AU9212682

INIS-mf--13327

ALLIGATOR RIVERS

ANALOGUE PROJECT

A STUDY OF URANIUM AND THORIUM MIGRATION AT THE KOONGARRA URANIUM DEPOSIT WITH APPLICATION TO ACTINIDE TRANSPORT FROM NUCLEAR WASTE REPOSITORIES

TIMOTHY E PAYNE

Being a dissertation submitted to
Macquarie University in
partial fulfillment of requirements
for the MEnvStud degree.

Supported by the Alligator Rivers Analogue Project

Managed by Ansto

Australian Nuclear Science and
Technology Organisation

January 1991

ansto

A STUDY OF URANIUM AND THORIUM MIGRATION AT THE KOONGARRA URANIUM DEPOSIT WITH APPLICATION TO ACTINIDE TRANSPORT FROM NUCLEAR WASTE REPOSITORIES

by TIMOTHY E PAYNE

Being a dissertation submitted to Macquarie University in partial fulfillment of requirments for the MEnvStud degree.

January 1991

CONTENTS

Summary
Acknowledgements
Figures
Tables

PART I - THE KOONGARRA ANALOGUE IN CONTEXT 1

1 INTRODUCTION 1

1.1 The Nuclear Waste Problem 1
1.2 Radwaste Disposal Strategies 2
1.3 Repository Design and Siting 3
1.4 The Need for Geochemical Analogues 5
1.5 Objectives and Outline of Dissertation 5

2 GEOCHEMICAL ANALOGUES OF REPOSITORIES 10

2.1 General Features of Analogues 10
2.2 Analogues of Geochemical Processes 11
2.3 Examples of the Analogue Approach 13

2.3.1 Oklo 13
2.3.2 Morro do Ferro 15
2.3.3 Sedimentary Roll-Front Uranium 16
2.3.4 Basalt Glass 16
2.3.5 The Salton Sea Geothermal Field 17

2.4 Koongarra Overview 18

3 KOONGARRA URANIUM DEPOSIT 21

3.1 Background to the Analogue Study at Koongarra 21
3.2 Geology and Uranium Distribiution 21
3.3 Mineralogy 22
3.4 Hydrogeology 23
3.5 Groundwater Chemistry 24

3.5.1 Groundwater Evolution 24
3.5.2 Surface Waters 25
3.5.3 Kombolgie Formation 25
3.5.4 Primary Mineralised Zone 26
3.5.5 Weathered and Transition Zones 26

3.6 Attributes of the Koongarra Site 27

PART II - URANIUM AND THORIUM MIGRATION AT KOONGARRA 38

4 MIGRATION OF URANIUM IN THE No. 1 ORE BODY 38

4.1 Formation of the Dispersion Fan 38
4.2 Uranium Concentrations in Groundwaters Intersecting the Ore Body 38
4.3 Uranium Solubility and Speciation in Groundwater 39
4.4 Distance-Concentration Relationship for Magnesium 40
4.5 A Conceptual Model 41

5 MODELLING RADIONUCLIDE MIGRATION IN THE WEATHERED ZONE 49

5.1 Open System Modelling 49
5.2 The Multiphase Model 52
5.3 Groundwater Interactions in the Multiphase and Open System Models 53

6 THORIUM MIGRATION IN KOONGARRA GROUNDWATER 55

6.1 Importance of Thorium Immobility 55
6.2 Measurement of Thorium Concentrations 55
6.3 Results 56
6.4 Discussion 57

7 RADIONUCLIDE TRANSPORT BY COLLOIDS AND FINE PARTICLES 60

7.1 Potential Role of Colloids and Particles 60
7.2 Sampling 60
7.3 Filter Treatment 61
7.4 Analysis for Uranium and Thorium 61
7.5 Elemental and Radionuclide Content of Ultrafiltrates and Colloidal Particles 62
7.6 Distribution of ^{238}U and ^{230}Th Amongst Particulate and Dissolved Phases 63
7.7 Mineralogy of Colloids and Particles 64
7.8 $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ Activity Ratios 65
7.9 Distribution Ratios for ^{230}Th and ^{238}U Associated with Groundwater Particulates and Colloids 65
7.10 Evidence for Mobility of Actinium-227 66
7.11 Summary and Implications 67

8 LABORATORY STUDY OF URANIUM SORPTION 78

8.1 Background 78
8.2 Experimental 78

8.2.1 Solid Phase 78
8.2.2 Synthetic Groundwater 78
8.2.3 Procedure 79

8.3 Adsorption of ^{236}U and Isotope Exchange With ^{238}U 80
8.4 Distribution Ratios for Uranium Adsorption 81
8.5 Surface Complexation Modelling 81

8.5.1 Amorphous Ferric Oxide Phase 82
8.5.2 Groundwater Phase 82
8.5.3 Surface Complexation Reactions 82

8.6 Discussion 83

PART III - APPLICATION TO ACTINIDE MIGRATION FROM A NUCLEAR WASTE REPOSITORY 89

9 MOBILITY OF ACTINIDES IN GROUNDWATER 89

9.1 Chemistry of Actinides of Major Concern 89
9.2 Actinium 90
9.3 Thorium 91
9.4 Protactinium 92
9.5 Uranium 92
9.6 Neptunium 93
9.7 Plutonium 94
9.8 Americium 96
9.9 Curium 96
9.10 Concluding Comments 97

10 OVERVIEW OF KOONGARRA AS AN ANALOGUE FOR ACTINIDE MIGRATION 103

10.1 Types of Information 103
10.2 Limitations 104
10.3 Possible Further Work 105
10.4 Summary of this Dissertation 105

REFERENCES 107

APPENDIX - Uranium-series Disequilibrium 115

SUMMARY

It is intended that nuclear waste repositories should isolate radionuclides from the biosphere for timescales exceeding a million years. Laboratory experiments cannot provide a satisfactory basis for predicting repository performance over such a period, therefore, natural systems which have existed for comparable timescales are being studied as models of relevant geochemical processes. Such systems are known as 'Natural Analogues'.

The Koongarra Uranium Deposit in the Northern Territory has several attributes which make it valuable as a natural analogue. These attributes include:

- it is relatively undisturbed.
- it has a fairly well understood and straightforward geology and hydrology.
- a large existing geochemical database.
- measurable levels of radionuclides of relevance to repository assessment are present.
- relevant timescales may be estimated with reasonable precision.

Koongarra provides a site for developing and testing physical, chemical and mathematical models of radionuclide migration. The validity of these models is dependent on the assumptions upon which they are based. These assumptions include:

(a) the immobility of thorium,

(b) the omission of terms for colloidal transport, and

(c) modelling uranium sorption by a distribution ratio (R_d).

The assumed immobility of thorium and neglect of colloidal transport appear to be justified in the Koongarra system. However, the R_d approach is an inadequate description of uranium sorption.

As well as providing a testing ground for general models of radionuclide migration, the actinides which are present at Koongarra can be used as chemical analogues of transuranic elements. In particular, thorium(IV) and uranium(VI) are analogues of tetravalent and hexavalent actinides. Furthermore, actinium could provide an analogue for the environmental behaviour of americium(III) and curium(III). Uranium (VI) is mobile as dissolved species in solution, whereas thorium and actinium, whilst relatively immobile, are associated with colloids in the Koongarra system.

A prerequisite to utilising these chemical analogues is to determine the likely oxidation state distribution of transuranic elements in the environment. Plutonium, which exhibits several oxidation states, and neptunium(V), which has no fully satisfactory chemical analogue element, appear to present the most difficult problems in predicting future radionuclide behaviour.

ACKNOWLEDGEMENTS

I gratefully acknowledge the organisations participating in the Alligator Rivers Analogue Project (ARAP), namely JAERI (Japan), PNC (Japan), SKI (Sweden), UKDOE (UK), USNRC (USA), and particularly ANSTO (Australia).

The ARAP project would not have existed without the enthusiastic efforts of Dr P Airey, Dr C Hardy (who co-supervised this dissertation) and P Duerden, who has been directing the project for several years. My thanks to R Edghill, D Garton, Dr C Golian, R Lowerson, T Nightingale, D Roman, Dr A Snelling and Dr T D Waite, who have made major contributions to the ARAP study.

Denison Australia kindly provided access to, and accommodation at, Koongarra, on numerous occasions.

I am grateful to my wife, Narelle, for continuing support and patience, and to Nancy Payne, for very thoroughly reading the final draft.

My thanks to my supervisor at Macquarie University, Dr Frank Cattell, who was generous with both time and expertise.

FIGURES

1.1 Radioactive decay of spent fuel from a power reactor 7

1.2 Possible repository in basalt 8

1.3 NAGRA disposal system 8

2.1 Geology in the neighbourhood of a reactor zone at Oklo 19

2.2 Roll-front uranium deposit 19

3.1 Location of the principal uranium ore bodies in the ARUF 29

3.2 Plan of the vicinity of Koongarra 29

3.3 Geological section through the No.1 ore body 30

3.4 Distribution of major minerals and hematite alteration 31

3.5 Koongarra boreholes open for water sampling and standing water level measurements 32

3.6 Simplified hydrogeological plan showing standing water level contours 33

3.7 Location of PH49, KD1, and w-series boreholes 34

3.8 (a) Uranium concentrations (KD1 and w-series boreholes) 35
(b) Bicarbonate concentrations (KD1 and w-series boreholes) 35
(c) Magnesium concentrations (KD1 and w-series boreholes) 36

4.1 Simplified cross-section of the No.1 ore body
(a) prior to weathering of primary ore 42
(b) present day 42

4.2 Location of boreholes sampling groundwaters intersecting the No.1 ore body 43

4.3 Uranium concentrations in groundwater as a function of distance 43

4.4 Distribution of uranyl species as a function of pH
(a) at equilibrium with air 44
(b) fixed carbonate of 2 mmol/L 44

4.5 Magnesium concentrations in groundwater as a function of distance 45

4.6 Simplified model of Koongarra No.1 ore body, with primary ore zone depicted as a linear source 45

7.1 Hollow fibre ultrafiltration system 69

7.2 Thorium α-spectrum for 1 μm filter (PH14b) showing prominent ^{227}Th peaks 69

7.3 Effect of filtration on radionuclide levels in groundwaters 70

8.1 Alpha-spectrum of uranium in solution phase on completion of adsorption/desorption experiment 84

8.2 ^{236}U adsorption on Koongarra DDH52 (15 m) sample 84

8.3 Relationship between ^{238}U leached from solid and ^{236}U in solution 85

8.4 Distribution ratios for ^{236}U adsorption 85

8.5 Uranium sorption on Ranger and Koongarra cores with curves computed using surface complexation model 86

9.1 Eh/pH diagram for system Th-S-O-H 98

9.2 Eh/pH diagram for system U-C-O-H 98

9.3 Eh/pH diagram for system Np-C-O-H 99

9.4 Eh/pH diagram for system Pu-C-O-H 100

9.5 Eh/pH diagram for system Am-C-O-H 101

TABLES

1.1 Total amounts of spent fuel estimated to be produced by the year 2000 9

2.1 Possible chemical analogues for the long-lived radionuclides present in High Level Waste 20

3.1 Groundwater chemistry in the Kombolgie Formation and the No.1 ore body 37

4.1 Uranium concentrations moving down-gradient 46

4.2 Uranium speciation with and without the uranyl phosphate species $UO_2(HPO_4)_2^{2-}$ 47

6.1 ^{232}Th, ^{230}Th and $^{230}Th/^{234}U$ in Koongarra groundwaters 58

6.2 Comparison of ^{230}Th concentrations in groundwaters and nearby core samples 59

7.1 Colloid sampling details 71

7.2 Partitioning of ^{238}U and ^{230}Th in 1 μm-filtered groundwater 71

7.3 Partitioning of cations in 1 μm-filtered groundwater 72

7.4 Distribution of ^{238}U and ^{230}Th amongst particles and ultrafiltrates 73

7.5 Extractable metals in groundwater particles and DDH52 core sample 73

7.6 Isotope ratios in ultrafiltrates, acid extractable particle phases, and residual phases
(a) $^{234}U/^{238}U$ 74
(b) $^{230}Th/^{234}U$ 74

7.7 Distribution ratios for ^{238}U and ^{230}Th in accessible phases 75

7.8 Distribution ratios based on total ^{238}U and ^{230}Th 76

7.9 Distribution ratios for ^{238}U and ^{230}Th on 'colloidal ferrihydrite' 76

7.10 $^{227}Th/^{230}Th$ in particulate fractions and ultrafilter backflush 77

8.1 Composition of ARUF synthetic groundwater 87

8.2 Triple layer model parameters for $Fe_2O_3.H_2O$ (amorphous) 87

8.3 Surface group hydrolysis and major ion surface complexation reactions with associated constants for $Fe_2O_3.H_2O$ (amorphous) in synthetic groundwater 88

8.4 'Best-fit' formation constants for uranyl surface species of major significance 88

9.1 Reported stability constants for (1,1) actinide complexes with major inorganic ligands 102

9.2 Reported actinide hydroxide solubility products 102

PART I THE KOONGARRA ANALOGUE IN CONTEXT

CHAPTER ONE

INTRODUCTION

1.1 The Nuclear Waste Problem

Radioactive nuclear wastes are an inevitable by-product of electric power generation by nuclear reactors, and have also been produced in substantial quantities by nuclear weapons programs. Smaller amounts have originated in reactors used for research or medical purposes. Some of these wastes have been deemed to be relatively harmless, and have been disposed of by shallow burial or pumped into the sea. More hazardous wastes have been "temporarily" stored, which has allowed some of the highly radioactive short-lived isotopes to decay while the problem of permanent disposal has been deferred. This problem is still awaiting a solution and the temporary storage has become indefinite.

Spent fuel from nuclear power generation contains a number of highly radioactive isotopes. These include transuranic elements such as plutonium, americium, curium and neptunium; and fission products such as cesium-137 and strontium-90.

After removal from the reactor, nuclear fuel rods are placed in cooling ponds for about a year to allow the decay of highly-active short lived fission products. The fuel rods may then be reprocessed to recover unused uranium and plutonium to be used as reactor-fuel. The remaining material is "high level waste" (HLW), which is initially converted to a solid form known as "calcine", and subsequently to a more durable waste form such as a borosilicate glass or a synthetic rock. This is then placed in resistant containers, which will ultimately be disposed of in a repository. An alternative strategy is the direct disposal of irradiated fuel without further processing other than encapsulation.

The required containment period for HLW is about a million years, by which time the waste will be no more radioactive than the original uranium which was mined to produce the nuclear fuel (Ringwood 1978). The decrease in activity over this time period is illustrated in figure 1.1. After about 600 years, the transuranic elements will be responsible for most of the radioactivity present.

The quantity of spent-fuel HLW accumulated in the United States until 1984 was 11 700 tonnes (5300 m^3), together with approximately 370 000 m^3 of lower level wastes. The amount of HLW in the United States increases by 1000-2000 tonnes annually (Krauskopf 1988). Estimates of the amounts of spent fuel expected to be produced by the year 2000, in all countries with significant nuclear power programs, are given in table 1.1. The total amount, some 200 000 tonnes is clearly going to present a significant problem, which at present has not been solved.

Finding an appropriate way to deal with nuclear waste and establishing its safety over timescales of the order of a million years is one of the most important environmental problems currently confronting mankind.

1.2 Radwaste Disposal Strategies

The design of repositories is far from settled. In fact there are several broad concepts being considered for the disposal of canisters containing HLW (Milnes 1985; Parker et al. 1984; Winograd 1981). These include:

- extra-terrestrial disposal - shooting the canisters into space
- emplacement within the ice-sheets covering Antarctica or Greenland
- disposal into sediments in the middle of stable areas of the ocean floor
- lowering down very deep boreholes drilled 10 km into the earth's crust
- direct injection of liquid waste into porous or fractured rock at depths over 1000 m
- burial near the ground surface in arid regions where the water table is very deep
- emplacement in deep mined repositories.

Extra-terrestrial disposal would provoke widespread apprehension amongst the community, particularly after the Chernobyl and Space Shuttle accidents. Because of enormous energy costs, only small volumes of waste could be accommodated. The possibility of catastrophic launch failure and resultant worldwide fallout ensures international opposition to this option.

The ice-sheet concept is not favourably regarded by relevant nations, partly because of the costs and risks associated with transport and disposal of radioactive waste in the remote and inhospitable polar environment. Also, the behaviour of the ice mass is not well understood, and it is likely that fluctuations in the polar ice caps occur over intervals comparable to or smaller than the required isolation time for radwaste (Parker et al. 1984). Possible changes caused by the greenhouse effect create further uncertainty. In addition to these problems, disposal of nuclear waste in Antarctica is contrary to the Antarctic Treaty of 1959, and access to Greenland is dependent on the approval of the Danish Government.

The subseabed disposal of nuclear waste remains the subject of intense investigation by several countries. A stable and remote area of the ocean floor would be chosen, and any radioactivity which escaped would be greatly diluted by seawater. However, transport processes in the marine environment are poorly understood, and it is possible that legal aspects of radwaste disposal under international waters would be a major obstacle. Critics also cite difficulties in monitoring the disposal area and the irretrievability of the waste packages as drawbacks of this technique.

The very deep hole (VDH) concept is unique because of the very great depths involved. This means that wastes emplaced in a VDH would be remote from the biosphere and surface events. Also, there would be no need to maintain a workforce underground whilst constructing and operating the facility, which would reduce occupational hazards. The VDH concept may provide a viable alternative to the other options, however it has not been thoroughly researched and knowledge of the interior of the earth at relevant depths is

scanty. Present technology limits the size of canisters which can be emplaced. Currently there is no drilling rig capable of drilling a hole with the modest diameter of 50 cm to a depth of 6 km (These dimensions correspond to the current USA reference VDH system). The VDH concept was studied in Germany but abandoned because of the volume limitations it would impose (Parker et al. 1984).

There is considerable previous experience with the technique of liquid waste injection in the petroleum industry. Nuclear waste could be disposed of at a relatively low cost by this method. However, a major problem is that the initial state of the injection zone is inherently poorly defined. Thus its long term behaviour cannot be predicted with any degree of certainty.

Burial near the surface (15-100 m depth) in arid regions has been advocated by Winograd (1981) and would involve a huge cost saving relative to other alternatives. This proposal has received little attention, probably because of the high risk of exhumation when wastes are buried within a hundred metres of the surface, and the possibility that a climatic change could result in the disposal site becoming a region of active groundwater flow.

The mined geological repository is favoured for several reasons. These include:

- apparent resistance to breaching either from natural processes or accidental human intrusion
- the feasibility of construction with existing technology, or projected technological advances, at costs which are not prohibitive
- the possibility of retrieving the waste, or mitigating the adverse impacts, if unexpected events occur which drastically reduce the safety of the system
- a variety of sites are available for comparative evaluation as host rocks.

Geologic disposal is the preferred option for ultimate disposal in most countries with nuclear power programs, including France, Germany, Japan, the UK, Holland, and Germany. In the USA, a federal committee in 1979 recommended geologic disposal above all other alternatives (Lemons et al. 1989), and Yucca Mountain in Nevada has recently being selected as the preferred site.

1.3 Repository Design and Siting

Nuclear waste repositories are being designed in accordance with an approach known as the "multiple barrier concept", in which a series of engineered and natural barriers prevent the escape of radwaste to the biosphere. The overall design involves a network of tunnels deep underground which are accessed by vertical shafts. A possible layout for a repository is shown in figure 1.2.

A representative system is that being considered by NAGRA (National Cooperative for the Storage of Radioactive Waste, Switzerland). The proposed NAGRA repository will be excavated between 1000 m and 1800 m below the surface in crystalline basement rocks overlain by a sequence of sedimentary rocks (Chapman et al. 1984). The nuclear waste will be converted to a borosilicate glass wasteform which will be enclosed in

stainless steel canisters. These will be encased in a thick cast iron shells, and the resulting assemblages placed in tunnels. The canisters will be surrounded by blocks of highly compacted bentonite clay, completely filling the tunnels (figure 1.3).The bentonite is expected to absorb water from the surrounding rock and expand to fill any remaining void space. At the completion of operations the access shafts will be backfilled, probably with bentonite clay mixtures.

A similar design is envisaged for repositories in the United States (Brookins 1984). In this case, the canister containing the fuel assembly will be held in another cylinder and this waste package inserted in a hole which is sleeved as an additional barrier. Outside the sleeve and filling the remaining volume will be a backfill material containing clay minerals and reductants. This is designed firstly to repel water and secondly to sorb radionuclides if they escape from the waste form.

The final barrier in both systems is the rock in which the repository is located. The host rock should impede the access of groundwater to the wasteform, and, if breaching occurs, should be capable of preventing the transport of radionuclides to the biosphere. This necessitates the following:

a) Geological stability

b) Long groundwater flow paths to the surface

c) Slow rates of groundwater flow and absence of major fractures

d) High sorptive capacity of the rock for the radionuclides contained in radwaste.

The host rock should not be in an area where extensive drilling for water or mineral resources is likely to occur, a requirement which is not satisfied if disused mines are used as repositories. It should be technically feasible to mine stable caverns in the selected rock.

Different countries have selected various rock types as being suitable for nuclear waste repositories.

Salt formations (either bedded salt or salt domes) are being investigated as host rocks in several countries, including Germany and the Netherlands (Lau 1987). Salt has several adverse characteristics. These include potential solubility, water content, heterogeneity and association with valuable resources. A significant attribute of salt is that it is self-sealing.

Granite and related coarse grained silicate rocks are favoured in many countries, including the UK, Sweden, and France. A problem with this rock type is that granite formations are invariably fractured. The preferred USA repository site (Yucca Mountain) is composed of tuff.

Repository sites in bedded clay and shale are being studied in some countries, including Italy and Belgium (Lau 1987). Several other rock types, including basalt and anhydrite are also being considered.

1.4 The Need For Geochemical Analogues

A nuclear waste repository system will be required to prevent the return of radionuclides to the biosphere over timescales exceeding a million years.

Demonstrating the safety of a proposed repository over such a timescale presents geoscientists with unprecedented challenges - not only in the scientific problems of understanding and modelling the behaviour of a modified geological system for thousands of years into the future, but also in convincing the community of the validity of the predictions.

The extrapolation of the results of laboratory experiments cannot alone provide a satisfactory guarantee of repository safety. This is because experimental timescales are restricted to a few years at most. Processes which are absent or negligible over such intervals may become significant over a period of thousands of years. In some cases the cumulative effect of thousands of years can be simulated over a shorter period. For example, radiation damage can be accelerated by exposure to high levels of radiation in a reactor. However, laboratory measurements take place on systems which cannot be proven to be adequately representative of the natural environment -indeed this may be impossible to simulate.

An approach which has received increasing attention in recent years is to study existing natural systems exhibiting physical and chemical properties which are similar to those of proposed nuclear waste repositories. No natural system could provide information about all aspects of an engineered repository. However, several geological environments which may be used for modelling particular aspects of repository behaviour have been identified. These are termed "natural analogues" or "geochemical analogues". These environments range from those applicable to the glass wasteform itself to geological systems which represent the migration of radionuclides through an unperturbed rock formation, the "far-field".

Ultimately the synthesis of information obtained from a variety of analogue systems may provide convincing evidence of the safety of nuclear waste repositories.

Uranium deposits have many similarities with mined radwaste repositories - both being rock systems containing an accumulation of radionuclides which may potentially be mobilised by groundwater. Therefore uranium ore bodies are obvious subjects for study as analogues of nuclear waste repositories.

1.5 Objectives and Outline of Dissertation

The subject of this dissertation is the Koongarra uranium deposit in the Northern Territory, Australia. Since 1982, this deposit has been studied as an analogue of a nuclear waste repository by a team of scientists from several countries.

The Koongarra No.1 ore body shows extensive evidence of movement of radionuclides in groundwaters. In particular, this is shown by the presence of a "dispersion fan" - which is an area containing elevated concentrations of uranium and other radionuclides which have been transported from the zone of original uranium accumulation (the primary ore zone) into the surrounding rocks. A quantitative understanding of this feature would be a significant step towards the modelling of the possible leakage of radionuclides from nuclear waste repositories.

The scope of this dissertation is restricted to actinide migration, both at Koongarra and in the repository situation. ("Actinide" refers to elements after actinium in the periodic table). The reasons for this are:

a) the toxicity and half-lives of actinides makes them the greatest potential threat if leakage from a repository occurs after several hundred years of storage

b) processes relevant to actinide migration occur at Koongarra

c) it places a reasonable limit to the scope of the study.

This dissertation particularly addresses the following:

- the relevance of Koongarra as a natural analogue and the way in which the study at Koongarra complements results from other analogue sites.

- the migration of uranium and thorium in groundwaters intersecting the deposit.

- the assumptions and data requirements of the mathematical models which have been proposed to describe radionuclide migration at Koongarra.

- the application of results from Koongarra to the possible migration of actinides from a nuclear waste repository.

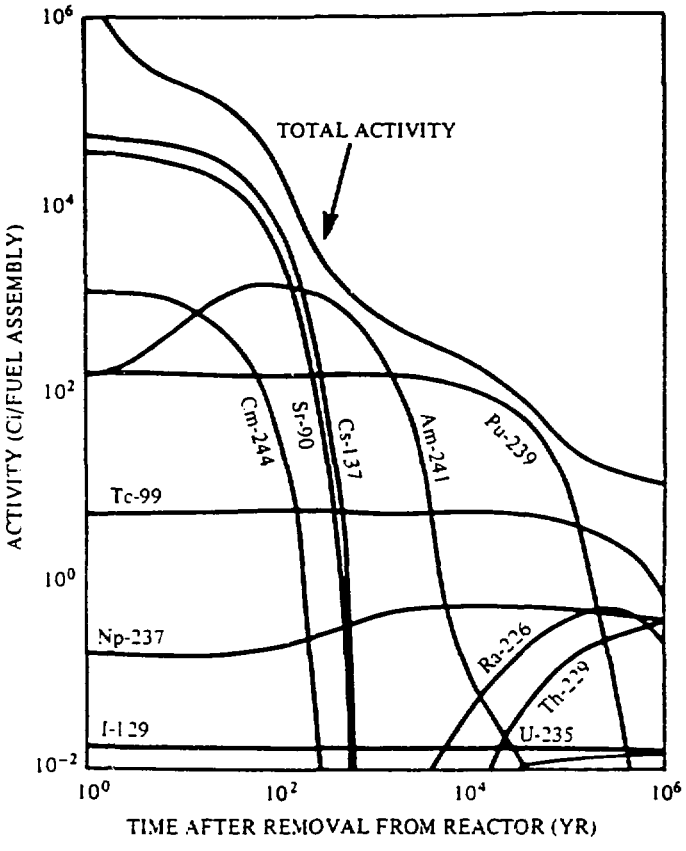


Figure 1.1 Radioactive decay of spent fuel from a power reactor (from Brookins 1984).

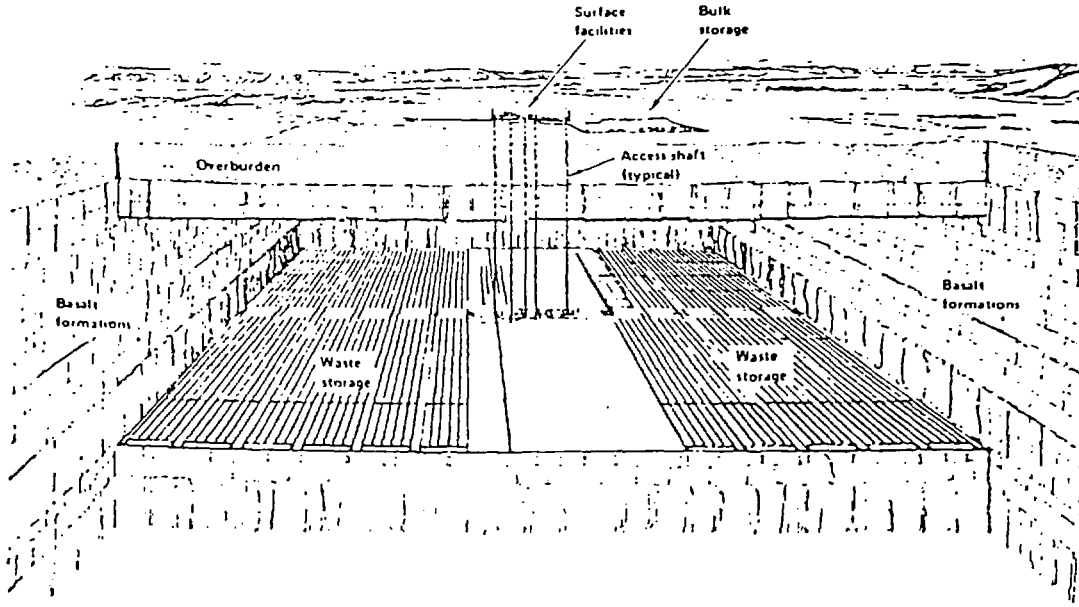


Figure 1.2 Possible repository in basalt (from Parker et al. 1984).

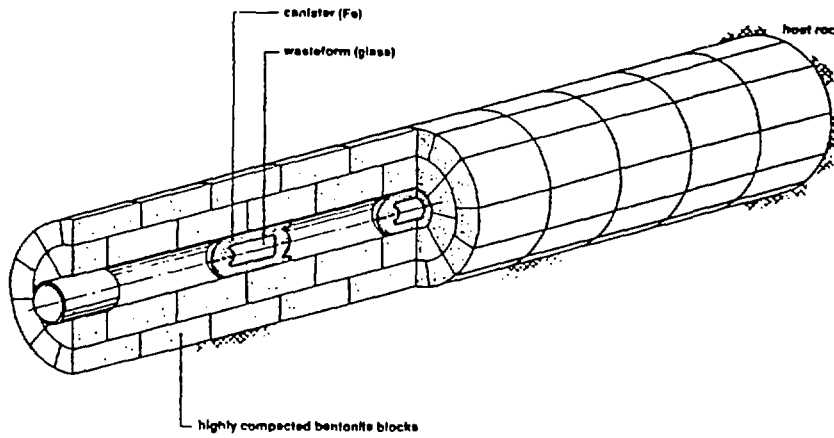


Figure 1.3 NAGRA disposal system (from Chapman et al. 1984)

Table 1.1 Total amounts of spent fuel estimated to be produced by the year 2000 (adapted from Krauskopf 1988).

Argentina	5800	Italy	3700
Belgium	3000	Japan	21000
Bulgaria	2500	Korea (south)	4400
Canada	38000	Romania	8200
China	1300	South Africa	1200
Czechoslovakia	3800	Spain	5100
Finland	1400	Sweden	5000
France	37000	Switzerland	2000
East Germany	2100	Taiwan	2600
West Germany	11000	United Kingdom	38000
Hungary	1400	United States	41600
India	5000	USSR	12600
	(tonnes)		(tonnes)

CHAPTER TWO

GEOCHEMICAL ANALOGUES OF REPOSITORIES

2.1 General Features of Analogues

The key issue in assessing the long-term safety of a nuclear waste repository is whether it is possible to predict the nature and consequences of events which may occur over long time periods far into the future. The major attributes of the geochemical analogue approach to this problem have been summarised (Birchard and Alexander 1983):

a) Relevant natural processes which have occurred over timescales exceeding thousands of years can be studied.

b) The behaviour of an artificial element in nature can be predicted by comparison with a natural element of similar chemistry.

c) Complex processes occurring over an extended area can be studied. Laboratory scale tests may overlook significant factors which become important in more complex systems.

No single analogue for a complete radioactive waste disposal system exists. However, natural analogues which are relevant to the most important geochemical processes leading to the release of radionuclides to the biosphere have been found.

For an analogue to be useful, it is essential that a timescale for the processes being studied can be established. This requirement may be satisfied if a geological process has a well defined start, or if it is at a steady state. A spatial discontinuity, which is some position or boundary from which migration of elements may be measured (such as an igneous intrusion) may provide a basis for establishing a time frame for the process (Airey and Ivanovich 1986). In the case of the Koongarra deposit, the initial mobilisation of radionuclides may be taken to coincide with the weathering of the primary uranium bearing minerals leading to radionuclide release to the groundwater (Airey 1986).

With the exception of uranium and thorium series radionuclides, the most important long-lived radionuclides present in HLW, such as technetium, neptunium, plutonium, americium and curium, are not normally present in measurable concentrations in relevant natural systems. Thus, in order to predict the behaviour of these critical radionuclides, chemical analogue elements with similar physico-chemical properties are required. These properties include redox characteristics, ionic radius, and stabilities of complexes (eg with OH^-, CO_3^{2-}, or organic ligands).

Table 2.1 indicates candidate analogue elements for nuclides present in HLW. Uranium is a possible analogue for several of the components of HLW, which is fortuitous, since it is a common radionuclide and has been extensively studied in the natural environment because of its importance as a nuclear fuel. Also, thorium is an analogue for some of the actinides in HLW. Thorium is present at Koongarra, because ^{230}Th is a member of the ^{238}U decay chain. Therefore, a uranium deposit such as Koongarra, as well as yielding information about the radioactive elements which it contains, is also useful as a model for other components of HLW.

2.2 Analogues of Geochemical Processes

The geochemical processes which may result in release of radionuclides to the biosphere, and the analogues which have been proposed to model them, relate to the following sequence of events (modified from Chapman et al. 1984):

1. Breakdown of buffer and seal materials.
   Process: The clay buffer functions as an impermeable flow barrier and impedes radionuclide transport. If it is subjected to elevated temperatures, its hydraulic conductivity will increase, possibly leading to groundwater intrusion.
   Analogues:
   a) Low grade metamorphism of thick sedimentary sequences which contain clay minerals.
   b) Igneous intrusions into clay formations.

2. Waste canister corrosion
   Process: The waste canister will be subject to corrosion in extreme thermal/chemical conditions.
   Analogues:
   a) Native iron metal in geological environments (steel canister).
   b) Native copper deposits (copper canister).
   c) Metal artefacts located in surface or near surface environments, such as early weaponry and tools.

3. Waste form dissolution and breakdown
   Process: The waste matrix, such as borosilicate glass, uranium oxide spent fuel, or synthetic crystalline wasteform (eg. SYNROC) will be leached or dissolved by groundwater, possibly of aggressive chemistry at high temperatures, and subjected to the effects of radiation damage.
   Analogues:
   a) Natural uraninite, particularly at Oklo, an African uranium deposit where natural nuclear reactions are known to have occurred.
   b) Volcanic glasses (for vitrified waste).
   c) Minerals such as zirconalite and hollandite (for crystalline waste forms).

4. Solubility and mobility of radionuclides in the near-field
   Process: In the immediate vicinity of the repository extreme physical and chemical conditions will exist. The movement of radionuclides will be determined by a number of complex interrelated processes - including adsorption, precipitation, complexation, and reduction/oxidation reactions.
   Analogues:
   a) Natural radionuclides and analogue elements (eg lanthanides) in groundwaters.
   b) Mobilisation of radionuclides from uranium deposits.

5. Fixation of radionuclides in minerals
   Process: Nuclides released from the waste will be incorporated within new minerals formed under the hydrothermal conditions in the near-field of the repository. This is probably of most significance if container failure occurs within the thermally active period shortly after disposal.
   Analogues:

a) Contact metamorphism reactions resulting from igneous intrusions into various rock types representative of bedrock formations of repositories.
b) Hydrothermal activity along fractures in various rock types.

6. Radiolysis
Process: Water, when subjected to intense radiation, decomposes giving products such as H_2, H_2O_2, OH^-, O_2, and H^+. It is thought the H_2 produced will be lost by diffusion giving an oxidising near-field, containing oxidants such as O_2, and H_2O_2 - creating a redox front. Oxidation of several important radionuclides (eg U, Np, and Tc) could increase their solubility and mobility by several orders of magnitude.
Analogues:
a) High grade uranium deposits, particularly Oklo, where nuclear reactions occurred.

7. Migration of redox-sensitive radionuclides
Process: Radiolysis will be a source of oxidants which could be transported along the flow path, causing the mobilisation of redox-sensitive species. Redox processes may also be important in the transition zone between reducing deep groundwater and more oxidising surface waters if the radionuclides migrate this far.
Analogues:
a) Roll-type uranium deposits (in these deposits, uranium is deposited as a result of reduction from the mobile U(VI) state to U(IV)).
b) Redox processes in natural waters.

8. Retardation during transport in the far-field
Process: The migration of radionuclides at some distance from the repository in an unchanged groundwater environment, the nature of which is determined by the properties of the host rock.
Analogues:
a) Natural reactor zones at Oklo.
b) Uranium ore bodies such as Koongarra.
c) Uranium and thorium series disequilibria in aquifers.
d) Releases from nuclear weapons tests or the nuclear industry.

