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RESEARCH ON RADIONUCLIDE MIGRATION UNDER SUBSURFACE GEOCHEMICAL CONDITIONS
- JAERI/AECL PHASE Ⅱ COLLABORATIVE PROGRAM YEAR 1 -
(Joint Research)

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(Ed.) Natural Barrier Laboratory

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Research on Radionuclide Migration under Subsurface Geochemical Conditions
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A radionuclide migration experiment program for fractured rocks was performed under the JAERI/AECL Phase-Ⅱ Collaborative Program on research and development in radioactive waste management. The program started in the fiscal year 1993, as a five-year program consists of Quarried block radionuclide migration program, Speciation of long-lived radionuclides in groundwater, Isotopic hydrogeology and Groundwater flow model development. During the first year of the program (Program Year 1 : March 18, 1994 ~ September 30, 1994), a plan was developed to take out granite blocks containing part of natural water-bearing fracture from the wall of the experimental gallery at the depth of 240 m, and literature reviews were done in the area of the speciation of long-lived radionuclides in groundwater, isotopic hydrogeology and the groundwater flow model development to proceed further work for the Program Year 2.

Keywords: Radioactive Waste Management, Geological Disposal, In-situ Conditions,
Long-lived Nuclides, Nuclide Migration, Speciation, Organic Compound,
Isotope Hydrology, Flow Model Development

地下環境下における放射性核種移行に関する研究
― 原研／ＡＥＣＬ共同研究フェーズ２計画第１年度 ―
(共同研究)

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日加放射性廃棄物処分安全性研究フェーズ２協定に基づき、地下環境下における放射性核種移行に関する研究を実施した。1993年度から５年計画で開始した本協定では、切り出し岩盤核種移行試験、地下水中における長寿命核種の化学形研究、同位体水文地質学的研究、及び地下水流解析モデルの開発を実施している。計画の初年度（第１計画年：1994年３月から1994年９月）は、切り出し岩盤核種移行試験のため、地下240mの実験坑道の壁面から実験用亀裂岩盤試料を取り出す準備を進めると共に、地下水中における長寿命核種の化学形研究、同位体水文地質学的研究、及び地下水流解析モデルの開発における文献調査を行い、第２計画年以降の準備を進めた。

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1. INTRODUCTION

For the most reliable predictions of radioactive nuclide migration under the depth, one needs to understand the actual behavior of the nuclides concerned under natural geochemical conditions. For this purpose, since 1987 many efficient studies have been performed under the collaborative program between Japan Atomic Energy Research Institute and Atomic Energy of Canada Limited. The JAERI/AECL Phase I (1987-1993) Agreement for Cooperation in Field Programs for Research and Development in Radioactive Waste Management was originally authorized in 1987 August. Under that Agreement, several programs have been performed on various aspects of radionuclide migration in the geosphere, and the need to perform radionuclide migration experiments under in situ conditions has been demonstrated. The results obtained from the one-dimensional migration experiments performed in columns of crushed fracture infilling materials in the URL showed that retardation of radionuclides tended to be higher than predicted on the basis of static sorption data obtained under a controlled atmosphere. In crystalline rock such as granite, fractures may play an important role for nuclides migration as well as groundwater flow. To obtain data concerning to the nuclide migration through fractured rocks such as crystalline rock, work scopes have been developed based on JAERI/AECL discussions for two programs to be included in the Phase II agreement as follows;

1) PROGRAM 1 ; **Radionuclide Migration Program**

Project 1: Quarried Block Radionuclide Migration Experiment

Study of radionuclide transport through natural fractures in the URL under in situ conditions. The study includes an assessment of the effect of colloids on transport of radionuclides.

Project 2: Speciation of Long-lived Radionuclides in Groundwater

Study of the effect of dissolved organic matter on radionuclide transport under in situ conditions at CRL.

2) PROGRAM 2 ; **Groundwater Flow Program**

Project 1: Isotopic Hydrogeology

Study of groundwater flow at depth, in Japan and at the URL, using ^{36}Cl and other isotopes.

Project 2: Groundwater Flow Model Development

Model development for radionuclide migration in heterogeneous geomedia.

This annual report summarizes the work done between 1994 March 18 and 1994 September 30 (Program Year 1). The details for each individual project with respect to key objectives, experimental design and procedures, results, and discussion of the data are included.

2. QUARRIED BLOCK RADIONUCLIDE MIGRATION PROGRAM (PROGRAM 1, PROJECT 1)

2.1 Radionuclide Migration Experiments in the URL

T.T. Vandergraaf

2.1.1 Introduction

The concept of the Quarried Block Radionuclide Migration Program is based on three experimental programs, the "Rockmass Experiment" and the "Radionuclide Retardation Mechanism Experimental Program" performed in a specially designed and dedicated facility in AECL Research's Underground Research Laboratory (URL) on behalf of the Japan Atomic Energy Research Institute (JAERI), and on the on-going "Radionuclide Migration Experimental Program" performed in the Large Block Radionuclide Migration Facility (LBRMF) at AECL Research's Whiteshell Laboratories. The results obtained from the one-dimensional migration experiments performed in columns of crushed fracture infilling materials in the URL clearly showed the importance of performing radionuclide migration experiments under in situ conditions: retardation of radionuclides tended to be higher than predicted on the basis of static sorption data obtained under a controlled atmosphere(1,2). The information obtained in the LBRMF showed the importance of performing migration experiments in natural fractures and the power of a radiometric analysis of the flow field at the completion of these migration experiments(3,4,5).

The experiments in the Quarried Block Radionuclide Migration Facility (QBRMF) in the URL form a synthesis between the experiments performed in the LBRMF and the in situ conditions in the URL. To perform these migration experiments under in situ conditions, access is needed to a water bearing fracture at depth in the URL. The only fracture that meets the required conditions and is readily accessible is a vertical "joint zone" that intersects Room 209 at the 240 level of the URL (Figure 2.1-1). This joint zone, JZ2, terminates just below the 240 level (Figure 2.1-2). It was perforated during construction of the 240 level and the intersection between the joint zone and Room 209 has been open to the atmosphere for a number of years. To ensure access to an area of JZ2 that has not likely been affected by the excavation of the 240 level, the QBRMF should be located as far from Room 209 as practicable. In addition, information obtained from drilling a limited number of boreholes into JZ2 suggested that the extent of fracture infilling increases as the distance from Room 209 increases (Figure 2.1-2), adding to the argument that the QBRMF should be located at some distance from Room 209.

2.1.2 Scope of the program

The scope of the Quarried Block Radionuclide Migration Program is to design, construct, and commission a new, dedicated experimental facility at the 240 level of the URL, to license this facility to allow the use of a limited quantity of radioisotopes, and to perform radionuclide and colloid migration experiments under in situ conditions in natural fractures in blocks of granite excavated or quarried from JZ2. The design of this new facility, the Quarried Block Radionuclide Migration Facility (QBRMF), would be based on that of the Large Block Radionuclide Migration Facility at the Whiteshell Laboratories(6). More specifically, the tasks under this program consist of the following;

- selection and characterization of a location in the URL for the QBRMF and a fracture zone that can be used as a source of granite blocks for the migration experiments,
- design, construction and licensing of the QBRMF,
- development of a quarrying method and obtaining granite blocks containing natural fractures for the migration experiments,
- performing migration experiments,
- post-experiments analysis and reporting of the results,
- development of a plan and methodology for an in situ migration experiment,

and,

- determination of the characteristics and impact of natural colloids and the stability of radiocolloids or pseudocolloids.

2.1.3 Design and engineering

A conceptual design of the QBRMF (Figure 2.1-3) that was prepared at an initial stage of the program was little modified to the final design of the facility (Figure 2.1-4). The major difference between the two designs is in the enclosure to contain the two quarried blocks during the migration experiments. In the conceptual design, two separate "walk in" fume hoods were envisaged. During discussions with design staff, it became clear that this conceptual design would limit the mobility in the QBRMF and that a single fume hood would be better suited for the QBRMF.

2.1.4 Exploratory boreholes

To ensure that the rock mass in the planed location of the QBRMF was as competent as expected and to further pinpoint the exact location of JZ2, two exploratory boreholes were drilled from the corner of Room 209 and the Buffer/Container Room (Room 213, Figure 2.1-5) to intersect the vertical jointed zone JZ2. Standard drilling procedures were used up to approximately 10 m from JZ2, at which point water from Fracture Zone 2 (FZ2) was used to cool the drill. The core obtained from approximately 10 m of either side of JZ2 was photographed immediately and then placed in acrylic tubes which were in turn filled with FZ2 groundwater. A small polyethylene bag containing metallic iron was placed in each acrylic tube to act as an oxygen scavenger. Following bubbling N_2 gas through the water in the tubes, the tubes were sealed and placed in storage in the existing JAERI Facility in the URL. A section of one of the cores retrieved from the boreholes was used in diffusion experiments.

The first borehole, JE-2 (209-067-JE2), intersected JZ2 approximately 8 m above the floor of the QBRM Facility and showed a series of three parallel fractures, at downhole distances of 49.01, 49.03, and 49.7 m. The fracture surfaces contained a thin calcite coating covering approximately 50 to 75% of the fracture surfaces. This borehole was extended approximately 40 m into the rock mass above the location of the QBRM Facility to a total length of 83.28 m. No fractures were found beyond JZ2. A temporary packer was installed in JE-2 as soon as possible after the borehole was drilled. Inflow of groundwater from JZ2 into JE-2 was approximately 300 mL/min.

An existing borehole, 206-036-OC1, that intersects JZ2 between the planed location of the QBRMF and Room 209, was extended to a total length of 50 m to obtain information on the rock mass in the planed location of the QBRM Facility. No fractures were identified, again suggesting that the planed location is acceptable. The packer that was originally in this borehole was replaced after drilling had been completed.

A second borehole, JE-5 (209-066-JE5), was drilled to obtain additional information on the uniformity of JZ2. It intersects JZ2 approximately 8 m below JE-2. A series of seven fractures were intersected between 44.66 and 46.41 m downhole distance. All fractures showed calcite and/or hematite fracture infilling covering up to 70% of the surface. A temporary packer was also installed into this borehole. Inflow of groundwater from JZ2 into JE-5 was approximately 2000 mL/min.

Instrumented packers were subsequently installed in boreholes JE-2 and JE-5, and OC-1. The location of these packers in the three boreholes are shown in Figures 2.1-6 to -8. Interval 4 in borehole JE-2 and interval 2 in OC-1 straddle the set of open fractures in JZ2 over a distance of 1 m. Since JE-5 was only drilled slightly beyond JZ2, interval 4 of the packer installed in this borehole contains the volume in the borehole beyond JZ2. Geokon vibrating pressure transducers with a range of 0 to 3500 kPa were installed in the boreholes at the same time as the packers. These transducers operate on a principle similar to that of the strings of a violin. Changes in pressure change the frequency of the vibrating wire. The frequency is recorded as a function of time. The transducers were connected to the URL Data Acquisition System and are monitored electronically on an hourly basis.

Hydraulic fluid withdrawal step tests were performed in the borehole intervals isolating the Room 209 vertical fracture FZ2. From these data the following hydraulic transmissivities were obtained:

JE-2	2.26×10^{-8} m^2/s
JE-5	5.21×10^{-7} m^2/s
OC-1	5.4×10^{-7} m^2/s

These values correspond to "equivalent single fracture apertures" of 34, 98, and 99 μm, respectively. Outflow from the JZ2 into the three boreholes under "open hole" conditions, i.e. no back pressure, were 0.14, ~1.0 and 1.15 L/min, respectively.

Hydraulic heads within the borehole packer isolated intervals that do not isolate JZ2 continued to show long, slow stabilization periods in general with hydraulic heads ranging from 375 to 1230 kPa in JE-2, 360 to 1075 kPa in JE-5 and 600 to 1450 kPa in OC-1, while the borehole intervals 4 in boreholes JE-2 and JE-5 and interval 2 in borehole OC-1 showed rapid head stabilization at about 1050 kPa and 950 kPa, respectively.

The groundwater in the vertical joint zone JZ2 was sampled during 1993 November and 1994 January. The concentration ranges that were obtained are presented in Table 2.1-1. Groundwater samples have been obtained from Boreholes JE-2, JE-5, PH-3, all intersecting Joint Zone JZ2 and from inflow from JZ2 into Room 209 in the URL. The groundwater is a dilute NaCl, with some Ca present. No Eh measurements were available by the end of Program Year 1, but values typically of -100 mV are expected.

2.1.5 Excavation

Excavation of Room 217 (Figure 2.1-5), the access heading to the new Quarried Block Radionuclide Migration Facility, was started on July 05. The first volume of rock was removed using a rock breaking method which does not involve explosives. This method has been used at the 420 level of the URL and will also be used in excavation the rock near vertical fracture JZ2 to minimize excavation damage to this fracture. The excavation schedule was based on the information obtained at the 420 level. However, since the stresses in the URL at the 240 level are lower than those at the 420 level, this method of excavation will take longer than anticipated. The target date for completing the excavation has therefore been revised from 1994 October 04 to 1994 November 07. This change in schedule was not expected to affect the overall schedule for the project.

By the end of Program Year 1, excavation of Room 217 and 218 had been completed and good progress was being made to the excavation of Room 219, the location of the Quarried Block Radionuclide Migration Facility. By the end of September, more than 60% of Room 219 had been excavated. Excavation proceeded smoothly, but a slight, one week, delay was encountered as a result of lower lithostatic pressures at the 240 level which in turn resulted in a lower rate of excavation using the rock breaker method. The delay does not affect the overall schedule. The volume of rock excavated to create Room 217 is 405 m^3 and that for Room 218 is 450 m^3. This compares with a total volume of the existing JAERI Facility in the URL of 140 m^3. The volume of the actual QBRMF will be in the order of 440 m^3.

2.1.6 Characterization

The exposed rock is being mapped as the excavation proceeds. The results continued to confirm pre-excavation predictions and no features were encountered that would affect the design or the construction of the QBRM Facility or have an adverse impact on the experiments.

The excavated area falls entirely within the alteration halo (pinking) between Fracture Zones 2 and 2.5. The predominant rock type is a weakly gneissic granite, which is host to early pegmatite sills, granodiorite and late pegmatite dykes. There are some minor fractures confined to the early pegmatitic sills, and two fractures in the widest part of this sill were observed in face 2, i.e., the face of the rock after the second round of excavation.

A small number of closed, subvertical fractures were encountered during the later parts of the excavation. These fractures were found mainly in a subhorizontal leucocratic zone. They were usually filled with hematite and were oriented roughly parallel to JZ2. None of these fractures are water bearing.

2.1.7 Licencing

The first phase of procurement of a Prescribed Substance License (PSL) has been completed an extension of the PSL for the existing JAERI Facility has been obtained from the Atomic Energy Control Board (AECB) including two additional radionuclides, ^{22}Na and ^{85}Sr. The second phase will involve a request to the AECB to extend the use of the PSL to the new QBRM Facility.

The Atomic Energy Control Board carried out an inspection of the facilities licensed under the current Prescribed Substance Licence (PSL) on May 18. No items of non-compliance were identified.

2.1.8 Public affairs

During the period leading up to the signing of the new cooperative agreement between JAERI and AECL, locally elected officials in the URL area were notified that negotiations were being held between JAERI and AECL for an experimental program similar to those of the "Rockmass Experiment" and the "Radionuclide Retardation Mechanism Experimental Program." The response from these elected officials was generally positive.

When the agreement between JAERI and AECL was signed, letters describing the QBRMF and the experimental programs planned for this facility were sent to the following agencies and individuals;

- Manitoba Department of the Environment
- Environment Canada, Winnipeg Office
- Elected Officials of the
  Rural Municipality of Lac du Bonnet
  Village of Lac du Bonnet
  Local Government District of Pinawa
- Royal Canadian Mounted Police (RCMP), Pinawa and Lac du Bonnet

Copies of the letters to the elected officials were sent to Minister of Labour and Northern Affairs, Province of Manitoba and Member of the Legislature for Lac du Bonnet and to Member of Parliament for the federal riding of Provencher.

No adverse reaction was received in response to these letters.

A film crew from the Aomori Broadcasting Corporation visited Whiteshell Laboratories and the Underground Research Laboratory. Dr. Keith Nuttall was interviewed about general issues regarding the Nuclear Fuel Waste Management Program. Mr. Yamaguchi was also interviewed and filmed while performing his diffusion experiments at Whiteshell. The film crew also filmed the Large

Block Radionuclide Migration Facility at Whiteshell. Filming in the URL included the excavation in progress in Room 219.

A film crew from the Canadian Broadcasting Corporation (CBC) also filmed the excavation in progress in Room 219 and the Large Block Radionuclide Migration Facility as part of a program to be broadcast on CBC "Newsworld."

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Table 2.1-1 Groundwater composition in vertical fracture JZ 2
(concentrations in mg/L)

Na^{+}	115-158
K^{+}	0.8 - 1.4
Ca^{++}	15.8 - 30.9
Mg^{++}	6.3 - 7.4
Si^{++++}	4.3 - 4.8
Sr^{++}	0.2 - 0.4
HCO_3^{-}	126 - 174
Cl^{-}	72 - 150
SO_4^{--}	61 - 120
F^{-}	4.9 - 6.4
Br^{-}	0.3 - 0.6
B^{-}	0.6 - 0.7
TDS	442 - 615

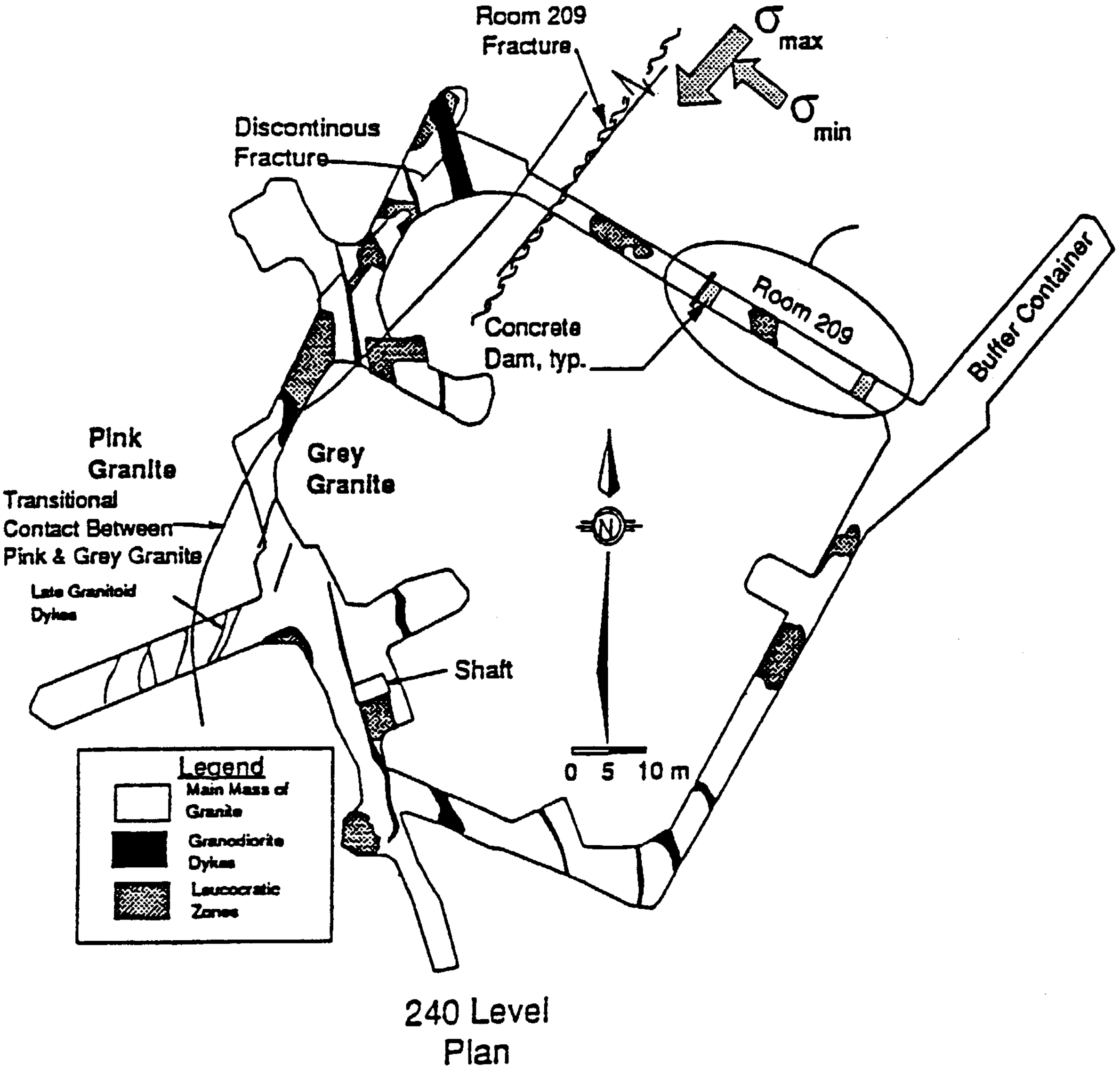


Fig.2.1-1 Plan view of 240 level in the URL showing location of vertical joint zone JZ2

