添付資料 2

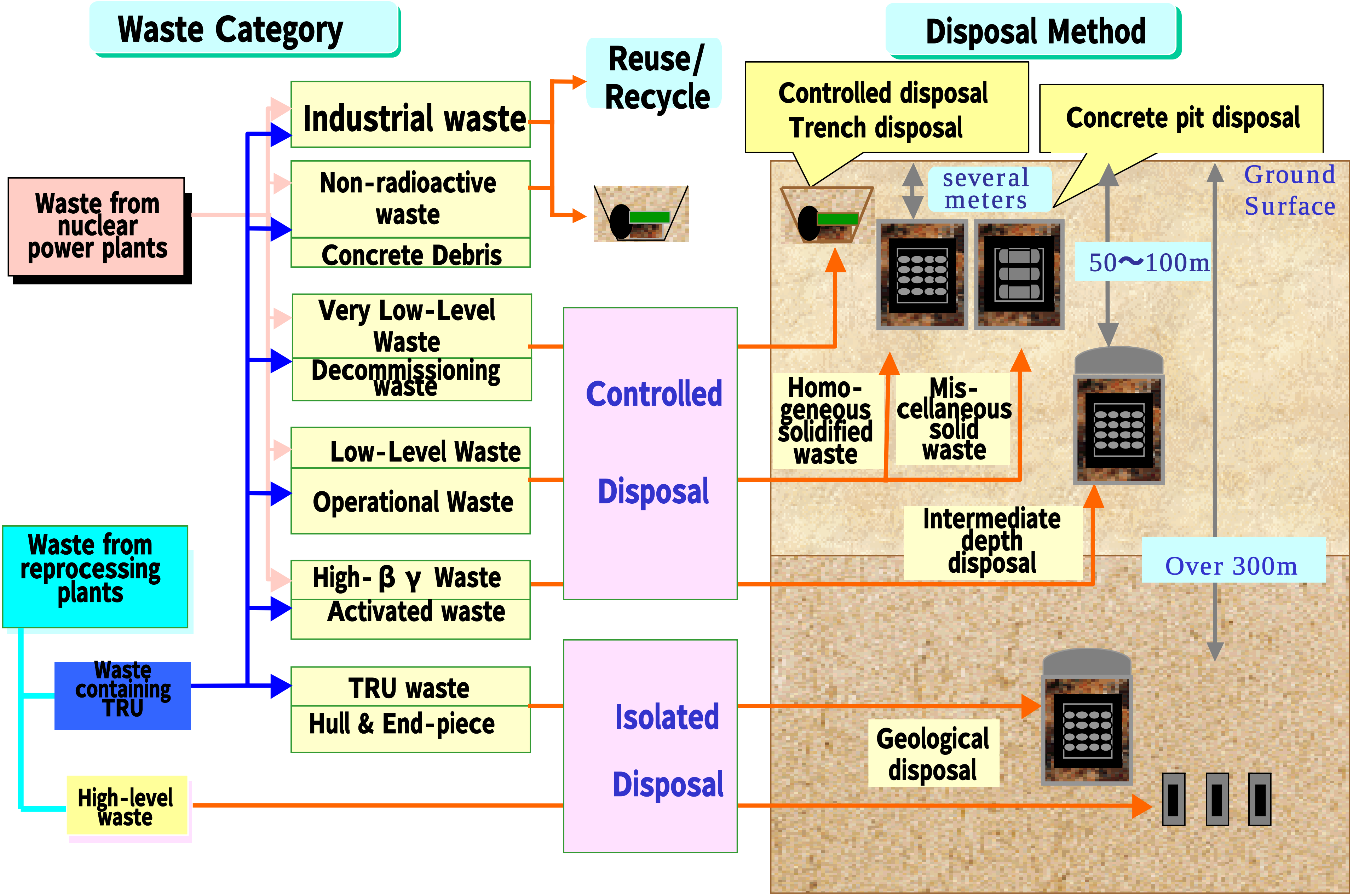
ワークショップの OHP 集

Impact of C-14 on the Safety Assessment of Radioactive Waste Disposal

Oct. 27-28, 2003
Workshop on C-14 Release and Transport in Repository Environments
Wettingen, Switzerland

Osamu Tochiyama (Tohoku University)
Hiromi Tanabe, Satoru Kaneko
(Radioactive Waste Management Funding and Research Center)

Radioactive Waste Categories and Disposal Concepts in Japan



Waste Category

Waste from nuclear power plants

Waste from reprocessing plants

Waste containing TRU

High-level waste

Industrial waste

Non-radioactive waste

Concrete Debris

Very Low-Level Waste

Decommissioning waste

Low-Level Waste

Operational Waste

High-β γ Waste

Activated waste

TRU waste

Hull & End-piece

Reuse/ Recycle

Controlled Disposal

Isolated Disposal

Disposal Method

Controlled disposal
Trench disposal

Concrete pit disposal

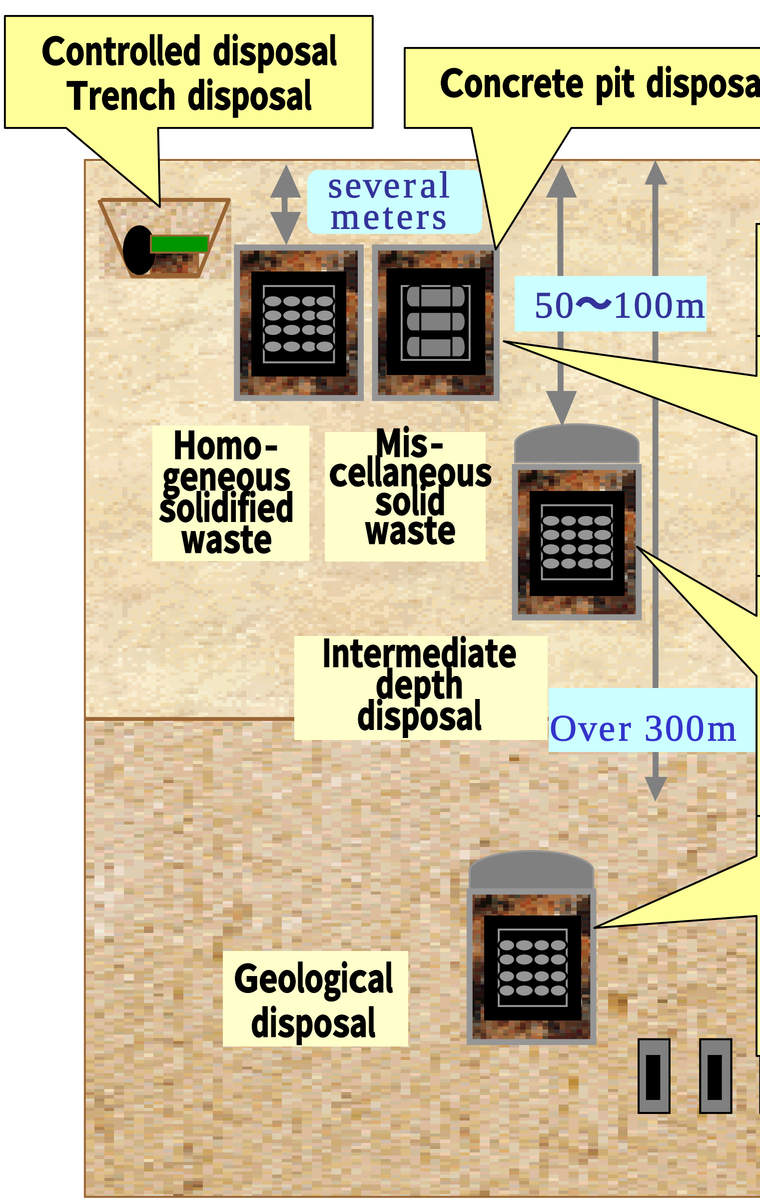
Homo-geneous solidified waste

Mis-cellaneous solid waste

Intermediate depth disposal

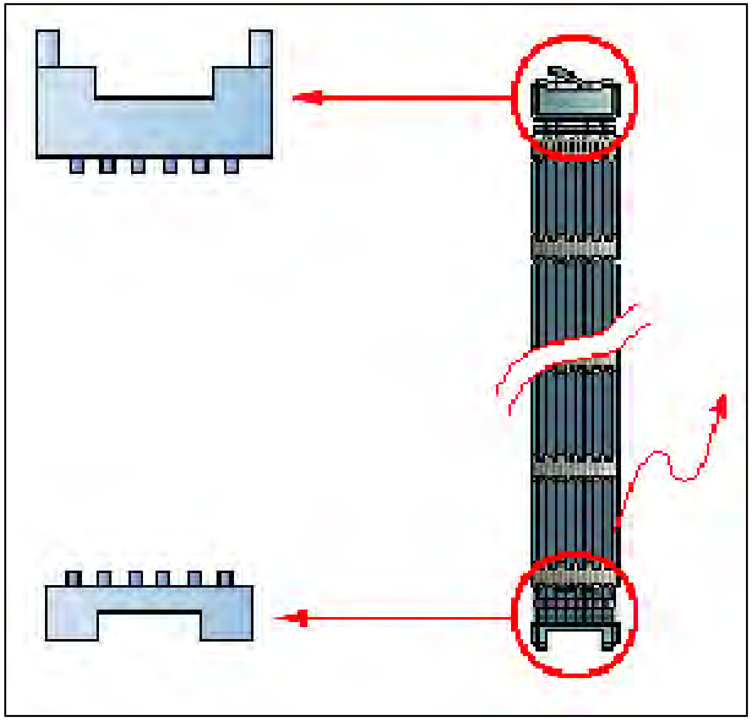
Geological disposal

Total inventory of C-14 for each type of waste



	C-14 Total inventory(Bq)
Low level waste	3.7E+10
High-βγ waste	3.5E+15
TRU waste	1.1E+15

Important C-14 containing TRU wastes

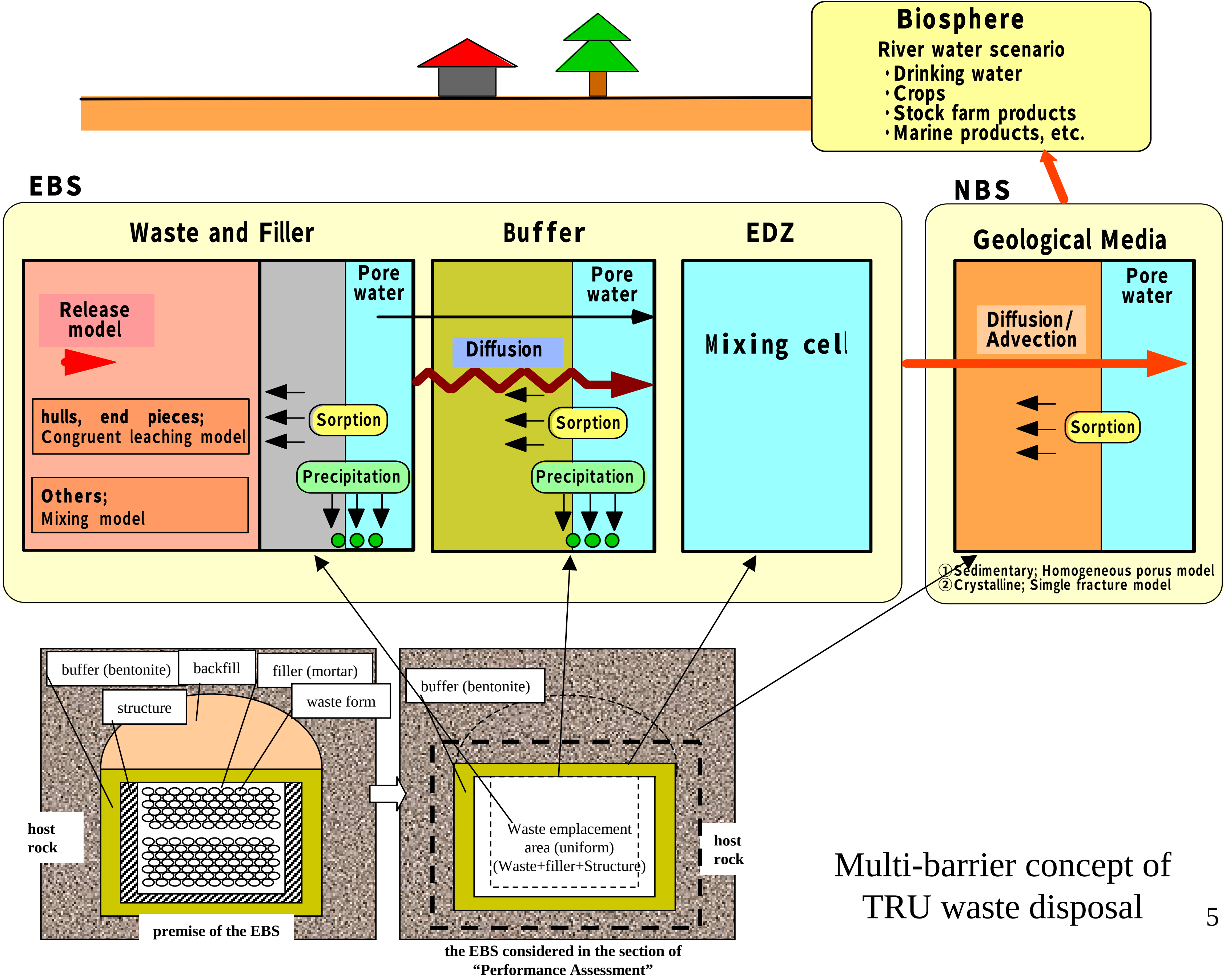


endpieces (SUS, Inconel)

cladding hulls (zircaloy)

Dose evaluation of C-14 contained in TRU wastes

Outline of the performance assessment of TRU waste disposal



Biosphere
River water scenario
- Drinking water
- Crops
- Stock farm products
- Marine products, etc.

EBS

Waste and Filler

Release model

hulls, end pieces;
Congruent leaching model

Others;
Mixing model

Pore water

Sorption

Precipitation

Buffer

Pore water

Diffusion

Sorption

Precipitation

EDZ

Mixing cell

NBS

Geological Media

Pore water

Diffusion/ Advection

Sorption

①Sedimentary; Homogeneous porus model
②Crystalline; Simgle fracture model

buffer (bentonite)

backfill

filler (mortar)

structure

waste form

host rock

premise of the EBS

buffer (bentonite)

Waste emplacement area (uniform)
(Waste+filler+Structure)

host rock

the EBS considered in the section of
“Performance Assessment”

Multi-barrier concept of
TRU waste disposal

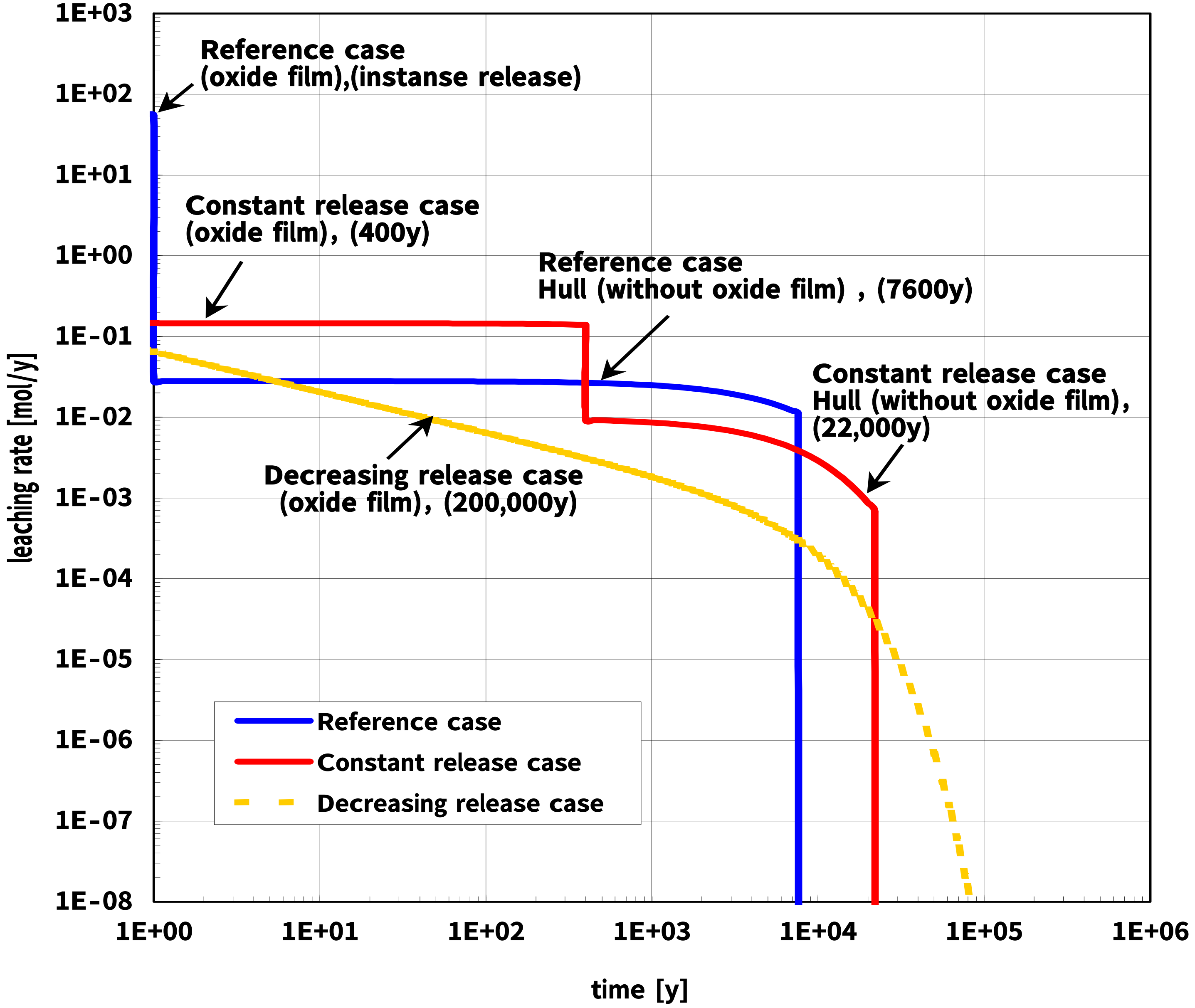
Transport parameters for the assessment

		base data	variation data	
inventory	oxide film	1.3E+14 Bq		
	matrix without oxide film	4.9E+14 Bq		
leaching period		reference case1)	constant release2)	decreasing release2)
	oxide film	instant release	400 y	200,000 y
	matrix without oxide film	7600 y	22,000 y	6.8E+8 y
hydraulic conductivity for NBS		1E-9 m/s	1E-10 m/s, 1E-8 m/s, 1E-7 m/s	
distribution coefficient of C-14 for cement and rock		0.1 ml/g	10 mg/l, 100 ml/g, 500 ml/g	

1) 「Progress Report on Disposal Concept for TRU Waste in Japan」 2000.3

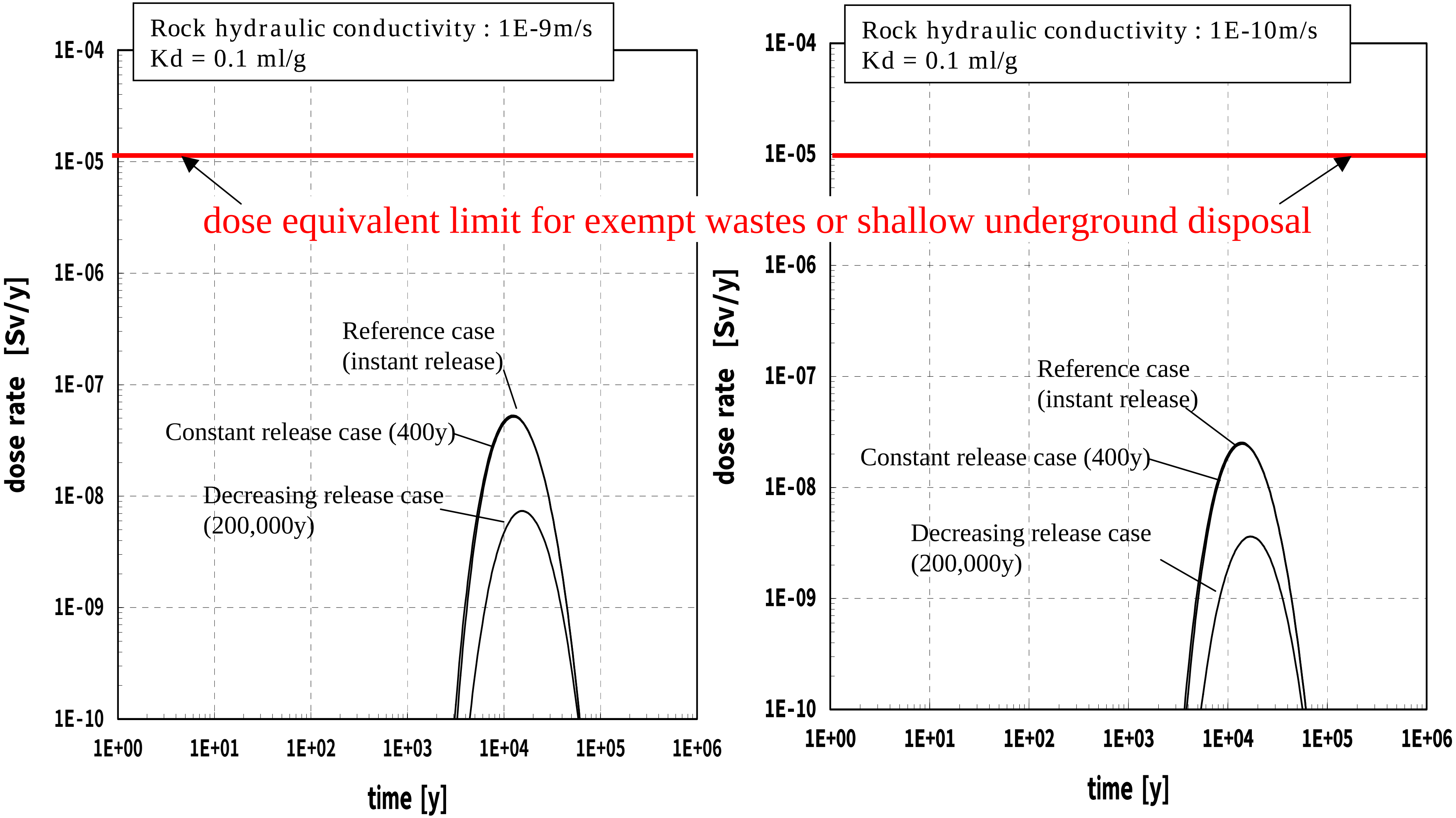
2) 「A Study on Chemical Forms and Migration Behavior of Radionuclide in Hull Waste」 ICEM’99

C-14 leaching rate of each case



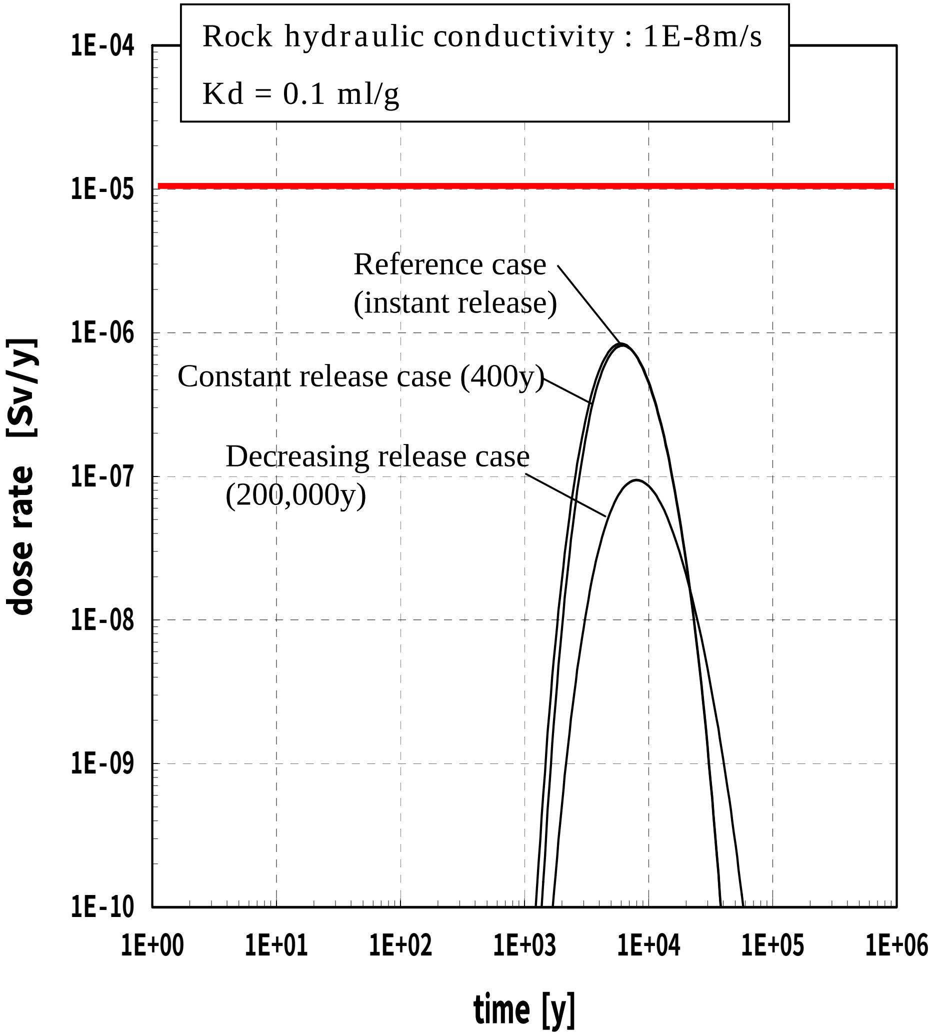
Dose evaluation of the case considering the variation of rock hydraulic conductivity and leaching period (1/2)

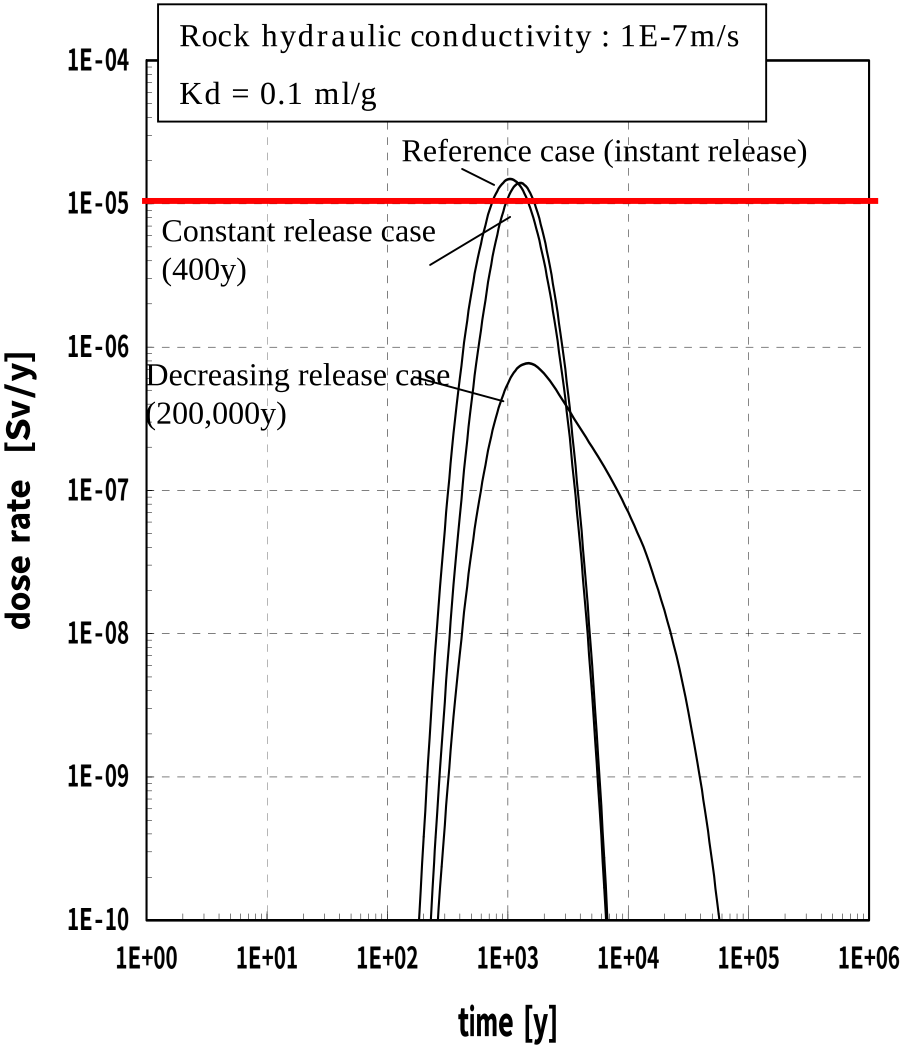
- oxide film -



oxide film: $K < 1\text{E-}9$ m/s → dose << 10 μSv/y

Dose evaluation of the case considering the variation of rock hydraulic conductivity and leaching period (2/2)
- oxide film -

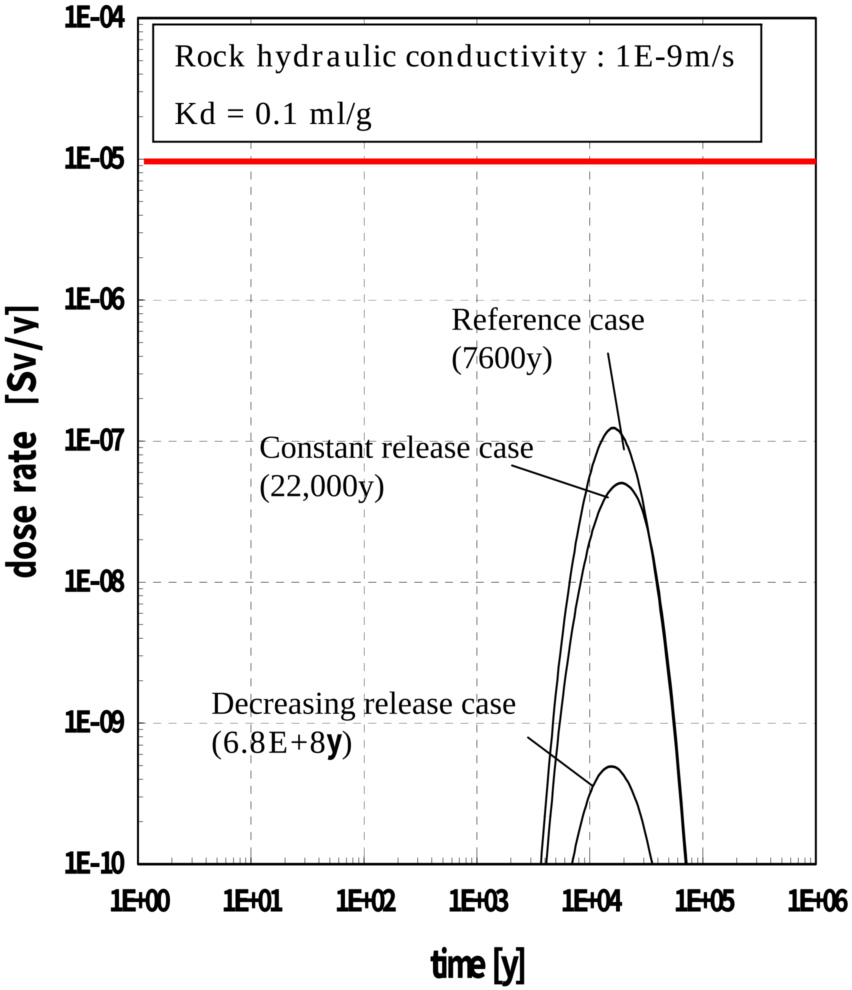


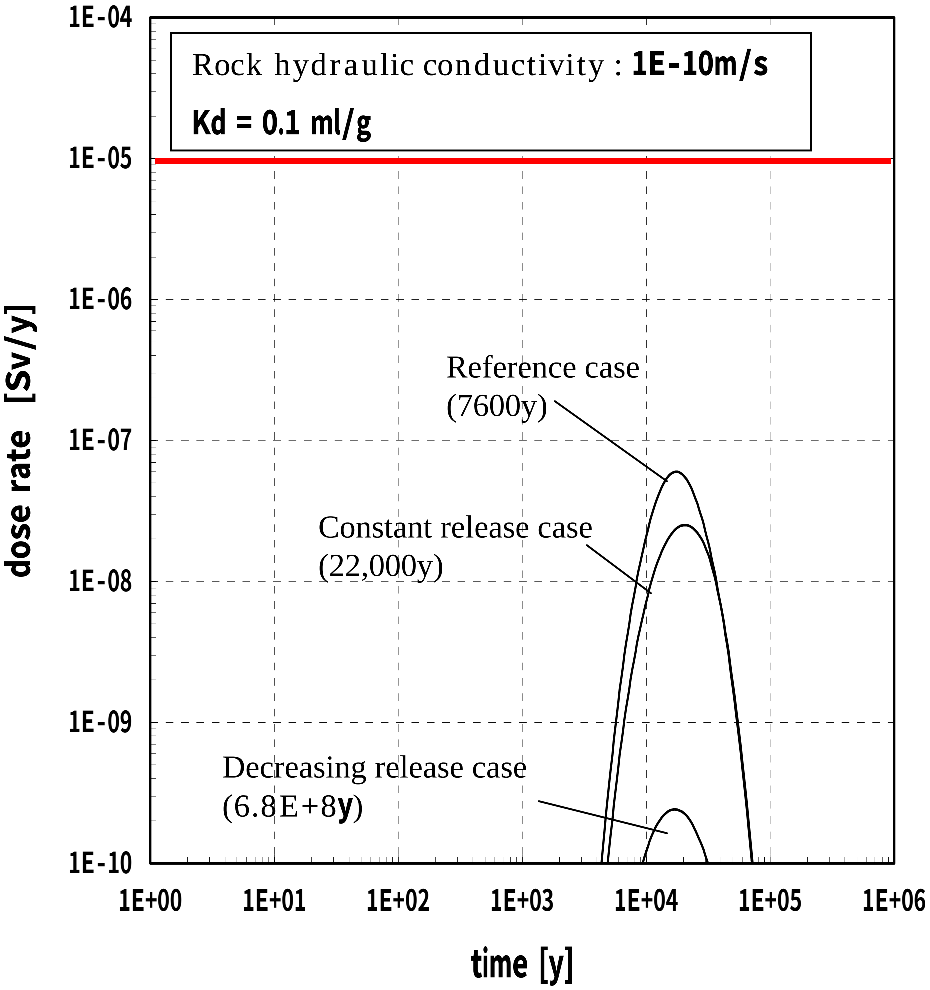


oxide film: $K \geq$ 1E-7 m/s → dose > 10 μSv/y

Dose evaluation of the case considering the variation of rock hydraulic conductivity and leaching period (1/2)

