α is found, the desorption coefficient β can be obtained. The revised model can thus deduce the number of available site in soils n_o, the sorption coefficient α and the desorption coefficient β.

6.2 Results and Discussion

Plots of $m/(N_o-N_{eq})$ against $1/N_{eq}$ for soils in location A, B and C are shown in Fig. 6.1, Fig. 6.2 and Fig. 6.3, respectively. Straight lines were obtained. By determining the slopes and intercepts, the distribution ratio z can be obtained. Results of the findings are summarized in Table 6.1.



```
Linear Regression:
Y = A + B * X

Parameter      Value       Error
------------------------------------------------
A        4.49184E-7     1.99777E-7
B        0.03141        9.25934E-4
------------------------------------------------

R        SD       N       P
------------------------------------------------
0.99697      4.08746E-7    9       <0.0001
------------------------------------------------
```

Fig. 6.1 Plot of $m/(N_o-N_{eq})$ against $1/N_{eq}$ for soils in location A.

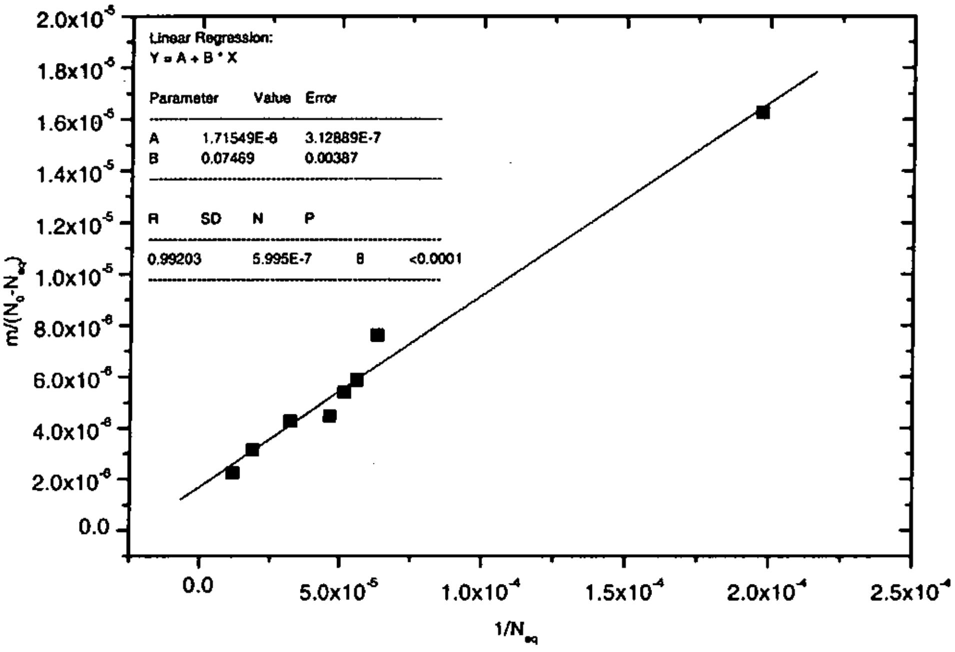


Fig. 6.2 Plot of m/(N_0-N_∞) against 1/N_∞ for soils in location B.

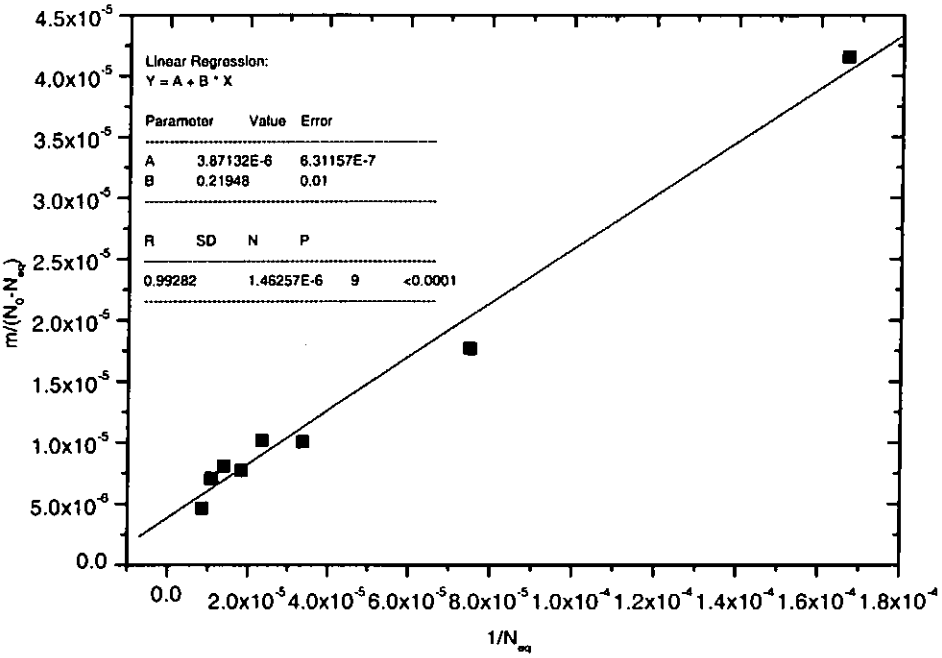


Fig. 6.3 Plot of m/(N_0-N_∞) against 1/N_∞ for soils in location C.

