PNC/CEA技術協力（放射性核種の地球化学）

（専門家会議報告）

1992年2月

動力炉・核燃料開発事業団
環境技術開発推進本部
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(Japan Nuclear Cycle Development Institute)
2005
PNC/CEA技術協力（放射性核種の地球化学）
（専門家会議報告）

報告者：大澤 正秀
石黒 勝彦
梅木 博之

要旨

今回の会議は、標記分野における研究開発方針、内容等に関する情報交換と施設調査を行い、協力の可能性のある項目、方法を協議したものである。

協議の結果、双方が関心を持った研究課題として6課題を摘出した。
今後、更に交換する情報の詳細を詰めた上で、双方の機関内の承認行為を経て合意に到ることとした。
1．会議概要

(1) 日時・場所
平成3年11月19～21日、フォンテネ・オ・ローズ研究所
22日 カダラッシュ研究所

(2) 出席者
（C E A）燃料サイクル局(DCC)  Michel CONTRE
Guy BAUDIN
DCC/DSD/廃棄物区分貯蔵研究室(SCS) Michel JORDA
DCC/DSD/SCS/地球化学課(SGC) JC. PETIT, M. T. MENAGER, V. MOULIN, P. VITORGE
DCC/DSD/SCS/溶液分析化学水理地球化学研究室(LCASH) Pierre TOULHOAT
IPSN A. BARBREAUV
DCC/廃棄物貯蔵部(DSD)（カダラッシュ） Denis ALEXANDRE
IPSN/DPEI/SERE/LETG（カダラッシュ） J. M. VINSON

(事業団) 環境技術開発推進本部 処分研究グループ 大澤、石黒、梅木

(3) 議事
① フランス側の報告 19日
② 日本側の報告 20日
③ 施設見学 フォンテネ・オ・ローズ研究所 20日
カダラッシュ研究所 22日
④ 共同研究の可能性に関する協議 20, 22日
2. 議事内容

(1) フランス側の報告

① 歓迎の挨拶（Michel CONTRE）

挨拶を兼ねて以下の紹介があった。

・C E Aの組織

(工業部門 3万人、研究部門 2万人 内 D C C 2千人、12研究所)

・フォンテネの沿革（1946年設立、2000名）

・フォンテネの活動内容（原子力安全、化学、ロボット、医学）

② 処分に関するフランスの現状（C. Baudin）

・D C Cの下に廃棄物貯蔵部（Département Stockage Déchets）がある。人員は

284名でカグラッシュ、フォンテネ、サクレイに研究部門を持っている。

・6月に国民議会に提出された放射性廃棄物法案は、上院を通じて今月25日に通

常の手続きに従って再度国民議会に付議される。

この法律が通過すればANDRAの組織変更と地下研究サイトの選定に入ること
になる。

【法律の骨子】

—サイト選定までに研究を進める

—地域住民等との協議プロセスの確立

—研究成果の公表（毎年国会に報告）

—2つの地下研究施設の設置

—15年以内の処分場設置の決定

—高度再処理研究（S P I N計画）

—使用済燃料処分については最小限の研究

・ANDRAを具体的にどのようにするかは今後決定される。

・地下研究サイトは、どこかは未定（4候補サイトの中から選ばれるかも知れない

しそうでないかも知れない。）但し、粘土層（エヌヌ県）については地元状況が

良好で期待は高い。

・地下研究サイトはANDRAが提案し国が承認することになる。
固体地球化学－ナチュラルアナログ (Marie Thérèse Ménager)
以下の項目に関する研究内容の説明があった。

(i) 固体／溶液反応の地球化学
   ・鉱物表面上の元素保持機構
   ・物質の水和溶解
   ・2次相の形成と変質
   ・酸化還元に関する岩石の緩衝能力
   ・コロイドと有機物の役割

(ii) ナチュラルアナログ → 発見的役割
   ・類似性自身の研究
   ・廃棄物固化体耐久性
   ・バリア間の相互作用（鉱－粘土）
   ・化学的類似物の移動

放射性元素の挙動に関係するコロイドと粒子状物質 (V. Moulin)
   ・天然水中のフミン酸とコロイド発生に関する研究
   ・放射性元素と陽イオン及びフミン酸とコロイドとの反応に関する研究
   ・鉱物表面上への陽イオンの保持性能に関するフミン酸とコロイドの影響

水理地球化学 (P. Toulhoat)
   ・ウラン鉱床回りの地下水中のウラン：ウラン探鉱と廃棄物管理への応用
   ・母岩との反応による地下水水中物質の変化
   ・実験室及び原位置における物質移行実験と水理・地球化学の連成モデリング
   ・還元性地下水中の二酸化ウラン挙動の実験
   ・分析化学

アクチニドの地球化学 (P. Vitorge)
   ・プルトニウム、アメリシウム、ネプチニウム等の熱力学データに関する測定値
     及び吸着に関する測定値を他の文献データと比較しつつ取りまとめている。
・ＮＥＡのＴＤＢのうちアメリシウムのレビューに参加している。

⑦ 実験施設（A. Barbreau）
・地下研究施設についてはＩＰＳＮが担当
・第1世代の地下研究施設において原位置試験手法の開発等を行っている旨の説明があった。
  粘土層（フランス南部 トルヌミル村付近） 鉱道トンネル跡
  頚岩（フランス北部 レバン町付近）発電用ダムの使用されていない立坑

② 日本側の報告
  ① 動燃事業団の研究開発の現状
  ② シナリオ開発
  ③ モデル開発
  ④ データ収集

③ 施設見学
  ① フォンテネ研究所
     (i) 固体地球化学／ナチュラルアナログ実験室
         ・ＳＥＭによる鉱物の表面観察（花崗岩の変質等）を調べている。
         ・研究者3名
     (ii) コロイド／地下水中の有機物に関する実験室
         ・地下水中のフミン酸／コロイドの定量分析
         ・使用装置（Laser Induced Time Resolved Spectrofluorometry）
         ・研究者10名程度
         ・地下水中のフミン酸／コロイドの定量分析
         ・日本の地下水もできたら分析して地下水の化学的性質の形成過程に関する一般論
         が導出できればと希望あり。
     (iii) 吸着に関する実験室
         ・プルトニウム等の吸着に関するパッチ試験（主に粘土）
・ストロンチウムを用いたカラム試験（準備中）
（iv）アメリシウム、プルトニウム等の熱力学データの測定実験室
・溶解度に関するコロイドの影響等の測定
・2種類の移行媒体を任意に注入できるカラム試験を準備中
・地球化学と物質移行の連成モデルに反映させる。

（v）ペントナイトの特性試験
・当初人工バリア設計のためのデータを採取していたが、最近は性能評価のための
データ採取が中心
・ペントナイト中の水分をγ線を使って測定
・ペントナイトの膨潤圧、透水係数を測定
・ペントナイトの原位置試験（Panay Silord鉱山）（ビデオ）

② IPSN及び事業所研究所（Jean-Marc VINSON IPSN/DPEI/SEBE/LETG）
（i）地層処分安全研究における化学的観点から現在進めている研究計画を説明
・試験孔内に実験装置を入れ、一種の原位置ラボを作り、放射性トレーサをもちい
た物質移行試験を計画しており、既に試験機器を試作済
（ii）地球化学測定機器の開発
・pH、Bh等を測定するための機器（2, 200m対応）を開発中。機器の開発のためカナ
ラッシュ研究所内に深さ 300m の試験孔が掘削されており、そこで適応試験を実
施中。
（iii）分析化学
・ICPマス等により放射性核種の定量分析
・α検出器、βγ検出器による従量分析技術の向上を図っている。
・本セクションはCEA共通（基盤分野）と位置づけられているが、今後処分研究
との関連をさらに強化する予定。
・地球化学の分析セクションを集約すべく装置を搬入中
（4）共同研究の可能性に関する協議

両方が関心を持った研究課題（①は除く）として次の6課題を確認した。この課題について両方で担当者を指名し、当面どの様な情報の交換や将来の共同作業が可能か更に詰めた上で、両方の機関内の承認行為を経て合意に至ることとした。

① 処分政策と概念
② ナチュラルアナログ
③ 深部地下水化学
④ 人工バリア内の地球化学的変化
⑤ 核種の地球化学
⑥ 核種廃棄機構

尚、ガラスの長期挙動については、ＣＥＡは、もう一つの協力課題である「固化体の長期挙動」（コーディネータ：伊藤）に含まれると認識していたので、伊藤－サス（ＣＥＡコーディネータ）間でガラスについては地球化学の分野で扱うとの文書確認を行った上で⑦として加えることとした。（この場合、マルクール研究所が加わる。）
List of topics of common interest for the PNC - CEA collaboration

Basis of the agreement in a first step is exchange of information

1. Policies and concepts concerning the disposal of radioactive waste disposal

2. Natural analogues
   * long-term behaviour of waste forms and engineered barriers (geochemical aspects)
   * migration of U and related elements in the geosphere
     - methodologies of study
     - modelling and extrapolation

3. Deep groundwater chemistry
   * in-situ sampling and measurement
   * analytical chemistry
   * colloids and organics
   * modelling

4. Geochemical evolution in engineered barriers systems
   * experiments and modelling

5. Radionuclides geochemistry
   * comparison of database

6. Radionuclide retardation mechanisms
   * solid/liquid interactions
CEA資料
DCC'S STAND ON R&D

RESPOND TO "SHORT TERM" NEEDS OF INDUSTRY

COGEMA: ON REPROCESSING
EDF: WASTES FROM REACTORS
ANDRA: WASTE DISPOSAL
CEA'S SUBSIDIARIES: EXPORTS

DEVELOP PROCESSES FOR TOMORROW

DCC'S INITIATIVES:

IN COORDINATION WITH INDUSTRY FOLLOWING GOVERNMENTAL GUIDELINES

FUEL CYCLE DIRECTION WE WORK FOR THE FUTURE
BACK END FUEL CYCLE FUTURE

SPIN

PURETEX

Pu IMPROVED SEPARATION
Np PARTIAL SEPARATION

ACTIVITY AND VOLUME REDUCTION
(ALPHA WASTES)

PRESENT PLANT (LA HAGUE)

ACTINEX

ADVANCED SEPARATION:
- Pu
- Np, Am, Cm
- LONG-LIVED FP

HIGHEST REDUCTION OF ALPHA WASTES

ACTIVITY

NEW FACILITIES

TRANSMUTATION

POWER PLANTS (FBR)
ACCELERATORS
MAJOR PROGRAMS ON WASTES

ON WASTES:
- Reduction in volume
- Characterization and monitoring of:
  . Matrices
  . Packages
- Study of long term behavior

ON DISPOSALS:
- Gather physico-chemical and geochemical data
- Migration
- Restore barrier imperiousness of sites

DIRECT STORAGE:
- Taking it into consideration for
  . Exotic fuels
  . Assessing external R&D
EQUIVALENT DOSE AT OUTLET OF GLASS DISPOSAL IN GRANITE

LWR GLASSES:
1: WITHOUT ACTINIDES SEPARATION
2: WITH ACTINIDES SEPARATION

Sv/y/ICRP limit
EVOLUTION OF POTENTIAL RADIOTOXICITY (1)

- PWR FUEL 33 GWD/1 3.5% U235
- VITRIFIED WASTE: REPROCESSING AFTER 3-YEAR COOLING
- HAW WASTE FROM ADVANCED REPROCESSING AND A TEN TO ONE RATIO FOR ACTINIDE SEPARATION
- HAW WASTE FROM ADVANCED REPROCESSING AND A HUNDRED TO ONE RATIO FOR ACTINIDE SEPARATION

potential radiotoxicity

Pu + Sr + Cm + Cs

Sr + Cm + Cs + Am

Sr + Cs

1

1/10

1/100

1/1000

1/10000

1/100000

time after fuel discharge (years)

Pu

Am

Pu

Am

Am
PRESENT STATUS

PRESENT FRENCH NUCLEAR POLICY CONSISTS IN THE REPROCESSING OF IRRADIATED FUELS FROM PWR'S AND IN THE RECYCLING OF PLUTONIUM IN PWR'S VIA MOX FUELS RELOADS AND POSSIBLY LATER ON ITS RECYCLING IN FBR'S. AT THE END OF 1990 THE CUMULATIVE TONNAGE OF FUEL REPROCESSED IN FRANCE REACHES 8,900 T OF GCR FUEL AND 3,900 T OF LWR FUEL.