- matrix without oxide film -

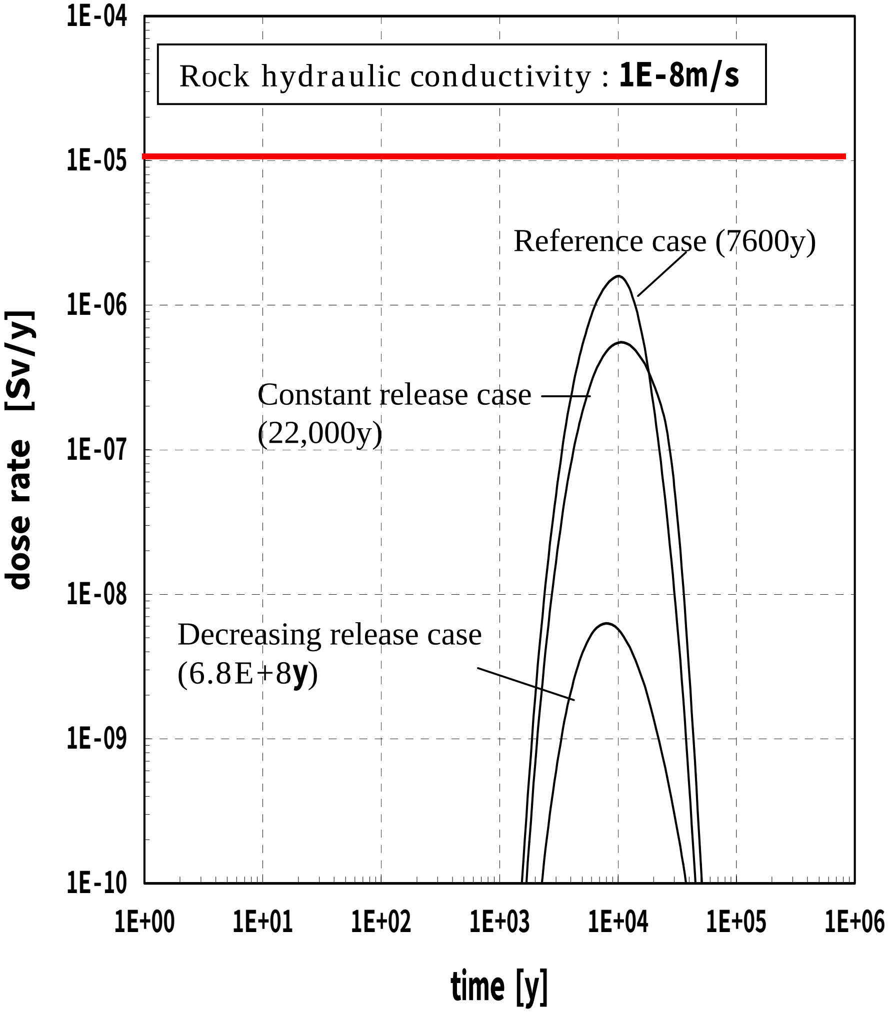


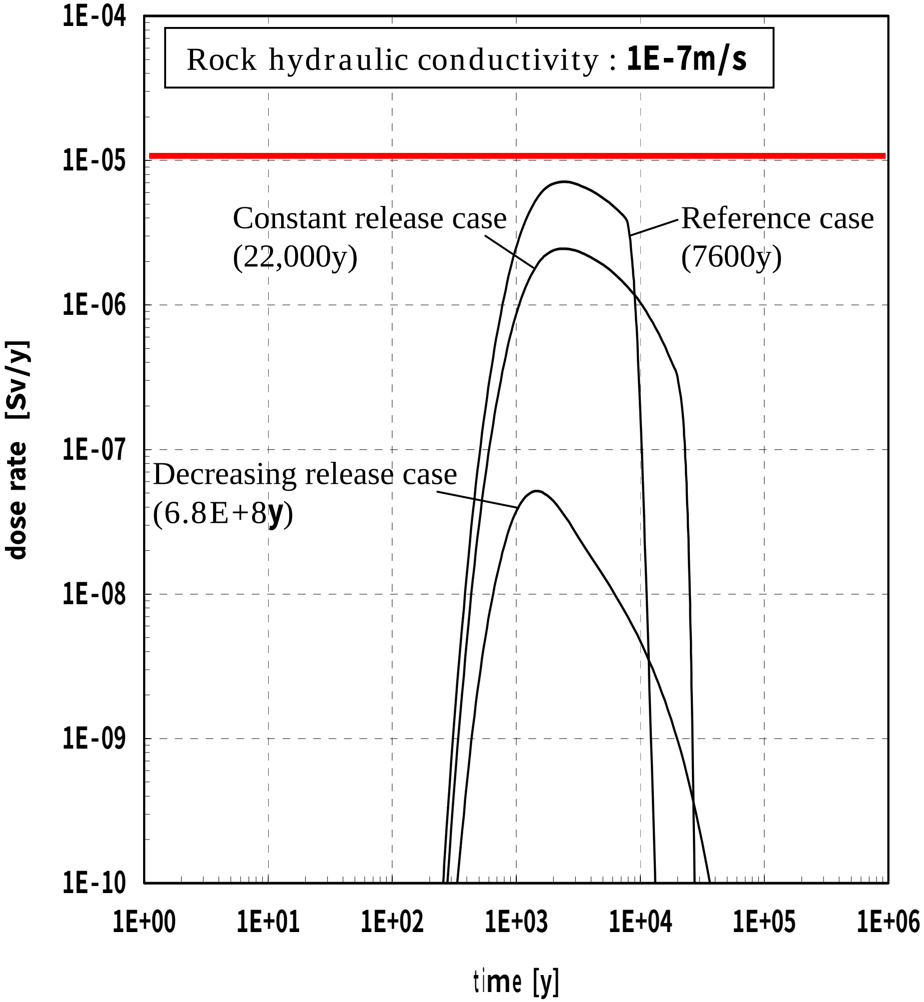


matrix: *K* < 1E-9 m/s → dose << 10 μSv/y

Dose evaluation of the case considering the variation of rock hydraulic conductivity and leaching period (2/2)

- matrix without oxide film -

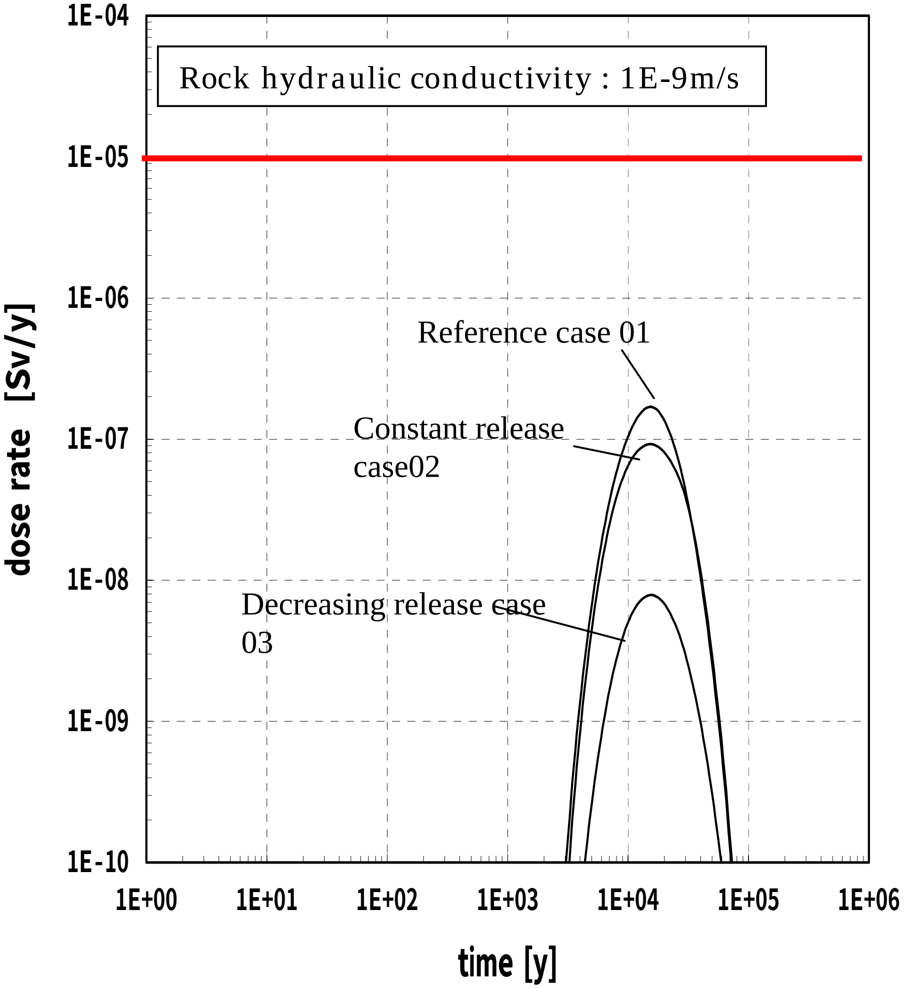


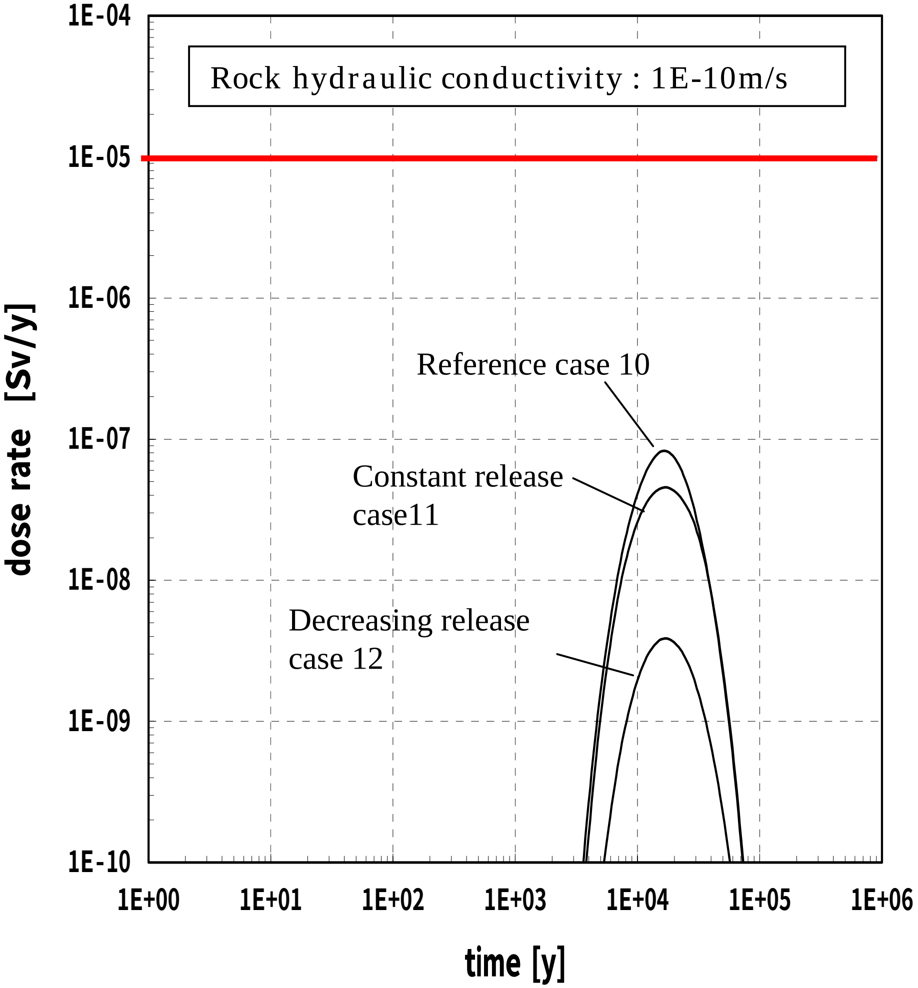


matrix: $K \geq$ 1E-7 m/s → dose $\cong$ 10 μSv/y

Dose evaluation of the case considering the variation of rock hydraulic conductivity and leaching period

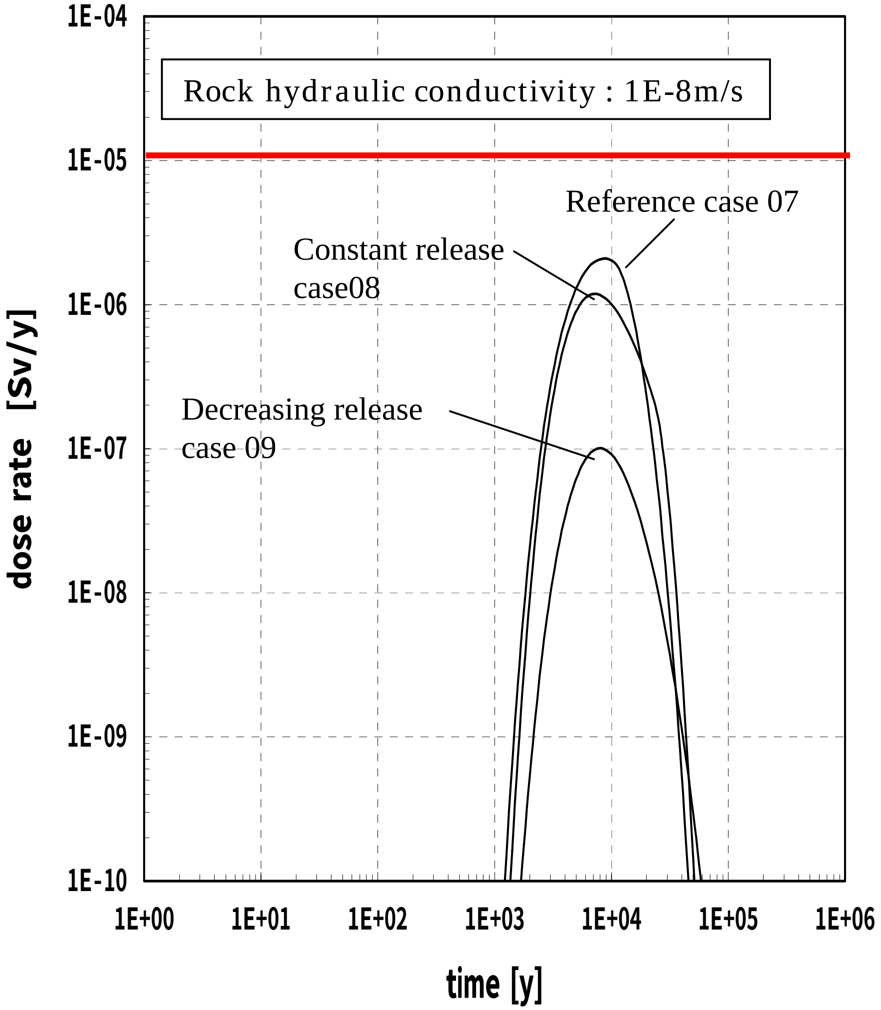
- oxide film plus matrix -

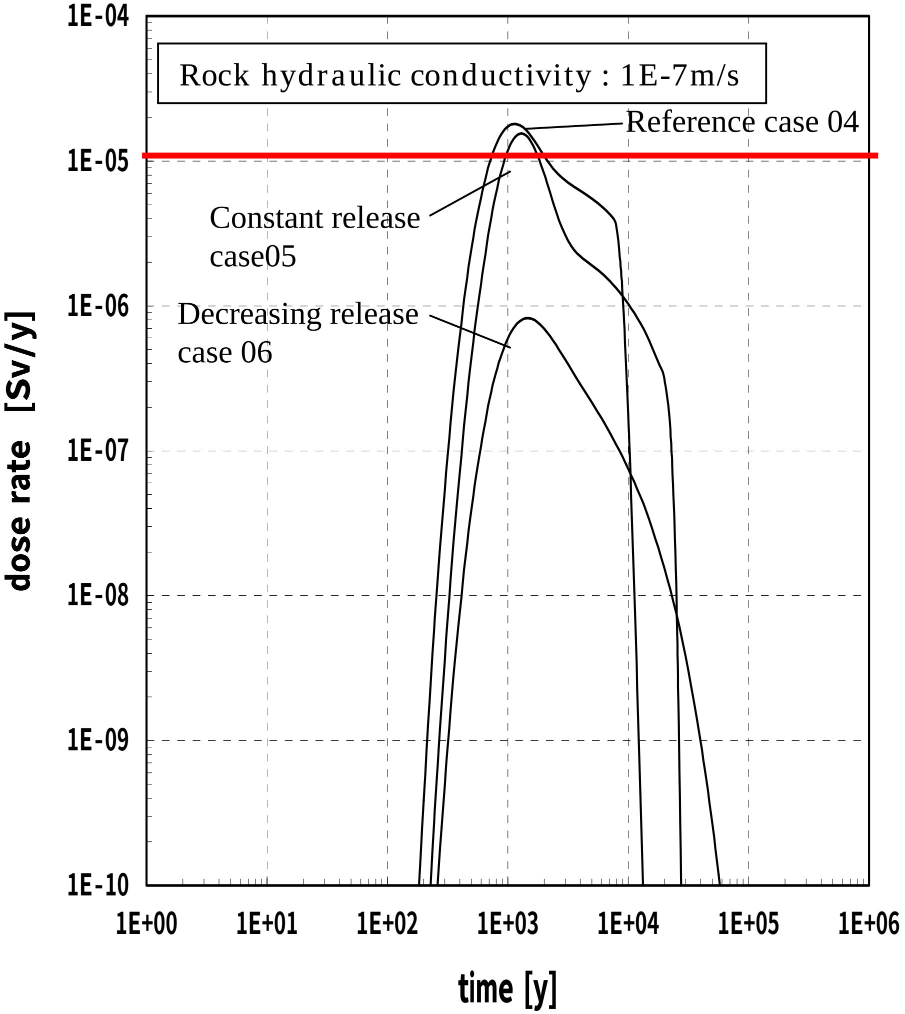




oxide film + matrix: K < 1E-9 m/s → dose << 10 μSv/y

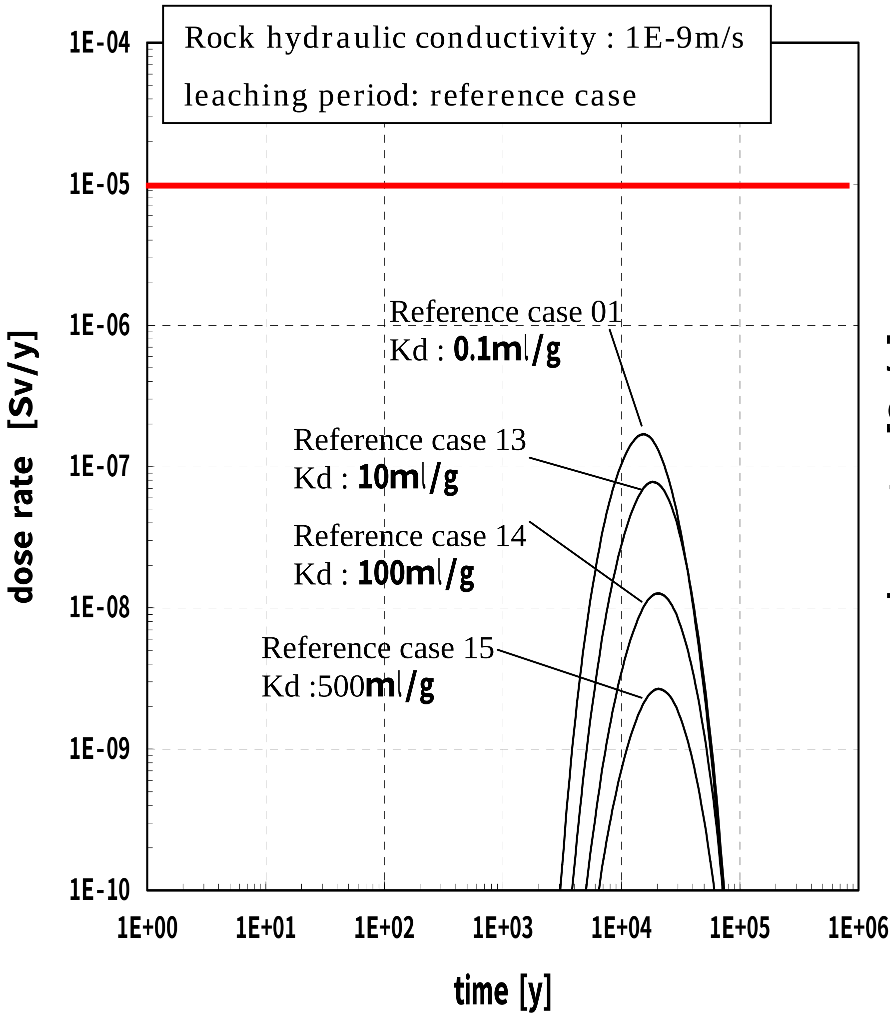
Dose evaluation of the case considering the variation of rock hydraulic conductivity and leaching period (2/2)
- oxide film plus matrix -

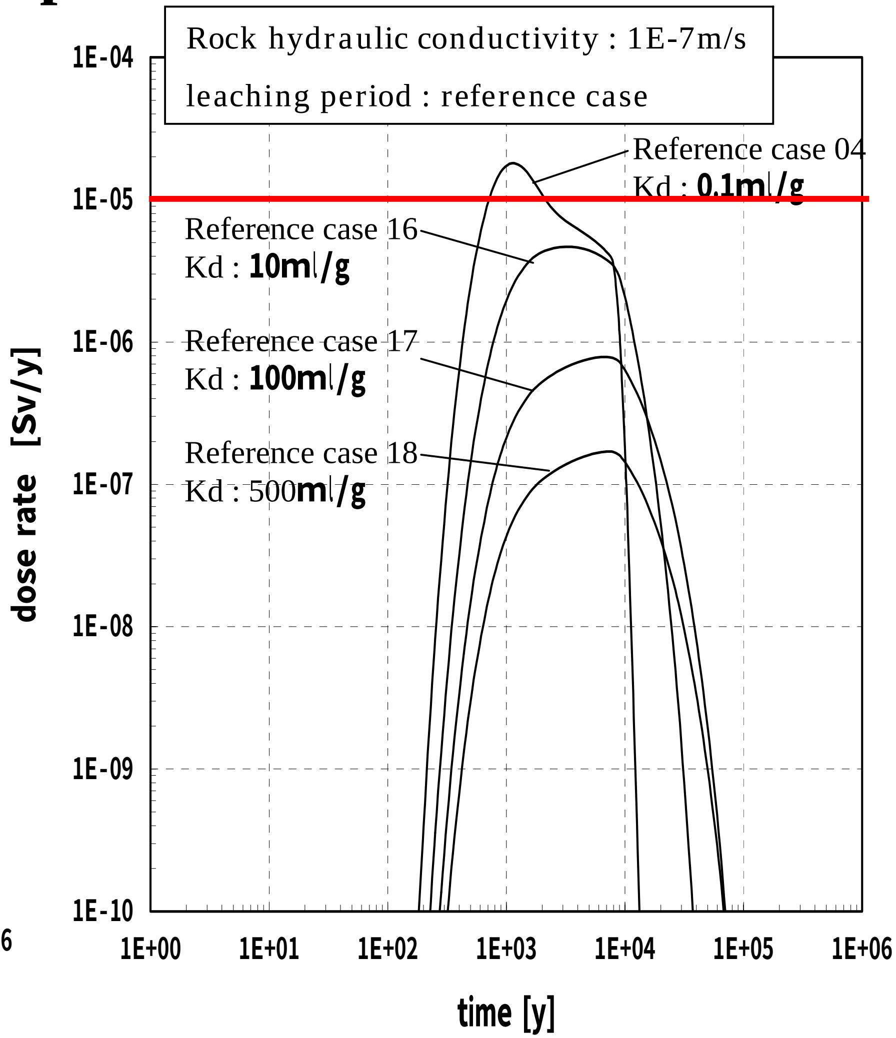




oxide film + matrix: *K* ≥ 1E-7 m/s → dose > 10 μSv/y

Dose evaluation of the case considering the variation of distribution coefficient for cement
- oxide film plus matrix -





Kd : 0.1 ml/g → higher → dose → lower

Dose evaluation of each case (Sv/y)
- oxide film plus matrix -

	Leaching period (years)		Rock hydraulic conductivity for NBS (m/s)	Distribution coefficient for Cement(C-14) (ml/g)	All radionuclide (Sv/y)	C-14 (Sv/y)
	Hull (oxide film)	Hull (without oxide film)				
case01	Instant release	7,600	1.00E-09	Base data 0.1	1.9E-07	1.7E-07
case02	400	22,000			1.0E-07	9.2E-08
case03	200,000	6.80E+08			1.1E-08	7.9E-09
case04	Instant release	7,600	1.00E-07		1.9E-05	1.8E-05
case05	400	22,000			1.6E-05	1.5E-05
case06	200,000	6.80E+08			9.4E-07	8.2E-07
case07	Instant release	7,600	1.00E-08		2.2E-06	2.1E-06
case08	400	22,000			1.2E-06	1.2E-06
case09	200,000	6.80E+08			1.2E-07	1.0E-07
case10	Instant release	7,600	1.00E-10		9.1E-08	8.2E-08
case11	400	22,000			5.1E-08	4.5E-08
case12	200,000	6.80E+08			5.7E-09	3.8E-09
case13	Instant release	7,600	1.00E-09	10	9.7E-08	7.8E-08
case14				100	3.4E-08	1.3E-08
case15				500	2.5E-08	2.7E-09

＊) 🟦 : Reference case , 🟨 : Constant release case , 🟥 : Decreasing release case

Conclusion

1. **C-14 is one of the dominant nuclide affecting dose from TRU or high $\beta\gamma$ wastes.**
2. **Safe disposal of C-14 containing waste is expected to be applicable for a wide range of geological condition in Japan, even when the target dose constraint is set to 10 μSv/y.**
3. **Fairly inferior geological condition (hydraulic conductivity > 10^{-7} m/s) may give the resultant dose higher than 10 μSv/y.**
4. **The above disadvantage can be overcome when we can set more favorable values for other parameters (leaching rates, distribution coefficients) by knowing the mechanism controlling these parameters.**
5. **Researches for more reliable migration data and more realistic transport models of C-14 are necessary for the safe disposal of radioactive wastes.**

Behaviour of ^{14}C in the Opalinus Clay Safety Case

L.H. Johnson and B. Schwyn

Workshop on C-14 Release and Transport in
Repository Environments

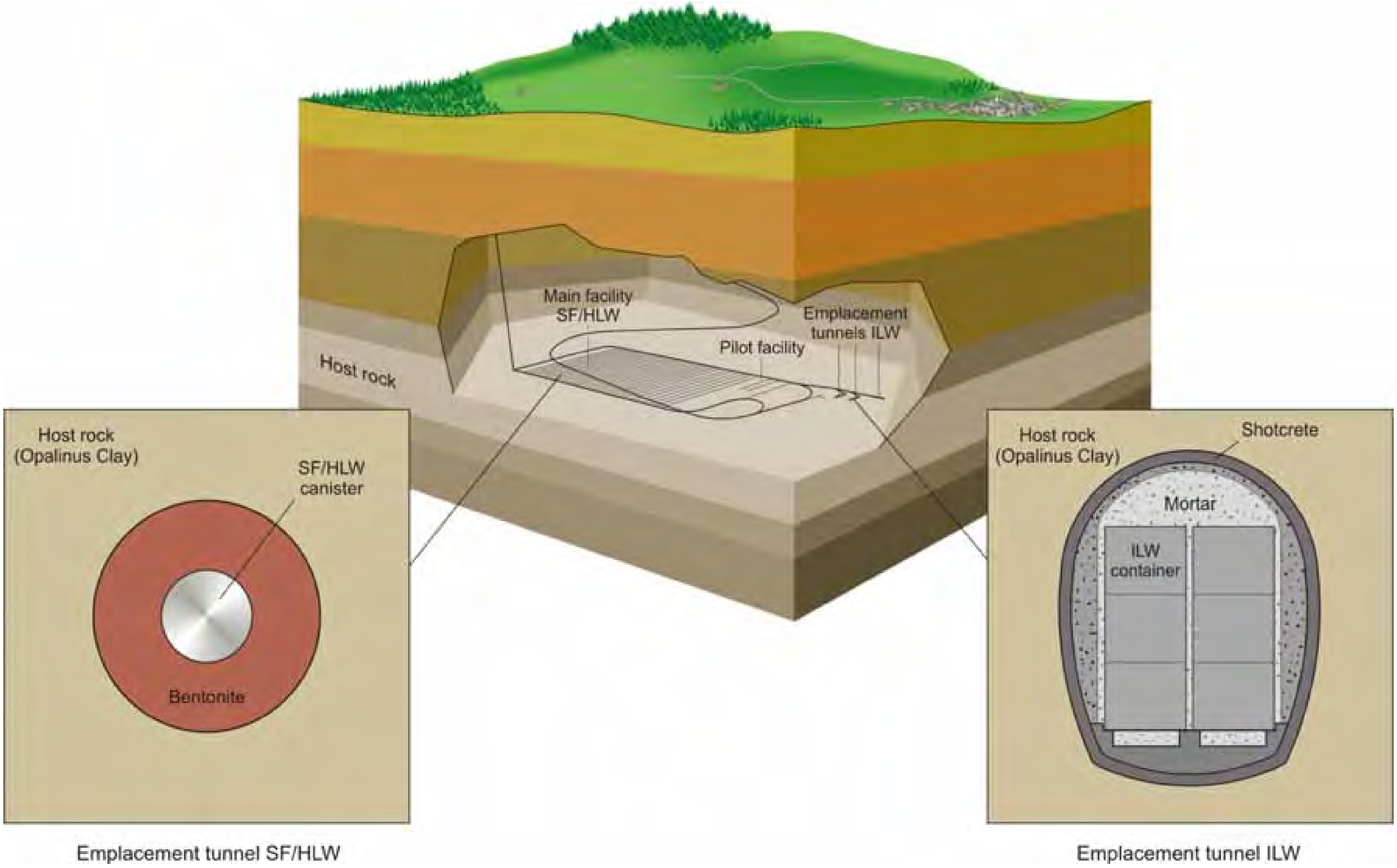
October 27 - 28, 2003

Wettingen, Switzerland

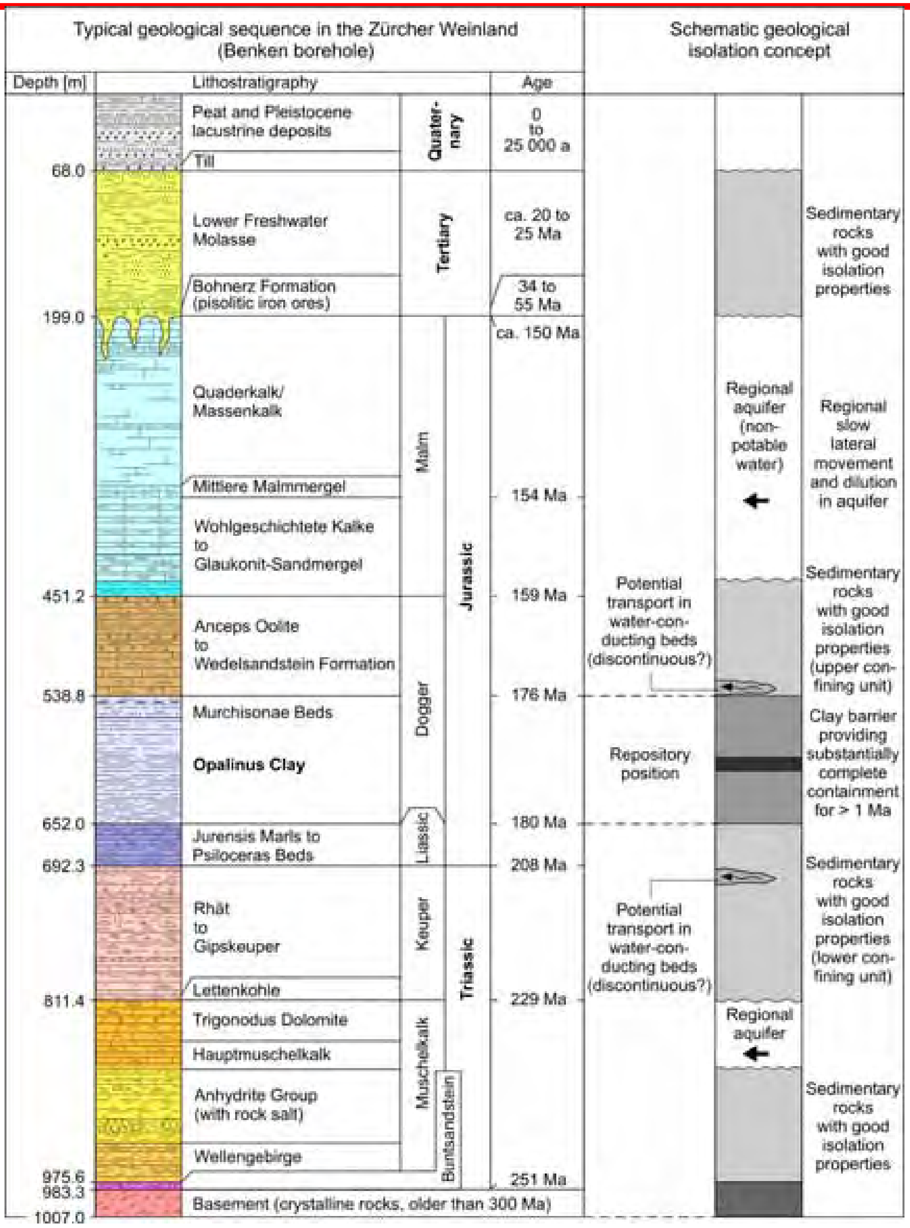
Scope

- Background on the Opalinus Clay study
- Waste Types and EBS
- Assumptions regarding chemical form of ^{14}C in different waste types (SF, HLW and ILW)
- Release of ^{14}C from the various wastes
- Treatment of solubility and sorption of released ^{14}C
- Results of various transport calculations
- Summary and research needs

Repository in Opalinus Clay



Geological sequence at Benken and isolation concept

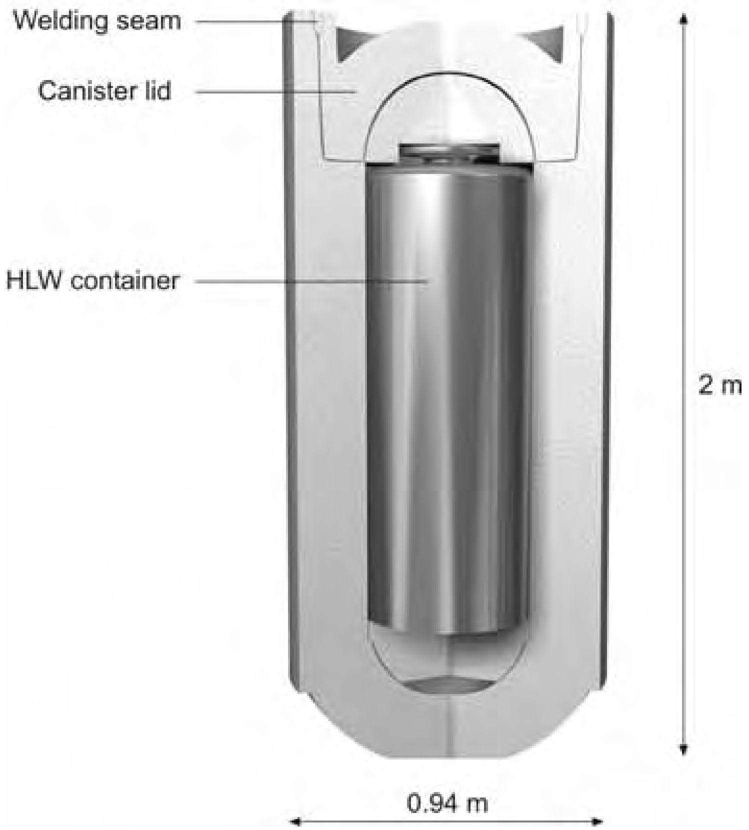


Repository depth - 650 m

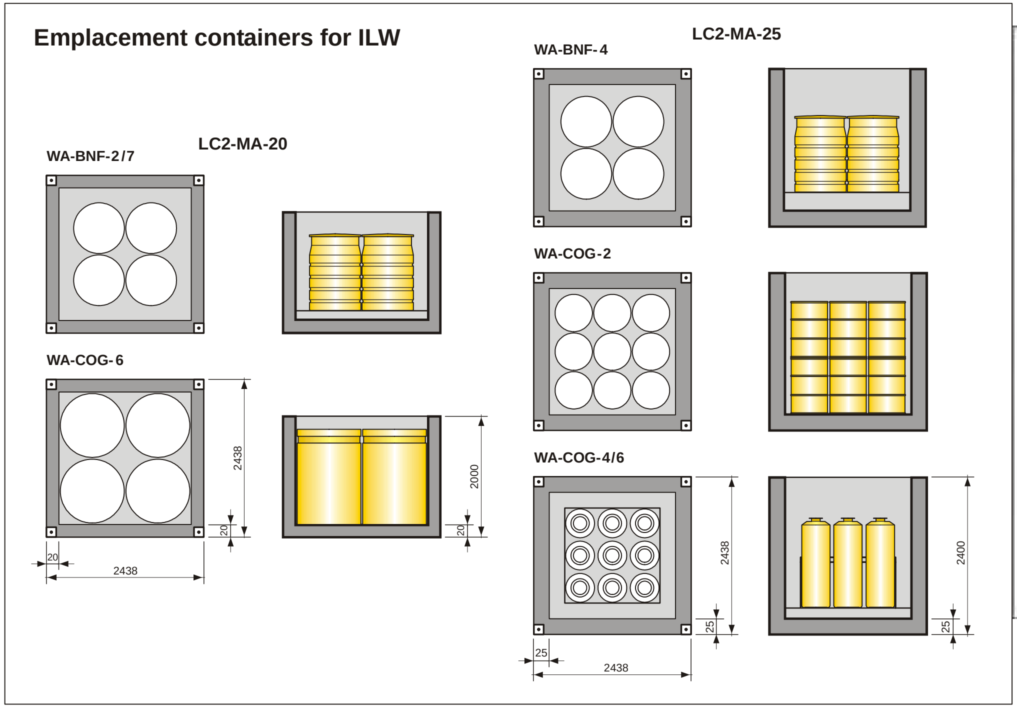
Thickness of Opalinus Clay - 100 to 130 m