Table 6.1 Parameters obtained for soils in location A, B and C.

Location	**Intercept (10^{-6})** $\frac{1}{k}$	**Slope** $\frac{\beta}{kS}$	**Distribution ratio (ml g^{-1}) (10^4)** $z = \frac{\beta}{S}$
A	0.45	0.032	6.99
B	1.72	0.075	4.35
C	3.87	0.221	5.67

The values of o, p, q and r for different masses can be found by using Eq. (6-27) to (6-30). The values of α were then varied, using Origin (Microcal Software, Inc), until a best fit was obtained between Eq. (6-26) and experimental data. Typical plots of the fitted curves for soils in location A are shown in Fig. 6.4, 6.5 and 6.6. Values of β can be obtained using found values of α and z. Values thus obtained and the calculated values of the distribution coefficient K_d for soils in location A, B and C are shown in Tables 6.2, 6.3 and 6.4, respectively.

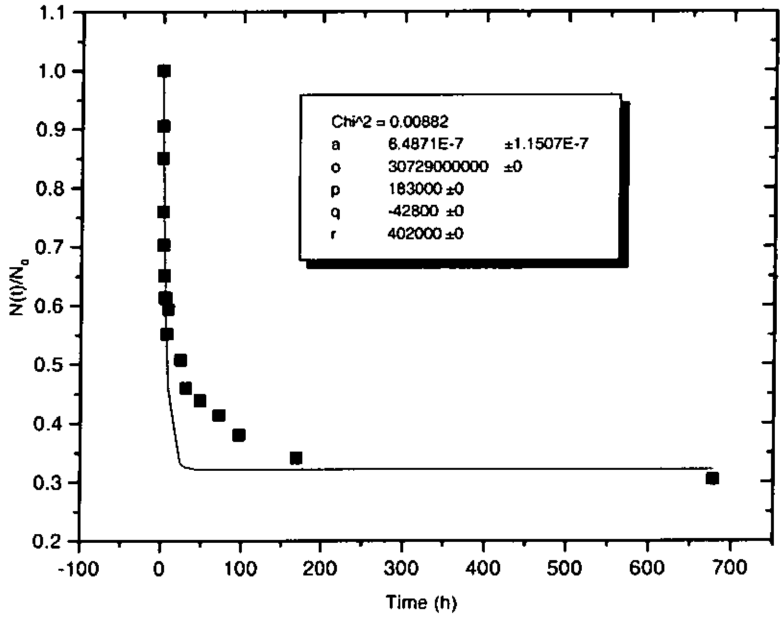


Fig. 6.4 Fitted curves for 0.1 g of soils in location A.

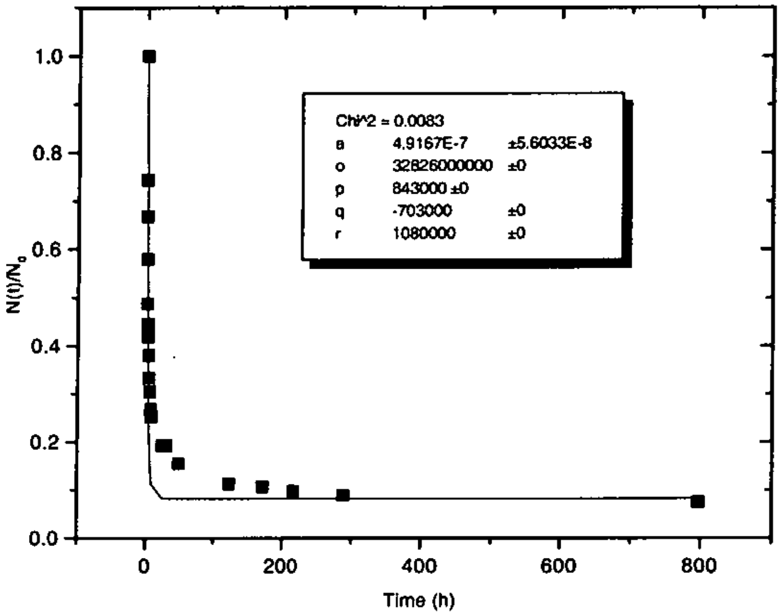


Fig. 6.5 Fitted curves for 0.4 g of soils in location A.

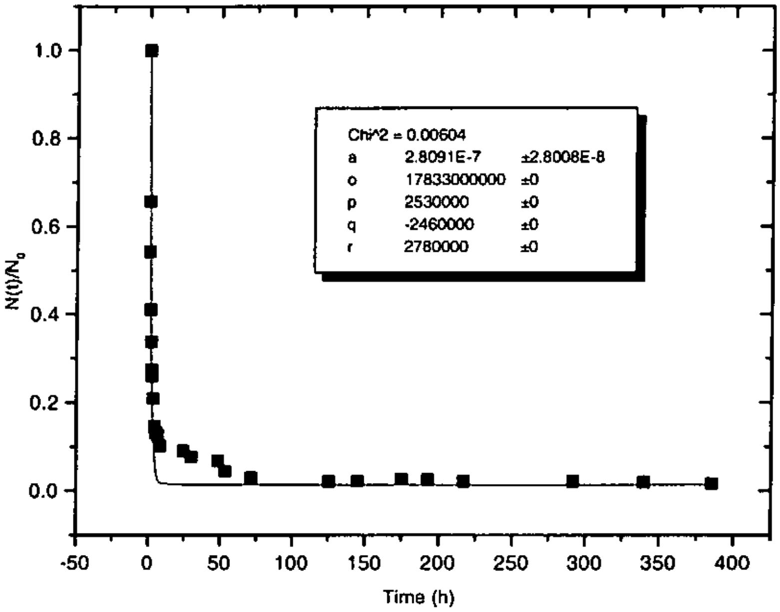


Fig. 6.6 Fitted curves for 2 g of soils in location A.

