JNC TN1200 2005-006

~~PNC ZB-0223 93-001~~

PNC/AEA(FC)-H-001 and S-001

13

~~限定資料~~

PNC／UKAEA技術協力

（熱力学データベースの構築及び吸着メカニズム）

―― 第1回専門家会議報告 ――

（海外出張報告）

平成5年12月

動力炉・核燃料開発事業団

本資料についての

〒107　東京都

動

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JNC TN1200 2005-006

~~限 定 資 料~~

~~PNC ZB 0223 93-001~~

PNC/UKAEA(FC)-H-001 and S-001

1993年12月

ＰＮＣ／ＵＫＡＥＡ技術協力

（熱力学データベースの構築及び吸着メカニズム）

── 第１回専門家会議報告 ──

（海外出張報告）

報告者：佐々木憲明[1)]

宮原　　要[1)]

吉川　英樹[2)]

要　旨

ＰＮＣ／ＡＥＡ協定に基づく、地層処分分野における第１回専門家会議が７月19日から３日間にわたり、英国ハーウェル研究所で開催された。熱力学データベースの開発・改良及び核種の吸着機構について双方の研究成果の報告を行い、協力の進め方について打ち合わせた。

その結果、今後世界的にデータのほとんどない重要元素の溶解度について情報交換を行うこと、核種の吸着に対する鉱物表面特性の影響を把握する実験を双方で検討する等の合意に達した。ＡＥＡは、英国の中低レベル放射性廃棄物の地層処分の安全評価及びそれに関連する研究開発を行っており、多くの実績を上げているが、今回その研究開発状況についても詳しく知ることができた。次回は、日本で開催する予定である。

本会議に加え、７月23日に英国における中低レベル放射性廃棄物処分の実施責任機関であるＵＫ Nirex社を訪問し、その活動の現状を調査したので合わせて報告する。

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1)　本社 環境技術開発推進本部 処分研究グループ

2)　東海事業所 環境技術開発部 地層処分開発室

BACK ROW:

Dr Adam Chambers, Mr Graham Baston, Dr Cherry Tweed, Mrs Ruth McCrohon, Dr Timothy Heath, Mr Malcolm Brownsword, Dr John Berry, Ms Ann Haworth, Dr Stephen Williams

FRONT ROW:

Dr Susan Sharland, Dr Noriaki Sasaki, Dr Keith Winters, Mr Kaname Miyahara, Mr Hideki Yoshikawa

目　次

1. 地層処分に係る熱力学データベース及び吸着機構に関するＡＥＡとの第１回専門家会議の概要

(1) 期　日

平成５年７月19日～21日

(2) 場　所

ＨＡＲＷＥＬＬ研究所

(3) 主な出席者

〔ＡＥＡ〕

Dr. K. H. Winters(Division Manager)

Dr. S. M. Sharland(Department Manager)

Dr. J. A. Berry （本協力の中の収着関係のテクニカルコーディネータ）

Dr. C. J. Tweed （本協力の中の熱力学データベース関係のテクニカルコーディネータ）

その他、Dr. S. M. Sharlandの率いる Chemecal Studies Departmentのメンバー多数。

〔動　燃〕

佐々木憲明（本社環境本部　処分研究グループ）
（本協力の中の吸着及び熱力学データベース関係のテクニカルコーディネータ）

宮原　　要（本社環境本部　処分研究グループ）

吉川　英樹（東海事業所環開部　地層処分開発室）

(4) 情報交換

双方の地層処分に係る研究開発の現状概要、熱力学データベース及び吸着機構の研究について、最近の状況を相互に発表。

(5) 合意事項

① 熱力学データベースの開発に関しては、次回の会議にて、世界的にもデータのほとんどないSe、Sn、Pdの溶解度について双方の情報の交換と議論を行う。

② 吸着機構の研究に関しては、吸着に関与する鉱物表面特性の影響を把握するため、純粋な物質を用いる実験を検討する。

ＡＥＡは、Al_2O_3 を用いる実験及び評価を行う。動燃は、ＡＥＡの実験状況を参考に検討する。また、緩衝材に対する吸着についても同様の評価を行うため、日本国内でFeを含まない（Feが吸着特性に大きく影響するため）純粋な合成モンモリロナイトの入手の可能性について調査する。

③　ＡＥＡの開発した熱力学データベースＨＡＴＣＨＥＳ（最新版）を、ＡＥＡは動燃に譲渡する（すでに入手した）。

（ＨＡＲＰＨＲＱ最新版及びＣＨＥＱＭＡＴＥについては、コストが必要とのこと）

④　高塩濃度溶液（１モル以上）で測定した熱力学データについて、イオン強度の補正を行う方法の開発については、動燃は高塩濃度の地下水を現在想定していないため、協力は当面保留する。

（ＡＥＡは、シェラフィールドサイトの地下水に、最高で海水の６倍の高濃度塩水を検出している。）

⑤　雰囲気制御グローブボックス内の 0.01ppm程度の CO_2濃度の測定法の詳細について、動燃はＡＥＡに連絡する。

⑥　次回の専門家会議は、日本にて平成６年（1994年）10月に、ＭＲＳ94京都会議の後に開催する。

AGENDA OF MEETING BETWEEN PNC AND AEA ON COLLABORATION ON RADIOACTIVE WASTE MANAGEMENT HELD AT HARWELL, UK.

19th-23rd July 1993

DAY 1: Monday 19th July 1993

1.1 Introductions and Welcome Address

1.2 Overview of AEA RDD Activities (Dr. S. Sharland)

1.3 Overview of PNC R&D Activities (Dr. N. Sasaki)

1.4 Presentation by AEA on Thermodynamic Databases and Speciation
  - HARPHRQ modelling including sorption modelling for PNC (Dr. T. G. Heath)
  - Coupled-chemistry transport and fundamental research on implementing sorption calculations (Ms. A. Haworth)
  - Coupled-chemistry transport and closely linked to assessment work (Dr. A. V. Chambers)

1.5 Presentation by PNC on Thermodynamic Database and Speciation
  - Status of PNC's Thermodynamic Database (Mr. K. Miyahara)
  - Solubility Measurements (Mr. H. Yoshikawa)
  - Measurements and Analyses of U in Groundwater of the Tono Mine as a Validation of the Database (Mr. K. Miyahara)
  - Analysis of the chemical reactions of the water-iron-glass system (Mr. K. Miyahara)

DAY 2: Tuesday 20th July 1993

2.1 Presentation by AEA on Understanding the Mechanisms of Sorption
  - Comparison of Batch and Through-Diffusion methods (Dr. J. A. Berry)
  - Discussion of Modelling Techniques for Batch and Through-diffusion Experiments (Dr. A. Haworth & Dr. J. A. Berry)

2.2 Presentation by PNC on Understanding the Mechanisms of Sorption
  - Status of Surface Complexation Model (Mr. H. Yoshikawa)
  - Sensitivity Analysis for Sorption of Uranium (Mr. K. Miyahara)
  - Validation Model for Sorption of Neptunium (Mr. K. Miyahara)

2.3 Round-up Discussion on Non-Commercial Collaboration
  - Ionic Strength Corrections
  - HATCHES Database

- Investigation of Sorption Behaviour
- Date of Next Meeting

DAY 3: Wednesday 21st July 1993

3.1 Presentation by AEA on other Experimental Studies

- Groundwater Evolution (Ms. A. Haworth)
- Glass Dissolution (Mr. J. A. C. Marples)
- Colloids (Dr. M. P. Gardiner)
- Microbial Action Under Repository Conditions (Dr. A. Rosevear)

3.2 Tour of Facilities

- Main Radiochemistry Building
- Non-active Laboratories
  1) Organic Degradation Work
  2) Physical Properties of Geological Materials
- Surface Analysis Facilities

DAY 4: Friday 23rd July 1993

4. Presentation by AEA on Performance Assessment

- Groundwater Modelling (Dr. A. Herbert)
- NAMMU/ADVIZE Demonstration (Mr. A. Cliffe & Mr. S. Morris)
- Hydrogeological Characterisation (Dr. T. Lineham)
- Introduction of Assessments (Mr. D. Billington)
- Gas Generation (Dr. P. Agg)
- Gas Migration (Dr. W. Rodwell)

PNC/AEA Agreement of Topics for their Collaboration on Radioactive Waste Management

19th -23rd July 1993

1. Discussions on topics for collaboration between PNC and AEA Technology in the field of radioactive waste management were held between 19th and 23rd July 1993 at Harwell.

2. Two of the three topics agreed as potentially suitable for future collaboration by Dr G Owen and Dr H Kaneko at their meeting in Tokyo on 17th July 1992 were discussed. The topics discussed were:

   Topic a) Thermodynamic database and speciation; and

   Topic b) Understanding the mechanisms of sorption.

Thermodynamic Database and Speciation

3. The agreements reached on the topic of thermodynamic database and speciation were:

   i) PNC and AEA will discuss the results of solubility experiments on Se, Sn, Pd at the next meeting;

   ii) AEA will model the solubility data on Se, Sn, Pd and Nd and amend HATCHES, as appropriate. The version of HATCHES containing these data (referenced to PNC) will be sent to PNC and the NEA.

Understanding the Mechanisms of Sorption

4. A work plan for the collaboration work on the topic of understanding better the mechanisms of sorption was agreed. The work would take place in three stages. More details of the work such as experimental conditions will be discussed before the start of the work.

Stage 1 - Aluminium Oxide Work

   i) AEA plan to carry out batch sorption experiments with aluminium oxide to test the suitability of this material for this investigation.

   ii) If the batch sorption experiments are successful, then AEA would send PNC pressed discs of aluminium oxide for in-diffusion experiments.

iii) If the batch sorption experiments with aluminium oxide are not successful then AEA and PNC would jointly choose an alternative mineral to investigate.

iv) AEA would model the batch sorption experiments with HARPHRQ and PNC would model the results with HYDRAQL; then an intercomparison of results would be made. AEA would also model the through-diffusion experiments with CHEQMATE.

Stage 2 - Goethite Work

i) AEA would carry out batch sorption and reservoir-depletion experiments using goethite.

ii) PNC would carry out in-diffusion experiments.

Stage 3 - Montmorillonite Work

i) PNC will check the possibility of purchasing synthesised montmorillonite, including an iron free version. When iron free montmorillonite is available, PNC would supply AEA with 20g of it.

ii) AEA would press part of the iron-free montmorillonite into discs, some of which would be sent to PNC.

iii) AEA would carry out batch sorption and through-diffusion experiments.

iv) PNC would carry out in-diffusion experiments with the iron-free montmorillonite discs prepared by AEA.

5. Further modelling studies on stages 2 and 3 would be discussed when experimental results are available and when modelling studies in stage 1 (iv) have been performed.

6. The programme will be reviewed regularly as work progresses. However, members of staff from AEA and PNC will meet to discuss the progress in the collaboration in Japan, in October 1994, after the MRS meeting.

7. It is understood by the parties that each party's work, as detailed above are supported on an annual basis by their own organisation, subject to internal reviews. Any changes to the programme will be communicated to the other party as soon as reasonably practicable.

[redacted] [redacted] [redacted]

N. Sasaki J.A. Berry C.J. Tweed

RMC008.DOC

24 September, 1993

MINUTES OF MEETING BETWEEN PNC AND AEA ON COLLABORATION ON RADIOACTIVE WASTE MANAGEMENT HELD AT HARWELL, UK.

19th - 23rd July 1993

DAY 1: 19th July 1993

1.1 Introductions and Welcome Address

The day began at 0930 with formal introductions.

Those present were:

Dr N Sasaki	PNC Tokyo
Mr K Miyahara	PNC Tokyo
Mr H Yoshikawa	PNC Tokai
Dr S M Sharland	AEA D&W Harwell
Dr J A Berry	AEA D&W Harwell
Dr S J Williams	AEA D&W Harwell
Mrs R McCrohon	AEA D&W Harwell
Dr C J Tweed	AEA D&W Harwell
Ms A Haworth	AEA D&W Harwell
Mr M Brownsword	AEA D&W Harwell
Mr G M N Baston	AEA D&W Harwell
Dr T G Heath	AEA D&W Harwell
Dr A V Chambers	AEA D&W Harwell
Dr D Brear	AEA D&W Harwell
Dr K H Winters	AEA D&W Harwell

A welcome address was then given by Dr K H Winters.

1.2 Overview of AEA RDD Activities

A presentation of the management structure within Radwaste Disposal Division, and an overview of the wide range of activities undertaken in the Division was given by Dr Sharland. The following discussion arose from the presentation.

Q. *KM (PNC).* How is AEA involved in safety assessments for Nirex?

A. *SMS (AEA).* AEA are the prime contractor on the post-closure safety assessment work for Nirex. We maintain close contacts with Nirex throughout the work.

Q. *NS (PNC).* Do AEA use guidelines for cut-off of the probability of events occurring?

A. *SMS (AEA).* The probabilities of events and scenarios are generally included in the risk assessments.

Q. *NS (PNC).* On the overhead of predicted timescales for the conditions in the repository, was it correct that chemical containment will persist for 100,000 years?

A. *SMS (AEA).* Yes, that is our best estimate at the current time, based on choosing a site with low groundwater flow and sufficient quantity of cement to buffer the pH.

Q. *KM (PNC).* On the overhead of near field porewater toxicity, when does the timescale start from?

A. *SMS (AEA).* From the time when the containment of the waste is breached.

Q. *NS (PNC).* What period of containment is assumed for these calculations?

A. *SMS (AEA).* For this calculation it was assumed that there was no containment. We also perform studies on how containers fail and the consequences to the activity in the near field.

Q. *KM (PNC).* How many containers will be in the repository?

A. *SMS (AEA).* Current figures are that more than 400,000 individual waste packages will be emplaced in the LLW/ILW repository up to 2030.

1.3 Overview of PNC R&D Activities

A presentation of the R&D activities of PNC, focusing on HLW disposal, was given by Dr Sasaki. Dr Sasaki gave copies of the latest research papers from PNC and a summary of the "H-3" report to AEA.

The following questions arose from the presentation.

Q. *SMS (AEA).* (Relates to overhead of position of radioactive waste related sites in Japan). Is the Kamaishi mine deeper than the Tono mine?

A. *NS (PNC).* Yes, it is deeper and there are a greater range of experiments.

Q. *JAB (AEA).* From which mine did the granodiorite supplied by PNC for experiments at Harwell come from?

A. *HY (PNC).* The granodiorite came from the Tono mine.

Q. *CJT (AEA).* The overhead of the Performance Assessment Model mentioned solubility and corrosion but did not appear to mention sorption; why?

A.	*NS (PNC).*	Sorption, desorption and precipitation are considered under Nuclide Transport in EBS.
Q.	*DB (AEA).*	What sort of model is used for the fracture work?
A.	*KM (PNC).*	A single phase fracture model is used. Channelling or network models are not used though they are being developed.
Q.	*SMS (AEA).*	(Relates to overhead on major tests in ENTRY project). We are interested to see that experiments to investigate coupling are being carried out at PNC as not many experiments of this type are being done. When will these experiments be carried out and when will results be available?
A.	*NS (PNC).*	They will be completed as soon as possible.

1.4 Presentation by AEA on Thermodynamic Databases and Speciation

Dr C J Tweed, head of Geochemical Modelling Section, first introduced her colleagues and described their fields of work.

Dr T G Heath	HARPHRQ modelling including sorption modelling for PNC.
Ms A Haworth	Coupled-chemistry transport and fundamental research on implementing sorption calculations.
Dr A V Chambers	Coupled-chemistry transport and closely linked to assessment work.

Dr Tweed then went on to say how she would cover the background to the three research areas listed below and that Ms Haworth would then go into more specific details on these subjects. The research areas covered by Dr Tweed and Ms Haworth were as follows:

1. thermodynamic database validation;
2. modelling of uranium in groundwater (natural analogue work and HARPHRQ); and
3. ionic strength corrections (including experience from the CHEMVAL project).

Dr Tweed and Ms Haworth suggested that two possible areas for collaboration with PNC were the thermodynamic database and the ionic strength corrections.

The following questions and comments arose from Dr Tweed's presentation.

Q.	*HY (PNC).*	Was the Ni and Cr mentioned in the overheads from engineered materials?
A.	*CJT (AEA).*	The Ni and Cr are from components of a number of compositions and the information was given for the purpose of showing the capabilities of HARPHRQ.

Comment

CJT (AEA). AEA's HARPHRQ is at the forefront of QA'd status databases in the world.

Q. *HY (PNC).* Was the sulphate ion concentration from the Poços de Caldas mine in reducing groundwater?

A. *CJT (AEA).* The groundwater was not very reducing, (0 to -200 mV) and so we would expect some SO_4^{2-} to be present.

Q. *KM (PNC).* The actinide decay scheme is considered very important in the radioactive waste; can CHEQMATE take this into account?

A. *CJT/AH/ (AEA)* Yes, CHEQMATE has been used to model some decay schemes, *SMS* but it is primarily intended to focus on the chemical and transport processes. Our assessment codes, MASCOT and STRAW consider actinide decay chains, but include much simpler representations of the chemical reactions.

Q. *NS (PNC).* Will a report on the verification and validation of the database be published; and if so, when?

A. *CJT (AEA).* Yes, the document is at present in the internal review system, and we hope that it will be published within the next twelve months.

Q. *NS (PNC).* Is this work a product of collaboration with the CEC?

A. *CJT (AEA).* No, some database validation has been performed as part of the CHEMVAL project, and that work is already available.

Q. *NS (PNC).* Has work on the verification and validation of the database been funded by Nirex?

A. *CJT (AEA).* Yes, this forms a key part of Nirex's safety case and therefore this document will eventually be in the public domain.

Q. *NS (PNC).* How is the regulatory authority related to Nirex?

A. *SMS (AEA).* Her Majesty's Inspectorate of Pollution (HMIP) acts as the regulatory body on behalf of the U.K. Government. HMIP will respond to Nirex's proposals for radioactive waste disposal and address any areas of particular concern. Data are sent to HMIP who are performing a parallel safety assessment programme.

Questions and comments arising from Ms Haworth's presentation.

Q. *NS (PNC).* Where do the data in HATCHES come from?

A. *AH (AEA).* We take literature data, mainly from critically-reviewed compilations such as from Bard, Parsons and Jordan, and from Smith and Martell, and tables published by NBS in Washington, plus in-house experimental results.

Q. *KM (PNC).* (Relates to overhead of uranium solubility predicted and measured). Uranium carbonate was not mentioned.

A. *CJT (AEA).* This species is not thought to occur at pH 10.

Q. *HY (PNC).* What solid data were used for the 80°C predicted time for uranium solubility?

A. *AH/CJT* (AEA) Predictions for uranium(VI) do not suggest a change in solubility-limiting solid phases. However, predictions for uranium(IV) do, but we do not have data to substantiate this.

Q. *HY (PNC).* How do you input a ligand grouping or molecular weight for organics into HATCHES?

A. *TGH (AEA).* This would be entered in a similar way to a new element.

Q. *KM (PNC).* How do you overcome the problems of organic ligands?

A. *JAB/CJT (AEA).* In experiments well characterised simulants such as polyhydroxycarboxylic acids are used and these are entered into HATCHES as individual complexes. We do not have specific information on fulvic and humic acids.

Q. *KM (PNC).* The present estimate for the ionic strength for the Japanese repository groundwater ionic strength is 0.5 M and a maximum 1 M. Why do the AEA think that consideration of ionic strength corrections are necessary?

A. *AH (AEA).* We have done work on ionic strength corrections because some of the deeper groundwaters at Sellafield are very saline. This topic was of interest to CEC, as a German repository is likely to be located in brine and work has been done relating to this.

1.5 Presentation by PNC on Thermodynamic Database and Speciation

1.5.1 Status of PNC'S Thermodynamic Database

A presentation was made by Mr Miyahara and the following questions arose.

Q. *CJT (AEA).* Have the groundwater cations been included in PNC's database?

A. *KM (PNC).* Not at present, but this will be addressed in the future.

Q. *NS (PNC).* What does AEA consider regarding change of phase with time?

A. *CJT (AEA).* Usually we model the amorphous and crystalline phases separately. These two solubility values are incorporated into the derivation of a probability distribution function for the solubility, which is used in performance assessment.

1.5.2 Solubility Measurements

A presentation was made by Mr Yoshikawa.

NB. On the overhead for the 3 methods of production of $NaOHCO_3$ there is an error in the table: where it says 40% it should read 60%.

The following comment arose from the presentation.

Q *JAB (AEA).* Please could you let us know the details of the make of instrument that can measure down to 0.01 ppm CO_2?

A *HY (PNC).* Details of this equipment will be found for AEA.

1.5.3 Measurements and Analyses of U in Groundwater of the Tono Mine as a Validation of the Database.

A presentation was given by Mr Miyahara and the following question and comments arose.

Q. *CJT (AEA).* Are there any U(V) species in the database?

A. *KM (PNC).* Yes, we use the NEA database, but it is not a predominant species.

Comments.

CJT (AEA). We have excluded U(V) species in the Harwell database as, when the NEA database was used at Harwell for UK conditions, it predicted U(V) species dominant.

JAB (AEA). Experience of U(V) chemistry leads *JAB* to consider that it is very unlikely to occur in groundwater.

DAY 2: 20th July 1993

Those present were:		
	Dr N Sasaki	PNC Tokyo
	Mr K Miyahara	PNC Tokyo
	Mr H Yoshikawa	PNC Tokai
	Dr S M Sharland	AEA D&W Harwell
	Dr J A Berry	AEA D&W Harwell
	Dr S J Williams	AEA D&W Harwell
	Mrs R McCrohon	AEA D&W Harwell
	Dr C J Tweed	AEA D&W Harwell
	Ms A Haworth	AEA D&W Harwell
	Mr M Brownsword	AEA D&W Harwell
	Mr G M N Baston	AEA D&W Harwell

2.1 Presentation by AEA on Understanding the Mechanisms of Sorption

2.1.1 Comparison of Batch and Through-Diffusion methods

Dr Berry gave a presentation of differences between batch and through-diffusion methods and described a set of experiments soon to be carried out at Harwell to investigate this situation using a single mineral. Dr Berry suggested that this may be an area for collaboration with PNC.

2.1.2 Discussion of Modelling Techniques for Batch and Through-diffusion Experiments.

Ms Haworth gave a presentation on modelling techniques and the following questions arose from both her, and Dr Berry's presentation.

Q. *HY (PNC).* The through-diffusion method is difficult to apply to some minerals and rocks and batch sorption results depend on particle size. How do you calculate the effects of differences between batch and through diffusion and of different particle sizes?

A. *AH (AEA).* Differences could be due to two main reasons:

1). new surfaces are exposed on grinding; and

2). available surface areas are different

We have not addressed the first reason but with CHEQMATE we can change the surface area in the calculations.

Q. *KM (PNC).* Have the through-diffusion and batch sorption experiments with the aluminium oxide been carried out yet?

A. *JAB (AEA).* We are currently in the process of preparing the discs of aluminium oxide.

Q. *KM (PNC).* Are the natural porewater and batch solutions very different?

A. *JAB (AEA).* In the far-field experiments we always use simulated groundwater and in the near field cement-equilibrated water is used and therefore no leaching occurs during the experiments. It is most important to get the aqueous phase composition correct from the start of the experiments.

Q. *HY (PNC).* Why was bentonite not chosen for these experiments?

A. *JAB (AEA).* Bentonite was not chosen for these experiments as bentonite free of iron could not be found by AEA. Experiments at Harwell with other minerals examined by various surface analytical techniques have clearly shown that sorption onto a very thin layer of iron oxide can dominate that of the surrounding minerals.

Comment.

NS (PNC). In Japan,we will check the possibility of purchasing synthesised montmorillonite, including an iron-free version.

Comment.

JAB (AEA). We would be very interested in an iron-free montmorillonite. Even 100 ppm of iron could dominate the sorption, so ideally the iron content should be undetectable.

2.2 Presentation by PNC on Understanding the Mechanisms of Sorption

2.2.1 Status of Surface Complexation Model

Mr Yoshikawa presented PNC's position in this area, and the following questions arose.

Q. *JAB (AEA).* On one of your overheads, the sorption of selenium on bentonite was said to be by surface complexation and yet on an earlier graph the Kd was shown to be zero or very low; can you explain this?

A. *HY (PNC).* The surface complexation model uses the percentage of goethite present and sorption is on the goethite.

2.2.2 Sensitivity Analysis for Sorption of Uranium

A presentation on this subject was given by Mr Miyahara.

2.2.3 Validation Model for Sorption of Neptunium

A presentation on this subject was given by Mr Miyahara.

2.3 Round-up Discussion on Non-Commercial Collaboration

The three areas proposed by AEA as candidates for collaboration with PNC were discussed in detail.

2.3.1 Ionic Strength Corrections

Q.	*KM (PNC).*	Our present value for groundwater concentration is not high in ionic strength. Why does AEA consider that it would be useful to PNC to consider high ionic strength corrections?
A.	*AH/SMS/ CJT (AEA)*	The truncated-Davies equation may be sufficient, but modelling is required to ensure that the model is working well for each particular groundwater.
Q.	*KH (PNC).*	Why concentrate on the ionic strength correction?
A.	*AH/CJT (AEA)*	There are not many situations where there is only one dominant reaction. HARPHRQ uses a complex array of reactions.
Q.	*NS (PNC).*	What is the ionic strength of the groundwater at Sellafield?
A.	*JAB (AEA).*	The most common analysis of the groundwater in the host rock at the proposed repository location shows an ionic strength of several times that of sea water.
Q.	*NS (PNC).*	What causes the very high salinity?
A.	*CJT/AH (AEA)*	It is likely that the evaporite layer in the rock close by is the cause of the high salinity.

Comment.

NS(PNC).	At present, the area of ionic strength corrections is not a priority for PNC, and so should not be included in the collaboration but this may change at a later date.

2.3.2 HATCHES Database

Comment.

KM (PNC).	The solubility of Se, Sn and Pd are not so well known as the actinides and Tc.

Comment.

CJT (AEA). The current status of the Harwell HATCHES database regarding these three elements is as follows.

Se	uses a compilation of data made by McKinley (1990) and has been tested against AEA measurements under cementitious conditions.
Sn	information under non-cementitious conditions from PNC would be very useful.
Pd	No modelling done at all so far Pd data is in the database but not many species are included.

Comment.

SMS (AEA). We would like to suggest that PNC take a copy of the latest version of HATCHES, (when you return to Japan). A user manual is currently available and more extensive documentation is at present being prepared. A conversion program also comes with HATCHES to convert it to HARPHRQ or EQ3/6 format.

Comment.

CJT (AEA). We have done much work since the publication of AERE R12324; for many elements we have additional species. For example, the data for uranium have been significantly changed since then.

Q. *CJT (AEA).* When PNC supply AEA with data on Se, Sn, Pd and Nd solubility, should the modified version of HATCHES be for the exclusive use of PNC, or should it go to the NEA with the data referenced to PNC?

A. *NS (PNC).* PNC would like the data to be published.

Comment.

SMS (AEA). HARPHRQ has been modified from PHREEQE in the following three ways and these modifications are included in the version sent to the NEA:

1) fixed pH;
2) truncated-Davies method of ionic strength correction;
3) finite minerals.

We can give you this modified version before you leave. The sorption module for use with HARPHRQ is available under a commercial licensing arrangement.

Q. *KM (PNC).* PNC have measured Nd as an analogue of Am; are there any data on Nd in HATCHES?

A. *CJT (AEA).* We have always worked with Am and not an analogue, and therefore there is no data in HATCHES on Nd.

Q. *SMS (AEA).* How much data do you use based on Paul Brown's theory?

A. *KM (PNC).* We use measured data where available, but when it is not, we use Brown's theory.

Q. *KM (PNC).* Do AEA have a set of guidelines for estimating values?

A. *SMS/CJT (AEA).* No, AEA does not have any formal guidelines.

Comment.

AH (AEA). Because there is such good referencing in HATCHES it is always clear where the data used come from.

Comment.

HY (PNC). PNC are just starting the $FeSe_2$ work.

Q. *CJT (AEA).* Are you also looking at FeSe? In HATCHES, Ian McKinley's reference only uses $FeSe_2$ data and FeSe data would be very valuable.

Q. *HY (PNC).* Does the database also include Se?

A. *CJT (AEA).* Yes. Se is predicted to precipitate at a higher Eh than FeSe or $FeSe_2$.

Q. *HY (PNC).* Which is more important; the Se/Fe compounds or the metallic Se?

A. *CJT (AEA).* This depends on other ions, as Se/Fe compounds give higher solubilities under UK conditions, we must consider these to give a conservative approach.

Q. *HY (PNC).* Which data are used in the database?

A. *CJT (AEA).* Only the database supplied by Ian McKinley.

Comment.

HY (PNC). We sometimes observe a metallic selenium precipitate in our solubility experiments.

Copies of the latest NEA versions of HATCHES and HARPHRQ were given to Mr Miyahara by Ms Haworth on 3½" discs.

2.3.3 Investigation of Sorption Behaviour

Q. *NS (PNC).* What kind of materials will be used for the experiments; and who will conduct the experiments?

A. *JAB (AEA).* The initial stages of the through-diffusion and batch sorption experiments with the aluminium oxide are already underway at Harwell. We will keep PNC informed of our progress. We will start simple experiments with Cs and Sr and, depending on the amount of sorption indicated by the batch experiments, we may also look at the sorption of actinides.

Q. *KM (PNC).* If we could provide the pure sodium montmorillonite, what would be our role?

A. *JAB (AEA).* We would be very pleased if PNC could obtain an iron-free sodium montmorillonite. PNC would, of course, be involved in the choice of elements to be investigated and would share the data from the experiments.

Comment.

KM (PNC). PNC could measure the retardation-factor in an in-diffusion experiment.

Comment.

NS (PNC). If the pure montmorillonite is available, then PNC will purchase it.

Comment.

JAB (AEA). If our preliminary work is successful, we could send you the aluminium oxide discs to perform in-diffusion experiments.

Comment.

KM (PNC). We have no experience of slicing anything other than bentonite.

Comment.

JAB (AEA). We could supply the aluminium oxide powder If our preliminary experiments indicate that aluminium oxide is not suitable, then we would inform PNC and jointly choose another material.

Comment.

SMS (AEA). Have you considered modelling the system with HYDRAQL? We will model the batch experiments with HARPHRQ, and then an intercomparison could be made. We will also model the through-diffusion experiments with CHEQMATE.

Comment.

KM (PNC). PNC have a coupled chemistry transport code, called CRACKER.

Comment.

CJT (AEA). CRACKER is a similar type of code to CHEQMATE, but it is simpler in some areas. The details of CHEQMATE are described in reports given to Mr Yui. We will send the updated CHEQMATE manuals when they are available.

Q. *NS (PNC).* How much montmorillonite is required.

A. *JAB (AEA).* About 20 g.

Q. *HY (PNC).* Could goethite be used for the batch and through-diffusion experiments?

A. *JAB (AEA).* Perhaps goethite could be used at the second stage in the experiment but it may not be suitable for through-diffusion if it is strongly sorbing. Thus, we will need to do a batch sorption experiment first.

Comment.

AH (AEA). There are some data available on aluminium oxide using a triple-layer model, but it is quite old. There is some interest in aluminium oxide to provide that part in clay behaviour modelling.

Comment.

HY (PNC). Perhaps goethite could be tried.

Comment.

JAB (AEA). Perhaps a batch experiment and reservoir-depletion and a breakthrough-curve with a tritium tracer could be carried out using goethite. We could consider the collaboration work in 3 stages as follows:

<u>Stage 1</u> Aluminium oxide work:
AEA batch and through-diffusion experiments;
PNC in-diffusion experiments.

<u>Stage 2</u> Goethite work:
AEA batch and reservoir-depletion experiments;
PNC in-diffusion experiments.

<u>Stage 3</u> Pure sodium montmorillonite work:
AEA batch and through-diffusion experiments;
PNC in-diffusion experiments.

2.4 Date of Next Meeting

October 1994, in Japan, after MRS Meeting.

DAY 3: Wednesday 21st July 1993

The PNC delegation was shown some of the laboratories in the main radiochemistry building (B220) by Dr J A Berry and Mr M M Cowper. The laboratories visited included the main glove box areas, the laboratories where work for PNC is undertaken as well as other laboratories used by Chemical Studies Department. The remote handling high-activity (αβγ) cells were also shown. In an adjacent building (B10), facilities for work on organic degradation studies were described by Dr N J Pilkington and Mr B F Greenfield; those for research on colloids by Dr M P Gardiner and for the measurement of physical properties of geological materials by Mr T R Lineham. The tour continued with a visit to the nuclear microprobe (B8) which was described by Mr J W McMillan and Mr P R Fozard. Further surface analysis equipment (SIMS - O and Ga beam machines, XPS, electron microprobe, XRD, laser Raman spectrophotometer etc) (B393 and B552) were described and shown by Mr B A Bellamy and Mr H E Bishop.

DAY 4: Friday 23rd July 1993

Presentations were made by AEA staff from Hydrogeology and Assessments Departments working on projects for UK Nirex Limited, for background information.

Mrs R McCrohon
Chemical Studies Department
AEA Technology
10.30 Harwell
Didcot
Oxon, OX11 0RA

30th July 1993

2. ＡＥＡにおける地層処分研究開発の現状

2.1 中低レベル廃棄物の地層処分研究開発の概要

英国の放射性廃棄物は極低レベル、低レベル、中レベル、高レベルの4カテゴリーに分類され、極低レベル廃棄物は、一般廃棄物とともに処分されている（表1参照）。中低レベル廃棄物については、1949～1982年まで海洋投棄による処分が実施された。また、低レベル廃棄物については、ドンレイ（1957年～）及びドリッグ（1959年～）で、現在まで浅地層処分が行われている。現在、中レベル及び高レベル廃棄物は、原子力施設のサイト内に貯蔵されている。放射性廃棄物の発生量を表2に示す。

中低レベル廃棄物については、地層処分を行うことを決めており、その実施責任機関は Nirexである。

地層処分に関する主なスケジュールとしては、すでに地下研究施設であるRock Characterization Facility（RCF）のサイトがシェラフィールドに決定され（1991年）、ここでのサイト特性に関する研究成果を踏まえた後、2005年に処分場の操業を開始し、2055年に処分場が閉鎖される予定である（表3参照）。

ＡＥＡは、中低レベル廃棄物の地層処分の安全評価、及びそれに関連する研究開発について、Nirex の中核的な受託機関である。実際に、このための研究を行っているのは、ＡＥＡハーウェル研究所の放射性廃棄物処分部（Radwaste Disposal Division；人員75名、部長Dr. K. H. Winters）においてであり、化学研究、水理、性能評価の3課室からなっている。ＡＥＡ全体及び放射性廃棄物処分部に関する組織図を、それぞれ図1及び図2、3に示す。個々の研究の現状について、紹介があったので以下にまとめる。

表１　英国における放射性廃棄物のカテゴリー

- Very Low-Level Wastes (VLLW):
  Disposal with household refuse, low activity or short half-life
- Low-Level Wastes (LLW):
  Not exceeding 4GBq/t alpha or 12GBq/t beta/gamma, not VLLW
- Intermediate-Level Wastes (ILW):
  Lower activity and heat output than HLW, not LLW
- High-Level Wastes (HLW):
  Wastes generating significant amounts of heat

表２　英国における放射性廃棄物発生量

	Low	**Medium**	**Alpha**	**High**
Interim store *(to 1990)*:	7,900	18,500	66,000	710
Disposed *(to 1990)*:				
Ocean bed (LLW & ILW)	<-------	26,000	------->	
Dounreay	14,000			
Drigg	775,000			
Production *(1990-2020)*:	644,000	65,000	65,000	560

(all quantities in cubic metres)

表3　中低レベル廃棄物の地層処分に関するスケジュール

1988:	Site comparison and selection of a limited number for further study
1991:	Selection of a single site for detailed geological characterisation, detailed design work in parallel
1992/3:	Application for planning permission and to move to underground work
2000(?):	Application for planning permission for disposal
2005:	Repository operational
2055:	Repository sealed

AEA Technology Structure

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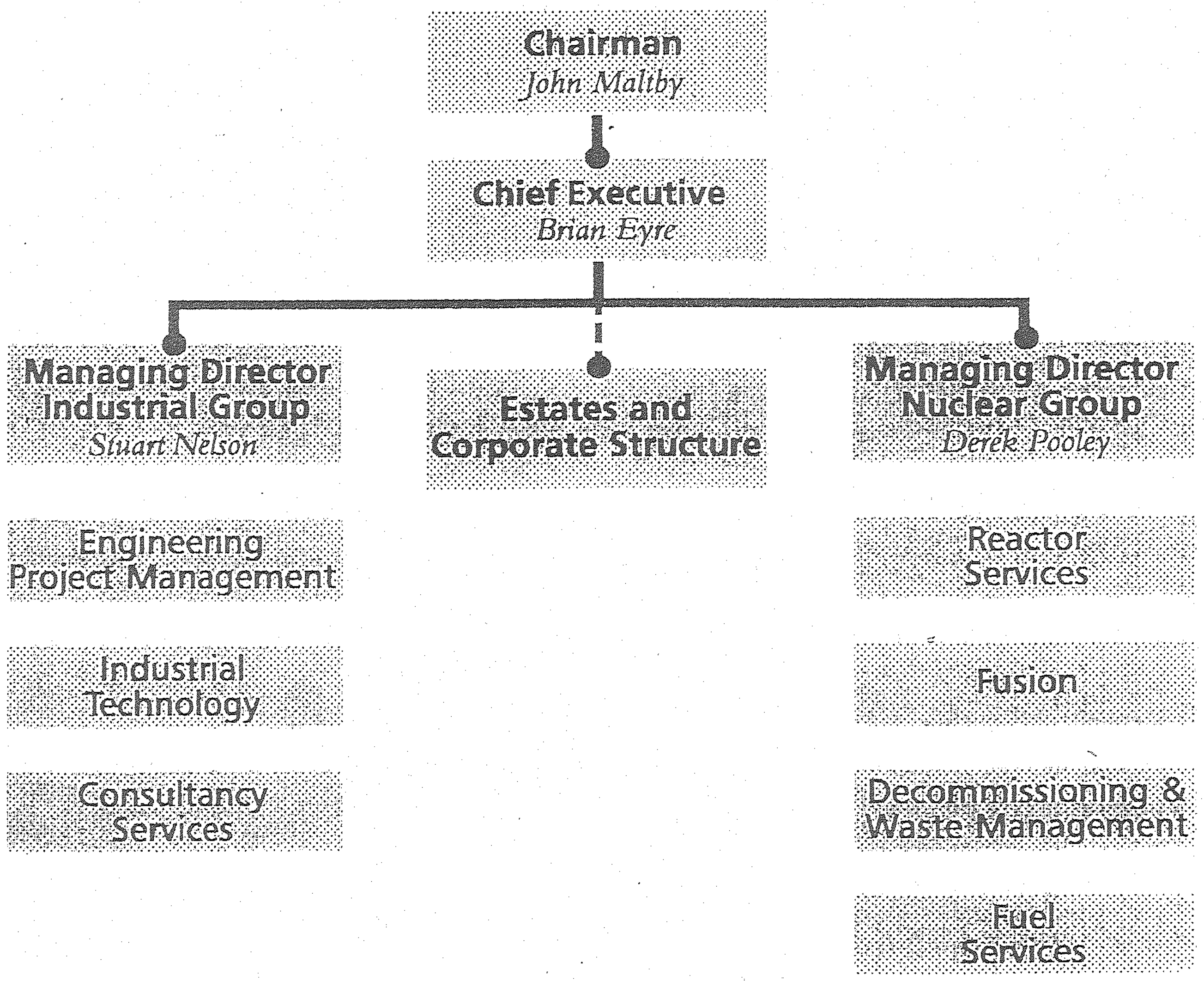


Chairman
John Maltby

Chief Executive
Brian Eyre

Managing Director
Industrial Group
Stuart Nelson

Estates and
Corporate Structure

Managing Director
Nuclear Group
Derek Pooley

Engineering
Project Management

Industrial
Technology

Consultancy
Services

Reactor
Services

Fusion

Decommissioning &
Waste Management

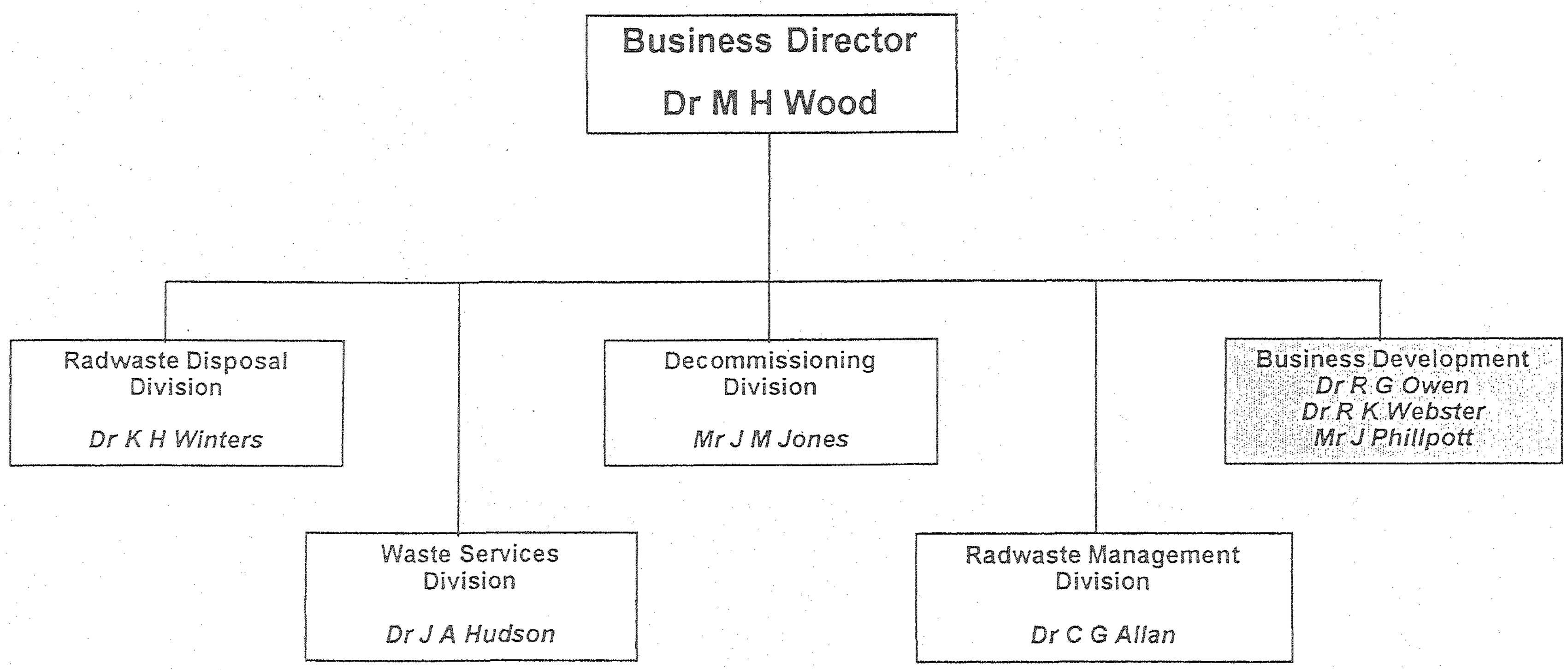
Fuel
Services

図１　ＡＥＡ全体の組織図

AEA

AEA Technology

Decommissioning & Waste Management



Business Director

Dr M H Wood

Radwaste Disposal Division

Dr K H Winters

Waste Services Division

Dr J A Hudson

Decommissioning Division

Mr J M Jones

Radwaste Management Division

Dr C G Allan

Business Development

Dr R G Owen

Dr R K Webster

Mr J Phillpott

図2　ＡＥＡ Decommissioning & Waste Management の組織図

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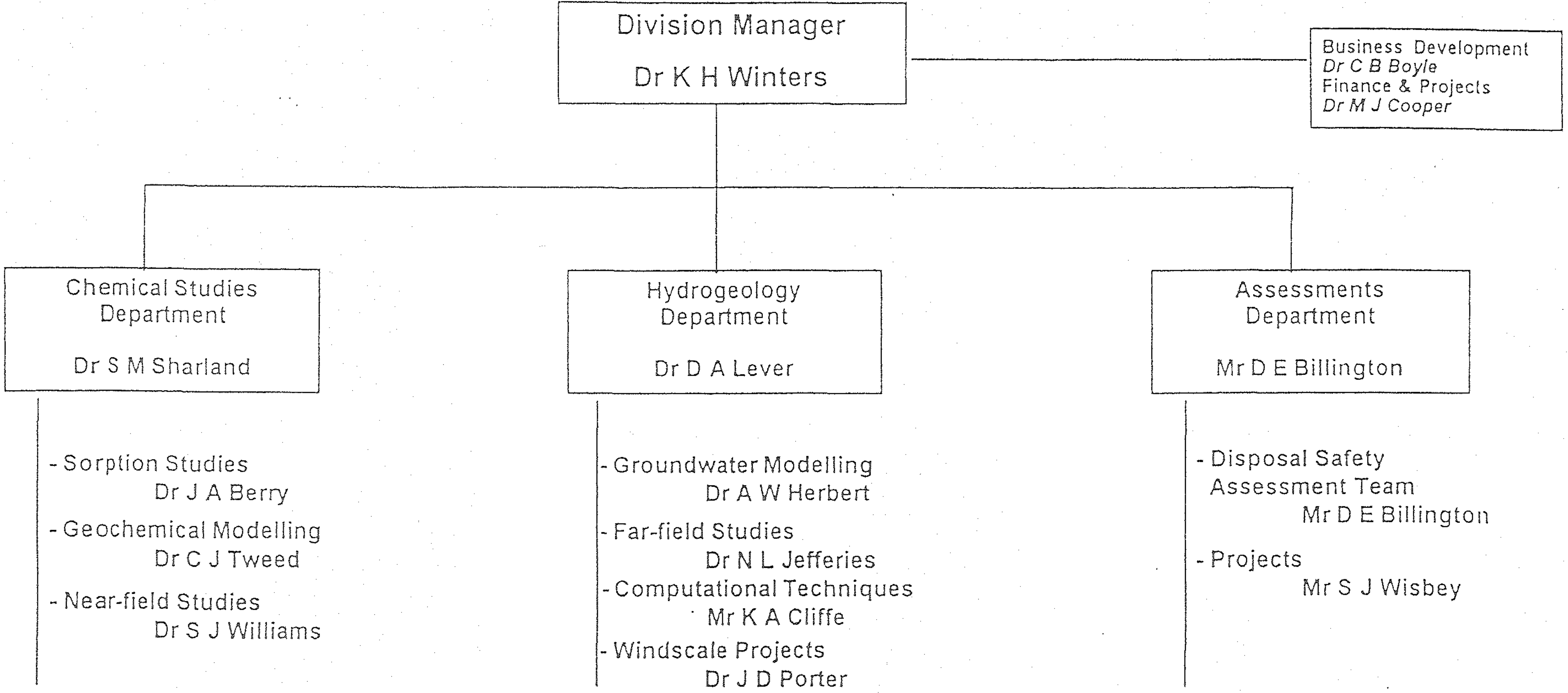
Waste Management

Radwaste Disposal Division



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  Dr J A Berry
- Geochemical Modelling
  Dr C J Tweed
- Near-field Studies
  Dr S J Williams

Hydrogeology Department
Dr D A Lever

- Groundwater Modelling
  Dr A W Herbert
- Far-field Studies
  Dr N L Jefferies
- Computational Techniques
  Mr K A Cliffe
- Windscale Projects
  Dr J D Porter

Assessments Department
Mr D E Billington

- Disposal Safety Assessment Team
  Mr D E Billington
- Projects
  Mr S J Wisbey

図 3　ＡＥＡ放射性廃棄物処分部の組織図

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Waste Management

2. 2　性能評価に係わる実験研究及び施設見学

(1)　ニアフィールドにおける有機物の影響について（Dr. S. J. Williams）

ニアフィールドでの放射性核種移行についての影響を増大すると思われる要因として次の事を考えている。

① 廃棄物中の有機物の作用
② 微生物の活動
③ コロイドの形成
④ 放射線の影響

有機物についての影響が説明された。廃棄物中の有機物は放射線または化学的な分解により低分子の物質として放出される。有機物化合物による影響として、放射性核種との錯体形成、微生物の餌、放射線分解や微生物作用を含めたガス発生、その他人工バリアとの相互作用が考えられる。実際に廃棄物中にどの様な有機物が存在するかというとＩＬＷにはＰＶＣ、イオン交換樹脂ゴムやプラスチックが、ＬＬＷには紙、木片、プラスチックやゴムが含まれている（図１参照）。Harwell では有機物の様々な条件下での分解実験、分解生成物存在下でのPu、Am等の溶解度実験また、吸着へ及ぼす有機物の影響等の実験を行っている。例えば、セルロースの分解生成物の研究では、調査研究、分解生成物の放射性元素の溶解度・吸着挙動に与える影響、全有機炭素分析・ガスクロマトグラフィー・ガスクロ質量分析計・高速液体クロマトグラフィー（HPLC）を用いた分析、そして予想される分解生成物の合成等を行っている。その結果、セメント間隙水中では10^{-10}mol／ℓであったPuの溶解度が10^{-3}mol／ℓまで変化する事が分かった（図２参照）。これらの実験は以下のメンバーで行っている。

Mr. B. F. Greenfield と Mr. M. W. Spindlerは分解の実験、放射性元素の溶解度変化の実験、ニアフィールド中での吸着に与える影響の実験、化合物の合成を、Dr. N. J. Pilington とMr. M. H. HudusはHPLCを用いた抽出液の分析を、そして実験によっては Dr. A. Rosevear と微生物の研究を、また、他の熱力学的モデル、性能評価、吸着研究とも関連して実施している。

(2)　放射性廃棄物処分におけるセメントの適用（Dr. A. W. Harris）

セメントの長期的性能に影響を及ぼす因子について研究を行っている。様々な因子があるが特に、熱による変質、アモルファス相の再結晶化等について調査している。熱は廃棄物自身から発生し、約80℃が最大と思われるが局所的なホットスポットの発生が懸念される。再結晶化についてはＣＳＨゲルが結晶化する事により表面積が小さくなり、化学的緩衝性の機能が低下するので重要と思われる。

(3)　粘土、花崗岩中における処分環境下での高レベルガラス固化体からの核種放出（Dr. J. A. C. Marples）

模擬ガラス固化体にＴｃ、Ｎｐ、Ｐｕ、Ａｍをドープして浸出実験を行っている。処分場の材料（ガラス粉末、鉄、セメント、粘土等）と混合し、水素５％含有のＡｒガスという還元雰囲気のグローブボックス中で60、90℃で１～12か月間浸出させ、Ｅｈ、ｐＨ、化学成分の分析を行っている。本装置の概略を図３に示した。例えばNpの場合、ポルトランドセメント混在下では2×10^{-10} mol／ℓであるが Boom Clay存在下では1200×10^{-10}mol／ℓ（図４参照）になる。Ｎｐの許容濃度は１日に２ℓ飲用し、年間１ｍSvの被ばく線量に抑えるのに2×10^{-10}mol／ℓとなる。結果として還元雰囲気の基では、ポルトランドセメントを含有する実験の結果、Ｔｃ、Ｎｐ、Ｐｕ、Ａｍの液中の濃度は許容濃度の0.1、1、2、0.4倍になる。バックフィルとしてのポルトランドセメントの使用により、ｐＨが高いにも係わらずガラスの重量減少量、浸出率は減少する等の結論が得られている。

(4)　ＡＥＡにおけるコロイド研究　（Dr. M. P. Gardiner）

研究対象のコロイドとは、大きさが１ｎｍ～１μｍの物で、水酸化酸化物、粘土、けい素の無機化合物やフミン酸、フルボ酸セルロースの分解物、糖類等の有機物を考えている。

これらは表面積が広く吸着剤として優れ、コロイドによってはバルクの水よりも速く移動するという実験結果を得ている。例として、トリチウム水とけい酸コロイドの亀裂中での移行挙動を図５に示した。トリチウム水よりもコロイドが速く移行している

事が分かる。 Harwell では分析方法として、粒度計、ＴＥＭ、電気泳動法を用いて研究を行っている。研究テーマとしては、①ニアフィールド条件下でのセメントコロイドの生成、②亀裂を通るコロイド挙動の実験とフィールド実験、③コロイド状分解生成物に対するＡｍ、Ｐｕの吸着実験、④コロイド状分解生成物とセメントコロイドの吸着に関する比較実験等を行っている。①に関してはバックフィル物質を 500～1000μｍの粒子サイズで、温度は室温、60℃、80℃、固液比は 1:5、1:10、1:50で、浸出時間１週間と３ヶ月の実験を行った。結果として、アモルファスＣＳＨ層の沈澱を形成し、Ｓｉで過飽和の状態でコロイドの形成が確認された。②については、けい素とヘマタイトのコロイドの移動について実験を行っている。けい素のコロイドとして Syton X30と Syton W30が用いられた。その結果、一定の流動のもとイオン強度と粒子サイズが増加するにつれコロイドの移行は減少した。

また、流速の減少については同様に減少した。ヘマタイトコロイドの移行率はけい素の移行率のわずか10％であった。フィールドでの実験の結果、30、70ｎｍのけい素コロイドの回収率はそれぞれ90％、70％であった。

(5) 微生物による放射性廃棄物の分解（Dr. A. Rosevear）

微生物の影響として、ガス生成、分解プロセスの補正、放射性炭素・トリチウムの挙動、空隙の閉塞性とバイオフィルムの形成、有機化合物の変化、錯体の形成、変質、吸着等への影響が考えられ、これらについての研究を行っている。

(6) ホット施設見学（Main radiochemistry building, B220）

① 雰囲気制御グローブボックスの見学

本施設には数多くのグローブボックスがあり、その中で雰囲気制御グローブボックスが23基設置されている。本装置を用いて深地層雰囲気を模擬した実験条件での各種研究が行われている。今回見学できたのは、ＰＮＣの委託研究の吸着実験で使用している通常タイプ型と低酸素濃度コントロール型の２タイプを見学した。通常タイプは縦、横、高さそれぞれ約１ｍ、1.5 ｍ、１ｍで鉄の枠組みで前面アクリル製で上下それぞれ２個づつグローブがセットでき、ガスは負圧で窒素ガスワンス

ルーである。本装置ではＰｕとＵの実験が可能で実際には約１mCiを取り扱っている。ガスは他に２％CO_2 ＋98％N_2 の使用も可能である。ボックス中には％オーダの CO_2メータが設置されていた。一方、低酸素濃度コントロール型の雰囲気制御グローブボックスは別の部屋に設置されていた。大きさは約 0.8m×２m×１mの横長のボックスでグローブは横に４個装着されていた。本装置のガスは精製筒を循環し15ℓ／分の交換速度である。ボックスは－1.75inH_2O の負圧で、グローブは特殊な物ではなくボックス全体でリーク率は 0.029％／ｈである。しかし、ＰＮＣと異なるのは、雰囲気を継続したままグローブ交換が可能である等、特殊な構造となっており、ＰＮＣのグローブボックス設計に参考になる。

② セルの見学

５連のセルを見学した。特徴的なのはセルが二重構造のステンレス製気密セルとなっており内側のセルの雰囲気が制御可能である事である。雰囲気ガスはＡｒである。２段階の負圧を取っておりリーク防止に努めていた。１つのセルでは小型の再処理実験を行っていた。また、さらに特徴的なのは２重構造になっているセルの内側のセルは取り外しが可能であり、５連セル近傍の大型セルに内側のセルを運び解体、除染ができる点である。マニピュレータの取合い等が特殊な構造であると思われる。

③ コールドの雰囲気制御グローブボックスの見学

グローブボックスはホット設備の通常タイプと同型で、唯一の違いは加圧で用いていることである。ボックス内に真空加熱炉を設置し、Ａｒ＋４％H_2 ガスを充塡して脱酸素還元製雰囲気を確保した有機物の分解実験をセメント－水－セルロース混合系80℃で行っていた。

④ 大型岩体実験装置等の見学

拡散の実験室には数トンもする大型の岩体を設置し、水平方向に走った亀裂に沿って、トリチウム水、色素をトレーサーとした拡散試験とコロイドの拡散試験を

行っていた。数学的モデルの確証のためのデータ取得を行っている（別添の写真を参照）。また、ボーリングコアの割れ目近傍部分でのトレーサの拡散試験を行い、割れ目近傍で空隙率が高い（割れ目のない部分に比べ）ことから、この部分で拡散が速いという結果を得た。

⑤ 機器分析設備の見学

有機物の分解実験のために使用している高速液体クロマトグラフィーを見学した。装置はMILLPORE、WATERS社製490Eであり、カラムに Resolve C18とWaters RCMの２本を用い有機物、コロイドの分離・同定を行っていた。コロイド実験には、市販の試薬Colloidal Silica、Syton W30 を用いて実験を行っていた。ＰＮＣでもコロイドの実験を計画しており、その際に用いる標準となりえる物質を検討しているので参考になった。本装置を用いた研究内容については、本報告書に記載されている７月20日午後に行われた Dr. S. J. Williamsの発表分に示した。

(7) 表面分布機器の見学

Materials charactarisation serviceについて、各分析機器を中心とした取り組みを図６に示した。これら機器を用いて Harwellの分析は、各Divisionからの依頼分析を一か所で行っており、また、各分析にDrクラスの研究者が専従し、専門的にかつ機能的に運営されているようである。

① Ｂ８施設（加速器棟）

案内者:Mr. J. W. McMillanとMr. P. R. Fozard

同施設には５Ｍｅｖの加速器が設置されていた。ｐで50μＡ、α、ｐ、^{3}He 、^{4}He の他、^{16}Ｏ、^{20}Ne、Kr^{84}等の粒子加速が可能である。地層処分研究には岩石の非破壊分析に荷電粒子放射化分析（ＰＩＸＥ）として用いられ、３ＭｅＶのｐのマイクロビームが利用できるそうだ。ただし、ベントナイト、凝灰岩のようにもろい試料は照射室を高真空にするので向かないとのことであった。また、ＲＢＳとしても利用でき、例えは花崗岩中のＵの濃度プロファイルを求めた結果、biotite と

sericiteへのUの吸着がquartzより大きいことや、表面からの深度分布を求めると、鉄の濃度とU吸着量が比例すること等が求まっている。図７、８にＲＢＳの代表的なスペクトル図と、濃度プロファイルを示す。）

② Ｂ393 、552 施設

案内者:Dr. H. BishiopとMr. B. Bellany

表面分析装置としてＳＩＭＳ、ＸＰＳ、ＥＰＭＡ、ＸＲＤ、レーザーラマン分光器を見学した。ＥＰＭＡは、日本電子社製のＪＸＡ－8600が稼動していた。

③ 総合印象

雰囲気制御グローブボックスは勿論のこと雰囲気制御セル、加速器からＨＰＬＣまで様々な実験機器を見学でき大いに参考になった。研究開発機関の分析に関する考え方として強い印象を受けた。

図１　廃棄物中に含まれる有機物

ILW	m^3
● Ion exchange resins	2000
● PVC	9000
● Rubber	3000
● Other plastics	3400
● Cellulose	700
● Mixed plastics, cellulose and rubber	2700
● Unspecified	200
LLW	
● Paper and wood	66,000
● Plastic and rubber	48,000

(From Biddle and Rees, UKAEA Report AERE R 12597 (1988))

図２　有機物存在下でのＰｕ溶解度

Organic Material	Pu solubility/(mol/l)
Cellulose (Tissue)	$1x10^{-3}$
Cotton Wool*	$1x10^{-5}$
Wood#	$1x10^{-3}$
Nylon	$1x10^{-10}$
Polythene	$1x10^{-10}$
PVC	$1x10^{-9}$
Polystyrene*	$5x10^{-10}$
Cement Leachate	$1x10^{-10}$

Organic material degraded anaerobically in contact with cement for 500 days at 80°C (except * = degradation time 240 days and # = time 120 days). Plutonium solubility measured at pH 12.

図3　浸出試験装置　(UKAEA, Harwell)

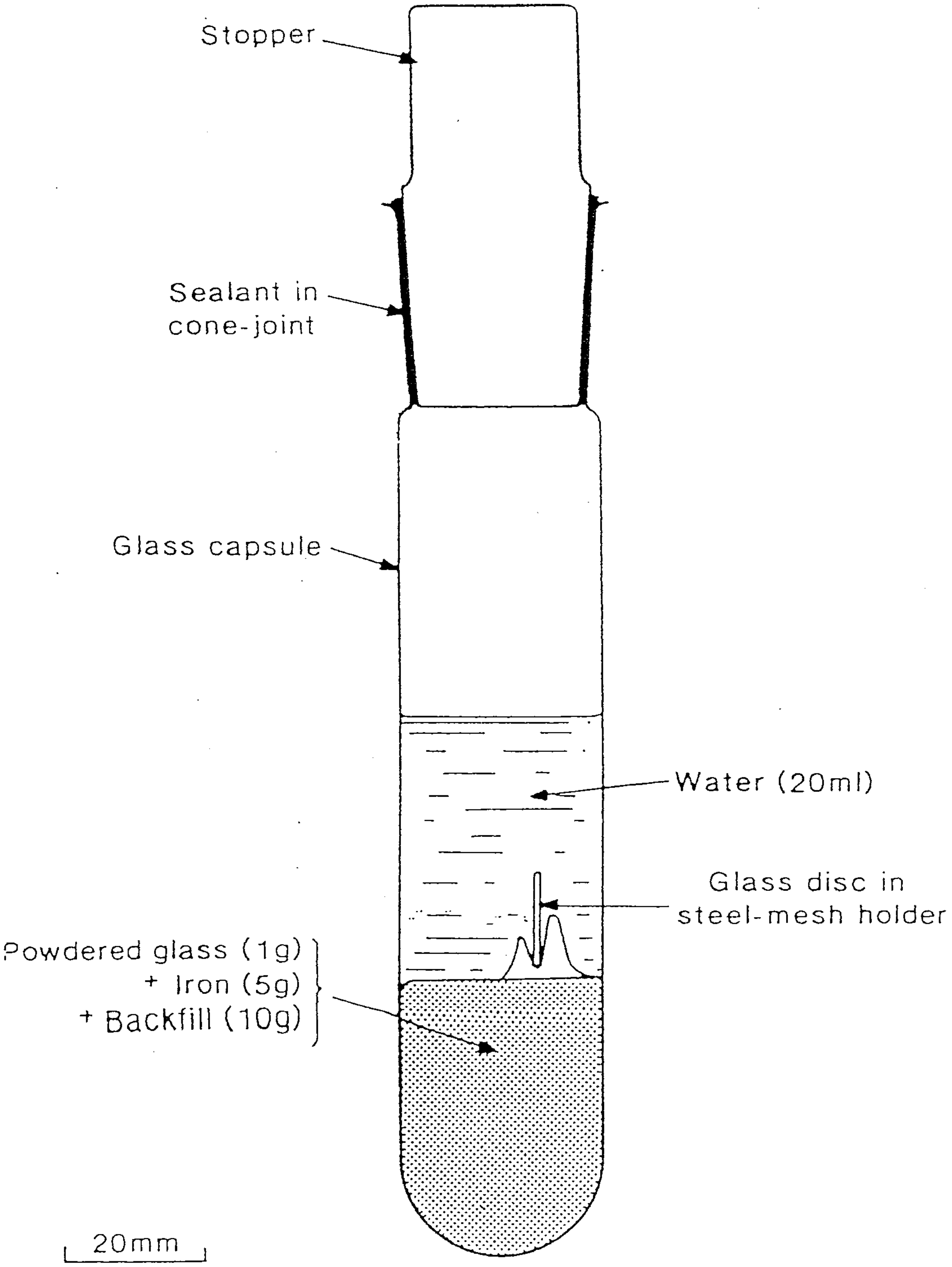


図 4　浸出試験結果

(Reducing conditions: MW Glass: 60°C)

Molar Concentrations

	Tc/E-08	Np/E-10	Pu/E-14	Am/E-13
Backfill				
OPC/PFA	3	2	0.5	2
Boom Clay	6	1200	40	15
Bentonite	3	70	60	40
Limiting Concentrations	7	2	230	0.5

OPC = Ordinary Portland Cement
PFA = Pulverised Fuel Ash

図５　トリチウム水とけい酸コロイドの亀裂中での移行挙動

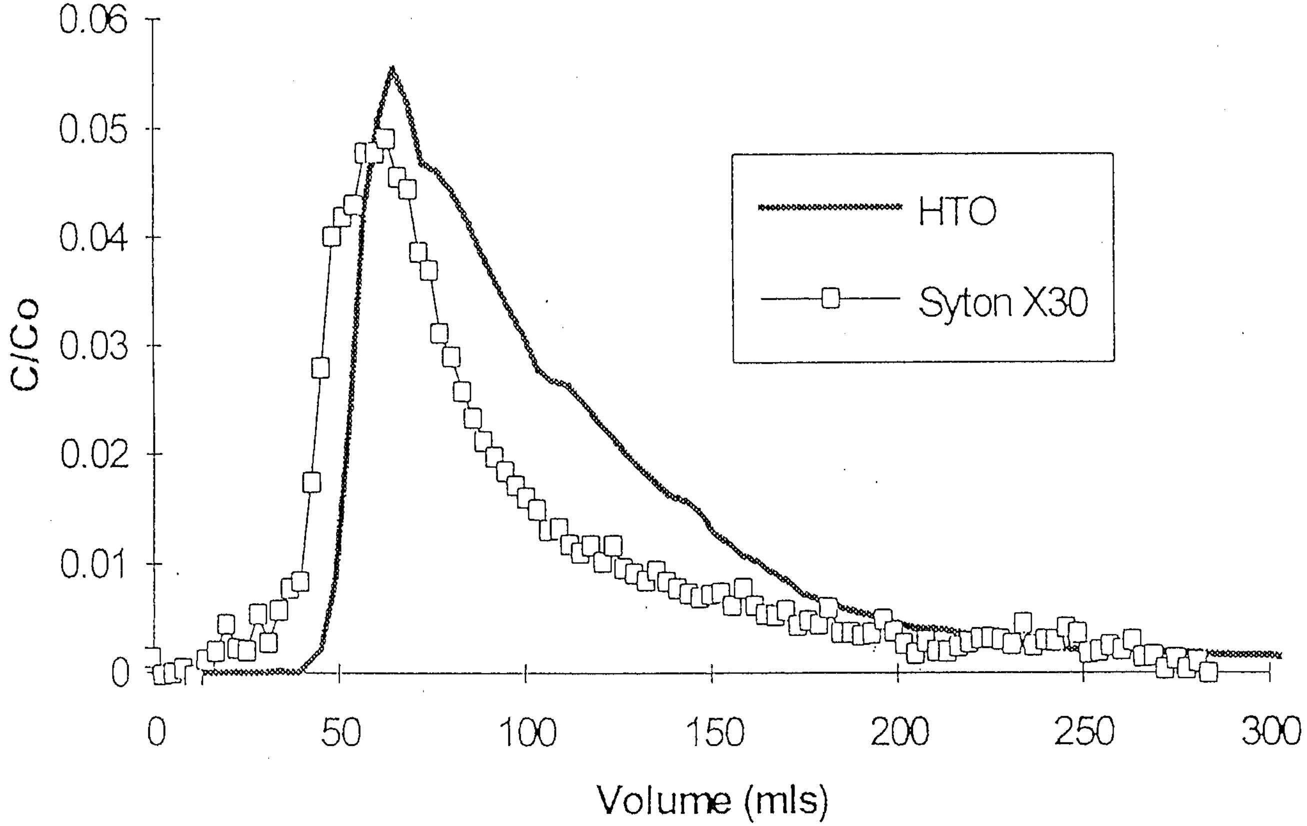


図6　Harwell研究所 Materials Characterisation Services での分析機器

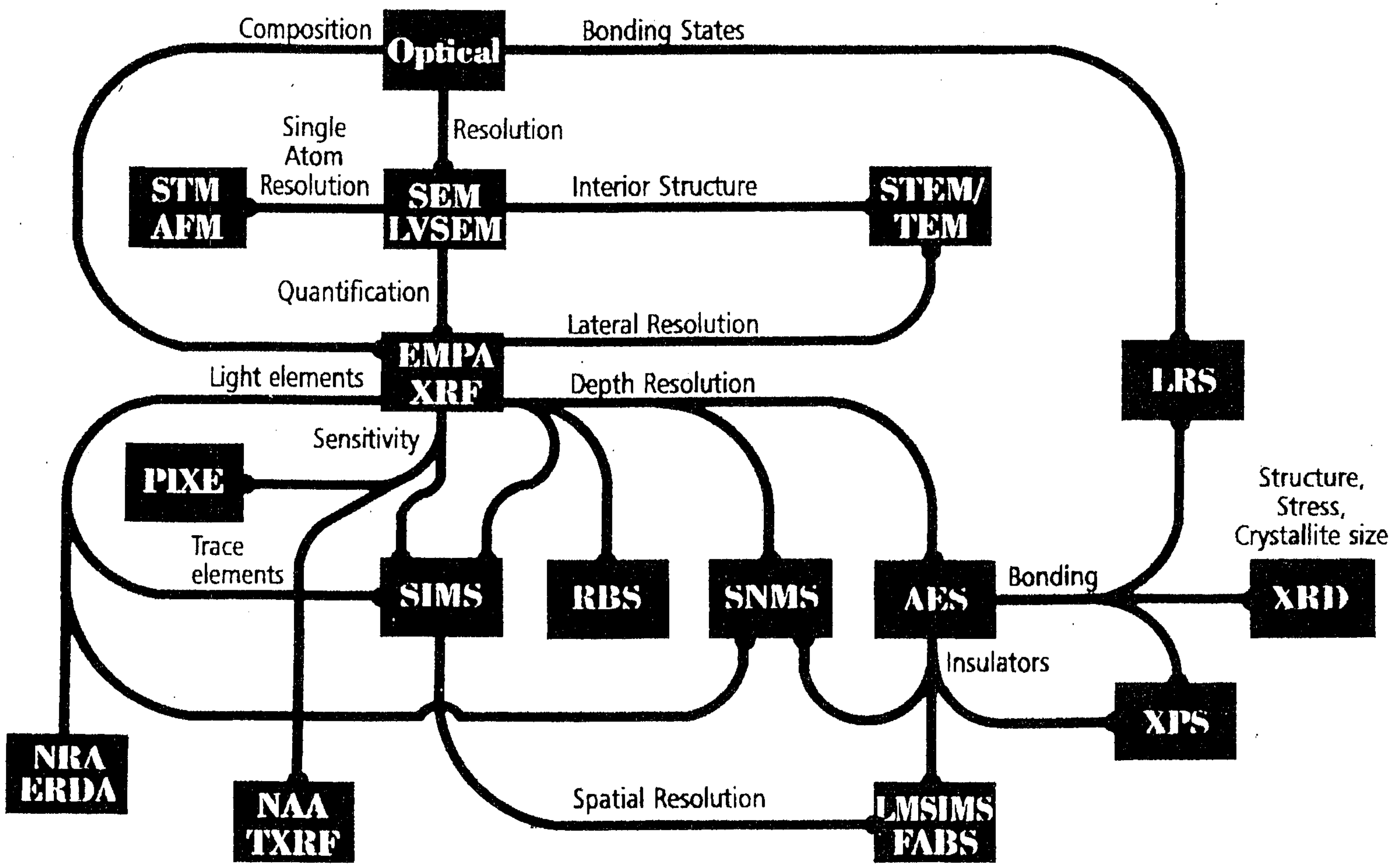


図7　Ilmite crystalの RBSスペクトル

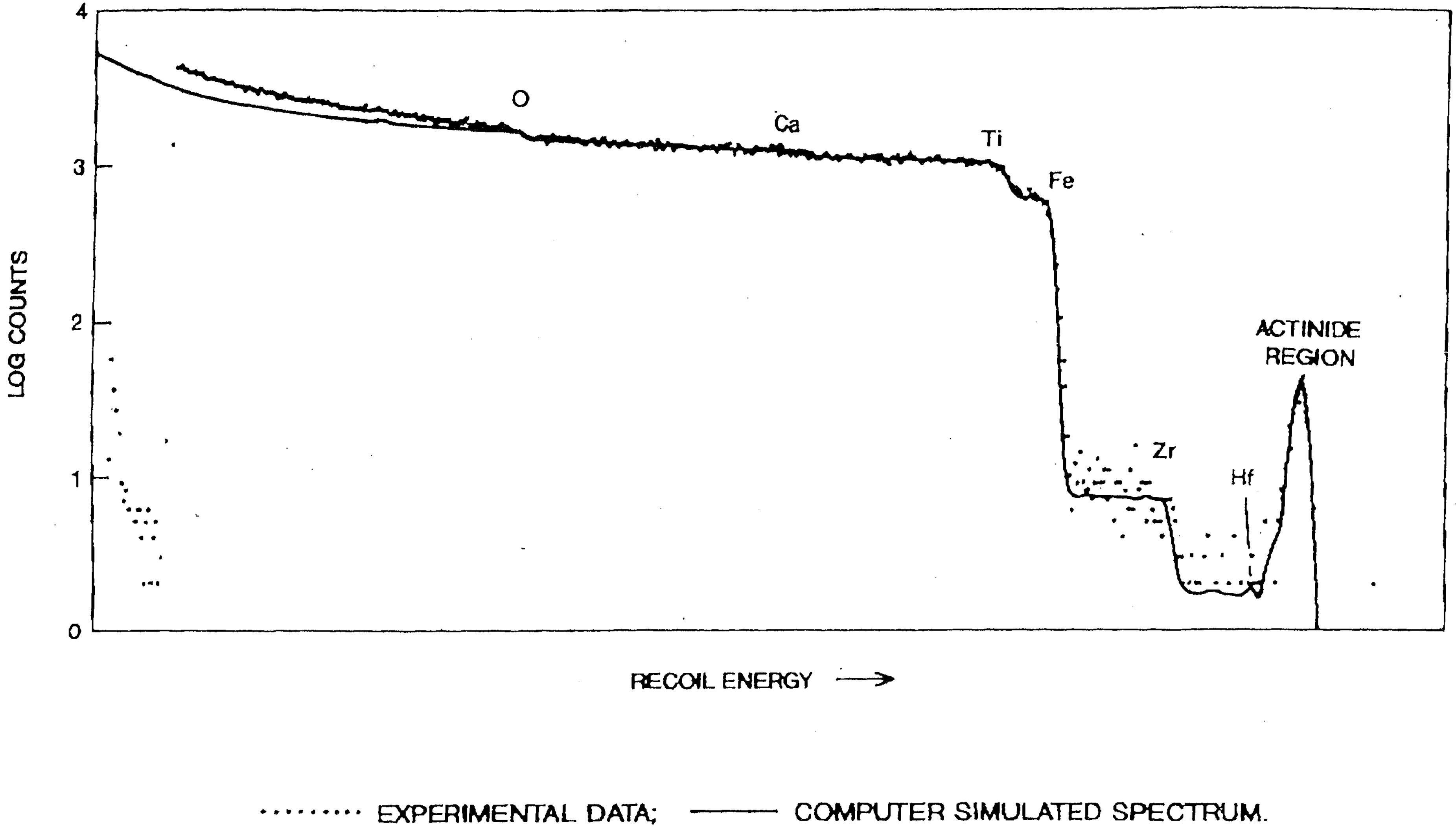
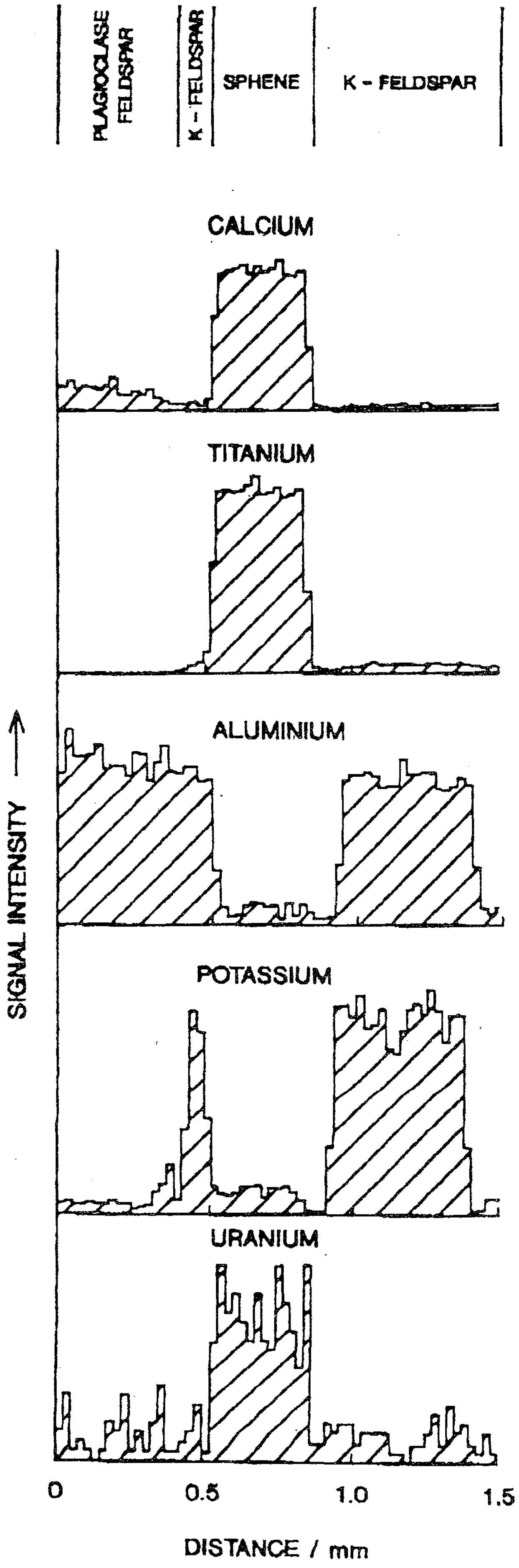


図8　Diorite Sampleの分析



2.3　ＡＥＡにおける水理・性能評価研究

(1)　水理研究

①　地下水モデル（Dr.A.Herbert）

ＡＥＡでは、地下水流動／物質移行モデリングのため、計算コードＮＡＭＭＵ（不均質多孔質媒体対象）、及びＮＡＰＳＡＣ（亀裂性媒体対象）を開発した。これらのコードは、これまでにStripaプロジェクト、INTRAVAL（WIPPサイトのケース）及び複合堆積盆地（Complex Sedimentary Basin）における評価に使用されてきた。

Stripaサイト（亀裂性媒体）において、ＮＡＰＳＡＣを用いて、3次元のフラクチャーネットワーク（図1参照）による地下水の流動経路、移動時間のモデル評価を行った（図2参照）。

INTRAVALのWIPPケース（不均質多孔質媒体）において、ＮＡＭＭＵを用いた評価を行った。この評価では、60本のボーリング孔からの情報（透水量係数など）に基づき、クリッジング、リアリゼーションといった統計的手法により、WIPPサイト周辺の透水係数の3次元分布を定め、地下水の流動特性を求めた。この結果、ボーリング孔での測定点数が増えるほど流動経路の不確実性が減ることが示された（図3参照）。

複合堆積盆地のケース（不均質多孔質媒体）では、ＮＡＭＭＵを用いて、地下水中の塩濃度の分布を予測する評価を行った。この評価では、シェラフィールドサイトを想定し、岩盤中に存在する高塩濃度地下水、及び岩盤中へ浸入した海水が、各々流動し、互いに混ざることによって生ずる、地下水中の塩濃度分布の経時変化を求めた。

その他、ＮＡＰＳＡＣでは、一次元に限定されるが、マトリクス拡散の取扱いも可能である。また、ＮＡＭＭＵのユーザーとしてはＵＫＮｉｒｅｘ以外にＳＫｉ、ＳＫＢ（スウェーデン）ＧＲＳ、ＢＧＲ、ＢＦＳ（ドイツ）、ＮＡＧＲＡ（スイス）が挙げられる。

② ＮＡＭＭＵ／ＡＤＶＩＺＥのデモンストレーション（Mr.A.Cliffe, Mr.S.Morris）

ＡＤＶＩＺＥは、ＮＡＭＭＵのための3次元グラフィックパッケージであり、市販のグラフィックパッケージＡＶＳと類似した機能を有するが、ＮＡＭＭＵの出力データと互換性がある点に特徴がある。

デモではドイツ、コンラッドサイトにおける3次元の水理特性のシミュレーションが示された。地下水流動ベクトルの表示（図4参照）や、処分場内の任意の点を起点としたパーティクルトラッキングを、処分場に対するあらゆる角度から示せるようになっていた。

今後さらに改良して、3次元領域を任意の平面で切り取った場合の、地下水流動特性の2次元表示を行えるようにしたいとのことであった。

③ 水理地質特性評価（Dr.T.Lineham）

実験室及び原位置での水理地質特性評価試験の実施例の紹介があった。室内実験の例では、岩盤の単一亀裂中に^{22}Naや^{18}Ｆのトレーサ溶液を含浸させ、γ線トモグラフィー測定を行い、亀裂幅の分布を調べた（ＰＥＴ法）。本手法の確度を確認するため、亀裂中に樹脂を充填して流し型を作り、流し型を取出した後、その幅の分布を測定することで、同一亀裂におけるＰＥＴ法の結果と比較する予定である（1994年）。

また岩石を用いた拡散試験では、ＰＮＣでも実施しているスルーディフュージョン法だけでなく、拡散の遅い核種を対象としたReservoir Depletion法を実施していた（図5参照）。Reser-voir Depletion法では、平板岩石試料の片面にトレーサ溶液を浸し、トレーサ溶液の濃度減少の経時変化により拡散係数を求めるものである。スルーディフュージョン法と異なり、岩石試料からトレーサを破過させる必要がないため、短時間での測定が可能となる。

原位置試験の例として、グレートブリテン島南西端のReskajeage農場テストサイト（シェラフィールドサイトに類似の地質構造）における亀裂ネットワーク中のガス移行試験の紹介があった。深さ50ｍのボーリング孔からヘリウムガスを注入し、地表に到達したガスをサンプリングし、質量分析によりヘリウムを検出して、地中

のガス移行のモデル評価結果の確証を行うものである。最も早いものでは、ガス注入後12日目に地表でヘリウムガスが検出された。

(2)　性能評価研究

①　性能評価の概要（Mr.D. Billington ）

ＡＥＡはＵＫＮｉｒｅｘからの委託により、ＬＬＷ、ＩＬＷ処分場閉鎖後の性能評価を担当している。10^{-6}の個人リスクを評価目標としており、性能評価報告書の政府への提出時期は未定(2000年以降？)だが、予察的性能評価報告書(ＮＳＡＲＰ)を作成中である。　評価のタイムフレームについては10^{4} 年といった制限を設けていず、10^{8} 年までの評価を行っている。評価の種類としては以下のものを実施している。

- 基本ケースによる決定論的評価
- 感度解析
- 代替ケースによる評価
- 確率論的評価（ＭＡＳＣＯＴコード）

（感度解析・代替ケースによる評価・確率論的評価）データとモデル中の不確実性の影響評価

コードとしてはニアフィールド核種移行評価のため、ＳＴＲＡＷ、ＳＴＲＡＷ2（溶解度制限、線型収着、崩壊連鎖生成）、ファーフィールド核種移行評価として、前述のＮＡＭＭＵ、ＮＡＰＳＡＣ、生物園評価としてＢＩＯＳを使用している。

安全評価のため研究として、(a)人工バリア、(b)ニアフィールド化学、(c)地層媒体中の物質移動、(d)生物園、(e)ガス生成・移行の５分野について室内実験、原位置試験及びモデリングを関連付けて実施している。

②　ガス発生・移行（Dr.P.Agg, Dr.W.Rodwell）

ＬＬＷ、ＩＬＷ処分後のガスの主な発生メカニズムとしては、嫌気性条件下での金属の腐食及び有機質（特にセルロース系）廃棄物の微生物による分解(degradation)が挙げられる。これらのメカニズムによる生成ガスの主なものは、

水素、CO_2 、メタンである。処分場の安全評価におけるガスが及ぼす潜在的危険性として以下のものが考えられる。

- ガスが処分場に閉じ込められた場合

  ⇨圧力上昇による処分環境下での動水勾配及び地下水流動への影響
- ガスが処分場から地層中へ放出された場合
  - (a) ガス／水の２相流による地下水の移動（生物圏への核種移行加速）
  - (b) 可燃性ガスの生物圏での炎上、爆発
  - (c) 放射性（毒性）ガスの生物圏への放出

ガス発生のモデル化のため金属腐食及び有機物の分解に関する反応として図６、７のものを考慮した。ガス生成速度に関する一次の微分方程式をコードＧＡＭＭＯＮにより解くことで長期のガス発生予測が可能となる。模擬ＬＬＷを充填したドラム缶中のガスの発生量の３年までの経時変化の実測値とＧＡＭＭＯＮによる予測値はよく一致した。

10^6 年までのガス発生量の予測結果では、約 100年まで嫌気性金属腐食により発生した水素が支配的であり、約 100～約 250年では、嫌気性微生物の増加によりCO_2 が支配的となる。約 250～3000年では、微生物分解システムの中でH_2が消費され、メタンが支配的となり、約3000年以降セルロース材が消費され、微生物が死滅し、再びH_2が支配的となる（図８参照）。

課題としては、処分場でのガスの蓄積、移動、ニアフィールドからのガス放出、ファーフィールドでのガス移行の予測評価が挙げられる。ニアフィールドガス移行に関しては、ＮＳＡＲＰプロジェクトで調査されている。またファーフィールドガス移行に関しては、ダルシー則、多孔質媒体中の２相流、亀裂ネットワークモデリングが実施されているところである。