Hydraulic conductivity - 2 x 10^{-14} m/s

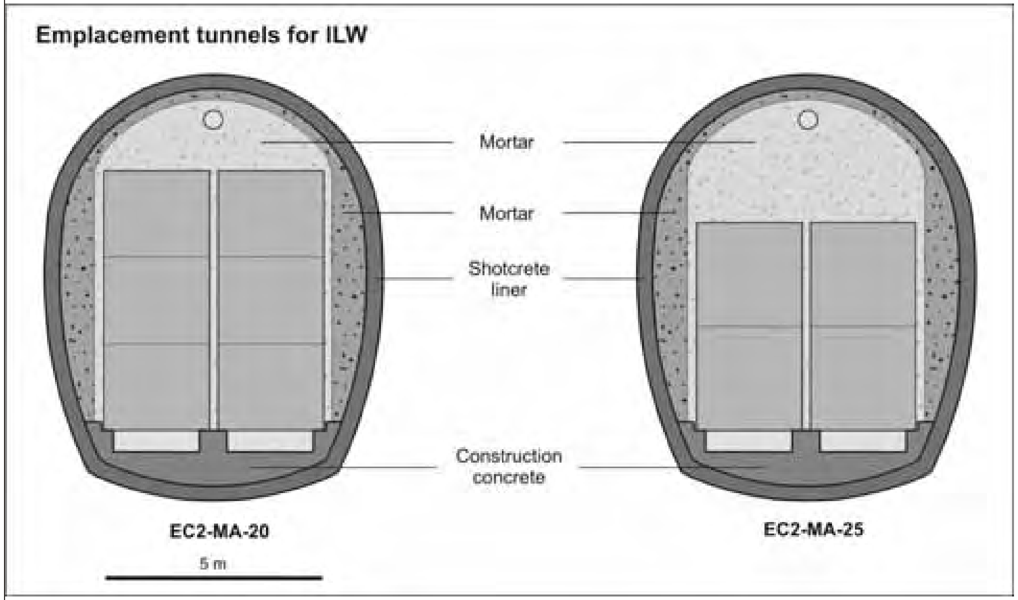
SF and HLW canisters



ILW containers and emplacement geometry



Emplacement containers for ILW

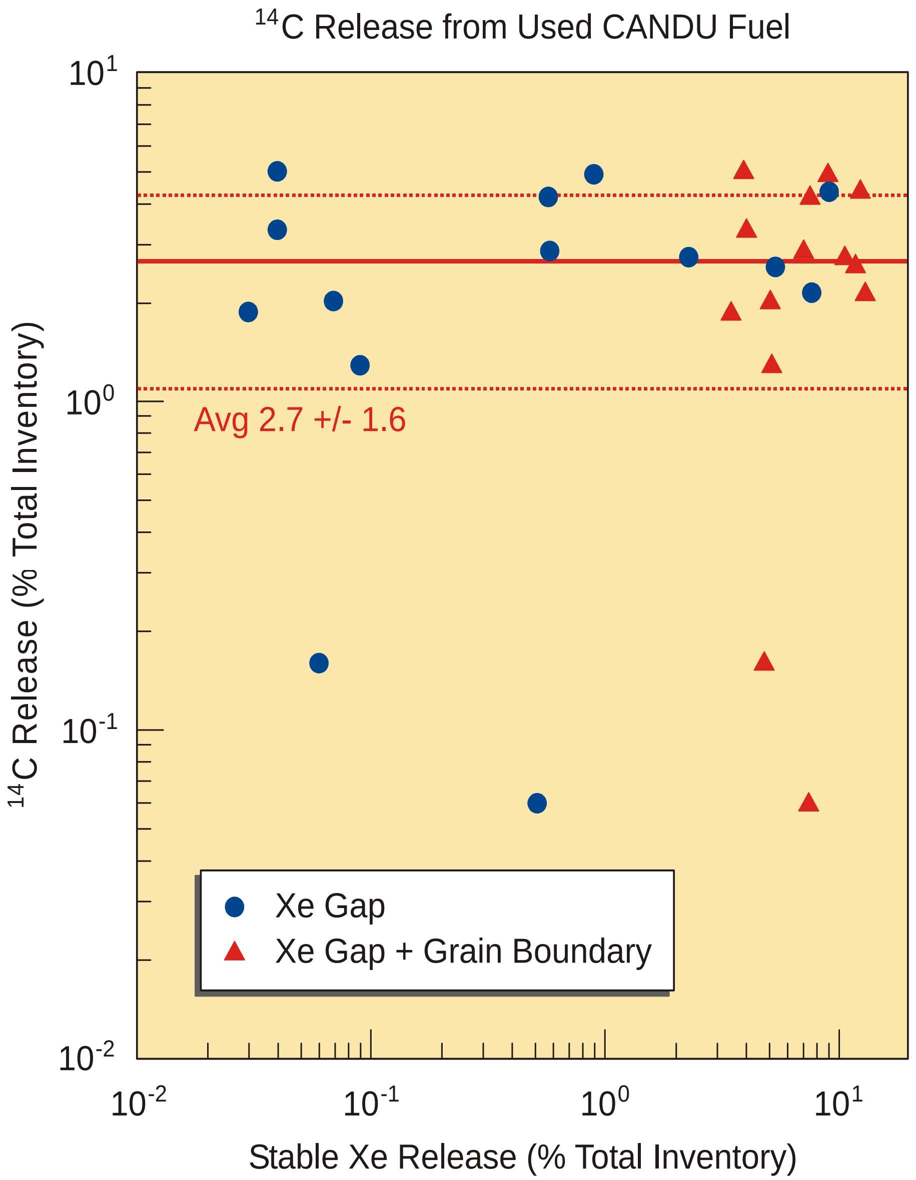


Emplacement tunnels for ILW

Assumptions regarding chemical form and release of ^{14}C from SF and HLW

- Spent fuel
  - Oxide matrix - Concentration of 25 ppm N is assumed for calculations of ^{14}C inventory. Chemical state uncertain (oxycarbide?) and ^{14}C is assumed to be released in inorganic form. Rapid release of 10 % is pessimistically assumed based on U.S. and Canadian leaching data.
  - Zircaloy - 80 ppm N assumed for calculations of ^{14}C inventory. Chemical state of ^{14}C is probably carbide, leading to release of organic ^{14}C upon corrosion. Rapid release of 20 % of ^{14}C in Zircaloy is assumed. Remainder is released slowly as Zircaloy corrodes (10 nm/a).
  - Steel and Ni-alloy assembly components - up to 800 ppm N present
- HLW
  - ^{14}C inventory about 1000x lower than for SF. Assumed to be inorganic, with no instant release fraction

Release of ^{14}C from SF



Releases range from 1 to 6 %

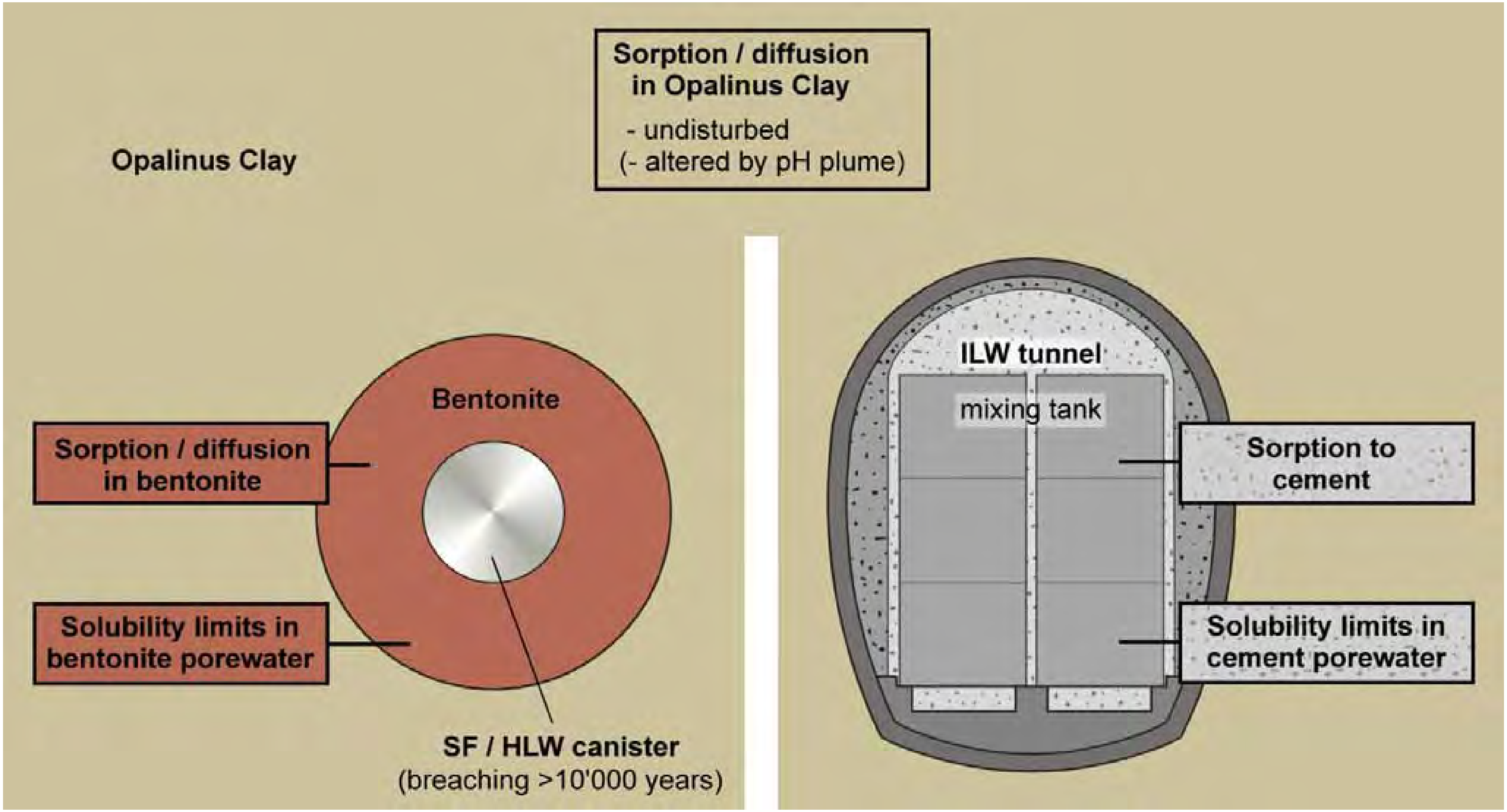
No relationship to fission gas release (C form is non-volatile)

Stroes-Gascoyne et al. 1994

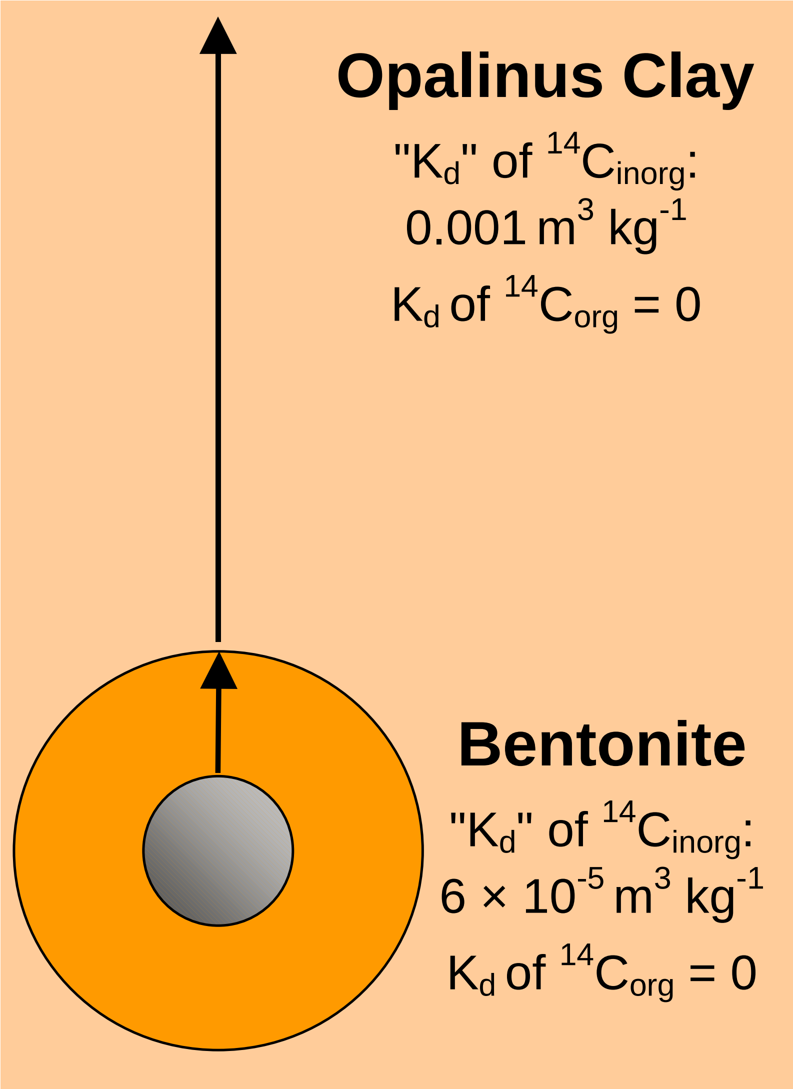
Assumptions regarding chemical form and release of ^{14}C from ILW

- Variety of reprocessing waste types from BNFL and COGEMA
- About half of the ^{14}C in the wastes is assumed to be organic (principally that present in Zircaloy hulls and ends wastes).
- In the release model, all of the ^{14}C in all waste types is assumed to be released 100 years after repository closure, i.e. no credit for the corrosion resistance of any of the wastes.

Retention processes considered in safety assessment



Diffusion of ^{14}C through bentonite and Opalinus Clay



Opalinus Clay

"K_d" of $^{14}C_{inorg}$:

$0.001\ m^3\ kg^{-1}$

K_d of $^{14}C_{org} = 0$

Bentonite

"K_d" of $^{14}C_{inorg}$:

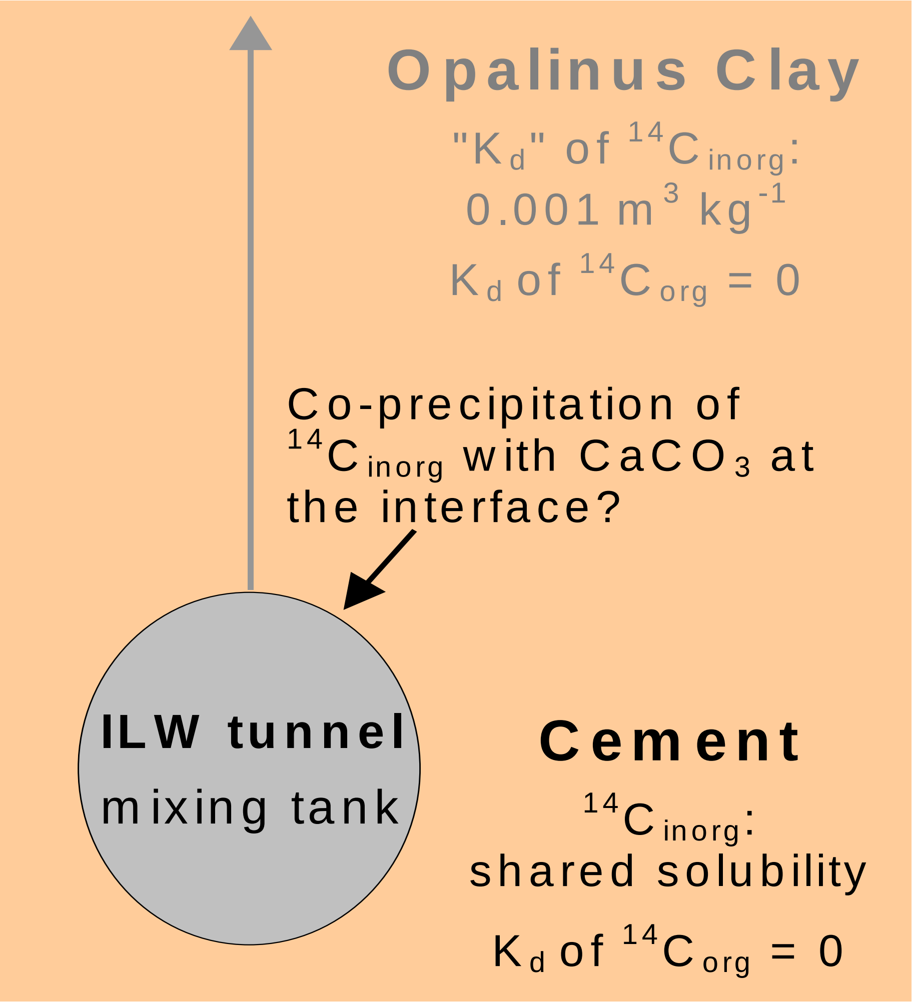
$6 \times 10^{-5}\ m^3\ kg^{-1}$

K_d of $^{14}C_{org} = 0$

- **Inorganic ^{14}C**
- Isotopic dilution with 0.27% of the calcite present
- Transformed into a pseudo sorption value "K_d"
- Opalinus Clay
  $CaCO_3$: 16 wt.%
  $[CO_3]_{porewater}$: 2.7 mol m^{-3}
- Bentonite
  $CaCO_3$: 0.7 wt.%
  $[CO_3]_{porewater}$: 2.8 mol m^{-3}

- **Organic ^{14}C**
- No retention assigned because of unknown structure

Sorption of ^{14}C in cementitious ILW tunnel



Opalinus Clay

"K_d" of $^{14}C_{inorg}$: 0.001 m^3 kg^{-1}

K_d of $^{14}C_{org}$ = 0

Co-precipitation of $^{14}C_{inorg}$ with $CaCO_3$ at the interface?

ILW tunnel

mixing tank

Cement

$^{14}C_{inorg}$: shared solubility

K_d of $^{14}C_{org}$ = 0

- **Inorganic ^{14}C**
- Isotopic dilution with 1% of the calcite present in cement
- Expressed as shared solubility

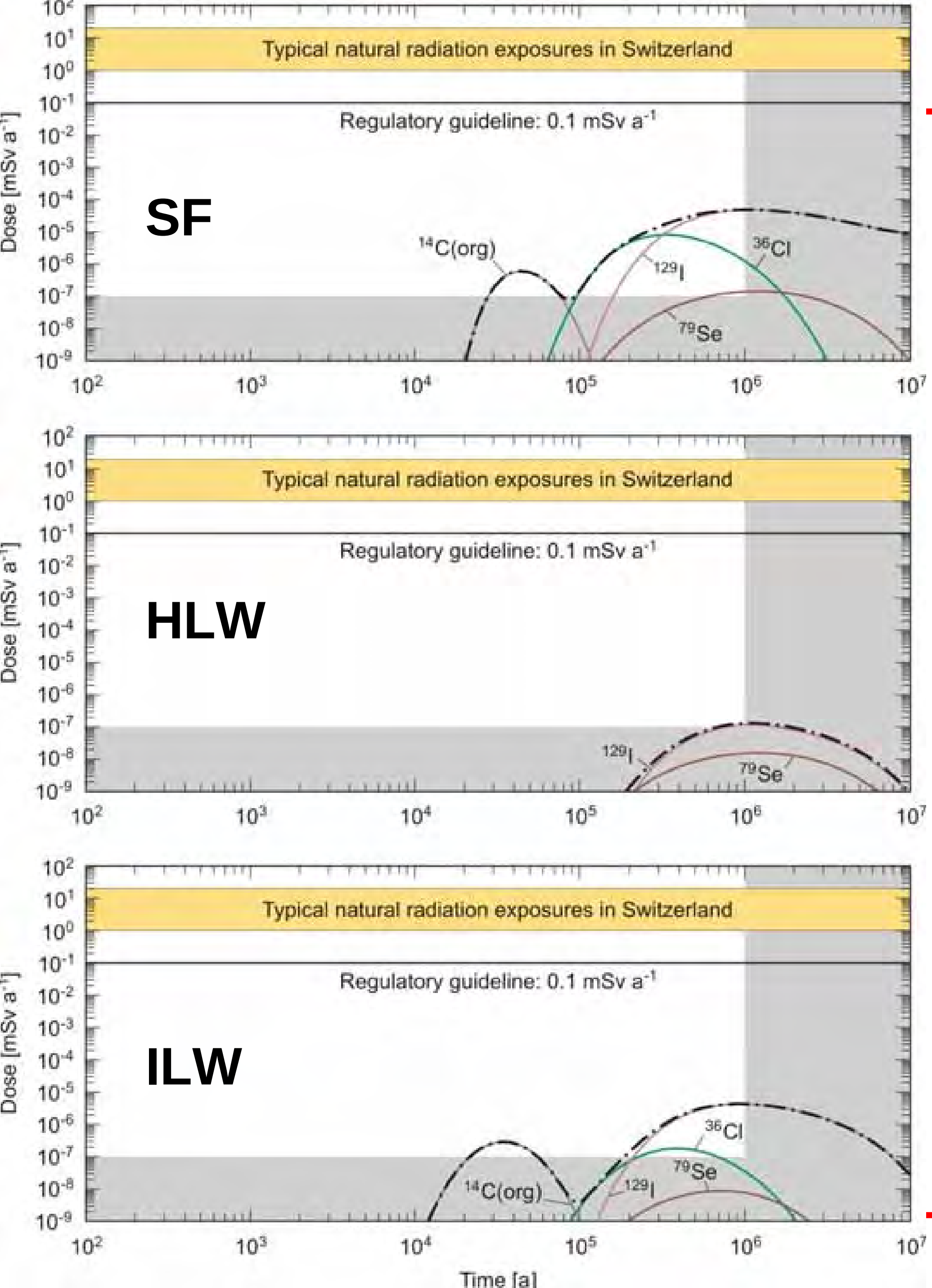
  1% of $CaCO_3$ in cement:

  4×10^{-4} mol kg^{-1}

  $[CO_3]_{porewater}$: 2×10^{-4} mol L^{-1}

- **Organic ^{14}C**
- No retention assigned because of unknown structure

Key results



Deterministic analyses

Reference Case results

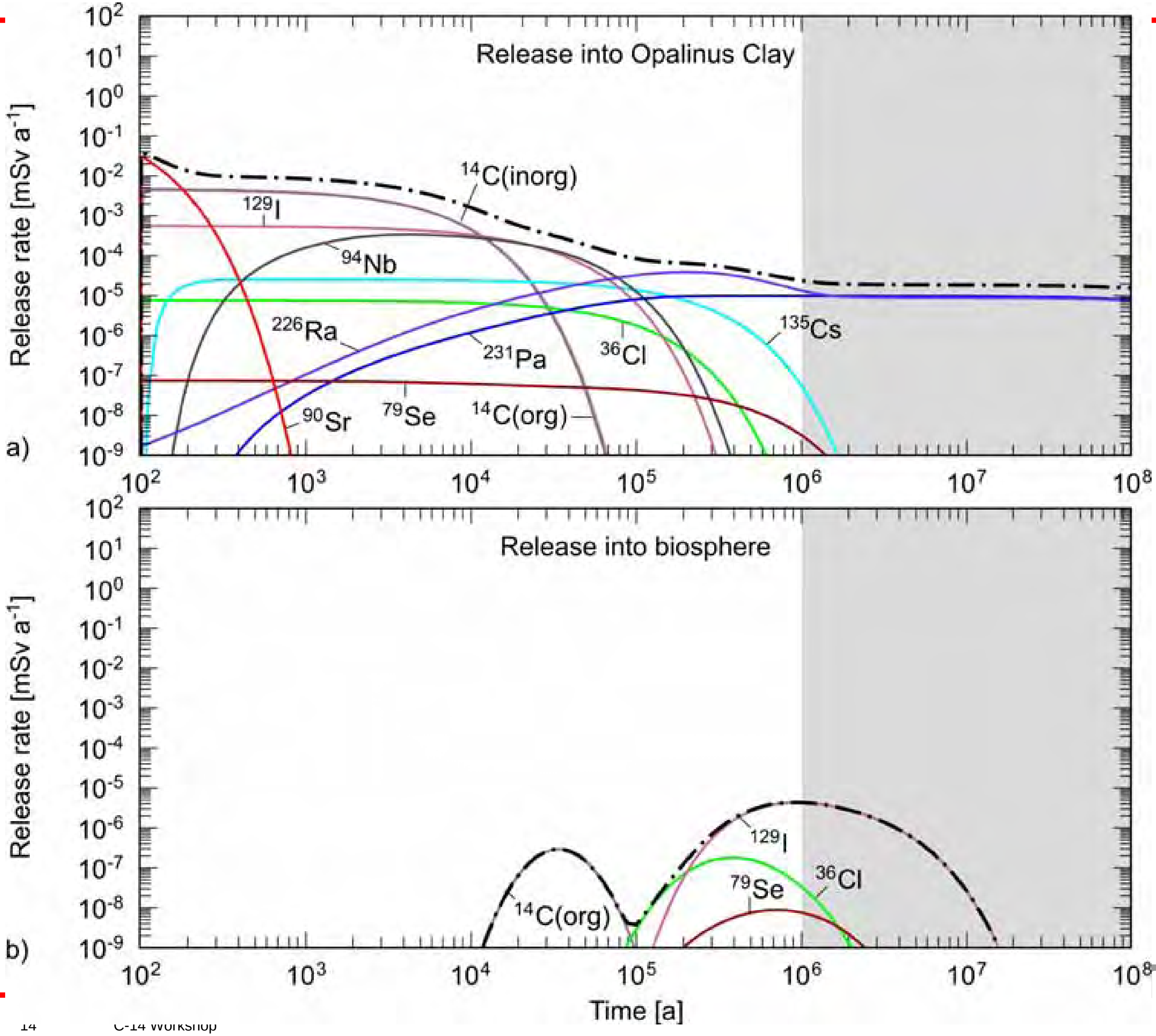
SF - Main dose contributors are ^{129}I ^{36}Cl, ^{14}C (org) and ^{79}Se

HLW - Main dose contributors are ^{129}I, ^{36}Cl and ^{79}Se

ILW - Main dose contributors are ^{129}I, ^{36}Cl, ^{14}C (org) and ^{79}Se

Max. doses are ~100x below regulatory limit

Release of radionuclides from ILW - reference case



Organisation of assessment cases

Scenarios	Conceptualisations	Parameters
Reference Scenario - Release of RN's in solution through host rock	Diffusion & advection	several sets
	NF alternatives	several sets
	Geo alternatives	several sets
	Role of access tunnels	several sets
	Gas & convergence effects	several sets
Release of volatile ^{14}C along gas pathway	Through host rock	several sets
	Affected by access	several sets
RN release affected by human action	borehole (near hit, direct hit)	several sets
	abstraction deep groundwater	several sets
	abandoned repository	
'What if?' cases (no scientific basis but to test system robustness)	high water flow	several sets
	discontinuities with flow	several sets
	several phenomena	several sets
	gas- induced	several sets
	instantaneous release volatile ^{14}C	several sets
	poor NF/Geo/flow	several sets
System options	more wastes	
	other ILW waste form	
	SF canister	several sets
Biosphere uncertainty	alternative geomorphologies	
	alternative climates	

Assessment case for instantaneous transport of ^{14}C

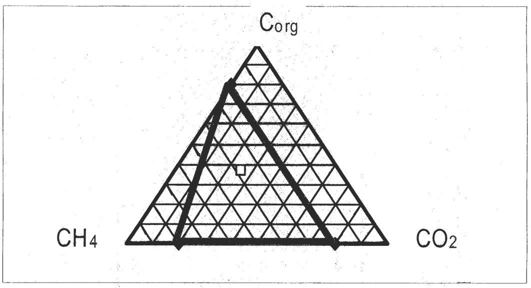
It is assumed that ^{14}C that is released in organic form from SF or ILW can be converted to a volatile form (e.g. methane) and be transported with H_2 formed by corrosion. Transport through the Opalinus Clay is assumed to be instantaneous. The case is hypothetical and meant to illustrate the robustness of the system with respect to uncertainties.

The results show that doses would be similar to the reference case.

Summary

- Conservative assumptions regarding ^{14}C release and transport lead to organic ^{14}C being one of the main dose contributors in calculations.
- Because of its relatively short half-life, any significant sorption would eliminate the dose contribution in Opalinus Clay host rock.
- It is clearly important to gain an improved understanding of the chemical form of released ^{14}C and its sorption characterisitics.
- By inference, the need for better data on ^{14}C behaviour is more important for host rocks with a confinement capacity that is lower than that of Opalinus Clay.

Part 1: Mobilisation and degradation of ^{14}C in waste



Part 1: Chemical Form and Mobilisation

- *Overview over Repository*
- *Different sources and types of waste (LLW)*
- *Kind of microbiological degradation*
- *Degree of microbiological degradation*

Part 1: Degree of microbial degradation

- ***extreme conditions for living***
  - *high salinity*
  - *high pH*
  - *little food*
- ***"There are extremophiles for every condition"***
  - *microbial activity found for pH up to ~11.0*
- ***"favourable" conditions because of Mg^{2+}***
  - *Mg^{2+} (from Carnallitit) lowers pH*
  - *sufficient Carnallitit close to all chambers containing organic ^{14}C*
  - *complete degradation of organic ^{14}C (to $^{14}CH_4/^{14}CO_2$) possible*

Part 1: Mobilisation and degradation of ^{14}C in waste

- ***Plain dissolution***
  - *hydrophilic organic compounds*
  - *carbonates*
    - *<oxalic acid, acetic acid, methanol, ethanol>?*
- ***Hydrolysis***
  - *14C-Carbide within irradiated AlN*
- ***microbial degradation***
  - *[no aerobic degradation]*
  - *anaerobic degradation (fermentation); $^{14}CH_4/^{14}CO_2$-ratio depending on*
    - *oxidizing agents (NO_3^-, SO_4^{2-})*
    - *content of oxygen in organic compound*
    - *highest $^{14}CH_4/^{14}CO_2$-ratio for aliphatic compounds (0.75)*

Part 1: Sources and types of ^{14}C-waste (LLW)

- ***^{14}C from Nuclear Power stations***
  - *(mainly) concentrated liquid waste:*
    - *carbonates*
    - *<oxalic acid, acetic acid, methanol, ethanol>?*
- ***^{14}C from Production of Radionuclides; Research***
  - *reagents for synthesis:*
    - *formiate, cyanide, cyanamide, methanol, methanal, carbonic acids*
  - *metabolites:*
    - *aliphatic alcohols and acids ("fatty alcohols and acids")*
  - *wastes from laboratories*
  - *remainings of plants*
  - *carcasses*
  - *radiation experiment:*
    - *steel box with irradiated AlN*

Part 1: Overview over Repository

- ***Geology***
  - *located in an old salt mine*
  - *rock salt (NaCl), potash salt (Carnallitit)*
- ***Solutions formed after access of water***
  - *NaCl-Solution*
  - *MgCl2-containing solutions ("Q-brine", "IP21")*
- ***Backfill materials***
  - *crushed salt*
  - *BFA (ashes of lignite)*
  - *"salt concrete" (concrete + crushed salt + SFA (ashes of hard coal) + brine)*

Nagra C-14 Workshop Meeting

Treatment of C-14 Release and Transport in the Long-Term Safety Assessment in the Final Repository in Morsleben

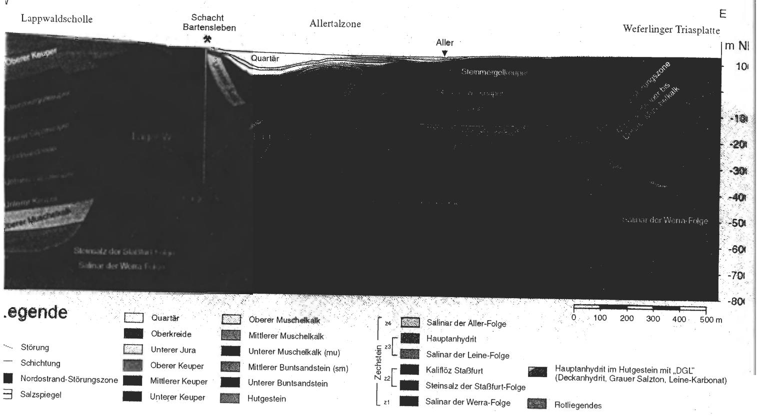
Part 1: Chemical Form and Mobilisation

Matthias J. Niemeyer, Colenco (Baden CH)

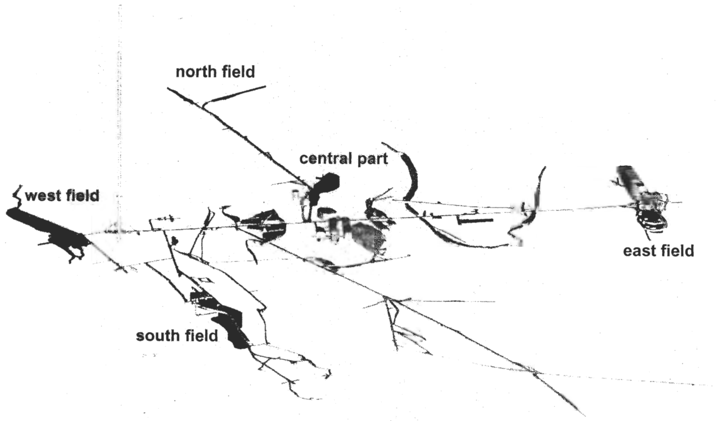
Part 2: Solubility and Transport

Ulrich Noseck, GRS (Braunschweig DE)

Morsleben repository: Geology



Morsleben repository: disposal areas



Form of C-14 in the waste

disposal area	organic form	alumina carbide	inorganic form
south field	1.56·10[illegible]	5.40·10[illegible]	[illegible]
west field	[illegible]	[illegible]	[illegible]
east field	1.60·10[illegible]	[illegible]	[illegible]
north field	5.00·10[illegible]	[illegible]	[illegible]
central part	[illegible]	[illegible]	[illegible]

- ❐ inorganic form: carbonate

脂肪酸→カルボン酸の一種

- ❐ organic form: fatty acids, fatty alcohols, ...
  - ❐ <u>reference case</u>: complete degradation of organics by microbial activity (75% CH_4, 25% CO_2)
  - ❐ <u>variant</u>: no degradation, transport in organic form
- ❐ alumina carbide: hydrolysis to CH_4

Treatment of retardation processes for C-14

- ❐ inorganic form
  - ❐ retardation in the near field by precipitation as calcite or dolomite
  - ❐ retardation in the far field by linear sorption
  - ❐ CO_2: transport in the gas phase
- ❐ organic form (only in the variant)
  - ❐ no retardation in the near field and far field
- ❐ CH_4 considered in separate calculations
  - ❐ transport in water: no retardation in the near field and far field
  - ❐ transport in the gas phase

Transport of C-14 in inorganic form (1)

- ❐ retardation as calcite and/or dolomite:

$$CO_2 + H_2O = HCO_3^- + H^+ = CO_3^{2-} + 2H^+$$
$$CO_3^{2-} + Ca^{2+} = CaCO_3$$
$$2\,CO_3^{2-} + Ca^{2+} + Mg^{2+} = MgCa(CO_3)_2$$

- ❐ CO_2 from degradation of cellulose and polyethelene
- ❐ $Ca(OH)_2$ from cementitious material, Mg^{2+} from the brine

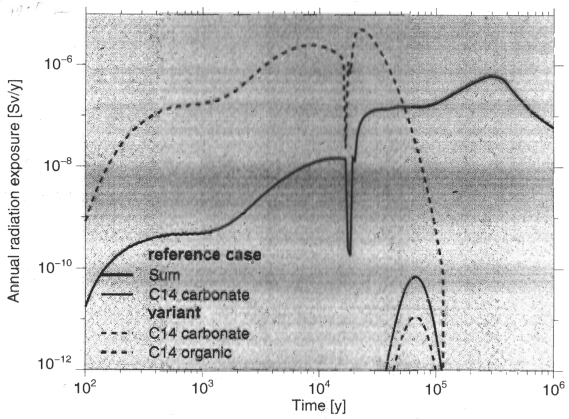
	south field	west field	east field	north field	central part
cellulose	$2.3\cdot10^{+4}$	$1.4\cdot10^{+5}$	[illegible]	[illegible]	$2.2\cdot10^{+3}$
polyethylene	$1.1\cdot10^{+5}$	$3.5\cdot10^{+5}$	[illegible]	[illegible]	$5\cdot10^{+3}$
cement	$1.0\cdot10^{+6}$	$6.9\cdot10^{+5}$	[illegible]	[illegible]	-
BFA	$2.0\cdot10^{+7}$	$1.4\cdot10^{+7}$	[illegible]	[illegible]	$5\cdot10^{+5}$
brine	46 813	19 816	[illegible]	[illegible]	18 355