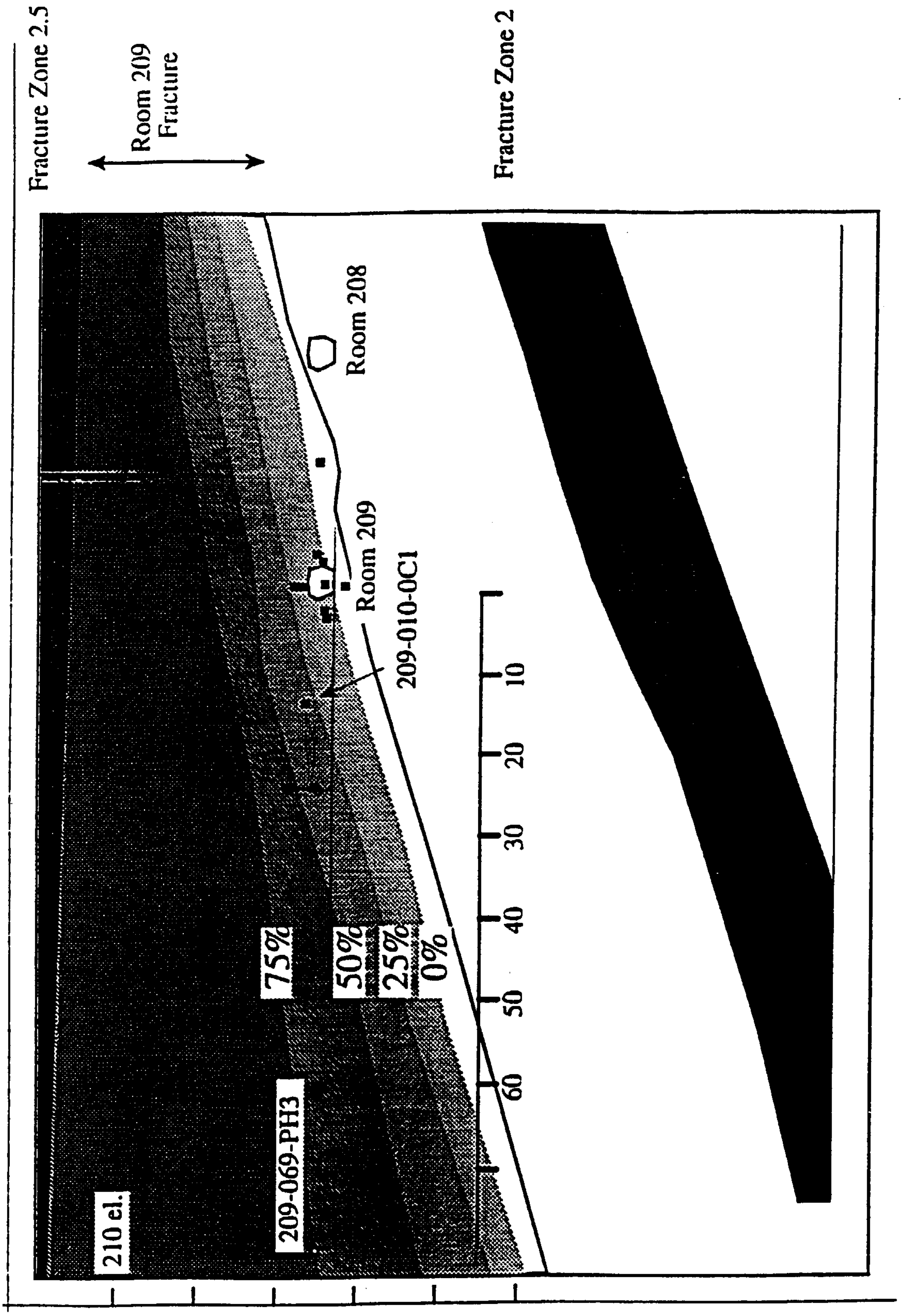


Fig.2.1-2 View of vertical joint zone JZ2 showing infilling coverage

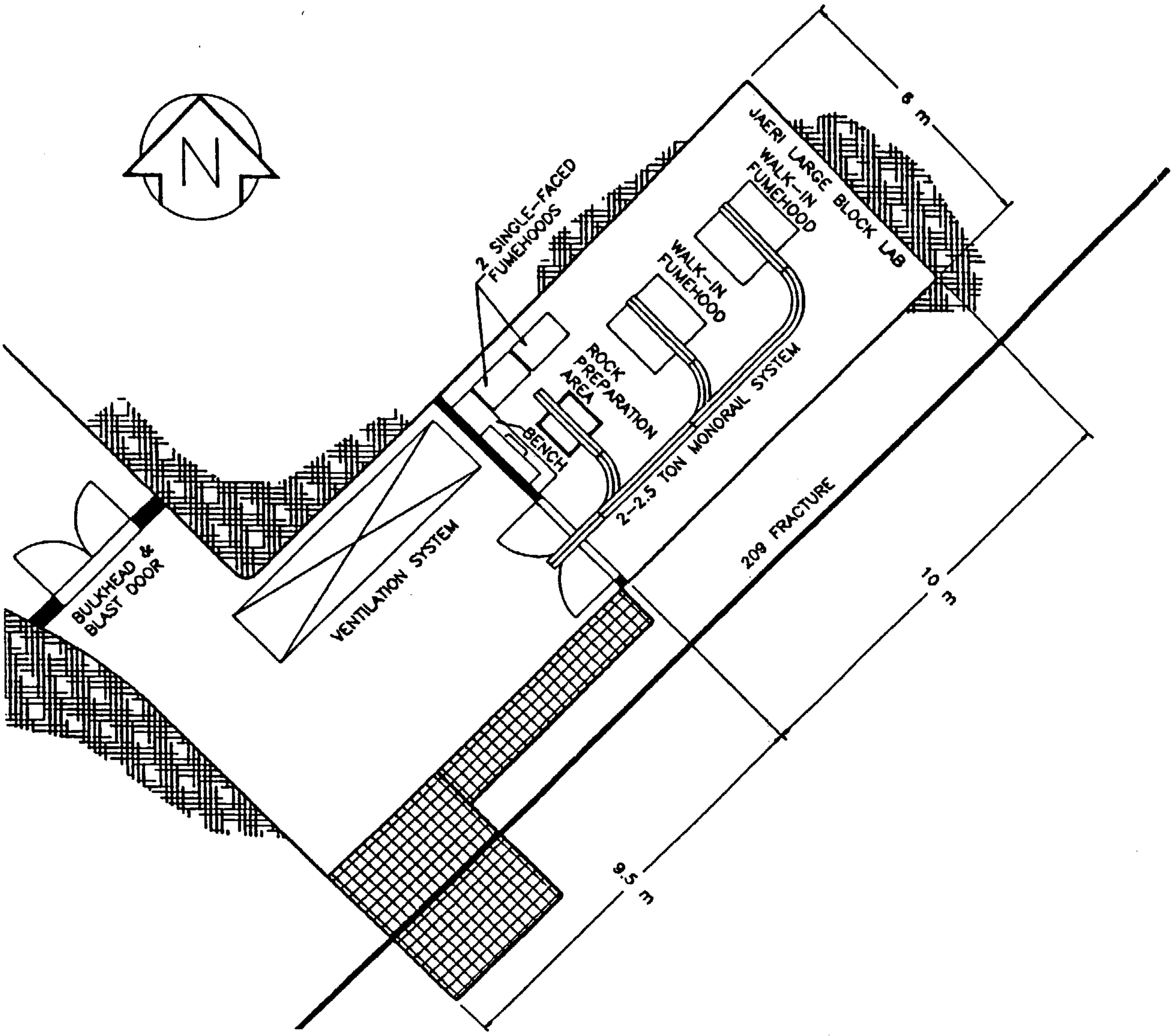


Fig.2.1-3 Initial layout of the QBRMF

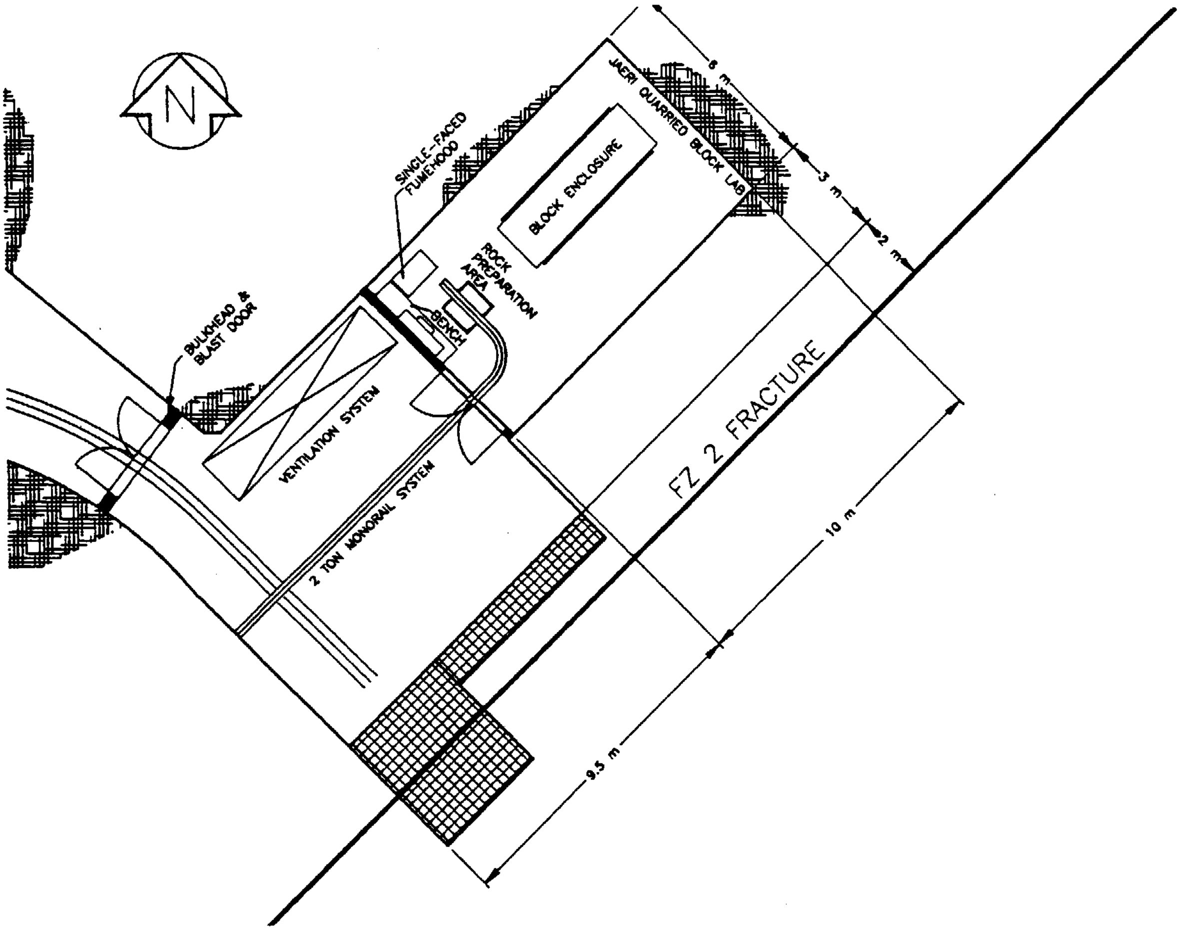


Fig.2.1-4 Final design of the QBRMF showing general layout

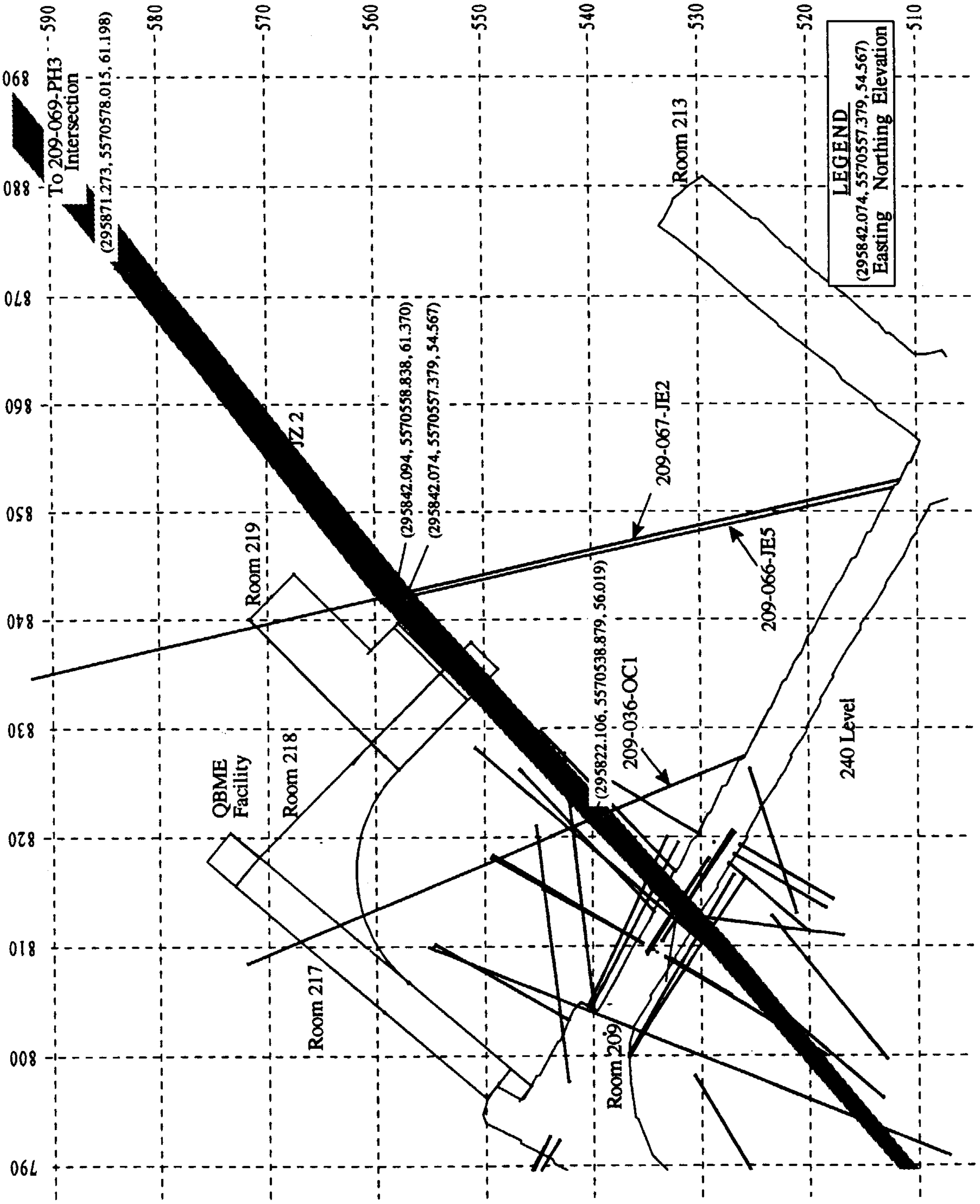
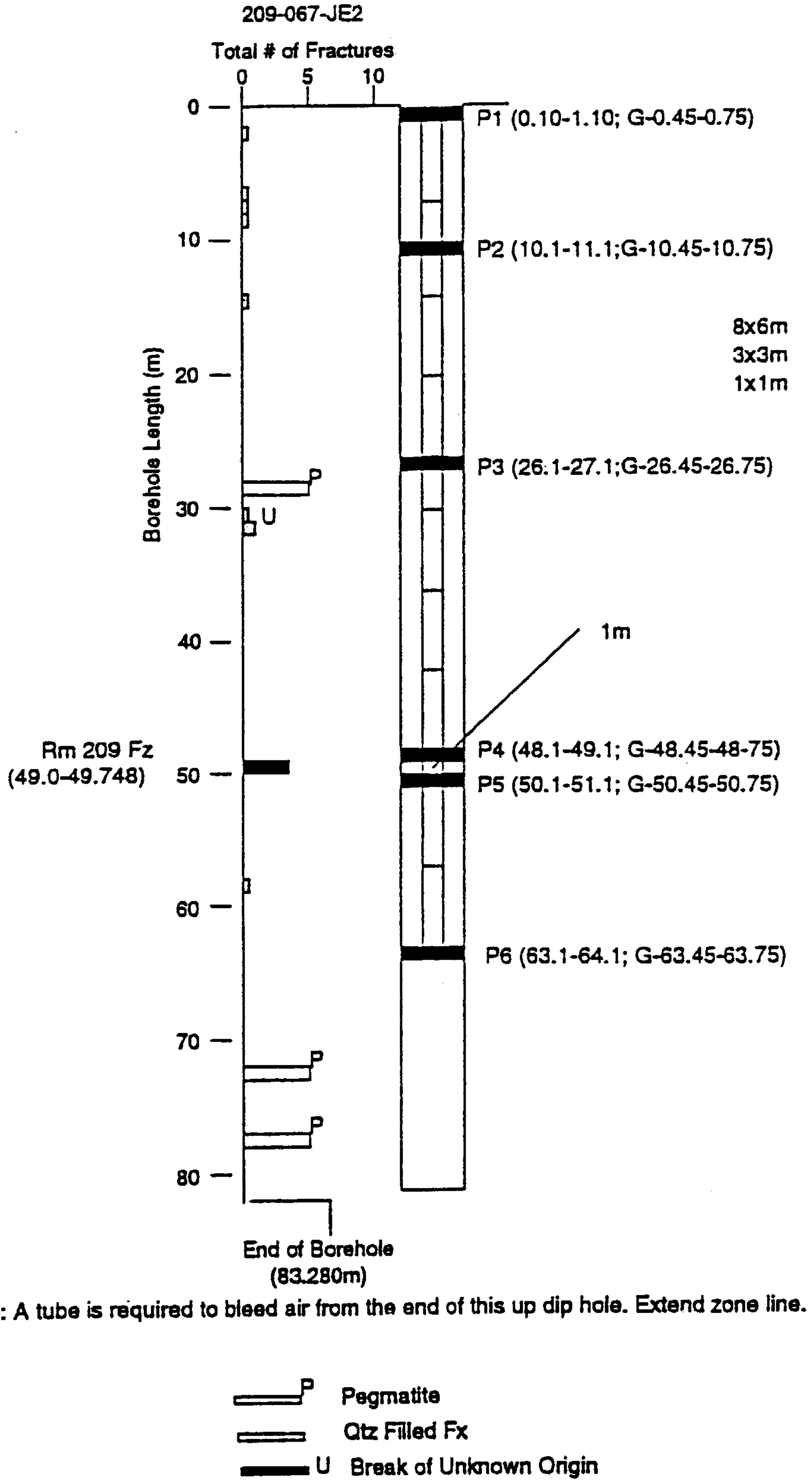
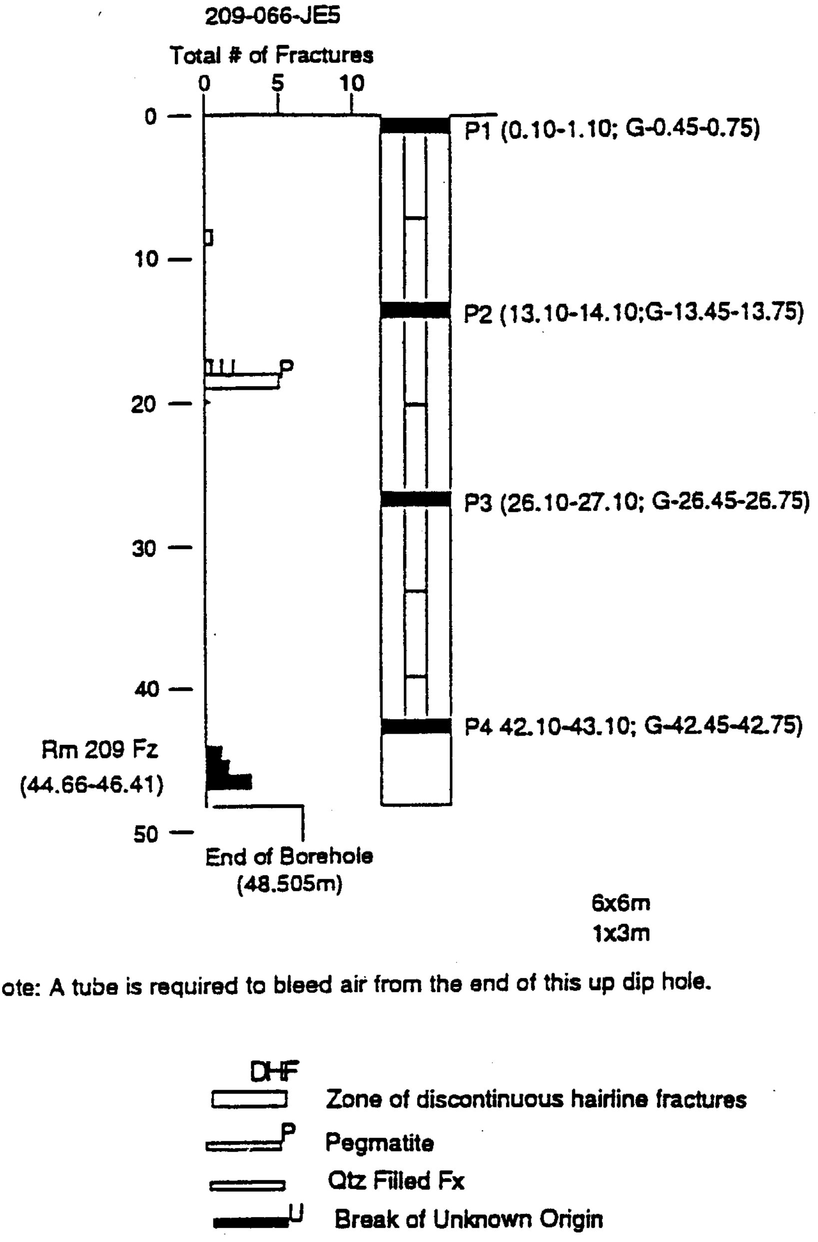


Fig.2.1-5 The quarried block radionuclide migration facility (QBRMF) and boreholes



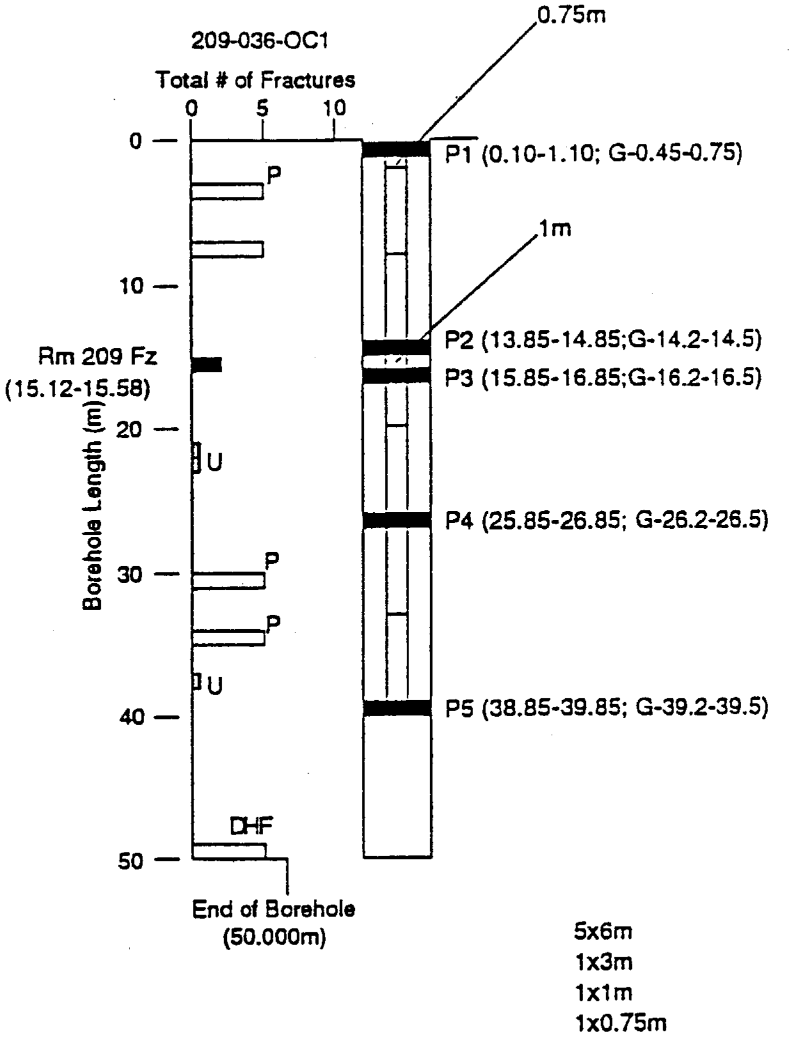
Note: A tube is required to bleed air from the end of this up dip hole. Extend zone line.