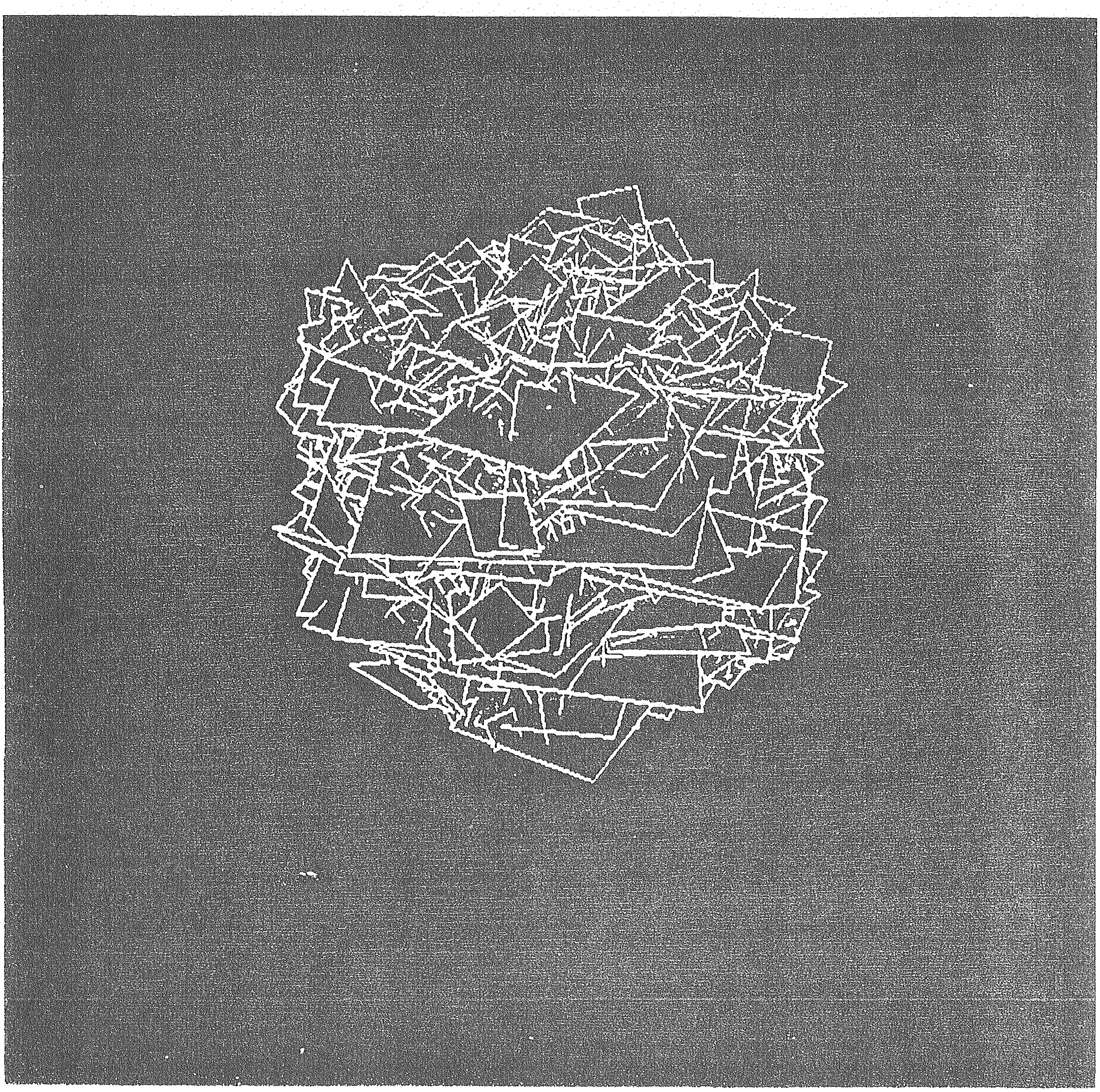


図1　3次元のフラクチャーネットワークモデル

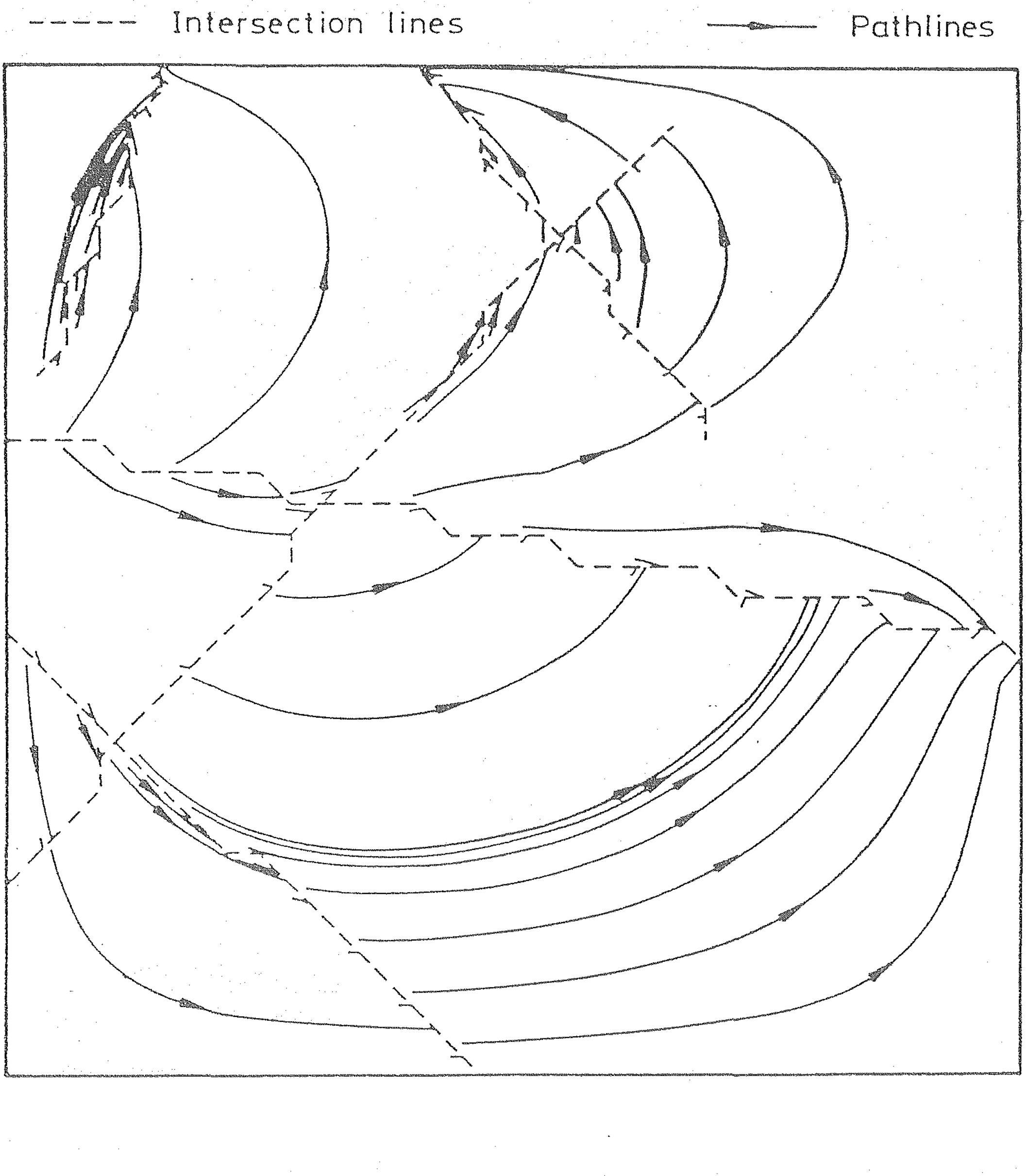
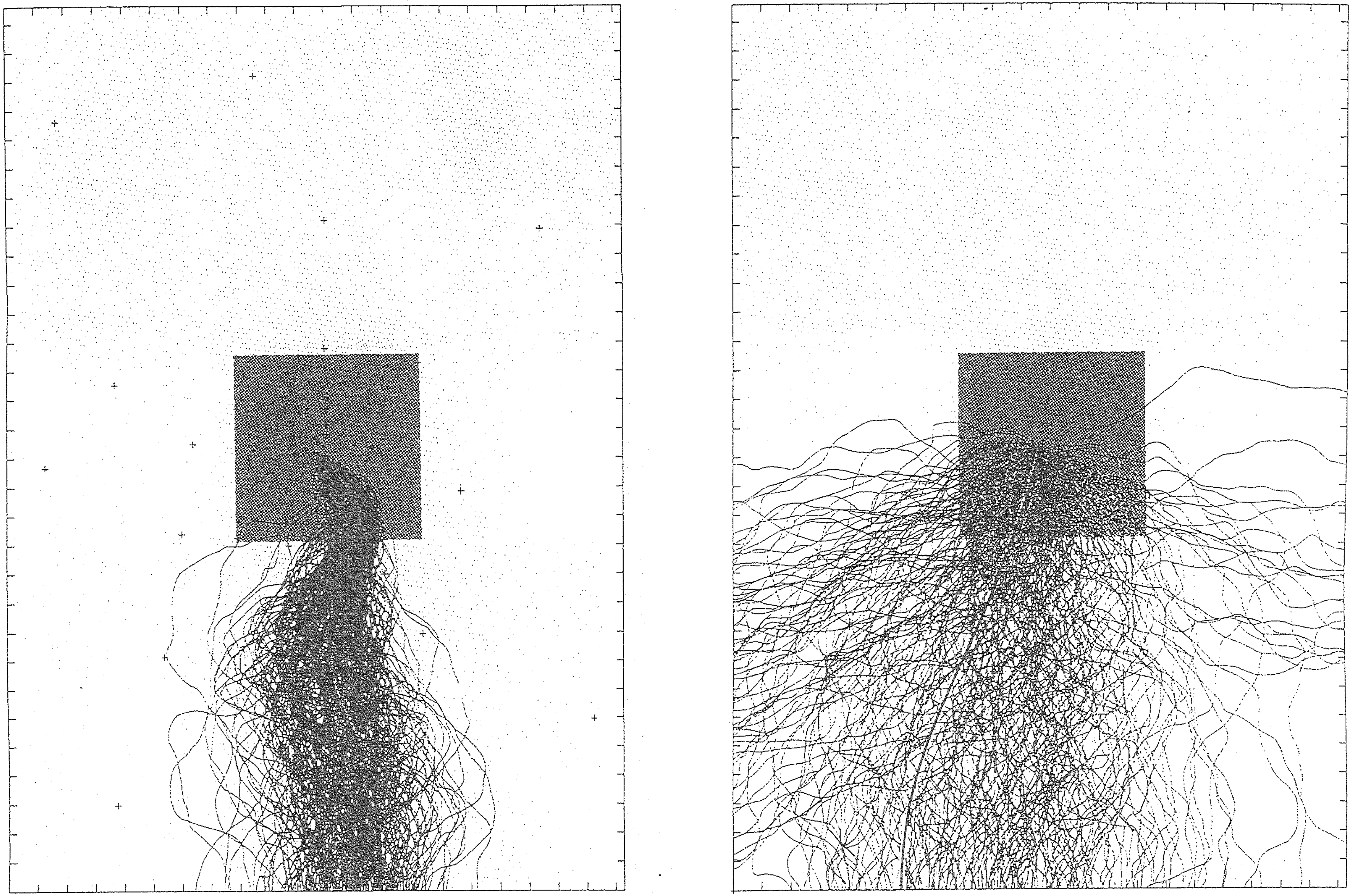


図2　ＮＡＰＳＡＣによる地下水流動経路の評価結果

（Stripaサイトのケース）



a） 透水量係数の測定データ点数が多い場合

b） 透水量係数の測定データ点数が少ない場合

図3　ＮＡＭＭＵにおける流動経路の評価結果（WIPPサイトのケース）

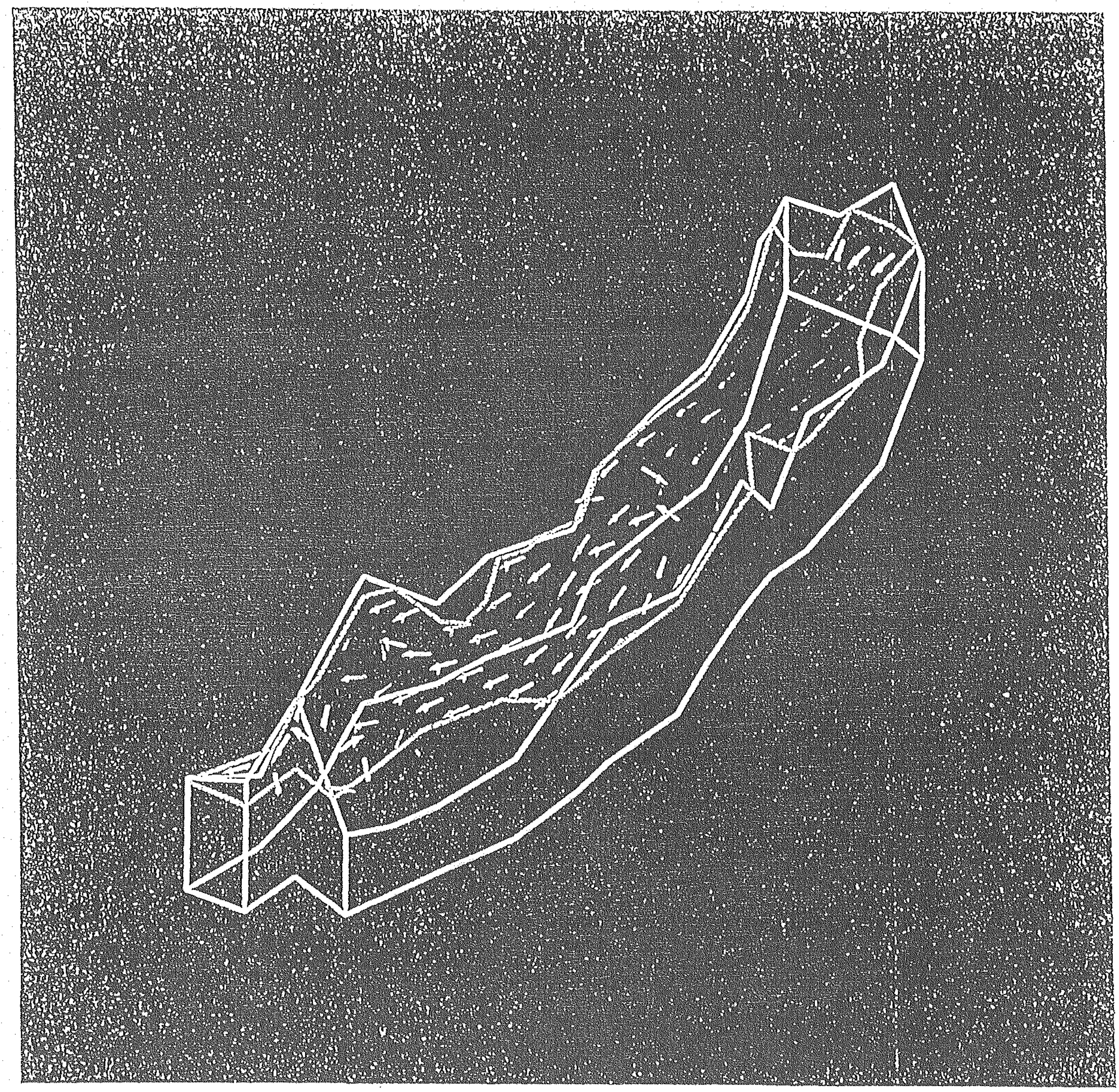


図4　ＮＡＭＭＵ／ＡＤＶＩＺＥによるデモの一例
（コンラッドサイトでの地下水流動ベクトルの分布）

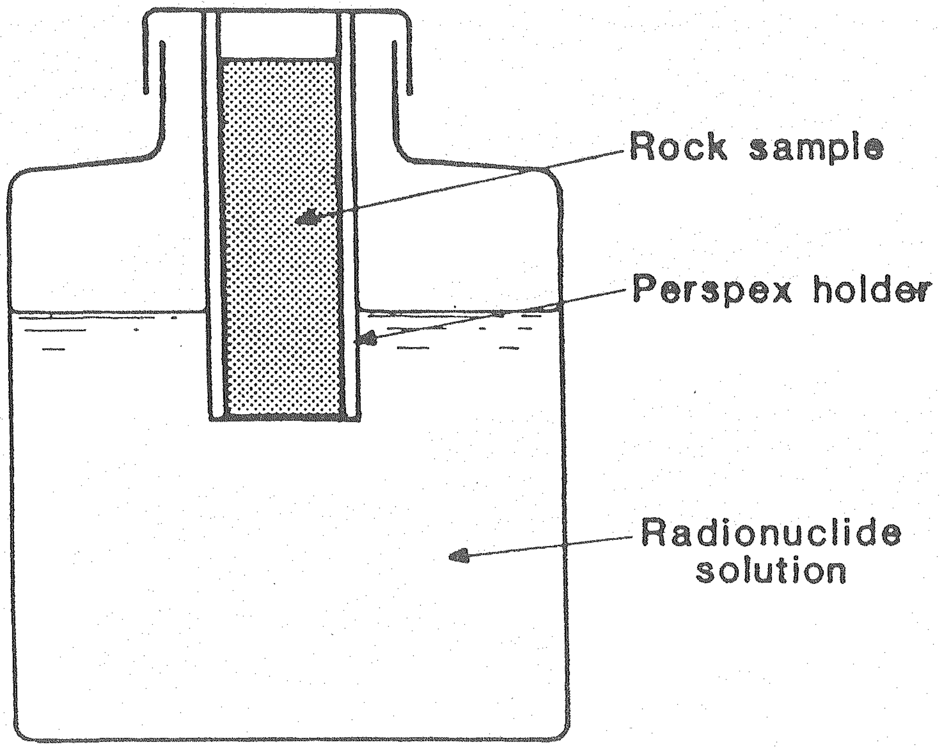


図5　Reservoir Depletion法

(a) *Aerobic corrosion*

(i) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
(ii) $4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3$

(b) *Oxide-film reduction*

(i) $4Fe_2O_3 + Fe \rightarrow 3Fe_3O_4$
(ii) $2Fe(OH)_3 + 4Fe + 2H_2O \rightarrow 2Fe_3O_4 + 5H_2$

(c) *Anaerobic corrosion*

(i) $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$
(ii) $Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$
(iii) $3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2$

図６　金属腐食プロセスによるガス生成反応

(a) *Physical degradation of bulk cellulose*
Bulk cellulose → Soluble cellulose/polysaccharide

(b) *Hydrolysis of soluble cellulose/polysaccharide*
$\underset{\text{cellulose}}{[C_6H_{10}O_5]_n} + nH_2O \rightarrow \underset{\text{glucose}}{nC_6H_{12}O_6}$

(c) *Further microbially-mediated degradation*
(i) *aerobic decomposition* (Microbe type 1)
$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
(ii) *nitrate decomposition* (Microbe type 2)
$5C_6H_{12}O_6 + 24HNO_3 \rightarrow 30CO_2 + 12N_2 + 42H_2O$
(iii) *acidogenesis* (Microbe type 3)
$C_6H_{12}O_6 + H_2O \rightarrow 2CO_2 + 2H_2 + C_2H_5OH + CH_3COOH$
(iv) *acetogenesis* (Microbe type 4)
$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2$
(v) *methanogenesis 1* (Microbe type 5)
$CH_3COOH \rightarrow CO_2 + CH_4$
(vi) *methanogenesis* 2 (Microbe type 6)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
(vii) *sulphate reduction 1* (Microbe type 7)
$CH_3COOH + H_2SO_4 \rightarrow H_2S + 2CO_2 + 2H_2O$
(viii) *sulphate reduction* 2 (Microbe type 8)
$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O$

図７　微生物による減成モデルにおけるガス生成反応

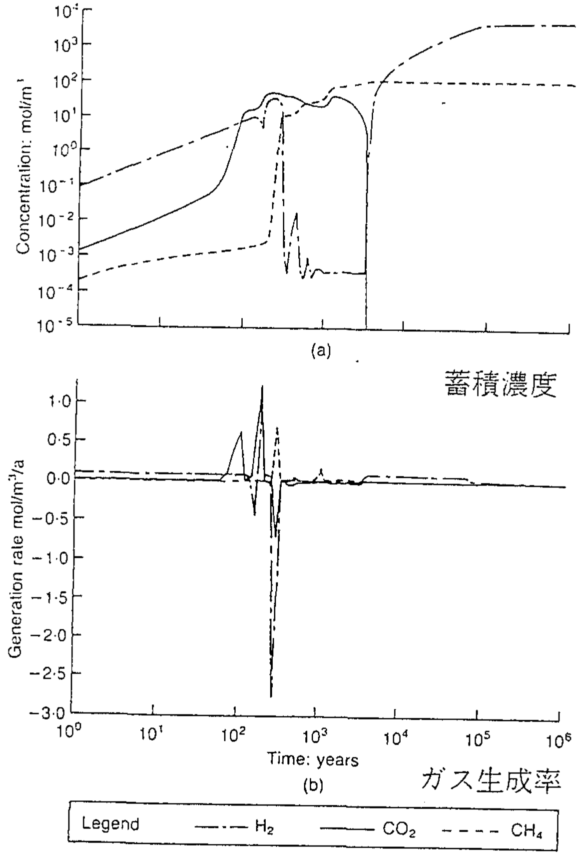


図８　ＧＡＭＭＯＮコードによるＬＬＷ，ＩＬＷによる廃棄物からのガス発生の長期予測結果

3. UK Nirexの現状

平成5年7月22日、英国 HarwellにあるUK Nirex本社を訪問し、Mr.H.Hudson (Publications Officer) 及びDr.R.Chaplow(Manager for the Site Characterization) より、同社の活動の状況について説明を得ることができた。UK Nirex社は、英国における中低レベル放射性廃棄物処分の実施責任機関であり、現在シェラフィールドに深地層処分場の建設計画を持って、研究開発等の活動を展開している。その内容は、動燃事業団にとって参考になると考えられるので、今回受けた説明、入手資料を基に、UK Nirex社の活動の現状をまとめてみた。

(1) 設 立

① 1982年に、The Nuclear Industry Radioactive Waste Executive (Nirex)として、英国政府の合意のもと、次の4社によって設立された。

- British Nuclear Fuels plc.（BNFL）
- The Central Electricity Generating Board
- The South of Scotland Electricity Board
- The UK Atomic Energy Authority

② 1985年11月に、UK Nirex Ltd. として再編され、このとき政府側からthe Department of Energyが参画した。

③ その後電力会社の再編成があり、また1992年4月には、the Department of Energyの機能がthe Department of Trade and Industryに移管された。その結果、現在の株主は次のとおりである。

株　　主	株数	割合
通常株主		
●British Nuclear Fuels plc.（ＢＮＦＬ）(注)	4,250	42.5%
●Nuclear Electric plc.(注)	4,250	42.5%
●Scottish Nuclear Ltd.(注)	750	7.5%
●UK Atomic Energy Authority	750	7.5%
特別株主		
●The Secretary of State for Trade and Industry	1	

（注）いずれも、民間企業ではなく、公共事業体とのことである。

④　ＵＫ Nirexは、廃棄物発生者がその責任を果たすために設立されたものである。資金は、原子力産業から直接提供されている。

(2)　職員数

現在約 100名。ただし、委託研究を多く行っており、これを含めると関与している人数は多数となる。

(3)　本社の所在地

英国、Curie Avenue, Harwell, Didcot, Oxfordshire　OX110RH

(4)　Nirex の役割

②　英国の原子力産業ならびに病院、産業、研究、国防において放射性物質を使用することによって発生する、中レベル及び低レベル放射性固体廃棄物を安全に処分すること。

（（注）現在のところ、高レベル放射性廃棄物の処分については、役割の中に含まれていない。高レベル放射性廃棄物の現在の管理責任者は、ＢＮＦＬ／ＵＫＡＥＡである。）

② Nirex の活動の中には、次のことが含まれる。

- 英国の放射性廃棄物について、包括的で最新の記録の維持
- 各廃棄物について、最適の処分方法の検討
- 廃棄物容器の標準化
- 好ましいサイトの調査
- 放射性廃棄物の輸送及び処分の新しい施設の立案、開発、運転
- 処分方法についての研究管理
- Nirex の活動について、公衆への情報の提供

③ Nirex は現在、深地層処分の研究、開発、設計、許認可、建設、運転を実施あるいは計画中である。

この50年間は、１つの処分場で十分であるとし、建設及び50年間以上にわたる運転のコストは、2.8 ～3.3 ×10^9 ポンドとしている。

(5) 英国における中低レベル放射性廃棄物の分類と発生量

① 低レベル放射性廃棄物（ＬＬＷ）

- α核種 4 GBq／ton 、$\beta\gamma$核種12GBq／ton を超えないもので、グローブ、壊れた実験器具、土壌、デコミ廃棄物など。通常 200ℓ ドラム缶に充填（この他に、2 m ＬＬＷ ＢＯＸ、4 mＬＬＷ ＢＯＸもあり）。年間発生量は30,000㎥。
- 現在は、ＤＲＩＧＧサイトに浅地中処分している。ＤＲＩＧＧサイトの運転はＢＮＦＬの責任で行っている。

② 中レベル放射性廃棄物（ＩＬＷ）

- ＩＬＷは、ＬＬＷの限界値を超えるもので、ハル、原子炉金属材、フィルター、スラッジ等著しい発熱のないもの。再処理によって、多量の長寿命核種を含むＩＬＷが発生する。セメント固化し、通常 500ℓ ドラム缶に充填する（この他に、3 ㎥ ＩＬＷＢＯＸ、4 mＩＬＷ ＢＯＸもあり）。
- 年間発生量は、5,000 ㎥であり、現在50,000㎥を貯蔵中。

(6) 処分の安全確保策

① ＤＯＥの安全基準は、個人の年間線量当量 0.1mSvに相当するリスクを受けないこと。時間制限(cut off time)は現在はない。

② 安全確保策は、いかなる時点においても生物圏へ有意な量の放射性核種が還流しないことを確かなものとすることであり、このために多重バリアシステムによる封じ込めを考えている。

③ 多重バリアは、物理的バリア、化学的バリア及び天然バリアであり、それぞれ次のとおり。

- 物理的バリア …… スチールドラム／ボックスあるいはコンクリートボックス。
  ドラム缶中のセメント固化体
- 化学的バリア …… 核種の溶解度を抑制するアルカリ性及び吸着性
- 天然バリア …… 地下水の流速が低く、物理的に安定なサイトに隔離

図1に多重バリアシステムの概念を示す。

(7) 調査サイトの選定

① 500 地点を12地点に絞り、最後に2地点とされた。調査項目は、地質、土地利用性、輸送／接近性、建設可能性、人口、環境影響、ＰＡなど。

② 1989年に公表されたアセスメントレポート(Nirexレポート№.71) において、ドーンレイ及びシェラフィールドについて、ＩＬＷ及びＬＬＷの深地層処分場としての適性を評価することとされた。この2地点が選定されたのは、ＰＡを考慮してのことである。既に原子力施設が稼動しており、したがって原子力産業に親近感があるからである。

③　1989年～91年に行われたボアホールドリルやその他の地質調査の結果、両サイトともに地質的には深地層処分場に適している可能性があることがわかったが、1991年7月にシェラフィールドを対象に、さらに調査を進めることとされた。

④　シェラフィールドが選定された大きな理由は、廃棄物の輸送及びそのコストである（処分場へ埋設する廃棄物の60％はシェラフィールドで発生）。

⑤　ただし、シェラフィールドが処分場サイトとして決まったわけではない。

⑥　図2にシェラフィールドの地図を、図3に地質断面を示す。

(8)　深地層処分場の概念

①　図4に、現在考えられている概念を示す。図5は、廃棄物受入れ施設の位置と建物のイメージを表したもので、既存の施設との位置関係が示されている。

②　深地層処分場の現在の概念は、

(a)　地上施設である廃棄物受入れ施設をＢＮＦＬの敷地内に置き、既存のインフラを最大限に利用する。

(b)　地下施設は深さ 800mであり、スパイラル状の2本のドリフト（長さ約5マイル、直径25フィート）で受入れ施設と結び、地上からコントロールするラックアンドピニオン式の電車で、廃棄物パッケージを1体ずつ運搬する。地下施設の大きさは約1.5 km四方である。

(c)　地下施設からは、2本の換気坑を立ち上げるのみとする。これは非常用の出入口ともなる。

(d)　このような設計を行うことによって、地上に存在する施設をほとんどなくし、必要な土地を少なくする。

というものである。

シェラフィールドサイトは、火山岩の岩盤上に堆積岩（砂岩など）が覆っており

（図３）、処分場は火山岩中に考えられている。

(9) シェラフィールドサイトの調査

① 1989年以来、シェラフィールドにおいて多くのボアホールドリルが行われてきている。図６にその場所を示す。1992年11月末までに、未許可のボアホールは、ＢＨ８、９及び13である。ボアホールドリルの深さは 2,000mに達する。全体で約15本のボアホールドリルが予定されている。

② 1992年10月にボアホールドリルと並行して、地下にRock Characterization Facility（ＲＣＦ）を建設することを発表。これは、サイトの特性を十分に評価し、処分場建設の申請を出すかどうかの判断情報を入手するためのものであり、また操業開始の許可を得るための情報を入手するためにも必要であるとしている。

具体的には、長期の安全性の評価、処分場の位置と方向・設計の決定、処分場建設の可能性の実証などを行う。

③ ボアホールドリルには、LiClをトレーサーとして用いている。

④ これまでの調査により、地下水は上層の堆積岩中を流れるものと下層の火山岩中を流れるものに分けられる。下層の方では、陸側からの流れと海側からの流れが混合しているという。

下層の地下水は、最高で海水の６倍、通常で３倍の塩濃度であるとのこと。

(10) Rock Characterization Facility（ＲＣＦ）の建設計画

① 目的は、次のとおり。

(a) 地質及び水理地質データの取得

(b) 長期安全性評価を行うためのモデル確証プログラムの実施

(c) 地質的に適切なゾーン内に処分場を建設するために、位置と方向、設計を決定するのに必要なデータの取得

(d) 処分場の建設方法を決めコスト評価を行うのに必要な、岩石の性質や割れ目の特性などの地質工学的なデータの取得

この他に、大容量の岩石について3次元のデータが入手できるし、その他地上ではできない試験が可能であるとしている。

② 図7にＲＣＦの概念図を示す。

③ 1993年に建設計画を申請する予定。年内に許可が下りれば、1994年に2本のアクセス立坑の掘削を開始し、1996年に終了を予定（Phase 1）。

場所は、ＢＮＦＬの所有地の地下で、Longlands Farm、Gosforth、Cumbria である（図2参照）。

立坑の直径は5ｍ、深さは 650m（処分場の想定深さ）、中心間距離は50mである。必要ならば、1本の立坑について 900mの深さまで延長することが考えられている。立坑掘削により、原位置でのロックマスの直接評価（掘削影響、割れ目の動きなど）及び地質構造の証明ができ、また地下水の流れの評価が可能となる。

④ 1996年にPhase 2を開始し、1999年にPhase 3の予定。

Phase 2は、3つの水平のテストギャラリーからなり、大きさは夫々3ｍ×3ｍ、長さ 150mである。

テストギャラリーでは、次の試験を行う計画である。

(a) 岩盤中の割れ目や断層の地図作りのためのドリリング

(b) 地下水理を明らかにするための水理地質学的測定

(c) 分散機構に関する情報を得るためのトレーサーテスト

(d) 地下水の起源と年代を評価するための地球化学的テスト

(e) 地下空洞を建設する技術を決めるための地質工学的テスト

(f) フラクチャーネットワークを通ってのガスの流れを研究するガス移行テスト

(g) ロックマスの化学的・熱的性質を調べるための実験

Phase 3は、ギャラリーをさらに水平に延長し、長さ 375m～600 mにする計画で

ある。目的は、特性調査及び確証プロセスを完了させることである。

図８は、地質断面中のＲＣＦの位置を示す。

⑤ ＲＣＦの建設費は、1.2 $\times 10^8$ ポンド（1992年レート）、必要な人員は 600人・年、期間は約５年と見積もられている。

⑥ なおＲＣＦでは、実廃棄物の使用は考えられていない。

(11) 処分場の建設計画

① ボアホールテスト、地震探査、ＲＣＦでの各種試験などの結果から、このサイトでの長期安全性が十分な信頼性でもって評価されたとき、処分場開発の申請が行われる。

② ＲＣＦの初期の結果として、地表からの調査によって地質及び水理地質の評価が十分確かなものとなれば、1996年遅く、または1997年の早い時期に処分場建設計画の申請が行われる予定。

ただし、申請について判断が得られるには、地下での研究が必要と考えられている。

③ 処分場建設計画が申請された時、Nirex は公聴会に対して、長期安全性に関するすべての情報を提供する。

④ 1996年遅く、または1997年の早い時期に処分場建設計画を申請したとすれば、Nirex は2006年～2007年に処分場の操業開始を目指す。

(12) 安全評価研究

Nirex が主にＡＥＡ Technology に委託している安全評価研究のほとんどは、現在動燃事業団が高レベル放射性廃棄物用に進めている研究内容と同じである。以下に主な項目を示す。

① 安全評価

- ニアフィールド評価

  地下水流れ、腐食、コンクリート、溶解度、収着、ガス発生と移行

- 地圏(Geosphere) 評価

  地下水流れ、核種移行、ガス移行

- 生物圏評価

  河川・湖、土壌・岩石、海・江湾、大気

② 安全性研究

- ニアフィールド研究

  腐食、コンクリート、ファーフィールドの化学、溶解度、収着、有機物、微生物、ガス発生と移行

- 地圏(Geosphere) 研究

  地下水流れ、核種移行、ガス移行

- 生物圏研究

  生物圏移行、気候変動

なお、処分場の安全評価に当たって、考慮すべき経路として次の4つを取り上げている。

(a) 地下水
(b) ガス
(c) 人間侵入
(d) 自然現象

安全評価研究にNirexが使っている予算は、年間600万ポンドであり、14の大学、11の研究機関に委託している。

(13) 感想

英国においては、高レベル放射性廃棄物は50年間冷却のために貯蔵するという方針が取られており、まず最初に中低レベル放射性廃棄物の深地層処分を実施するという政策

となっている。そのため、これまでどちらかというと、Nirex あるいは研究開発を中核的に実施しているＡＥＡの活動状況に関心が薄かったように思われる。

しかし実態は、中低レベル放射性廃棄物を対象としているといえども、深地層処分の研究開発であり、しかも候補サイトを決めて、特性調査、処分場設計、地下研究施設の建設、安全評価研究などが行われており、相当に研究が進んでいるとの印象である。

別途訪問したＡＥＡ Technology においては、Nirex からの受託研究を行っており、その人材の豊富さ、設備の充実ぶり、研究開発の進展などに強く印象づけられたが、これらを合わせて考えてみると、英国における深地層処分の研究開発あるいは実施に向けての活動に対し、今後一層の関心を払うことが重要であると思われる。

以　上

Multi-Barrier Containment

Physical
Containment

Chemical
Conditioning
- Alkaline
- Sorbing

Geological Isolation
- Low water flow
- Physical stability

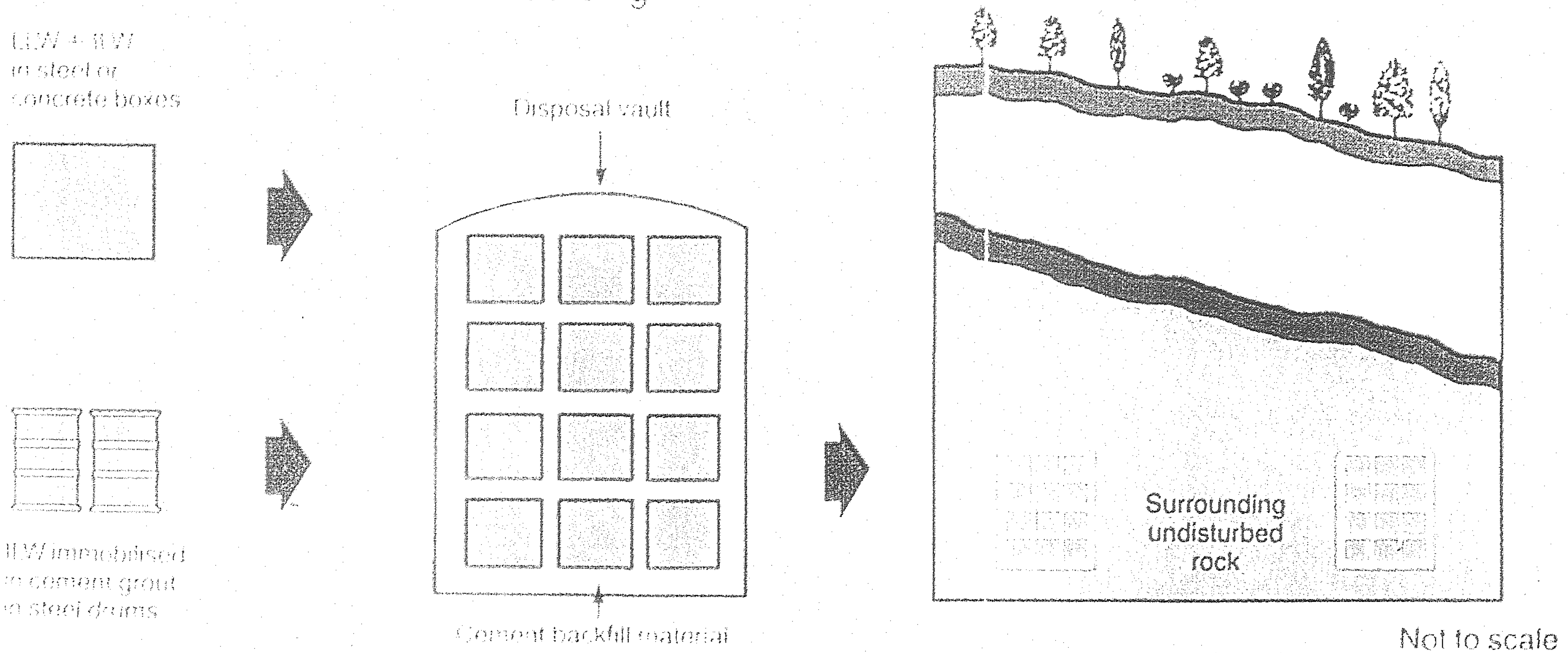


図１　多重バリアシステムの概念

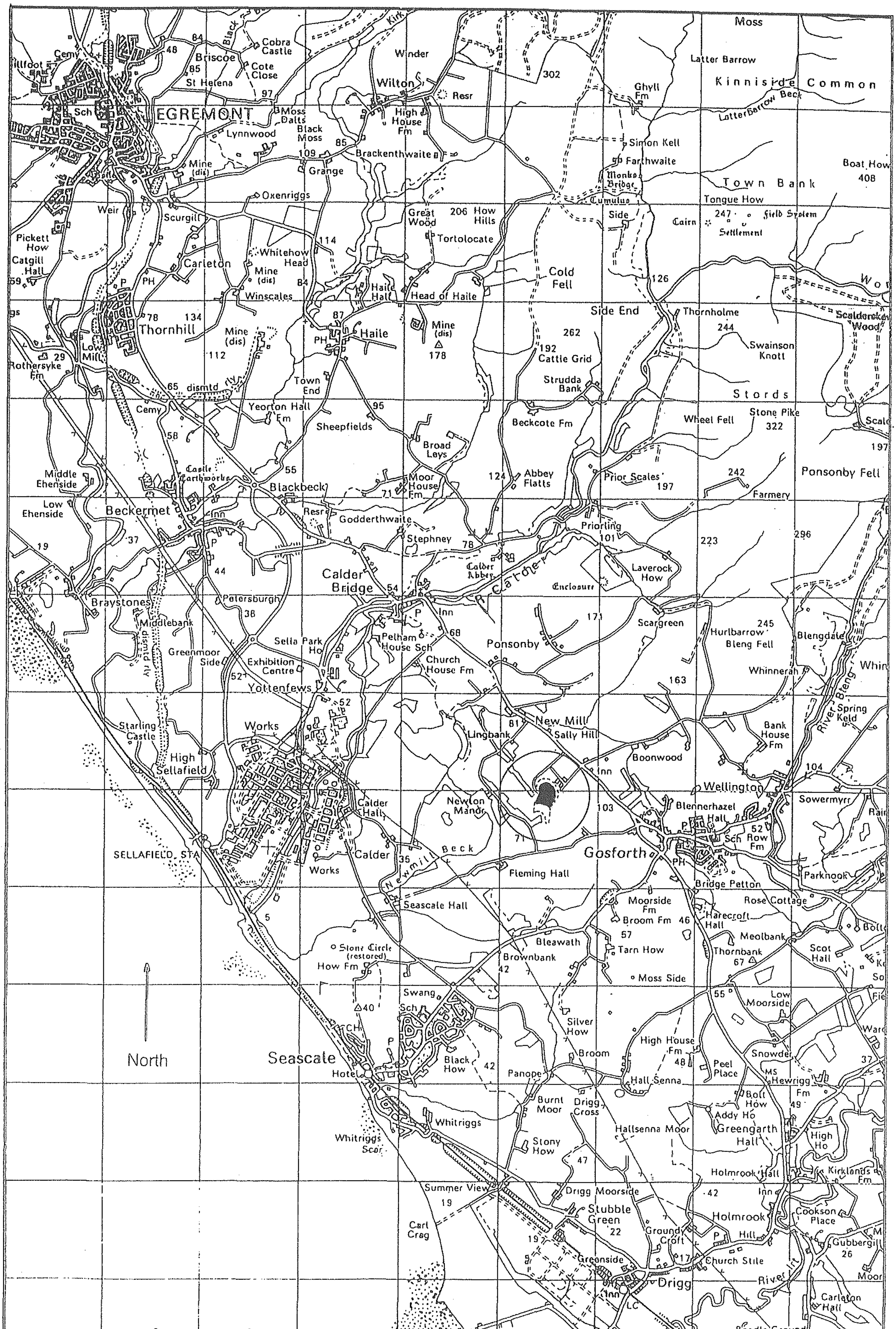


図２　シェラフィールドサイトの地図（赤く印づけられている

ところは、Rock Characterization Facilityの建設予定地）

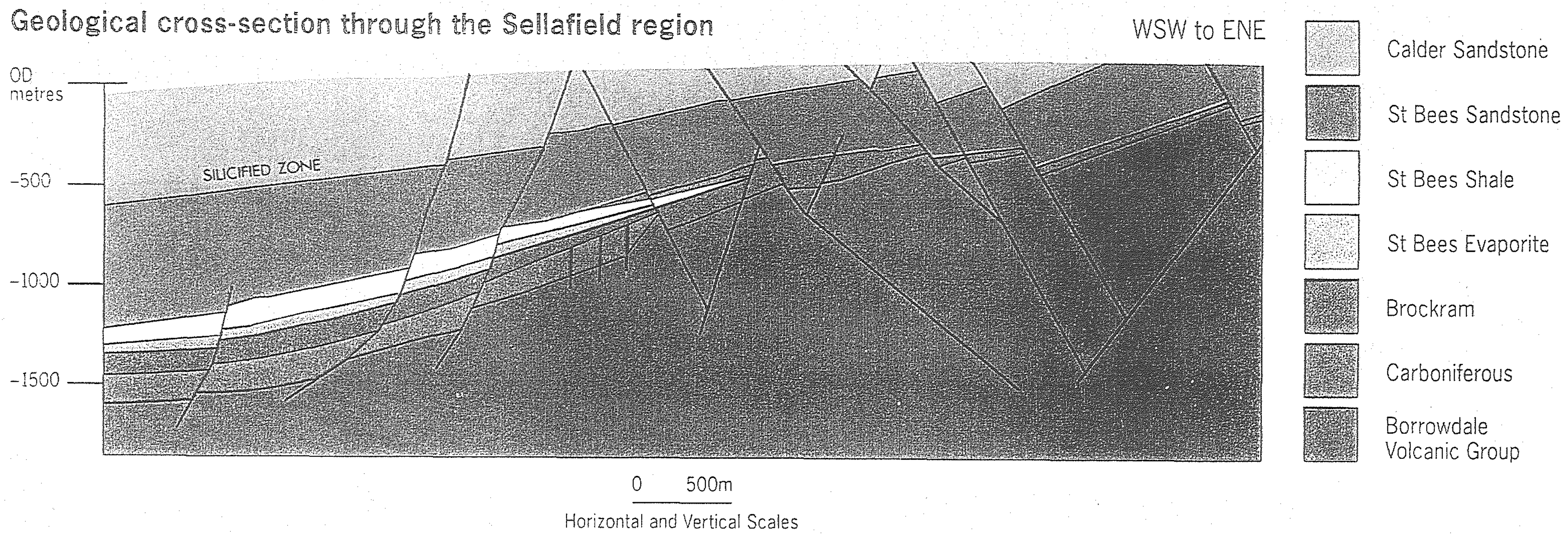


図３　シェラフィールドの地質断面図

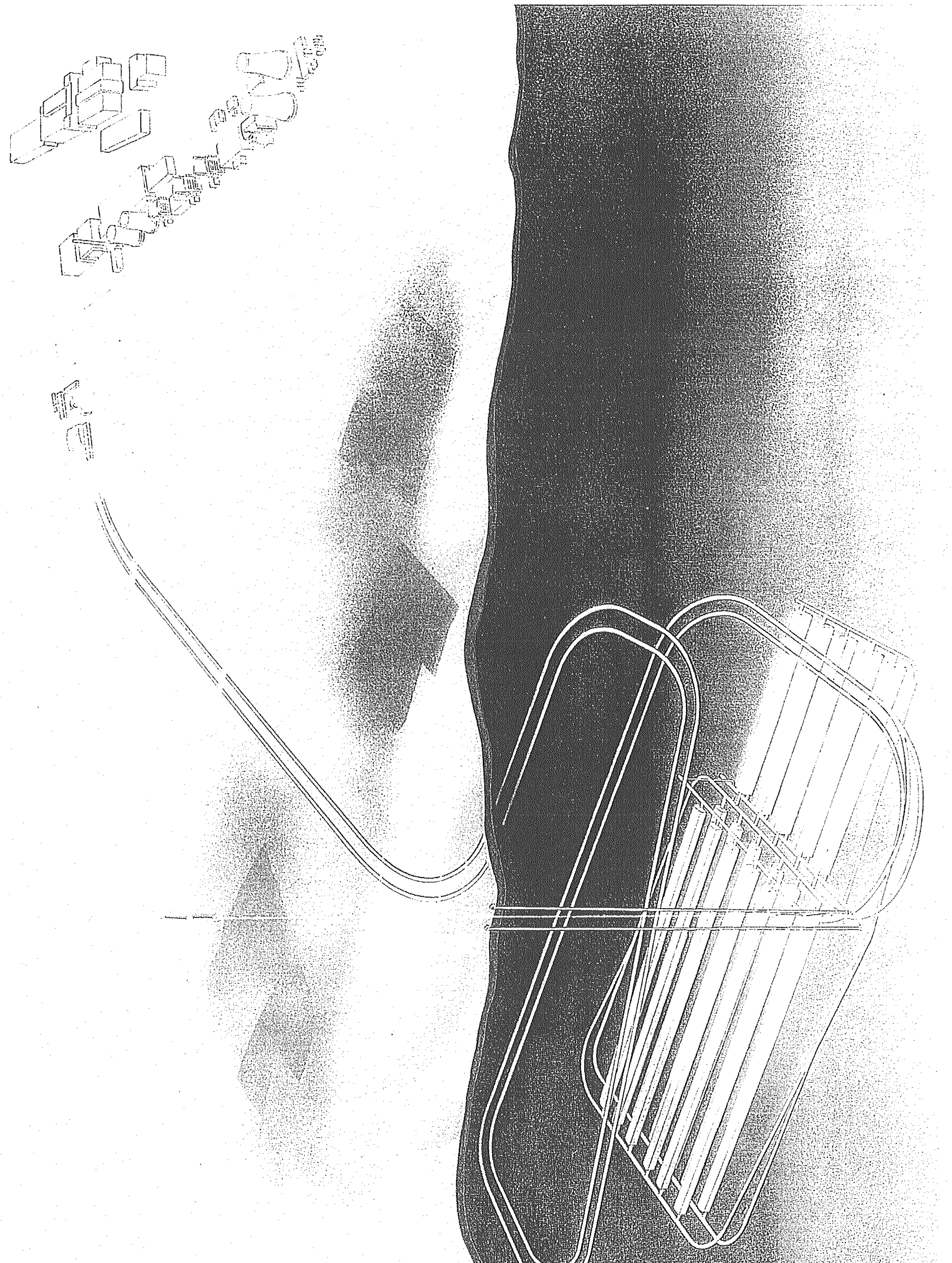
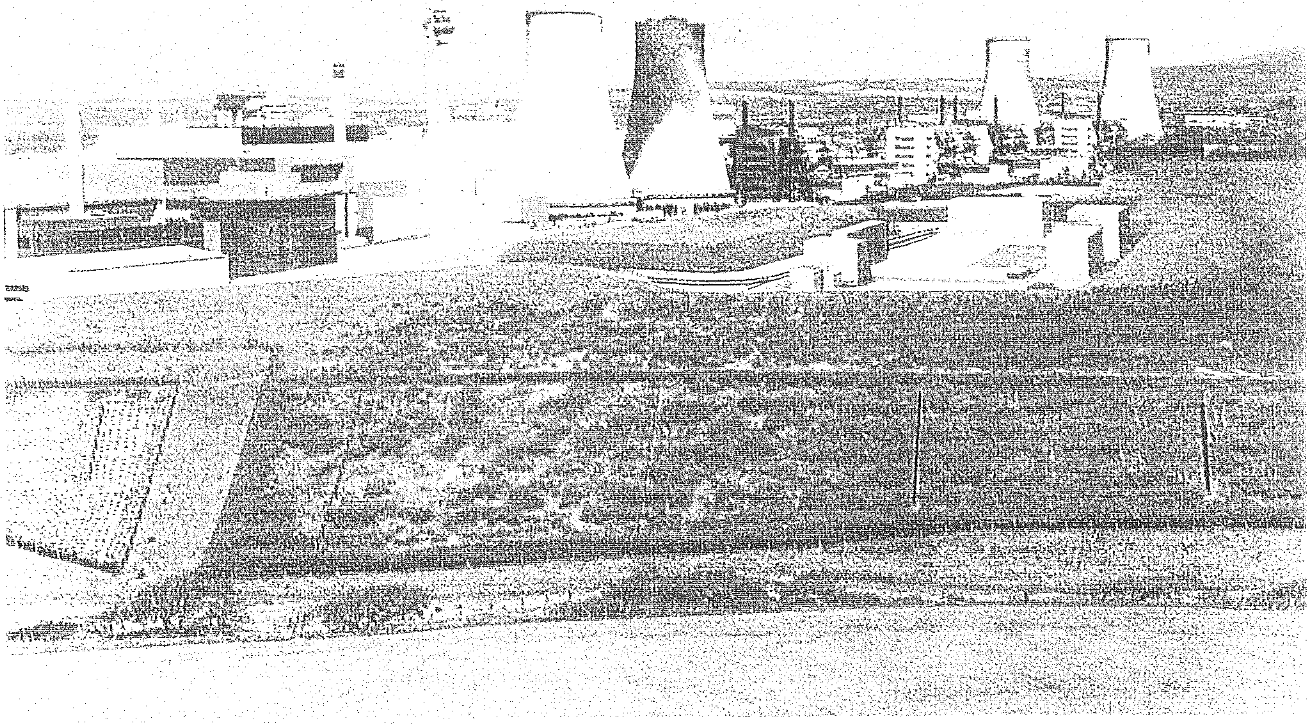


図４　深地層処分場の概念図



View of the

Sellafield site showing

proposed location

of the waste receipt

facilities.

図５　廃棄物受入れ施設の位置と建物のイメージ

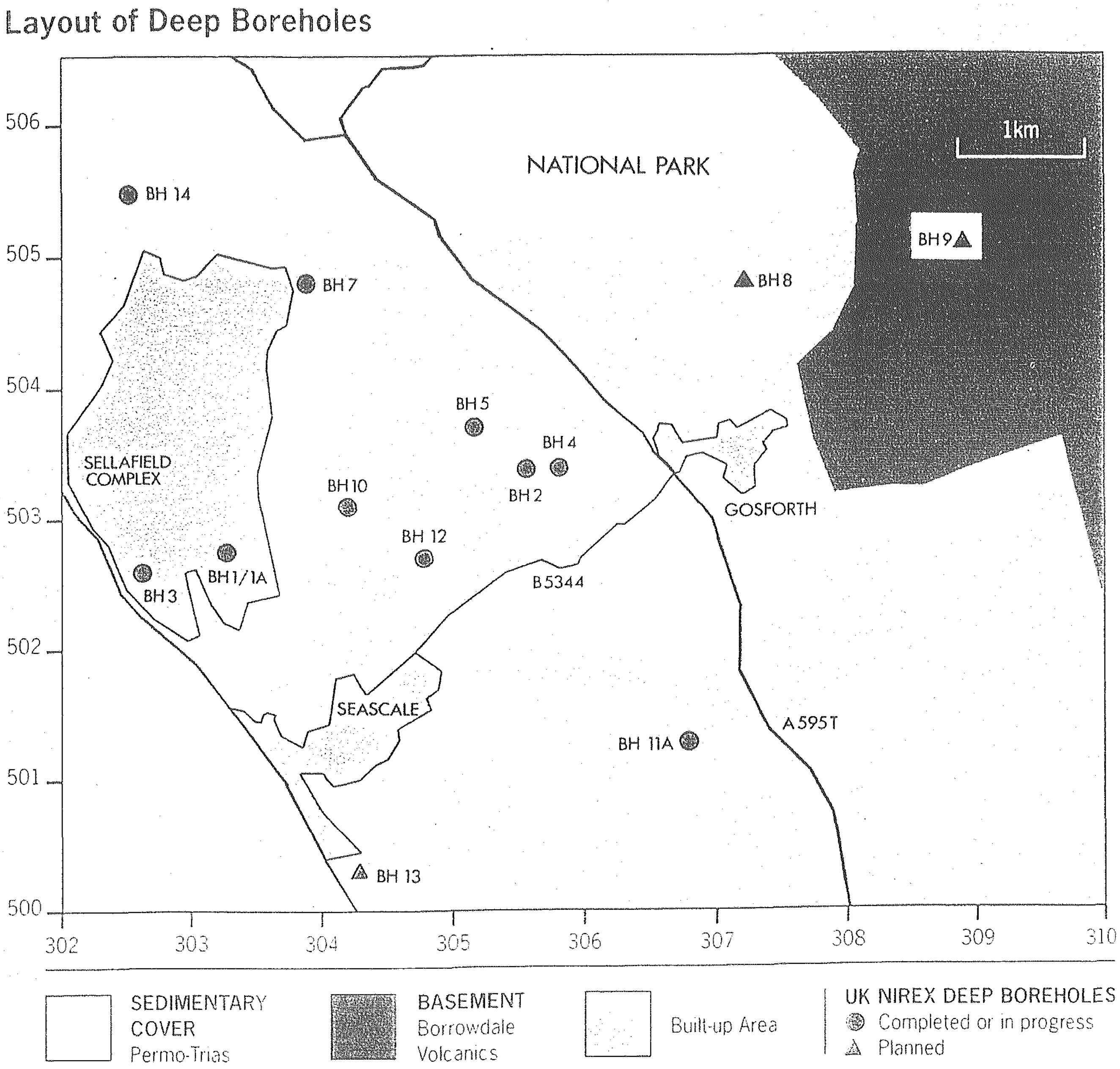


図６　ボアホールドリルの位置

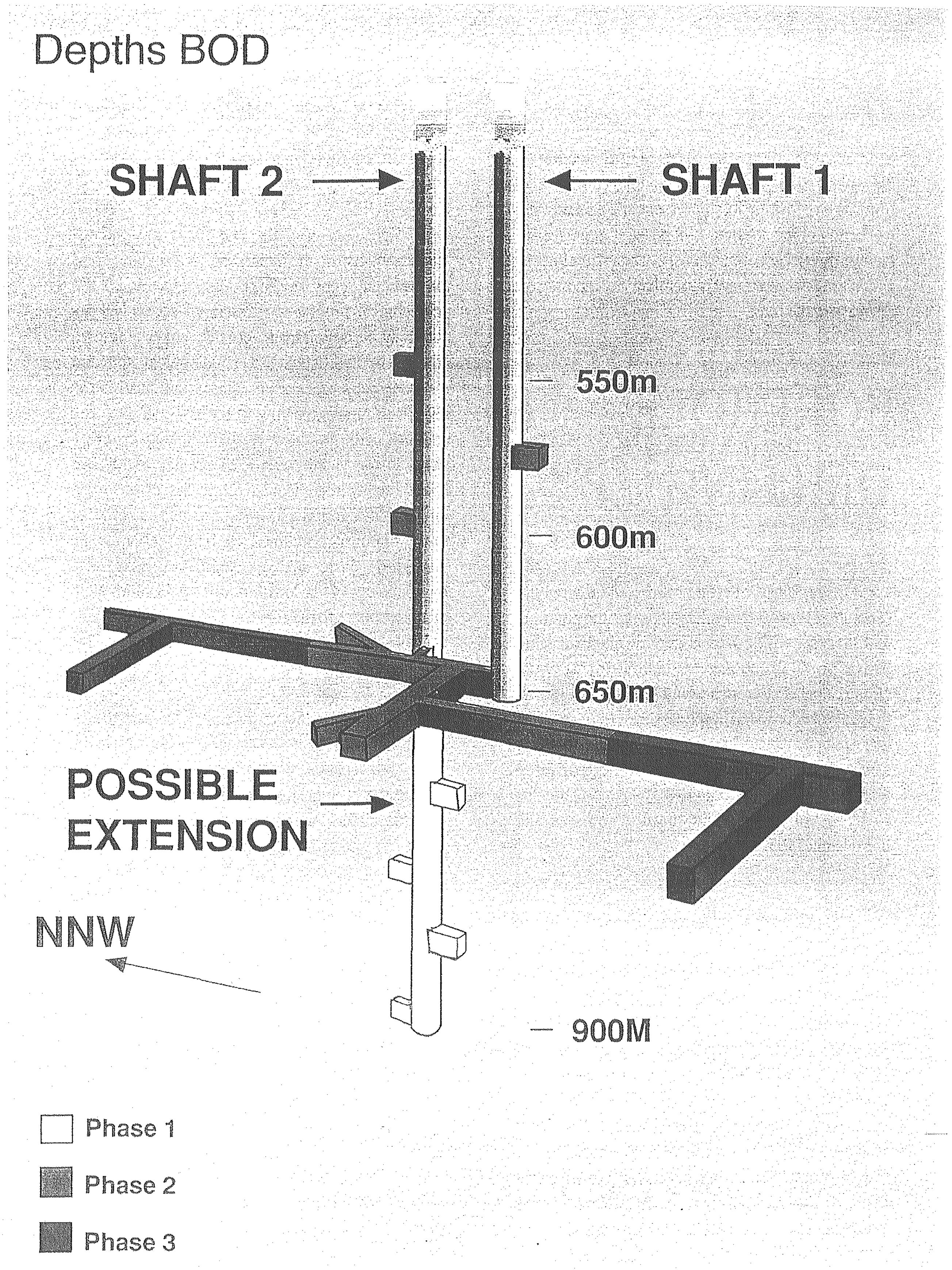

Depths BOD
SHAFT 2
SHAFT 1
550m
600m
650m
POSSIBLE
EXTENSION
NNW
900M
Phase 1
Phase 2
Phase 3

図7　ＲＣＦの概念図

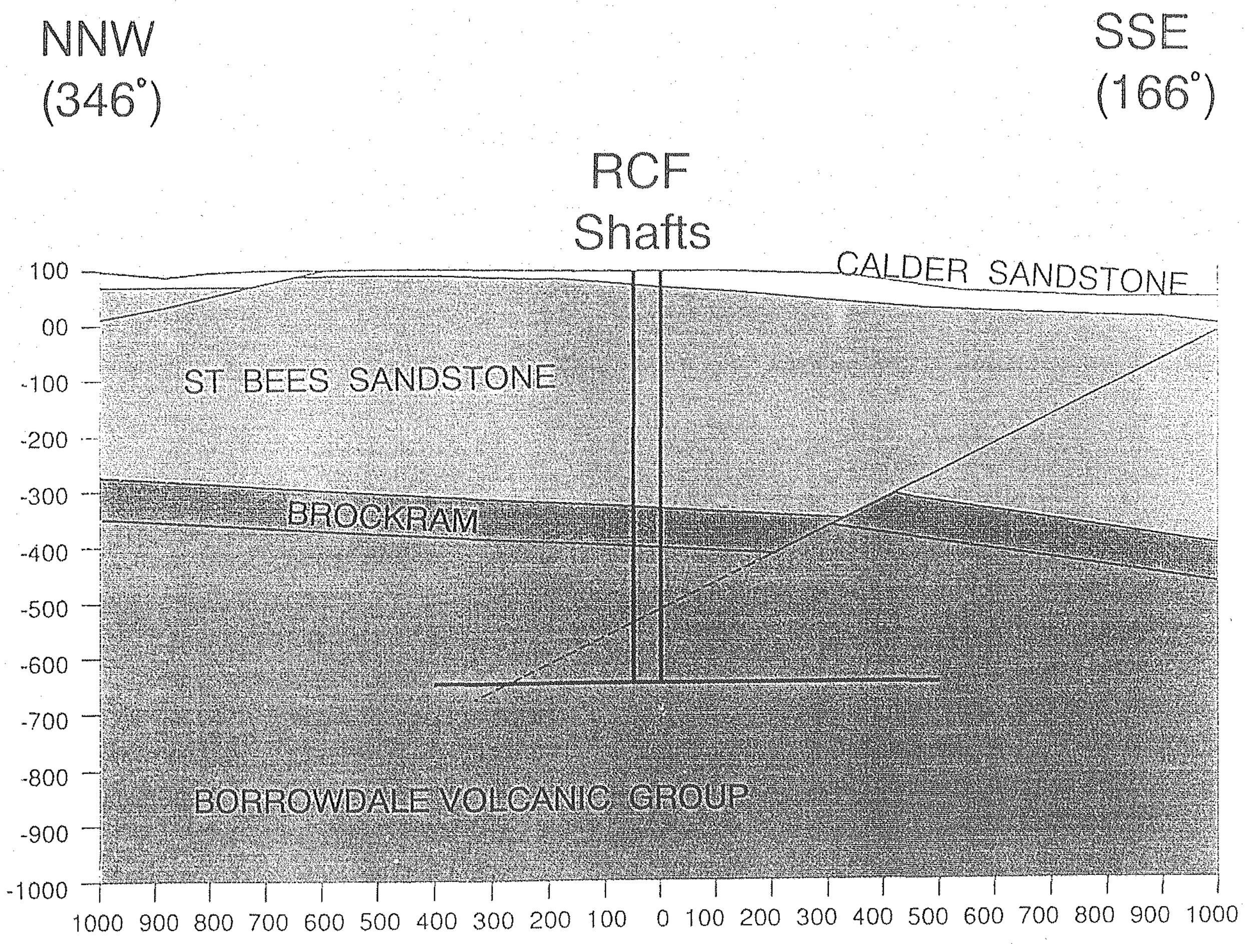
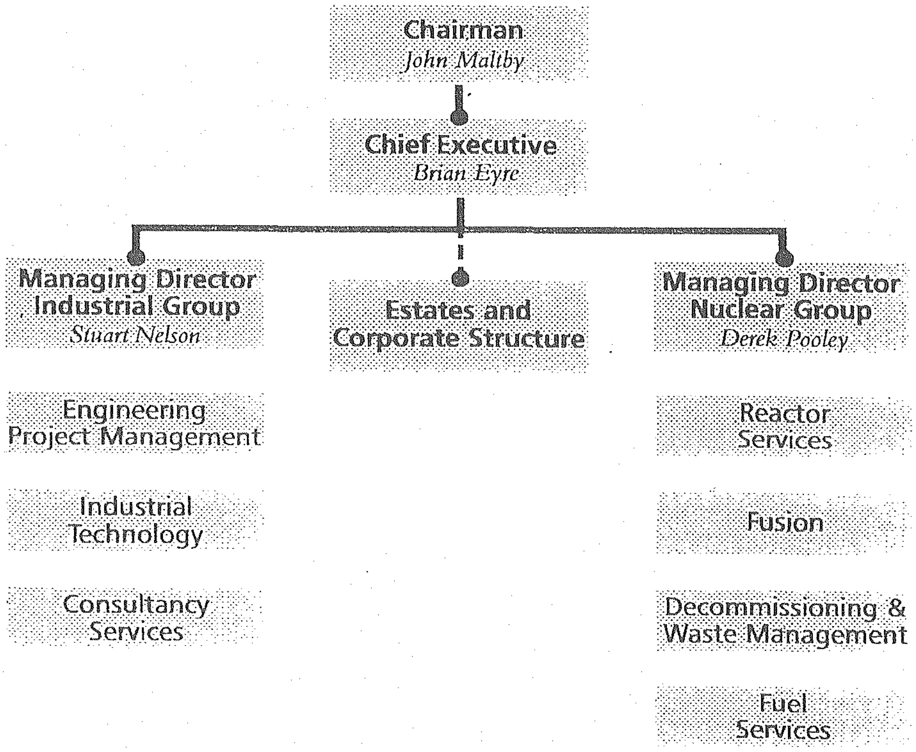


図８　地質断面図中のＲＣＦの位置（ＷＳＷから見たもの）

ＡＥＡ資料

AEA Technology Structure

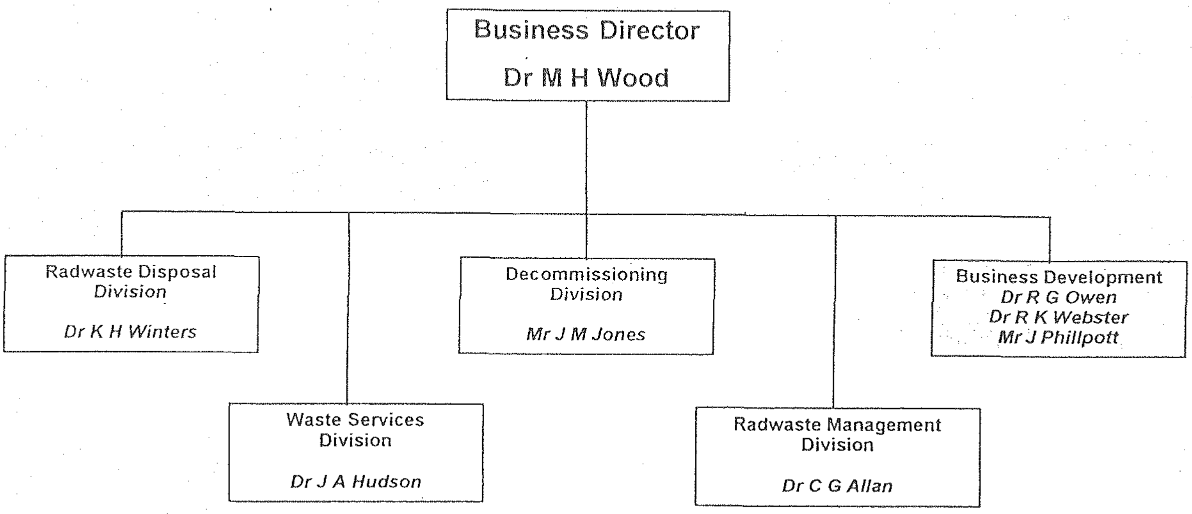
1590T01A



- **Chairman** *John Maltby*
  - **Chief Executive** *Brian Eyre*
    - **Managing Director Industrial Group** *Stuart Nelson*
      - Engineering Project Management
      - Industrial Technology
      - Consultancy Services
    - **Estates and Corporate Structure**
    - **Managing Director Nuclear Group** *Derek Pooley*
      - Reactor Services
      - Fusion
      - Decommissioning & Waste Management
      - Fuel Services

AEA Technology

Decommissioning & Waste Management



- Business Director
  Dr M H Wood
  - Radwaste Disposal Division
    Dr K H Winters
  - Waste Services Division
    Dr J A Hudson
  - Decommissioning Division
    Mr J M Jones
  - Radwaste Management Division
    Dr C G Allan
  - Business Development
    Dr R G Owen
    Dr R K Webster
    Mr J Phillpott

AEA Technology
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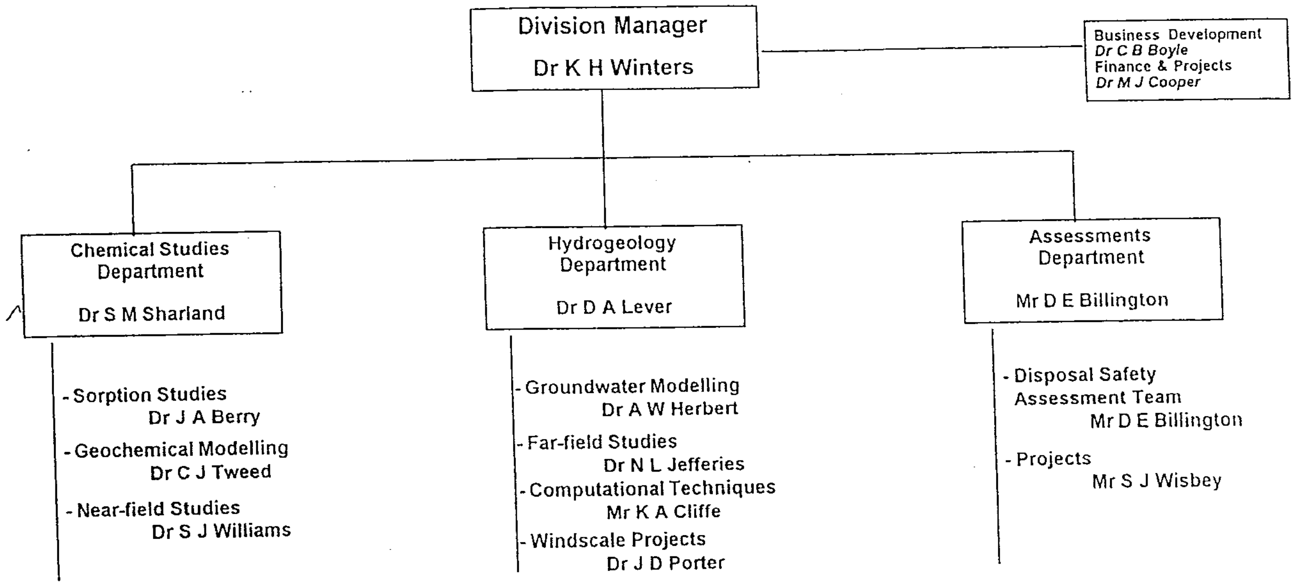
Waste Management

Radwaste Disposal Division



Division Manager
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Business Development
Dr C B Boyle
Finance & Projects
Dr M J Cooper

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Dr S M Sharland

- Sorption Studies
  Dr J A Berry
- Geochemical Modelling
  Dr C J Tweed
- Near-field Studies
  Dr S J Williams

Hydrogeology Department
Dr D A Lever

- Groundwater Modelling
  Dr A W Herbert
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  Dr N L Jefferies
- Computational Techniques
  Mr K A Cliffe
- Windscale Projects
  Dr J D Porter

Assessments Department
Mr D E Billington

- Disposal Safety Assessment Team
  Mr D E Billington
- Projects
  Mr S J Wisbey

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Work for UK Nirex Ltd: Role of AEA D&W

- Responsible for the post-closure safety case
- Lead contractor for safety assessments
- Lead contractor for supporting R&D

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AEA Experience in Post Closure Safety Assessment and Research (Overseas)

SOME CURRENT CUSTOMERS

- Japan (PNC &JNFL)
- Switzerland (NAGRA)
- CEC
- Germany (GRS)

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Decommissioning
& Waste Management

Teams for Safety Assessment Research Work

- An assessment team capable of carrying out full assessment of radiological and other hazards associated with waste repositories
- A mathematical modelling team with particular expertise in groundwater and geochemical modelling
- A radionuclide chemistry team with skills and facilities which enable the measurement of radionuclide properties in repository conditions as well as interactions with host geologies, performance of engineered barriers etc
- A field investigation team that assists in the characterisation of sites, the measurement of geological properties, etc

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Aims of the Nirex Safety Assessment Research Programme

- To understand the important processes governing the transport of radionuclides and to provide parameters for the safety assessment
- To construct models that provide a good representation of these processes
- To provide advice to Nirex on matters such as repository materials

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Nirex Safety Assessment Research Programme

Large Programme of Research, Coordinated into 5 areas:

- Engineered barriers
- Near-field chemistry
- Mass transfer in the geosphere
- Biosphere
- Gas evolution and migration

Consists of Field experiments, laboratory experiments and modelling studies (for interpretation and prediction)

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Gas Evolution and Migration

- Gas type and quantity, and dispersal mechanism
- Sources
  - Corrosion of metals
  - Microbial activity

Mass Transfer in the Geosphere

- Physical and chemical processes affecting migration of radionuclides
- Key parameters for Safety Assessment
  - Hydrogeology
    - Groundwater Flows
  - Geochemistry
    - Sorption
    - Colloids

Engineered Barriers

- Physical and chemical containment
- Detailed studies of behaviour of waste canisters, backfill materials and structural materials

● Cementitious materials	● eg evolution of pH in porewater
● Carbon and stainless steels	● eg corrosion

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Near-Field Chemistry

- Chemical behaviour of radioelements in near-field
- Key parameters for safety assessment
  - Solubility
  - Sorption
- Study effects of
  - Degradation of organic materials
  - Degradation of repository materials
  - Microbiological activity

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Biosphere

- Climatology
- Geomorphology
- Radionuclide transport in near surface region

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Categories of Radioactive Waste in the UK

- Very Low-Level Wastes (VLLW):
  Disposal with household refuse, low activity or short half-life
- Low-Level Wastes (LLW):
  Not exceeding 4GBq/t alpha or 12GBq/t beta/gamma, not VLLW
- Intermediate-Level Wastes (ILW):
  Lower activity and heat output than HLW, not LLW
- High-Level Wastes (HLW):
  Wastes generating significant amounts of heat

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Radwaste Disposal in UK

1949-1982	**Some disposal of LLW/ILW to deep ocean bed**
1957-present	**Disposal of LLW at Dounreay**
1959-present	**Disposal of LLW at Drigg**

(storage of HLW and ILW at nuclear sites)

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Deep Repository Programme

1988: Site comparison and selection of a limited number for further study

1991: Selection of a single site for detailed geological characterisation, detailed design work in parallel

1992/3: Application for planning permission and to move to underground work

2000(?): Application for planning permission for disposal

2005: Repository operational

2055: Repository sealed

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Quantities of waste

	Low	Medium	Alpha	High
Interim store *(to 1990)*:	7,900	18,500	66,000	710
Disposed *(to 1990)*:				
Ocean bed (LLW & ILW)	<------	26,000	------->	
Dounreay	14,000			
Drigg	775,000			
Production *(1990-2020)*:	644,000	65,000	65,000	560

(all quantities in cubic metres)

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Levels of Containment

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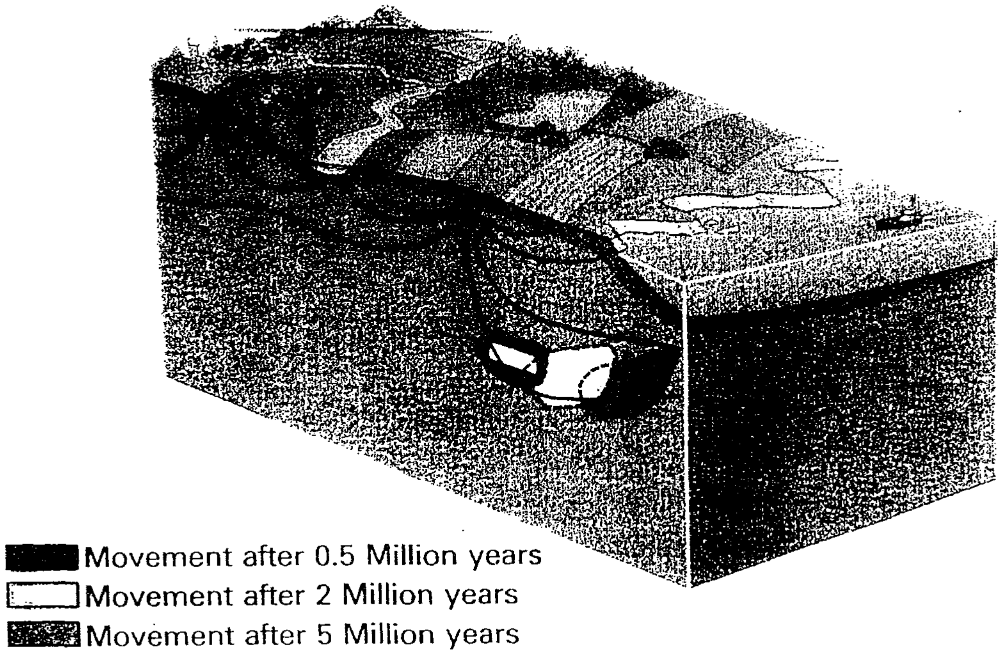
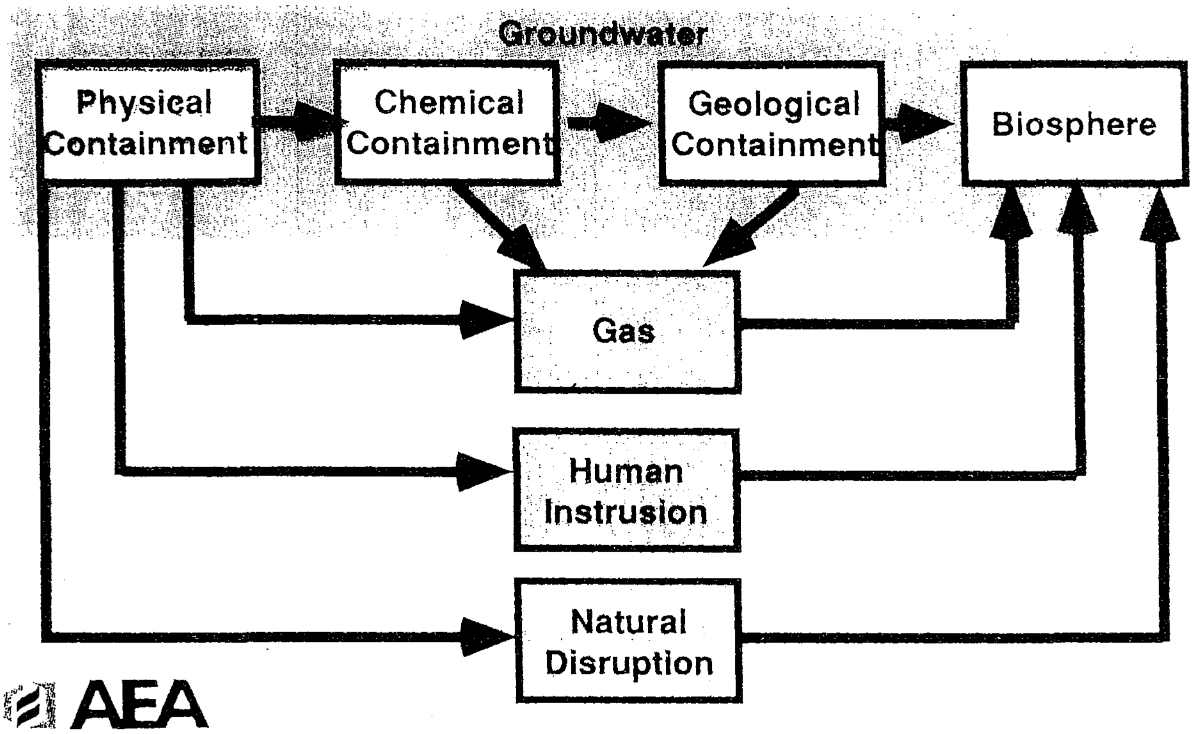


Requirements of Authorising Departments

- Individual risk target in any one year equivalent to that associated with a dose of 0.1mSv
  About 1 chance in a million
- No significant increase in radioactivity in the general vicinity of the site
- Choose a site with a low probability of disturbance by man
- Discharges ALARP to ensure that individual and collective doses are ALARA
- Analyse probability of disruption by external events

Assessment Pathways



Groundwater

Physical Containment

Chemical Containment

Geological Containment

Biosphere

Gas

Human Instrusion

Natural Disruption

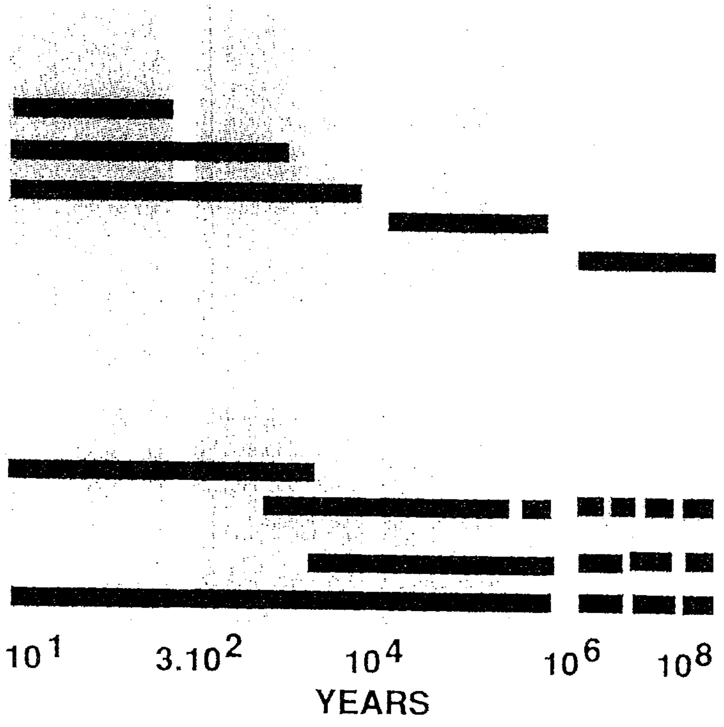
Timeframes and Pathways

TIMEFRAMES

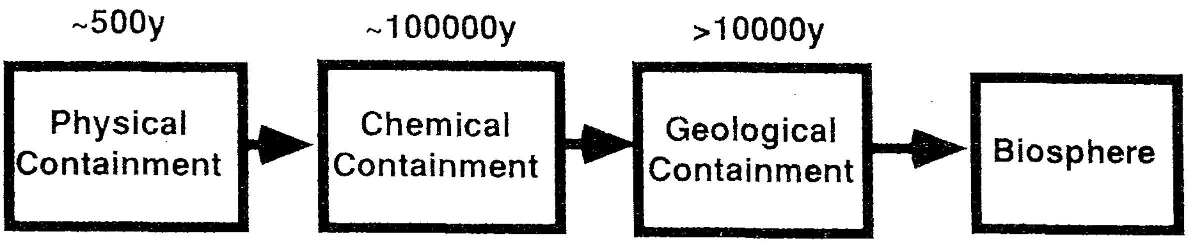
- Institutional controls
- Long-term societal changes
- Current interglacial conditions
- Glacial cycling
- More stable climatic and tectonic system

PATHWAYS

- Gas
- Intrusion
- Groundwater
- Natural disruption



Groundwater Pathway: Geosphere Model


~500y

Physical Containment

~100000y

Chemical Containment

>10000y

Geological Containment

Biosphere

- Groundwater flow
- Radionuclide transport
  - Advection
  - Diffusion
  - Hydrodynamic dispersion
  - Sorption
  - Radioactive decay and ingrowth

Codes:

NAMMU • Homogeneous rock

NAPSAC • Fractured rock

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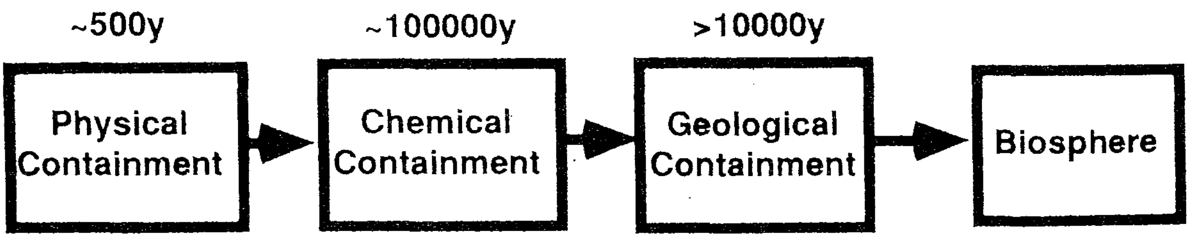
Groundwater Pathway: Near-Field Model


~500y

Physical Containment

~100000y

Chemical Containment

>10000y

Geological Containment

Biosphere

- Limited solubility
- Sorption
- Transfer to far field
- Radioactive decay and in growth

Codes:

STRAW

STRAW 2

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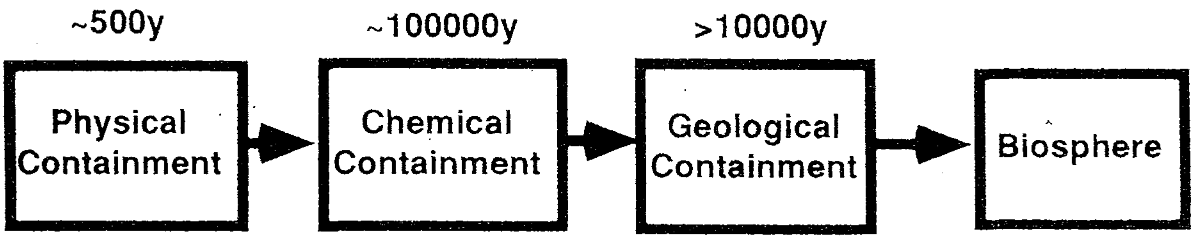
Groundwater Pathway - Biosphere Model



Potential receptors

- Deep soil
- Stream or river
- Local marine environment
- Lake
- Well water

Variation in climate and sea-level could result in different receptors at different times

Codes:

BIOS

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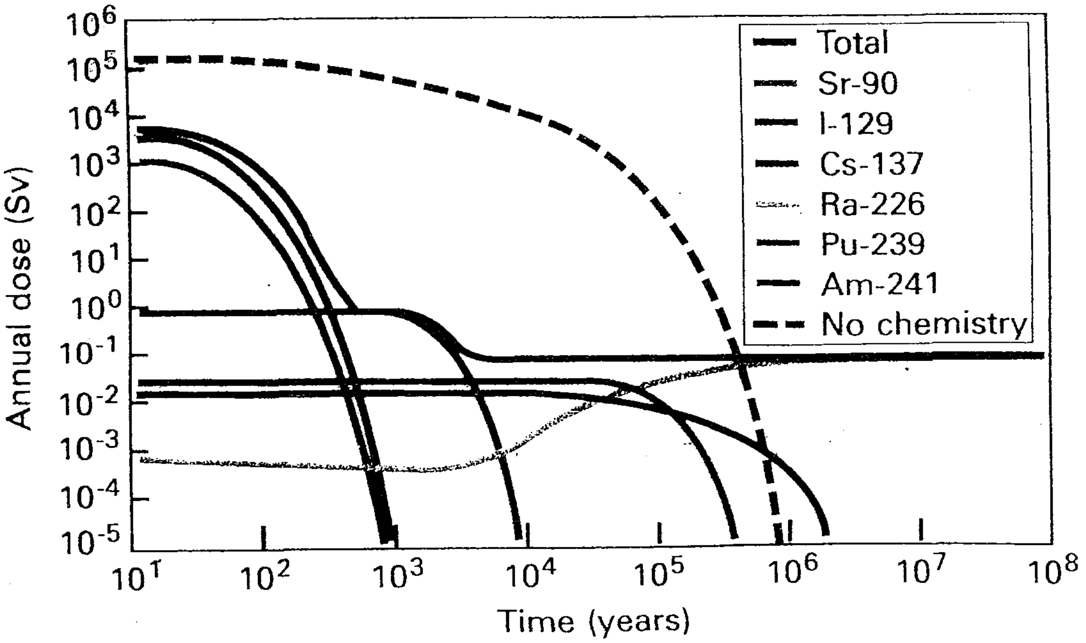
Toxicity of Near-field Porewater for Mixed LLW and ILW