9. Matrix Diffusion
Process: Diffusion of radionuclides into a water-saturated rock matrix in the far-field. Radionuclides may diffuse from fracture surfaces into crystalline rocks via a pore system of microfissures between crystals in the rock matrix, making the rock a sink for radionuclides. It is not yet certain that this process actually occurs.
Analogues:
a) Water conducting fracture zones transporting measurable amounts of uranium which intersect a host rock profile.
b) Hydrothermal vein-type uranium deposits.

From this summary, it is apparent that a full understanding of repository performance can only be arrived at through combining results from studies of a wide range of natural systems.

However, it is thought that far-field processes will be more likely to be determining factors in the safety of particular repository sites over long timescales than near-field processes. This is because most models of repository behaviour have shown that transit times to the surface are a function of solubility and sorption in the host rock formation rather than the stability of the wasteform. Indeed, Burkholder(1983) arrived at the conclusion that waste containers with lifetimes over 100 years were

unnecessary, and, if all the waste from a repository entered the final (geologic) barrier within 10 000 years after burial, eventual doses would not be significantly increased relative to much slower failure of engineered barriers.

These lines of argument show that natural analogues for far-field processes, such as the Koongarra uranium deposit, have an important role to play in the overall verification of the safety of nuclear waste repositories.

2.3 Examples of the Analogue Approach

In the last two decades, many geologic systems have been suggested as analogues of nuclear waste repositories. Studies of these systems range in scale from international projects involving a large effort at a particular analogue site, down to isolated reports where a system is applied as an analogue, possibly as an afterthought, or an interesting sideline, to an unrelated research program. In view of this, it is worthwhile to consider the value of an analogue study such as that of Koongarra. The following questions need to be considered in this context:

a) Does a particular study have the potential to lead to significant progress?
b) Does it duplicate other work elsewhere?
c) Can it provide useful information, which, when combined with results from other studies, will lead to a comprehensive understanding of the processes in question?

To help resolve these questions, several analogue studies will be briefly discussed in this section. The range of geochemical analogues being considered, and their application to specific problems, will be illustrated. This will enable the Koongarra study to be placed in context with other natural analogues.

2.3.1 Oklo

About two billion years ago, a naturally occurring nuclear fission reactor existed in a uranium deposit at Oklo, in what is today the west African country of Gabon. At this time, the ^{235}U content of normal uranium was about 3.2 % (comparable to the enriched uranium used in some present day reactors). This, together with a favourable water:uranium ratio and a lack of neutron poisons, allowed criticality to occur.

The initial step in achieving criticality was the mobilisation of uranium soon after sedimentation occurred around two billion years ago, followed by concentration and precipitation in zones where locally reducing conditions prevailed. The reactor zones consisted of block-shaped accumulations of uranium ore, about 20 m long and 1 m thick (figure 2.1). At the time of criticality the reactor zones were buried approximately 3500 m below the surface. These zones were able to sustain nuclear reactions because the uranium was separated from neutron poisons such as V, Se, Mo, and most of the Fe, during remobilisation (Brookins 1984).

Over a period of approximately 300 000 years, the Oklo reactor produced, and exposed the surrounding rocks to, more than 30 elements which are the products of neutron capture, nuclear fission and radioactive decay. About 800 000 kg of uranium was involved in nuclear reactions, and 12 000 kg of ^{235}U was fissioned. The reactions produced 2000 kg of plutonium, 730 kg of ^{99}Tc, and numerous other reaction products. The inventory at Oklo at the

end of nuclear events corresponded to about 15 % of the uranium and 1-2 % of the plutonium and fission products in the United States spent fuel inventory as of 1980 (Curtis et al. 1981).

During the thermal period, the rocks which comprised the reactors received large radiation doses, and the local thermal loading resulted in vigorous circulation of hydrothermal fluids through the reactor zone. This temperature increase in the near-field environment is analogous to that produced during the thermal period of proposed repositories.

The apparently unique combination of conditions occurring at Oklo has led to detailed investigations of the migration of numerous elements being undertaken. For many components of the system, high-precision mass spectrometry techniques have allowed relative amounts of isotopes originating from nuclear reactions and non-nuclear sources to be measured.

Measurement of ruthenium isotopes by these techniques has enabled the migration of ^{99}Tc, which is of major concern in nuclear waste, to be studied. Natural ruthenium consists of seven isotopes of which four are fission products. Three of these are produced instantaneously (on geologic timescales) but one, ^{99}Ru is formed by the decay of ^{99}Tc, which has a half-life of 213 000 years. If migration of ^{99}Tc had occurred at Oklo, this would be detected by the distribution of ^{99}Ru differing from that predicted as the outcome of nuclear processes. Zones of ^{99}Ru enrichment have been identified, within several metres of the reactor core, from which it has been concluded that ^{99}Tc migrated from the reactor but was then retained (Curtis et al. 1981).

Actinide migration at Oklo appears to have been limited. Thorium, neptunium and plutonium were mostly retained, whereas some local redistribution of uranium occurred. The retention of americium seems likely, based on crystal chemical and Eh/pH considerations, although this cannot be inferred directly (Brookins 1984). The retention of actinides over timescales of two billion years, during which the surface of the earth has been constantly changing, has provided support for the proposition that nuclear repositories can be relied on to prevent release of actinides to the biosphere over timescales which are comparatively much shorter (de Laeter 1985).

The relative levels of the uranium isotopes, ^{238}U, ^{235}U and ^{234}U, were measured, using α-spectrometry, in a chemically leached sample of uranium ore from Oklo (Sheng and Kuroda 1984). An unusually high ^{235}U/^{238}U ratio was found, apparently due to the production of ^{239}Pu during reactor operation, which subsequently produced ^{235}U by α-decay.

Sheng and Kuroda also reported a ^{234}U/^{238}U isotope ratio exceeding 60 in a resistant mineral phase obtained from this ore sample after chemical leaching of accessible phases (the value of this ratio is unity in the absence of isotope fractionation). They attributed this to 'α-recoil', a process which caused an excess of the daughter ^{234}U over its precursor ^{238}U in some mineral phases. (Disequilibria between isotopes in the ^{238}U decay series, and related phenomena such as α-recoil, are discussed in Appendix I). Commonly, α-recoil leads to mobilisation of the daughter nuclide, however, it may result in emplacement of the daughter in less readily leached sites, as apparently occurred in the sample studied by Sheng and Kuroda. The study of α-recoil effects in systems such as Oklo and Koongarra is of relevance to the safety assessment of nuclear waste repositories because several of the radionuclides in HLW are α-emitters.

Oklo is the only known example of a natural reactor, and has provided a unique opportunity to study the transport of fission products and transuranic elements in a geologic environment. The very fact that evidence of criticality still exists attests to the possibility that radionuclides may be immobilised over timescales approximating to half the age of the earth and much longer than would be required of a repository (Curtis et al. 1981).

2.3.2 Morro do Ferro

The Morro do Ferro is a hill located near the centre of the Pocos de Caldas plateau in Brazil. The region has a subtropical climate, with rainfall of about 170 cm/year, mostly occurring in a four-month rainy season (Eisenbud et al. 1984).

An ore body on the south face of the Morro do Ferro contains about 30 000 tonnes of thorium, 100 000 tonnes of light rare earth elements (REE's), and about 300 tonnes of uranium (Eisenbud et al. 1986). Thorium is chemically similar to Pu(IV), which is a common form of plutonium in environmental conditions. As well, the rare earth elements Nd(III) and La(III) can serve as analogues for both Am(III) and Cm(III).

The Morro do Ferro deposit is near the surface, in weathered rock, and is intersected by groundwater with a short transit time to the surface. A nuclear repository would be deep in unweathered rock and therefore its contents would be much less likely to reach the surface than the elements present in the Morro do Ferro, which may be considered to be a model of a "worst case" repository scenario.

The thorium concentrations in local streams carrying surface runoff from the deposit were determined (Eisenbud et al. 1984; 1986). The mobilisation rate for thorium was extremely low. If the Th-Pu analogue is valid, then it would be predicted that if all the plutonium expected to exist in the United States by the year 2050 was emplaced under conditions comparable to those existing at Morro do Ferro, then the level of plutonium in the streams would be well below the maximum permissible concentrations for waste discharges set by the USNRC (Eisenbud et al. 1986).

Further measurements of thorium levels in natural surface waters from the highest radioactivity region of the deposit, gave some extraordinarily high levels of ^{232}Th (up to 261 $\mu g/L$), exceeding the solubility of $Th(OH)_4$ by a factor of about 200 (Miekeley and Kuchler 1987). This was attributed to the presence of soluble thorium-humate complexes, as the levels of dissolved organic carbon were also very high (up to 250 mg/L). This result indicates that it will be necessary to isolate radioactive waste from organic matter. This conclusion is in agreement with that of Cleveland and Rees (1981), who established a strong relationship between the levels of plutonium and organic ligands, such as ethylenediaminetetraacetic acid (EDTA), in leachates from a radioactive waste disposal site in the USA. The presence of EDTA in unprocessed nuclear waste may derive from the use of cleaning agents containing EDTA for decontamination in nuclear facilities.

Evidence of the validity of the Th-Pu comparison at the Morro do Ferro is urgently needed. It has been suggested that the high level of organic carbon in the water limits its applicability to more relevant environments (Parker et al. 1984).

The light REE's abundantly present in the Morro do Ferro are also of significance, since the lanthanides are chemical analogues to the trivalent actinides americium and curium which are present in HLW (table 2.1). The mobilisation of lanthanum due to stormflow erosion was found to be of the order of 0.0001 % per year, whereas mobilisation by groundwater solubilisation was a thousand times lower (Lei et al. 1986). This indicated that lanthanum was rather immobile, and residence times long, even under the subtropical weathering conditions prevailing at the site. The authors concluded: 'This gives some assurance that long-lived isotopes of Cm and Am, which would be expected to behave similarly, would decay in-situ if emplaced under similar conditions... The majority of the La that is being transported from the ore body is by surface erosion, a condition that is very unlikely in nuclear HLW repositories proposed for 600-1000 metre depths'.

2.3.3 Sedimentary Roll-front Uranium Deposits

Roll-front deposits comprise an accumulation of uranium occurring when oxidising groundwater containing low (ppb) levels of uranium in its relatively mobile (+VI) oxidised state reaches a reducing barrier, causing the reduction to the highly immobile U(IV) form (figure 2.2). This geochemical environment is analogous to the vicinity of a radioactive waste repository containing redox-sensitive elements in its post-thermal period (Deutsch and Serne 1983). Several roll-front deposits have been discovered in the Shirley Basin, Wyoming (Levinson 1980).

The uranium in roll-front deposits is believed to originate from source rocks such as granites, tuffs and tuffaceous sandstones which contain uranium in accessory minerals. This uranium may be leached by groundwater - particularly oxidising, carbonate-bearing groundwaters, as may be found near recharge zones - and will migrate as U(VI) carbonate complexes. The uranium is then deposited at a reducing barrier, such as a zone rich in hydrogen sulfide. Organic matter or microbial activity can play an important role in establishing a redox front. The barrier may slowly migrate due to the ongoing influx of oxidising groundwater at its upstream edge.

Similar processes could occur near a repository. Local oxidising conditions resulting from radiolysis may cause uranium and other radionuclides to dissolve. Groundwater movement may then carry them into backfill material or fresh rock, where interaction with reducing materials such as sulfide or ferrous silicates would cause precipitation (Krauskopf 1988).

The study of roll-front deposits provides a contrast to the study of Koongarra, where, as will be shown, the major processes occurring are weathering, oxidation and dispersion of uranium from minerals such as uraninite rather than reduction and precipitation. The two types of geologic environment provide complementary information, because they relate to distinct parts of the overall radionuclide release scenario.

2.3.4 Basalt Glass

A close analogue for the initial release of radionuclides from a borosilicate glass wasteform has proved difficult to find. This is because few natural materials have a similar chemical composition.

Basalt glasses, which are formed by the very rapid cooling of flows of injected magma, seem to be the closest analogue, since they have a very similar content of SiO_2 to nuclear waste glass (approximately 45 %). The SiO_2 content of glass has a major influence on glass/water interactions. Natural glasses like rhyolitic obsidian (which often contains more than 80 % SiO_2), and glass objects preserved from ancient times, are of questionable value due to their vastly different composition (Krauskopf 1988).

Laboratory experiments on basalt glasses and borosilicate glasses suggest the two react via similar processes (Byers et al. 1985). However, basalt glasses contain virtually no boron or lithium, which makes comparison with wasteforms difficult (Chapman et al. 1984).

In general, natural glass analogues only provide qualitative information, due to their dissimilar chemistry, and also because nuclear effects such as radiolysis and recoil are rarely seen in natural glasses. Furthermore, studies tend to relate to the stability of the glass itself, whereas loss of the containment integrity (ie ability to retain radionuclides) probably occurs long before the glass breaks down.

2.3.5 The Salton Sea Geothermal Field

This analogue site provides a contrast to those already discussed, since it specifically relates to the environment of a repository in a salt formation. Salt is potentially fully soluble, and its mechanical properties are totally unlike granite or basalt. The Salton Sea geothermal field in California was chosen as an analogue to a salt repository for the following reasons (Elders and Moody 1985):

a) Detailed knowledge of the system exists due to its commercial development as a source of electric power.

b) Temperatures within it range up to 300°C, thus covering the temperature range expected in a salt repository.

c) Highly saline deep groundwaters (up to 25 % TDS) span the range of brines expected around a salt repository.

d) Sedimentary rocks similar to those surrounding potential salt host rock horizons are present.

e) Geothermal activity has been occurring for 25 000 years which is a relevant timescale for a repository.

Studies at this site have included sampling of fluids and rocks, evaluation of hydrology and permeability, observation of geothermal alteration, measurement of pressures at burial depths, and studies of the duration, extent and effects of heating.

Measurements on brine samples and rock cores from this site have shown that uranium, thorium and REEs are immobile over a wide range of temperature and salinity, with strontium and cesium being slightly mobile.

Zukin et al. (1987) calculated rock/brine concentration ratios (R_c = (dpm/g)rock/(dpm/g)brine) for the various radionuclides in the system. R_c values for isotopes of radium, polonium and lead were near unity, which indicated potential mobility of these elements in this environment. The relatively high solubility of radium and lead was attributed to the

formation of chloride complexes. In addition, the reducing conditions prevent the formation of MnO_2 and $RaSO_4$, hence tending to increase radium mobility.

Calculated R_c values for actinides were much higher, about 5×10^5 for ^{232}Th, and 5×10^4 for ^{238}U and ^{234}U. As the R values for thorium and uranium isotopes differed by only an order of magnitude, it was suggested that uranium was retained in the +IV oxidation state by the reducing conditions in the brines (Zukin et al. 1987).

Measurements of isotopic ratios in the rocks and brines enabled estimates of residence times to be made. The residence time of ^{228}Ac in the brine before sorption onto solid surfaces was estimated to be below 70 minutes, indicating the potential for rapid removal of reactive isotopes from brines (Zukin et al. 1987).

2.4 Koongarra Overview

The preceding survey shows the variety of natural analogue studies and the different aspects of the nuclear waste disposal problem which they address. Where does the study at Koongarra fit in?

In the context of studying radionuclide movement, the most important feature of the Koongarra deposit is the dispersion fan, a zone of uranium enrichment which extends approximately 100 m from the zone of original uranium accumulation, and results from the movement of uranium by groundwater away from the primary ore zone. This movement has taken place over approximately two million years (Airey et al. 1986b).

The weathered rock system within which uranium movement is occurring is essentially unchanged by the proximity of the orebody, except that it contains measurable levels of radionuclides originating from the deposit. Koongarra, therefore provides an analogue to the 'far-field' of a repository. This is the region some distance from the waste canisters, which is not affected by local thermal and radioactive perturbations caused by the nuclear waste.

From a scientific viewpoint, Koongarra offers an opportunity to derive and validate models of radionuclide movement over long timescales, which are comparable to the isolation periods required of waste repository systems.

To the non-specialist, Koongarra is an example of a geological system in which radionuclide migration has been limited to distances of the order of tens of metres over timescales exceeding a million years, under conditions that are apparently not ideal for radionuclide containment. It therefore offers some degree of assurance about repository safety to a public which is clearly not convinced by theoretical predictions or laboratory experiments. When combined with results from other analogue studies, this could lead to an increased confidence in the capability of repositories to prevent the release of radionuclides to the biosphere.

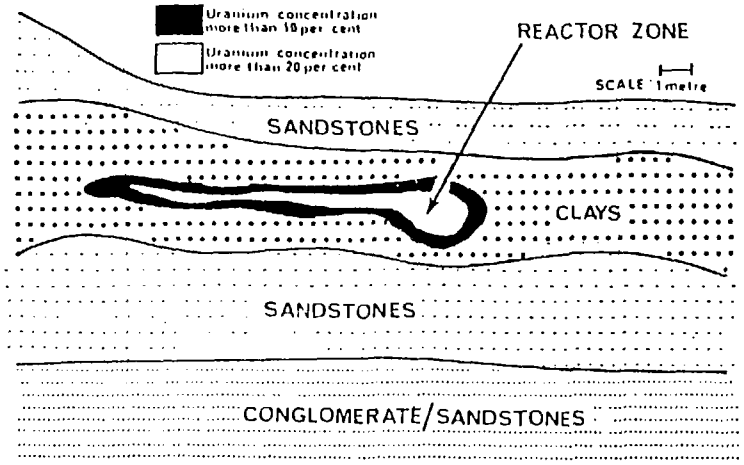


Figure 2.1 Geology in the neighbourhood of a reactor zone at Oklo (from de Laeter 1985).

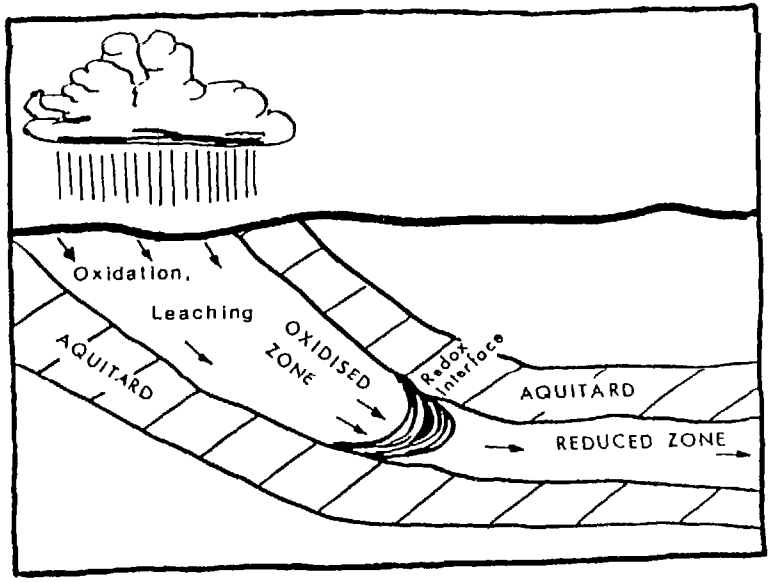


Figure 2.2 Roll-front uranium deposit.

Table 2.1 Possible chemical analogues for the long-lived radionuclides present in High Level Waste (HLW)

(Adapted from Chapman et al. 1984)

Nuclide	Redox Conditions[a]	Oxidation State	Ionic Radius[b] (Å)	Hydrolysis Coefficient[c] (log K1)	Possible Analogue[d]
Tc	Red	IV			Re (IV)
	Ox	VII	0.64		Re (VII)
Pa	Red	V	0.78	9.5	Th, U (IV)[e]
	Ox	V	0.78	9.5	Th, U (IV)[e]
U	Red	IV	0.76	13.4	U (IV)
	Ox	VI	0.73	8.2	U (VI)
Np	Red	IV	0.87	12.5	U (IV) (Th Zr Hf)
	Ox	V	0.75	5.1	U (VI)
Pu	Red	III or	1.00	6.5	Lanthanides[f]
		IV	0.86	13.5	U (IV), Th (Zr, Hf)
	Ox	IV or	0.86	13.5	U (IV), Th (Zr, Hf)
		V	0.74	4.3	U (VI)
Th	Red	IV	0.94	10.8	Th
	Ox	IV	0.94	10.8	Th
Am	Red	III	0.98	6.5	Lanthanides
	Ox	III	0.98	6.5	Lanthanides
Cm	Red	III	0.97	6.5	Lanthanides
	Ox	III	0.97	6.5	Lanthanides

Other important radionuclides (I, Cs, Pd, etc) have naturally occurring stable isotopes which can be used as direct analogues.

(a) Red (Reducing) : Eh derived from Fe(II)/Fe(III).
Ox (Oxidising) : Eh derived from O_2.
(b) For the 6 co-ordination state.
(c) For $M^{n+} + OH^- = M(OH)^{n-1}$.
(d) Most suitable given first.
(e) The chemistry of Pa(V) is more similar to the 4-valency actinides than to 5-valency actinides.
(f) Best analogue is Nd. Other acceptable lanthanides are Ce, Pr, Sm, Eu, Gd, Tb, Dy and Ho. Less acceptable are La (too large), Er, Yb, Tm, Lu (too small) and Y.

CHAPTER THREE

KOONGARRA URANIUM DEPOSIT

3.1 Background to the Analogue Study at Koongarra

Koongarra is in the Alligator Rivers Uranium Field (ARUF) which contains several other uranium deposits including Jabiluka, Ranger and Nabarlek. The ARUF approximately coincides geographically with the Kakadu National Park. The national park surrounds the Koongarra site, but the immediate vicinity of the ore body was excluded.

The Koongarra deposit was discovered by Noranda Australia Limited in ty 1970, within two years of the company commencing exploration in the Northern Territory. A draft environmental impact statement (EIS) for the proposed open-cut mine was prepared in 1978 (Noranda 1978). This was followed by a supplementary volume which addressed several criticisms, and deficiencies, which were identified after public examination of the draft EIS. The draft and supplementary volumes comprise the EIS for the proposed mine. The Government has not given approval for mining. The ownership of the lease has been transferred to Denison Australia Ltd, and a company presence has been maintained at the site.

The uranium deposits of the ARUF were first proposed as analogues of radwaste repositories by Shirvington (1979; 1983), who studied the Austatom Prospect (located about 30 km west of Ranger), and the Nabarlek ore body. This work established the potential of the deposits as natural analogues.

A systematic study commenced in 1981 when the Australian Atomic Energy Commission (AAEC) set up a project with substantial support from the United States Nuclear Regulatory Commission (USNRC). The USNRC is responsible for assessing safety aspects of the disposal of high level wastes at geologic sites in the United States. The USNRC-sponsored study included several of the uranium deposits in the ARUF, and was reviewed by Airey (1986). During this project, the Koongarra No.1 ore body was identified as being the most suitable analogue site.

An international study of Koongarra was commenced in 1988. The Australian Nuclear Science and Technology Organisation (ANSTO - the successor to the AAEC) was the major participant, with collaboration from several countries including the USA, Great Britain, Japan and Sweden. The first stage of this study, known as the Alligator Rivers Analogue Project (ARAP) was completed during 1990.

3.2 Geology and Uranium Distribution

The Koongarra deposits are located about 225 km east of Darwin, in the Alligator Rivers region of the Northern Territory within the Pine Creek Geosyncline (figure 3.1). This geosyncline is a region of Late Proterozoic sediments, with interlayered tuff units, resting on a granitic late Archaean Basement - the Nanambu Complex (Foy and Pedersen 1975).

There are two major ore bodies at Koongarra, both located in a zone of deeply dipping Cahill formation schists adjacent to the Koongarra reverse fault. Figure 3.2 is a plan view of the vicinity.

The No.1 ore body is located on a gently sloping plain, about 100 m from the Kombolgie sandstone escarpment. This escarpment rises between 200 m and 300 m above the plain. The Kombolgie formation is almost flat lying and rests unconformably on the schists of the Cahill formation. The Koongarra fault is close to the foot of the escarpment. A dolomite outcrop exists to the southwest of the deposits.

A cross-section of the No.1 ore body is shown in figure 3.3. The primary mineralisation occurs in a series of uraninite lenses, which extend from the base of the weathered zone (approximately 25 m below the surface), to about 100 m depth. These lenses dip at 55°, roughly parallel to the fault.

The secondary uranium mineralisation in the weathered zone extends as a horizontal tongue for about 100 m to the south east of the primary ore. This 'dispersion fan' is the result of the redistribution of uranium by groundwaters, which move in a generally southern direction away from the escarpment. The direction of this movement is indicated by arrow 'a' in figure 3.2.

The No.2 ore body is located to the north east of the No.1 ore body, and is separated from it by a barren gap of about 100 m. The uranium ore extends from 50 m depth to over 250 m, and is entirely below the weathered zone. There is only minor secondary mineralisation, and no dispersion fan is present (Snelling 1980a).

The distribution of uranium and daughter radionuclides in the solid phase of the No.1 ore body has been extensively investigated (Nightingale 1988; Snelling 1980a; 1980b). The essential features of the uranium distribution are shown in figure 3.3. The primary mineralisation contains veins of uraninite, and therefore grades exceeding 50 % are encountered over limited areas. Uranium concentrations in the weathered zone decrease from the rich ore-grade secondary mineralisation adjacent to the primary orezone (>10 %) to 0.1 % at the nominal boundary of the dispersion fan (defined for mining purposes), eventually decreasing to background levels some hundreds of metres downgradient from the primary zone. The unweathered Cahill formation schists below the dispersion fan are not significantly enriched in uranium.

3.3 Mineralogy

The primary ore veins at Koongarra are uraninite (UO_2) containing about 1 % to 5 % of CaO; trace levels of silicon, iron, manganese, thorium and rare earth elements (<0.5 %); ^{238}U-series and ^{235}U-series radionuclides; and the ultimate product of radioactive decay, lead. The distribution of uranium minerals in the No.1 ore body is shown in figure 3.4.

The Koongarra reverse fault marks the geological footwall of the primary mineralised zones. The strongest uranium mineralisation is in a zone of quartz chlorite schist, stratigraphically just below a layer of graphitic quartz-mica schist which is the boundary of uranium mineralisation in the unweathered zone. Within the primary ore body, the ore consists of lenses containing veins of uraninite conformable to the host schists, together with uranium/lead oxides.

Chlorite, predominantly magnesium chlorite, is the principal gangue, and its intimate association with the uraninite suggests that the two formed together.

A variety of secondary uranium minerals has been identified, including oxides, silicates, phosphates, a sulfate mineral, and a single reported occurrence of a vanadate. Some of these secondary minerals were formed as a result of in-situ alteration of uraninite by relatively oxidising groundwaters originating from the fault zone (Snelling 1980a). This groundwater introduced silicon, and possibly some calcium to the uraninite, and redistributed the uranium, lead and calcium. Thus, some uraninite veins were replaced by uranyl silicates, such as sklodowskite and uranophane. These minerals are found close to the uraninite in the unweathered zone, located in veins, between grain boundaries and within fractures. Uraninites situated furthest from the fault, in the high grade zone below the graphitic hanging wall, remain unaltered.

Uranyl phosphates, such as saleeite ($Mg(UO_2)_2(PO_4)_2.8\text{-}10H_2O$) and torbernite ($Cu(UO_2)_2(PO_4)_2.8\text{-}10H_2O$) are found in the weathered schists immediately above the primary ore zone. This is a region of weathered and leached primary ore which was formerly the upper part of the primary ore.

Down gradient of the uranyl phosphate zone, the uranium content gradually decreases, with uranium dispersed in the weathered schists, and, in the leading edge of the dispersion fan, adsorbed on clays.

The clays and iron minerals in the weathered zone form, at least in part, by alteration of chlorite, the major rock-forming mineral of the quartz-chlorite schist (Murakami and Isobe 1990). The extent of alteration is a function of depth. In the unweathered zone, chlorite is abundant, but at lesser depths the chlorite has been transformed to vermiculite. The final alteration product, kaolinite, is found close to the ground surface. During the transformation process, Fe is released and this is found as ferrihydrite coating minerals and other iron minerals in the weathered zone.

3.4 Hydrogeology

The Koongarra area experiences a humid monsoonal wet season from November to early April, during which 95 % of the annual rainfall (1800 mm) occurs. As a result, water tables vary by up to 15 m throughout the year.

The major source aquifer in the Koongarra system is considered to be the 'footwall' aquifer in the Kombolgie formation. The Koongarra fault forms the hydraulic boundary between the footwall aquifer and the other major aquifer, the 'hanging-wall' aquifer. The latter consists of (a) unweathered Cahill formation schists (b) weathered schists and (c) surficial sands (Norris 1989).

The direction of the dispersion fan indicates that, in general, groundwater flows away from the fault, towards the Koongarra creek. However, the groundwater flowlines are not necessarily parallel to the cross-section in figure 3.3, which corresponds to a line of drill holes which form part of the exploration drilling grid. The orientation of the grid was arbitrarily chosen.

Standing water level measurements and drawdown tests provide data which can be used to infer the hydrogeology of the system. Figure 3.5 shows all boreholes which are currently open for groundwater sampling, water level measurements and pumping tests.

Drawdown tests on the PH-series boreholes (Norris 1989), indicated that the system is heterogeneous, with major transmissivity axes aligned from northeast to southwest (parallel to the schistosity in the unweathered zone). In the drawdown tests, the water in a given borehole was pumped down to well below its natural levels (ie into unweathered rock), and the levels in surrounding wells were monitored. Hence drawdown results may be more related to the unweathered Cahill formation, rather than to the weathered zone.

Standing water level data have been primarily obtained from PH-series bores that are cased through the weathered zone to prevent their collapse. Recent water level data from w-series boreholes, which have independent sampling points in both the weathered zone at 13-15 m depth, and the transition zone at 23-25 m depth, are also available (Duerden 1989; Norris 1989).

The water level contours (figure 3.6) show that the hydraulic gradient dips primarily to the south, but the concentric nature of the contours suggests that flow paths tend to radiate outwards rather than remain parallel to one another. Figure 3.6 shows an anomolous region of water gradients near the south-west end of the ore zone.

The different orientations of the transmissivity axes and the hydraulic gradients introduce complexity into interpreting the data. A reasonable interpretation is that the drawdown data reflect the heterogeneity and anisotropy amongst the layers of the Cahill formation rocks. The standing water level data were obtained when the system was unstressed, and may therefore be the best indicator of natural groundwater flow directions in the weathered zone.

The hydraulic gradient across the No.1 ore body, which is indicated by the water level data, is consistent with the direction in which the dispersion fan extends (figure 3.6). However, the question of whether the current flow patterns have been maintained throughout the development of the dispersion fan remains a subject of research.

3.5 Groundwater Chemistry

3.5.1 Groundwater Evolution

The chemistry of groundwater sampled at Koongarra shows a geochemical evolution as it passes along aquifer paths. The changes in groundwater composition result from mixing, dilution, dissolution (and possibly precipitation) of minerals, adsorption/desorption, evaporation, and outgassing.

The major sources of groundwater entering the flow-system of the deposit are:

(a) the footwall aquifer in the Kombolgie Formation

(b) shallow groundwaters intersecting the top of the ore body, and

(c) direct infiltration from the surface.

Upon moving into the mineralised zones of the Cahill formation, the groundwaters acquire a characteristic composition, with elevated levels of uranium and other radionuclides, and also of magnesium. The concentrations of these ions diminish with distance downgradient, due to a combination of dilution and sorption processes.

Changes of groundwater chemistry can have a dramatic influence on radionuclide migration. For example, oxidation of U(IV) to U(VI) increases uranium solubility by several orders of magnitude. Furthermore, the presence of complexing ions such as phosphate or carbonate can have a major effect on the solution phase chemistry of uranium (see section 4.3).

The evolution of groundwater chemistry will be discussed with particular reference to the w-series boreholes, which take samples of groundwater from the weathered zone, and also KD1 and PH49. The positions of these boreholes are shown in figure 3.7.

3.5.2 Surface Waters

Surface waters sampled during the 1977/1978 wet season were slightly acidic (pH 5), with low alkalinity, conductivity, and correspondingly low levels of dissolved constituents (Noranda 1978). In the most dilute surface waters sampled, Na and Cl were the only ions present in significant amounts (0.57 mg/L and 0.51 mg/L respectively).

During the wet season, surface waters typically comprise recent rainwater, whereas samples taken in the dry season are more influenced by groundwater inflow. Rainfall always contains some traces of dissolved sea-salt, originating from the evaporation of droplets of seawater to a fine aerosol of NaCl (Drever 1988). Thus, the wet season surface water compositions reported by Noranda (1978) probably reflect the chemistry of recent rainfall.

3.5.3 Kombolgie Formation

Boreholes KD1 and w6 intersect the Kombolgie sandstone, however, there is no significant water inflow into the recently-drilled w6 over the 25 m depth of this hole, hence it has not been possible to take representative samples of groundwater. The drilling log for nearby KD1 also shows no water inflow within 30 m of the surface, but substantial water intersections at greater depths (Noranda 1978). Inflowing groundwater was encountered throughout the interval between 30 m and the bottom of the hole at 120 m.

Kombolgie waters sampled at KD1 had a low pH and also low levels of dissolved constituents (Table 3.1). Redox measurements indicated the presence of quite oxidising groundwater. This was verified by down-hole probe profiles obtained for KD1 (Duerden and Payne 1988). The downhole probe consists of a sonde which is lowered down the borehole, equipped with sensors for pH, redox, conductivity, dissolved oxygen and temperature measurements, providing in-situ data for these parameters. The profiles showed that an aquifer (presumably a fracture system), at a depth of approximately 70 m, introduced acidic, oxidising and oxygen-containing groundwater into the borehole. An important aspect of these data is that the pH-profiles obtained after the borehole was pumped with a high-capacity submersible pump indicated that this aquifer was the main source of water in this borehole.

The data indicate that groundwater moves across the fault from the Kombolgie sandstone into the Cahill formation. A substantial proportion of this water traverses the fault at considerable depth, with no evidence for movement within 30 m of the ground surface. The chemistry of this groundwater is oxidising and relatively acidic, and may well be responsible for the in-situ oxidation and alteration of uraninite observed in core samples taken from the No.1 ore body in regions close to the fault.

The uranium concentrations in KD1 groundwaters have been determined on several occasions (table 3.1). Values of 0.5-1.0 $\mu g/L$ are typical, with reported measurements ranging up to 5 $\mu g/L$.

3.5.4 Primary Mineralised Zone

The major ion chemistry for PH49, which intersects the primary orebody, is included in Table 3.1. This borehole is cased through the weathered zone, and has been sampled on several occasions both with and without packers to restrict the source of water.

The water chemistry is fairly constant, without major seasonal or depth-related variations, and is representative of groundwaters intersecting the orebody. Relatively high levels of Mg^{2+} are present, which corresponds to the abundance of magnesium in the chloritised mine-series rocks which accompany uranium mineralisation. This enrichment of magnesium is characteristic of the uranium deposits in the ARUF (Giblin and Snelling 1983). Significant levels of Ca^{2+} are also present in the PH49 samples, particularly those from greater depths. The main anion is bicarbonate (HCO_3^-) and these groundwaters tend to outgas CO_2 when brought to the surface. Significant levels of PO_4 have also been measured in groundwater from PH49 and other boreholes in the Cahill formation (Payne and Waite 1989).

Redox and pH measurements suggest that uranium is present in its mobile U(VI) state. The data indicate that uraninite would be unstable if contacted by this groundwater (Sverjensky 1989). Not surprisingly, the total uranium concentrations in PH49 groundwaters (around 200 $\mu g/L$) are amongst the highest measured at Koongarra.

3.5.5 Weathered and Transition Zones

The dispersion fan of the No.1 ore body is in the weathered zone, within approximately 25 m of the surface. Prior to the drilling of the w-series boreholes in November 1988, the chemistry of groundwaters in this zone was poorly understood, because all existing boreholes were cased through the weathered zone. The w-series boreholes have two sampling intervals between 13-15 m and 23-25 m depth, making possible sampling of groundwaters from the zone of the uranium dispersion.

The location of the w-series boreholes is shown on figure 3.7. W6 is in the Kombolgie Sandstone near KD1, upgradient of the deposit. As there is no significant water inflow into w6 this borehole will be excluded from further consideration.

The remaining w-series holes intersect the weathered Cahill formation. In order of increasing distance from the fault, these boreholes are w1, w4, w2, w5 and w7. The standing water levels (figure 3.6) show that this order corresponds to a sequence moving downgradient.

The w-series boreholes in the Cahill formation intersect 3-4 m of surface sands, then 15-20 m of weathered and decomposed schist, grading into partially weathered or fresh schists at the base of the hole. The 23-25 m sampling interval therefore samples groundwater from the partially weathered base of the weathered zone (or transition zone).

The uranium, magnesium and bicarbonate concentrations in groundwaters from KD1, w1, w4, w2, w5, and w7 (23-25 m depth) are shown in figures 3.8(a-c). KD1 has been included in place of w6 to represent the upgradient

groundwater. These figures show the trends in water chemistry as the groundwater flows into the mineralised zones of the Cahill Formation, and the subsequent changes moving downgradient.