Fig.2.1-6 Location of packers in borehole JE-2



Note: A tube is required to bleed air from the end of this up dip hole.

Fig.2.1-7 Location of packers in borehole JE-5



Note: A tube is required to bleed air from the end of this up dip hole. Extend zone line.

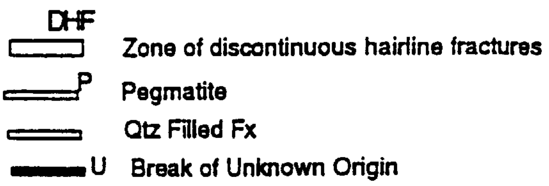


Fig.2.1-8 Location of packers in borehole OC-1

2.2 Plutonium Diffusion and Sorption Experiments

Tetsuji Yamaguchi and Shinichi Nakayama

2.2.1 Introduction

Retardation of radionuclide transport through fractures in a groundwater flow system can be affected by diffusion into the interconnected pore space in the rock mass adjacent to a fracture. Results obtained from radionuclide migration experiments performed in a natural fracture in the Large Block Radionuclide Migration Facility at Whiteshell Laboratories showed that diffusion into the rock mass had a significant effect on retardation of ^3H_2O transport through the fracture(1). The diffusion of radionuclides into the rock mass is an important phenomenon that has to considered in radionuclide migration experiments that will be performed under in situ conditions in a specially designed facility, the Quarried Block Radionuclide Migration Experiment (QBRMF) in AECL Research's Underground Research Laboratory near Lac du Bonnet, Manitoba.

JAERI has been studying diffusion of ions in rocks by a through-diffusion method(2-5). The objective of this experimental study is to measure the diffusivity of a selected number radionuclides in the rock surrounding the natural fracture using a technique developed by JAERI and to support the analysis of the Quarried Block Radionuclide Migration Experiment.

2.2.2 Preliminary sorption experiment

A meaningful through diffusion curve can be obtained within a reasonable time period if the Kd for Pu on granite is less than 0.02 ml/g. A batch sorption experiment was therefore performed with Pu on granite prior to the start of the diffusion experiments to determine if Pu through-diffusion experiments can be performed within a reasonable time period. Groundwater was obtained from vertical joint zone JZ 2, the source of groundwater for the migration experiments in the QBRMF, and filtered through a 0.2 μm filter. Plutonium-238 was prepared as a 0.01 mol/l $NaHCO_3$ solution and mixed with the groundwater to prevent precipitation of Pu hydroxide. $NaNO_2$ was added to the solution as a reducing agent. Concentrations of Pu, HCO_3^- and NO_2^- in the solution were 9×10^{-9}, 5×10^{-3} and 1.7×10^{-3} mol/l, respectively.

A core of Inada granite was crushed and sieved and the size fraction between 0.850 and 2.00 mm used. The crushed granite was preconditioned with groundwater in a polycarbonate test tube for a period of 10 days. The groundwater was replaced by the Pu solution and agitated manually. The water/rock ratio was 26.7 ml/17.9 g. Sorption of Pu on the tube was checked by placing another 25 ml of the Pu solution in a polycarbonate test tube (blank test). After 30 minutes, the test tubes were centrifuged and a 0.2 ml portion was withdrawn to measure Pu concentration by liquid scintillation counting. The pH and Eh of the solution were measured with a pH test paper and a Pt/AgCl electrode, respectively. Sampling and analysis were repeated after 1 and 2 weeks.

The results are tabulated in Table 2.2-1. The Pu concentration in the mixture decreased from 6.25×10^{-9} to 5.82×10^{-11} mol/l in 2 weeks. The distribution coefficient (Kd) for Pu on the granite was calculated to be 159 ml/g. The Pu concentration in the blank solution also decreased over the same time period. The observed decrease in Pu concentration in the sorption test may therefore not only be due to sorption on the granite but also to adsorption on the tube walls and/or possibly precipitation. To account for this observation, the distribution coefficient for Pu on the granite was recalculated using the following assumptions:

(1) the decrease observed in the blank is due to sorption on the vial wall and the Ka of Pu on the tube wall (2.91 ml/cm^2) is the same in the sorption test. This gives a Kd of 149 ml/g.

(2) the final concentration in the blank test (1.36 x 10^{-9} mol/l) is the Pu solubility under the condition of the sorption experiment and the difference in Pu concentration between the solubility and the final Pu concentration in the sorption test is due to the sorption on the granite. This gives a Kd of 33 ml/g.

These Kd values may be underestimated because equilibrium conditions in the Pu concentration may not have been reached after 2 weeks.

Sorption of Pu under the conditions of these experiments is much greater than 0.02 ml/g. Therefore, the rate of diffusion of Pu is too low to complete the through-diffusion experiments within a reasonable time period. Instead, the experimental diffusion program was changed as follows:

(1) Diffusion of Sr and I in granite from the URL The effective diffusivity of SrI_2 will be measured by a through diffusion method.

(2) Sorption of Pu on URL granite disks Pu sorption on URL granite disks will be studied. Sorption is expected to be controlled by diffusion of Pu into the granite. The concentration of Pu in solution will be measured as a function of time. From the concentration decrease curve, overall diffusivity of Pu in the granite will be obtained.

2.2.3 Preparation of granite disks

A granite core was obtained from the exploratory borehole JE 2 that was drilled into the rockmass surrounding the vertical fracture JZ 2 in the URL. Four liters of groundwater from FZ 2 was also obtained from this borehole. In a Pu diffusion experiment that had been performed in JAERI, Pu(IV) was gradually oxidized during the experiment. It seemed to be necessary to exclude atmospheric oxygen as much as possible to avoid air oxidation of the granite. The rock sawing equipment was modified by enclosing the diamond rotary blade and motor with an acrylic/polyethylene housing. Compressed N_2 gas was used to displace as much of the atmospheric oxygen as possible. To hold the rock core as firmly as possible to prevent chipping during cutting, a new holder was designed and constructed to hold the core. Eleven 5-mm thick disks of granite were cut from the core, using groundwater from Fracture Zone 2 in the URL to cool the blade during cutting. The 11 disks were placed in an acrylic vessel filled with groundwater from Fracture Zone 2. A small polyethylene bag filled with iron powder was added to this vessel to scavenge atmospheric and dissolved oxygen and to maintain reducing conditions.

The locations along the core from which the 11 disks were cut are illustrated in Fig. 2.2-1.

These disks will be used in SrI_2 diffusion experiments, Pu sorption experiments and porosity measurements as follows:

G1: porosity measurement
F1:porosity measurement
F2: SrI_2 diffusion experiment
G2:porosity measurement
F3: Pu sorption experiment
F4:porosity measurement
F5: SrI_2 diffusion experiment
F6:Pu sorption experiment
F7: porosity measurement
F8:SrI_2 diffusion experiment
F9: Pu sorption experiment
F10: porosity measurement
F11: porosity measurement

The samples denoted by G indicate samples with a thickness greater or smaller than the samples marked F. These samples are not suitable for diffusion experiments and will be used to determine porosity. Inada granite cores have been cut into 5 mm thick, 40 mm diameter disks under aerated conditions.

2.2.4 Diffusion cells

The diameter of the URL granite core is 60 mm, compared with 40 mm for the Inada granite. Since the diffusion cells were designed for the 40 mm diameter disks, either the diameter of the granite would have to be reduced, or the diffusion cells modified. The decision was made to modify some of the diffusion cells to accommodate the granite disks, for the following reasons;

(1) The porosity of the URL granite is lower than that of the Inada granite and any reduction in diffusion can be offset by using disks with a larger diameter.

(2) By modifying the diffusion cells, handling of the granite is minimized. This is important since the granite should be kept from atmospheric oxygen as much as possible.

Six granite disks were attached to acrylic frames with silicone gaskets. Any water leakage through the silicone/granite joint will be checked after the diffusion/sorption run by placing a dye solution in one compartment of the diffusion cells, evacuating the other cell, and visually observing any location where dye exits. Diffusion cells have been assembled as shown in Fig. 2.2-2. These operations have been done in a glove box under N_2 with an oxygen concentration of less than 1 ppm.

2.2.5 Porosity measurement

The porosity of the rock is an essential parameter in this study and must therefore be determined with as high a precision as possible. However, the porosity of the rock samples used in the diffusion and sorption experiments should not be measured before the diffusion and sorption runs because the porosity measurement may cause air oxidation of the rock samples. The porosity of the samples will instead be obtained from that of the adjacent disks by interpolation or, if necessary, will be measured on the disks after the diffusion and sorption experiments have been completed.

The porosity of Inada granite disks was measured by water saturation. The results are presented in Table 2.2-2. The determination of the porosity was started for URL granite disks. Saturated weight, dry weight and thickness of a URL granite disk (G2) were measured to be 32.9810.004 g, 32.916 g and 4.230.07 mm, respectively. The porosity was calculated to be 0.510.03%. Additional porosity determinations will be determined for the following reasons;

1) The measured porosity is much higher than previously measured values (0.2-0.3%).
2) The rock disk saturated with water was weighed in a balance after wiping surface water off with a piece of tissue paper. A large error may be associated with this measurement because of incomplete wiping surface water. A more precise technique has been developed at Whiteshell based on following weight changes due to drying as a function of time(6). This technique will be used and results compared with those obtained on G2.
3) The porosity of Inada granite will be measured for comparison using the Whiteshell technique.

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(1) Vandergraaf, T. T., C. K. Park and D.J. Drew (1994) : Migration of Conservative and Poorly Sorbing Tracers in Granite Fractures, Proceeding of the Fifth International High Level Radioactive Waste Management Conference, Las Vegas, USA, pp.2251-2256.
(2) Kita, H., T. Iwai and S. Nakashima (1989) : Diffusion Coefficient Measurement of an Ion in Pore Water of Granite and Tuff, Journal the Japan Society of Engineering Geology, 30 (2), 84-90 (in Japanese).
(3) Kumata, M., T. Iwai, T. Sagawa, T. Suzuki and K. Nishiyama (1990) : Diffusion Experiment of a Radionuclide in Granitic Rock Cores, JAERI-M-90-179, (in Japanese).
(4) Nishiyama, K., S. Nakashima, R. Tada and T. Uchida (1990) : Diffusion of an Ion in Rock Pore Water and its Relation to Pore Characteristics, Mining Geology, 40 (5), 323-336 (in Japanese).
(5) Yamaguchi, T., Y. Sakamoto and M. Senoo (1993) : Consideration on Effective Diffusivity of Strontium in Granite. Journal of Nuclear Science and Technology, 30 (8), 798-803.
(6) Melnyk, T. W. and A. M. M. Skeet (1986) : An Improved Technique for the Determination of Rock Porosity, Canadian Journal of Earth Science, 23, 1068-1074.

Table 2.2-1 pH, Eh and plutonium concentration in blank and sorption tests (Ionic strength: 0.01, bicarbonate concentration: 0.003-0.005 mol/l)

	blank test				sorption test			
	pH	Eh	Pu concentration		pH	Eh	Pu concentration	
		(mV)	(Bq/ml)	(mol /l)		(mV)	(Bq m/l)	(mol/l)
initial	9		1260	8.34×10^{-9}			943	6.25×10^{-9}
30 minutes			1240	8.21×10^{-9}			796	5.27×10^{-9}
1 week	9		219	1.45×10^{-9}	8.5		13.4	8.87×10^{-11}
2 weeks	9	295.3	206	1.36×10^{-9}	8.5	292.8	8.79	5.82×10^{-11}

Table 2.2-2 Dry weight (Wd), saturated weight (Ws) and underwater weight (Wu) for Inada granite disks. Density, porpsity and thickness are given by: density = Wd/(Ws - Wu), porosity = (Ws - Wd)/(Ws - Wu) and thickness = (Ws - Wu)/(cross section).

disk No.	dry weight (g)	saturated weight (g)	underwater weight (g)	density (kg/dm^3)	porosity (%)	thickness (cm)
D1	16.778	16.826	10.415	2.617	0.75	0.510
D2	16.790	16.834	10.429	2.621	0.68	0.510
D3	15.888	15.925	9.877	2.627	0.61	0.481
D4	16.412	16.451	10.209	2.629	0.63	0.497
D5	16.214	16.251	10.079	2.627	0.61	0.491
D6	16.203	16.245	10.077	2.627	0.69	0.491
D7	15.946	15.988	9.903	2.621	0.69	0.484
D8	16.145	16.186	10.011	2.615	0.67	0.491
D9	15.496	15.536	9.610	2.615	0.67	0.472
E1	16.180	16.219	10.048	2.622	0.63	0.491
E2	16.312	16.351	10.136	2.625	0.62	0.495
E3	15.953	15.994	9.906	2.620	0.68	0.485
E4	17.143	17.184	10.656	2.626	0.63	0.519
E5	15.584	15.621	9.679	2.623	0.61	0.473

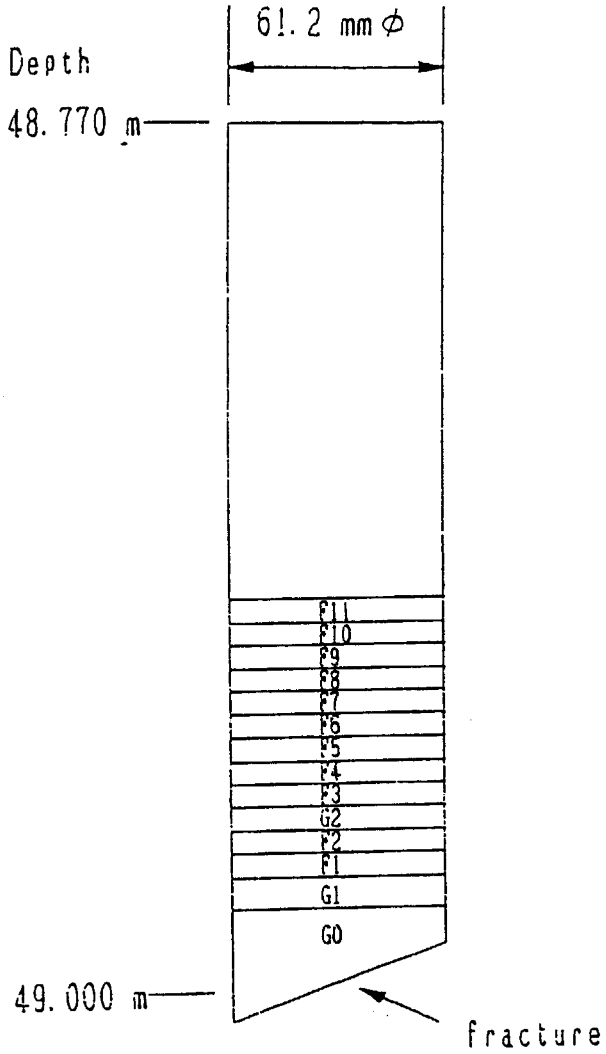


Fig.2.2-1 Schematic of the granite core selected for the diffusion experiments from the borehole JE-2.
Eleven 5-mm thick granite disks (F1-F11) were cut from the core between the depths of 48.770 and 49.000m

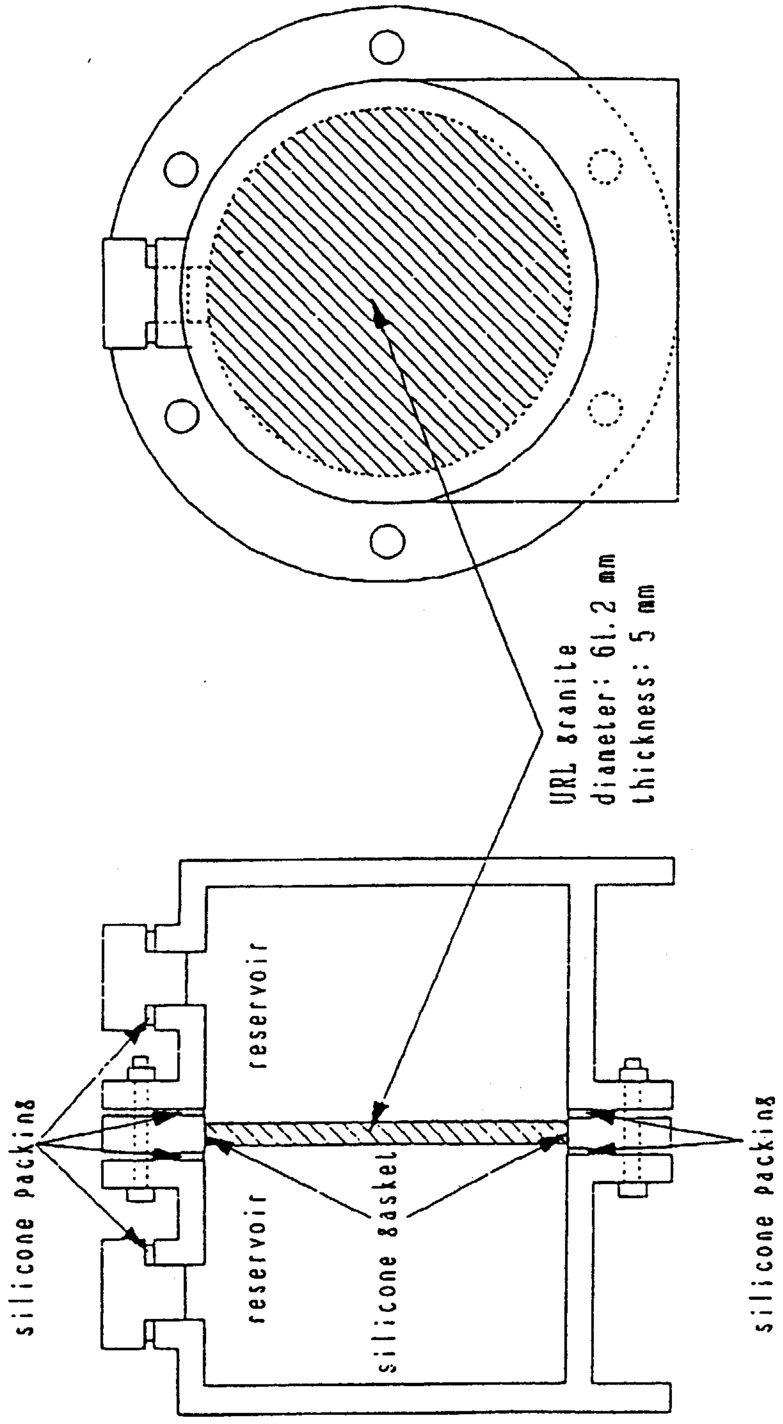


Fig.2.2-2 Diffusion cell used in SrI_2 diffusion experiment and Pu sorption experiment

3. SPECIATION OF LONG-LIVED RADIONUCLIDES IN GROUNDWATER (PROGRAM 1, PROJECT 2)

The overall objective of this program is to investigate the effect of naturally-present dissolved organic carbon (DOC) compounds on the mobility of selected long-lived radionuclides. This project seeks to improve our understanding of the processes involved in the formation of complexes between selected radionuclides and organic compounds that are naturally found in groundwaters. Such complexes may enhance the mobility of these nuclides in geologic systems.

A literature review on characteristics of humic substances (major part of naturally-present DOC compounds) in groundwaters, GPC method, and sorption behavior of humic-radionuclide complexes onto geomaterials has been done.

3.1 Method Development-High Performance Gel Permeation Chromatography

S. Nagao and Y. Sakamoto

Apparent molecular weight distribution (MWD) is an important physico-chemical property related to migration behavior of humic substances and humic-radionuclide complexes. High-performance gel permeation chromatography (GPC) can be used successfully for analysis of MWD of aquatic humic substances isolated from river, lake and groundwater. In this program, the GPC method with UV or fluorescence detector has been applied to aquatic humic substances without any pretreatment such as concentration and purification of humic substances. The data may represent the natures of aquatic humic substances at *in-situ* environmental conditions.

High-performance GPC system consists of a Hitachi Model L-6000 pump, a Model L-5020 column oven, a Model L-4250 UV-VIS detector, a Model D-2500 computing integrator, and a Rheodyne Model 7125 injection valve with 20 μL-loop. The GPC separation was carried out with a stainless steel column (Hitachi GL-W530: 30 cm x 10.7 mm I.D.) packed with water soluble polyacrylate gel resins. The approximate upper exclusion limit was molecular weight of 50,000 daltons calibrated with pullulan, according to the industrial catalogue. The Aldrich humic acid and natural water samples, 100 μL water volume, were injected into the high-performance GPC column with a carrier flow-rate of 1 ml/min. Mobile phase was 0.01 mol/L Tris-HCl buffer solution including 0.01 mol/L NaCl at pH 8.0. Absorbance was monitored at 280 nm by the UV-VIS detector.