PWR'S EXPLOITATION AND REPROCESSING PRODUCE WASTES TO BE DISPOSED OF:


**GLASSES AND ALPHA WASTES** WOULD BE DISPOSED OF IN A SITE TO BE DECIDED ON, ONE OPTION RETAINED IS THEIR ISOLATION IN A DEEP UNDERGROUND GEOLOGICAL REPOSITORY. IN 1987 ANDRA STARTED FIELD INVESTIGATIONS, BUT DUE TO STRONG PUBLIC OPPOSITION, THE GOVERNMENT DECIDED IN FEBRUARY 1990 TO DEFER FIELD INVESTIGATIONS FOR A 12 MONTHS PERIODS.
BEFORE RESUMING FIELD INVESTIGATIONS AND TAKING A DECISION ON THE CHOICE FOR A FINAL DISPOSAL, TWO PEER REVIEWS HAVE BEEN REQUESTED BY THE FRENCH GOVERNMENT ON THE BASIC OPTIONS CONCERNING THE MANAGEMENT OF THE BACK-END OF THE FUEL CYCLE:

ONE FROM THE "OFFICE PARLEMENTAIRE D'ÉVALUATION DES CHOIX SCIENTIFIQUES ET TECHNOLOGIQUES" (parliamentary office for scientific and technological choice assessment). PUBLISHED IN DECEMBER 1990 IT IS DUBBED THE "BATAILLE REPORT".


FOLLOWING DISCUSSION OF THESE REPORTS, THE FRENCH NATIONAL ASSEMBLY (DEPUTIES) APPROVED, LAST JUNE, THE FIRST DRAFT OF A NEW LEGISLATION COVERING A 15 YEARS PROGRAM FOR HLW GEOLOGICAL DISPOSAL. THIS LEGISLATION IS BEING DEBATED BY THE SENATE BEFORE A FINAL VOTE OF THE NATIONAL ASSEMBLY. THIS LAW TAKES INTO ACCOUNT THE MAIN CONCLUSIONS OF THESE REPORTS:
STUDIES ARE REQUIRED BEFORE OF A GEOLOGICAL DISPOSAL SITE MAY BE SELECTED,
-A BROAD PROCESS OF CONSULTATING WITH COMMUNITIES AND REGION CONCERNED BY A POTENTIAL WASTE DISPOSAL MUST BE ESTABLISHED,
-SAFETY STUDIES FOR DISPOSAL MUST BE PURSUED,
-TWO UNDERGROUND LABORATORIES ARE DESIRABLE,
-A DECISION ON THE CREATION OF A DISPOSAL MUST BE TAKEN WITHIN THE COMING 15 YEARS,
-GREATERT EFFORT MUST BE DONE ON ADVANCED REPROCESSING,
-A MINIMUM OF WORK SHOULD BE DONE TO EVALUATE DIRECT DISPOSAL OF SPENT FUEL.

THE BILL SUBMITTED TO VOTE STIPULATES THAT:
-EVERY YEAR A REPORT WILL BE SENT TO THE PARLIAMENT ON THE PROGRESS OF R&D ON SITE STUDIES, ACTINIDES SEPARATION AND IMPROVEMENTS IN THE EMBEDDING OF WASTES.
-WITHIN A 15 YEARS PERIOD THE GOVERNMENT WILL SUBMIT TO PARLIAMENT THE CONDITIONS CONCERNING THE CREATION OF A GEOLOGICAL DISPOSAL WHEN REQUIRED.
TWO SCENARIOS ARE CONSIDERED:

- A NORMAL SCENARIO - I.E EXCLUSIVE OF A MAJOR ACCIDENT - FOR WHICH RADIOTOXICITY AT THE OUTLET IS EVALUATED BY TAKING MIGRATIONS THROUGH THE BARRIERS INTO ACCOUNT.

- ACCIDENTAL SCENARIOS; THE MOST PESSIMISTIC ONE BEING A SIMULTANEOUS RELEASE OF ALL THE RADIONUCLIDES CONTAINED IN THE STORED WASTES. THIS UNREALISTIC SITUATION ALLOWS AN ESTIMATE OF THE MAXIMUM HARMFUL EFFECT CALLED POTENTIAL TOXICITY TO BE MADE.

NORMAL SCENARIO

Figure 1 SHOWS THE EVOLUTION OF EQUIVALENT DOSES VERSUS TIME FOR DISPOSAL, IN GRANITE, OF GLASSES CORRESPONDING TO FRENCH PRODUCTION TILL 2010.

THE GRANITE CHARACTERISTICS ARE THOSE MEASURED AT AURIAT, AN EXPERIMENTAL LABORATORY IN THE CENTER OF FRANCE.

CALCULATIONS ARE MADE WITH THE PAGIS MODEL DEVELOPED BY THE EUROPEAN COMMISSION.

RELEASE OF ACTIVITY INTO THE BIOSPHERE WOULD BEGIN BEYOND 400 000 YEARS; THEN DOES WOULD REACH A MAXIMUM AROUND $10^6$ YEARS AND DECREASE TO A CONSTANT VALUE OVER $2.10^7$ YEARS BEFORE DISAPPEARING. THE MAXIMUM LEVEL REMAIN $10^4$ TIMES LOWER THAN ACCEPTABLE LIMITS.
CEA GENERAL ORGANIZATION CHART
AS AT 1 MAY 1991

ADMINISTRATOR GENERAL
Philippe Rouvillois
DEPUTY ADMINISTRATOR GENERAL
Guy Paillotin
HIGH COMMISSIONER
Jean Teillac

SCIENTIFIC DIRECTOR
Robert Dautray
NUCLEAR SAFETY GENERAL INSPECTOR
François Cogné

GENERAL INSPECTORATE
Claude Moranville
MANAGEMENT CONTROL UNIT
Daniel Leroy

OPERATIONAL DIVISIONS

MILITARY APPLICATIONS DIVISION
Roger Baléras
NUCLEAR FUEL CYCLE DIVISION
Jean-Yves Barré
NUCLEAR REACTORS DIVISION
Jacques Bouchard
PHYSICAL SCIENCES DIVISION
Robert Aymar
LIFE SCIENCES DIVISION
Michel Suscillon
ADVANCED TECHNOLOGIES DIVISION
Yannick d'Escatha

NUCLEAR PROTECTION AND SAFETY INSTITUTE
Jean Rastoin
FRENCH RADIOACTIVE WASTE MANAGEMENT AGENCY
Henri-Edme Wallard
NATIONAL INSTITUTE FOR NUCLEAR SCIENCE AND TECHNOLOGY
Yves Chelet
HISTORIC OF THE CEN-FAR

- 1945  FRENCH AEC CREATION
- 1946  CHATILLON CENTER
- 1957  CEN-FAR CENTER
- 1948  FIRST ATOMIC FRENCH PILE - STOPED IN 1976
- 1953  FIRST PILOT PLAN FOR NUCLEAR FUEL REPROCESSING
         - transfert to ATALANTE in MARCOULE since 1993)
- 1956  FIRST PU METALLURGY LAB - STOPED IN 1981
- 1956  FIRST GRAMME WEIGHT OF PU
         STARTING OF NEUTRON STUDIES IN NUCLEAR CORE AND ARTIFICIAL RADIOELEMENTS MAKING
         in
         \[\{\]
         1959 - 1982 TRITON
         1959 - 1977 MINERVE (transfert to Cadarache)
         \[\}\]
- 1973  STARTING OF NUCLEAR FUSION TOKAMAK
         - STOPED in 1985 -
         (TORE SUPRA in CADARACHE)
- 1990  FIRST DISMANTLING OF HIGH ACTIVITIES LAB.
THE OLDEST CENTER
BORN IN 1946
Birth-place of the nuclear physics (civilian and military)

THE MORE DENSE
2 000 PERSONS/130 000 m²

THE MORE FLEXIBLE
AEC CENTER
all the nuclear lines started in CEN-FAR
CEN-FAR ACTIVITIES

NUCLEAR SAFETY

HUMAN
ENVIRONMENTAL
PLANTS

PROTECTION

CRISES TECHNICAL NATIONAL CENTER

CHEMISTRY

* CHEMISTRY OF IRRADIATED NUCLEAR FUEL
  - Reprocessing
  - Solid and liquid wastes treatment
  - Actinides production (sources)

* ANALYTICAL CHEMISTRY
* CORROSION CHEMISTRY
* WASTES CONDITIONNING AND DISPOSAL STUDIES

ROBOTIC for hostile environment, services and medical applications.

* TELEOPERATION
* MOBILE AND AUTONOMUS ROBOTS
* INDUSTRIAL PROCESSES AUTOMATISATION
* SIMULATION AND REMOTE CONTROL

MEDICAL

* TOXICOLOGY
* PATHOLOGY
EFFECTIF DES UNITES DU CENTRE
AU 30/10/90 hors stagiaires et thésards

DIRECTIONS
OPERATIONNELLES

DCC 305
DTA 142
DSV 37

SUPPORT
LOGISTIQUE
GIE-INTRA
ANDRA
SCSIN
EXTERIEUR

IPSN

25 %
19 %
1 %
6 %
2 %
11 %

CEN/FAR

FAR/O1GB 10/90
DIRECTIONS OPERATIONNELLES
(DCC - DTA - DSV)

NUCLEAIRE

BIOTECHNOLOGIE

CHIMIE

ROBOTIQUE

CEN/FAR

FAR/OIGB 10/90
MATERIALS, for waste embedment and disposals

CEMENT BASE MATERIALS
  Liquid & REI waste solidification
  Solid technological waste immobilization
  Concrete shallow land burrial & deep disposal structure
  Long term durability

  CUSTOMERS : EDF, CEA Centers, COGEMA, ANDRA,...

CLAY (NATURAL FRENCH BENTONITE) BASE MATERIALS
  Deep disposal & borehole backfilling and sealing

  CUSTOMERS : ANDRA, ENRESA (SPAIN)

GEOCHEMISTRY, of radionuclides and groundwaters

  Actinide chemistry & speciation
  Chemistry of deep groundwater
  Solid-solution interactions
  Radionuclide interactions with disposal materials
  Kinetics of migrations
  Natural analogs

  CUSTOMERS : CEA, ANDRA, IPSN
WASTE PACKAGES EVALUATION

Full size leaching tests
Coring samples for agreement tests

CUSTOMERS: WASTE PRODUCERS

MODELLING

Long term behavior of materials
Radionuclide migration (source-term)

CUSTOMERS: ANDRA, IPSN
DURABILITY STUDIES, to guarantee cement and concrete behavior on 300 years, in disposal conditions

Basic studies on compared microstructure of the different type of french cements after setting
Effect of water leaching
  .Influence of type of cement
  .Influence of pH
  .Influence of ions (Cl-, SO4--, CO3--, NO3-, NH4+, ...)
  .Influence of microfractures
Modelling of cement decalcification

FORMULATION STUDIES of mortars, grouts, concretes

WASTE EMBEDMENT
  Chemical liquid waste (evaporator concentrates, sludge, REI, ...)
    Setting, durability
  Choice of cement
  Choice of waste pretraitment and/or cement additives (setting)
  Process implementation
  Waste form behavior
  Example: concentrate and sludge from CEA centers, REI and concentrate from EDF reactors
Solid technological waste

Rheology, confinement

Compound choice
Confinement power of the grout (or mortar) measurement
Process implementation
Waste form behavior

Example: hulls of EDF PWR reactors, technological waste from COGEMA and CEA centers

ENGINEERED BARRIERS FOR SHALLOW LAND BURRIAL AND DEEP DISPOSAL

Long durability concretes (structure parts of disposals)
High confinement mortars (filling material of monoliths)

CHARACTERIZATION OF CEMENTITIOUS WASTE FORM
(homogeneous and heterogeneous ones)

Bleeding before setting
Workability time
Shrinkage or swelling (depending on storage condition)
Mechanical strength
Permeability to N2
Diffusion coefficients (HTO, Cs,...)
Leaching rate
CLAY BARRIERS STUDIES

SELECTION OF A CLAY (1983 - 1985)

Choice of a french natural clay (Ca "bentonite"), in collaboration with BRGM and ANDRA, coming from one among 18 surface natural deposits.

Mineralogical identification

Physical and chemical property measurements

Densification ability

LONG TERM STABILITY of the selected bentonite (1985-1995)

in terms of mineralogy, swelling pressure, ionic exchange capacity evolution

Temperature effect

Effect of chemical species coming from the near-field

(geological and engineered media)

Radiation effects
STUDY OF CLAY DENSIFICATION (1985 - 1988)

Bloc compaction
In-situ packing

Compacted bentonite properties as a function of density and water content:

Permeability
Thermal conductivity
Mechanical properties

Compaction and properties of bentonite/sand mixtures as a function of the sand content

INDUSTRIAL VALIDATION (1987 - 1990)

Block manufacture
Setting in basket of the clay blocks
Handling of the baskets
In-situ validation (Fanay-Silord) : Pits of 1m diameter and 30m deep

FULL SIZE BEHAVIOR (1985 - 1995)

evaluated in mock-up
in-situ
OBJECTIVE

==> TO PREDICT THE MIGRATION OF RADIOELEMENTS IN THE GEOSPHERE OVER LARGE PERIODS OF TIME NOT DIRECTLY ACCESSIBLE TO THE LAB (1,000 TO 1,000,000 YEARS)

IMPORTANCE OF

* TIME SCALES
* DIMENSIONAL SCALES
* COMPLEXITY OF SYSTEM
FOUR METHODOLOGICAL APPROACHES

1. LABORATORY STUDIES
2. IN SITU EXPERIMENTS
3. NATURAL ANALOGUES
4. MODELLING
FOUR MAIN DIRECTIONS OF INVESTIGATION

1. GEOCHEMISTRY OF LONG-LIVED RADIONUCLIDES

=> SPECIATION

* THERMODYNAMIC DATA BASE (OECD/NEA)
* CARBONATE SYSTEM (U, Pu, Np, Am)
* OTHER LIGANDS
* EXTENSION OF STUDIES TO TC, SE...