Transport of C-14 in inorganic form (2)

- geochemical calculation with EQ3/6:
  - quantity of C-14 in solid, solution and gas phase
  - mobile fraction of C-14
  - large amount of immobile C-14 in south field and central part

	south field	west field	east field	north field	central part
precipitate [mol]	$8.7 \cdot 10^{+6}$	[illegible]	$1.1 \cdot 10^{+7}$	[illegible]	$9.6 \cdot 10^{+4}$
dissolved [mol]	[illegible]	[illegible]	[illegible]	[illegible]	$1.9 \cdot 10^{+2}$
gaseous [mol]	-	[illegible]	[illegible]	[illegible]	-
mobile fraction	$7 \cdot 10^{-5}$	0.46	0.67	[illegible]	$2 \cdot 10^{-3}$

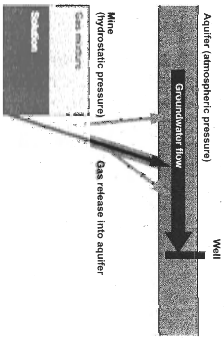
Results for reference case and variant



CH$_4$ transport in water: conceptual model

Assumptions

- Homogeneous mixture of methane, hydrogen and air in distinct areas of the repository
- Dissolution of the gaseous components in water according to their partial pressure
- Percentage composition of the gas mixture not changed during transport
- Immediate transport into near surface aquifer after flooding of the repository area
- Radioactive decay of C-14
- Degassing of methane from solution due to pressure decrease is neglected
- Dilution in the near surface aquifer



Calculation of radiation exposure

$$D = \frac{c_M \beta_M q_{C\text{-}14}}{f} a_{C\text{-}14} D_{C\text{-}14}$$

with:

Parameter	Sign	Value
Maximum methane solubility at 4.9 MPa [mol/m^3]	c_M	17.64
Dilution in aquifer (25 000 m^3/a / 10 m^3/a)	f	2 500
Dose conversion factor for C-14 [(Sv/a)/(Bq/m^3)]	$D_{C\text{-}14}$	$1.1 \cdot 10^{-7}$
Specific activity of C-14 [Bq/mol]	$a_{C\text{-}14}$	$2.31 \cdot 10^{12}$

to be determined:

Parameter	Sign
Methane fraction in gas mixture	β_M
Isotope fraction of C-14 in methane	$q_{C\text{-}14}$

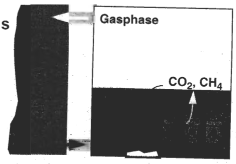
Determination of β_M and $q_{C\text{-}14}$

- Isotope fraction of C-14 in methane: $q_{C\text{-}14}$
  - Active methane from organic waste and aluminum carbide
  - Inactive methane from cellulose and polyethylene
- Methane fraction in gas mixture: β_M
  - Methane from cellulose and polyethylene
  - Hydrogen from iron, aluminium, zinc, cellulose and polyethylene
  - Air from operational phase
- Results

	south field	west field	east field	remaining
β_M [%]	9.4	13.2	9.6	4.6
$q_{C\text{-}14}$	$1.8 \cdot 10^{-8}$	[illegible]	[illegible]	[illegible]
D [Sv/a]	$3.0 \cdot 10^{-6}$	[illegible]	[illegible]	[illegible]

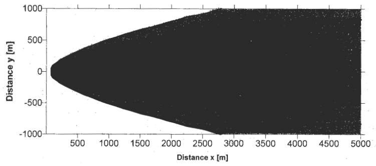
Gas release from the repository

- Three scenarios for the repository
  - Dry mine without any inflow of brine
  - Not isolated emplacement areas (north field and central part)
  - Isolated emplacement areas (west-south field and east field)
- Scenario für west-south field
  - Inflow of brine driven by hydrostatic pressure at lowest sealing
  - Pressure build-up reduces brine inflow
  - Gas release starts when gas pressure exceeds hydrostatic pressure at highest sealing
  - Displacement of gas by brine inflow and convergence
  - Gas release constant in time: $2.5 \cdot 10^{+8}$ Bq/y starts at 17 700 y, lasts 1 200y



Transport in the Geosphere / Biosphere

- Transport in the Geosphere
    - Unresisted, instantaneous release to the surface
    - CH_4 is transformed to CO_2 by microbes in the unsaturated zone
      Only release of CO_2
- Transport in the Biosphere
    - Release from point-source
    - Spreading of radionuclides in atmosphere by Gauss-Plume
    - Wind speed: 2.8 m/s
    - Release: $2.5 \cdot 10^{+8}$ Bq/y



Calculation of dose rate

- Critical group
    - Reference Biosphere from Biomass 2000
    - 7.6 km^2 arable land completely located within plume
    - 300 - 1 000 people living within plume all year
- Inhalation: Inhalation of conataminated air in 1.7 m height
    - Mean C-14 concentration in the air in 1.7 m $1.8 \cdot 10^{-5}$ Bq/m^3
    - radiation exposure by inhalation $9.0 \cdot 10^{-13}$ Sv/y
- Ingestion: Plants assimilating air in 0.5 m height; food pattern according to AVV
    - Mean C-14 concentration in the air in 0.5 m $2.1 \cdot 10^{-5}$ Bq/m^3
    - Mean C-14 concentration in plants $1.1 \cdot 10^{-2}$ Bq/kg
    - radiation exposure by ingestion $1.1 \cdot 10^{-8}$ Sv/y

---

Conclusions

- Calculations performed for different chemical forms of C-14:
  water pathway:
- C-14 as *carbonate* is efficiently reduced
    - by precipitation as calcite/dolomite if enough $Ca(OH)_2$ from cementitious materials and Mg^{2+} from the brine is present
    - by sorption on clayey material during transport through the overburden
- If no degradation of *organic* C-14 containing substances by microbial reactions, → strong impact on the dose rate due to no retardation in the near and far field
- C-14 as *methane* will cause
    - higher dose rates compared to carbonatic C-14 due to no sorption in near and far field
    - dose rates are in the same range as calculated for organic C-14
- gas pathway: Contribution of C-14 released on the gas phase two orders of magnitude lower than highest dose rates caused by methane / organic C-14 in solution

The Study for The Chemical Forms of C-14 Released from Activated Metals

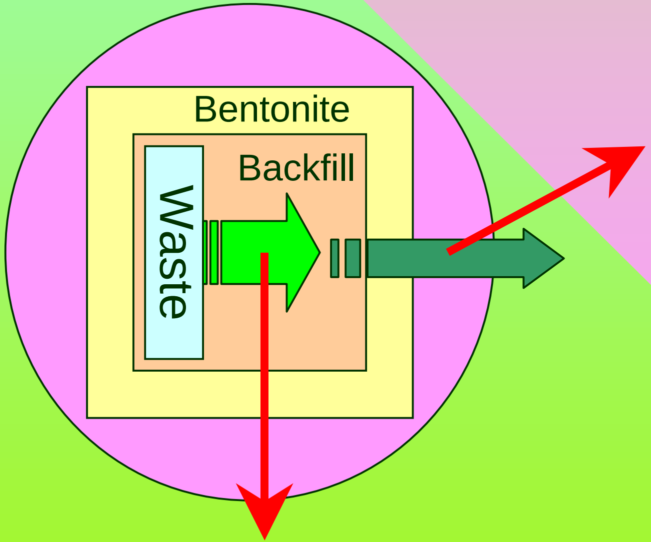
October 27-28, 2003

JNFL
RWMC
MHI
NDC
TOSHIBA

Contents

1. Objective

- The distribution coefficients of C-14 for barrier materials, e.g. cement, bentonite and so on, would be low, if the form of C-14 is mainly organic. The distribution coefficient for C-14 released from activated metal would depend on the chemical form
- In this study, the chemical forms of C-14 released from activated metals at a disposal site were investigated.



Chemical form：influences to flow rate of C-14, and Kd-values

Refer to the distribution of C-14

Release Rate：Dependent on Corrosion Rate of Material

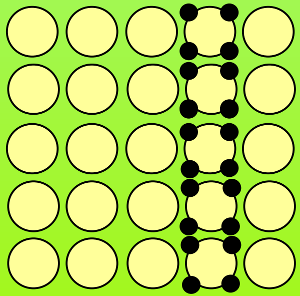
Refer to the Distribution of C-14

2. Procedure (Material)

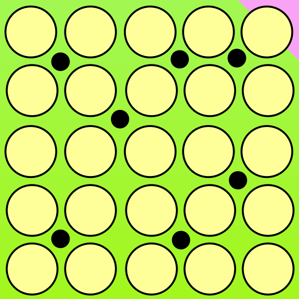
Investigation on chemical forms：activated stainless steel

Investigation on generation of carbon compounds from some materials：Fe_3C、ZrC etc

No.	Material	Carbon in Metal		
		Carbide	Solute	
1	Activated Stainless Steel	△*	○*	
2	Fe_3C	○		
3	Pearlite	○		Carbon 1wt%
4	Carbon Steel	○	△	
5	Martensite		○	Carbon 1wt%
6	ZrC	○		
7	Zr	△	△	



Carbide



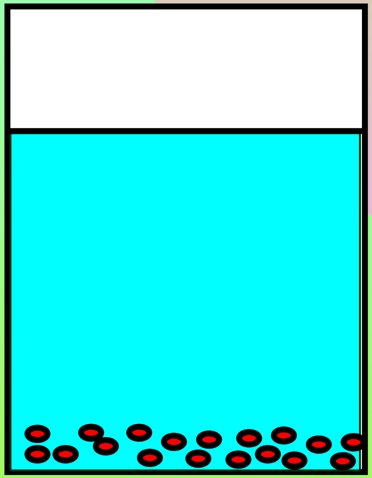
Solute

* The part of C-14 nuclides generated by neutron activation of N-14 would be carbide.

2. Procedure (Conditions etc)

① Materials	7 materials including activated sample
② Atmosphere	Anaerobic alkaline condition
③ pH	pH12～pH８
④ Leaching Time	1～15 months
⑤ Analytical Method	Activated Sample ：high performance liquid chromatography + liquid scintillation analyzer Cold Samples：high performance liquid chromatography or GC-MS

2. Experimental Method (Objects for Detection)



Gas Phase

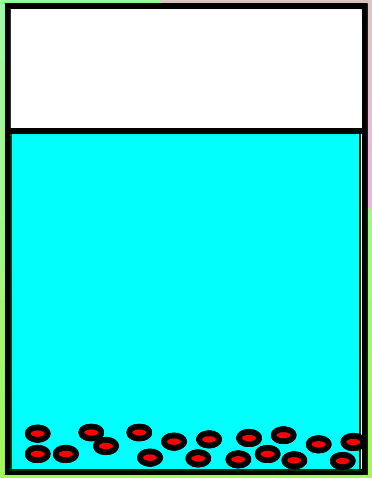
- The concentration ratio of each organic compound in gas phase

Liquid Phase

- The concentration ratio for TOC in total carbon in the solution
- The concentration ratio of each organic compounds in the TOC in the solution

3. The Results of Leaching Test(No.1) (1/2)

- The ratio of organic and inorganic C-14 in gas and liquid phase



Material		Activated Stainless Steel
Org. in Gas Phase		Not Measured
Liquid Phase	Org.	66～75%
	Inorg.	25～34%

3． The Results of Leaching Test(No.1) (2/2)

- Organic carbon in liquid phase

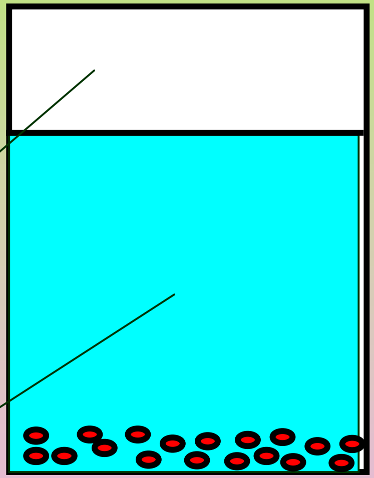
No.	Material	pH *	The ratio of organic carbon compounds in liquid phase (%)							
			Formic Acid	Acetic Acid	Acet-aldehyde	Form-aldehyde	Methanol	Ethanol	Propanol	Un-known
1	Activated Stainless Steel	10	10	43	N.D	9	10	6	N.D	22

● The concentration ratio for TOC in total carbon in the solution is **66%～75%**

* pH10 Simulated Groundwater

4. The Results of Leaching Test (No.2～7)(1/2)

- The ratio of organic/inorganic carbon in liquid and gas phase



Solid Carbon in Each Phase		Carbon Steel	Zr	Fe_3C	ZrC
Organics in Gas Phase (Organics)		～0.01%	～0.01%	Not Measured	Not Measured
Carbon in Liquid Phase	Organics	70～85%	55～85%	55～65%	88～90%
	Inorganic	15～30%	15～45%	35～45%	10～12%

4. The Results of Leaching Test (No.2～7)(2/2)

- The ratio of each organic carbon compound in the liquid phase

Solid	pH for the solution *	The Ratio of Organic Carbon Compounds For Liquid Phase (%)							
		Formic Acid	Acetic Acid	Acetaldehyde	Formaldehyde	Methanol	Ethanol	Propanol	Unknown
Fe_3C	8	51	49	N.D	N.D	N.D	N.D	N.D	—
	12.5	52	48	N.D	N.D	N.D	N.D	N.D	—
Pearlite	10	23	77	D	D	D	D	N.D	—
Carbon Steel	8	36	45	N.D	12	N.D	7	N.D	—
	12.5	20	71	N.D	6	N.D	3	N.D	—
Martensite	10	14	26	9	N.D	12	33	6	—
ZrC	8	3	97	N.D	N.D	N.D	N.D	N.D	—
	12.5	6	94	N.D	N.D	N.D	N.D	N.D	—
Zr	8	17	33	N.D	20	N.D	30	N.D	—
	12.5	9	56	N.D	16	3	16	N.D	—

- pH１０ Simulated Groundwater、pH8and pH12.5:sodium hydroxide Solution
- D：Detected Slightly　ND: Not Detected

5. Conclusion (1/2)

⟨Gas Phase⟩

- The experiments with cold samples (No.2 ～7) indicate a slight concentration of organic carbon in gas phase.

⟨Liquid Phase⟩

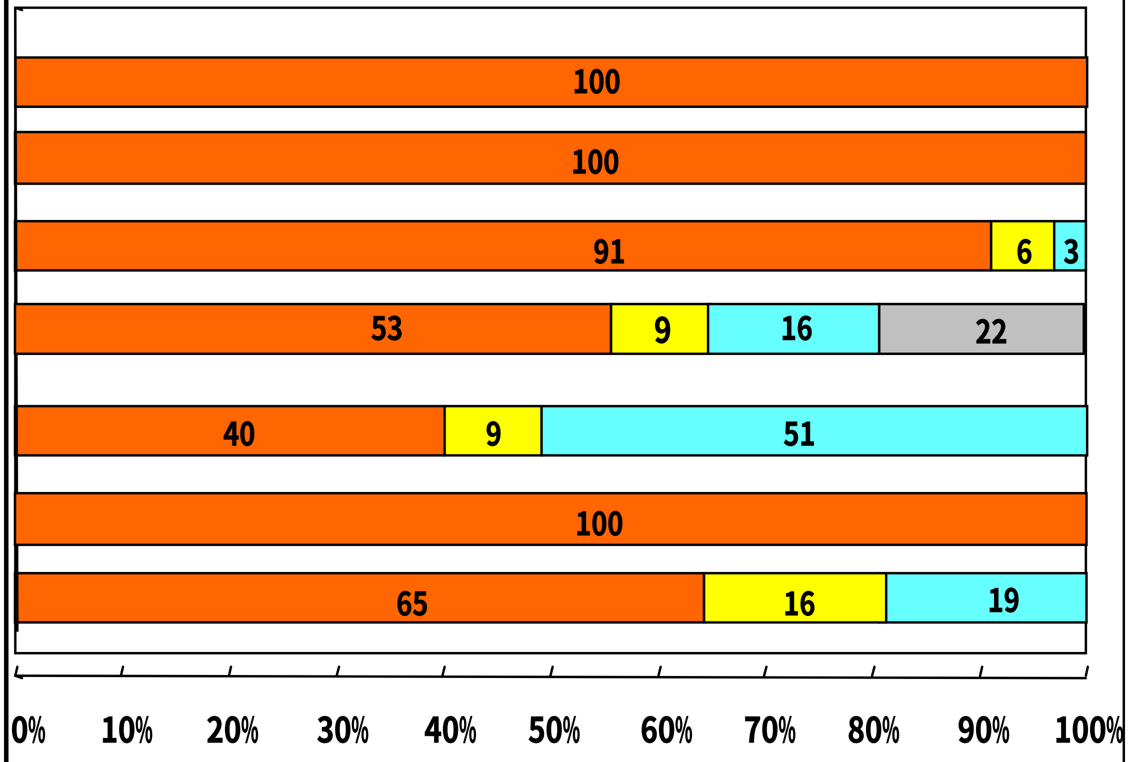
- The experiments with hot samples (No.1) indicate the ratio of organic C-14 released from activated metal in liquid phase is 66～75% (The ratio for inorganic C-14 is 23～34%).
- From carbides and non- activated metals

→Generated organic carbon compounds might be not only carboxylic acid but also alcohols owing to increasing the ratio of solute carbon in metallic phase

→The ratio of acetic acid concentration from ZrC is higher than that from Fe_3C.

5． Conclusion (2/2)

- **The organic compounds of each material**

Material	pH	The ratio of each organic compound
Fe_3C	12.5	
Pearlite	10	
Carbon Steel	12.5	
Activated Stainless	10	
Martensite	10	
ZrC	12.5	
Zr	12.5	

🟧 Carboxylic 🟨 Aldehyde 🟦 Alcohol ⬜ unknown

There are no differences in the kinds of organic carbon from the metals.

6. Discussion (1/2)

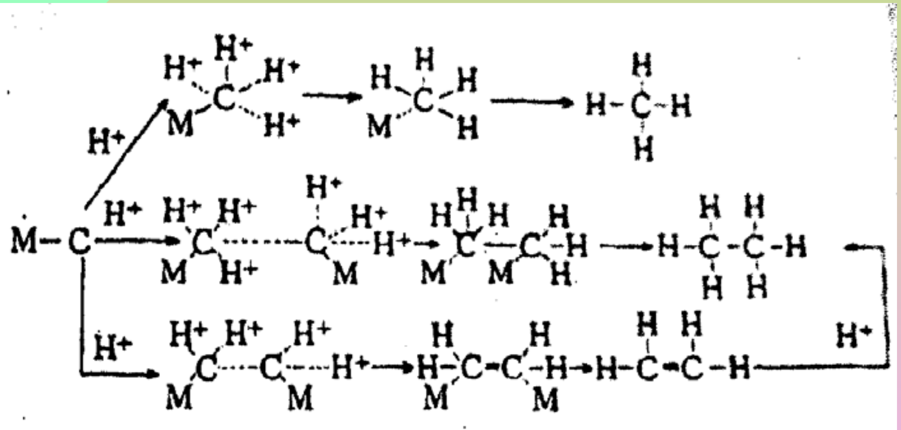
The chemical forms released from metals would be dependent on the chemical condition in the metallic phase.

① Generated organic carbon compounds might be carboxylic acid for carbides (hydrolysis for carbides).

②Generated organic carbon compounds might be not only carboxylic acid but also alcohols owing to increasing the ratio of solute carbon in metallic phase (Fischer-Tropsch reaction).

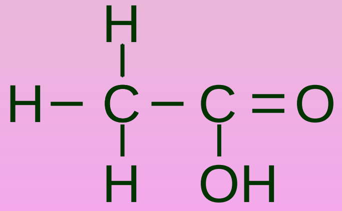
6. Discussion (2/2)

①



+

2OH →



CH_3COOH

② $CO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$

$\Rightarrow CO + 2H_2 \rightarrow CH_3OH$

‥‥ Fischer-Tropsch Reaction

7．Summary

- The ratio for organic C-14 released from activated metal in liquid phase is 66～75% (The ratio for inorganic C-14 is 23～34%).There is slight concentration of organic carbon in gas phase from carbides and non- activated metals.
- Generated organic carbon compounds might be carboxylic acids for carbides. Increasing the ratio of solute carbon in metallic phase would cause the generation of not only carboxylic acid but also alcohols .
- There are no differences in the kinds of organic carbon from the metals.
- Future Study

The investigation on generation of organic forms of C-14 from activated metals

i.e.. The leaching experiment for activated Zirconium alloy or non-activated stainless steel.

Methods for measuring ^{14}C on spent ion exchange resins – a review

Kristina Stenström and Åsa Magnusson
Div of Nuclear Physics
Lund University, Sweden

^{14}C in reactor coolant

<u>BWR</u>: mainly $^{14}CO_2$/carbonates

<u>PWR</u>: mainly CO, hydrocarbons (formaldehyde, formic acid, acetaldehyde, methanol, ethanol, acetone and acetic acid)

^{14}C on ion exchange resins

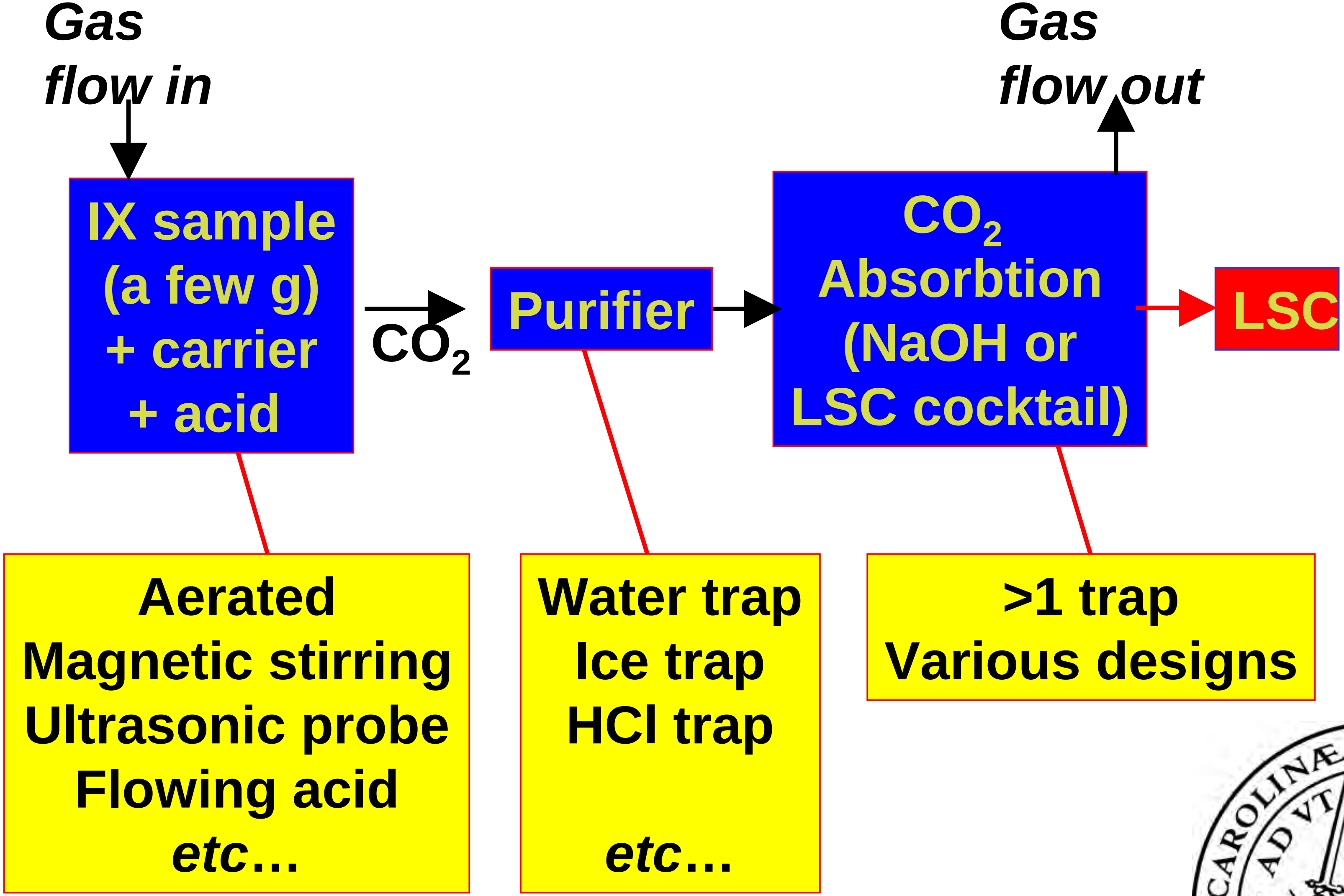
Many different opinions in the literature…
Varying results…

^{14}C needs to be measured!

Author (year)	Acid stripping		Combustion	
	carbonate	organic	speciation	total
Aitolla and Olsson (1980)	X			
Speranzini and Buckley (1981)			X	X
Nott (1982)	X			
Salonen/Snellman (1981-1985)	X	X		
Bleier (1983)				X
Martin (1986)	X			X
Chang *et al* (1989)	X			
Martin *et al* (1993)	X			X
Moir *et al* (1994)	X			X
Vance *et al* (1995)	X			X

Supercritical fluid extraction – Dias and Krasznai (1996)
Microbial treatment (total ^{14}C) – Tusa (1989)

Acid stripping in general



Gas flow in

IX sample (a few g) + carrier + acid

CO_2

Purifier

CO_2 Absorbtion (NaOH or LSC cocktail)

Gas flow out

LSC

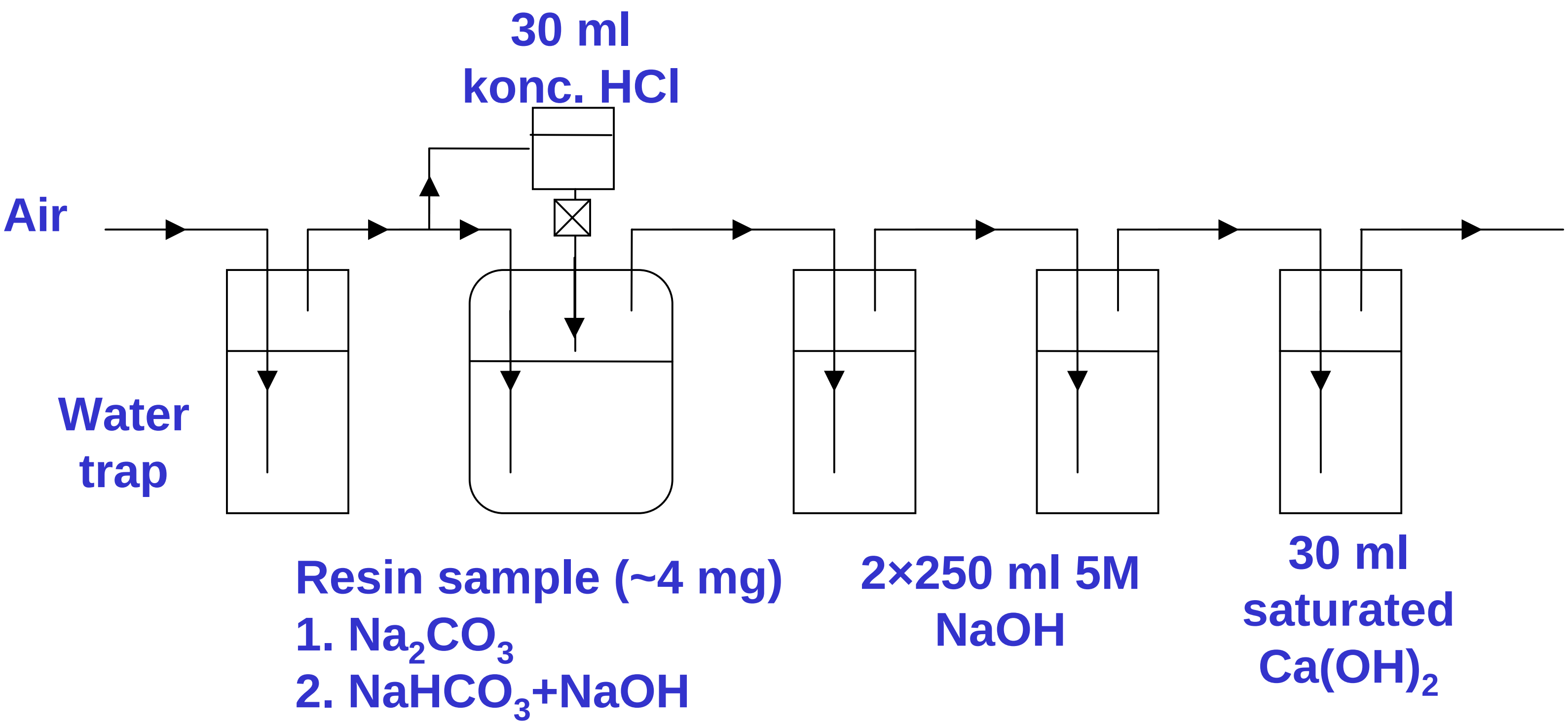
Aerated
Magnetic stirring
Ultrasonic probe
Flowing acid
etc…

Water trap
Ice trap
HCl trap

etc…

>1 trap
Various designs

Aittola and Olsson (1980)



30 ml
konc. HCl

Air

Water
trap

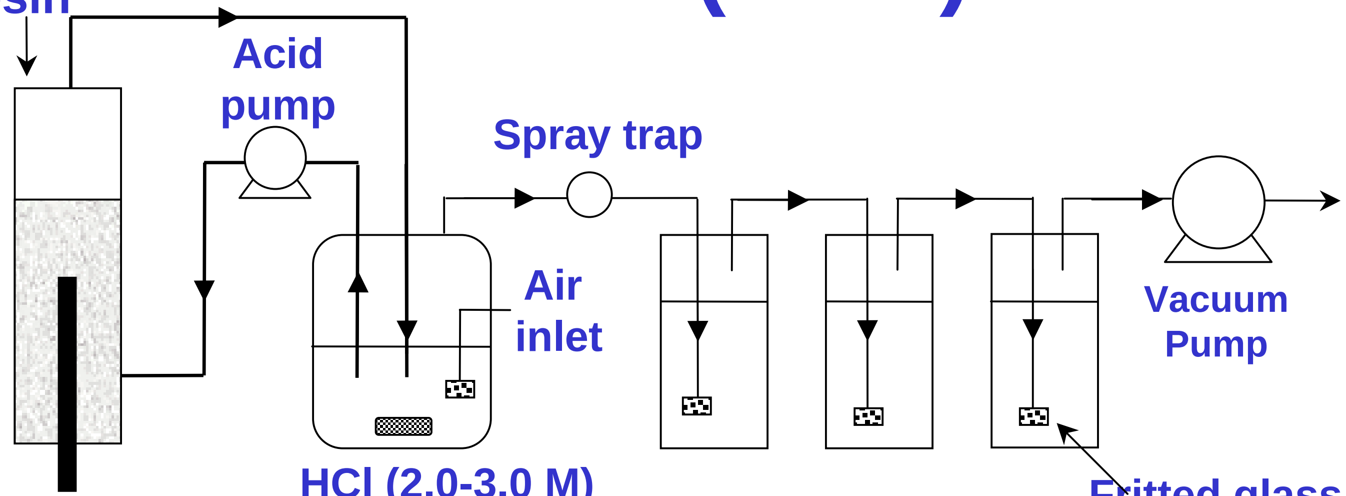
Resin sample (~4 mg)
1. Na_2CO_3
2. $NaHCO_3$+NaOH

2×250 ml 5M
NaOH

30 ml
saturated
$Ca(OH)_2$

- Recovery (^{14}C-labelled standard) :
  1) 33%-49%   2) 85%
- Precipitate as $BaCO_3$ (modified in test 2))
- No info about reproducibility, interference or memory effect

Nott (1982)



Stripping column with resin

Acid pump

Spray trap

Exhaust to fume hood

Air inlet

Vacuum Pump

Ultrasonic probe and generator

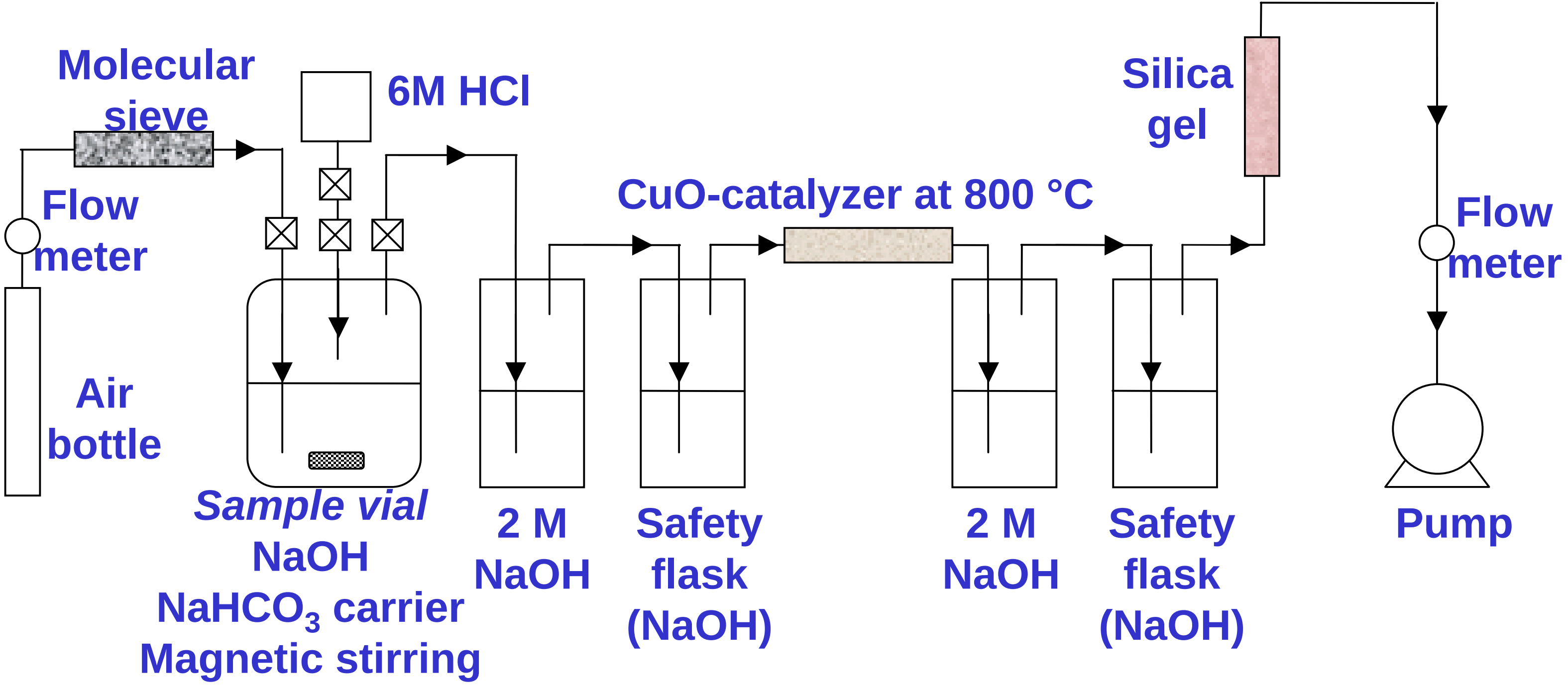
HCl (2.0-3.0 M) magnetic stirring

0.5-2.0 M NaOH (first two 250 ml; third 150 ml)