The initial step in releasing uranium into the groundwater is the weathering of primary U(IV) minerals, such as uraninite (UO_2), to secondary U(VI) minerals, such as saleeite and torbernite. As these U(VI) minerals are weathered, they release uranium as the mobile UO_2^{2+} species. Such processes are responsible for the increase in uranium concentrations in the vicinity of w4.

The decrease in uranium concentrations moving downgradient (figure 3.8a) is due to dilution and sorption processes. Similar patterns are seen in bicarbonate and magnesium concentrations. Herczeg (1990) suggests that the bicarbonate arises from weathering of dolomite according to the following reaction:

$$2CO_2 + 2H_2O + MgCa(CO_3)_2 = Mg^{2+} + Ca^{2+} + 4HCO_3^-$$

Such a process would also release Mg^{2+}, however much of the Mg^{2+} present in the groundwater probably results from the weathering of chlorite in the mine-series rocks to form vermiculite and ferrihydrite (Murakami and Isobe 1990). Strong evidence for this process arises from mineralogical investigations which show abundant chlorite in the unweathered rock and vermiculite in the base of the weathered zone.

The weathering of chlorite also releases aluminium, iron and silicon. The aluminium is either precipitated as aluminium hydroxide or adsorbed - Al concentrations in the groundwaters are very low, as might be expected of this rather insoluble element. Fe^{3+} is also highly insoluble, so Fe released during weathering is reprecipitated as the abundant ferrihydrite mineral coatings found in the weathered zone at Koongarra.

3.6 Attributes of the Koongarra Site

Compared to the other ore bodies in the ARUF, the Koongarra deposit is the most suitable site for analogue studies. The attributes of Koongarra may be summarised as follows:

a) The deposit is undisturbed apart from exploratory drilling.

b) Extensive hydrological data are available, and there is a consensus on the general direction of groundwater flow.

c) A substantial body of data on the geochemistry of the deposit exists.

d) The Koongarra deposit has a relatively straightforward geology, and has well defined regions of primary, weathered primary, and secondary ore.

e) The mobilisation and retardation of radionuclides in the dispersion fan is directly comparable to the far field of a nuclear waste repository.

f) The base of weathering intersects the ore zone. This provides a basis for estimating the timescales of radionuclide migration, since the time of initial radionuclide mobilisation may be taken to coincide with the onset of weathering.

The Nabarlek and Ranger deposits have been mined, which, as well as removing some of the potential study material, has perturbed natural groundwater flow patterns. The massive Jabiluka deposit is relatively poorly understood and would require extensive study before a database comparable to that for Koongarra could be built up. The Austatom prospect (studied by Shirvington 1979) has a virtually unknown hydrologial regime. Information about groundwater is limited to a few observations made during exploratory drilling.

The advanced state of knowledge but limited extent of disturbance to the Koongarra site, as well as its superiority from a geological viewpoint make it the preferred natural analogue study location.

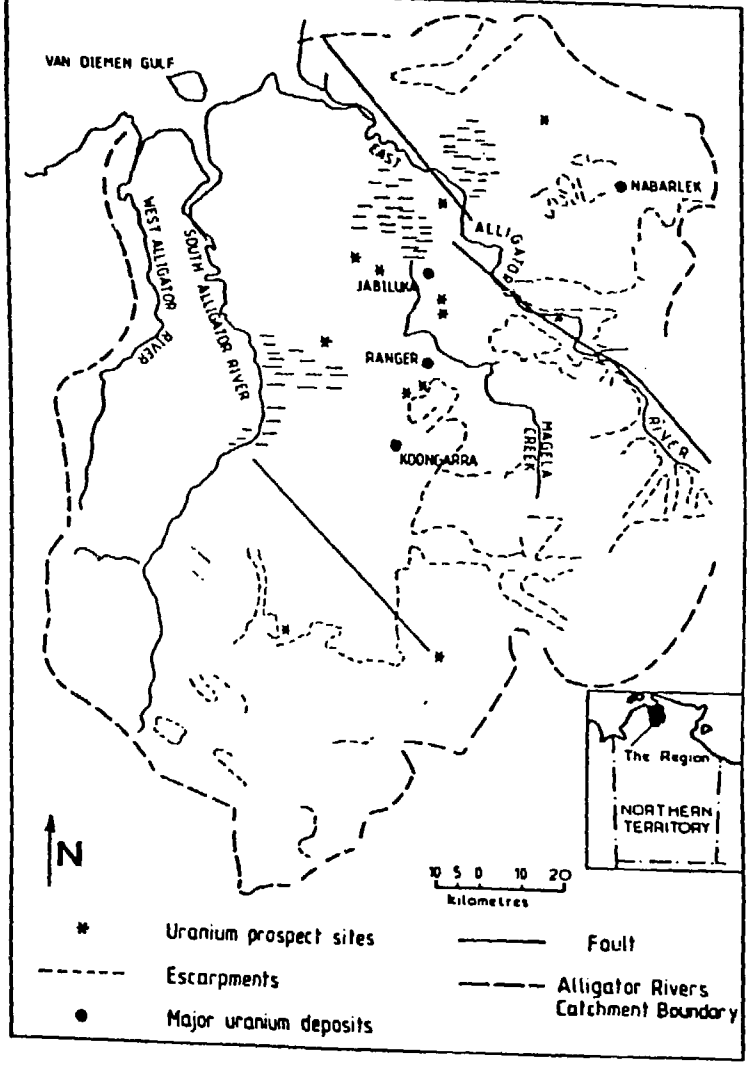


Figure 3.1 Location of the principal uranium ore bodies in the ARUF (from Airey at al. 1984).

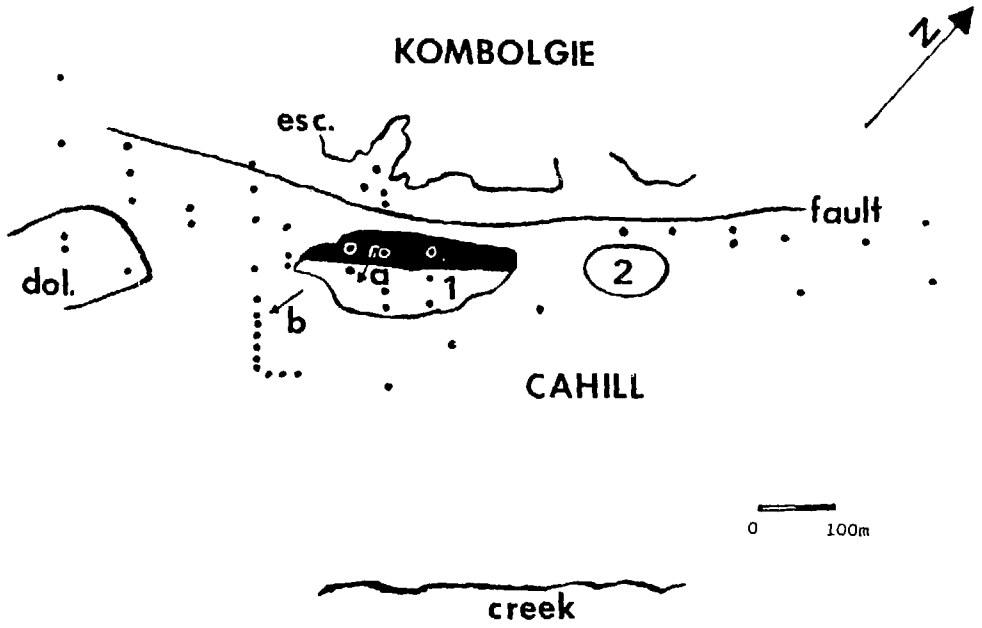


Figure 3.2. Plan of the vicinity of Koongarra, showing No.1 and No.2 ore bodies. The primary zone of the No.1 ore body is shaded. Arrows 'a' and 'b' indicate approximate directions of groundwater flow. 'Esc' - escarpment, 'dol' - dolomite.

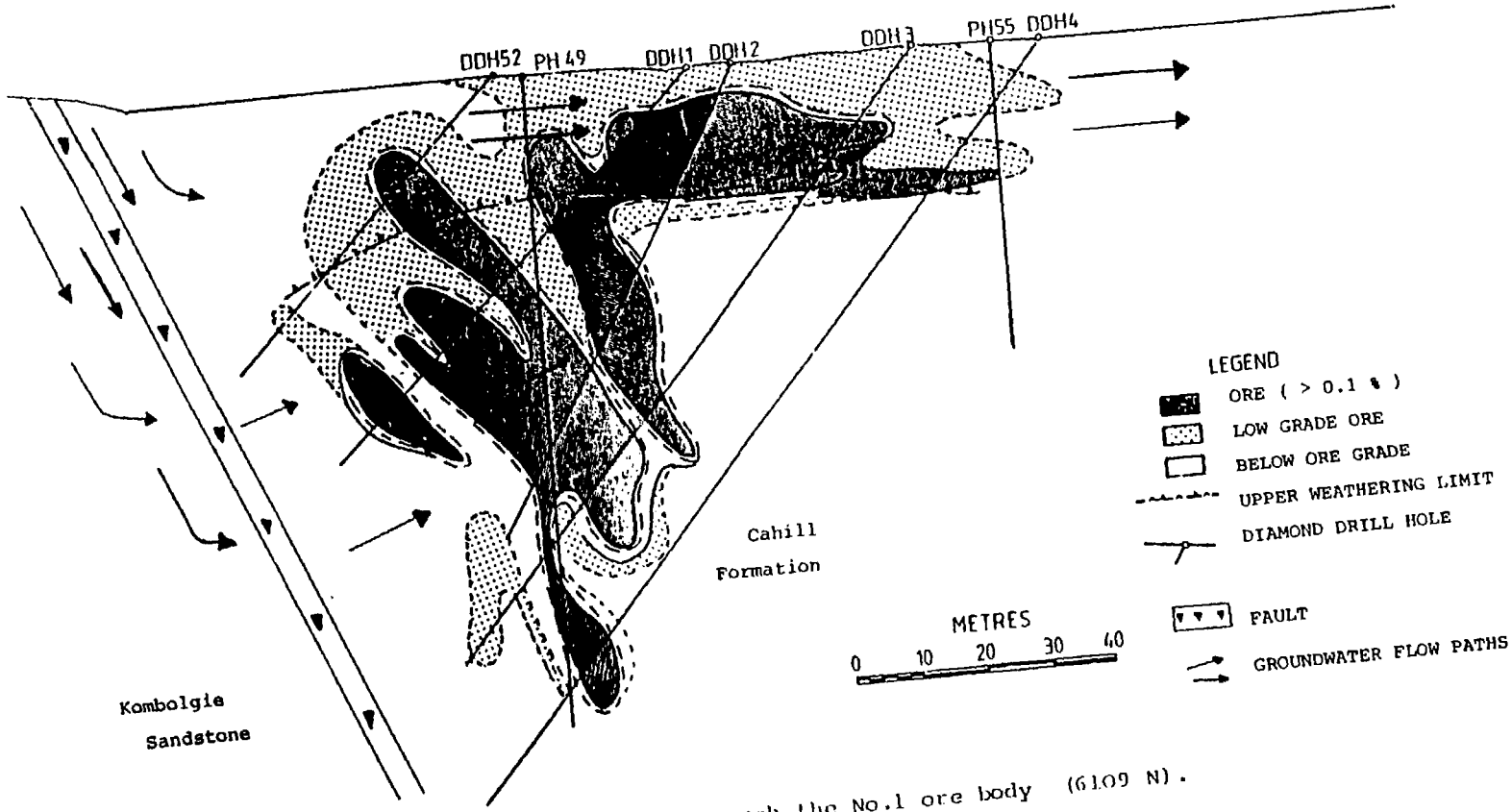


Figure 3.3. Geological section through the No.1 ore body (6109 N).

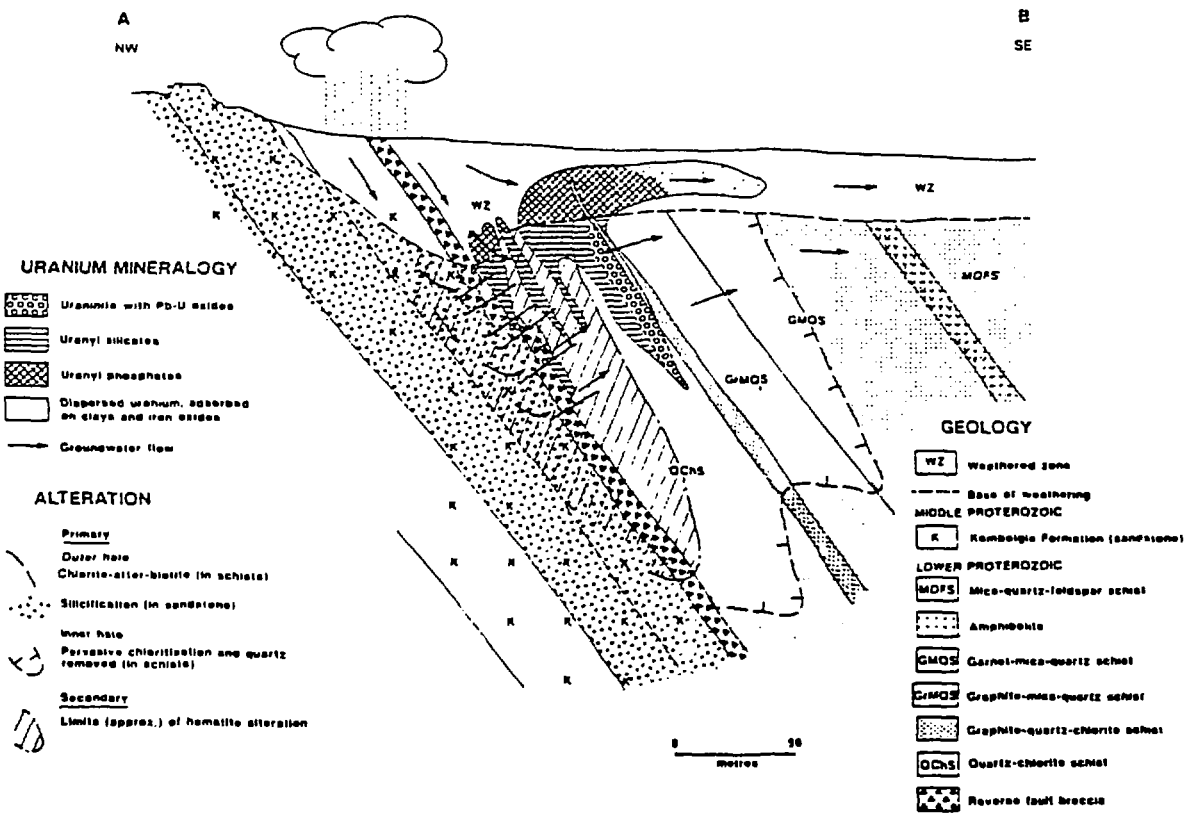


Figure 3.4. Distribution of major minerals and hematite alteration (from Snelling 1989).

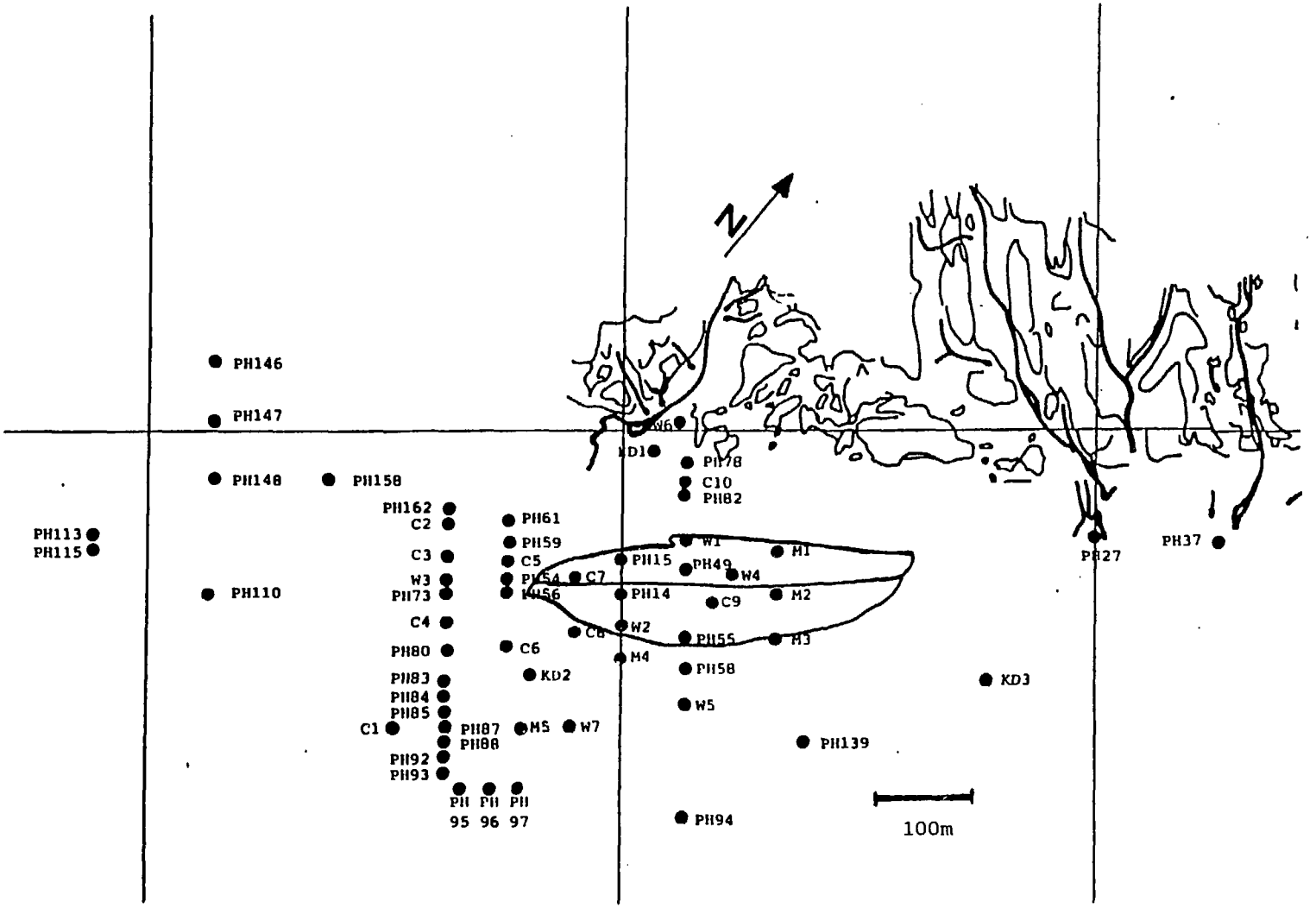


Figure 3.5. Koongarra boreholes open for water sampling and standing water level measurements.

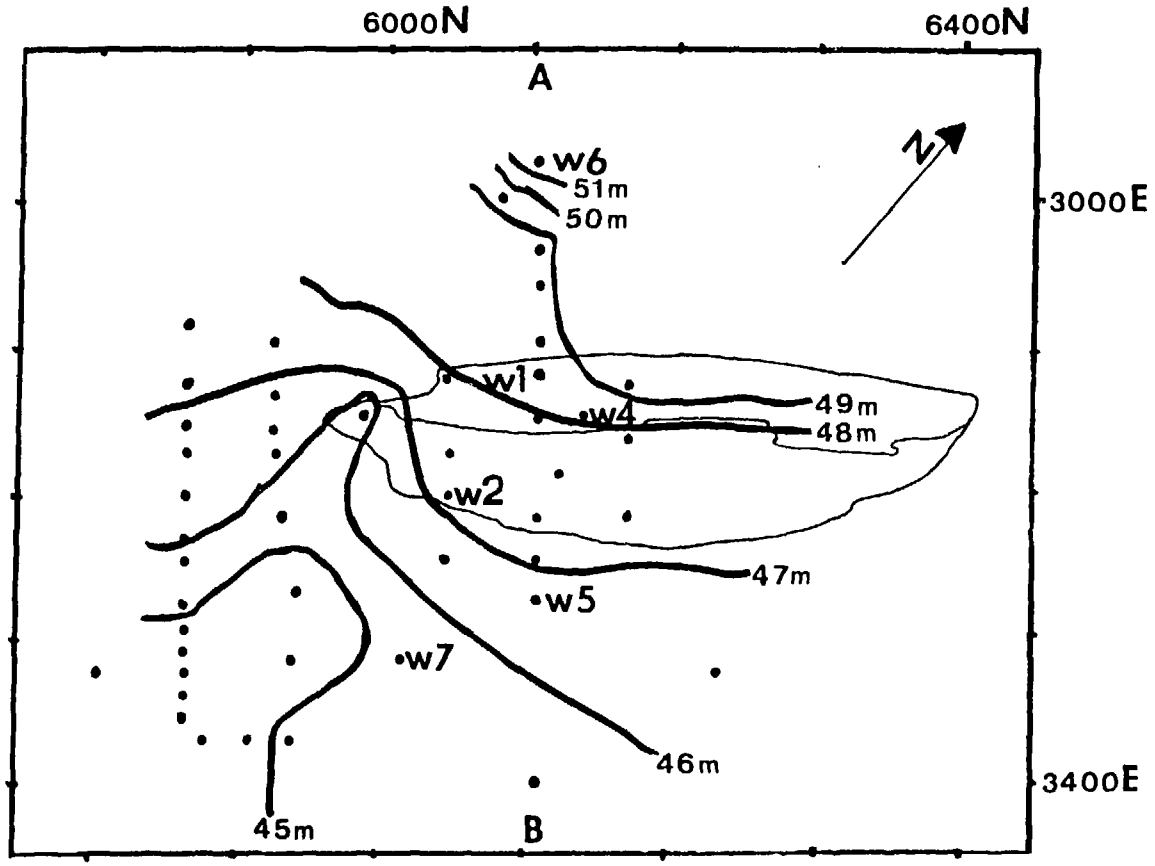


Figure 3.6. Simplified hydrogeological plan showing s.w.l. contours (drawn from data of Norris 1989) and outline of the No.1 ore body. The cross-section in figure 3.3 is along the line A-B.

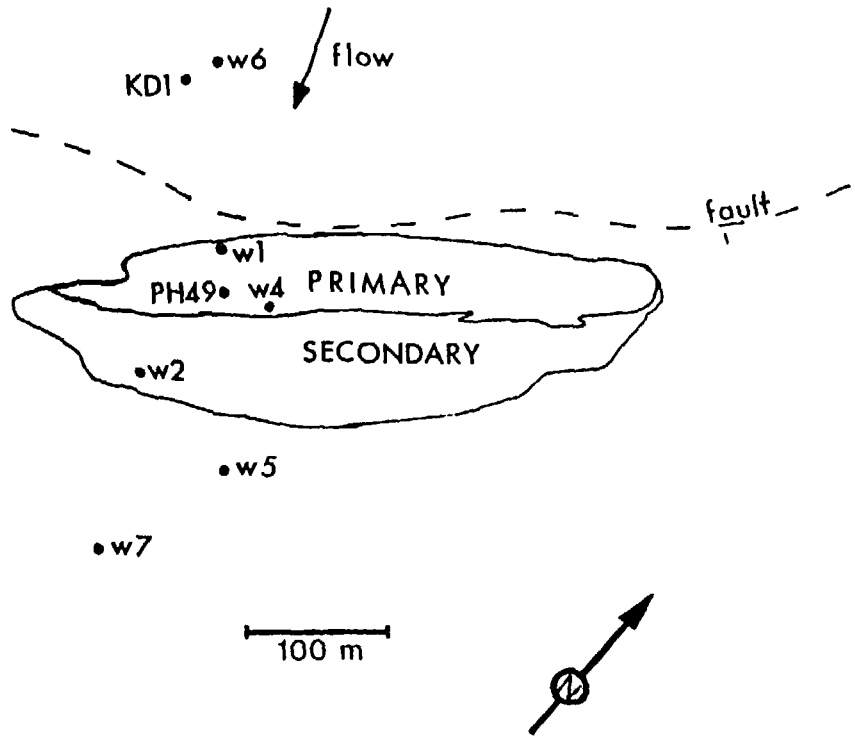
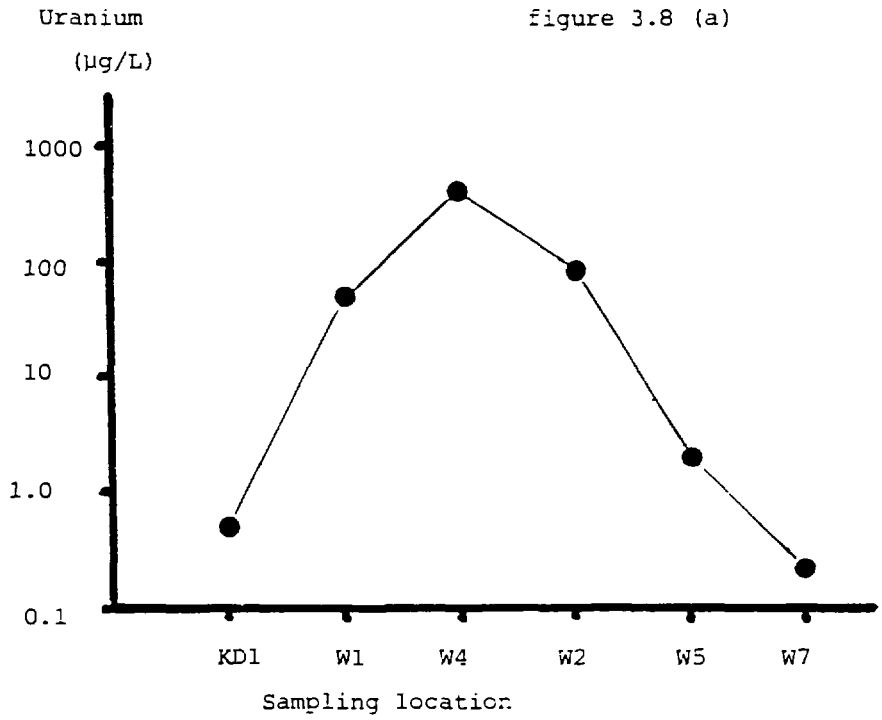


Figure 3.7. Location of PH49, KD1, and w-series boreholes.



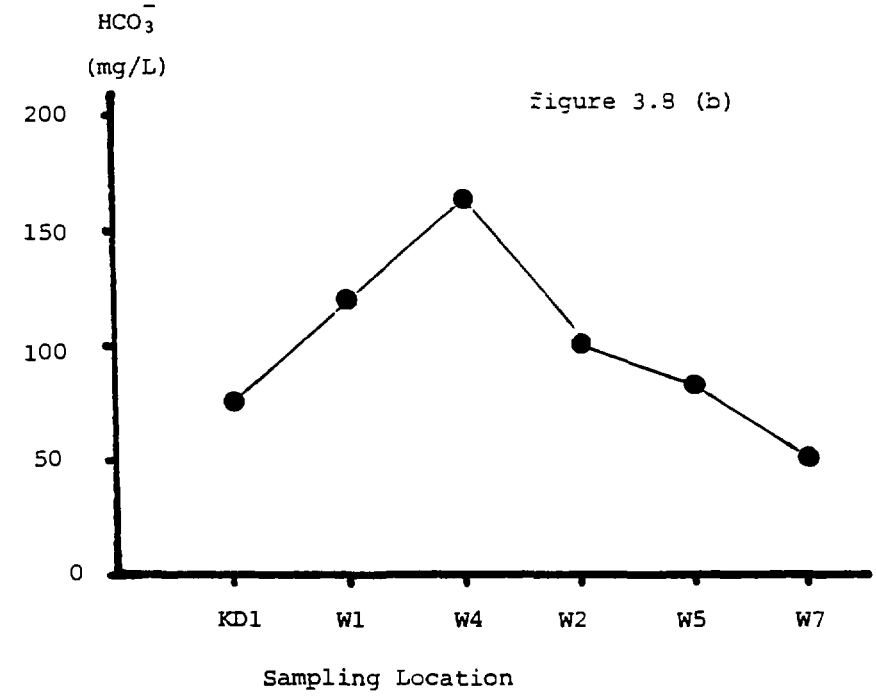


Figure 3.8 Uranium (a) and bicarbonate (b) concentrations (KD1 and w-series boreholes).

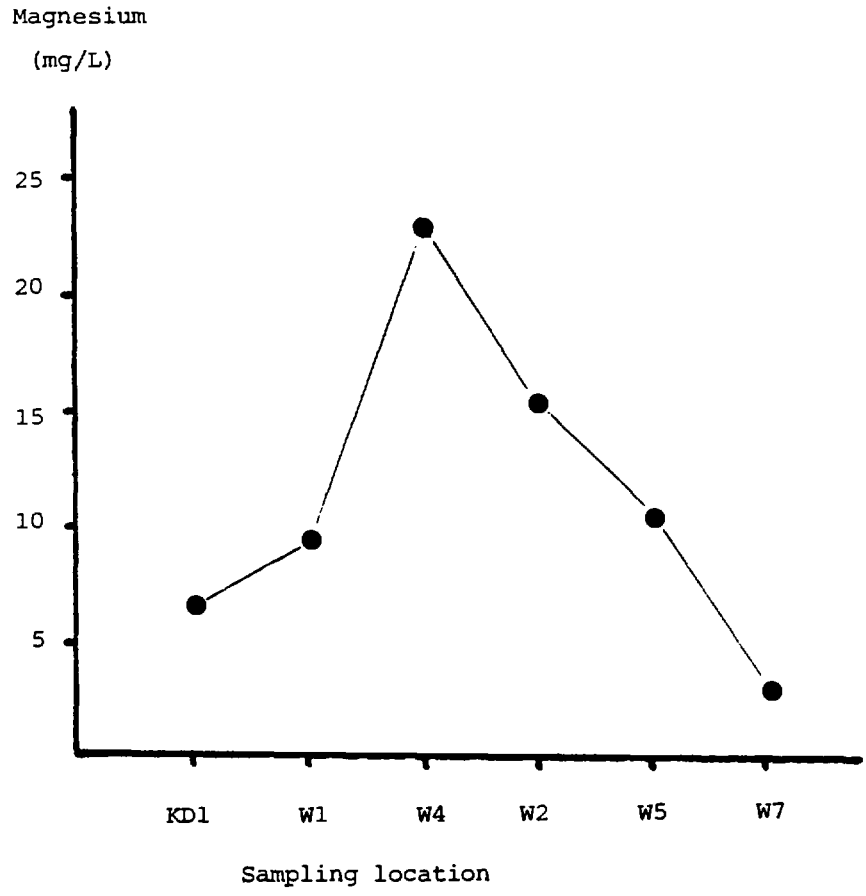


Figure 3.8 (c) Magnesium concentrations (KD1 and w-series boreholes).

Table 3.1 Groundwater Chemistry in the Kombolgie Formation and the No 1 Ore Body

Formation	Kombolgie		Cahill (No 1 ore body)			Analyst
Borehole	KD1		PH49			
Depth	70.5-72.5 m	80-82 m	28-30 m	28-30 m	44-46 m	
Date	Nov 1988	May 1988	May 1988	Nov 1988	Nov 1988	
pH	6.18	5.82	6.74	6.84	7.01	1[c]
Eh (mV)	+220	+235	+130	+130	+280	1
Cond (μS/cm)	108	124	236	230	247	1
Mg^{2+} (mg/L)	8.9	2.4[b]	26.4	25.0	24.0	2
Ca^{2+}	4.6	2.0	3.9	5.2	8.5	2
Fe^{2+}	1.6	1.0	0.8	1.1	0.5	2
K^{+}	0.2	0.3	0.7	0.8	0.9	2
Na^{+}	0.9	1.0	1.4	1.2	1.3	2
Si	8.2	6.5	8.9	9.2	8.7	2
HCO_3^-	67	43	154	159	180	1
Cl^-	3.4	2.6	4.9	8.5	2.0	3
F^-	0.3	0.1	0.2	0.3	0.4	3
PO_4^{2-}	<0.005	0.030	0.310	0.090	0.060	1
SO_4^{2-}	0.20	<1	2	0.29	0.11	3
U (μg/L)	0.5	3.7	274	102	131	1
Σ +ve (meq/L)[a]	1.07	0.39[b]	2.48	2.45	2.51	
Σ -ve (meq/L)[a]	1.22	0.78	2.67	2.87	3.03	

Units are mg/L except where otherwise stated.

(a) Σ +ve and Σ -ve are the sum of cations and anions respectively.

(b) The Mg^{2+} value for this analysis is anomolously low, and is probably the reason for the poor charge balance. Samples taken at KD1 at other times gave Mg^{2+} values in the range 4.8 to 10.2 mg/L, average 6.7 mg/L. If this figure is used, Σ +ve = 0.71 meq/L.

(c) Analysts were: (1), T E Payne (ANSTO), (2) L Dale (CSIRO), (3) S McEvoy (CSIRO).

PART II URANIUM AND THORIUM MIGRATION AT KOONGARRA

CHAPTER FOUR

MIGRATION OF URANIUM IN THE NO 1 ORE BODY

4.1 Formation of the Dispersion Fan

One of the objectives of the present study is to examine the assumptions underlying the mathematical model of radionuclide migration in the ore body which is being developed as part of the ARAP study. Two key elements of the model are:

(a) defining the starting point, and

(b) identifying the main processes involved in the evolution of the system.

The initial condition of the system can be considered to be an accumulation of uranium ore located in unweathered rock, some distance below the ground surface (figure 4.1a). The primary ore body formed after uranium leached into fractures within basement granitoids and sediments during metamorphism (Snelling 1980b). Subsequently, concentration occurred by adsorption onto chlorites, together with redox reactions involving graphite, chlorite and/ or pyrite, followed by precipitation of pitchblende. The age of the primary ore body is estimated to be 1800 million years.

The mobilisation of uranium from the primary ore body occurred when the weathering front, which is slowly moving downwards as the formation weathers, intersected the primary uranium mineralisation. This event occurred between 1 and 3 million years ago (Airey et al. 1986b). Groundwaters moving through the weathered zone then dissolved uraninite and other minerals in the primary ore and transported the uranium into the surrounding rocks. This process has continued to the present day and has led to the formation of the characteristic dispersion fan (figure 4.1b).

The cross-sections of the No 1 and No 2 ore bodies are very similar (Snelling 1980a), except that the No 2 ore body has not been intersected by the weathering front, hence no dispersion fan is present. The current state of the No 2 ore body is similar to the unaltered No 1 ore body, as depicted in figure 4.1a.

It is therefore reasonable to conclude that the dispersion fan of the No 1 ore body is a consequence of horizontal movement of groundwaters within the weathered zone. These groundwaters have leached uranium from a former upward extension of the primary ore body located in the present-day weathered zone and redeposited it in the surrounding rocks.

4.2 Uranium Concentrations in Groundwaters Intersecting the Ore Body

The aim in this section is to quantify uranium concentrations as a function of distance from a suitably defined origin. This may then allow simplification of the system for modelling purposes.

General trends in uranium concentrations from KD1 and five w-series boreholes were presented in section 3.5.5. A larger, and potentially more useful database can be assembled by including data from all Koongarra boreholes which have been sampled since 1988. This approach reduces the influence of localised inhomogeneities and shows up overall trends. To

some extent, these advantages are offset by the fact that the boreholes other than the w-series are only open at depths below about 22 m, and therefore may give anomolously low concentrations by sampling groundwater from the barren unweathered rock underlying the dispersion fan.

In this section, attention will be restricted to boreholes which are on flow paths which intersect the orebody. These boreholes are shown in figure 4.2.

For the purpose of analysing the data, the 3000 m east line (on the exploration grid) was selected as the origin of distance (figure 4.2). The distance of each borehole downgradient was then readily calculated by subtracting 3000 m from the easterly grid reference.

Table 4.1 gives uranium data for filtered (<0.45 μm pore size) groundwaters from these boreholes. The order of boreholes in the table corresponds to increasing distance downgradient.

The plot of uranium concentration as a function of distance is shown on figure 4.3. The curve on this figure was drawn qualitatively. The data point for borehole M2 was omitted from the figure because M2 is cased through the entire dispersion fan (to 40 m depth) and sealed, therefore the uranium concentration is not an accurate reflection of groundwater concentrations in the dispersion fan which would be expected to be very high at this location.

Figure 4.3 shows that there is a sharp increase in uranium concentrations when moving groundwaters intersect the ore body. Subsequently, there is a gradual decrease to background levels, over a distance of some 200 m. This distance is greater than the extent of the economic orezone as defined for mining purposes, which extends over approximately 75 m.

Considerable scatter is seen in the data. This is attributed to inhomogeneities in uranium distribution which may arise from preferential aquifer paths in the area surrounding the ore body.

Uranium concentrations downgradient appear to be below the input uranium concentrations at KD1 and C10. This may be because the pH/Eh conditions of the Kombolgie groundwater favour uranium solubilisation relative to conditions downgradient. Furthermore, the rock-type downgradient is clay-rich weathered schist which probably sorbs uranium more strongly than sandstone.