521T12



Types of Calculations

- Base-case deterministic calculations

- Sensitivity studies
- 'What if' studies
- Probabilistic - MASCOT - 3 code

} Assess implications of uncertainties in data and models

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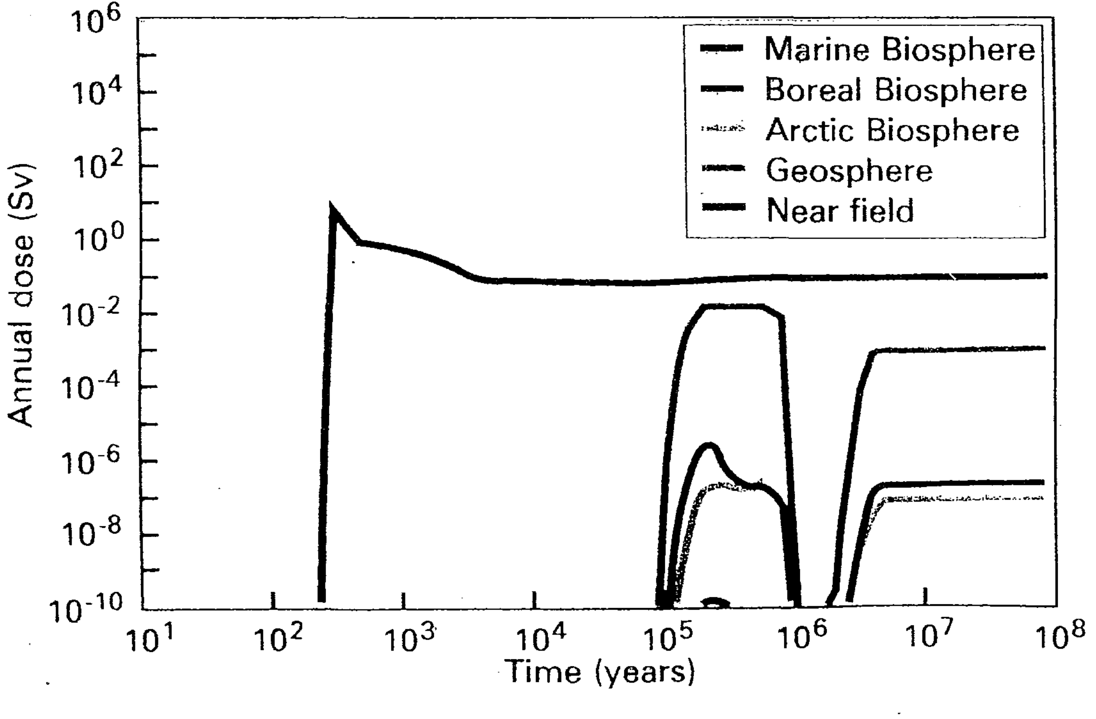
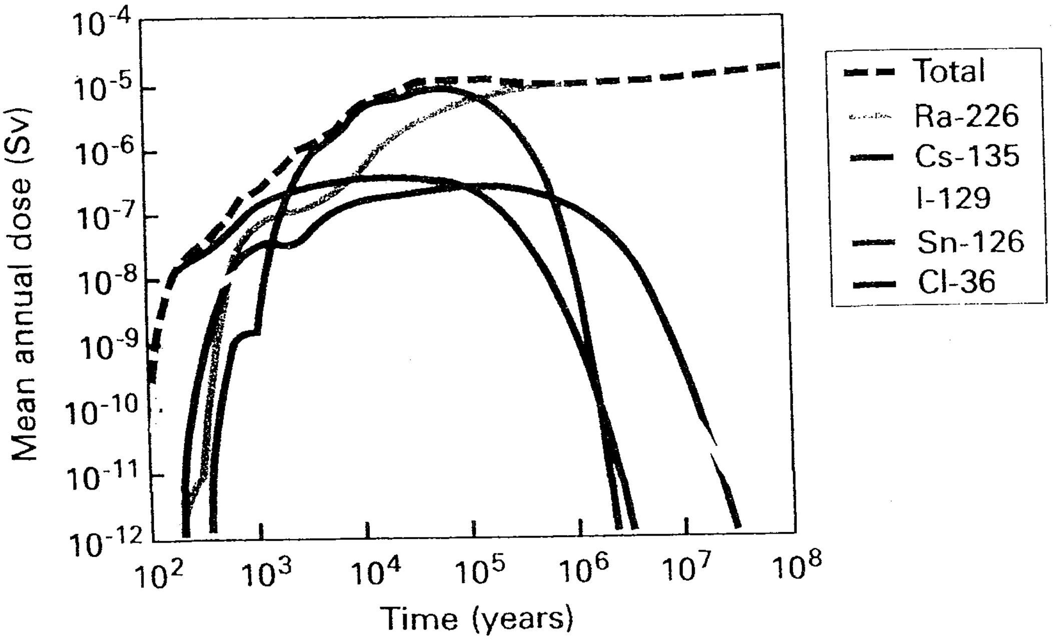
Contribution of the Chemical and Physical Barriers to Limiting the Dose to Man



Probabilistic Calculation of Mean Annual Dose for a Future Boreal Biosphere

621T16



Nirex Safety Assessment Research Programme

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- **Engineered barriers**
- **Near-field chemistry**
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- **Biosphere**
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Consists of Field experiments, laboratory experiments and modelling studies (for interpretation and prediction)

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- To provide advice to Nirex on matters such as repository materials

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Priority Radionuclides

Choice depends on:-

- Pathway - groundwater/gas/intrusion/natural
- Inventory in waste
- Contribution to heat generation
- Half life and decay chains

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AEA Experience in Post Closure Safety Assessment and Research (UK)

- **Nirex:** Shallow disposal assessment (LLW & ILW)
- **Nirex:** Deep repository programme (LLW & ILW)
- **UKDoE:** HLW programme
- **BNFL:** Support to shallow disposal (LLW) at Drigg
- **UKDoE:** Support to regulator
- **Nuclear Generators:** Strategic

AEA Experience in Post Closure Safety Assessment and Research (Overseas)

SOME CURRENT CUSTOMERS

- Japan (PNC &JNFL)
- Switzerland (NAGRA)
- CEC
- Germany (GRS)

Aims of Geochemical Modelling

To model the chemical evolution of complex aqueous systems

- To help interpret experimental data and to guide design of experiments
- To investigate reaction mechanisms
- To predict the behaviour of geochemical systems over long timescales
- To help select parameters for performance assessment
- To assess the effect of assumptions made in performance assessment models

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Geochemical Modelling Techniques

- Chemical Modelling - HARPHRQ code
- Chemical and Transport Modelling - CHEQMATE code

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The HARPHRQ Code

- Based on USGS speciation code PHREEQE which calculates equilibrium water chemistry for a particular chemical inventory and associated minerals

- HARPHRQ extended to include:-

  Full finite minerals accounting

  Option to fix pH

  Choice of several sorption models in a seperate module

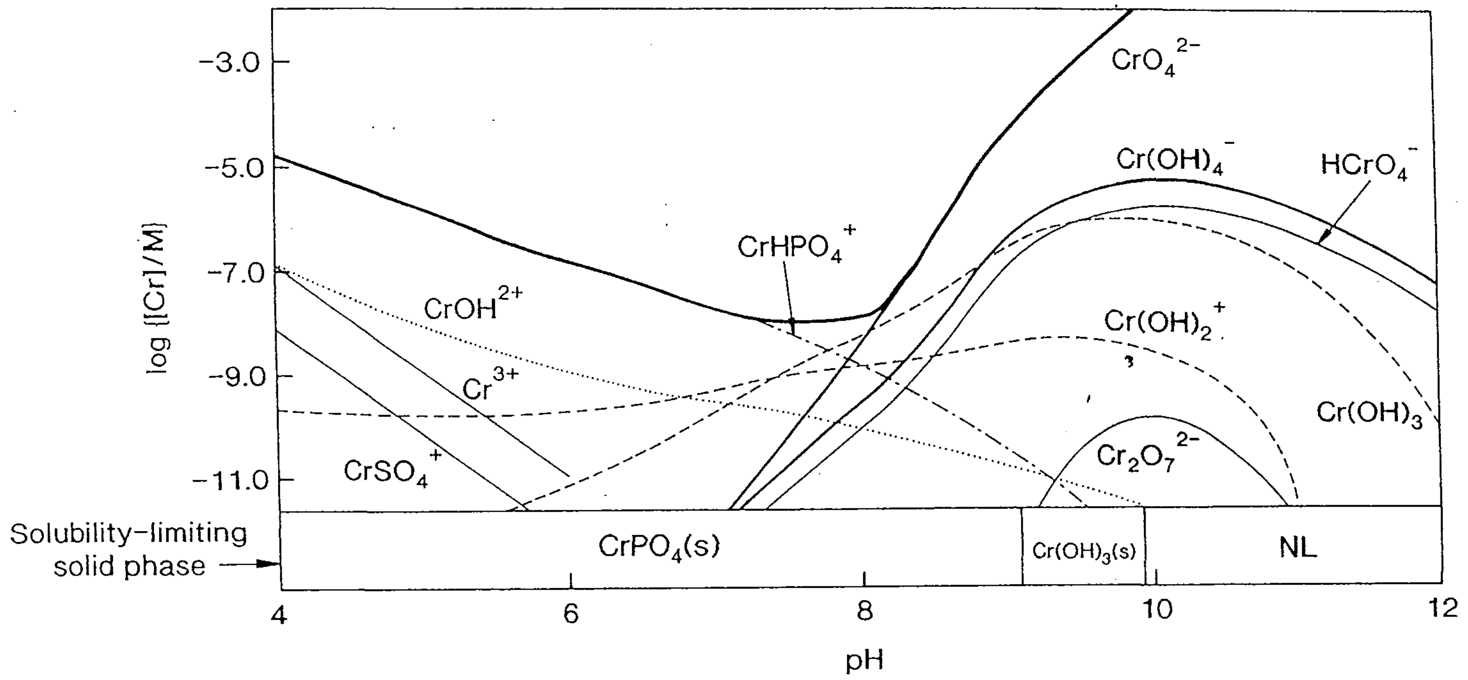
Applications of Chemical Thermodynamic Modelling

- RADIOACTIVE/TOXIC SOLID WASTE DISPOSAL
  solubility/speciation of contaminants in groundwater
  adsorption/ion-exchange of contaminants onto rocks/clays
  migration of contaminants away from disposal

- LIQUID EFFLUENT TREATMENT
  solubility/speciation of contaminants/reagents during processing
  process optimisation (better clean-up)
  reduction of secondary wastes
  reduced costs (capital, reagent and waste disposal)

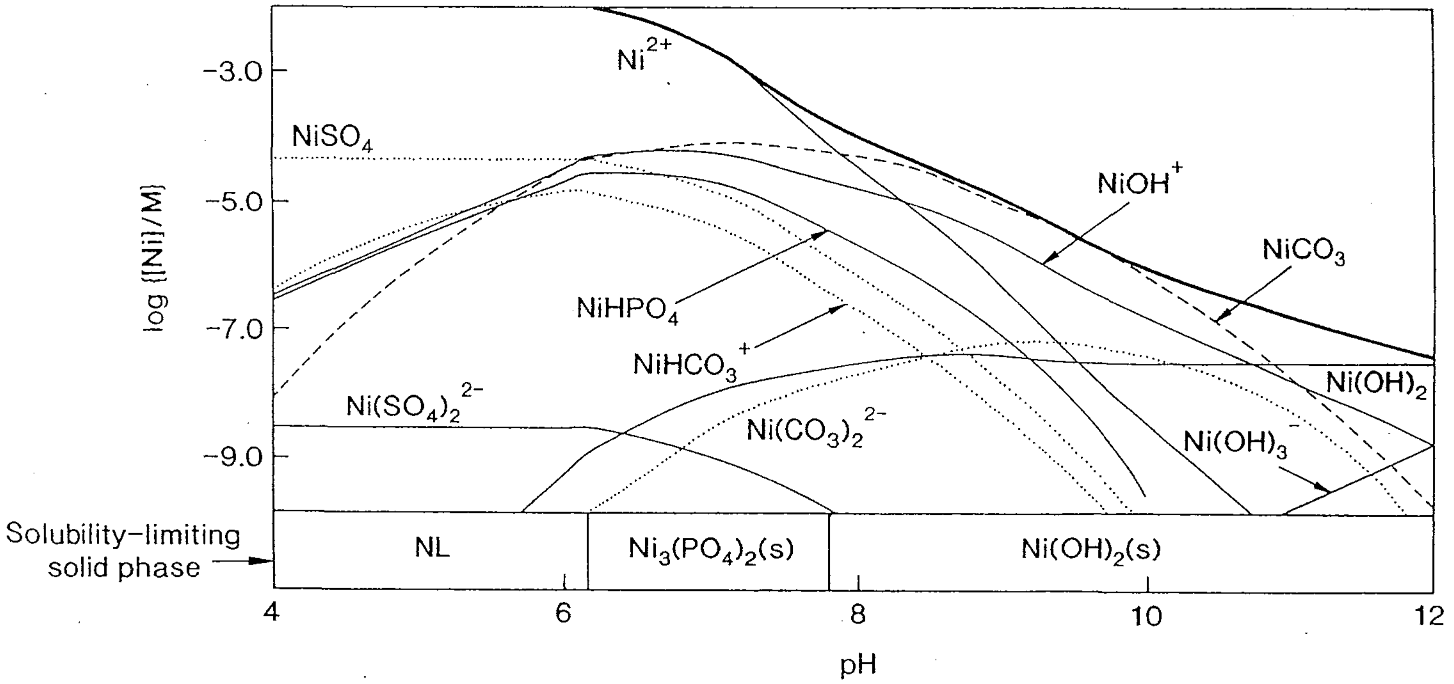
- INORGANIC CHEMICAL PROCESSING
  seperations, leaching. precipitation. solvent extractions, etc
  improved methods, increased efficiency, reduced costs

Figure 2. Chromium Solubility and Speciation



Total elemental concentration of sulphur, chlorine, phosphorus and carbon is 10^{-4} M
NL indicates that no solid limits the solubility to less than 10^{-2} M

Figure 4. Nickel Solubility and Speciation



Total elemental concentration of sulphur, chlorine, phosphorus and carbon is 10^{-4} M
NL indicates that no solid limits the solubility to less than 10^{-2} M

The HATCHES Database

- HATCHES - a database and management system
- Operates on a PC and uses dBASEIII+
- Contains thermodynamic data for use with PHREEQE, HARPHRQ and CHEQMATE
- Has text field describing data source and derivation of PHREEQE data from this
- Has conversion programs which automatically convert dBASE output to a PHREEQE- or EQ3/6- format database

---

The CHEQMATE Program

- Assumes chemical processes generally faster than transport - local chemical equilibrium
- Transport by diffusion, electromigration, advection and dispersion
- Chemical processes include aqueous speciation, precipitation/ dissolution and sorption
- Some mineral kinetics can be included

Input Data

CHEMICAL DATA

- Thermodynamic data - equilibrium constants for reactions ➠ HATCHES database
- Initial chemistry for each cell

TRANSPORT DATA

- Physical properties - diffusion coefficient, porosity
- Flow properties - Darcy velocity, dispersion length
- Grid length, timestep

Output Data

For each cell and time step:

- Full aqueous speciation
- Changes in mineral amounts
- pH, Eh, concentration of elements
- Sorbed concentration of elements

Applications

- PREDICTIVE MODELLING

  Aeration period of repository

- LABORATORY EXPERIMENTS

  Through-diffusion (radionuclides)
  Concrete degradation
  Alkali/rock interaction
  Corrosion studies

- FIELD STUDIES

  Pocos de Caldas natural analogue
  Chlorine migration throughout clay
  Jordan natural analogue

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Prediction of the Aeration Period of the Repository

Modelling assumptions

- Regular array of steel cans embedded in concrete backfill
- Porewater is initially saturated with oxygen at the concentration in equilibrium with atmosphere
- After closure no further oxygen enters system
- Oxygen consumed by corrosion of steel canisters
- Transport is by diffusion only

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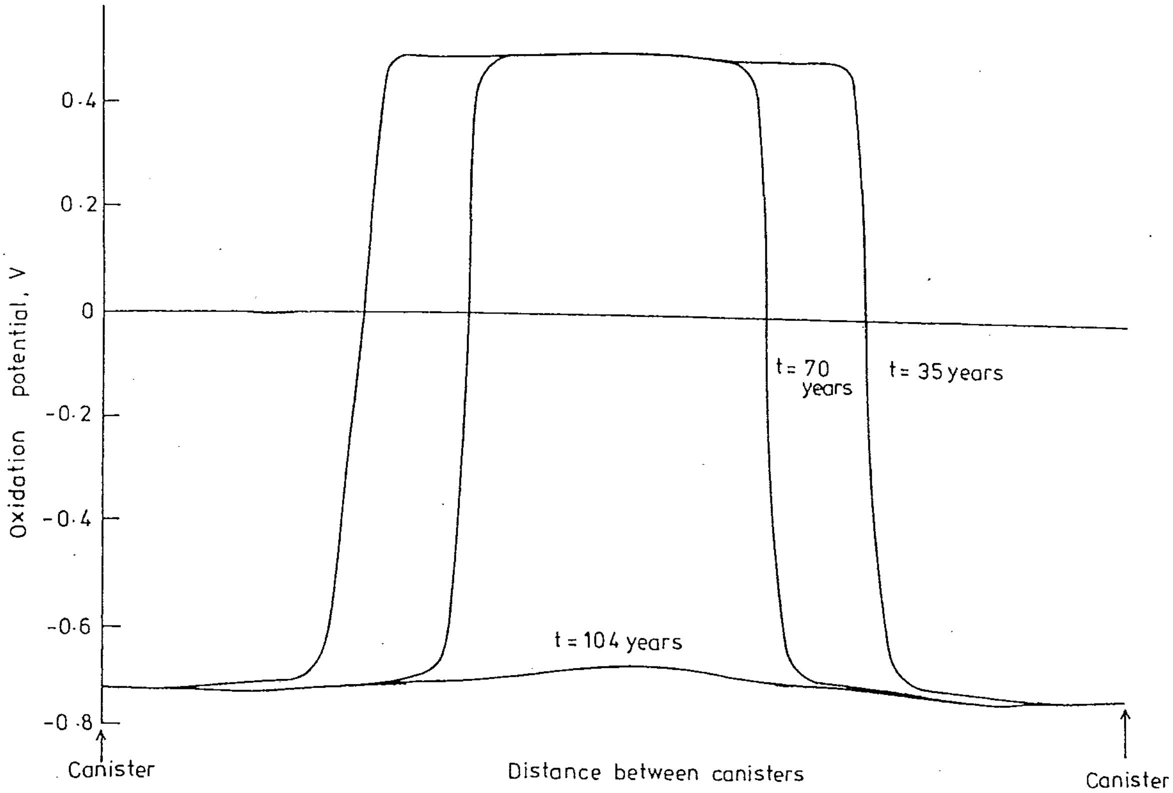

AERE R 12442 Fig. 4
Profiles of oxidation potential (Eh) between two uniformly corroding steel canisters at 35, 70 and 104 years

Sorption Modelling

- **HARPHRQ used to model batch sorption experiments and to parameterise chemical model**
- **CHEQMATE couples the chemical model with transport to simulate through-diffusion experiments**
- **Systems modelled**
  - **uranium sorption onto clay with or without organics**
  - **plutonium sorption onto sandstone with organics**
  - **americium and lead sorption onto cement**

Modelling of the Poços de Caldas Natural Analogue

Description of the uranium distribution at the site

- **Deeper rocks contain pyrite, associated groundwater is strongly reducing**
- **Rock near surface contains ferric oxyhydroxides (red/orange colouration)**
- **Sharp redox front divides the two regions**
- **Enriched zone of uraninite is observed just below the redox front, in the reduced layer**

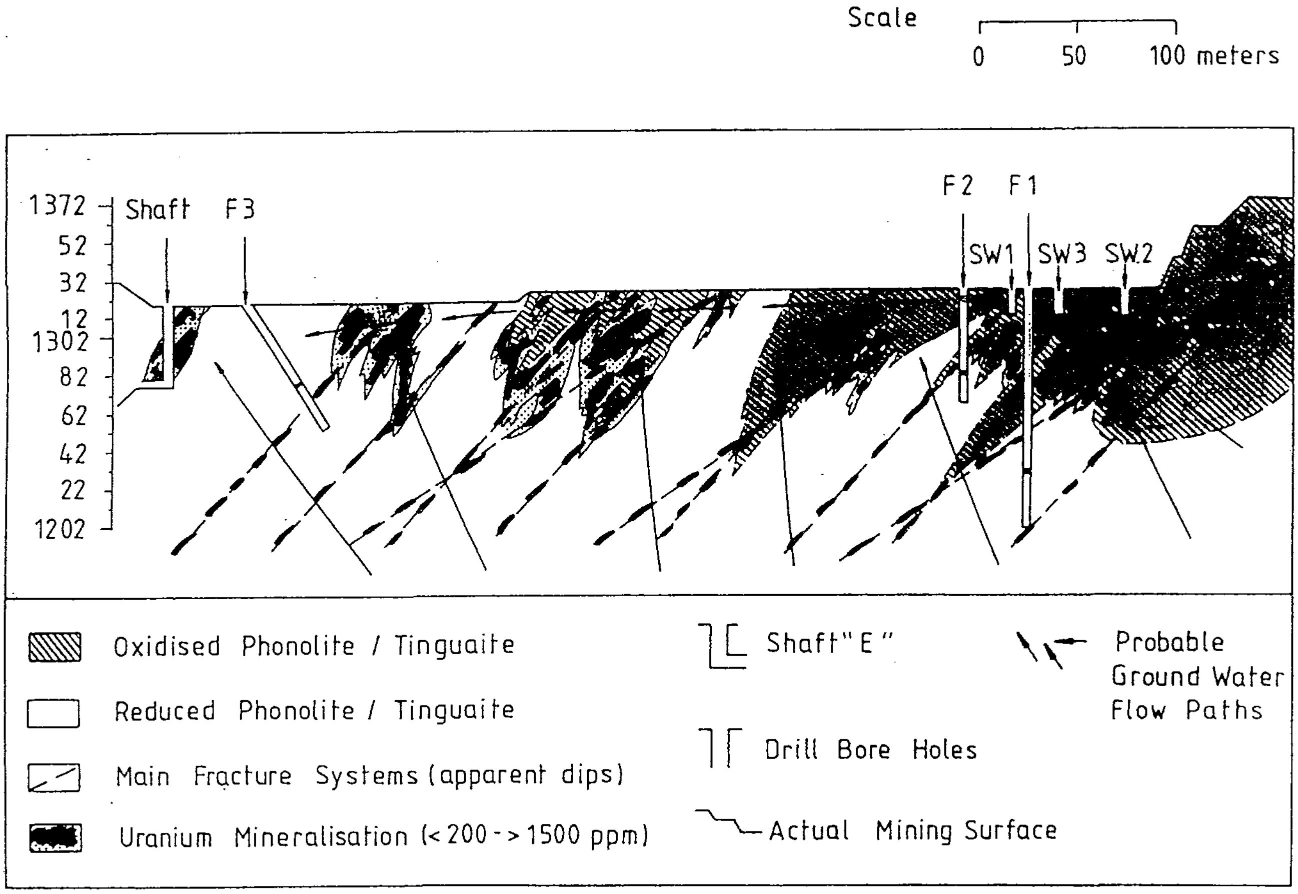

FIG. 1. CROSS-SECTION OF OSAMU UTSUMI MINE, BRAZIL.

Modelling of the Poços de Caldas Natural Analogue

Conceptual model of system

- Original rock contains pyrite and uraninite
- Inflowing oxidising water reacts with the upper portion of the rock and oxidises U(IV) to U(VI), which is more soluble
- Soluble U(VI) is carried in the groundwater across the redox front, is reduced to U(IV) and reprecipitates

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Table 5 Water chemistry calculated with and without precipitation of chalcedony and observed values[5] just downstream (reduced) and upstream (oxidised) of the redox front.

Reduced region

	Field	Calculated	Calculated No SiO_2 Solid
pH	5.5-6.1	6.7	5.9
SO_4^{2-} (mg/l)	9-20	16.8	16.8
K (mg/l)	8-13	15.9	15.7
SiO_2 (mg/l)	29-37	18.2	48

Oxidised region

	Field	Calculated	Calculated No SiO_2 Solid
pH	5.6-6.2	6.8	6.0
SO_4^{2-} (mg/l)	10-300	13.0	13.0
K (mg/l)	-	17.0	18.7
SiO_2 (mg/l)	-	18.2	42.0

Concluding Remarks

HARPHRQ and CHEQMATE are flexible modelling tools which have applications in many areas including radwaste treatment and disposal, toxic waste management and other environmental problems.

Sorption Modelling

Why model?

Modelling approach.

Modelling of batch experiments.

Modelling of through-diffusion experiments.

Why Model?

- Important to understand how sorption parameters obtain from experiments relate to in-situ values.
- Help interpret experimental results and identify reasons for differences between techniques.
- After validation model could be used to predict sorption over long timescales or in different conditions.

Sorption: Modelling Approach

- Use some batch results to parameterise static chemical model.
- Test chemical model by predicting results from the remaining batch experiments.
- Couple chemical model with transport to simulate diffusion experiments.

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Modelling of Batch Experiments

Chemical model used dependent on complexity of the system - may be simple mass-action or surface complexation.

Chemical model developed using HARPHRQ equilibrium constants for aqueous species from HATCHES.

Sorption reactions from literature, previous experiments or by fitting to experiment.

'Fitting' to small range of conditions, testing against remaining experiments.

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Modelling of Through-Diffusion Experiments

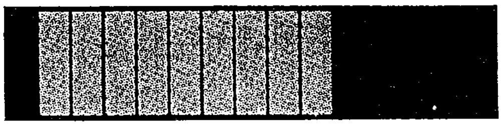
- Use CHEQMATE program to couple transport with chemical equilibrium model.
- Can use chemical model without simplification, therefore, easier to identify important additional processes.
- Simulate through-diffusion experiments and compare with results.
- Examine effect of assumptions such as surface area.

CHEQMATE Model

➡ flux into cell J) from finite
➡ flux out of cell J) difference

ΔC calculated from difference between flux in and flux out
ΔC passed to HARPHRQ to calculate new equilibrium chemistry

Sorption: Through-Diffusion Model



■ High Concentration Reservoir

▨ Rock/Mineral

■ Measurement Reservoir

PNC Collaboration

AIMS - To help interpret differences between results obtained from batch and through-diffusion techniques.

- Parameterise static chemical model from batch experiments.
- Simulate through-diffusion experiments.
- Compare predictions with experimental results to examine effect of assumptions made.

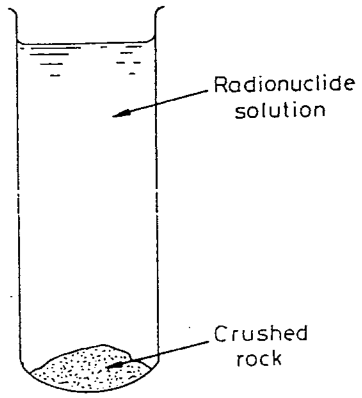
Study of techniques to measure sorption

Many techniques have been used at AEA Harwell:

batch, through-diffusion, in-diffusion, reservoir depletion, column, high-pressure convection (HPC) and uranium-series disequilibrium (USD for Th, U, Ra)

Relatively high R_D values have been observed from batch, HPC, reservoir depletion and where appropriate USD.

Through-diffusion results tend to be lower than batch however.



$$R_D = \frac{V}{M} \frac{(C_0 - C_1)}{C_1}$$

- where

R_D = distribution ratio

V = volume of solution

M = mass of solid

C_0 = initial concentration of radionuclide

C_1 = equilibrium concentration of radionuclide

FIG. 3. BATCH EXPERIMENT.

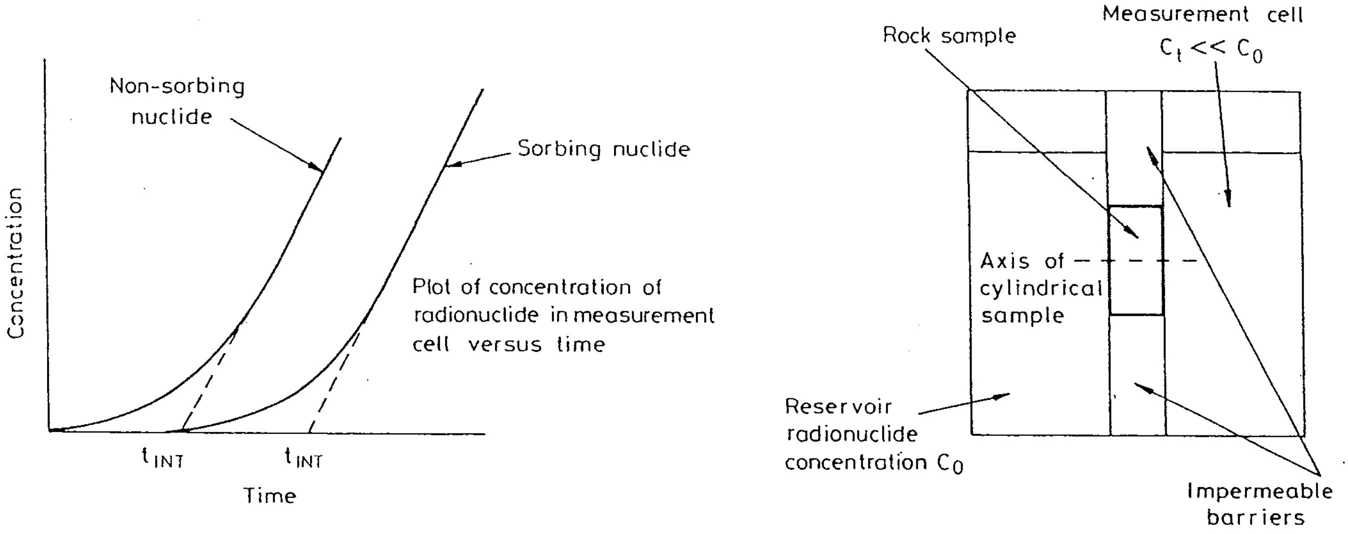


FIGURE 1. THROUGH-DIFFUSION EXPERIMENT.

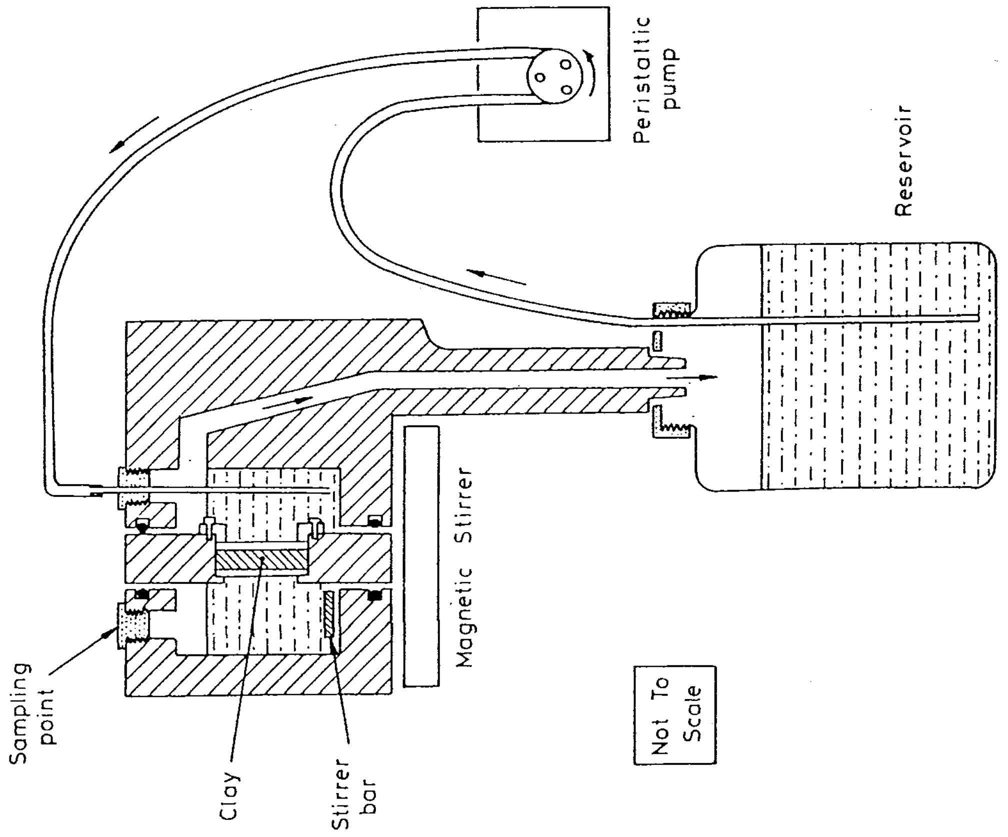


FIG. 8. THROUGH-DIFFUSION CELL.

2. Through-diffusion theory

A schematic through-diffusion cell is shown in Figure 1. A sample of rock is sandwiched between two reservoirs, one of which contains the radionuclide at a constant concentration. The radionuclide diffuses from the high concentration reservoir through the rock and into the other reservoir (measurement cell), where the concentration is monitored.

The increase in concentration in the measurement cell, (C_t), is given by [4]:

$$C_t = \frac{A\ell C_0}{V_2}\left[\frac{D_i t}{\ell^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2}\sum_1^\infty \frac{(-1)^n}{n^2} \exp\left\{-\frac{D_i n^2\pi^2 t}{\ell^2\alpha}\right\}\right]$$

where A = cross-sectional area of rock sample
ℓ = thickness of rock sample
V_2 = volume in the measurement cell
C_0 = concentration in the high-concentration reservoir
D_i = total intrinsic diffusion coefficient
α = rock capacity factor = $\phi - s'$
ϕ = porosity
s' = ds dc
s = quantity of nuclide sorbed per unit volume of porous material
c = concentration of nuclide in pore water
t = time.

At long times, the exponentials fall away to zero, so the solution is approximately:

$$C_t = \frac{A\ell C_0}{V_2}\left[\frac{D_i t}{\ell^2} - \frac{\alpha}{6}\right].$$

The slope of the curve whilst steady-state diffusion

4)

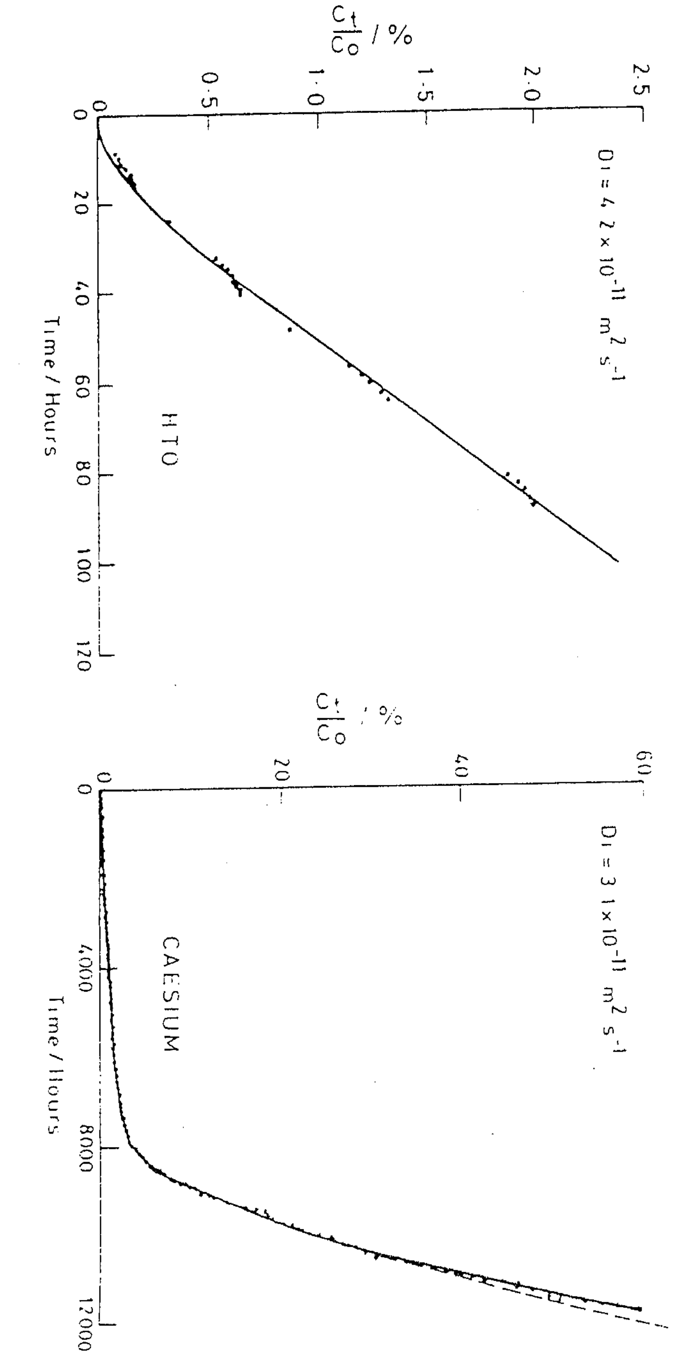


FIG.4. HTO, CAESIUM - DARLEY DALE SANDSTONE THROUGH DIFFUSION BREAKTHROUGH CURVES

Compare batch and through-diffusion on a single mineral phase at comparable radioelement concentrations.

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Through-diffusion reservoir concentration should be approximately twice the steady-state batch experiment concentration.

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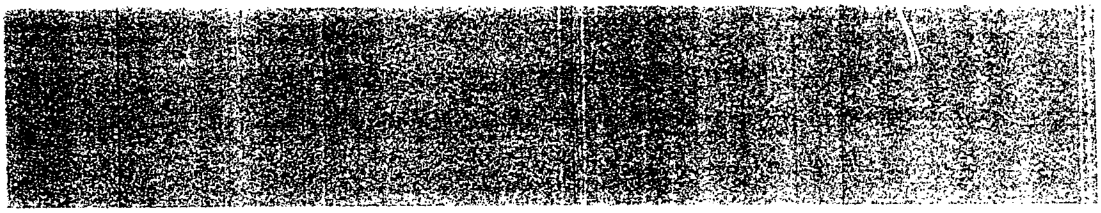
Is R_D a direct function of available surface area?



Development work will include containment of disc of single mineral phase, measurement of surface areas of both discs and powders.

Ionic Strength Corrections

- Background.
- Ionic strength correction methods commonly implemented.
- Alternative methods.
- Data requirements.

Background

- Chemical equilibria depend on solution conditions particularly ionic strength.
- Ionic strength corrections used to calculate ‘effective concentrations’.
- Constants in database corrected to I = 0 from experimental conditions.
- Then corrected again for ionic strength of solution in calculation.
- Need consistency between two corrections.

Ionic Strength Correction Methods

1. Debye-Huckel - only true theoretical model but only valid for <10-3M.

2. Extended Debye-Huckel (Guggenheim) - valid for low ionic strength.

3. Davies equation valid for ionic strength <0.5M.

4. Truncated Davies equation <1M.

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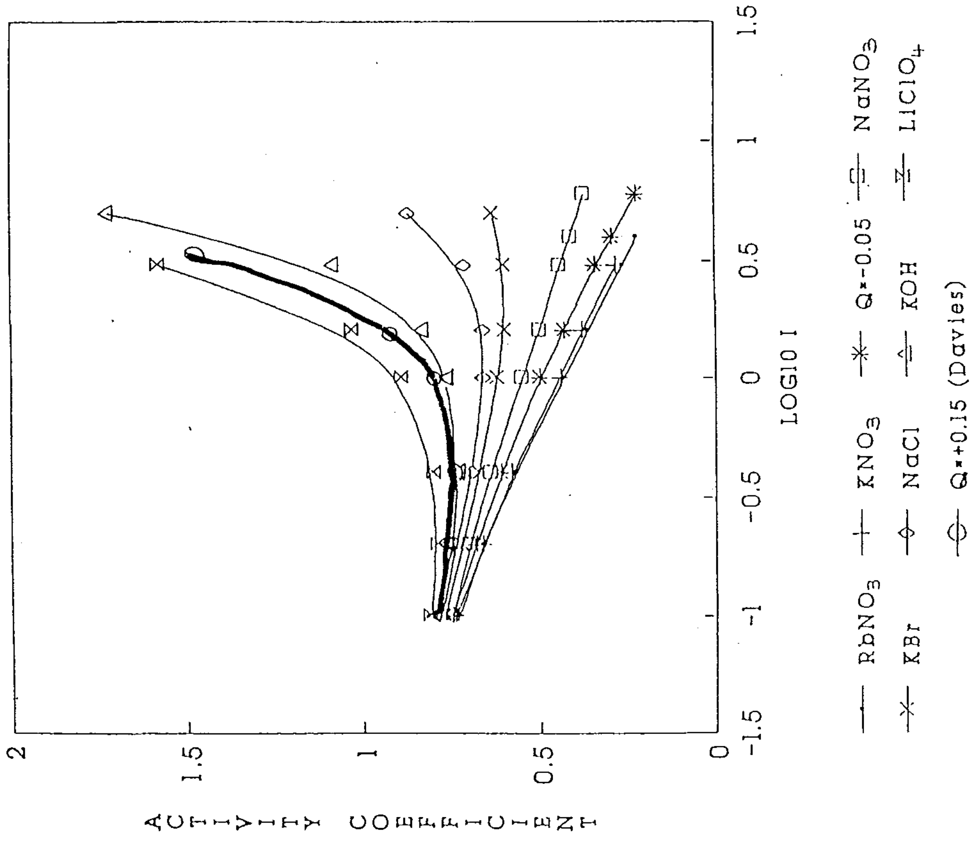

Figure 1: Experimental Activity Coefficients for 1:1 Electrolytes

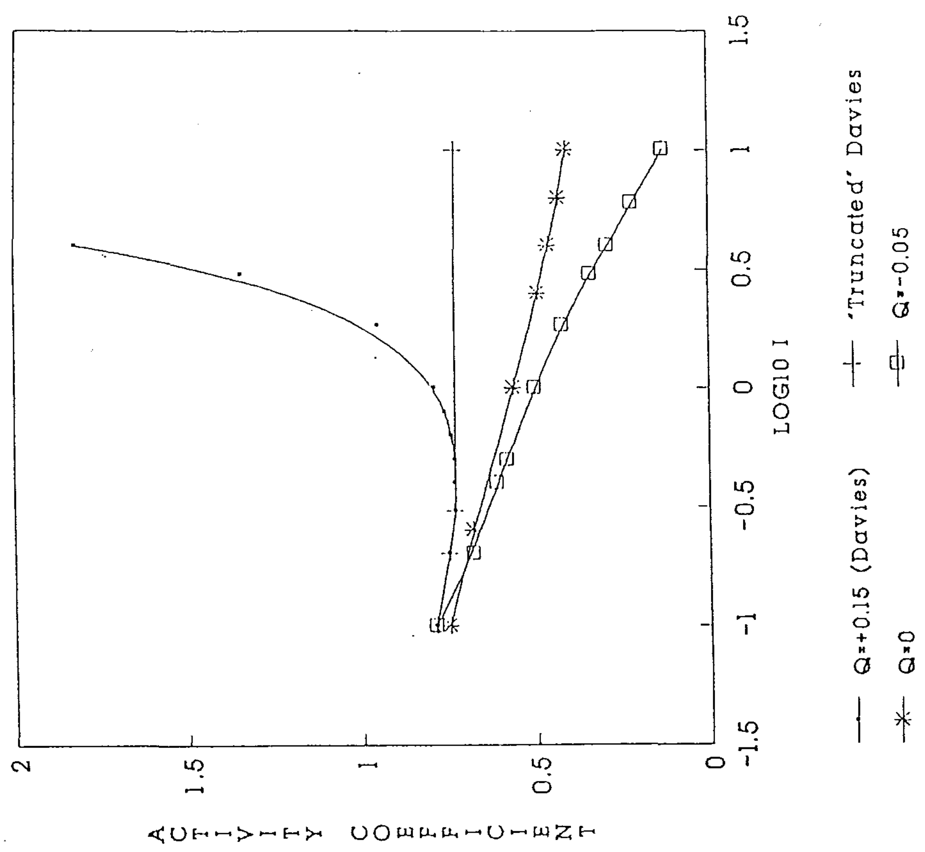

Figure 6: Variations of the Davies Equation for 1:1 Electrolytes

Alternative Ionic Strength Correction Methods

1 **Specific Interaction Theory (SIT) I <3.5.**

2 **Pitzer equation - takes into account interactions with cations, anions and solvent molecules. Valid to very high ionic strength.**

Data Requirements

Debye-Huckel, Guggenheim and Davies corrections require no ion specific data.

SIT requires one interaction parameter for each ion pair (ε) - available for major and some minor groundwater ions.

Pitzer requires three ion specific data - available for small number of test cases only.

Proposed Collaboration with PNC

AIM - To test ionic strength correction methods against data obtained by PNC in more concentrated solutions.

- Use methods currently implemented in HARPHRQ and compare against experimental data.
- Assess data availability for alternative methods.
- Test appropriate alternatives, taking into account data availability.

HATCHES Database

- Why do we need a database?
- Sources of data.
- Validation of data.
- Contents and structure of database.
- Update and release of database.

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Why do we Need a Database?

- Thermodynamic modelling important to gain confidence in parameters for processes such as solubility and sorption used in performance assessment.
- PHREEQE, HARPHRQ and CHEQMATE all need thermodynamic data for calculations.
- Quality of results dependent on quality of data.
- Accurate, complete database is therefore essential.

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Sources of Data

- Based on USGS database supplied originally with PHREEQE.
- New data from in-home comparisons of critical reviews of data and recently published experimental data.

Validation of Data

- Comparison against laboratory experiments focussed on cementitious conditions relevant to UK disposal scenarios - e.g. U solubility.
- 'Validation' against field studies e.g. Poços de Caldas, Jordan, Oman natural analogues.
- Participation in international code comparisons e.g. CHEMVAL.

Table 5.13 Results of interpretive modelling: TIN

TIN MQ2 pH=12.53
pe=5.2

	AEA	Nagra
Aqueous species (%)		
$Sn(OH)_6^{2-}$	85	
$Sn(OH)_5^-$	14	
SnO_3^{2-}	1	
$Sn(OH)_3^-$		100
Solubility controlling solid (saturation index)		
SnO_2	-3.8	29.6
$Sn(OH)_4$	-11.3	

NAGRA predict that as the pe is reduced to -4 and -8, SnO_2 becomes more soluble with the saturation index changing from 16.6 to 8.6. The aqueous speciation remains the same. Harwell predict no change with pe.

TIN MQ5 pH=12.60
pe=2.05

	AEA	Nagra
Aqueous species (%)		
$Sn(OH)_6^{2-}$	88	
$Sn(OH)_5^-$	11	
SnO_3^{2-}	1	
$Sn(OH)_3^-$		100
Solubility controlling solid (saturation index)		
SnO_2	-4.0	28.6
$Sn(OH)_4$	-11.4	-

NAGRA predict that as the pe is reduced to -4 and -8, SnO_2 becomes more soluble with the saturation index changing from 16.6 to 8.6. The aqueous speciation remains the same. Harwell predict no change with pe.

Contents and Structure of Database

- **55 elements, 932 aqueous species and 784 minerals.**
- **Common groundwater cations e.g. Ca and Na.**
  Radioelements, actinides, fission products e.g. U, Th, Pu.
  Some toxic metals e.g. Cr, Zn, Mn.
  Inorganic ligands e.g. N, Cl, C.
  Some organic ligands e.g. EDTA and Citrate.

Contents and Structure of Database

- On PC based DBASE III includes text field which gives source of data, details of any manipulation, details of any supporting data and update history.
- Automatic conversion programs from DBASE III to PHREEQE/HARPHRQ and EQ3/6 format.

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Update and Release of Database

- Released annually in October through NEA in Paris for distribution worldwide.
- Strict QA and checking procedure followed in updating.
- Used on all Nirex programmes including NSARP and site investigation.

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Proposed Collaboration with PNC

AIM - To produce a thermodynamic database especially tailored to the key elements and conditions of importance to PNC.

- Test HATCHES against experimental solubility data provided by PNC for key elements and conditions.
- Refine HATCHES if necessary.

Experimental [illegible]

Work on near-field and far-field materials related

to LLW, ILW and HLW studies

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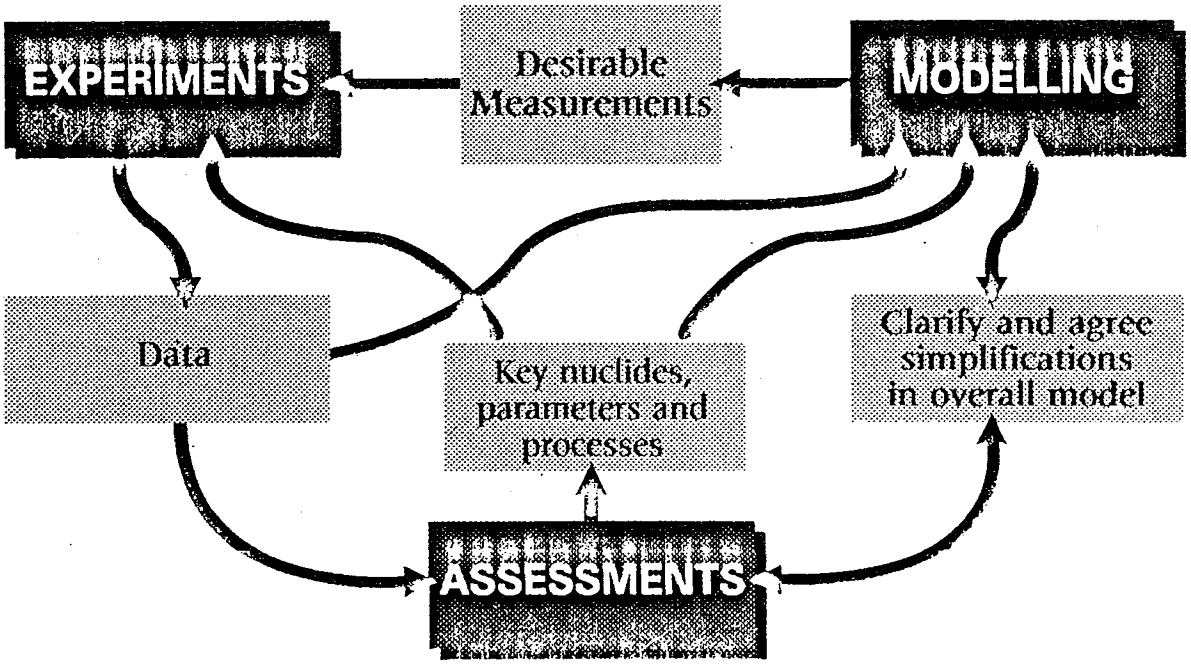
Structure of Post-Emplacement Radiological Assessment



WORK CARRIED OUT FOR:

BNFL

Department of Environment

JNFL

NAGRA

Nirex

PNC

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Near-field work for Site Safety Assessment Studies

(Mrs R M^{c}Crohon)

Far-field work for Site Safety Assessment Studies

(Dr J A Berry)

Far-field Work for Study of Mechanisms for Sorption

(Mr M M Cowper)

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Far-field Studies

Objectives:

- To obtain a physical and chemical description of processes affecting the migration of radionuclides in the geosphere

- To provide input data needed for risk assessment models

Far-Field Studies

CURRENT STUDIES INCLUDE:

- Effects of temperature
- Effects of ionic strength
- Effects of competitive ions
- Effects of organic materials (natural and degradation products)
- Effects of pH
- Effects of redox potential
- Effects of radionuclide concentration (isotherms)

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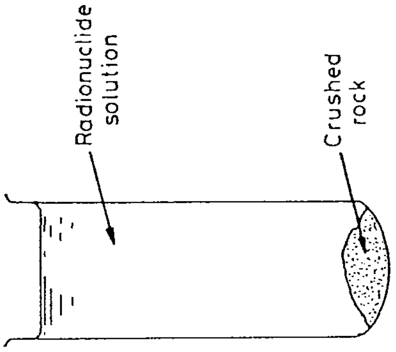


$$R_D = \frac{V}{M} \frac{(C_0 - C_1)}{C_1}$$

- where

R_D = distribution ratio
V = volume of solution
M = mass of solid
C_0 = initial concentration of radionuclide
C_1 = equilibrium concentration of radionuclide

FIG. 3. BATCH EXPERIMENT.

Table 8. Plutonium sorption on St. Bees sandstone

Organic materials present	Water-to-rock ratio	Final pH	R_D/cm^{3}g^{-1} Centrifuged	0.45μm	30000 MWCO
None	50:1	11.7	$>10^4$	$>10^4$	$\sim 10^4$
	50:1	11.7	$>10^4$	$>10^4$	$\sim 10^4$
	5:1	11.2	>3000	>3000	~ 3000
	5:1	11.2	>3000	>3000	~ 3000
Gluconate	50:1	11.7	130 ± 6	130 ± 5	140 ± 6
	50:1	11.7	120 ± 6	160 ± 8	190 ± 10
	5:1	11.5	25 ± 1	33 ± 2	23 ± 1
	5:1	11.5	24 ± 1	29 ± 2	31 ± 2
Degradation products	50:1	12.0	970 ± 90	960 ± 80	980 ± 90
	50:1	12.0	1200 ± 100	940 ± 90	1300 ± 100
	5:1	11.8	1400 ± 500	1500 ± 500	2400 ± 1000
	5:1	11.7	2300 ± 1000	1500 ± 500	1300 ± 500
None	50:1	8.8	$>10^4$	$>10^4$	$\sim 10^4$
	50:1	7.9	$>10^4$	$>10^4$	$>10^4$
	5:1	8.2	>3000		2800 ± 1000
	5:1	8.1	>3000	>3000	>3000
Gluconate	50:1	8.3	<1	<1	1 + 2/− 1
	50:1	7.9	3.3 ± 1.2	1 ± 1	19 ± 2
	5:1	8.2	4.6 ± 0.2	5.6 ± 0.2	11 ± 1
	5:1	8.7	5.9 ± 0.3	5.1 ± 0.4	6.5 ± 0.4
Degradation products	50:1	8.6	480 ± 40	480 ± 30	420 ± 20
	50:1	8.7	620 ± 40	820 ± 70	930 ± 80
	5:1	9.0	240 ± 30	700 ± 100	510 ± 100
	5:1	8.3	300 ± 40	1200 ± 400	1100 ± 400

Errors shown on R_D values are $\pm 2\sigma$ based on the statistics of counting

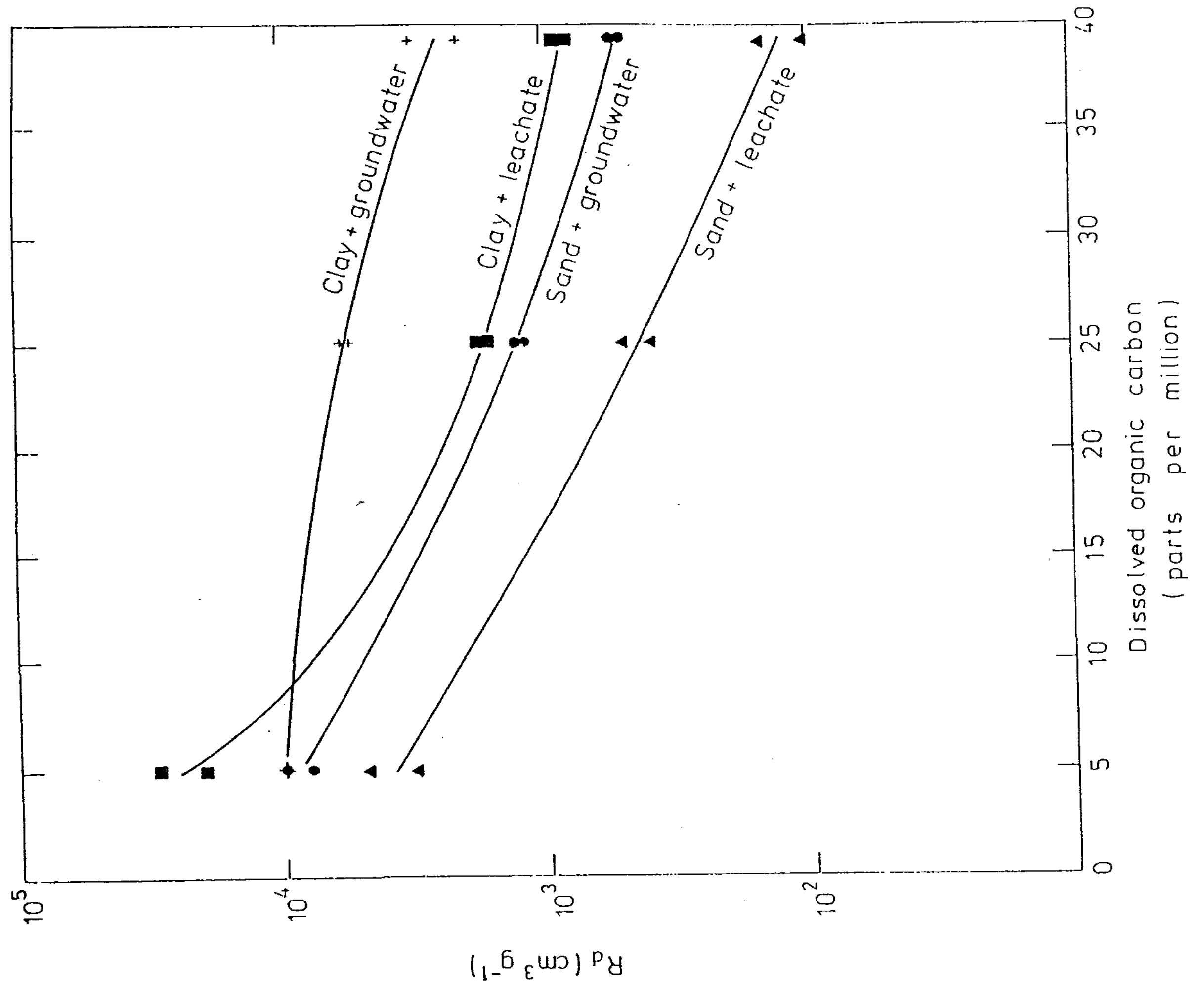


FIGURE 25. THE EFFECT OF HUMIC ACID CONCENTRATION ON DISTRIBUTION RATIOS OF PLUTONIUM

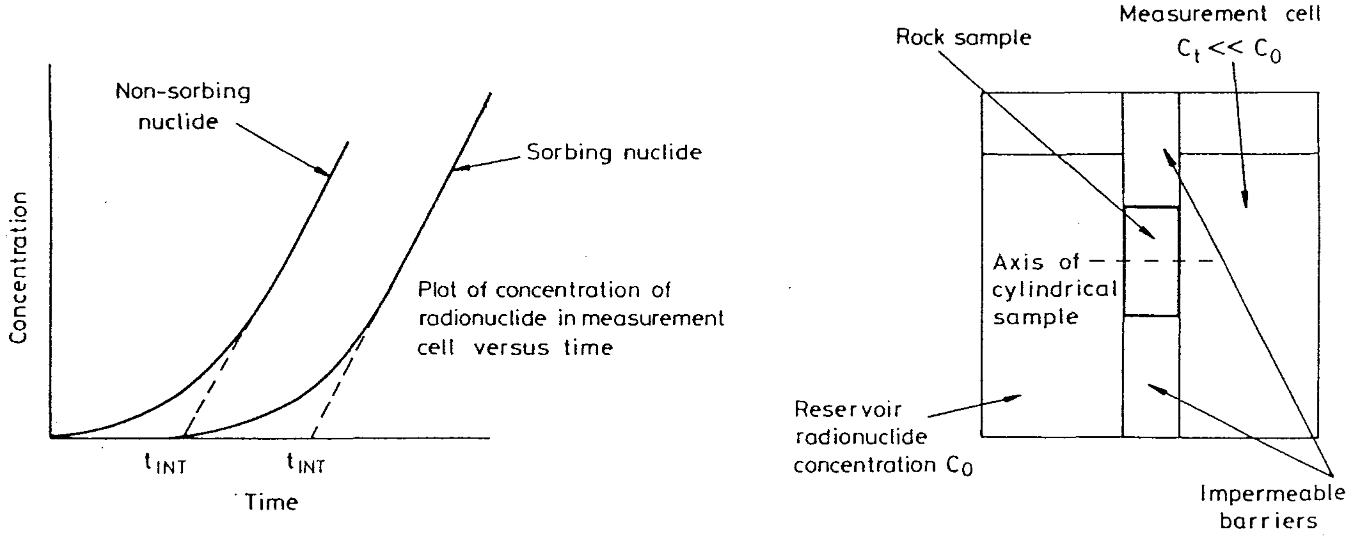


FIGURE 1. THROUGH-DIFFUSION EXPERIMENT.

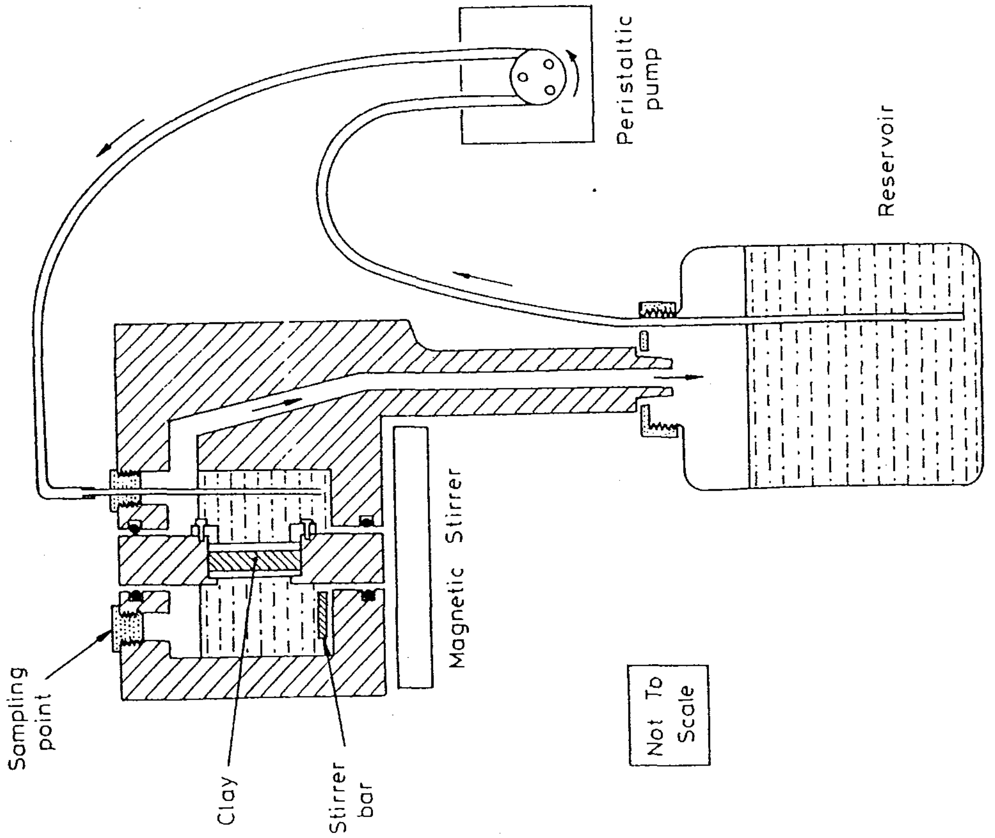


FIG. 8. THROUGH-DIFFUSION CELL.

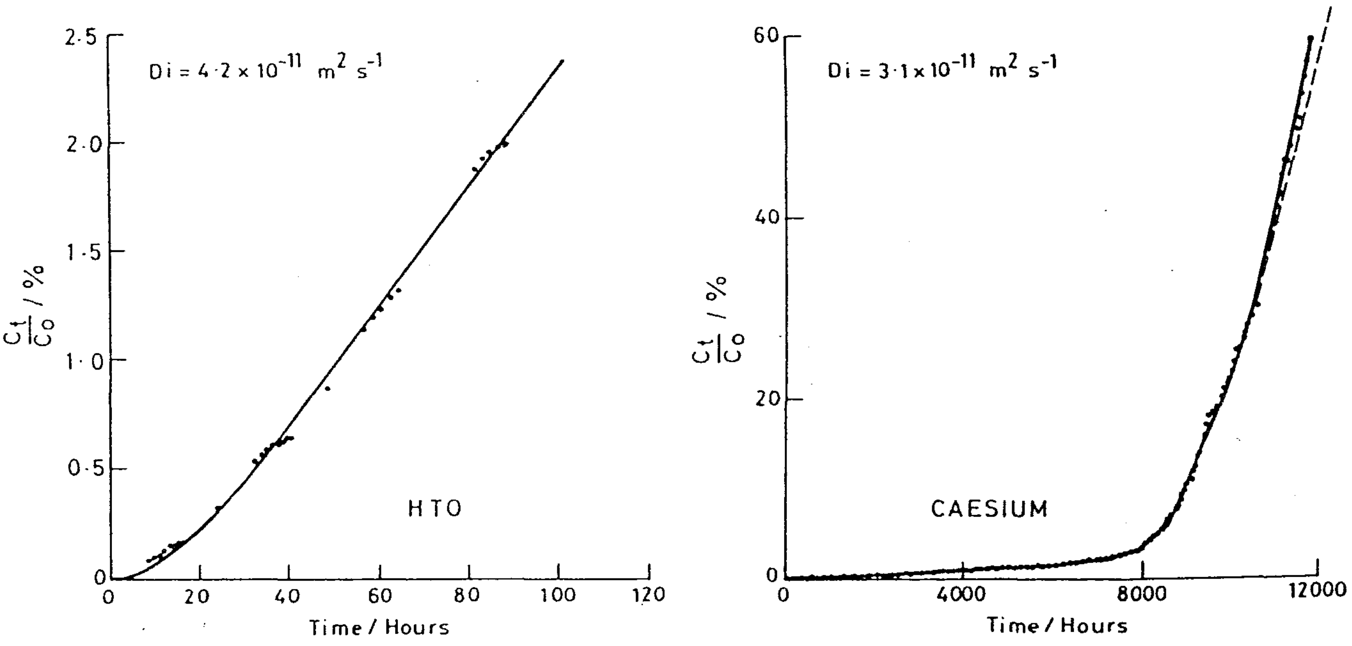


FIG.4. HTO, CAESIUM-DARLEY DALE SANDSTONE THROUGH DIFFUSION BREAKTHROUGH CURVES

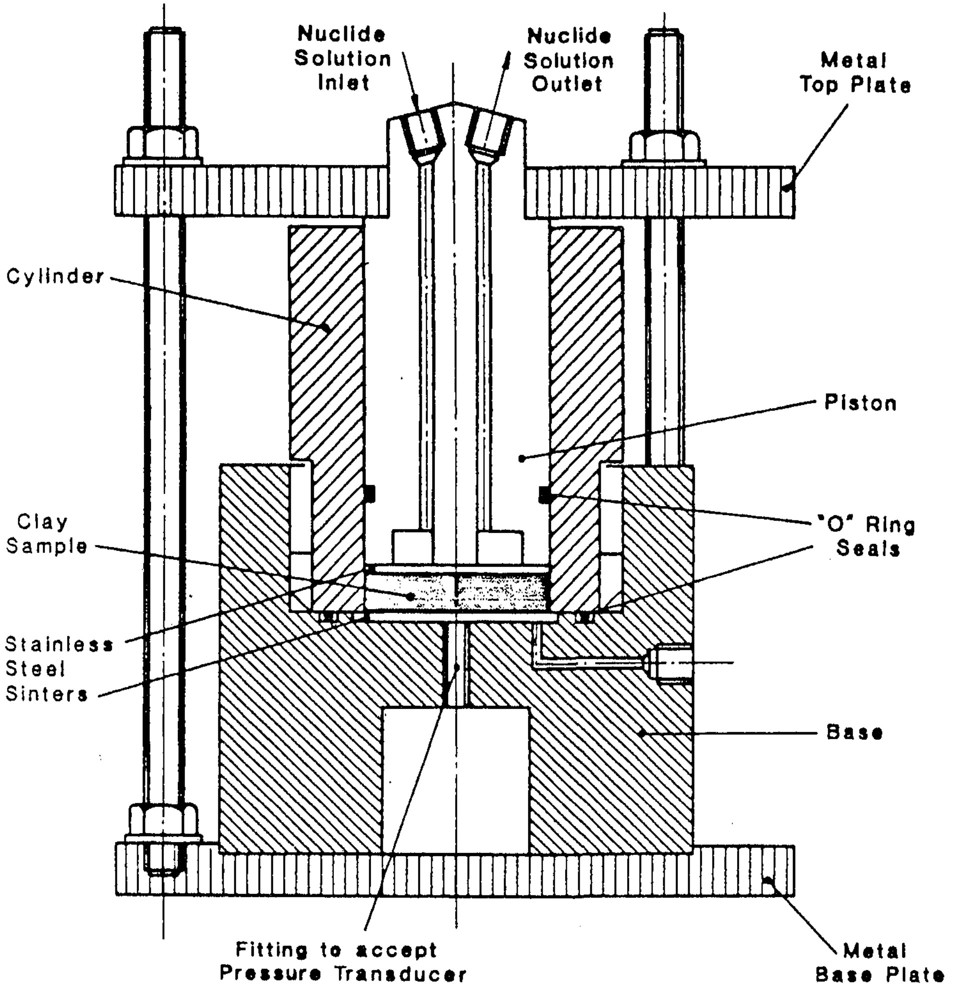


FIG. 5. IN-DIFFUSION CELL FOR CLAY SAMPLES

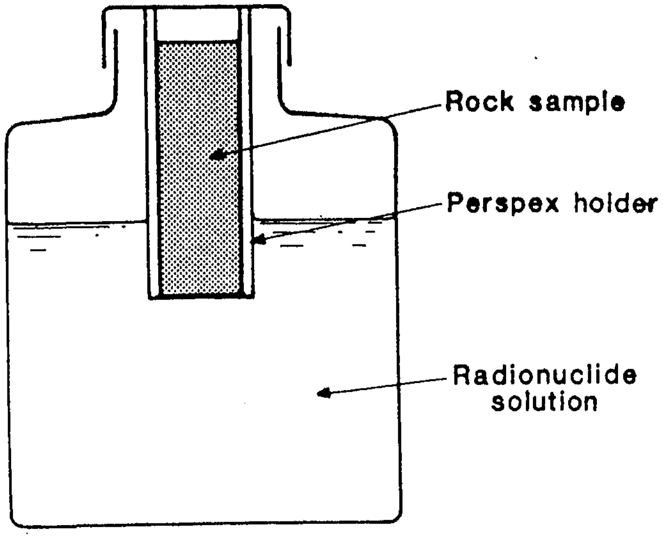
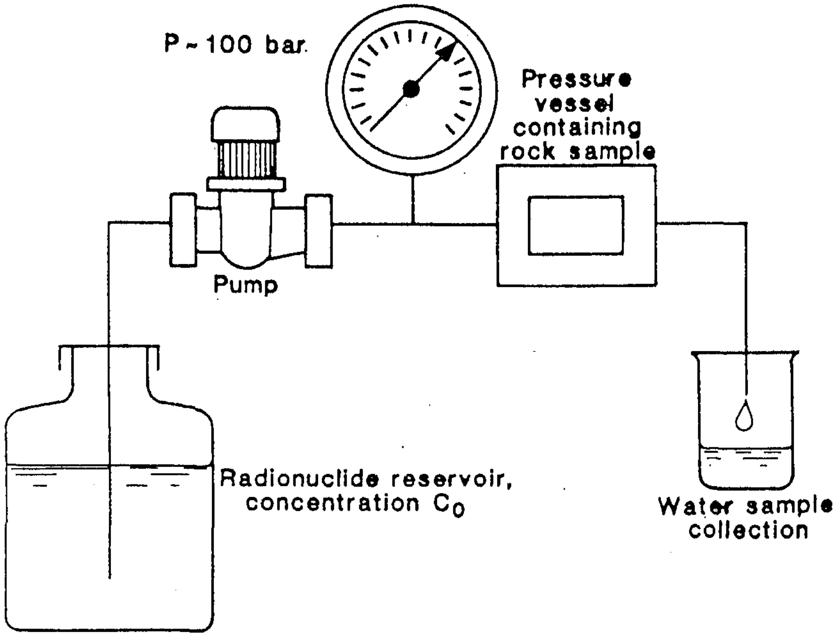


FIGURE 8 IN-DIFFUSION EXPERIMENT



In this experiment a radionuclide solution flows through the rock under a high hydraulic gradient.

FIGURE 2. HIGH-PRESSURE CONVECTION EXPERIMENT

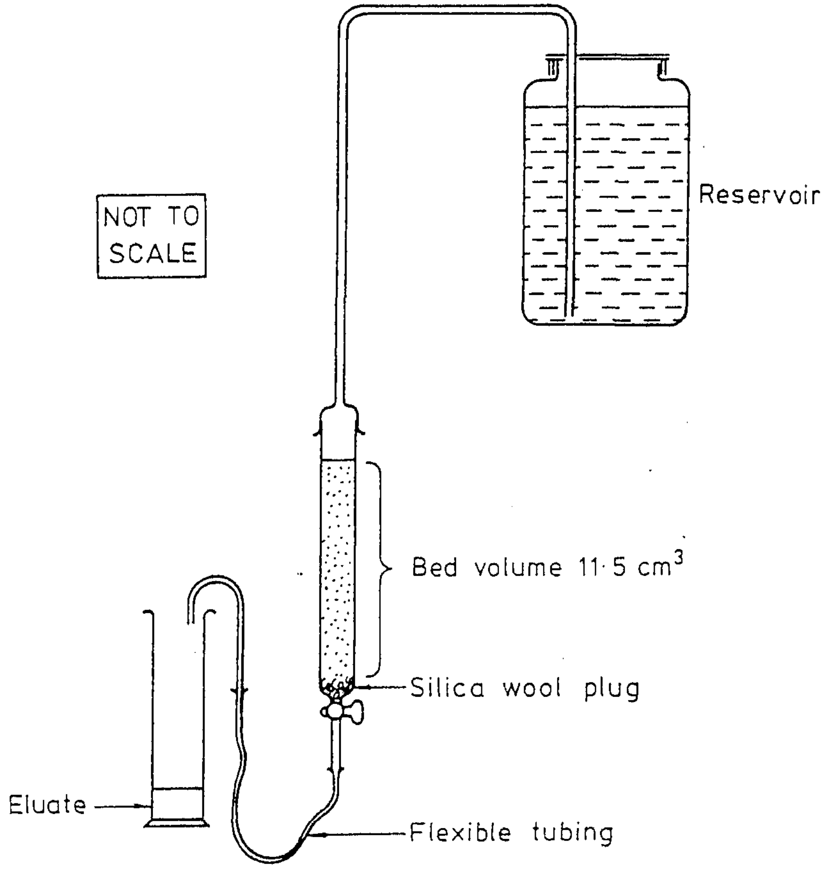


FIGURE 2. APPARATUS USED IN COLUMN EXPERIMENTS

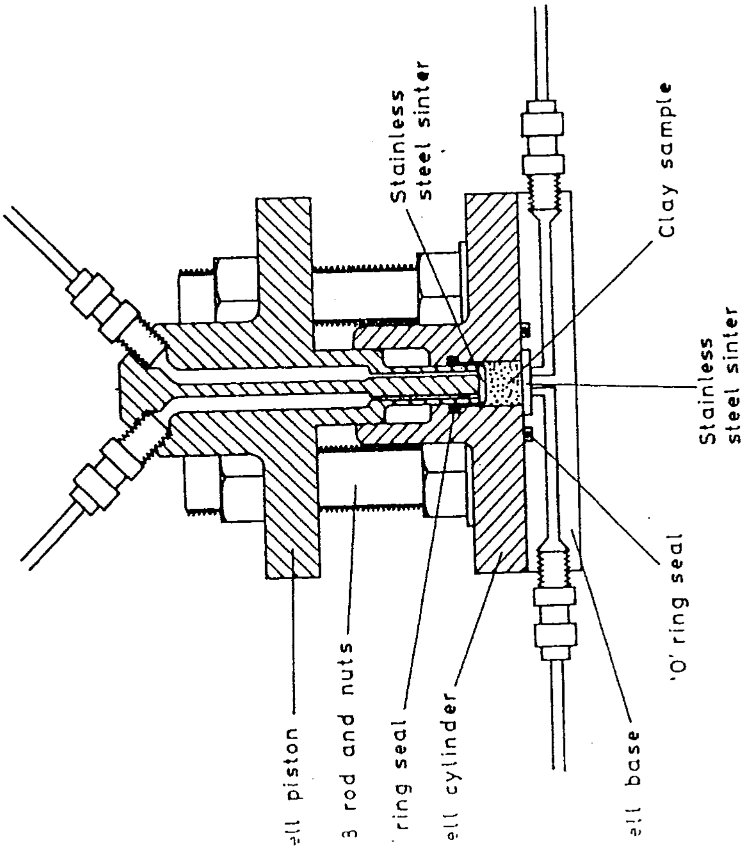


FIGURE 7. HIGH-PRESSURE CONVECTION CELL: CROSS SECTION

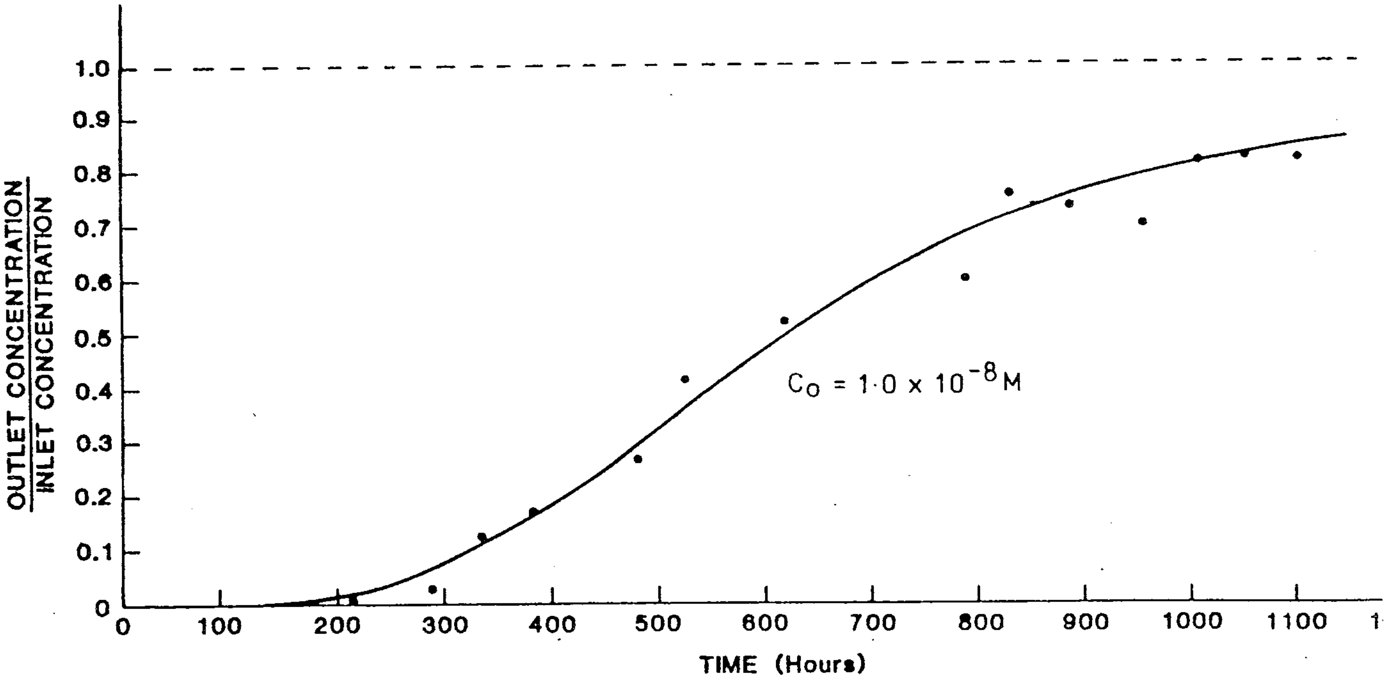


FIGURE 15. STRONTIUM-CLAY HIGH PRESSURE CONVECTION BREAKTHROUGH CURVE

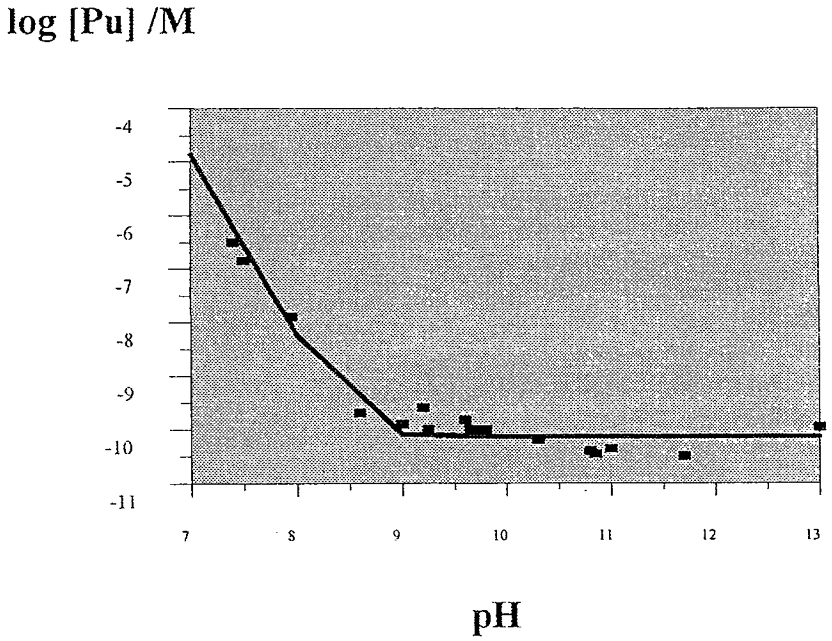
The Effects of Organics in the Near Field

S J WILLIAMS

Near-field Solubilities

Element	Solubility/(mol/l)
Americium	3×10^{-11}
Plutonium	7×10^{-11}
Neptunium	8×10^{-9}
Protactinium	1×10^{-10}
Thorium	4×10^{-9}
Radium	$\leq 1 \times 10^{-6}$
Lead	4×10^{-4}
Tin	1×10^{-4}
Palladium	$\leq 1 \times 10^{-7}$
Zirconium	1×10^{-8}
Technetium	1×10^{-7}

Effect of pH on Plutonium Solubility



Perturbations

Possible perturbations of the behaviour of radioelements in the near field could arise from:

a) organic materials present in the waste;

b) microbiological action;

c) colloids; and

d) radiolysis.

Range of Effects

The radiolytic or chemical degradation of organic materials in radioactive wastes may result in the release of small molecules

Organic molecules

- **Complexation of radionuclides**
- **Carbon source for microbial activity**
- **Gas generation - either directly from radiolysis or indirectly through microbial action**
- **Interaction with materials of the Engineered Barriers**

Inorganic molecules

- **Gas generation - mainly from radiolysis**
- **Interaction with materials of the Engineered Barriers**

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Combustible PCM

Major Components

- PVC (plasticised)
- Polyethylene
- Neoprene (polychloroisoprene)
- Latex (natural polyisoprene)
- Hypalon (chlorosulphonated polyethylene)
- Cellulose

Minor Components

- Perspex (polymethylmethacrylate), PTFE, polycarbonate, polystyrene, polypropylene, 'O'-rings, unplasticised PVC, nylon, polmethylpentene, glass fibre reinforced epoxy resin, Bakelite and traces of almost any other rubber or plastic

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Potential Volumes of Unconditioned Organic Wastes

ILW	m^3
Ion exchange resins	2000
PVC	9000
Rubber	3000
Other plastics	3400
Cellulose	700
Mixed plastics, cellulose and rubber	2700
Unspecified	200
LLW	
Paper and wood	66,000
Plastic and rubber	48,000

(From Biddle and Rees, UKAEA Report AERE R 12597 (1988))

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Organic Degradation Experiments

Solid organic materials are chemically degraded in the presence of a crushed cement.

The atmosphere may be air or may be anaerobic, for example argon/hydrogen or nitrogen.

The degradations may be carried out at room temperature or at up to 80°C.

Typically, the organic material may be 10% of the total of organic and cement. However, variations in organic content can be studied.

Leachates containing degradation products are removed, cooled and the radioelement solubility measured at pH 12 by adding a small volume of a concentrated solution of radioelement.

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Pu Solubilities in Organic Leachates

Organic Material	Pu solubility/(mol/l)
Cellulose (Tissue)	$1x10^{-3}$
Cotton Wool*	$1x10^{-5}$
Wood#	$1x10^{-3}$
Nylon	$1x10^{-10}$
Polythene	$1x10^{-10}$
PVC	$1x10^{-9}$
Polystyrene*	$5x10^{-10}$
Cement Leachate	$1x10^{-10}$

Organic material degraded anaerobically in contact with cement for 500 days at 80°C (except * = degradation time 240 days and # = time 120 days). Plutonium solubility measured at pH 12.

Strategy for Cellulose Degradation

Understanding of impact of cellulose degradation developed by pursuing several areas of work

- **Effect of leachates from cellulose degradation on radionuclide solubility and sorption behaviour**
- **Review of likely products and degradation chemistry from published literature**
- **Analysis of leachates and identification of degradation products (TOC, GC, GC-MS, HPLC)**
- **Synthesis of likely degradation products - use as standards for analyses and for studies of radionuclide behaviour**

Experimental Programmes

Mr B F Greenfield and Mr M W Spindler
- Chemical and radiolytic degradation experiments
- Effects on radionuclide solubilities
- Effects on sorption in the near field
- Synthesis of compounds (university sub-contract)

Dr N J Pilkington and Mr M H Hurdus
- Analysis of leachates (HPLC)
- Isolation of compounds from leachates (HPLC)

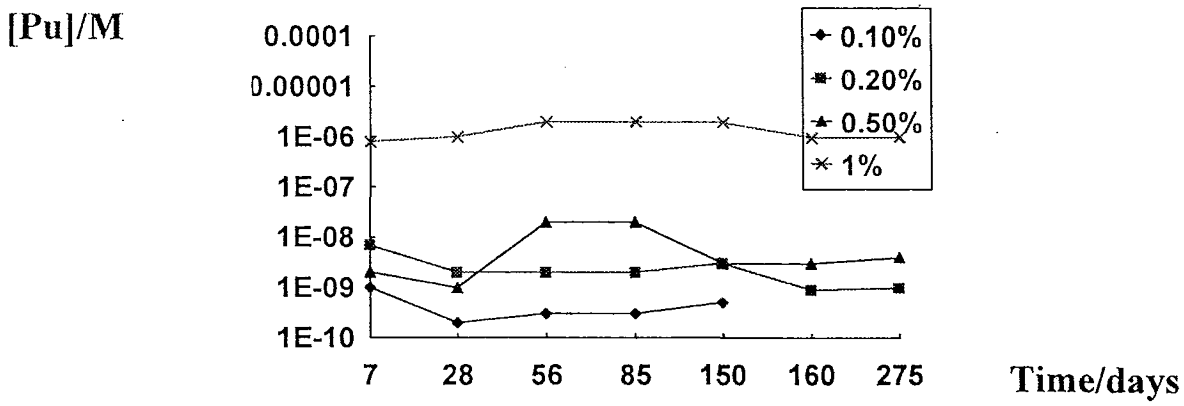
Linked to
- Microbiological studies (Dr A Rosevear)
- Thermodynamic modelling, assessments and sorption studies

Solubilities in Cellulose Leachates

Radioelement	Solubility/(mol/l) Cellulose	 Cement Water
Plutonium(IV)*	$1x10^{-3}$	$1x10^{-10}$
Plutonium(IV)	$1x10^{-4}$	$1x10^{-10}$
Americium(III)	$1x10^{-6}$	$1x10^{-10}$
Thorium(IV)	$1x10^{-5}$	$\leq 8x10^{-10}$
Uranium(IV)	$1x10^{-5}$	$1x10^{-7}$
Uranium(VI)	$5x10^{-4}$	$5x10^{-6}$
Neptunium(IV)	$1x10^{-6}$	$1x10^{-8}$
Technetium(IV)	$1x10^{-6}$	$1x10^{-7}$
Tin(IV)*	$1x10^{-3}$	$1x10^{-7}$

Measured at pH 12 in leachates from a 10% loading of cellulose in OPC/BFS degraded aerobically (except * = anaerobic).