3.1.1 UV detection

The validity of the direct GPC method was checked with humic acid purchased from Aldrich. Effects of humic concentration, pH and ionic strength on chromatograms were studied because these chemical properties had an influence on the MWD and varied with natural environments.

Chromatograms of the humic acids show two peaks above the humic concentration of 0.5

mg/L (Figure 3.1-1). The two peaks were not be detected for the humic acid having the concentration of 0.1 mg/L. The variation of retention times is only 0.1-0.2 min. The peak height ratio (7.5/8.4 min) is almost constant among these samples having the concentration of 0.5 to 100 mg/L. Relative standard deviation of the integrated peak area is 3~5% at the concentrations of 1, 5, 10 and 100 mg/L for 8 determinations. The chromatograms have basic features and good reproducibility at the concentration of 0.5 to 100 mg/L.

The effects of pH and ionic strength of natural waters on chromatograms were studied. The peak area and peak height ratio (7.5/8.4 min) are almost constant with pH value from 5.2 to 8.4, but are 30% and 13% lower values for the humic acid solution at pH 4.0 (Figure 3.1-2a). The variations of chromatograms is negligible at pH 5.2 to 8.4. The chromatograms vary with ionic strength from 0.001 to 1.0 mol/L $NaClO_4$ (Figure 3.1-2b). The peak height ratio is 2.7 at 0.001~0.01 mol/L, 2.0 at 0.05 mol/L and 1.7 at 0.1~1.0 mol/L $NaClO_4$. On the other hand, the peak area is 4.5 at 0.001~0.1 mol/L and 3.7 at 0.5~1.0 mol/L $NaClO_4$. In basis of the results on peak height ratio and area, the shapes of chromatograms are divided into three groups as follows; 1) ionic strength of 0.001~0.01 mol/L; 2) 0.05~ 0.1 mol/L; 3) 0.5~1.0 mol/L. The typical range of ionic strength is ~0.003 mol/L for terrestrial waters and about 0.75 mol/L for sea water and marine pore water. Typical concentrations of total organic carbon of aquatic humic substances are 0.5 mg/L in sea water, 7 mg/L in rivers, and 25 mg/L in marshes and bogs. The pH of natural waters ranges from 6 to 9. Therefore variations of chromatograms of aquatic humic substances on three chemical properties are negligible for freshwater and marine water samples, respectively.

At a first step, the direct GPC method was applied to aquatic humic substances in five ponds and three marine sedimentary pore waters with the DOC concentration of 2.5 to 32 mgC/L. Typical chromatograms are shown in Figure 3.1-3. Chromatograms of pond waters from dystrophic lakes show 4 peaks and their retention times agree well each other. Chromatogram of the marine pore water sample shows 6 peaks. Four retention times below 12.2 min of the pore water agree with those of pond water samples. The agreement indicates that the humic substances separated by the GPC have similar four types of molecular sizes in spite of different environmental conditions. The differences in peak height are considered to be due to variations of characteristics of humic substances.

The percentage of aquatic humic substances with each molecular weight to total humic substances was calculated from the integrated peak area of the chromatograms. The major part (65-98%) of humic substances in the pond and pore waters has apparent molecular weight of less than 10,000 daltons. These results are consistent with data obtained for lake waters and sea waters by other scientists. Consequently, the direct GPC method can be applied to aquatic humic substances in natural waters.

3.1.2 Fluorescence detection

The concentrations of dissolved organic carbon in most uncontaminated groundwaters are low, typically ranging from 0.1 to 2 mg/L. Aquatic humic substances with the concentration of less than 0.5 mg/L can not be detected with the UV detection. Fluorescence detection was chosen to detect humic substances with low concentration (<0.5 mg/L) because of high sensitivity compared to that of UV detection. Fluorescence spectra of humic substances have been measured with a three dimensional fluorescence spectrophotometer to clarify analytical conditions at the GPC method.

Three dimensional excitation-emission matrix spectra for humic acid (Aldrich) solutions were measured with a fluorescence spectrophotometer (Hitachi Model F-4500). As shown in Figure 3.1-4, the humic acid has two excitation/ emission maxima at Ex 260 nm/ EM 495 nm and Ex 440 nm/EM 515 nm. Fluorescence intensity at the two maxima was plotted as a function of the humic concentrations (Figure 3.1-5). There are good positive correlation ($r^2=0.99$) between the fluorescence intensity and the humic concentrations from 0.1 to 10 mg/L. The fluorescence intensity of humic substances is used as a simple indicator of the concentration of humic substances in groundwaters.

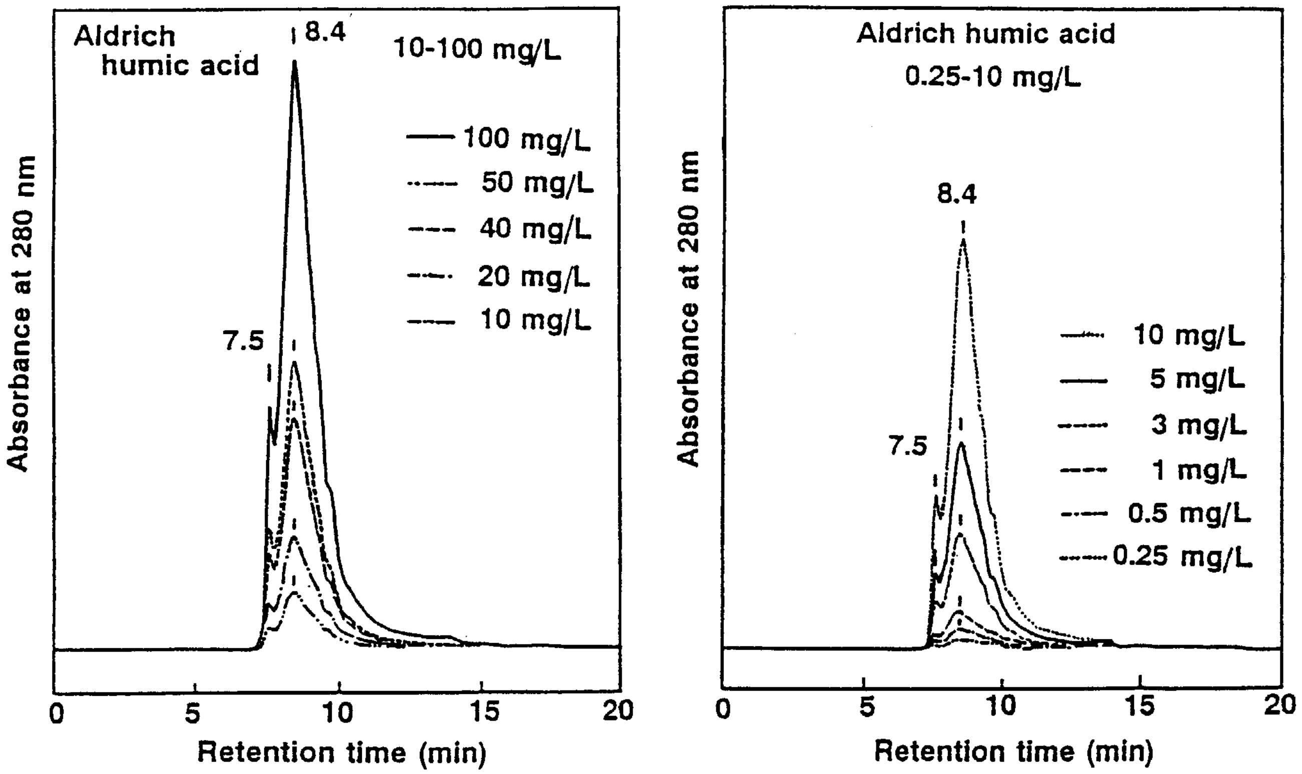


Fig.3.1-1 Chromatograms of humic acid (Aldrich) solutions with the concentration of 0.25 to 100 mg/L. The absorbance unit in the right panel is four times as large as the left panel.

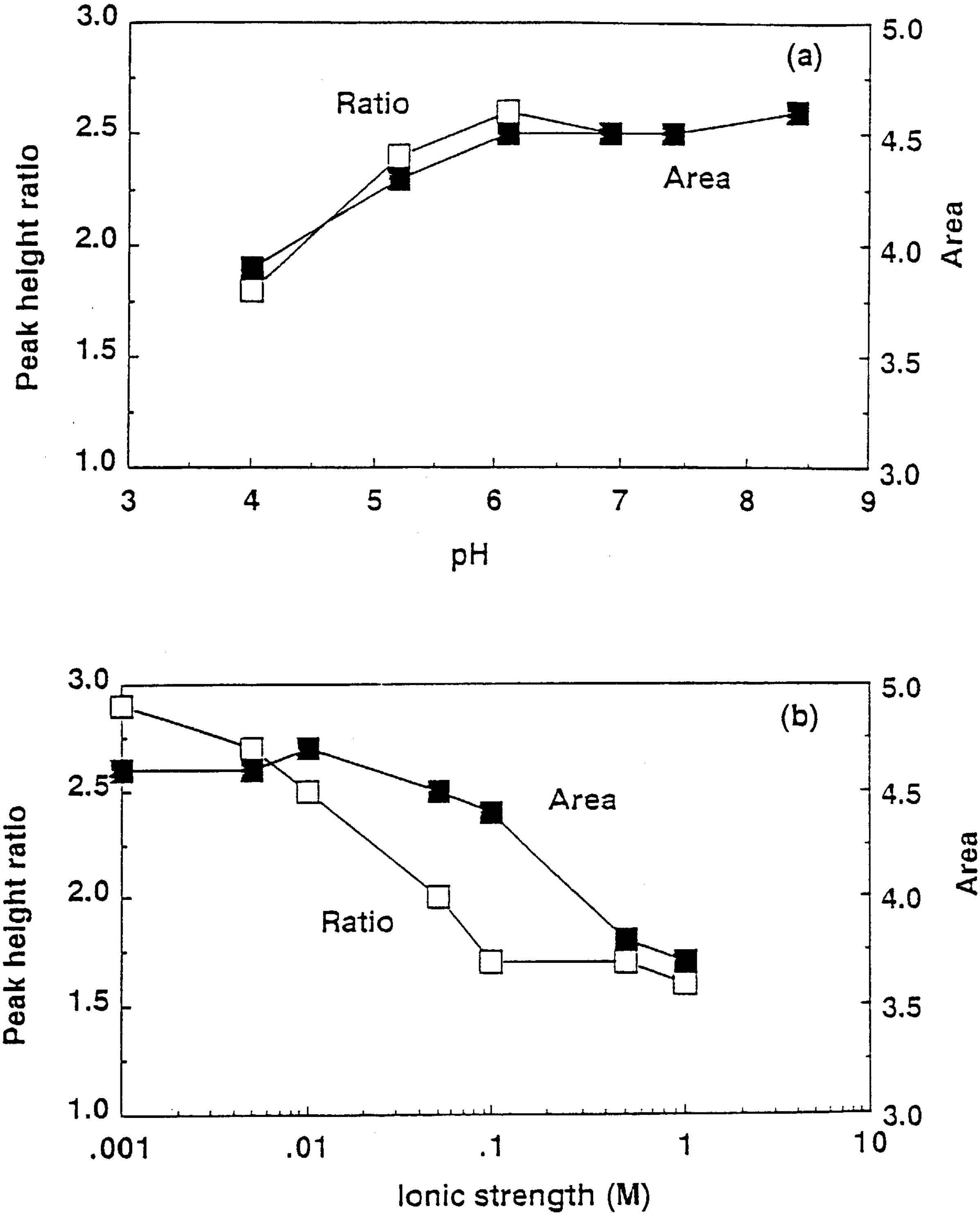


Fig.3.1-2 Peak height ratio (8.4/7.5 min) and peak area of humic acid (Aldrich) solutions with the concentration of 20 mg/L as a function of pH (a) and ionic strength (b).

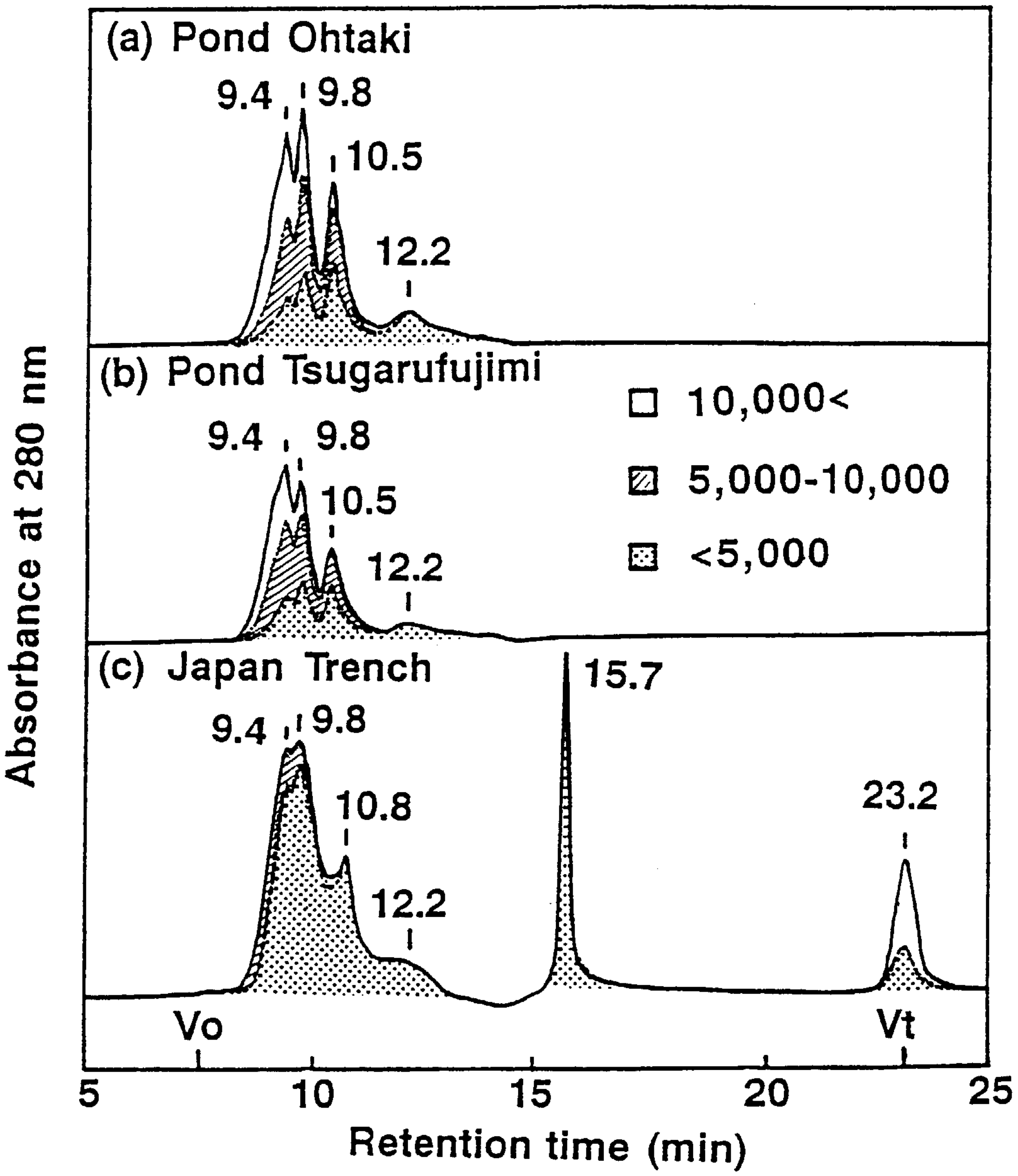


Fig.3.1-3 Chromatograms of aquatic humic substances in lake waters from Pond Ohtaki (a) and Tsugarufujimi (b), and a marine pore water © from the Japan Trench sediment. The chromatograms of the same solutions ultra-filtered by molecular size filters of 5,000 daltons (dashed lines) and 10,000 (dotted lines) are also shown. The void volume (Vo) and total effective column volume (Vt) of the column were about 7.5 min and 23.2 min, respectively.

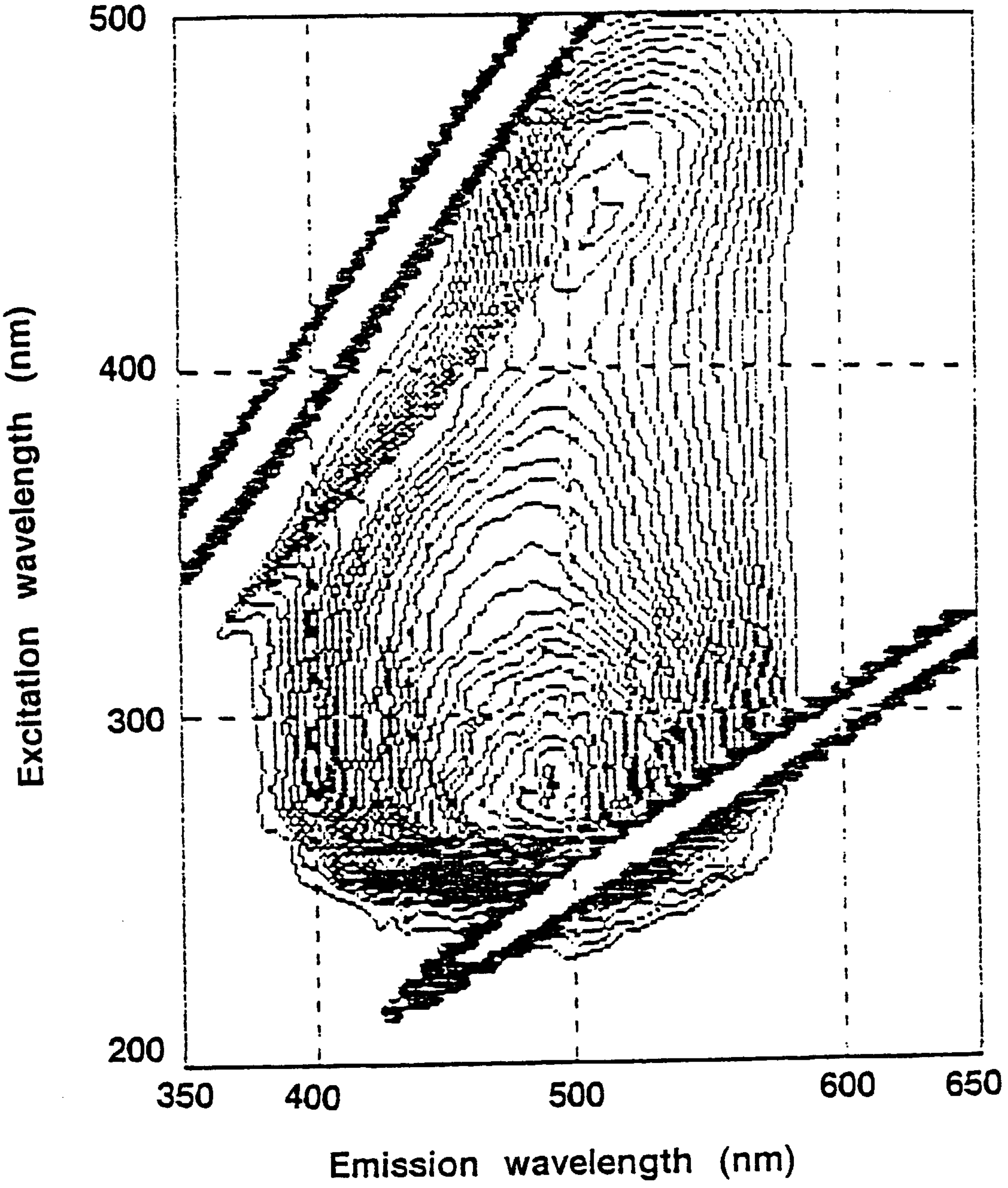


Fig.3.1-4 Contour plot of fluorescence excitation-emission matrix spectra for a humic acid (Aldrich) solution with the concentration of 8.0 mg/L and pH 8.0. The two dark rows of running diagonally across the left side of the figure are from first-order Rayleigh scatter. The humic water has two excitation-emission maxima at Ex 260 nm/EM 495 nm and Ex 440nm/EM 515 nm.

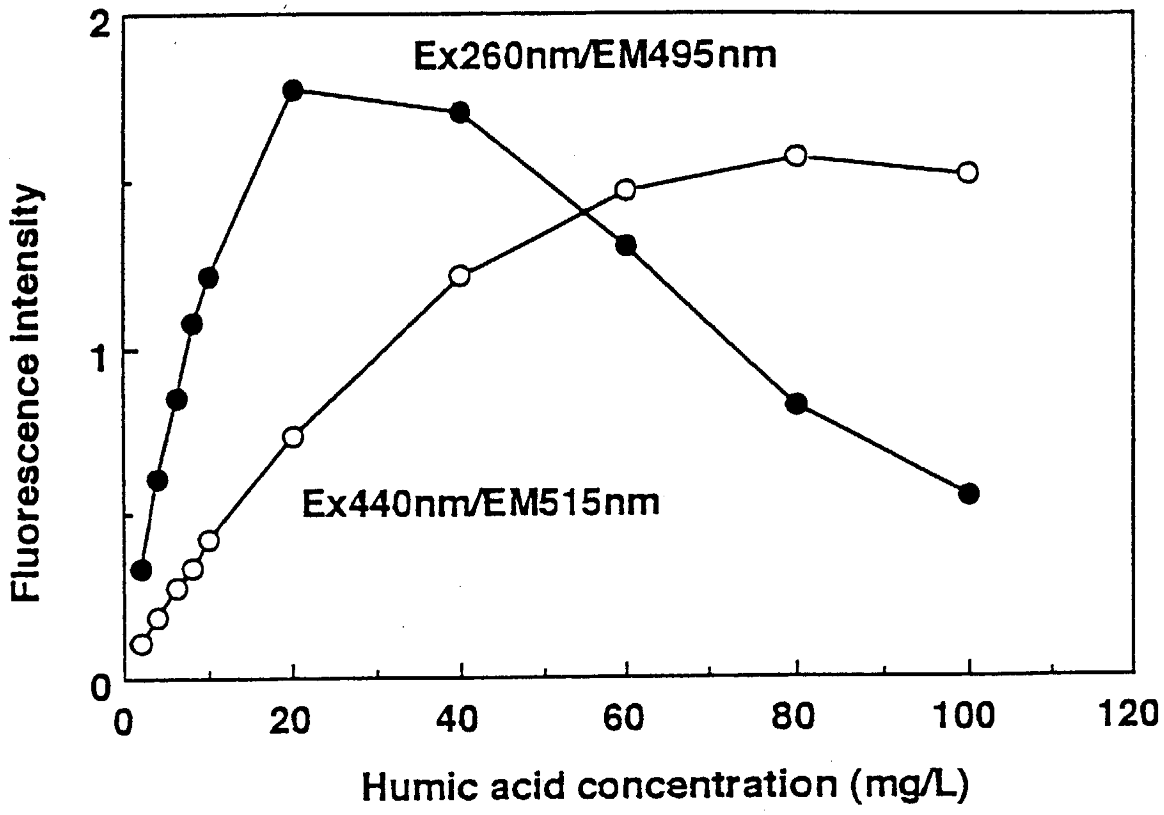


Fig.3.1-5 Fluorescence intensity of the two peaks detected at EX 260 nm/EX 495 nm and EX 440 nm/EX 515 nm for the humic acid (Aldrich) solutions as a function of the humic concentration from 0.1 mg/L to 100 mg/L.