Fritted glass disc

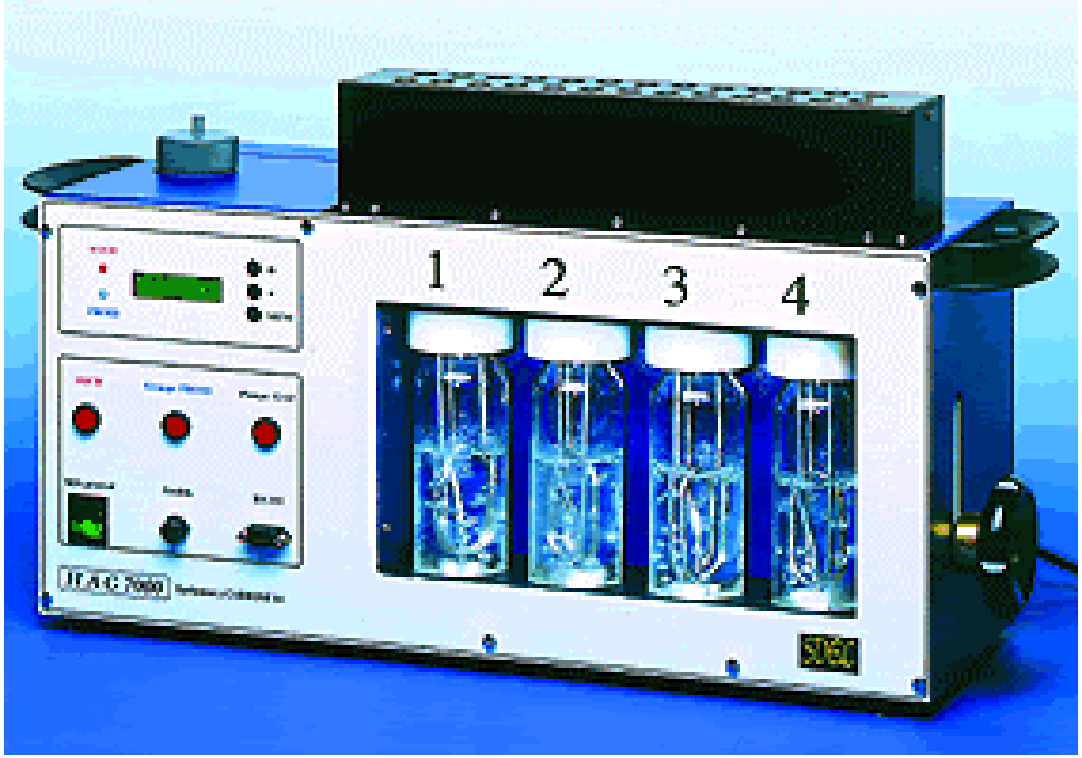
- <u>Recovery:</u> Range (91.8 - 102.1)% Mean (97.4 ± 3.6)%
- No info about memory effect
- Potential problem of interfering radionuclides

Salonen/Snellman (1981, 1982, 1985)

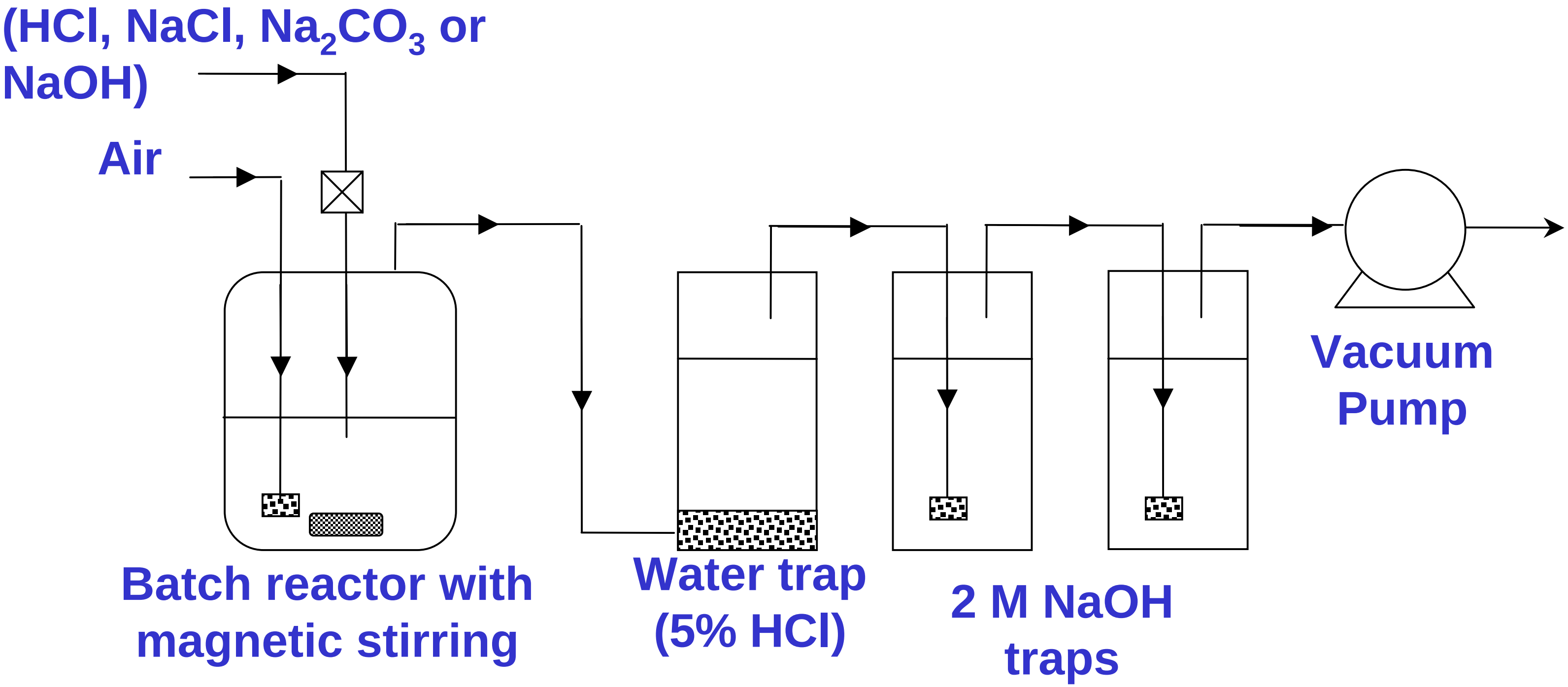


- Recovery: 93% with minor variations
- Precipitate as $BaCO_3$
- No memory effect
- No interference from other radionuclides
- Catalyst efficiency?
- CO/hydrocarbons are easily lost
- Drying the resin evaporates ^{14}C

SDEC-France



Chang *et al* (1989)



(HCl, NaCl, Na_2CO_3 or NaOH)

Air

Batch reactor with magnetic stirring

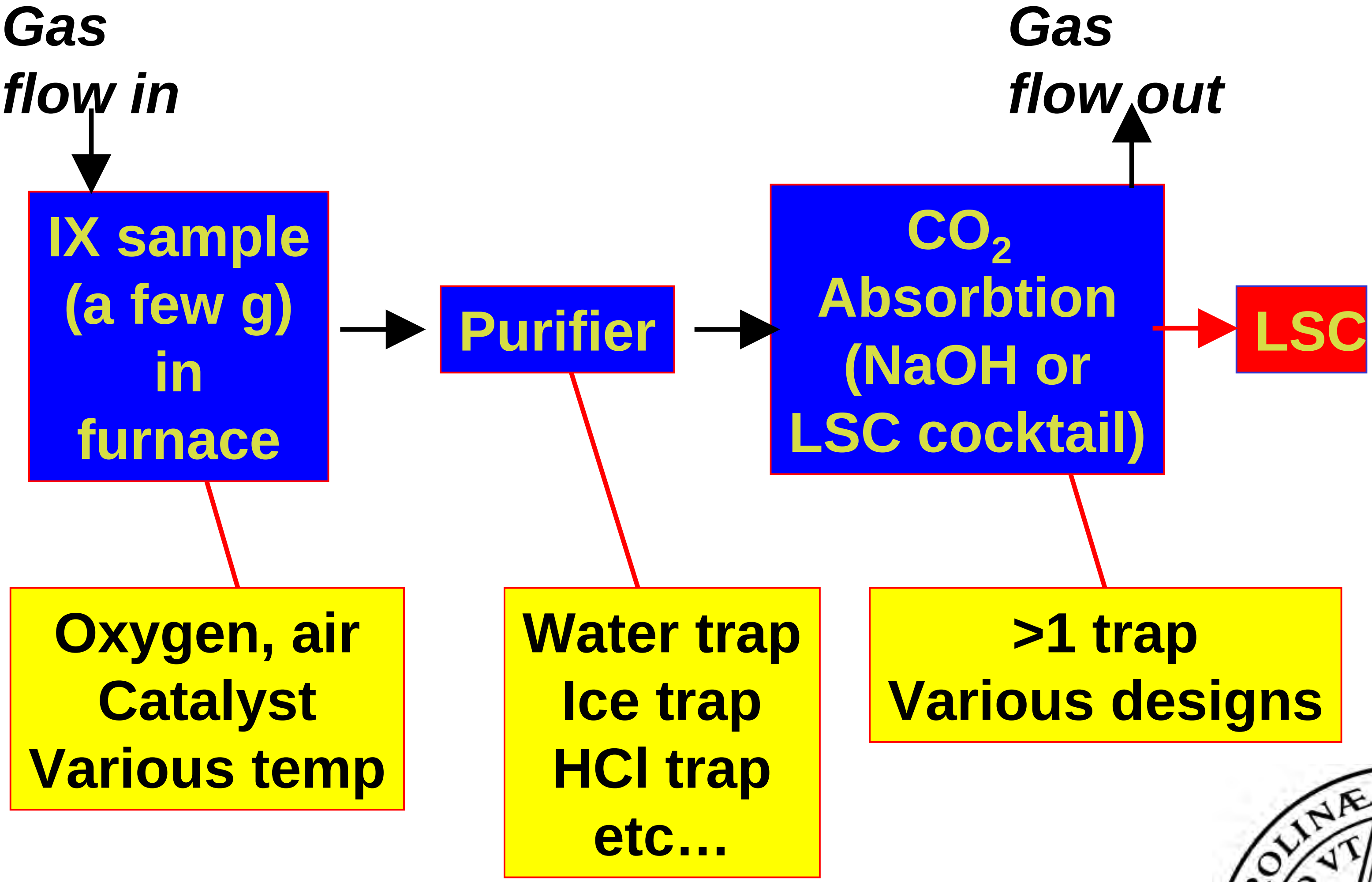
Water trap (5% HCl)

2 M NaOH traps

Vacuum Pump

- Best results with aerated agitated HCl
- Recovery: (98.5-100)%
- No interfering radionuclides in the NaOH (but in water trap) and no memory effect
- Real samples: remaining 0.5% removed with $K_2S_2O_8$

Combustion in general



Gas flow in

IX sample (a few g) in furnace

Purifier

CO_2 Absorbtion (NaOH or LSC cocktail)

LSC

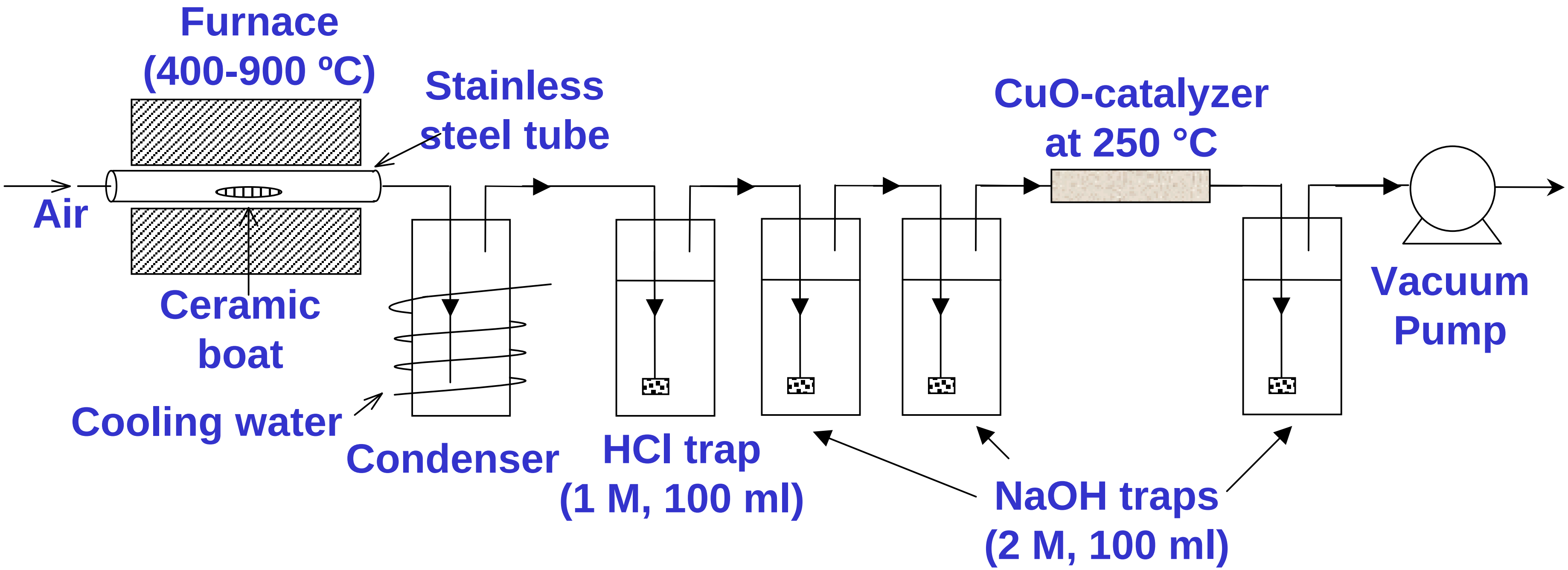
Gas flow out

Oxygen, air
Catalyst
Various temp

Water trap
Ice trap
HCl trap
etc…

>1 trap
Various designs

Speranzini and Buckley (1981)



Furnace
(400-900 ºC)

Stainless
steel tube

CuO-catalyzer
at 250 °C

Air

Ceramic
boat

Vacuum
Pump

Cooling water

Condenser

HCl trap
(1 M, 100 ml)

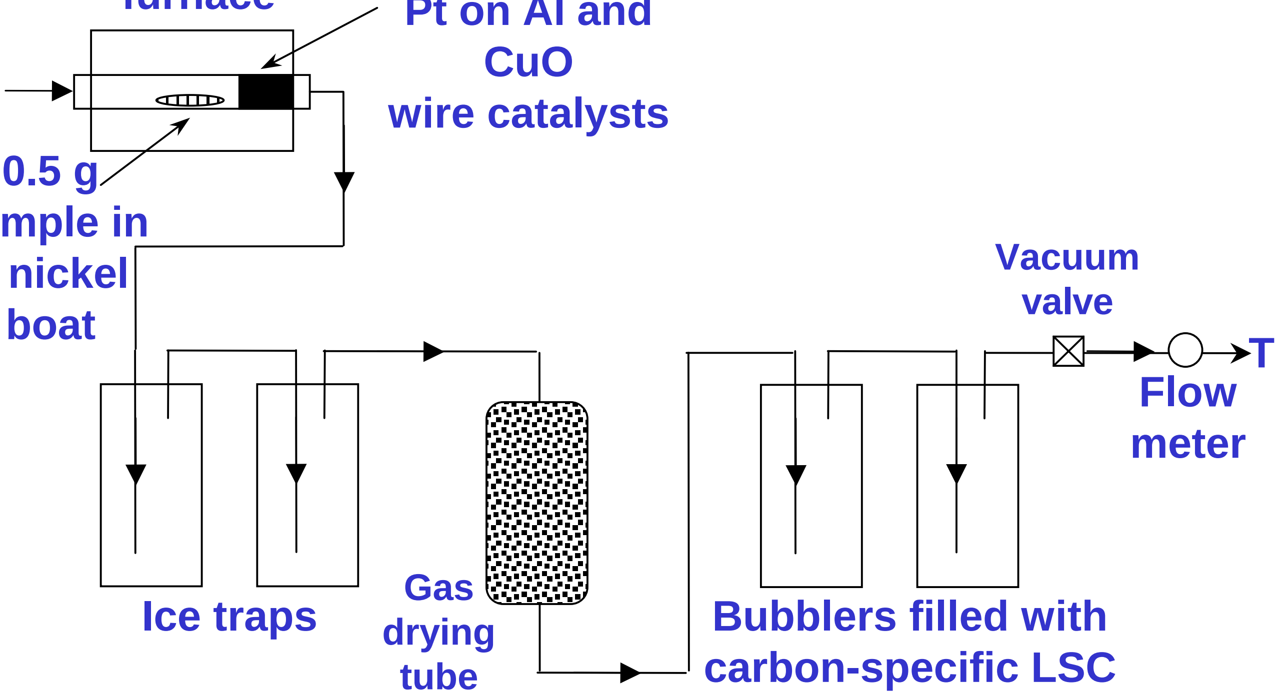
NaOH traps
(2 M, 100 ml)

- Recovery: (93-98)%
- Ion exchanged carbonates are not thermally stable:

  $CaCO_3 + SO_2 + ½\ O_2 \rightarrow CaSO_4 + CO_2$

  Reaction rate increases in the presence of $CaCl_2$

Martin *et al* (1993): Combustion



Electric tube furnace

Pt on Al and CuO wire catalysts

Air

0.5 g sample in a nickel boat

Vacuum valve

To vacuum

Flow meter

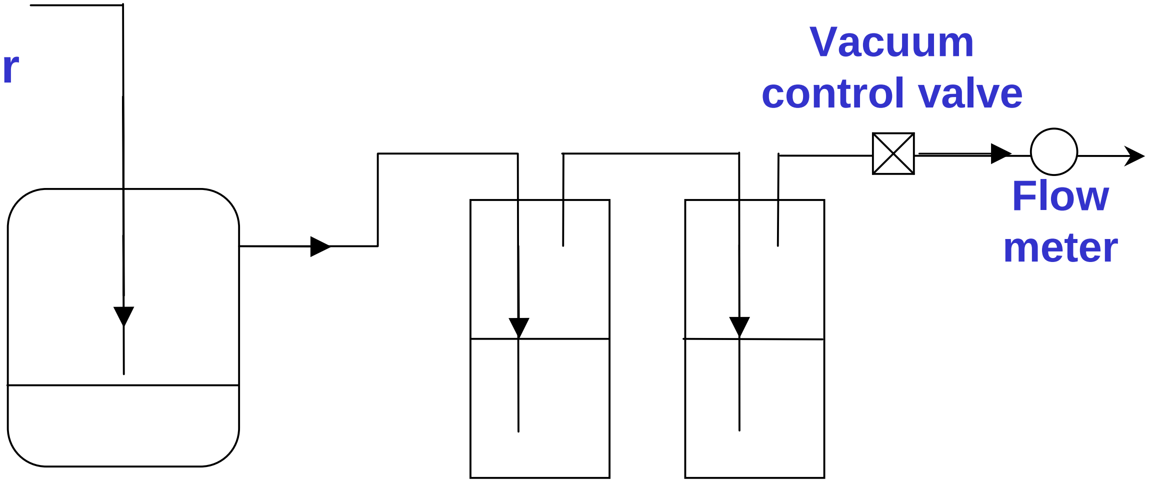
Gas drying tube

Ice traps

Bubblers filled with carbon-specific LSC cocktail

- 740 °C for 30 minutes
- Recovery: (63±9)%
- Not clear how well optimized

Martin *et al* (1993): Acid stripping



Room air
and acid or
base

Vacuum
control valve

To vacuum

Flow
meter

Flask and bubbler
containing resin sample

Bubblers filled
with
carbon-specific
LSC cocktail

- Recovery: (85±7)% (combustion (63±9)%)
- No memory effect
- ^{60}Co does not interfere

Moir *et al* (1994)

- Anion/cation separation by a sugar solution
- Parr bomb combustion for total ^{14}C
- Acid stripping for ^{14}C/carbonates

- Recoveries:
  - acid stripping (93±5)%
  - Parr bomb combustion (100±10)%
- No cross-contamination or memory effect
- Sugar separation ⇒ microbial activity?

Vance *et al* (1995)

Acid stripping (inorganic ^{14}C)
6 M H_2SO_4
↓
purification traps
↓
$Ca(OH)_2$/methanol trap
↓
purification of $CaCO_3$ precipitate

Combustion (total ^{14}C)

No information about recovery etc.

What do we want to do?

- **Organic/inorganic fraction**

Author (year)	**Acid regeneration**		**Combustion**	
	carbonate	**organic**	**speciation**	**total**
Aitolla and Olsson (1980)	X			
Speranzini and Buckley (1981)			**X**	**X**
Nott (1982)	X			
Salonen/Snellman (1981-1985)	**X**	**X**		
Bleier (1983)				X
Martin (1986)	X			X
Chang *et al* (1989)	X			
Martin *et al* (1993)	X			X
Moir *et al* (1994)	X			X
Vance *et al* (1995)	X			X

N and C-14 Contents of Spent Fuel

P. MARIMBEAU, DEN / DER / SPRC

E. ESBELIN, DEN/DRCP/SE2A

C14 contents of Spent Fuel - PRECCI SP1 goals

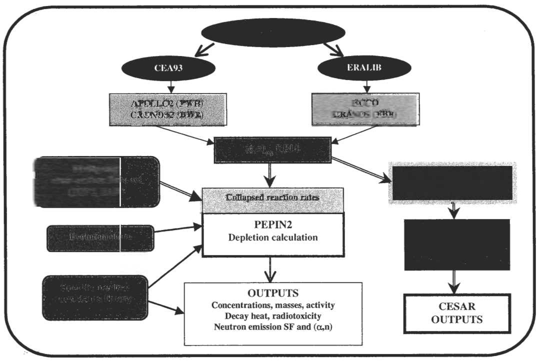
The aims of SP1 are
- to provide the source term to other PRECCI SPs
- to constitute a qualified reference database on spent fuel intrinsic data

- ➢ To characterise the spent fuel for a range of realistic cases by a qualified depletion code
- ➢To identify the PRECCI isotopes of interest
- ➢ To make out the qualification documents for these isotopes
- ➢ To lead a deliberate step to supply the identified failures

---

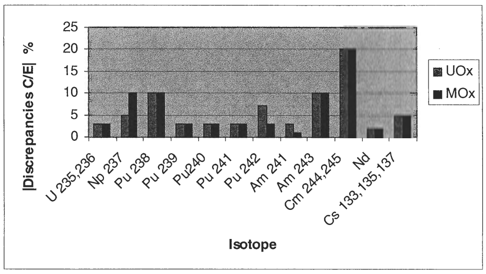
C14 contents of Spent Fuel - Source term calculation

The DARWIN - CESAR Package



C14 contents of Spent Fuel - Source term calculation

State of DARWIN-CESAR qualification -
Actinides and FPs



C14 contents of Spent Fuel - PRECCI isotopes

Isotopes of interest for PRECCI

- Actinides : Present isotopes in fuel :
  U, Np, Pu, Am, Cm
  + their decrease products
- Fission products : ^{90}Sr/Y, ^{137}Cs/Ba
  The LLFPs : ^{79}Se, ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs
- Impurities activation products (IAP) of fuel
  activation products of structural materials (APS) :
  ^{3}H, ^{60}Co, ^{63}Ni, ^{14}C, ^{36}Cl, ^{41}Ca, ^{59}Ni, ^{93}Mo, ^{94}Nb, ^{99}Tc

---

C14 contents of Spent Fuel - PRECCI analytical program

Analyses for inventories qualification

- Fuels : 2 PWR-UOx, 2 MOx ➔ ~35 and 60 GWd/t
- Dissolutions : COMIR and ATALANTE
- 3 groups of LLRN, 3 analyses laboratories
  - LLFPs : ^{79}Se, ^{90}Sr, ^{93}Zr, ^{107}Pd, ^{126}Sn ➢ SECR /Saclay
  - IAPs: ^{59}Ni, ^{93}Mo, ^{94}Nb ➢ LARC /Cadarache
  - Gaseous and volatile : ^{14}C, ^{36}Cl, ^{129}I ➢ SE2A /Marcoule

Progress state :
- Measuring techniques are operational (except ^{36}CL)
- ^{14}C and ^{129}I analyses on MOx fuel in process
- LLFPs : analyses on UOx fuel in process
- ^{36}Cl : R&D

Formation of ^{14}C for PWR fuels at 50 GWd/t

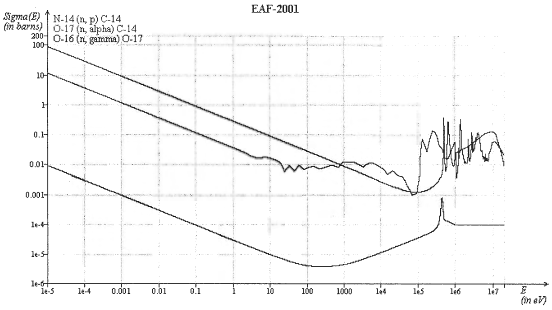
Channels of formation	Contributions (%)	
	UOx	MOx
$^{17}O\ (n,\alpha)\ ^{14}C$	59.6	63.5
$^{14}N\ (n,p)\ ^{14}C$	35.6	27.9
ternary fission ➔ ^{14}C	4.1	7.8
$^{16}O\ (n,\ ^{3}He)\ ^{14}C$	0.23	0.35
$^{16}O\ (n,\gamma)\ ^{17}O\ (n,\alpha)\ ^{14}C$	0.22	0.19
$^{18}O\ (n,\ n\alpha)\ ^{14}C$	0.14	0.20

- Masses of ^{14}C in grams contained in a 900 MWe assembly

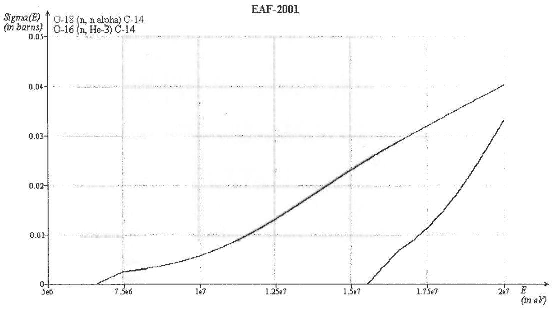
Masses of C14 /assembly	10 years	300 years	3,000 years	10,000 years
UOX – 33GWd/t	4.09E-2	3.95E-2	2.85E-2	1.222E-2
MOx – 37 GWd/t	3.67E-2	3.54E-2	2.55E-2	1.095E-2
UOx- 50 GWd/t	5.72E-2	5.52E-2	3.98E-2	1.707E-2
Structures for 50 GWd/t				

[redacted]

Main cross-sections for C-14 formation



Threshold cross-sections for C-14 formation



Statistical study of industrial analyses of manufacturers' batches

- Results for UOx and MOx fuels (~10 000 t and 400 t)
  - ➢LD = 8 ppm for N impurity
- Activities of some IAPs in UOx fuel at 50 GWd/t

Activities in UOx fuel (Bq/g)	10 years	300 years	10,000 years
^{14}C	2.05E+4	1.978E+4	6.12E+3
^{36}Cl	5.37E+2	5.37E+2	5.25E+2
^{59}Ni	1.387E+2	1.383E+2	1.265E+2
^{63}Ni	1.984E+4	2.66E+3	0.0

The aim is to compare CESAR results with those coming from other international codes

- ➢ using their own tools : basic nuclear data, calculation schemes…

- ➢ Domain : Fuel cycle and back-end of the cycle
- ➢ Fuel : PWR UOx and MOx (1^{st} phase)
- ➢ Results : Inventories of actinides, FPs, IAPs

- ➢ Framework : WPPR of the OECD

- ➢ Progress : specifications currently being drafted

^{14}C in a graphite reflector-
method development and measurement of organic and inorganic ^{14}C

Å. Magnusson, K. Stenström, M. Faarinen,
R. Hellborg, P. Persson, G. Skog

Aim: To develop a suitable method for measuring the fractions of organic and inorganic ^{14}C in graphite

LUND
UNIVERSITY

SKB

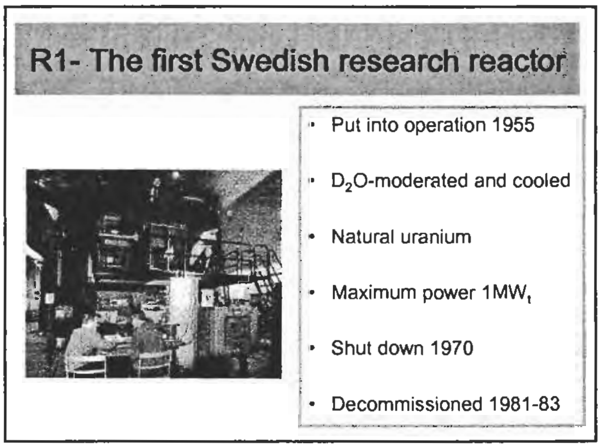
Why measuring the fractions of organic/inorganic ^{14}C?

- Different chemical properties...
- ...important for classification and disposal

Our definitions

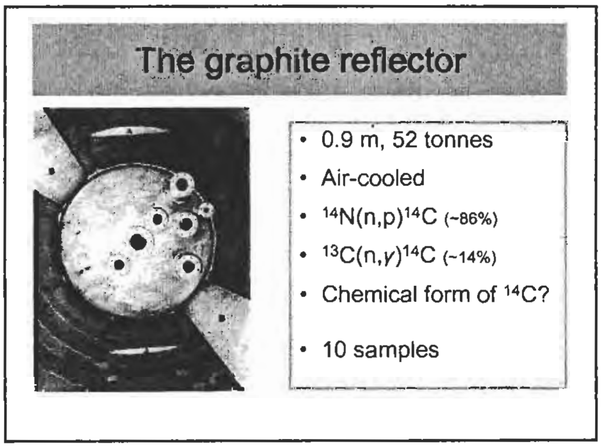
Organic: Compounds oxidized at T<600°C

Inorganic: Compounds oxidized at 600°C<T<900°C



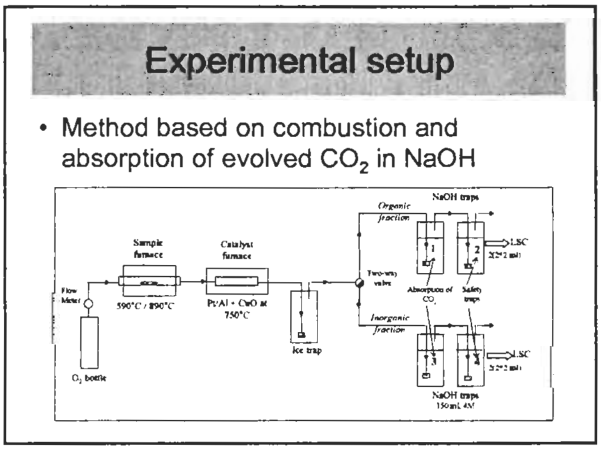
R1- The first Swedish research reactor

- Put into operation 1955
- D_2O-moderated and cooled
- Natural uranium
- Maximum power $1MW_t$
- Shut down 1970
- Decommissioned 1981-83



The graphite reflector

- 0.9 m, 52 tonnes
- Air-cooled
- $^{14}N(n,p)^{14}C$ (~86%)
- $^{13}C(n,\gamma)^{14}C$ (~14%)
- Chemical form of ^{14}C?
- 10 samples



Experimental setup

- Method based on combustion and absorption of evolved CO_2 in NaOH

Results

Sample	Organic ^{14}C (Bq/g)	Inorganic ^{14}C (Bq/g)
R1-020	443	1011
R1-030	131	371
R1-045	346	1104
R1-055	596	1099
R1-058	1561	2760
R1-088	570	238
R1-093	77	377
R1-108	308	964
R1-109	737	1855
R1-113	272	800
Mean value	**519**	**1033**

Total amount

Organic ^{14}C: 27 GBq

Inorganic ^{14}C: 54 GBq

System performamce

Proof of complete oxidation:

- *No signs of CO*
- *No visible traces of remaining sample material*

Proof of complete absorption of CO_2:

- *No signs of CO_2*
- *No activity above background level*

System performance

Proof of non-existing cross contamination:

- *No activity above background level*

Proof of a nearly 100% system recovery of ^{14}C:

- *No signs of remaining ^{14}C*
- *Complete CO_2 absorption*
- *No signs of remaining sample material*

System performance

Proof of reproducibility:

Sample	Organic ^{14}C Bq/g (mean value)	Inorganic ^{14}C Bq/g (mean value)	Total ^{14}C Bq/g
R1-058	1685	2573	**4258**
R1-058	1370	2800	**4170**
R1-058	1629	2907	**4536**
R1-093	77	376	**453**
R1-093	76	377	**453**
R1-108	278	1026	**1304**
R1-108	337	901	**1238**

Uncertainties

- Errors arising during combustion and measuring procedure: **3 - 20%**
- Errors arising due to the inhomogenity of ^{14}C within the sample material:
  - **19%**, organic ^{14}C fraction
  - **11%**, inorganic ^{14}C fraction

[illegible]

- Simple system construction
- Oxidation and CO_2 absorption
- System recovery of ^{14}C
- Contamination
- Decreasing the errors
- Complete separation of the organic and inorganic ^{14}C fractions?

Study on Photocatalytic Decomposition of Organic C-14 in Waste Packages

October 27-28, 2003

RWMC

(Radioactive Waste Management Funding and Research Center)

Kobe Steel, Ltd.

1. Expected Performance and Tasks of Waste Packages

Characteristics of organic C-14

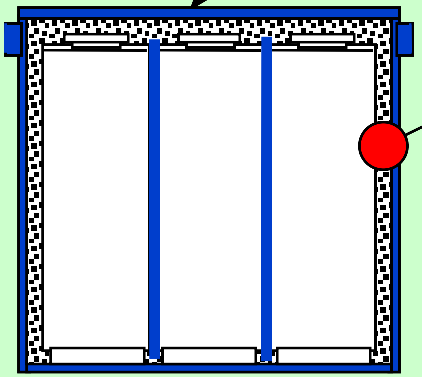
- Long half-life (5730 years)
- Low adsorption to clay, rock
- Low propensity to precipitate

Difficult to reduce organic C-14 release by present barrier materials

Barrier of waste packages

●Corrosion resistance

●Restriction of water permeability/nuclide release



Barrier of infilling material

●Decomposition of organic C-14 by photocatalysts

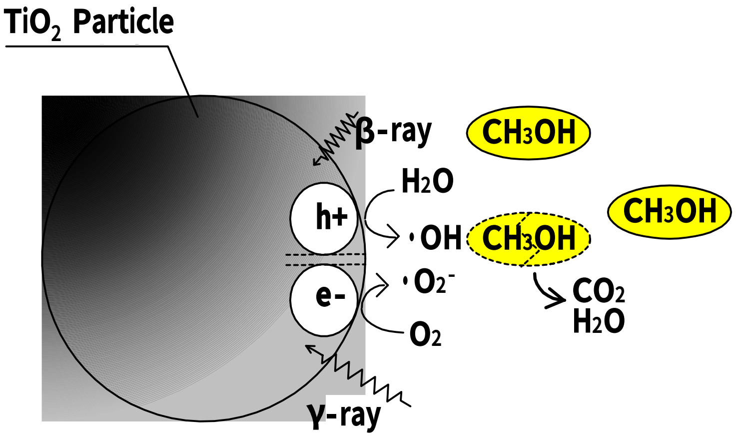
Improvement of distribution coefficient by decomposition

＜Objectives of this study＞

- Evaluation of corrosion resistance of package material (local corrosion, bending/welding parts)

◎ Evaluation of photocatalytic effect for decomposition of organic C-14

(1) Reactions on Photocatalysts



Schematic model of photoelectrochemical reactions

$TiO_2 + h\nu \rightarrow TiO_2 + e^- + h^+$

Reduction ① $e^- + O_2 \rightarrow {\cdot}O_2^-$ (Aerated)

② $2e^- + 2H_2O \rightarrow H_2 + 2OH^-$ (Deaerated)

Oxidation ① $h^+ + H_2O \rightarrow {\cdot}OH + H^+$

② $h^+ \rightarrow h_{trap}^+$

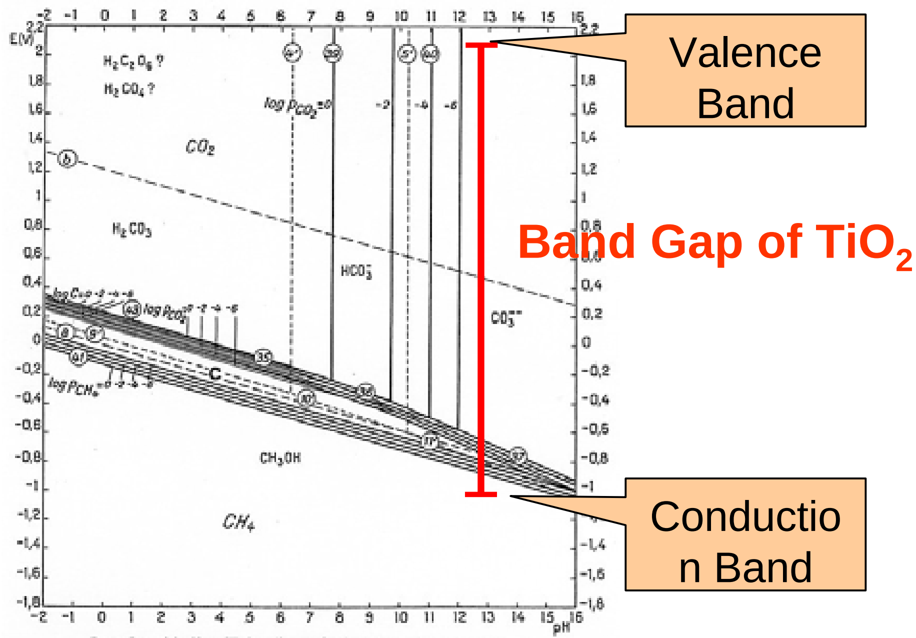
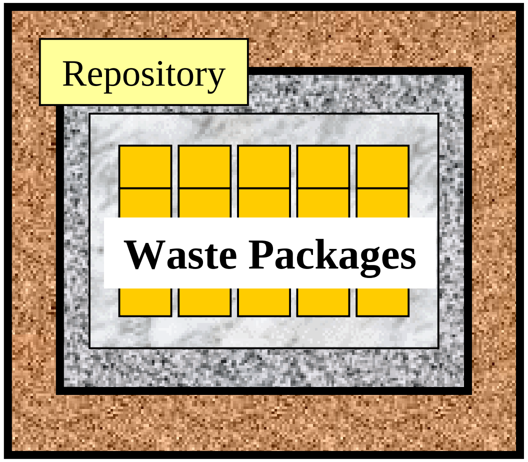
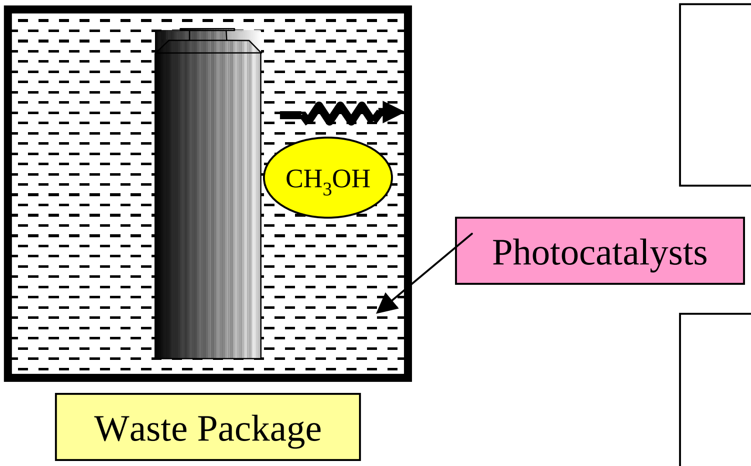


FIG. 7. Potential-pH equilibrium diagram for the system carbon-water, at 25°C.
(Considering carbon in the form of graphite.)
The portion of the diagram above the line log C = 0 refers to solutions containing 1 g-at of dissolved carbon per litre in the form of $H_2CO_3 + HCO_3^- + CO_3^{--}$. The portion of the diagram below this line refers to solutions thermodynamically saturated with solid carbon.