2. GEOCHEMISTRY OF SOLID-SOLUTION INTERACTIONS

 => MOBILITY OF ELEMENTS
 => RULING PARAMETERS

* MECHANISMS OF ELEMENTAL RETENTION ONTO MINERAL SURFACES

* AQUEOUS DISSOLUTION OF GLASSES AND MINERALS
* FORMATION AND EVOLUTION OF SECONDARY PHASES (GELS)

* ROLE OF COLLOIDS AND HA/FA (ORGANIC MATTER)

* BUFFERING CAPACITY OF ROCKS FOR THE REDOX POTENTIAL

3. COUPLING OF HYDRODYNAMICS AND GEOCHEMISTRY

    => MASS TRANSFER

* PERCOLATION EXPERIMENTS
* CHROMATOGRAPHIC MODEL

4. NATURAL ANALOGUES

    => HEURISTIC ROLE

* STUDIES ON THE ANALOGY ITSELF

* DURABILITY OF WASTE FORMS
* INTERACTIONS BETWEEN BARRIERS

* MIGRATION OF CHEMICAL ANALOGUES (U, TH, REE...)
CEA-PNC Meeting

19th November 1991

Marie Thérèse Ménager

"Laboratoire d'Etude des Comportements À Long Terme"
To predict the migration of radioelements in the geosphere over large periods of time not directly accessible to the laboratory (1,000 to 1,000,000 years)

* Time scales
* Dimensional scales
* Complexity of system
FOUR METHODOLOGICAL APPROACHES

1. Laboratory studies
2. In situ experiments
3. Natural analogues
4. Modelling
1. Geochemistry of solid/solution interactions

Mobility of elements

Controlling parameters (Eh, pH, ligands)

2. Natural analogues
1. Geochemistry of solid/solution interactions

# Oxides, silicates, cement minerals...
# Adsorption, ion exchange, coprecipitation...

# Minerals and glasses

# Mechanisms
(Hydrolysis, polymerization, ion exchange, accumulation of heavy elements)
**Formation and evolution of secondary phases**

# Amorphous/crystalline (hydroxides, hydrosilicates ...)

# Trapping ability

# Distribution during organization of gels

# Effects of radiation damages on solubility

---

**Buffering capacity of rocks for the redox potential**

# Ionic valence --- geochemical mobility

---

**Role of colloids and of organic matter**
2. Natural analogues

* Studies on the analogy itself

# Chemical elements
(actinides/U, Th, REE)

# Materials
(nuclear and natural glasses, bitumens ...)

# Geochemical systems
(hydrothermal sites ...)

* Studies on the durability of waste containers

# Nuclear glasses

# U-oxide

# Concretes

# Bitumens
Interactions between near-field barriers

# Glass/iron canister/Clayey backfill materials

# U, Th, REE (mineralized systems)

# granites, clays, schists

# Oklo natural fossil reactors
RETENTION OF RADIONUCLIDES IN POORLY ORGANIZED PHASES
IN THE NEAR FIELD OF A HLW NUCLEAR DISPOSAL

CREACH M., MAGONTHIER MC.
CEA / CEN Fontenay aux Roses
HLW NUCLEAR DISPOSAL:

- WASTE PACKAGING: GLASS IN STAINLESS STEEL (Fe) CANISTER.
- DISPOSAL DESIGN: BACKFILL MATERIAL UNDER DEVELOPMENT.

SIMULATION OF NEAR FIELD CONDITIONS:

- NATURE OF SECONDARY PHASES?
- TRAPPING OF HEAVY ELEMENTS?

5 MONTHS - 150°C
Présentation du verre et de la pellicule d'altération (MH 1)

1. Verre
2. Zone poreuse
3. Zone mixte claire
4. Zone mixte sombre
5. Argile
MAJOR COMPONENTS OF THE HYDRATED LAYER:

§ Si - Al (GLASS NETWORK)
§ Fe (STAINLESS STEEL)

HEAVY ELEMENTS PARTITION:

§ HYDRATED LAYER / SOLUTION
§ AMORPHOUS / CRYSTALLINE SUBLAYERS

?? EVOLUTION OF AMORPHOUS MATERIAL WITH TIME ??

• ABILITY TO TRAP HEAVY ELEMENTS
• INFLUENCE OF HEAVY ELEMENTS UPON CRYSTALLOGENESIS
• BEHAVIOUR OF HEAVY ELEMENTS

TOO COMPLEX COMPOSITION OF NUCLEAR GLASS:
MULTICOMPONENTS HYDRATED LAYER

AGING OF THREE-COMPONENTS GELS
PRELIMINARY RESULTS

NO STRUCTURAL AND CHEMICAL EVOLUTIONS AFTER 5 MONTHS OF AGING (90°C).

INHIBITION OF CRYSTALLIZATION (SILICA EXCESS?)

PERSISTENCE OF TRAPPING

SILICA-RICH GELS AS THOSE DEVELOPED ONTO NUCLEAR GLASS COULD BE EFFICIENT TRAPPING BARRIERS AS LONG AS ENVIRONMENTAL CONDITIONS ARE PRESERVED
EVALUATION OF REDOX BUFFER CAPACITY OF GEOLOGICAL FORMATIONS

Trotignon L et Turpault M.-P.

BIOSPHERE

EQUILIBRATED SOLUTION AFTER ROCK-WATER INTERACTION

ROCK
- QUARTZ
- BIOTITE
- K-FELDSPAT
- PLAGIOCLASE

BIOTITE

\[ \text{Fe}^{2+} \implies \text{Fe}^{3+} \]

OXYDIZING SOLUTION

PERTURBATION

WASTE DISPOSAL

CEA DCC/DSD/SCS/SGC/LECAP : 18/11/91
AIM:

Evaluate the response of the geological medium to a chemical perturbation caused by the waste disposal.

What is the redox buffer capacity of a rock volume through which oxidizing solutions flow?

APPROACH:

Laboratory experiments on the oxidative corrosion of iron(II) minerals and on representative volumes of rock samples.

Study of natural analogues: oxidative perturbation at long term.

SELF-RADIATION EFFECTS ON THE SOLUBILITY OF ACTINIDE-
CONTAINING SECONDARY PHASES

Thierry PROT

Scope of this work: investigate possible effect of α-decay on the
solubility of several mineral phases:
- carbonate (examplified by calcite, CaCO₃)
- ferric oxide (haematite, α-Fe₂O₃)
- ferric oxihydroxide (goethite, FeOOH)
- hydrated layer of amorphous silica
- hydrated layer of simulated nuclear waste glass
  (R7T7)

Use of external bombardment of He and Pb of appropriate energies to
simulate both the α-particle (He, 1.8 MeV) and the α-recoil nuclei (Pb, 200
keV).

Analysis methods:
- optical microscopy with Nomarsky interferential
  contrast
- diamond stylus device to measure possible irradiation
  effect
  (Dektak, Talystep)
- Rutherford Backscattering Spectrometry (RBS)
- Resonant Nuclear Reaction Analysis (RNRA)
- Elastic Recoil Detection Analysis (ERDA)
- X-ray Photoelectron Spectroscopy (XPS)
- Scanning Electronic Microscopy
- Transmission Electronic Microscopy (ultrathin
  sections)
RESULTS

- Radiation enhanced solubility of calcite with partial decomposition of calcium carbonate into oxide for high fluences (> $10^{12}$ ions Pb/cm$^2$ $\leq$ equivalent doses of $\approx 2.5 \times 10^{17}$ events $\alpha$/g). For a given fluence, decomposition is higher with Pb ions than He ions (different mechanisms of energy loss).

- Partial dehydration of FeOOH into $\alpha$-Fe $\mathcal{O}_3$

- Not change observed in $\alpha$-Fe $\mathcal{O}_3$ (Fe $\mathcal{O}_4$ amorphization,..) ?

- Radiation enhanced hydration of the hydrated layer of amorphous silica in deionised water.

- During aqueous corrosion, retention of heavy elements (Fe, REE, actinides) in simulated nuclear glass.
Contribution of old analog material for radionuclides migration modelling in cemented engineering barriers.

Rougeau Patrick

* Sampling of concrete in contact with radionuclides:
  - Uranium mine.
  - Archeological cements.

* Petrographic studies:
  - Optical microscopy and cathodoluminescence.
  - XRD, SEM and EDX.
  - Uranium fission tracks.
  - ICP analysis.

* Modelling of radionuclides migration in concrete
ELEMENTAL REMOBILIZATIONS AROUND THE U-MINERALIZED VEIN OF THE JALERYS (MORVAN-FRANCE)

M.T. MENAGER, J.C. PETIT, C. MENET

DRDD-SESD-SCPCS-LECALT, CEN-FAR, BP6
92265 FONTENAY-AUX-ROSES FRANCE

FINANCIAL SUPPORT OF CEC

ISSUE

IS AN INTRAGRANITIC U-MINERALIZED ORE BODY ANALOGOUS TO A RADWASTE DISPOSAL IN A GRANITIC FORMATION?

* FLUIDS PATHS

* ALTERATION STAGES

* TRACE ELEMENT MOBILIZATION AND SUBSEQUENT TRAPPING

DISPERSION PROCESSES

ASSESSMENT OF CONFINEMENT CAPABILITY
THE SITE: THE JALERYS

GRURY GRANITE (MORVAN-FRANCE)

* MINE

* SAMPLING AT -170 M

* SUBALKALINE K GRANITE

* AGE: 348 MY

* MINERALIZATION IN M-WIDE VEINS
  PITCHBLende-QUARTZ-PYRITE

U
"SOURCE-TERM"

GRANITE
U TH REE

XXX

XXX X X X

30 M

* SMECTITIC SELVAGE ANALOGOUS TO ENGINEERED BARRIER
IMPlications FOR HLW DISPOSAL

URANIUM

WATER/ROCK INTERACTIONS LEAD TO

U-MIGRATION FROM ORE BODY THROUGH
GRANITIC FORMATION

* T'C RANGE CONSISTENT WITH
DISPOSAL CONDITIONS

* COMPARABLE FLUID COMPOSITIONS (?)

FLUID CIRCULATION AND U DISPERSION/TRAPPING

* FISSURAL TRANSPORT

* "MATRIX DIFFUSION"

U TRAPPED IN VARIED ALTERATION MINERALS

ZONATION FROM VEIN TO BULK GRANITE
DISTINCTIVE RETENTION SCALES
FOR U RELEASED

* "NEAR FIELD" (0 TO 10 M)

PHYLLOSILICATES

FE HYDROXIDES

U-SECONDARY MINERALS (?)

* "FAR FIELD"

CARBONATES

RETENTION MECHANISMS

* INCORPORATION : PHYLLOSILICATES

* SORPTION : FE HYDROXIDES
PHYLLOSILICATES

* PRECIPITATION : THORITE
REE-CARBONATES

THORIUM AND REE

MIGRATION ONLY ON MICROSCALE DISTANCES

T°C AND FLUID COMPOSITION(?)
A TWO BILLION YEARS
OLD NATURAL DISPOSAL
OF ACTINIDES AND FISSION PRODUCTS:

THE NEW NUCLEAR OKLO REACTORS
(GABON)

C. MENET

CEA
CEN-FAR
FONTENAY aux ROSES
FRANCE
COLLOID AND PARTICULATE
MATTER IN RELATION WITH THE
BEHAVIOUR OF RADIOCHEMICALS

CEA - PNC COLLABORATION

TECHNICAL MEETING ON GEOCHEMISTRY

NOVEMBER 19, 1991

V. MOULIN
MOBILITY OF TRACE RADIOTOXIC ELEMENTS IN NATURAL AQUIFERS

===> COMPLEX PHYSICO-CHEMICAL INTERACTIONS FUNCTION OF

* ELEMENT
* ROCK MATRIX
* WATER:

===> PRESENCE OF COLLOIDS:

♦ 1-1000 nm size
♦ organic, inorganic nature
♦ dissolution/precipitation, complexation
filtration and sorption
1. Study of the occurrence of colloids and humic substances in natural waters

* concentration?
* composition?
* properties?