3.2 Concentrate Natural Organic Compounds from Large Volumes of Groundwaters

R.R. Rao, J.L. Young and R.W.D. Killey

Speciation of long-lived radionuclides in groundwaters depend on the nature and concentration of both the nuclides and ligands present as well as the host environment. It has been considered that natural organics play an important role in the speciation of contaminants and thereby influence their migration. However, organic compounds naturally present in groundwaters have a wide range of molecular weights, charge characteristics, and chemical compositions. To evaluate the effects of naturally occurring dissolved organic materials (DOMs) on the mobility of radionuclides, one has to characterize these DOMs to understand their complexing and sorption properties. However, the concentrations of DOMs, expressed in terms of dissolved organic carbon, in most uncontaminated groundwaters are low, typically ranging between 0.1 to 2 ppm. One has to preconcentrate the DOMs from large groundwater samples of 5000-10000 litre size to get at least 1-5 g required for the laboratory tests.

A literature search on: (i) methods for concentrating the DOMs from groundwaters, and (ii) the effect of DOMs on the mobility of actinides has been done. Some literature papers were already collected and requests for certain other reports were sent. A review of the literature studies is in progress. Reverse osmosis (RO) and nanofiltration (NF) procedures may be suitable for preconcentration of DOMs from large volumes of groundwater. Once the groundwaters containing these DOMs are preconcentrated to about 5-10 liter, they can be further enriched by adsorption chromatography. Then cation exchange and size-exclusion chromatographic techniques can be applied to de-salt, purify and fractionate the materials.

We have recently undertaken and completed the scoping studies to test the feasibility of a bench scale RO unit by concentrating DOMs from a 200 L sample of groundwater from the glass block site at Chalk River Laboratories. The sampling location is shown in the Glass Block Hydrogeologic Grid (Figure 3.2-1). The groundwater sample was collected from the borehole PLS-63A which is -1.5 metres south-west of PLS-63. The water was pumped into pre-cleaned 20 L Nalgene polyethylene Carboys and taken to the Environment Canada Laboratories in Ottawa for processing through a Seprotech RO unit.

A diagram showing the schematics of the unit is given in Figure 3.2-2. The unit primarily consists of a security screen to remove particulate, a pump to generate a maximum of 1500 psi pressure, a cartridge filter of 0.4 μm pore size, a cartridge chamber to house an RO (or NF) membrane, and 2 or 3 reservoirs, one each for collecting feed water, RO concentrate and permeate. Flow and pressure indicators are to provide information on operating parameters and indirectly on the extent of enrichment of DOMs.

Sub-samples were taken from the concentrate and permeate after processing the groundwater through the RO unit. These samples along with the feed water were analyzed for pH, conductivity and total organic carbon (TOC). The results are presented in Table 3.2-1. The concentration factor calculated from measurements of volume reduction and conductivity is ~20. The experience gained from this exercise suggests that unless the membrane, plumbing and reservoirs of the RO unit are thoroughly leached and checked for TOC, there is a potential for contamination of the concentrated organics mainly both from the preservatives of the membrane and the residual organics in the plumbing. The size speciation of the RO concentrate was performed using Amicon Stirred Cell Ultrafiltration Cascade method (Figure 3.2-3) under positive nitrogen pressure ranging between 5 and 50 psi. The size fractionation results indicate that (i) ~40% of DOMs fall in the size range between <10 000 and > 1 000 MW. (ii) another ~50% between <1 000 and >500 MW and (iii) ~2% are > 10 000 MW.

The Eh and pH of the groundwater from the borehole PLS-63A measured on 1994 July 29 are reported in Table 3.2-2. The present feed water geochemical data (Table 3.2-1) are similar to the values measured in 1983 at the Glass Block Site (Table 3.2-3). The mean Eh of the groundwater is 38010 mV. This indicates that aerobic conditions prevail in the host environment at the Glass Block Site.

The scoping studies suggest that the bench scale RO/NF unit is suitable for concentrating the DOMs by conveniently taking the unit into the field rather than bringing in large volumes of water to the laboratory. Since 50% of the DOMs are low MW species, we are considering to purchase an RO/NF unit that could accommodate both RO and NF membrane cartridges so that a combination could be used for site specific operations. This would allow us to concentrate the organics without the build up of high ionic strengths which could alter the integrity of the DOMs. We have requested quotations from different suppliers for the RO unit. We plan to acquire a suitable system by 1994 November, complete the initial concentration steps of CRL groundwaters before the end of 1995 January, and process URL groundwaters by the end of March.

Table 3.2-1 Test of reverse osmosis technique for concentrating organics in groundwaters.

Sample	Temp. (°C)	pH	Conductivity (μS/cm)	TOC (mg/L)
Feed water	16.1	5.19	0.084	1.57
Permeate				
(a) at ¾ complete	20.9	5.33	0.006	
(b) at completion	19.9	5.88	0.028	
Concentrate				
(a) at ½ complete	20.9	6.21	0.228	
(b) at completion	20.9	7.41	1.520	32

Mode of operation:

RO concentrate was returned to the feed reservoir and recycled through the system until maximum concentration was achieved.

Table 3.2-2 Information and groundwater chemical data for PLS-63A.

Time	Volume of groundwater pumped (L)	Temp. (°C)	pH	E_h[a] (mV)
09:50	0			
10:00	86	12.0	5.12	394
10:04	120	12.0	5.10	377
10:10	172	11.8	5.15	373
10:15	215	12.0	5.13	386
10:20	258	11.8	5.20	390

[a] measurements made on 1994 July 29

Table 3.2-3 Glass Block Site geochemical data -1983.

Component	Unit	1 m	5 m
Conductance	µS	82	80
pH		5.7	5.7
E_h	mV	420	425
O_2	mg/L	0.7	3.1
Alkalinity (by titration)	mg/L	5.8	7.0
SO_4^{2-}	mg/L	17.1	16.6
Total S^{2-}	mg/L	0.09	0.08
NO_3^-	mg/L	0.2	0.3
Cl^-	mg/L	0.9	1.0
Total Fe	mg/L	0.09	0.02
Fe^{2+}	mg/L	<0.06	0.01
Total Mn	mg/L	<0.01	0.01
Ca^{2+}	mg/L	5.6	5.6
Mg^{2+}	mg/L	1.7	1.7
K^+	mg/L	0.9	0.7
Na^+	mg/L	1.9	3.4
Total Si	mg/L	5.7	5.8
DOC	mg/L	2.4	2.1
TIC	mg/L	2.3	2.1
Charge balance error	%	- 3.6	3.4

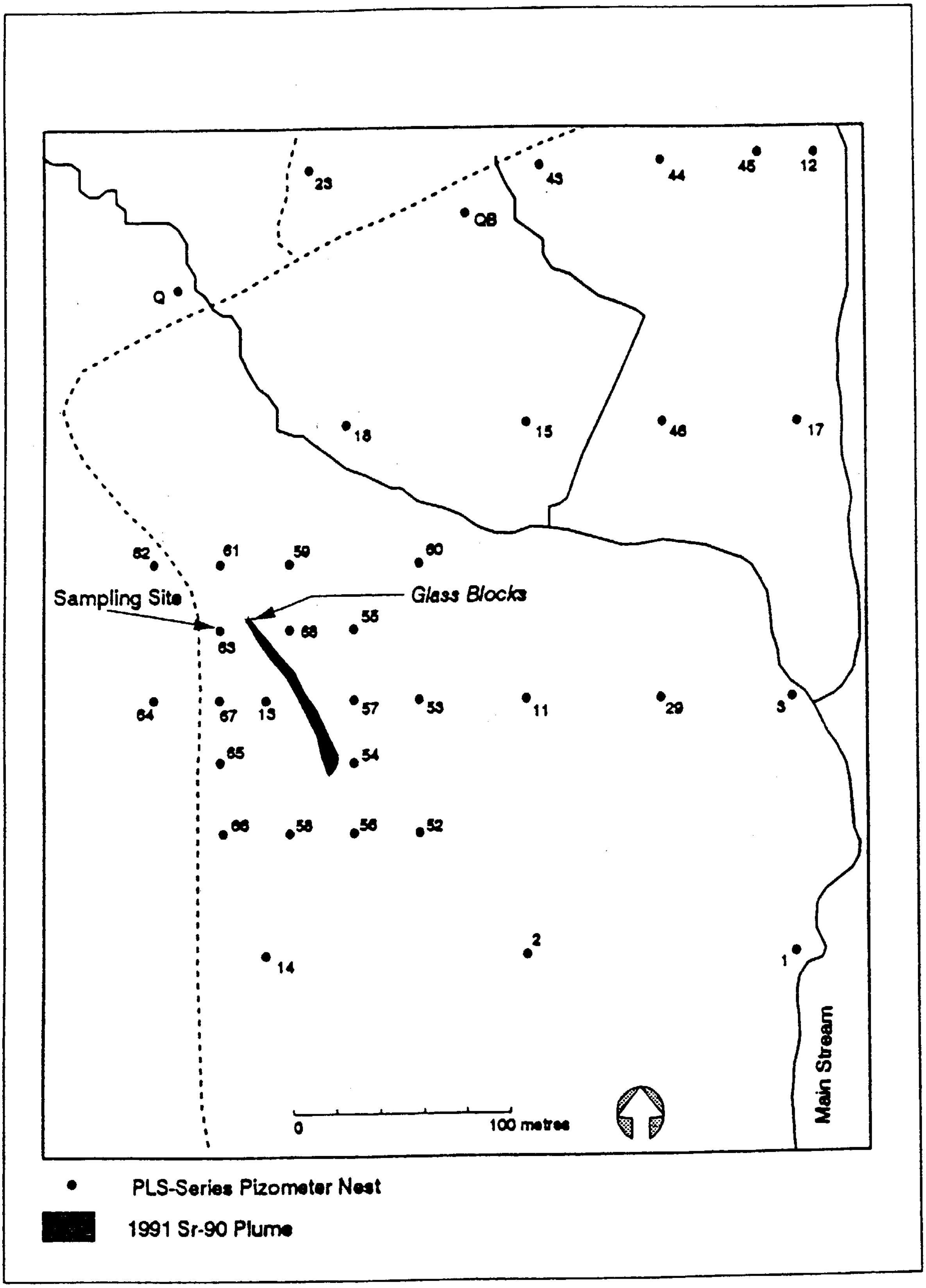


Fig.3.2-1 Glass block hydrogeologic grid.

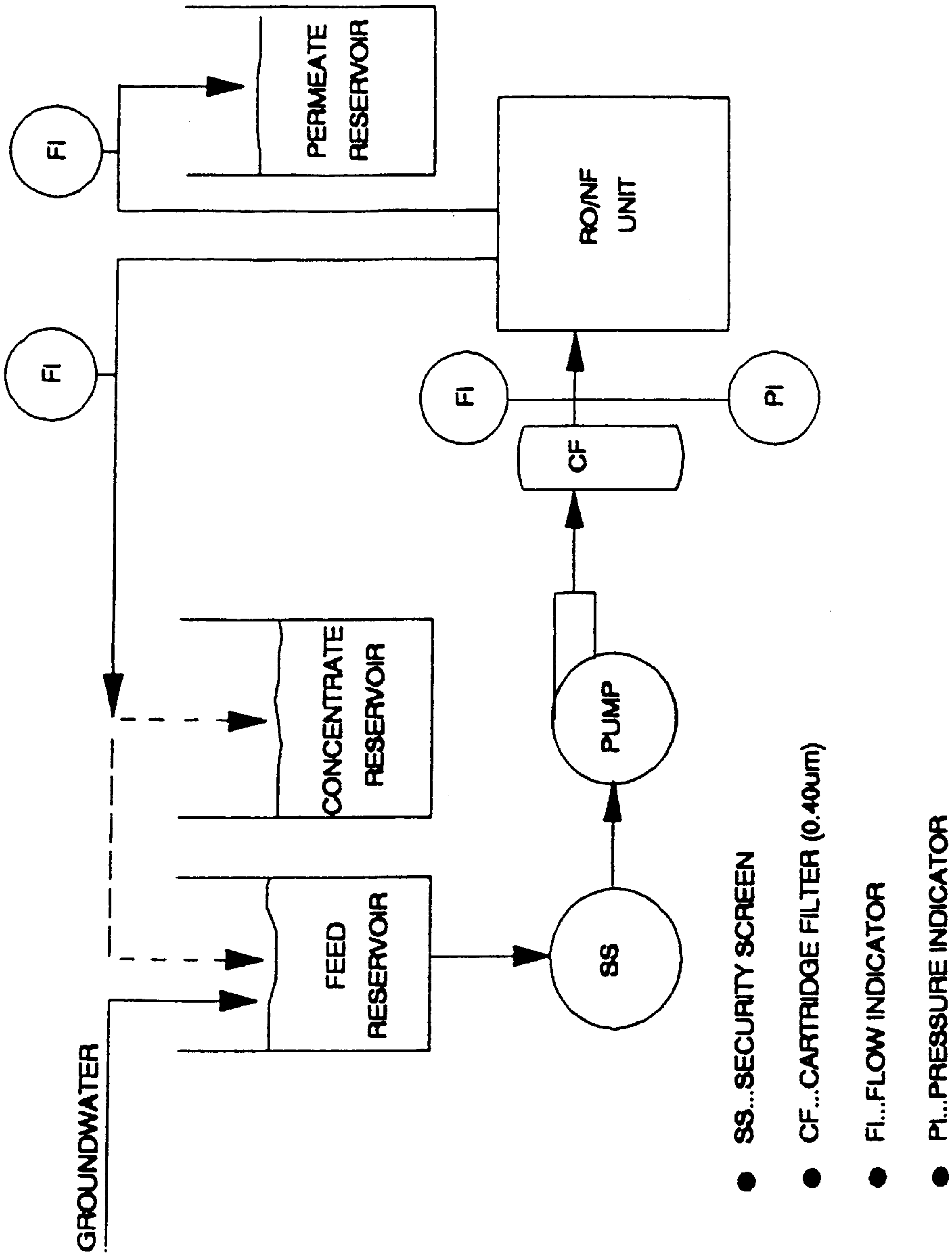
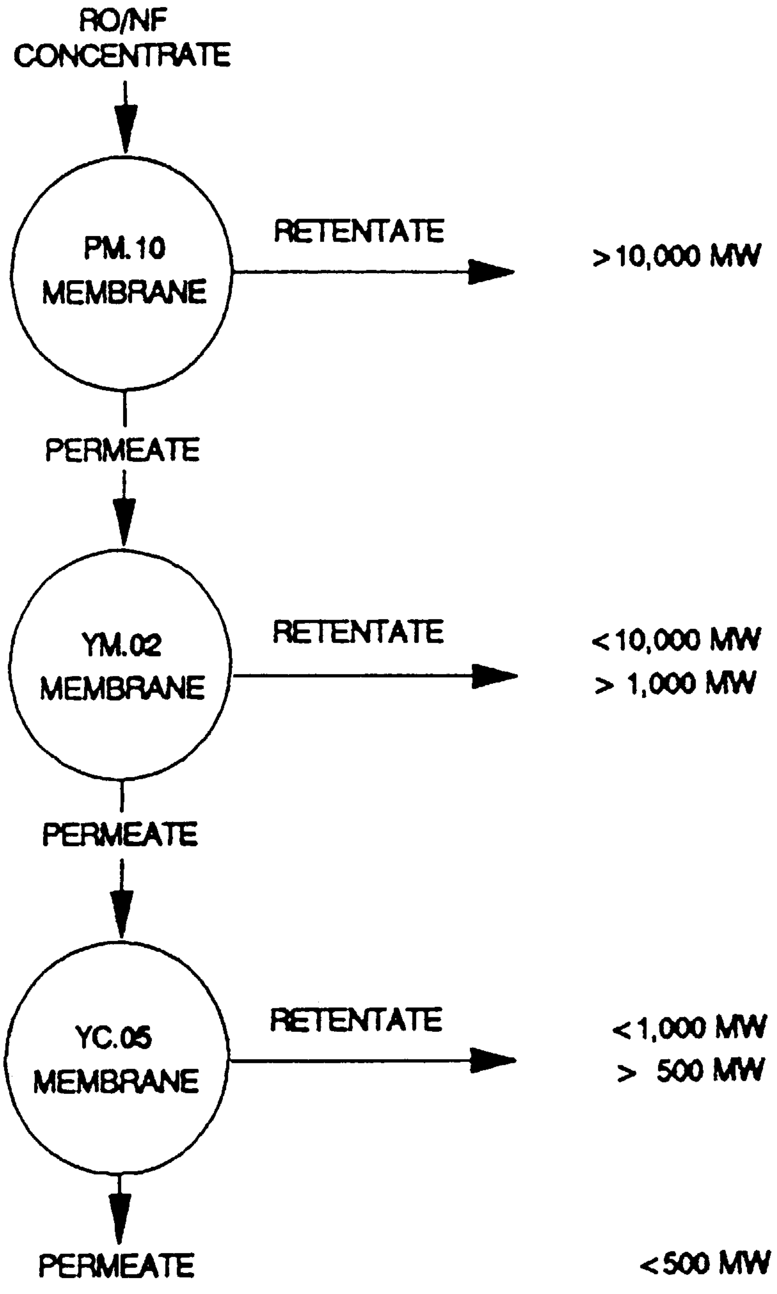


Fig.3.2-2 Reverse osmosis (RO) / nanofiltration (NF) system.



- Cells pressurized with nitrogen.

Fig.3.2-3 Stirred cell ultrafiltration.

4. ISOTOPIC HYDROGEOLOGY (PROGRAM 2 - PROJECT 1)

The overall objectives of this program are the assessment and application of specific isotopic methods in order to study the origin and evolution of groundwaters and to determine the residence ages of waters in deep formations. The principle objectives for Year l, involving a critical review of the literature on these methods, and development work on the analytical and field techniques required by the program, have largely been accomplished.

4.1 Stable Isotope Hydrology

M.Kumata, M.Mukai

Long-term groundwater flow at depth is major concern for safety assessment of radioactive waste disposal. Low-flow and low-permeability regions are expected to be selected for disposal site, however, it is not considered to be negligible very slow water movement through geomedia over periods of up to one hundred thousand years. Relating to waste disposal hydrology, isotope techniques has been considered to be particularly valuable (1,2). Traditional groundwater hydrology techniques, such as well-pumping tests, are less useful in large-scale, long-term groundwater flow analysis. Capabilities offering by isotope techniques using environmental tracer enable one to estimate past and present behavior of groundwater system, and therefore establish a basis for future predictions.

In Switzerland the hydrogeochemical program including isotope analysis started in 1981 and comprehensive field investigation have been performed to assess the feasibility and safety of a high-level radioactive waste repository. Waters were collected from about 140 springs and wells of different aquifers in northern Switzerland and adjacent areas. Seven deep boreholes with depths between 1306 and 2482 m have been drilled. About 60 waters from the deep boreholes were also sampled and analyzed(3). Isotopes and elements analyzed in the program were listed in Table 4.1-1. Also, the hydrogeochemical investigations carried out in the Stripa Project since 1977, in Sweden. Adding to enormous chemical data, oxygen-18 and deuterium were measured for stable isotope geochemistry. Carbon-14, tritium and chlorine-36 were also measured for the determination of residence time and in-situ production(4).

Stable isotopes of hydrogen and oxygen are very suitable tools for hydrogeological investigations because these environmental isotopes are part of the water molecules and follow their behavior through hydrological cycles, and are conservative in chemical reactions. Accordingly, stable isotope hydrology play an important role in both hydrogeochemical programs mentioned above.

Considering the natural abundance of the isotopes, it is only the molecules of $H_2{}^{16}O$, $H_2{}^{18}O$, $HD^{16}O$ and $H_2{}^{17}O$ which are of any importance among the possible stable isotope water species. Further, ^{18}O is in existence 5.5 times more abundant than ^{17}O. Hence, the abundance ratios of the isotopic pairs $^{18}O/^{16}O$ and D/H are using in the stable isotope hydrology. For reasons dictated by the measurement technique the absolute abundance ratio of isotopes is not usually measured in natural waters. Only the relative difference in the ratio of the heavy isotope to the more abundant light isotope of the sample with respect to a reference is determined. This difference is defined as follows:

$$\delta = \frac{R_{sample} - R_{reference}}{R_{reference}}$$

where the R's are the $^{18}O/^{16}O$ or the D/H isotope concentration ratio. As the differences between samples and reference are quite small, it is convenient to express the δ-values in per mill differences, i.e.

$$\delta(‰) = \delta \times 1000.$$

For the international comparison, isotopic concentrations expressed as δ(‰) are refer to Standard Mean Ocean Water (SMOW). Since SMOW is not a real water sample, a water sample, called VIENNA-SMOW (abbreviated as V-SMOW) is used as reference⁽⁵⁾.

The various isotopic forms of water have slightly different vapor pressures and freezing points. These two properties give rise to differences in ^{18}O and ^{2}H concentrations in water as a result of isotopic fractionation.