4.3 Uranium Solubility and Speciation in Groundwater

Calculations of the state of saturation of groundwaters sampled at Koongarra, using the equilibrium computer code EQ3NR, showed that the groundwaters were significantly undersaturated with respect to the primary and secondary uranium minerals present in the ore body (Sverjensky 1989). Therefore, the groundwaters would be expected to be actively dissolving these minerals. Consequently, adsorption rather than precipitation would be expected to be the major process retarding uranium migration in the dispersion fan at Koongarra.

The chemical speciation of uranium in the solution phase is dependent on the concentrations of complexing ligands (both organic and inorganic) in the groundwater. Koongarra groundwaters are quite low in total organic

carbon (Mathews 1989), therefore inorganic species, such as hydroxyl, carbonate and phosphate are likely to be the main uranyl complexants in these groundwaters.

In the absence of significant amounts of organic complexants or phosphate, the speciation of uranyl (UO_2^{2+}) in solution is primarily dependent on the amount of dissolved uranyl in a solution at equilibrium with air was calculated as a function of pH, using the chemical equilibrium code MINTEQA2, and stability constants from Tripathi (1983). The results showed that a sequence of complexes containing carbonate and/or hydroxyl ions dominated uranyl speciation over the pH range 4 to 10 (figure 4.4a).

In Koongarra groundwaters, the dissolved CO_2 is significantly higher than the air-equilibrium value, maintaining the dissolved carbonate level at about 2.0 millimolar. MINTEQA2 calculations for these conditions indicated that hydroxyl-containing uranyl species were much less significant, and uranyl carbonate species dominated uranyl speciation in the pH range above 5.0 (figure 4.4b).

Uranium phosphate minerals, such as saleeite and renardite, are common at Koongarra, and literature values for the formation of the $UO_2(HPO_4)_2^{2-}$ species (Dongarra and Langmuir 1980; Langmuir 1978) indicated that this complex could dominate uranyl speciation in Koongarra groundwaters. The results of MINTEQA2 calculations for a number of bores in the vicinity of the deposit (Table 4.2) showed that within the Cahill formation, up to 98.9% of the uranyl ion in solution could be complexed by phosphate (Payne and Waite 1989). Upgradient, in Kombolgie groundwater (KD1), uranyl phosphate complexes were insignificant.

The calculations showed that uranyl phosphate complexes could play a major role in solution phase uranium speciation, despite the fact that phosphate concentrations are about 100 times lower than bicarbonate concentrations. However, considerable controversy surrounds the importance of the $UO_2(HPO_4)_2^{2-}$ complex in uranyl speciation. The strength of this complex, indeed its very existence, have been questioned (Markovic and Pavkovic 1983; Tripathi 1983). If this species is excluded from the calculations, the speciation results are entirely different (table 4.2).

In summary, the solution phase speciation of uranium in Koongarra groundwater appears likely to be dominated by carbonate and/or phosphate complexes, with the relative importance of the major postulated uranyl species remaining a matter for debate.

4.4 Distance-Concentration Relationship for Magnesium

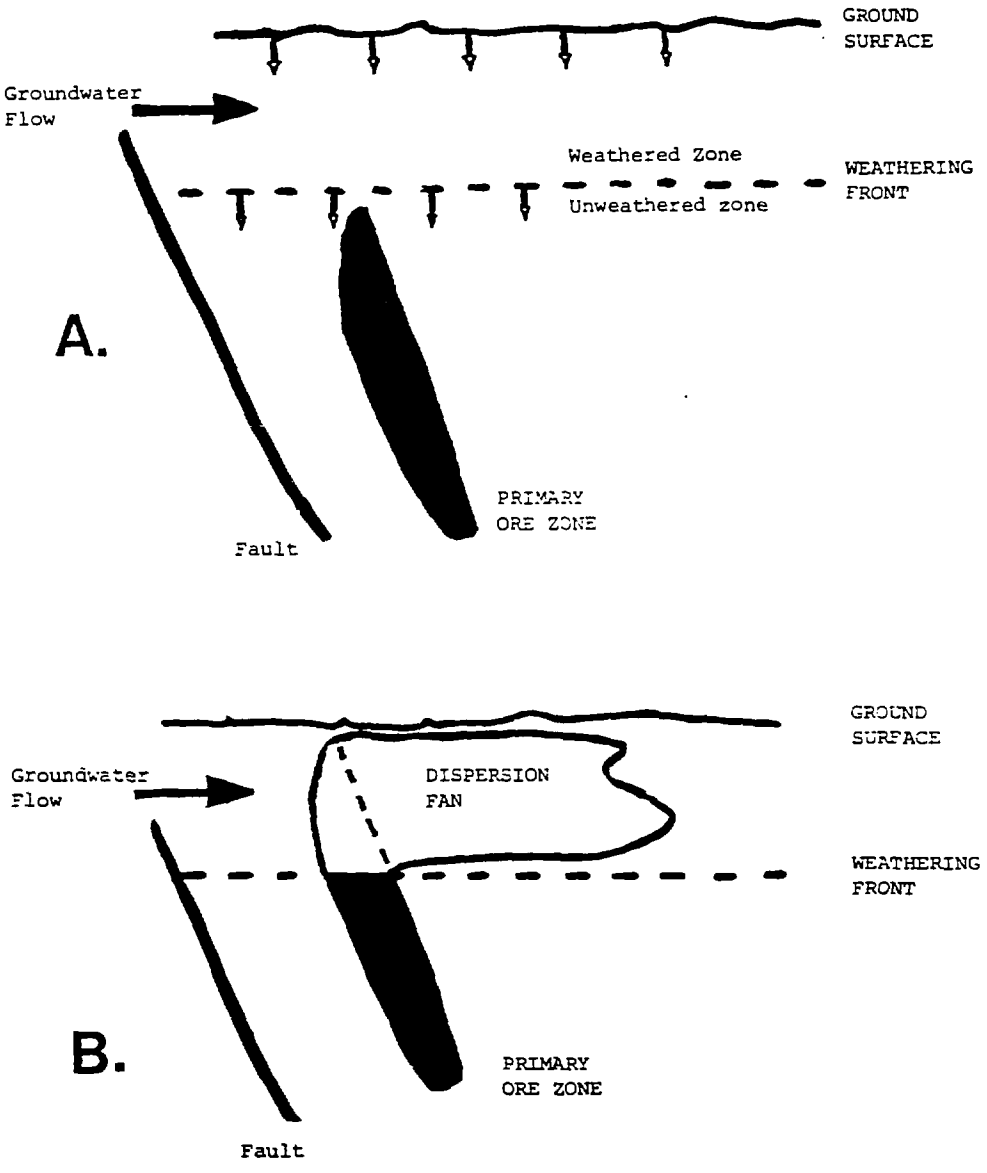
Magnesium is important at Koongarra because it is released by weathering of the chloritised schists of mine series host rocks. Hence a magnesium "source" can be considered to exist over approximately the same area as the uranium "source".

The data on magnesium concentrations (compiled from ARAP progress reports) were treated in exactly the same fashion as the uranium data, and indicated an enrichment over approximately the same area as the elevated uranium levels (figure 4.5). However, magnesium levels varied by a factor of approximately five, as opposed to around 500 for uranium. This suggested that magnesium behaves more conservatively than uranium and dilution plays a relatively more important role than sorption processes in reducing its concentration.

4.5 A Conceptual Model

The distribution of elevated concentrations of magnesium and uranium in groundwaters suggested that the primary zone of the No 1 ore body could be represented by a "linear source" intersected almost perpendicularly by moving groundwater. The orientation of this linear source is along a line commencing in the vicinity of PH15 and extending beyond M1 in figure 4.2.

A simplified model of the ore body is presented in figure 4.6. The primary orezone is represented by a planar rectangular source perpendicular to the groundwater flow, with its exposed upper edge acting as a line source of uranium input. Elevated uranium concentrations are found in groundwaters over a distance approximately 200 m downgradient from this source.



Simplified cross section of the No 1 orebody -

A Prior to weathering of primary ore (small arrows indicate downward movement of ground surface and weathering front).

B Present day.

Figure 4.1

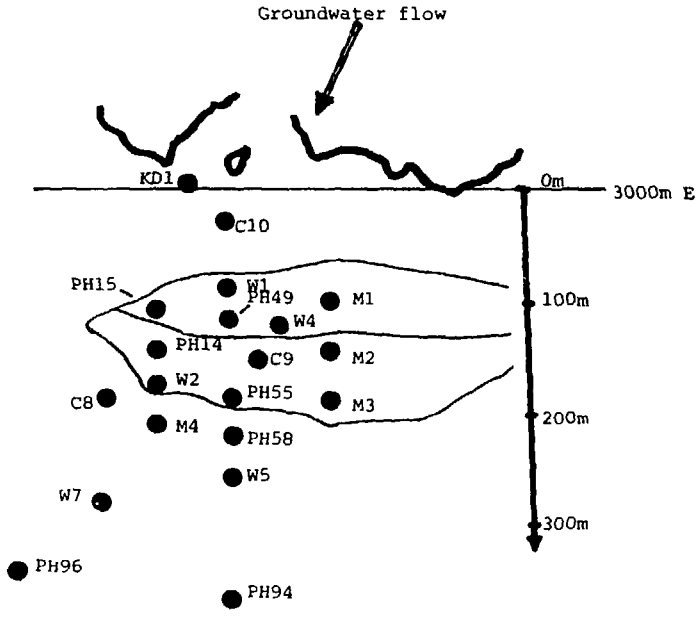


Figure 4.2 Location of boreholes sampling groundwaters intersecting the No.1 ore body

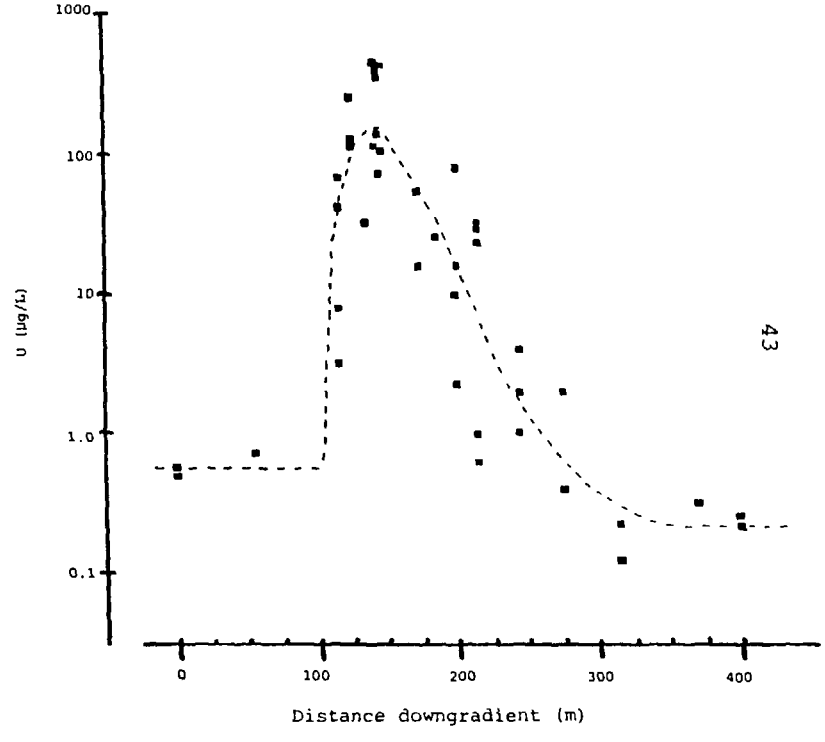


Figure 4.3 Uranium concentrations in groundwater as a function of distance.

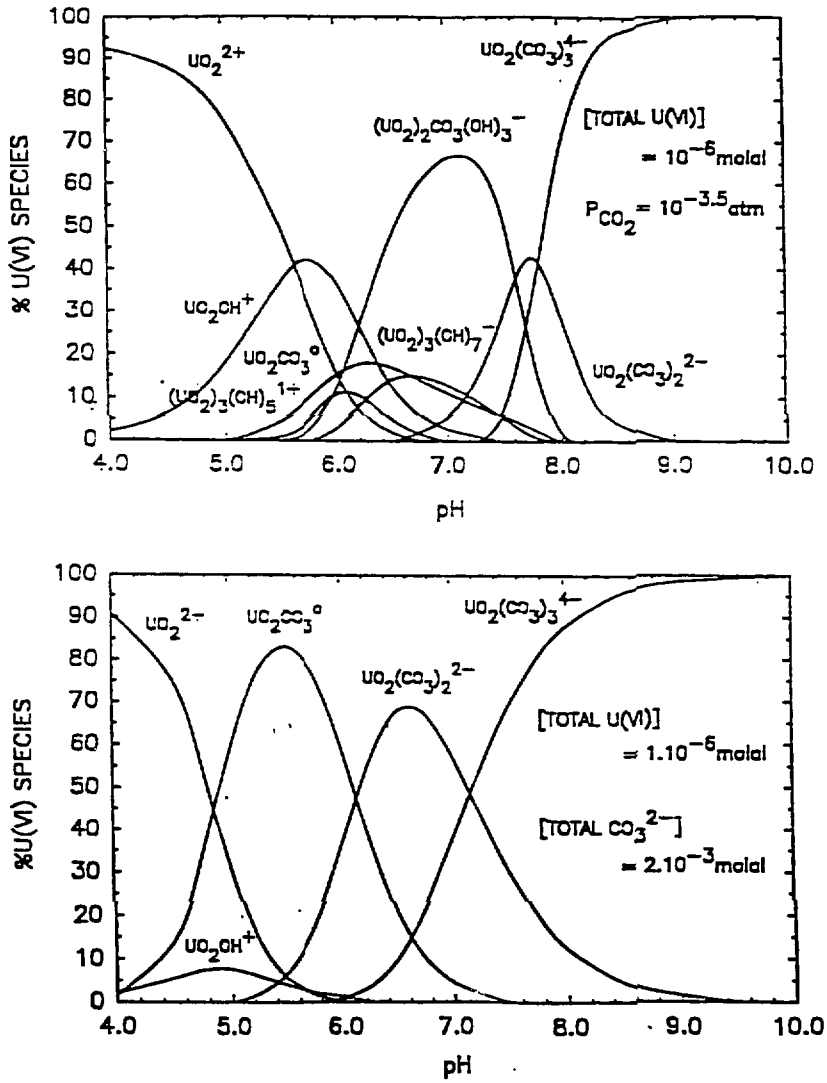


Figure 4.4

Distribution of major uranyl species as a function of pH, for a total uranyl concentration of 10^{-6}M (a) at equilibrium with air (b) fixed carbonate 2mmol/L

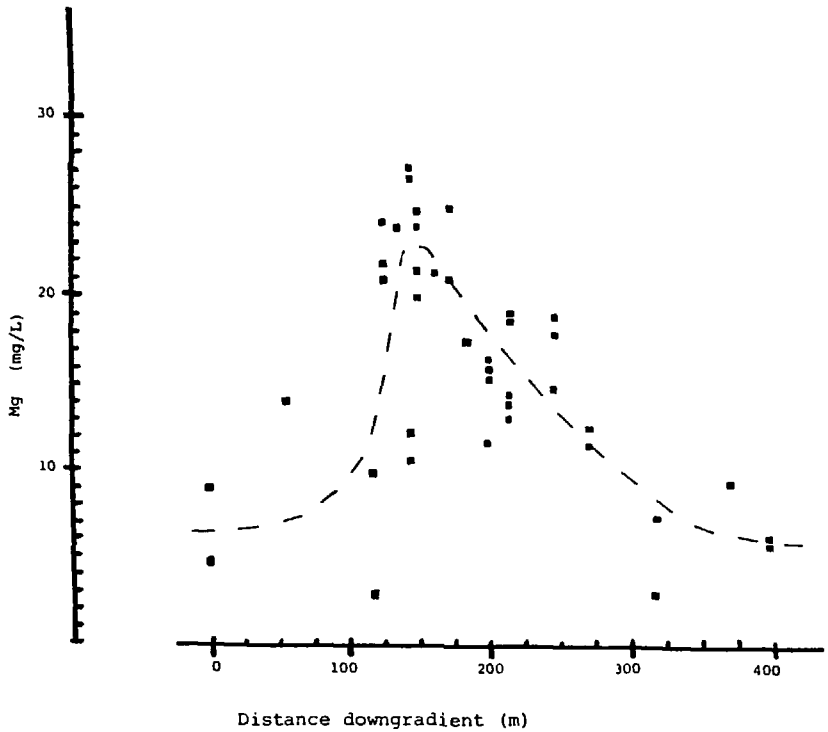
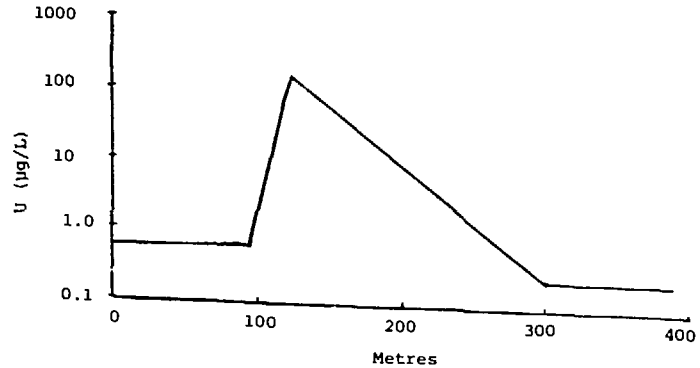
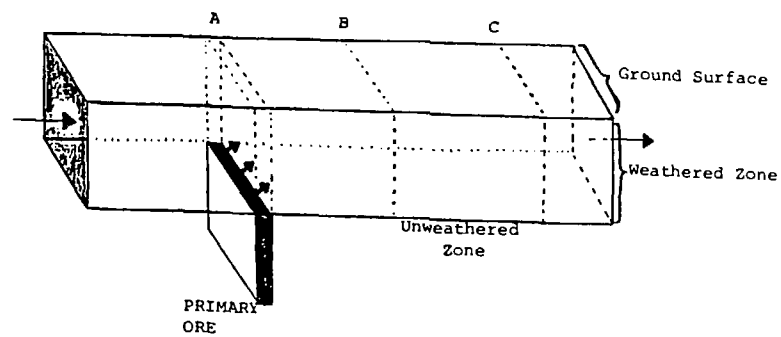


Figure 4.5 Magnesium concentrations in groundwater as a function of distance.





Simplified model of Koongarra No 1 orebody, with primary ore zone depicted as a linear source (groundwater uranium concentrations are shown above).

→ Groundwater flow path.
A Zone of former upward extension of primary ore.
B Limit of economic mineralisation.
C Limit of elevated U-conc in groundwater.
Small arrows indicate uranium input to groundwater.

Figure 4.6

Table 4.1 Uranium Concentrations Moving Down-Gradient

(0.45 μm filtered groundwater)

Borehole	Location (m)		Distance Down-Gradient (see text) (m)	Depth Sampled (m)	Uranium μg/L	Analysis Method	Date Sampled
	N	E					
KD1	6081	2998	-	40-42	0.49	α	Nov 1988
				70.5-72.5	0.49	α	Nov 1988
C10	6109	3056	56	<40	0.70	ICPMS	May 1989
W1	6109	3117	117	13-15	3.2	α	5 Oct 1989
				13-15	7.9	α	7 Oct 1989
				23-25	65.9	α	5 Oct 1989
				23-25	39.8	α	7 Oct 1989
M1	6170	3124	124	24-26	128	ICPMS	May 1989
				35-50	248	ICPMS	May 1989
				46-48	109	ICPMS	May 1989
PH15	6046	3134	134	<21	30.6	α	Nov 1988
W4	6139	3146	146	13-15	412	α	6 Oct 1989
				13-15	440	α	7 Oct 1989
				23-25	431	α	6 Oct 1989
				23-25	345	α	7 Oct 1989
PH49	6109	3147	147	27-29	107	ICPMS	May 1989
				28-30	102	α	Nov 1988
				33-35	71.2	ICPMS	May 1989
				44-46	139	α	Nov 1988
M2	6170	3162	162	40-46	3.11	α	May 1989
PH14	6048	3171	171	<26	17.8	α	Nov 1988
				<22	46.6	ICPMS	May 1989
C9	6124	3185	185	34-40	26.4	ICPMS	May 1989
W2	6048	3200	200	13-15	16.1	α	Oct 1989
				23-25	79.4	α	Oct 1989
C8	5987	3200	200	24-26	9.71	ICPMS	May 1989
				38-40	2.27	ICPMS	May 1989

Table 4.1 (Continued)

Borehole	Location (m)		Distance Down-Gradient (see text) (m)	Depth Sampled (m)	Uranium μg/L	Analysis Method	Date Sampled
	N	E					
M3	6170	3216	216	20-22	22.0	ICPMS	May 1989
				26-28	28.8	ICPMS	May 1989
				34-40	31.0	ICPMS	May 1989
PH55	6109	3216	216	26-28	0.62	α	Nov 1988
				38-40	1.01	α	Nov 1988
M4	6048	3246	246	34-40	4.08	ICPMS	May 1989
PH58	6109	3246	246	25-27	2.02	α	Nov 1988
				38-40	1.01	α	Nov 1988
W5	6109	3273	273	13-15	0.42	α	Oct 1989
				23-25	1.89	α	Oct 1989
W7	6018	3314	314	13-15	0.12	α	Oct 1989
				23-25	0.22	α	Oct 1989
PH96	5911	3370	370	<26	0.30	α	Nov 1988
PH94	6109	3399	399	26-28	0.23	α	Nov 1988
				40-42	0.26	α	Nov 1988

Compiled from results in Alligator Rivers Analogue Project Progress Reports.

Analysis: α-spectrometry (T Payne, ANSTO)
ICPMS (L Dale, CSIRO)

Bore No.	Depth (metres)	Total Mg (mg/L)	Total U (µg/L UO_2)	Total P (µg/L PO_4)	Alkalinity (mg/L CO_3^{2-})	pH	% U(VI) Species (>1%)				% U(VI) Species (>1%) ($UO_2(HPO_4)_2^{2-}$ excluded)			
							$UO_2(HPO_4)_2^{2-}$	$UO_2CO_3^{0}$	$UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$	$UO_2CO_3^{0}$	$UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$	$UO_2HPO_4^{0}$
PH49	28-30	26.4	240	310	46.8	6.80	86.8	2.0	10.8		14.8	81.2	2.5	
PH55	26-28	17.9	0.47	650	62.2	6.57	98.9				18.4	78.3	1.8	1.2
PH61	43.5-45.5	18.0	4.6	130	74.0	7.03	54.0	2.7	40.0	3.2	5.9	87.0	7.0	
PH94	26-28	5.7	0.20	290	18.6	7.17	98.8				16.9	79.7	1.7	1.1
PH14		20.3	61	160	62.7	6.42	78.6	5.2	15.8		24.2	73.8	1.2	
PH88	28-30	14.1	2.5	110	43.1	6.54	83.7	4.3	11.6		26.5	71.5		
KD1*	70.5-72.5	8.9	0.55	10	32.8	6.18	6.3	49.1	43.0		52.4	45.9		
KD1†	70.5-72.5	8.9	0.55	5	32.8	6.18	1.7	51.6	45.2		52.5	46.0		

* Phosphate at detection limit (10 µg/L PO_4)

† Phosphate at half detection limit

Table 4.2 Uranyl speciation with and without the uranyl species $UO_2(HPO_4)_2^{2-}$ for Koongarra groundwater samples.

CHAPTER FIVE

MODELLING RADIONUCLIDE MIGRATION IN THE WEATHERED ZONE

5.1 Open System Modelling

Mathematical modelling of radionuclide migration from uranium deposits in the ARUF has been undertaken since the original USNRC-sponsored work commenced in 1981. The emphasis at Koongarra has been on modelling the distribution of the radionuclides of the U-series decay chain (particularly ^{238}U, ^{234}U and ^{230}Th) within the dispersion fan (Duerden and Golian 1988).

Isotopes in the ^{238}U series become fractionated during transport processes, leading to differences in their distribution throughout the deposit. This phenomenon is known as uranium series disequilibrium and is critical to modelling radionuclide migration at Koongarra. More details are given in Appendix I.

In the model, it is assumed that mobilisation of uranium commenced when the weathering front, which is moving downward, intersected the primary ore (see figure 4.1). This event is considered to have occurred at time zero (t_0). Groundwater moving in the weathered zone then started to solubilise uranium and transport it into the dispersion fan where redeposition occurs.

A key assumption of the model is that ^{230}Th is immobile. (The validity of this assumption will be investigated in chapter six). In contrast, ^{238}U and ^{234}U are considered to be mobile in the groundwater, hence their distribution will be modified by groundwater movement. It follows that any ^{230}Th present in the solid phase at a particular point must have formed by in-situ decay of ^{234}U, rather than by transport of ^{230}Th from elsewhere.

These assumptions about the system yield the following generating equations for ^{238}U, ^{234}U and ^{230}Th:

	production by decay	depletion by decay	leaching/ deposition	
$\frac{-d(^{238}U)}{dt} =$		$\lambda_{238}(^{238}U)$	$+ \xi(^{238}U)$	(6.1)
$\frac{-d(^{234}U)}{dt} =$	$-\lambda_{238}(^{238}U)$	$+ \lambda_{234}(^{234}U)$	$+ R\xi(^{234}U)$	(6.2)
$\frac{-d(^{230}Th)}{dt} =$	$-\lambda_{234}(^{234}U)$	$+ \lambda_{230}(^{230}Th)$		(6.3)

The terms in brackets denote solid phase concentrations; λ_{238}, λ_{234}, and λ_{230}, are decay constants for ^{238}U, ^{234}U and ^{230}Th, respectively; ξ is the uranium leaching/deposition rate; and R is the ratio of the leaching/deposition rate for ^{234}U to that of ^{238}U (usually the $^{234}U/^{238}U$ ratio in intersecting groundwater). At Koongarra the value of R varies from unity because of isotope fractionation processes (see section 7.8).

Equations 6.1 to 6.3 show the processes leading to changes in radionuclide levels which are considered in this model. Increased levels result from production of a nuclide by decay of its parent, or deposition; and decreases are due to leaching or decay. The sign of ξ indicates whether net leaching or deposition occurs. Note the absence of a production term for ^{238}U, since it is primordial, and of a leaching/deposition term for ^{230}Th in accordance with its assumed immobility.

The solution for the isotope ratio $^{234}U/^{238}U$ (R1) has been developed (Airey et al. 1986b):

$$R1 = R1(t_o)\exp(b - a)t + \frac{\lambda_{234}}{(b - a)}(\exp(b - a)t - 1) \qquad (6.4)$$

with:

$$a = \lambda_{234} + R\xi \ , \quad b = \lambda_{238} + \xi$$

$R1(t_o)$ is the value of R1 at t_o.

A more complex solution for R2 (the $^{230}Th/^{234}U$ isotope ratio) has been derived (see Airey et al. 1986b).

The steps in applying the model are as follows:

1) Specify initial conditions, ie. values of $R1(t_o)$ and $R2(t_o)$.

2) Select an appropriate range of values for ξ and R.

3) Calculate R1 and R2 and compare with measured values.

4) Identify sets of parameters in which calculated and measured values of R1 and R2 agree satisfactorily (eg. to within 10%) and are internally self consistent.

The values of $R1(t_o)$ and $R2(t_o)$ can be determined by consideration of the initial state of the system. It is assumed that at t_o, the primary ore body was at radiometric equilibrium (R1 = R2 = 1.0). In the region in which the dispersion fan now exists, a relatively small, 'background' concentration of uranium was present, which has now been inundated by far greater amounts. Hence, for a given location in the dispersion fan, the value of $R1(t_o)$ is unimportant since the value of R1 at that point will

quickly become equal to the value in the groundwater. In accordance with the assumption that thorium does not migrate, the value of $R2(t_0)$ is set to zero.

Equations 6.1 to 6.3 only include terms for the radionuclide contents of the solid phase, and a more complete description of the system is possible when a variable relating solid and liquid phase concentrations is added (Duerden and Golian 1988).

The distribution of radionuclides between solid and aqueous phases may be expressed as a distribution coefficient (K_d) or distribution ratio (R_d), the latter term being appropriate for laboratory experiments where equilibrium may not be achieved. The R_d (or K_d) for a radionuclide ('Z') is defined as:

$$R_d = \frac{\text{amount of Z sorbed on solid per unit mass}}{\text{amount of Z in solution per unit volume}} \qquad (6.5)$$

and has the units mL/g.

The R_d value may be included within models which simulate contaminant transport. In its simplest form, the relationship between the average groundwater velocity (V) and the average relative velocity of a contaminant (V_c) in a porous medium is given by:

$$\frac{\overline{V}}{\overline{V}_c} = 1 + \frac{\rho_b}{\eta} R_d \qquad (6.6)$$

where ρ_b is the bulk density, and η is the porosity (Freeze and Cherry 1979). The quantity V/V_c is often referred to as the retardation factor (R_f). Because of the direct relationship between R_d and R_f, the R_d concept has been widely used in modelling radionuclide migration. This application has recently been reviewed (Serne and Muller 1987).

In the mathematical model of Koongarra (Duerden and Golian 1988), an in-situ uranium distribution ratio (R_d) was incorporated. This was defined as the ratio of the total uranium content of the rock (g/g) to that of the groundwater (g/mL).

The resulting mathematical model is still highly simplified, because the in-situ R_d is a function of the total uranium content of the solid phase. This includes uranium held in a variety of ways - ranging from adsorption on surface sites to incorporation within stable mineral phases. The degree of interaction of uranium in such diverse sites with the groundwater would be expected to range from rapid exchange to almost zero.

The term 'accessible' has been suggested for the proportion of uranium which is readily available for leaching (Shirvington 1979). Such a definition allows a distinction to be made between uranium which may be mobilised by groundwater ('accessible'), and 'inaccessible' uranium.

Further refinement leads to a model where the solid phase is visualised as comprising several distinct phases which have various interactions between one another and with the groundwater.

5.2 The Multiphase Model

In this more complex model, the solid phase is viewed as consisting of an assemblage of minerals of differing characteristics and radionuclide content.

The mineralogical categorisation which has been used for samples from the weathered zone at Koongarra comprises the following radionuclide-containing phases:

1) Soluble phases and exchangeable ions.

2) Amorphous minerals: species which are coprecipitated with, occluded in, or otherwise associated with non-crystalline or coating minerals, such as ferrihydrite.

3) Crystalline iron minerals, such as goethite and hematite.

4) Resistant clay/quartz and other minerals.

The distribution of radionuclides amongst these phases has been extensively investigated by a chemical procedure, referred to as a 'sequential extraction', in which the solid is successively treated with reagents which specifically dissolve the desired phases.

The selective phase separation applies the following procedure (or a close variant) to a sample of crushed rock or disaggregated material (Lowson et al. 1986):

1) Soluble salts and exchangeable ions. The sample (1-2 g) is shaken with 0.1 M NH_4Cl at room temperature for 24 hours.

2) Amorphous oxide minerals. The sample is shaken with 80 mL of Tamm's Acid Oxalate (TAO) solution (10.92 g oxalic acid, 16.11 g ammonium oxalate in 1 L of water) at room temperature, and in the dark, for four hours.

3) Crystalline Iron Minerals. The residue from (2) is treated with 80 mL of DCB solution (85.72 g sodium citrate 5.5 hydrate, 16.8 g sodium bicarbonate in 1 L of water, with 1 g of sodium dithionite per gram of sample added just prior to extraction), at 80°C for half an hour. This extraction is repeated.

4) Resistate. The residue is digested with a sequence of nitric, hydrofluoric and perchloric acids, followed by fusion with sodium carbonate and borax.

It is emphasised that the resulting distribution of radionuclides is operationally defined by the extractants used. However, physical analyses by XRD, and other techniques, have shown that the sequential extraction dissolves the various mineral phases with a high degree of specificity (Lowson et al. 1986; Yanase et al. 1990).

In the multiphase model (Airey et al. 1986b), it is assumed that:

i) Uranium of the amorphous mineral phase is directly accessible to the groundwater.

ii) On the geological timescale, exchange occurs between the amorphous and crystalline iron phases.

iii) The clay/quartz phases have relatively low concentrations of uranium and thorium.

iv) By the process of α-recoil (see Appendix I), the clay/quartz phase tends to become enriched in daughter radionuclides.

Assumptions (i), (iii) and (iv) were supported by a study of four Ranger samples (Lowson et al. 1986). In this study, similar $^{234}U/^{238}U$ activity ratios were measured in the groundwater and amorphous iron phases, indicating that these phases were in adsorption/desorption equilibrium. Furthermore, the concentrations of ^{238}U and ^{230}Th in the resistate clay/quartz phase (expressed as dpm per gram of phase) were about an order of magnitude lower than in the combined iron phases. Finally, the $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ isotope ratios were above unity in resistate phases.

The assumed exchange between amorphous and crystalline iron phases is more difficult to substantiate. Laboratory data have shown that recrystallization of amorphous iron (ferrihydrite) to crystalline iron (goethite or hematite) phases does occur (Johnson and Lewis 1983), particularly at elevated temperatures. However, the fate of associated (adsorbed or occluded) species is a matter for conjecture. It is not known whether they are released or retained during recrystallisation. This unresolved matter is of relevance both in natural systems and in repository safety assessment in many geological environments.

5.3 Groundwater Interactions in the Multiphase and Open System Models

The following chapters aim to investigate several aspects of the above models which relate to radionuclide migration in the groundwater phase. These are:

A) The assumed immobility of thorium.
Leaching and deposition of thorium are excluded from the model, as this element is assumed to be immobile. If this assumption is invalid, the basis of the model, (particularly equation 6.3) is called into question.

B) The omission of terms for colloidal transport.
It is assumed in the model that only dissolved radionuclides can move in groundwater. However, it is possible that very fine (colloidal) particles (<1 μm in size) may be entrained and move with the groundwater. Such particles could carry with them highly insoluble radionuclides, thereby accelerating their migration.

C) The distribution of radionuclides between groundwater and solid phases.
The issue here is the extent to which uranium in the groundwater is sorbed by the mineral phases present. A related question is whether a parameter such as R_d is adequate to model this interaction.

D) The identification of accessible phases and quantification of the amounts of contained uranium.

In the model, uranium associated with coating minerals is considered to be accessible ie. exchanging with the groundwater over short timescales. It is therefore necessary to quantify the amount of uranium which is accessible and determine whether it does correspond to the TAO-extractable phase.

The remainder of Part II of this study is occupied with considering these issues.

CHAPTER SIX

THORIUM MIGRATION IN KOONGARRA GROUNDWATER

6.1 Importance of Thorium Immobility

There are two main reasons for studying thorium mobility in Koongarra groundwater. These are:

i) The immobility of ^{230}Th is assumed in the open-system model of the system (chapter five). If ^{230}Th is mobile in Koongarra groundwater, then the modelling approach is undermined.

ii) Thorium is a chemical analogue for several components of HLW, including Pa(V), Np(IV) and Pu(IV) (table 2.1). As was shown in chapter two, there is evidence of the immobility of thorium from the Morro do Ferro analogue site, and the Salton Sea Geothermal Field. At the Morro do Ferro, in particular, thorium is being used as an analogue for plutonium. Therefore, any evidence for thorium movement could have implications to the migration of plutonium.

The most direct way to study thorium mobility at Koongarra is to measure the levels of thorium isotopes, particularly ^{230}Th, in groundwater which has passed through a filter with a nominal 450 nm pore size. This separation is accepted as defining the dissolved or soluble fraction (Batley and Gardner 1977). However, this is largely an operational definition, and a smaller pore size membrane, such as an ultrafilter, may give a better indication of truly dissolved species. While filtration through a 450 nm membrane is a standard technique in water analysis, it should be regarded as a practical separation procedure rather than a true measure of dissolved species.

6.2 Measurement of Thorium Concentrations

Levels of ^{232}Th and ^{230}Th were measured in filtered groundwater samples collected during a field visit to Koongarra in November, 1988 (Payne 1989).

Groundwater was obtained from the boreholes using a submersible pump, which in most cases was suspended between inflatable packers, thereby defining a specific sampling interval. Where packers were not used, the source of the water was at depths between the bottom of the hole and the end of the casing (boreholes at Koongarra are cased through the weathered zone to about 20m depth). The boreholes sampled were PH14, PH15, PH49, PH55, PH56, PH61, PH88, PH94 and PH96. The location of these boreholes is shown on figure 3.5.

During pumping, groundwater pH and conductivity were monitored until they stabilised, after which sampling commenced. Thorium was coprecipitated (with ferric hydroxide) from 20 L samples of filtered groundwater (450 nm membrane). The concentrations of ^{232}Th and ^{230}Th were determined using α-spectrometry, after separation using anion exchange techniques (Payne 1989). ^{229}Th was used as a yield tracer.