2. Study of their interactions with radionuclides and cations

* complexation reactions with HA/FA
* flocculation of HA/FA
* sorption of cations onto colloids (model)

3. Their role on retention properties of cations on mineral surfaces (oxides, ...)

as a function of important physico-chemical parameters:
$pH$, ionic strength, presence of competing cations (Ca), ratio cation/HA-FA, HA/FA concentration
PRESENCE IN NATURAL WATERS

CONCENTRATION - ISOLATION
CHARACTERISATION:

HUMIC SUBSTANCES

Concentration: sorption onto an anionic resin

Fonay-Augères/Massif Central: 2 ppm TOC
(10 grammes of humic/fulvic acids isolated: site specific materials for CEC)

Surface waters: 4 ppm TOC

Characterisation:
- elementary, mineral analysis,
- spectroscopic analysis,
- acido-basic properties,
- size analysis (UF, SEC, PCS)
APPLICATION TO HUMIC SUBSTANCES

selection of a groundwater characteristic of a geological formation:

FANAY-AUGERES/Massif-Central/France

- a granitic formation
- a U mine
- a fracturated and mineralised formation

--- Water (2 ppm TOC)

- sampling from a borehole
- 280 m depth

- chemical analysis
- application of geochemical codes
- datation (tritium)

in order to know the geological and geochemical environment of humic substances
Extraction, separation and purification of humic substances

GROUND WATER

CONCENTRATION

Anion-Exchange Resin
DEAE-Cellulose

Elution with NaOH

ORGANIC SUBSTANCES

SEPARATION

Precipitation with HCl
Centrifugation

Precipitate
(Humic Acids)

NaOH/HCl treatment
Dialysis

PURIFICATION

Solute
(Fulvic acids + others)

Amberlite XAD-8

Elution with NaOH

Cation-Exchange resin

Lyophilisation

HUMIC ACIDS

FULVIC ACIDS
By using this procedure it has been isolated:

4.5 grammes of humic acids
10 grammes of fulvic acids

Fanay-Augères humic substances represent 41% of TOC present in the water.

Fanay-Augères humic substances:

*site specific humic substances*

in the Complex Colloid (CoCo) group in the frame of a CEC programme distributed to the laboratories involved in this group.
CHARACTERIZATION OF HUMIC SUBSTANCES

<table>
<thead>
<tr>
<th>Elemental analysis</th>
<th>HUMIC ACIDS</th>
<th>FULVIC ACIDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C</td>
<td>46.2</td>
<td>49.2</td>
</tr>
<tr>
<td>% H</td>
<td>6.3</td>
<td>4.8</td>
</tr>
<tr>
<td>% O</td>
<td>30.6</td>
<td>44.7</td>
</tr>
<tr>
<td>% N</td>
<td>8</td>
<td>1.4</td>
</tr>
<tr>
<td>% ash</td>
<td>&lt; 1</td>
<td>3.5</td>
</tr>
<tr>
<td>H/C</td>
<td>1.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral composition (ppm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>340</td>
<td>20</td>
</tr>
<tr>
<td>Fe</td>
<td>670</td>
<td>40</td>
</tr>
<tr>
<td>Ca</td>
<td>5080</td>
<td>2200</td>
</tr>
<tr>
<td>U</td>
<td>7760</td>
<td>30</td>
</tr>
<tr>
<td>Mg</td>
<td>2200</td>
<td>110</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acidity (meq/g)</th>
<th>3.4</th>
<th>5.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Datation</td>
<td>-</td>
<td>625 y</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spectroscopic analysis</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-Visible E4/E6 (pH8, Tris 0.1 M)</td>
<td>3.6</td>
<td>17.5</td>
</tr>
<tr>
<td>FTIR</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Size analysis
**RECAPITULATIVE TABLE ON SIZE DETERMINATION**

<table>
<thead>
<tr>
<th>Method</th>
<th>HA</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Size exclusion chromatography</em> (Tris 0.1 M, pH 7, UV detection 254 nm)</td>
<td>5000 D (1000 %)</td>
<td>5000 D (100 %)</td>
</tr>
<tr>
<td><em>Ultrafiltration</em> (Tris 0.1 M, pH 7, UV detection 254 nm)</td>
<td>&lt;1.5 nm (30 %) and 3-25 nm (60 %)</td>
<td>&lt;1.5 nm (95 %)</td>
</tr>
<tr>
<td><em>Photon Correlation Spectroscopy</em> (laser 1 W, 90°)</td>
<td>100 nm (2.4 %)</td>
<td>70 nm (0.03 %)</td>
</tr>
</tbody>
</table>

Valérie MOULIN        CEA        DSD/SCS/SGC
APPLICATION TO COLLOIDS

* SELECTED WATERS:

Grimsel/Switzerland (CEC Programme)

El Berrocal/Spain (CEC Programme)

Pyrénées/France

Oklo/Gabon

* CONCENTRATION TECHNIQUE:

TRANSVERSAL ULTRAFILTRATION IN SITU

ON FILTERS OF DIFFERENT POROSITIES

(3, 15, 100, 220, 450 nm)

* CHARACTERIZATION

Scanning Electron Microscopy + EDX: size, composition, concentration

Photon Correlation Spectroscopy: size determination

(directly on the water/filtrates)
RESULTS OBTAINED ON GRIMSEL WATER

<table>
<thead>
<tr>
<th>Pore size (nm)</th>
<th>Size range (nm)</th>
<th>[Colloid] part/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>70-1000</td>
<td>4.5 $10^9$</td>
</tr>
<tr>
<td>15</td>
<td>70-1000</td>
<td>3.8 $10^9$</td>
</tr>
<tr>
<td>15</td>
<td>70-1000</td>
<td>4.4 $10^8$</td>
</tr>
<tr>
<td>100</td>
<td>100-1000</td>
<td>6.0 $10^8$</td>
</tr>
<tr>
<td>220</td>
<td>220-1000</td>
<td>1.8 $10^8$</td>
</tr>
<tr>
<td>450</td>
<td>450-1000</td>
<td>2.6 $10^8$</td>
</tr>
<tr>
<td>SITE</td>
<td>DESCRIPTION</td>
<td>[COLLOID]</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Alligator</td>
<td>U or body, metasediments</td>
<td>-</td>
</tr>
<tr>
<td>Cigar Lake</td>
<td>U or body unconformity</td>
<td>1 to 260 mg/l</td>
</tr>
<tr>
<td>Gorleben</td>
<td>sedimentary</td>
<td>$10^{17}$ part/l</td>
</tr>
<tr>
<td>Grimsel</td>
<td>crystalline</td>
<td>$10^{10}$ part/l</td>
</tr>
<tr>
<td>Mannitoba</td>
<td>crystalline</td>
<td>$10^{14}$ part/l</td>
</tr>
<tr>
<td>Nevada</td>
<td>volcanic rocks</td>
<td>0.1 to 16 mg/l</td>
</tr>
<tr>
<td>Pocos de Caldas</td>
<td>altered volcanic rocks</td>
<td>&lt;1 mg/l</td>
</tr>
</tbody>
</table>

Published data on colloid concentration in different natural waters
INTERACTIONS OF HUMIC SUBSTANCES AND COLLOIDS WITH RADIOELEMENTS

* COMPLEXATION

* FLOCULATION

* SORPTION
COMPLEXATION

--- use of suitable analytical techniques for studying complex formation due to
  
  * heterogeneity and polydispersity of humic substances
  
  * specificity of radioelements (Am, Np, Pu, U, Th)

--- humic substances - trivalent cations
  
  * effect of pH
  
  * effect of ionic strength
  
  * effect of competing cations (Ca, Al, Fe)
METHODS

- based on titration of humic/fulvic acids
  o spectrophotometry
    \( (Am) = 3 \times 10^{-5} M \)
  o laser induced time resolved spectrofluorimetry (LITRS)
    \( (Cm) = 5 \times 10^{-8} \) to \( 10^{-6} M \)

Conditions:
  * pH, ionic strength constant
  * addition of increasing HA-FA
  * measurement of absorbance or fluorescence

- based on the separation of the complex and cation
  o size-exclusion chromatography (SEC)
    \( (Am) = 10^{-7} M \)
    \( (Cu, Eu, Th, U) \)

Conditions:
  * pH, ionic strength constant
  * measurement of bound cation

\[ \Rightarrow \text{variable (M)/(HA,FA)} \]
LASER INDUCED

TIME RESOLVED

SPECTROFLUOROMETRY
IN COLLABORATION WITH THE LASER SPECTROSCOPY GROUP/CEA-FAR
$C_m / H_A$

**Fluorescence Titration Curve**

$C_m : 5 \times 10^{-7}$ M

pH 5.2

$NaClO_4 : 0.1$ M

$W = 0.5$ mmol/g

$[H_A] \text{ mg/l x c.l.}$

$C_m + H_A \rightleftharpoons C_m H_A$

$\beta = [C_m H_A] / [C_m][H_A]$

$[H_A] = W \cdot C_0 - [C_m H_A]$

CEA/DCC/DPE

Valérie MOULIN  CEA  DSD/SCS/SGC
INFLUENCE OF pH ON THE INTERACTION CONSTANT

λ excitation : 337 nm, λ fluorescence : 601 nm for curium

λ excitation : 355 nm, λ fluorescence : 576 nm for dysprosium

CEA/DCC/DPE

Valérie MOLLIN  CEA  DSD/SCS/SGC
CONCENTRATION EFFECT
ON THE INTERACTION CONSTANT

\[ \Delta C_m \quad \bullet \text{Dy} \quad \bullet \text{Am} \]

NaClO$_4$ 0.1 M

\[ \log [M] \]

- \( \lambda \) excitation: 307 nm, \( \lambda \) fluorescence: 596 nm
- \( \lambda \) excitation: 355 nm, \( \lambda \) fluorescence: 576 nm

CEA/DCC/DPE
SORPTION PROCESSES OF RADIOELEMENTS ONTO COLLOIDS

* BATCH EXPERIMENTS

MODEL COLLOIDS (SILICA)/ Am(III), Np(V), U(VI)

* DESCRIPTION OF SORPTION MECHANISMS
ACTINIDE SORPTION ONTO SILICA COLLOIDS

I = 0.1 M NaClO₄

log Kd (ml/g)

U

Am

Np

U
100 ppm

Np
500 ppm

Am
500 ppm

pH
DESCRIPTION OF THE SORPTION PROCESSES ON SILICA COLLOIDS?

LIMITATION OF THE USE OF Kd:
* just a quantitative description of the sorption
* no relation between the different species present
  * not related to a specific mechanism

⇒

IN ORDER TO PREDICT THE CATION SORPTION BEHAVIOUR:

REQUIREMENT OF A SORPTION MODEL
PROPOSAL OF MECHANISMS TO FIT THE EXPERIMENTAL DATA: CASE OF U (VI)

\[ \text{SiOH} + \text{UO}_2 \rightleftharpoons \text{SiO} \text{UO}_2 + \text{H} \]
\[ \log K_{S1} = -0.9 \]

\[ \text{SiOH} + \text{UO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{SiO} \text{UO}_2(\text{OH}) + 2\text{H} \]
\[ \log K_{S2} = -7.3 \]

\[ \text{SiOH} + 3\text{UO}_2 + 5\text{H}_2\text{O} \rightleftharpoons \text{SiO} (\text{UO}_2)_3(\text{OH})_5 + 6\text{H} \]
\[ \log K_{S3} = -17 \]

\[ \text{SiOH} + \text{UO}_2 + 2\text{CO}_3 + \text{H} \rightleftharpoons \text{SiO} \text{UO}_2(\text{CO}_3)_2 + \text{H}_2\text{O} \]
\[ \log K_{S4} = 29 \]

\[ \text{SiOH} + \text{UO}_2 + 3\text{CO}_3 + \text{H} \rightleftharpoons \text{SiO} \text{UO}_2(\text{CO}_3)_3 + \text{H}_2\text{O} \]
\[ \log K_{S5} = 36 \]

Compared with Kurbatov plot:
\[ \log K_S = -7.2 \]
[SiO₂] = 100 ppm    [UO₂] = 1.5 \times 10^{-6} \text{ M}
ROLE OF HUMIC SUBSTANCES AND COLLOIDS ON RETENTION PROPERTIES OF CATIONS ONTO MINERAL SURFACES
INFLUENCE OF HUMIC SUBSTANCES ON THE RETENTION OF RADIOELEMENTS

* SORPTION OF ACTINIDES ONTO MINERAL SURFACES (OXIDES: SILICA, ALUMINA, ...) IN THE PRESENCE OF HUMIC SUBSTANCES AS A FUNCTION OF:
  - pH
  - VALENCE OF THE ACTINIDE:
  - IONIC STRENGTH
  - PRESENCE OF COMPETING CATIONS

* PROPOSITION OF RETENTION MECHANISMS:

SURFACE COMPLEXATION MODEL
Alumina - Am(III)
in the presence of humic acids

$\text{Al}_2\text{O}_3 \ 10 \text{ g/l} \ I = 0.1 \text{ M NaClO}_4$
Adsorption of Am on silica as a function of pH and ionic strength