The δD and $\delta^{18}O$ of world-wide fresh-water sources have been measured by Craig(1961)⁽⁶⁾ and the relation between δD and $\delta^{18}O$ was described as follows:

$$\delta D\ (‰) = 8\ \delta^{18}O + 10.$$

A line of projection of the relation on the δ diagram defined as the (global) meteoric water line by Craig(1961)⁽⁶⁾. The departure of ^{18}O and ^{2}H concentrations from the meteoric water line is a feature of the isotopes that can be used in a variety of hydrologic investigations, including studies of origin of groundwater.

4.1.1 Sample preparation for deuterium and oxygen-18

Sample preparation methods for δ D and $\delta\ ^{18}O$ have been investigated for gas samples in mass spectrometric analysis. Two different preparation methods were examined for the analysis of δ D of sampled groundwater. Isotope exchange technique for preparation of hydrogen gas in mass spectrometric D/H analysis⁽⁷,⁸⁾ and the reduction of water with zinc for hydrogen isotope analysis⁽⁹⁾. Based on our experimental results of preparation of hydrogen gas in D/H analysis, careful selection of zinc was required for complete reduction of the water sample. Such an appropriate zinc is not so easy to obtain. Therefore, although the isotope exchange technique needs many experiences to obtain good results, we decided to apply this method.

For the oxygen-18 analysis, the CO_2 equilibration method was reviewed. As the conventional method(10) is time-consuming, a new simplified method(11) was considered to be used. A plastic syringe is used as an equilibration vessel for the simplified method. Based on the literature, the differences between the simplified method and the conventional one have been found to be within +/- 0.1(11). Accordingly, we concluded that it worth to exam this method.

Followings are the sample gas preparation method for the measurement of isotopic ratio by using a mass spectrometer.

1) Oxygen-18
   a) take a 5 ml water sample in a reaction vessel (a 25 ml plastic syringe) and remove air bubbles.
   b) introduce pure CO_2 gas (99.9%) into the vessel at a volume of about 7ml. Then seal the vessel.
   c) immerse the vessel into the water bath and keep 4 hours at a temperature of 25 ℃.
   d) separate the CO_2 gas from the liquid phase by using a vacuum system for CO_2 gas purification (Fig. 4.1-1).

2) Deuterium
   a) take a 10 mg of hydrophobic-platinum catalyst in a reaction vessel (a 30 ml glass flask).
   b) put a 2 ml water sample into the vessel and seal with a high-vacuum greased stopcock.
   c) introduce pure H_2 gas (99.999%) into the vessel under a vacuum condition.
   d) immerse the vessel into the water bath and keep 2 hours at a temperature of 30 ℃.
   e) separate the H_2 gas from the liquid phase by using a vacuum system for H_2 gas purification (Fig. 4.1-2).

Separated gas phase is introduced into a mass spectrometer (VG-SIRA 10) and isotopic ratio of D/H or $^{18}O/^{16}O$ of the sample gas is measured. A working standard solution is used as reference gas. At each preparation the working standard is triplicate, one for reference gas and two for background correction.

For the international comparison, water samples, called VIENNA-SMOW (abbreviated as V-SMOW) and Standard Light Antarctic Precipitation (abbreviated as SLAP) were prepared as standards. Measured isotopic ratios using a working standard were recalculated based on the V-SMOW - SLAP line in order to obtain delta values for SMOW.

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Table 4.1-1 List of analyses mode as part of the Nagra programme (from Pearson et al. Ed. 1991)

Determination	Substance
Stable Isotope Ratios	
$^{2}H/^{1}H$	Water
$^{4}He/^{3}He$	Dissolved helium
$^{13}C/^{12}C$	Dissolved carbonate
	Carbonate minerals
$^{18}O/^{16}O$	Water
	Carbonate minerals
	Sulphate minerals
	Dissolved sulphate
$^{34}S/^{32}S$	Dissolved sulphate
	Sulphate minerals
	Dissolved sulphide
	Sulphide minerals
$^{40}Ar/^{36}Ar$	Dissolved argon
Radioisotopes	
^{3}H	Water
^{14}C	Dissolved chloride
^{36}Cl	Dissolved chloride
	Chloride leached from rock
^{39}Ar	Dissolved argon
^{85}Kr	Dissolved krypton
$^{87}Sr/^{86}Sr$	Dissolved strontium
	Minerals
U and Th	Dissolved and Minerals
Dissolved Gases	
Helium	Dissolved
Argon	Dissolved
Neon	Dissolved
Krypton	Dissolved
Xenon	Dissolved

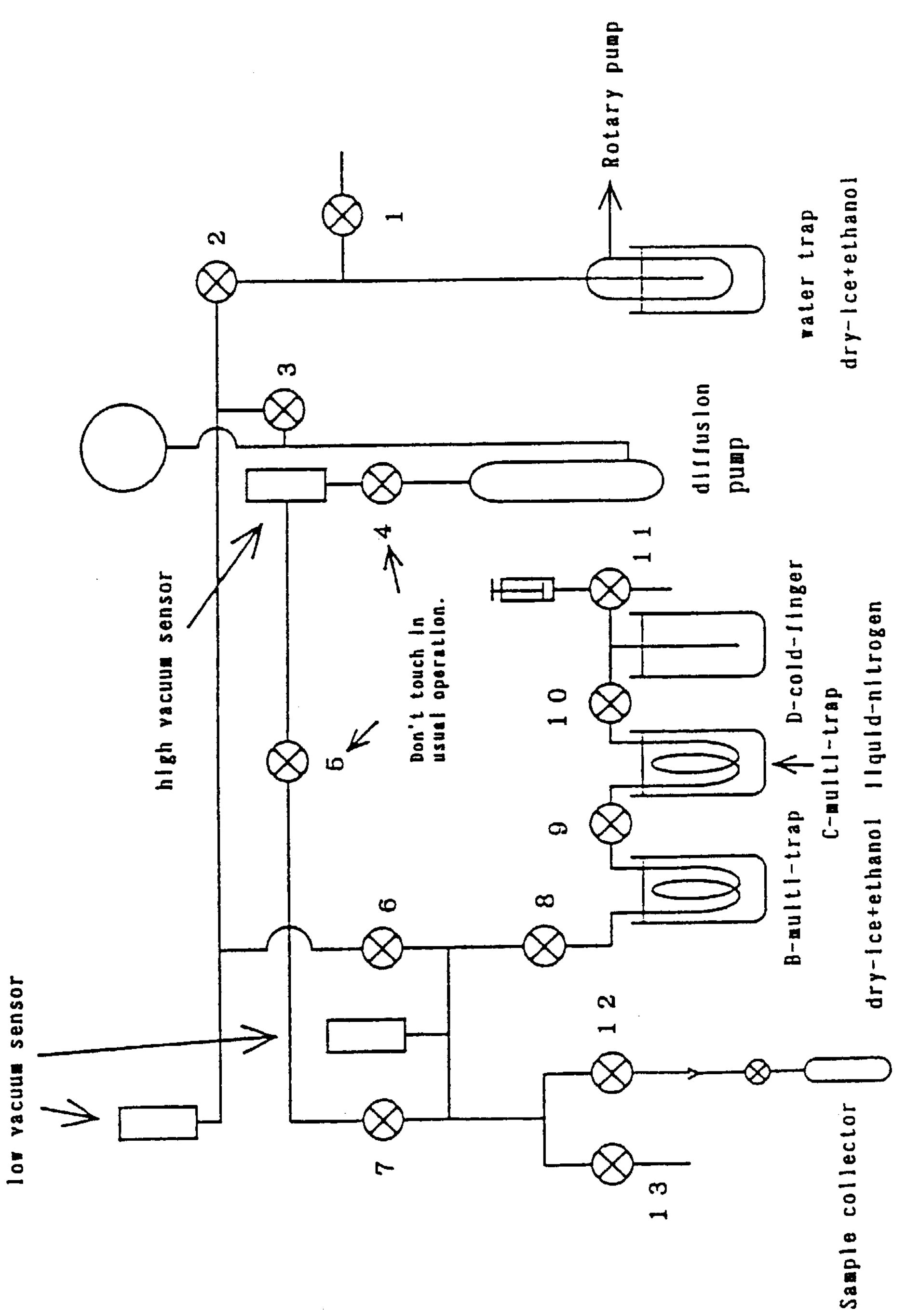

Fig.4.1-1 Schematic diagram of vacuum system for CO_2 gas purification.

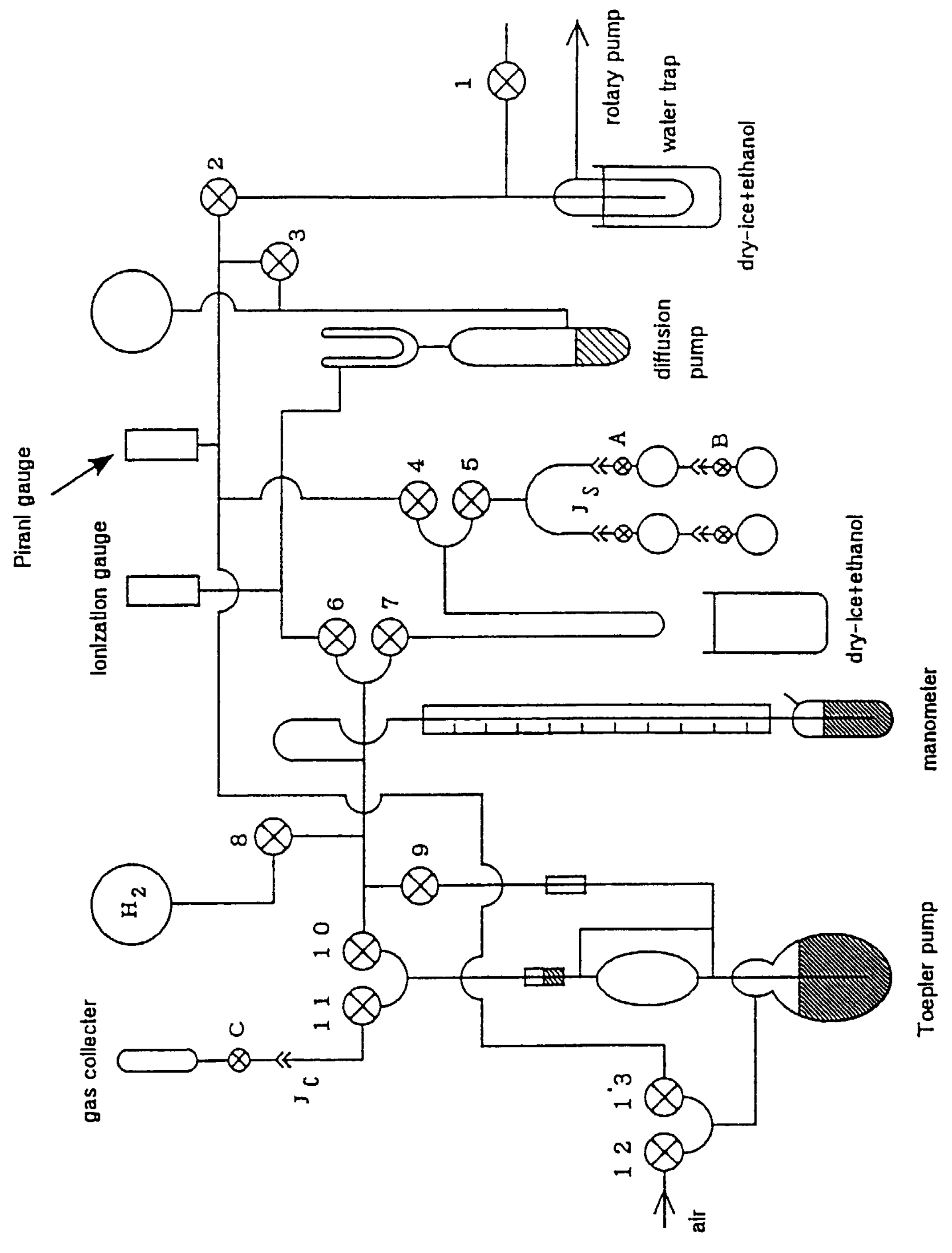

Fig.4.1-2 Schematic diagram of vacuum system for H_2 gas purification.

4.2 Isotopic Methods Used in Hydrogeological Studies

R.J. Cornett, M. Gascoyne, T.G. Kotzer, G.M. Milton

The review of available literature by M. Gascoyne and T. Kotzer on isotopic methods used in hydrogeological studies is near completion. Sections on applications of isotopic methods in hydrogeology, specific isotopic techniques (e.g. ^{3}H/^{3}He, He, Ne, ^{7}Li/^{6}Li, ^{11}B/^{10}B and ^{36}Cl/Cl) and the application to the URL area in Manitoba have been finished (Table 4.2-1 and -2).

The review has helped the authors to focus more clearly on the usefulness of some of the isotopic methods in determining groundwater residence times, water-rock interaction mechanisms and sources of dissolved salts. Current hydrologic methods used for sampling shallow groundwaters and their in situ produced gases, as described in the literature, have been adopted and modified where necessary. For instance, recent developments and results of the applications of ^{3}H in groundwaters and use of the ^{3}H/^{3}He dating method, at Chalk River Laboratories and elsewhere, have clearly demonstrated the power of this technique in identifying drill water contamination, infiltration rates of groundwaters and residence times of groundwaters in a fast-flowing aquifer(1−4). He and Ne analyses on deep groundwaters in ancient terranes at the URL and elsewhere indicate that, in general, deep groundwaters have ^{4}He concentrations and ^{3}He/^{4}He ratios indicating equilibrium with the rocks, thus yielding old residence ages(5). Use of the ^{4}He method for determining groundwater ages, requires that the spatial distributions of U, Th and fractures and rock porosity be well characterized in addition to having some prior knowledge of the hydrogeology of the aquifer or host rocks(6).

The review has shown that in situ production of ^{36}Cl is a common characteristic of many sites worldwide(7) including the granite at the URL, where concentrations of U and Th in the host rocks are significant. This therefore limits the potential of the ^{36}Cl/Cl dating technique as a groundwater dating tool in some cases. However in these areas the technique has been found to be very useful in identifying recently recharged groundwaters (beyond the range of ^{3}H/^{3}He dating) and in identifying the source of salts in the groundwaters(8). In some cases, if closed system conditions to Cl^{-} exist, as has been demonstrated for the Great Artesian Basin, Australia for instance, decay of recharge ^{36}Cl can be used as a dating tool for waters up to approximately 2 million years old.

Determining the sources of salinities in groundwaters using B and Li isotopes has been reviewed. At the present time, ^{7}Li/^{6}Li isotopic data on groundwaters are not very comprehensive. Application and interpretation of boron isotopic analyses in groundwater and mineral systems, suggests they have potential for delineating salinity origins and could be a useful tool when combined with several isotopic systems such as stable isotopic analyses (D/H, ^{18}O/^{16}O) and ^{36}Cl/Cl. Clearly the most successful studies for characterizing groundwater systems will result from integrating noble gas, radioisotope and stable isotopic systematic.

4.2.1. Groundwater age dating and noble gas analysis of deep groundwaters

1) ^{3}H/^{3}He age dating

Development of analytical methods for characterization of groundwaters was accomplished by conducting a $^3H/^3He$ study on a series of groundwater samples from a shallow (<15 m depth), semi-confined, sandy aquifer at Chalk River Laboratories(4). Helium and neon isotopic compositions and tritium concentrations were determined on a series of groundwater samples collected from multi-level wells along the length (approximately 500 m) of the aquifer at Chalk River Laboratories for the purpose of calculating $^3H/^3He$ residence ages and determining the flow velocities for these groundwaters. Velocities of waters in the aquifer, determined by independent tracer and borehole dilution tests, are typically on the order of cm/day, resulting in total transit times for waters in the aquifer of approximately 5 years(9). Groundwaters recharging into the aquifer are dominantly meteoric waters with elevated ^3H concentrations of approximately 600 to 1200 TU (1 TU = 1 $T/10^{18}H$ atoms) due to the close proximity of a low-level waste management site to the aquifer recharge area, resulting in a significant spike of ^3H which has been injected into the shallow hydrologic regimes. Since ^3H has a relatively short half-life ($t_{1/2}$ = 12.43 yrs), a substantial amount of ^3He above solubility equilibrium will accumulate in the groundwaters over their residence time thereby making the aquifer an ideal location to test the $^3H/^3He$ method of age dating using the recently-commissioned noble gas mass spectrometer system at Chalk River Laboratories.

Groundwater samples were collected in copper tubes which were sealed on both ends with helium leak-tight clamps. Samples for determining tritium concentrations by liquid scintillation methods were collected in Nalgene bottles. Separation of the dissolved gases was done by degassing the groundwaters under vacuum (10^{-5} torr) and collecting the exsolved gases in leak-tight ampoules on activated charcoal cooled to liquid nitrogen temperatures (-196℃). The samples for noble gas analysis were then inlet into a stainless steel high vacuum system (10^{-7} to 10^{-9} torr) where He and Ne were cryogenically separated from other atmospheric gases (CO_2, SO_2, H_2O) and from each other.

Isotopic ratios and concentrations of ^3He and ^4He were measured by noble gas mass spectrometry. As well, concentrations and isotopic ratios of Ne were determined to correct for excess air in the samples which would affect both the ^3He and the ^4He concentrations and result in increased $^3H/^3He$ ages if not corrected for.

Mass spectrometer analyses indicated that the groundwaters contained concentrations of Ne and He which were as much as 30 to 40 per cent greater than solubility equilibrium at 6 ℃ (Table 4.2-3). The He and Ne values measured are typical of the amounts in groundwaters which recharge through the unsaturated zone and contain excess air due to entrainment of air bubbles(10). ^{20}Ne, the most abundant isotope of neon and a very sensitive indicator of excess air in samples, is not produced in the subsurface by nucleogenic processes and hence was used to correct the helium isotopic data for any excesses.

^3He concentrations, corrected for excess air, exceeded atmospheric solubility equilibrium ^3He concentrations by as much as 10 to 15 x (Table 4.2-3) suggesting a substantial tritogenic ^3He component due to the decay of ^3H to ^3He ($^3He_{trit}$). $^3He_{trit}$ was calculated(1) as,

$$ {}^{3}He_{trit} = {}^{3}He_{sample} - {}^{3}He_{excess} - {}^{3}He_{recharge} $$

where ${}^{3}He_{sample}$; total dissolved ${}^{3}He$ in the sample, ${}^{3}He_{excess}$; ${}^{3}He$ contributed by excess air, and ${}^{3}He_{recharge}$; additional ${}^{3}He$ after recharge.

Since ${}^{3}He_{recharge}$ is negligible, ${}^{3}He_{trit}$ can be calculated based on the estimation of ${}^{3}He_{excess}$. Spatially, the helium isotopic data indicated a linear increase of ${}^{3}He_{trit}$ with distance (Figure 4.2-1A) indicating there was negligible diffusive loss of helium from the relatively shallow groundwaters and that the ${}^{3}H/{}^{3}He$ method would yield reliable ages for the groundwaters.

Residence ages for the groundwaters were calculated using the measured ${}^{3}H$ and calculated ${}^{3}He_{trit}$ concentrations (Table 4.2-3) in the groundwaters and the relationship:

$$ t_{3H/3He} = \lambda^{-1} \ln({}^{3}He_{trit}/{}^{3}H + 1) $$

The ${}^{3}H/{}^{3}He$ method of age dating groundwaters, relative to other methods which monitor the decrease in bomb-produced ${}^{3}H$ with time, is ideal, as it is relatively insensitive to any variations in the concentration of ${}^{3}H$ in recharge waters through time(1).

Residence ages varied from approximately 0.8 to 7.3 years (Table 4.2-3) and displayed a linear relationship with distance from recharge (Figure 4.2-1B). Groundwater velocities calculated on the basis of the ${}^{3}H/{}^{3}He$ ages and distance from recharge were approximately .09 to .25 m/day, similar to that determined by previous borehole dilution testing. Changes in the slope of the velocities (Figure 4.2-1B) were evident and may indicate: a) anisotropy in the hydrogeologic characteristics of the aquifer, b) decreasing groundwater velocities down the flow path due to decreasing hydraulic gradients, or c) biases in interpreting the isotopic data due to a relatively limited data set.

In summary, the ${}^{3}H/{}^{3}He$ age dating method has proved successful for characterizing aspects of a relatively shallow groundwater system. The linear trend of ${}^{3}He$ with distance suggests no diffusive loss of tritogenic ${}^{3}He$ from the aquifer groundwaters resulting in ${}^{3}H/{}^{3}He$ groundwater residence ages that are quite representative of the actual residence time for waters in the aquifer.

2) Noble gas analysis of deep groundwaters

A series of deep groundwater samples were collected from surface boreholes and during subsurface sampling programs at the Whiteshell Underground Research Laboratory and supplied to Chalk River Laboratories for development of noble gas isotopic analysis on ancient groundwaters. The samples were collected in copper tubes sealed with helium leak-tight clamps. Initial He, N_2, O_2, CO_2 and Ar concentrations supplied by Whiteshell indicated the waters contained substantial quantities of noble gases. To date several of these waters have been analyzed for their He and Ne isotopic compositions and concentrations to facilitate development of quantitative sample splitting methods for noble gas analysis by mass spectrometry. For the deep groundwaters, splitting of the samples before analysis was required as the samples typically contain several orders of magnitude more helium than is required for the high sensitivity noble gas mass spectrometer.

Degassing of the groundwater samples to obtain the dissolved gas constituents was done using the same method described for the $^{3}H/^{3}He$ method. A quadruple mass spectrometer was used initially to determine semi-quantitatively the amounts of total He in the sample before reducing the amounts of sample for quantitative noble gas mass spectrometry.

^{4}He concentrations in the groundwaters varied between 9.29×10^{4} and 9.89×10^{-3} ccSTP/g H_2O, which are several orders of magnitude above that expected for groundwaters in equilibrium with atmosphere at 6 ℃ (4.8×10^{-8} ccSTP/g H_2O - Table 4.2-4). $^{3}He/^{4}He$ ratios were near 10^{-8} indicating ^{4}He-enrichment in the groundwaters, relative to groundwaters in equilibrium with atmosphere ($^{3}He/^{4}He = 1.37 \times 10^{-6}$). Such high ^{4}He concentrations and low $^{3}He/^{4}He$ ratios for the groundwaters are typical of groundwaters from granitic rocks(6) and are identical to the noble gas concentrations in previously analyzed Whiteshell URL waters reported by Bottomley et. al. (1984)(5) (Figure 4.2-2).