6.3 Results

The measured thorium levels are given in table 6.1. The data will be discussed with reference to reported measurements of thorium levels in Koongarra groundwaters (Ivanovich et al. 1988; Short et al. 1988). Packers were not used in either of these previous studies, and in both cases groundwaters were ultrafiltered through membranes with nominal cutoffs at 100 000 molecular weight (Short et al.), or 10 000 MW (Ivanovich et al.). These pore sizes are at least an order of magnitude smaller than the 450 nm filter used in the present study.

Thorium-232:

Although ^{232}Th is not a member of either the ^{238}U or ^{235}U decay series, it is commonly detected in Koongarra core samples. Being an α-emitter, it could, in principle, be measured in groundwater using α-spectrometry.

The results of Short et al. indicated ^{232}Th levels below 0.002 dpm/L, and Ivanovich et al. gave an upper limit of 0.001 dpm/L. Considering the tendency of thorium to be associated with particulate rather than dissolved forms, it might have been expected that levels in 450 nm filtered groundwater would have been higher. However, most values were not significantly different from zero (Table 6.1). It therefore appears that dissolved ^{232}Th concentrations in Koongarra groundwaters are comparable to, or below, the detection limit of this technique (0.001 dpm/L or 0.005 μg/L).

Thorium-230:

In many cases, ^{230}Th peaks were discernible in the α-spectra, and after allowing for all sources of error, the values given in table 6.1 tend to be significantly different from zero. The highest ^{230}Th level measured, 0.050 dpm/L at PH49, is greater than the maximum value of 0.0096 dpm/L reported for ultrafiltered groundwater, using a 10000 MW membrane (Ivanovich et al. 1988; see also chapter 7). This suggests that measured ^{230}Th concentrations in filtered groundwaters are dependent on the pore size of the filters used, which is consistent with the possible inclusion of fine particles in the 450 nm filtered samples. The relatively high levels of ^{230}Th measured for PH49 (Table 6.1) may therefore be ascribed to fine particles passing through the 450 nm filter. This would be consistent with the nature of the solid phase at this location, which, being near the centre of the ore body, contains large amounts of ^{230}Th.

Apart from PH49, there was no apparent trend relating ^{230}Th concentrations to location in the ore body. Any such trend would be extremely difficult to measure, on account of the extremely low dissolved ^{230}Th levels, and the strong association of thorium with particles (see also chapter seven).

Overall, the results showed that the mobility of ^{230}Th is extremely low. The most conclusive evidence for this was the ^{230}Th/^{234}U ratio, which was less than 0.022 in these groundwater samples (table 6.1). For boreholes with significant uranium concentrations (>10 μg/L) this ratio was below 0.001. This is conclusive evidence of the immobility of Th(IV) relative to U(VI).

6.4 Discussion

Thorium has long been considered to be extremely immobile in natural waters (Langmuir and Herman 1980), and this was assumed in the mathematical model of Koongarra (Airey et al. 1986b). The present study has confirmed the immobility of thorium by showing that the levels of both ^{232}Th and ^{230}Th are extremely low in Koongarra groundwaters, despite the presence of readily measurable levels of both thorium isotopes in Koongarra core samples.

Thorium concentrations for groundwaters, and reported values for some solid core samples from the vicinity of the water sampling location (from Edghill 1989), are compared in table 6.2. A more extensive comparison of data will be possible when further solid phase ^{230}Th concentrations have been measured. Nonetheless, it is clear that the groundwaters have very low relative thorium contents. The value of the in-situ thorium distribution ratio, R_d (defined in section 5.1), ranges from approximately 4 X 10^5 mL/g to 2 X 10^9 mL/g for these samples. The spread of values is largely due to the inhomogeneous thorium distribution in the solid phase, corresponding to the localised nature of the primary uranium mineralisation. The very high R_d values for ^{230}Th are further verification of the immobility of thorium in nature.

These conclusions are in concordance with those of previous studies in the ARUF (Ivanovich et al. 1988; Short et al. 1988). The results are also in qualitative agreement with other studies of natural waters. For example, in ocean waters total ^{232}Th contents of 0.01 to 0.1 dpm/1000 L have been reported (Bacon and Anderson 1982; Kaufman 1969). Very low thorium levels were also generally found in surface waters at the Morro do Ferro (Eisenbud et al. 1984; 1986).

There are some exceptional cases where high levels of thorium have been reported in natural waters. Elevated thorium concentrations up to 261 μg/L at Morro do Ferro were ascribed to the presence of high levels of humic compounds (Miekeley and Kuchler 1987 - see section 2.3.2).

A $^{230}Th/^{234}U$ activity ratio of approximately unity was found in several deep briny groundwaters from Texas (Laul and Smith 1988). This uncommon situation (implying roughly equal mobilities of uranium and thorium) was attributed to the uranium being present in its immobile (+IV) oxidation state, rather than to significant mobility of thorium. This was a reasonable explanation, considering the low measured uranium concentration. The highest value for ^{230}Th was 0.80 dpm/L (average 0.19 dpm/L), about an order of magnitude above that measured at Koongarra. The higher thorium levels were probably due to the briny nature of the groundwaters. Increased mobility of radionuclides in saline groundwaters was also found in the Salton Sea Geothermal Field study (see section 2.3.5). A laboratory study of dissolution of uranium minerals in non-oxidising brines (with uranium present in its U(IV) state) suggested that uranium mobility was also greater in high ionic strength conditions (Giblin and Appleyard 1987).

In conclusion, it can be stated that the mobility of thorium is very low in most natural systems, with the major exceptions being a slightly increased mobility in highly saline groundwaters and a very much greater mobility in cases when organic complexants are present. The low measured levels of thorium isotopes in Koongarra groundwaters, which have a very low ionic strength and only trace levels of organics (Mathews 1989), are therefore not exceptional.

Table 6.1

^{232}Th, ^{230}Th and $^{230}Th/^{234}U$ in Koongarra Groundwaters

(errors in brackets)

Hole (depth)	^{232}Th (dpm/L)	^{230}Th (dpm/L)	^{234}U (dpm/L)	$^{230}Th/^{234}U$
PH14 (<26m)	0.0007(0.0010)	0.0014(0.0011)	11.6 (0.5)	1.2×10^{-4}
PH15 (<30m)	0.0008(0.0010)	0.0034(0.0011)	22.5 (0.7)	1.5×10^{-4}
PH49 (28-30m)	0.0002(0.0016)	0.050 (0.005)	76.5 (2.2)	6.5×10^{-4}
PH49 (44-46m)	<0.006	0.036 (0.006)	105 (3)	3.4×10^{-4}
PH55 (40-42m)	0.000 (0.003)	0.001 (0.005)	0.83 (0.06)	$<7 \times 10^{-3}$
PH56 (26-28m)	0.0009(0.0014)	<0.0017	4.93 (0.16)	$<4 \times 10^{-4}$
PH61(43½-45½m)	0.0006(0.0015)	0.0024(0.0022)	1.63 (0.08)	1.5×10^{-3}
PH88 (38-40m)	<0.0009	0.0055(0.0017)	1.52 (0.08)	3.6×10^{-3}
PH94 (40-42m)	0.0015(0.0010)	0.0052(0.0012)	0.24 (0.04)	2.2×10^{-2}
PH96 (<26m)	0.0018(0.0019)	0.0114(0.0025)	0.21 (0.02)	5.5×10^{-2}

All measurements were corrected for detector backgrounds and chemical blanks.

In cases where samples gave smaller signals than blanks, upper limits are given.

Table 6.2

Comparison of ^{230}Th concentrations in groundwaters and nearby core samples.

WATER SAMPLE (percussion hole)		CORE SAMPLES (diamond drill hole)		RANGE OF IN-SITU R_d VALUES
hole(depth)	^{230}Th dpm/L	hole(depth)	^{230}Th dpm/g	mL/g
PH49(28-30m)	0.050	DDH1 (19.4,29.3,34.5m)	62500,21,165	4.2×10^5 to 1.3×10^9
PH49(44-46m)	0.036	DDH2 (33.0,63.4m)	60500,26200	7.3×10^8 to 1.7×10^9
PH55(40-42m)	<0.006	DDH4 (23.6,31.5m)	145,11	$> 1.8 \times 10^6$

Note that percussion holes are vertical whereas diamond drill holes are at an angle. Therefore, DDH1 and DDH2 intersect the vicinity of PH49 at different depths.

(solid phase data from Edghill 1989)

CHAPTER SEVEN

RADIONUCLIDE TRANSPORT BY COLLOIDS AND FINE PARTICLES

7.1 Potential Role of Colloids and Particles

High rates of pollutant transport can occur even when the pollutant is strongly bound by solid phases. This is the situation in some rivers, where highly insoluble and/or strongly sorbed substances are transported because the sediments and particles to which they are attached are themselves moving with the flowing water. Gibbs (1973) showed that over 83% of Fe, Cu, Ni, Co, Cr and Mn in the Yukon and Amazon Rivers was associated with particles above 450 nm in size.

In recent years, it has been recognised that fine particles could accelerate radionuclide migration in groundwaters. Colloids (particles in the size range below 1 μm) have a high surface area per unit mass, and are potentially smaller than the cracks and pores in fractured and permeable media. Therefore, they may adsorb and transport radionuclides. However, the low flow rates and filtration effects of the rock matrix prevent entrainment of all but the finest particles.

There have been some reports of contaminants migrating with groundwater colloids. A recent study of the vicinity of a nuclear detonation cavity at the Nevada Test Site indicated that Mn, Co, Ce and Eu were being transported in a colloidal form (Buddemeier and Hunt 1988). A study of groundwaters from the Nabarlek and Koongarra ore bodies found that ^{230}Th was associated with colloids, whereas ^{238}U and ^{234}U were mostly present as soluble species (Short et al. 1988).

To date, colloidal terms have been omitted from the open-system multiphase transport model being developed for the Koongarra system. Furthermore, both uranium and thorium are analogues of several components of HLW. It is therefore important to investigate whether significant amounts of radionuclides are associated with colloids in Koongarra groundwaters.

During a field trip to Koongarra in August 1986, groundwater was sampled, with the objective of investigating the association of radionuclides amongst particles in various size ranges. This work was carried out by several personnel from ANSTO and AERE, Harwell, UK. The levels of uranium and thorium isotopes in each size fraction were subsequently measured at the ANSTO laboratories, Lucas Heights. An early summary of some of the results was published (Ivanovich et al. 1987), and this was followed by a detailed report (Ivanovich et al. 1988). This chapter will review this study and present some further results.

7.2. Sampling

Groundwater was sampled at KD2, PH55, PH14 (twice) and PH49. The locations of these boreholes are shown in figure 3.5. Groundwater was pumped through a 5 μm (nominal) cellulose fibre filter cartridge, and then a 1 μm Nuclepore cartridge filter. This latter filter is a 'membrane' filter, with a very uniform pore size distribution. Colloidal (<1 μm) particles were concentrated using an Amicon DC10LA ultrafiltration system fitted with hollow fibre filters with a nominal cutoff at 10 000 MW. The equipment was isolated from atmospheric oxygen to prevent oxidation of Fe^{2+}, which would have led to the formation of fine particulate iron oxides.

The ultrafiltration system (figure 7.1) basically consists of a loop around which groundwater is pumped. The system is designed to ensure a high velocity of water along the hollow fibres that comprise the ultrafiltration membrane. Ultrafiltered water continuously passes through the membrane, and is replaced by an equivalent amount of fresh groundwater. Hence, the volume of liquid in the system remains constant, but gradually becomes enriched in colloids from the entire volume which has passed through the membrane. The colloid-enriched portion in the recirculation vessel is referred to as the 'colloid concentrate'. Thus, the amount of radionuclides and other species associated with the colloid can be determined by subtracting their concentration in the ultrafiltrate from that of an equivalent volume of colloid concentrate.

In practice, some radionuclide activity is retained by the filter cartridge, despite the high tangential velocities employed. Therefore, at the end of sampling, the ultrafilter cartridge was backflushed with 0.1 M HCl.

Both the colloid concentrate and the ultrafilter backflush contain radionuclides concentrated from the entire volume passed through the ultrafilter. Therefore, to interpret the results it is necessary to know the ultrafiltrate volume, and the ratio of the ultrafiltrate volume to that of the colloid concentrate. This latter quantity is known as the concentration factor (CF). This data is provided in table 7.1. The large volumes of groundwater processed ensured that any significant association of radionuclides with colloidal particles would be readily detected.

During sampling, the pH, redox potential, dissolved oxygen and conductivity were measured in the incoming groundwater and ultrafiltrate, and bicarbonate levels were determined by titration with 0.006 M HCl. At the completion of operations, the 5 μm and 1 μm filters, the ultrafiltrate, colloidal concentrate and backflush were collected for physical, elemental and radiochemical analyses.

7.3 Filter Treatment

The 5 μm and 1 μm filters were leached to remove potentially mobile precipitated or adsorbed phases from the retained particles. An overnight leach with 0.5 M HCl has been used to dissolve these phases from sediments (Agemian and Chau 1976), and a similar 30 minute leach with 0.3 M HCl at near boiling temperatures (Malo 1977) has also been utilised. The procedure adopted in the present study was to heat briefly to 70°C with 0.5 M HCl, then soak in this solution for 2-3 days. A relatively long leaching time was employed because the bulky nature of the filters was expected to inhibit the leaching process.

The filters were then ashed and the masses of the residues determined. The mass of the retained particles was calculated by subtracting the mass of an ashed, unused filter of the same type. Finally, the ashed filter residues were digested using concentrated HCl, $HClO_4$ and HF.

7.4 Analysis for Uranium and Thorium

The extremely low levels of thorium in the ultrafiltrates were determined after co-precipitation from 25 L samples with ferric hydroxide. Uranium concentrations in ultrafiltrates were measured after either precipitation or evaporation of the sample. Radionuclide levels in the colloidal fraction

were determined after evaporation of the sample in aqua-regia. In the particle fractions, radionuclides in accessible phases were determined by analysis of the filter leaches, and in residual phases, by analysis of the digested filter residues.

After the addition of known quantities of ^{232}U and ^{229}Th as yield tracers, uranium and thorium were isolated by conventional anion exchange methods (Korkisch 1969; Lally 1982), and electrodeposited on stainless steel discs for α-spectrometry.

7.5 Elemental and Radionuclide Content of Ultrafiltrates and Colloidal Particles

For all boreholes sampled, the colloid concentrate(CC), ultrafiltrate(UF), and ultrafilter backflush(BF), were analysed in order to determine the fractionation of species in the sub-1 μm fraction between dissolved and colloidal forms. The concentrations of ^{238}U and ^{230}Th found in the CC, UF, and BF fractions are given in table 7.2.

For each experiment, the ^{238}U content of the CC was somewhat higher than that of the UF, but the difference was surprisingly small, considering that the CC contained colloidal ^{238}U concentrated from over 1000 L.

Significant amounts of ^{238}U and ^{230}Th were found in the BF fractions. This raised the question of whether this fraction contained colloidal material which had adhered to the membrane (rather than being recirculated into the CC), or whether the ultrafilter had sorbed dissolved species from solution.

It was concluded that the BF fraction should be treated as being colloidal particles, for the following reasons:

a) Sorption is usually most serious on unconditioned membranes (Salbu et al. 1984). Hundreds of litres of groundwater were passed through the membrane in each experiment, thereby decreasing the probability of unsaturated sorption sites being present.

b) The possibility of sorption on filters of any size is rarely considered - all retained material is simply assumed to be particulate. Therefore the inclusion of this material as particulate would follow standard practice.

c) In the next section it will be shown that there were large quantities of particles in the 1-5 μm size range in these groundwaters. It is therefore likely that there would also have been some particles below 1 μm. As SEM analysis of the 1 μm filter membranes showed the pores were not obstructed (see below), these colloidal particles should have passed through the 1 μm filter, and been found in either the CC or BF fractions.

The amount of colloidal ^{238}U (U_c) was calculated using the following equation:

$$U_C = \frac{U_{CC} - U_{UF}}{CF} + U_{BF} \qquad (7.1)$$

U_{CC}, U_{UF} and U_{BF} are the ^{238}U concentrations in the CC, UF and BF fractions, respectively (the latter expressed per litre of groundwater processed), and CF is the concentration factor.

The percentage of ^{238}U (in the < 1μm fraction) carried by colloids (P) was then calculated using the expression:

$$P = \frac{U_C}{U_C + U_{UF}} \times 100 \qquad (7.2)$$

The results are given in table 7.2. Even after assuming that the ^{238}U in the BF is colloidal, the percentage of ^{238}U associated with colloids is only 1-3 % of the total ^{238}U content.

The ^{230}Th concentrations in both the CC and UF were found to be extremely low (bordering on detection limits) but there was an apparent enrichment of ^{230}Th in the CC (table 7.2). Indeed, when the ^{230}Th content of the backflush was taken into account, the proportion of ^{230}Th in 1 μm-filtered groundwater which was associated with colloids ranged up to 82 %. This was much greater than the corresponding percentage for ^{238}U. However, it must be remembered that the total amount of ^{230}Th which passed through the 1 μm filter was extremely low. In fact, the absolute activity of ^{230}Th associated with colloids was lower than for ^{238}U.

The results for major cations (table 7.3) showed no significant enrichment of any cation in the CC, despite the concentration of the colloid from large volumes. However, there was retention of Fe on the ultrafilter membrane (as determined by Fe analysis of the BF) for every experiment. This amounted to 0.5-1.4 % of the total Fe which passed through the ultrafilter.

The concentrations of anions (Cl^-, F^-, SO_4^{2-}) in the CC were similar to their respective values in the UF, and the difficulty of measuring anions (particularly HCO_3^-, the dominant anion in these groundwaters) in the acidified BF samples precluded conclusions being made about anion distributions.

In summary, the elements which appear to be associated with colloidal (<1 μm) particles in Koongarra groundwaters are uranium, thorium and iron. (A possible addition to this list is actinium, which is discussed below).

7.6 Distribution of U and Th Amongst Particulate and Dissolved Phases

PH14 and PH49 are near the centre of the Koongarra ore body, in a region of high radionuclide levels. Therefore it was possible to undertake a detailed study of the particle-size distribution of ^{230}Th and ^{238}U in groundwaters from these boreholes. The distribution of ^{238}U and ^{230}Th in particles in the size ranges defined by the 5 μm filter, 1 μm filter, and ultrafilter; and in solution are given in table 7.4.

The values associated with particulate material were determined by dividing the total ^{238}U and ^{230}Th retained on the filters by the filtrate volume. The colloidal (<1 μm) size range includes both the colloid-associated nuclides determined to be present in the CC, and the amounts found in the BF fraction.

Even when the quantities of ^{238}U associated with large particles are included, it can be seen the ^{238}U is mostly present in dissolved forms, which pass through the ultrafilter. In contrast, virtually all the ^{230}Th is

associated with larger particles above 1 μm in size. The small amount of ^{230}Th found in the colloidal size range is probably the low-end 'tail' of this distribution.

The extremely low levels of thorium measured in the ultrafiltrate and colloids reflect the extreme immobility of this element, particularly considering the high levels of ^{230}Th which are present in the solid phases near these boreholes.

The results show that only a small proportion of the total ^{238}U and ^{230}Th in these groundwaters is carried by colloidal particles. In the case of ^{238}U, this is because almost all the ^{238}U in pumped groundwaters is dissolved. On the other hand ^{230}Th is overwhelmingly associated with large particles which are above 1 μm in size.

7.7 Mineralogy of Colloids and Particles

The particles on the 1 μm filters were examined by scanning electron microscopy (SEM) using energy dispersive spectroscopy (EDS) to determine their chemical composition (Davey et al. 1988). The particles in PH14 and PH49 borewaters were mostly kaolinite, with a few chlorite particles present. Kaolinite is a product of weathering and is abundant within 20 m of the surface at Koongarra. Iron rich material was associated with many of the clay particles, possibly as iron-oxide coatings. A few particles showing only Si in the EDS spectra were probably quartz grains.

The SEM analysis of the filters showed that the pores remained unobstructed, hence the effective filter pore-size remained constant during the filtration procedure.

The presence of amorphous coating minerals in the particles was confirmed by chemical analysis of the acid extractants used for the 1 μm and 5 μm filters. The amounts of Fe, Al and Mn extracted (table 7.5) were much higher than for extractions of a typical weathered core sample from nearby drillhole DDH52, using several techniques suggested for extracting non-residual or amorphous phases (Agemian and Chau 1976; Malo 1977; McKeague and Day 1966).

These results imply that the particles are heavily coated with amorphous minerals, attributable to their exposure to groundwater. Iron oxides are known to be strong uranium adsorbers (Ames et al. 1983; Hsi and Langmuir 1985), and these iron containing phases probably strongly influence the mobility of radionuclides in the Koongarra system.

The SEM analysis of the colloid concentrate detected very little colloidal material. The main difference between the CC and UF samples was a greater number and variety of Fe-containing particles in the CC, suggesting the presence of Fe-rich colloids. Some of the Fe-rich particles were attributed to post-sampling oxidation, but the morphology of particles in the CC suggested that some of the Fe-rich particles were formed prior to sampling (Davey et al. 1988).

7.8 $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios

The $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ isotope ratios in the PH14 and PH49 ultrafiltrates, and in the accessible and residual particle phases, as determined by acid extraction and digestion respectively, are given in table 7.6.

In both experiments at PH14, the $^{234}U/^{238}U$ activity ratios in acid extractable phases were below unity and close to that of the UF. This suggested that the acid extractable uranium was accessible to the groundwater, whereas the residual phases, which had higher $^{234}U/^{238}U$ ratios, contained inaccessible uranium.

The $^{230}Th/^{234}U$ activity ratios at PH14 again showed the immobility of thorium relative to uranium, with the $^{230}Th/^{234}U$ ratio in the UF several orders of magnitude below unity. This deficiency of mobile thorium was reflected by the $^{230}Th/^{234}U$ ratio in accessible phases which was also substantially below unity.

At PH49, the $^{234}U/^{238}U$ ratios in the acid-extracted phases of the particles retained by the 1 μm and 5 μm filters were similar, but differed from that of the UF. A possible explanation for this is mixing of particle-bearing groundwaters from two aquifers during sampling. The $^{230}Th/^{234}U$ isotope ratio was again substantially below unity in the ultrafiltrate, and (to a lesser extent), in accessible phases. In resistate phases, both $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ ratios were above unity, which may be attributed to recoil emplacement processes (see Sheng and Kuroda 1984; 1986).

7.9 Distribution Ratios for ^{230}Th and ^{238}U Associated with Groundwater Particulates and Colloids

A distribution ratio (R_d) can be derived for the distribution of ^{238}U and ^{230}Th between the groundwater and the particles retained by the 5 μm and 1 μm filters. The calculated R_d values, based on the levels of accessible ^{238}U and ^{230}Th found in the acid leaches of the particles are given in Table 7.7. The R_d values for uranium lie within a narrow range, varying by less than a factor of three, between 2.6 X 10^4 mL/g and 6.5 X 10^4 mL/g. The values for the 1-5 μm sized particles are in the upper part of this range, with the R_d for the >5 μm particles all below 4 X 10^4 mL/g. This may be attributed to the higher surface area of the smaller particles, which leads to a greater adsorption on a mass basis.

The ^{230}Th distribution ratios are two to four orders of magnitude higher than for ^{238}U, being in the range 2.6 X 10^6 mL/g to 1.1 X 10^9 mL/g. The greater range of R_d indicates that the thorium distribution may not be a result of sorption equilibria.

Although ^{232}Th was not detected in the ultrafiltrates, these waters probably contain a greater mass of ^{232}Th than ^{230}Th, as is known to be the case in the contacting rocks. The absence of ^{232}Th in the α-spectra is due to its low specific activity relative to ^{230}Th. Hence, the groundwater level of ^{230}Th may be limited by solubility (dominated by ^{232}Th) rather than sorption processes, which would explain the range of calculated R_d values for ^{230}Th.

The distribution ratios in table 7.7 are based on radionuclide levels found in accessible phases as determined by an acid leach. Table 7.8 shows R_d values calculated after a total digestion of the particles. This includes radionuclides in inaccessible phases, and therefore results in higher calculated R_d values for both ^{238}U and ^{230}Th. This is particularly the case for ^{230}Th, which was shown in section 7.7 to be more associated with inaccessible phases.

Although R_d values calculated using total radionuclide content are sometimes used in modelling migration phenomena, this approach is inferior to using R_d values based on accessible phases. This is because radionuclides trapped in inaccessible phases probably have little interaction with the aqueous phase. Comparison of tables 7.7 and 7.8 shows that the resulting R_d values can be quite different.

It is possible to use the collected data to calculate R_d values for the colloidal particles retained by the ultrafilter. If the particles are assumed to be $Fe(OH)_3$ then their mass can be simply calculated from the measured Fe content of this phase (Fe being the only element other than ^{238}U or ^{230}Th which was significantly enriched in the colloid fraction). The resulting R_d values (Table 7.9) are an indication of the likely R_d on ferrihydrite which has been postulated to be a major adsorbing phase in groundwater rock/systems (Payne and Waite 1990).

7.10 Evidence for Mobility of Actinium-227

The thorium α-spectra for some of the fine particle and colloid fractions showed an unusual feature - substantial ^{227}Th peaks were present, as well as peaks from its daughters ^{219}Rn, ^{215}Po, and ^{211}Bi (figure 7.2). These are all members of the ^{235}U decay chain (see Appendix I), and are not normally prominent in α-spectra on account of the much greater activity of the isotopes of the ^{238}U series. The peaks from ^{227}Th indicated the presence of ^{227}Ac in the samples (since the half-life of ^{227}Th is only 19 days, and the samples had been stored for some months at the time of analysis).

The amount of ^{227}Ac was determined using the integral of the higher energy ^{227}Th doublet at 5.9-6.1 MeV, thus avoiding the more complex corrections required in the 5.6-5.9 MeV energy region (Golian et al. 1984). The count rate was corrected for a minor contribution of ^{211}Bi, and allowance was made for decay of unsupported ^{227}Th after separation from its parent.

For samples at secular equilibrium, the $^{227}Th/^{230}Th$ activity ratio is 0.046 and is derived from the ratio of the respective parents ^{235}U and ^{238}U. Golian et al. (1984) reported values in the range 0.032 to 0.052 for bulk core samples taken from the Ranger Uranium Deposit.

The $^{227}Th/^{230}Th$ ratio for the spectrum in figure 7.2 was 2.9. This α-spectrum is for the accessible phases of particles in the 1-5 μm size range collected in the second sampling experiment at PH14 (denoted PH14b). Unusually high $^{227}Th/^{230}Th$ ratios were also measured in the extractable phases of >5 μm particles, and in the BF fractions at PH49 and PH14 (table 7.10).

The high $^{227}Th/^{230}Th$ ratios in the BF fractions suggest that ^{227}Ac is more mobile than ^{230}Th in the particle fraction below 1 μm in size, and of all the radionuclides studied is the one most associated with colloids. Due to large errors in measuring the low levels of ^{227}Th and ^{230}Th in CC and UF fractions, the $^{227}Th/^{230}Th$ ratio in the CC could only be measured at PH49,

where radionuclide levels were the highest. In this instance the $^{227}Th/^{230}Th$ ratio was 11±3, and this supported the assertion that actinium is associated with colloids and fine particle phases in the Koongarra groundwaters.

The $^{227}Th/^{230}Th$ activity ratios in the digested particle residues (after removal of labile phases by an acid leach) were close to equilibrium values (table 7.10), therefore being similar to the isotope ratio in the bulk rock. The ^{227}Ac excess is therefore confined to the more mobile accessible coating phases.

A high $^{227}Th/^{230}Th$ ratio has been previously reported for a water sample in a rainwater puddle at the Ranger uranium mine (Dickson and Meakins 1984). This result supports the conclusion that there is excess actinium in accessible phases of rock samples from the ARUF, which in this case could have been dissolved by acidic rain or mine-waters.

The evidence therefore suggests that actinium is more mobile than thorium, and is highly associated with fine particles. However, actinium is far less mobile than uranium as can be inferred from the $^{227}Ac/^{235}U$ ratios in the ultrafiltrate which were <0.02 in all cases. The secular equilibrium value of this ratio is unity in the absence of preferential mobility since ^{235}U is the ultimate parent of ^{227}Ac.

7.11 Summary and implications

The distributions of ^{238}U and ^{230}Th at PH49 are summarised in figure 7.3. In this figure, the total radionuclide level is indicated, first for unfiltered groundwater, then for 5 μm-filtered, 1 μm-filtered and finally ultrafiltered groundwater. The reduction in levels upon passing through each filter therefore indicates the radionuclide load in each size range. The diagram clearly shows that virtually all the thorium in groundwater pumped from these boreholes was associated with particles above 1 μm in size, whereas most of the uranium was dissolved. Thorium is extremely immobile and was present at very low levels in the ultrafiltrates.

In 1 μm-filtered groundwater only 1-2 % of the ^{238}U was associated with colloidal particles, with the corresponding figures for ^{230}Th being 12-82 %. This greater association of ^{230}Th with colloidal particles agrees with the previous study (Short et al. 1988).

The levels of ^{238}U and ^{230}Th carried by particles in larger size ranges have never previously been investigated, and are much greater than the amounts associated with colloidal particles. The importance of larger particles in natural groundwater systems is likely to be limited since the low flow rates and filtration effects of the rock matrix will tend to prevent their entrainment. In fact, these particles may only be mobilised when natural systems are perturbed, as occurs when these boreholes are pumped. This may also be the case with the colloidal particles.

The particles entrained by the groundwater originated in the weathered zone and consisted predominantly of clay-like minerals. The strong adsorption of uranium and thorium by these particles was attributed to coating minerals rich in Fe, Al and Mn.

Distribution ratios for ^{230}Th were variable and suggested groundwater thorium levels may be limited by solubility constraints. Uranium R_d values were within a relatively narrow range and indicated that uranium migration could be modelled by adsorption/desorption processes. Higher R_ds were found when the total ^{238}U and ^{230}Th rather than just accessible phases were considered.

There were unexpectedly high amounts of ^{227}Ac in accessible phases of particles in the groundwater. ^{227}Ac was mobile in a fine phase which passed through the 1 μm filter and was retained by the ultrafilter.

The only elements significantly enriched in the colloidal phase were iron, uranium, actinium and thorium. This suggested that a potentially mobile ferrihydrite-like colloid was present, to which radionuclides were adsorbed. In the Koongarra system the amount of radionuclides transported in this fashion is very small, but such a colloidal phase could conceivably be important in the environment of a nuclear waste repository.

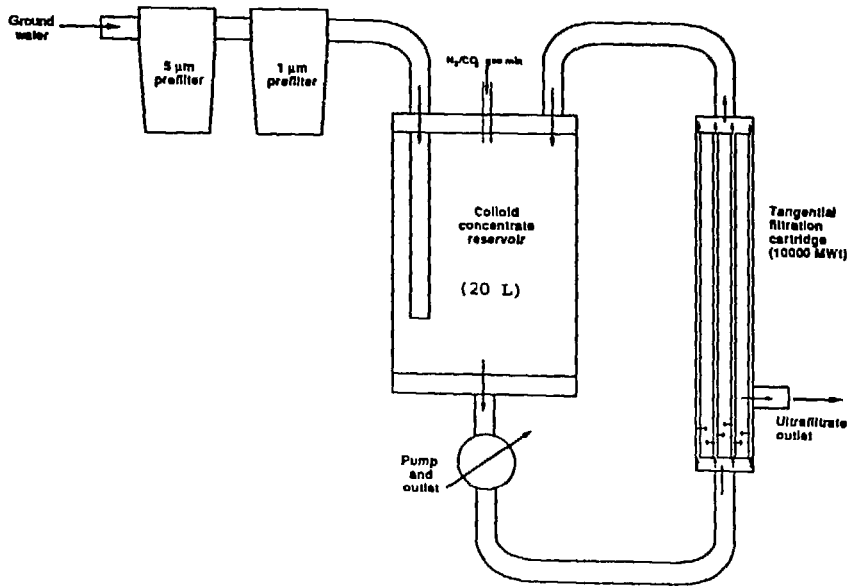


Figure 7.1

Hollow fibre ultrafiltration system

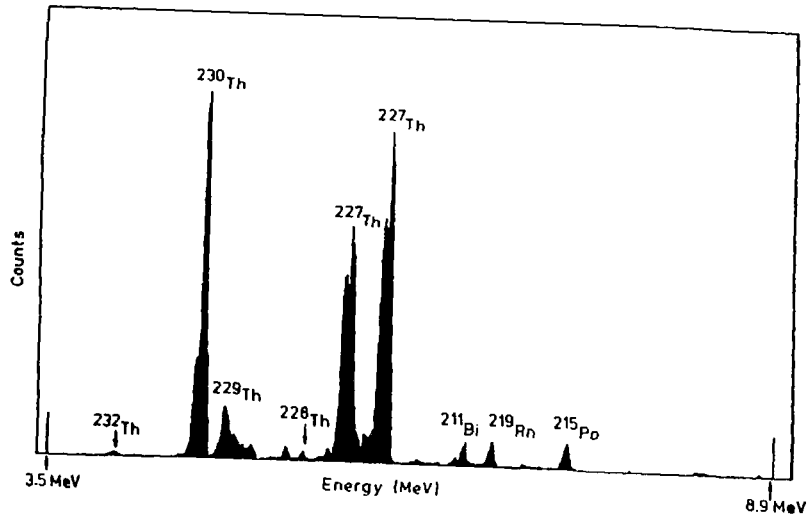


Figure 7.2

Thorium alpha-spectrum for 1 µm filter (PH14b) showing prominent ^{227}Th peaks (^{229}Th is added as an analytical yield tracer)

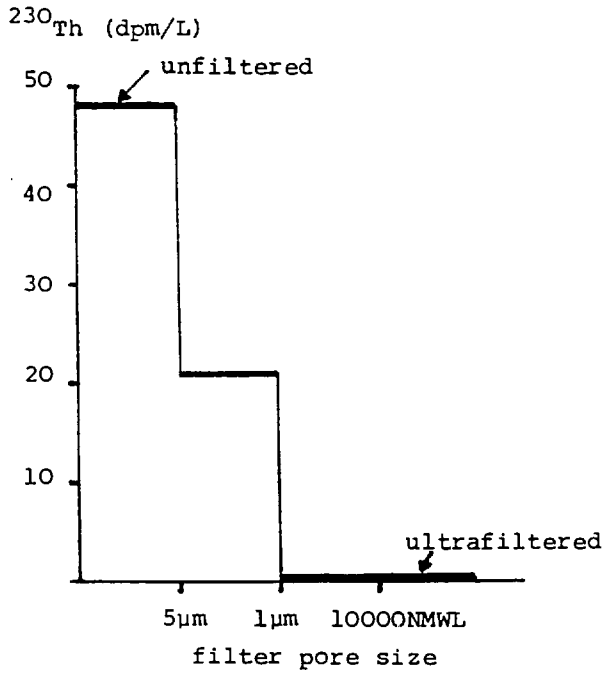


Figure 7.3

Effect of filtration on radionuclide levels in groundwater

Table 7.1

Colloid Sampling Details

Borehole	Ultrafiltrate Volume (L)	Concentration Factor*
KD2	2060	147
PH55	1313	66
PH14(a)**	1182	131
PH14(b)	1115	56
PH49	891	45

* Ratio of ultrafiltrate volume to colloid concentrate volume

** PH14 was sampled twice

Table 7.2 Partitioning of ^{238}U and ^{230}Th in 1 μm-filtered groundwater

A. ^{238}U

Borehole	UF dpm/L	CC dpm/L	Backflush dpm/L *	Colloidal ^{238}U
KD2	0.059	0.075	0.0010	1.8 %
PH55	0.30	0.33	0.0071	2.5 %
PH14(a)	65.4	71.1	0.90	1.4 %
PH14(b)	153	161	1.51	1.1 %
PH49	133	156	1.35	1.4 %

B. ^{230}Th

Borehole	UF dpm/L	CC dpm/L	Backflush dpm/L *	Colloidal ^{230}Th
KD2	<0.0004	0.0024	-	-
PH55	0.0044	0.068	0.0013	33 %
PH14(a)	0.0096	0.070	0.00088	12 %
PH14(b)	0.0037	0.018	0.0011	27 %
PH49	0.0032	0.081	0.0128	82 %

* Radionuclide concentrations in the ultrafilter backflush are in dpm per litre of UF passed through the membrane.