Effect of Cellulose Loading



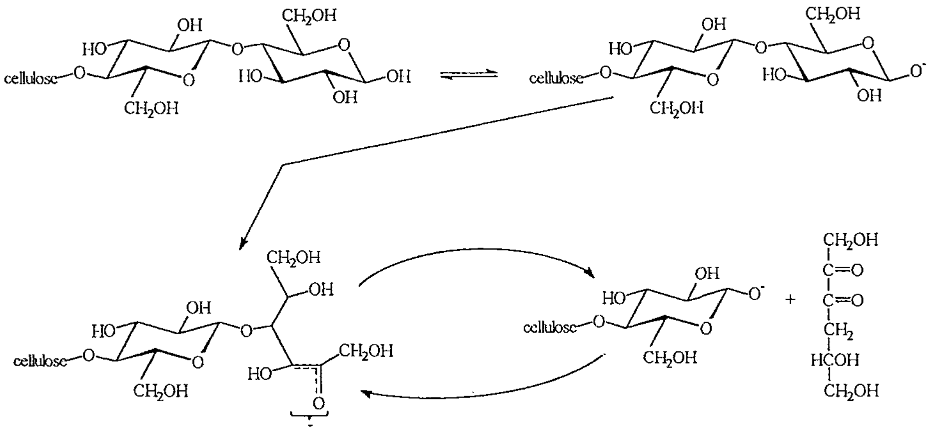
Plutonium solubilities measured in leachates obtained from different loadings of cellulose in cement

Organic Effect on Sorption

10% cellulose in	Rd/ $cm^3 g^{-1}$
9/1 BFS/OPC	400-600
3/1 PFA/OPC	100-200
No Organics	$1x10^4$ - $1x10^5$

Sorption of plutonium by OPC/PFA from cellulose leachates produced under anaerobic conditions.

'Peeling' Reaction of Cellulose



Alkaline degradation

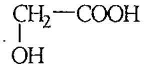
Cellulose Degradation Products

$H-COOH$

formic acid

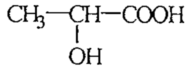
CH_3-COOH

acetic acid



$CH_2(OH)-COOH$

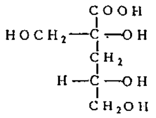
glycolic acid



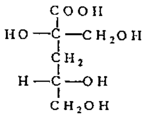
$CH_3-CH(OH)-COOH$

lactic acid

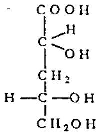
Cellulose Degradation Products



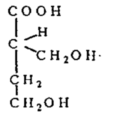
2-*C*-(hydroxymethyl)-3-deoxy-
D-*erythro*-pentonic acid
erythro-iso-saccharinic acid (ISA)



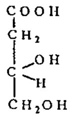
2-*C*-(hydroxymethyl)-3-deoxy-
D-*threo*-pentonic acid
threo-iso-saccharinic acid (ISA)



3-deoxy-D-pentonic acid



2-*C*-(hydroxymethyl)-
3-deoxy-tetronic acid



3,4-dihydroxy-butanoic acid

Analyses

A number of techniques are used to analyse cellulose leachates

- Total Organic Carbon (TOC) - indicates extent of degradation
- Gas Chromatography (GC) - requires preparation of volatile derivatives and standards
- Gas Chromatography - Mass Spectrometry (GC-MS) - requires preparation of volatile derivatives
- High Performance Liquid Chromatography - requires standards but may be used on aqueous samples, can be used for both analytical and preparative work

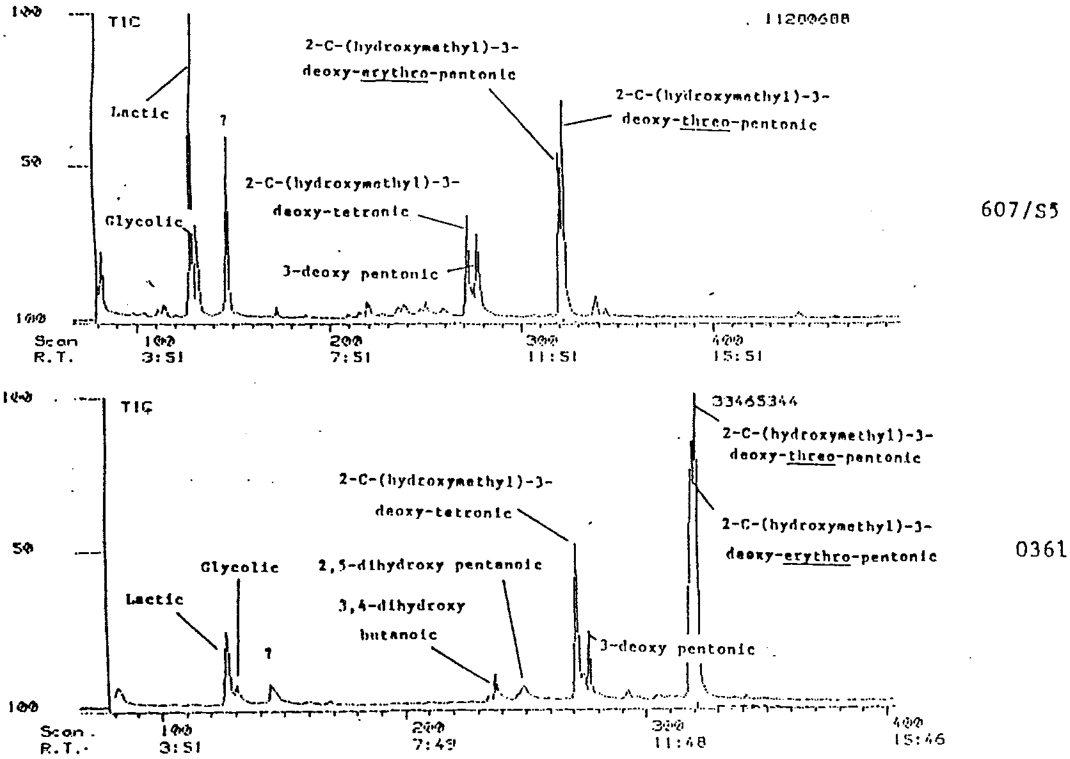
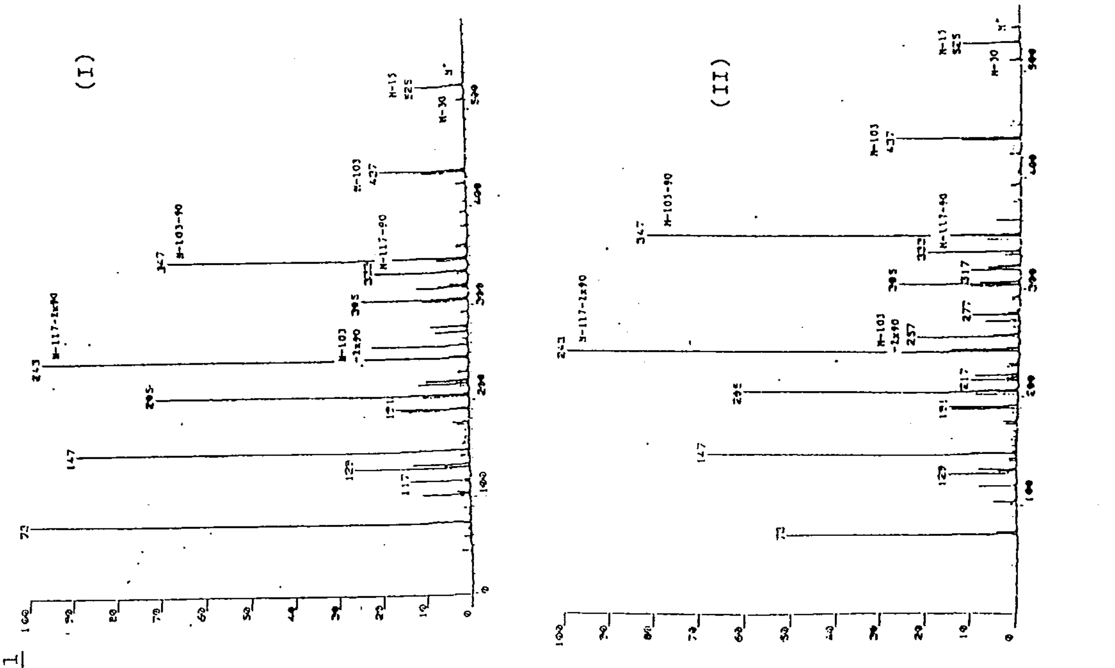


Figure 26. GC-MS of Test Leachates

Figure 31



Mass Spectra of 2-C-(hydroxymethyl)-3-deoxy-D-erythro-pentonic (I) and 2-C-(hydroxymethyl)-3-deoxy-D-threo-pentonic acids

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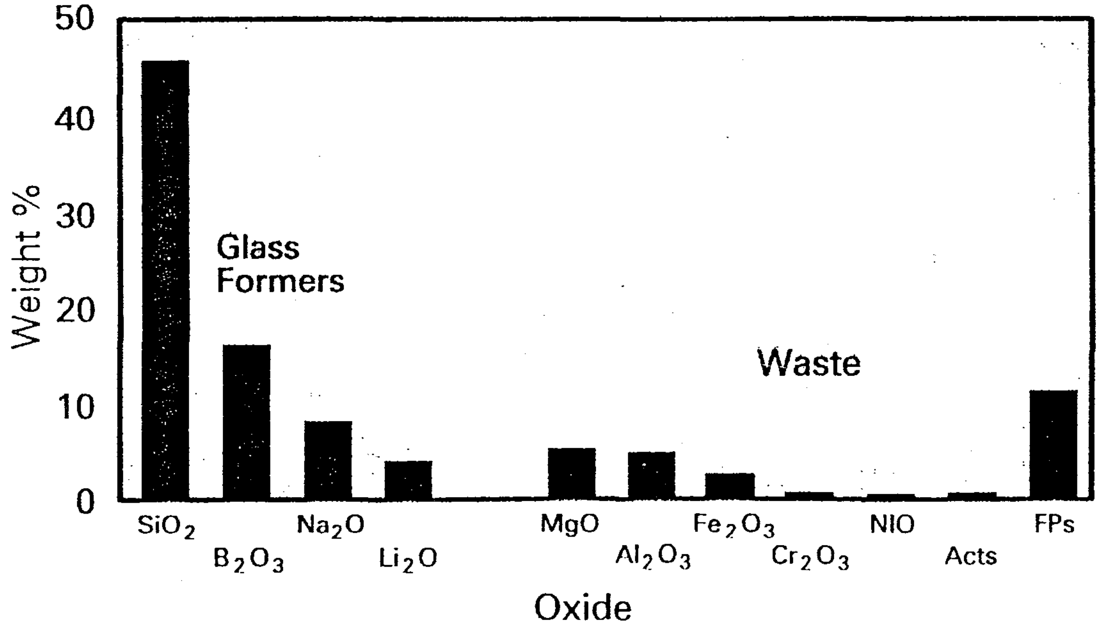
RADIONUCLIDE RELEASE
from
VITRIFIED HIGH-LEVEL WASTE
UNDER REPOSITORY CONDITIONS
in
CLAY OR GRANITE.

JAC Marples
AEA Technology
Harwell Laboratory

Composition of MW Glass

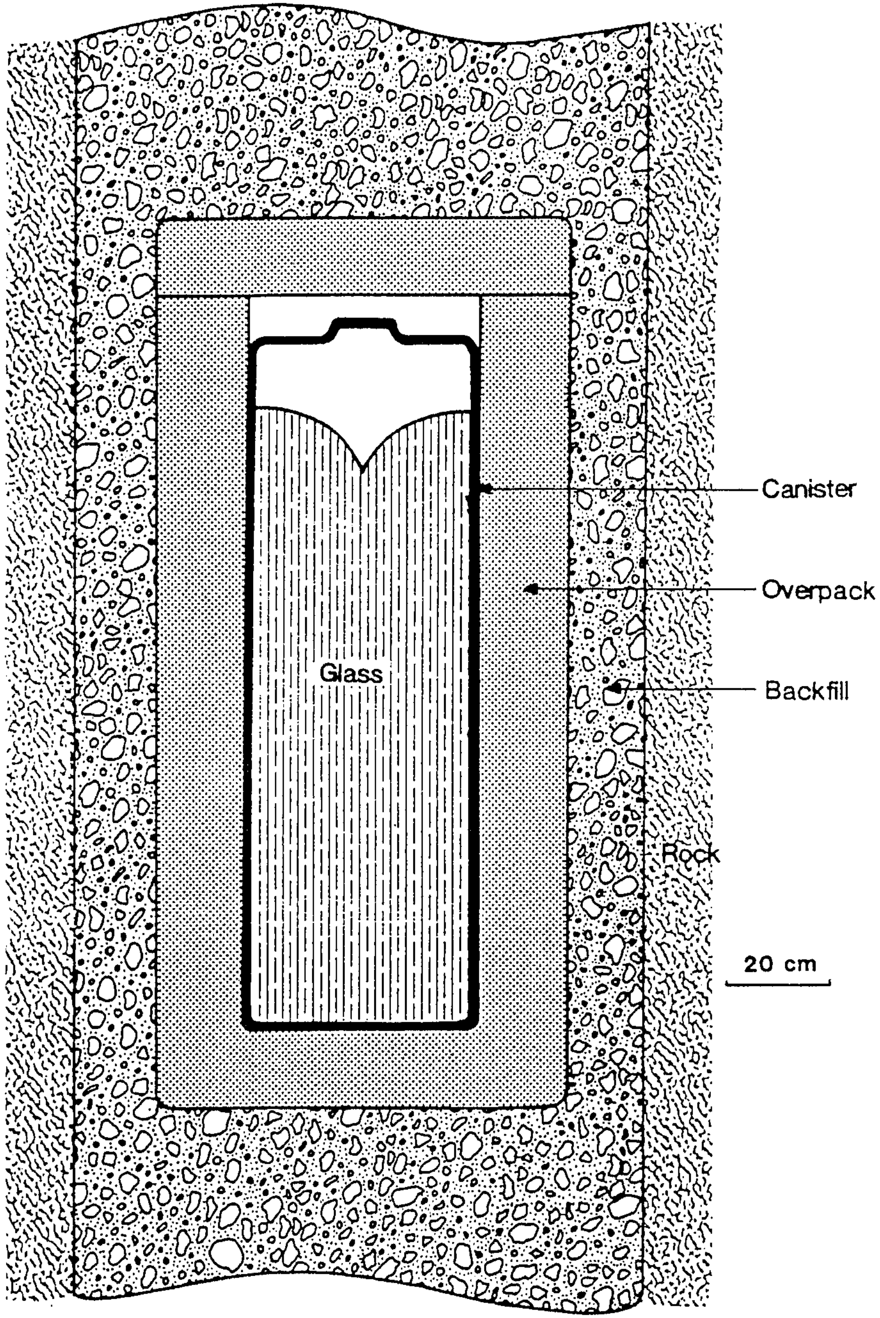


TOTAL INGESTION HAZARD FOR MAGNOX HLW

(Relative to Tc = 1)

AT 1000 YEARS		AT 10000 YEARS	
ELEMENT	RELATIVE HAZARD	ELEMENT	RELATIVE HAZARD
Am	12000	Pu	240
Pu	370	Am	120
Np	30	Np	36
Tc	1	Tc	1
Sn	0.6	Sn	0.6
Cs	0.4	Th	0.6
U	0.3	Cs	0.4
Cm	0.3	Pb	0.4
Zr	0.2	U	0.3
		ZR	0.3

HAZARD (Sv/te) = QUANTITY PRODUCED (Bq/Te) X DOSE PER UNIT INTAKE (Sv/Bq)



SCHEMATIC CROSS-SECTION OF THE NEAR-FIELD OF A HIGH-LEVEL WASTE REPOSITORY

REPOSITORY SOURCE-TERM

AT HIGH WATER FLOWS

RELEASE = LEACH RATE X AREA X TIME

AT LOW WATER FLOWS

RELEASE = CONCENTRATION IN WATER IN REPOSITORY X WATER FLOW RATE X TIME

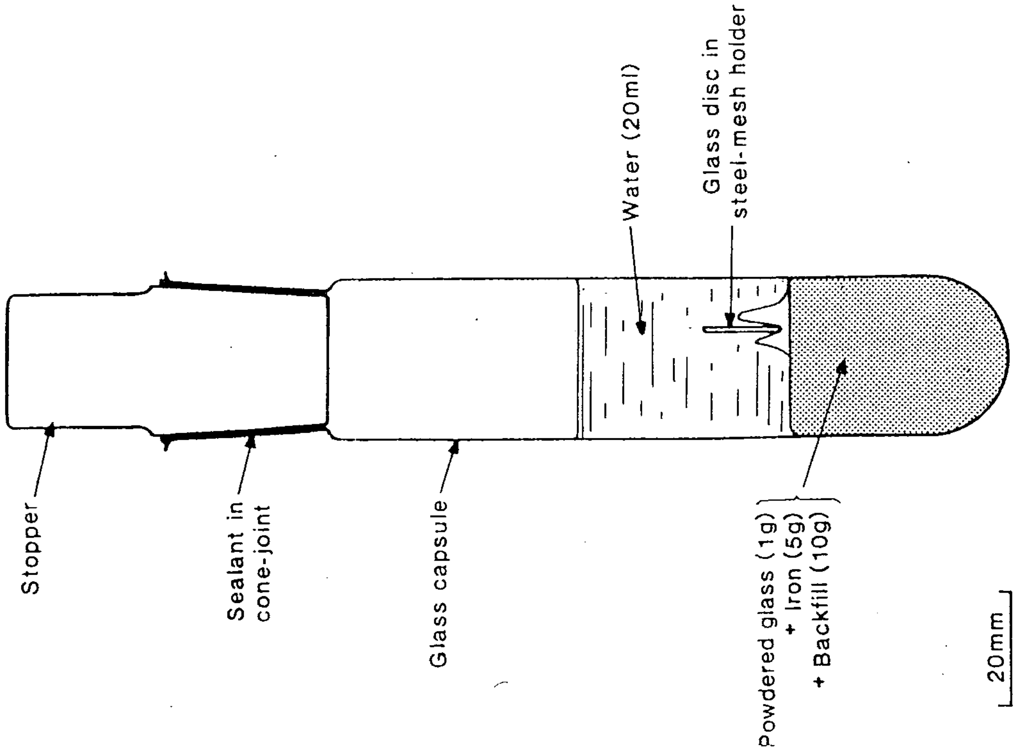
CONCENTRATION IN WATER = SOLUBILITY MODIFIED BY SORPTION ON BACKFILL ETC.

EXPERIMENTAL METHOD

- MW Glass with full inactive waste simulant
- Samples separately doped with:
  Tc, Np, Pu, Am
- Crush glass
- Mix with "Repository Components"
- Load into capsule
  - in argon-5% hydrogen filled glove-box

EXPERIMENTAL METHOD
(Continued)

- Seal capsule - transfer to oven.
- Hold at temperature (60 or 90C) for
  1, 3, 6 or 12 months
- Return to glove box
  - measure Eh and pH
- Take water samples for counting
- Filter to remove particles
  - and colloids



CAPSULE FOR EQUILIBRIUM-CONCENTRATION EXPERIMENTS

Capsule Experiments (I)

(Reducing conditions: MW Glass: 60°C)

Molar Concentrations

	Tc/E-08	Np/E-10	Pu/E-14	Am/E-13
Backfill				
OPC/PFA	3	2	0.5	2
Boom Clay	6	1200	40	15
Bentonite	3	70	60	40
Limiting Concentrations	7	2	230	0.5

OPC = Ordinary Portland Cement
PFA = Pulverised Fuel Ash

Capsule Experiments (II)

(OPC/PFA Backfill: 60°C)

Molar Concentrations

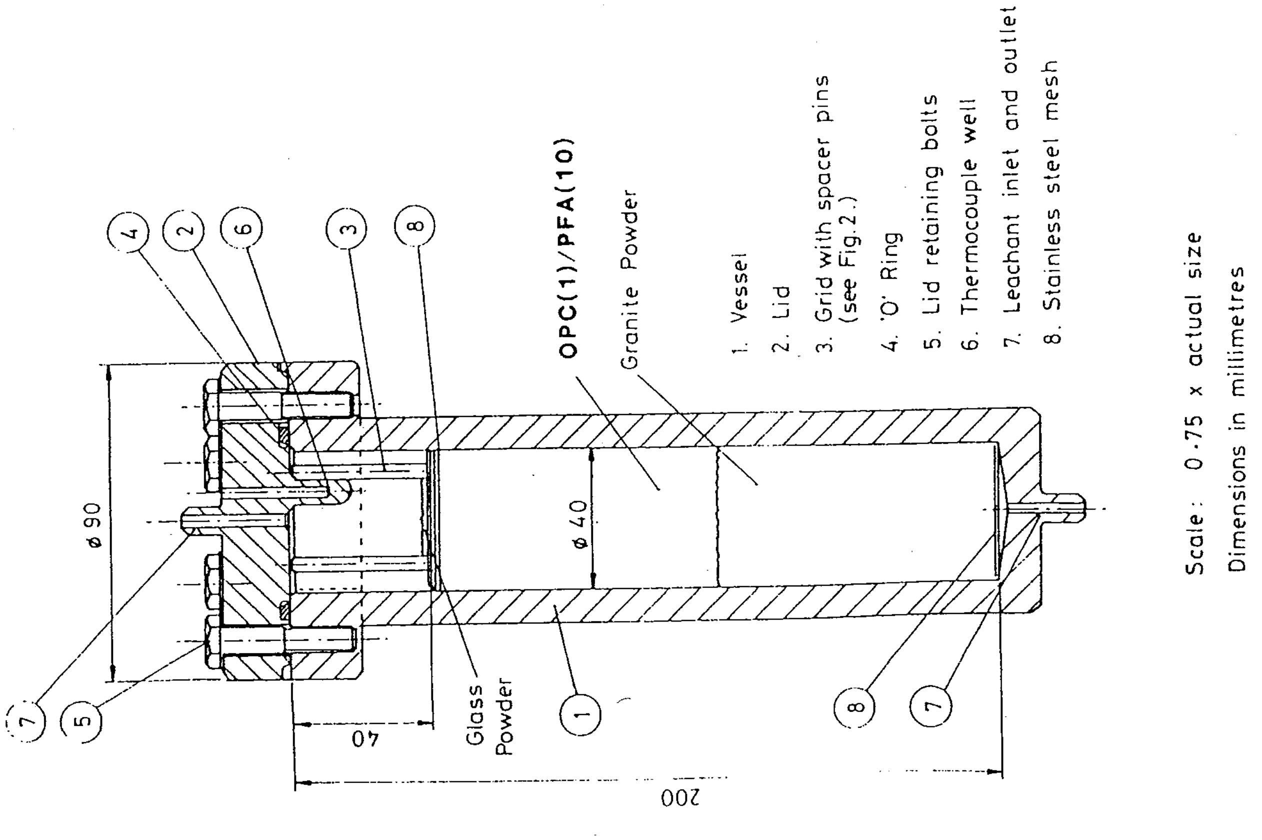
	Tc/E-08	Np/E-10	Pu/E-14	Am/E-13
Reducing Conditions				
SON68	3	6	0.5	2
MW	3	2	0.5	2
Oxidising Conditions				
MW	8000	15	0.5	2
Limiting Concentrations	7	2	230	0.5

(1mSv per year if you drink 2 litres per day)

Weight-loss Leach-rates

1 year at 60°C in capsules

Components	pH	Leach-rate (g/sq cm/day)
Fe only	9.1	7 E-6
Fe + OPC/PFA	11.5	0.2
Fe + Bentonite	8.0	27
Fe + Boom clay	7.7	21



Scale: 0·75 x actual size

Dimensions in millimetres

FIG.1. "SEMI-INTEGRAL" TEST - LEACHING CELL.

Repository System Simulation Test

Molar Concentrations: 60°C: 1.8nm filter

Water	Backfill	Tc	Np	Pu	Am
Volvic	OPC/PFA	2E-8	3E-10	2E-11	2E-13
	Smectite	2E-5	5E-7	2E-10	4E-12
Sea	OPC/PFA	4E-9	1E-11	1E-11	2E-13
	Smectite	7E-7	4E-8	5E-11	8E-13

Conditions were not properly reducing in the experiments with the sand/smectite backfill

Conclusions

In granite repository simulations,
with backfills containing OPC and
under reducing conditions:

- The concentrations of Tc, Np, Pu and Am in solution were respectively 0.2, 1, 20 and 4 times the "Limiting Concentration."
- This is the concentration which, if present in drinking water, would lead to an annual dose of 1mSv to someone drinking 2 litres per day.

Conclusions

In granite repository simulations:

- The use of OPC as a backfill decreased the weight-loss leach-rate of the glass rather than increasing it, despite the high pH.
- If sea-water entered the repository, it would not increase the amounts of Tc and of the actinides in solution.

Colloid Capability within AEA Technology

Dr M P Gardiner

Experimental Studies Section
Hydrogeology Department

What are Colloids?

Particles in the size range 1 nm to 1 µm.

Inorganic

- Oxyhydroxides
- Clays
- Silica

Organic

- Humic Acid/Fulvic Acid
- Cellulose Degradation Products
- Exopolysaccharides

Why are we Interested in Colloids?

- Colloids have a high surface to volume ratio: Good sorbers.
- Colloids can move faster than the bulk water.
- Partitioning is assumed to occur between an immobile solid phase and the aqueous solution phase.
- Colloids constitute a third, potentially mobile, phase onto which radioelements may sorb.
- The effect of a mobile colloidal phase will be to enhance radioelement migration by decreasing partitioning onto immobile solid surfaces.

Routine Experimental Methods

- Photon Correlation Spectroscopy.
- Transmission Electron Microscopy (EDAX).
- Particle Electrophoresis.

Current Work

1. Studies of the formation of cementitious colloids under conditions representative of the near field.
2. Colloid migration experiments through a large slate fracture.
3. Field scale colloid migration experiments through a fractured slate aquifer.
4. Sorption of Americium and Plutonium onto colloidal corrosion product simulants.
5. Competitive sorption between colloidal corrosion product simulants and cements.

Near-Field Colloids

Laboratory Studies.

Objectives:

- Characterisation of the size and concentration of colloids formed in leachates of a candidate backfill.
- Identification of chemical and physical nature of colloids formed in leachates of a candidate backfill.
- Investigation of the changes brought about to colloids formed in the near-field when transposed to the far-field.

Near-Field Colloids

Materials and Experimental Procedures.

- Backfill: 500 to 1000 micron particle size.
- Temperatures: Room temperature, 60°C and 80°C.
- Solid to liquid ratio: 1:5, 1:10 and 1:50.
- Leaching timescale: One week and three months.

Near-Field Colloids

Results.

- Colloids formed by over saturation of the solution with silica followed by the precipitation of amorphous CSH phases.
- Colloid burden is dependent upon the concentration of soluble silica available from the backfill.
- Final colloid concentration in a leachate is very sensitive to the thermal history of that leachate.

Colloid Transport in Fracture Systems

Objectives.

1. To investigate the transport of well characterised inorganic colloids in fractured rock as a function of colloid type, size, ground water chemistry and fracture aperture.

2. To investigate the colloidal stability of particles under representative far field conditions.

3. To develop a simple code capable of describing colloid transport in fractured systems.

Colloid Transport in Fracture Systems

Laboratory studies of colloid transport.

- Silica and Hematite colloid migration studied over a distance of 1 m.
- Ionic strength range: 10^{-2} to 10^{-5}M.
- Volumetric flow rate range: 0.2 to 4.0 cm^3/min

Colloid Transport in Fracture Systems

Laboratory Results.

- Colloid breakthrough is in advance of the conservative tracer.
- Colloid transmission decreases as a function of increasing particle size and ionic strength at constant flow rate.
- Colloid transmission decreases as a function of decreasing flow rate.
- Colloid tracer accesses a smaller volume of the fracture that the conservative tracer.
- Hematite colloid transmission only 10% of silica colloid transmission.

Colloid Transport in Fracture Systems

Field Studies of Colloid Transport.

- Colloid migration experiments are conducted at Reskajeage Quarry, Cornwall in an engineered borehole array.
- Syton X30/Rhodamine-WT and Syton W30/Rhodamine-WT systems studied.
- Experiments performed between borehole 17 and borehole 15 15.4 m) and between borehole 12 and borehole 15 (5 m)

Colloid Transport in Fracture Systems

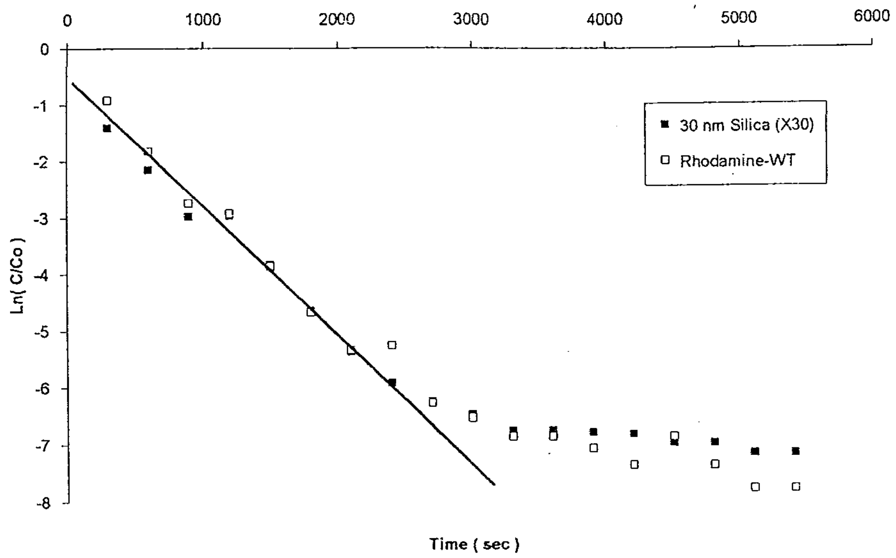
Field Results.

- 30 nm silica colloid recovery 90% relative to dye.
- 70 nm silica colloid recovery 70% relative to dye.
- Retardation factors not calculated.
- No partitioning of colloid or dye in release well.

Sorption of Plutonium and Americium onto Haematite, Magnetite and Zirconium Hydroxide in 3:1 BFS/OPC Cement Equilibrated Water

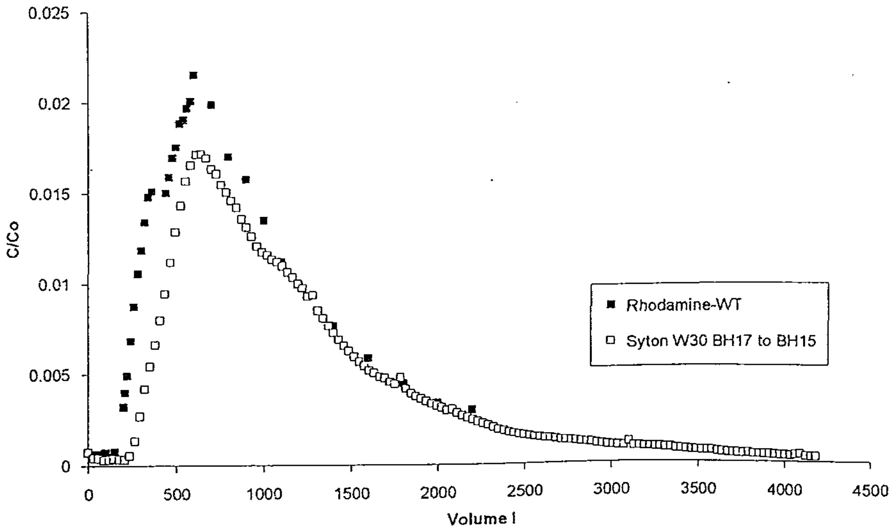
Colloid	Plutonium R_d/ml g^{-1}	Americium R_d/ml g^{-1}
Haematite	1×10^5	3×10^6
Magnetite	3×10^6	2×10^6
Zirconium Hydroxide	2×10^6	1×10^7

Syton X30 and Rhodamine Tracer Decay Function Borehole 12



AEA Technology
Decommissioning
& Waste Management

Syton W30 and Rhodamine Tracer Breakthrough (BH15)



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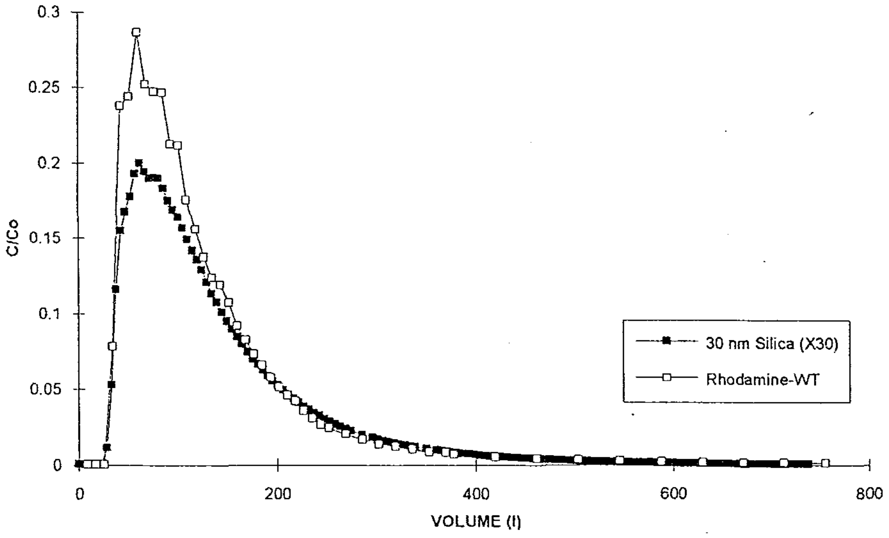
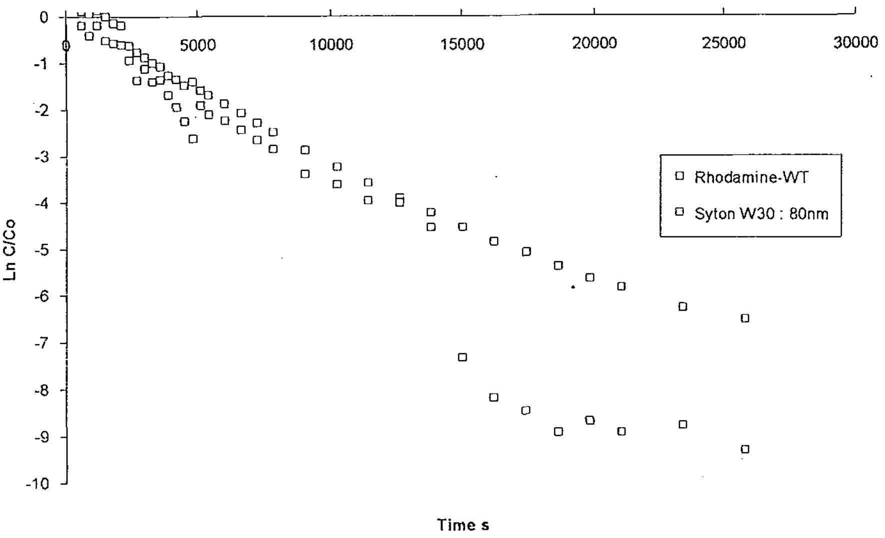
& Waste Management

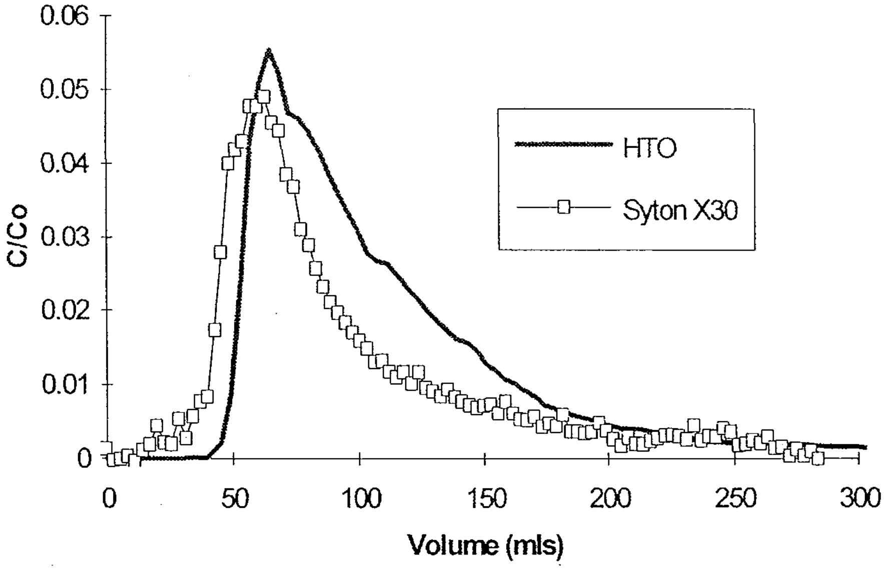
Syton X30 and Rhodamine Tracer Breakthrough Curve Borehole 15



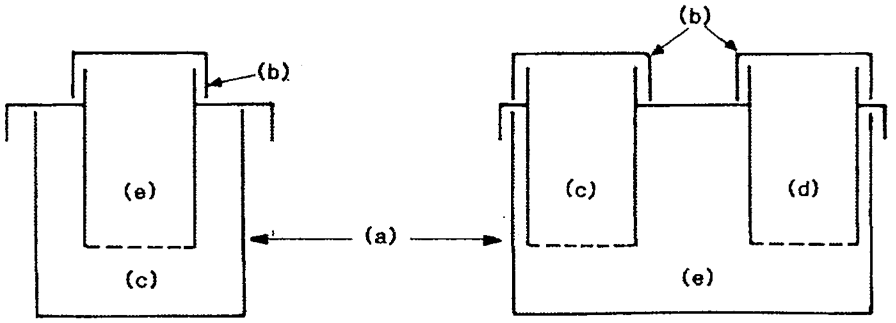
Syton W30 and Rhodamine Tracer Decay Function Borehole 17



Syton X30 and Tritiated Water Migration Through Large Slate Fracture



Experimental Rigs for Competitive Sorption Experiments



Single Solid Experiments

Competitive Sorption Experiments

(a) Poly Pot
(b) Ultrafree PF, 30,000 molecular weight cut off filter unit
(c) Colloid suspension /3:1BFS/OPC (single solid expt.only)
(d) 3:1 BFS/OPC competitive sorption experiments
(e) Actinide hydroxide solid phase

Sorption of Am and Pu on to Colloids

Single Solid Experiments

- Solid actinide was precipitated in a polysulphone filter unit
- Sorption carriedout on to Magnetite, Haematite and Zirconium Hydroxide each dispersed in 3:1 BFS/OPC equilibrated water

Competitive Sorption of Am and Pu on to Colloids and Cement

Two solid experiments

- Colloid and cement contained in separate filter units
- Actinide solid precipitated in pot

Sorption on to Colloids

Method

- Iron and Zirconium colloids were neutron activated to give either ^{59}Fe or ^{95}Zr γ-radiolable.
- Solid actinide (Plutonium or Americium) was pptd in a 30000 MWCO Millipore Ultrafree PF filter unit.
- The unit containing actinide and equilibrated cement water is placed in contact with the colloidal solution.
- Dissolving actinde diffuses continuously through the membrane to sorb on to the colloids.

Sorption on to Colloids

Objective:

- To measure sorption and 'desorption' R_d's on to μg quantities of colloidal corrosion product simulants.
- To measure the competitive sorption coefficients between colloidal corrosion product and cement.

Groundwater flow and transport modelling

- **Flexible tools to solve problems**
  - **NAMMU**
  - **NAPSAC**
- **Fracture network flow at Stripa**
- **Heterogeneous porous medium at Wipp**
- **Complex sedimentary basin**

1) Fracture network modelling at Stripa -

Flow and transport in fractured rock

- Groundwater flow is restricted to the fracture network
- Rock matrix is often effectively impermeable
- We observe localised flows that may be widely spaced
- Conventional modelling with porous media is successful on large scales

The fracture network modelling approach

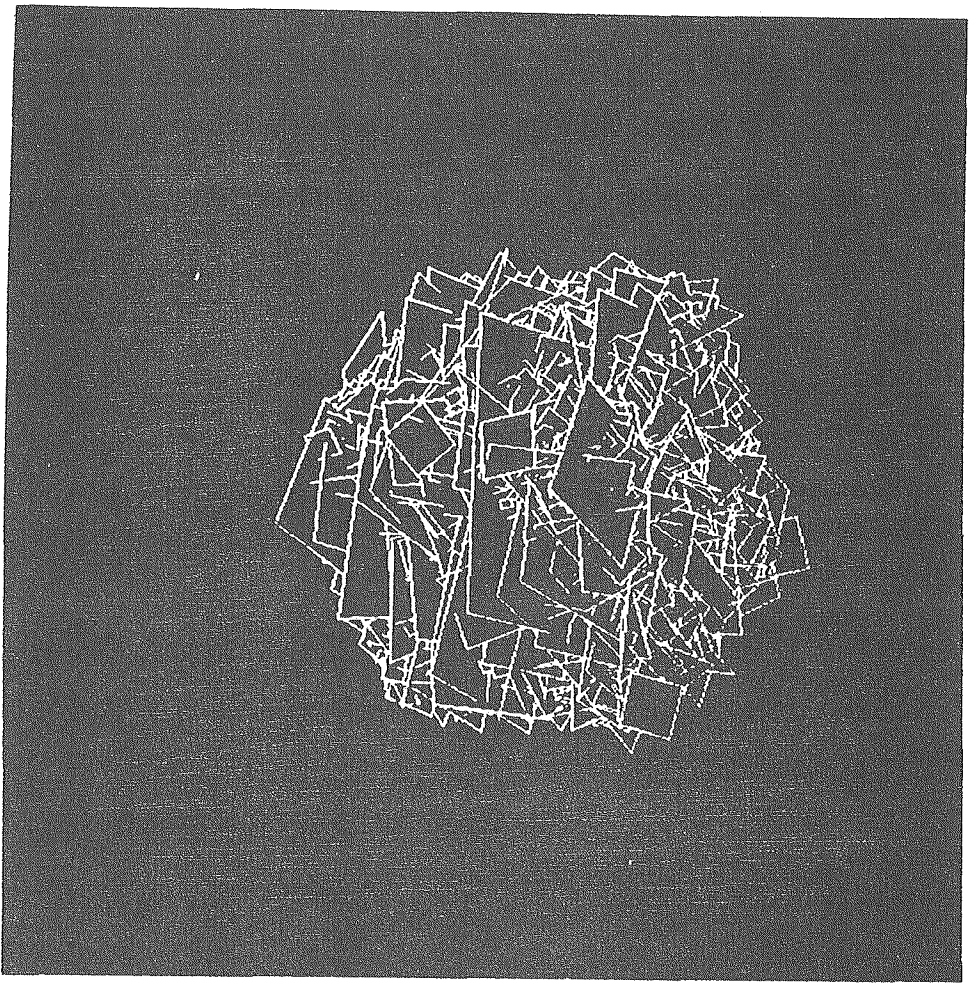
- We need to demonstrate understanding of the flow system
- We need to justify our use of continuum approximations on large scales
- We need to interpret measurements and observations on the scale of the fractures

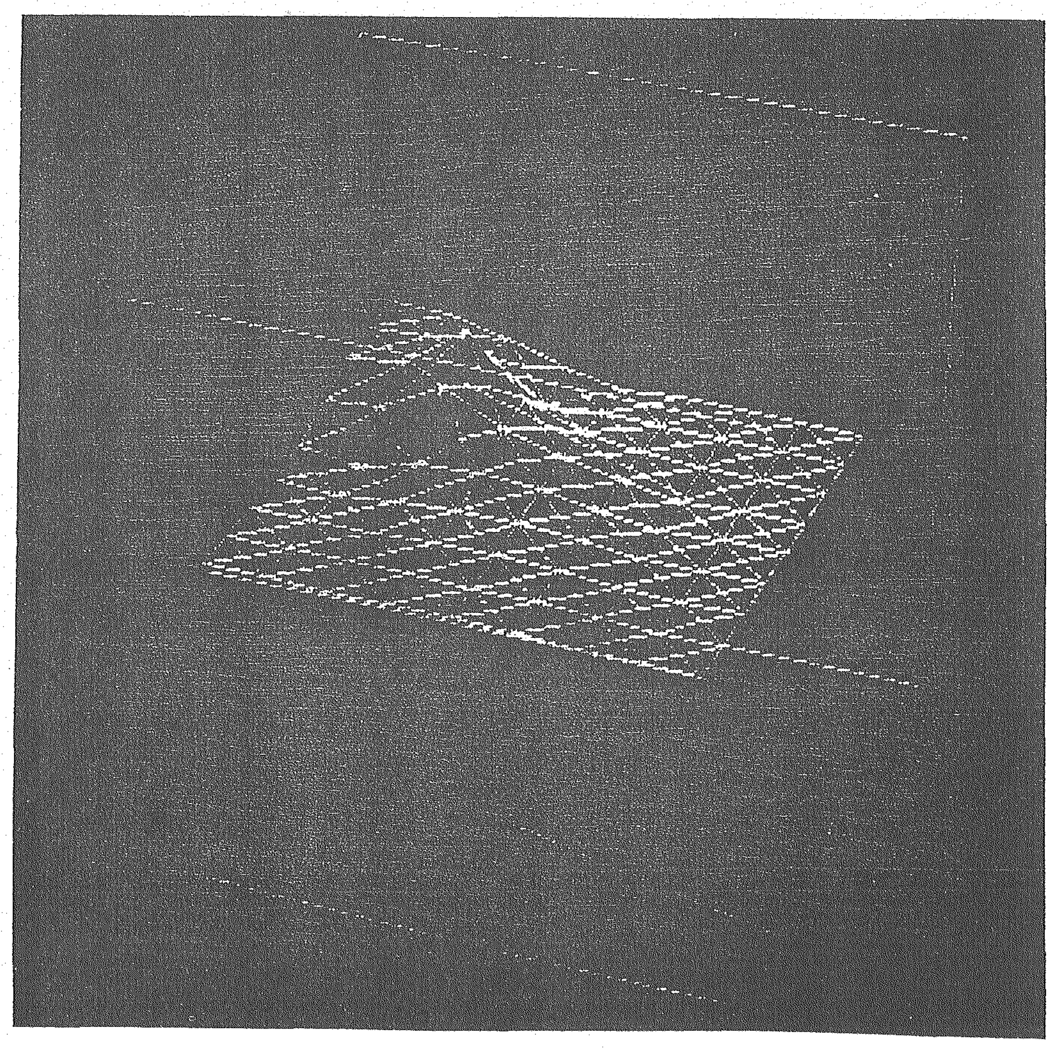
NAPSAC Capabilities

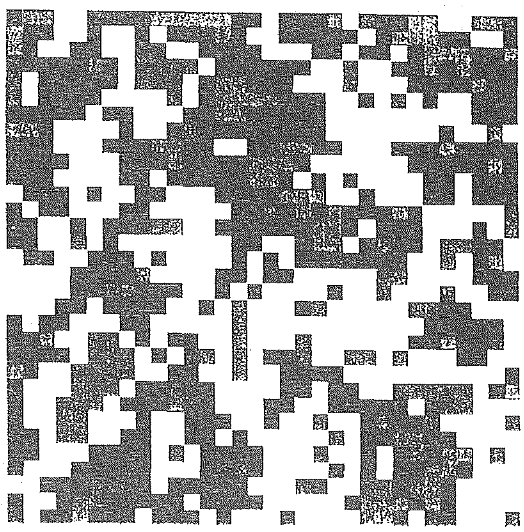
- three-dimensional steady-state fracture flow
- three-dimensional steady-state fracture transport
- borehole model
- three-dimensional transient fracture flow
- one-dimensional coupling to matrix
  eg. thermal
- two-dimensional steady-state fracture flow

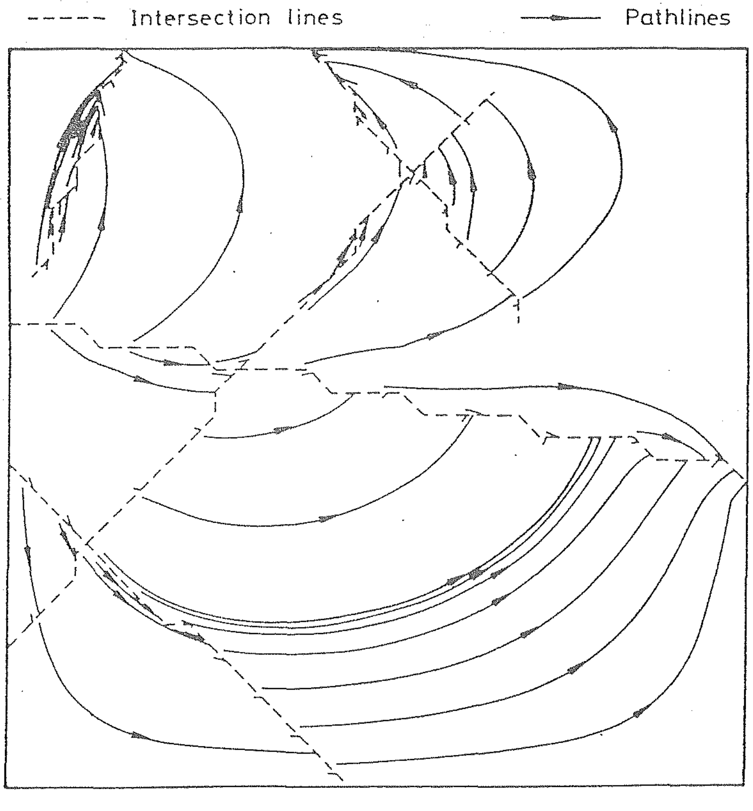
NAPSAC Applications

- Radioactive waste disposal
    - Nirex
    - Stripa project
    - Overseas nuclear industry
- Geothermal energy
- Oil industry
    - Block size and permeability
    - Interpretation of geology








Intersection lines
Pathlines

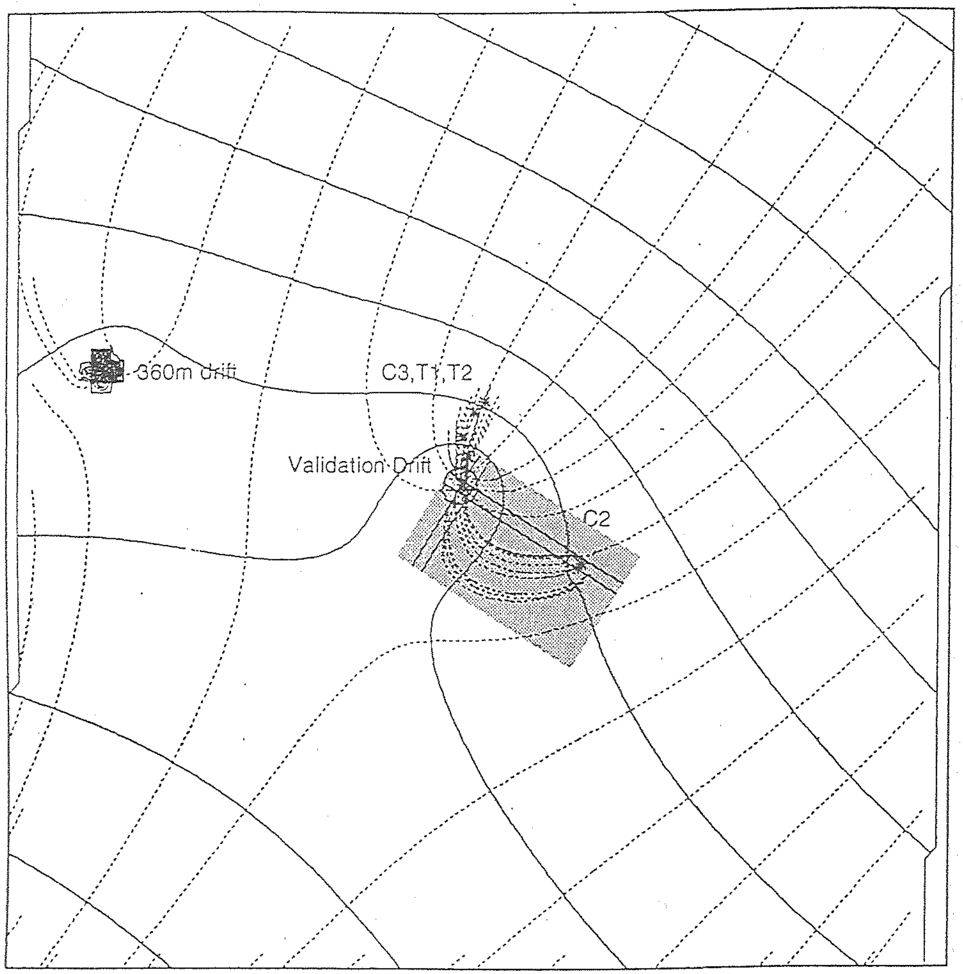
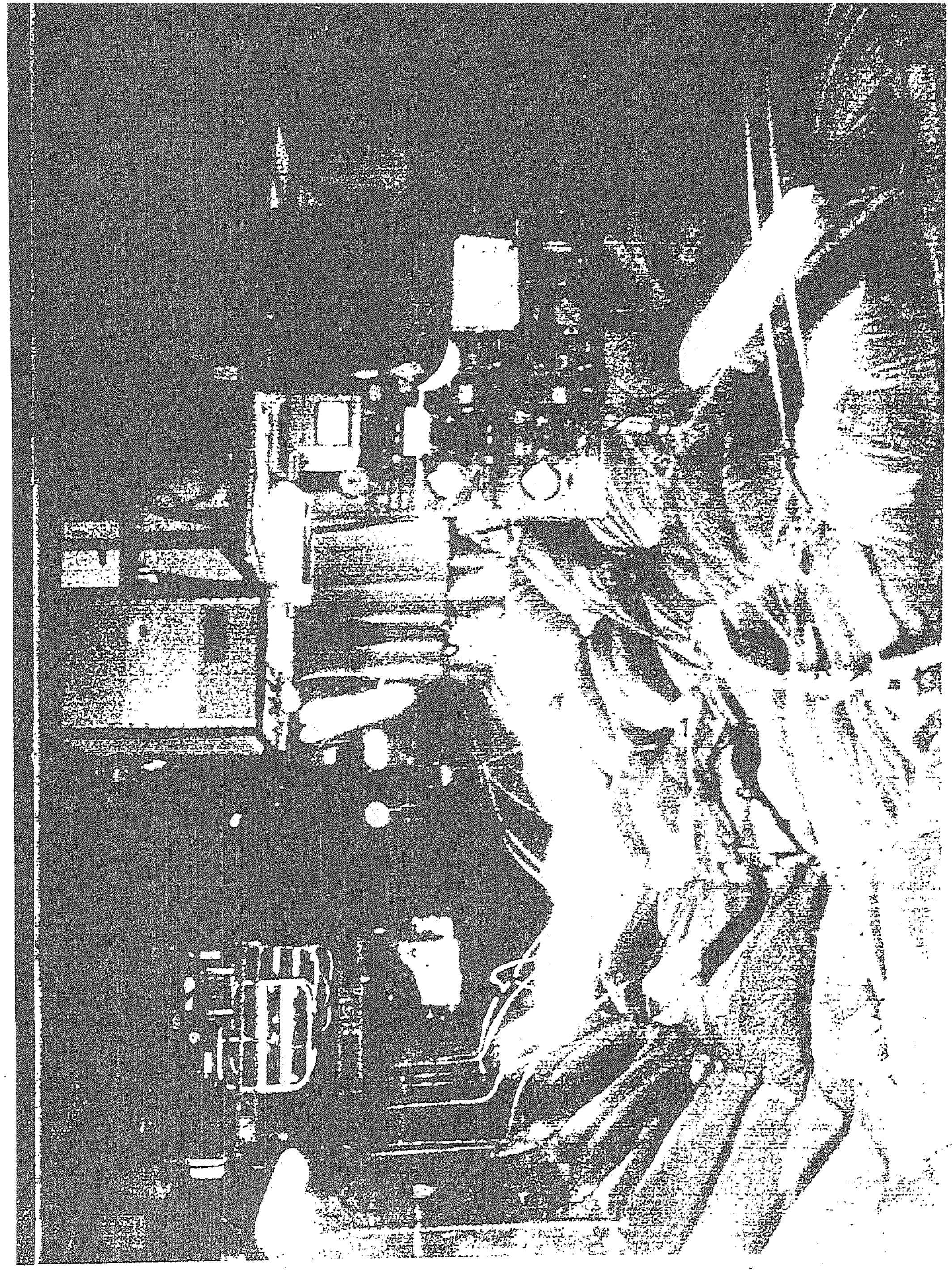
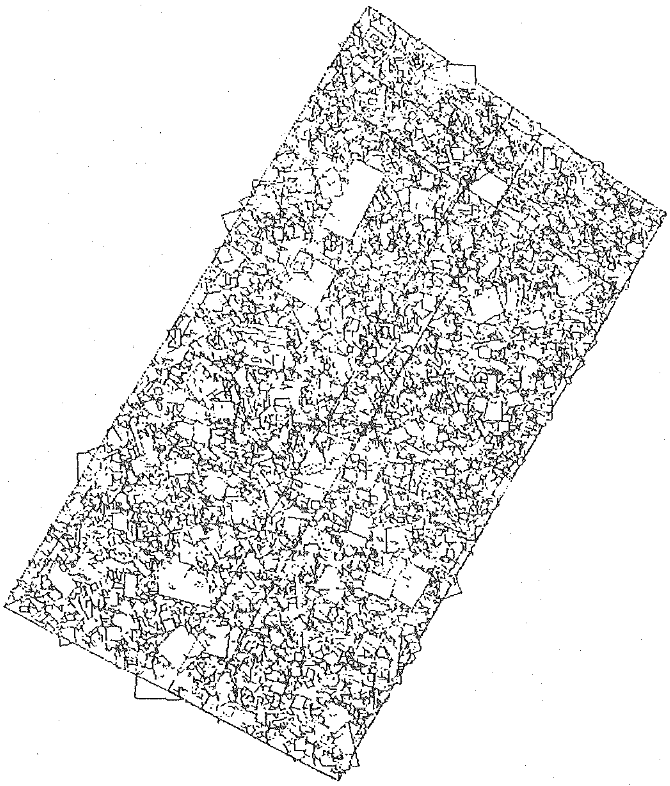


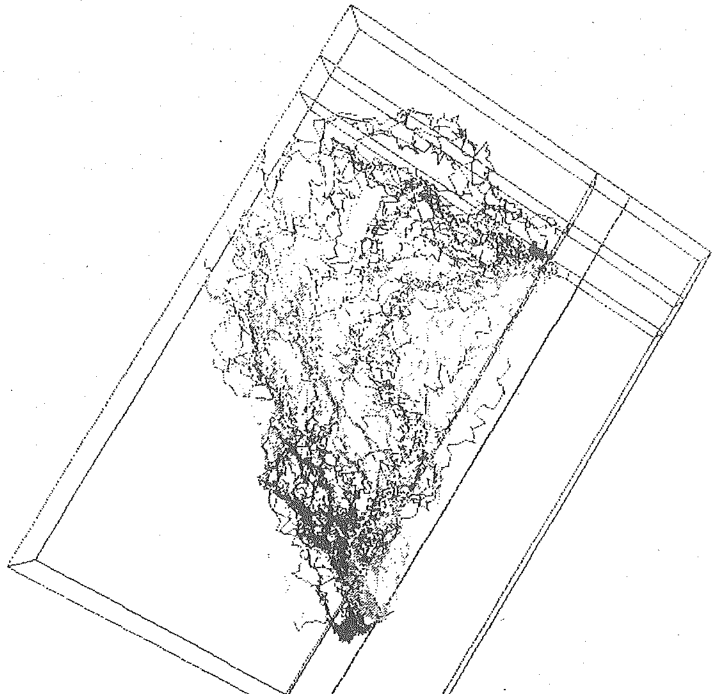
Figure 6.1 Head contours and flow pathlines for tracer experiments with recovery in Validation Drift

Sub-model region for model TR4*** shown in grey

Pathlines shown in dashed lines







NAMMU

* Extremely powerful groundwater flow and transport code.

* Widely used.

* Applicable to a wide range of physical problems.
    - saturated and unsaturated flow
    - coupled flow and heat transport
    - solute transport
    - solute transport with density effects
    - etc.

* Continuum model (Far Field)

* Geometric Flexibility (Finite Element)

* Efficient solution methods (CRAY 2)

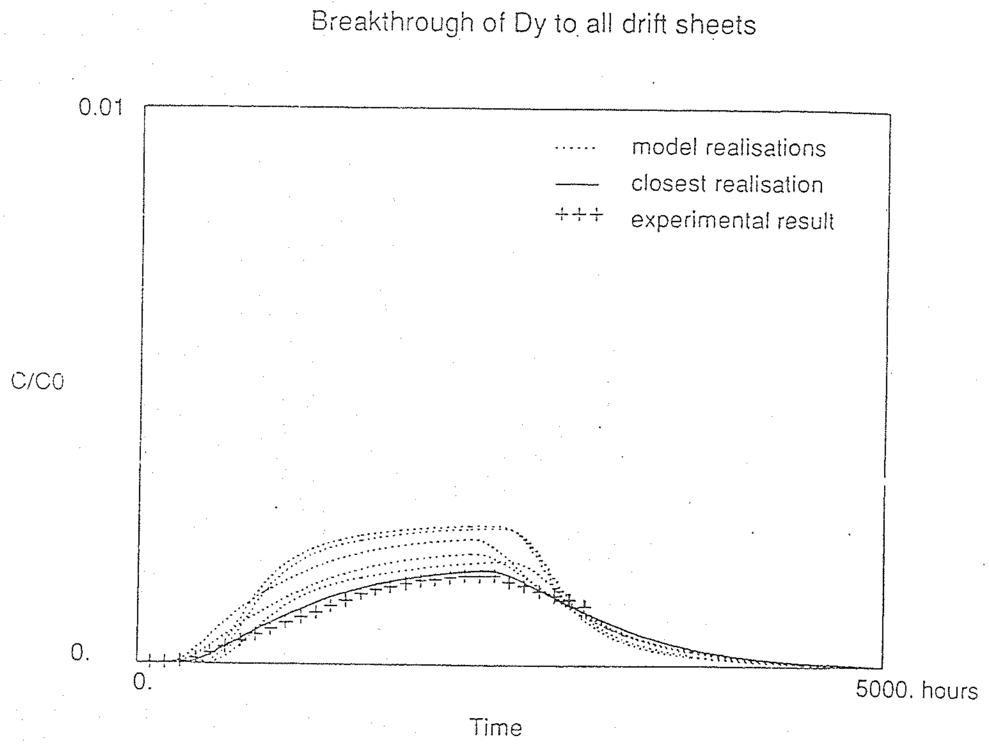
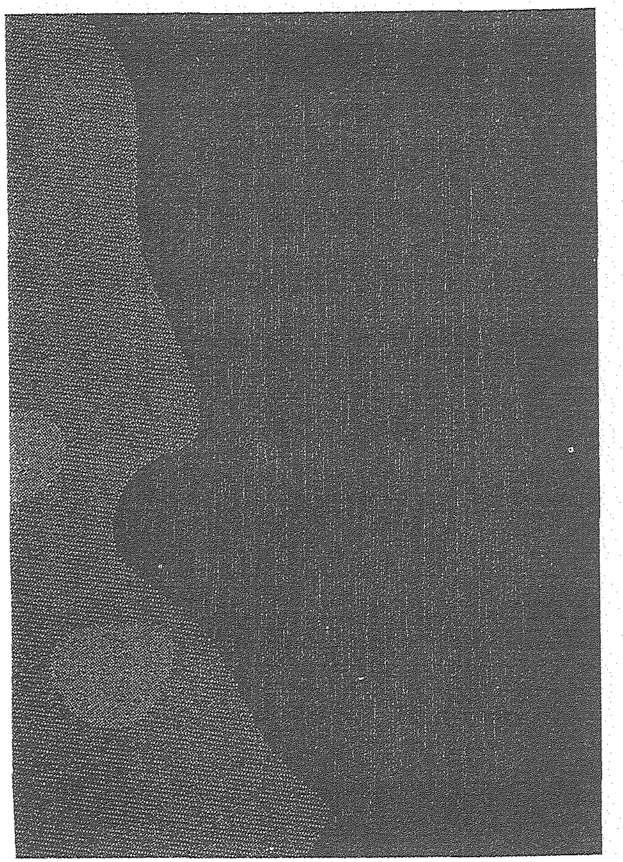


Figure 6.11 Comparison of predicted and experimental breakthrough for Dy tracer experiment: injection in C2 and recovery in the Validation Drift. All realisations of 1m injection intervals shown.

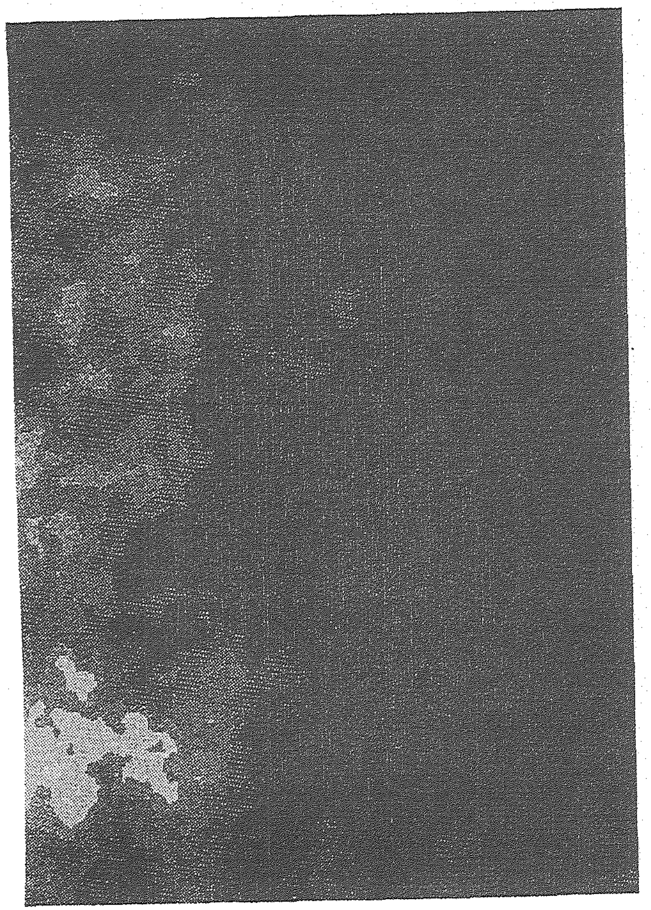
2) Heterogeneous porous medium modelling for INTRAVAL

WIPP-2 TEST CASE

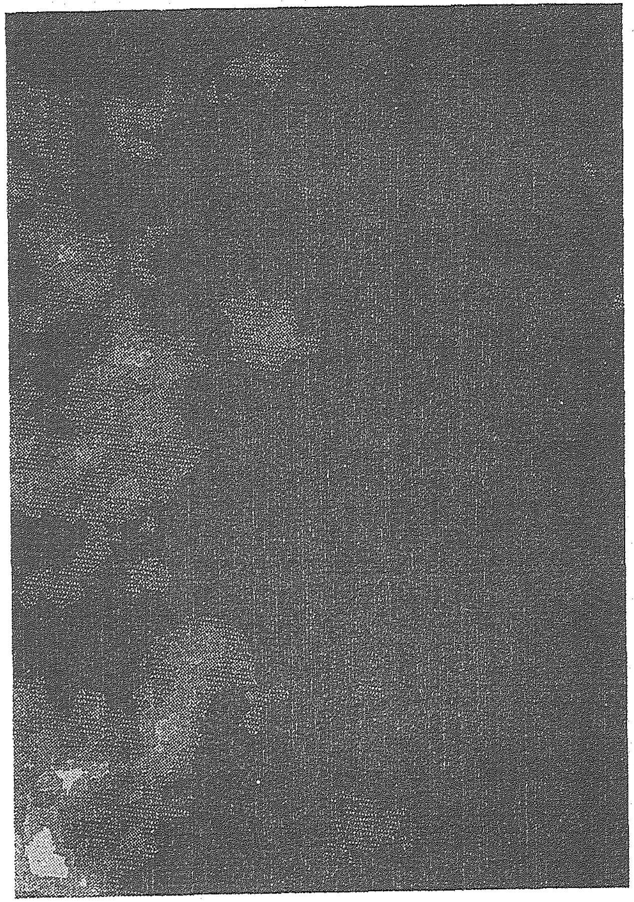
- Waste Isolation Pilot Plant in the US
- Culebra Dolomite main path for radionuclide transport off site following inadvertent borehole intrusion
- Culebra Dolomite is thin, extensive layer
- Well-investigated
    - 60 boreholes
    - 39 measurements of transmissivity
- Well-documented
    - Cauffman T L, LaVenue A M, and McCord J P, 1990
- INTRAVAL test case
    - opportunity to study validation of stochastic models



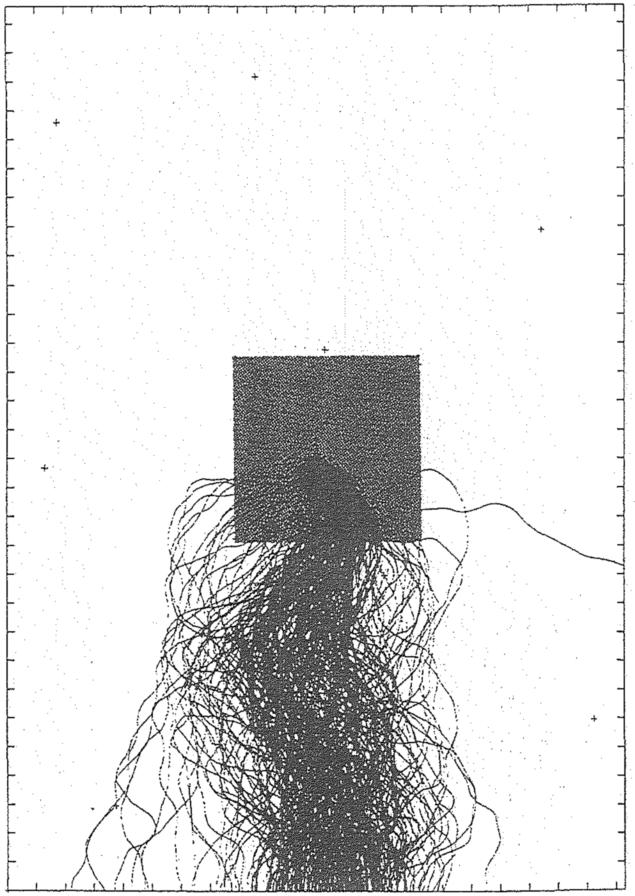
(wipp101m.tr)



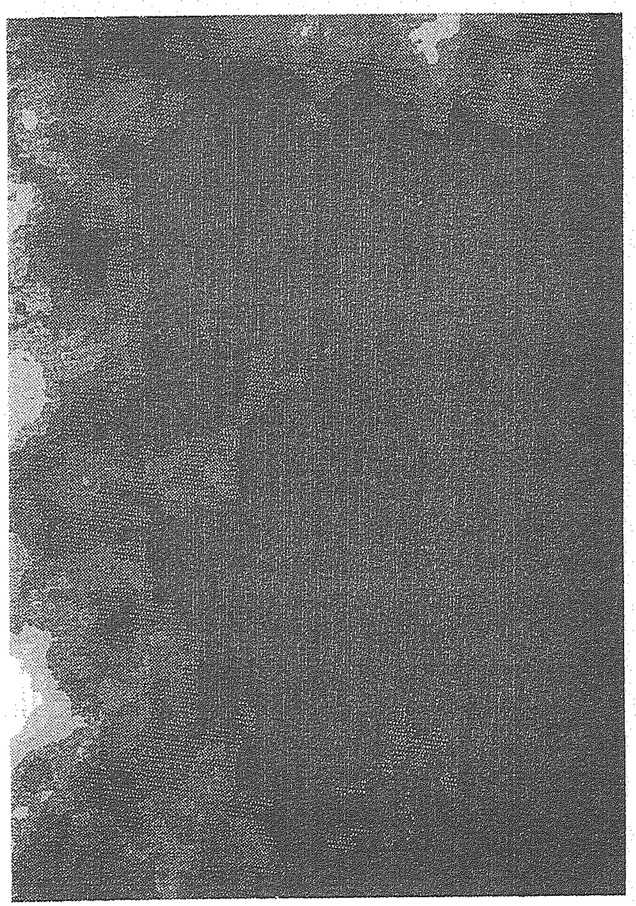
(wipp101.tr2)



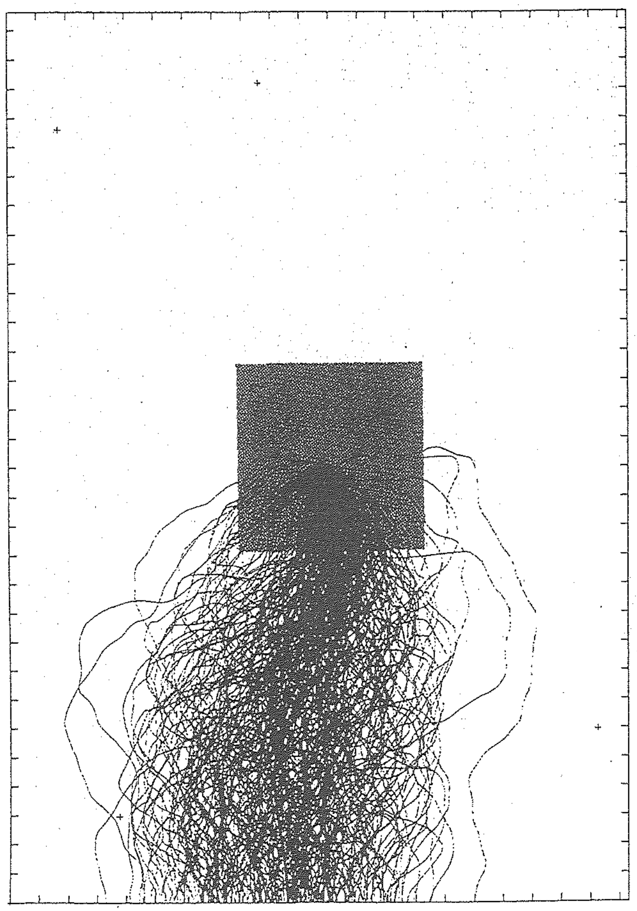
(wipp101.tr3)



(wipp106)



(wipp101.tr1)



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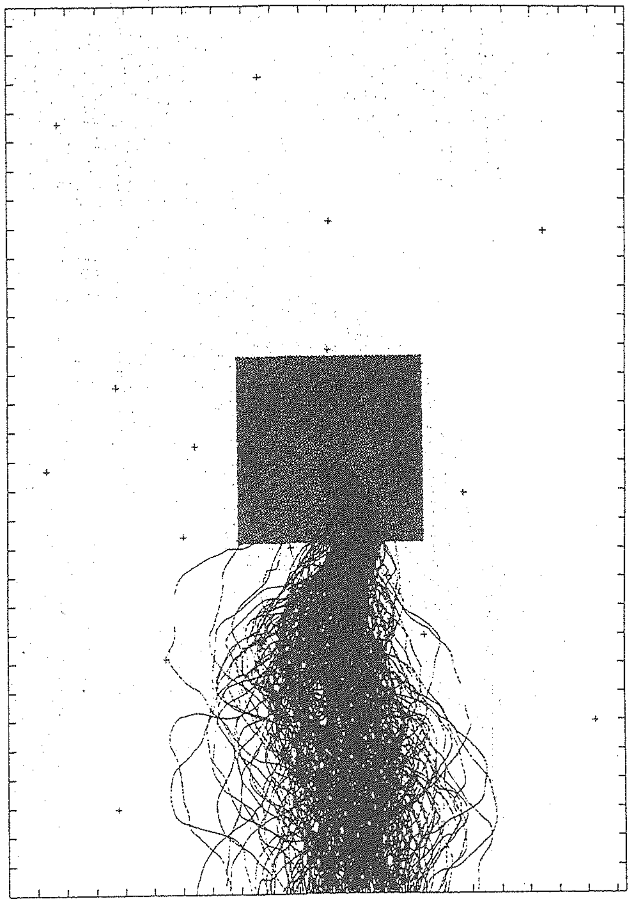
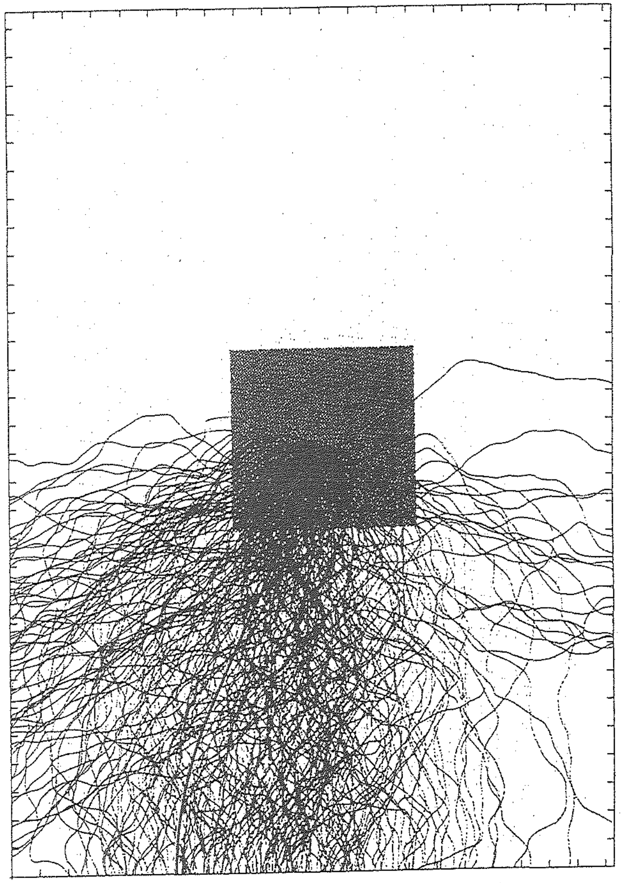


(wipp101)

CONCLUSIONS

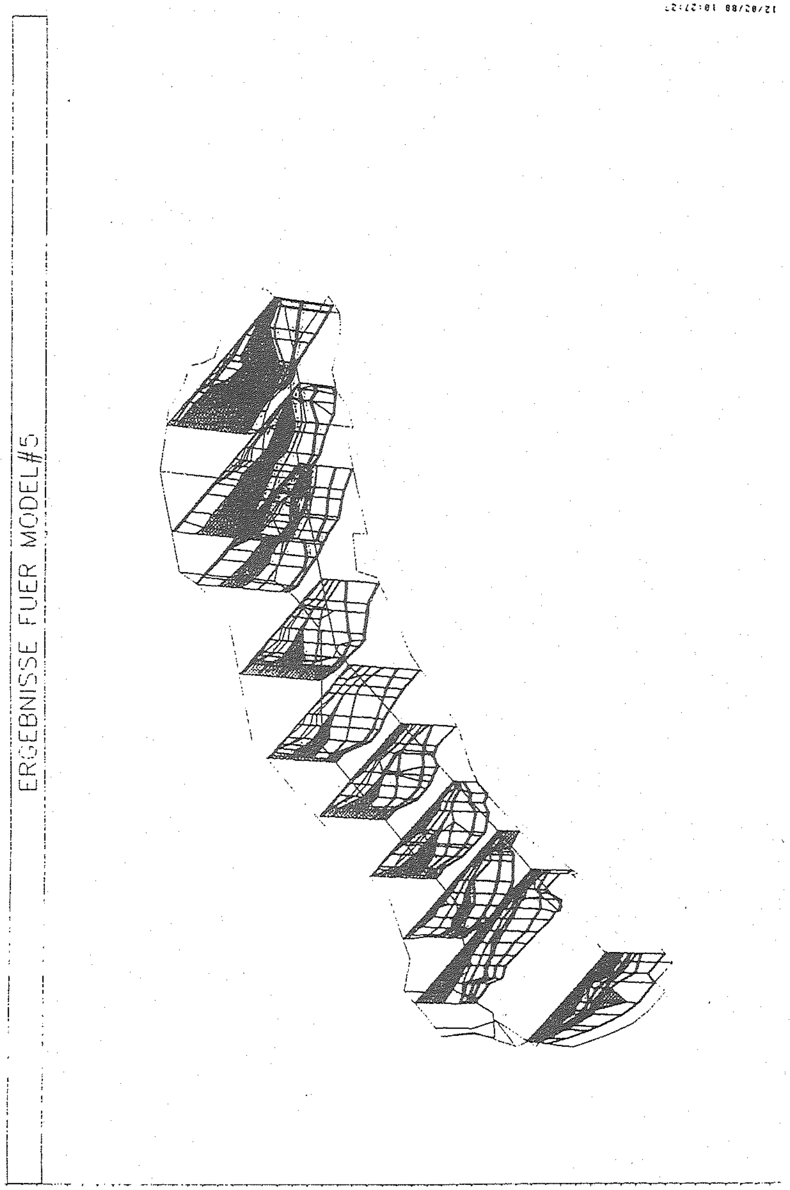
- Conditioning reduced uncertainty
- Correlation length cannot be reliably estimated if it is comparable to domain size
- Statistical hypothesis-testing framework appropriate for validation
- Stochastic groundwater flow and transport modelling is a viable tool for use in a repository performance assessment

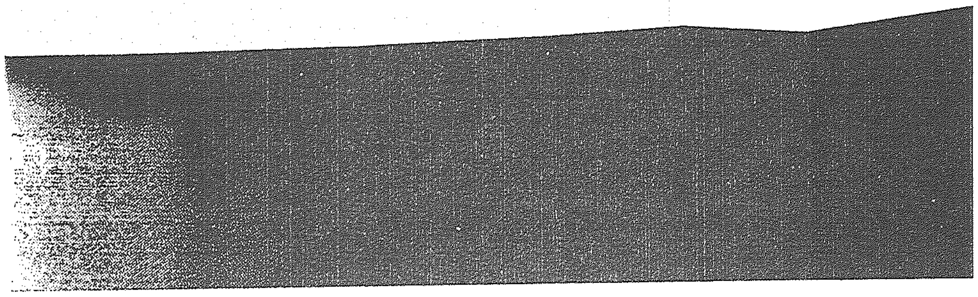


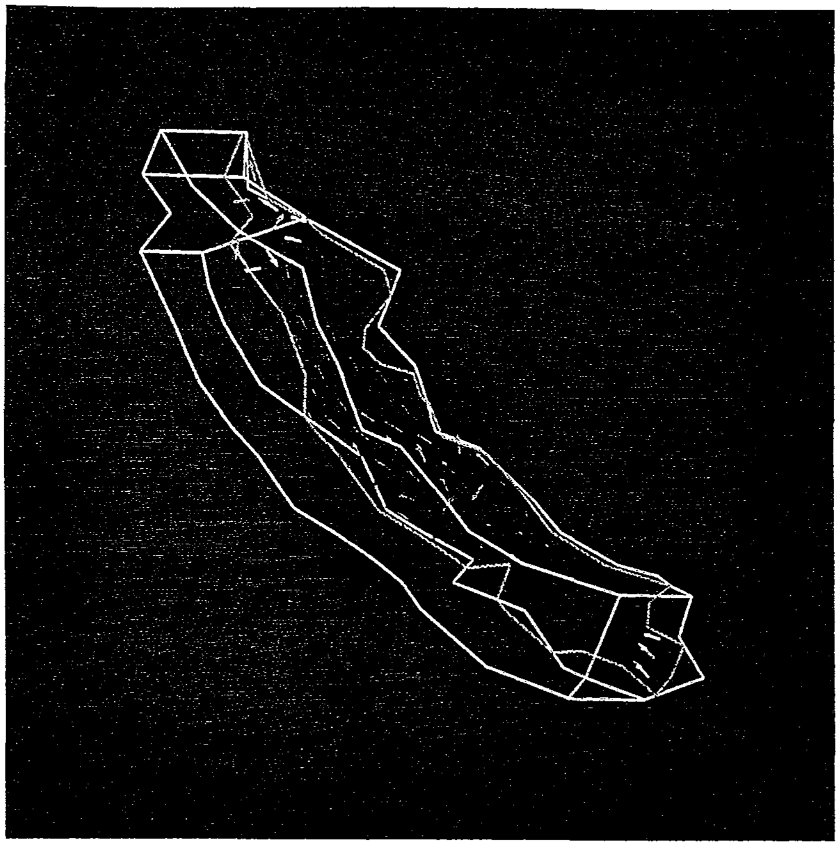
(wipp108)

-) Modelling a complex basin

5) Modelling two sources of salinity for integration of site geochemistry







NAMMU/ADVIZE

- **NAMMU**
  - groundwater flow
  - heat and mass transport
  - continuous porous media

NAMMU/ADVIZE

- **Finite-element method**
  - modelling flows through complex geological strata
  - one, two or three spatial dimensions
  - wide range of elemnts
    - » triangles and quadrilaterals
    - » hexahedra, prisms and tetrahedra
  - options for grid generation
  - sophisticated techniques for nonlinear problems
  - time stepping
    - » Crank-Nicholson
    - » Gear's method

NAMMU/ADVIZE

- Modular design
  - groundwater flow in saturated and unsaturated regions
  - coupled flow and solute transport with concentration dependent density
  - contaminant transport including rock matrix diffusion
  - stochastic treatment of heterogeneity

NAMMU/ADVIZE

- Verification
  - INTRACOIN
  - HYDROCOIN
  - INTRAVAL

NAMMU/ADVIZE

- Platforms
  - portable subset of FORTRAN77
  - machine dependencies confined to a few routines
  - IBM PC and compatibles
  - workstations
    - IBM RS/6000, SUN, Dec
  - supercomputers
    - Cray 2, Cray YMP, Convex
  - optimised through the use of BLAS

NAMMU/ADVIZE

- Users
  - UK Nirex
  - SKi & SKB (Sweden)
  - GRS, BGR & BFS (Germany)
  - NAGRA (Switzerland)