- ▲ I = 0.001 M
- ● I = 0.01 M
- ■ I = 0.1 M

% of Am on silica vs pH

log Kd in ml/g

2 3 4 5 6 7 8 9

2 2.3 2.6

0.7 1.1 1.3 1.5 1.7 1.9 2 2.3 2.6
Adsorption of Am(III) as a function of pH, [HA] and I

- [HA] = 1 ppm, I = 0.1 M
- [HA] = 10 ppm, I = 0.1 M
- [HA] = 1 ppm, I = 0.001 M
- [HA] = 10 ppm, I = 0.001 M
SURFACE COMPLEXATION MODEL

Silica - Am(III)

\[ \text{SiOH} + \text{Am} \rightleftharpoons \text{SiOAm} + \text{H} \]

\[ \log K = -0.5 \]

Silica - Humic acids

\[ \text{SiOH} + \text{HA} \rightleftharpoons \text{SiOHA} + \text{H} \]

\[ \log K = 2.2 \]

Silica - Humic acids - Am(III)

\[ \text{SiOH} + \text{HA} + \text{Am} \rightleftharpoons \text{SiOHAAm} + \text{H} \]

\[ \log K = 9.7 \]
• COMPLEMENTARY APPROACHES USING:
  - colloidal suspensions
  - mineral monoliths

===> USE OF ION BEAM TECHNIQUE
(RUTHERFORD BACKSCATTERING SPECTROMETRY = RBS)
  * RETENTION MECHANISMS
  * QUANTITATIVE DETERMINATION OF THE AMOUNT FIXED

IN COLLABORATION WITH TWO LABORATORIES:
CNRS/Orsay; INFM/Padova
MONOLITHS
SILICA / IRON OXIDE / MUSCOVITE MICA

COLLOIDS
CERIA / SILICA / IRON OXIDE / MICA

associated with U(VI), Th(IV)

=====>

* EFFECT OF THE CHARGE (interface, colloid)
* EFFECT OF THE SIZE (colloid, porosity)

FORMATION OF A MONOLAYER
STUDIES PERFORMED WITH

M. Caceci/T. Dellis/N. Labonne/M.T. Tran/D. Stammose/M. Theyssier/J.C. Petit/J.P. Vilarem/J. Tits/ M.C. Magonthier/M.T. Ménager:
CEA, DSD
C. Moulin/P. Decambox/O. de Ruty: CEA, DPE

IN COLLABORATION WITH

B. Allard/Sweden
J.C. Dran/CNRS
G. Della Mea/INFM
J. Ramsay/AEA
P. Gomez, M. Turrero/CIEMAT
HYDROGEOCHEMISTRY

1) uranium and uranium series in groundwaters around uranium deposits. (French deposits, Oklo, Cigar Lake). Application to uranium prospection and waste management.

2) evolution of major and trace elements in groundwaters during progressive interaction with host-rocks: application to waste disposal studies, field studies of granitic thermal waters and mine waters (Limousin, Lodève, Oklo).

3) experimentation and modelling of trace element transport (laboratory and in situ experiments). Achievement of a coupled hydrodynamical-geochemical code with DRN/DMT/SEMT/TTMF

4) experimental study of UO2 behaviour in presence of reducing groundwaters

5) analytical chemistry (neutron activation, ion chromatography, alpha spectrometry, electrochemistry, laser spectrofluorimetry)
Uranium and uranium series in groundwaters

- uranium speciation in groundwaters around uranium deposits
- influence of oxido-reduction
- control of uranium concentration in reducing groundwaters
- U series disequilibrium in groundwaters, application to water-rock interaction and uranium prospection
- lead isotopes in groundwaters, application to uranium prospection.
Cigar Lake: ○ sterile  ● mineralized
Lodeve: △ sterile  ▲ mineralized
Jarvan: □ sterile  ■ mineralized
major and trace elements in groundwaters

- the evolution of groundwater during the progress of water rock interaction is studied. Many granitic sites have been studied. A predictive model of major and trace element behaviour has been established

- efforts now converge towards the understanding of clay interstitial water
CORRELATION BETWEEN CA, K AND DEEP TEMPERATURE IN EQUILIBRATED THERMAL WATERS AND GROUNDWATERS FROM DIFFERENT AREAS.
<table>
<thead>
<tr>
<th></th>
<th>&lt; 450nm</th>
<th>&lt;10 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>moles/Kg</td>
<td>moles/Kg</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>8.0 10^{-8}</td>
<td>1.0 10^{-9}</td>
</tr>
<tr>
<td>Ca</td>
<td>4.0 10^{-5}</td>
<td>4.0 10^{-5}</td>
</tr>
<tr>
<td>Ce</td>
<td>5.5 10^{-9}</td>
<td>&lt;8.5 10^{-11}</td>
</tr>
<tr>
<td>Co</td>
<td>5.0 10^{-10}</td>
<td>5.0 10^{-10}</td>
</tr>
<tr>
<td>Cs</td>
<td>1.0 10^{-7}</td>
<td>1.0 10^{-7}</td>
</tr>
<tr>
<td>Eu</td>
<td>3.5 10^{-11}</td>
<td>&lt;1.5 10^{-12}</td>
</tr>
<tr>
<td>Hf</td>
<td>7.7 10^{-9}</td>
<td>&lt;4.7 10^{-12}</td>
</tr>
<tr>
<td>La</td>
<td>3.0 10^{-9}</td>
<td>2.6 10^{-11}</td>
</tr>
<tr>
<td>Mo</td>
<td>4.4 10^{-8}</td>
<td>4.0 10^{-8}</td>
</tr>
<tr>
<td>Na</td>
<td>2.5 10^{-3}</td>
<td>2.5 10^{-3}</td>
</tr>
<tr>
<td>Nd</td>
<td>7.1 10^{-9}</td>
<td>&lt;6.1 10^{-10}</td>
</tr>
<tr>
<td>Rb</td>
<td>3.0 10^{-7}</td>
<td>3.0 10^{-7}</td>
</tr>
<tr>
<td>Sc</td>
<td>1.0 10^{-9}</td>
<td>5.5 10^{-12}</td>
</tr>
<tr>
<td>Sm</td>
<td>3.7 10^{-10}</td>
<td>5.6 10^{-12}</td>
</tr>
<tr>
<td>Sr</td>
<td>2.8 10^{-7}</td>
<td>2.8 10^{-7}</td>
</tr>
<tr>
<td>Ta</td>
<td>1.1 10^{-10}</td>
<td>&lt;2.3 10^{-12}</td>
</tr>
<tr>
<td>Tb</td>
<td>6.3 10^{-11}</td>
<td>&lt;2.2 10^{-12}</td>
</tr>
<tr>
<td>Th</td>
<td>5.5 10^{-10}</td>
<td>&lt;4.3 10^{-12}</td>
</tr>
<tr>
<td>Zr</td>
<td>6.5 10^{-7}</td>
<td>&lt;6.2 10^{-8}</td>
</tr>
<tr>
<td>Zn</td>
<td>2.1 10^{-8}</td>
<td>1.2 10^{-8}</td>
</tr>
</tbody>
</table>

part. : associated with particles (colloids)
diss. : present as dissolved species
experimentation and modelling of trace elements transport

- column and in situ tracing experiments
- laboratory sorption experiments
- coupled hydrogeochemical transport code (3D capabilities, inclusion of speciation, precipitation dissolution and sorption (surface complex models)
SITE CHARACTERIZATION

1) in-situ analysis

* development of chemical fiber-optics sensors (pH, Fell, etc...). Sensors allow a distant monitoring of chemical parameters which measurement generally induces some perturbation of the geochemical systems. They are to be used in underground laboratories (Mol, Belgium) and drill holes (down to some hundred meters)

* development of "clean" on site water and particle sampling (ultrafiltration, dialysis)

2) study of radiolytic gas production in rocksalt

* experimental program carried out in the frame of the european HAW project on samples from ASSE (Germany)

* development of new analytical techniques which could be used in underground facilities (Fourier Transform Infrared Spectroscopy)
FIBER-OPTICS BASED SENSORS

physical sensors

displacement,
stress,
temperature,
distributed temperature, etc...

chemical sensors

pH
Eh
Organics (benzene, dyes)
uranium
potassium
enzymes
etc...
Available references


Commissariat à l'Energie Atomique, DCC/DSD/SCS/LCASH 13.09.91
SORPTION OF AMERICIUM (III)
FIXATION SUR UNE MONTMORILLONITE

Concentration initiale de M(II) : $5 \times 10^{-4}$ M

$\text{NaClO}_4 \times 10^{-2}$ M

SORPTION OF SODIUM IONS

Kaolinite

\[ [\text{Na}^+]_{\text{clay}} \text{ (m e.q./g)} \]

EC  EC\(_1\)  EC\(_2\)
0.09  0.04  0.05

pH

Illite

\[ [\text{Na}^+]_{\text{clay}} \text{ (m e.q./g)} \]

EC  EC\(_1\)  EC\(_2\)
0.40  0.135  0.265

pH

Bentonite

\[ [\text{Na}^+]_{\text{clay}} \text{ (m e.q./g)} \]

EC  EC\(_1\)  EC\(_2\)
0.95  0.45  0.50

pH
SORPTION OF AMERICIUM (III)
DATA TREATMENT

Fa

\[
\begin{align*}
\{ \text{AmOH}^2+ \} \\
\{ \text{Am(OH)}_2^+ \text{ or AmCO}_3^+ \}
\end{align*}
\]

log [Na\(^+\)]

bentonite
kaolinite
illite
NaNpO2CO3 solubility

\[ \text{lg}[\text{Np}] \]

\[ \text{lg}[\text{CO}_3^{2-}] \]
Minor species influence on the Ig Ks201' error distribution.
Np(V) absorbance in carbonate hydroxide media
Experimental domain

Ig[CO3 2⁻]

-1g[H⁺]
$$k_3 = \frac{[\text{NpO}_2(\text{CO}_3\text{)}_3^{\sigma-}]}{([\text{NpO}_2(\text{CO}_3\text{)}_3^{\sigma-}]) [\text{CO}_3^{\sigma-}]}$$

\[ \lg k_3(0) = -0.86 \pm 0.13 \ ( -0.87 \pm 0.54 ) \]

\[- \Delta \varepsilon_3(\text{Na}^+) = 0.04 \pm 0.02 \ (0.06 \pm 0.20) \]

- \[ \circ [81 \text{ BIL}]^* \]
- \[ \circ [75 \text{ UEN/SAI}]^* \]
- \[ \circ [83 \text{ MAY}] \]
- \[ \circ [89 \text{ RIG}] \]
- \[ \circ [86 \text{ GRE/ROB}] \]
- \[ \circ [71 \text{ MOS5}]^* \]
\[ K_{S_2\beta_3} = [M^+]^3[NpO_2(CO_3)_3^{5-}] / [CO_3^{2-}] \]

\[
\begin{array}{cccc}
M & Na & K & NH_4 \\
\lg(K_{S_2\beta_3}(0)) & -8.96 \pm 0.30 & -9.04 \pm 0.03 & -9.30 \pm 0.25 \\
\end{array}
\]

\[ [77 \text{ SIM}]^* \]
[77 SIM] indicates a potentially significant observation.

\[ [86 \text{ GRE/ROB}] \]
[86 GRE/ROB] indicates another observation or study.

\[ [66 \text{ GOR/ZEN}]^* \]
[66 GOR/ZEN] indicates another significant observation.

\[ [71 \text{ MOS5}]^* \]
[71 MOS5] indicates another significant observation.

\[ \text{NaClO}_4 \]

\[ (\text{NH}_4)_2\text{CO}_3 \]

\[ \text{K}_2\text{CO}_3 \]

\[ \text{redetermination} \]

The graph shows a plot of \( \lg(K_{S_2\beta_3}) \) against mole/kg for various ions, with different markers indicating different sources or observations.
SAFETY RESEARCH PROGRAMS PERFORMED IN UNDERGROUND LABORATORIES BY CEA - IPSN

The Institut de Protection et de Sûreté Nucléaire of the Commissariat à l'Energie Atomique is developing, in the framework of its R and D safety programs, in situ research concerning the confining properties of geological formations. Two sites have been selected, one in clay and the other in shales. These kinds of underground laboratories are called "LEMI": Laboratoires d'Etudes Methodologiques et Instrumentales".

1. THE CLAY UNDERGROUND LABORATORY OF TOURNEMIRE

In situ reasearch work concerning argillaceous formations has been started at the end of 1990. The selected site is an old abandoned railway tunnel, 1885 meters long, in the close vicinity of the village of Tournemire, in the south of France. This tunnel crosses a thick toarcian clay formation, about 200 meters thick; the overlying limestone layers are 270 meters thick, so the geotechnical and hydrogeological conditions are representative of those of a deep repository.

This site is unfit for any radioactive waste disposal operation but very interesting for basic studies on clay. Considering the large possibilities of scientific investigations presented by this site, ELF, a french oil company, is associated with the CEA/IPSN in the use of the tunnel.