Neon isotopic compositions and ratios were also measured on the groundwaters. Concentrations of neon in the groundwaters show evidence for excess air and also undersaturation due to bubble stripping during sampling; however, the neon concentrations are comparable to those expected for equilibrium solubility with atmosphere at 6 ℃ (Table 4.2-3). No corrections for excess He based on the neon analyses were done as the large amounts of nucleogenic He make any corrections for excess air meaningless. $^{21}Ne/^{20}Ne$ and $^{22}Ne/^{20}Ne$ ratios in the groundwaters show similar variations to URL groundwaters analyzed by Bottomley et. al. (1984)(5) (Figure 4.2-3) and suggest nucleogenic production of ^{21}Ne and ^{22}Ne by (α,n) and (n,α) reactions, the dominant mechanisms being,

$$^{18}O(\alpha,n)^{21}Ne$$
$$^{25}Mg(n,\alpha)\,^{22}Ne$$

The isotopic data suggest a correlation between increasing ^{4}He and ^{21}Ne, which may result from radiogenic ^{4}He produced by a decay of U and Th and ^{21}Ne produced from (α,n) reactions on ^{18}O.

The isotopic results obtained to date at Chalk River Laboratories on deep groundwaters from the Whiteshell URL are comparable to previous noble gas analyses on deep groundwaters reported by Bottomley et. al. (1984)(5). Procedures developed for degassing the groundwater samples to obtain the in situ gases and for splitting the samples have yielded quantitative and accurate results.

4.2.2 Determinations using accelerator mass spectrometry

1) ^{36}Cl

The precision in our measurements of known ^{36}Cl standards varies from 5% for $^{36}Cl/Cl$ ratios of E-11 to 10% for ratios of E-11, with measured values for "dead" KCl ranging between (0.5-2) E-14. Full procedural blanks are in good agreement with these "dead" KCl measurements. Recent experience in the analysis of water samples of unknown origin has shown that our error for ratios of

^{36}Cl/Cl of the same order of magnitude as our blanks is approximately 15%, dropping to 5% for ratios roughly 10 times higher than the blank Stable chlorine concentrations are determined by eluent-suppressed anion chromatography using a Dionex. In the concentration range of our samples, the precision is approximately 5. The lower limit of detection is 0.02 ppm.

A recent publication entitled, "Origin of groundwater salinity in the Lac du Bonnet granite, southeastern Manitoba, from ^{36}Cl measurements"(8), has plotted Cl concentrations against ^{36}C/Cl ratios measured in the Nuclear Structure Laboratory, University of Rochester. We have performed similar measurements on these waters, and as shown in Figure 4.2-4, our values are in good agreement with the earlier measurements. Ratios in the low Cl- shallow sub-surface waters agree well with local precipitation values.

We are currently studying a zone of near vertical recharge near Sturgeon Falls, Ontario, for which tritium and ^{3}H/^{3}He data have been used very successfully to date the time of recharge of the nuclear weapons testing peak(1). A plot of two sets of measurements is shown in Figure 4.2-5. The most recent data add support to our hypothesis that additions from a sand-gravel aquifer, or deep groundwaters seeping across the bedrock - overburden interface immediately beneath it, are causing increases in ^{36}Cl concentrations in the deepest samples. However, the very anomalous values measured in the near surface (2.1 m and 3 m) appear to be real. At the moment, we have no testable hypothesis to explain these higher than expected values.

2) ^{129}I

A technique for the concentration of I from samples of up to 60 L of groundwater has been developed at the Whiteshell Laboratories and tested on several URL groundwaters of varying salinity. The technique involves the use of ion exchange resin to concentrate iodine followed by differential elution and purification by organic phase extraction. Preliminary results indicate iodine recoveries of between 60 and 100. Stable iodide concentrations are determined by ICPMS at Trent University. The precision of these measurements is 10, with an LLD of 1 ppb. Reduced recoveries of the stable isotope have been observed at low mass levels, and the steps in the procedure at which these losses occur are being checked by the addition of ^{125}I tracer.

To date, the precision in our measurements of known standards of this isotope has been ~10% for an ^{129}I/I ratio of E-11, and ~15% for a ratio of E-12. A detailed search for the causes of the poor beam transmission frequently observed during these measurements has indicated that the presence of oxygen in the mounted sample (presumably in the oxide form), can decrease beam currents very effectively. Our routine method of sample preparation involves the recovery of I^- as AgI. Scanning electron microscopy has revealed the presence of Si, Al and Fe contamination in a number of our AgI sources, particularly those recovered from water samples. Any one of these elements could be coprecipitated or occluded in the oxide or hydrous form, particularly if present in the water in the colloidal state. We are currently testing other methods for iodine recovery, especially for water samples containing large amounts of organic material, which may interfere with preconcentration on ion exchange resin.

Methods of mounting admixtures of Au, AgBr, Nb, etc. to the source have been tested for their effect on current output. No significant relationship of current to mode of preparation was observed. The mass 128 peak seen in the data from the samples measured has been tentatively identified as tellurium, a common trace component of copper ores. (Our samples are mounted in copper cones.)

4.2.3 $^{11}B/^{10}B$ isotopic analysis

Development of the $^{11}B/^{10}B$ isotopic analysis method was done at McMaster University in conjunction with work done at Whiteshell Laboratories. Analyses are made using the method of negative-ion thermal ionization mass spectrometry (NTIMS) directly on nanogram amounts of samples without any preconcentration techniques. While this method prevents any isotopic fractionation of B prior to analysis (e.g., during preconcentration techniques) some fractionation has been found to occur during the NTIMS analysis itself. Correction factors determined from a boric acid isotopic standard are applied but some enhancement of ion yield may be occurring due to the presence of other (groundwater-derived) salts in the sample matrix. Work is continuing on this effect. Nevertheless, the preliminary results are promising and appear to indicate a trend of increasing $^{11}B/^{10}B$ with increasing groundwater salinity.

4.2.4 URL sampling program

1) Dissolved gas sampling

Preliminary analyses at CRL of the He and Ne gas contents of groundwater samples obtained in earlier sampling activities at the URL has shown the need for a modification of one of the gas sampling techniques used by AECL at the Whiteshell Laboratories. Groundwater samples taken at the surface directly from the pump discharge line have previously been adequate to medicate the relative concentrations of one gas with respect to another. However, they have often shown poor reproducibility of duplicates because of gas bubble formation due to pressure release in the pumping line. This can result in higher or lower gas concentrations than is actually present in the groundwater. The preliminary analyses at CRL have also shown this effect because some samples are under- or over-saturated with Ne (relative to atmospheric concentrations) indicating either bubble-stripping or preferential gas bubble entrainment. In all future work for the program, down-borehole sampling using a fully pressurized line will be used to prevent this phenomenon. In addition, because of the abundance of He in URL groundwaters and the sensitivity of the mass spectrometer at CRL, smaller groundwater samples are required for this analysis. The gas sample vessels will be modified therefore as part of future design and testing work.

2) URL sampling program

The design of the URL Sampling Program is essentially complete. It requires the careful sampling of groundwaters across a 1 km cross-section of flow path, from an elevated outcrop of the Lac du Bonnet granite south-east of the URL shaft, to a known low-lying discharge area to the north-west. Approximately 20 surface-collared boreholes lie along or near this section and a further 40 can be sampled from within the URL facility. A detailed chemistry is available for most of the permeable borehole zones that have been selected for special sampling and analyses in this project,

About 20 groundwater samples will be taken from the following locations:

(1) shallow and deep zones in the recharge area (to identify isotopic changes associated with flow of dilute groundwater recharge to depths of 200-400 m).

(2) brackish groundwaters in the intermediate flow-path at depths of 200-300 m (to examine isotopic changes caused by mixing with underlying saline groundwaters and uptake of salts from granite wall-rock along the flow-path), and;

(3) from brackish-saline groundwaters at depths of 10-200 m in the discharge area to estimate total resident time in the flow-path, and to determine principal rock-water interactions and sources of dissolved salts.

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Table 4.2-1 Stable Isotope Systems Commonly used for Characterizing Groundwaters

Isotope	Mass	Hydrologic Applications
H	1, 2	Possibly only truly conservative element in groundwaters, as water is dominant source of H. Can be used to determine paleoclimates, recharge elevations, water-rock interactions, fluid reservoirs and fluid evaporation.
O	18, 16	Non-conservative at elevated temperatures due to large reservoir of O in rocks which are ^{18}O-enriched. Used to predict paleoclimates during recharge, hydrothermal activity and water-rock interactions.
B	10, 11	Two isotopically-distinct reservoirs, seawater and crustal rocks, can be used to discriminate between marine and non-marine sources. Has been used to characterize both marine and non-marine waters and evaporite minerals. Ratio can be affected by adsorption of ^{10}B onto clays, leaching of ^{10}B from host rocks and rayleigh fractionation processes during progressive evaporation (similar to O and H isotopes).

Table 4.2-2 Summary of Radioisotopes and Noble Gases Commonly used in Hydrogeologic Applications

Isotope $(t_{1/2})$a	**Atmospheric sources**	**Lithospheric sources**	**Hydrologic applications**
^{3}H (12.34)	cosmogenic anthropogenic	^{6}Li(n,α)^{3}H	$H_2O<40$ years, travel time if input ^{3}H function known
^{3}He	atmosphere	^{3}H decay. primordial	mantle water origins and ^{3}H/^{3}He ages
^{4}He	atmosphere	U,Th α decay primordial	"old" waters in crust, and flow ages if system characterized
^{14}C (5736)	cosmogenic anthropogenic	^{14}N(n,p)^{14}C ^{18}O(n,α)^{14}C	residence ages if rock contribution of C-12 can be estimated
^{20}Ne	atmosphere	-	excess air in samples
^{21}Ne	atmosphere	^{18}O(α,n)^{21}Ne from U, Th α	"old" waters have more ^{21}Ne - similar uses to decay ^{4}He?
^{36}Cl (3 x 10^5)	cosmogenic anthropogenic	^{35}Cl(n,γ)^{36}Cl	residence ages of waters as old as 2 Ma in certain areas
			origin of Cl$^-$ if waters in equilibrium with rocks
			rates of infiltration based on depth to bomb pulse
^{129}I (1.7x10^7)	cosmogenic fission anthropogenic	^{238}U spontaneous	origins of water, residence ages of waters of 10^6 to 10^7 years if U, Th distributions, initial ^{129}I /I ratios and transfer of ^{129}I from rock to water are known

Table 4.2-3 Tritogenic ^{3}He, ^{4}He and Ne isotopic concentrations determined by noble gas mass spectrometry, tritium concentrations determined by liquid scintillation methods and ^{3}H/^{3}He ages for groundwaters collected from drillholes along aquifer flowpath. [from Noack and Kotzer, 1994]

Site	**^{3}H** (10^7 atm/g)	**^{3}He$_{trit}$** (10^{-14} cc/g)	**^{4}He** (10^{-8} cc/g)	**Ne** (10^{-7} cc/g)	**^{3}H/^{3}He age** (years)
c179-2	4.72	10.39	7.58	2.72	1.03
c179-3	4.72	10.80	7.71	2.63	1.07
c136-2	4.65	7.96	-	1.89	0.81
c134-1	5.12	48.75	6.51	2.39	4.09
c134-2	5.10	50.99	6.91	2.48	4.27
c134-3	5.26	47.38	-		3.89
c130-1	4.56	84.21	6.43	2.29	7.23
c130-2	4.55	78.63	5.89	2.02	6.84
c130-3	4.68	80.86	6.79	2.56	6.84
c133-2	4.93	88.33	6.35	2.32	7.06
air solubility at 6 C		6.323	4.65	2.10	

Table 4.2-4 Preliminary He and Ne isotopic results for WNRE samples

Sample No.	**^{4}He** (cc STP/g H_2O)	**Ne**	**^{3}He/^{4}He**	**^{22}Ne/^{20}Ne**	**^{21}Ne/^{20}Ne**
ATK8-14-12DH	9.29×10^{-4}	6.2×10^{-7}	0.82×10^{-8}	0.10194	0.00293
B37-1-2A	4.43×10^{-3}	-	1.01×10^{-8}	0.10374	0.00309
WB1-7-8A	9.89×10^{-3}	1.7×10^{-7}	0.93×10^{-8}	0.11678	0.01304
Solubility and equilibrium ratios in air (5 C)	4.8×10^{-8}	2.12×10^{-7}	1.37×10^{-6}	0.10219	0.00298

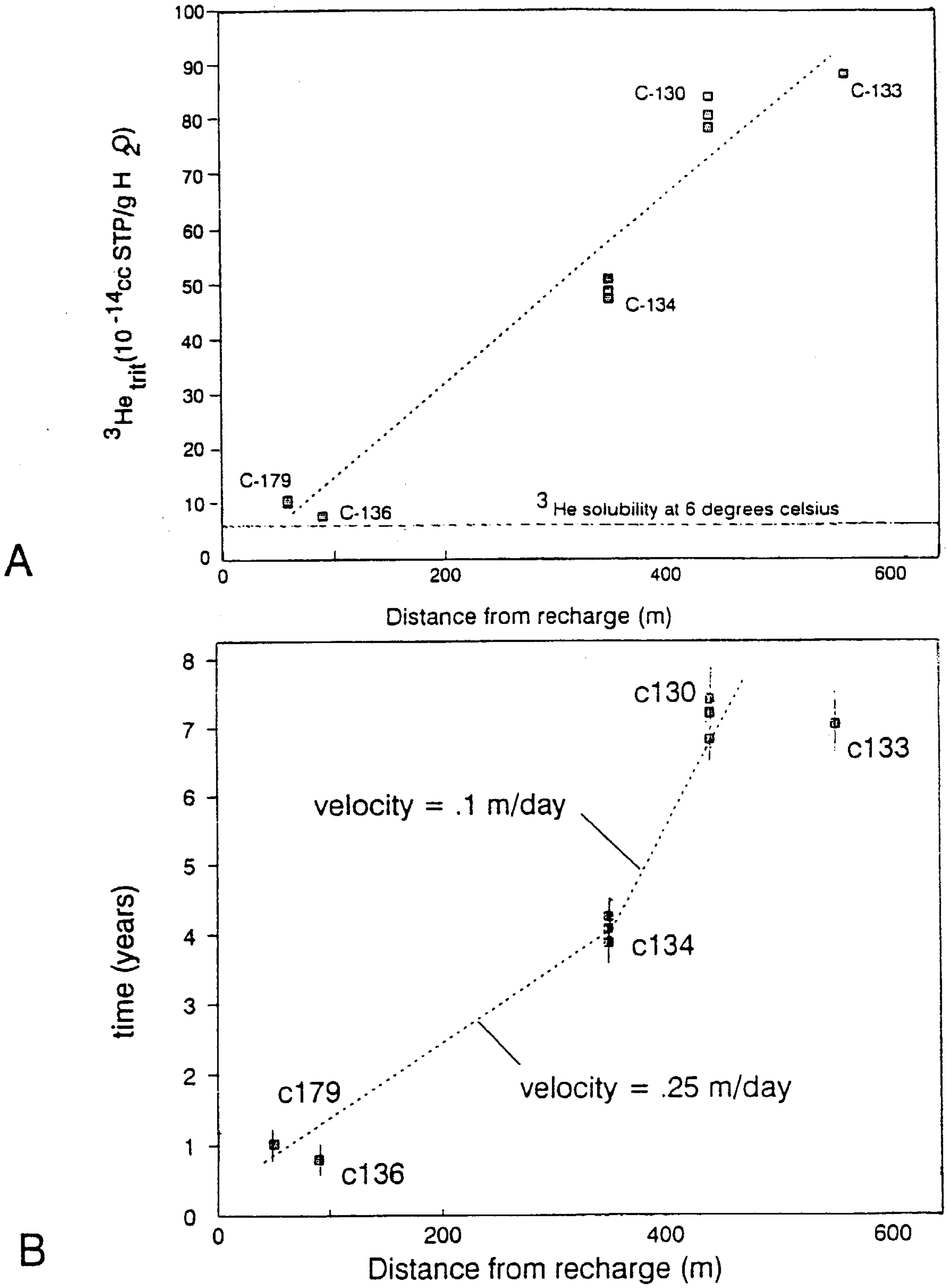

Fig.4.2-1 A) Linear increase in tritiogenic ^{3}He with increasing distance from aquifer recharge suggesting negligible diffusive loss of helium from the groundwaters. B) Increase in ^{3}H/^{3}He ages with increasing distance from aquifer recharge (see Noack and Kotzer, 1994).

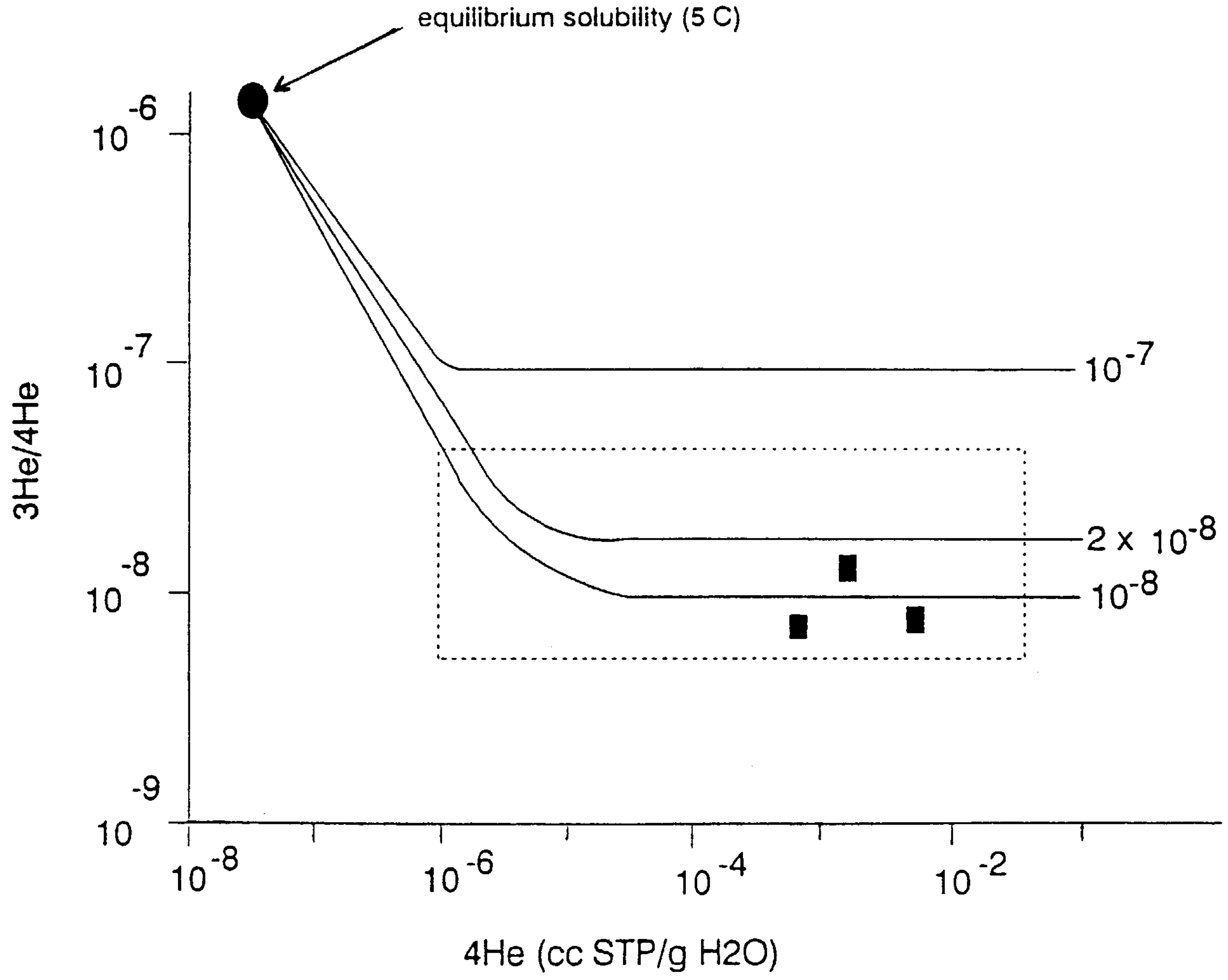

Fig.4.2-2 Plot of ^{3}He/^{4}He ratios versus ^{4}He concentrations for Whiteshell groundwaters analyzed to data at Chalk River Laboratories (solid squares). Curves indicate the expected trends in ^{4}He concentrations for subsurface ^{3}He/^{4}He production rates of between 10^{-7} and 10^{-8}. Field outlined by dashed rectangle indicates range of helium isotopic data for previously analyzed Whiteshell groundwaters reported by Bottomley et al. (1984).