Table 6.2 Calculated and fitted values obtained for soils from location A.

Mass (g)	*N_0 (10^5)*	*n_o (10^5)*	*α (s^{-1}) (10^{-7})*	*β (s^{-1}) (10^{-2})*	*Chi-square (10^{-3})*	*K_d (24h) (10^3) (ml g^{-1})*	*K_d (equil) (10^4) (ml g^{-1})*
0.05	1.18	1.11	1.36	0.95	7.83	7.16	1.29
0.10	1.10	2.23	6.49	4.54	8.82	9.70	2.28
0.20	1.16	4.45	4.36	3.05	14.3	7.52	2.23
0.30	1.24	6.68	4.36	3.05	14.7	8.96	2.23
0.40	1.17	8.91	4.92	3.44	8.30	10.5	3.08
0.60	1.20	13.4	4.14	2.89	5.75	10.2	2.83
0.80	1.15	17.8	5.41	3.78	6.09	14.0	3.34
1.00	1.19	22.3	4.94	3.46	7.62	8.88	3.06
2.00	1.23	44.5	2.81	1.96	6.04	5.01	3.02

Table 6.3 Calculated and fitted values obtained for soils from location B.

Mass (g)	*N_0 (10^5)*	*n_o (10^5)*	*α (s^{-1}) (10^{-7})*	*β (s^{-1}) (10^{-2})*	*Chi-square (10^{-3})*	*K_d (24h) (10^3) (ml g^{-1})*	*K_d(equil) (10^3) (ml g^{-1})*
0.10	1.30	0.58	2.31	1.01	1.20	1.96	5.18
0.20	1.17	1.17	1.64	7.14	3.25	2.66	5.93
0.40	1.25	2.33	3.13	1.36	7.77	3.03	7.50
0.50	1.34	2.91	6.98	3.04	5.69	3.75	10.40
0.60	1.31	3.50	4.83	2.10	7.69	3.36	9.53
0.70	1.37	4.08	5.17	2.25	8.71	3.32	9.50
0.80	1.21	4.66	3.77	1.64	4.83	3.41	8.25
2.00	1.28	11.70	6.30	2.74	7.95	4.64	12.1

Table 6.4 Calculated and fitted values obtained for soils from location C.

Mass (g)	*N_0 (10^5)*	*n_o (10^5)*	*α (s^{-1}) (10^{-7})*	*β (s^{-1}) (10^{-2})*	*Chi-square (10^{-3})*	*K_d (24h) (10^3) (ml g^{-1})*	*K_d(equil) (10^3) (ml g^{-1})*
0.10	1.38	0.26	5.03	2.85	0.39	0.73	1.85
0.20	1.22	0.52	1.35	0.76	0.66	0.64	1.50
0.30	1.34	0.78	1.79	1.01	2.31	1.02	1.55
0.50	1.34	1.29	1.40	0.79	4.99	0.85	1.72
0.60	1.32	1.55	5.95	3.37	3.54	1.21	2.37
0.80	1.21	2.07	2.16	1.22	4.40	1.12	2.27
1.00	1.29	2.58	4.84	2.74	2.28	1.76	3.35
2.00	1.26	5.17	4.89	2.77	2.26	2.30	4.24
5.00	1.26	12.90	6.25	3.54	1.16	2.70	4.01

It can be seen from Table 6.2 that the Chi-square values were quite low, ranging from 0.58% to 1.47%, implying that the fitting was reasonably good. As apparent from Figs. 6.4 - 6.6, the fitting is generally very good for initial and final experimental data. The sorption coefficient α for different masses ranged from 1.36 to 6.49 (in unit of 10^{-7} s^{-1}), with a mean value of 4.31 (in unit of 10^{-7} s^{-1}) and a standard deviation of ± 1.49 (35%). The desorption coefficient β for different masses ranged from 0.95 to 4.54 (in unit of 10^{-2} s^{-1}), with a mean value of 3.55 and a standard deviation of ± 1.04 (35%). Considering the simplicity of the theory, the values of the sorption and desorption coefficients obtained were reasonably constant for a given type of soils, independent of masses of soils added and the time of contact between soils and ^{137}Cs solution.

In contrast, the values of the distribution coefficients K_d evaluated at 24 h were different from those evaluated at equilibrium. The values of K_d at 24 h ranged from 5.01 to 14.0 (in unit of 10^3 ml g^{-1}), with a mean value of 9.10 and a standard deviation of ± 2.51 (28%), whereas those evaluated at equilibrium ranged from 12.9 to 33.4 (in unit of 10^3 ml g^{-1}), with a mean value of 26.0 and a standard deviation of 0.65 (25%). Even though the standard percent deviations for K_d were smaller than that of the sorption and desorption coefficients, the values of K_d depended on the sorption time. The use of the distribution coefficient K_d may thus create some ambiguity when intercomparisons were to be made.