The IPSN research program concerns geotechnical, hydrogeological and thermal properties of clay and more particularly, to develop new methods, apparatuses and devices, for the investigation of very low permeability medium and modelling.

After a general geological survey of the area, the first stage, in order to qualify the site and get basic informations on the hydraulic environment, includes to carry out cored boreholes; five boreholes (5 downwards and 1 upwards) have been drilled, respectively 169 m, 144 m, 118 m, 30 m, and 65m long, with
A lot of permeability tests have been performed (pulse tests) as well as geophysical loggings: natural gamma, gamma gamma, acoustic log, and neutron log. Four boreholes have been equipped with the ground water monitoring system, the BAT filter tip, which allows pressure measurement and water sampling in very low permeability rocks. One of the BAT filter tips has been set at the top of the domerian formation, constituted also of clay, which is just below the toarcian clay, and three other BAT filter tips have been located at different levels of the toarcian clay, in order to get informations on hydraulic characteristics; the upwards borehole has been equipped with a pressure gauge set in the upper limestone formation overlying the toarcian clay. Dilatometer tests have also been carried out in the Toarcian and additional dilatometer tests are planned.

An other downwards borehole, 230 m long, has been drilled, in order to investigate the hydrogeology of the carixian limestones, below the domerian clays. Aquifer head, at the different levels, will be continuously monitored.

After this first reconnaissance phase, it is contemplated to perform ventilation tests in a drift specially excavated from the tunnel, in order to evaluate the scale effect on the permeability coefficient and to determine the permeability values at a large scale. The detailed characteristics of these tests will be settled by considering the results of the first stage.

A lot of geophysical tests are also planned in the drift in order to study strain, swelling and convergence of clay and their influence on permeability.

A program of isotopic studies is also under way. The objective is to determine the age of the ground waters in order to precise their transfert time through the clay. Considering the very low quantity of water available, microanalyses by mass spectrometry will be used; measurement will concern 3H, 14C, 36Cl, 129I, and the ratio U/Th.

A thermo-hydro-mechanical experiment is also contemplated in the long run.

Hydrogeological and coupled phenomena models will be developed, in order to describe water flow in clay.

2. THE SHALE UNDERGROUND LABORATORY OF REVIN

A research program concerning the confining properties of a shale formation will start on september 1991 in a non used drift of an electric dam in the northern part of France, in the vicinity of the town of Revin.

The drift is excavated in a thick shale formation of paleozoic age (Upper Cambrian), at a depth of about 170 meters below the surface of the ground. The mechanical, geological and hydrogeological characteristics of the formation has been already studied by Electricité de France, the owner of the dam, for the purpose of the dam making. It is formed by an alternation of shales and quartzites.
It has been strongly folded during the Caledonian orogenesis. It is fissured but the permeability looks to be low.

The present research program includes, in a first stage:

- The geotechnical characterization of the rocks (laboratory study and in situ dilatometer measurement)
- A detailed investigation of fracturing along the wall of the drift.
- Detailed study of the hydrogeological properties of the medium: investigation of the part of matrix, fissures and foliation-planes in the permeability will be carried out by means of a 200 meters long borehole drilled from the surface of the ground and three 100 meters long boreholes drilled from the drift.
- An isotopic study of groundwater similar to the study contemplated at Tournemire will be also carried out.
  - Water flow will be modelled.
  - Additional geophysical studies are also planned.
CHEMICAL ASPECTS OF THE SAFETY STUDY FOR A STORAGE SITE

J.M. VINSON SERE-LETO

The confining of radioactive waste in geological formations is based on three fundamental principles:

- safety,
- long-term considerations,
- the natural environment.

The storage is based around the notion of a barrier, as in other nuclear installations. The criteria for the selection and optimization of the barriers are based on the definition and the risk assessment of this structure.

Except in accident situations, where the geological barrier's integrity comes into question, the normal situation is naturally "accidental" because of the long-term aspect. The risk, represented by mobilizing and transporting a pollutant into the natural environment is, in this case, principally of chemical nature. Its prevention must be carried out in several stages, in space and in time.

Where the installation is concerned, the artificial barriers role is to differ and then limit the pollutant's mobility. The natural environment (geological barrier and interfaces) must contribute to the dilution if not immobilization of elements that are potentially dangerous for man.

Apart from the preventive stress exerted by the installation and the residual stress, linked to irreversible reactions (thermic, chemical or bacteriological), it is the medium and the medium only which, through its chemical properties, conditions the behaviour of an element in low concentration.

The selection and designation of a geological barrier must be based on the criteria; favourable, unfavourable or redhibitory. Only using an advanced knowledge of
the medium and a global strategy for studying its particular properties with specific investigation methods, parametric laboratory studies and exhaustive models can reliable selection criteria be defined.

The geological barrier cannot be selected outside its environment. Its position in space (in particular its depth) cannot be separated from the quality of its interfaces which are not necessarily the biosphere. The variation of chemical parameters at the interfaces can play a vital role in the mobility of pollutants.

We generally define the state of a body in its medium by its thermodynamic equilibria. These equilibria relative to possible energetic states can be calculated using certain geochemical models. The acquisition of chemical data "in situ" must place emphasis on the validation and their possible improvement. The data available can be:

- General parameters: pressure, temperature, ionic conductivity, pH, Eh, etc..., which can be acquired in the form of diagrapies giving the bore profile.
- A global chemical composition. Major traces and infratraces, gas, solid mineralogy.
- Approaching the space variability by punctual sampling at all levels in the bore and by non destructive geophysical studies.
- Evaluation of the experimental destruction by comparative studies of the free water and the reconstituted interstitial medium.

All media and especially all natural media, which are very complex, possess properties likely to modify either globally or locally the range of theoretical reactional possibilities. This means the kinetic factors and electrical interaction phenomena, which require more detailed speciation studies, "in-situ". They are made more delicate by the difference between thermodynamic conditions in the surface and subterranean media.

Kinetic factors, linked to suitable energetic levels, can favorize activation reactions by the free motion of oxydization or reduction overstresses. The latter can be evaluated using a more detailed study of oxydo-reduction couples. The Carbon, Suffer, Nitrogen families, as well transition metals (Iron, Manganese and Zinc). These investigations must be carried out in close correlation with the measuring of bacterial activities, likely to provoke significant physical-chemical modifications in an ecosystem:

- Consumption or modification of organic or mineral molecules.
- Production of gaseous metabolites.
pH and Eh variations caused by acidic, alkaline, oxidizing or reducing metabolites.
- Porous network clogging caused by the production of biomass or of exopolymers.

Electrical interaction phenomena linked to the charge of surface solids, other ions in solution and the solvent have a considerable significance. They are likely to modify the behaviour of the pollutant in relation to its theoretical equilibria:

- In solution:
  - by the majority competition effect,
  - by orientation in the solvent field and creation or organic and mineral colloids,
  - by coagulation of these colloids (electrolyte effect, free Calcium),

- On the substratum by saturation of the double layer.

These properties approaches can be revealed by an "in-situ" speciation study. It shows, in particular the coverage of each element in the anion and cation and particular forms, with an aim to studying the medium’s effect on:

- Endogenous trace elements (Ln, Re).
- Natural tracers (U, Th).
- Artificial tracers (Eu, Gd).

The principal means for putting this strategy into operation are boring (least disruption), whether made from the surface or from a subterranean laboratory. We note, paradoxically, that a good site for putting this strategy into operation is generally a poor site for storage. Over the last ten years, it has been necessary to develop a specific instrumentation to make an "in-situ" study plausible.

As a complement to the conventional boring equipment, the laboratory was initially and with CCE help, devoted to the study and creation of the methods required. This phase is nearing its end and its findings will be put into operation in collaboration with other teams (CIEMAT, CCR ISPRA, BGS, HARWELL, OVIEDO, CINNE) as part of a program coordinated by ENRESA, for the study of transfers based on an uranium deposit, on the "EL BERROCAL" site.
The tools are the following:

1. **Probes for direct measurement by diagraphy**:
   - Natural gamma,
   - Pressure-temperature,
   - Differential temperature,
   - Ionic conductivity (normal and differential), conventional probes (G.O.) widely used in the petroleum industry,
   - pH-Eh, pH-Ca++, developed in 1983 by the LESS, which allows the obtention of pH, Eh and free Calcium profiles down the length of a bore.

2. **Probes for Indirect measurement (punctual sampling)**:
   - **SAMPLERS H.P. and P.V.V.**

   The high pressure sampler, created in 1982, is made up of one or several 2 litre bottles, vacuum conditioned in advance, which are opened and then closed at the desired height, by an electrovalve. It allows the quantitative analysis of dissolved elements, particles and gases which are conserved by the use of self-blanking unions. The system's simplicity permits the bottles to the changed rapidly allowing several samples to be taken in a short on site period.

   This type of probe is however open to criticism due to:

   - the nature of the bottles (Inox 316),
   - the initial pressure shock,
   - the small water input and passage through an electrovalve which must be protected by prefiltration.

   For all the above reasons but also for the obtention of reliable microbiological sampling, a sampler conceived along different lines (P.V.V.) is being built.

   The P.V.V. is designed to meet four essential objectives:

   - Easy internal and external sterilization.
   - Chemical and biological inertia of all the parts in contact with the fluid sample.
   - The absence of an initial pressure shock and of a degassing front in the sample.
- Possibility of sample treatment on surface in the nominal sampling conditions.

The sampler is thus built around a bottle made of PEEK whose initial volume is made rendered null by a mobile piston. The latter is pushed up by degassed sterile water. On opening, under the effect of the boring effect, the piston slowly retreats pushing the sterile water into a second empty volume through a capillary tube whose load loss regulates the filling time.

The mouth of the sampler is closed by a mobile piston, also inert. The dead volume between the sampler’s mouth and the bottle is filled in advance with sterile water. The mouth piston opening and closing control is assured by an independent secondary circuit comprising two electrovalves and a pressure sensor.

The bottles are devised in order to allow, on the surface, connection with an equal pressure bench for the addition of specific markers for the study of a bacterial activity. The system must also allow multiple identical sampling using the CHROMATO probe, but on the surface, so as to allow the harmonization of transfer and analysis protocol.

- **CHROMATOLAB**

  This probe has a double function:

- Quantitative analysis using the "in-situ" concentration of trace and infra-trace elements.

- Qualitative analysis by the separation of anion and cation species.

The correlation of the results obtained using the samplers, the Chromato probe and the ultrafiltration probe, under study, should allow us to obtain a precise description of the state of the elements present in the subterranean water.

The chromato probe constitutes a specially adapted volumetric chromatographic pump which allows the boring water to percolate onto a specific anionic or cationic support. A second pump linked to a tank allows the medium to be buffered when circumstances demand. The concentration can be made on eight parallel lines so
as to reduce the intermediary handling operations on the surface. When there is no chemical aid, the effluents are disposed of in the bore, otherwise they are stored in a tank.

Since the technical development, part of the MIRAGE program, was completed in early 1990, much work has been done on the study of diverse supports, concentration and analysis protocols, in order to prepare the on site study at "EL BERROCAL".

3. MIGRATION STUDY PROBES

- **FORALAB (dispersive mode)**

  This probe allows the study of the migration of a tracer through a column filled with a ground material which simulates a saturated porous medium.

  A pump identical to that of the chromato probe allows the compensation of the column with water from the bore. A chromatography valve next carries out an instantaneous punctual injection of the tracer (Eu). A fraction collector allows the study of the impulsion response of the head of the column.

  In a modified version, during the study, an ultra-filtration stage and specific ionic support should allow an evaluation of the qualitative behaviour of the tracer and the bacterial activity of the reconstituted porous medium in order to establish a comparison with the measurements in the free water from the bore.

- **AUTOLAB (diffusive mode)**

  The Autolab probe is designed to spend a long time in the bore and has no metallic link with the surface (carrying or conductor cable). The probe is entirely autonomous.

  Inside a chamber of approximately 5 litters, clay samples made on site or reconstituted from the rock's alteration materials are available.

  At the required depth, the chamber is opened by the hydrostatic boring pressure. A diffusion front with the water among the samples is established. After about 1 month, the chamber is closed by lowering the probe a few meters into the bore. Using
a messenger, an ampoule of tracer is broken inside the chamber and a battery powered agitation system homogenizes the solution. One month later, the probe is brought back-up, carefully depressurized and the tracer’s migration can be measured.

4. ULTRA-FILTRATION (project)

The speciation study in subterranean water must also look at the suspension phases (colloids). A probe element comprising several filtration stages in line with control of the load loss and anionic and cationic support is being developed. This element can be used below the Foralab column but also directly on the pump for particle measurements.

A pump with a higher flow rate will later to be used with the system and specific supports for organic matter.

5. GEOPHYSICAL SYSTEMS

- RADAR

A study of the possibilities offered by using non destructive electromagnetic methods for volumic analysis of a site’s structure has been carried out in the form of a thesis.