Table 7.3

Partitioning of cations in 1 μm-filtered groundwater

Hole	Fraction	K	Na	Mg	Ca	Al	Fe	Mn	Si
KD2	UF mg/L	0.65	1.69	15.5	0.92	<0.02	1.14	0.037	12.5
	CC mg/L	0.63	1.63	11.1	0.70	0.02	1.06	0.027	9.8
	BF*	-	-	-	-	(0.1%)	0.8%	-	-
PH55	UF mg/L	1.07	1.58	17.1	1.28	<0.02	0.77	0.067	12.5
	CC mg/L	1.11	1.62	18.2	1.38	0.02	0.80	0.070	12.6
	BF*	-	-	-	-	(0.05%)	0.5%	-	-
PH14a	UF mg/L	0.71	1.49	21.7	2.29	0.04	0.43	0.36	9.2
	CC mg/L	0.74	1.44	22.2	2.38	<0.02	0.46	0.37	9.0
	BF*	-	-	-	-	(0.15%)	1.4%	-	-
PH14b	UF mg/L	0.65	1.36	19.8	1.50	0.02	0.14	0.20	9.5
	CC mg/L	0.69	1.37	18.2	1.43	<0.02	0.13	0.17	9.0
	BF*	-	-	-	-	(0.2%)	1.1%	-	-
PH49	UF mg/L	0.58	1.12	24	1.60	0.02	0.40	0.13	8.3
	CC mg/L	0.60	1.09	23	1.60	<0.02	0.46	0.13	8.0
	BF*	-	-	-	-	(0.4%)	1.1%	-	-

* Percentage of total found in ultrafilter backflush. In cases not assigned a numeric value, ultrafilter retention was below 0.03%. Data for Al in BF fraction are bracketed because the Al values were close to detection limits.

Table 7.4

Distributions of ^{238}U and ^{238}Th amongst particles and ultrafiltrates.

	Experiment	Particles >5 µm (dpm/L)	Particles 1-5 µm (dpm/L)	Particles <1 µm (dpm/L)	Ultrafiltrate (dpm/L)	Percentage of total in ultrafiltrate
^{238}U	PH 14(a)	3.64(0.11)	4.86(0.14)	0.94(0.04)	65.4(2.5)	87.4(3.3)
	PH 14(b)	32.8(1.0)	30.4(0.8)	1.65(0.12)	153(4)	70.2(1.8)
	PH 49	43.3(0.7)	27.1(0.6)	1.86(0.15)	133(3)	65.0(2.0)
^{230}Th	PH 14(a)	0.77(0.04)	1.23(0.05)	0.0013(0.0002)	0.0096(0.0018)	0.48(0.09)
	PH 14(b)	3.86(0.10)	0.96(0.04)	0.0014(0.0002)	0.0037(0.0010)	0.08(0.02)
	PH 49	26.7(0.6)	20.9(0.6)	0.015(0.002)	0.0032(0.0005)	0.0067(0.0011)

Errors are given in brackets.

Table 7.5

Extractable metals in groundwater particles and DDH52 core sample (15 m depth)

A. Groundwater Particles (extraction described in text)

borehole	Particle size range	Metal Extracted (mg/g) Al	Fe	Mn
PH14a	>5 µm	2.45	36.4	0.36
PH14a	1-5 µm	15.5	24.5	0.20
PH14b	>5 µm	4.3	14.0	0.20
PH14b	1-5 µm	3.3	15.7	0.17
PH49	>5 µm	2.4	8.4	0.05
PH49	1-5 µm	11.2	25.3	0.12

B. DDH52 core sample (15m depth)

Extraction technique	Al	Fe	Mn
Agemian and Chau (1976)	0.75	0.072	0.003
Malo (1977)	1.58	0.082	0.007
McKeague and Day (1966)	0.77*	0.67*	-
McKeague and Day (1966)	0.83*	1.20*	-

* - data supplied by T. Nightingale

Table 7.6

Isotope ratios in ultrafiltrates, acid-extractable particle phases, and residual phases.

A. $^{234}U/^{238}U$

	PH 14(a)	PH 14(b)	PH 49
Ultrafiltrate	0.75±0.02	0.78±0.01	1.02±0.01
Particles			
>5 μm - acid extraction	0.80±0.01	0.78±0.01	0.90±0.01
1-5 μm - acid extraction	0.74±0.02	0.75±0.01	0.88±0.02
>5 μm - residual phases	0.93±0.01	0.84±0.04	1.08±0.01
1-5 μm - residual phases	0.92±0.02	0.90±0.03	1.17±0.02

B. $^{230}Th/^{234}U$

	PH 14(a)	PH 14(b)	PH 49
Ultrafiltrate	2.0×10^{-4}	3.1×10^{-5}	2.3×10^{-5}
Particles			
>5 μm - acid extraction	0.012	0.026	0.37
1-5 μm - acid extraction	0.17	0.0072	0.69
>5 μm - residual phases	0.86	0.40	1.03
1-5 μm - residual phases	0.91	0.80	1.39

The accuracy of $^{230}Th/^{234}U$ is ±20 % for the ultrafiltrates, and ±5 % for all other phases.

Table 7.7

Distribution ratios for ^{238}U and ^{230}Th in accessible phases

A. Particle size >5 µm.

	Particles mass (g)	^{238}U in acid leach (dpm/g)	$R_d(^{238}U)$ (mL/g)	^{230}Th in acid leach (dpm/g)	$R_d(^{230}Th)$ (mL/g)
PH14a	9.9	2470	3.8×10^4	23.2	2.4×10^6
PH14b	28.6	3990	2.6×10^4	80.7	2.2×10^7
PH49	33.8	3820	2.9×10^4	1270	4.0×10^8

B. Particle size 1-5 µm

	Particles mass (g)	^{238}U in acid leach (dpm/g)	$R_d(^{238}U)$ (mL/g)	^{230}Th in acid leach (dpm/g)	$R_d(^{230}Th)$ (mL/g)
PH14a	2.0	2500	3.8×10^4	313	3.3×10^7
PH14b	3.5	9940	6.5×10^4	53	1.4×10^7
PH49	10.0	5630	4.2×10^4	3390	1.1×10^9

Table 7.8

Distribution ratios based on total ^{238}U and ^{230}Th.

	Experiment	^{238}U dpm/g	$R_d(^{238}U)$ mL/g	^{230}Th dpm/g	$R_d(^{230}Th)$ mL/g
Particles > 5 μm	PH 14(a)	3300	5.1×10^4	696	7.3×10^7
	PH 14(b)	5700	3.7×10^4	664	1.8×10^8
	PH 49	6000	4.5×10^4	3700	1.2×10^9
Particles 1-5 μm	PH 14(a)	3000	4.6×10^4	770	8.0×10^7
	PH 14(b)	10000	6.5×10^4	330	8.9×10^7
	PH 49	6700	5.0×10^4	5200	1.6×10^9

Table 7.9

Distribution ratios for ^{238}U and ^{230}Th on 'colloidal ferrihydrite'

Borehole	$Fe(OH)_3$ (mg)	^{238}U (dpm/g)	$R_d(^{238}U)$ (mL/g)	^{230}Th (dpm/g)	$R_d(^{230}Th)$ (mL/g)
KD2	32.9	62	1.1×10^6	-	-
PH55	13.2	740	2.5×10^6	132	3×10^7
PH14a	14.1	78700	1.2×10^6	77	8×10^6
PH14b	3.6	490000	3.3×10^6	352	1×10^8
PH49	8.0	160000	1.2×10^6	1500	5×10^8

Table 7.10

$^{227}Th/^{230}Th$ in particulate fractions and ultrafilter backflush.

filter	PH14a	PH14b	PH49
5μm- extractable phase	2.37	0.99	0.14
5μm- residual phase	0.04	0.07	0.05
1μm- extractable phase	0.22	2.87	0.09
1μm- residual phase	0.04	0.05	0.05
ultrafilter backflush	3.1	3.5	2.8

The radiometric equilibrium value of $^{227}Th/^{230}Th$ is 0.046.

CHAPTER EIGHT

LABORATORY STUDY OF URANIUM SORPTION

8.1 Background

The first step in the mobilisation of uranium from the primary ore zone at Koongarra occurs when uraninite is oxidised and altered to product secondary minerals, usually with a change in oxidation state from U(VI) to U(VI) (Snelling 1980a). The U(VI) state is more soluble in groundwater, and uranium movement may then occur in the direction of groundwater flow. If the solubility product for a particular uranium mineral is locally exceeded, precipitation may occur. Alternatively the uranium may be adsorbed by a mineral surface. At sufficient distance from the primary ore the level of uranium is invariably below solubility limits (Sverjensky 1989), and adsorption becomes the main restriction on migration.

The extent of uranium sorption under a range of conditions was measured in the laboratory, using samples from Koongarra borehole DDH52 as the solid phase. In these experiments, an artificial uranium isotope (^{236}U) was adsorbed from a synthetic groundwater onto the Koongarra sample, which contained natural uranium isotopes (^{238}U, ^{235}U, and ^{234}U). The different uranium isotopes are readily distinguishable by α-spectroscopy, so a determination of the levels of both ^{236}U and ^{238}U in the synthetic groundwater at the end of each experiment allowed both adsorption and desorption to be studied.

The experiments with samples from the Koongarra deposit were carried out parallel with similar work on samples from the geologically similar Ranger deposit. A full account of this work including surface complexation modelling of both data sets has been prepared (Payne and Waite 1990).

8.2 Experimental

8.2.1 Solid Phase

A rock sample from Koongarra borehole DDH52 (depth approximately 15 m) was crushed (to less than 0.15 mm), using a ring grinder. The sample was a highly weathered schist, consisting of 31% quartz, and with kaolinite the dominant clay mineral. Significant amounts of goethite and hematite, and traces of aluminium hydroxides were present. The total uranium content was 392 μg/g (Airey et al. 1984).

The surface area was determined using an ethylene glycol monoethyl ether (EGME) technique (Bower and Goertzen 1959; Eltantawy and Arnold 1973). The samples were saturated with excess EGME after being thoroughly dried in a vacuum. The weights of the samples were recorded daily, with the system being kept under a vacuum between measurements. After four days the weights were constant, and it was assumed that monolayer coverage had been achieved. The surface areas were calculated from the mass of EGME adsorbed per gram of rock sample, using a value of 0.377 mg of EGME per square metre of surface. Standards of known surface area were run concurrently with the samples to check the accuracy of the procedure. The rock samples were run in triplicate, and the surface area was found to be 29±4 m^2/g.

8.2.2 Synthetic Groundwater

Natural groundwater was not used because of the remoteness of the region and the instability of the groundwater during storage. The aqueous phase

used in the experiments with both Ranger and Koongarra samples was a synthetic groundwater which simulated the natural groundwaters of the region, made by dissolving analytical grade chemicals in distilled water. The composition (Table 8.1) was determined after analyses of more than 100 groundwaters from the ARUF (Airey et al. 1984).

A wide pH range was used for the adsorption experiments so the main features of uranium sorption could be established. The pH was adjusted using NaOH or HCl.

The levels of sodium and chloride were approximately an order of magnitude higher than natural groundwaters, because readily soluble sodium and chloride salts were used to achieve the groundwater composition, and because of pH adjustments. The elevated level of sodium is unlikely to have affected the results, since the presence of competing cations even at 0.1 M concentrations displaced only a small proportion of uranium from similar samples (Airey et al. 1986a), indicating that uranium was specifically adsorbed.

Calculations using the chemical equilibrium code MINTEQA2 confirmed that the elevated levels of sodium and chloride did not significantly affect the solution phase speciation. Apart from sodium and chloride, the levels of other ions were comparable to those in baled Koongarra groundwater samples (Giblin and Snelling 1983), and to more recent data for pumped water samples (Table 3.1).

The mobility of many elements, including uranium, radium and iron, is dependent on the redox potential. Natural redox conditions may be simulated in the laboratory with chemicals which impose the required Eh (Barney 1984). For experiments with the Ranger and Koongarra samples, the redox conditions were controlled by adding 100 ppm of hydroxylamine to the synthetic groundwater. Previous experiments with samples from the Ranger deposit (Airey et al. 1986a) had indicated that within the natural pH range, this would produce an Eh close to that measured in the field.

8.2.3 Procedure

Approximately 200 mg of crushed ore and 100 mL of synthetic groundwater were equilibrated overnight at the desired pH prior to the sorption experiments. The required amount (59 dpm) of ^{236}U was slowly evaporated to dryness, then dissolved in the synthetic groundwater. The pre-equilibrated ore sample was added to the spiked groundwater, and the pH measured and adjusted if necessary. The contact time was seven days, during which the pH was checked and adjusted if it had drifted. No pH adjustments were made within the 48 hours prior to sampling.

Polyethylene bottles were used for the sorption experiments, because this material adsorbs only a small proportion of uranium from solution, particularly when geologic material is present (Airey et al. 1986a).

The pH and Eh of the system were determined at the time of sampling, the Eh meter being standardised with ZoBell's solution (Nordstrom 1977). A sample of the aqueous phase was then separated from the solid by centrifugation, a known amount of ^{232}U yield tracer was added, and the uranium separated and electrodeposited on a planchette for α-spectrometry.

The uranium spectrum for one of the experiments is shown in figure 8.1. The ^{238}U peak results from the leaching of natural uranium into the synthetic groundwater, whereas the ^{236}U indicates the amount of ^{236}U

remaining in solution after adsorption. The amounts of ^{238}U and ^{236}U in the synthetic groundwater were calculated from their count rate relative to the ^{232}U peak.

All measurements were corrected for detector background, which in the region of ^{238}U and ^{236}U was only a few counts per day. The continued use of ^{232}U results in the slow emplacement of ^{228}Th in the detectors by α-recoil. A shoulder of the ^{228}Th peak is close to the ^{232}Th peak, which necessitates subtraction of this contribution from the integral of the ^{232}U peak. The integral of the ^{236}U peak was corrected by subtracting the counts from ^{235}U, present in the same spectral region with 4 per cent of the activity of ^{238}U. These corrections are relatively minor as can be inferred from inspection of figure 8.1.

One of the significant advantages of studying adsorption of ^{236}U on samples bearing natural uranium is that both adsorption and leaching may be readily measured from the one α-spectrum.

8.3 Adsorption of ^{236}U and Isotope Exchange with ^{238}U

The adsorption of ^{236}U was dependent on the pH, reaching a maximum for both samples between approximately pH 7 and pH 8 (figure 8.2). Adsorption on the Ranger sample was generally greater than for the Koongarra sample, reflecting their surface areas (145 m^2/g and 29 m^2/g respectively). The results of these experiments are qualitatively similar to those obtained in other studies of uranium sorption on geologic substrates (Ames et al. 1983; Giblin 1980; Hsi and Langmuir 1985; Tripathi 1983).

The uranium α-spectrum (figure 8.1) showed that leached ^{238}U was present in the synthetic groundwater. This indicated that the total uranium participating in sorption interactions in this system was comprised of the ^{236}U initially in the synthetic groundwater plus a proportion of the natural uranium present in the solid phase. The proportion of total uranium available for leaching by the groundwater has been termed "accessible" (Shirvington 1979), and can be estimated by studying the isotopic exchange between ^{236}U and ^{238}U.

The experimental relationship between the level of ^{238}U leached into solution ($\mu g/g$ of solid) and the ^{236}U in solution (expressed as a percentage of the ^{236}U initially added to the synthetic groundwater) at the end of each experiment is shown in figure 8.3. The linear relationship suggests that isotope exchange was occurring between ^{236}U in the aqueous phase and ^{238}U bound in surface sites.

The line of best fit on figure 8.3 has been extrapolated to the point corresponding to zero ^{236}U sorption, at which all accessible ^{238}U would be expected to be in solution. This construction shows that the amount of accessible uranium in the Koongarra and Ranger samples was 90 $\mu g/g$ and 14 $\mu g/g$, respectively.

The result for the Koongarra sample is in excellent agreement with the amount which was extractable with the Tamm's Acid Oxalate (TAOO reagent, which removes accessible uranium (see section 5.2). The TAO-extractable uranium in the Koongarra sample was 90 $\mu g/g$, with the corresponding figure for the Ranger sample being 20 $\mu g/g$. The agreement is somewhat fortuitous, since figure 8.3 shows appreciable scatter. One of the reasons for this is inhomogeneity in the solid phase.

The isotope exchange results suggest that there is a fixed amount of accessible uranium (approximately 20 per cent of the ^{238}U) which takes part in adsorption/desorption equilibria, with the remainder of the uranium in the solid phase being relatively inaccessible. Therefore the total uranium participating in sorption interactions is the total of the ^{236}U spike and the accessible ^{238}U in the 200 mg of ore, ie 4.4 μg for the experiments with the Ranger sample and 18.4 μg for the Koongarra sample.

8.4 Distribution Ratios for Uranium Adsorption

The distribution ratio for ^{236}U adsorption (see section 5.1) was calculated for each experiment, using the expression:

$$R_d = \frac{(A_o - A_f)}{A_f} \cdot \frac{V}{m}$$

with V the groundwater volume, m the mass of crushed rock, and A_o and A_f the initial and final activities of ^{236}U in the synthetic groundwater (Airey et al. 1984). The variation of R_d as a function of pH is shown in figure 8.4. The maximum R_d values were close to 10^4 mL/g, at pH values near 8.0.

Several studies of uranium sorption have been reported. Giblin (1980) found that uranium adsorption on kaolinite was pH-dependent, with R_d reaching a maximum of 35 000 mL/g at pH 6.5. Borovec (1981) summarised uranyl R_d values (mL/g) on a variety of substances including humic acids (10^4), Fe(iii) hydroxides (10^6), fine grained natural goethite (10^3) and quartz (0). Distribution ratios for clay minerals were in the range 50-1000 mL/g, with kaolinite at the lower end of the range. When competing ions were present at the same molar concentrations as uranyl, adsorption on clays was reduced.

Hsi and Langmuir (1985) studied uranyl sorption onto ferric oxyhydroxides, with an aqueous phase consisting of 0.1 M $NaNO_3$ with total carbonate of 1.0 mM. Distribution ratios were at a maximum between pH 6 and 7, reaching approximately 5 x 10^6 mL/g for amorphous iron oxyhydroxide, 5 x 10^5 mL/g for goethite, and below 10^3 mL/g for hematite.

The comparison of the measured R_d values with reported values provides only qualitative information, since experimental conditions and solid phases are vastly different. The R_d values measured for the Koongarra DDH52 sample are generally higher than values reported for pure clay phases. This may indicate that a highly sorptive solid phase, such as amorphous ferric oxyhydroxide, is playing a role in uranyl sorption.

R_d values are a useful tool in modelling the migration of contaminants in groundwater systems (section 5.1). In the Koongarra case, uranium R_d values have been used in modelling the evolution of the dispersion fan (Airey et al. 1986b). However, in order to provide data which is transferable to other geological environments, a more fundamental approach is required.

8.5 Surface Complexation Modelling

The overall objective of the ARAP is to provide a detailed understanding of the Koongarra system, and, in particular, to trial geochemical models of

the system. Experimental relationships, such as in figures 8.2 or 8.4 do not in themselves fulfil these goals - the phenomena must be modelled as specific examples of geochemical processes.

The surface complexation model aims to mathematically describe the interaction of solution phase species with a sorbing phase. It has been utilised to model the sorption data on the Ranger and Koongarra samples (Payne and Waite 1990). The modelling of this data presented considerable problems due to the complexity of both the solid phase, and the solution phase chemistry of uranium. Due to the complex and iterative calculations, the computer code MINTEQA2 was used in the modelling.

8.5.1 Amorphous Ferric Oxide Phase

In order to fully implement the model, all surface site types exerting a significant influence on uranium adsorption must be identified and their characteristics defined. Given the multiplicity of phases in these weathered zone solids, this task is almost impossible.

Amorphous ferric oxide coating phases have very high surface areas (around 700 m^2/g), and are known to be strong adsorbers of radionuclides. Therefore, in the initial modelling of the results it was assumed that these amorphous coatings dominated the sorption behaviour in the system. A similar approach has been used to model the adsorption of chromate to soils (Zachara et al. 1989). The triple layer parameters for amorphous ferric oxide were obtained from the literature (table 8.2).

The amount of iron present in amorphous mineral coatings was determined by elemental analysis of the TAO extraction of the samples. The TAO-extractable uranium in the sample, together with the ^{236}U added to the solution phases, was assumed to participate in sorption interactions. The isotope exchange results had shown that this was a reasonable assumption.

8.5.2 Groundwater Phase

As was shown in section 4.3, the speciation of uranium in groundwater is quite complex. Therefore, the solution phase uranyl speciation was computed for each set of experimental conditions.

In the calculations, it was assumed that the experimental system was closed, because the polyethylene bottles were sealed throughout the equilibration period. Consequently, the uranyl speciation in the system was found to be very similar to that shown in figure 4.4b, which was calculated for a system with fixed total carbonate of 2.0 mmol/L.

8.5.3 Surface Complexation Reactions

For the next step in modelling, attention was initially restricted to modelling the data for the Ranger samples. The modelling proceeded by incorporating surface complexation reactions of species present in the synthetic groundwater (summarised in TAble 8.3), and, by a process of trial and error, arriving at a series of "best fit" formation constants for the major uranyl surface species (table 8.4).

The criteria for "best fit" was basically the extent to which the adsorption curve computed from the model fitted the experimental data. Figure 8.5a shows the curve calculated using the parameters in table 8.4, compared to the sorption data for the Ranger sample.

While the adsorption data for the Koongarra sample was somewhat scattered, a reasonable description of this data was also obtained by using the constants derived for the Ranger results (figure 8.5b). Such a fit was considered satisfactory considering that the Koongarra sample contained significantly more TAO-extractable ^{238}U than the Ranger sample, and contained a smaller proportion of amorphous iron oxide (Payne and Waite 1990).

8.6 Discussion

The study of uranyl sorption within the ARAP project provides a case study showing the different types of data that can be derived in a study of this nature.

Firstly, the sorption study provides site-specific information, such as the uranium R_d values, which can be directly incorporated into the model of uranium migration at the site (Airey et al. 1986b).

Secondly, the study provides details about the nature of groundwater/solid interactions which, as well as being applicable to the Koongarra system are relevant to other geological systems. In this category could be placed the apparent importance of ferric oxide coatings as sorbing surfaces, and the isotopic exchange processes, which could be a useful tool in measuring accessible contaminants in a variety of systems.

Finally, the data from Koongarra provide the opportunity to test models of geochemical interactions which are applicable in a wide range of natural systems, such as the surface complexation model. While the application of this model to sorption results is at an early stage, it provides the potential for a quantitative understanding of complex sorption interactions in natural systems. At this stage, one of the main problems in applying the model is the large amount of input data which is required, including surface site density, surface area, and the inner- and outer-layer capacitance for all potentially sorbing phases. To obtain this data would require a major experimental undertaking. However, such an approach offers the possibility of applying general predictive models of adsorption, rather than using more descriptive parameters such as R_d and K_d.

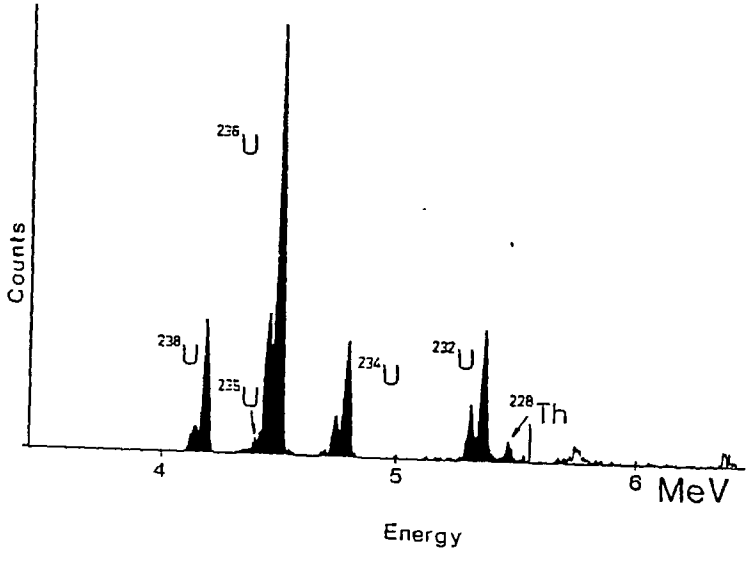


Figure 8.1

Alpha-spectrum of uranium in solution phase on completion of adsorption/desorption experiment.

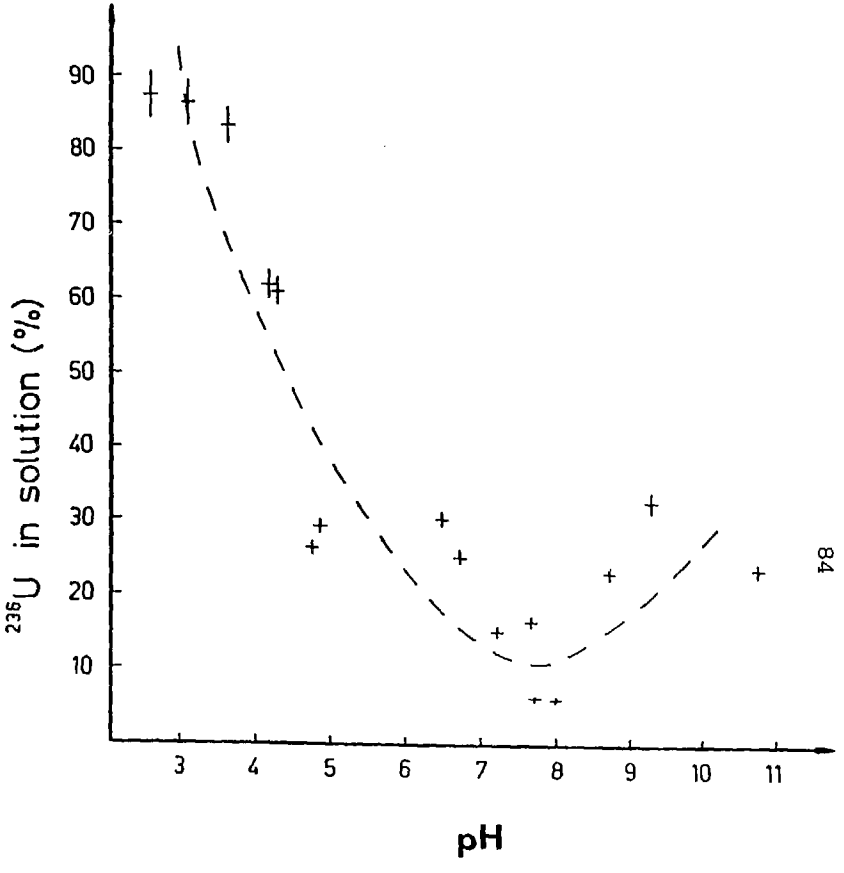
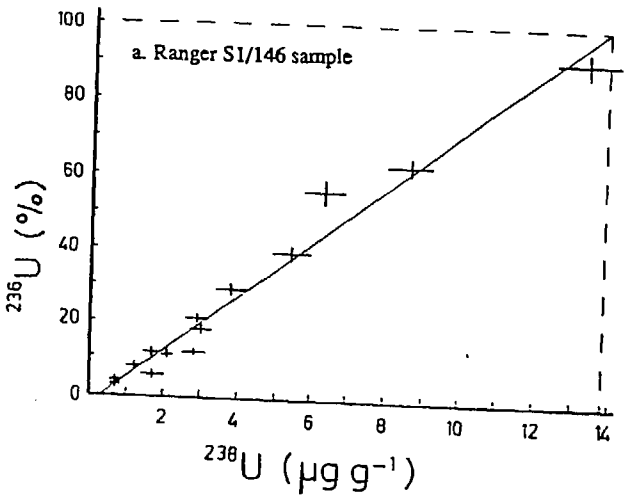


Figure 8.2

^{236}U adsorption on Koongarra DDH52 (15m) sample



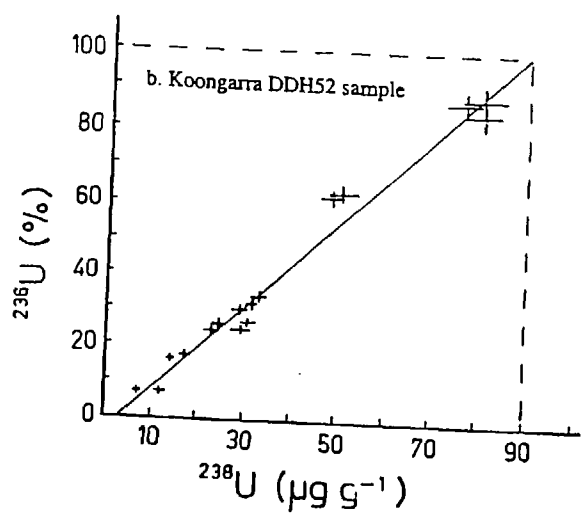


Figure 8.3

Relationship between ^{238}U leached from solid and ^{236}U in solution

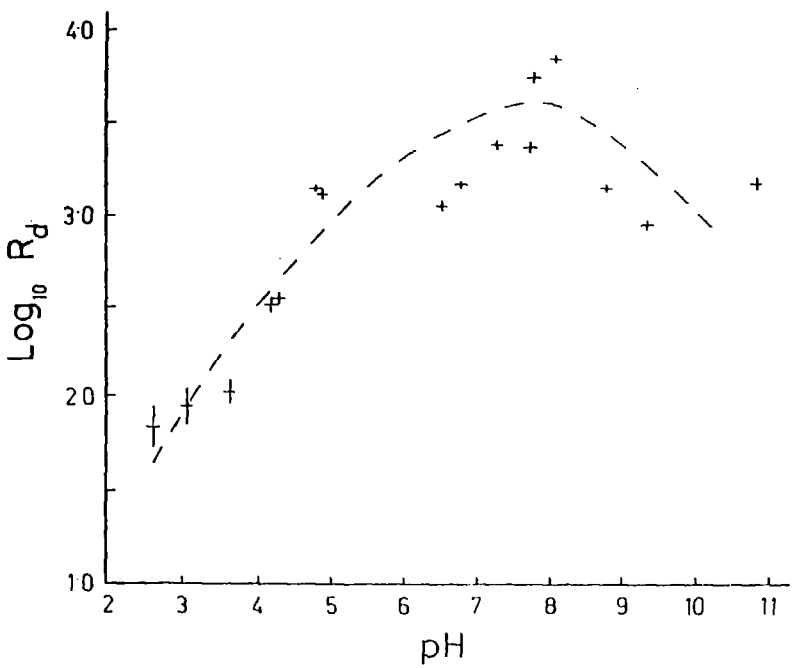
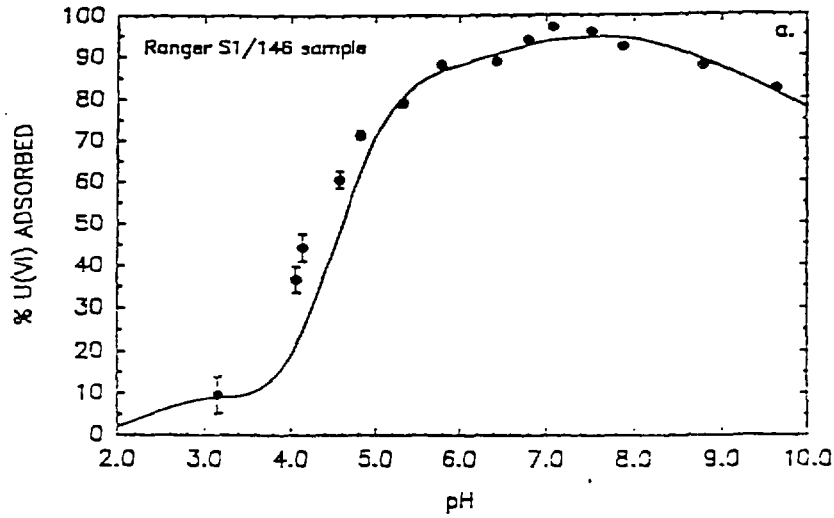


Figure 8.4

Distribution ratios for ^{236}U adsorption



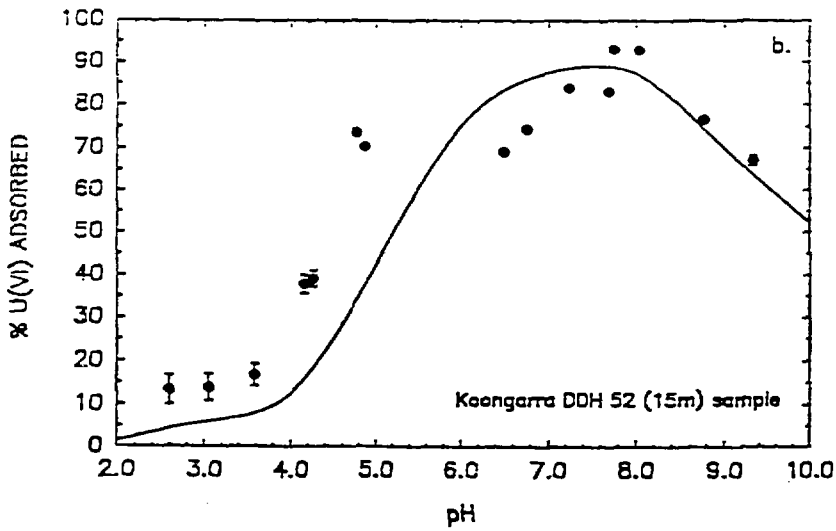


Figure 8.5

Uranium sorption on Ranger and Koongarra cores with curves computed using surface complexation model

Table 8.1

Composition of ARUF synthetic groundwater

Component	Concentration (mg/L)
Na^+	86
K^+	3.1
Ca^{2+}	11.5
Mg^{2+}	17
SiO_3^{2-}	50
Cl^-	73
SO_4^{2-}	4.3
HCO_3^-	145

Table 8.2

Triple layer model parameters for $Fe_2O_3.H_2O$ (amorphous).

Parameter	Value
surface site density (N_s)[a]	20 sites/nm^2
surface area (S)[a]	700 m^2/g
outer-layer capacitance (C_2)[b]	0.2 F/m^2
inner-layer capacitance (C_1)[b]	1.4 F/m^2

a. Hsi and Langmuir (1985)

b. Davis et al. (1978)

Table 8.3

Surface group hydrolysis and major ion surface complexation reactions with associated constants for $Fe_2O_3.H_2O$ (amorphous) in synthetic groundwater.

Reactions	Intrinsic Constants (log K)
$FeOH_2^- = FeOH + H^+$	- 5.1[a]
$FeOH = FeO^- + H^+$	-10.7[a]
$FeOH + Na^+ = (FeO^- - Na^+)^0 + H$	- 9.0[b]
$FeOH + Cl^- + H^+ = (FeOH_2^+ - Cl^-)^0$	7.0[b]
$FeOH + CO_3^{2-} + 2H^+ = (FeOH_2^+ - HCO_3^-)^0$	20.7[c]
$FeOH + CO_3^{2-} + 2H^+ = (FeOH - H_2CO_3)^0$	20.0[c]
$FeOH + SO_4^{2-} + H^+ = (FeOH_2^+ - SO_4^{2-})^-$	11.6[c]
$FeOH + SO_4^{2-} + 2H^+ = (FeOH_2^+ - HSO_4^-)^0$	17.3[c]
$FeOH + Ca^{2+} = (FeO^- - Ca^{2+}) + H^+$	- 6.3[c]
$FeOH + Mg^{2+} = (FeO^- - Mg^{2+}) + H^+$	- 6.3[d]

a. Davis et al. (1978)

b. Hsi and Langmuir (1985)

c. Zachara et al. (1989)

d. Considered similar to $FeO^- - Ca^{2+}$

Table 8.4

'Best-fit' formation constants for uranyl surface species of major significance.

Species	Constant
	(log K)
$FeO^-UO_2OH^+$	- 8.2
$FeOH_2^+UO_2CO_3^0$	23.3
$FeOH_2^+UO_2(CO_3)_2^{2-}$	31.2
$FeOH_2^+UO_2(CO_3)_3^{4-}$	34.7

PART III APPLICATION TO ACTINIDE MIGRATION FROM A NUCLEAR WASTE REPOSITORY

CHAPTER NINE

MOBILITY OF ACTINIDES IN GROUNDWATER

9.1 Chemistry of Actinides of Major Concern

The actinides which are major components in spent nuclear fuel are ^{241}Am, ^{239}Pu, ^{237}Np, ^{229}Th, ^{244}Cm, and ^{235}U (see figure 1.1). In this chapter, the chemistry and potential hazard of each of the actinides up to curium will be outlined, with reference to relevant information from Koongarra.

In many respects, the aqueous chemistry of all the actinides is similar, for example, they all form strong complexes with oxygen-containing ligands such as hydroxide, sulfate, carbonate or phosphate. The similarities between actinides are most evident when they are in the same oxidation state. The following oxidation states could exist in natural systems (Allard et al. 1984):

III - Ac, Pu, Am, and Cm
IV - Th, U, Np, and Pu
V - Pa, U, Np, and Pu
VI - U, Np, and Pu.

Any one system may contain actinides in several oxidation states. A typical oxic environment could contain Am(III), Th(IV), Np(V) and U(VI) (Allard et al. 1982) as well as Pu in every one of these oxidation states.