NAMMU/ADVIZE

- ADVIZE
  - developed by IBM BSC
  - Open solution
  - visualisation of complex 3- data
  - NAMMU/ADVIZE
    - » NAMMU plus
    - » ADVIZE tailored to NAMMU data structures

AEA

NAMMU/ADVIZE

- Program structure
  - User interface
  - Kernal
  - Graphics drivers
    - » makes use of high performance 24-bit 3D solour graphics processor

AEA

NAMMU/ADVIZE

- Unique features
  - handling of irregular data
  - no automatic resampling onto a regular mesh
  - displays exactly what NAMMU calculates
  - diagnostic tool

PNC資料

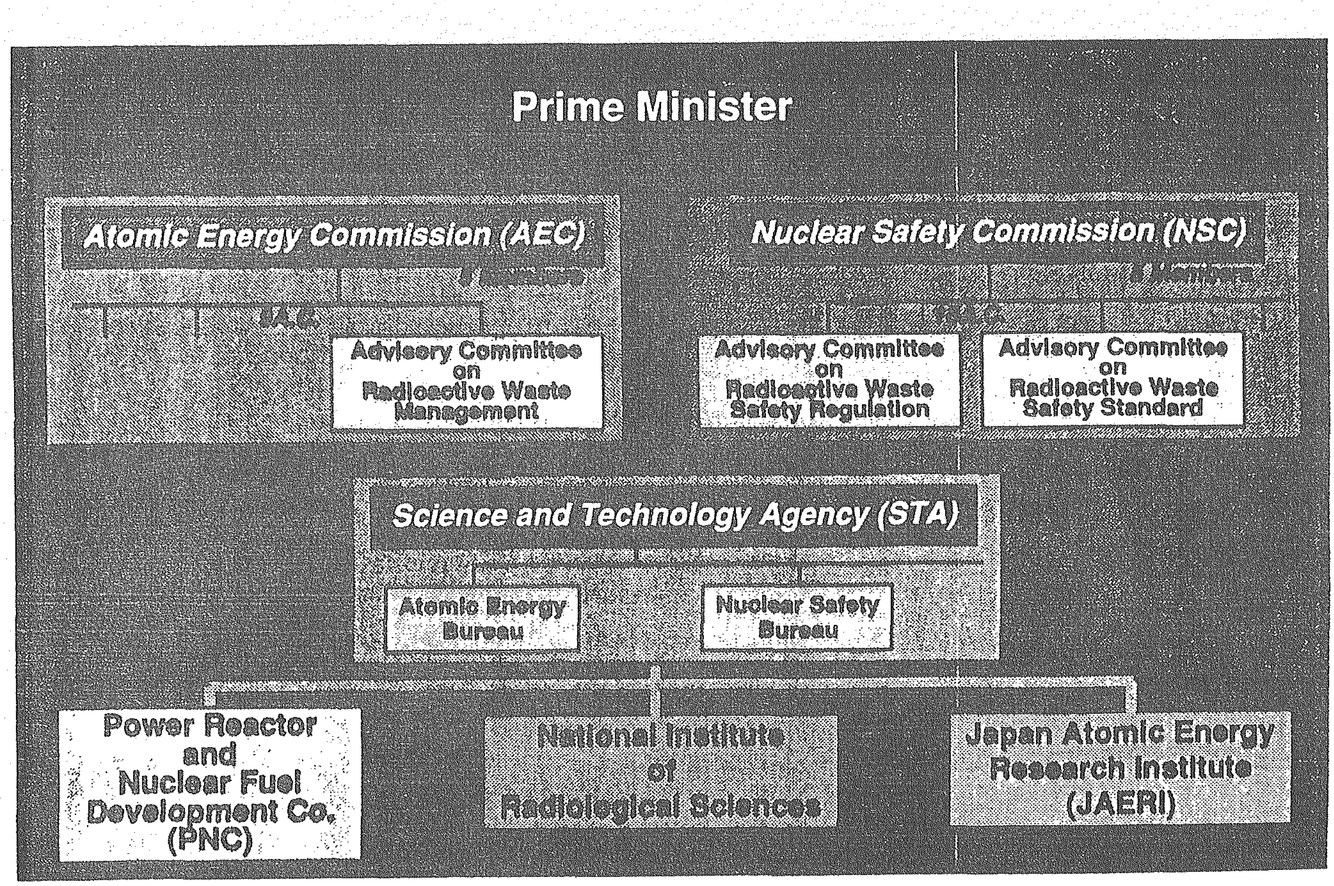
Overview of PNC R&D activities

The 1st AEA/PNC Collaboration Meeting at Harwell

19-21 July 1993

N.Sasaki(PNC)

PNC



Prime Minister

Atomic Energy Commission (AEC)

Advisory Committee
on
Radioactive Waste
Management

Nuclear Safety Commission (NSC)

Advisory Committee
on
Radioactive Waste
Safety Regulation

Advisory Committee
on
Radioactive Waste
Safety Standard

Science and Technology Agency (STA)

Atomic Energy
Bureau

Nuclear Safety
Bureau

Power Reactor
and
Nuclear Fuel
Development Co.
(PNC)

National Institute
of
Radiological Sciences

Japan Atomic Energy
Research Institute
(JAERI)

PNC Organization

(Relevant to Isolation System Research Program)

PNC / HQ

Radioactive Waste Management Project

Executive Director :M.Yamamoto
Director :Y.Asakura
Director :A.Yamato
Deputy Director :K.Tsurumaki

Coordination Section
[illegible]
N.Oda

Conditioning Research Program
[illegible]

Isolation System Research Program
[illegible]
[illegible]

Geoscience Research Program
K.Tsurumaki
[illegible] Yamasaki

Presentation Management Research Program
M.Ohsawa

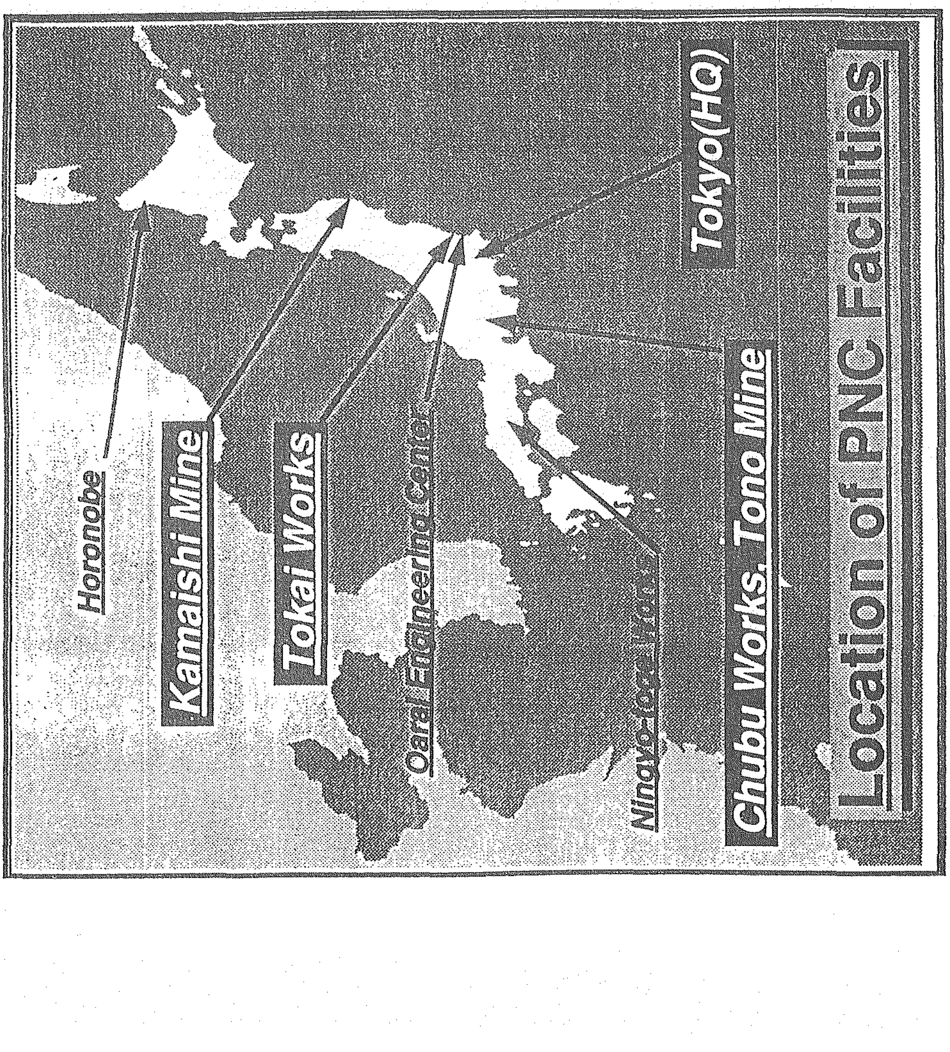
Tokai Works
[illegible]

Waste Technology Development Division
Director : [illegible]

Geological Isolation Technology Section
[illegible]

Chubu Works
Senior Director : T.Tsuboya
Deputy Senior Director : M.Yamakawa

Waste Isolation Research Section
Y.Yusa
T.[illegible]



Location of PNC Facilities

Roles and Responsibilities

Government
- Overall Responsibility
- Policy and Rule Making

PNC
- Research and Development
- Geological Environment Study

Utilities
- Collection of Disposal Cost
- Cooperation in R&D as Waste Producers

Overall Procedures & Schedule

1993

Steering Committee on High-level Radioactive Waste Project(SHP) Established on 28th of May

~2000

Implementing Organization Will be Established

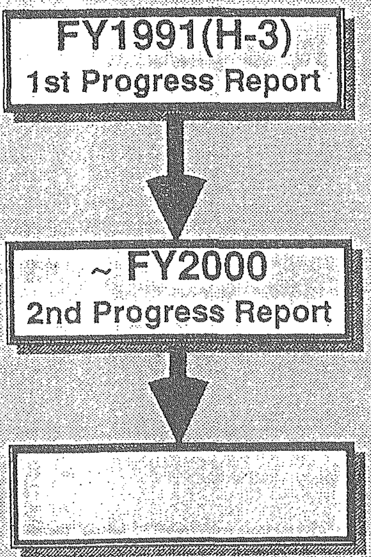
- Site Selection with Local Acceptance
- Site Characterization Studies & Demonstration of Disposal Technology
- Application for Operating License

Safety Investigations for Granting License by the Government

2030 ~ Mid of 2040's

Start of Repository Operation

Milestone & Major Documentation



FY1991(H-3)
1st Progress Report

- Clarify Scope & Priority of Near-field Study
- Initiate Projective Near-field P.A. Study

Milestone #1
Detailed Analysis of Engineered Barrier System Performance & the Geological Environment of the Repository Package

~ FY2000
2nd Progress Report

- Clarify Requirement to Far-field P.A. Study
- Initiate Projective Far-field P.A. Study

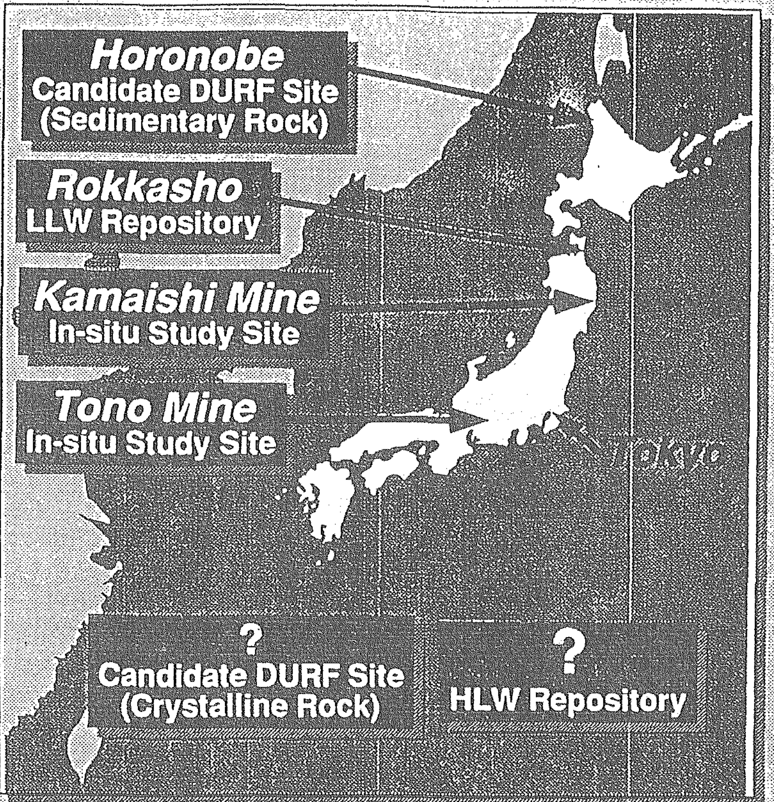
Milestone #2
Analysis of Far-field System Performance & Compliance with Requirements of Total System Performance

- Demonstrate Feasibility of Geological Disposal in Japan

To Promote HLW Disposal Program

It is Considered Highly Important:

- To Provide Clear Distinction between Implementation of Disposal Strategies and Research & Development as Independent Processes
- To Increase the Transparency of the Overall Disposal Program by Defining Concrete Schedules and the Roles & Responsibilities of the Organization Involved
- To Review the Results of Research & Development Work out by Governmental Authorities at Appropriate Intervals
- To Ensure that the Local Communities' Views and Wishes are Reflected in the Decision-making Process during each Stage of the Program



Horonobe
Candidate DURF Site
(Sedimentary Rock)

Rokkasho
LLW Repository

Kamaishi Mine
In-situ Study Site

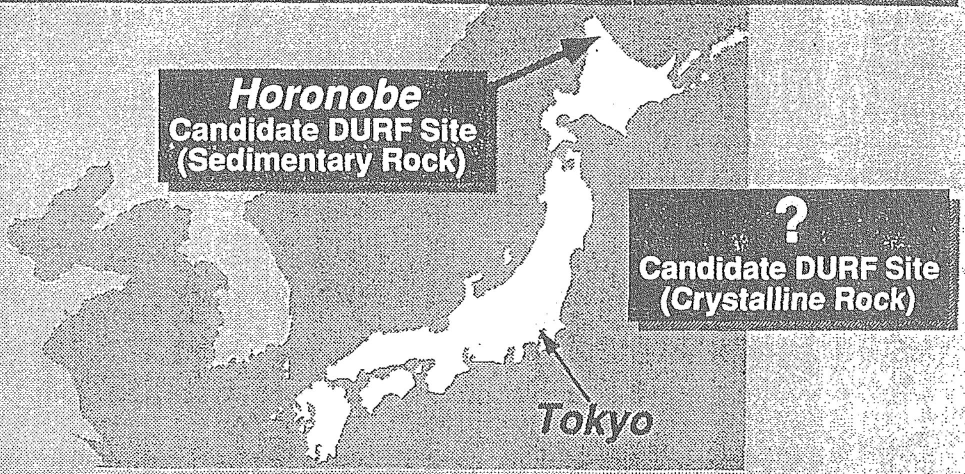
Tono Mine
In-situ Study Site

?
Candidate DURF Site
(Crystalline Rock)

?
HLW Repository

DURF: Deep Underground Research Facility

Deep Underground Research Facilities



Horonobe
Candidate DURF Site
(Sedimentary Rock)

?
Candidate DURF Site
(Crystalline Rock)

- Independent from Repository Program
- For Sedimentary and Crystalline Environment
- Local Public Relations

Major Field of R&D Activities

- *Geology*
  - Geological Components of Japan
  - Geological Setting of Japan
  - Groundwater Hydrology and Chemistry
  - Tectonic and Volcanic Activities
  - Weathering and Alteration
- *Engineering*
  - Materials, Design and Engineering for Reference EBS
  - Repository Design and Engineering

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Major Field of R&D Activities

- *Performance Assessment*
  - FEP List
  - Scenario Development & Classification
  - Identify Scope of Geological and Engineering Studies
  - Isolated Scenarios
  - Groundwater Scenarios
  - (- Combined Scenario)

PNC

R&D Approach: Geological Environment

- *Isolated Scenarios*
  - Geoscientific Study on Relevant Natural Phenomena
- *Groundwater Scenarios*
  - Characterisation of Groundwater Hydrology and Geochemistry
  - Characterisation of Geochemical Properties

PNC

R&D Approach: Engineering

- Design Reference EBS and Repository
- Carry out Technical Assessment

PNC

R&D Approach: Performance Assessment

- Scenario Development & Classification
(Identify Scope of Geological and Engineering Studies)
- Isolated Scenarios:
  - ■ Define Characteristics of Relevant Phenomena
- Groundwater Scenarios:
  - ■ Predictive Modelling
  - ■ Site Independent N.F. Performance

(- Combined Scenario)

PNC

Site Generic Assessment Approach

- ■ Identify Natural System Attributes which Optimize EBS Performance
  - *Favorable Chemistry*
  - *Low Groundwater Flux*
  - *Relative Tectonic Stability*
  - *Low Risk of Disruptive Events*
- ■ Attributes should be Present in any of Several Geologic Settings
- ■ Conduct Performance Assessment Studies Based on for Generic Site Having Favorable Attributes

PNC's First Progress Report (H-3)

- Published in September 1992
- Provided Information for the Public to Find out the Current Status of R&D
- Submitted to the Authority (AEC) in December 1992
- Review Comment by AEC (in July 1993)
- The Second Progress Report is Scheduled to be Submitted before the Year 2000

H-3 Report Overview

Objectives

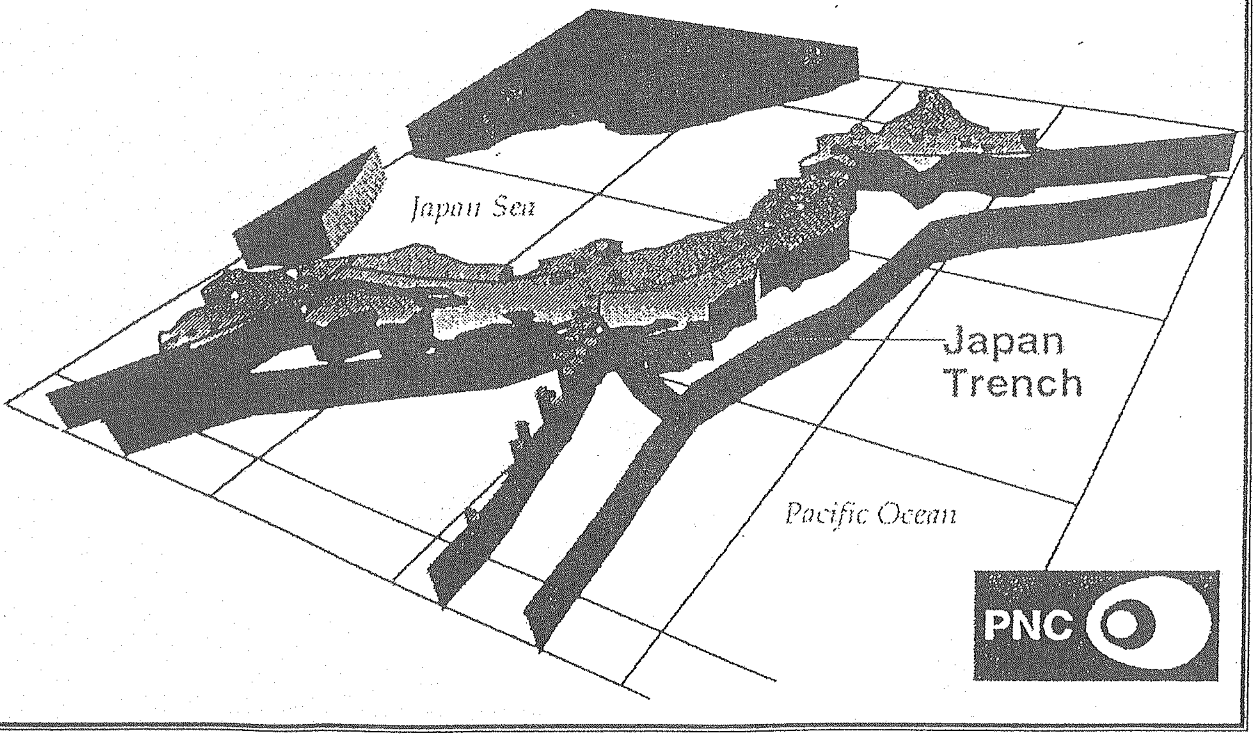
- Conduct Preliminary Performance Analysis to Evaluate the Technical Feasibility of the Geological Isolation System Taking Variety of Geological Environment into Account
- Make Clear the Issues for the Further R&D Items

PNC

Contents of Progress Report (H-3)

- *Preface*
- *Executive Summary*
- *Introduction*
    - Waste description
    - Principle of Geological Disposal
    - Assignments to PNC
- *Geology*
- *Engineering*
- *Long Term Performance Assessment of Geological Disposal System*
- *Summary and Conclusion*
- *Glossary*

Distribution of Volcanoes in Japan



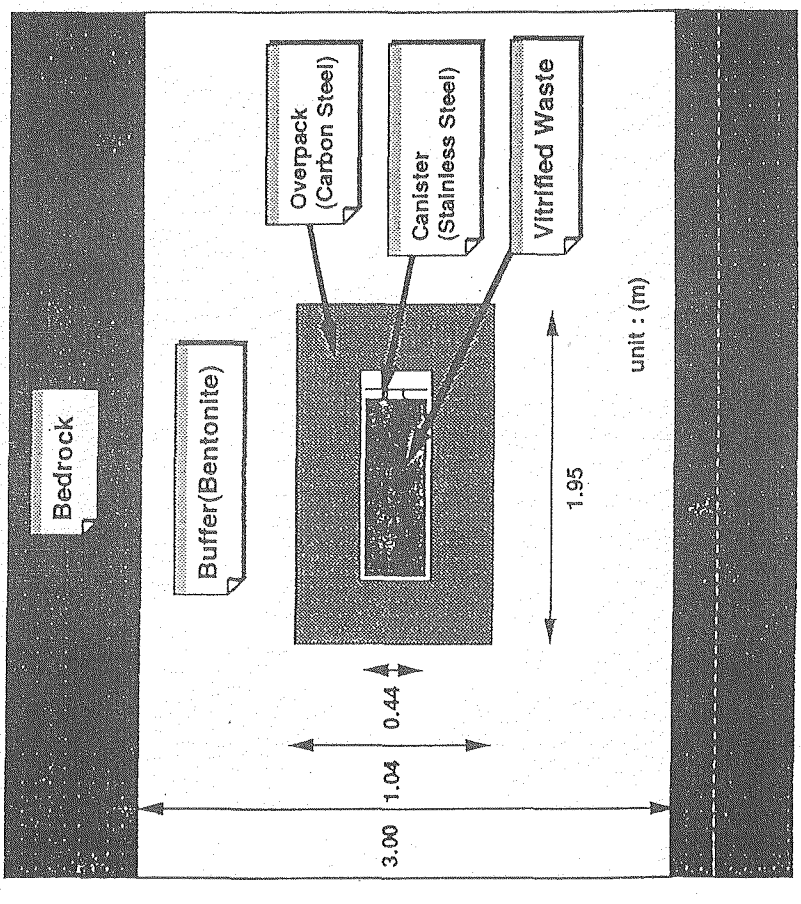
Classification of Scenarios

Isolated Scenarios (Direct Impact)

- Human Intrusion
- Meteorite Impact
- Eruption (Volcanic Activity)
- Uplift / Erosion

Groundwater Scenarios (Indirect Impact)

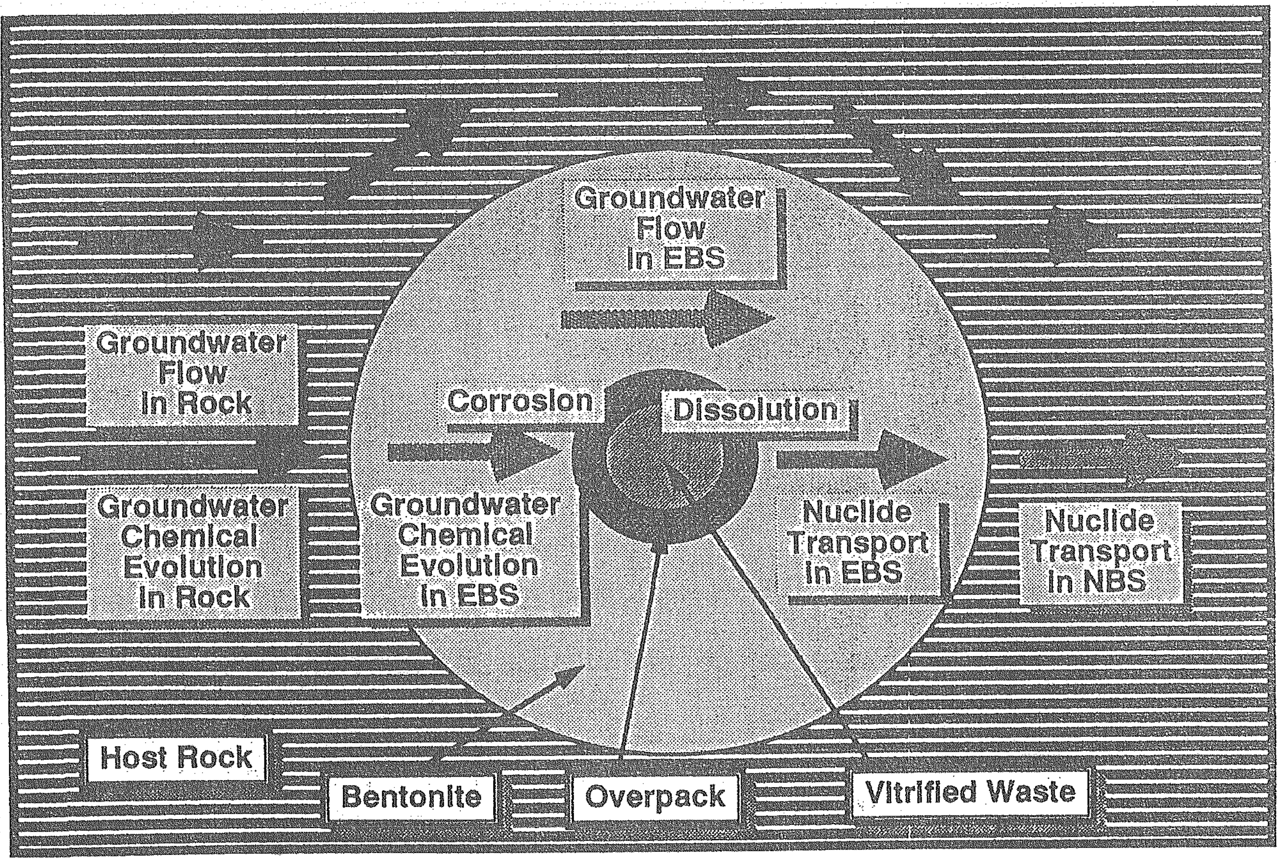
- Base Case Scenario for Quantitative Analysis
  [Stationary Geological Environment, No EBS Deficiency]
- Alternative Scenarios
  1. Climate Change [Sea-Level Change, etc.]
  2. Tectonic Movement [Change in Fracture Network, etc.]
  3. Human Activity [Drilling, etc.]
  4. EBS Deficiency [Channelling of Bentonite, etc]

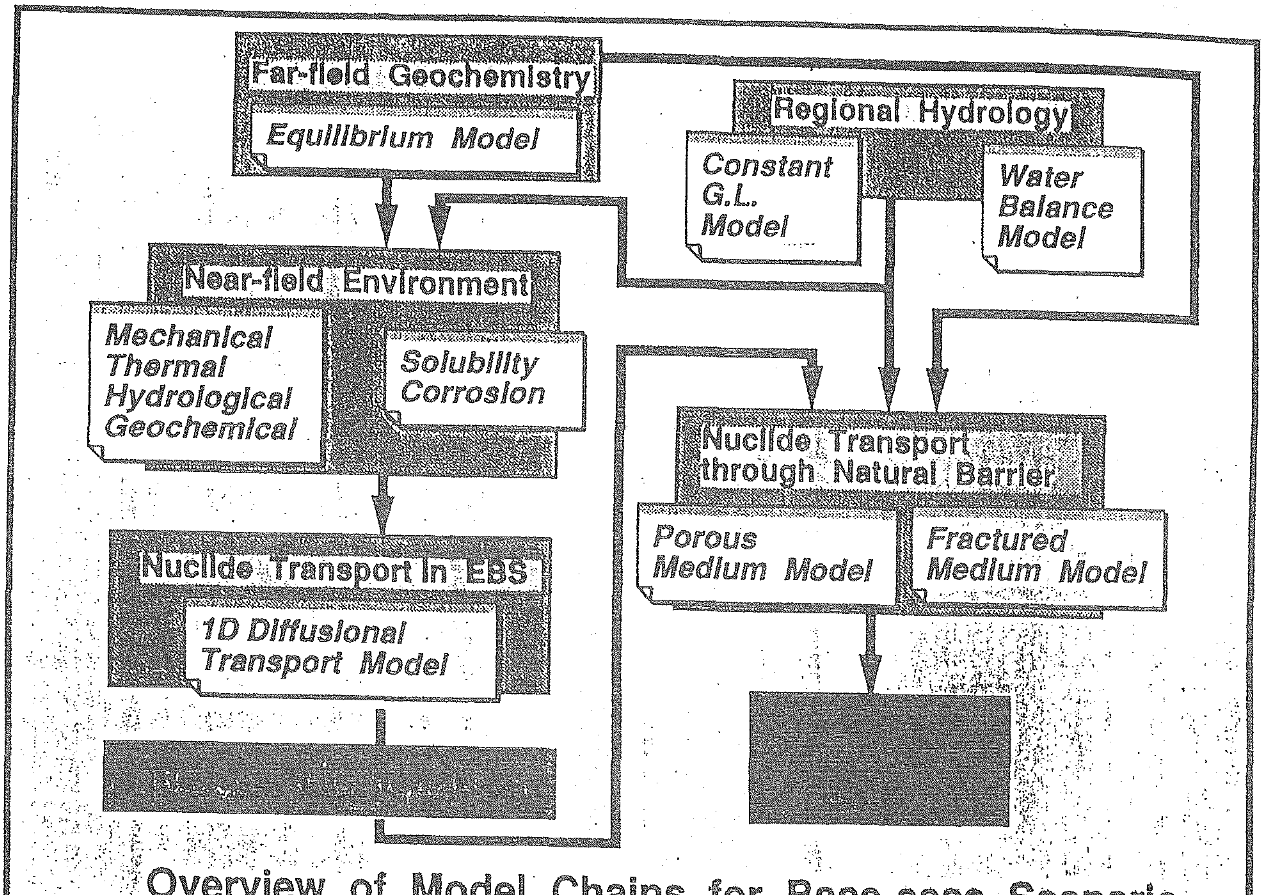


Reference Design of EBS

Basic Characteristics of Engineered Barrier System

- *Vitrified Waste Form*
  - Low Solubility
  - High Stability
- *Massive Steel Overpack*
  - Physical Isolation
  - Maintain Reducing Conditions
- *Thick Bentonite Buffer*
  - Low Permeability
  - Sorptive Capacity
  - Buffering to Maintain Reducing Conditions





Far-field Geochemistry

Equilibrium Model

Regional Hydrology

Constant G.L. Model

Water Balance Model

Near-field Environment

Mechanical Thermal Hydrological Geochemical

Solubility Corrosion

Nuclide Transport through Natural Barrier

Porous Medium Model

Fractured Medium Model

Nuclide Transport in EBS

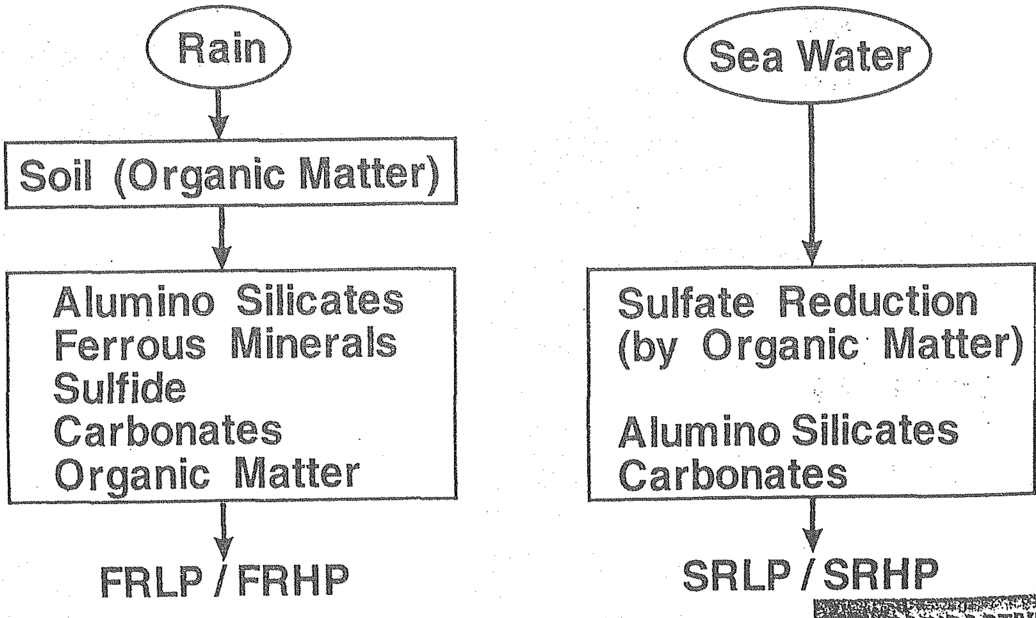
1D Diffusional Transport Model

Overview of Model Chains for Base-case Scenario

PNC

Geochemical Calculation

Geochemical Code : PHREEQE
TDB : Original PHREEQE-TDB,NEA-TDB



Rain

Soil (Organic Matter)

Alumino Silicates
Ferrous Minerals
Sulfide
Carbonates
Organic Matter

FRLP / FRHP

Sea Water

Sulfate Reduction
(by Organic Matter)

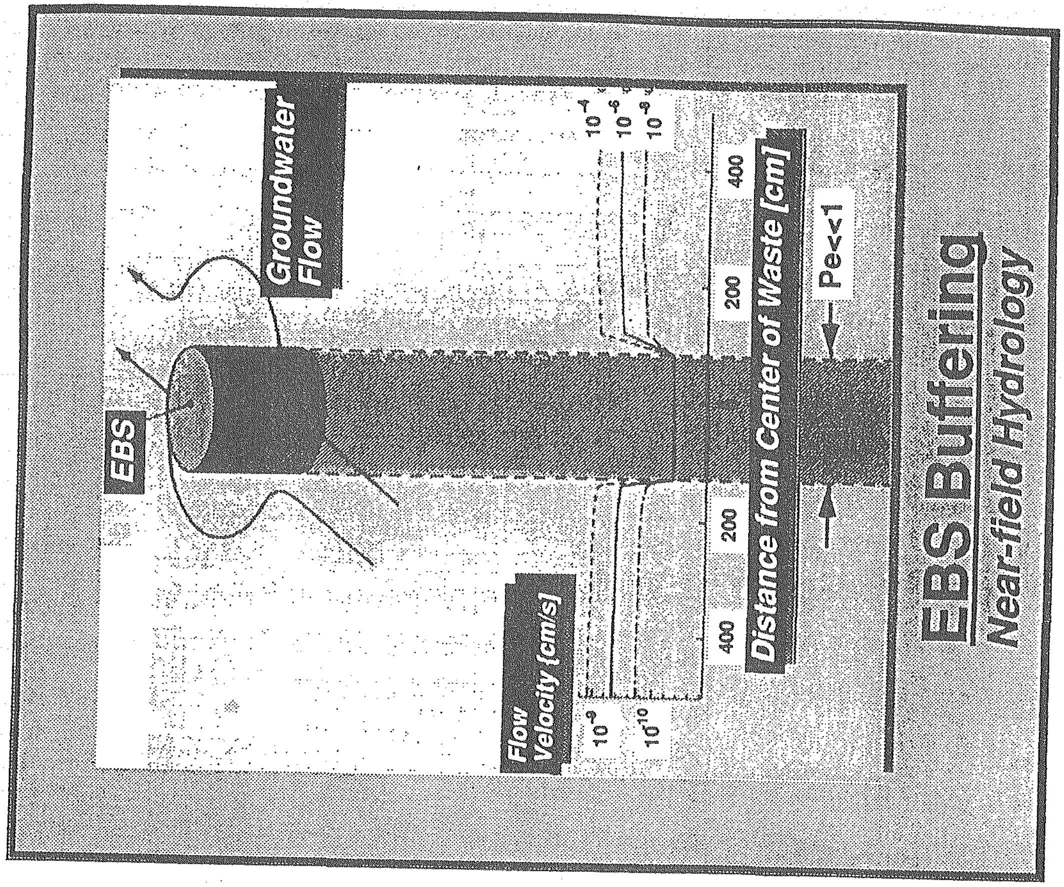
Alumino Silicates
Carbonates

SRLP / SRHP

PNC

Groundwater Geochemistry
[Calculated vs In-situ]

Groundwater	pH	Eh(mV)	Concentration (mol/l)		
			HCO_3^-	Na^+	Cl^-
FRHP	8.74	-281	6.928E-3	7.212E-3	————
Tono (Sedimentary Rock)	8.6	-300	1.5E-3	1.5E-3	2.9E-5
FRLP	5.74	-161	1.289E-1	2.515E-3	————
SRHP	7.98	-306	4.840E-2	6.023E-1	5.539E-1
SRLP	6.30	-183	4.144E-2	4.752E-1	5.539E-1



EBS Buffering
Near-field Hydrology

PNC

Bentonite Model
(Based on "Wanner Model")

1. Ion exchange reaction
   (Z^- ; ion exchange site of bentonite)

$ZNa = Z^- + Na^+$
$ZK = Z^- + K^+$
$Z_2Ca = 2Z^- + Ca^{2+}$
$Z_2Mg = 2Z^- + Mg^{2+}$

2. Dissolution / precipitation

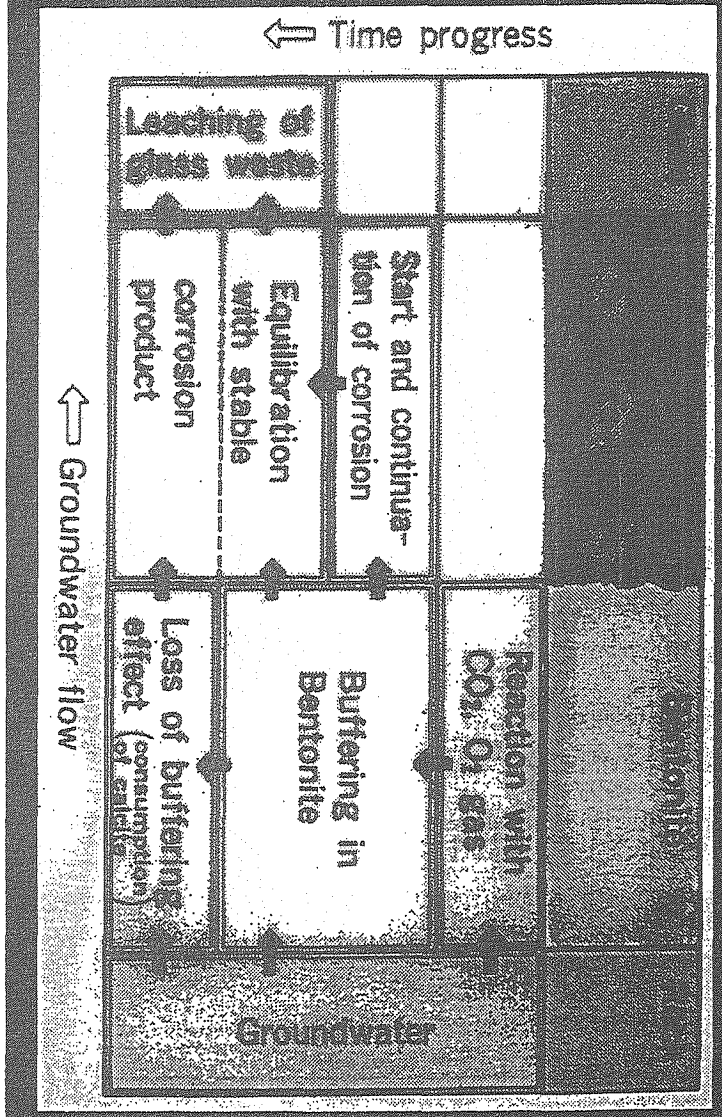
calcite + $H^+ = Ca^{2+} + HCO_3^-$ (pH buffer)
quartz + $2H_2O = Si(OH)_4(aq)$

3. Eh buffering effects by pyrite

$$FeS_2 + 15/4\ O_2(aq) + 1/2\ H_2O \longrightarrow Fe^{3+} + 2SO_4^{2-} + H^+$$

RADIOACTIVE WASTE MANAGEMENT PROJECT

The Conceptual Diagram of Groundwater Evolution in N.F.



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Summary and Conclusion - Corrosion Overpack

We estimated corrosion allowance with taking account of following items.

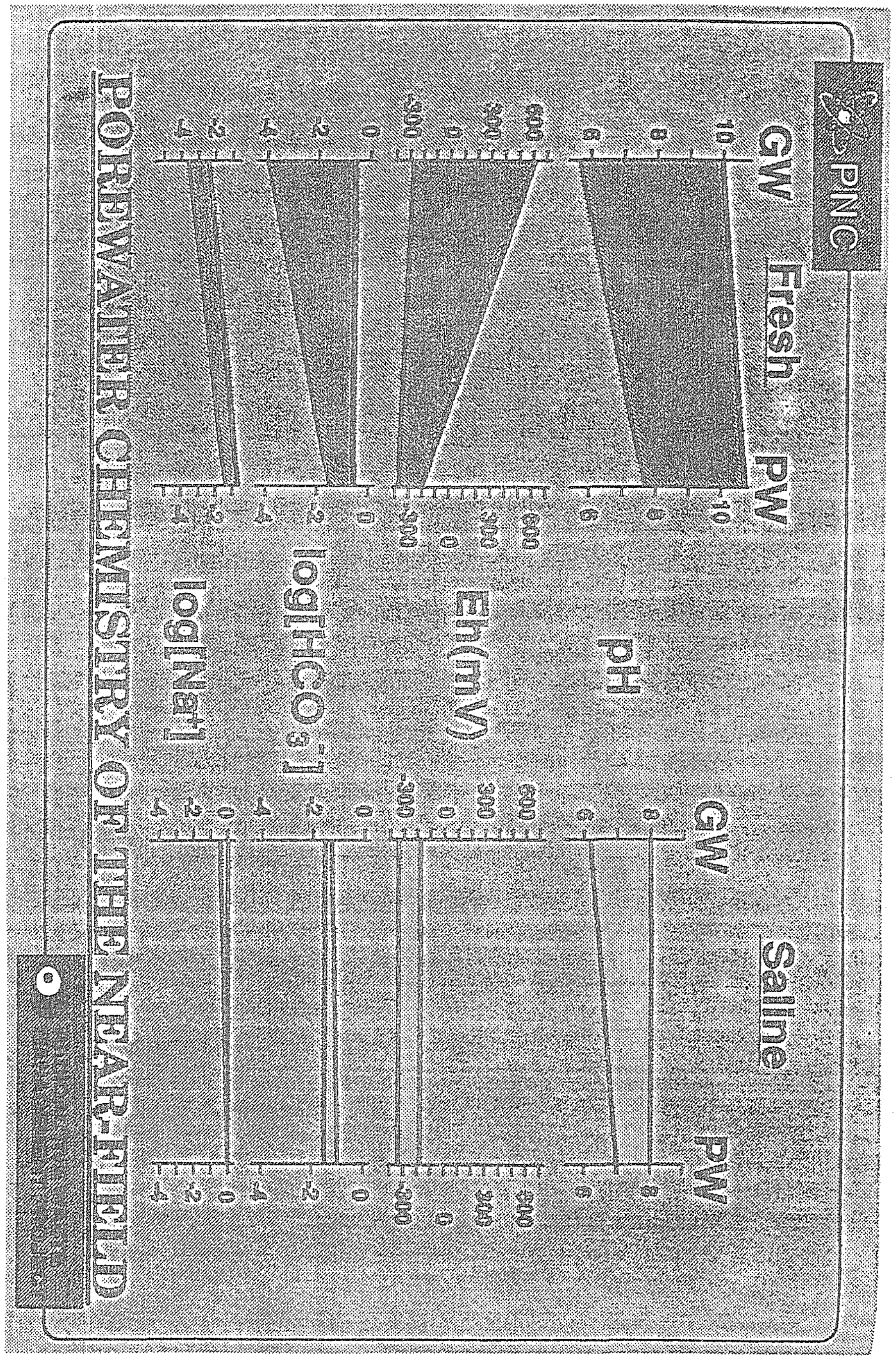
Corrosion due to oxygen.
→ 9.9mm/1000y
(To assume that all of oxygen in buffer will be consumed by corrosion of overpack)

Corrosion due to water reduction
→ 20mm/1000y
(To extraplate corrosion rate acquired by experiment)

Corrosion due to sulfide / sulfate
→ 1.8mm/1000y
(To assume activity of SRB and that this type of corrosion will be controlled by transport of sulfate)

Total 9.9 + 20 + 1.8 ≈ 32mm

RADIOACTIVE WASTE MANAGEMENT PROJECT



POREWATER CHEMISTRY OF THE NEAR-FIELD

Glass Dissolution

- Reaction Limited Release : Cs

$$\frac{dx_j}{dt} = \alpha \cdot S \cdot f_j \{ K_r + K_+ \ (1 - \frac{C_{si}}{C_{si}^*}) \}$$

α : Factor for Surface Area Increase
S : Surface Area
f_j : Mass Fraction of the Nuclide, j
K_r : Long-term Dissolution Rate of Glass Matrix

- Parameter Values for H-3 Analysis

α : 10
S : 1.7 m^2
K_+ : 2.0 $g / m^2 / d$
K_r : 5 · 10^{-3} $g / m^2 / d$

Calculated Solubility of Important Radioelements

[mol/l]

Element	Solubility limiting solid	Fresh		Saline	
		FRHP	FRLP	SRHP	SRLP
Tc	TcO_2	1.0E-12* $TcO(OH)_2$	1.0E-12* $TcO(OH)_2$	1.0E-12* $TcO(OH)_2$	1.0E-12* $TcO(OH)_2$
Np	NpO_2	2.0E-12 $Np(OH)_4$	2.0E-12 $Np(OH)_4$	1.7E-12 $Np(OH)_4$	1.8E-12 $Np(OH)_4$
Pu	PuO_2	2.5E-11 $Pu(CO_3)_4^{4-}$	5.3E-6 $Pu(CO_3)_4^{4-}$	6.4E-10 $Pu(CO_3)_3^{2-}$ $Pu(CO_3)_4^{4-}$	2.8E-7 $Pu(CO_3)_3^{2-}$
Am	$AmOHCO_3$	6.3E-8 $Am(CO_3)_3^{3-}$	3.1E-7 $AmCO_3^+$	6.3E-9 $Am(CO_3)_2^-$ $AmCO_3^+$	1.0E-7 $Am(CO_3)_3^{3-}$ $Am(CO_3)_2^-$
Se	$FeSe_2$	5.4E-7 HSe^-	1.0E-8* HSe^-	1.0E-8* HSe^-	1.0E-8* HSe^-

* Detection limit of ICP-MASS

Radionuclide Transport in Near-field

- *Mathematical Model*
  - ☐ Diffusion in Bentonite
  - ☐ Sorption
  - ☐ Decay Chain - Ingrowth
  - ☐ Precipitation

$$R_i \frac{\partial C_i}{\partial t} + \frac{\partial Cp_i}{\partial t} = Dp \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i}{\partial r} \right) - R_i \lambda_i C_i + R_{i-1} \lambda_{i-1} C_{i-1} - \lambda_i Cp_i + \lambda_{i-1} Cp_{i-1}$$

C_i : Concentration of Radionuclide i in Pore Water
Cp_i : Concentration of Precipitate on Radionuclide i in Pore
Dp : Pore Diffusivity
λ_i : Decay Constant of Radionuclide i
R_i : Retardation Factor of Radionuclide i

Radionuclide Transport in Near-field

$$R_i = 1 + \frac{1-\varepsilon}{\varepsilon} \rho Kd_i$$

ε : Porosity of Bentonite
ρ : Density of Bentonite
Kd_i : Distribution Coefficient of Radionuclide i

$$\frac{\partial Cp_i}{\partial t} = u(Cp_i)\ k\ (C_i - C_{sol\,i})$$

k : Reaction Rate
$C_{sol\,i}$: Solubility of Radionuclide i

$$u(Cp_i) = \begin{cases} 1 & (Cp_i > 0 \quad \text{or} \quad C_i > C_{sol\,i}) \\ 0 & (Cp_i = 0 \quad \text{and} \quad C_i \leq C_{sol\,i}) \end{cases}$$

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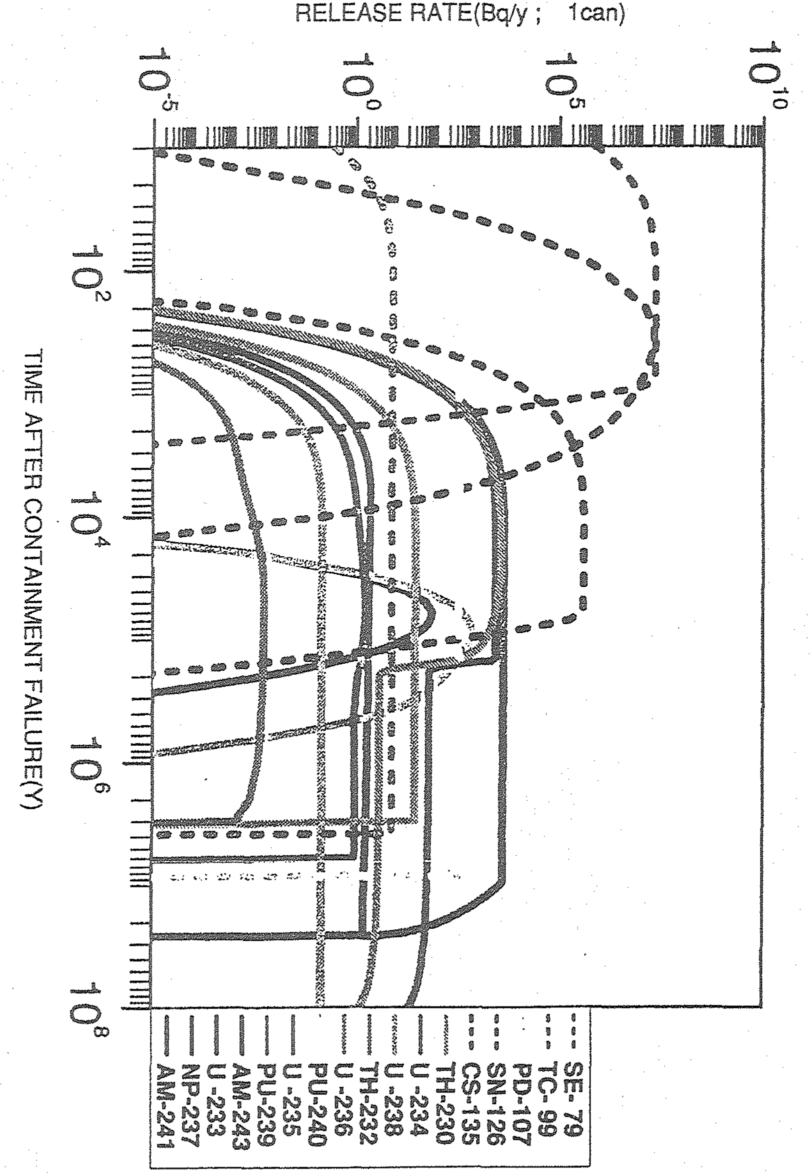
Summary and Conclusion - Nuclide Transport in EBS

1. The radionuclide transport in the EBS was analyzed by considering the diffusive transport in the bentonite buffer, as well as the processes of sorption / desorption, precipitation / dissolution, and decay-chain in-growth.

2. The retardation factor in the bentonite buffer is defined by assuming an instantaneous local equilibrium and a linear relationship between the concentrations in the solid and the liquid phases under isothermal condetions. The precipitation / dissolition term is determined from reaction rates and solubility .

3. The release rates from EBS are significantry low and this shows the effectiveness of the buffering of the EBS.

RADIOACTIVE WASTE MANAGEMENT PROJECT



TIME-DEPENDENT RELEASE RATE (FRHP:OXIDE:NOS)

Analytical Method

Mathematical Model

- ☐ Advection-Dispersion (Porous Media)
- ☐ Advection-Dispersion with Matrix Diffusion (Fractured Media)
- ☐ Linear Sorption

Simplified Analysis

Sensitivity analysis by analytical steady-state solution

Detailed Analysis

- Transient-State
- Degree of Matrix Diffusion (Fractured Media Only)
- Decay-Chain

Porous Media; Analytical solution derived by Lung et al.(1987)

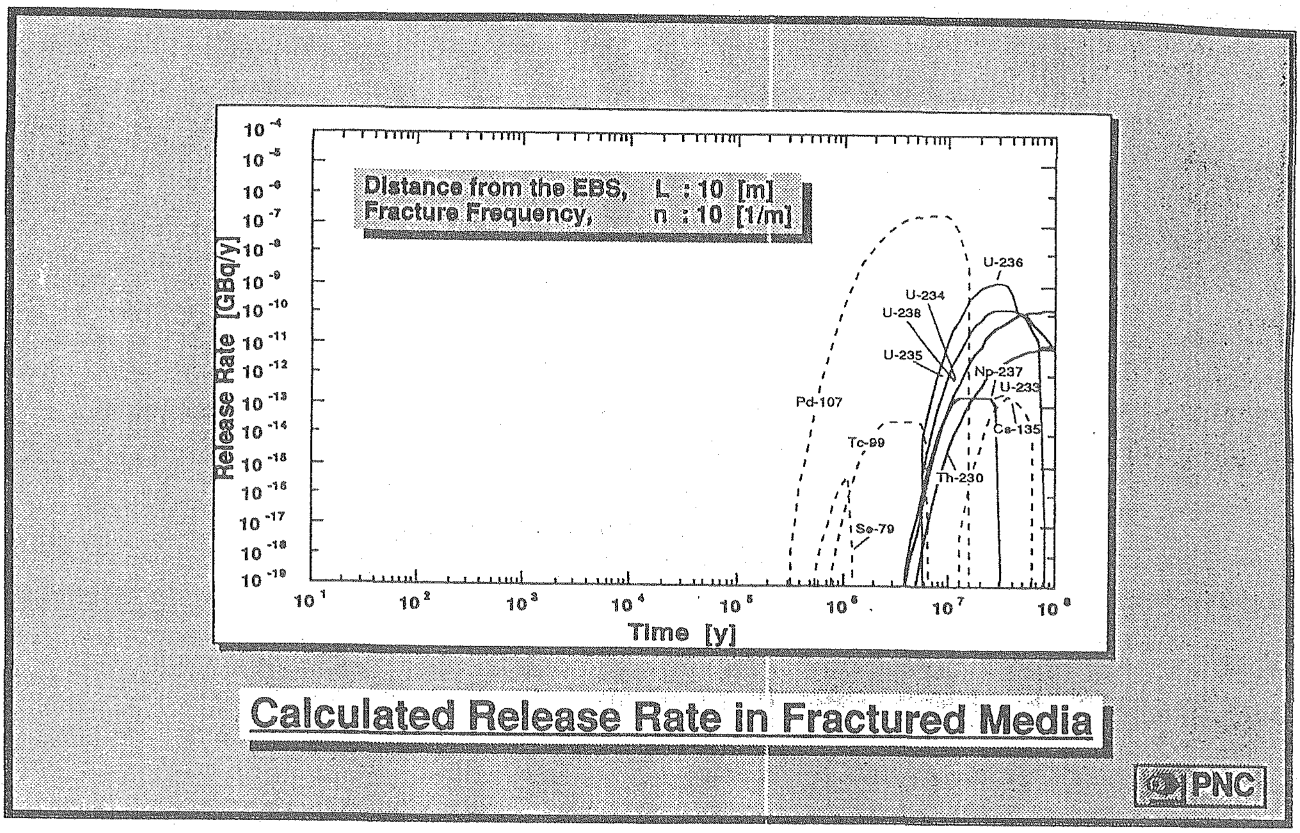
Fractured Media; Numerical solution by Talbot algorithm for solving Laplace-transformed equations

RADIOACTIVE WASTE MANAGEMENT PROJECT

Parameters for Detailed Analyses on the Performance of the NBS

Dispersivity : α_L [m]	L/10
Distance from the EBS : L [m]	10, 100, 1000
Hydraulic Conductivity : K_e [m/s]	1×10^{-10}
Hydraulic Gradient : ΔH [-]	0.05
Fracture Frequency : n [1/m]	10
Effective Diffusion Coefficient in Matrix : De [m^2/s]	1×10^{-12}
Porosity of Matrix : ε^m[-]	0.01
Density of Matrix : ρ^m [kg/m^3]	2.7×10^3

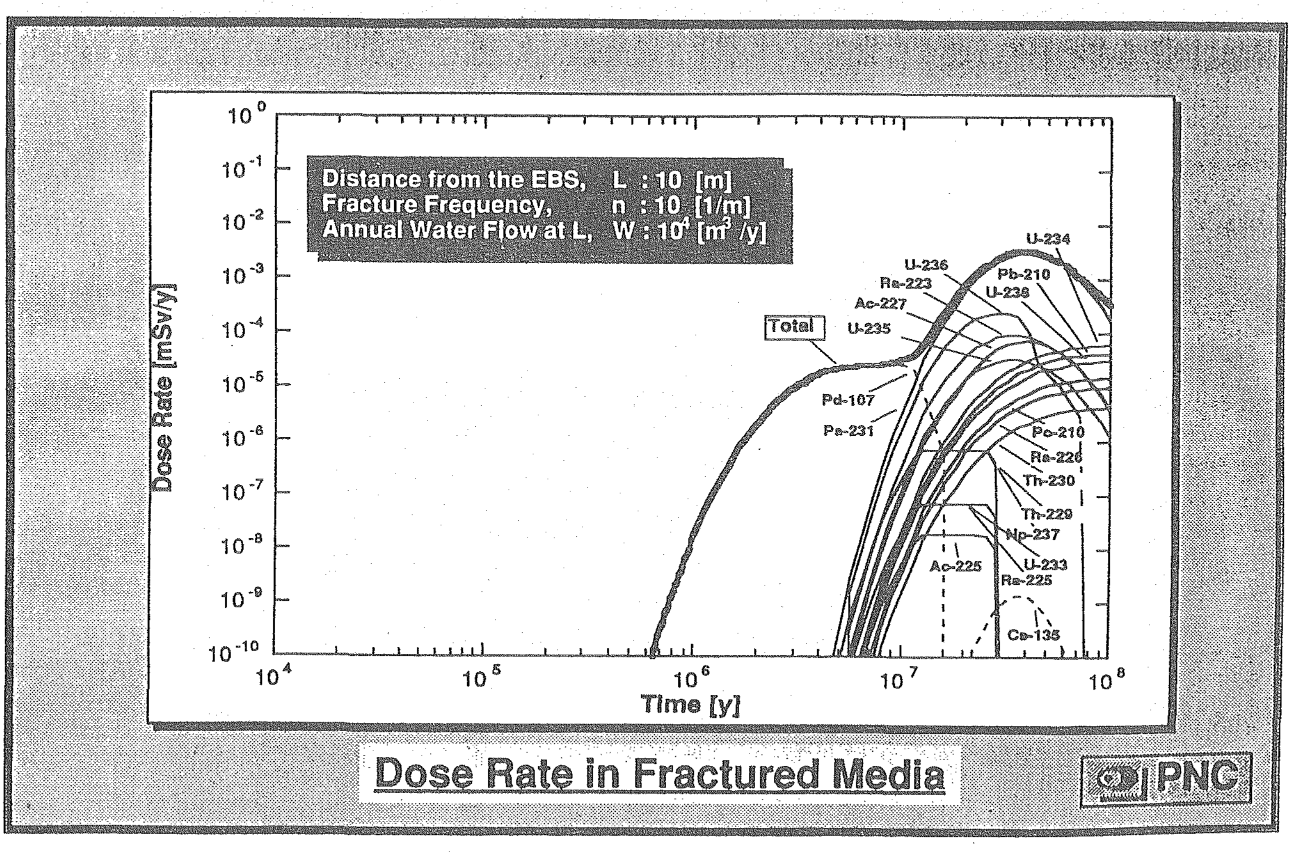
PNC



Distance from the EBS, L : 10 [m]
Fracture Frequency, n : 10 [1/m]

Calculated Release Rate in Fractured Media

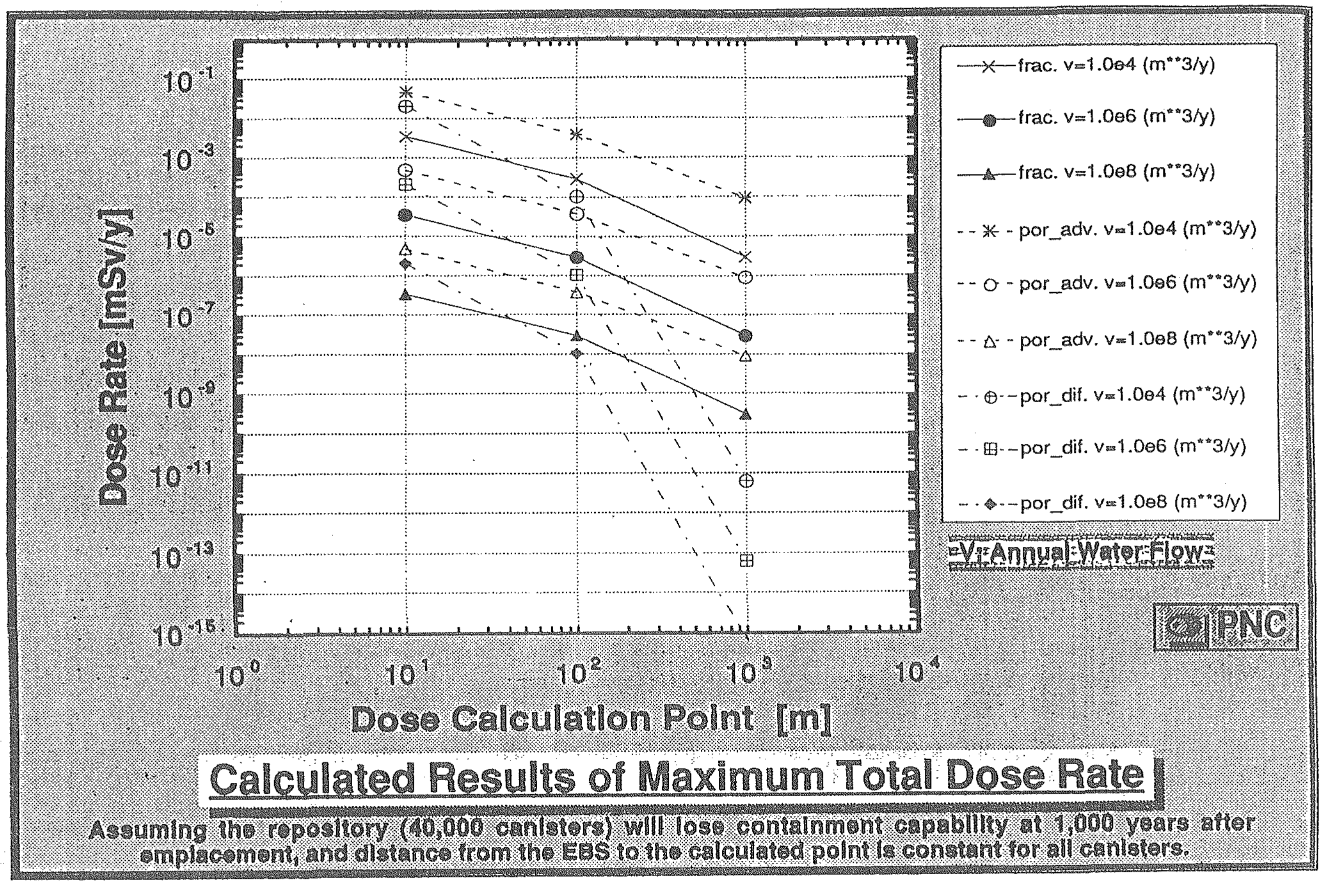
PNC



Distance from the EBS, L : 10 [m]
Fracture Frequency, n : 10 [1/m]
Annual Water Flow at L, W : 10^4 [m^3 /y]

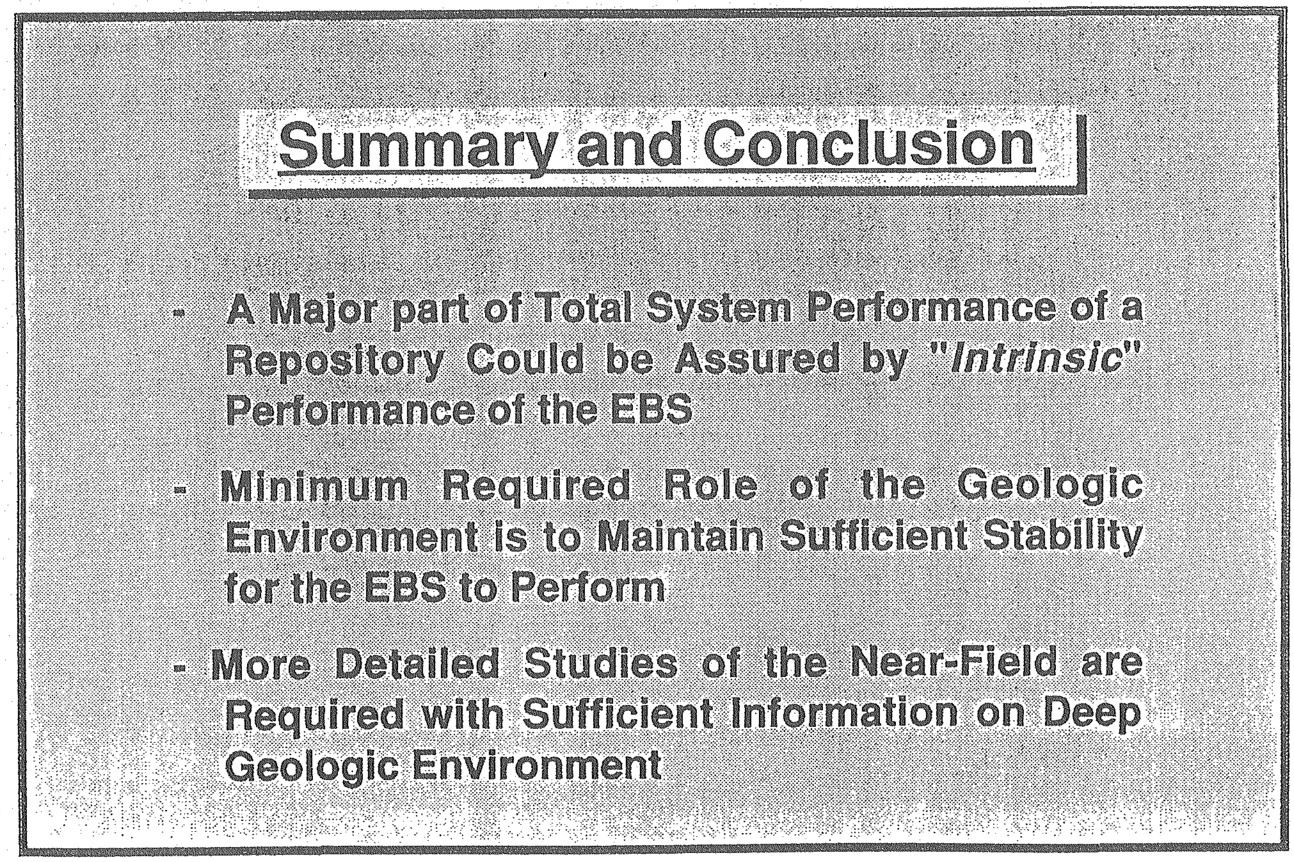
Dose Rate in Fractured Media

PNC



Calculated Results of Maximum Total Dose Rate

Assuming the repository (40,000 canisters) will lose containment capability at 1,000 years after emplacement, and distance from the EBS to the calculated point is constant for all canisters.



Summary and Conclusion

- A Major part of Total System Performance of a Repository Could be Assured by "*Intrinsic*" Performance of the EBS
- Minimum Required Role of the Geologic Environment is to Maintain Sufficient Stability for the EBS to Perform
- More Detailed Studies of the Near-Field are Required with Sufficient Information on Deep Geologic Environment

発表 3

Status of Surface Complexation Model Development and Fundamental Data Such as Surface Charasterisation of Solid

C.ODA, H.YOSHIKAWA, M.YUI

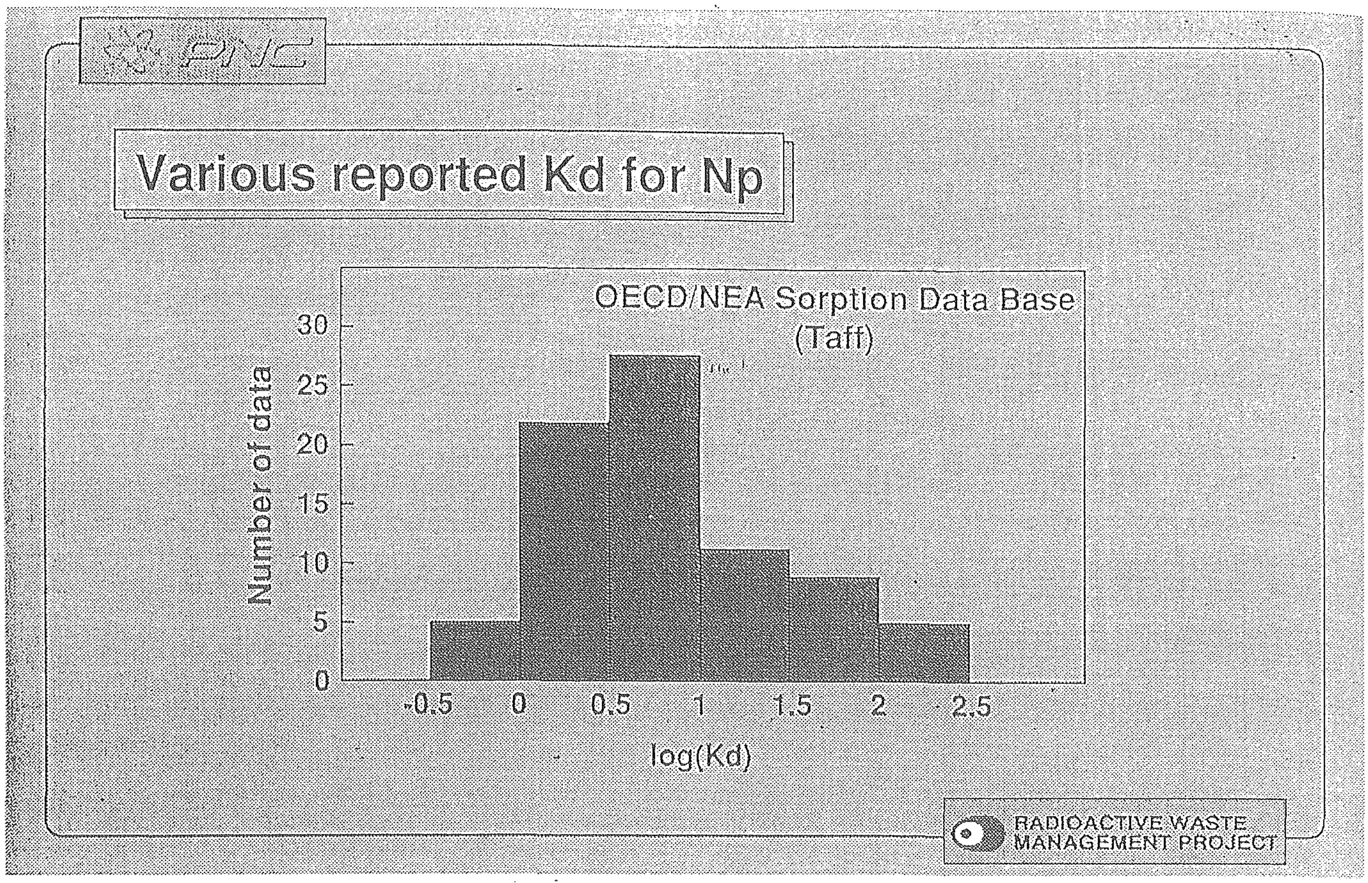
RADIOACTIVE WASTE
MANAGEMENT PROJECT

PNC

Why are there various Kd value

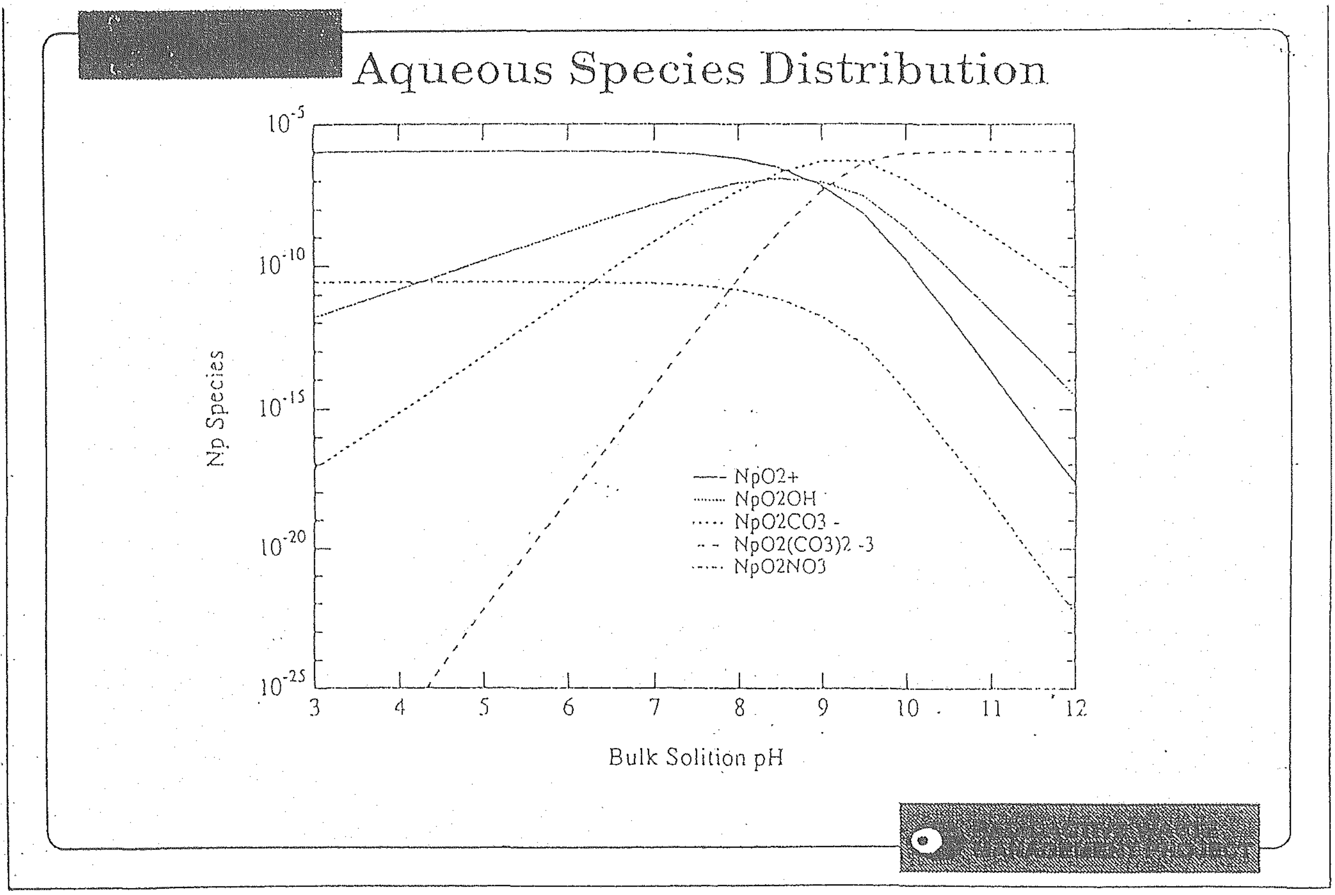
in reports for sorption experiment?

RADIOACTIVE WASTE
MANAGEMENT PROJECT

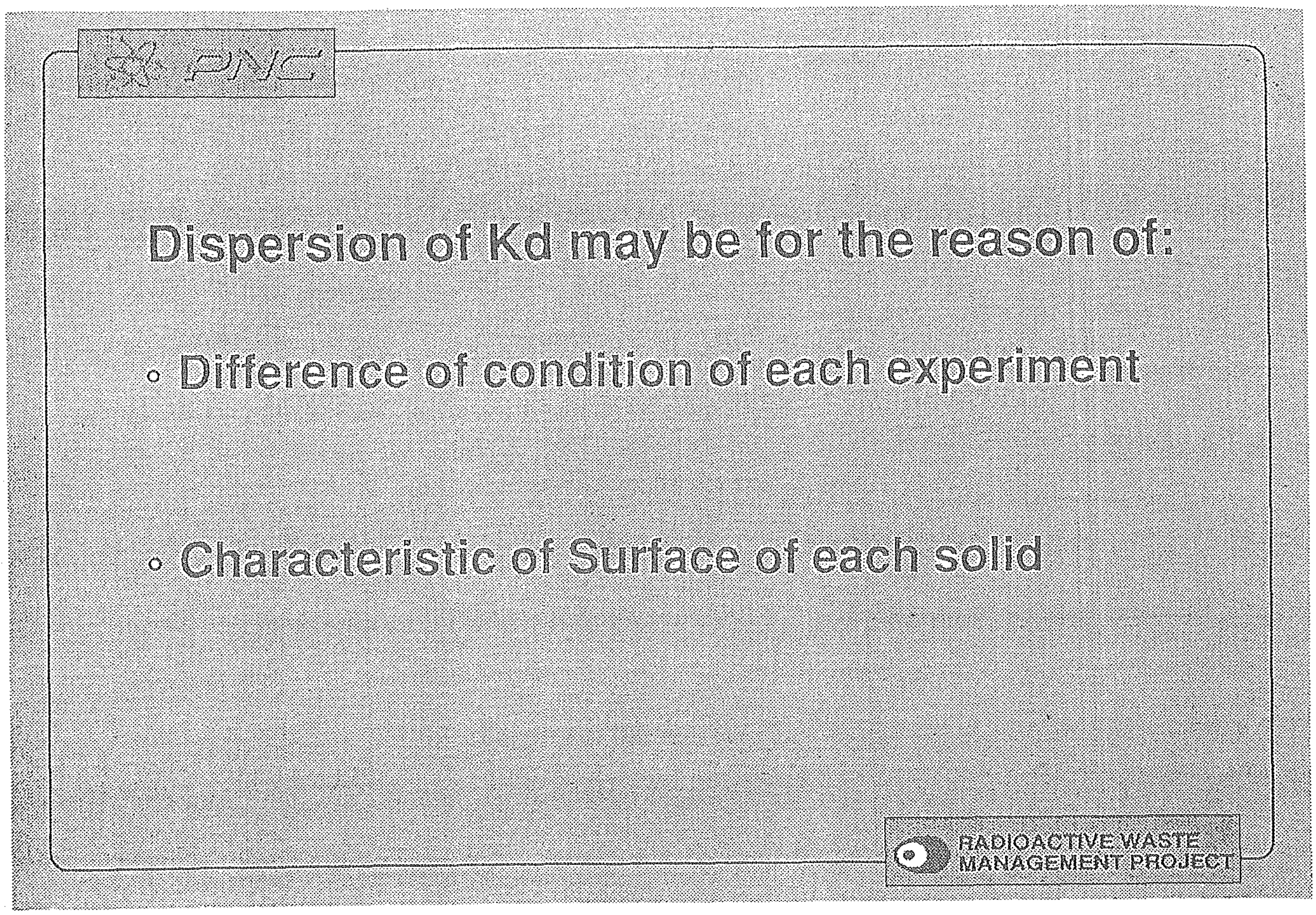


Various reported Kd for Np

RADIOACTIVE WASTE
MANAGEMENT PROJECT

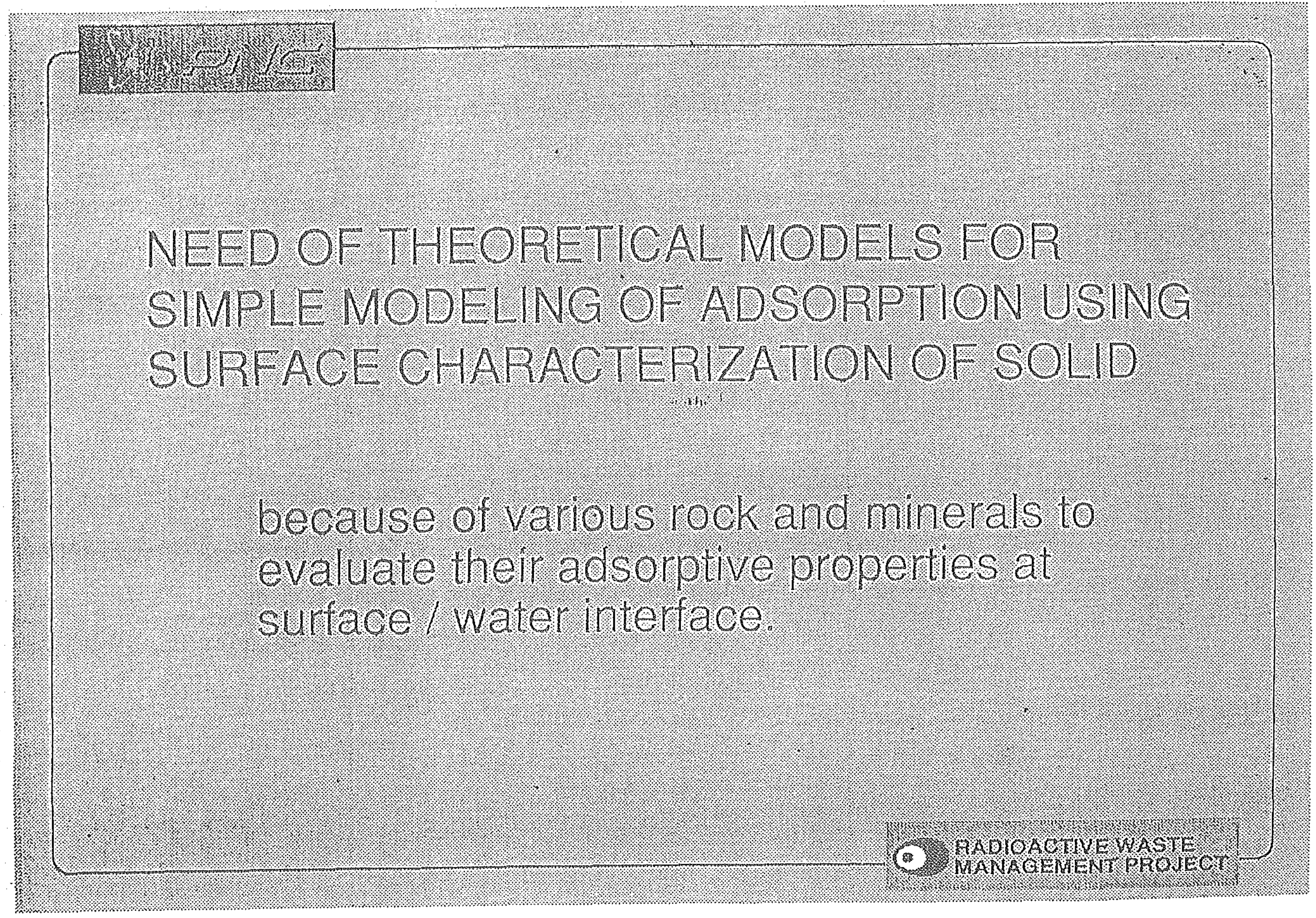


Aqueous Species Distribution



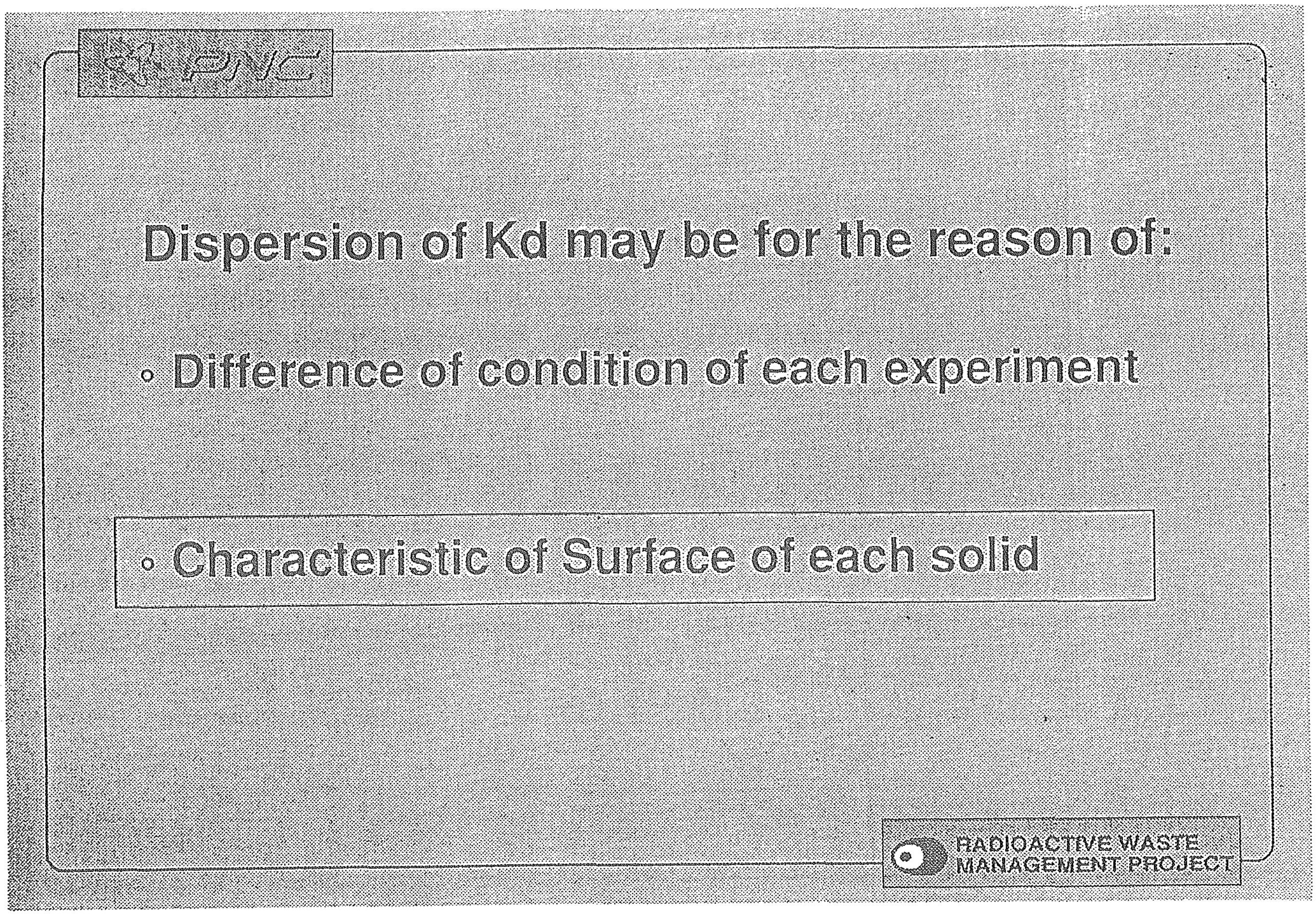
Dispersion of Kd may be for the reason of:

- ○ Difference of condition of each experiment
- ○ Characteristic of Surface of each solid



NEED OF THEORETICAL MODELS FOR SIMPLE MODELING OF ADSORPTION USING SURFACE CHARACTERIZATION OF SOLID

because of various rock and minerals to evaluate their adsorptive properties at surface / water interface.