From Table 6.2, the number of available sites n_o for sorption was found to increase with the mass of soils added. According to Eq. (6-20), n_o should be linearly proportional to the mass m. Linearity has not been strictly observed as the shapes and surfaces of the soil particles were highly irregular, as evidence from the SEM pictures presented in Chapter 5. Eq. (6-20) is valid only if soil particles were all of the same size and shapes and with smooth surfaces.

Table 6.2 shows that the number of available sites n_o is larger than the initial number of ^{137}Cs in water solution N_o for all masses, with the exception of the smallest mass used (0.05 g). In principle, all sites should be filled, leaving no ^{137}Cs in the water solution. The experimental data indicated that ^{137}Cs was never absolutely zero in the water solution even after very long time (400 h), implying that desorption process may in fact be simultaneously occurring.

Similar conclusions can be drawn for soils in location B and C. The mean values of the sorption coefficient α, the desorption coefficient β and the mass constant k for soils from the three locations are shown in Table 6-5. The sorption coefficients α for soils in location A and B were about the same and were higher than that in location C. This may be due to the higher clay contents in these two locations and clay contents have been found to play an influential role in the sorption behavior of radiocaesium to soils (Boggs et al., 1985; Buckau et al., 1986; Kim, 1986). The highest K-contents in soils in location C may also lead to lower sorption coefficient as K-ions have the ability to block cesium sorption sites (Shenber and Erikkson, 1993). The desorption coefficient β for soils in location B was the smallest. This may be due to the relatively low value of pH associated with soils in location B as pH affects the adsorption process and influence the retention of radiocaesium in soils (Matkar et al., 1992). The value of the mass constant k was the highest for soils in location A and the lowest for soils in location C. For a given mass, the higher the mass constant k the more sites there are available for sorption. This is probably due to that the total clay and slit content (particle of size less than 0.02 mm diameter) in location A, B and C were 81.5%, 47.6% and 20.0%, respectively. For equal mass, the total surface area of smaller size particles is larger than that of larger size and this may lead to more sorption sites.

Table 6.5 Mean values of the sorption coefficient α, the desorption coefficient β and the mass constant k for soils in the three locations.

Location	α (s^{-1}) (10^{-7})	β (s^{-1}) (10^{-2})	k (10^{5})	K_d (24 h) (ml g^{-1}) (10^{3})	K_d (Equil.) (ml g^{-1}) (10^{3})
A	4.31	3.01	22.30	9.10	26.0
B	4.26	1.86	5.83	3.27	8.55
C	3.74	2.12	2.58	1.37	2.54

6.3 Conclusions

A revised model has been proposed, based on the simultaneous occurrence of the sorption and desorption processes. By fitting with experimental data, reasonably constant sorption and desorption coefficients were obtained. The coefficients were independent of the masses of soils used and the sorption time between soils and ^{137}Cs solution. The two new parameters were found to be more consistent than the conventional distribution coefficient K_d, the values of which were found to depend on the sorption time. The theory also provides an estimate of the number of sorption sites for different masses of soils. One of the drawbacks of the theory is that it takes longer time and more samples to determine the coefficients. It is proposed that the distribution coefficient K_d be used as a preliminary and then the present model be adopted to more unambiguously characterize the sorption behavior of ^{137}Cs to soils.

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.1 Conclusions

The general purpose of this study is to investigate the sorption behavior of ^{137}Cs in soils in Hong Kong reservoirs. This is important as the sorption of radiocaesium to soil constituents is one of the factors which determines the availability of radiocaesium to biological systems. Such information provides the long-term mobility of radiocaesium for remedial decisions and effective response to any accidental releases from the nearby Daya Bay nuclear power plants.

Removal of radiocaesium from water by settlement and sorption has been claimed by some researchers to have more influence than by diffusion across sediment-water interface. In this project, experiments were carried out to determine the sorption capability of soils in the Shek Lei Pui Reservoir. It is generally believed that physical and chemical properties, such as pH level, soil structure, soil texture, organic matter, cation exchange capacity and the potassium content determined the capacity for radiocaesium sorption by soils. Soils from three different locations (A, B and C) in the reservoir were analyzed and the variations of the physical and chemical properties of the soils were found to be high. Types of soils in location A, B and C can be classified as loam soil, clay loam and sandy loam, respectively. Soils from location A (water-level) had the largest percentage of slit and the lowest K-content. It also contained the largest percentage of sodium. Soils from location B (ground-level) was the most acidic and contained the highest value of aluminum. Soils in location C (catchment) had the largest percentage of sand, the smallest percentage of clay, the highest pH and the highest CEC value. In general, soils in Hong Kong were relatively low in organic matter and consistently more acidic than those in other countries. Results of scanning electron microscope (SEM) images showed that the shapes of soils were highly irregular. From energy dispersive X-ray (EDX) analysis, the main compositions found in the soils were Aluminum (Al), Silicon (Si), Iron (Fe) and Potassium (K). It was also observed that the high density polyethylene (HDPE) container used in experiments played a part in the sorption process and ways have to be devised to minimize its effect.