The Canadian radar "PULSE EKKO III" has been used on the surface and in tunner in :

- granite,
- slate,
- chalk,
- salt,
- sand,
- a glacier.

The results found are promising and detailed work on the data treatment is in progress in collaboration with the IFP. The utilization of this kind of system in boring could provide a source of information very complementary with seismic methods. A partnership has been embarked upon with SKB in order to use the probe in RAMAC boring.
Using all these methods together, we should, in the first phase of the "EL BERROCAL" project be able to test their validity and to develop the collaboration necessary for the integration of their results into a global study strategy for the site.

Complementary work is also going on for the study of dispersion in a saturated fractured medium in collaboration with the CEA/FAR on the Montalba site. A study of sonic methods and in particular the interpretation of STONELY waves for calculating weak permeabilities is also on the way.

The laboratory must also carry out the geochemical instrumentation on the Swedish ASPO site and in so doing assess the problems of a subterranean cavity in a granite medium. A study strategy identical to that prepared for the study of the "EL BERROCAL" site on the clayey TOURNEMIRE (IPSN) site has been agreed in principle.
PNC資料
PNC's RESEARCH AND DEVELOPMENT PROGRAM
FOR
GEOLOGICAL DISPOSAL

PREPARED FOR
CEA/PNC TECHNICAL MEETING ON GEOCHEMISTRY

20 NOV. 1991
MASAHIDE OHSAWA
It is a great pleasure for me to present an outline of Research Programme for High-level Radioactive Waste Disposal in Japan.

Before I go into the detail, let me briefly explain the General Scheme of Japanese HLW Management.

In this programme, it is stated that "high-level radioactive waste is to be solidified in a stable form and stored for cooling for an appropriate period, and then finally disposed of into deep underground formation".

Measures to be taken for such a geological disposal are
- vitrification into borosilicate glass,
- storage for cooling for a period between 30 to 50 years to mitigate the effect of decay heat,
- and disposal into geological formation deeper than several hundred meters with multibarrier system consists of engineered and natural barriers.
Since then, considering the increasing degree of public concern about nuclear issues, the General Scheme of HLW Disposal Project was reviewed with the objective of adding more impetus to the future R&D activities.

As the result of the review, the report titled "Major Targets and Implementation of R&D for HLW Geological Disposal" has been released by the Advisory Committee on Radioactive Waste Management of the Atomic Energy Commission (AEC) of Japan in December 1989.

Policy of R&D Program for HLW Isolation Project

Major Targets and Implementation of R&D for HLW Geological Disposal

1989.12

Advisory Committee of Atomic Energy Commission
As a general background when considering HLW Management in Japan, there are two significant issues, natural and administrative as follows.
- one is a wide variety of geological environment including eight potential rock types with different groundwater flow system and geochemistry.
- and the other is the fact that regulatory criteria for HLW still remains to be established and hence the concept of site generic performance assessment has been applied.

NOTE  Eight rocktypes
1  Granite    5  Neogene Sediment
2  Gabbro    6  Pre-Neogene Sediment
3  Rhyolite    7  Limestone
4  Basalt     8  Crystalline schist
As a major conclusion, the report states that implementation of R&D program should be based upon following guidelines.

1 - to depend on integrating and systematic approach
2 - to accommodate a wide range of geological environment
3 - to give a higher priority on near field studies while steadily advancing study on far field
   - and it was considered more than a decade will be required for the final conclusion based on public understanding.

Implementation of R&D should be

(1) depended on integrating and systematic approach

(2) accommodated diverse geological environment

(3) given a priority on near-field studies while steadily advancing study on far-field

(4) taken more than a decade for final conclusion with public understanding

PNC
RADIOACTIVE WASTE MANAGEMENT PROJECT
This viewgraph shows the national waste management organization.

Atomic Energy Commission (AEC) consists of five members and has eight Advisory Committees, one of which is Advisory Committee on Radioactive Waste Management. On the other hand, Nuclear Safety Commission (NSC) consists of six members and has fifteen Advisory Committees, including that on Radioactive Waste Safety Regulation and that on Radioactive Waste Safety Standard.

Science and Technology Agency supervises PNC, Japan Atomic Energy Research Institute implements a regulatory research, National Institute of Radiological Sciences implement a research on radiological effect.

PNC has been assigned a leading role on the R&D in Japan, with 90% of the overall budget for HLW R&D in Japan.
Now, let me turn into PNC's R&D programme.

Before I explain our R&D activities, I present PNC’s organization, research site, and budget.

This viewgraph shows the waste management organization within PNC.

In the head office, R&D of the geological isolation is assigned to Isolation system research program and Geosciences research program with a total number of 16 staff members.

Geological isolation research section at Tokai Works and Waste isolation research section at Chubu Works have 39 and 22 staff members respectively.
Head office is in Tokyo.

Performance assessment, natural analogue study on engineered barrier and disposal technology development are carried out at Tokai Works.

Chubu Works takes in-situ tests in sedimentary rocks, performance assessment on natural barrier, natural analogue study at the uranium mine, and geological survey.

At Kamaishi city, in-situ test on granitic rock is implemented in an abandoned iron mine.

Horonobe is the candidate site for vitrified wastes and TRU wastes storage facility and underground research laboratory in the sedimentary environment. At this site, preliminary site evaluation by deep borehole investigation was conducted. However, in 1989, the prefectual assembly of Hokkaido passed a resolution which will not allow the construction of URL at Horonobe reflecting the negative attitude of the local public.
This viewgraph shows the budget for waste isolation program. The total budget of this fiscal year is 4.5 billion yen and about 70% of the total is allocated for the performance assessment study.

<table>
<thead>
<tr>
<th></th>
<th>FY87</th>
<th>FY88</th>
<th>FY89</th>
<th>FY90</th>
<th>FY91</th>
<th>FY92 (Proposed)</th>
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<td>166</td>
<td>205</td>
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<td>3,228</td>
<td>3,936</td>
<td>4,268</td>
<td>4,599</td>
<td>4,921</td>
</tr>
</tbody>
</table>
This viewgraph shows the Japanese concept of Multibarrier system for Geological Disposal.

Repository is to be located deep enough that the Human Intrusion scenario is considered to be less significant than groundwater scenario.

Engineered barrier system consists of vitrified waste, mild steel-overpack and compacted bentonite as buffer material.

Concept for safety assurance consists of three levels.
- 1st level of safety is achieved by complete confinement of high radioactivity in the waste by preventing groundwater comes into contact with the waste.
- Second level of safety is achieved by keeping radionuclides within near-field by limiting dissolution and diffusion.
- Third level of safety is achieved by guaranteeing no radiological impact by retarding radionuclide migration through geosphere.
This is PNC's 15-year strategic program to demonstrate the feasibility of geological disposal in Japan. Two milestones are placed and three documentations will be submitted.

First progress report will be compiled by the end of fiscal year 1991 in order to clarify the scope and giving priority to the near-field study and to initiate projective near-field performance assessment approach.

Our first milestone is a detailed analysis of engineered barrier system and the geological environment for the repository package. Then on the basis of such an analysis, draft concept assessment report will be compiled in fiscal year 1996 to clarify requirement to the far-field performance and to introduce a projective far-field study.

Second milestone is an analysis of the far-field system performance and compliance with requirement of the total system performance. Finally by fiscal year 2003, the concept assessment report will be prepared.
This viewgraph shows an approach which was chosen for the first progress report now under compilation.

In this report, we adopt a site generic performance assessment - to clarify the range of parameter values which dominate important geological conditions such as hydrology and geochemistry of groundwater - to quantify performance of engineered barrier system under a given parameter range - to classify the types of transport media and to perform sensitivity analyses for a given parameter range.

Dr. Isiguro and Dr. Umeki will present these issues in detail following my presentation.
The aim of this viewgraph is to explain how each of R&D subprogram contributes to the performance assessment processes.

Global data from in-situ test programs are used for geological system comprehension.

Shaft Excavation Experiment, namely SEE Project, and hydrogeological study supply data for modeling of hydrogeological structure.

Process models are developed through the PACE Program which is carried out under an agreement between Battelle Pacific Northwest Laboratory. And PNC's BIG-BEN test also provide the data for the hydrothermal-mechanical coupled process, the name of which is derived from big bentonite and which means a large scale experiment of engineered barrier system.

These models are validated by system specific data from the ENTRY Project and the natural analogue studies. In the ENTRY Project, we plan, for example, data acquisition in a equipments which has precise atomospheric control capacity as well as hydrological experiment in an artificial heterogeneous medium.

For the assessment, application specific data are set by geological survey, nuclide geochemistry and characterisation of waste form and engineered barrier system.
Here, I will present major activities in each research site. At first, Tokai Works implements performance assessment, natural analogue study focusing on engineered barrier materials, and disposal technology development.

**Tokai Works**

- Performance Assessment Study
  - Model development
  - Extention and version up Computer system (PACE program)
  - Model Data Set for H-3 Report
  - Data acquisition (Lab. Test)
  - Validation Study (ENTRY, Big-Ben)

- Natural Analogue Study
  - Engineered Barrier Materials

- Disposal Technology Development
This atmosphere control glove box is to be used as a part of the ENTRY project for the acquisition of data such as corrosion, chemical interaction of bentonite with groundwater, Kd value or solubility, on various parameters under the simulated repository condition.

NOTE 1 m³

O₂ below 1 ppm
This viewgraph shows the BIG-BEN, which is the Large scale experiment of engineered barrier sysytem for observation of re-saturation process and the hydro-thermo-mechanical coupled processes in the near field. This installation consists of a heater, full scale overpack of carbon-steel, buffer material of compacted bentonite and artificial rock bed. The first series of heater test has been carried out since March 1990. Re-saturation test is now under way.
This photograph shows the artificial rock under construction. This is made of reinforced concrete and has 3 m of thickness and 5 m of height.
At Tokai works, natural analogue studies on the engineered barrier materials are also carried out, one of which is on basaltic volcanic glass as a analogy for vitrified waste.

Samples of basaltic glass were obtained from Mt. Fuji and Izu-Oshima and the alteration surfaces of the glass-samples were observed. Result of the observation revealed no significant difference among the different groundwater composition. The alteration rate is estimated about 2 to 3 micro-meter per 1000 years.

NOTE

Mt. Fuji: calcium carbonate type
Izu-Oshima: sodium chlorride
R&D activities at Chubu Works include in-situ test such as Shaft excavation effect project, regional hydrological study and hydrogeological modelling, instrumentation development, performance assessment study such as preparing model data set for H 3 report, data acquisition, natural analogue on the uranium migration at uranium deposit, and geological survey.

**Chubu Works**

- In-situ Test
  - Shaft Excavation Effect (SEE) project
  - Hydraulic test (regional) and model development
  - Instrumentation development

- Performance Assessment Study
  - Model Data Set for H-3 Report
  - Data acquisition

- Natural Analogue
  - Uranium Migration

- Geological Survey
This is a schematic view of SEE Experiment in Tono uranium mine at Chubu works. This shaft is 150 m deep with 6 m diameter.

Excavation has been completed, and rock stress and hydraulic conductivity before and during excavation were measured. Hydraulic potential distribution around the shaft has continuously been measured. Comparison between the measurement and a simulation model which was developed for hydorauric analysis reveals a good agreement. We also evaluate excavation effect on the rocks around the shaft using the result of this experiment.
This photograph shows upward view from the bottom of the shaft.
At Kamaishi city which is about 400 km north from Tokyo, we conduct in-situ test in a granitic environment at an abandoned iron mine.

First phase started in 1988 and will terminate in 1992.

Main activities are hydrogeological experiment, seismic study, rock mechanics.

---

**Kamaishi mine**: Granite
- Hydraulic test (Cross hole injection)
- Seismic study
  - (Magnitude, Hydro-pressure)
- Rock Mechanics (Excavation Effect)

**Horonobe**: Sedimentary Rock (mudstone)
- Candidate URL site
- Water Sampling
One of the major activities in Kamaishi is a monitoring of seismic activities and their effects on hydraulic pressure and groundwater geochemistry.

For this purpose, three seismographs and a monitoring system for groundwater are set up as shown in this photograph.
A number of organizations outside PNC are actively participating in the subject field. We have bilateral collaboration with:
- Japan Atomic Energy Research Institute
- Geological Survey of Japan
- National Research Institute for Pollution and Resources
- National Research Institute for Metals

Major Contractors include:
- Engineering Companies
- Construction Companies
- Steel Companies
- Mining Companies
- Geological Consultants
- Software Companies

DOMESTIC CO-OPERATION

Bilateral Co-operation
- JAERI (Performance Assessment)
- GSJ (Predictive Geology)
- NARIIP (Measurement Technology)
- NRIM (Metal Corrosion)

Major Contractors
- Engineering Company (Performance Assessment: PA)
- Construction Company (PA. Disposal Technology, NA)
- Mining Company (Geological Survey, PA)
- Steel Company (PA, NA)
- Geological Survey Company (Data Acquisition)
- Software Company (PA. Integration)
Last but not least, international collaborations.