PNC

Dispersion of Kd may be for the reason of:

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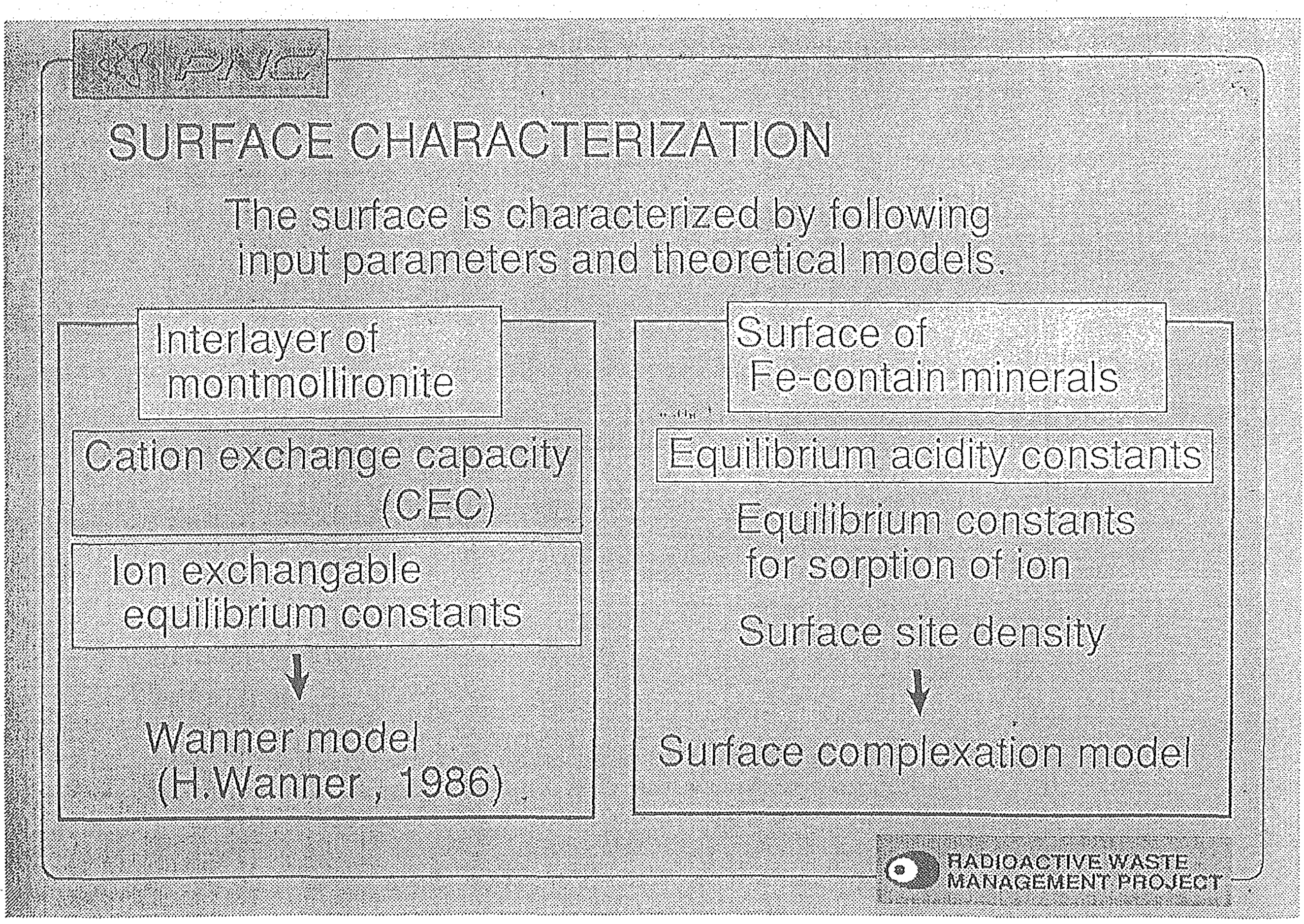
RADIOACTIVE WASTE
MANAGEMENT PROJECT



PNC

SURFACE CHARACTERIZATION

The surface is characterized by following input parameters and theoretical models.

Interlayer of montmollironite

Cation exchange capacity (CEC)

Ion exchangable equilibrium constants

↓

Wanner model (H.Wanner , 1986)

Surface of Fe-contain minerals

Equilibrium acidity constants

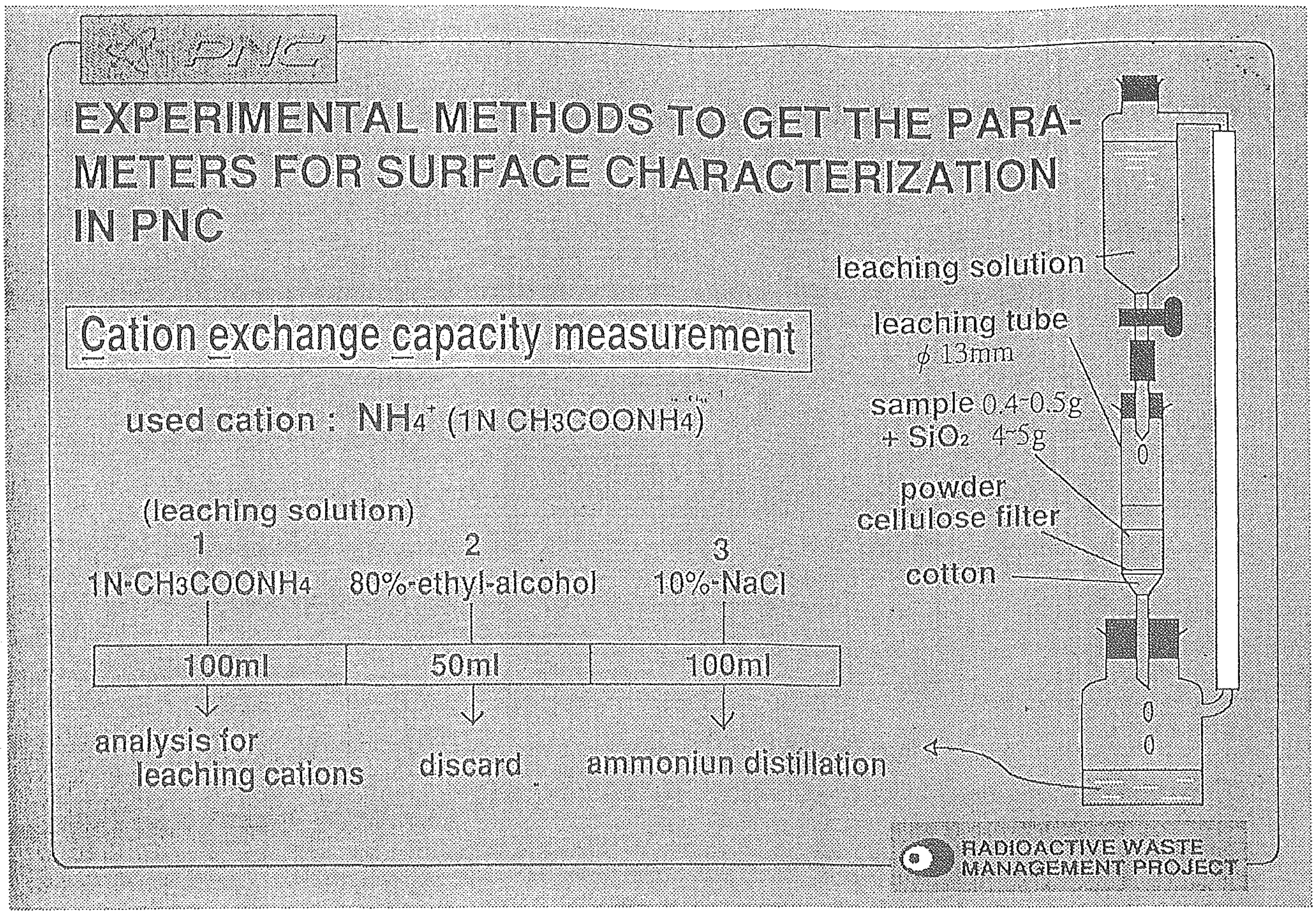
Equilibrium constants for sorption of ion

Surface site density

↓

Surface complexation model

RADIOACTIVE WASTE
MANAGEMENT PROJECT



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EXPERIMENTAL METHODS TO GET THE PARAMETERS FOR SURFACE CHARACTERIZATION IN PNC

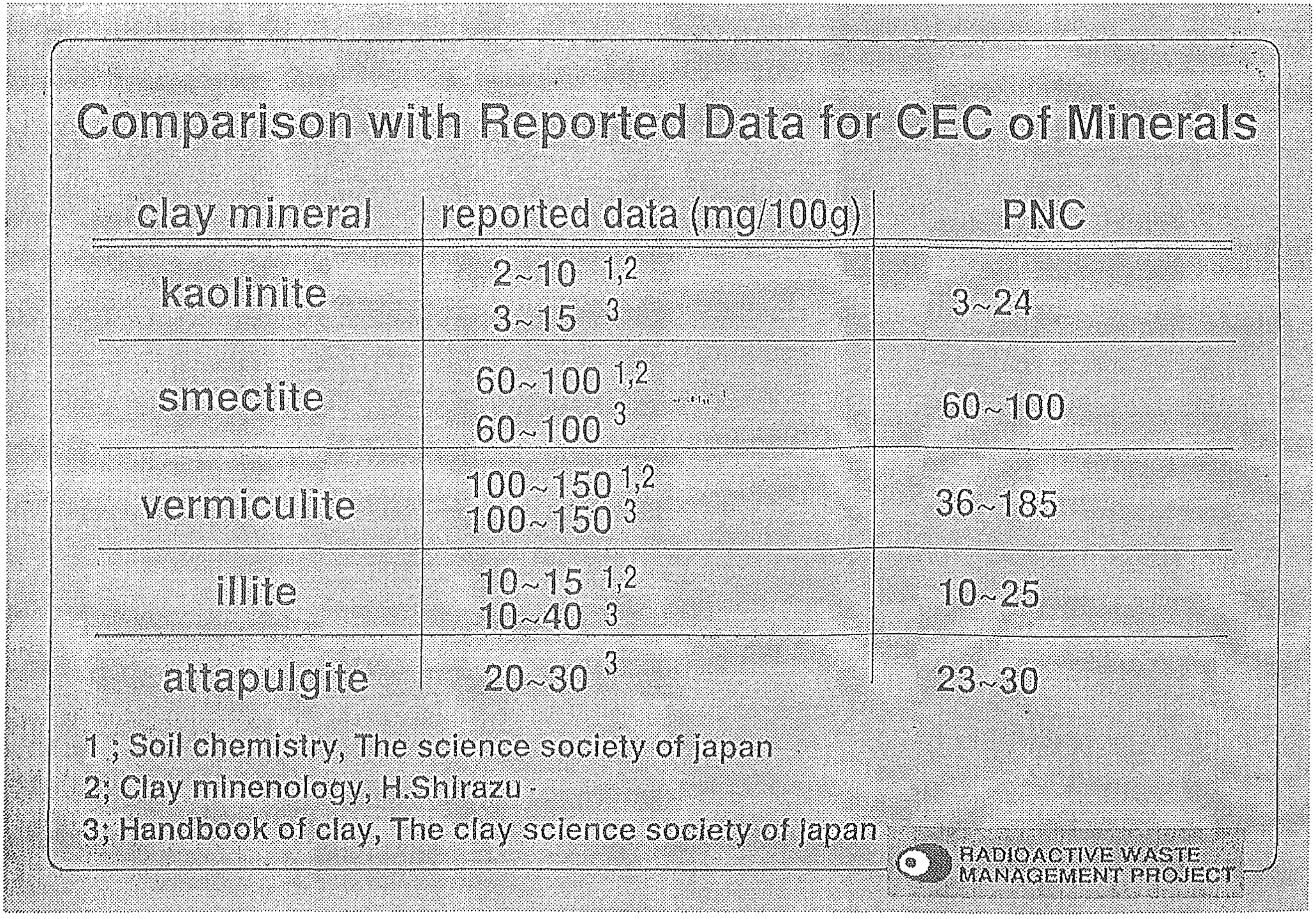
Cation exchange capacity measurement

used cation : NH_4^+ (1N CH_3COONH_4)

(leaching solution)

1	2	3
1N-CH_3COONH_4	80%-ethyl-alcohol	10%-NaCl
100ml	50ml	100ml
analysis for leaching cations	discard	ammoniun distillation

RADIOACTIVE WASTE MANAGEMENT PROJECT



Comparison with Reported Data for CEC of Minerals

clay mineral	reported data (mg/100g)	PNC
kaolinite	2~10 [1,2] 3~15 [3]	3~24
smectite	60~100 [1,2] 60~100 [3]	60~100
vermiculite	100~150 [1,2] 100~150 [3]	36~185
illite	10~15 [1,2] 10~40 [3]	10~25
attapulgite	20~30 [3]	23~30

1 ; Soil chemistry, The science society of japan
2; Clay minenology, H.Shirazu
3; Handbook of clay, The clay science society of japan

RADIOACTIVE WASTE MANAGEMENT PROJECT

Results of CEC mesurements of KUNIPIA F

Cation in layer	Na	Ca	K	Mg	total (meq/100g)
Capacity	107.2	19.5	1.3	4.2	132.2
	108.3	19.5	1.2	4.0	133.0
	108.7	17.5	1.2	2.1	129.4
	106.5	17.4	1.1	2.7	127.7
	108.7	17.5	1.2	2.5	129.9
Mean	107.9	18.3	1.2	3.1	130.5
	82.7%	14.0%	0.9%	2.4%	100%

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↓

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(H.Wanner , 1986)

Surface of Fe-contain minerals

Equilibrium acidity constants

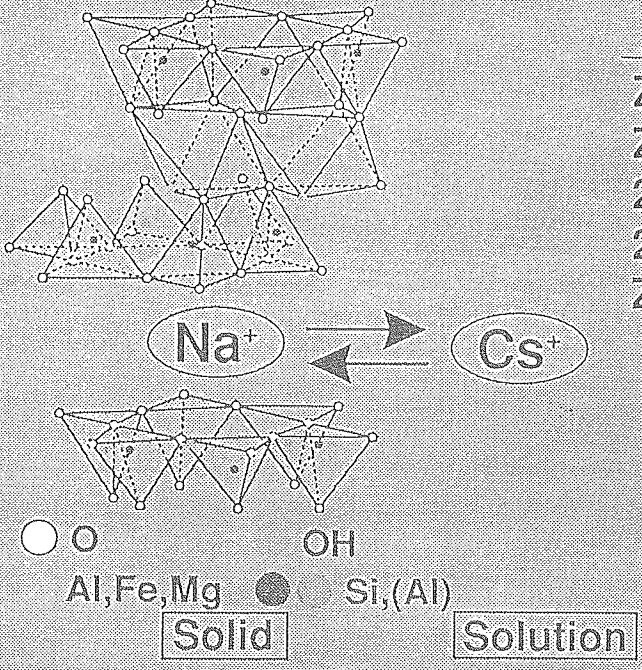
Equilibrium constants for sorption of ion

Surface site density

↓

Surface complexation model

Modelling



Schematic view of Cs sorption

Ion exchange constant

reaction	logK
$Z^- + Na^+ = ZNa$	20.0 [1]
$Z^- + K^+ = ZK$	20.6 [1]
$2Z^- + Ca^{2+} = Z2Ca$	41.8 [1]
$2Z^- + Mg^{2+} = Z2Mg$	40.2 [1]
$Z^- + Cs^+ = ZCs$	20.8

[1] Wanner et al. 1986

Site dencity → CEC

element		CEC
Na	:	1.078 meq/l
K	:	0.012 meq/l
Ca	:	0.183 meq/l
Mg	:	0.031 meq/l

SURFACE PROPERYTIES OF BENTONITE

Surface/water interface described with own dominant mechanisms of adsorption.

Interlayer of smectites

montmollironite 45～50wt%

Cage of zeolites

analcite 3～4wt%

↓

Ion exchange

Surface of Fe-contain minerals

pyrite 0.5～0.7wt%

(goethite as weathered minerals)

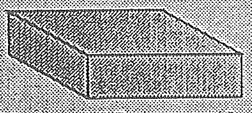
↓

Surface complexation

PNC

Characteristics of altered surface material

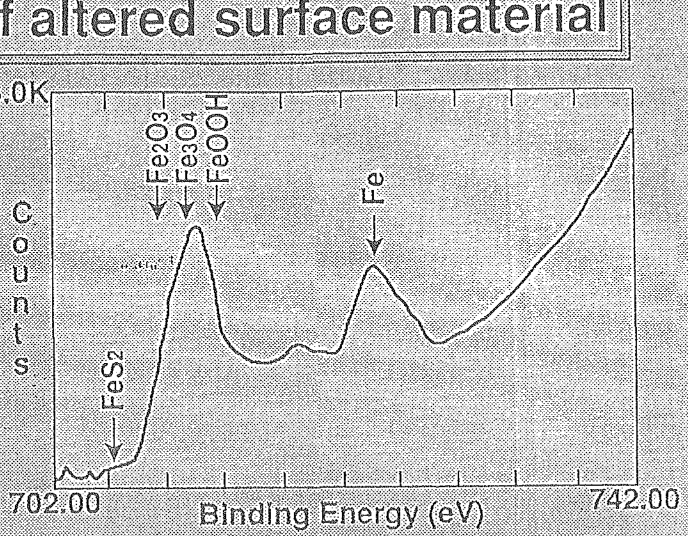
Sample (altered FeS_2)



(10mm × 10mm × 4mm)

↓

ESCA



ESCA Spectrum

Altered surface layer of FeS_2 ⇒ Ferrosic oxide or hydroxide (ex. Fe_2O_3, Fe_3O_4, FeOOH)

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SURFACE CHARACTERIZATION

The surface is characterized by following input parameters and theoretical models.

Interlayer of montmollironite

- Cation exchange capacity (CEC)
- Ion exchangable equilibrium constants

↓

Wanner model (H.Wanner , 1986) .

Surface of Fe-contain minerals

- Equilibrium acidity constants
- Equilibrium constants for sorption of ion
- Surface site density

↓

Surface complexation model

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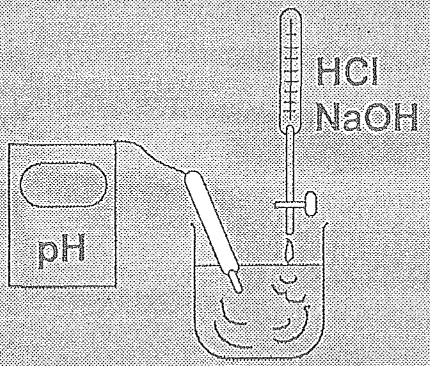
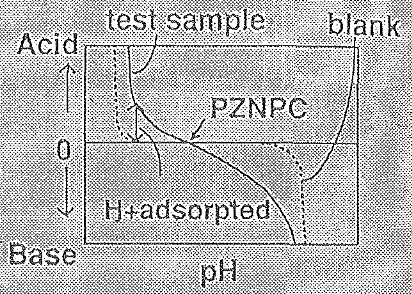
EXPERIMENTAL METHODS TO GET THE PARAMETERS FOR SURFACE CHARACTERIZATION IN PNC

Acid-base titration measurement

Point of zero net proton charge (PZNPC),
Amount of H^+ adsorpted on solid





RADIOACTIVE WASTE
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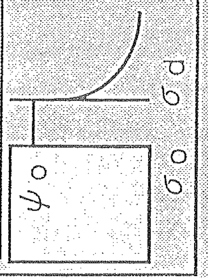
APPROACHES TO INTERPRITATION OF TITRATION RESULTS

Describe with
surface complexation models

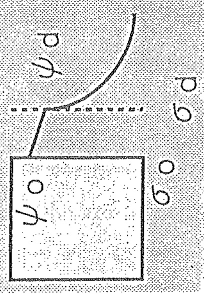
· Diffuse Layer model



$\sigma_o + \sigma_d = 0$

$\sigma_d = 0.1774C^{1/2} \sinh(Z\psi_o \cdot 19.46)$

· Basic stern model

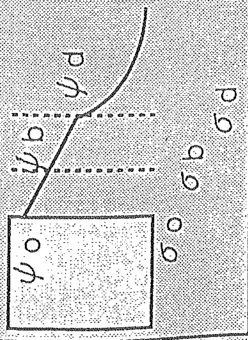


$\sigma_o + \sigma_d = 0$

$\sigma_d = 0.1774C^{1/2} \sinh(Z\psi_d \cdot 19.46)$

$\sigma_o / C_1 = \psi_o - \psi_d$

· Triple layer model

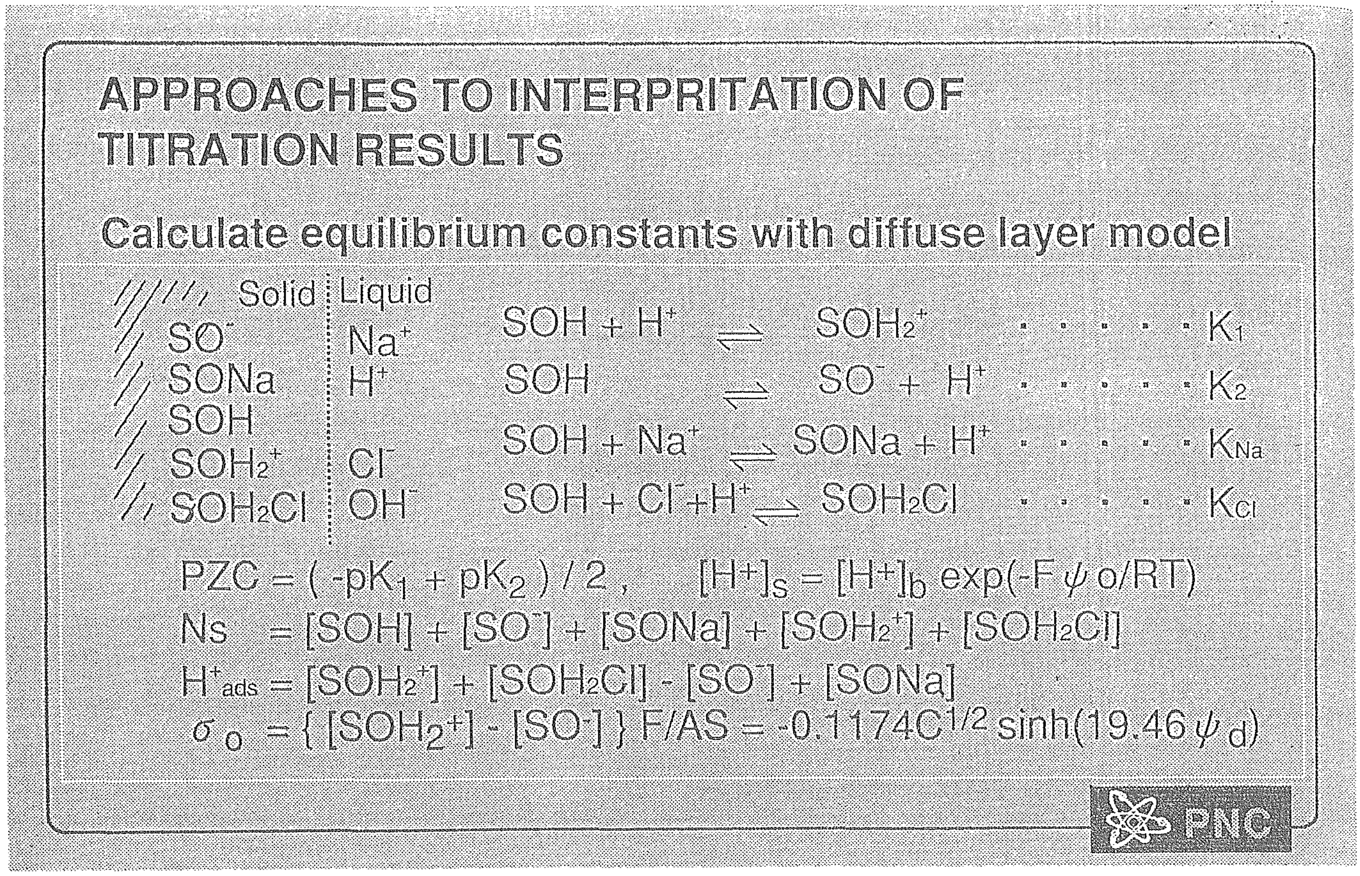


$\sigma_o + \sigma_b + \sigma_d = 0$

$\sigma_d = 0.1774C^{1/2} \sinh(Z\psi_d \cdot 19.46)$

$\sigma_o / C_1 = \psi_o - \psi_b$

$(\sigma_o + \sigma_b) / C_2 = \psi_b - \psi_d$



APPROACHES TO INTERPRITATION OF TITRATION RESULTS

Calculate equilibrium constants with diffuse layer model

Solid	Liquid
SO^-	Na^+
SONa	H^+
SOH	
SOH_2^+	Cl^-
SOH_2Cl	OH^-

$SOH + H^+ \rightleftharpoons SOH_2^+$ · · · · · · K_1

$SOH \rightleftharpoons SO^- + H^+$ · · · · · · K_2

$SOH + Na^+ \rightleftharpoons SONa + H^+$ · · · · · · K_{Na}

$SOH + Cl^- + H^+ \rightleftharpoons SOH_2Cl$ · · · · · · K_{Cl}

$PZC = (-pK_1 + pK_2)/2$, $[H^+]_s = [H^+]_b \exp(-F\psi_o/RT)$

$Ns = [SOH] + [SO^-] + [SONa] + [SOH_2^+] + [SOH_2Cl]$

$H^+_{ads} = [SOH_2^+] + [SOH_2Cl] - [SO^-] + [SONa]$

$\sigma_o = \{[SOH_2^+] - [SO^-]\} F/AS = -0.1174C^{1/2} \sinh(19.46\psi_d)$

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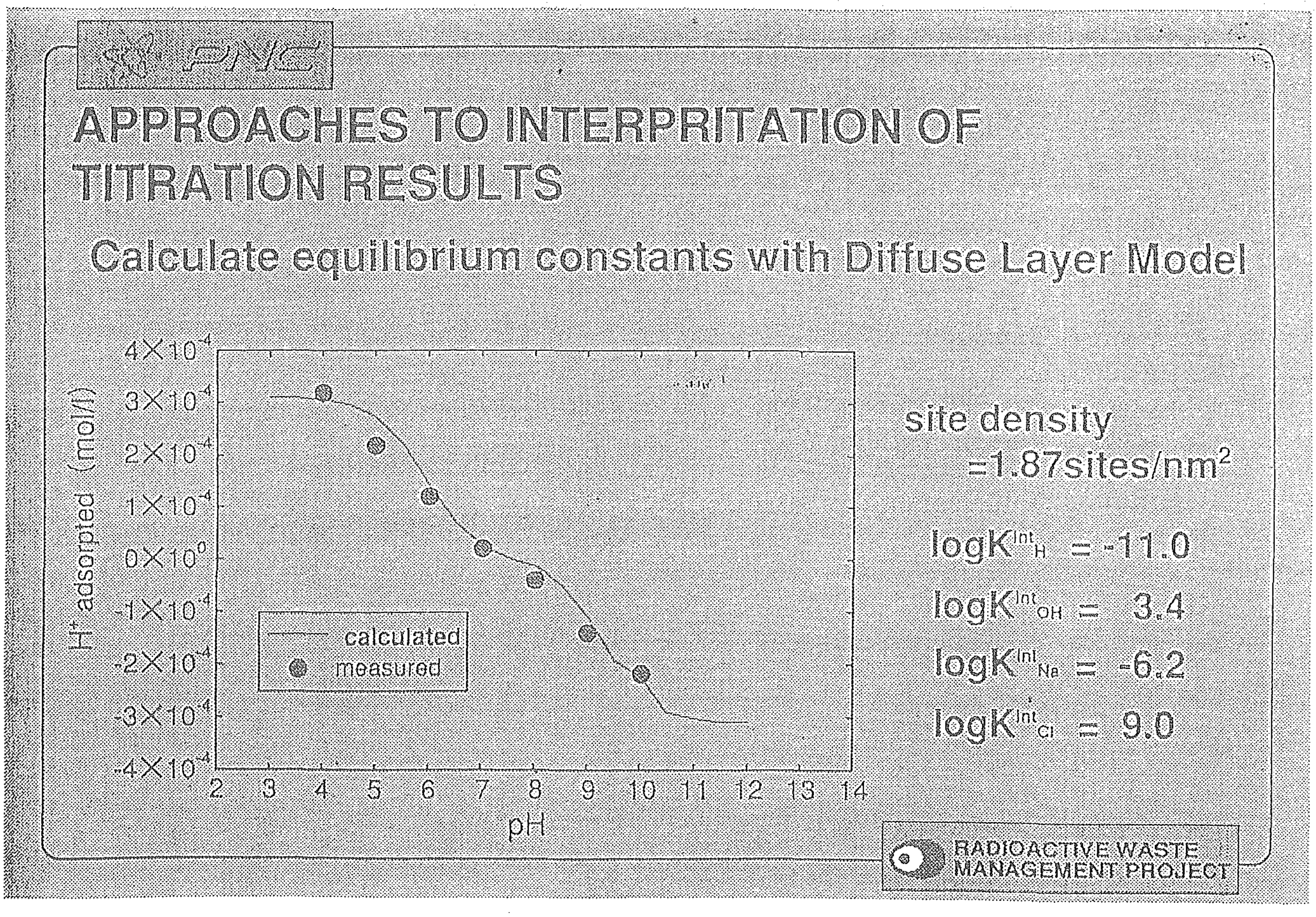

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APPROACHES TO INTERPRITATION OF TITRATION RESULTS

Calculate equilibrium constants with Diffuse Layer Model

site density
=1.87sites/nm^2

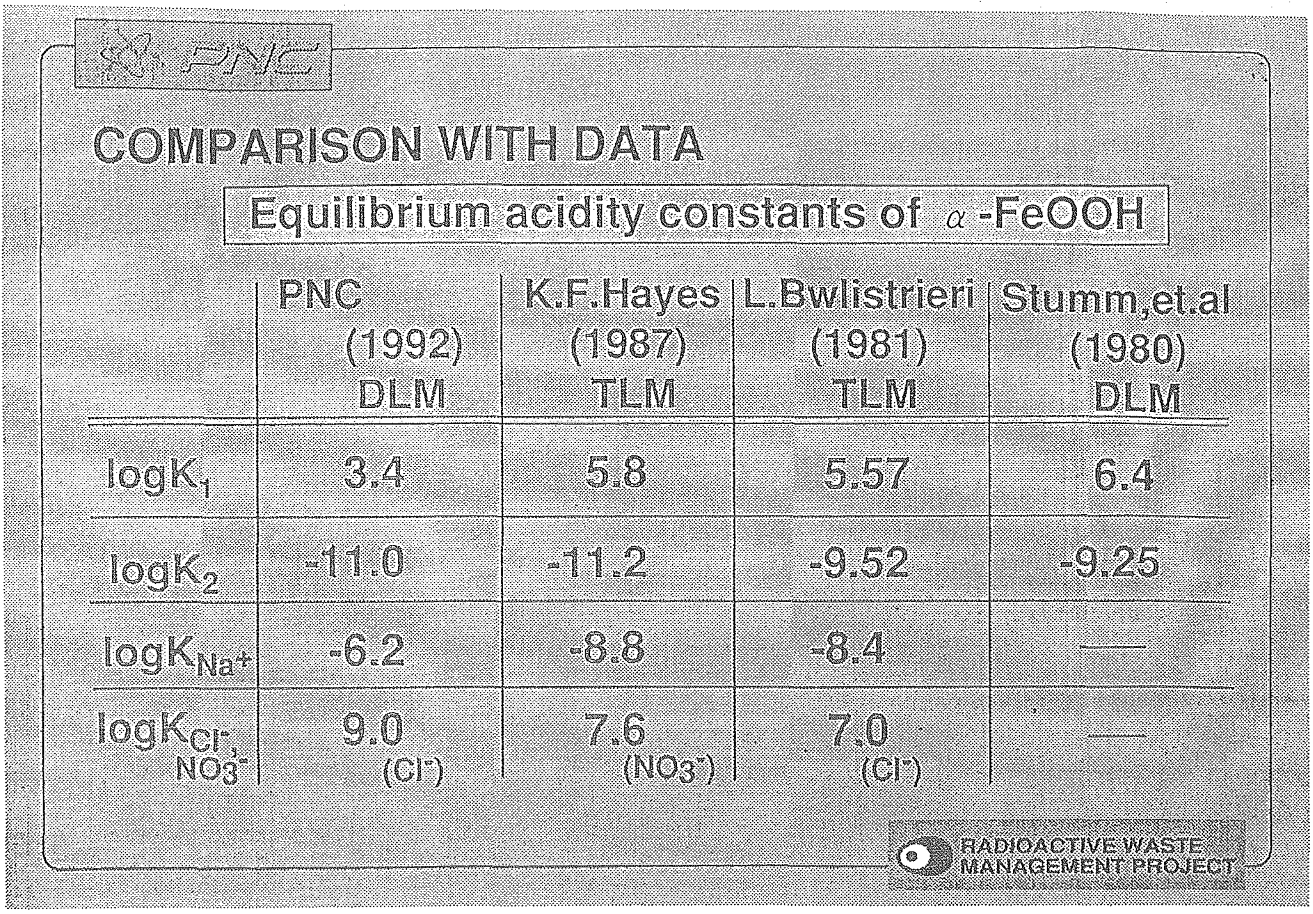
$\log K^{Int}_H = -11.0$

$\log K^{Int}_{OH} = 3.4$

$\log K^{Int}_{Na} = -6.2$

$\log K^{Int}_{Cl} = 9.0$

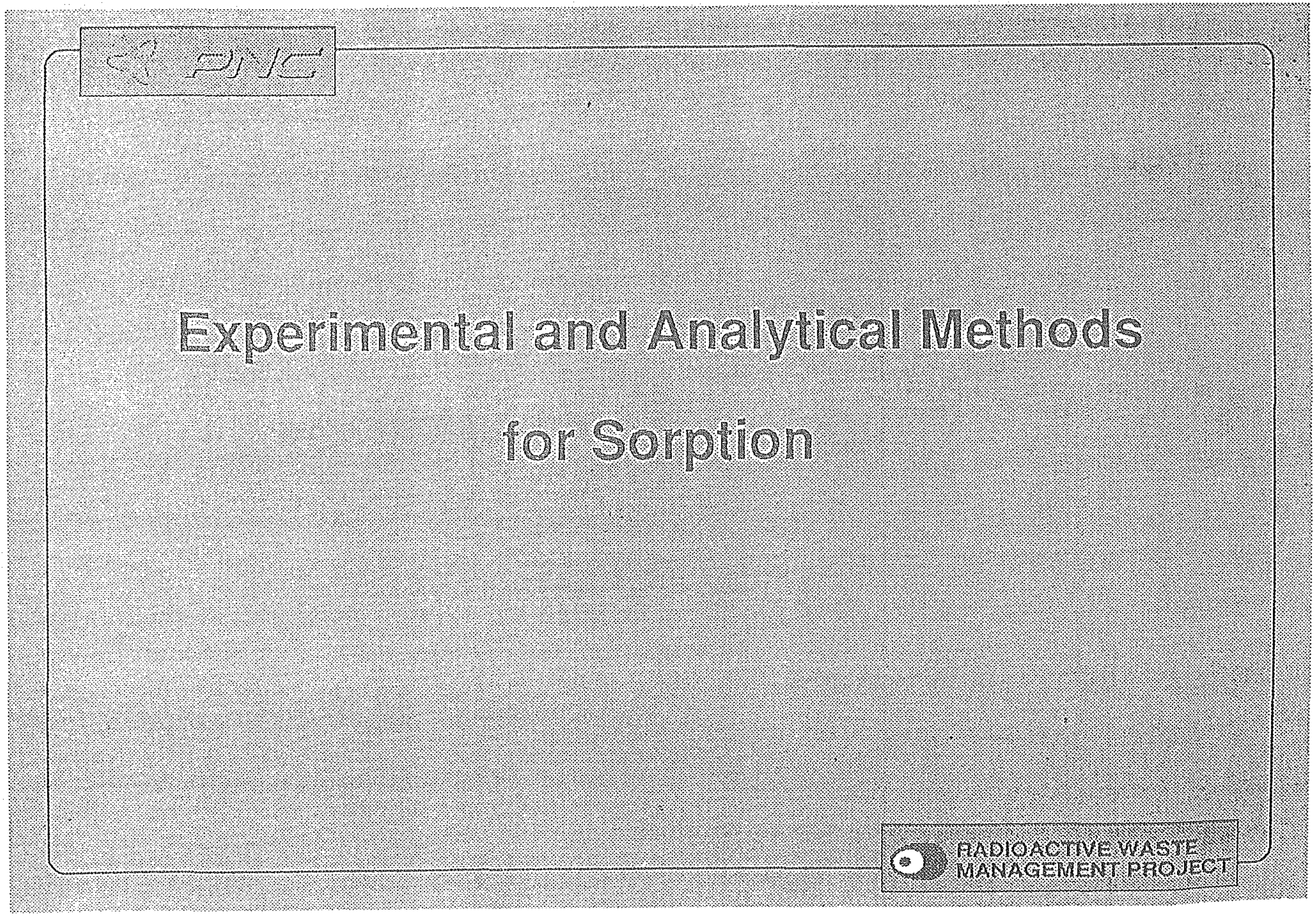
RADIOACTIVE WASTE MANAGEMENT PROJECT



COMPARISON WITH DATA

Equilibrium acidity constants of α-FeOOH

	PNC (1992) DLM	K.F.Hayes (1987) TLM	L.Bwlistrieri (1981) TLM	Stumm,et.al (1980) DLM
$\log K_1$	3.4	5.8	5.57	6.4
$\log K_2$	-11.0	-11.2	-9.52	-9.25
$\log K_{Na^+}$	-6.2	-8.8	-8.4	—
$\log K_{Cl^-, NO_3^-}$	9.0 (Cl^-)	7.6 (NO_3^-)	7.0 (Cl^-)	—



Experimental and Analytical Methods for Sorption

Study on sorption behavior of Cs and Se on bentonite

T.Shibutani , H.Yoshikawa and M.Yui

PNC RADIOACTIVE WASTE MANAGEMENT PROJECT

Object

- Experimental study of the sorption of Cs and Se on bentonite.
- Modelling of the sorption of Cs and Se on bentonite.

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Experimental Condition

	Cs		Se
method	batch	column	batch
Solid	KunigeruV1[*1]	KunigeruV1[*1]	KunigeruV1[*1] KunipiaF[*2] α FeOOH
Solution	equilibrated water with solid		
Solid/Solution	1g/50ml 1g/500ml	———	1g/50ml
Parameter	Cs concentration $10^{-9} \sim 10^{-2}$	drydensity $0.4 \sim 1.8$	pH $4 \sim 11$
Atmosphere	Air	Air	N_2
Time	30days	2~20days	30days

[*1] KunigeruV1 : Bentonite (50~55% Na-montmorillonite)

[*2] Kunipia F : Bentonite (95% Na-montmorillonite)

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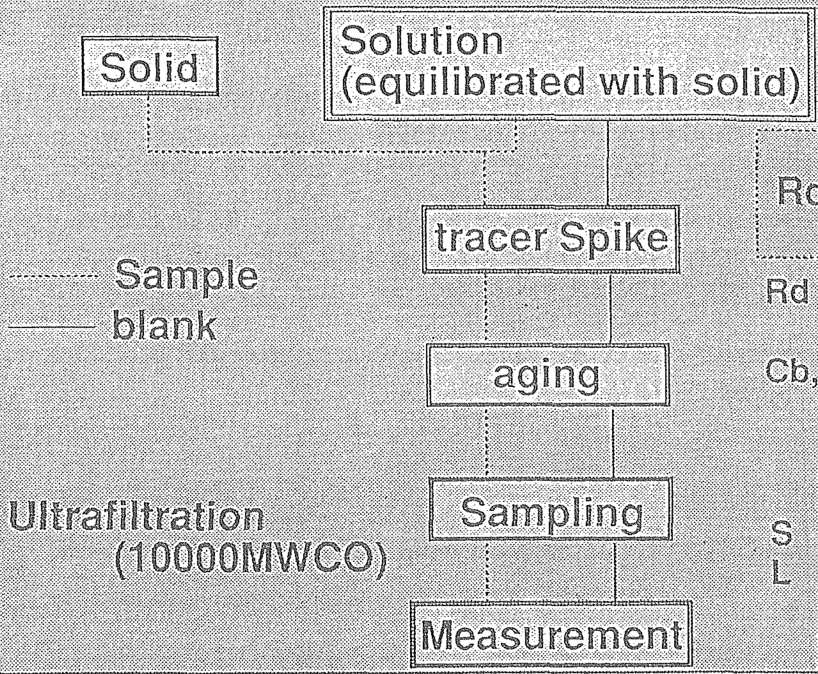
Mineral Composition of Bentonite (%)

	Kunigel V-1		Kunipia F	
Na-montmorillonite	46 - 49	(1)	99	(1)
Quartz	19 - 23	(2)(3)	0.5	(2)
Chalcedony	~ 23	(2)(3)	D.L.	
Plagioclase	1 - 5	(2)(3)	trace	(2)
Calcite	1 - 4	(2)(3)(4)	0.5	(2)
Dolomite	2 - 4	(2)(3)	D.L.	
Pyrite	0.5 - 0.9	(3)(4)(5)	D.L.	
Analcime	3 - 4	(2)(3)	D.L.	
Biotite	trace	(3)	D.L.	
Chlorite	trace	(3)	D.L.	
Analitical Method	(1)Methylene Blue Capacity,(2) XRD (3)Modal Analysis,(4)DTA (5)Chemical Analysis		(1)Methylene Blue Capacity (2) XRD	
ref.	Ito et. al,1992		Private Commu.	

RADIOACTIVE WASTE MANAGEMENT PROJECT

Experimental procedure for batch method



Ultrafiltration
(10000MWCO)

$$Rd = \frac{Cb - Ct}{Ct} \times \frac{L}{S}$$

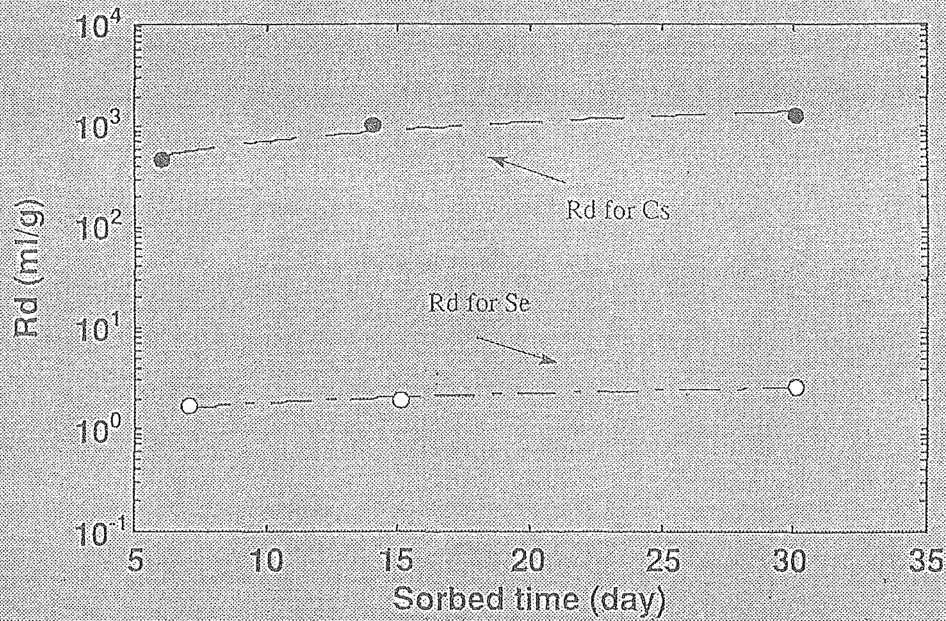
Rd : Distribution coefficient(ml/g)

Cb,Ct : Concentration of tracer in blank (Cb) and sample (Ct) (mol/l)

S : Solid(g)

L : Solution(ml)

Time Dependency of distribution ratio



Time dipendency of distribution ratio of Cs and Se on bentonite

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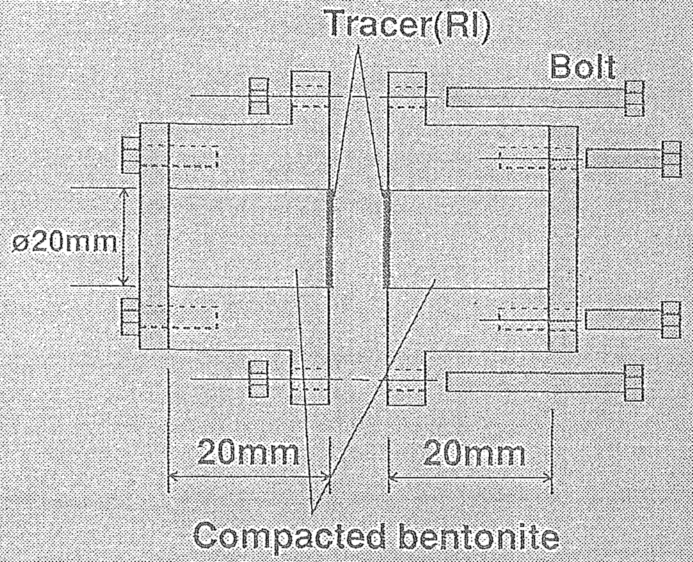
Experimental method

- Column method



Procedures

[1] Compaction of bentonite dried at 110 °C.
[2] Immersion in distilled water.
[3] Putting of tracer on Surface of bentonite.
[4] Diffusion.
[5] Slicing of bentonite and measurement of radioactivity.

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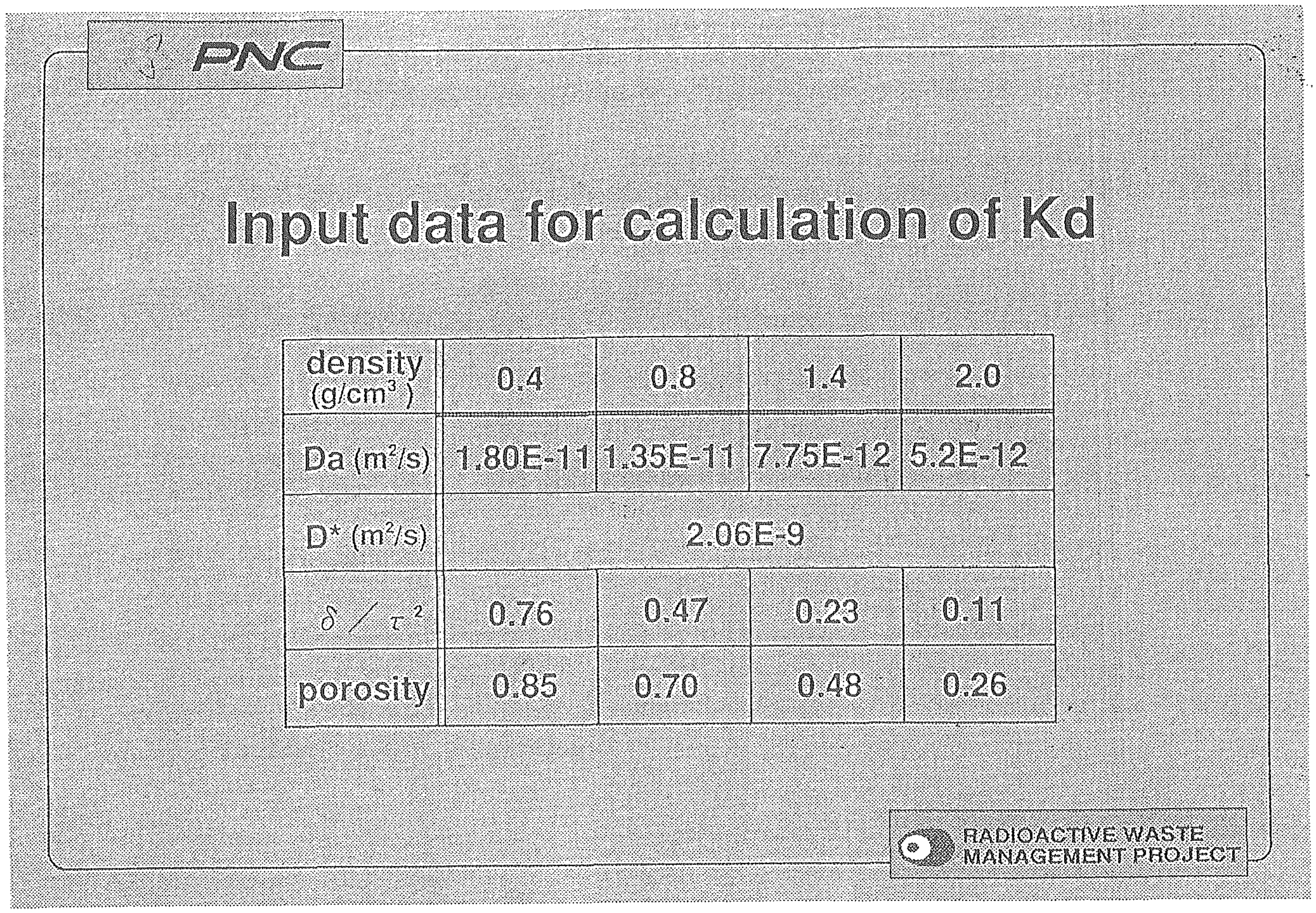
Estimation of distribution coefficient from apparent diffusion coefficient

$$Kd = \frac{\varepsilon}{\rho}\left(\frac{D^*}{Da}\frac{\delta}{\tau^2} - 1\right)$$

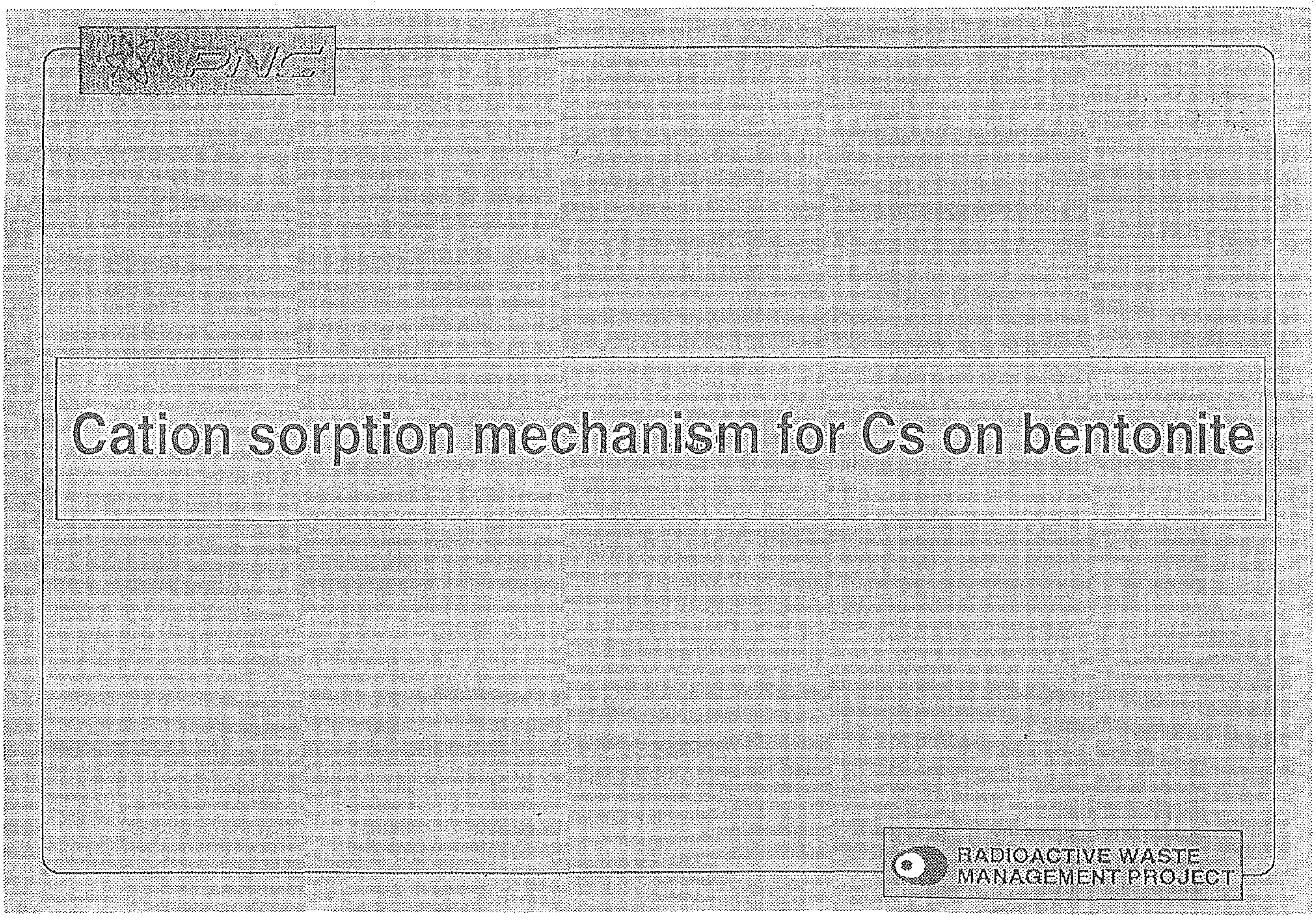
D^* : Diffusion coefficient of nuclide in free water (m^2/s)
Da : Apparent Diffusion coefficient of nuclide into solid (m^2/s)
ε : Porosity
ρ : Density (kg/m^3)
δ : Constrictivity
τ : Tortuosity

RADIOACTIVE WASTE MANAGEMENT PROJECT

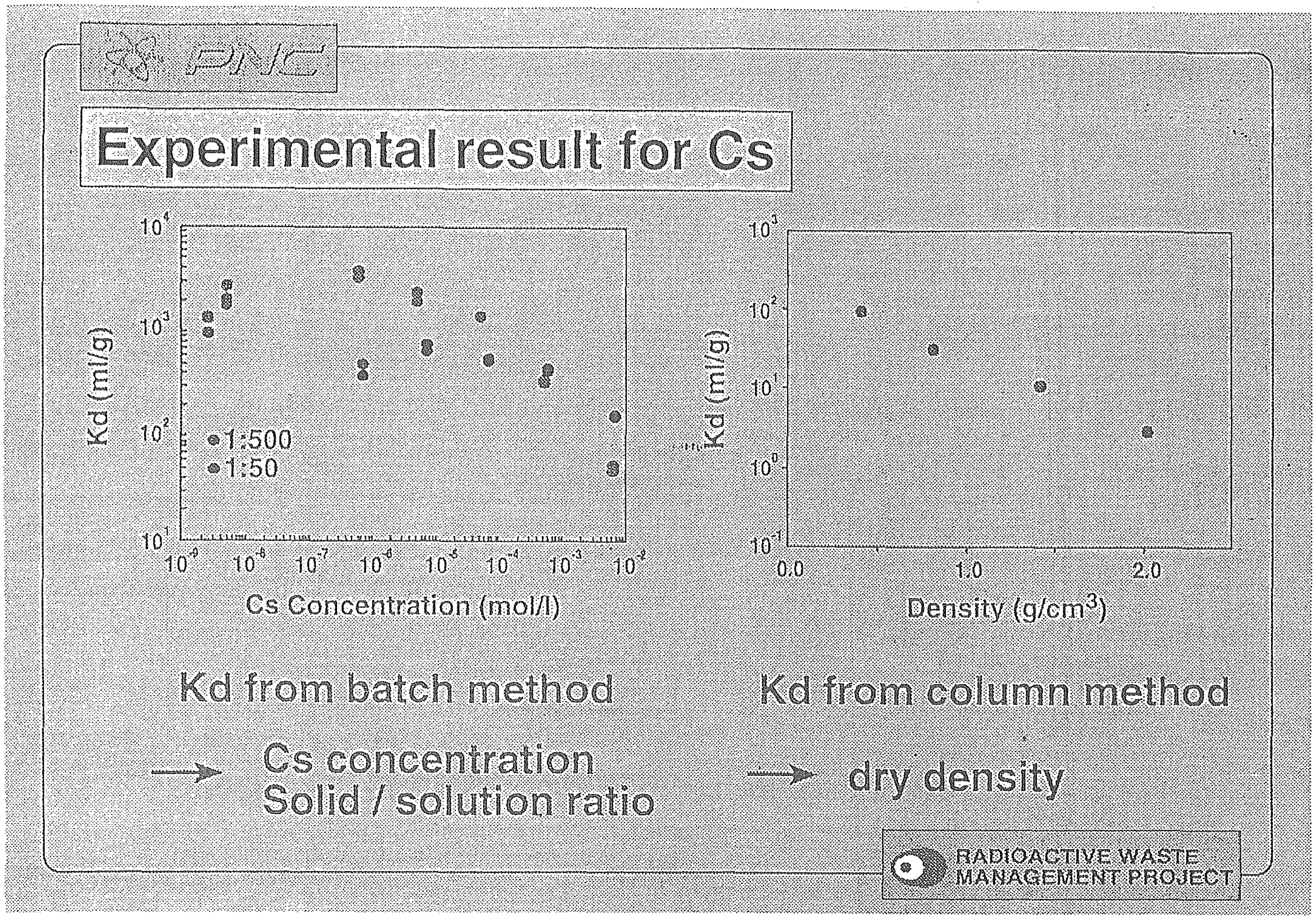


Input data for calculation of Kd

density (g/cm^3)	0.4	0.8	1.4	2.0
Da (m^2/s)	1.80E-11	1.35E-11	7.75E-12	5.2E-12
D* (m^2/s)	2.06E-9			
δ / τ^2	0.76	0.47	0.23	0.11
porosity	0.85	0.70	0.48	0.26



Cation sorption mechanism for Cs on bentonite



Experimental result for Cs

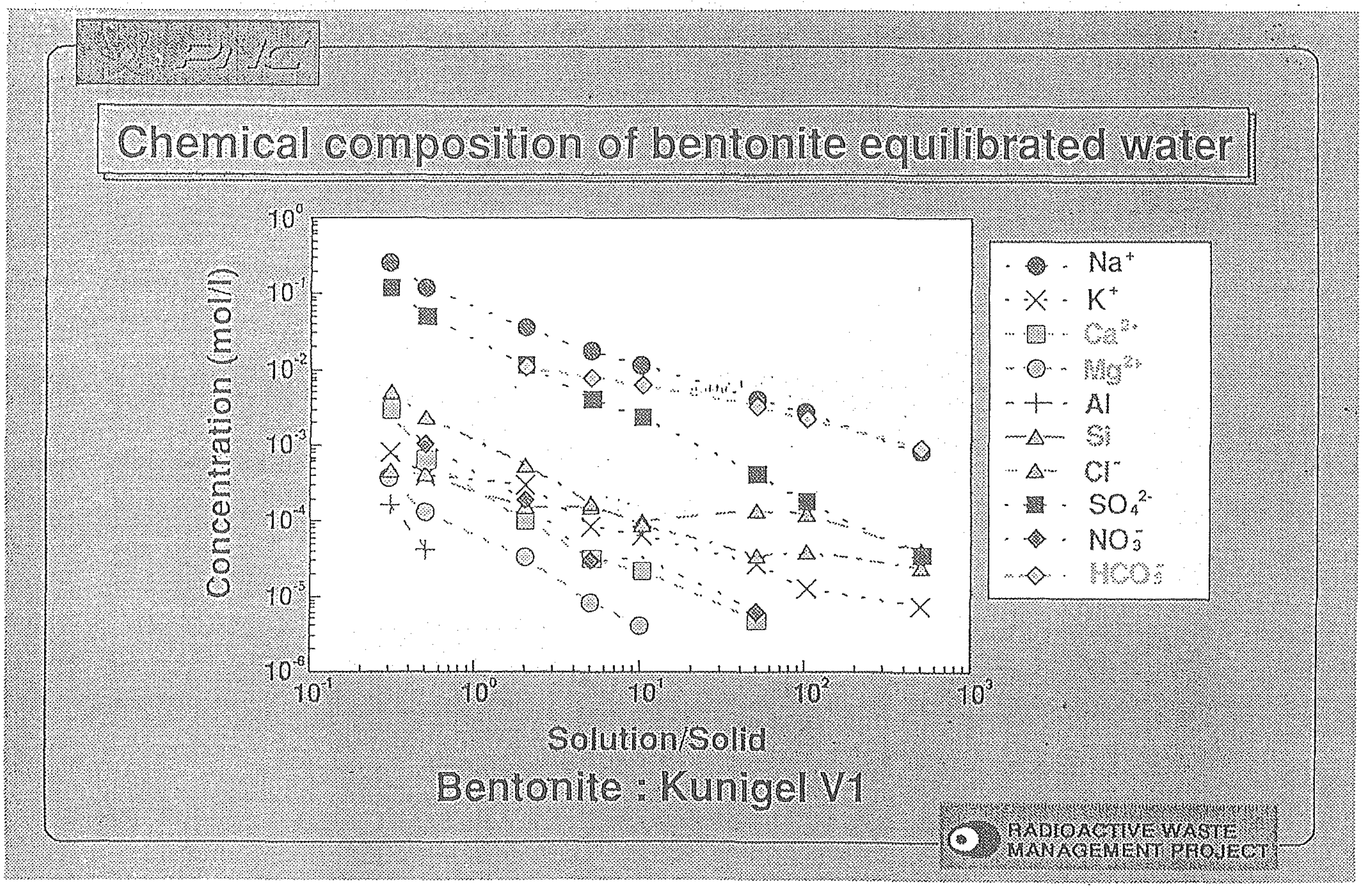
Kd from batch method

→ Cs concentration
Solid / solution ratio

Kd from column method

→ dry density

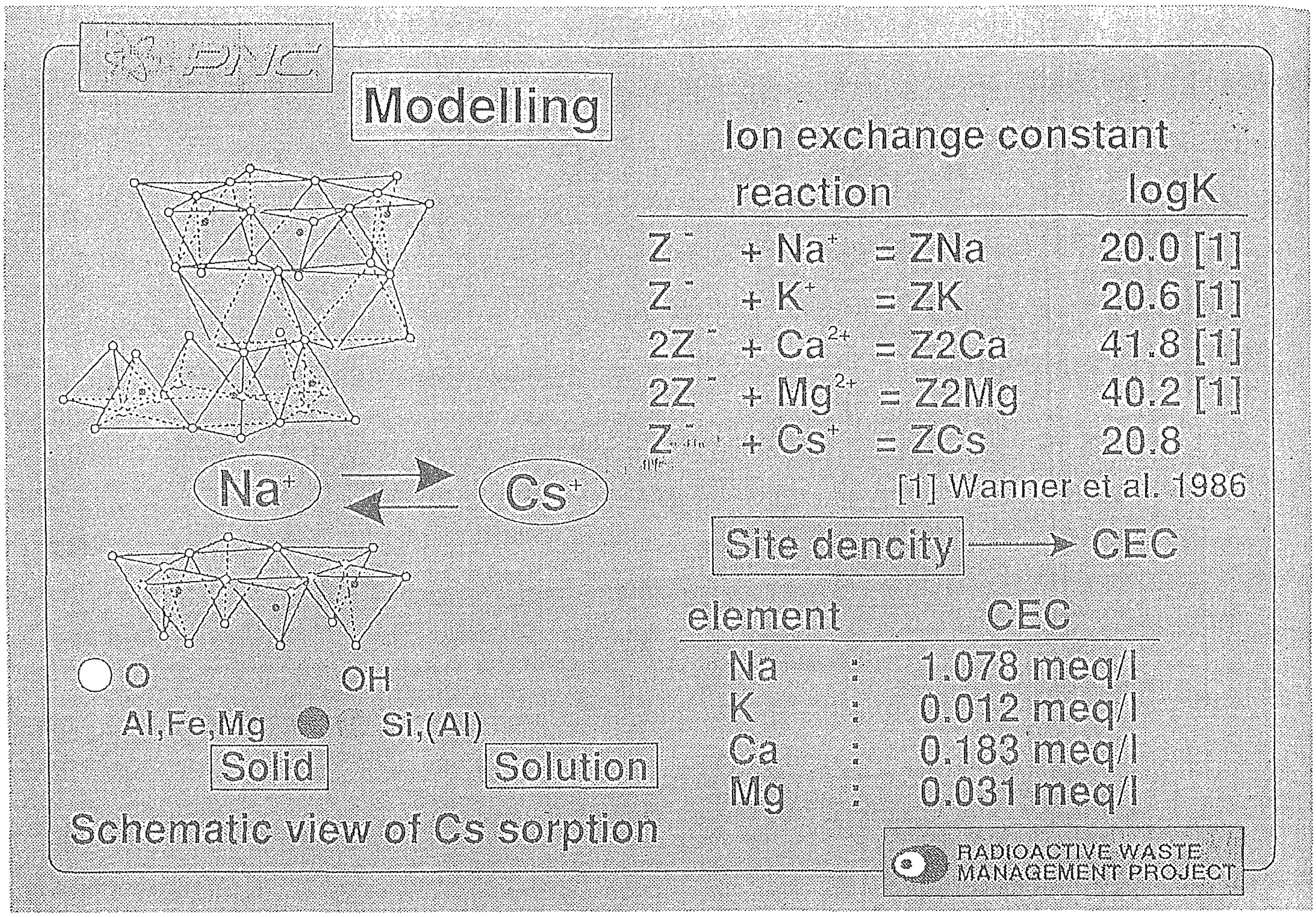
RADIOACTIVE WASTE MANAGEMENT PROJECT



Chemical composition of bentonite equilibrated water

Bentonite : Kunigel V1

RADIOACTIVE WASTE MANAGEMENT PROJECT



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Modelling

○ O OH

Al,Fe,Mg ● Si,(Al)

Solid **Solution**

Schematic view of Cs sorption

Ion exchange constant

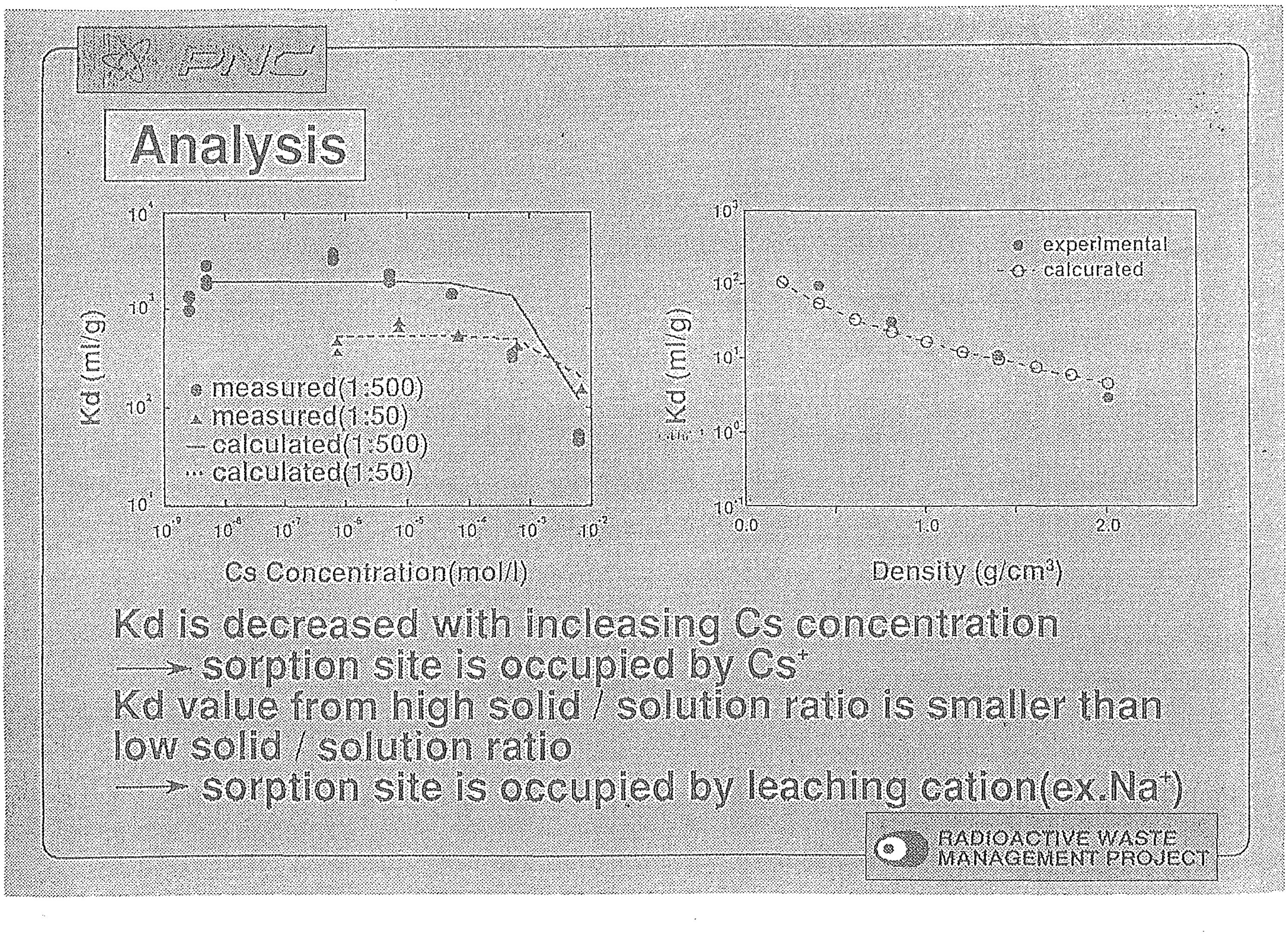
reaction	logK
$Z^- + Na^+ = ZNa$	20.0 [1]
$Z^- + K^+ = ZK$	20.6 [1]
$2Z^- + Ca^{2+} = Z2Ca$	41.8 [1]
$2Z^- + Mg^{2+} = Z2Mg$	40.2 [1]
$Z^- + Cs^+ = ZCs$	20.8

[1] Wanner et al. 1986

Site dencity → CEC

element	CEC
Na :	1.078 meq/l
K :	0.012 meq/l
Ca :	0.183 meq/l
Mg :	0.031 meq/l

RADIOACTIVE WASTE MANAGEMENT PROJECT



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Analysis

Kd is decreased with incleasing Cs concentration

→ sorption site is occupied by Cs^+

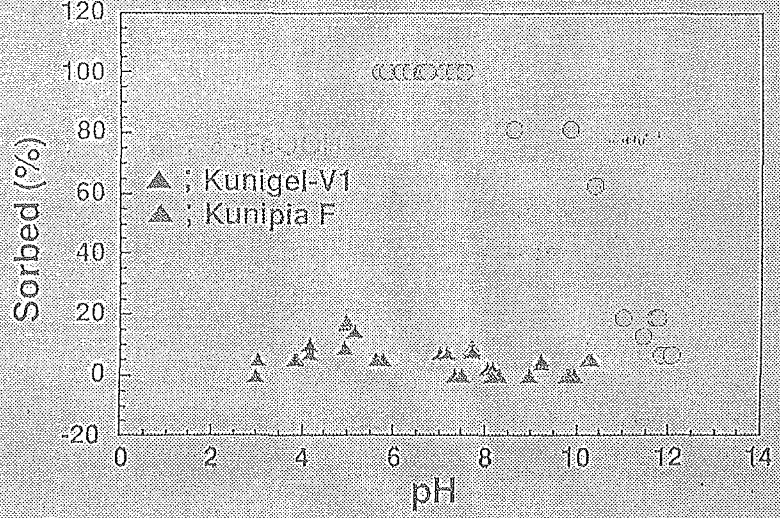
Kd value from high solid / solution ratio is smaller than low solid / solution ratio

→ sorption site is occupied by leaching cation(ex.Na^+)

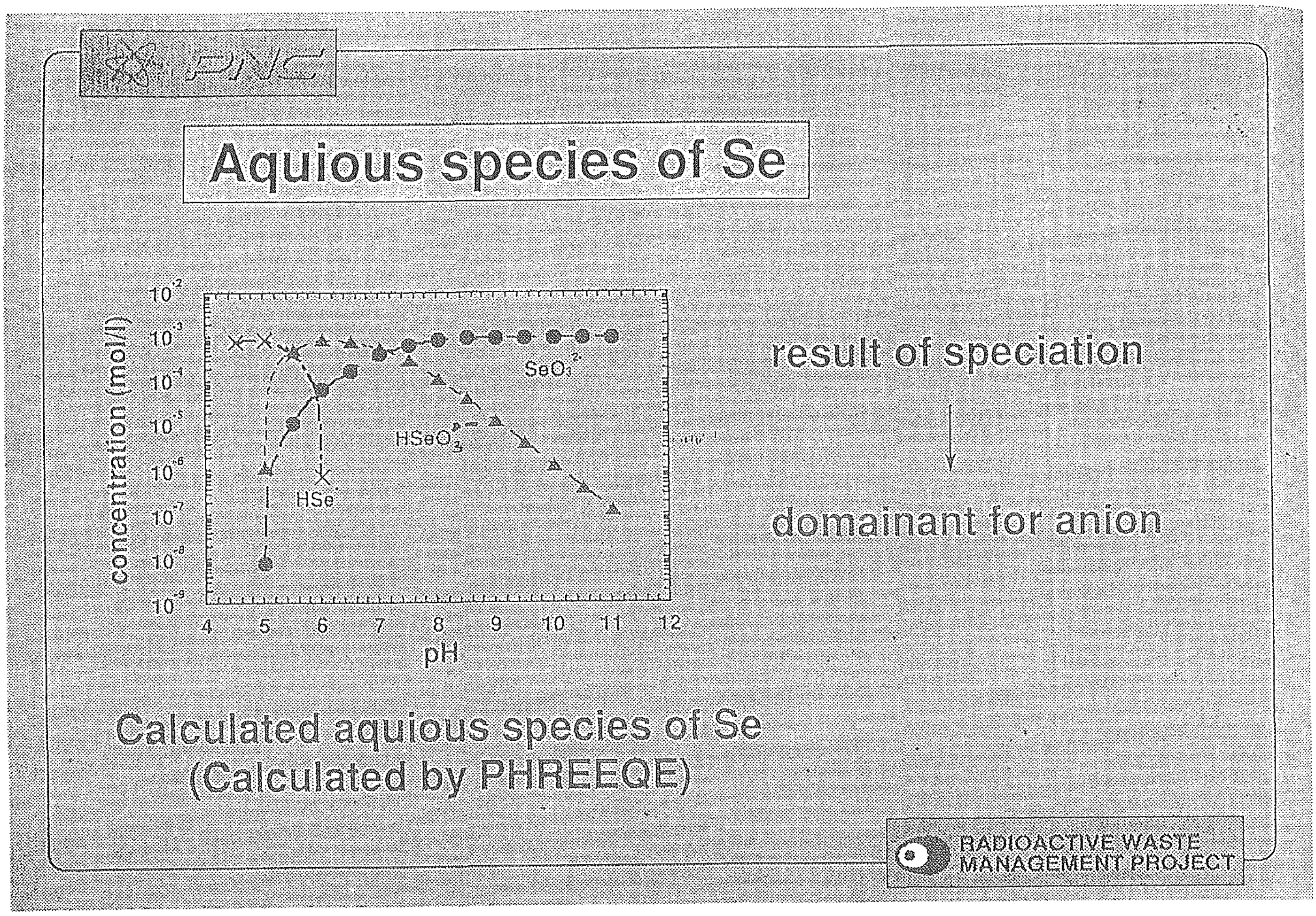
RADIOACTIVE WASTE MANAGEMENT PROJECT

Anion sorption mechanism for bentonite

Experimental result for Se



- Sorbed ratio of Se on α-FeOOH are decreased with pH increasing



Aquious species of Se

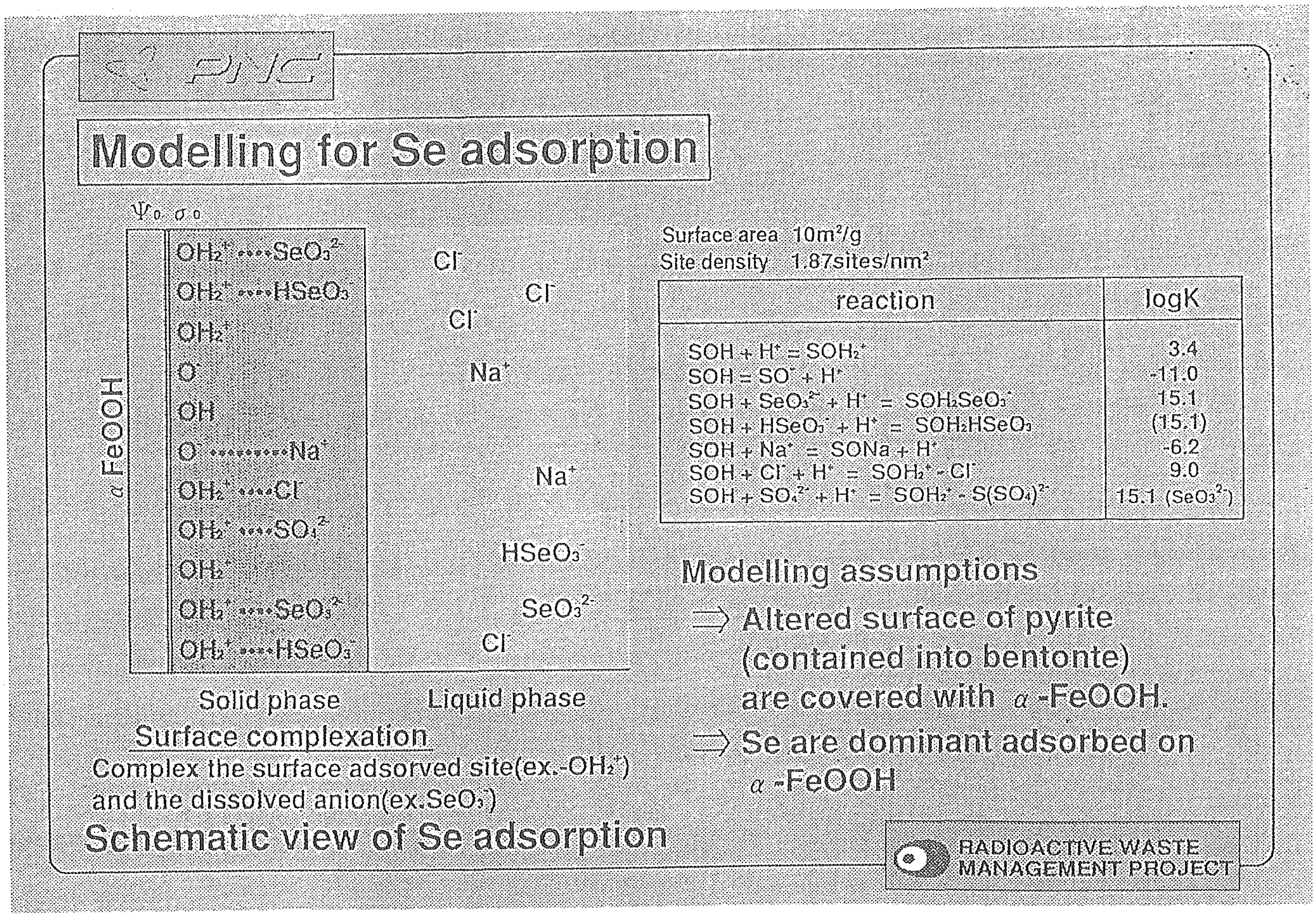
result of speciation

↓

domainant for anion

Calculated aquious species of Se
(Calculated by PHREEQE)

RADIOACTIVE WASTE
MANAGEMENT PROJECT



Modelling for Se adsorption

Surface complexation
Complex the surface adsorved site(ex.-OH_2^+)
and the dissolved anion(ex.SeO_3^-)

Schematic view of Se adsorption

Surface area 10m^2/g
Site density 1.87sites/nm^2

reaction	logK
$SOH + H^+ = SOH_2^+$	3.4
$SOH = SO^- + H^+$	-11.0
$SOH + SeO_3^{2-} + H^+ = SOH_2SeO_3^-$	15.1
$SOH + HSeO_3^- + H^+ = SOH_2HSeO_3$	(15.1)
$SOH + Na^+ = SONa + H^+$	-6.2
$SOH + Cl^- + H^+ = SOH_2^+ - Cl^-$	9.0
$SOH + SO_4^{2-} + H^+ = SOH_2^+ - S(SO_4)^{2-}$	15.1 (SeO_3^{2-})

Modelling assumptions

⇒ Altered surface of pyrite
(contained into bentonte)
are covered with α -FeOOH.

⇒ Se are dominant adsorbed on
α -FeOOH

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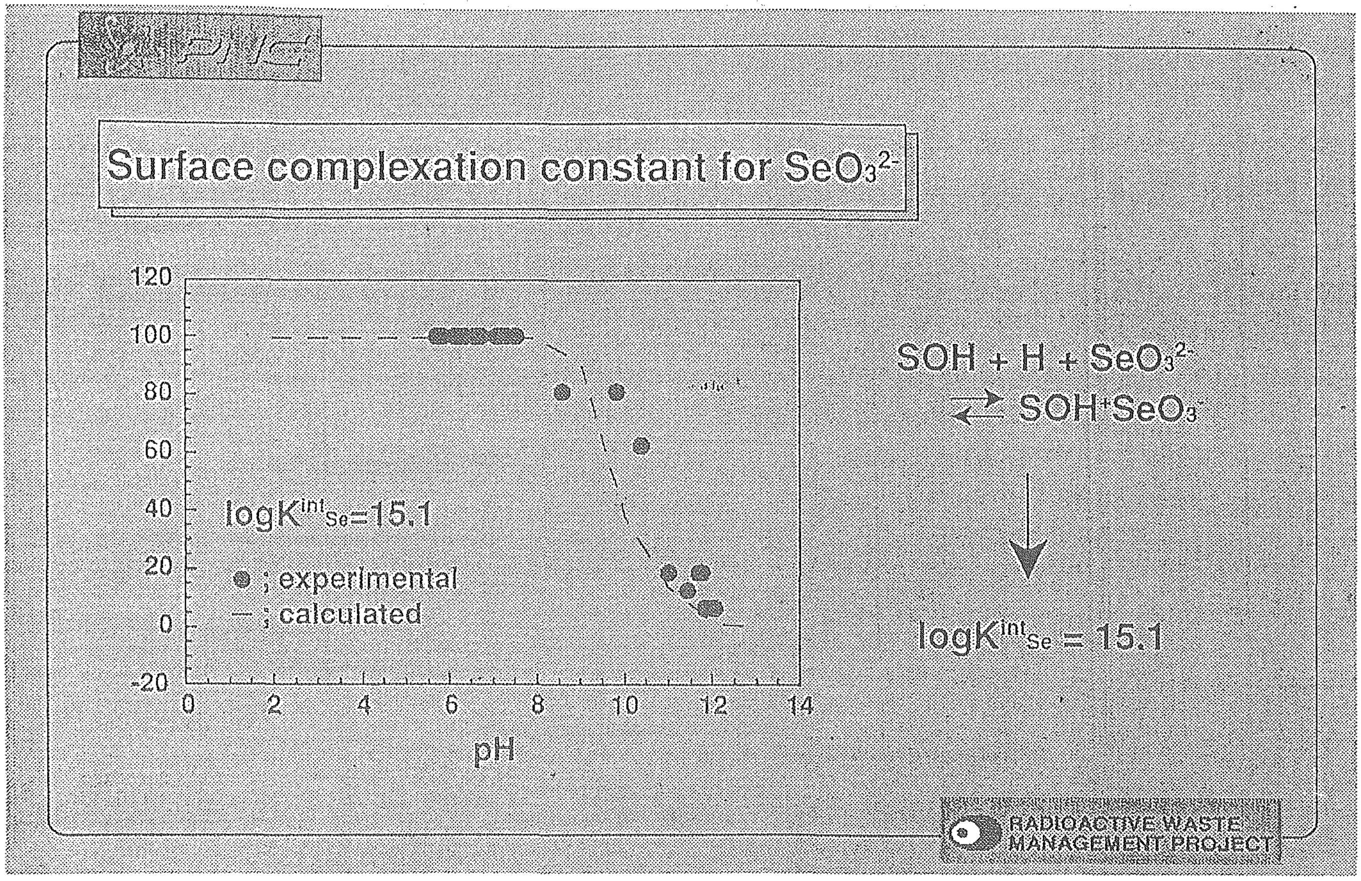
MANAGEMENT PROJECT

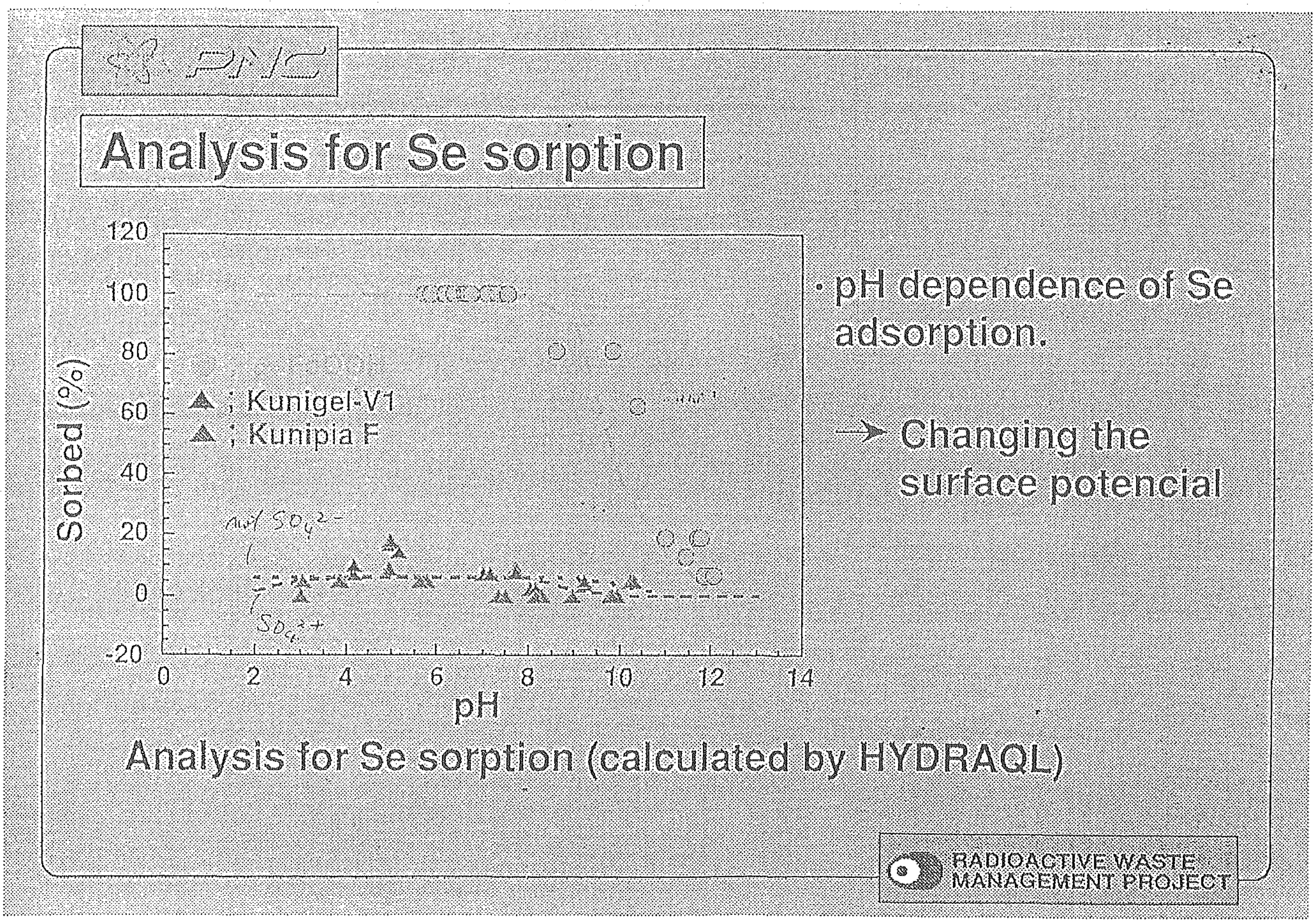


Surface complexation constant for SeO_3^{2-}

$$SOH + H + SeO_3^{2-} \rightleftarrows SOH^{+}SeO_3^{-}$$

$$\downarrow$$

$$\log K^{int}_{Se} = 15.1$$



Analysis for Se sorption

- pH dependence of Se adsorption.