The time variations of ^{137}Cs concentration in water were monitored using five different isotherms until equilibrium has been established. The conductivity and the pH of the water-soil mixture were also monitored. The first isotherm was defined by varying the mass of soils added while maintaining a constant initial ^{137}Cs activity concentration. The mass of soils ranged from 0.05 g to 5 g. The second isotherm was defined by varying the initial water concentration with constant mass of random sizes. The concentrations varying from 29 kBq ℓ^{-1} to 120 kBq ℓ^{-1}. The third isotherm was defined by varying the sizes of soil particles while keeping constant initial activity concentration and mass of soil. The diameters of soils ranged from 0.15 mm to 2 mm. The fourth isotherm was defined by varying the mass of soil added in one specific pH value while maintaining constant initial activity concentration. The mass varied from 2 g to 7 g and three different pH values of 2.6, 3.0 and 3.6 were used. The fifth isotherm was defined by varying the pH values of water but maintaining constant mass of soil.

In general, the rates of decrease in water concentration were initially very high, higher for larger mass of soils added, and then slowed down. The larger the mass, the shorter was the time for equilibrium. Increased slurry ratio led to increased conductivity in soil-water mixture. The initial decrease in water concentration increased with larger slurry ratio and smaller size of particles and was independent of initial water concentration. The equilibrium fraction sorbed to soils increased with larger slurry ratio of soils of random sizes at constant initial water concentration. For constant mass of soils of random sizes, increased initial water concentration decreased fraction sorbed to soils and decreased values of K_d. At constant slurry ratio and initial water concentration, K_d and % sorption increased as the size of the soil particles decreased.

The sorption behavior of ^{137}Cs to soils has generally been described by the distribution coefficient K_d, a quantity commonly used by other researchers to the understanding and determination of the eventual fate of metal and radionuclides released in aquatic environments. However, it was found in this project that K_d depended on initial activity concentration, slurry ratio and sorption time.

A logistic model, based on irreversible exchange of ^{137}Cs to soil, was devised. The model was able to explain many of the experimental findings but failed to describe some of the quantitative aspects. Agreement between theory and experiment was good only for small masses. The theory also failed to fit theoretical values with experimental data to consistently deduce a sorption coefficient, which should be unique for a particular type of soils.

A revised model was devised to better describe the experimental data. Experiments showed that the fraction of activity concentration remaining in water was never zero, indicating that there may be some reversible exchange mechanism going. The new model was thus based on the simultaneous occurrence of the sorption and desorption processes. By fitting theoretical with experimental data, reasonably constant sorption and desorption coefficients have been obtained for a particular types of soils, independent of mass of soils added and the sorption time. The model also provides an estimate on the number of sorption sites for different types and masses of soils. One of the drawbacks of the theory is that it takes longer time and more samples to determine the coefficients.

7.2 Suggestions For Future Work

For further research work, the following investigations may be carried out:

- In our model, the number of available sites n_0 for sorption was postulated to increase linearly with the mass of soils added, but this had not been strictly observed. It might due to the fact that the shapes and surfaces of the soil particles were highly irregular, as evident from the SEM images. The postulate is valid only if soils particles were all of the same size and shapes and with smooth surfaces. We thus propose to use well-defined shape materials (e.g. resin) to test our model.

- Our model was based on the simultaneous occurrence of the sorption and desorption processes at irreversible and reversible sites, respectively. However, more than two types of sites in soils may be involved, as suggested by some researchers (Sanchez et al., 2000). Possible types of sites may be associated with fractions due to exchange, carbonates, ion oxide, organic matter and other constitutes. Experiments should be carried out to isolate these sites and the sorption behavior determined. The model should be revised to take these different sites into account.

REFERENCES

Antonopulos-Domis, M., Clouvas, A., Tervisidis, F. "Depot au sol dans la Grece du nord de Cs-134 a la suite de l' accident de Chernobyl". Radioprotection, Vol. 23, pp. 115-119 (1988) (in French)

Baeza, A., del Rio, M., Jimenez, A., Miro, C. & Paniagua, J. "Relative sorption of ^{137}Cs and ^{90}Sr in soil: Influence of particle size, organic mattercontent and pH". Radiochimica Acta, Vol. 68, pp. 135-140 (1995)

Bogg, S., Livermore, D. and Seitz, M. G. "Humic substances in natural waters and their complexation with trace metals and radionuclides". Argonne National Laboratory Report ANL, pp. 84-78 (1985)

Bolt G. H., Bruggenwert, M.G.M., Kamphorst, A. "Adsorption of cations by soil. In: Bolt, G.H., Bruggenwert, M.G.M. (Eds), Soil Chemistry. A Basic Elements". Elservier, Amsterdam, pp. 73-75 (1976)

Brady, Nyle C. The nature and properties of soils. Prentice Hall, Upper Saddle River, N.J., 740pp (1996)

Brobberg, A. "Distribution of cesium-137 in lake sediments". In: Proceedings of conference: 15. Regional congress of the international Radiation Protection Association (IRPA) on the radioecology of natural and artificial radionuclides, 10-14 September 1989, Visby, Sweden (1989)

Brouwer, E., Baeyens, E., Maes, B., and Cremers, A. "Cesium and rubidium ion equilibria in illite clay". Journal of Physical Chemistry, Vol. 87, pp. 1213-1219 (1983)

Buckau, G., Stumpe, R. and Kim, J. I. "American colloid generation in groundwaters and its speciation by laser-induced photoacoustic spectroscopy". Journal of the Less-Common Metals, Vol. 122, pp. 555-562 (1986)