Table 9.1 shows the stability constants for actinides (represented generically as An) in the same oxidation state complexed with some inorganic ligands (L). For simplicity, only values for (1,1) complexes are given (ie. An_xL_y where both x and y are unity). Data for numerous other complexes exist. For example, plutonyl ion (PuO_2^{2+}) forms (1,2), (1,3), (2,2), and (3,5) hydroxo complexes, as well as the (1,1) complex. The formation constants for these species, as given by Jensen (1982), are all similar to the corresponding uranyl values. In general, the differences between the formation constants for U, Np, Pu, or Am (in a particular oxidation state) with inorganic ligands are often within experimental error (Allard et al. 1984), as shown by the similar complex stabilities in table 9.1.

The actinides also exhibit a similar tendency to form hydroxide solids, when in the same oxidation state (table 9.2). This is likely to also be the case with other actinide precipitates, however, the existing database does not allow a conclusive comparison. Accurate data for many potentially important complexes and solid phases have not yet been obtained. Currently, the OECD is coordinating a major project to compile thermodynamic data for the actinides.

Actinides in their lower (III or IV) oxidation states tend to be less soluble and more strongly adsorbed, and have a greater tendency to colloidal behaviour (Olofsson et al. 1982), than actinides in the higher (V or VI) oxidation states.

Therefore, the chemistry of actinides in geological environments is determined more by oxidation state than by the particular actinide in question. Many of the possible analogues in table 2.1 were selected on the

basis of their oxidation state. A major part of predicting the migration behaviour of a nuclide is, therefore, to determine its oxidation state in a particular system.

9.2 Actinium

The oxidation state of actinium in natural environments is limited to a Ac(III). Actinium is not a major concern in nuclear waste, but has a similar chemistry to Am and Cm, which, like Ac, are lanthanide-like and have an important +3 oxidation state (Cotton and Wilkinson 1980). The chemistry of Pu(III) is also similar. Therefore, actinium may be worth study as an analogue of trivalent transuranic elements.

The presence of ^{227}Th in some thorium α-spectra in the colloid part of the present study suggested that actinium was associated with colloids, and adsorbed on fine particles entrained in the groundwater. The mobility of actinium was greater than thorium, but substantially less than uranium, in the Koongarra system (section 7.10).

Although information on the geochemistry of actinium is sparse, these observations agree with reports in the literature. Dickson and Meakins (1984) reported that ^{227}Ac was readily leached from Ranger uranium ore, and presented a thorium alpha spectrum qualitatively similar to figure 7.2. These authors reasoned that the mobility of ^{227}Ac (and possibly ^{227}Th) could account for the presence of ^{223}Ra, frequently measured in groundwaters.

In a study of ^{231}Pa mobility, it was decided to determine the concentration of ^{231}Pa in uranium ore by measuring its second-order daughter ^{227}Th, thereby making the assumption that the intermediate ^{227}Ac was immobile (Golian et al. 1984). However, the calculated ^{231}Pa/^{235}U activity ratios indicated that either ^{231}Pa or ^{227}Ac must be mobile under conditions where ^{230}Th was at equilibrium with its parent ^{234}U. The authors concluded that the most likely explanation of their data was leaching of ^{227}Ac at a significant rate.

Excess concentrations of ^{227}Ac were measured in deep ocean waters (Nozaki 1984; Nozaki and Horibe 1983), where the ^{227}Ac/^{230}Th activity ratio was found to be approximately 1.0. This value is well above the equilibrium value for members of the ^{235}U and ^{238}U decay chains respectively, but is similar to that measured for fine particulate phases in Koongarra groundwaters.

The colloidal transport of actinium has not been previously studied. However, it has been found that lanthanides of similar chemistry (cerium(III) and europium(III)) are associated with colloids (Buddemeier and Hunt 1988).

In conclusion, there is growing evidence for mobility of Ac(III) in dissolved and also fine particulate phases, although in all environments studied, actinium is much less mobile than hexavalent uranium. These results have implications for the mobility of trivalent actinides, particularly americium and curium.

9.3 Thorium

Thorium is not considered to present a major hazard in nuclear waste, but it is the subject of study on account of its geochemical similarity to plutonium(IV). Its sole oxidation state is +4 and it is an analogue element for actinides exhibiting this oxidation state (Pu, U, Np).

The immobility of thorium was assumed in the modelling of Koongarra, and this was supported by measurement of thorium levels in groundwaters (chapter 6). The levels of ^{230}Th in filtered groundwater were about three orders of magnitude lower than uranium levels. In-situ distribution ratios for ^{230}Th were calculated to be above 4×10^5 mL/g.

There was an association of thorium with colloids, with 12 - 82 % of ^{230}Th in 1 μm-filtered groundwater being colloidal. This conclusion agrees with previous results (Short et al. 1986). However, the total amount of ^{230}Th which passed through a 1 μm filter was extremely small. Thorium was associated to a much greater extent with larger particles which are probably immobile under normal groundwater conditions. The R_d values for ^{230}Th on groundwater particles were above 2×10^6 mL/g (chapter 7).

These R_d values were about a hundred times higher than for uranium. Therefore, as the uranium dispersion fan extends for about 200 metres, thorium would have travelled only a few metres. Thus, it is reasonable to assume that ^{230}Th in the dispersion fan arises from in-situ decay of transported uranium.

The groundwater colloids found at Koongarra consisted mainly of Fe, together with U, Th and Ac. This suggested the presence of mobile iron-rich colloids with adsorbed radionuclides. Similar colloids could provide a transport mechanism for radionuclides from waste repositories.

The results at Koongarra are in general agreement with results from other analogue studies. Thorium was retained at Oklo, and mobilised extremely slowly at Morro do Ferro, almost entirely by the mechanism of surface erosion. High levels of dissolved thorium were only found at the Morro do Ferro when dissolved organics were also present (Miekeley and Kuchler 1987).

Thorium shows a slightly greater mobility in saline environments. In highly reducing saline groundwater from the Salton Sea Geothermal Field, R_d values for U and Th were within an order of magnitude of one another (Zukin et al. 1987). This indicated that U(IV) was present. A similar result was obtained for briny groundwaters from Texas (Laul and Smith 1988).

The immobility of thorium in most (organic free) natural systems is in accordance with theoretical predictions, as shown on an Eh/pH diagram (figure 9.1). This diagram shows the dominating thorium species as a function of the redox potential (Eh) and pH. The solid species ThO_2 dominates thorium speciation over a wide domain (Brookins 1988). Only at low pH is a solution phase species present at a significant concentration. In this diagram, sulfate was assumed to be present at relatively high levels. Therefore, at Koongarra, the stability field of ThO_2 would be even greater and it is therefore not surprising that thorium is highly immobile.

9.4 Protactinium

^{231}Pa is a decay product of ^{235}U and is only present in small amounts in nuclear waste (Brookins 1984). Therefore it has received little attention except presumably at AERE, Harwell, UK, where 125 g of ^{231}Pa was separated from 60 tonnes of uranium sludge from Congo ore.

The aqueous chemistry of protactinium is dominated by the +5 oxidation state. It tends to hydrolyse and form colloidal hydroxo species (Cotton and Wilkinson 1980), and is thought to be highly immobile in the geological environment. However its geochemistry has not been studied in detail.

Although in the present study evidence for the mobility of its daughter ^{227}Ac was found, protactinium itself has a unique chemistry and is not addressed by analogy to uranium or thorium.

9.5 Uranium

In nature, the chemistry of uranium is dominated by the oxidation states U(IV) and U(VI), which have totally different chemistries. U(IV) is quite immobile and has a similar chemistry to thorium, whereas U(VI) is comparatively soluble, and present at appreciable levels in many natural waters, including seawater (approx. 4 μg/L).

The chemistry of the +6 state is that of the dioxo ion UO_2^{2+}, which is also exhibited by neptunium and plutonium in their +6 oxidation states. Inorganic ligands, particularly carbonate (and possibly phosphate), are the main complexants for uranyl in natural groundwaters. The speciation of uranium in oxidising environments is dominated by a series of uranyl carbonate complexes above a pH of about 5 (figure 9.2, see also figure 4.4a).

Under reducing conditions, the solubility of uranium is much lower, (due to the dominance of U(IV)) and is controlled by the solubility of UO_2. Figure 9.2 shows a large stability domain for UO_2 in reducing of conditions.

In the present study, the levels of dissolved uranium in field samples were lower than solubility limits, and suggested uranium levels at Koongarra were controlled by sorption. Only in the immediate vicinity of the primary ore is it likely that uranium concentrations are high enough to be limited by solubility.

Uranium in Koongarra groundwater migrates predominantly as dissolved species which pass through ultrafilter membranes. A small proportion, about 1 - 3 %, is carried by iron-rich colloids. Uranium is sorbed to fine particles, with distribution ratios of 2-7 X 10^4 mL/g. R_d values on the colloids were substantially higher, about 10^6 mL/g.

Uranium sorption was studied in laboratory experiments, using the artificial isotope ^{236}U. Adsorption of ^{236}U was dependent on the pH, and isotope exchange occurred between ^{236}U and accessible ^{238}U (section 8.3). This study showed that uranium associated with amorphous iron mineral phases (as determined by a TAO-extraction), was in short term exchange with the groundwater. Surface complexation modelling of the sorption data was undertaken, based on the assumption that amorphous ferric oxide was the major sorbing phase. The model was able to provide a satisfactory fit to the data, but was only applied in a greatly simplified form.

Ferrihydrite produced by co-weathering processes, or by waste canister corrosion, will be an important sorbing phase near waste repositories. The potential importance of such a phase can be inferred from both the uranium sorption study, and the colloid part of the present work.

Although conditions at Koongarra are apparently not ideal for radionuclide containment, and uranium is present in its relatively mobile U(VI) state, uranium migration has been limited to less than 200 m over about a million years. If Pu(VI) migrated at similar rates, this would provide some assurance about repository safety, particularly when it is considered that a repository would be deep underground. Under such conditions, flow paths to the biosphere would be longer, and plutonium would be reduced to its less mobile lower oxidation states.

9.6 Neptunium

Compared to other long-lived transuranics, the behaviour of neptunium in natural aquatic systems has received little attention, apparently because major releases of neptunium into the environment have not resulted from nuclear weapons testing. Neptunium has been described as the 'neglected actinide' (Cleveland et al. 1983).

However, after about 100 000 years, the total biological hazard of spent fuel will be dominated by ^{237}Np and its decay products, including ^{229}Th (Allard et al. 1984). In the last decade it has been realised that the hazards of ^{237}Np may have previously been underestimated. In an analysis where HLW radionuclides were ranked by factors including half-life, solubility, adsorption affinity, wasteform nuclide inventory and biological toxicity, ^{237}Np was concluded to be the most hazardous actinide, despite comprising a relatively low proportion of the initial actinide inventory (Serne and Relyea 1981). A similar conclusion was reached by Brookins (1984), who also noted the toxicity of daughter nuclides of ^{237}Np.

Under reducing conditions, such as deep groundwaters, tetravalent neptunium species dominate (Allard et al. 1984). Experimental evidence and analogy with Th(IV) indicate that Np(IV) would be relatively immobile.

The Eh/pH diagram for neptunium shows that with NpO_2 selected as the solubility limiting phase (figure 9.3a), neptunium is highly insoluble over a broad domain. However, more soluble phases such as $NpO(OH)_2$ could dominate, and the Eh/pH diagram for this system shows a substantial region of potential neptunium mobility as NpO_2^+ or $Np(OH)_5^-$ (figure 9.3b). The effect is even greater if $Np(OH)_4$ is chosen as the dominant Np(IV) phase, in which case neptunium is mobile over a wide Eh/pH domain (Brookins 1988). Whilst it would be expected that both $NpO(OH)_2$ and $Np(OH)_4$ would age to NpO_2, these phases would greatly increase neptunium migration if they formed in the environment of a repository (Brookins 1988).

Speciation studies of natural surface waters showed Np(V) was the most stable oxidation state and was comparatively soluble (Nash et al. 1988). In general, Np(V) species dominate in oxic conditions - NpO_2^+ at low pH, and $NpO_2(CO_3)_2^{5-}$ or $NpO_2(CO_3)_2^{3-}$ at higher pH when carbonate is present (Allard et al. 1984). These anionic neptunium carbonate complexes are chemically similar to analogous U(VI) complexes (Beall and Allard 1981). However U(VI) is an imperfect analogue, since the pH of neptunium hydrolysis is much higher. Considering the similar pH of hydrolysis and adsorption edges, the sorption of Np(V) would therefore be expected to be weak across a broad pH range.

Pentavalent actinides probably have a lower surface affinity than any other oxidation state, behaving as a simple monovalent ion (Keeney-Kennicutt and Morse 1984). These authors reported that adsorption of Np(V) occurred on synthetic and natural solids for some solution compositions, but strong desorption occurred in seawater. Like uranyl, neptunium sorption would be expected to be highly dependent on solution conditions, and this may explain the variable results obtained.

Most studies indicate Np(V) to be mobile, present in a soluble form, and not associated with colloids (eg Bidoglio et al. 1987). In a speciation study of several actinides, Allard et al. (1983) found that sorption of Np(V) was minimal across a wide pH range. At a pH of 8.5 the order of actinide sorption was:

Th(IV) > Am(III) > Pa(V) > Pu(?) >> U(VI) > Np(V).

Therefore, fears of neptunium migration centre on the possible mobility of Np(V) species. The chemistry of this state is difficult to predict - Np(V) is, perhaps surprisingly, totally unlike Pa(V), and U(VI) is not a close analogue.

Clearly, it would be desirable to select a reducing deep repository environment where Np(IV) would dominate. The presence of Fe(II) minerals would assist in favouring Np(IV) (Beall and Allard 1981). Reduction of Np(V) to the tetravalent state would give 2-3 orders of magnitude higher distribution coefficients in the environmental pH range and result in a similar immobility to Th(IV). Such conditions apparently prevailed at Oklo, where neptunium produced in the natural reactor was retained.

9.7 Plutonium

Plutonium is highly toxic and long-lived, and is the major radioactive component of spent fuel between 1000 and 100 000 years after removal from reactors. Two isotopes, ^{239}Pu and ^{240}Pu, are present. Both are alpha-emitters and they are usually grouped together.

Plutonium has been spread throughout the environment. About 4200 kg has been injected into the atmosphere from nuclear explosions (Allard et al. 1984), a further 300 tonnes resides in nuclear weapons, and additional amounts have been released in accidents. It has been dumped on land and into the sea as low-level effluent. These releases have allowed its environmental behaviour to be studied in greater detail than other transuranic elements.

The solution phase chemistry of plutonium is complex, and it exhibits oxidation states +3, +4, +5 and +6. Under strongly reducing conditions Pu(III) dominates, with Pu(IV) having a significant stability field. The transfer from predominant Pu(IV) to Pu(V) occurs around the redox potential normally encountered in natural systems. This change dramatically increases plutonium solubility and reduces its sorption affinity (Allard et al. 1984).

The Eh/pH diagram for plutonium shows that, with PuO_2 as the dominant solid phase, plutonium would be immobile over a broad domain (figure 9.4a). This diagram is similar to that for the analogue element thorium (figure 9.1). If $Pu(OH)_4$ is chosen as the preferred Pu(IV) solid, the stability fields of solution complexes, such as $Pu(OH)_5^-$, are dramatically increased (figure 9.4b).

The behaviour of Pu(IV) is similar to that of U(IV) or Th(IV), and Pu(III) is analogous to actinium. These comparisons, and direct evidence, suggest an association with colloids in the lower oxidation states. In the higher (V and VI) states, Np(V) or U(VI) are reasonable analogues although the understanding of Np(V) chemistry is not comprehensive (as noted above). However the study of Np(V) is not complicated by the presence of several other possible oxidation states. The analogy with Np(V) indicates the possible mobility of PuO_2^+.

In systems where mixed oxidation states are present, adsorbed plutonium is usually in the +3 or +4 oxidation state (Cleveland and Rees 1981). In an experimental study, the R_d for plutonium was investigated after separating lower (III + IV) and higher (V + VI) states. The R_d of Pu(III + IV) was about 1000 times greater than for Pu(V + VI) (Mahara and Matsuzura 1989). Similarly, Sanchez et al. (1985) reported that the sorption edge for Pu(IV) on goethite occurred at pH 4 as opposed to pH 5 for Pu(V). These authors considered that adsorption of Pu(V) could occur with a change in oxidation state.

Nelson and Lovett (1978), noted that open ocean U(VI) concentrations were about 10 000 times higher than Th(IV) concentrations, although crustal abundances of the two elements are similar. They therefore predicted, and confirmed, that in this environment distribution coefficients for Pu(IV) would exceed those of Pu(VI) by factors of up to 1000.

The relatively low mobility of plutonium in its lower oxidation states provides further support for including reducing barriers in waste repository design. Numerous examples in the literature indicate that when plutonium is not reduced, its migration is difficult to predict and may be dramatically underestimated (eg Mahara and Matsuzura 1989).

Plutonium produced in the US nuclear weapons program was disposed of hastily, starting in 1943, by releasing it into sorption beds in canyons in the vicinity of Los Alamos. About 370 000 MBq of waste were discharged in the subsequent decade. Despite predictions of retention within a few millimetres, the plutonium penetrated to 30 m depth (Nyhan et al. 1983). This may be ascribed to the variable oxidation state of plutonium, or the rather unwise pH of the discharged waste of approximately 3.0 to 4.0. Released plutonium tended to be less mobile than americium, which was also released.

In a recent report, it was revealed that in the Mortandad Canyon (another recipient of Los Alamos waste), plutonium and americium were detectable in monitoring wells up to 3390 m from the discharge point (Penrose et al. 1990). Again, laboratory studies had predicted migration of only a few metres. Plutonium was mostly in the reduced state, and the mobility of plutonium and americium in the silt/sand aquifer was attributed to colloidal transport in the 25-450 nm size range, with a possible contribution by surface flow in storm events.

The results of laboratory studies and inadvertent experiments in natural environments show that the mobility of plutonium has been generally underestimated, because of its multiple valence states, and, in some cases, colloidal transport. Furthermore, the Maxey Flats study (Cleveland and Rees 1981) showed a strong mobilisation as EDTA complexes which were only weakly sorbed. This result shows the importance of complete destruction of organic matter in transuranic wastes, and of selecting a repository environment in which the groundwater is free of strongly complexing ligands.

Overall, the results indicate that the mobility of plutonium in its reduced state is limited, as verified by its retention at Oklo (section 2.3.1). Studies at the Morro do Ferro and Koongarra have demonstrated the immobility of Th(IV), and, if the analogy of Pu(IV) with Th(IV) is valid, these results indicate immobility of Pu(IV). However, the possibility of colloidal transport of plutonium in its lower oxidation states, and particularly the greater mobility of higher oxidation states, indicate that further investigation of plutonium mobility is required.

9.8 Americium

^{241}Am and ^{243}Am are alpha-emitters with half-lives of 458 and 7950 years respectively, and are produced after long irradiation of nuclear fuel in a reactor. ^{241}Am is the most active actinide in spent fuel in a time period between approximately 100 and a few thousand years after removal from the reactor.

Americium is trivalent in both oxidising and reducing environments. The Eh/pH diagram for americium shows that, in the presence of moderate levels of dissolved carbonate, Am(III) is immobilised as $Am_2(CO_3)_3$ over a substantial Eh/pH field (figure 9.5). Therefore, americium would probably be relatively immobile if repository host rocks contain significant amounts of carbonate (Brookins 1988).

There is limited data on the geochemistry of americium. At Oklo, indirect evidence suggested retention of americium (section 2.3.1). Mobilisation rates for lanthanum (a chemical analogue of americium) at Morro do Ferro (section 2.3.2) were very low, and mostly due to stormflow erosion rather than solubilisation.

As noted previously, actinides in low oxidation states tend to be associated with colloids. Americium released into the Mortandad Canyon has, within 30 years of being released, traversed a distance of some 3390 metres (Penrose et al. 1990). The americium was found to be mobile both in a colloidal form, and also as a stable, anionic complex of unknown composition.

In a study of several actinides, Allard et al. (1984) found a significant particle fraction for Am(III) and Pu(IV), even at low concentrations, in contrast to hexa-and pentavalent actinides. These authors reported Am(III) to be strongly sorbed on geologic media, particularly on a fine colloid assumed to be $Fe(OH)_3$.

In the present study, Ac(III) and Th(IV) were the radionuclides most strongly associated with colloids in Koongarra groundwaters, and furthermore Fe, (assumed to be particles of $Fe(OH)_3$) was significantly enriched in the colloid fraction.

Therefore, the limited experimental evidence, and analogue studies, show that americium is somewhat mobile, with colloidal transport (in common with Th(IV) and Pu(IV)) being a possible migration mechanism.

9.9 Curium

The long term hazard of actinides above americium is almost negligible, and curium has only been studied to a limited extent. It has been reported to have a low solubility in seawater (Nash et al. 1988).

Analogy with actinium, americium and lanthanides of similar chemistry (for example, lanthanum at the Morro do Ferro) indicate that curium is unlikely to be mobile in a repository environment within timescales comparable to its 100 year half-life.

9.10 Concluding Comments

Overall, understanding of the chemistry of the transuranic elements (as opposed to their concentrations) in natural environments is quite limited. The mobility of these radionuclides in the environment does not always correspond to predictions based on theory or experiment.

Plutonium has received the most study, due to its wide dispersion in the environment, and also because of a (correct) public perception of its toxicity. Neptunium, in particular, requires attention, due to its recently revised risk factors, and its possible mobility in the pentavalent state, for which no satisfactory chemical analogue element has been found.

Koongarra provides analogues for the behaviour of actinides in their +3, +4 and +6 states, by actinium, thorium and uranium respectively. Specific processes occurring at Koongarra, such as adsorption, alpha-recoil and colloidal transport, are likely to occur in the vicinity of a waste repository. Furthermore, Koongarra may be used to test generally applicable models of radionuclide migration.

In order to apply data for analogue elements to the behaviour of transuranic elements in geological environments, it is necessary to know the dominant oxidation states, or the distribution of oxidation states, of the transuranic in question. Furthermore, the assumption that the chemistry of an actinide is primarily determined by its oxidation state needs further verification. For the use of chemical analogues to be fully convincing, the similarities (and differences) between actinides in particular oxidation states require further study.

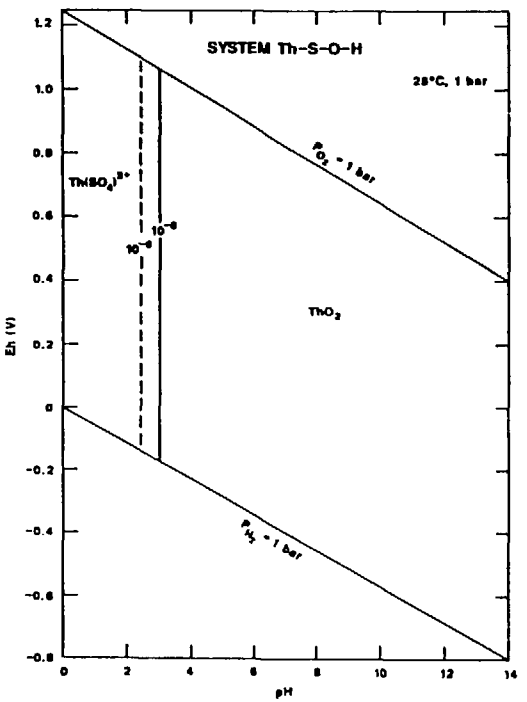


Figure 9.1

Eh/pH diagram for system Th-S-O-H. Assumed activities for dissolved species are

Th = $10^{-6,-8}$ S = 10^{-3} (from Brookins 1988).

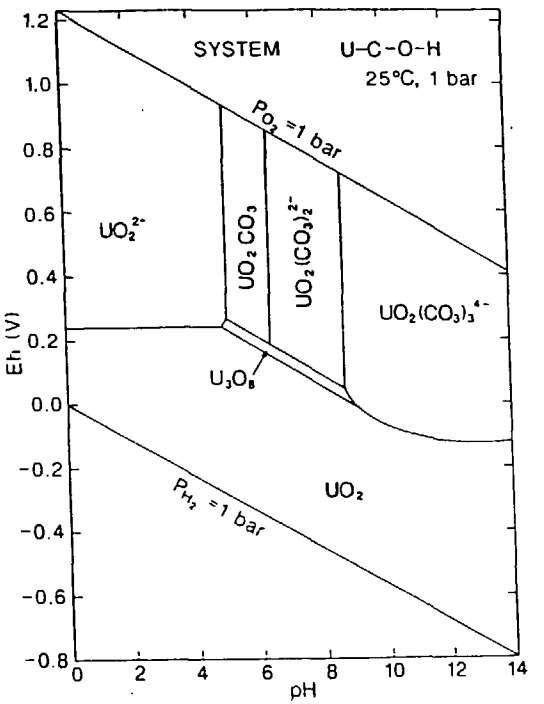


Figure 9.2

Eh/pH diagram for system U-C-O-H. Assumed activities for dissolved species

U = 10^{-8}, C = 10^{-3} (from Brookins 1988).

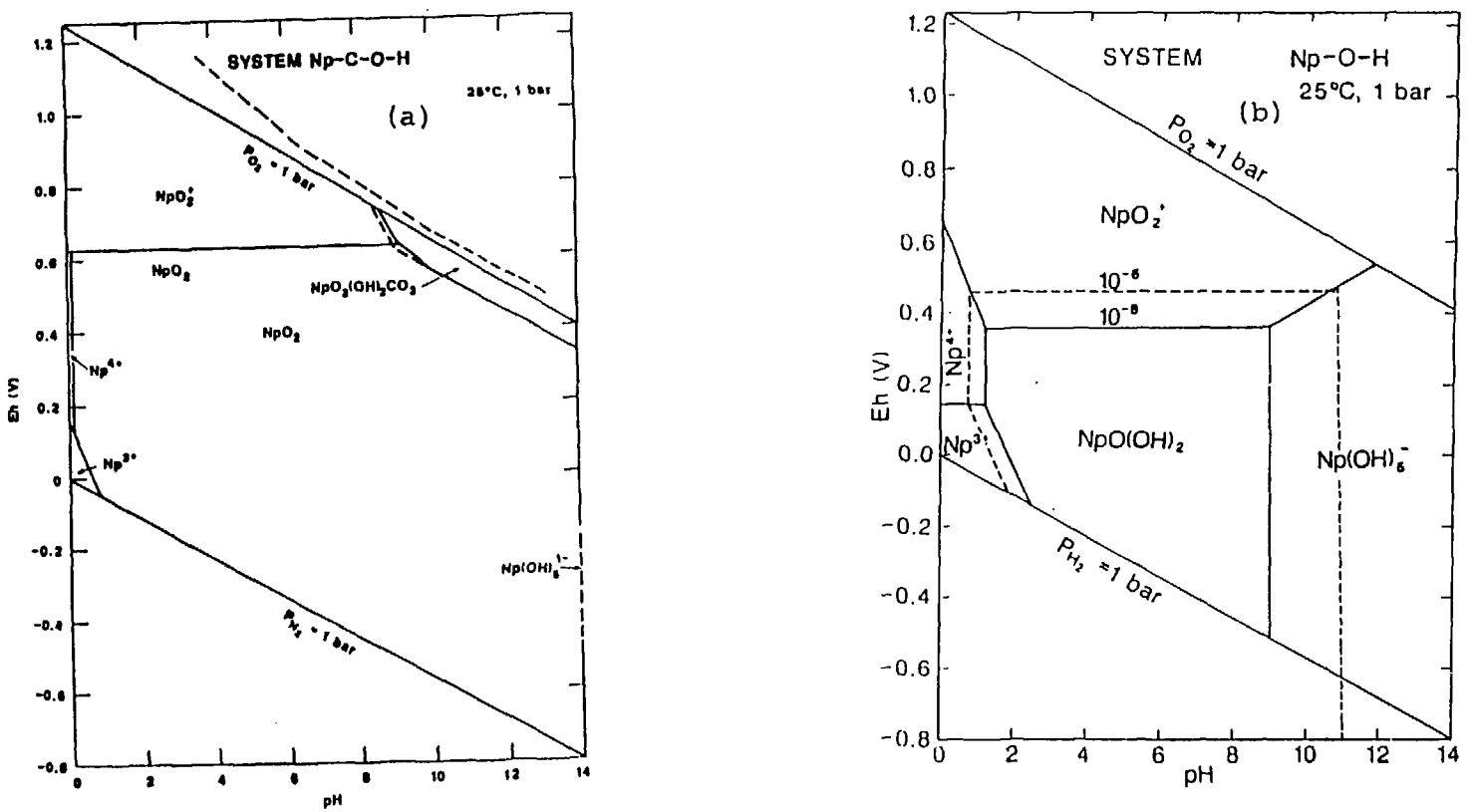


Figure 9.3 Eh/pH diagram for the system Np-C-O-H (from Brookins 1988).

(a) with NpO_2 the dominant Np(IV) oxysolid (b) with $NpO(OH)_2$ the dominant Np(IV) oxysolid.

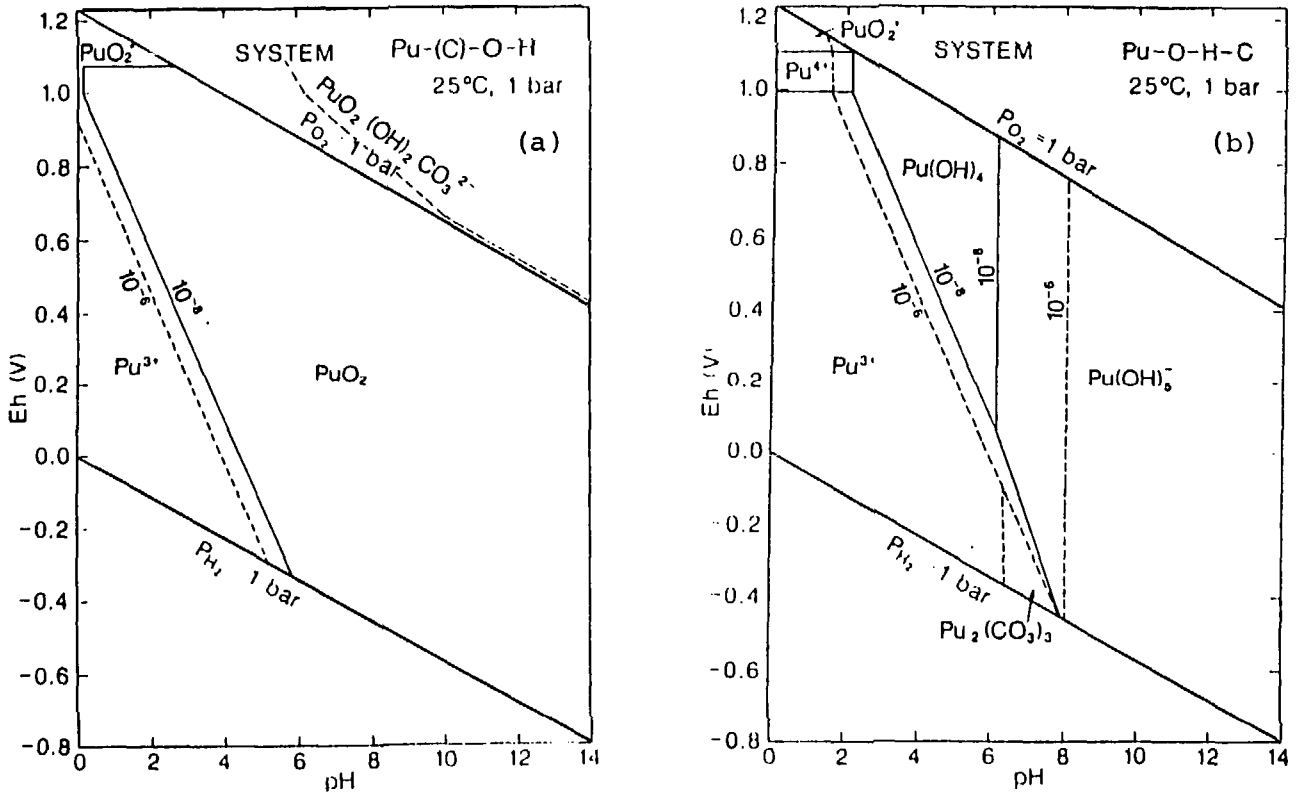


Figure 9.4 Eh/pH diagram for system Pu-C-O-H (from Brookins 1988).

(a) PuO_2 chosen as dominant Pu(IV) oxide solid (b) $Pu(OH)_4$ as dominant Pu(IV) oxide solid.

Assumed activities Pu = 10^{-8}, C = 10^{-3}

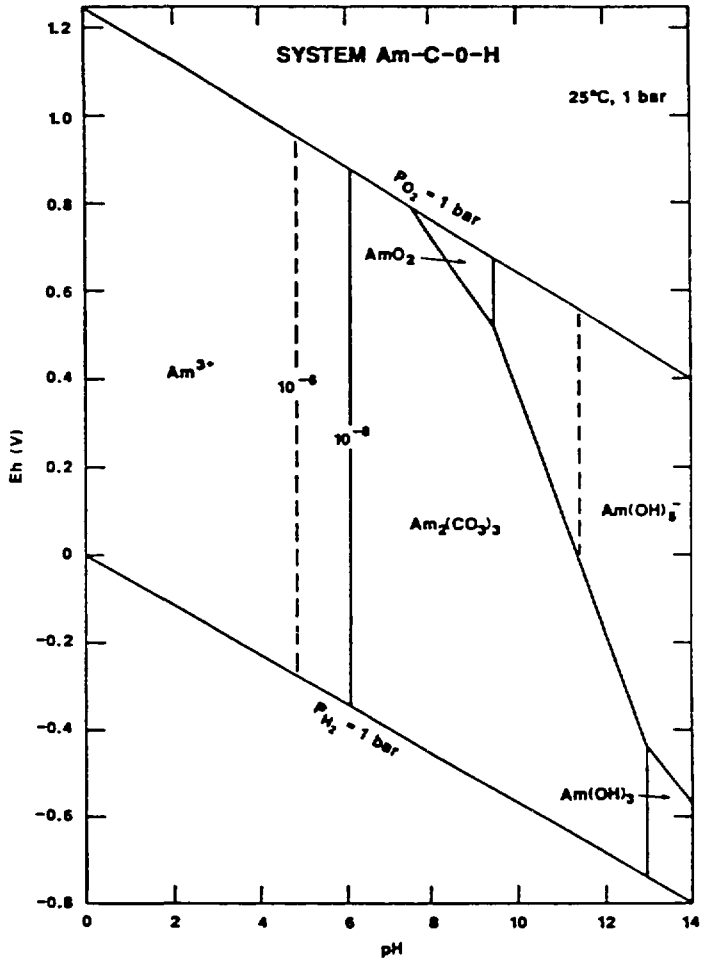


Figure 9.5 Eh/pH diagram for system Am-C-O-H
Assumed activities for dissolved species
Am = $10^{-6,-8}$ C = 10^{-3} (from Brookins 1988).

Table 9.1

Reported stability constants for (1,1) actinide complexes with some major inorganic ligands.

(log K_1 for $An + L \rightarrow AnL$; $I = 0$)

		Hydroxide ($L = OH^-$)	Chloride ($L = Cl^-$)	Carbonate ($L = CO_3^{2-}$)
An^{3+}	Range[a]		< 1	
	Pu[b]	6.7	-0.1	
	Am	7.9	-0.1	
	Cm	7.9		
An^{4+}	Range	12.5-13.7	< 2	
	U	12.2	0.26	
	Np	11.7	0.15	
	Pu	13.6	0.14	
AnO_2^+	Range	4.0-5.1	< 0	5-5.9
	NpO_2^+	4.0	-0.3	
	PuO_2^+	4.3	-0.17	
AnO_2^{2+}	Range	8.1-9.1	< 2	9.9-12
	UO_2^{2+}	8.1	-0.1	10.1
	NpO_2^{2+}	8.6	-0.1	
	PuO_2^{2+}	7.9	0.1	

a. Range given by Allard et al. (1984)

b. Values selected by Jensen (1982)

Only environmentally significant oxidation states have been included in this table.

Table 9.2

Reported actinide hydroxide solubility products.

(for $xAn + yL \rightarrow An_xL_y$ (s); $-\log K_s$)

$An(OH)_3$	Range[a]	
	Pu[b]	19.7
	Am	19.6
$An(OH)_4$	Range	46-63
	U	56.2
	Np	55.4
	Pu	56
AnO_2OH	Range	8.5-9.3
	NpO_2^+	9.1
	PuO_2^+	9.3
$AnO_2(OH)_2$	Range	22.2-24.5
	UO_2^{2+}	22.4
	NpO_2^{2+}	22.7
	PuO_2^{2+}	24.5

a. Range given by Allard et al.(1984)

b. Values selected by Jensen (1982)

CHAPTER TEN

OVERVIEW OF KOONGARRA AS AN ANALOGUE FOR ACTINIDE MIGRATION

10.1 Types of Information

The safety of nuclear waste repositories concerns individuals from a broad cross section of the community. Natural analogues have the potential to give a general response to such concerns. However, at some stage, it will be necessary to attempt to apply the knowledge gained from Koongarra and other analogues to specific questions relevant to repository assessment.