- OECD/NEA International Projects
- SCK/CEN on migration experiments in clay formation
- AECL on technological development on hydrological investigation and migration experiment in fractured rock
- NAGRA on migration experiment in a single fracture

**International Co-operation**

1. OECD/NEA International Project
   - Alligator River Analogue Project (1988-1992)

   - Migration Experiment in Clay Formation

   - Technological Development on Hydrological Investigation
   - Migration Experiment in Fractured Zone

   - Migration Experiment in Single Fracture
- SKB on HRL Project
- PNL on PACE Program
- SAIC on system integration
- Golder Associates on fracture flow model development
- AEA Harwell on corrosion and sorption study.

  - HRL Project

  - PACE Program
  SAIC (1990- )
  - System Integration
  GOLDER ASSOCIATES (1991- )
  - Fracture Flow Model

  - Corrosion
  - Sorption
And finally, our latest collaboration with you, for which we got together this time in order to confirm the details.

Thank you for your attention.
Safety Assessment

Scenario Analysis → Model Development → Consequence Analysis → Safety Criteria

Information Requirement
- Geology
- Repository/Waste Processes
- Natural Evidence
- Biosphere
- Radiological
- Human Protection
- Behavior

Framework for Repository Safety Assessment
REFERENCE DESIGN OF EBS
FEP (Features, Events and Processes)

[1] Natural Phenomena
   7 categories - 60 FEPs

[2] Human Activities
   4 categories - 30 FEPs

   4 categories - 17 FEP
POSSIBLE IMPACT TO FUTURE GENERATIONS

INDIRECT
- GAS
- LIQUID
  - NATURAL
  - REPOSITORY
    - GROUNDWATER
    - MAGMA
  - EROSION

DIRECT
- NATURAL PHENOMENA
  - REPOSITORY EFFECT
- HUMAN INTRUSION
  - ADVENTENT
  - INADVENTENT

HIERARCHY OF IMPACT MODE
Groundwater Circulation

P: hydraulic potential
L: water level
F: flow rate
K: hydraulic transmissivity
H: hydraulic gradient
W: water content
I: major ion activity
S: stress
CONCLUSION

Practical Number of Scenarios were Identified for Consequence Analysis by Iterating

- Top-Down Approach to Clarify Scope of Analysis
- Bottom-Up Approach to Define Cause/Effect Relationship among FEP's

Major Modification for Original FEP List are

- Change in Level of Description to Fit Site-Generic Analysis Emphasizing EBS Performance
  - Stress on Correlation Structure of Generic Hydrological/Geochemical Conditions
  - Lumping Site-Specific Feature for Far-Field Migration
- Screening of Unlikely FEP's in Japan
  - Glaciation
- Screening of FEP's whose Relation to EBS Performance were not Specified
  - Changes in Earth's Magnetic Field
  - Biotabation etc.
OVERALL MODEL CHAINS FOR BASE-CASE SCENARIO
REGIONAL HYDROLOGY

- Actual System
- 3D Analysis

EXPANSION OF WELL DEFINED HYDROLOGY

VICINITY OF SHAFT

TONO STUDY SITE

CHUBU AREA

TOPOGRAPHY

GEOLOGICAL STRUCTURE

WATER BALANCE

NATION WIDE

→ Hydraulic Gradient ≤ 0.03
   (Realistic)
REGIONAL HYDROLOGY

- Hypothetical System
- 2D Analysis

IN FLOW FROM ADJACENT SYSTEM (HIGH MOUNTAIN)

FAULT

TOPOGRAPHY = G.W. LEVEL

→ Hydraulic Gradient ≤ 0.35
(Conservative)
EBS BUFFERING

Water Flux

GROUNDWATER FLOW

HYDRAULIC GRADIENT = 0.35

FLOW VELOCITY (cm/sec)

10^-8
10^-10

400 200 0 200 400

DISTANCE FROM CENTER OF WASTE (cm)

k1 = 1.0e-4
k1 = 1.0e-6
k1 = 1.0e-8

PE << 1

NEAR-FIELD HYDROLOGY

RADIOACTIVE WASTE MANAGEMENT PROJECT
POWER REACTOR AND NUCLEAR FUEL
DEVELOPMENT CORPORATION
Flow Chart for Geochemical Modelling of Groundwater Evolution using Thermodynamic Model

Categorization of Groundwater Based on Dominant Characteristics which Affect Nuclide Migration

Extraction of Geochemical Reactions which Dominate Groundwater Characteristics

Minerals and Deep Groundwater Composition Observed in Japan

Modelling of Groundwater Evolution

Calculation by using Geochemical Code

Representative Observed Data → Categorized Groundwater Composition
Categorization of groundwater composition for "Site-generic" approach

- **Rain water origin = Fresh**
  - (FRLP) (FRHP)
  - (FOHP: hypothetical)

- **Sea water origin = Saline**
  - (SRLP) (SRHP)
  - Sea water

The degree of redox reaction

High $\leftarrow$ Eh $\rightarrow$ low

The degree of weathering reaction

Low $\leftarrow$ pH $\rightarrow$ high
Geochemical Calculation
Geochemical Code: PHREEQE

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
### Modeled Groundwater and Example Data

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<th>Groundwater</th>
<th>pH</th>
<th>pe</th>
<th>$\text{HCO}_3^-$</th>
<th>$\text{Na}^+$</th>
<th>$\text{Cl}^-$</th>
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<td>7.212E-3</td>
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<td>1.5E-3</td>
<td>2.9E-5</td>
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<td>SRHP</td>
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<td>-5.18</td>
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THERMAL EFFECTS OF HEAT FROM RADIOACTIVE WASTE ON ENGINEERED BARRIER MATERIALS

![Graph showing heat emitted from the waste package](image)

Fig. Heat emitted from the waste package

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<td>Buffer material</td>
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<td>Initial condition (50% saturated)</td>
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<tr>
<td>Saturated condition (100% saturated)</td>
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<td>Overpack</td>
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<td>Vitrified waste</td>
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</table>
Fig. Change of near-field temperature with time
The conceptual diagram of groundwater evolution in near-field
Bentonite Model
(Based on "Wanner Model")

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

   \[ Z\text{Na} = Z^- + \text{Na}^+ \]
   \[ Z\text{K} = Z^- + \text{K}^+ \]
   \[ Z_2\text{Ca} = 2Z^- + \text{Ca}^{2+} \]
   \[ Z_2\text{Mg} = 2Z^- + \text{Mg}^{2+} \]

2) Dissolution/precipitation

   calcite + \( H^+ \) = \( \text{Ca}^{2+} + \text{HCO}_3^- \)  
   (pH buffer)

   quartz + 2\( H_2O \) = \( \text{Si(OH)}_3(aq) \)

3) Eh buffering effects by pyrite

   \( \text{FeS}_2 + \frac{15}{4} \text{O}_2(aq) + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{H}^+ \)
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<td>Pu</td>
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<td>Am</td>
<td>—</td>
<td>AmOHCO$_3$</td>
<td>Rai et. al</td>
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<td>( \text{FRLP} )</td>
<td>( \text{SRHP} )</td>
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<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
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<td>RaSO(_4)</td>
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<tr>
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<td>Ra(^{2+})</td>
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## Calculated Solubility (Oxide)

(mol/l)

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<th>S R H P</th>
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<td>Pu (CO₃)₄⁻³</td>
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<td>HSe⁻</td>
<td>HSe⁻</td>
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Experimental and modelling results on the interaction of bentonite with water
Experimental results of coupled leaching test of fully radioactive glass waste with compacted bentonite saturated with water.
Experimental results of MCC-1 type leaching tests of fully radioactive waste glass
CONCEPTUAL MODEL OF NUCLIDE TRANSPORT IN BENTONITE

Diffusion (Inlet)

\[-\varepsilon D_p \frac{Cl(r,t) - Cl(r-\Delta r,t)}{\Delta r}\]

Concentration

\[-\varepsilon \frac{dCl}{dt} - \varepsilon(\lambda_1 Cl_1 - \lambda_1 Cl_{-1})\]

Diffusion (Outlet)

\[\varepsilon D_p \frac{Cl(r+\Delta r,t) - Cl(r,t)}{\Delta r}\]

Sorption

\[-(r_{in}) Cl + \varepsilon \frac{dCl}{dr} - \lambda_{in} Cl_{in} - \lambda_{in} Cl_{-1}\]

Precipitation

\[-\varepsilon \frac{dCl_{p}}{dt} - \lambda_{p} Cl_{p} - \lambda_{p} Cl_{p-1}\]
RADIONUCLIDE TRANSPORT IN NEAR-FIELD

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

\[ R_i \frac{\partial C_i}{\partial t} + \frac{\partial C_{pi}}{\partial t} = D_p \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_i}{\partial r} \right) - R_i \lambda_i C_i + R_{i-1} \lambda_{i-1} C_{i-1} - \lambda_i C_{pi} + \lambda_{i-1} C_{pi-1} \]

- \( C_i \): Concentration of Radionuclide \( i \) in Pore Water
- \( C_{pi} \): Concentration of Precipitate on Radionuclide \( i \) in Pore
- \( D_p \): Pore Diffusivity
- \( \lambda_i \): Decay Constant of Radionuclide \( i \)
- \( R_i \): Retardation Factor of Radionuclide \( i \)
RADIONUCLIDE TRANSPORT IN NEAR-FIELD

\[ R_i = 1 + \frac{1 - \varepsilon}{\varepsilon} \rho K_{di} \]

\( \varepsilon \) : Porosity of Bentonite

\( \rho \) : Density of Bentonite

\( K_{di} \) : Distribution Coefficient of Radionuclide \( i \)

\[ \frac{\partial C_{pi}}{\partial t} = u(C_{pi}) \ k \ (C_i - C_{sol \ i}) \]

\( k \) : Reaction Rate

\( C_{sol \ i} \) : Solubility of Radionuclide \( i \)

\[ u(C_{pi}) = \begin{cases} 
1 & (C_{pi} > 0 \ or \ C_i > C_{sol \ i}) \\
0 & (C_{pi} \leq 0) 
\end{cases} \]
DESCRIPTION OF TRANSPORT MEDIA (1)

- Homogeneous Transport Media Dominated by Molecular Diffusion
  - Micrometer Pore Size Scale  \[\Rightarrow\]  Clay Stone
  - Homogeneous Pore Distribution  \[\Rightarrow\]  Compacted Sedimentary Rocks
  - Matrix of Crystalline Rocks

[Diagram of sedimentary layers with labels for sandy facies, silty or clayey layer, compacted matrix, matrix, organic matter, quartz grain, clay mineral, order of millimeter, and order of meter.]
DESCRIPTION OF TRANSPORT MEDIA (2)

A: Transport Media Dominated by both Advection/Dispersion and Molecular Diffusion
- Hierarchical Pore Structure System
  - Advection/Dispersion
  - Molecular Diffusion

Large Scale Pore $\leftrightarrow$ Small Scale Pore

(Ex.) Conglomerate Rocks which are Less Tightly Cemented by Clay Minerals and Other Detrital Grains
DESCRIPTION OF TRANSPORT MEDIA (3)

B: Transport Media Dominated by both Advection/Dispersion and Molecular Diffusion B

- Hierarchical Fracture Structure System
  Fracture $\rightarrow$ Dominated by Avection $\rightarrow$ Advection/Dispersion
  Matrix $\rightarrow$ Advective Flow = 0 $\rightarrow$ Molecular Diffusion
  ↓

  Crystalline Rocks with Fractures

Microfracture

Filling Materials

Without Filling Materials

Order of millimeter
• Diffusion [J. Bear (1979)]

\[ f_{in} \quad \text{time} \quad \text{input} \quad \text{Rock} \quad \text{output} \quad f_{out} \]

\[ 0 \quad T \]

EBS \quad NBS

• Advection/Dispersion with Matrix Diffusion [D.H. Tang (1981)]

\[ f_{in} \quad \text{time} \quad \text{input} \quad \text{Rock} \quad \text{output} \quad f_{out} \]

\[ 0 \quad T \]

EBS \quad NBS

Performance of Natural Barrier Subsystem = \( f_{out} / f_{in} \)
Parameters on Hydrology & Nuclide Migration

- Hydrology
  \( \nabla H = 0.05, \quad 2b = 1.0 \times 10^{-4} \text{ (m)}, \quad 2S = 5.0 \text{ (m)}, \quad \text{Path Length} = 10 \text{ (m)} \)

- Nuclide Migration
  - Distribution Coefficient

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<tr>
<th>Nuclide</th>
<th>Kd</th>
<th>Nuclide</th>
<th>Kd</th>
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<td>Th-232</td>
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</table>

- De : [Fracture] = 3.2E-4 (m²/y), [Porous] = 4.7E-3 (m²/y)
- \( \varepsilon \) : [Fracture] = 2.0E-2 (-), [Porous] = 3.0E-1 (-)
Reduction of Release Rate through Natural Barrier