Bunzl, K.and Kracke, W. "Soil to plant transfer of $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{137}Cs and ^{90}Sr from global fallout in flour and bran from wheat, rye, barley and oats, as obtained by field measurements". Science of the Total Environment, Vol. 63, pp. 111-124 (1987)

Bunzl, K., Forster, H., Kracke, W. "Residence times of fallout ^{239,240}Pu, ^{238}Pu, ^{241}Am and ^{137}Cs in upper horizons of an undistributed grassland soil". Journal of Environmental Radioactivity, Vol. 22, pp. 11-27 (1994)

Carlsson S. "A model for the movement and loss of ^{137}Cs in a small watershed". Health Physics, Vol. 34, pp. 33-37 (1978)

Champbell, L. S. and Davies, B. E. "Soil sorption of cesium modeled by the Langmuir and Freundlich isotherm equations". Applied Geochemistry, Vol. 10, pp. 715 (1995)

Clough, P. N. "Severe accident in :Energy and the environment, Dunderdale, J. (Ed)" Whitstable Kent :Whitstable Litho Ltd (1990)

Comans R. N. J., Middelburg J. J., Zonderhuis J., Woittiez J. R. W., De Lange G. J., Das H. A. and Van Der Weijden C. H. "Mobilization of radiocaesium in pore water of lake sediments". Nature, Vol. 339, pp. 367-369 (1989)

Cornell, R. M. "Adsorption of cesium on minerals: a review". Journal of Radioanalytical and Nuclear Chemistry, Vol. 171, pp. 483-500 (1993)

Cremers, A., Elsen A., De Preter P. and Maes A. "Quantitative analysis of radiocaesium retention in soils". Nature, Vol. 335, pp. 247-249 (1988)

DePeter, P "Radiocesium retention in the aquatic, terrestrial and urban environment: A quantitative and unifying analysis." Dissertations De Agriculatura, Katholieke University Universiteit te Fakulteit der Landbouwwetenschappen (1990)

De Koning, A., Geelhoed-Bonouvrie, P.A., Comans, R.N.J. "Comparing in situ distribution coefficients and exchangeability of radiocaesium in freshwater sediments with laboratory predictions". The Science of the Total Environment, Vol. 257, pp. 29-35 (2000)

Du, J., Dong, W., Wang, X., Liu, H., Tao, Z. "Sorption and desorption of radiocesium on calcareous soil and its solid components". Journal of Radioanalytical and Nuclear Chemistry, Vol. 231, pp. 183-185 (1998)

Dumat, C. and Staunton, S. "Reduced adsorption of caesium on clay minerals caused by various humic substances". Journal of Environmental Radioactivity, Vol. 46, pp. 187-200 (1999)

Duvernet, F. "Prévoir la trajectoire d' un nuage pollué: un pari gagné". La Recherche, Vol. 20, pp. 1406-1408 (1989) (in French)

Elejalde, C., Herranz, M., Legarda, F., Romero, F. "Determination and analysis of distribution coefficients of ^{137}Cs in soils from Biscay (Spain)". Environmental Pollution, Vol. 110, pp. 157-164 (2000)

Erten, H. N., Aksoyoglu, S., Hatipoglu, S., Gokturk, H., "Sorption of cesium and strontium on montmorillonite and kaolinite". Radiochimica Acta., Vol. 44/45, pp. 147-151 (1988)

Evans D. W., Alberts J. J. and Clark R. A. "Reversible ion-exchange fixation of cesium-137 leading to mobilization from reservoir sediements". Geochimica et Cosmochimica Acta, Vol. 47, pp. 1041-1049 (1983)

Frysinger, G. R. and Thomas, H. C. "Adsorption studies on clay minerals, III. Yttrium-caesium and cerium (III) caesium on montmorillonite". Journal of Physical Chemistry, Vol. 64, pp. 224-228 (1960)

Fredriksson, L., Eriksson, Å. and Lönsjö, H. "Studies on plant accumulation of fission products under Swedish conditions VIII: Uptake of ^{137}Cs in agricultural crops as influenced by soil characteristics and the rate of potassium fertilization in a three year microplot experiment". Research Institute of National Defense, Stockholm, Report FOA 4, pp. A4486-A4623 (1966)

Fredriksson, L. "Plant uptake of fission products III. Uptake of ^{137}Cs by Trifolium pratence as influenced by potassium and calcium level in the soil". Lantbrukskögskolans annaler, Vol. 36, pp. 41-60 (1970)

Gerrard, J. Fundamentals of soils. Routledge, New York, 230 pp (2000)

Gudiksen, P. H.; Harvey, T. F.; Lange, R. "Chernobyl source term, atmospheric dispersion and dose estimation". Health Physics, Vol. 57, pp. 697-706 (1989)

Hakonson, T. E. and Whicker, F. W. "Cesium kinetics in a montance lake ecosystem". Health Physics, Vol. 28, pp. 699-706 (1975)

Haward, B. J., Beresford, N.A., Burrow, L. Shaw, P.V., Curtis, E.J.C. "A comparison of caesium 137 and 134 activity in sheep remaining on upland areas contaminated by Chernobyl fallout with those removed to less active lowland pasture". Journal of the Society of Radiological Protection, Vol. 72, pp. 71-73 (1987)

Henry D. Foth. Fundamentals of soil science. Wiley , New York, 360pp (1990)