Potential-pH equilibrium diagram for the system carbon-water at 25°C

(2) Application of Photocatalysts to Waste Packages





Infill photocatalysts in waste packages

↓

Photocatalytic decomposition of organic C-14

↓

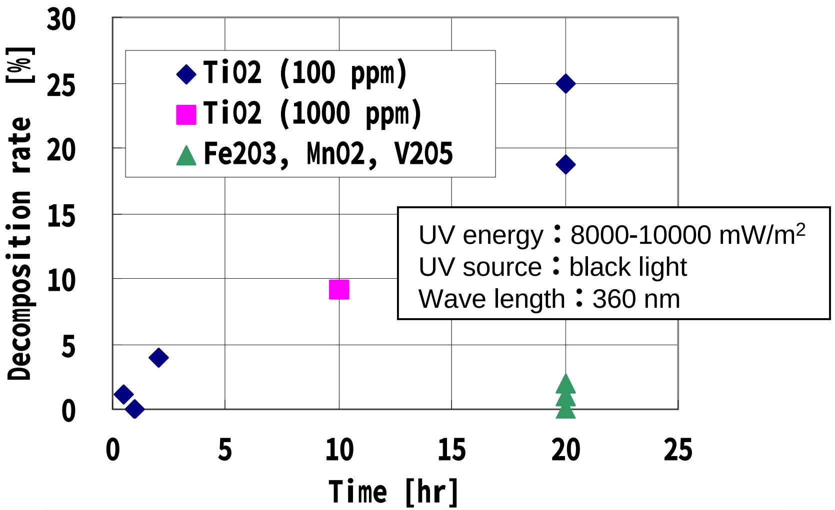
Retention of C-14 by sorption (Improve Distribution Coefficient)

↓

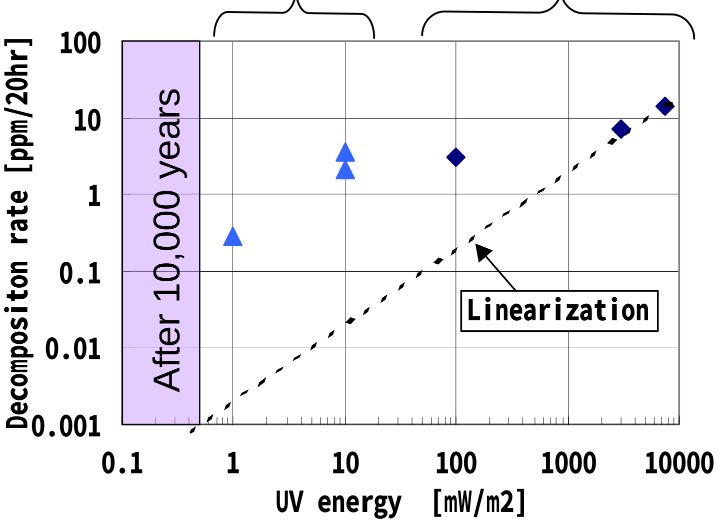
Improve barrier performance by infilling

(3) Studies with UV

Decomposition test of methanol by TiO_2 with UV



UV energy：8000-10000 mW/m^2
UV source：black light
Wave length：360 nm



UV Source：D_2, Xe lamp
Wave length：360 nm

UV Source：Black light
Wave length：360 nm

1) TiO_2 can decompose methanol.

2) The decomposition proceeds with time.

3) TiO_2 can act with low energy UV.

→ Improved Quantum efficiency

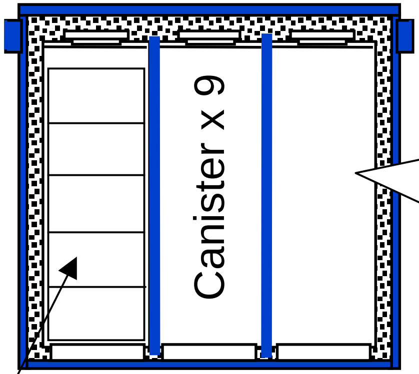
Possibility of photocatalysts with low energy radiation

(4) C-14 in Waste Packages

<Dimensions>

Waste package:1.4 x 1.4 x 1.4 m

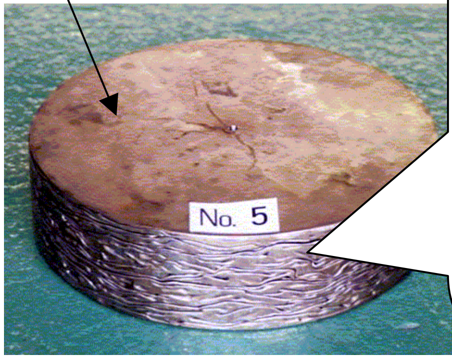
Canister: ϕ0.43 x 1.34 mH x 9



C-14 inventory
in a canister

5.5E+10 Bq/canister*1)

Compressed hull waste



(image sample)

(1) C-14 in oxide film: 20%*2)

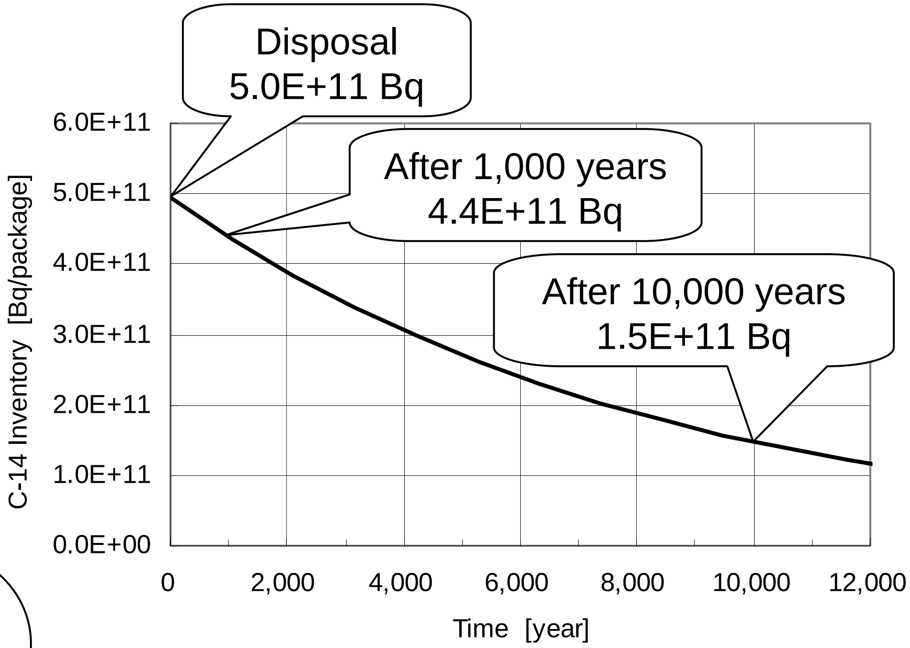
⇩

Leach immediately

(2) C-14 in base material: 80%

⇩

Leach with corrosion gradually



C-14 concentration
in waste package

⇩

10^{-5} mol/L order*3)

---

*1) RWMC, Development of radioactive wastes treatment system (1998).

*2) Noma et al., Study for TRU waste disposal system (2000).

*3) Specific activity of C-14: 2.31TBq/mol, filling factor of packages: 60%.

2. Objectives

- Photocatalysts oxidize organics by converting photon energy to electro-chemical energy.
- Activation of photocatalysts by **γ** - rays has been reported.

1) Activation by low energy radiation in repository conditions

2) Decomposition of suggested organic matters

Evaluate technical possibility of

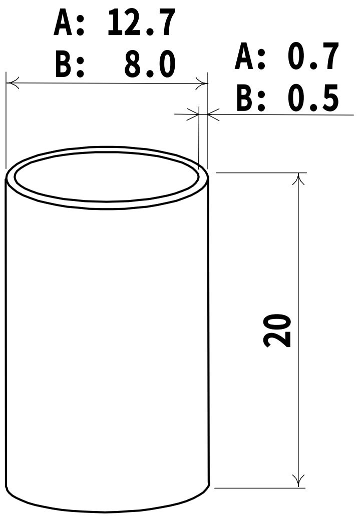
Decomposition of organic C-14 by photocatalysts with **β** - rays

3. Materials

- Photocatalysts :

Anatase TiO_2 sintered on titanium plate (Kobe Steel,ltd.)

high photoactivity, stable physically and chemically



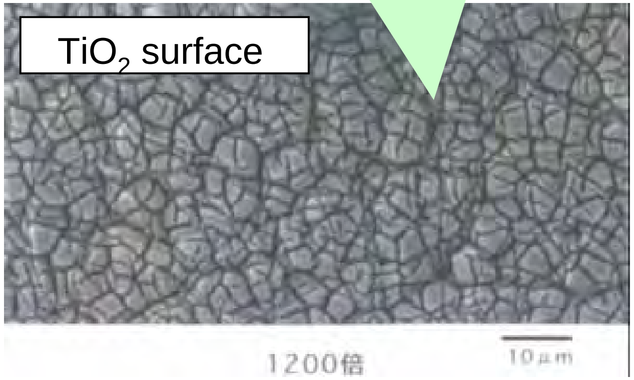
- Organic matters :

C-14 labeled Methanol (ICN Biochemicals)

C-14 labeled Formaldehyde (ICN Biochemicals)

C-14 labeled Formic Acid (American radiolabeled chemicals)

Micro grooves on surface



Crystal structure (<100 nm)

4. Methods

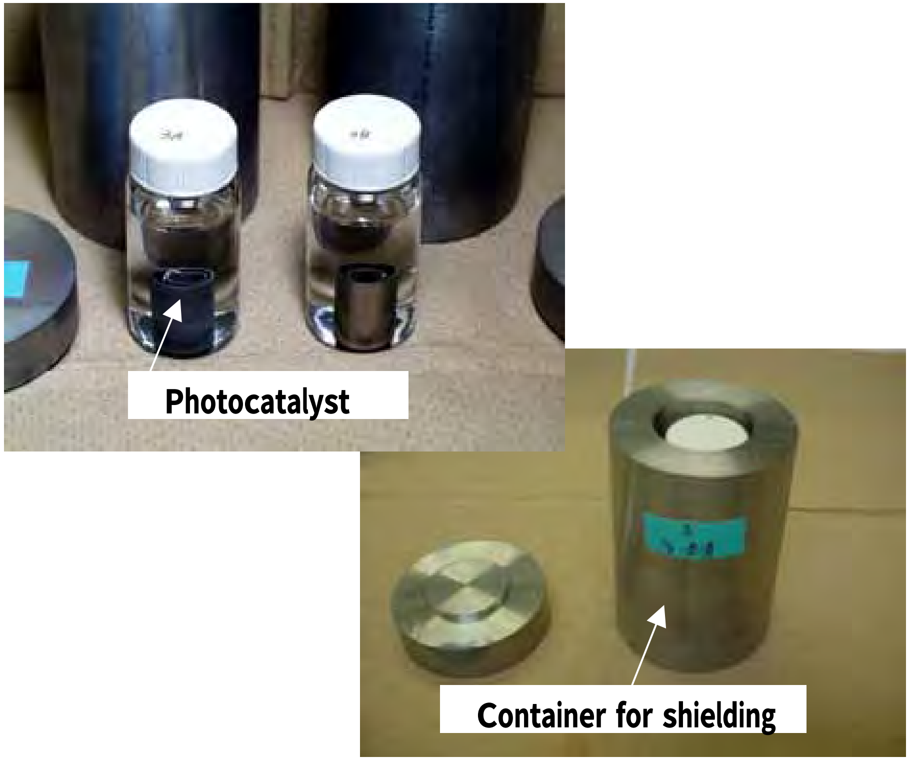
Prepare test solution

Install photocatalysts and test solution

Seal glass vials

Place in container for shielding

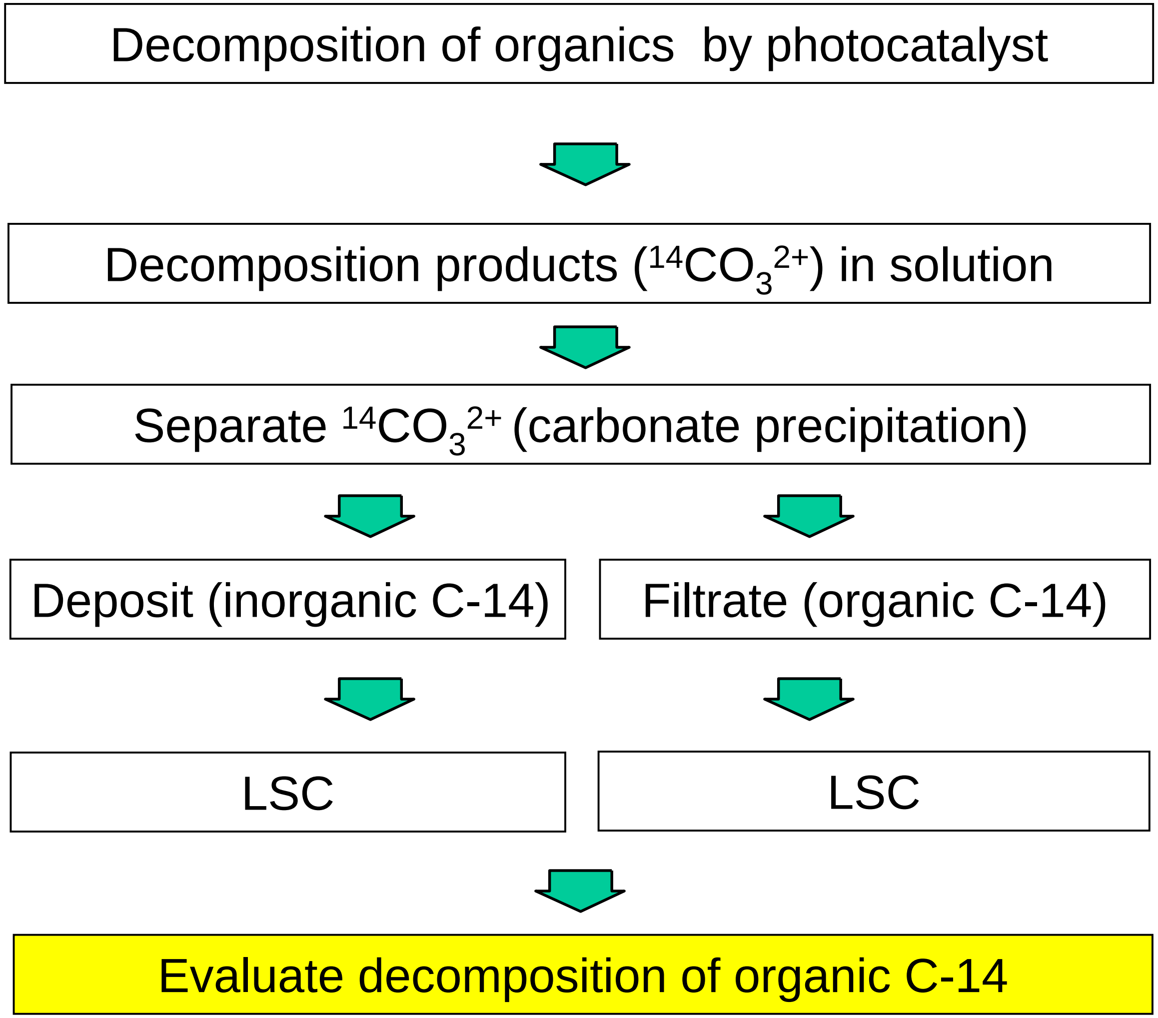
β - ray irradiation



5. Conditions

(1) Temp : Room temperature
(2) Solution pH : pH11 (NaOH)
(3) Organic matters : Methanol
Formaldehyde
Formic acid
(4) Radioactive concentration : 25 MBq/L
(5) Organics concentration : $1.2 - 1.4 \times 10^{-5}$ mol/L
(6) Surface area/water volume : 1.27 cm^2/ml
(7) Irradiation time : 10, 20, 40, 80 days
(8) Analysis : Radioactive concentration
（Liquid Scintillation Counter）

6. Procedure for Analysis



Decomposition of organics by photocatalyst

Decomposition products ($^{14}CO_3^{2+}$) in solution

Separate $^{14}CO_3^{2+}$ (carbonate precipitation)

Deposit (inorganic C-14)

Filtrate (organic C-14)

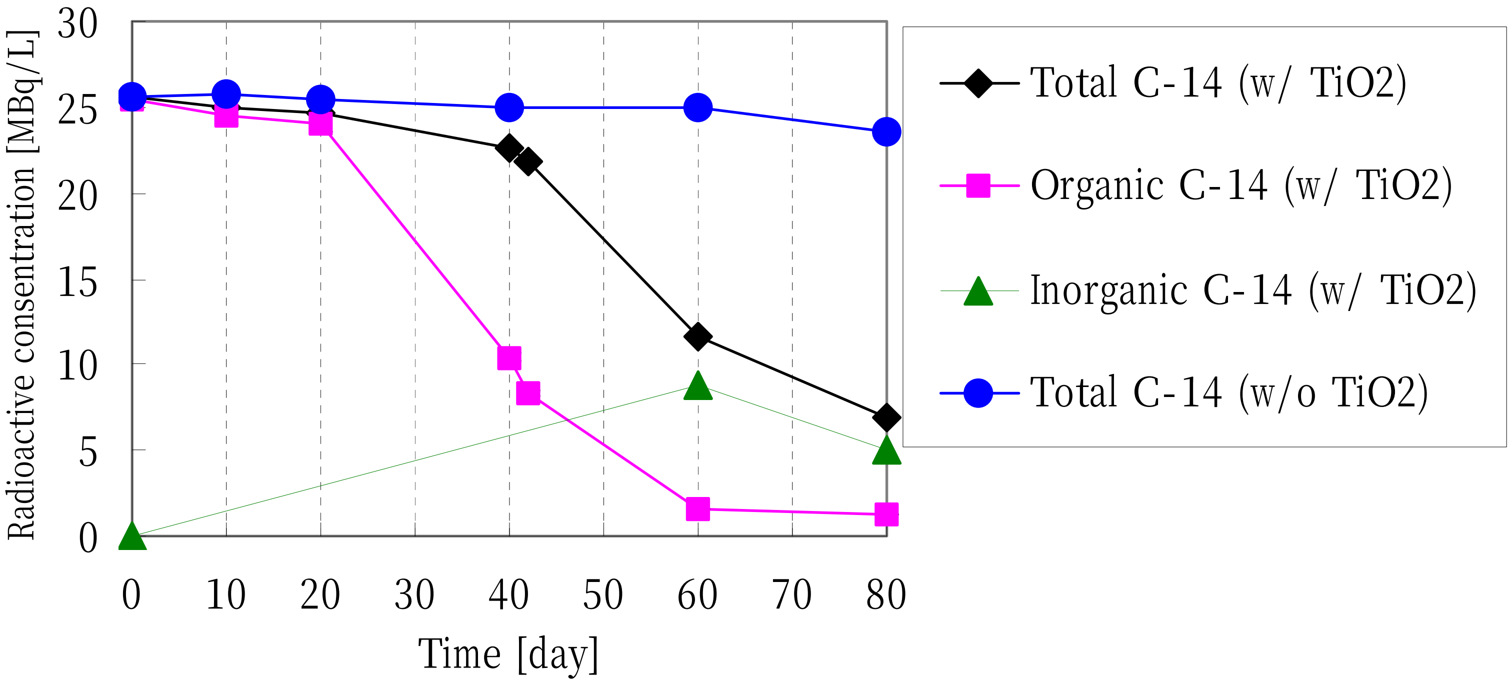
LSC

LSC

Evaluate decomposition of organic C-14

7. Results - Methanol

Variation of C_R (radioactive concentration) in methanol solution

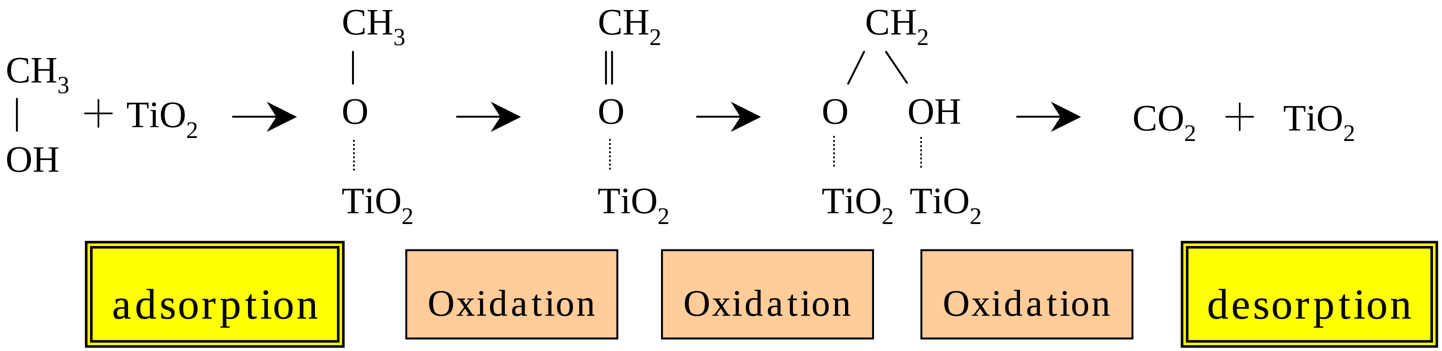


- C_R of inorganic C-14 increased. (decomposition rate: 20%/80days)
- C_R of organic C-14 decreased.

  → 90 % of organic C-14 removed by 60 days.
- C_R of total C-14 (w/o TiO2) not changed. ← No evaporation of C-14

8. Decomposition Reaction of Methanol

<Proposed decomposition reaction of methanol*5)>



(1) Adsorbed onto TiO_2, then decomposed

→ Removed organic C-14 in solution could contain

“adsorbed” and “decomposed” C-14

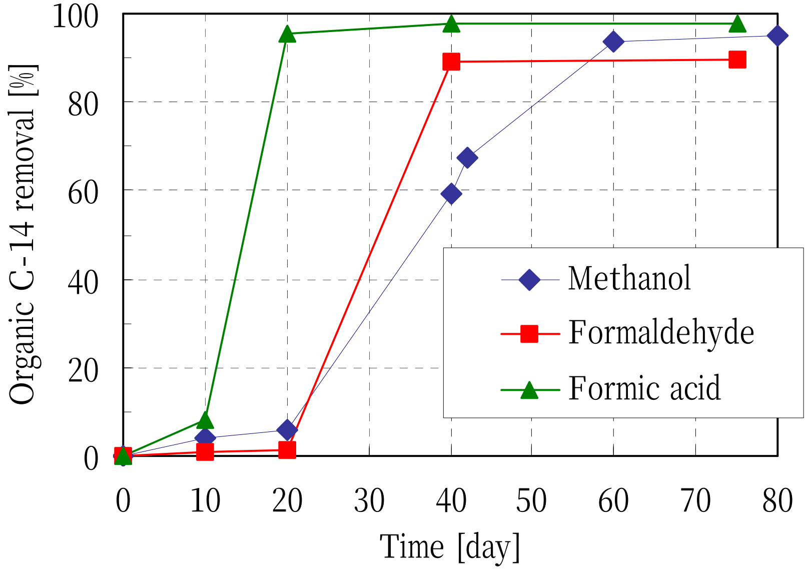
(2) Oxidized to CO_2, then desorbed.

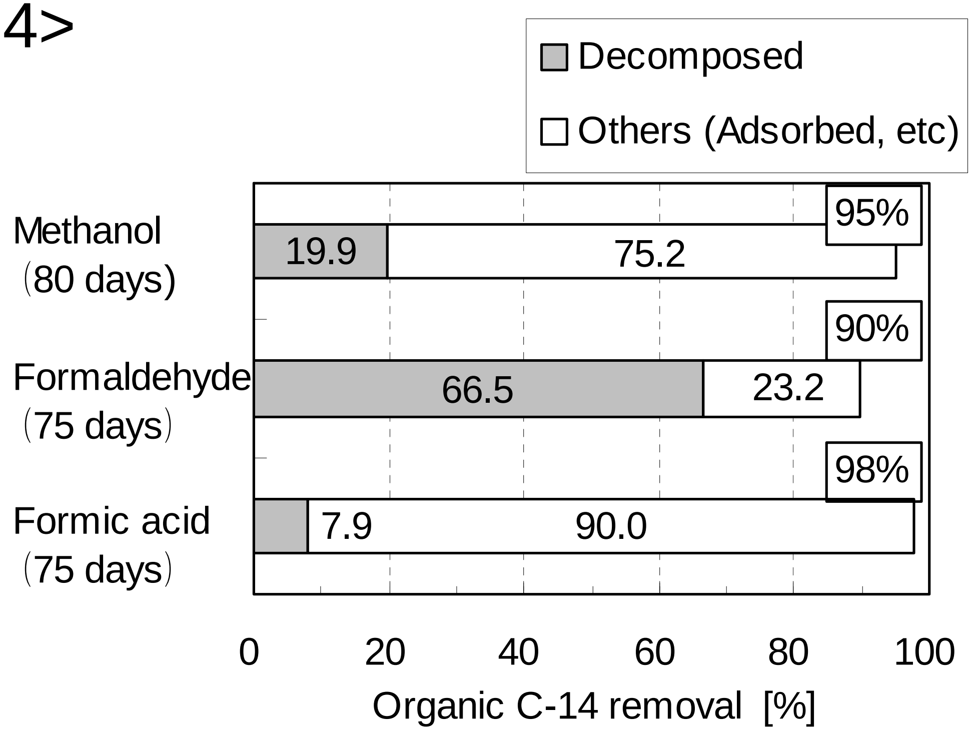
→ “Adsorbed” C-14 would be finally decomposed

*5) Yamagata et al.: Bull. Chem. Soc. Jpn., Vol.62, No.4, pp.1004-1010 (1989).

9. Results – Effect of Organic Forms

<Removal rate of organic C-14>



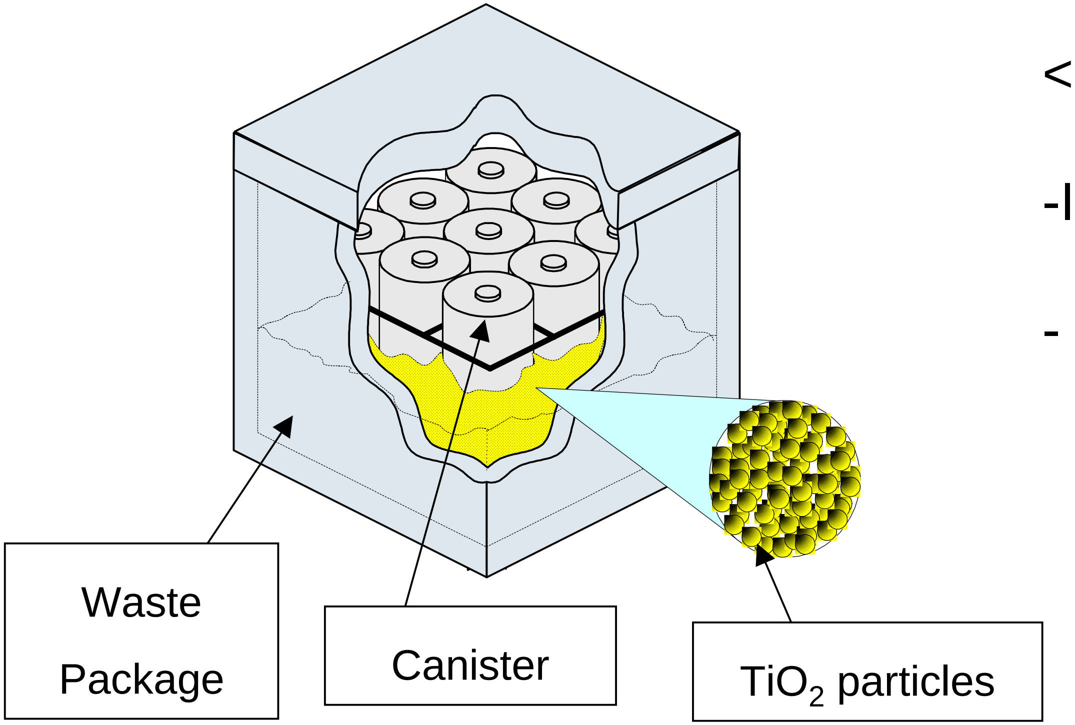


- Clarified decomposition of 3 organics by TiO_2
- Removal rate ("adsorbed"+ "decomposed")

Formaldehyde < Methanol < Formic Acid

10. Application to Waste Packages
Installation of Photocatalysts

Infill photocatalyst particles in waste packages.



<Conditions>

-Infill TiO_2 particle (ϕ2 mm)

- Filling factor : 60%

Surface area/water volume：

35 times as the experiments

11. Conclusions

- Clarified decomposition of organic C-14
  by photocatalysts irradiated with β - rays
- Decomposition rate of organic C-14 (75 - 80days)
  - Methanol : 20%
  - Formaldehyde : 67%
  - Formic Acid : 8%
- Confirmed possibility of decomposition of organic C-14
  in waste packages

12. Future Tasks

1. Performance of photocatalysts in repository

- Reaction mechanism (sorption, decomposition)
- Performance in reduced condition
- Effect of components in ground water (Ca^{2+}, other organics, etc.)

2. Reliability of photocatalysts

- Durability of photocatalysts
- Resistance to ionized radiation, heat

3. Effect to environment

- Effect of H_2 gas generated by photocatalytic water decomposition
- Effect to corrosion of waste package materials and metal wastes

4. Others

- Productivity, cost
- Handling, infilling method

Appendix

Results – Decomposition Rate with Time

<Decomposition reaction of methanol>

$CH_3OH+2H_2O \rightarrow H_2CO_3+3H_2$

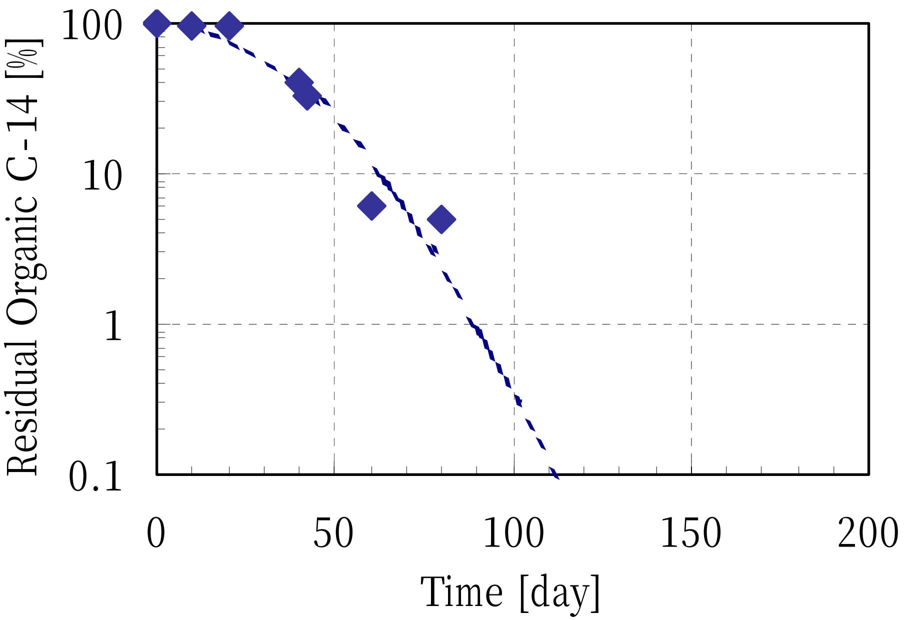
Description as a Langmuir formula*6)

$$-\frac{1}{dt}[CH_3OH] = \frac{k_1 K [CH_3OH]}{1+K[CH_3OH]}$$

(k_1:rate constant、K:equilibrium constant)

Organic C-14 can reduced to 1/1000 by 110 days

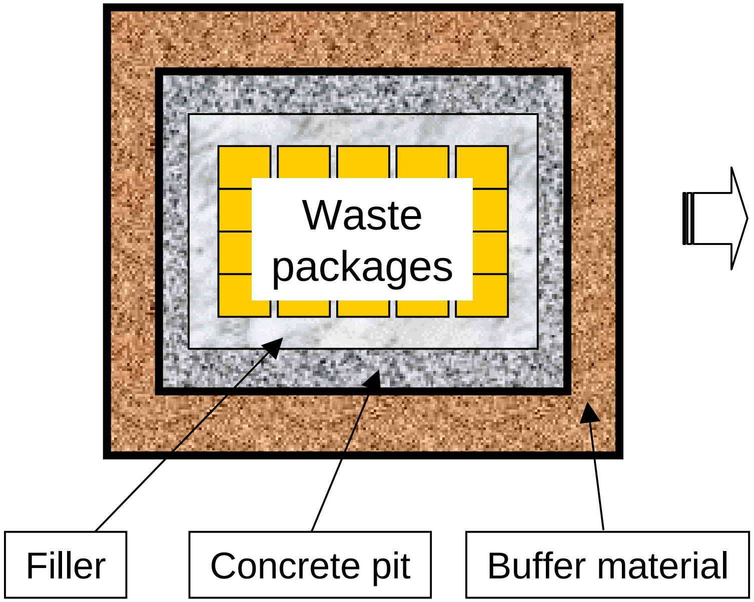
<Residual organic C-14 in methanol solution>



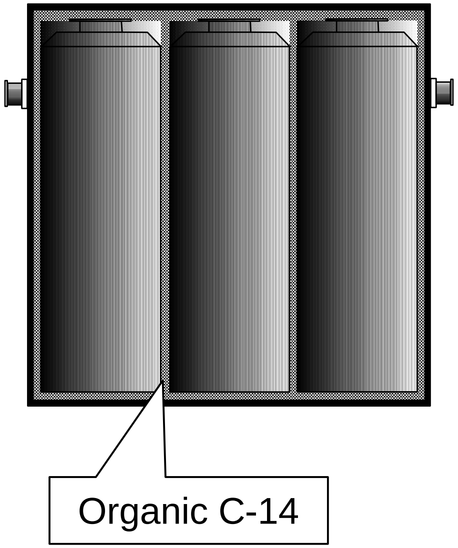
＊6) Jian Chen et al., Water Research, Vol.33, No.5, pp.1173-1180, 1999

Application to Waste Packages
Reaction in Waste Package

Underground repository



Waste Package



Proposed formula

$$-\frac{1}{dt}[C-14]=\frac{k_1K[C-14]}{1+K[C-14]}$$

(k_1:rate constant、K:equilibrium constant)

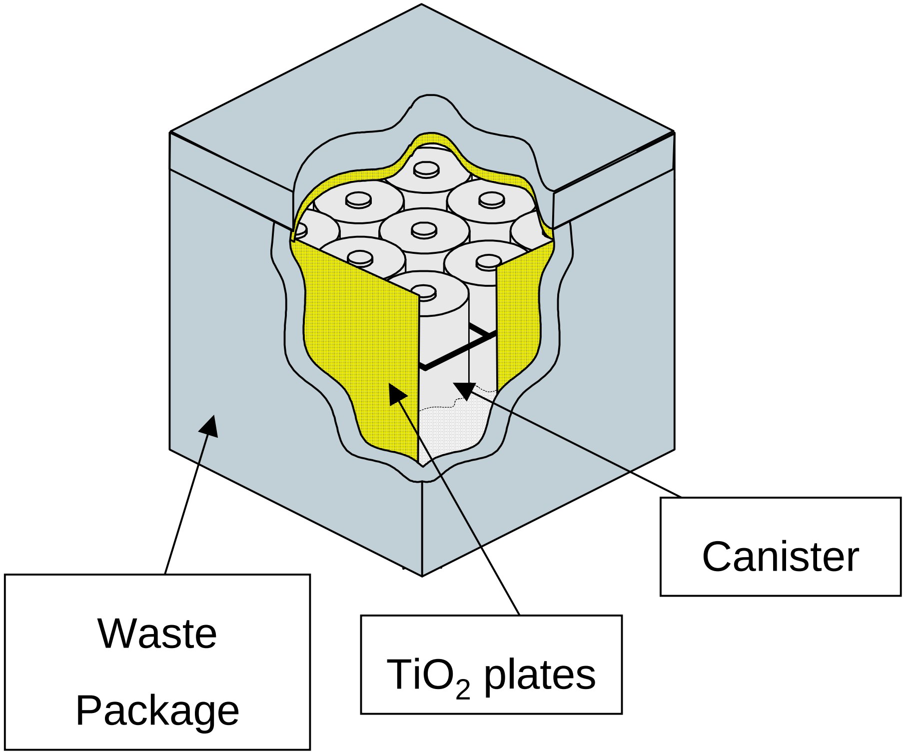
Consider surface area

Flow rate of groundwater would be very slow inside of bentonite layer.