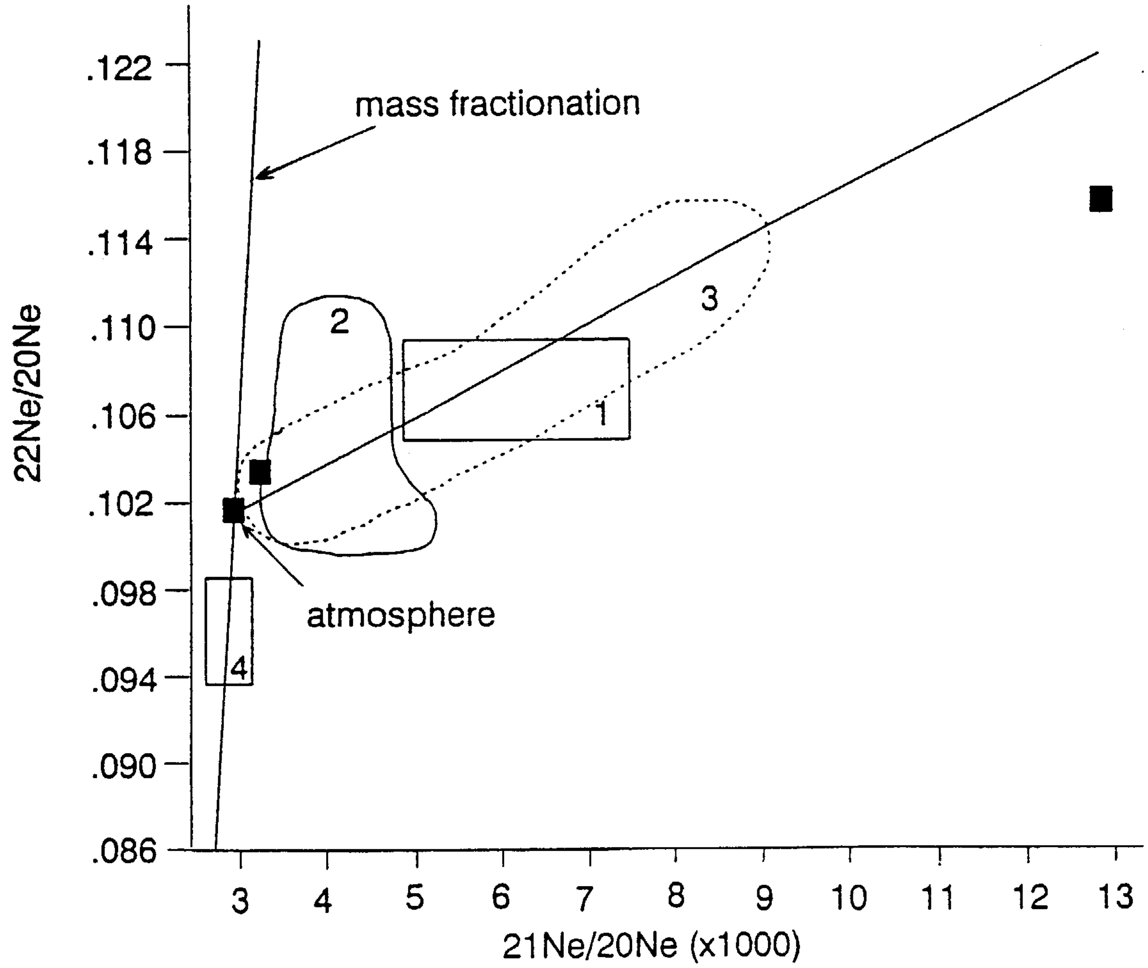

Fig.4.2-3 $^{22}Ne/^{20}Ne$ and $^{21}Ne/^{20}Ne$ ratios for Whiteshell groundwaters analyzed at Chalk River Laboratories (solid squares). Field indicated represent: 1) crustal natural gases; 2) crustal rocks; 3) neon isotopes in Whiteshell waters reported by Bottomley et al. (1984) (A least square regression curve for Whiteshell waters is shown.); 4) ancient granites.

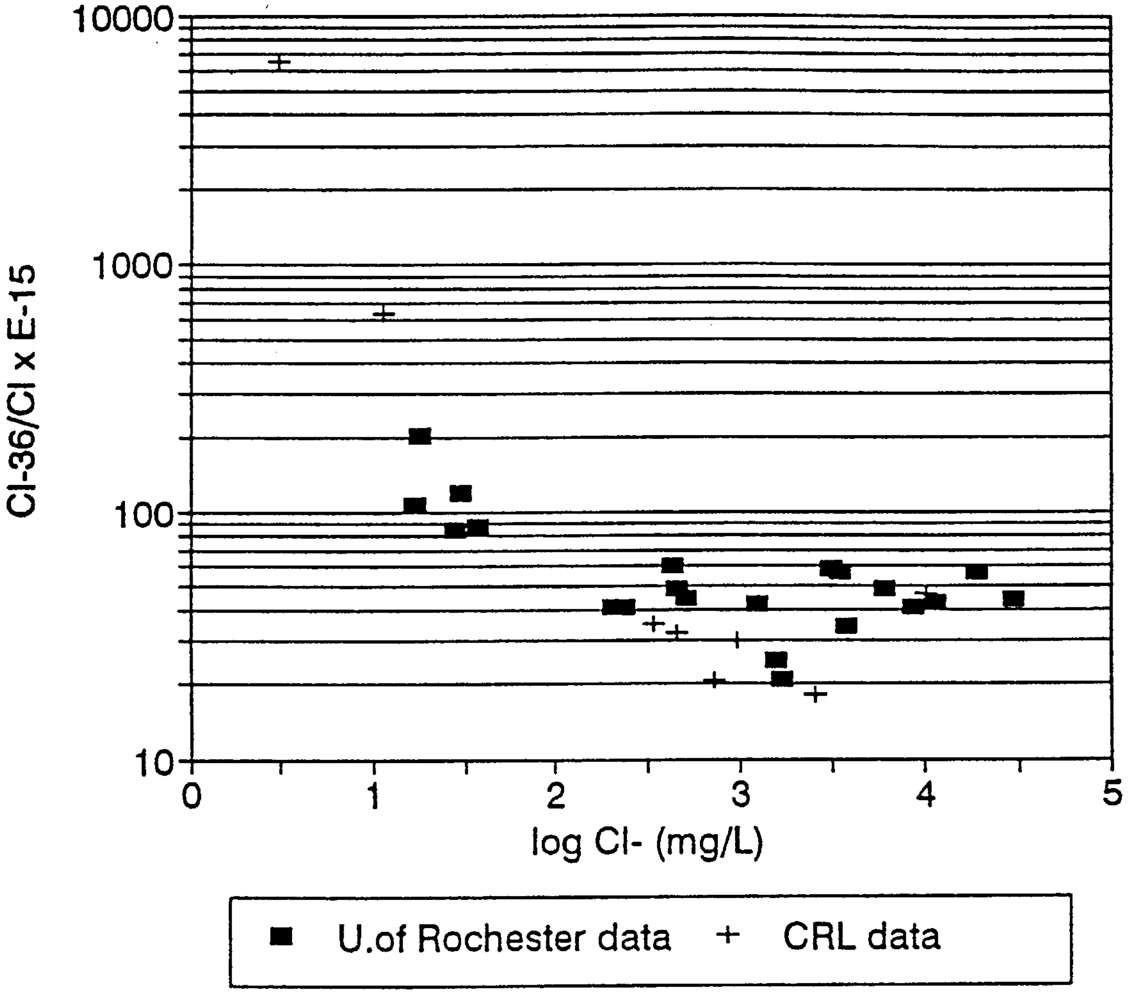

Fig.4.2-4 Variation of ^{36}Cl/Cl ratio with log Cl$^-$ concentration in groundwaters from the Lac du Bonnet granite, and some borehole leaching experiment waters (Gascoyne et al., 1994).

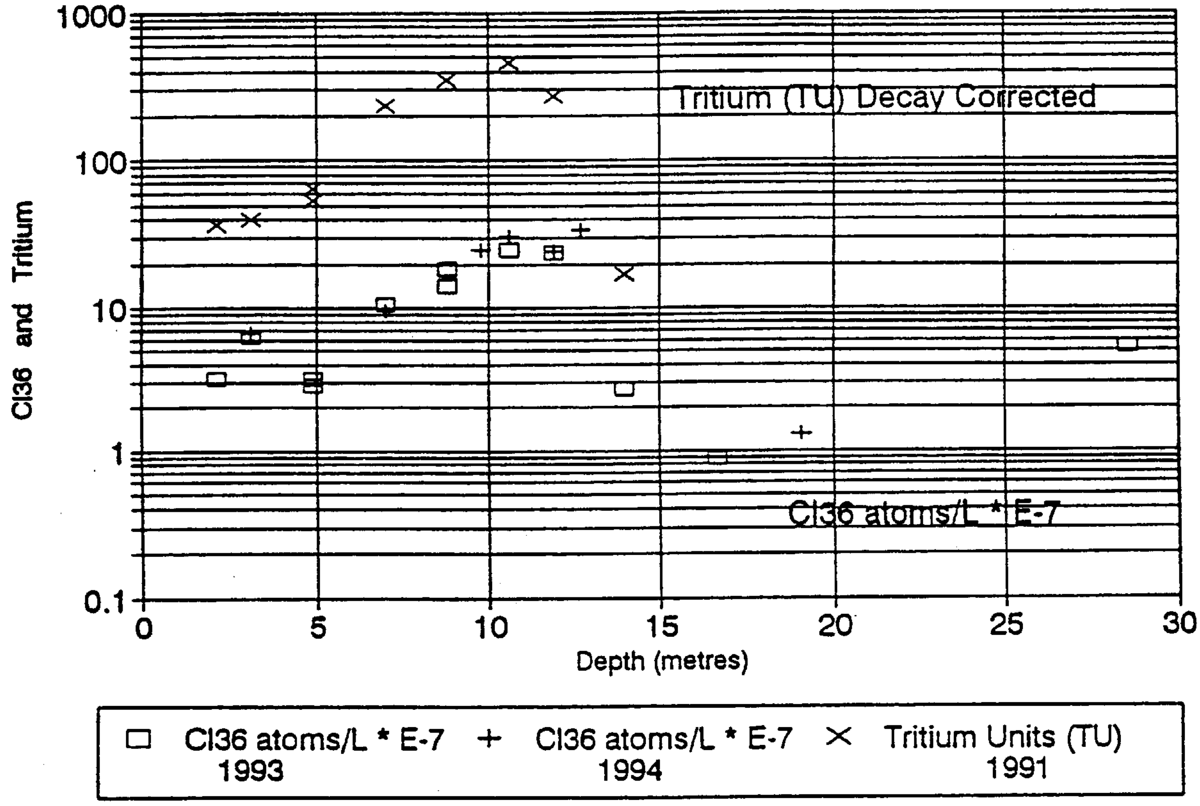

Fig.4.2-5 ^{36}Cl/Cl ratios in zone of near vertical recharge, Sturgeon Falls, Ontario (tritium data from Solomon et al., 1993).

5. GROUNDWATER FLOW MODEL DEVELOPMENT (PROGRAM 2, PROJECT 2)

The overall objective of this task is to develop an improved basis for modelling groundwater flow and radionuclide transport through unconsolidated heterogeneous geologic media. The specific objective is to develop a theoretical basis from which an improved methodology for measuring field hydrogeological parameters can be estimated.

H. Kimura, M. Munakata

The most attractive point of the Twin Lake experiments for modelers is to get some information about tracer transport in a natural geological media. These experiments show that tracer movement in the Twin Lake aquifer is strongly affected by a geologic heterogeneity. It is important to estimate flow parameters of heterogeneous media in this kind of simulation. To estimate flow parameters and generate heterogeneous flow field are interest to us.

We have initiated literature reviews of hydrological and geostatistical methods used for characterizing heterogeneities in geologic media, and the development of geostatistical models will be used for analyses of the Twin Lake data.

G. Moltyaner, M. Klukas, A. Wills, L. Yamazaki

We have completed a brief review of geophysical methods used for characterizing heterogeneities in geologic media. The review concentrates on methods relevant to the problem of groundwater flow and contaminant transport, and subdivides these methods by scale and location (borehole vs. surface surveys) and by the physical principle underlying each method (electro-magnetic, acoustic, nuclear etc.). For each method we have specified the type of information obtained (petrophysical or hydrological aquifer characterization, geological and geophysical description of subsurface structure) and how the information can be used as input for flow and transport models (parameter input, definition of boundary conditions, etc.).

In reviewing geological heterogeneity characterization methods, we have subdivided them into qualitative (visual) and quantitative deterministic or stochastic methods. Qualitative methods, based mostly on the depositional scenario of sediments, are useful for the development of conceptual heterogeneity model. Quantitative deterministic methods assume that a textural property such as the effective grain diameter is distributed in space in a known way. Stochastic methods treat the grain size as a random field. We have searched the available literature for 'recipes' on how to relate the effective grain diameter distribution and variability in the groundwater flow characteristics. The review of literature showed that there is a need to start from first principles and develop a new way for relating the effective grain size distribution and groundwater flow velocity.

We have been successful in establishing empirically the correlation between flow velocity and effective grain diameter (Figure 5-1). An effort to explain theoretically the observed correlation is underway. We have organized a special AGU session on the topic of heterogeneity characterization and shall make two presentations on experimental observations and theoretical developments at this session, We have also been successful in bringing more researches into the program through bilateral international collaborations.

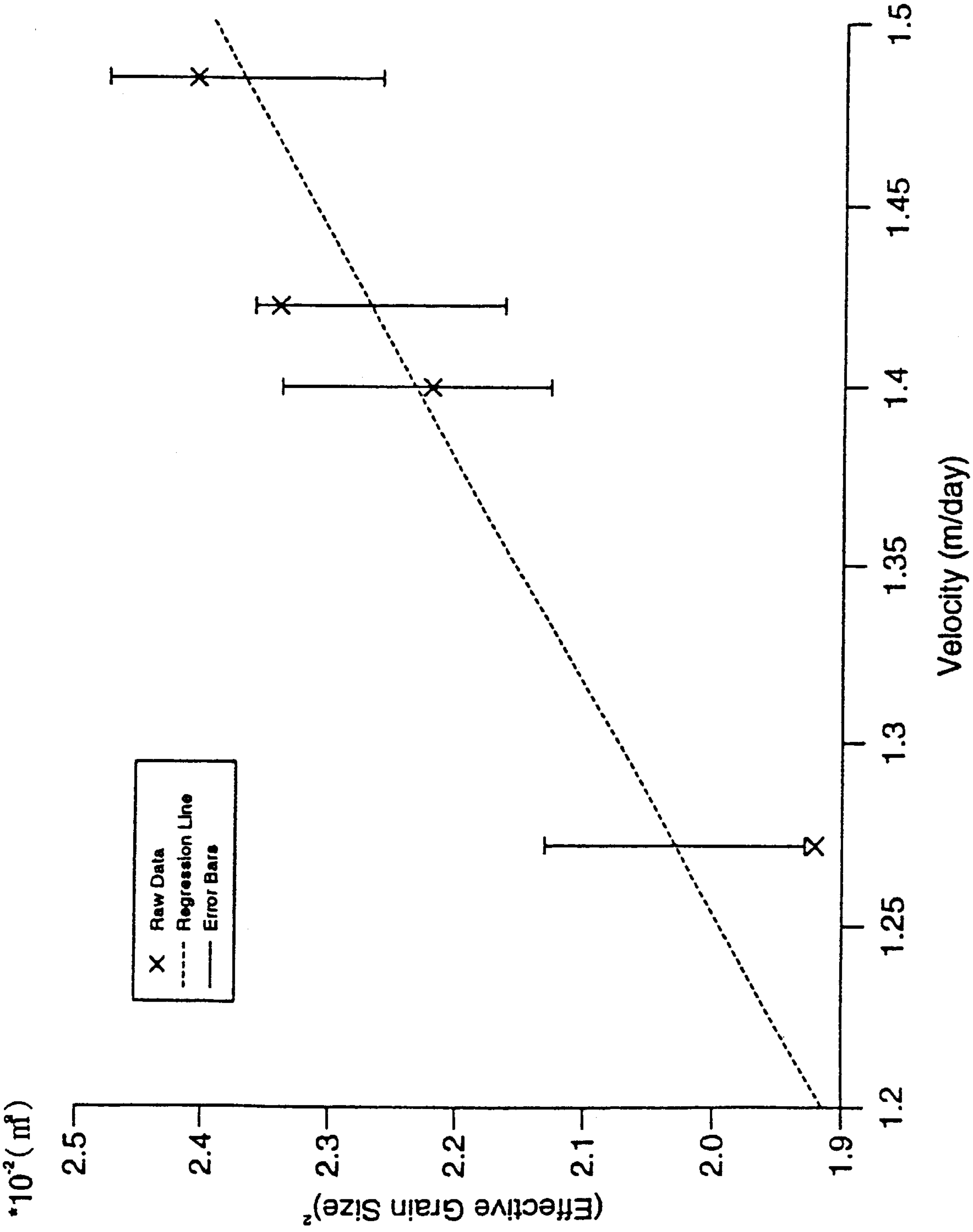

Fig.5-1 Correlation between velocity and effective grain size for individual layers.

国際単位系（SI）と換算表

表1　SI基本単位および補助単位

量	名　称	記　号
長　さ	メートル	m
質　量	キログラム	kg
時　間	秒	s
電　流	アンペア	A
熱力学温度	ケルビン	K
物質量	モル	mol
光　度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表3　固有の名称をもつSI組立単位

量	名　称	記号	他のSI単位による表現
周波数	ヘルツ	Hz	s^{-1}
力	ニュートン	N	$m\cdot kg/s^2$
圧力，応力	パスカル	Pa	N/m^2
エネルギー,仕事,熱量	ジュール	J	N·m
工率，放射束	ワット	W	J/s
電気量，電荷	クーロン	C	A·s
電位，電圧，起電力	ボルト	V	W/A
静電容量	ファラド	F	C/V
電気抵抗	オーム	Ω	V/A
コンダクタンス	ジーメンス	S	A/V
磁束	ウェーバ	Wb	V·s
磁束密度	テスラ	T	Wb/m^2
インダクタンス	ヘンリー	H	Wb/A
セルシウス温度	セルシウス度	℃	
光束	ルーメン	lm	cd·sr
照度	ルクス	lx	lm/m^2
放射能	ベクレル	Bq	s^{-1}
吸収線量	グレイ	Gy	J/kg
線量等量	シーベルト	Sv	J/kg

表2　SIと併用される単位

名　称	記　号
分，時，日	min，h，d
度，分，秒	°，′，″
リットル	l，L
トン	t
電子ボルト	eV
原子質量単位	u

$1\ eV = 1.60218\times10^{-19}J$

$1\ u = 1.66054\times10^{-27}kg$

表4　SIと共に暫定的に維持される単位

名　称	記　号
オングストローム	Å
バーン	b
バール	bar
ガル	Gal
キュリー	Ci
レントゲン	R
ラド	rad
レム	rem

$1\ Å = 0.1nm = 10^{-10}m$

$1\ b = 100fm^2 = 10^{-28}m^2$

$1\ bar = 0.1MPa = 10^5Pa$

$1\ Gal = 1cm/s^2 = 10^{-2}m/s^2$

$1\ Ci = 3.7\times10^{10}Bq$

$1\ R = 2.58\times10^{-4}C/kg$

$1\ rad = 1cGy = 10^{-2}Gy$

$1\ rem = 1cSv = 10^{-2}Sv$

表5　SI接頭語

倍数	接頭語	記　号
10^{18}	エクサ	E
10^{15}	ペタ	P
10^{12}	テラ	T
10^9	ギガ	G
10^6	メガ	M
10^3	キロ	k
10^2	ヘクト	h
10^1	デカ	da
10^{-1}	デシ	d
10^{-2}	センチ	c
10^{-3}	ミリ	m
10^{-6}	マイクロ	μ
10^{-9}	ナノ	n
10^{-12}	ピコ	p
10^{-15}	フェムト	f
10^{-18}	アト	a

(注)

1. 表1－5は「国際単位系」第5版，国際度量衡局 1985年刊行による。ただし，1 eVおよび1 uの値はCODATAの1986年推奨値によった。
2. 表4には海里，ノット，アール，ヘクタールも含まれているが日常の単位なのでここでは省略した。
3. bar は，JISでは流体の圧力を表わす場合に限り表2のカテゴリーに分類されている。
4. EC閣僚理事会指令では bar，barnおよび「血圧の単位」mmHgを表2のカテゴリーに入れている。

換　算　表

力	$N(=10^5dyn)$	kgf	lbf
	1	0.101972	0.224809
	9.80665	1	2.20462
	4.44822	0.453592	1

粘　度　$1\ Pa\cdot s(N\cdot s/m^2) = 10\ P$(ポアズ)$(g/(cm\cdot s))$

動粘度　$1m^2/s = 10^4St$(ストークス)(cm^2/s)

圧力	MPa(=10bar)	kgf/cm^2	atm	mmHg(Torr)	$lbf/in^2(psi)$
	1	10.1972	9.86923	7.50062×10^3	145.038
	0.0980665	1	0.967841	735.559	14.2233
	0.101325	1.03323	1	760	14.6959
	1.33322×10^{-4}	1.35951×10^{-3}	1.31579×10^{-3}	1	1.93368×10^{-2}
	6.89476×10^{-3}	7.03070×10^{-2}	6.80460×10^{-2}	51.7149	1

エネルギー・仕事・熱量	$J(=10^7\ erg)$	kgf·m	kW·h	cal(計量法)	Btu	ft·lbf	eV
	1	0.101972	2.77778×10^{-7}	0.238889	9.47813×10^{-4}	0.737562	6.24150×10^{18}
	9.80665	1	2.72407×10^{-6}	2.34270	9.29487×10^{-3}	7.23301	6.12082×10^{19}
	3.6×10^6	3.67098×10^5	1	8.59999×10^5	3412.13	2.65522×10^6	2.24694×10^{25}
	4.18605	0.426858	1.16279×10^{-6}	1	3.96759×10^{-3}	3.08747	2.61272×10^{19}
	1055.06	107.586	2.93072×10^{-4}	252.042	1	778.172	6.58515×10^{21}
	1.35582	0.138255	3.76616×10^{-7}	0.323890	1.28506×10^{-3}	1	8.46233×10^{18}
	1.60218×10^{-19}	1.63377×10^{-20}	4.45050×10^{-26}	3.82743×10^{-20}	1.51857×10^{-22}	1.18171×10^{-19}	1

1 cal＝ 4.18605J（計量法）

＝ 4.184J（熱化学）

＝ 4.1855J（15℃）

＝ 4.1868J（国際蒸気表）

仕事率　1 PS(仏馬力)

＝ 75 kgf·m/s

＝ 735.499W

放射能	Bq	Ci
	1	2.70270×10^{-11}
	3.7×10^{10}	1

吸収線量	Gy	rad
	1	100
	0.01	1

照射線量	C/kg	R
	1	3876
	2.58×10^{-4}	1

線量当量	Sv	rem
	1	100
	0.01	1

（86年12月26日現在）

RESEARCH ON RADIONUCLIDE MIGRATION UNDER SUBSURFACE GEOCHEMICAL CONDITIONS – JAERI/AECL PHASE II COLLABORATIVE PROGRAM YEAR 1 – (JOINT RESEARCH)