Hesslein R. H. "Whole-lake radiotracer movement in fertilized lake basins". Canadian Journal of Fisheries and Aquatic Sciences, Vol. 44, pp. 74-82 (1987)

Hird, A.B., Rimmer, D.L., Livens, F.R., "Factors affecting the sorption and fixation of cesium in acid organic soil". Europe Journal of Soil Science, Vol. 471, pp. 97-104 (1996)

HKSAR, the Hong Kong Special Administrative Region. Daya Bay Contingency Plan, Part 1. Government Printer, Hong Kong (1999)

Hsu, C. N., Liu, D. C., Chuang, C. L. "Equilibrium and kinetic sorption behaviors of cesium dand strontium in soils". Applied Radiation and Isotopes, Vol. 45, pp. 981 (1994)

Hsu, C. N., and Chang K. P. "Study of factors dominating sorption and desorption of Cs in soil". Radiochimica Acta, Vol. 68, pp. 129-133 (1995)

IAEA "Sediment K_d and concentration factors for radionuclides in the marine environment". IAEA Technical Reports Series No. 247, Vienna. (1985)

Ijuin , M., Picat, P. Sass, A., Grauby, A. "Determination of the diffusion coefficient of radioelements in the Rhone sediments". Health Physics, Vol. 24, pp. 665-672 (1973)

Jia Guogang, Testa Corrado, Desideri Donatella, Guerra, Meli Maria A., Roselli Carla and Belli Maria E. "Soil Concentration, vertical distribution and inventory of Plutonium, ^{241}Am, ^{90}Sr and ^{137}Cs in the Marche Region of Central Italy". Health Physics, Vol. 77, pp.52-61 (1999)

Kim, J. I. "Chemical behavior of transuranic elements in natural aquatic systems. In Handbook on the Physics and Chemistry of the Actinides, ed. A. J. Freeman and C. Keller". North Holland, Amsterdam, pp. 413-456 (1986)

Kirikopoulos A. V., Bulgakov, A. A., Popov V. E., Hilton J. and Comans R. N. J. "Long-term investigation of ^{137}Cs fixation by soils" Radiation Protection Dosimetry, Vol. 64. pp. 15-18 (1996)

Lee M. H. and Lee C. W. "Association of fallout-derived ^{137}Cs, ^{90}Sr and ^{239,240}Pu with natural organic substances in soils". Journal of Environmental Radioactivity, Vol. 47, pp. 253-262 (2000)

Lieser, K. H. and Steinkopff Th., "Chemistry of radioactive cesium in the hydrosphere and in the geosphere". Radiochimica Acta Vol. 48, pp. 79-87 (1989)

Linsalata, P. "Sources, distribution and mobility of plutonium and radiocesium in soils, sediments and water of the Hudson River and watershed, New York". New York University, Ph.D. dissertation (1984)

Livens, F. R., Loveland, P.J. "The influence of soils properties on the environmental mobility of caesium in Cumbria". Soil Use and Management, Vol. 43, pp. 69-75 (1988)

Maes, A. and Cremers, A. "Highly selective ion-exchange in clay minerals and zeolithes. In: J. A. Davies, K. F. Hayes (Eds)". Geochemical processes at mineral surface, Washington, DC: American Chemical Society, pp. 254-295 (1986)

Matkar, V. M., Narayanan, U., Bhat, I. S. & Pillai, K. C. "Geochemical association of plutonium in sediments of the Trombay coastal environment ". Journal of Radioanalytical and Nuclear Chemistry, Vol. 156, pp. 119-127 (1992)

Maubert, H., Duret, C., Combes, C., Roussel, S. "Behaviour of the radionuclides deposited after the Chernobyl accident in a mountain ecosystem of the French Southern Alps. In: Desmet, G., Nassimbeni, P., Belli, M., eds. Transfer of radionucides in natural and semi-natural environments". Elsevier Applied Science, London and New York (1990)

Muller, R. N. & Sprugel, D. G. "Distribution of local and stratospric plutonium in Ohio soils". Health Physics, Vol. 33, pp. 405-409 (1977)

Müller, P. "Caesium–137 in Rehwild der Bundersprepublik Deutchland". Der Saarjäger, Vol. 3, pp. 3-6 (1986)

Nathalie Kruyts and Bruno Delvaux "Soil organic horizons as a major source for radiocesium biorecycling in forest ecosystems". Journal of Environmental Radioactivity, Vol. 58, pp. 175-190 (2002).

Nishita, H., Kowalewsky, B.W. Steen, A. J. and Larson, K. H. "Fixation and extractability of fission products contaminating various soils and clays: ^{90}Sr, ^{91}Y, ^{106}Ru, ^{137}Cs and ^{144}Ce". Soil Science, Vol. 81, pp. 317-326 (1956)

Nishita, H., Taylor, P., Alexander, G. V. and Larson, K. H. "Influence of stable Cs and K on the reactions of ^{137}Cs and ^{42}K in soils and clay minerals". Soil Science, Vol. 94, pp. 187-197 (1962)

Ohnuki, T., "Sorption characteristics of cesium on sandy soils and their components". Radiochimica Acta, Vol. 65, pp. 70 (1994)

Periañez, R., Abril, J. M., Garcia-León, M. "Ra-isotopes in suspendend matter in an esturarine system at the southwest of Spain". Journal of Radioanalytical and Nuclear Chemistry, Vol. 183, pp. 395-407 (1994)