Condition in waste package would be assumed to be static.

Application to Waste Package
Installation of Photocatalysts-2

Place photocatalytic plates in waste packages.



<Conditions>

- Install TiO_2 plate
- Infill quartz sand

(Filling factor: 60%)

⇩

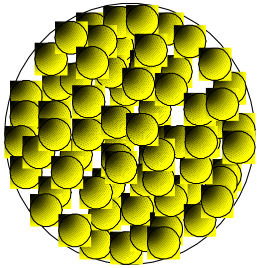
Surface area/water volume：

1/4 as the experiments

Application to Waste Package Evaluation

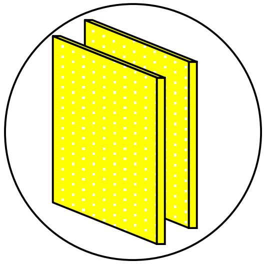
Evaluation on results of methanol experiments

<Time required to reduce organic C-14 to 1/1000>



Case－1） TiO$_2$ particles

4 days



Case－2） TiO$_2$ plates

485 days

Released organic C-14 can be reduced in a shorter period by photocatalysts.

Fundamental study of C-14 chemical form under irradiated condition

NAGRA/RWMC Workshop on C-14, Oct. 27-28, 2003

JNFL
Japan Nuclear Fuel Ltd.

RWMC
Radioactive Waste Management Funding and Research Center

Hitachi Ltd.

Outline

1. **Introduction**
2. Basic decomposition model
3. Application to actual disposal system
4. Evaluation of C-14 chemical form
5. Conclusion

Background

Activated metal

- zirconium alloy
- steel alloy

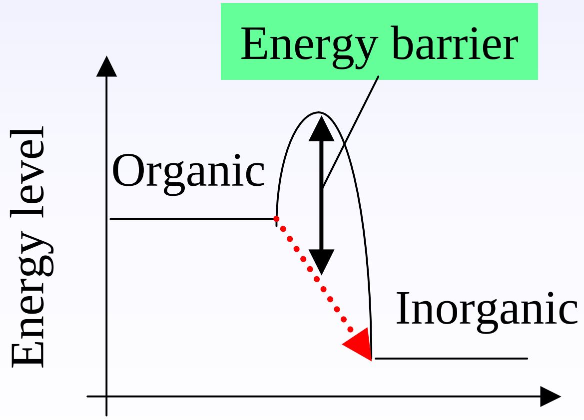
corrosion →

Low molecular weight of organic C-14

- formic acid, acetic acid
- formaldehyde
- methanol, ethanol

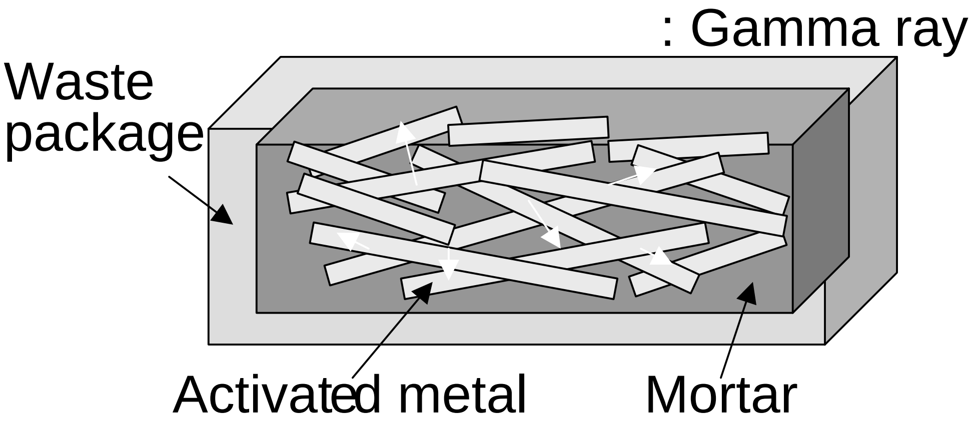
Due to low sorption abilities of organic C-14, it is very important to evaluate the long-term stability of organic forms

- ➢An inorganic form is more stable thermodynamically in the disposal condition (pH=12.5, Eh= -600mV).
- ➢However, high energy is required to decompose an organic matter.
- ➢In this study, irradiation effect was investigated.



Objective

Disposal system of activated metal



: Gamma ray

Waste package

Activated metal

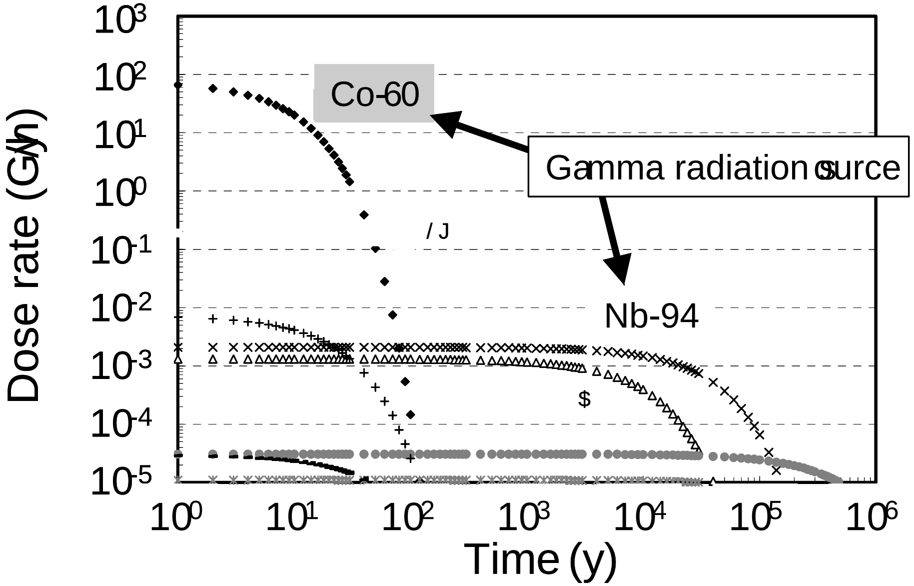
Mortar

In the actual disposal system, it is possible to expect Nb-94 as a long-term gamma radiation source.

Objective

To evaluate the C-14 chemical form in the waste package considering the radiolysis by Nb-94.

Calculated dose rate in the waste package



Outline

1. Introduction
2. **Decomposition model**
3. Application to actual disposal system
4. Evaluation of C-14 chemical form
5. Conclusion

Decomposition model

Direct decomposition

Organic C-14 $\rightsquigarrow CO_3^{2-}$

Indirect decomposition

$H_2O \rightsquigarrow OH\cdot$

$OH\cdot$ + Organic C-14 $\rightarrow CO_3^{2-}$

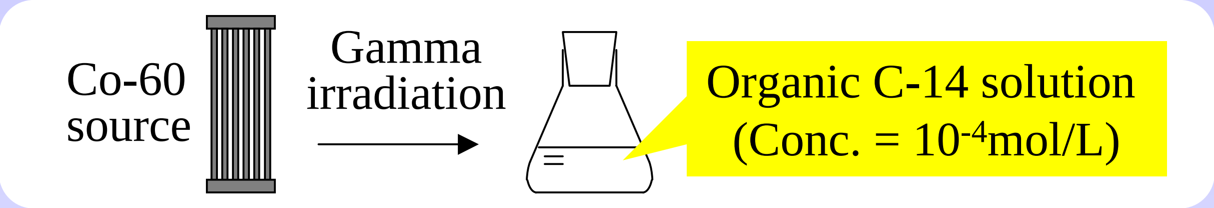
Indirect decomposition is a dominant process in a low organic concentration.

Decomposition model

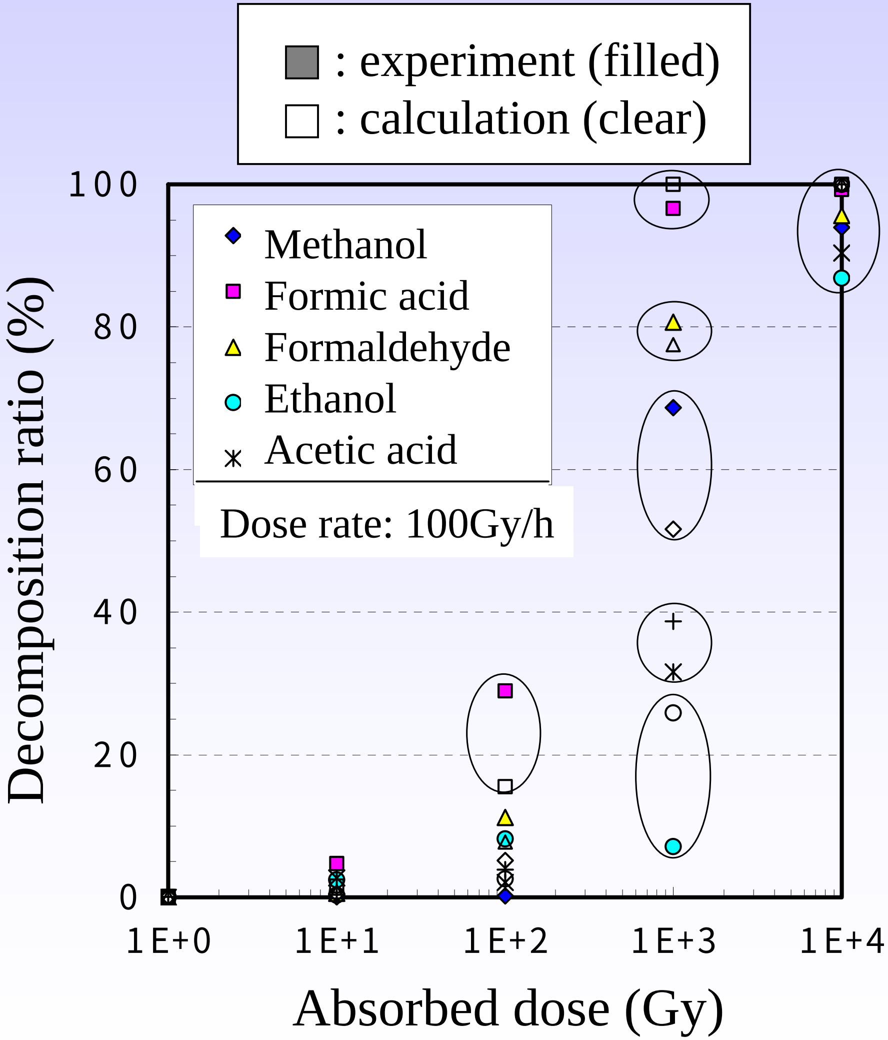
- Decomposition reactions of organic matters should be described as follows.
- Firstly, the validity of this model was investigated by a simple irradiation test.

Formic acid	$HCOOH + 2OH\cdot \rightarrow CO_2\uparrow + H_2O$
Formaldehyde	$HCHO + 4OH\cdot \rightarrow CO_2\uparrow + 3H_2O$
Methanol	$CH_3OH + 6OH\cdot \rightarrow CO_2\uparrow + 5H_2O$
Acetic acid	$CH_3COOH + 8OH\cdot \rightarrow CO_2\uparrow + 6H_2O$
Ethanol	$C_2H_5OH + 12OH\cdot \rightarrow CO_2\uparrow + 9H_2O$

Irradiation test



Organic C-14 solution (Conc. = 10^{-4}mol/L)



The experimental results agreed with the calculated results obtained by an absorbed energy and G-value*.

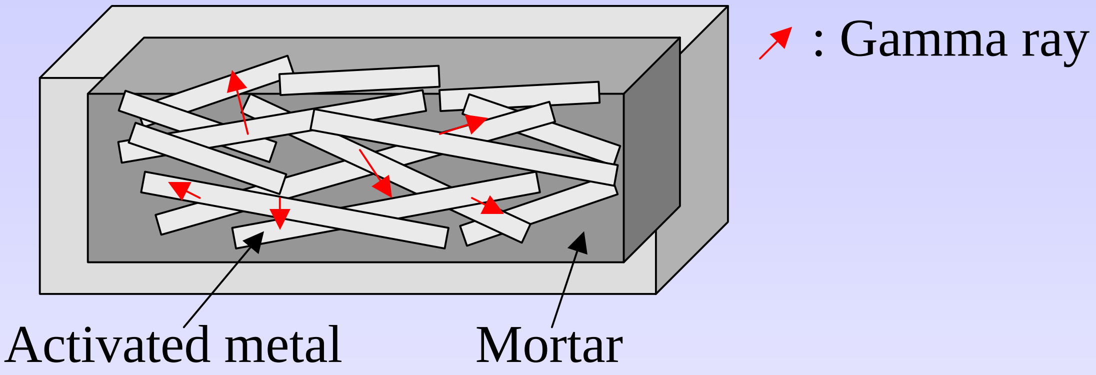
*G-value : OH radical number which is generated, when the water absorbed 100eV.

Outline

1. Introduction
2. Decomposition model
3. **Application to actual disposal system**
4. Evaluation of C-14 chemical form
5. Conclusion

Actual conditions

Waste package (4.6m^3)



Organic C-14 concentration

- ●Concentration of C-14 in activated metal
- ●Corrosion rate
- ●Surface area
- ●The ratio of organic form
- ●Porosity in a waste package

↓

Leaching rate of Organic C-14

Irradiation conditions

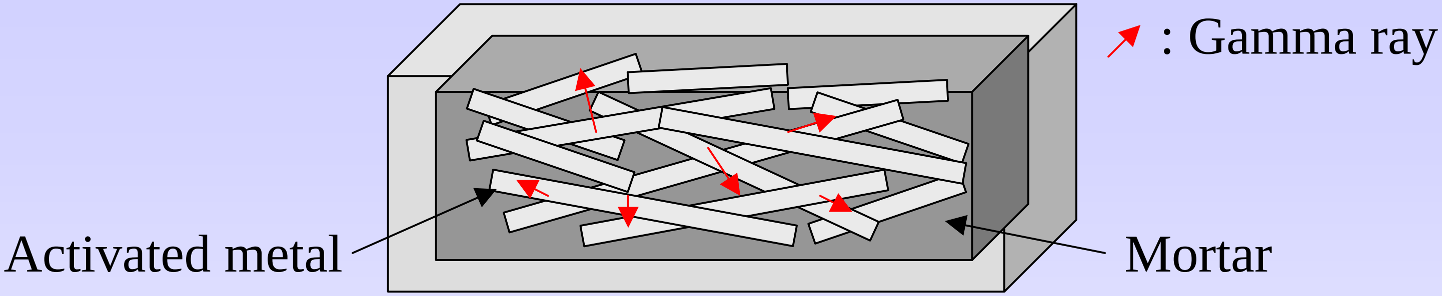
- ●Dose rate by Nb-94
- ●Amount of water in a waste package
- ●G-value of OH radical

↓

Generation rate of OH radical

Estimation

Waste package (4.6m^3)



Leaching rate of Organic C-14

6.6×10^{-9} mol/L/y

*1: Calculated from the surface area of metal, corrosion rate, porosity, etc.

Generation rate of OH radical

4.7×10^{-6} mol/L/y

*2: Calculated by the dose rate of Nb-94

8mol of OH radicals are necessary in order to decompose the 1mol acetic acid.

Theoretical maximum decomposition rate

5.9×10^{-7} mol/L/y

Organic C-14 becomes almost inorganic, when 1% of OH radical is consumed for the decomposition.

Irradiation conditions

The value evaluated in the experiment

Decomposition efficiency*

*: The ratio of OH radicals used for the decomposition of organic C-14

Task

- Concentration dependence
- Dose rate dependence

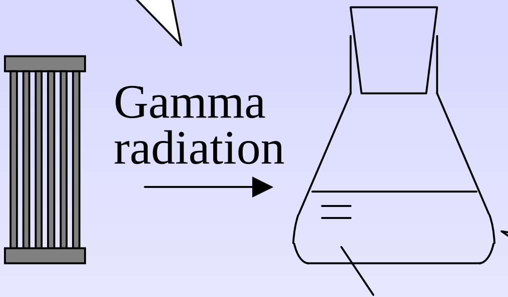
Irradiation conditions

Item	Conditions
Dose rate	2×10^{-1} - 2×10^{2} Gy/h (Actual dose rate: 10^{-3} - 10^{-2}Gy/h)
Organic C-14 Conc.	10^{-7} - 10^{-5} mol/L (Actual concentration: 10^{-7} -10^{-5} mol/L)

Experimental conditions

Irradiation condition
Dose rate: 2×10^{-1} - 2×10^{2} Gy/h
Absorbed dose: 3 - 3000 Gy

- C-14 form
  Acetic acid, Methanol
- Concentration
  10^{-7} - 10^{-5}mol/L



●Temp.	25℃
●Atmosphere	Anaerobic(3%-H_2 gas)
●Solution	Alkaline solution(pH=10) Actual groundwater

Addition of carrier and HCl
+Ar purge

C-14 Analyses → **Total C-14**

C-14 Analyses → **Organic C-14**

$$\textbf{Decomposition Ratio(\%)} = \frac{\text{Total C-14} - \text{Organic C-14}}{\text{Total C-14}}$$

$$\textbf{Decomposition Efficiency(\%)} = \frac{\textbf{Decomposition Ratio(\%)}}{\text{Irradiation factor*}}$$

* Irradiation factor : Theoretical dose necessary for 100% decomposition

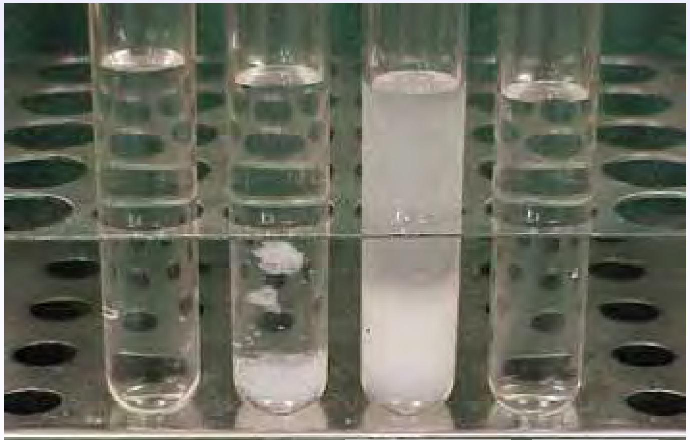
Appearance

Irradiation

Irradiated samples*

$*10^1$ - 10^4Gy

Inorganic C-14 separation



purge

Addition of HCl

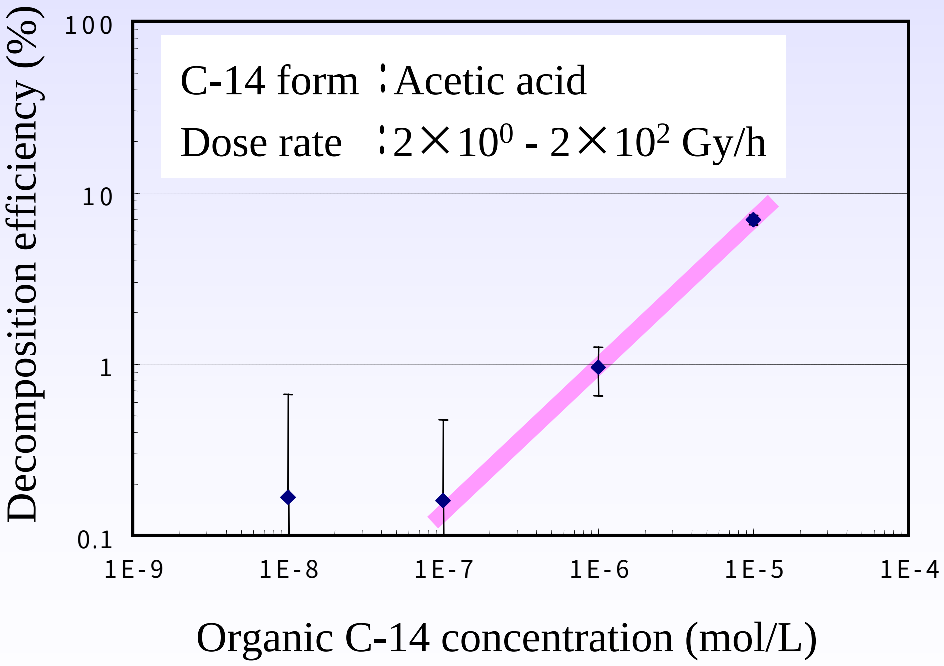
Addition of carrier

Irradiated sample

←

Experimental results

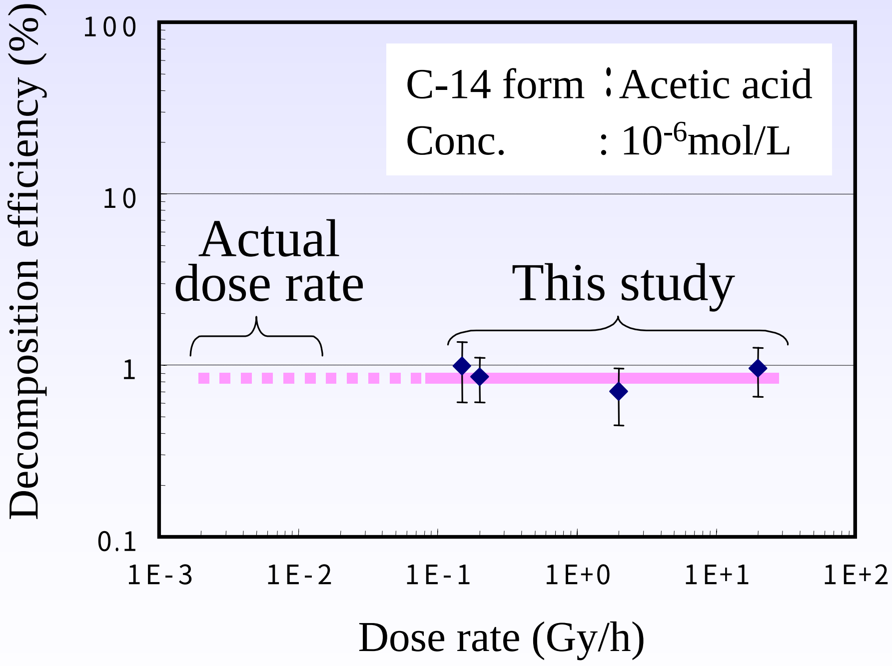
- The decomposition efficiency increased in proportion to the organic C-14 concentration.
- The dose rate dependence was not observed in this study.



Concentration dependence

C-14 form : Acetic acid

Dose rate : 2×10^{0} - 2×10^{2} Gy/h



Dose rate dependence

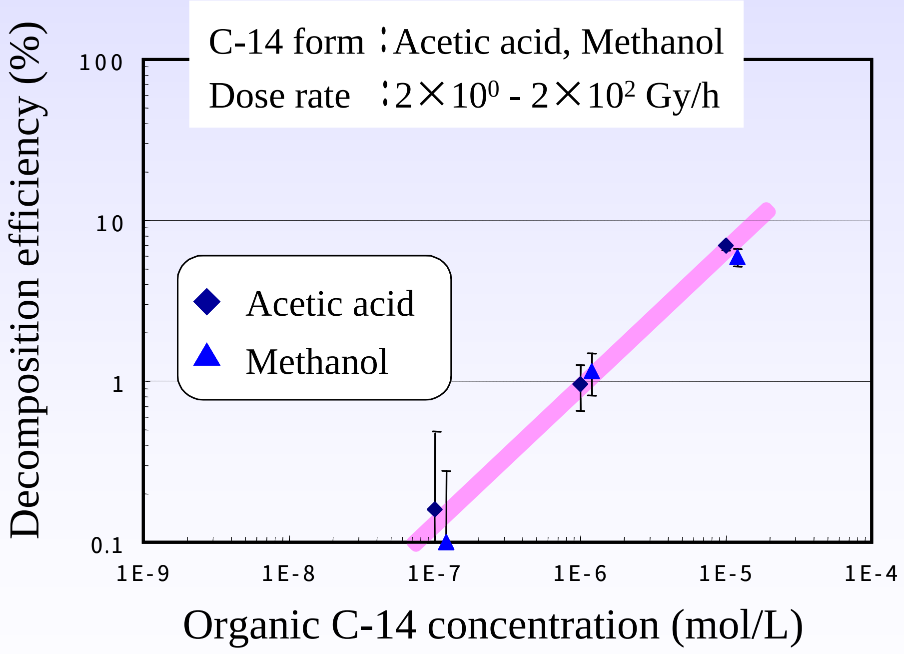
C-14 form : Acetic acid

Conc. : 10^{-6}mol/L

Effects of C-14 form and groundwater

- The effect of chemical form and groundwater composition was very small.

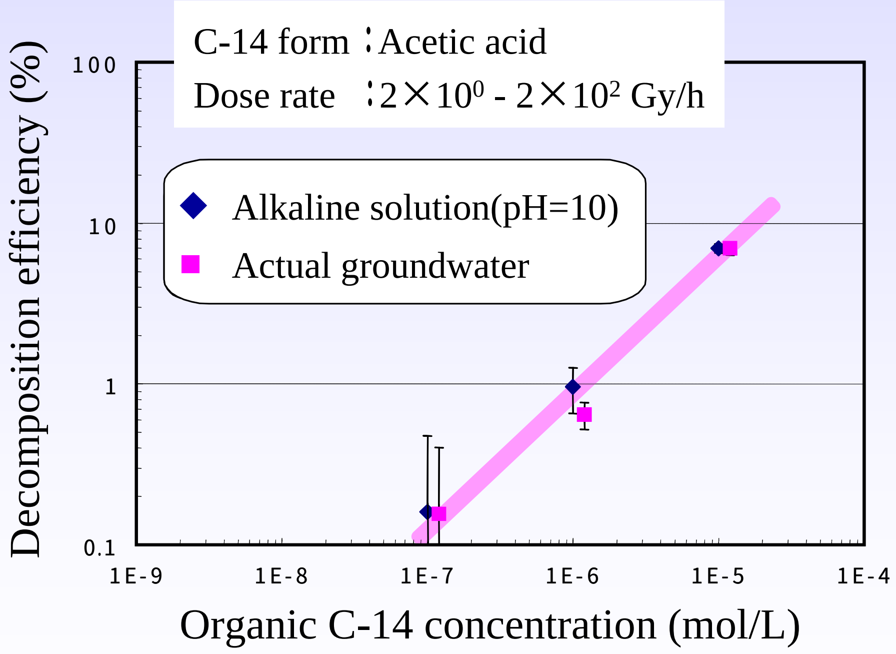
Effect of organic form



C-14 form ：Acetic acid, Methanol

Dose rate ：2×10^0 - 2×10^2 Gy/h

Effect of Groundwater



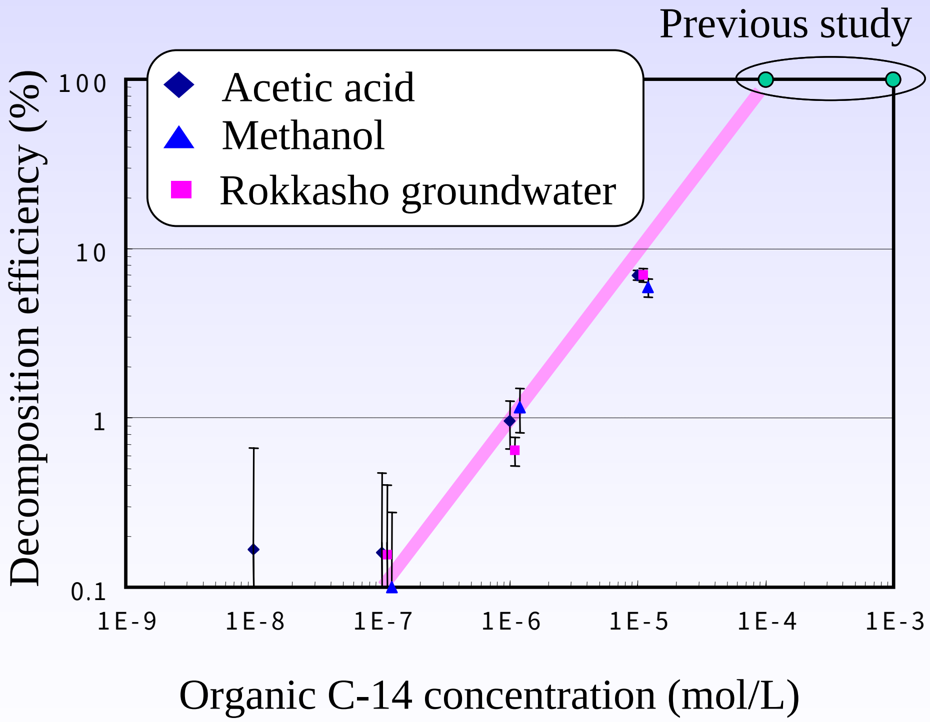
C-14 form ：Acetic acid

Dose rate ：2×10^0 - 2×10^2 Gy/h

Discussion

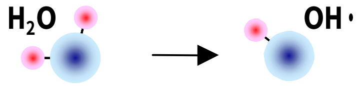
Experimental results

The decomposition efficiency increased in proportion to the organic C-14 concentration.



Reaction of OH radical

Generation of OH･



Decomposition

OH･ + Org. C-14

→ Inorg.C-14

Competitive reaction

OH･ + X → H_2O

X : Competitive material

Competition model

- The decomposition efficiency should be dependent on the organic C-14 concentration.
- This model agrees with the experimental result.

It is considered that the decomposition efficiency is not dependent on dose rate.

Outline

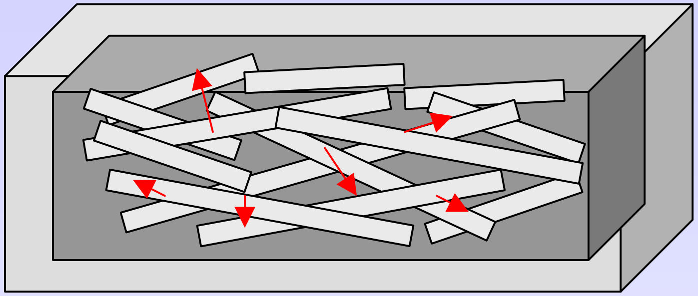
1. Introduction
2. Decomposition model
3. Application to actual disposal system
4. **Evaluation of C-14 chemical form**
5. **Conclusion**

Evaluation of chemical form

Generation

- **Leaching rate**

Waste package (4.6m^3)



Decomposition & migration

- **Chemical form**
- **Dose rate**
- **Staying time in a waste package**

Evaluation of organic C-14 concentration in the waste package

$$C_n = \left\{ C_{n-1} + G \cdot dt \cdot \left(\frac{1}{2}\right)^{\frac{(t-dt)}{T}} \right\} \times \left(1 - \frac{1}{U} \cdot dt\right) \times \left\{ 1 - \frac{1}{C_{temp}} \cdot (D \cdot dt) \cdot (C_{temp} \cdot E) \right\} \times \left(\frac{1}{2}\right)^{\frac{dt}{T}}$$

C_n: Organic C-14 conc. (mol/L)

G: Organic C-14 leaching rate (mol/L/y)

T: Half life of C-14(5730y)

U: Staying time of Organic C-14 in waste package(y)

D: Theoretical maximum decomposition rate(mol/L/y)

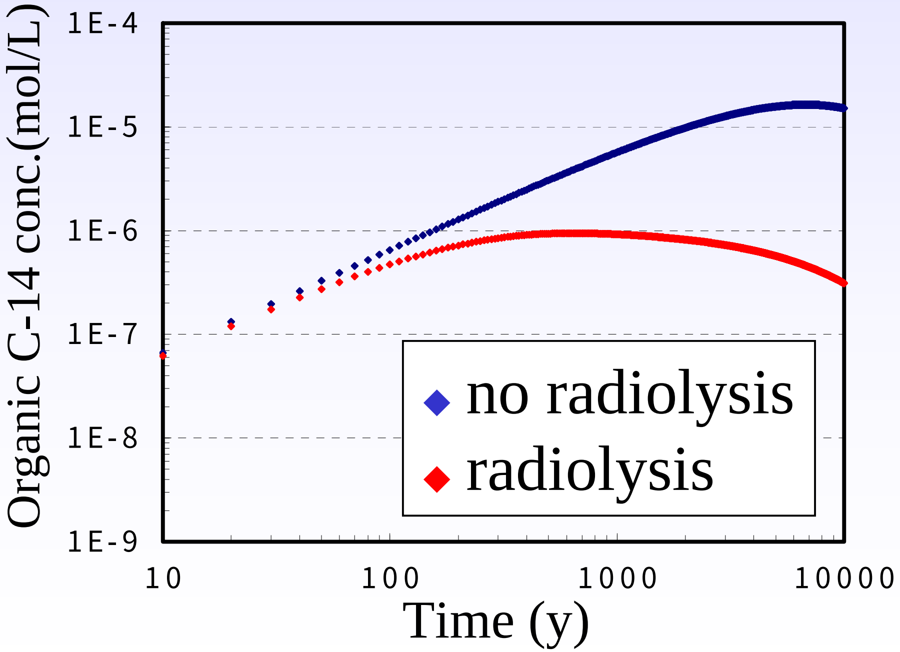
E: Decomposition efficiency(mol^{-1}・L)

Estimated results

It was found that the rate of an organic form might fall sharply by considering the irradiation effect.