This dissertation has covered a small part of this process. Results from one analogue site (Koongarra) have been applied to a particular aspect of repository safety (actinide release). This has provided a case study of natural analogues - indicating the kind of information available and the questions which can be answered.

Koongarra provides information at a number of levels, meeting the concerns of various groups in the community.

These levels can be categorised as follows:

i) General qualitative information.
To a completely non-technical audience, Koongarra, in common with other natural analogues such as Oklo, Morro do Ferro, and the Salton Sea Geothermal Field, provides a qualitative reassurance about the ability of natural systems to retain radionuclides over long time-periods.

ii) General scientific information.
Geological and chemical information can be derived at Koongarra and incorporated within a general understanding of the way in which natural or modified geological systems evolve. This category includes:

- the role of ferrihydrite coatings as radionuclide sorbing phases.
- the transport of uranium as inorganic carbonate or phosphate solution complexes.
- the chemical behaviour of actinides in particular oxidation states.
- the apparent immobility of thorium.
- the tendency of thorium and actinium to be associated with particulate and colloidal phases.

iii) Specific data

Into this category can be placed scientific data, including numeric values of specific parameters, which are site-specific to Koongarra. While such detailed information can be useful in testing general models of geological systems, it is not generally applicable outside the Koongarra system.

For example:

- radionuclide migration rates.
- patterns of isotope disequilibria.
- in-situ uranium and thorium distribution ratios.

10.2 Limitations

The study of natural analogues can resolve questions about the future safety of waste repositories, in a way that is possibly more convincing than results from laboratory experiments, or predictions based on theory. However, the approach has certain limitations.

Koongarra, like several other analogues, demonstrates qualitatively the ability of geological systems to prevent the dispersion of radionuclides. However, it could be argued that many similar systems once existed, which have been completely dispersed and released their radionuclide inventory to the environment. Therefore such qualitative conclusions have limited generality.

Another limitation of the analogue approach is that certain components of a nuclear waste repository have no close analogues. For example, the migration of neptunium, which appears to have no satisfactory analogue element, is difficult to predict.

The site-specific data obtained at Koongarra provides an opportunity to test models of radionuclide migration, but even a completely successful test-run of a model on a particular analogue site such as Koongarra would not completely validate the model. This is because the result of geological processes acting at Koongarra is already known. Therefore by iteratively fine-tuning the model, in accord with what is observed at Koongarra, it should be possible to eventually recreate the system to any required degree of accuracy.

Nonetheless, if a model performs well in the Koongarra case, greater confidence in its predictive ability will be justified. Ideally, at some future stage, models developed at other analogue sites could be tested at Koongarra, and vice-versa. The success of such an exercise would provide grounds for confidence in predictions derived from migration models.

10.3 Possible Further Work

In this dissertation I have attempted to relate the study of actinide migration at Koongarra to the possible release of transuranics from a nuclear waste repository. In several areas knowledge appears to be limited. The following questions are presented as worthwhile avenues of further study:

i) When ferrihydrite recrystallises to forms such as goethite and hematite, are adsorbed radionuclides retained or released?

ii) Is the uranyl phosphate complex $UO_2(HPO_4)_2^{2-}$ as stable as suggested by Dongarra and Langmuir (1980)?

iii) Is actinium a worthwhile analogue of trivalent actinides such as americium and curium? If so, further study of its geochemistry is warranted.

iv) Can the surface-complexation model be extended to more fully describe uranium adsorption in complex systems, such as Koongarra?

v) How do pentavalent actinides, particularly Np(V) behave in the natural environment? Does a satisfactory analogue element for Np(V) exist?

To some extent these questions can be answered by further study of geological systems such as Koongarra.

10.4 Summary of this Dissertation

The disposal of nuclear waste is currently a significant environmental problem. Several radionuclides, particularly long-lived actinides, present a major threat to human well-being should they be released from geological waste repositories and migrate towards the biosphere.

Predicting the behaviour of repositories over long time periods presents unprecedented challenges to the scientific community. One way to gain confidence in modelling possible radionuclide releases is to study natural systems which are similar to components of the multibarrier waste repository.

Several such analogues are currently under study and these provide useful data about radionuclide behaviour in the natural environment. One such system is the Koongarra uranium deposit in the Northern Territory. In this dissertation, the migration of actinides, primarily uranium and thorium, in this system has been studied as an analogue for the behaviour of transuranics in the far-field of a waste repository.

The major conclusions of this study are:

1) The main process retarding uranium migration in the dispersion fan at Koongarra is sorption, which suppresses dissolved uranium concentrations well below solubility limits. Ferrihydrite appears to be a major sorbing phase, based on sequential extraction data, isotope exchange data and the apparent success of a simplified uranyl sorption model in which ferrihydrite was the only major uranium sorbing phase.

2) Thorium is extremely immobile, with very low dissolved concentrations and corresponding high distribution ratios for ^{230}Th. This supports an underlying assumption of the model of the Koongarra system developed by Golian et al. (1986). This result has implications for the migration of tetravalent actinides, particularly Pu(IV), in a repository environment.

3) Overall, colloids (particles below 1 μm in size) are relatively unimportant in Koongarra groundwater. Uranium migrates mostly as dissolved species, whereas thorium and actinium are mostly adsorbed to larger, relatively immobile particles and the stationary phase. However, of the small amount of ^{230}Th that passes through a 1 μm filter, a significant proportion is associated with colloidal particles. Actinium appears to be slightly more mobile than thorium and is associated with colloids to a greater extent, although generally present in low concentrations. These results suggest the possibility of colloidal transport of trivalent and tetravalent actinides in the vicinity of a nuclear waste repository.

REFERENCES

Agemian, H. and Chau, A.S.Y. 1976, 'Evaluation of Techniques for the Determination of Metals in Aquatic Sediments', Analyst 101, 761-767

Airey, P.L., Roman, D., Golian, C., Short, S., Nightingale, T., Lowson, R.T. and Calf, G.E. 1984, 'Radionuclide Migration Around Uranium Ore Bodies - Analogue of Radioactive Waste Repositories', Annual Report 1982-83 (AAEC/C40), AAEC, Lucas Heights, Australia.

Airey, P.L. 1986, 'Radionuclide Migration Around Uranium Ore Bodies in the Alligator Rivers Region of the Northern Territory of Australia - Analogue of Radioactive Waste Repositories - A Review', Chemical Geology 55, 255-268

Airey, P.L., Duerden, P., Roman, D., Golian, C., Nightingale, T.J. and Payne, T.E. 1986a, 'Radionuclide Migration Around Uranium Ore Bodies - Analogues of Radioactive Waste Repositories', Annual Report 1984-85 (AAEC/C55), AAEC, Lucas Heights, Australia.

Airey, P.L., Golian, C. and Lever, D.A. 1986b, 'An Approach to the Mathematical Modelling of Uranium Series Redistribution Within Ore Bodies', Topical Report (AAEC/C49), AAEC, Lucas Heights, Australia.

Airey, P.L. and Ivanovich, M. 1986, 'Geochemical Analogues of High-Level Radioactive Waste Repositories', Chemical Geology 55, 203-213

Allard, B., Olofsson, U., Torstenfeldt, B., Kipatsi, H. and Andersson, K. 1982, 'Sorption of Actinides in Well-Defined Oxidation States on Geologic Media', in Scientific Basis for Nuclear Waste Management V, (ed) W. Lutze, Elsevier Science, New York.

Allard, B., Olofsson, U. and Torstenfelt, B. 1984, 'Environmental Actinide Chemistry', Inorganica Chimica Acta 94, 205-221

Ames, L.L., McGarrah, J.E., Walker, B.A. and Salter, P.F. 1983, 'Uranium and Radium Sorption on Amorphous Ferric Oxyhydroxide', Chemical Geology 40, 135-148

Bacon, M.P. and Anderson, R.F. 1982, 'Distribution of Thorium Isotopes Between Dissolved and Particulate Forms in the Deep Sea', Journal of Geophysical Research 87, 2045-2056

Barney, G.S. 1984, 'Radionuclide Sorption and Desorption Reactions with Interbed Materials from the Columbia River Basalt Formation', in Geochemical Behaviour of Disposed Radioactive Waste, (eds) G.S. Barney, J.D. Navratil and W.W. Schulz, American Chemical Society, Washington.

Batley, G.E. and Gardner, D. 1977, 'Sampling and Storage of Natural Waters for Trace Metal Analysis', Water Research 11, 745-756

Beall, G.W. and Allard, B. 1981, 'Sorption of Actinides from Aqueous Solutions Under Environmental Conditions', in Adsorption from Aqueous Solutions, (ed) P.H. Tewari, Plenum Press, New York.

Bidoglio, G., Offerman, P. and Saltelli, A. 1987, 'Neptunium Migration in Oxidising Clayey Sand', Applied Geochemistry 2, 275-284

Birchard, G.F. and Alexander D.H. 1983, 'Natural Analogues - A Way to Increase Confidence in Predictions of Long Term Performance of Radioactive Waste Disposal', in Scientific Basis for Nuclear Waste Management VI, (ed) D.G. Brookins, Elsevier Science, New York.

Borovec, Z. 1981, 'The Adsorption of Uranyl Species by Fine Clay', Chemical Geology 32, 45-58

Bower, C.A. and Goertzen, J.O. 1959, 'Surface Area of Soils and Clays by an Equilibrium Ethylene Glycol Method', Soil Science 87, 289-292

Brookins, D.G. 1984, Geochemical Aspects of Radioactive Waste Disposal, Springer-Verlag, New York.

Brookins, D.G. 1988, Eh-pH Diagrams for Geochemistry, Springer-Verlag, New York.

Buddemeier, R.W. and Hunt, J.R. 1988, 'Transport of Colloidal Contaminants in Groundwater: Radionuclide Migration at the Nevada Test Site', Applied Geochemistry 3, 535-548

Burkholder, H. 1983, 'Engineered Components for Radioactive Waste Isolation Systems - Are They Technically Justified?', Technical Report (ONWI-286), Office of Nuclear Waste Isolation, Battelle, Columbus.

Byers, C.D., Jercinovic, M.J., Ewing, R.C. and Keil, K. 1985, 'Basalt Glass: An Analogue for the Evaluation of the Long-Term Stability of Nuclear Waste Form Borosilicate Glass', in Scientific Basis for Nuclear Waste Management VIII, (eds) C.M. Jantzen, J.A. Stone, and R.C. Ewing, Materials Research Society, Pittsburgh.

Chapman, N.A., McKinley, I.G. and Smellie, J.A.T. 1984, 'The Potential of Natural Analogues in Assessing Systems for Deep Disposal of High-Level Radioactive Waste', Technical Report 84-41, Nationale Genossenschaft fur die Lagerung radioaktiver Abfalle, Baden.

Cleveland,J.M. and Rees, T.F. 1981, 'Characterization of Plutonium in Maxey Flats Radioactive Trench Leachates', Science 212, 1506-1509

Cleveland, J.M., Rees, T.F. and Nash, K.L. 1983, 'Neptunium and Americium Speciation in Selected Basalt, Granite, Shale, and Tuff Ground Waters', Science 221, 271-273

Cotton, F.A. and Wilkinson G. 1980, Advanced Inorganic Chemistry, John Wiley & Sons, New York.

Curtis, D.B., Benjamin, T.M. and Gancarz, A.J. 1981, 'The Oklo Reactors: Natural Analogues to Nuclear Waste Repositories', in The Technology of High Level Nuclear Waste Disposal, (ed) P.L. Hofmann, United States Department of Energy, Washington.

Davey, B.G., Edghill, R.B., Cockayne, D.J. and Hunter, R.J. 1988, Report on Electron Microscope Studies of Groundwater Colloids from the Koongarra Uranium Ore Body, Northern Territory, Australia, Appendix C in Ivanovich et al. 1988 (see below)

Davis, J.A., James, R.O. and Leckie, J.O. 1978, 'Surface Ionization and Complexation at the Oxide/Water Interface', Journal of Colloid and Interface Science 63, 480-499

de Laeter, J.R. 1985, 'The Oklo Reactors: Natural Analogues to Nuclear Waste Repositories', Search 16, 193-196

Deutsch, W.J. and Serne, R.J. 1983, 'Uranium Mobility in the Natural Environment - Evidence from Sedimentary Roll-front Deposits', in Geochemical Behavior of Disposed Radioactive Waste, (eds) G.S. Barney, J.D. Navratil and W.W. Schulz, American Chemical Society, Washington.

Dickson, B.L. and Meakins, R.L. 1984, 'An Observation of Rapid Mobilisation of Uranium and its Decay Products', Nuclear Instruments and Methods in Physics Research 223, 593-597

Dongarra, G. and Langmuir, D. 1980, 'The Stability of UO_2OH^+ and $UO_2(HPO_4)_2^{2-}$ Complexes at 25°C', Geochimica et Cosmochimica Acta 44, 1747-1751

Drever, J.I. 1988, The Geochemistry of Natural Waters (second edition), Prentice-Hall, New Jersey.

Duerden, P. and Golian, C. 1988, 'Open System Modelling Approach', in Alligator Rivers Analogue Project, Progress Report, 1 September 1987 - 30 April 1988, ANSTO, Lucas Heights, Australia.

Duerden, P. 1989, 'Well Surveys and Data', in Alligator Rivers Analogue Project, Progress Report 1 June - 31 August 1989, ANSTO, Lucas Heights, Australia.

Duerden, P. and Payne, T.E. 1988, 'May 1988 Field Trip', in Alligator Rivers Analogue Project, Progress Report, 1 May 1988 - 31 Aug 1988, ANSTO, Lucas Heights, Australia.

Durrance, E.M. 1986, Radioactivity in Geology, Ellis Horwood, Chichester.

Edghill, R. 1989, 'The Distribution of Uranium and Thorium Between Phases in Weathered Core from Koongarra', in Alligator Rivers Analogue Project, Progress Report, 1 June 1989 - 31 August 1989, ANSTO, Lucas Heights, Australia.

Eisenbud, M., Krauskopf, K., Franca, E.P., Lei, W., Ballad, R., Linsalata, P. and Fujimori, K. 1984, 'Natural Analogues for the Transuranic Actinide Elements: An Investigation in Minas Gerais, Brazil', Environmental Geology Water Science 6(1), 1-9

Eisenbud, M., Linsalata, P. and Franca, E.P. 1986, 'Use Of Natural Analogues to Predict the Behavior of Transuranic Actinide Elements in the Environment', in Radioactive Waste, National Council on Radiation Protection and Measurement, Betheda.

Elders, W.A. and Moody, J.B. 1985, 'The Salton Sea Geothermal Field as a Natural Analog for the near-field in a Salt High-Level Nuclear Waste Repository', in Scientific Basis for Nuclear Waste Management VIII, (eds) C.M. Jantzen, J.A. Stone and R.C.Ewing, Materials Research Society, Pittsburgh.

Eltantawy, I.M. and Arnold, P.W. 1973, 'Reappraisal of Ethlene Glycol Mono-ethyl Ether (EGME) Method for Surface Area Estimations of Clays', Journal of Soil Science 24(2), 232-238

Foy, M.F. and Pedersen, C.P. 1975, 'Koongarra Uranium Deposit', in Economic Geology of Australia and Papua-New Guinea, 1. Metals, (ed) C.L. Knight, Australasian Institute of Mining and Metallurgy, Melbourne.

Freeze, R.A. and Cherry, J.A. 1979, Groundwater, Prentice-Hall, New Jersey.

Gibbs, R.J. 1973, 'Mechanisms of Trace Metal Transport in Rivers', Science 180, 71-73

Giblin, A.M. 1980, 'The Role of Clay Adsorption in Genesis of Uranium Ores', in Uranium in the Pine Creek Geosyncline, (eds) J. Ferguson and A.B. Goleby, IAEA, Vienna.

Giblin, A.M. and Appleyard, E.C. 1987, 'Uranium Mobility in Non-oxidising Brines: Field and Experimental Evidence', Applied Geochemistry 2, 285-295

Giblin, A.M. and Snelling, A.A. 1983, 'Application of Hydrogeochemistry to Uranium Exploration in the Pine Creek Geosyncline, Northern Territory, Australia', Journal of Geochemical Exploration 19, 33-55

Golian, C., Nightingale, T. and Airey, P.L. 1984, 'Protactinium-231 Measurement and Application to a Uranium Series Transport Model', Nuclear I. truments and Methods in Physics Research 223, 577-581

Herczeg, A. 1990, 'Geochemistry and Stable Isotopes in Groundwaters at Koongarra', in Alligator Rivers Analogue Project, Progress Report, 1 December 1989 - 28 February 1990, ANSTO, Lucas Heights, Australia.

Hsi, C-K. and Langmuir, D. 1985, 'Adsorption of Uranyl onto Ferric Oxyhydroxides: Application of the Surface Complexation Site-binding Model', Geochimica et Cosmochimica Acta 49, 1931-1941

Ivanovich, M., Duerden, P., Payne, T.E., Nightingale, T.J., Longworth, G., Wilkins, M., Edghill, R.B., Cockayne, D. and Davey, B. 1987, 'Natural Analogue Study of the Distribution of Uranium Series Radionuclides Between the Colloid and Solute Phases in the Hydrogeological System of the Koongarra Uranium Deposit, N.T., Australia', Natural Analogues in Radioactive Waste Disposal (CEC Symposium, Brussels, 1987), Graham and Trotman, London.

Ivanovich, M., Duerden, P., Payne, T., Nightingale, T., Longworth, G., Wilkins, M.A., Hasler, S.E., Edghill, R.B., Cockayne, D.J. and Davey, B.G. 1988, Natural Analogue Study of the Distribution of Uranium Series Radionuclides Between the Colloid and Solute Phases in the Hydrogeological System of the Koongarra Uranium Deposit, Australia (Report AERE-R 12975), United Kingdom Atomic Energy Authority, Harwell.

Jensen, B.S. 1982, Migration Phenomena of Radionuclides into the Geosphere, Harwood Academic, Chur, Switzerland.

Johnson, J.H. and Lewis, D.G. 1983, 'A Detailed Study of the Transformation of Ferrihydrite to Hematite in an Aqueous Medium at 92°C', Geochimica et Cosmochimica Acta 47, 1823-1831

Kaufman, A. 1969, 'The ^{232}Th Concentration of Surface Ocean Water', Geochimica et Cosmochimica Acta 33, 717-724

Keeney-Kennicutt, W.L. and Morse, J.W. 1984, 'The Interaction of $Np(V)O_2^+$ with Common Mineral Surfaces in Dilute Aqueous Solutions and Seawater', Marine Chemistry 15,133-150

Korkisch, J. 1969, Modern Methods for the Separation of Rarer Metal Ions, Pergamon Press, London.

Krauskopf, K.B. 1988, Radioactive Waste Disposal and Geology, Chapman and Hall, London.

Lally, A.E. 1982, 'Chemical Procedures', in Uranium Series Disequilibrium - Applications to Environmental Problems, (eds) M. Ivanovich and R.S. Harmon, Clarendon Press, Oxford.

Langmuir, D. 1978, 'Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits', Geochimica et Cosmochimica Acta 42, 547-569

Langmuir, D. and Herman, J.S. 1980, 'The Mobility of Thorium in Natural Waters at Low Temperatures', Geochimica et Cosmochimica Acta 44, 1753-1766

Lau, F-S. 1987, Radioactivity and Nuclear Waste Disposal, Research Studies Press, Letchworth.

Laul, J.C. and Smith, M.R. 1988, 'Disequilibrium Study of Natural Radionuclides of Uranium and Thorium Series in Cores and Briny Groundwaters from the Palo Duro Basin, Texas', Radioactive Waste Management and the Nuclear Fuel Cycle 11(2), 169-225

Lei, W., Linsalata, P., Franca, E.P. and Eisenbud, M. 1986, 'Distribution and Mobilisation of Cerium, Lanthanum, and Neodynium in the Morro do Ferro Basin, Brazil', Chemical Geology 55, 313-322

Lemons, J., Malone, C. and Piasecki, B. 1989, 'America's High Level Nuclear Waste Repository : A Case Study of Environmental Science and Public Policy', International Journal of Environmental Studies 34, 25-42

Levinson, A.A. 1980, Introduction to Exploration Geochemistry (second edition), Applied Publishing, Wilmette, Illinois.

Lowson, R.T., Short, S.A., Davey, B.G. and Gray, D.J. 1986, '^{234}U/^{238}U and ^{230}Th/^{234}U Activity Ratios in Mineral Phases of a Lateritic Weathered Zone', Geochimica et Cosmochimica Acta 50, 1697-1702

Mahara, Y. and Matsuzura, H. 1989, 'Mobile and Immobile Plutonium in a Groundwater Environment', Water Research 23(1), 43-50

Malo, B.A. 1977, 'Partial Extraction of Metals from Aquatic Sediments', Environmental Science and Technology 11(3), 277-282

Markovic, M. and Pavkovic, N. 1983, 'Solubility and Equilibrium Constants of Uranyl in Phosphate Solutions', Inorganic Chemistry 22, 978-982

Mathews, R. 1989, 'Total Organic Carbon in Groundwaters', in Alligator Rivers Analogue Project, Progress Report, 1 December 1988 - 28 February 1989, ANSTO, Lucas Heights, Australia.

McKeague, J.A. and Day, J.H. 1966, 'Dithionite- and Oxalate-Extractable Fe and Al as Aids in Differentiating Various Classes of Soils', Canadian Journal of Soil Science 46, 13-22

Miekeley, N. and Kuchler, I.L. 1987, 'Interactions Between Thorium and Humic Compounds in Surface Waters', Inorganica Chimica Acta 140, 315-319

Milnes, A.G. 1985, Geology and Radwaste, Academic Press, London.

Murakami, T. and Isobe, H. 1990, 'Alteration of Chlorite and its Relevance to Uranium Migration', in Alligator Rivers Analogue Project, First Annual Report 1988-1989, ANSTO, Lucas Heights, Australia.

Nash, K.L., Cleveland, J.M. and Rees, T.F. 1988, 'Speciation Patterns of Actinides in Natural Waters: a Laboratory Investigation', Journal of Environmental Radioactivity 7, 131-157

Nelson, D.M. and Lovett, M.B. 1978, 'Oxidation State of Plutonium in the Irish Sea', Science 276, 599-601

Nightingale, T.J. 1988, Mobilisation and Redistribution of Radionuclides During Weathering of a Uranium Ore Body. Unpublished MSc Thesis, University of Sydney, Australia.

Noranda 1978, Koongarra Project - Draft Environmental Impact Statement, Noranda Australia Limited, Melbourne.

Nordstrom, D.K. 1977, 'Thermochemical Redox Equilibria of ZoBell's Solution', Geochimica et Cosmochimica Acta 41, 1835-1841

Norris, J.R. 1989, 'Preliminary Hydraulic Characterisation of a Fractured Schist Aquifer at the Koongarra Uranium Deposit, Northern Territory, Australia', in Alligator Rivers Analogue Project, Progress Report, 1 March 1989 - 31 May 1989, ANSTO, Lucas Heights, Australia.

Nozaki, Y. and Horibe, Y. 1983, 'Alpha-emitting Thorium Isotopes in Northwest Pacific Deep Waters', Earth and Planetary Science Letters 65, 39-50

Nozaki, Y. 1984, 'Excess ^{227}Ac in Deep Ocean Water', Nature 310, 486-488

Nyhan, J.W., Drennon, B.J., Abeele, W.V., Wheeler, M., Purtymun, W.D., Trujillo, G., Herrera, W.J. and Booth, J.W. 1985, 'Distribution of Plutonium and Americium Beneath a 33 year old Liquid Waste Disposal Site', Journal of Environmental Quality 14, 501-509

Olofsson, U., Allard, B., Torstenfelt, B. and Andersson, K. 1982, 'Properties and Mobilities of Actinide Colloids in Geologic Systems', in Scientific Basis for Nuclear Waste Management V, (ed) W. Lutze, Elsevier Science, New York.

Osmond, J.K., Cowart, J.B. and Ivanovich, M. 1983, 'Uranium Isotopic Disequilibrium in Ground Water as an Indicator of Anomolies', International Journal of Applied Radiation and Isotopes 34, 283-308

Parker, F.L., Broshears, R.E. and Pasztor, J. 1984, The Disposal of High-Level Radioactive Waste (Volumes I and II), The Beijer Institute of The Royal Swedish Academy of Sciences, Stockholm.

Payne, T.E. 1989, 'Thorium Levels in Koongarra Groundwaters', in Alligator Rivers Analogue Project, Progress Report, 1 March 1989 - 31 May 1989, ANSTO, Lucas Heights, Australia.

Payne, T.E. and Waite, T.D. 1989, 'Modelling of Radionuclide Sorption Processes in the Weathered Zone of the Vicinity of the Koongarra Orebody', in Alligator Rivers Analogue Project, Progress Report, 1 March 1989 - 31 May 1989, ANSTO, Lucas Heights, Australia.

Payne, T.E. and Waite T.D. 1990, 'Surface Complexation Modelling of Uranium Sorption Data Obtained by Isotope Exchange Techniques', Radiochimica Acta, in press.

Penrose, W.R., Polzer, W.L., Essington, E.H., Nelson, D.M. and Orlandini, K.A. 1990, 'Mobility of Plutonium and Americium Through a Shallow Aquifer in a Semiarid Region', Environmental Science and Technology 24, 228-234

Ringwood, A.E. 1978, Safe Disposal of High Level Nuclear Wastes: A New Strategy, Australian National University Press, Canberra.

Salbu, B., Steinass, E. and Bjornstad, H. 1984, 'Use of Different Physical Separation Techniques for Trace Element Speciation Studies in Fresh Waters', in Hydrochemical Balances in Freshwater Systems, IAHS-AISH Publication No. 150.

Sanchez, A.L., Murray, J.W. and Sibley, T.H. 1985, 'The Adsorption of Plutonium IV and V on Goethite', Geochimica et Cosmochimica Acta 49, 2297-2307

Serne, R.J. and Muller, A.B. 1987, 'A Perspective on Adsorption of Radionuclides onto Geologic Media', in The Geological Disposal of High Level Radioactive Wastes, (ed) D.G. Brookins, Theophrastus, Athens.

Serne, R.J. and Relyea, J.F. 1981, 'The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program', in The Technology of High-Level Nuclear Waste Disposal, (ed) P.L. Hofmann, United States Department of Energy, Washington.

Sheng, Z.Z. and Kuroda, P.K. 1984, 'The α-Recoil Effects of Uranium in the Oklo Reactor', Nature 312, 535-536

Sheng, Z.Z. and Kuroda, P.K. 1986, 'Isotopic Fractionation of Uranium: Extremely High Enrichments of ^{234}U in the Acid-Residues of a Colorado Carnotite', Radiochimica Acta 39, 131-138

Shirvington, P.J. 1979, '$^{234}U/^{238}U$ Disequilibria as a Measure of Uranium Migration in Clay over the Past 250,000 years', in Underground Disposal of Radioactive Waste II, IAEA, Vienna.

Shirvington, P.J. 1983, 'Fixation of Radionuclides in the ^{238}U Decay Series in the Vicinity of Mineralized Zones: 1. The Austatom Uranium Prospect, Northern Territory, Australia', Geochimica et Cosmochimica Acta 47, 403-412

Short, S.A., Lowson, R.T. and Ellis, J. 1988, '$^{234}U/^{238}U$ and $^{230}Th/^{234}U$ Activity Ratios in the Colloidal Phases of Aquifers in Lateritic Weathered Zones', Geochimica et Cosmochimica Acta 52, 2555-2563

Snelling, A.A. 1980a, 'Uraninite and its Alteration Products, Koongarra Uranium Deposit', in Uranium in the Pine Creek Geosyncline, (eds) J. Ferguson and A.B. Goleby, IAEA, Vienna.

Snelling, A.A., 1980b, A Geochemical Study of the Koongarra Uranium Deposit, Northern Territory, Australia. Unpublished PhD Thesis, University of Sydney, Australia.

Snelling, A.A. 1989, 'Koongarra Uranium Deposits', in The Geology of the Mineral Deposits of Australia and Papua New Guinea, (ed) F.E. Hughes, The Australasian Institute of Mining and Metallurgy, Melbourne.

Sverjensky, D.A. 1989, 'Geochemical Modeling of the Koongarra Uranium Deposit', in Alligator Rivers Analogue Project, Progress Report, 1 December 1988 - 28 February 1989, ANSTO, Lucas Heights, Australia.

Tripathi, V.S. 1983, Uranium(VI) Transport Modelling: Geochemical Data and Submodels. Unpublished PhD Thesis, Stanford University, California.

Winograd, I.J. 1981, 'Radioactive Waste Disposal in Thick Unsaturated Zones', Science 212 1457-1464

Yanase, N., Nightingale, T., Payne, T. and Duerden P. 1990, 'Uranium Distribution in Mineral Phases of Rock by a Sequential Extraction Procedure', Radiochimica Acta, in press.

Zachara, J.M., Ainsworth, C.C., Cowan, C.E. and Resch, C.T. 1989, 'Adsorption of Chromate by Subsurface Soil Horizons', Soil Science Society of America Journal 53, 418-428

Zukin, J.G., Hammond, D.E., Ku, T-L. and Elders, W.A. 1987, 'Uranium-thorium Series Radionuclides in Brines and Reservoir Rocks from two Deep Geothermal Boreholes in the Salton Sea Geothermal Field, Southeastern California', Geochimica et Cosmochimica Acta 51, 2719-2731

APPENDIX I

URANIUM SERIES DISEQUILIBRIUM

Natural uranium is comprised almost entirely of ^{238}U (>99 % by mass). ^{238}U has a half-life of 4.5 X 10^6 years and decays through the short lived intermediates ^{234}Th (24 day half-life) and ^{234}Pa (1.2 minutes) to ^{234}U, which is comparatively stable, with a half life of 2.5 X 10^5 years. This in turn decays to ^{230}Th (half-life of 75 000 years), ^{226}Ra (1600 years), and then through a series of short lived isotopes to the stable isotope, ^{206}Pb.

The entire decay series is shown in figure A1. Two types of decay occur: α-decay, which involves the emission of an α-particle (He nucleus) with a consequent decrease in mass; and β decay which results in a change in atomic number without a significant mass decrease. The different modes of decay, the range of half-lifes, and the number of different elements present in this series, lead to the complex pattern of their distribution in nature.

Members of the chain can become separated by several mechanisms (Osmond et al. 1983):

a) differences in chemical properties such as solubility (for example, uranium is generally more soluble then thorium)

b) diffusion of gaseous intermediates (^{222} Rn is a gas and during its 3.8 day halflife can move considerable distances from its point of formation - even into the earths atmosphere) and

c) isotope fractionation processes associated with radioactive decay (see below).

As a result, the distribution of the different isotopes can be quite dissimilar. In this section, attention will be mostly restricted the three longest lived isotopes in the chain: ^{238}U, ^{234}U and ^{230}Th.

Several broad scenarios for the movement of these isotopes in a groundwater system are possible. If no migration of any radionuclide occurs, there will be no isotopic fractionation and the system is said at 'secular equilibrium'. The Koongarra No.1 orebody was in this state prior to the onset of weathering about 1-3 million years ago, and this would appear to be the current situation of the No.2 orebody.

In systems where uranium is being carried in groundwater, ^{238}U, ^{234}U and ^{230}Th can become fractionated from one another. A common situation is that ^{234}U will be preferentially mobilised, in which case it travels faster than its parent, ^{238}U, in the system. The preferential mobilization of ^{234}U may be brought about by:

a) lattice damage induced by radioactive decay,

b) location of daughter atoms in weakly bound or interstitial sites,

c) oxidation state change from +4 to +6 during decay, leading to enhanced solubility, or,

d) direct α-recoil from the solid into the aqueous phase (Osmond et al 1983).

The process of recoil results from a sudden movement of a daughter nucleus when an α-particle of several MeV energy is emitted, analogous to the recoil of a gun. The distance through which the recoiling nucleus is displaced is approximately 20 nm (Sheng and Kuroda 1986). If a ^{238}U atom located near the surface of a mineral grain decays, throwing out an α-particle, the daughter ^{234}Th nucleus could be recoiled into the surrounding water. Subsequent decay to ^{234}U will lead to an excess of ^{234}U in the aqueous phase relative to ^{238}U.

Koongarra is an exception to the general rule, because ^{234}U is generally slower moving than ^{238}U in the system. This is seen, for example, by the $^{234}U/^{238}U$ ratio in the groundwater, which is often measured to be below unity. The reduced mobility of ^{234}U has been attributed to α-recoil emplacement of daughter nuclides in inaccessible mineral phases, reducing their availability for leaching (Nightingale 1988).

Compared to ^{238}U and ^{234}U, ^{230}Th is highly immobile, as was verified for the Koongarra system in Chapter 6. This provides a basis for calculating the rate of movement of the uranium isotopes in the system. The distribution of ^{230}Th gives an indication of the previous position of the ^{234}U, which can be compared its current distribution. The ^{230}Th is essentially a marker, showing the situation which prevailed at some time in the past.

Disequilibria in the ^{235}U decay series can also be studied at Koongarra. This decay chain includes the nuclides ^{231}Pa, ^{227}Ac and ^{230}Th. Thorium α-spectra containing unusually high amounts of ^{227}Th were obtained for some of the size fractions separated from Koongarra groundwaters in the experiments described in chapter seven. This was attributed to the mobility of ^{227}Ac in the system, possibly in a fine-particle or colloidal form. The ^{235}U decay series is shown in figure A2.

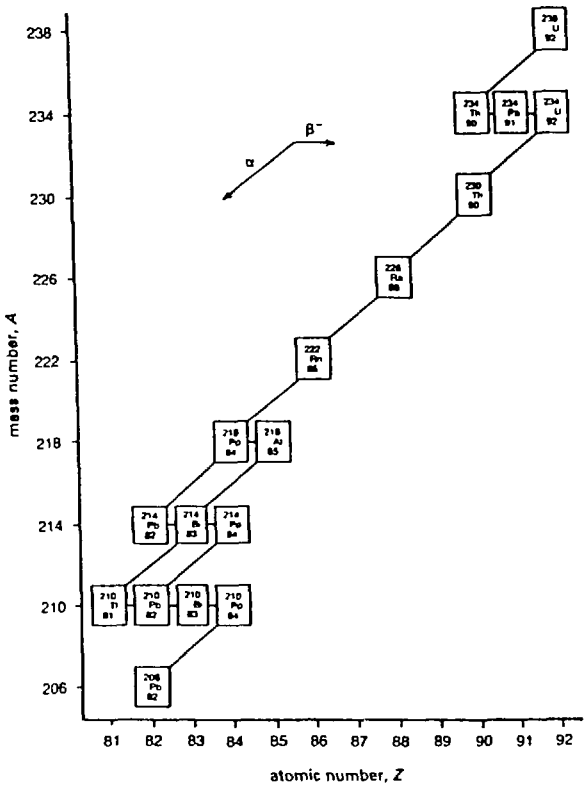


Figure A.1 The ^{238}U decay series (from Durrance 1986).

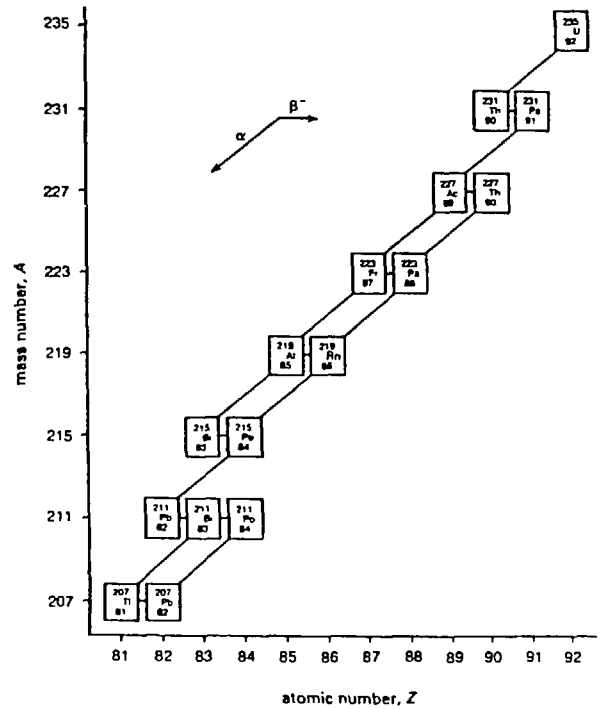


Figure A.2 The ^{235}U decay series (from Durrance 1986).