→ Changing the surface potencial

Analysis for Se sorption (calculated by HYDRAQL)

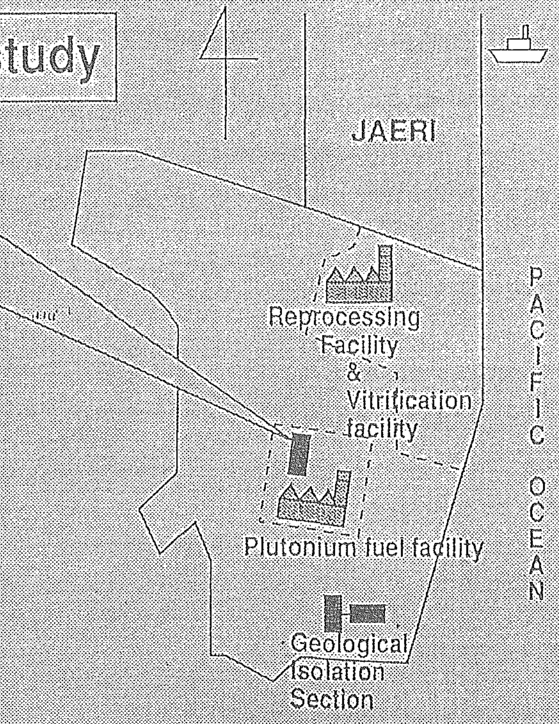
Discussion and conclusion

- Sorption behavior of Cs on bentonite were interpreted by using ion-exchange model.
  - ⟶ Dominant cation sorption mechanism
  - ⟹ Ion-exchange
- Sorption behavior of Se on bentonite were interpreted by using surface complexation model.
  - ⟶ Dominant anion sorption mechanism
  - ⟹ Surface complexation
- The Kd value from column method could be simulated by ion-exchange model for batch method.
  - ⟹ Kd of nuclides into compacted bentonite could be estimated from batch method.

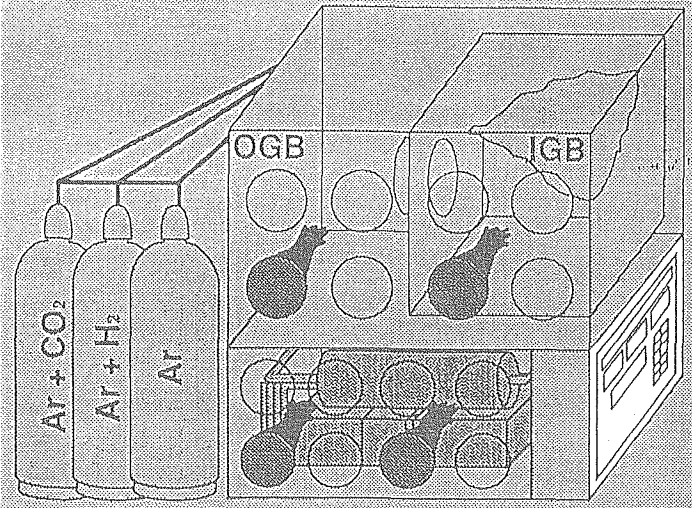
Equipment for plutonium study

Plutonium fuel facility
Room No.230 (for HLW isolation study)

- Atomospheric controlled glove box
  - - - - test run - - - -
- Glove box
  - Sorption experiment
  - Diffusion experiment
  - Solubility experiment
  - Leaching experiment
  - Vitrification experiment
- Open port box
  - Sample treatment



Main component of atmospheric controlled glove box



Upper Section (glove box)

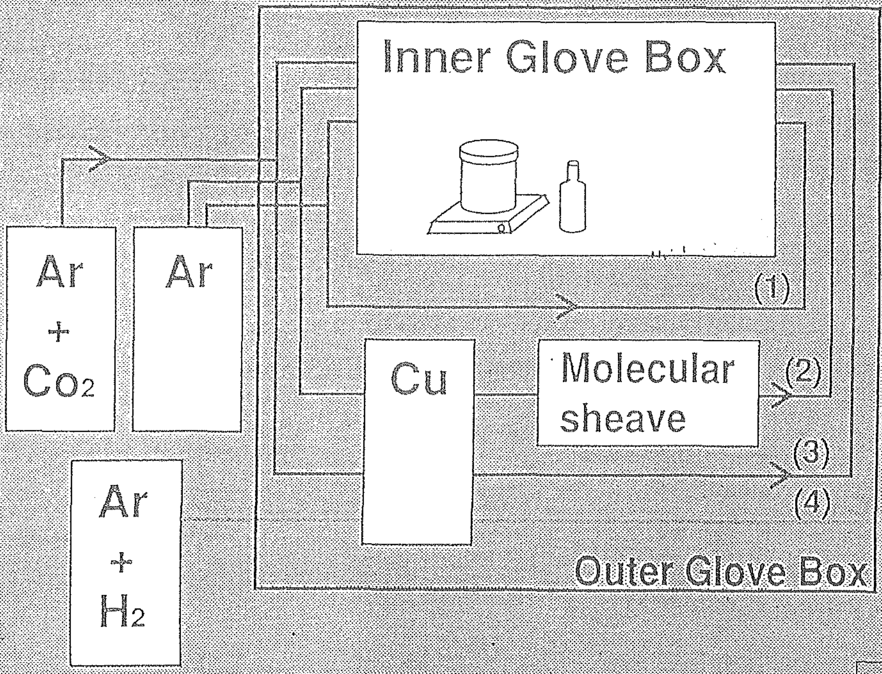
This equipment is composed with double glove box.

- Inner glove box
  Experimental area
  ⇒ Ar (O_2 < 1ppm)
  or Ar + CO_2
- Outer glove box
  Sample treatment area
  ⇒ Air

Lower Section (glove box)

- Atmospheric control system

Atmospheric controlled system



(1) Ar Purge Line

(2) O_2,CO_2,H_2O remove Line

(3) O_2 remove Line

(4) Regeneration Line

Characteristic of Atmospheric Controlled Glove box

- $O_2 < 1ppm$
- $CO_2 <$ controllable
- Total amount of Pu : 200mg
- Atmosphere : Ar

Future study

- Thermodynamic study for Pu oxide, hydroxide and carbonate.
- Migration study for Pu under reducing condition.
  — sorption and diffusion study —

Experimental and Analytical Methods for Solubility Measurement

H.MAKINO, S.SHIBUTANI, H.YOSHIKAWA, M.YUI

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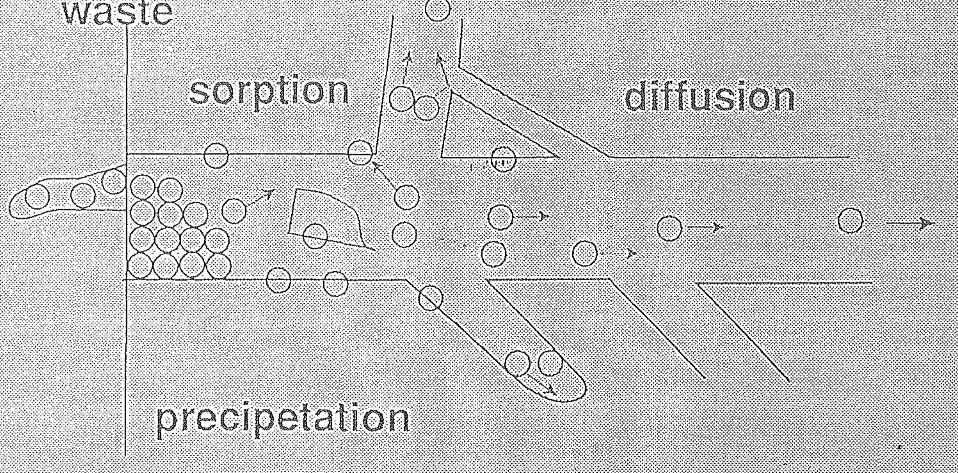
Reterdation



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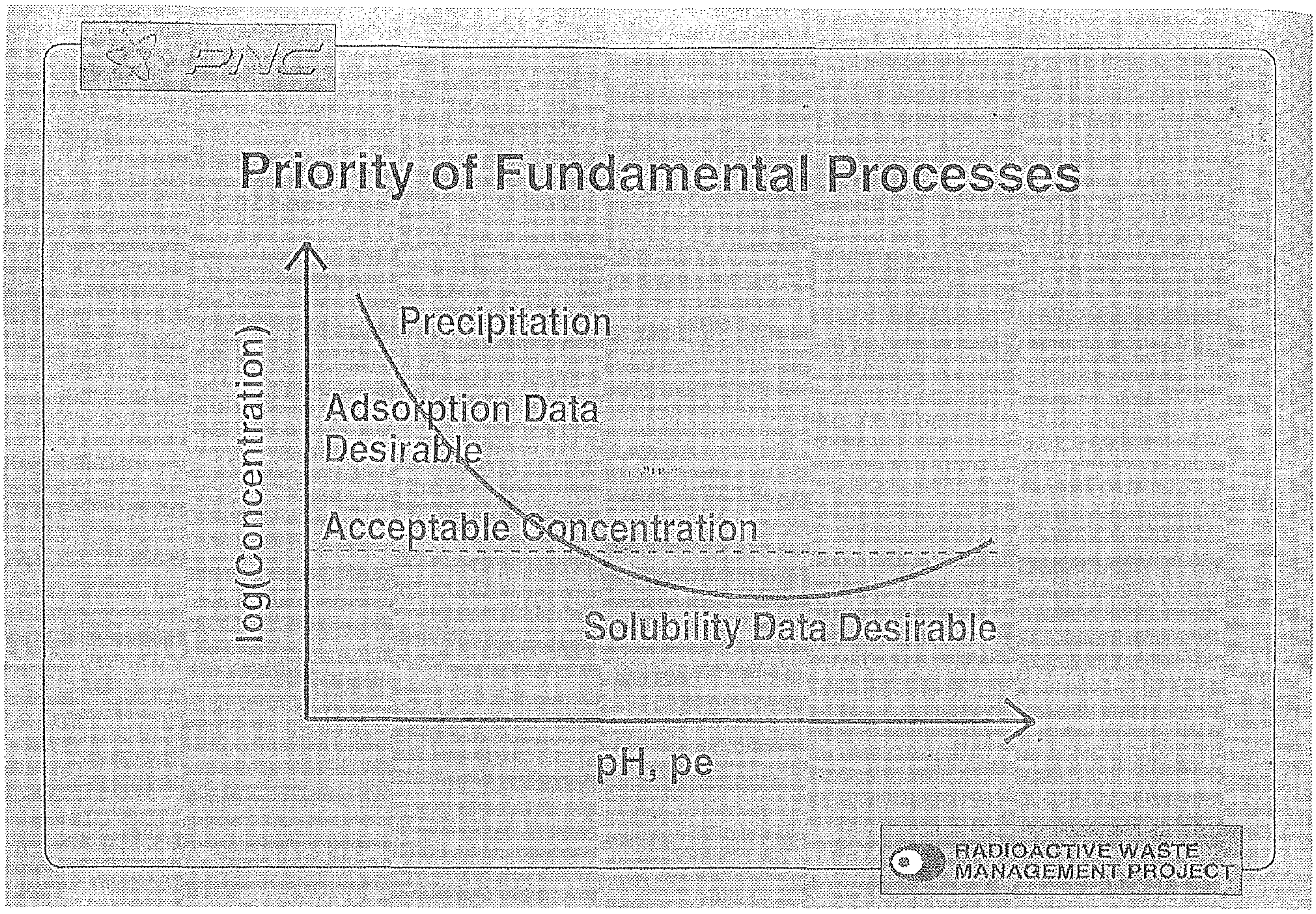

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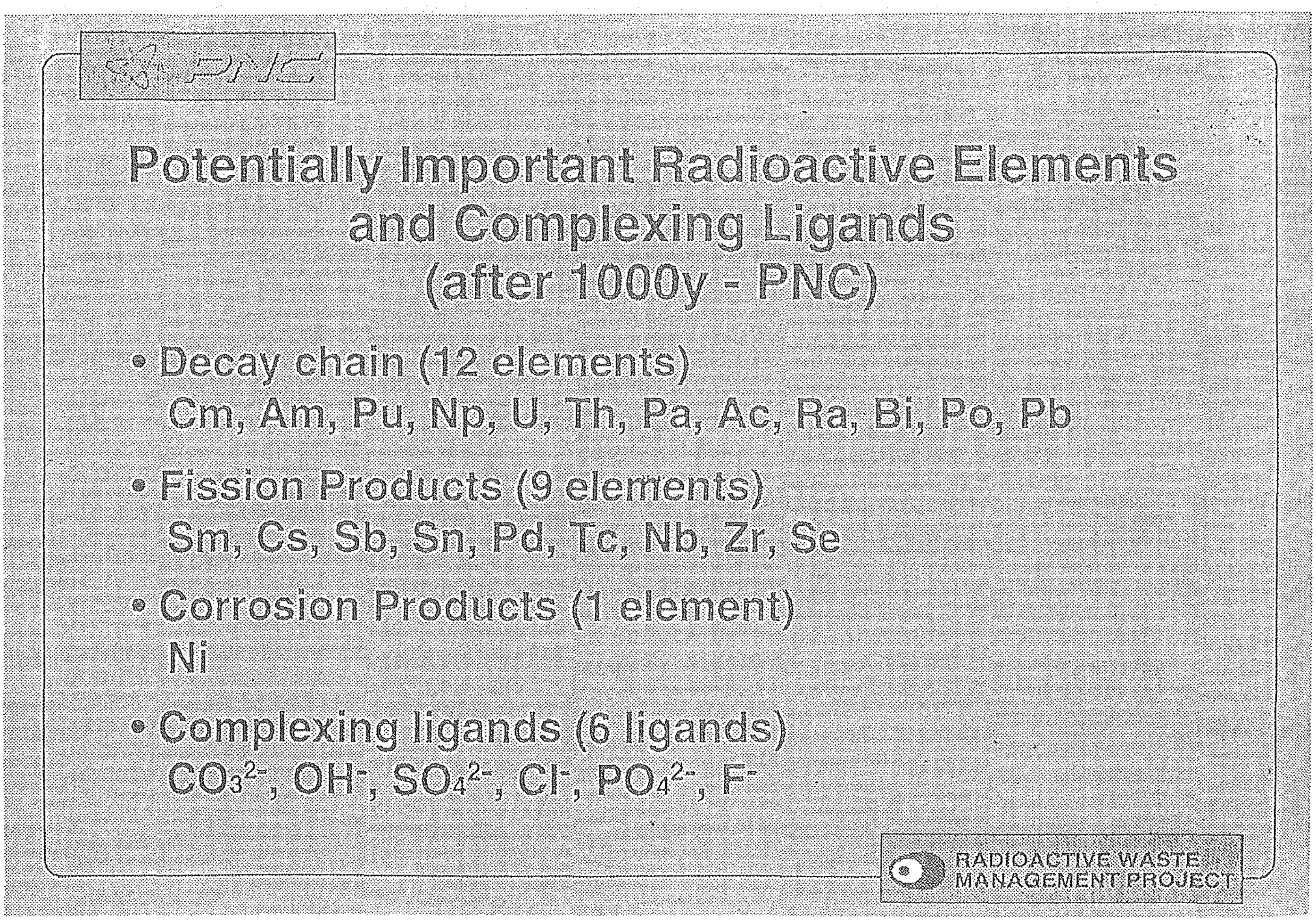
Priority of Fundamental Processes



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Potentially Important Radioactive Elements and Complexing Ligands
(after 1000y - PNC)

- Decay chain (12 elements)
  Cm, Am, Pu, Np, U, Th, Pa, Ac, Ra, Bi, Po, Pb
- Fission Products (9 elements)
  Sm, Cs, Sb, Sn, Pd, Tc, Nb, Zr, Se
- Corrosion Products (1 element)
  Ni
- Complexing ligands (6 ligands)
  CO_3^{2-}, OH^-, SO_4^{2-}, Cl^-, PO_4^{2-}, F^-

Reasons for Study

- Actinide elements (e.g.,Cm,Am,Pu) are important components of nuclear wastes.
- Some lantanide elements (e.g.,Nd) can be used as an analog for actinide elements and be expected dominant non-radioactive elements themselves.
- Accurate data for complexation constants with groundwater anions (e.g., CO_3^{2-},OH^-) and solubility products required to set upper limits on radionuclide concentrations.
- Data necessary for accurate performance assessment.

CALCULATED SOLUBILITY OF SOME IMPORTANT NUCLIDES

[mol/l]

Element	Solubility limiting solid	Fresh		Saline	
		FRHP	FRLP	SRHP	SRLP
Tc	$TcO_2 \cdot 2H_2O$	3.5E-8 $TcO(OH)_2$	3.4E-8 $TcO(OH)_2$	3.4E-8 $TcO(OH)_2$	3.4E-8 $TcO(OH)_2$
Np	NpO_2	2.0E-12 $Np(OH)_4$	2.0E-12 $Np(OH)_4$	1.7E-12 $Np(OH)_4$	1.8E-12 $Np(OH)_4$
Pu	PuO_2	2.5E-11 $Pu(CO_3)_3^{2-}$	5.3E-6 $Pu(CO_3)_4^{4-}$	6.4E-10 $Pu(CO_3)_3^{2-}$ $Pu(CO_3)_4^{4-}$	2.8E-7 $Pu(CO_3)_3^{2-}$
Am	$AmOHCO_3$	6.3E-8 $Am(CO_3)_3^{3-}$	3.1E-7 $AmCO_3^{+}$	6.3E-9 $Am(CO_3)_2^{-}$ $AmCO_3^{+}$	1.0E-7 $Am(CO_3)_3^{3-}$ $Am(CO_3)_2^{-}$
Se	$FeSe_2$	8.0E-7 HSe^-	6.0E-9 HSe^-	7.6E-9 HSe^-	6.9E-10 HSe^-

Solubility of TcO_2 is less than 1.0E-20 mol/l.

Syntheses and Solubility Measurement of Crystalline of Nd(Ⅲ) Ion.

1) Hydroxide
2) Hydroxocarbonate

OBJECTIVE

Develop and Verify thermodynamic data for dominant Am solid and aqueous phase reactions that are expected to occur in the repository environment using analogue of Np.

Chemical properties of Nd and Am.

M^{3+}	Nd	Am
electron configuration	$[Xe]\ 4f^{3}6S^{0}$	$[Rn]\ 5f^{6}7S^{0}$
effective ionic radii * [pm]		
CN6	98.3	97.5
CN8	110.9	109

Shannon.R.D. , Acta Cryst. A32, 751(1976)

Nd(Ⅲ) are chosen because of

- the similarity ionic radii of Am(Ⅲ) .
- the similarity chemical behavior of Am(Ⅲ) .

Validation of Am thermodynamic data .

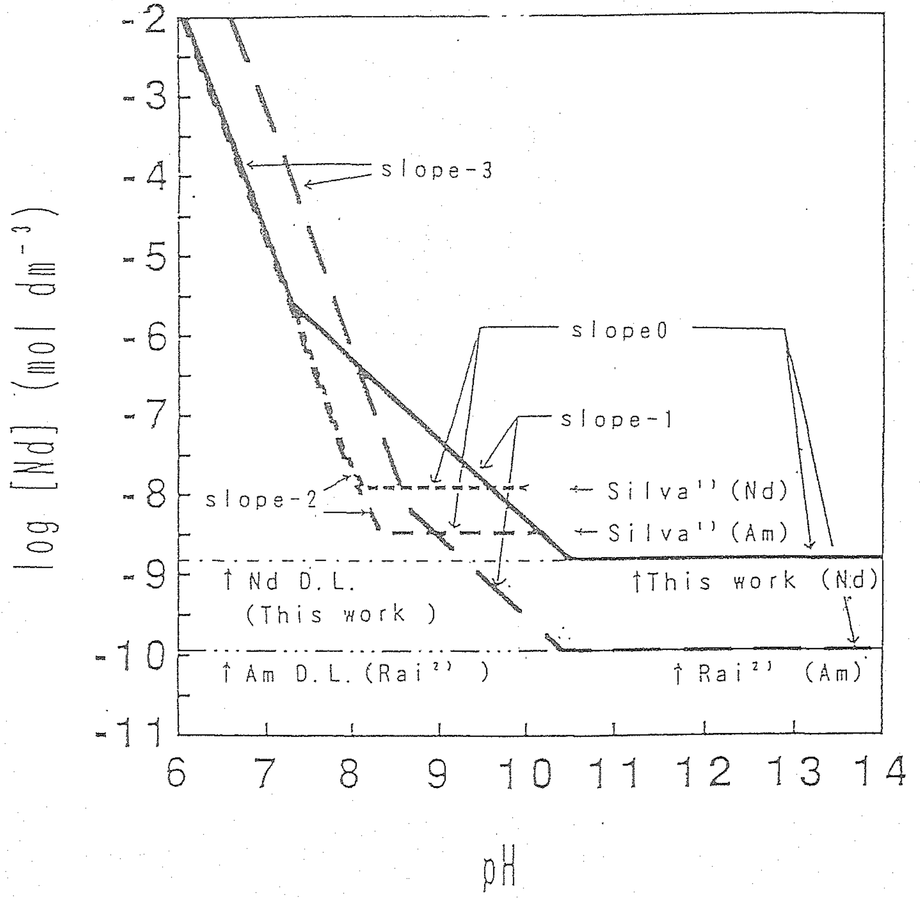
Dominant species of Nd(III) and Am(III) at different pH ranges

Dominant species	pH range of Nd	pH range of Am
M^{3+}	< 7.3	< 8.7
$[MOH]^{2+}$	———— *	———— *
$[M(OH)_2]^{+}$	7.3～10.5	8.7～10.4
$[M(OH)_3](aq)$	10.5 <	10.4 <

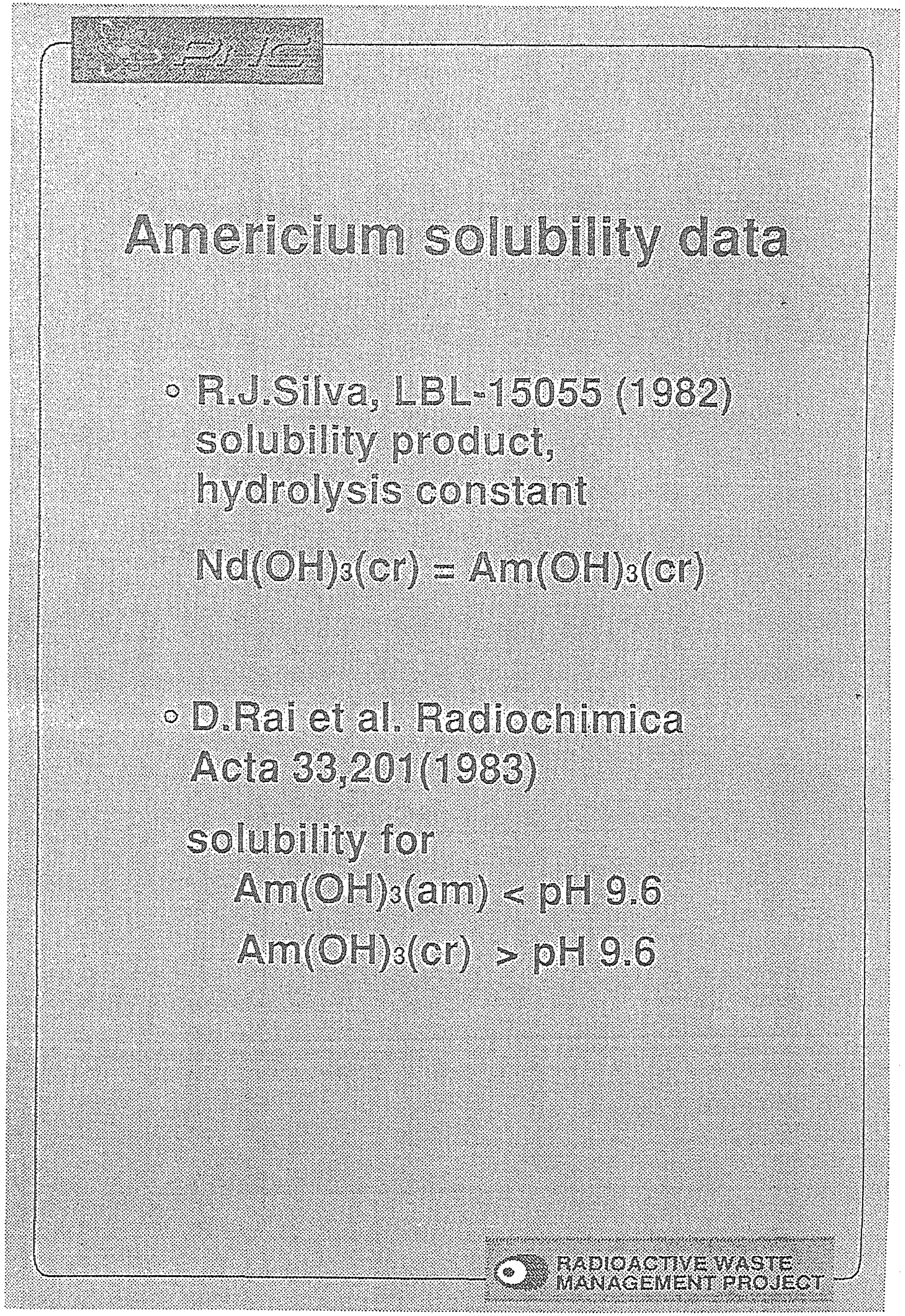
* : Not dominant

Syntheses and Solubility Measurement of Crystalline of Nd(Ⅲ) Ion.

1) Hydroxide
2) Hydroxocarbonate



Solubility of Nd(OH)$_3$(c) (this work) compared with data reported by Silva1) and Rai2) (D.L. : detection limit)



Americium solubility data

- R.J.Silva, LBL-15055 (1982)
  solubility product,
  hydrolysis constant

  Nd(OH)$_3$(cr) = Am(OH)$_3$(cr)

- D.Rai et al. Radiochimica Acta 33,201(1983)

  solubility for
  Am(OH)$_3$(am) < pH 9.6
  Am(OH)$_3$(cr) > pH 9.6

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The results of solubility experiments for $Am(OH)_3$

under pH9 by Silva and Rai are compared.

Silva data < *Rai data*
(cristalline) (amorphous)

above pH9

Rai data < Silva data
reportedly conducted equally for cristalline.

⇓

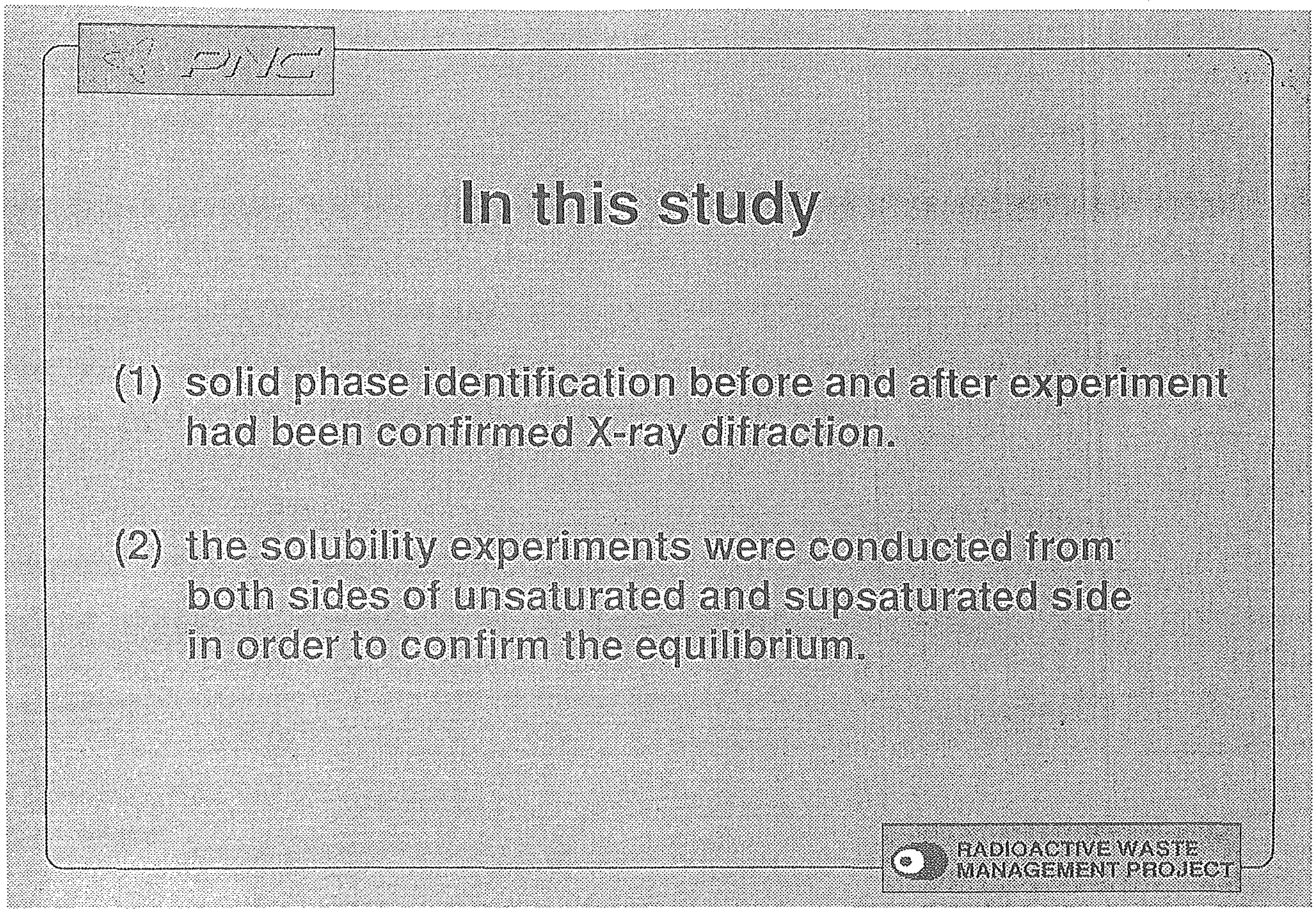
Why ?

Difference of the solid phase identification

- ◦Silva
  - SEM experimenting from the unsaturated side.
- ◦Rai
  - X-ray diffraction after the experiment from the supersaturated side.

⇓

Solid phase identification in a solubility experiment becomes a significant theme.



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In this study

(1) solid phase identification before and after experiment had been confirmed X-ray difraction.

(2) the solubility experiments were conducted from both sides of unsaturated and supsaturated side in order to confirm the equilibrium.

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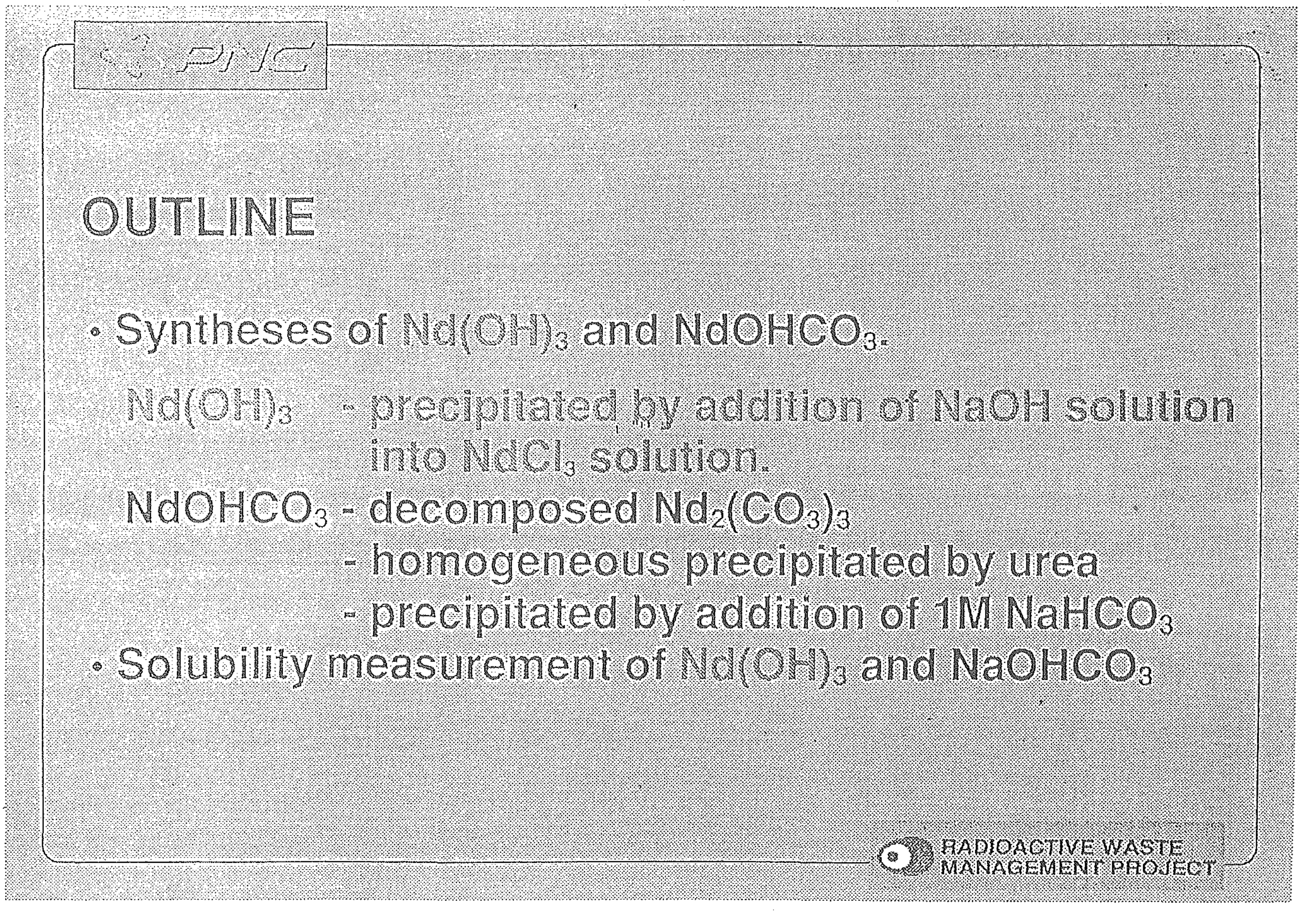

PNC

OUTLINE

- Syntheses of $Nd(OH)_3$ and $NdOHCO_3$.

  $Nd(OH)_3$ - precipitated by addition of NaOH solution into $NdCl_3$ solution.
  $NdOHCO_3$ - decomposed $Nd_2(CO_3)_3$
  - homogeneous precipitated by urea
  - precipitated by addition of 1M $NaHCO_3$
- Solubility measurement of $Nd(OH)_3$ and $NaOHCO_3$

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Experimental Condition

Atmoshere : < 0.01ppm CO_2

< 1ppm O_2

in order to prevent formation of carbonate

Water : distilled twice

removed of dissolved CO_2

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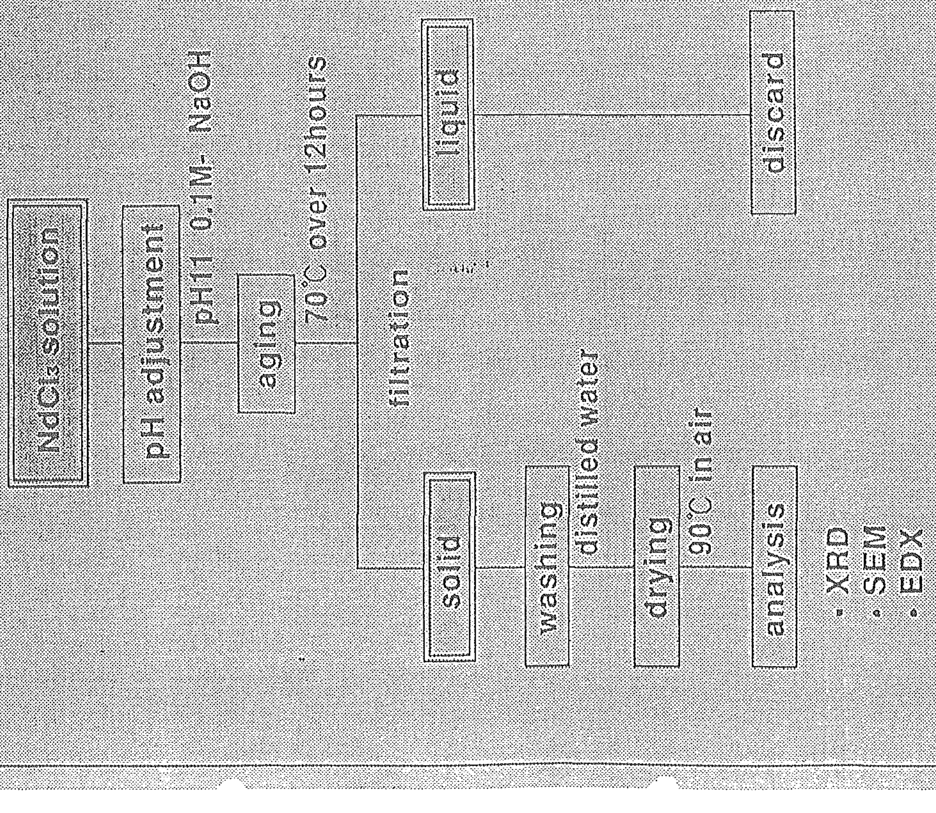
MANAGEMENT PROJECT

Scheme of Production of $Nd(OH)_3$



$NdCl_3$ solution

pH adjustment

pH11 0.1M- NaOH

aging

70°C over 12hours

filtration

liquid

discard

solid

washing

distilled water

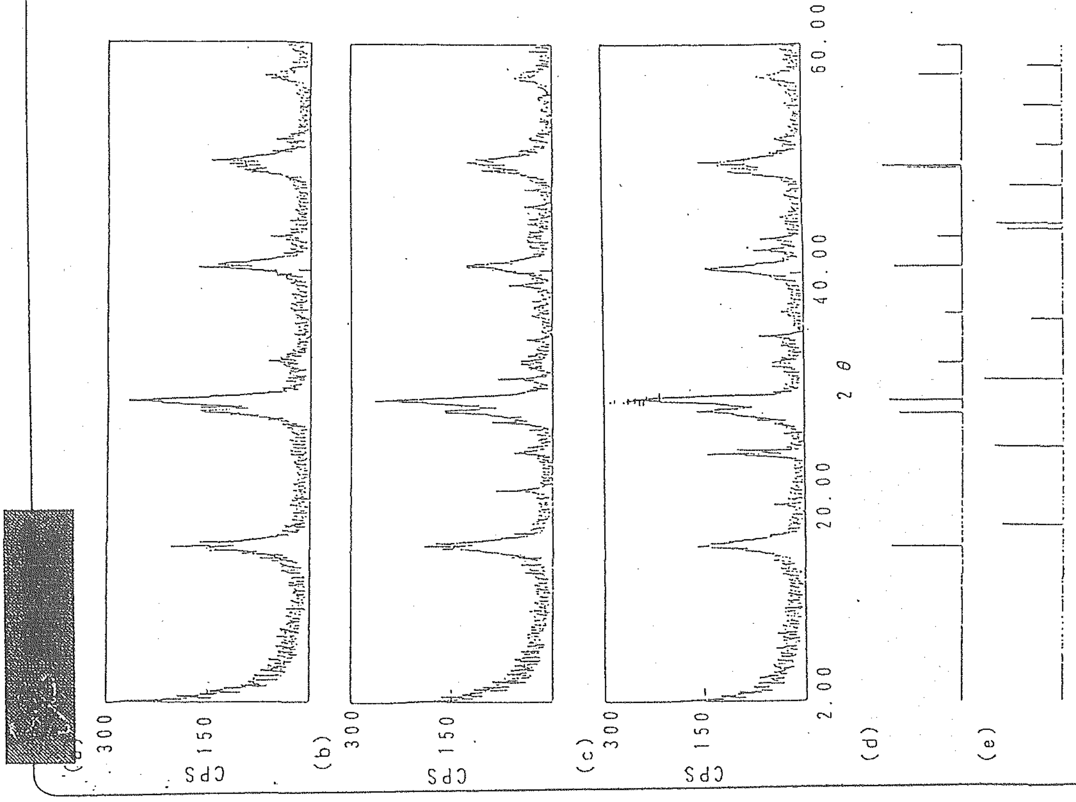
drying

90°C in air

analysis

- XRD
- SEM
- EDX

RADIOACTIVE WASTE
MANAGEMENT PROJECT



(X-ray diffraction patterns
(a): Before experiment, (b): After experiment (initial pH 7.0 and aged for 48 days), (c): After experiment (initial pH 13.0 and aged for 48days), (d): Diffraction pattern of Nd(OH),(c)'' (e): Diffraction pattern of Nd(OH)CO,(c)'')

RADIOACTIVE WASTE MANAGEMENT PROJECT

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Analytical Approach

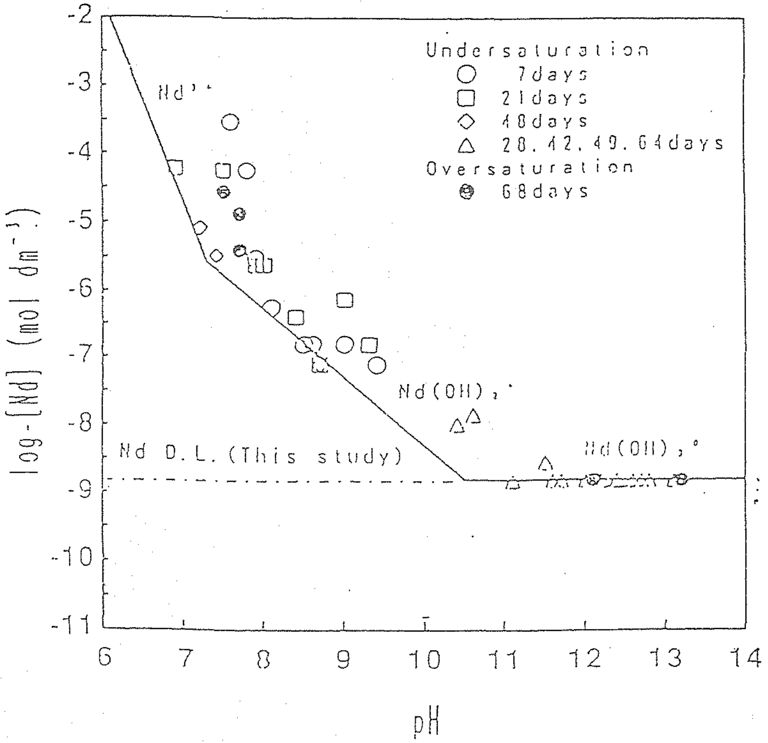
Solid phase

- Crystallinity
  - XRD : X-ray powder diffraction.
  - SEM : Scanning electron microscope.
- Elementary
  - DTA : Differential thermoanalysis
  - FT-IR : Fourier transformation infrared spectroscopy.

Liquid phase

- total concentration
  - ICP-MS : Inductively coupled plasma mass analysis.

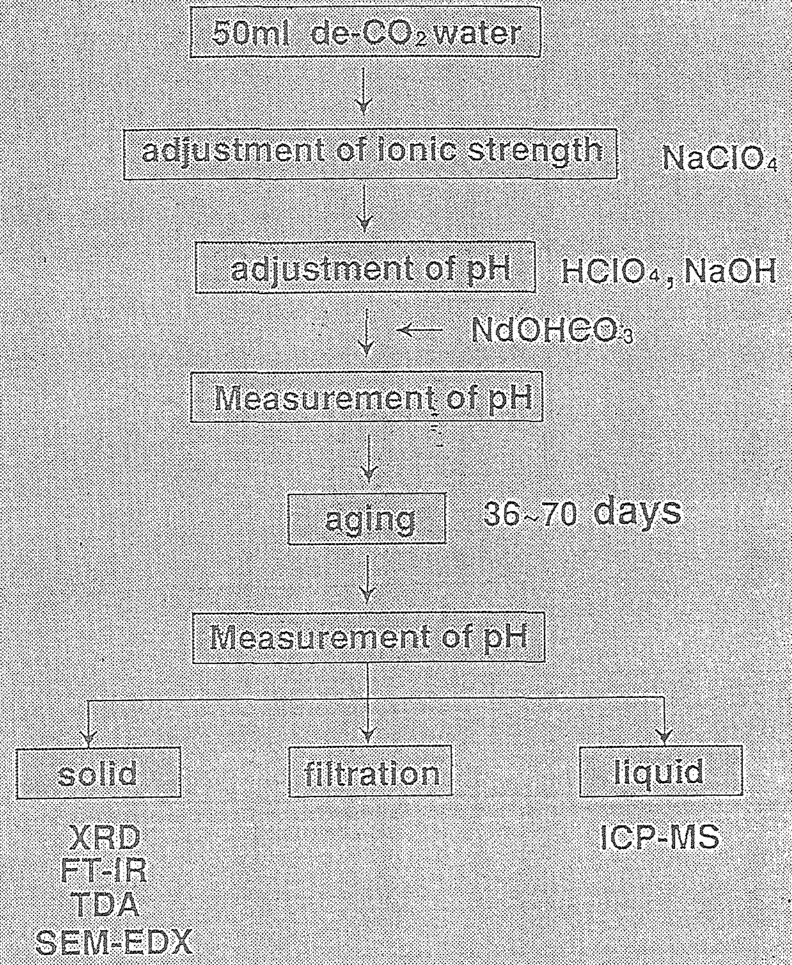
RADIOACTIVE WASTE MANAGEMENT PROJECT



Experimental data for solubility of $Nd(OH)_3(c)$ in 0.01 mol dm^{-3} $NaClO_4$ at 22 °C

D. L.: detection limit

Measurement of Solubility
(from the unsaturated side)



50ml de-CO_2 water

↓

adjustment of ionic strength — $NaClO_4$

↓

adjustment of pH — $HClO_4$, $NaOH$

↓ ← $NdOHCO_3$

Measurement of pH

↓

aging — 36~70 days

↓

Measurement of pH

↓

solid — filtration — liquid

XRD
FT-IR
TDA
SEM-EDX

ICP-MS

Hydrolysis reaction of Nd(III)

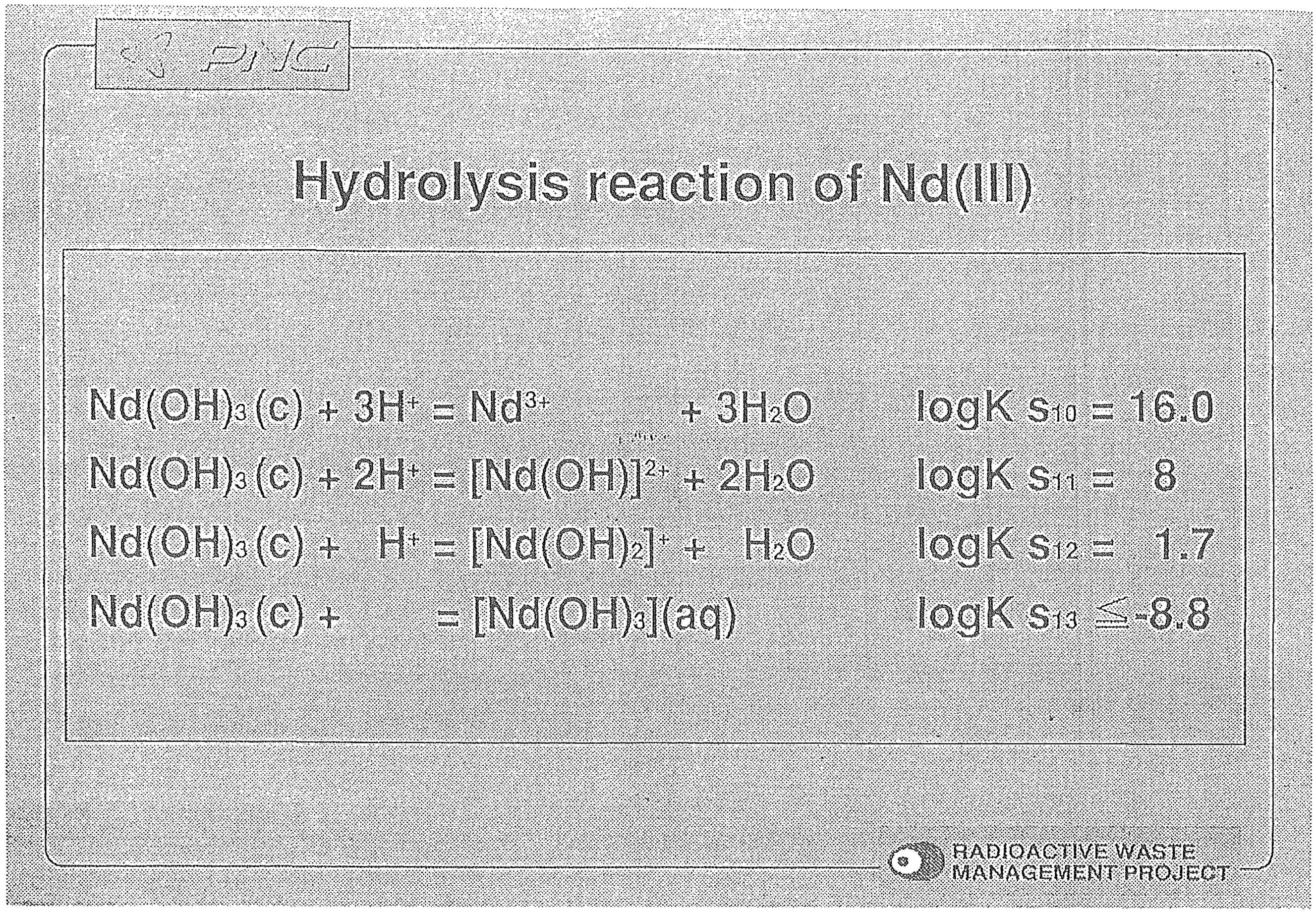
$Nd(OH)_3(c) + 3H^+ = Nd^{3+} + 3H_2O$	$\log K_{s10}$
$Nd(OH)_3(c) + 2H^+ = [Nd(OH)]^{2+} + 2H_2O$	$\log K_{s11}$
$Nd(OH)_3(c) + H^+ = [Nd(OH)_2]^+ + H_2O$	$\log K_{s12}$
$Nd(OH)_3(c) + \quad = [Nd(OH)_3](aq)$	$\log K_{s13}$

Observed Nd concentration

$$m_{Nd}=Nd^{3+}+[Nd(OH)]^{2+}+[Nd(OH)_2]^{+}+[Nd(OH)_3]_{(aq)}$$

$$=\frac{K_{S10}}{\gamma_1}\underbrace{\gamma_{H^+}{}^3 m_{H^+}{}^3}_{X^3}+\frac{K_{S11}}{\gamma_2}\underbrace{\gamma_{H^+}{}^2 m_{H^+}{}^2}_{X^2}+\frac{K_{S12}}{\gamma_3}\underbrace{\gamma_{H^+} m_{H^+}}_{X}+\frac{K_{S13}}{\gamma_4}$$

γ_1=activity of Nd^{3+}
γ_2=activity of $[Nd(OH)]^{2+}$
γ_3=activity of $[Nd(OH)_2]^+$
γ_4=activity of $[Nd(OH)_3]_{(aq)}$ (=1)
γ_{H^+}=activity of H^+
m_{H^+}=concentration of H^+ ($=10^{-PH}/\gamma_{H^+}$)



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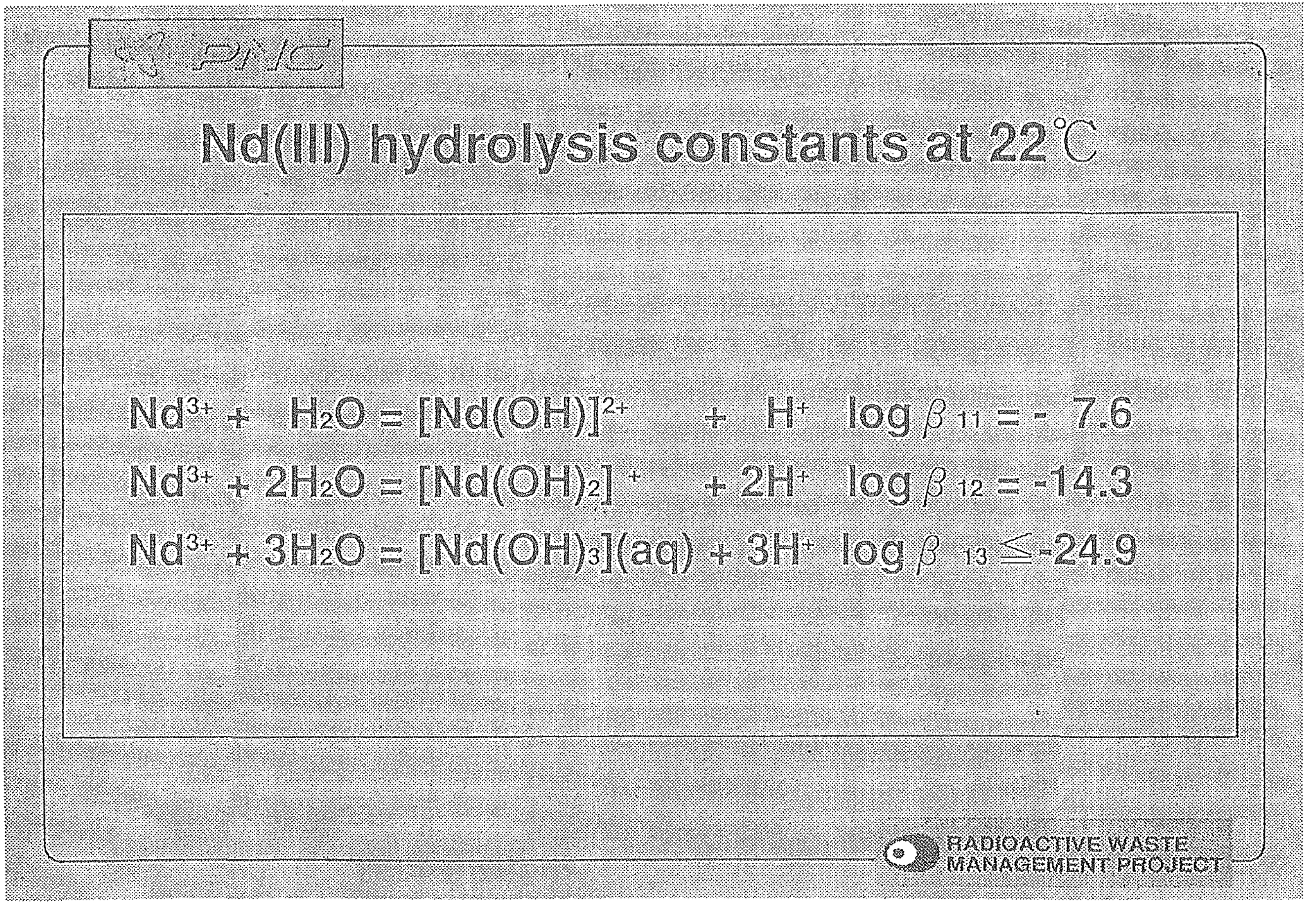
Hydrolysis reaction of Nd(III)

$\mathrm{Nd(OH)_3(c) + 3H^+ = Nd^{3+} + 3H_2O}$ $\log K_{s10} = 16.0$

$\mathrm{Nd(OH)_3(c) + 2H^+ = [Nd(OH)]^{2+} + 2H_2O}$ $\log K_{s11} = 8$

$\mathrm{Nd(OH)_3(c) + H^+ = [Nd(OH)_2]^+ + H_2O}$ $\log K_{s12} = 1.7$

$\mathrm{Nd(OH)_3(c) + \; = [Nd(OH)_3](aq)}$ $\log K_{s13} \leqq -8.8$



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Nd(III) hydrolysis constants at 22℃

$\mathrm{Nd^{3+} + H_2O = [Nd(OH)]^{2+} + H^+}$ $\log \beta_{11} = -7.6$

$\mathrm{Nd^{3+} + 2H_2O = [Nd(OH)_2]^+ + 2H^+}$ $\log \beta_{12} = -14.3$

$\mathrm{Nd^{3+} + 3H_2O = [Nd(OH)_3](aq) + 3H^+}$ $\log \beta_{13} \leqq -24.9$

Comparison of the hydrolysis constants of Nd(III) and Am(III)

	Nd(III)		Am(III)	
	This work (A)	Silva[1)] (A)	Silva[1)] (B)	Rai[2)] (C)
log β_{11}	-7.6	-7.7[8)]	-7.7[8)]	≦ -8.2
log β_{12}	-14.3	-16.0	-16.0	-17.1
log β_{13}	< -24.9	-23.9	-24.3	≦ -27.0
log β_{14}	———	< -35	< -36	———
logK_{s10}	16.0	16.0	15.9	17.5

(A) : $Nd(OH)_3$ (c) , (B) : $Am(OH)_3$ (c) , (C) : $Am(OH)_3$ (am)

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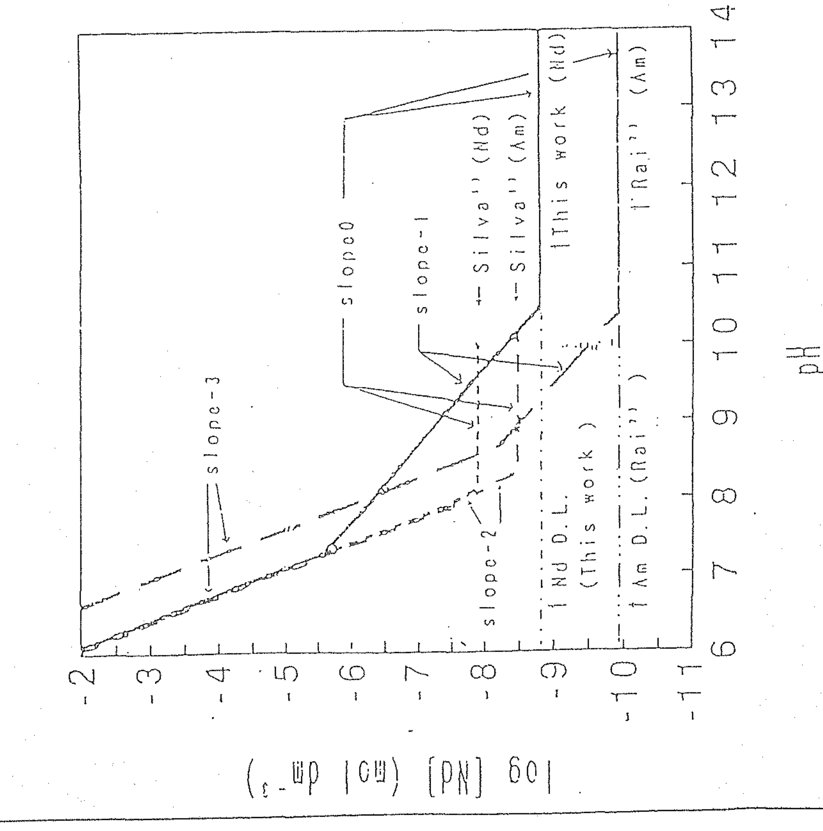


Solubility of $Nd(OH)_3$(c)(this work) compared with data reported by Silva[1)] and Rai[2)]

D.L.: detection limit

RADIOACTIVE WASTE MANAGEMENT PROJECT

Conclusion

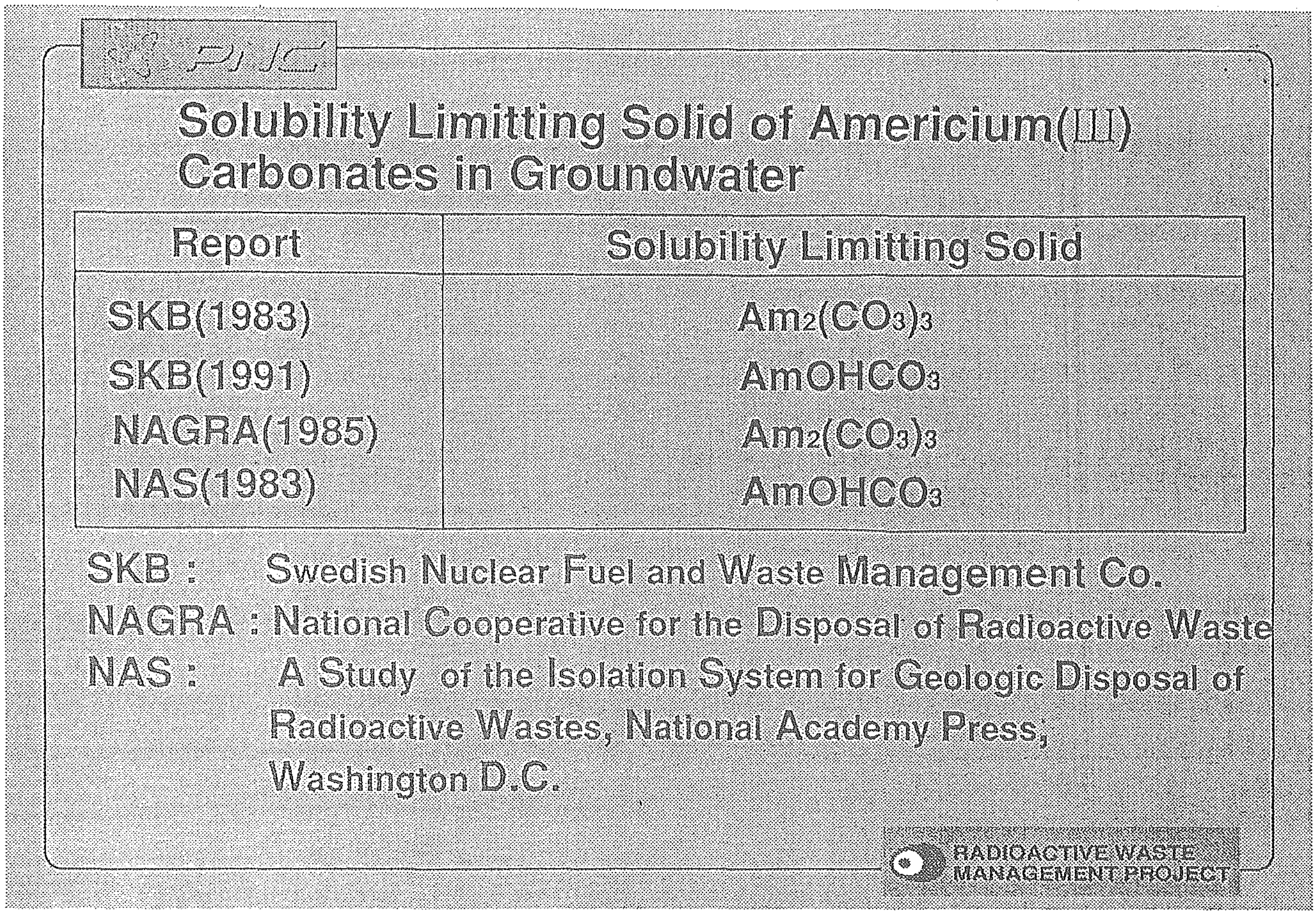
- Solubility experiments of crystalline neodymium hydroxide were conducted.

- There were no change of solid phases between before and after the experiment by the confirmation with X-ray diffraction and SEM.

- The solubility product ($\log K_{s10} = 16.0$) and hydrolysis equilibrium constants ($\log \beta_{11} \sim \log \beta_{13} = -7.6, -14.3, < -24.9$) of $Nd(OH)_3(cr)$ were determined.

Syntheses and Solubility Measurement of Crystalline of Nd(Ⅲ) Ion.

1) Hydroxide
2) Hydroxocarbonate

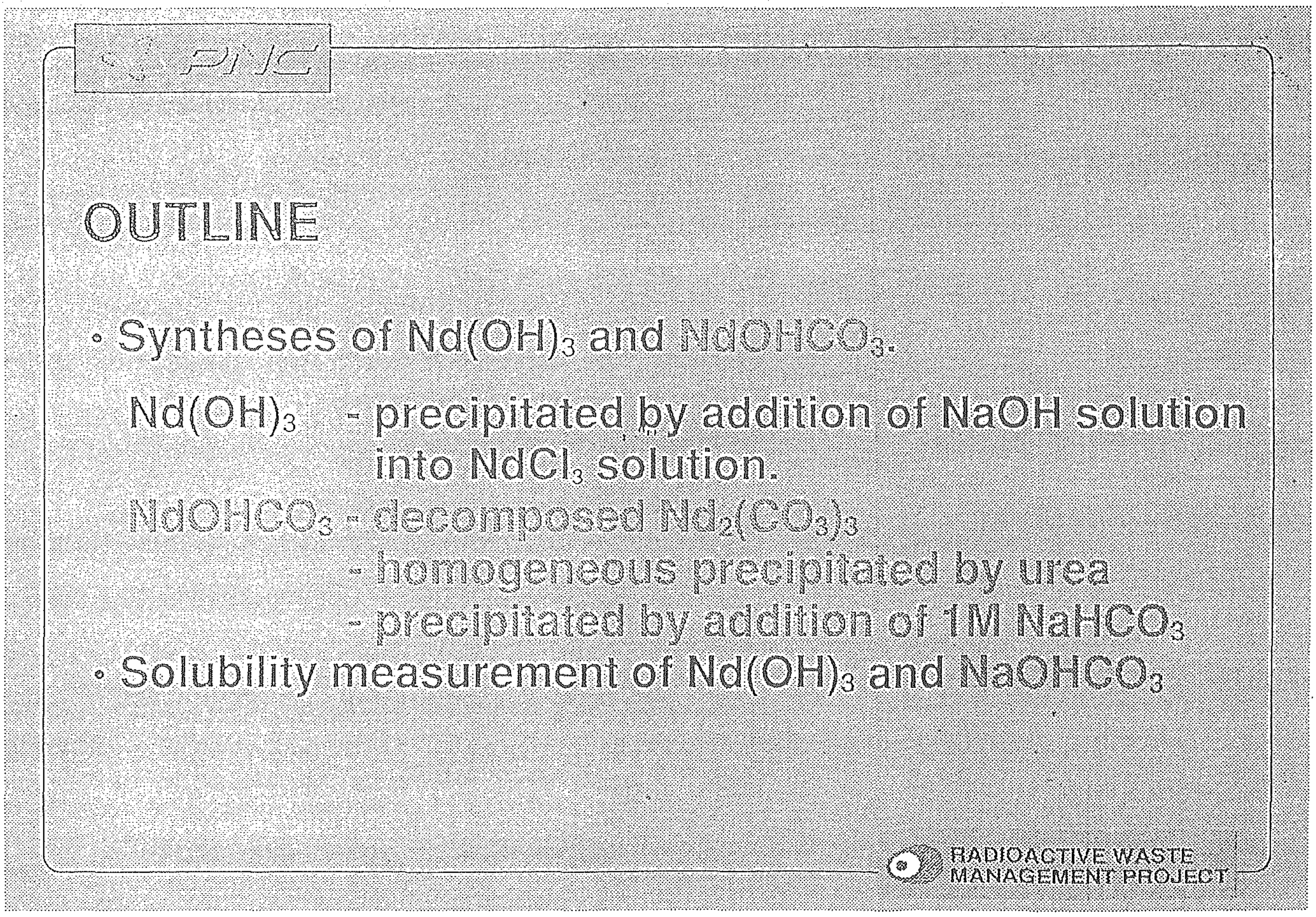


Solubility Limitting Solid of Americium(Ⅲ) Carbonates in Groundwater

Report	Solubility Limitting Solid
SKB(1983)	$Am_2(CO_3)_3$
SKB(1991)	$AmOHCO_3$
NAGRA(1985)	$Am_2(CO_3)_3$
NAS(1983)	$AmOHCO_3$

SKB : Swedish Nuclear Fuel and Waste Management Co.
NAGRA : National Cooperative for the Disposal of Radioactive Waste
NAS : A Study of the Isolation System for Geologic Disposal of Radioactive Wastes, National Academy Press; Washington D.C.

RADIOACTIVE WASTE MANAGEMENT PROJECT



OUTLINE

- Syntheses of $Nd(OH)_3$ and $NdOHCO_3$.

  $Nd(OH)_3$ - precipitated by addition of NaOH solution into $NdCl_3$ solution.

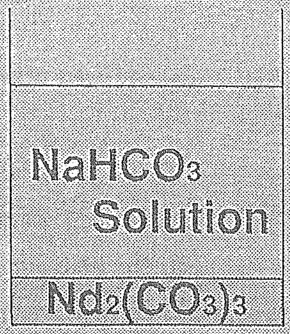
  $NdOHCO_3$ - decomposed $Nd_2(CO_3)_3$
  - homogeneous precipitated by urea
  - precipitated by addition of 1M $NaHCO_3$
- Solubility measurement of $Nd(OH)_3$ and $NaOHCO_3$

RADIOACTIVE WASTE MANAGEMENT PROJECT

SYNTHESIS $NdOHCO_3(C)$ - decomposed $Nd_2(CO_3)_3$

- Used by Rai and Kim in solubility measurement of $AmOHCO_3$.

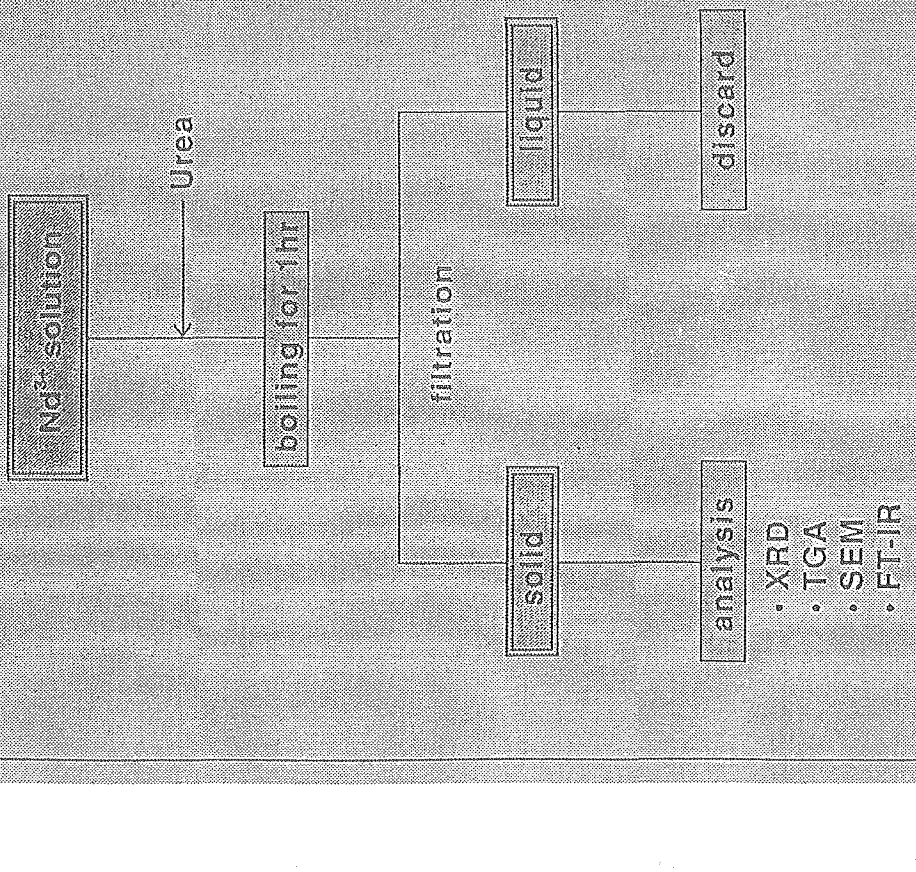
Aging $Nd_2(CO_3)_3$ in $NaHCO_3$ solution to transform into $NdOHCO_3$.



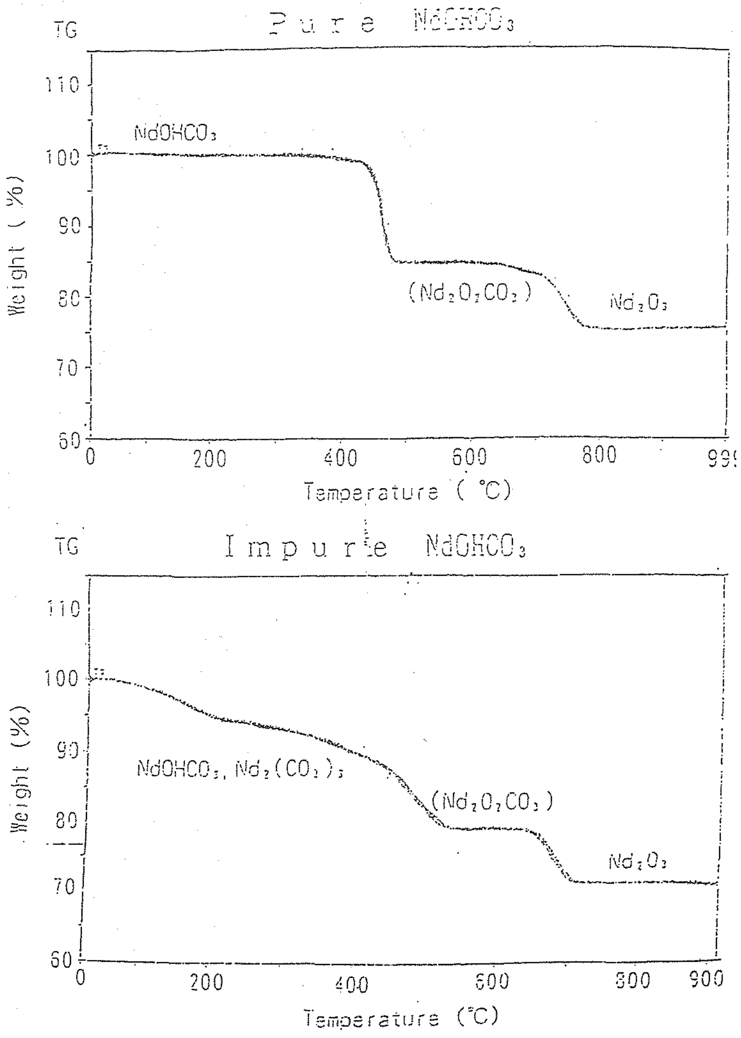
$$Nd_2(CO_3)_3 + H_2O \rightarrow 2NdOHCO_3 + CO_2$$

Aging for 2 months

Synthesis $NdOHCO_{3(cr)}$ by Homogeneous Preparation

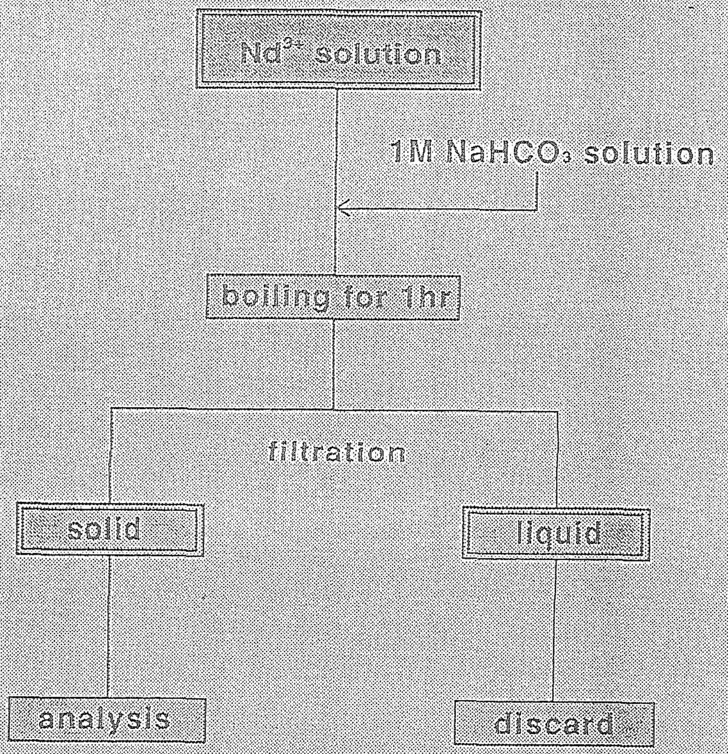


- XRD
- TGA
- SEM
- FT-IR



Thermal Decomposition of Products

Synthesis $NdOHCO_{3(cr)}$ precipitated by addition of $1M NaHCO_3$



- XRD
- TGA
- SEM
- FT-IR

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Comparison with 3 method for $NdOHCO_3$ Synthesis

	Transformation	Urea Hydrolysis	Adding $NaHCO_3$ Solution
Cristallinity	○	○	○
Vield	—	20 %	30 %
Reproducibility	×	○	○
Time for Synthesis	about 2 manths	3 hours	2 hours

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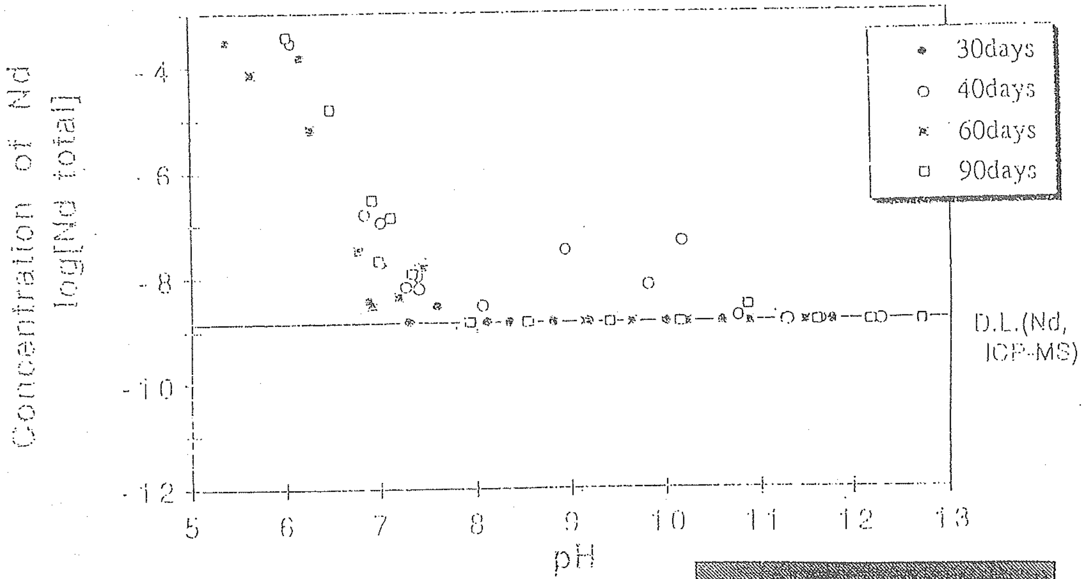
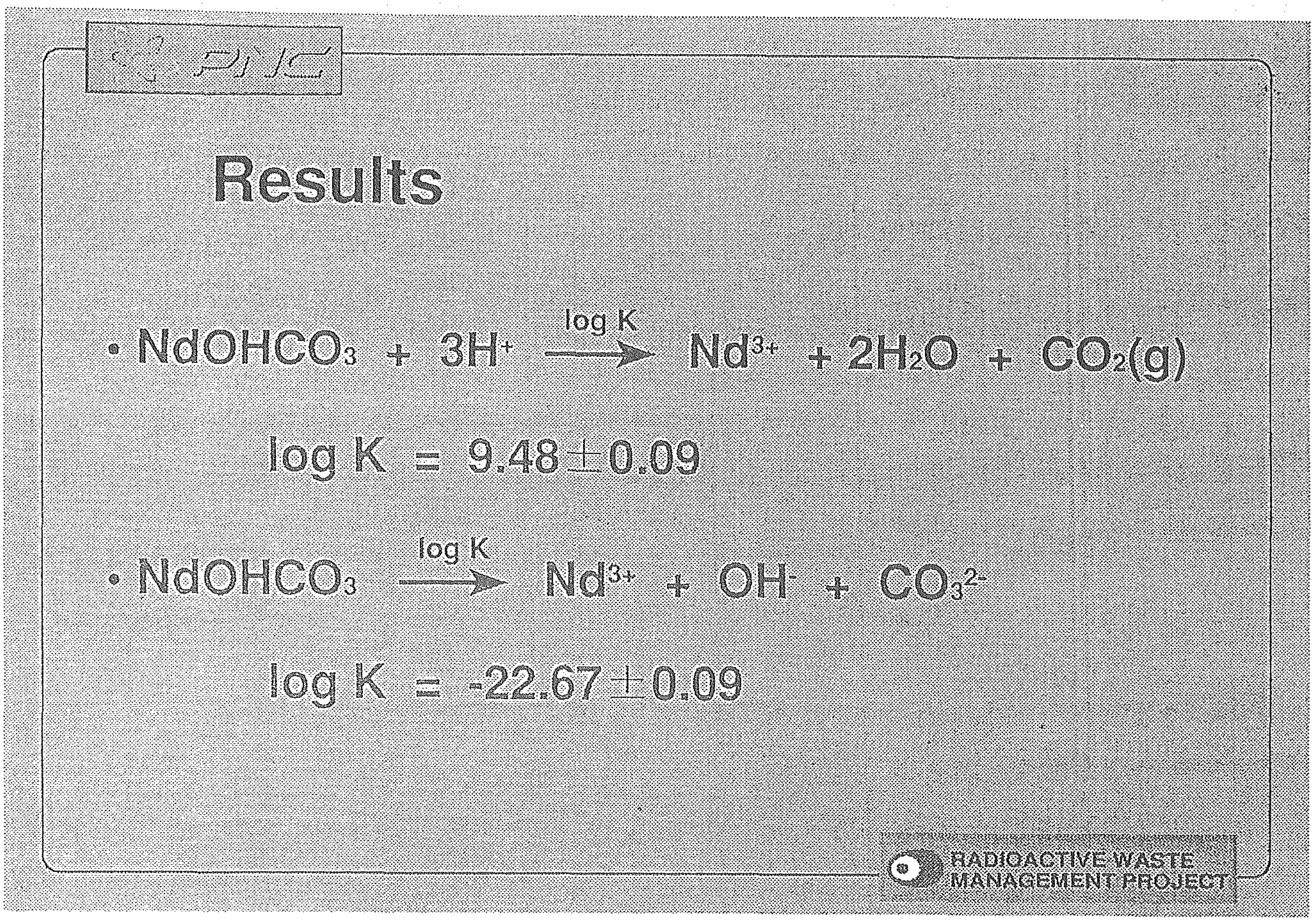
Experimental Results on Solubility of NdOHCO3(c) (undersaturation,Pco2=0.5ppm,25 ℃)



RADIOACTIVE WASTE MANAGEMENT PROJECT



Results

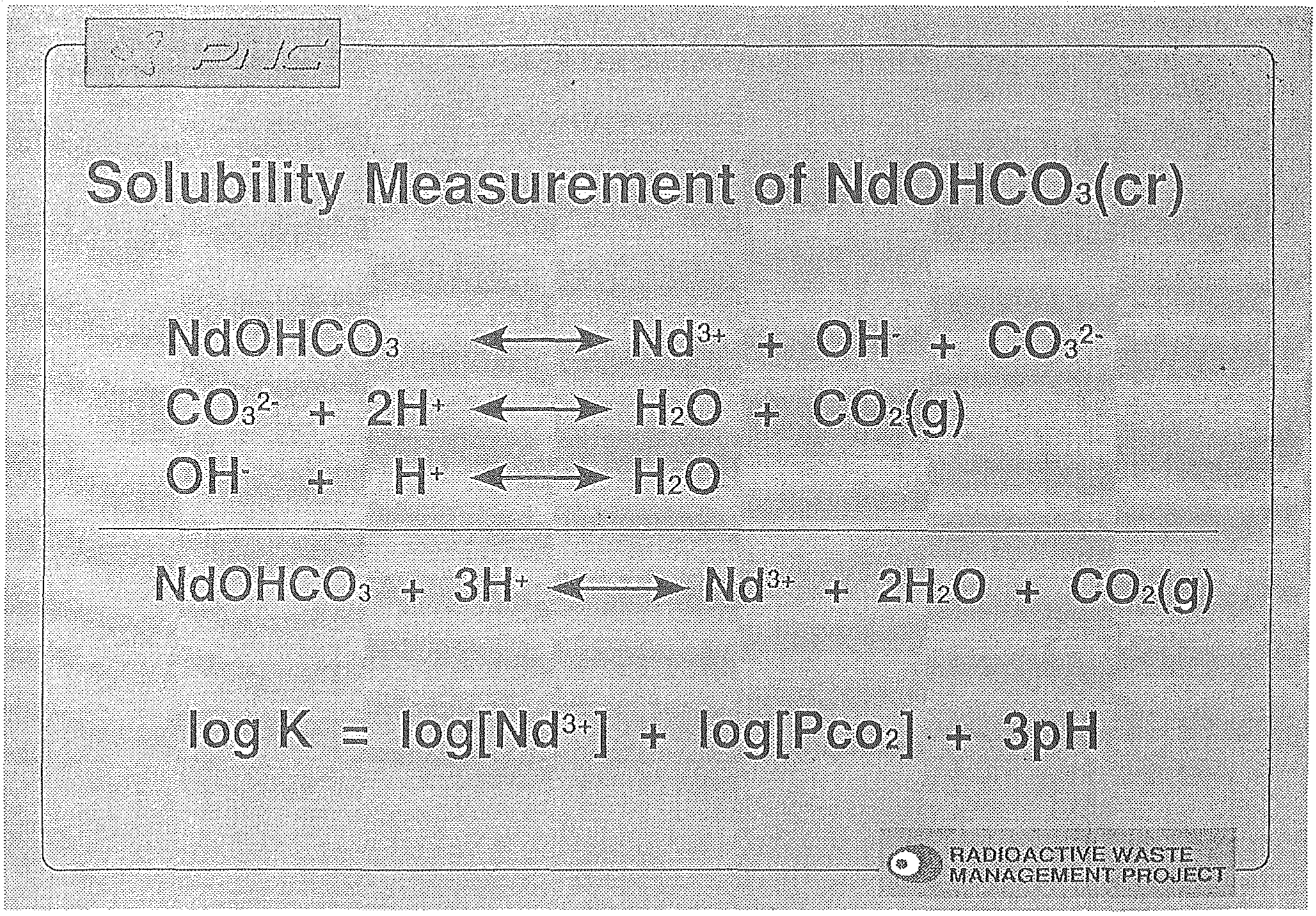
- $NdOHCO_3 + 3H^+ \xrightarrow{\log K} Nd^{3+} + 2H_2O + CO_2(g)$

  $\log K = 9.48 \pm 0.09$

- $NdOHCO_3 \xrightarrow{\log K} Nd^{3+} + OH^- + CO_3^{2-}$

  $\log K = -22.67 \pm 0.09$

RADIOACTIVE WASTE MANAGEMENT PROJECT



Solubility Measurement of $NdOHCO_3(cr)$

$$NdOHCO_3 \longleftrightarrow Nd^{3+} + OH^- + CO_3^{2-}$$
$$CO_3^{2-} + 2H^+ \longleftrightarrow H_2O + CO_2(g)$$
$$OH^- + H^+ \longleftrightarrow H_2O$$

$$NdOHCO_3 + 3H^+ \longleftrightarrow Nd^{3+} + 2H_2O + CO_2(g)$$

$$\log K = \log[Nd^{3+}] + \log[P_{CO_2}] + 3pH$$

RADIOACTIVE WASTE MANAGEMENT PROJECT

Conclusion

$pH < 7.4$ Ionic Strength $I=0.1$

$NdOHCO_3 = Nd^{3+} + OH^- + CO_3^{2-}$

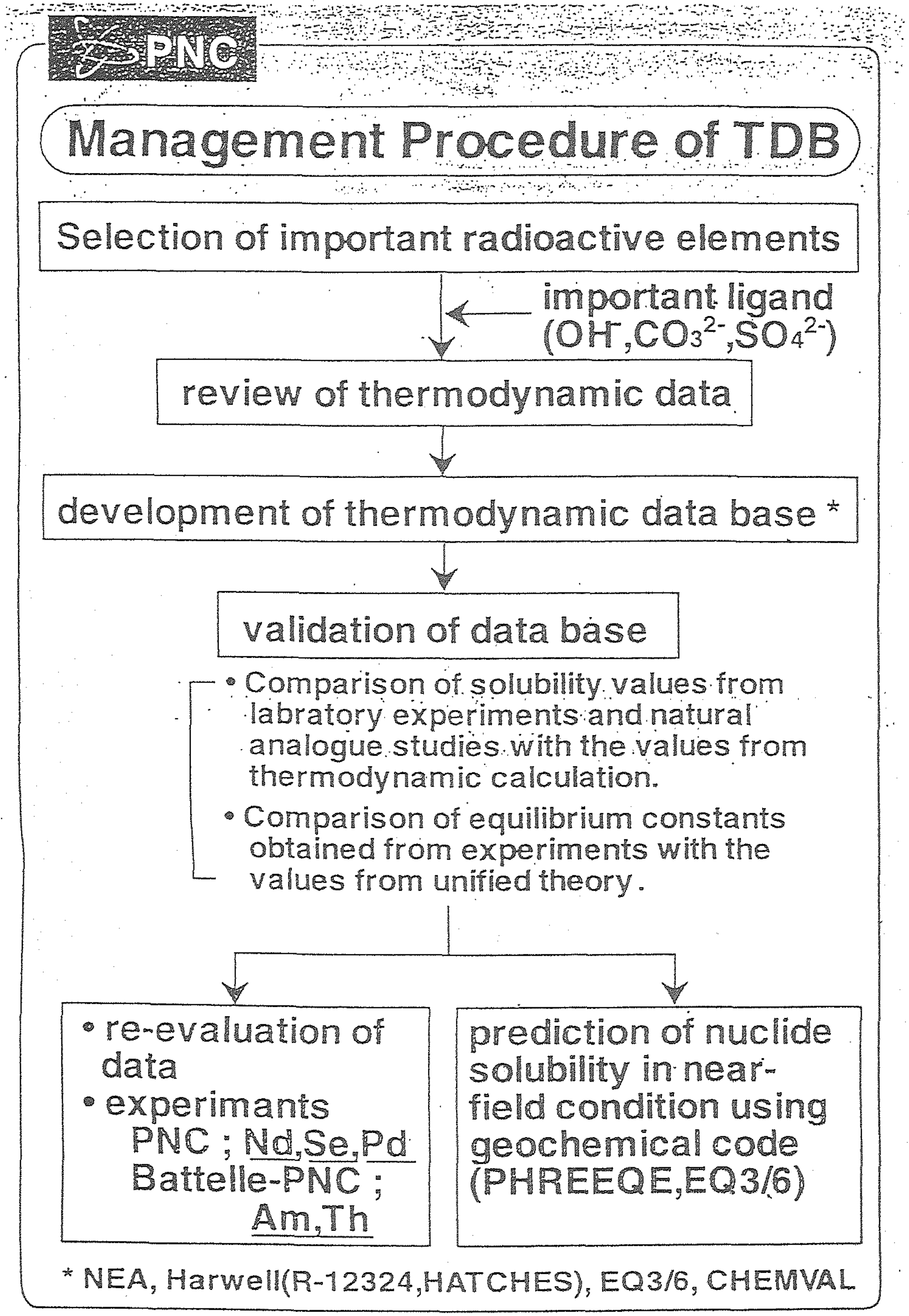
	PNC	Rai	Kim	
log K	-22.67	-22.50	-21.03	-19.19

☐ Nd

☐ Am

Status of PNC’s Thermodynamic Database

P N C



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Management Procedure of TDB

Selection of important radioactive elements

important ligand (OH^-, CO_3^{2-}, SO_4^{2-})

review of thermodynamic data

development of thermodynamic data base *

validation of data base

- Comparison of solubility values from labratory experiments and natural analogue studies with the values from thermodynamic calculation.
- Comparison of equilibrium constants obtained from experiments with the values from unified theory.