Persson, Ch., Rohde, H., De Geer, L. E. "The Chernobyl accident — A meterorological analysis of how radiobnuclides reached and were deposited in Sweden". Ambio, Vol. 16, pp. 20-31 (1987)

Polemio, M. and Rhodes, J. D., "Determining cation exchange capacity: A new procedure for calcareous and gypsiferous soil". Soil Science Society of America, Vol. 41, pp. 524-528 (1977)

Robbins J. A., Lindner G., Pfeiffer W., Kleiner J., Stabel H. H. and Frenzel P. "Epilimnetic scavenging of Chernobyl radionuclides in Lake Constance". Geochimica et Cosmochimica Acta, Vol. 56, pp. 2339-2361 (1992)

Robbins J. A. and Jasinski A. W. "Chernobyl fallout radionuclides in Lake Sniardwy Poland". Journal of Environmental Radioactivity, Vol. 26, pp. 157-184 (1995)

Rosner, G., Hötzl, H. and Winkler, R. "Simultaneous radiochemical determination of plutonium , strontium, uranium and iron nuclides and application to atmospheric deposition and aerosol sample". Journal of Analytical Chemistry, Vol. 338, pp. 606-609 (1990)

Sanchez A. L., Parekh N. R., Dodd B. A. and Ineson P. "Microbial component of radiocaesium retention in highly organic soils". Soil Science and Biochemistry, Vol. 32, pp. 2091-2094 (2000)

Santschi P. H., Nyffeler U. P., Anderson R. F., Schiff S. L., O'Hara P. and Hesslein R. H. "Response of radioactive trace metals to acid-base titrations in controlled experimental ecosystems: evaluation of transport parameters for application to whole-lake radiotracer experiements". Canadian Journal of Fisheries and Aquatic Sciences, Vol. 43, pp. 60-77 (1986)

Sawhney, B. L. "Kinetic of cesium sorption by clay minerals". Soil Science Society of America, Vol. 30, pp. 565-569 (1966)

Sawhney, B. L. "Selective sorption and fixation of cations by clays minerals: a review" Clays and Clay Minerals, Vol.20, pp. 93-100 (1972)

Schimmack, W., Bunzl, K., Kreutzer, K. and Schierl, R. "Effect of acid irrigation liming on the migration radiocaesium in a forest soil as observed by field measurements". Science of the Total Environment, Vol. 101, pp. 181-189 (1991)

Schulz, R. K., Overstreet, R. and Barshad, I. "On the soil chemistry of caesium-137". Soil Science, Vol. 89, pp. 16-27 (1960)

Shenber, M. A. and Eriksson, Å. "Sorption behaviour of caesium in various soils". Journal of Environmental Radioactivity, Vol. 19, pp. 41-51 (1993)

Smith J. T. and Comans R. N. J. "Modelling the diffusive transport and remobilization of ^{137}Cs in sediments: the effects of sorption kinetics and reversibility". Geochimica et Cosmochimica Acta, Vol. 60, pp. 995-1004 (1996)

Smith J. T., Comans R. N. J. and Elder D. G. "Radiocaesium removal from European lakes and reservoirs: key processes determined from 16 Chernoby-contamined lakes". Water Research, Vol. 33, No. 18, pp. 3762-3774 (1999)

Sposito G. The surface chemistry of soils. Oxford University Press, New York, pp. 234 (1984)

Stephens John A., Whicker Ward F. and Ibrahim Shawki A. "Sorption of Cs and Sr to Profundal sediments of a Savannah River Site Reservoir". Journal of Environmental Radioactivity, Vol. 38, pp. 293-315 (1998)

Tessier, A., Campbell, P. G. C., Bisson, M. "Sequential extraction procedures for the speciation of particulate trace metals". Analytical Chemistry, Vol. 51, pp. 844-850 (1979)

Valcke, E. and Cremers. A. "Sorption-desorption dynamics of radiocaesium in organic matter soils". The Science of the Total Environment, Vol. 157, pp. 275-283 (1994)

Wang Xiangke, Dong Wenming, Li Zhi, Du Jinzhou and Tao Zuyi "Sorption and desorption of radiocesium on red earth and its solid components: relative contribution and hysteresis". Applied Radiation and Isotopes, Vol. 52, pp. 813-819 (2000)

Wauters J, Elsen A, Cremers A, Konoplev AV, Bulgakov AA and Comans RNJ "Prediction of soild/liquid distribution coefficients of radiocaesium in soils and sediments. Part one: a simplified procedure for the solid phase characterization". Applied Geochemistry, Vol. 11, pp. 589-594 (1996)

WHO, "Chernobyl: Health Hazards from Radiocesium". Environmental Health, Vol. 24, World Health Organization, Copenhagen (1987)

Winegardner, Duanr L. An introduction to soils for environmental professionals. Lewis Publishers, Boca Raton, 270pp (1996)

LIST OF PUBLICATIONS

1. Man C. K. and Cheung Y.P. “Determination and analysis of sorption of ^{137}Cs to soils in Hong Kong reservoir”, accepted for publication in Environmental Pollution.

2. Man C. K. and Cheung Y.P. “Sorption behaviour of ^{137}Cs to soils in Hong Kong reservoir”, presented in 2001 American Radiation Safety Conference and Exposition (ARSCE), Cleveland, Ohio, USA, on June 10-14, 2001.