- re-evaluation of data
- experimants
  PNC ; Nd,Se,Pd
  Battelle-PNC ; Am,Th

prediction of nuclide solubility in near-field condition using geochemical code (PHREEQE,EQ3/6)

* NEA, Harwell(R-12324,HATCHES), EQ3/6, CHEMVAL

PNC

PNC IN-HOUSE TDB FOR GEOCHEMICAL CALCULATION

Geochemical Elements	Key Elements				
Original PHREEQE TDB +NEA-TDB	Harwell R12324 (1988)	NEA-TDB	EQ 3/6 (1988)	Rai et al (1980)(1990)	Phillips et al (1988)
	Zr, Ra, Th, Pa, Np, Pu, Se	U (1990) Tc (1989)	Sn	Am	Pd

RADIOACTIVE WASTE MANAGEMENT PROJECT

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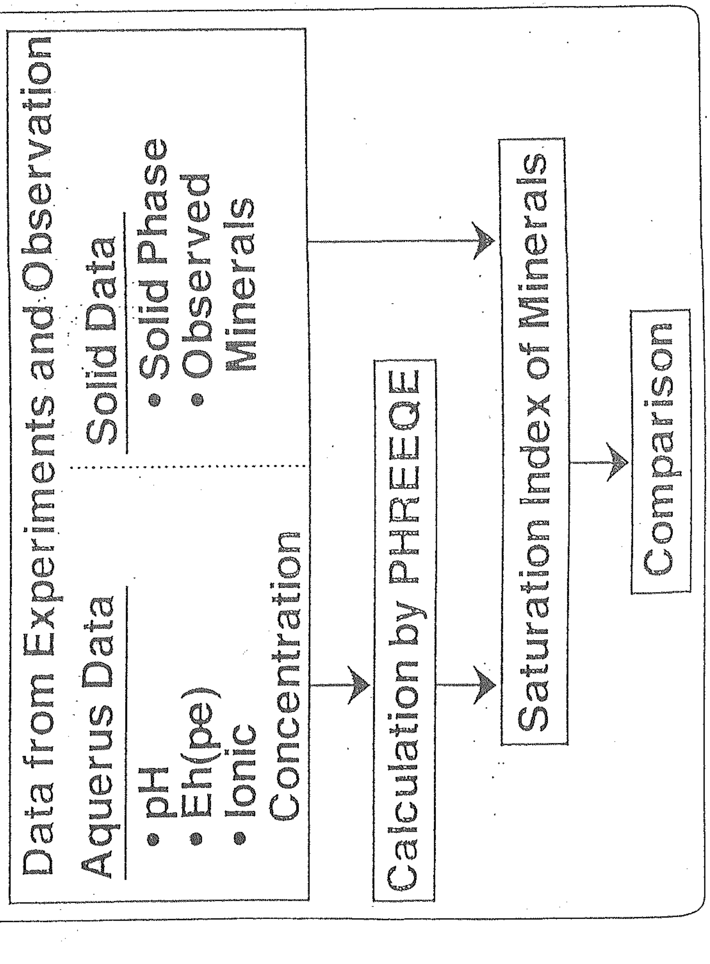
Validation

Example Problem

- Groundwater Composition of Sandstone Type of Uranium Deposit (Chatham et al , 1981)
- Uranium Concentration of Tono-Uranium Deposit in Japan (Ochiai et al. , 1988)

Flowchart of Validation



Data from Experiments and Observation

Aquerus Data
- pH
- Eh(pe)
- Ionic Concentration

Solid Data
- Solid Phase
- Observed Minerals

Calculation by PHREEQE

Saturation Index of Minerals

Comparison

Validation

Observed Data in Sandstone Uranium Deposit (Texas)

- Major Groundwater Composition

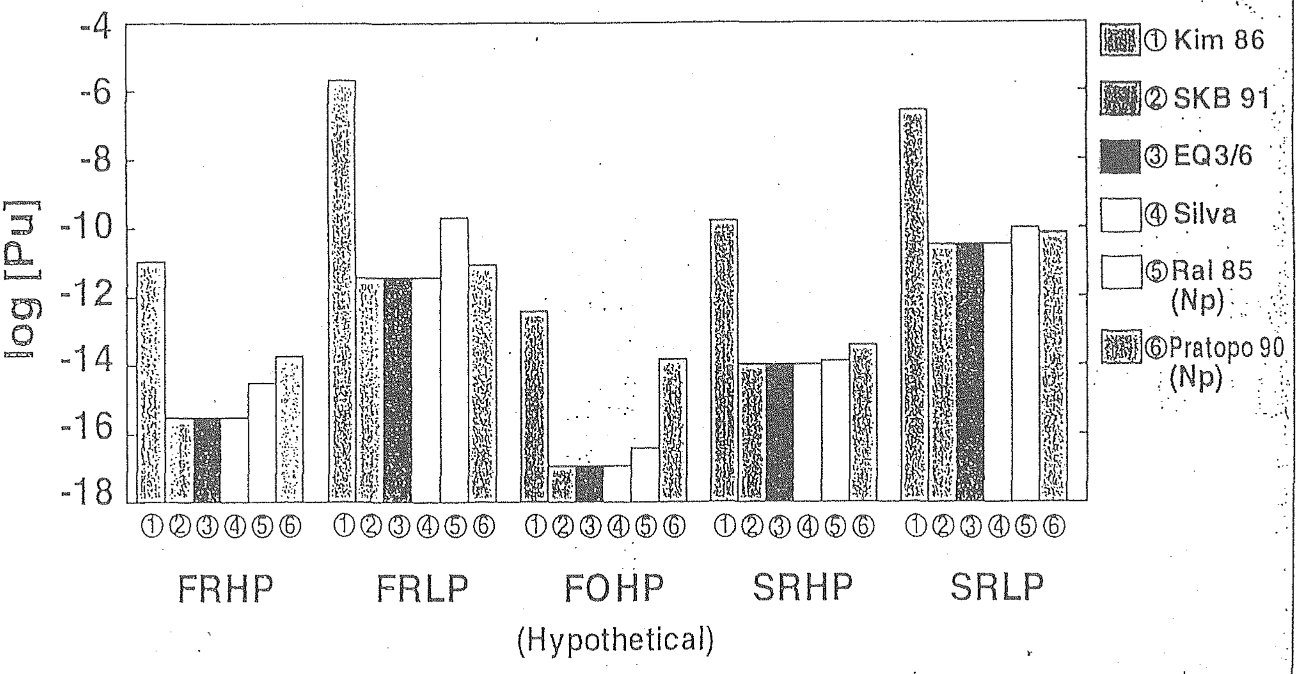
sample#	T31	T33	T34
pH	6.9	6.8	7.1
Eh(mV)	-176	-238	-203
Na	290	270	440
Ca	150	320	180
HCO_3	360	261	294
SiO_2	50	41	50
U	0.0013	0.0004	0.0003

(Unit : ppm)

- Observed Minerals Uraninite , Coffinite

Calculated Results by PHREEQE
Saturatin Index[log(IAP/KT)]

sample#	T31	T33	T34
Uraninite	1.12	0.61	0.49
Coffinite	0.81	0.22	0.18



Pu Solubilities calculated with various data bases

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Solubility limiting solid phases and TDB selected for analyses

Element	Solubility limiting solid phase		TDB selected for analyses
	Oxide	Hydroxide	
Zr	—	$Zr(OH)_4$	Harwell R12324
Tc	TcO_2	$TcO_2.2H_2O$	NEA-TDB
Sn	SnO_2	—	EQ3/6
Ra	$RaSO_4$	$RaSO_4$	Harwell R12324
Th	ThO_2	$Th(OH)_4$	Harwell R12324
Pa	Pa_2O_5	—	Harwell R12324
U	$UO_2(cr)$	$UO_2(am)$	NEA-TDB
Np	NpO_2	$Np(OH)_4$	Harwell R12324
Pu	PuO_2	$Pu(OH)_4$	Harwell R12324
Am	—	$AmOHCO_3$	Rai et. al
Ac	—	$AmOHCO_3$	Analogy of Am
Pd	PdO	$Pd(OH)_3$	Phillips et. al
Se	$FeSe_2$	$FeSe_2$	Harwell R12324

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CALCULATED SOLUBILITY OF IMPORTANT RADIOELEMENTS

[mol/l]

Element	Solubility limiting solid	Fresh		Saline	
		FRHP	FRLP	SRHP	SRLP
Tc	TcO_2	1.0E-12 $TcO(OH)_2$	1.0E-12 $TcO(OH)_2$	1.0E-12 $TcO(OH)_2$	1.0E-12 $TcO(OH)_2$
Np	NpO_2	2.0E-12 $Np(OH)_4$	2.0E-12 $Np(OH)_4$	1.7E-12 $Np(OH)_4$	1.8E-12 $Np(OH)_4$
Pu	PuO_2	2.5E-11 $Pu(CO_3)_3^{2-}$	5.3E-6 $Pu(CO_3)_4^{4-}$	6.4E-10 $Pu(CO_3)_3^{2-}$ $Pu(CO_3)_4^{4-}$	2.8E-7 $Pu(CO_3)_3^{2-}$
Am	$AmOHCO_3$	6.3E-8 $Am(CO_3)_3^{3-}$	3.1E-7 $AmCO_3^+$	6.3E-9 $Am(CO_3)_2^-$ $AmCO_3^+$	1.0E-7 $Am(CO_3)_3^{3-}$ $Am(CO_3)_2^-$
Se	$FeSe_2$	5.4E-7 HSe^-	1.0E-8 HSe^-	1.0E-8 HSe^-	1.0E-8 HSe^-

Summary and Conclusion
TDB Management

1. Themodynamic data for H3 analysis have been retrieved from recent, well-known databases such as NEA-TDB, Harwell R12324 and EQ3/6 Data 0 through review works and validation studies.
2. The modelling studies indicate that uranium concentrations are nearly saturated with uranium minerals, uraninite and coffinite which are observed in the corresponding zone. This shows the reliability of uranium of NEA-TDB used in PNC in-house database.
3. The following examines of PNC's database have been carried out.
   - CHEMVAL Examples
   - Brown's unified theory

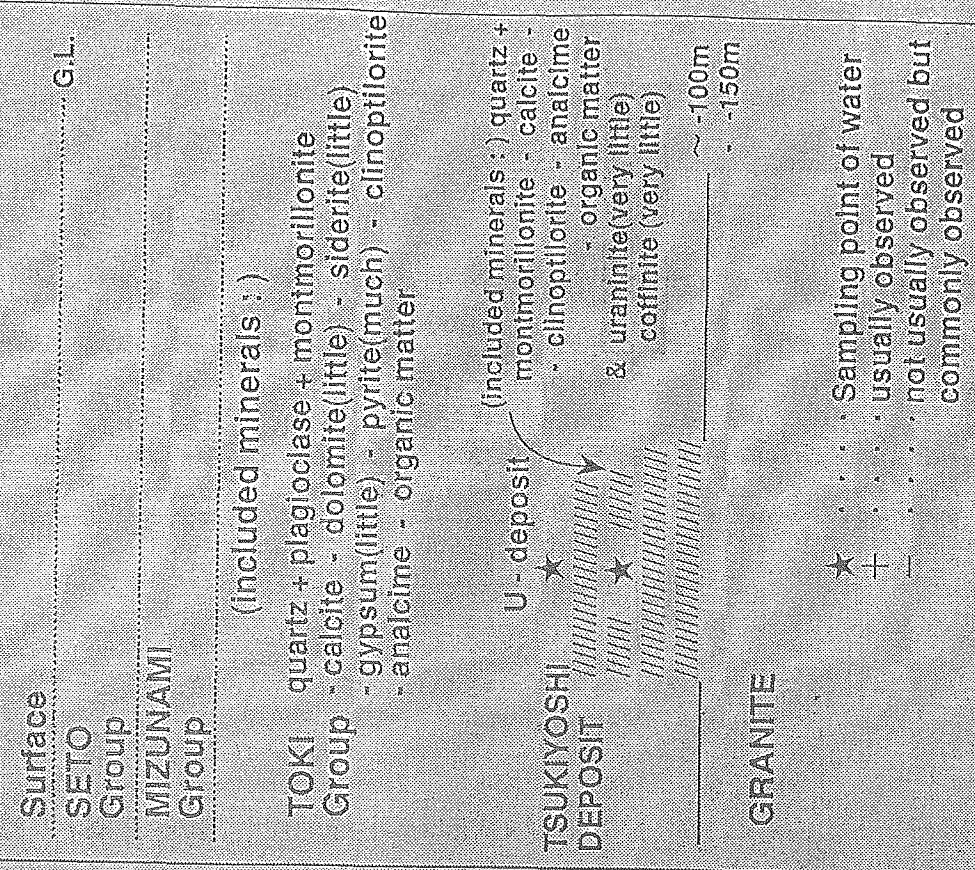
Validation Studies of the NEA·TDB Uranium Thermodynamic Data Base by Speciation of Uranium at TONO Site

YUI Mikazu
TAKEDA Seietsu
HANS WANNER(OECD/NEA)

Analayzed Data of Groundwater Samples in TOKI Group (ppm)

Elements \ Sample	TOKI Group (over U-deposit)	U-deposit*
pH	8.6	8.56±0.17
Eh(mV)	-300	
HCO_3	90	80.02±6.87
CO_3		10.46±3.33
Cl	1	0.97±0.06
SO_4	1	0.26±0.07
F	3	4.55±0.09
Na	35	39.64±0.59
K	0.3	0.35±0.11
Ca	5	2.78±0.06
Mg	0.1	0.05±0.01
Fe	0.1	Fe^{2+}<0.05 Fe^{3+}<0.05
Si		8.05±0.09
U(ppb)	0.1~1.0	0.39±0.29

Included Minerals in TOKI Group



(included minerals :)

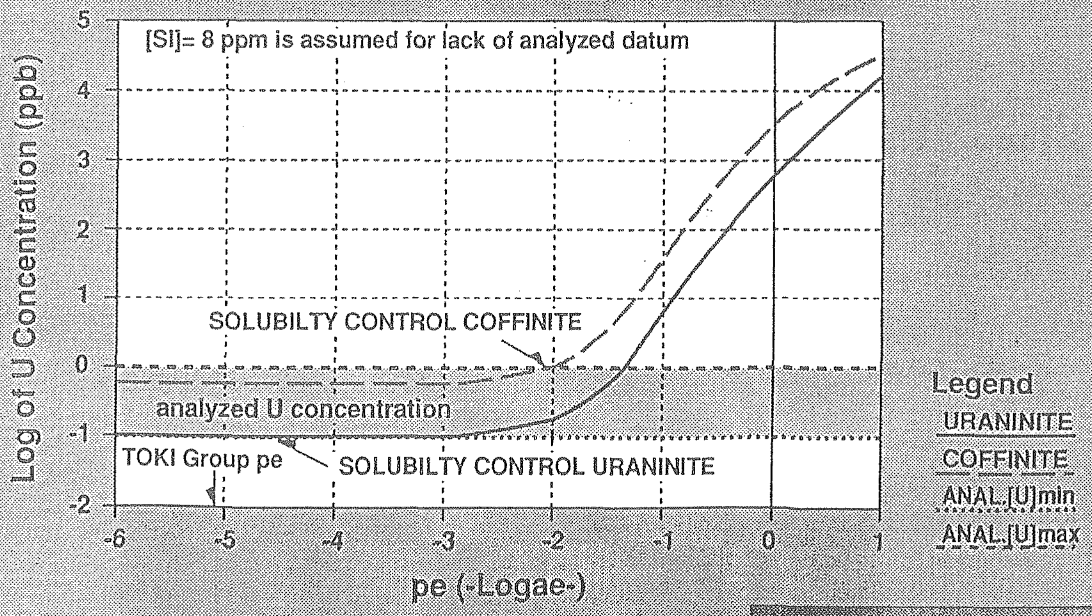
TOKI Group quartz + plagioclase + montmorillonite
- calcite - dolomite(little) - siderite(little)
- gypsum(little) - pyrite(much) - clinoptilorite
- analcime - organic matter

(included minerals :) quartz +
montmorillonite - calcite -
- clinoptilorite - analcime
- organic matter
& uraninite(very little)
coffinite (very little)

★ · · · · Sampling point of water
\+ · · · · usually observed
− · · · · not usually observed but commonly observed

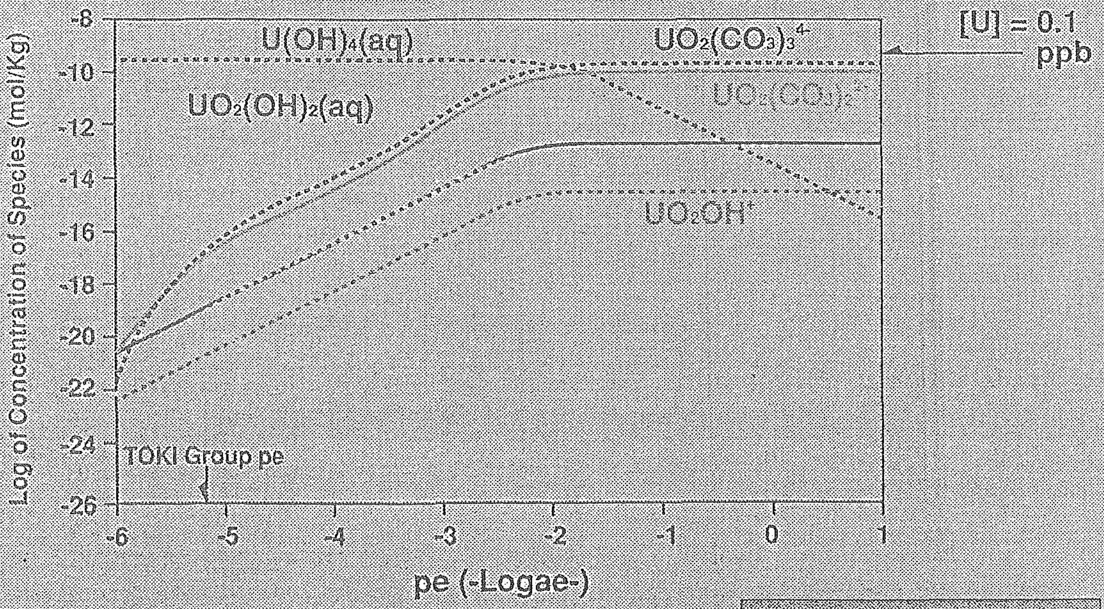
RADIOACTIVE WASTE MANAGEMENT PROJECT

U CONC. OF TOKI G.W. EQUILIBRATED WITH MINERALS AS A FUNCTION OF PE.



RADIOACTIVE WASTE MANAGEMENT PROJECT

AQ. SPECIATION OF TONO GROUNDWATER IN TOKI GROUP



RADIOACTIVE WASTE MANAGEMENT PROJECT

Summary

1. Geochemical Calculation Shows the Following Uranium Speciation in Groundwater of TOKI Group including Uranium Deposit

   (1) Dominant aqueous species($pe<-2$)
   $U(OH)_4(aq)$

   (2) Solubility controlled minerals of Uranium ($pe<-2$)
   Uraninite ($UO_2(c)$) or
   Coffinite ($USiO_4(c)$)

   (3) Another equilibrium minerals
   calcite, pyrite, quartz, etc

2. Comparison of predicted minerals with observed shows good agreement

→

Data of Uraninite, Coffinite and $U(OH)_4(aq)$ of NEA-TDB are validated at least by this study.

RADIOACTIVE WASTE MANAGEMENT PROJECT

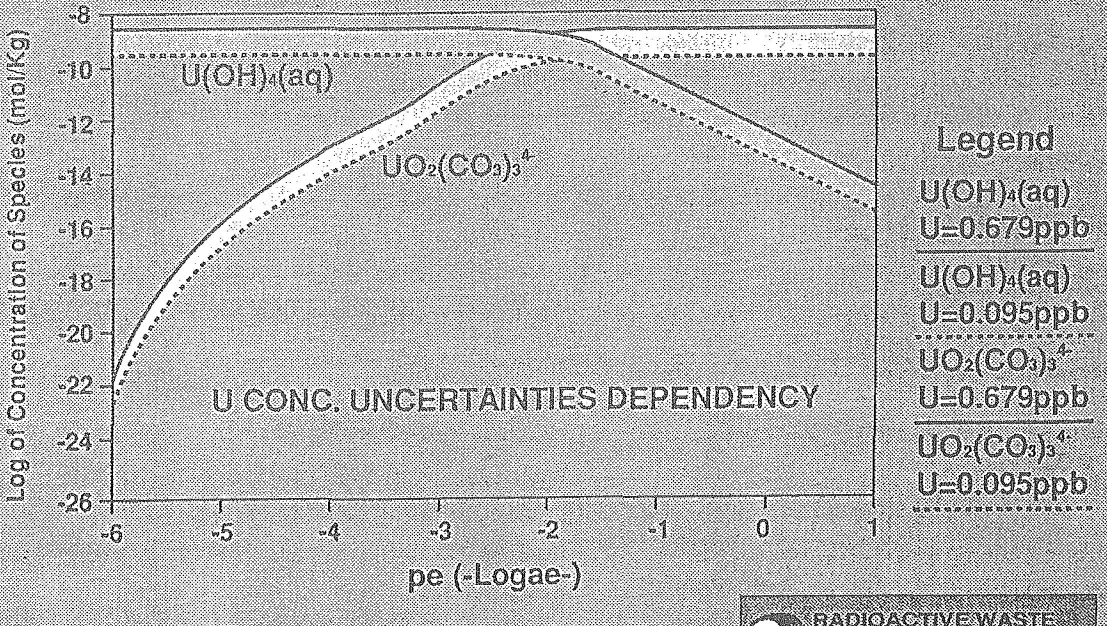
Predicted Equilibrium Minerals except for Uranium in TOKI Group
(Si = 8 ppm)

calcite
siderite
quartz
pyrite
momtmorillonite
fluorite

(Thermodynamic affinity = RTlnQ/K| ≤ 0.5)

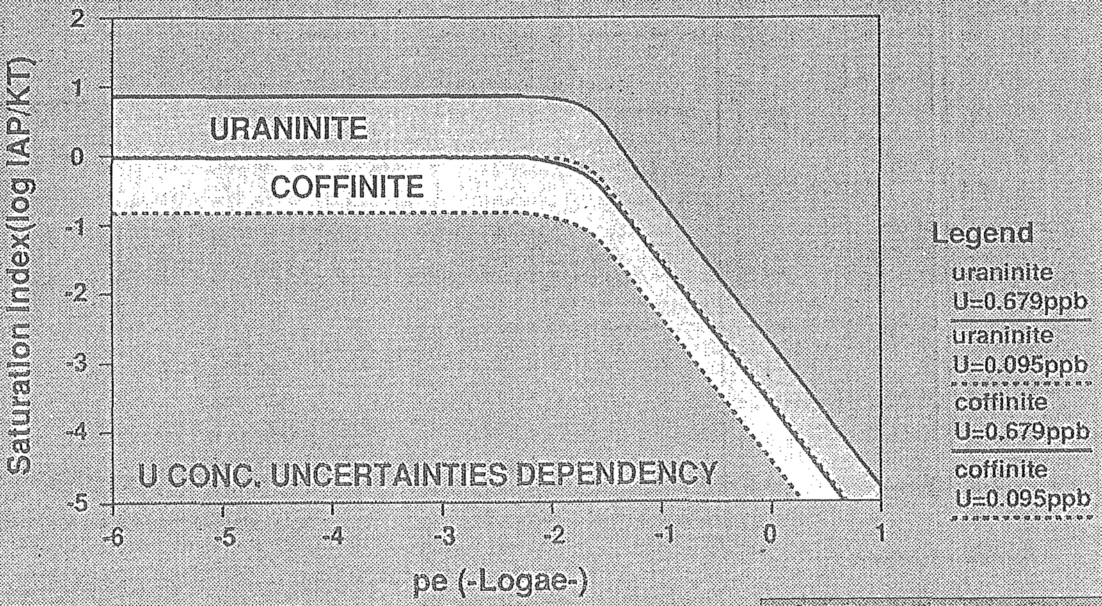
RADIOACTIVE WASTE MANAGEMENT PROJECT

AQ. SPECIATION OF TONO G.W. IN URANIUM DEPOSIT

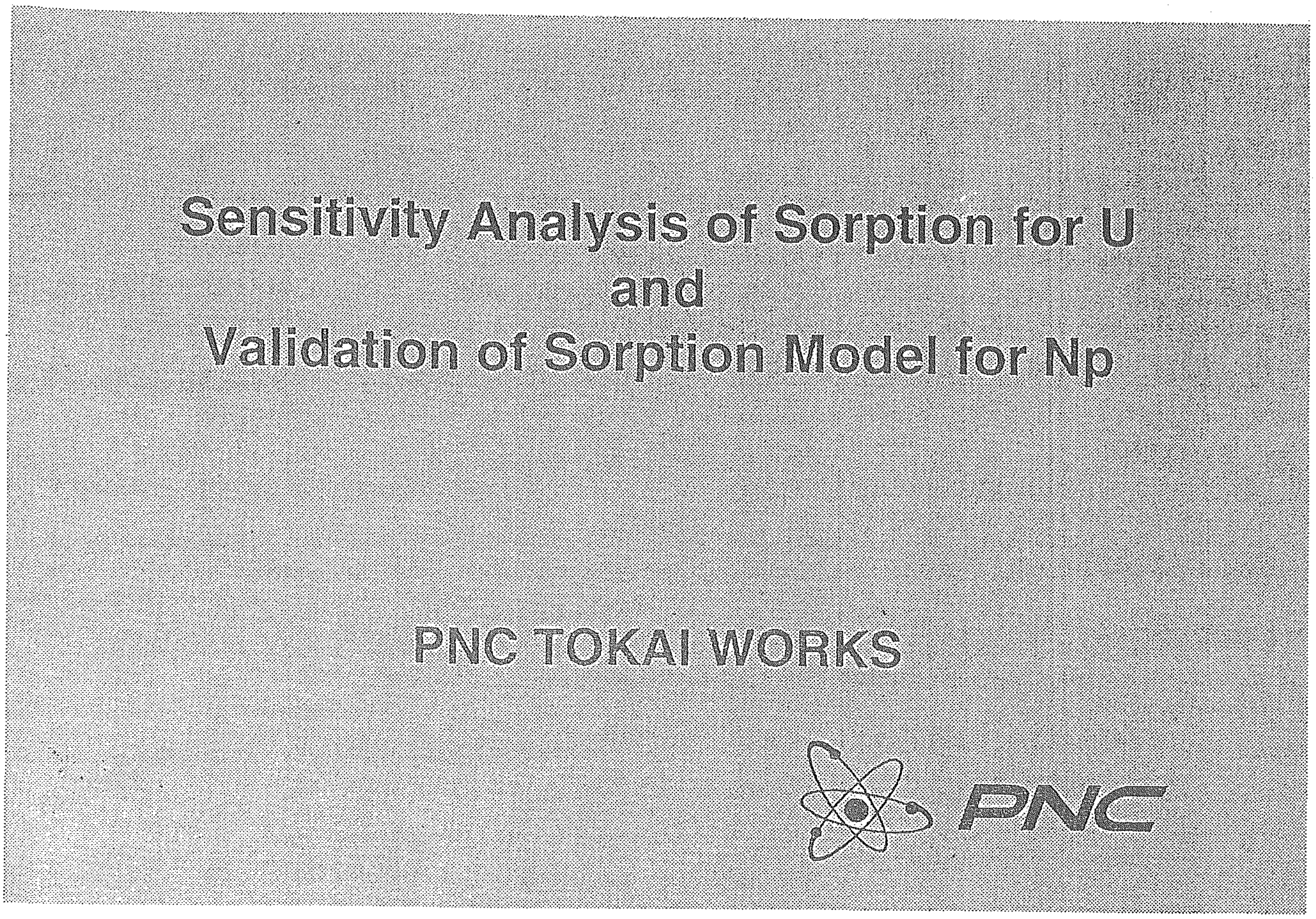


RADIOACTIVE WASTE MANAGEMENT PROJECT

MINERAL SATURATION INDEX OF TONO G.W. IN URANIUM DEPOSIT AS A FUNCTION OF PE



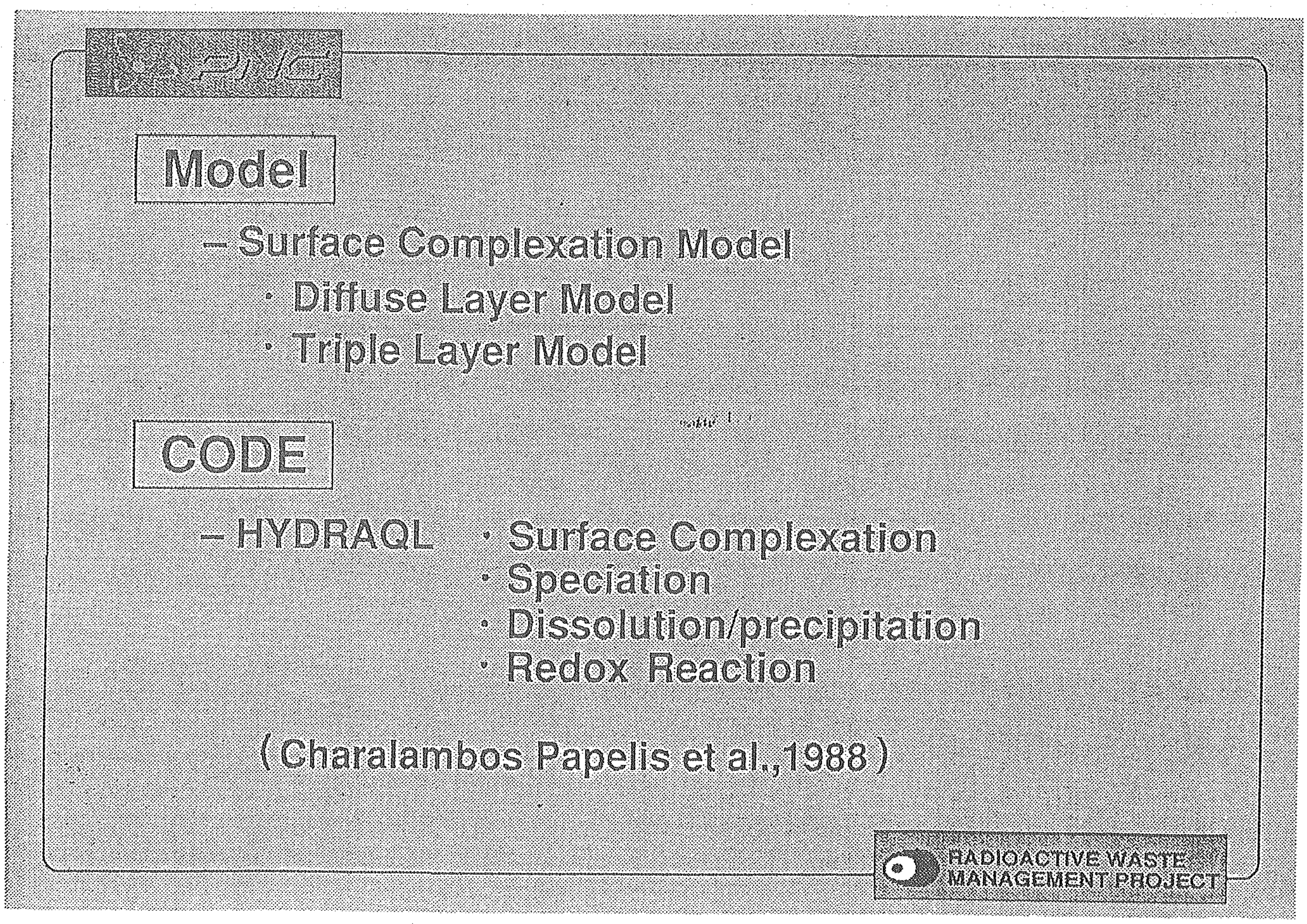
RADIOACTIVE WASTE MANAGEMENT PROJECT



Sensitivity Analysis of Sorption for U
and
Validation of Sorption Model for Np

PNC TOKAI WORKS

PNC



Model

- Surface Complexation Model
  - · Diffuse Layer Model
  - · Triple Layer Model

CODE

- HYDRAQL · Surface Complexation
  - · Speciation
  - · Dissolution/precipitation
  - · Redox Reaction

(Charalambos Papelis et al.,1988)

Objective

① Predict Sensitivity of U(VI) Sorption Behavior to C concentration by Using HYDRAQL CODE.

② Predict Np(V) Sorption Behavior on Some Minerals by Using HYDRAQL CODE, and Compare the Prediction with Experimental Result (Allard, 1982) Based on Bradbury's Approach (NEA,Sorption Workshop '91)

Calculation Condition-1-

Solution : Cement equilibrated solution

Subject : ferric oxyhydroxide in London Clay

Site Density : 9.85×10^{-3} (mol/g)

Surface Area : 600(m^2/g)

Model : Triple - Layer Model

Liquid/Solid : 50 (ml/g)

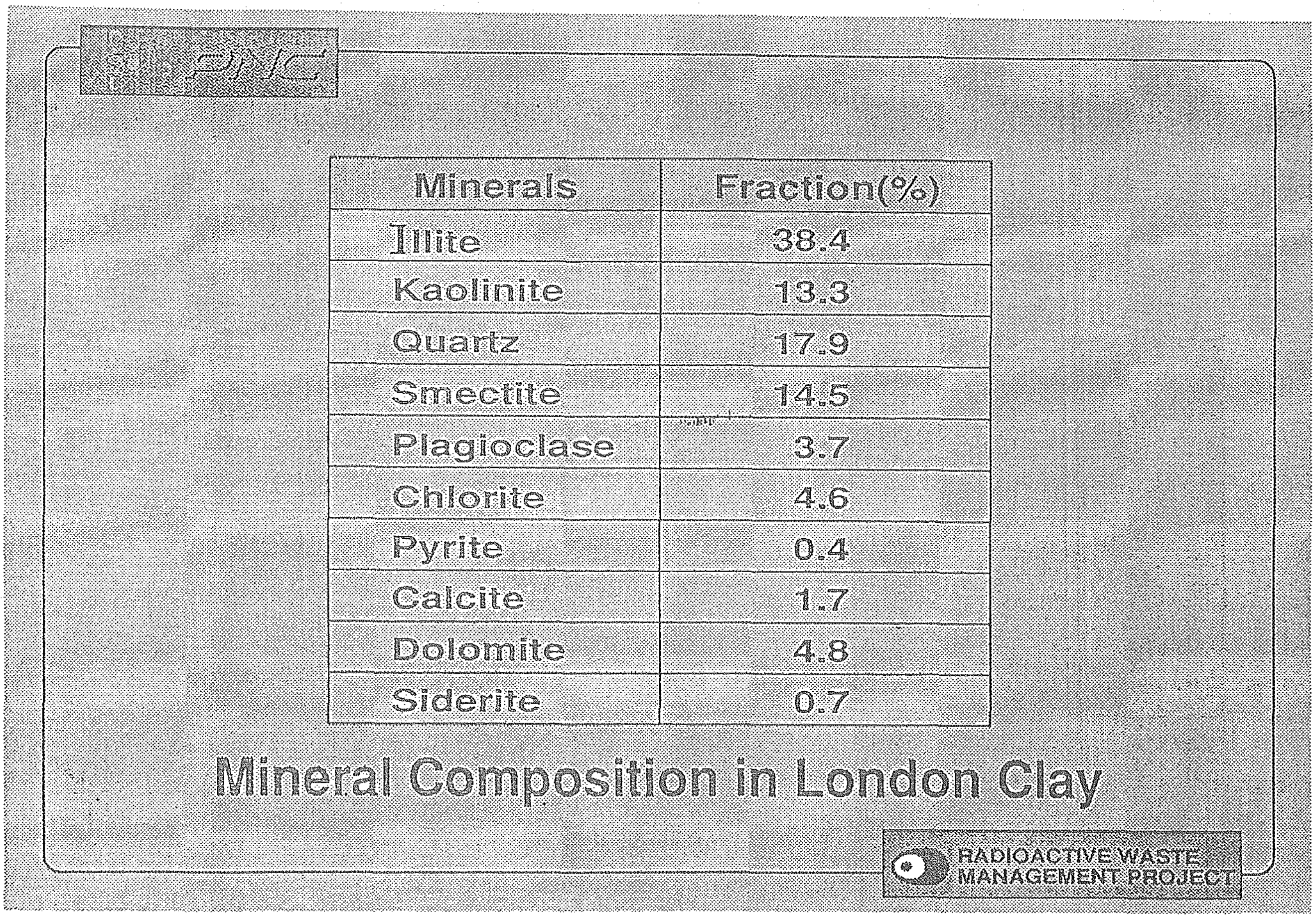
Temperature : 25 (℃)

Oxidation Condition : U(VI)

pH Range : 2～12

Data of Species : U TDB in NEA

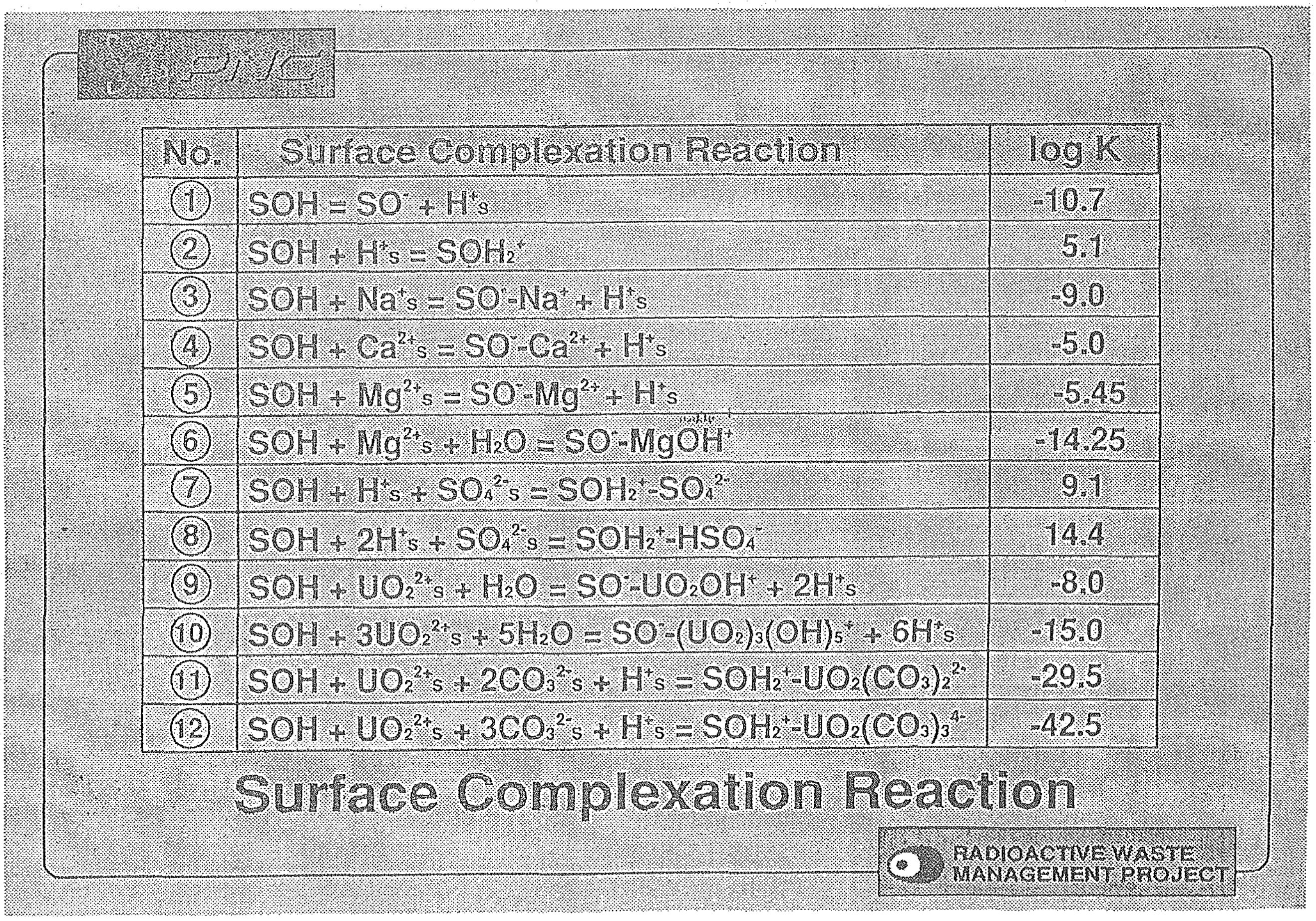
Based on Bond (1990)



Minerals	Fraction(%)
Illite	38.4
Kaolinite	13.3
Quartz	17.9
Smectite	14.5
Plagioclase	3.7
Chlorite	4.6
Pyrite	0.4
Calcite	1.7
Dolomite	4.8
Siderite	0.7

Mineral Composition in London Clay

RADIOACTIVE WASTE
MANAGEMENT PROJECT

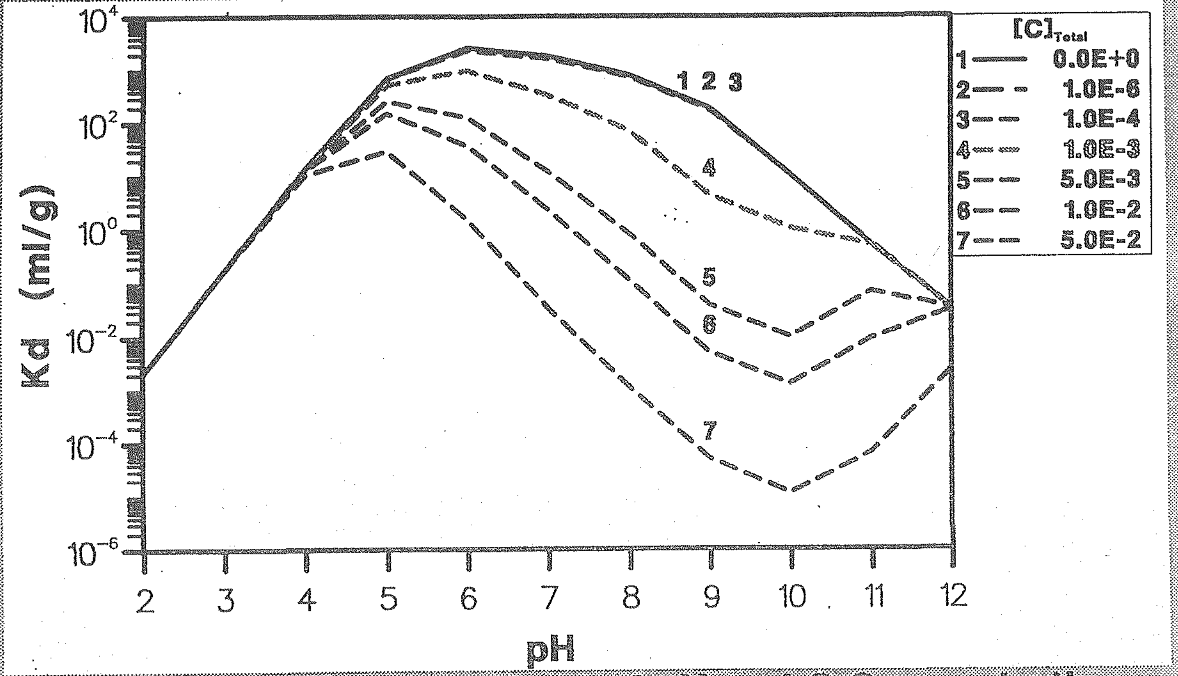


No.	Surface Complexation Reaction	log K
①	$SOH = SO^- + H^+_s$	-10.7
②	$SOH + H^+_s = SOH_2^+$	5.1
③	$SOH + Na^+_s = SO^-\text{-}Na^+ + H^+_s$	-9.0
④	$SOH + Ca^{2+}_s = SO^-\text{-}Ca^{2+} + H^+_s$	-5.0
⑤	$SOH + Mg^{2+}_s = SO^-\text{-}Mg^{2+} + H^+_s$	-5.45
⑥	$SOH + Mg^{2+}_s + H_2O = SO^-\text{-}MgOH^+$	-14.25
⑦	$SOH + H^+_s + SO_4^{2-}{}_s = SOH_2^+\text{-}SO_4^{2-}$	9.1
⑧	$SOH + 2H^+_s + SO_4^{2-}{}_s = SOH_2^+\text{-}HSO_4^-$	14.4
⑨	$SOH + UO_2^{2+}{}_s + H_2O = SO^-\text{-}UO_2OH^+ + 2H^+_s$	-8.0
⑩	$SOH + 3UO_2^{2+}{}_s + 5H_2O = SO^-\text{-}(UO_2)_3(OH)_5^+ + 6H^+_s$	-15.0
⑪	$SOH + UO_2^{2+}{}_s + 2CO_3^{2-}{}_s + H^+_s = SOH_2^+\text{-}UO_2(CO_3)_2^{2-}$	-29.5
⑫	$SOH + UO_2^{2+}{}_s + 3CO_3^{2-}{}_s + H^+_s = SOH_2^+\text{-}UO_2(CO_3)_3^{4-}$	-42.5

Surface Complexation Reaction

RADIOACTIVE WASTE
MANAGEMENT PROJECT

① Result



Change of Kd as functions of pH and C Concentration

Conclusion -1-

Sensitivity Analysis about C Concentration for U Sorption

- $[C] < 10^{-4}$(mol/l) : Kd values of U do not depend on C concentration

  $[C] > 10^{-4}$(mol/l) : Kd values of U decrease following the change of dominant aqueous species (Hydroxide → Carbonate Species)

- Kd values of U have a peak around pH5 (Competition of surface complexation and aqueous species with pH)

Class of Surface Area of Minerals

Class	Figure	Mineral	[1]Approximate formulac	[2]Surface area [m^2g^{-1}]
Ortho-, ring- and chain-silicates	6a	Almandine	$Fe_3^{2+}Al_2Si_3O_{12}$	2.1
	6b	Epidote	$Ca_2Fe^{3+}Al_2O.OHSi_2O_7SiO_4$	4.2
	6c	Olivine	$(Mg,Fe)_2[SiO_4]$	5.0
	6d	Augite	$(Ca,Mg,Fe,Al)_2(AlSi)_2O_6$	6.3
	6e	Hornblende	$(Na,K)_{0\text{-}1}Ca_2(Mg,Fe^{2+},Fe^{3+},Al)_5[Si_{6\text{-}7}Al_{2\text{-}1}O_{22}](OH,F)_2$	4.6
Sheet-silicates	7a	Kaolinite	$Al_4[Si_4O_{10}](OH)_8$	11.0
	7b	Serpentine	$Mg_3[Si_2O_5](OH)_4$	15.7
	7c	Attapulgite	—	190
	7d	Biotite	$K_2(Mg,Fe^{2+})_{6\text{-}4}(Fe^{3+},Al,Ti)_{0\text{-}2}[Si_{6\text{-}5}Al_{2\text{-}3}O_{20}](OH,F)_4$	7.0
Tecto-silicates	8a	Microcline	$(K,Na)[AlSi_3O_8]$	4.2
	8b	Bytownite	$Na[AlSi_3O_8]$-	3.1
	8c	Albite	$Ca[Al_2Si_2O_8]$	2.9
Oxides	9a	Magnetite	$Fe^{2+},Fe_2^{3+}O_4$	2.1
	9b	Limonite	$FeO\text{-}OH.nH_2O$	80
	9c	Hematite	$\alpha\text{-}Fe_2O_3$	1.8(7)
	9d	Corundum	$\alpha\text{-}Al_2O_3$	2.1
	9e	Gibbsite	$Al(OH)_3$	13
Sulphides	10a	Pyrite	FeS_2	7.0
	10b	Chalcopyrite	$(Cu,Fe)S_2$	7.2

1) Deer, Howic and Zussmann, 1977.
2) Allard et al. 1983.

Calculation Condition-2-

Assumption

Surface of minerals is covered by hydrous ferric oxide (Bradbury, 1991 NEA SORPTION WORK SHOP)

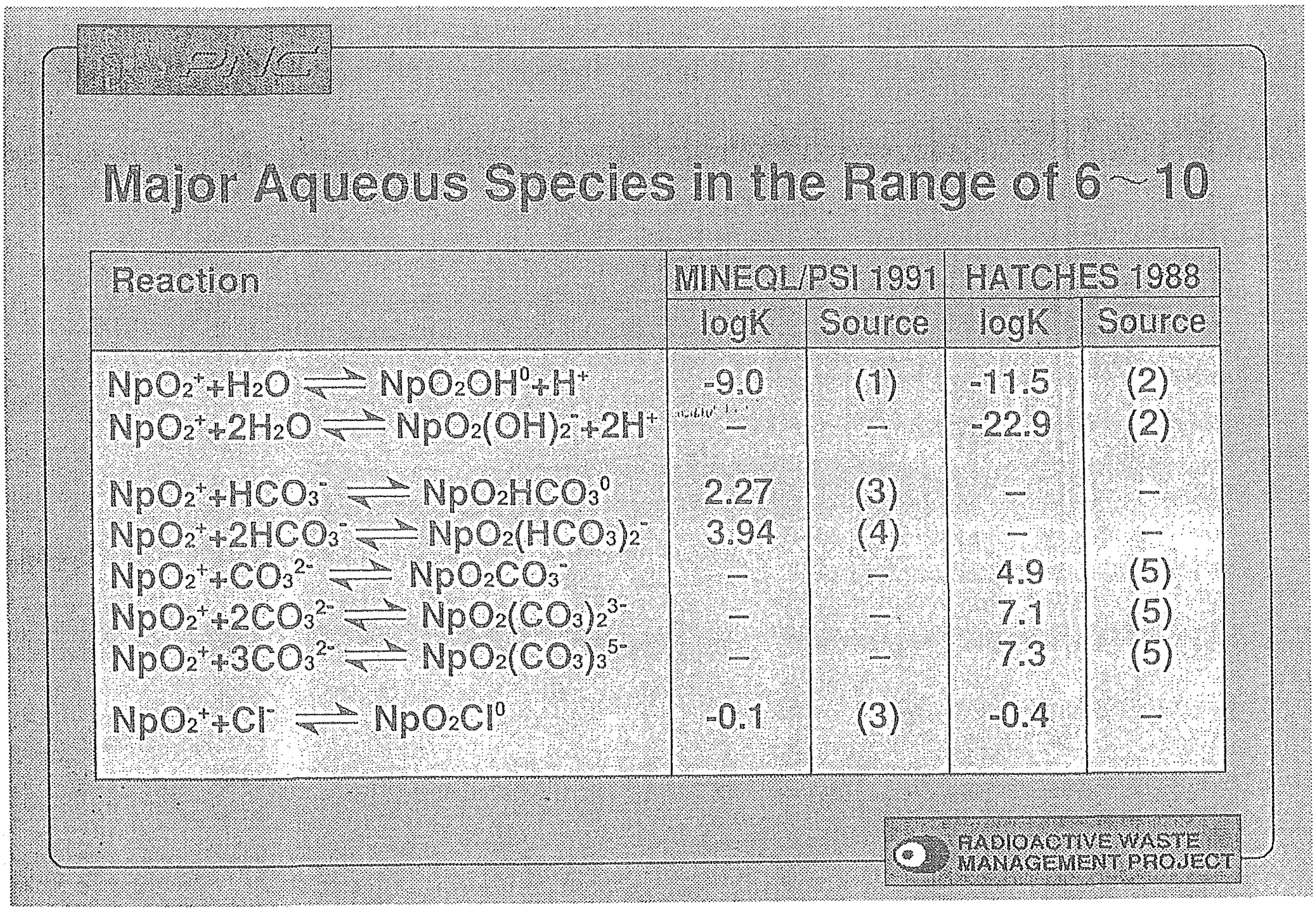
Condition

Solution : pH = 8.2 Ca^{2+} 3.8E-4(mol/l)
Na^+ 65(mg/l) Cl^- 70(mg/l)
K^+ 3.9(mg/l) SO_4^{2-} 9.6(mg/l)
Mg^{2+} 4.3(mg/l) ΣCO_3^{2-} 110(mg/l)

Surface Area : value of each mineral

Site Density : Strong Site 9.4×10^{-8}(mol/m^2)
Weak Site 3.75×10^{-6}(mol/m^2)

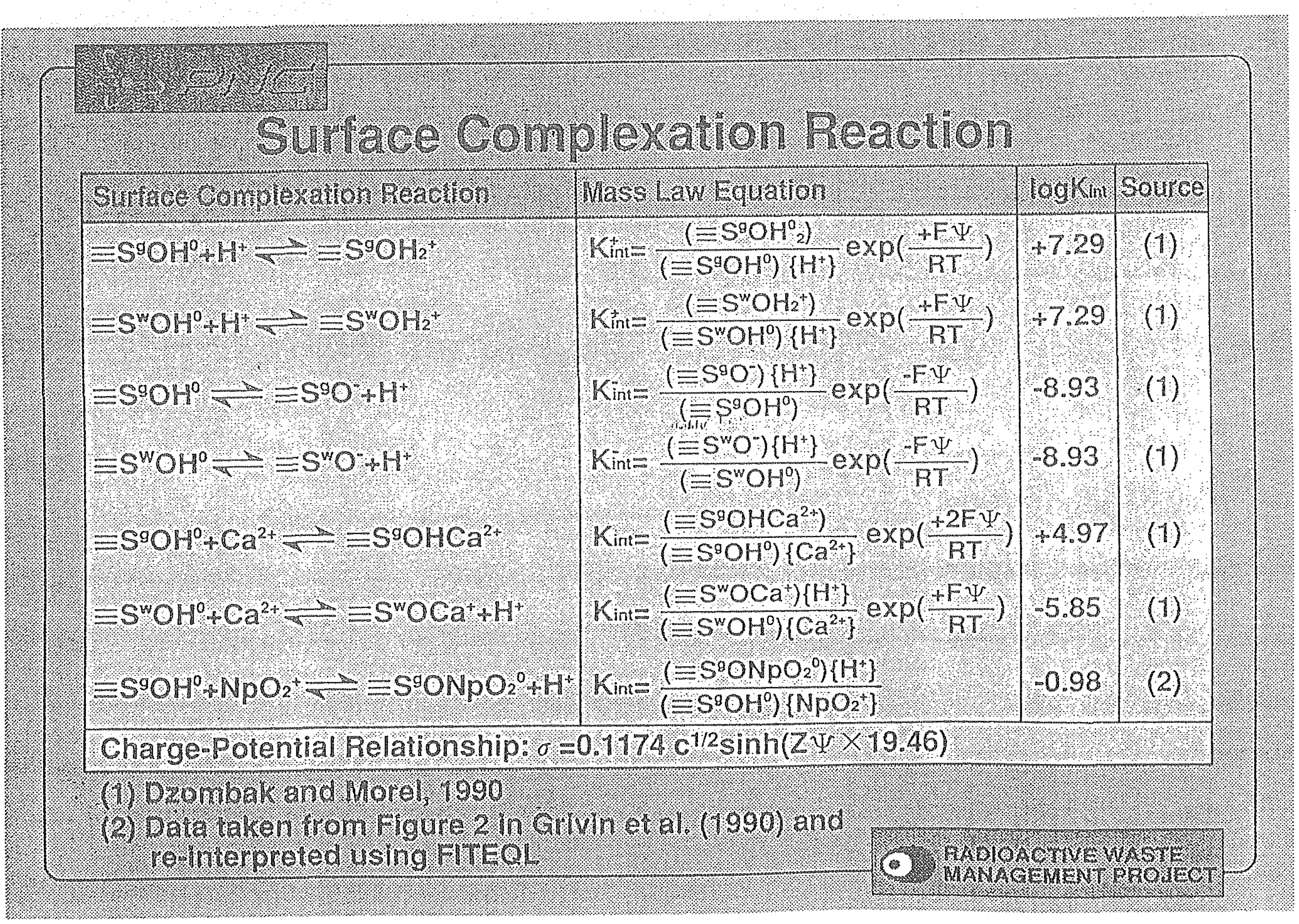
Surface Complexation Model : Diffuse Layer Model



Major Aqueous Species in the Range of 6～10

Reaction	MINEQL/PSI 1991		HATCHES 1988	
	logK	Source	logK	Source
$NpO_2^+ + H_2O \rightleftharpoons NpO_2OH^0 + H^+$	-9.0	(1)	-11.5	(2)
$NpO_2^+ + 2H_2O \rightleftharpoons NpO_2(OH)_2^- + 2H^+$	–	–	-22.9	(2)
$NpO_2^+ + HCO_3^- \rightleftharpoons NpO_2HCO_3^0$	2.27	(3)	–	–
$NpO_2^+ + 2HCO_3^- \rightleftharpoons NpO_2(HCO_3)_2^-$	3.94	(4)	–	–
$NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2CO_3^-$	–	–	4.9	(5)
$NpO_2^+ + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3-}$	–	–	7.1	(5)
$NpO_2^+ + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-}$	–	–	7.3	(5)
$NpO_2^+ + Cl^- \rightleftharpoons NpO_2Cl^0$	-0.1	(3)	-0.4	–

RADIOACTIVE WASTE
MANAGEMENT PROJECT



Surface Complexation Reaction

Surface Complexation Reaction	Mass Law Equation	$\log K_{int}$	Source
$\equiv S^gOH^0 + H^+ \rightleftharpoons \equiv S^gOH_2^+$	$K^{+}_{int} = \frac{(\equiv S^gOH^0_2)}{(\equiv S^gOH^0)\{H^+\}} \exp\left(\frac{+F\Psi}{RT}\right)$	+7.29	(1)
$\equiv S^wOH^0 + H^+ \rightleftharpoons \equiv S^wOH_2^+$	$K^{+}_{int} = \frac{(\equiv S^wOH_2^+)}{(\equiv S^wOH^0)\{H^+\}} \exp\left(\frac{+F\Psi}{RT}\right)$	+7.29	(1)
$\equiv S^gOH^0 \rightleftharpoons \equiv S^gO^- + H^+$	$K_{int} = \frac{(\equiv S^gO^-)\{H^+\}}{(\equiv S^gOH^0)} \exp\left(\frac{-F\Psi}{RT}\right)$	-8.93	(1)
$\equiv S^wOH^0 \rightleftharpoons \equiv S^wO^- + H^+$	$K^{-}_{int} = \frac{(\equiv S^wO^-)\{H^+\}}{(\equiv S^wOH^0)} \exp\left(\frac{-F\Psi}{RT}\right)$	-8.93	(1)
$\equiv S^gOH^0 + Ca^{2+} \rightleftharpoons \equiv S^gOHCa^{2+}$	$K_{int} = \frac{(\equiv S^gOHCa^{2+})}{(\equiv S^gOH^0)\{Ca^{2+}\}} \exp\left(\frac{+2F\Psi}{RT}\right)$	+4.97	(1)
$\equiv S^wOH^0 + Ca^{2+} \rightleftharpoons \equiv S^wOCa^+ + H^+$	$K_{int} = \frac{(\equiv S^wOCa^+)\{H^+\}}{(\equiv S^wOH^0)\{Ca^{2+}\}} \exp\left(\frac{+F\Psi}{RT}\right)$	-5.85	(1)
$\equiv S^gOH^0 + NpO_2^+ \rightleftharpoons \equiv S^gONpO_2^0 + H^+$	$K_{int} = \frac{(\equiv S^gONpO_2^0)\{H^+\}}{(\equiv S^gOH^0)\{NpO_2^+\}}$	-0.98	(2)

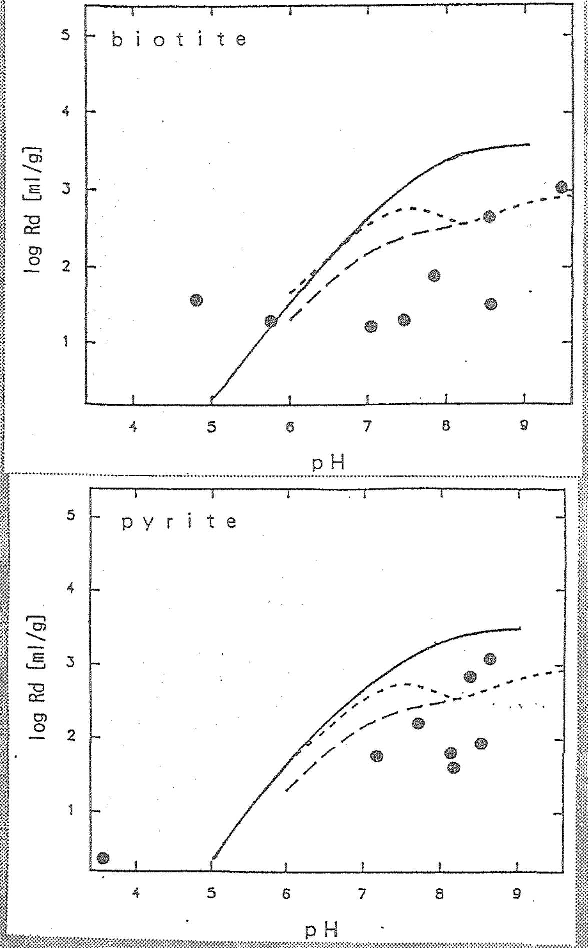
Charge-Potential Relationship: $\sigma = 0.1174\, c^{1/2} \sinh(Z\Psi \times 19.46)$

(1) Dzombak and Morel, 1990
(2) Data taken from Figure 2 in Grivin et al. (1990) and
re-interpreted using FITEQL

RADIOACTIVE WASTE
MANAGEMENT PROJECT

PNC

② Result

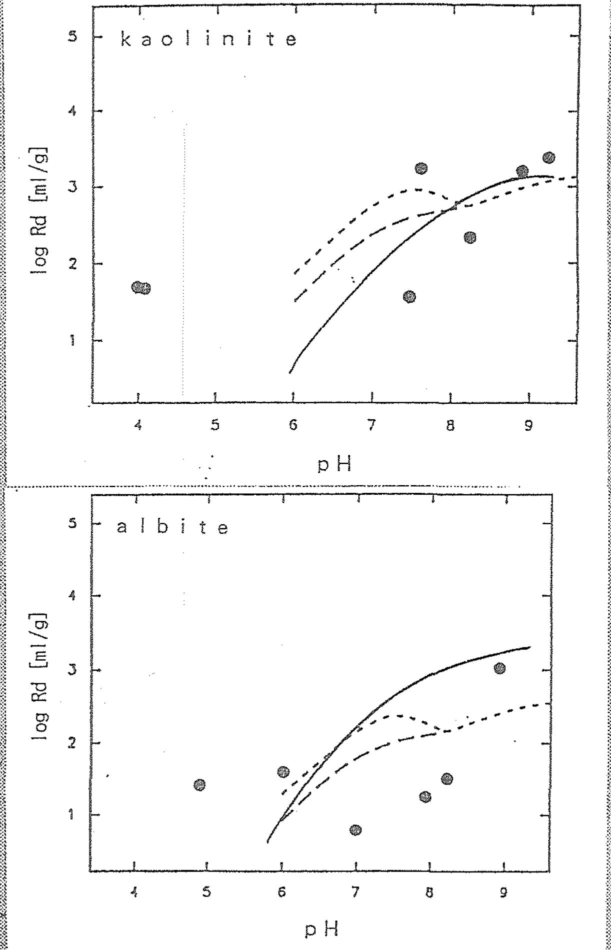


Comparison of Predicted Kd Value
with Experimental Result
(——; pH<8.2 [Ca^{2+}]= 3.8 × 10^{-4} M, pH>8.2
calcite Equilibrium;- - - calcite Equilibrium)

RADIOACTIVE WASTE
MANAGEMENT PROJECT

PNC

② Result



Comparison of Predicted Kd Value
with Experimental Result
(——; pH<8.2 [Ca^{2+}]= 3.8 × 10^{-4} M, pH>8.2
calcite Equilibrium;- - - calcite Equilibrium)

RADIOACTIVE WASTE
MANAGEMENT PROJECT

Analysis of the chemical reactions of the water-iron-glass system

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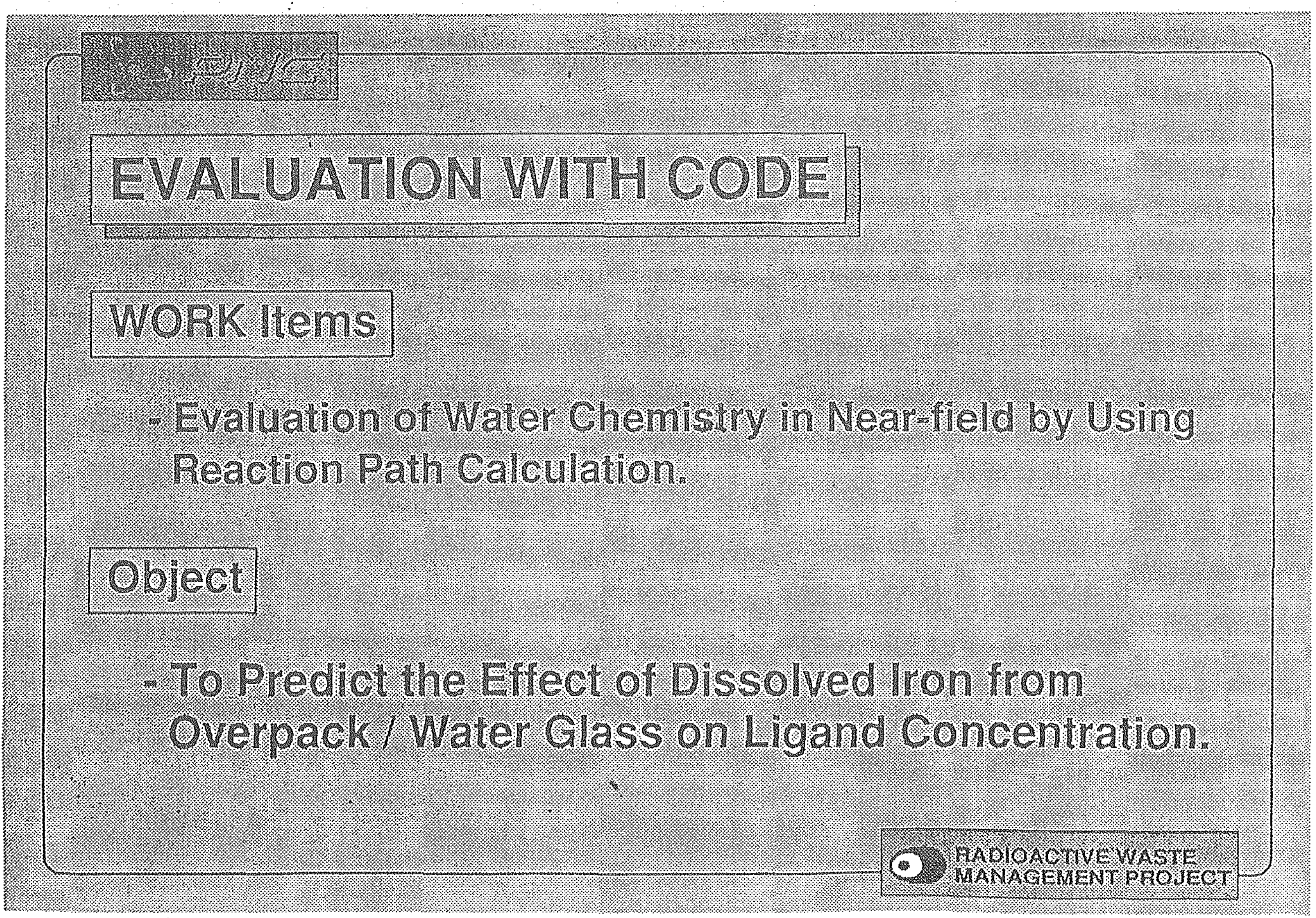


EVALUATION WITH CODE

WORK Items

- Evaluation of Water Chemistry in Near-field by Using Reaction Path Calculation.

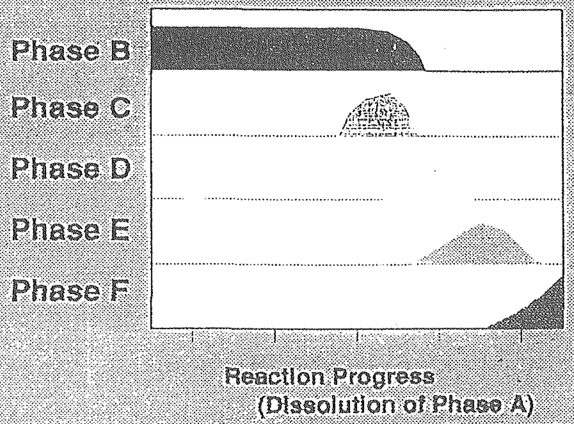
Object

- To Predict the Effect of Dissolved Iron from Overpack / Water Glass on Ligand Concentration.

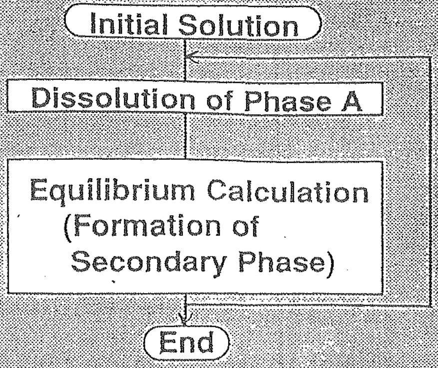
RADIOACTIVE WASTE
MANAGEMENT PROJECT

Reaction Path Calculation

Formation of Secondary Phases with Progress of Dissolution Reaction



Flow of Reaction Path Calculation


Initial Solution

Dissolution of Phase A

Equilibrium Calculation (Formation of Secondary Phase)

End

Assumption

- Close System
- EQ 3/6 (Reaction Progress)
- Corrosion Product of Overpack ⇨ magnetite (Fe_3O_4)
  Iron Solid in Glass ⇨ hematite (Fe_2O_3)
- 25℃, 1atm

Procedure of Reaction Path Calculation

Pore Water in Bentonite

⇩

Reaction Path Calculation 1 : Dissolution of Corrosion Product till magnetite Saturation

⇩

Reaction Path Calculation 2 : Dissolution of Glass till SiO_2(am) Saturation

Assumption : Precipitation of Secondary Phase Occurs Rapidlly

PNC

Calculation Case

- Sulphide (Sulphate), Carbonate, Phosphate, pH, pe are Noted

Case		Solution Composition	Corrosion Product	Dissolution Component of Glass
①	Single Ligand System	Sulphide/Carbonate/Phosphate	magnetite	hematite, SiO_2(am)
②	Mixed Ligands System	Sulphide and Carbonate		hematite, SiO_2(am), P_2O_3
③	Groundwater, Buffered Solution System	Groundwater and Pore Water		
④	Plural Ligands System + Glass Component	Sulphide and Carbonate		Glass waste (Include Other Major Component)
⑤	Groundwater, Pore Water system + Glass Component	Groundwater and Pore Water		

Case ①②④ : Ligand Concentration ~0.1M, pH/pe correspond to Equilibrium of magnetite/hematite
Case ③⑤ : Cited from Literature (Seo et al., 1992)

RADIOACTIVE WASTE MANAGEMENT PROJECT

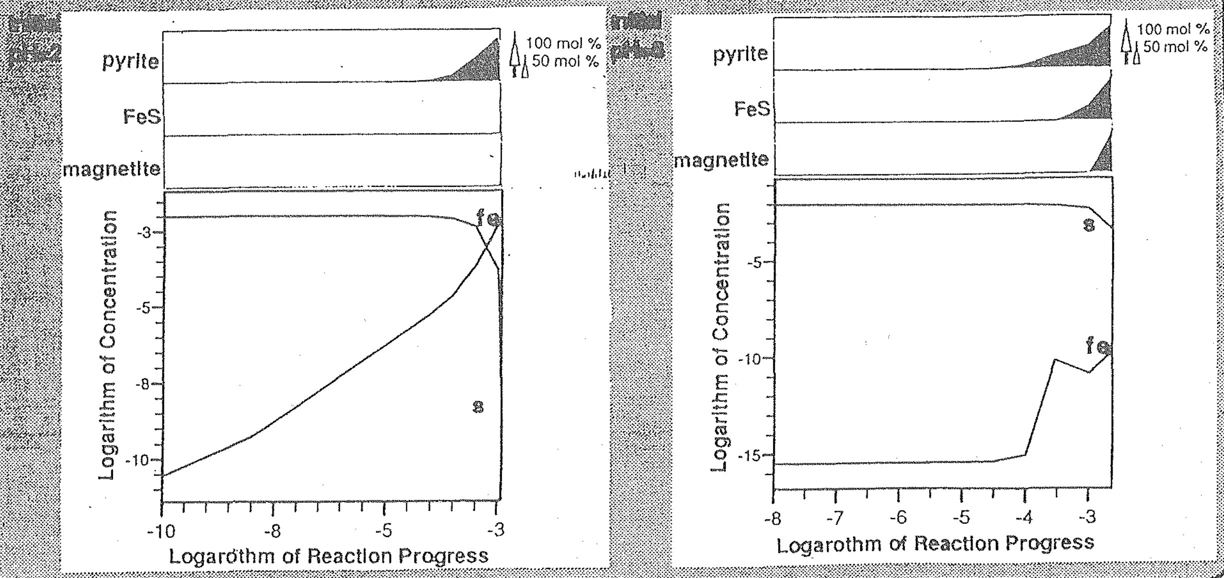
Case ① Single Ligand

Evolution of Water Chemistry with Reaction Progress (Fe-S-H_2O system)

- Dissolution of Corrosion Product (Fe_3O_4)

Major Reactions : $Fe_3O_4 + 8H^+ + 2e^- \longrightarrow 3Fe^{2+} + 4H_2O$

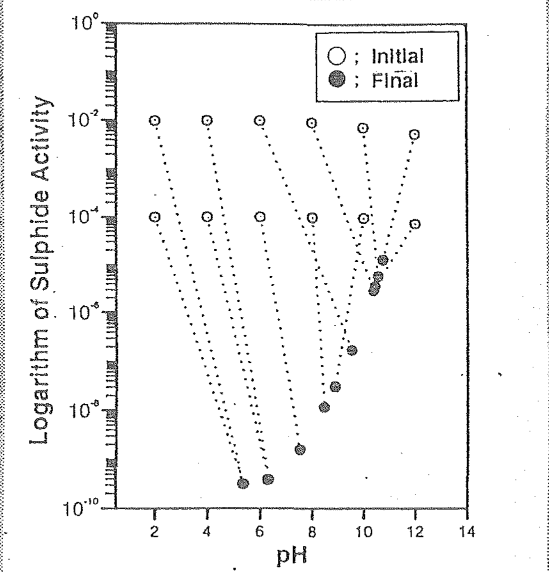
$Fe^{2+} + 2HS^- \rightleftarrows FeS_2\downarrow + 2H^+ + 2e^-$

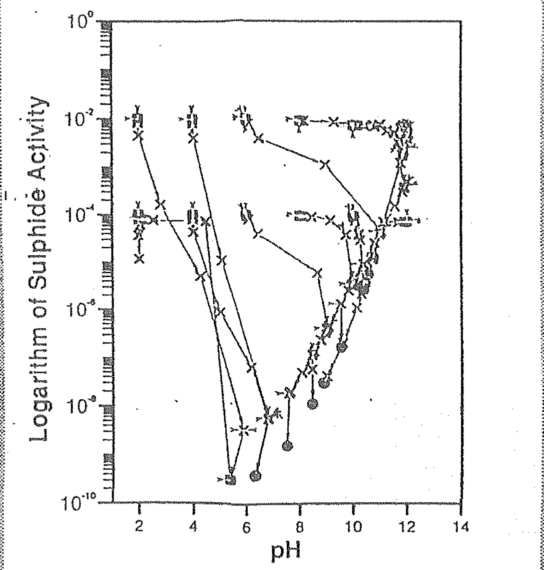


Case ①

Single Ligand System

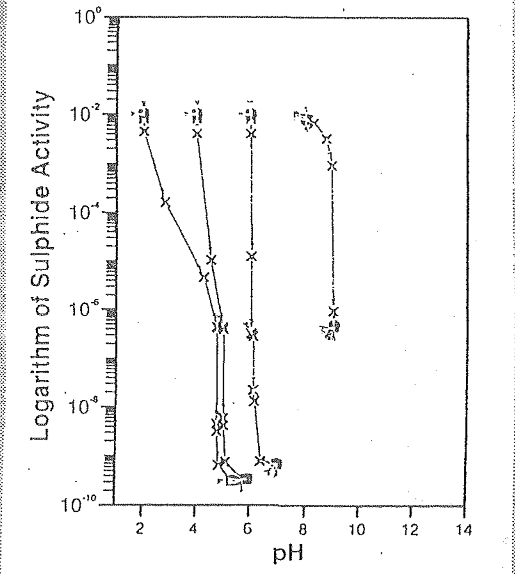
Changes of pH and Sulphide Activity with Reaction Progress



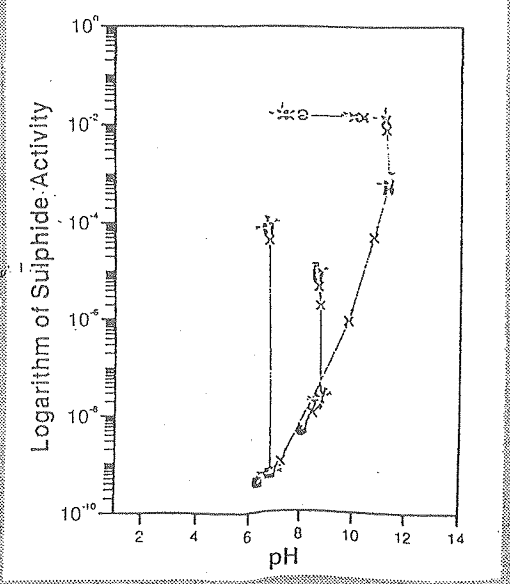


Case ④, ⑤

Changes of pH and Sulphide Activity with Reaction Progress



Case ④
(Plural ligands System + Glass component,
Case② is same.)

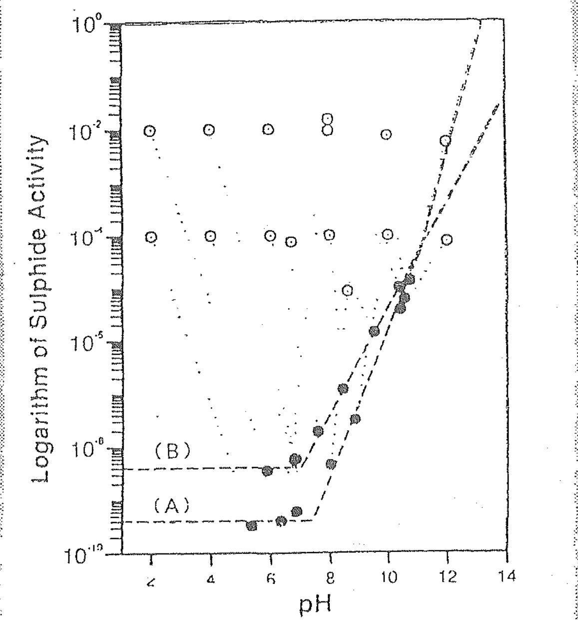


Case ⑤
(Groundwater, Pore Water System
+ Glass component, Case③ is same.)

Calculation Result

- Ligand concentrations were limited by the precipitation of iron - ligand solid (pyrite, siderite, vivianite)
- Ligand concentration had pH dependency after reaction

Relationship between pH and Ligand Activity after the Reaction paths



Result of Case ① and Case ⑤

(A) pyrite/magnetite/hematite

H_2S log $a_{H_2S} = -9.4$

HS^- log $a_{HS^-} = pH - 16.9$

SO_4^{2-} log $a_{SO_4^{-2}} = 2pH - 26.5$

(B) pyrite/FeS/magnetite

H_2S log $a_{H_2S} = -8.4$

HS^- log $a_{HS^-} = pH - 15.4$

SO_4^{2-} log $a_{SO_4^{-2}} = 2pH - 37.6$

Summary

- Dissolution of iron from overpack could limit ligand concentrarion by precipitation of iron - ligand solid.
- Reaction with overpack and glass could buffer pH of solution.
- Relationships between pH and ligand activity after reaction were interpreted by the linear equation for pH.