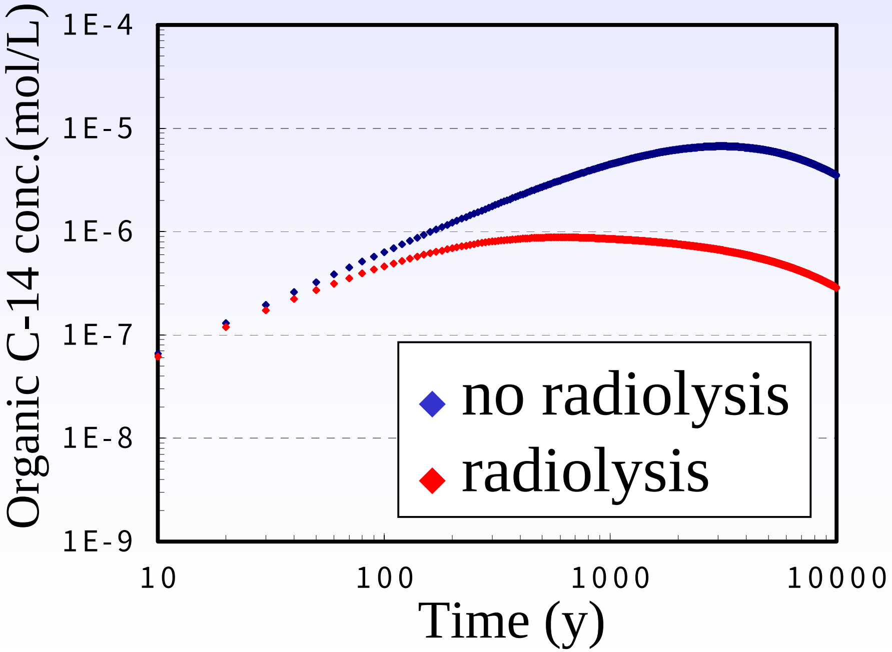
Calculated results in case1

C-14 form	Acetic acid
Dose rate	2×10^{-3} Gy/h
Leaching rate	6.6×10^{-9}mol/L/y
Staying time	18000 y



Calculated results in case2

C-14 form	Acetic acid
Dose rate	2×10^{-3} Gy/h
Leaching rate	6.6×10^{-9}mol/L/y
Staying time	1800 y



Future work

1. The effect of competitive substance

The effect on the decomposition efficiency must be evaluated on the substance which coexists in the actual disposal condition.

2. The effect of low dose rate

The effect of low dose rate must be theoretically examined, since to simulate the low dose rate experimentally is difficult.

3. Evaluation of C-14 staying time in the waste package

C-14 staying time should be evaluated considering the waste package design.

Interactions of Carbon in a Repository Environment

Workshop on ^{14}C Release and Transport in Repository Environments
Wettingen, Switzerland - Oct. 27-28, 2003

B. Kienzler, V. Metz, M. Kelm,
Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung (INE)
C. Nebelung, L. Baraniak
Forschungszentrum Rossendorf, Institut für Radiochemie

^{14}C disposal in Germany

- $^{14}N(n,p)^{14}C$ $\sigma = 1.48$ barn
  $^{17}O(n,\alpha)^{14}C$ $\sigma = 0.183$ barn
  ^{14}C specific activity: 1.65×10^{11} Bq g^{-1}
- Zircalloy cladding ^{14}N: max. 65 ppm
  UO_2, moderator (H_2O): ^{17}O: 0.038%
- Zircalloy per ton heavy metal: 520kg(GKN I), 550kg(GKNII)
  ^{14}N ~ 2 mol / t HM
  ^{17}O ~ 3.2 mol / t HM
- LWR: 370 - 390 GBq / (GWe yr)
  installed nuclear power in Germany: 22 GWe
  phase-out, total life-time: 32 yrs.
  Total ^{14}C inventory in a disposal: 2.8×10^{5} GBq
  1700 g (120 mol)
- pebble bed HTR (total 5×10^{12} Bq), LLW, tracers…..

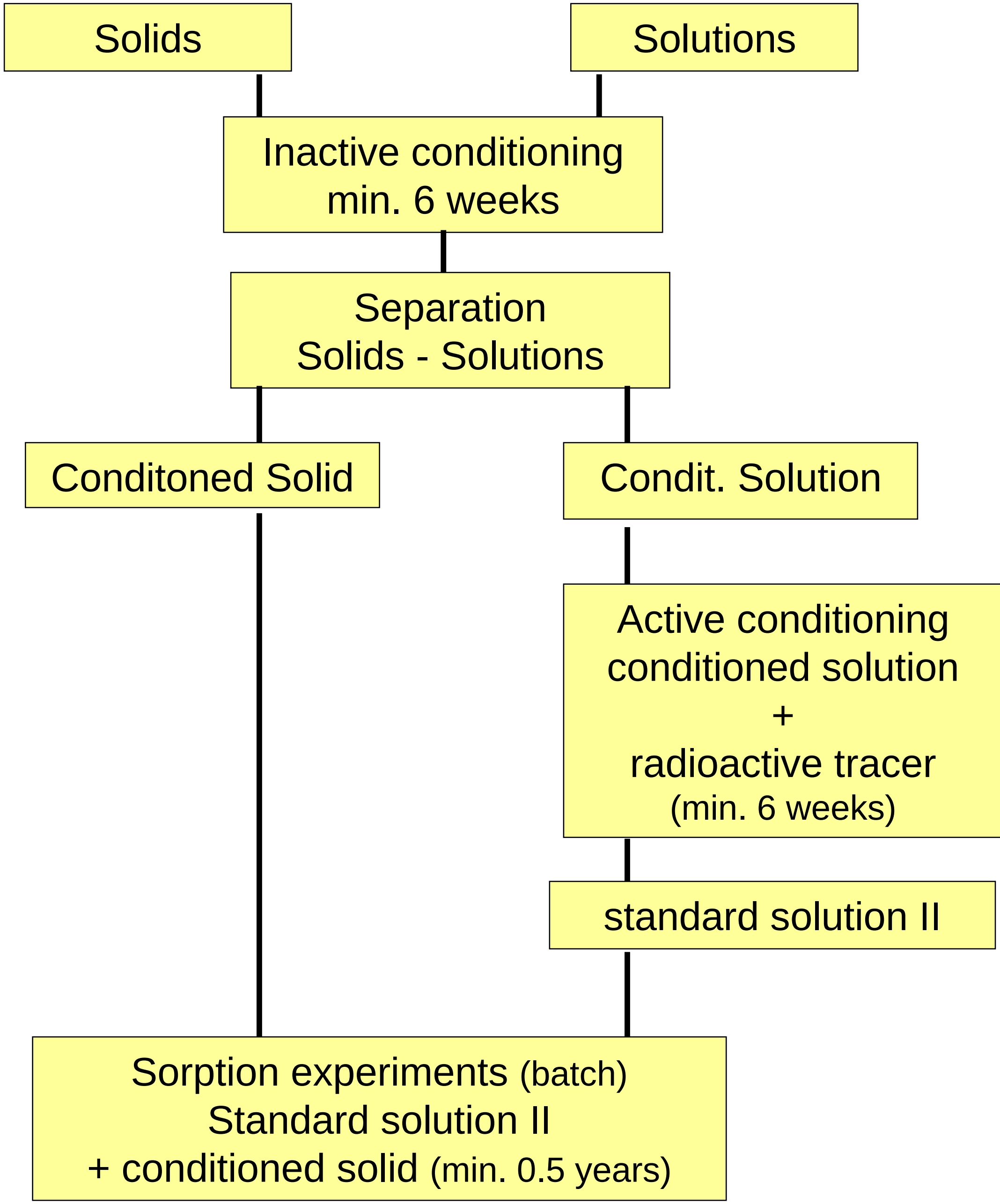
Behaviour of ^{14}C loaded waste

- Zircalloy: (Kaneko 2002), ZrC
  Release: DOC from carbides ~2 x DIC
- HTR fuel: $^{14}CO_2$, depending on O_2
  total release < 2%
- ERAM: Al-carbides from ^{14}C production → methane
- ^{14}C labelled organic material: biodegradation depending on
  - pH
  - electron acceptors (O_2, NO_3^-, Fe^{3+}, SO_4^{2-}, CO_2)

$CH_2O + O_2$	$\rightarrow CO_2 + H_2O$	ΔG°=-502.4 kJ mol-1
$CH_2O + 4/5\ NO_3 + 4/5\ H^+$	$\rightarrow CO_2 + 2/5\ N_2 + 7/5\ H_2O$	ΔG°=-476.9 kJ mol-1
$CH_2O + 8\ H^+ + 4\ Fe(OH)_3$	$\rightarrow CO_2 + 11\ H_2O + 4\ Fe^{2+}$	ΔG°=-116.0 kJ mol-1
$CH_2O + ½\ CO_2$	$\rightarrow CO_2 + ½\ CH_4$	ΔG°=-92.9 kJ mol-1

Recent Experimental Investigations for FB Asse ERAM

Steps for conditioning
-solids
- solutions



Solids

Solutions

Inactive conditioning
min. 6 weeks

Separation
Solids - Solutions

Conditoned Solid

Condit. Solution

Active conditioning
conditioned solution
+
radioactive tracer
(min. 6 weeks)

standard solution II

Sorption experiments (batch)
Standard solution II
+ conditioned solid (min. 0.5 years)

^{14}Methane Sorption

Solids: sorel concrete

Solutions: $MgCl_2$-rich brine

Monitoring the CH_4/Ar ratio

Result:

CH_4/Ar ratio constant within a deviation of 5%

➦ Total methane sorption onto sorel phases below 0.2 mmol CH_4/kg solid material

^{14}Carbonate Solubility / Sorption

Solids: salt concrete
sorel concrete
“Grauer Salzton”

Solutions: $MgCl_2$-rich brine
NaCl brine

pH	**NaCl**	**$MgCl_2$**
salt concrete	10.6	6
sorel concrete	9	6.7
Grauer Salzton	7.3	5.7

Solubility	**NaCl**	**$MgCl_2$**
	$2.5x10^{-5}$ - $1.2x10^{-4}$ mol/l	$1.6x10^{-3}$ - $6.7x10^{-3}$ mol/l

Sorption	**NaCl**	**$MgCl_2$**
$R_s = \frac{A_0 - A}{A} \cdot \frac{V_0}{m}$	$R_s \sim 3000$ ml/g	$R_s = 2.3$ ml/g to 11 ml/g

Asse Salt Mine

13 emplacement rooms

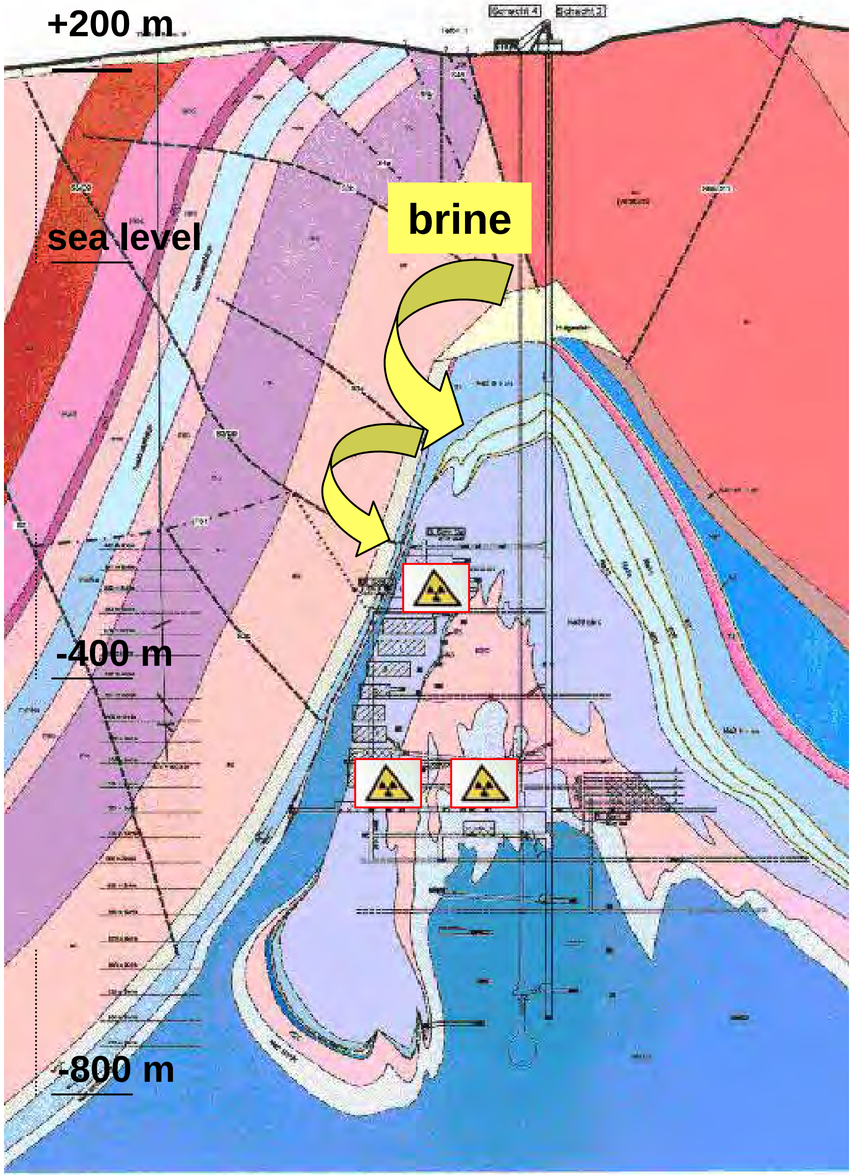
≈1300 drums intermediate-level waste

- ≈125000 drums low-level waste
- ≈10^{15} Bq total RN inventory
  mainly An: ≈120 t U, ≈80 t Th, ≈12 kg Pu
- intrusion of $MgCl_2$-rich brine expected
- >30000 t Portland cement (OPC)
- > 670 t NO_3^-
- 2800 t organic carbon ⇒ degradation
  to CO_2, inorganic carbon (DIC), e.g.

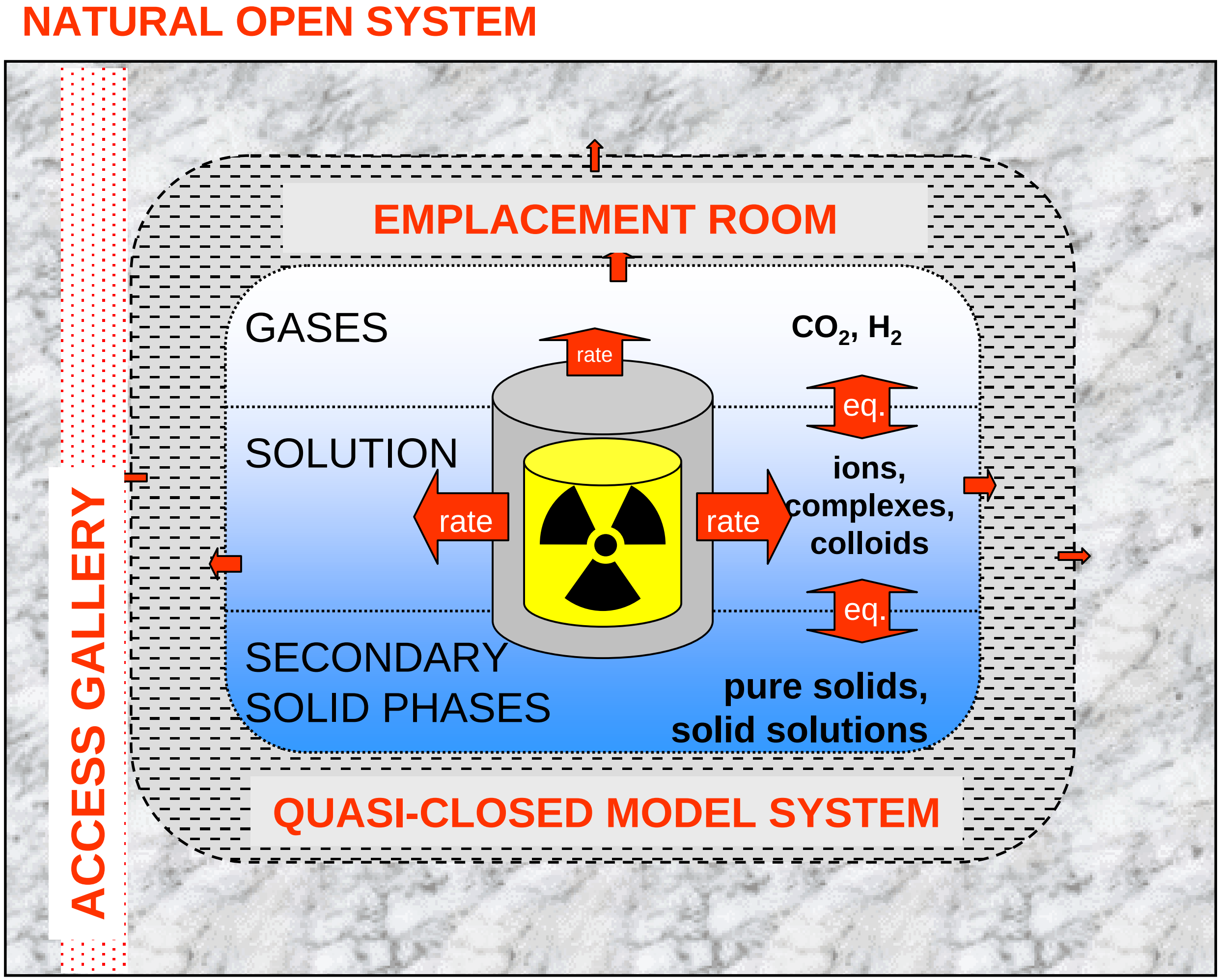
$$C_6H_{10}O_5 + 4.8H^+ + 4.8NO_3^- = 7.4H_2O + 6CO_2 + 2.4N_2$$

affecting geochemical environment

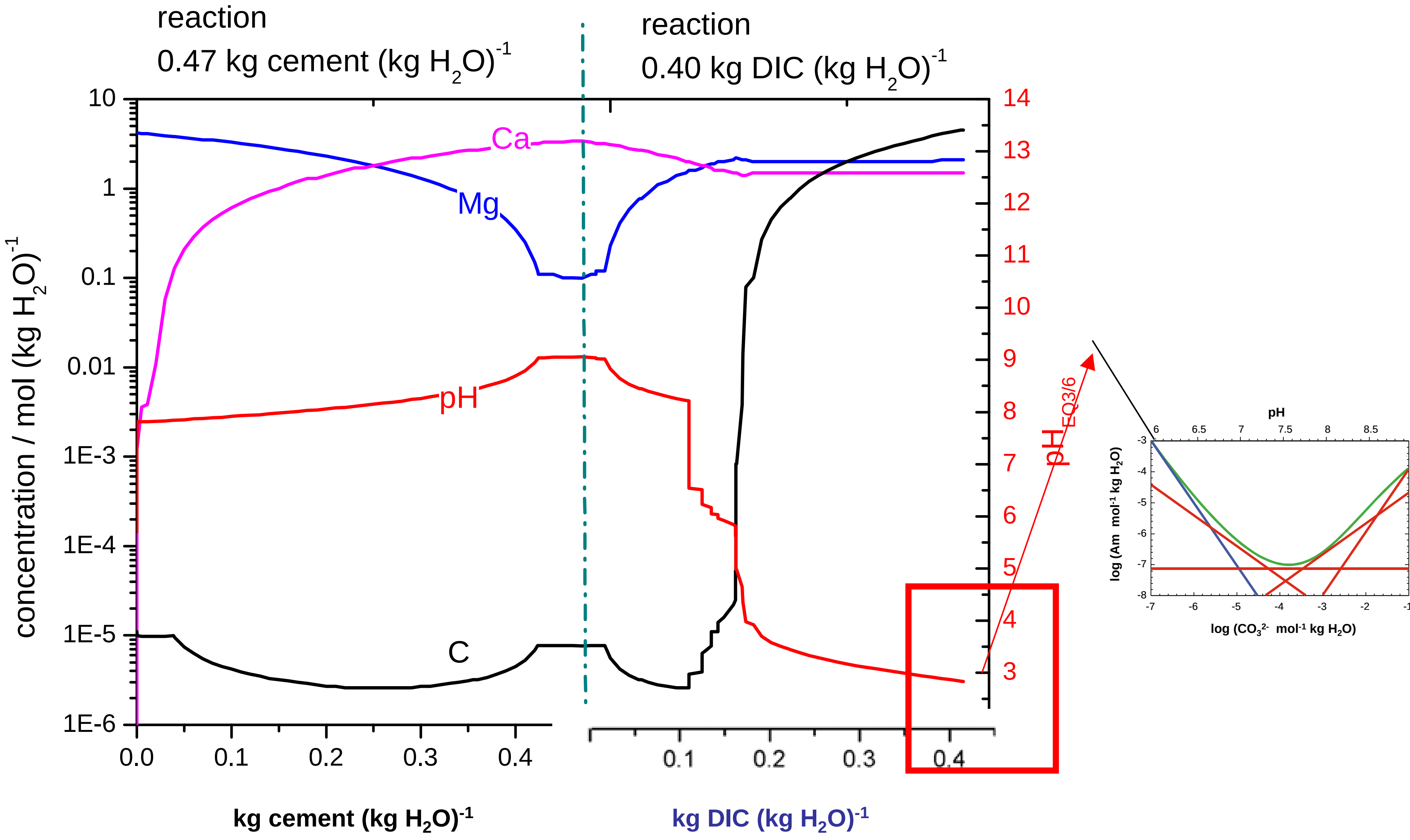
⇒ **affecting radionuclide release**



Quasi-closed system modeling approach

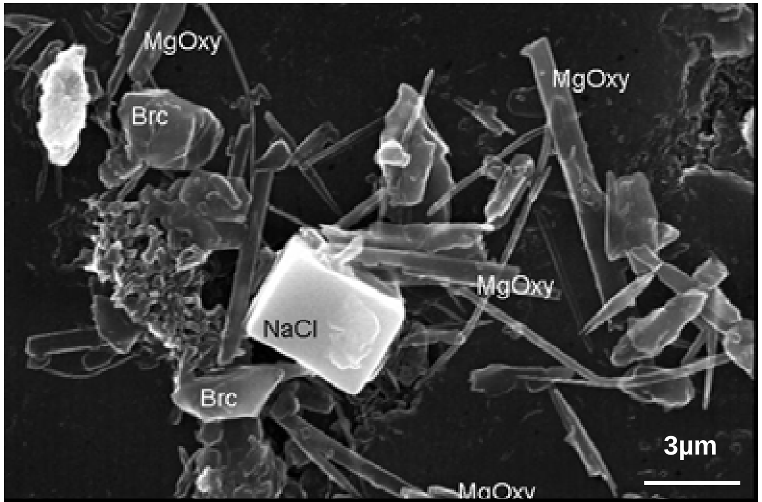


Reaction of cement in Q-brine + *DIC* input

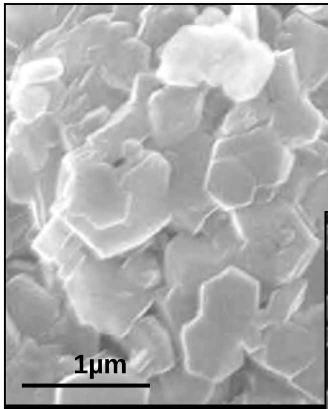


Recommended buffer material

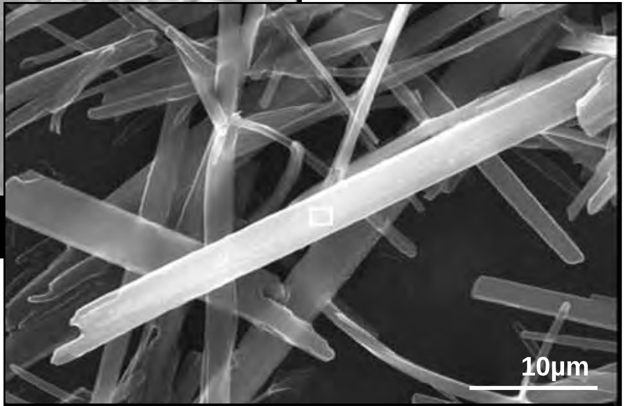
Mg-depot provided by *K-UTEC* GmbH
- ≈69 wt.% *brucite* + *Mg-oxychloride*
- ≈25 wt.% *halite*
- ≈ 6 wt.% accessory minerals



Mg-depot (SEM: Klaus Spieler, INE)



brucite (SEM: INE)



Mg-oxychloride (SEM: INE)

INE recommendation to FB Asse:

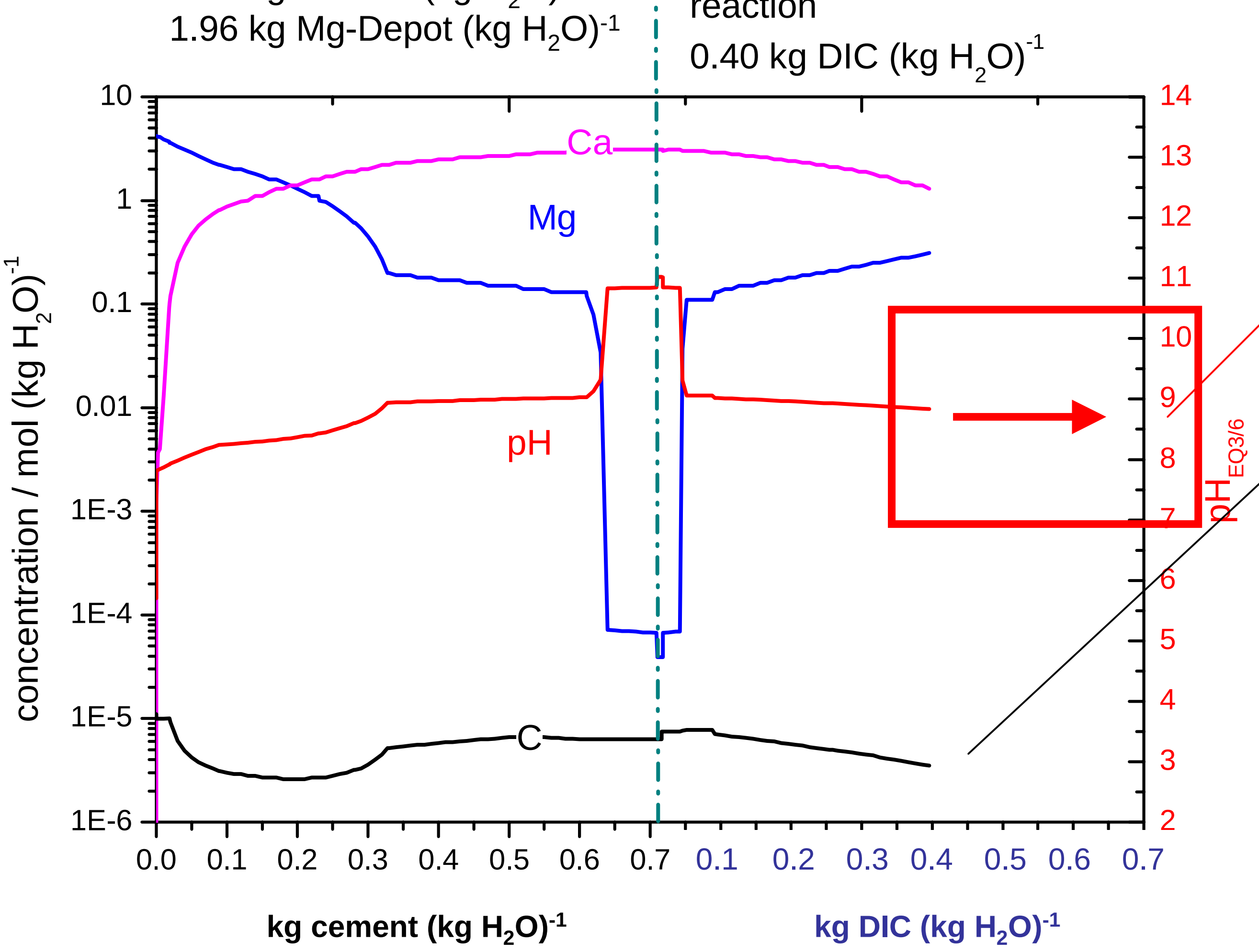
brucite + Mg-oxychloride
“Mg depot”

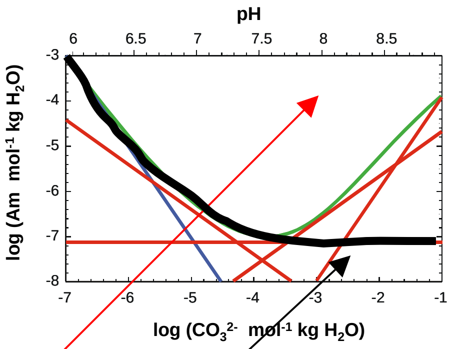
studying effectivness
- **buffering pH**
- **limiting [CO_3^{--}]**
- **resulting in low [An]**

Reaction of cement + Mg-depot in Q-brine + *DIC* input

reaction
0.71 kg cement (kg H_2O)$^{-1}$
1.96 kg Mg-Depot (kg H_2O)$^{-1}$

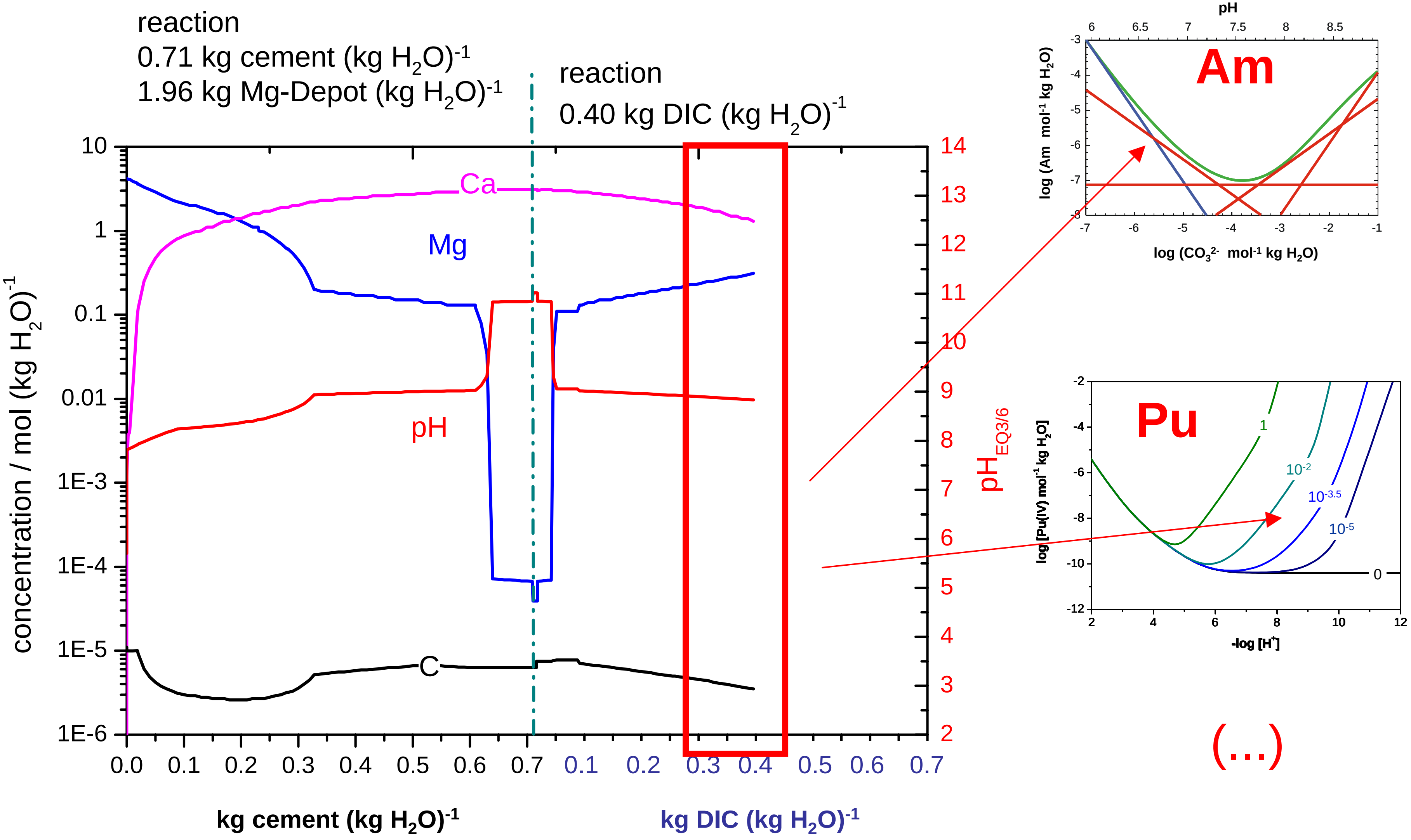
reaction
0.40 kg DIC (kg H_2O)$^{-1}$





Magnesite precipitation

Reaction of cement + Mg-depot in Q-brine + *DIC* input

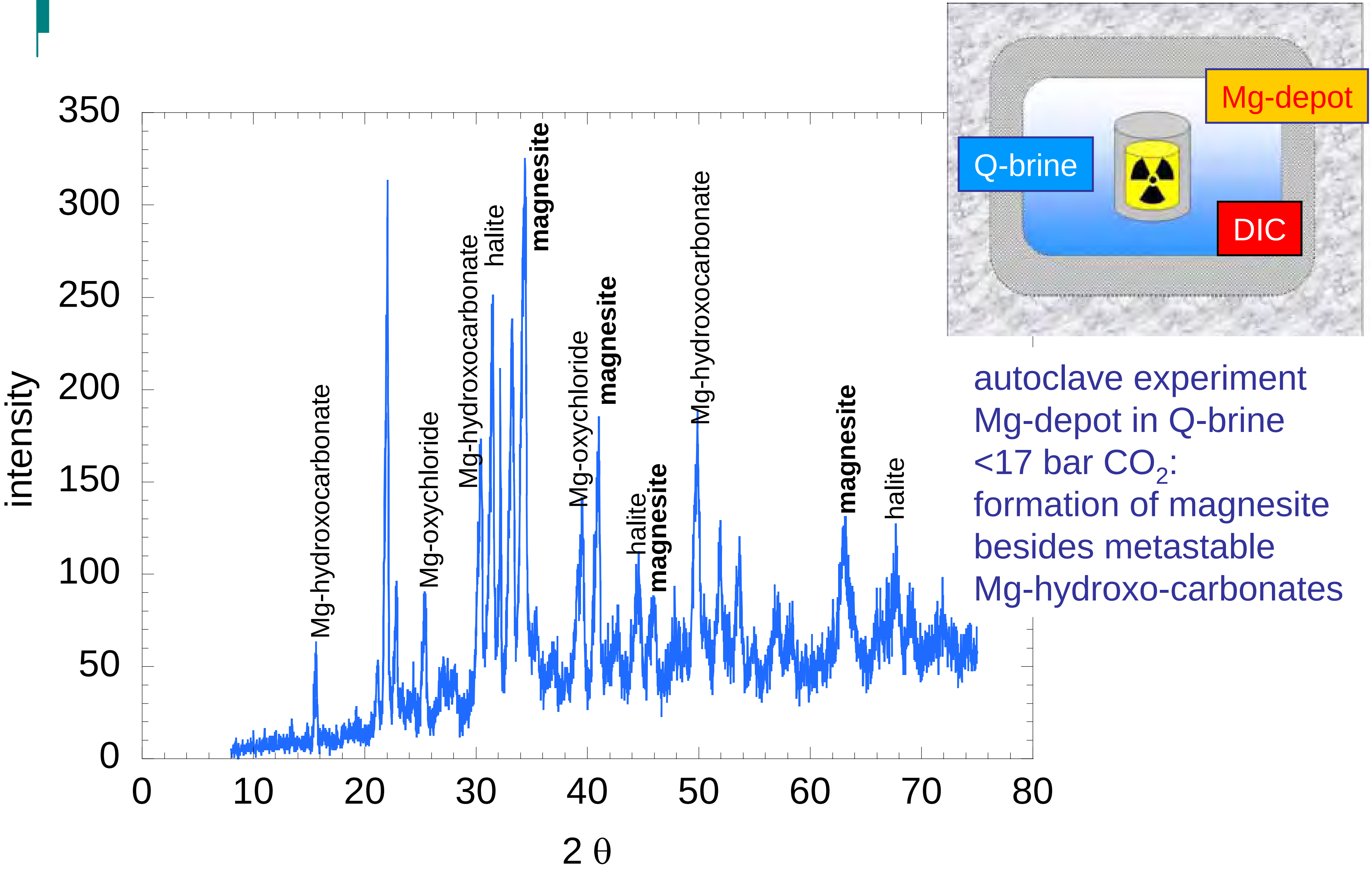


reaction
0.71 kg cement $(kg\ H_2O)^{-1}$
1.96 kg Mg-Depot $(kg\ H_2O)^{-1}$

reaction
0.40 kg DIC $(kg\ H_2O)^{-1}$

(...)

Autoclave experiment: formation of carbonates



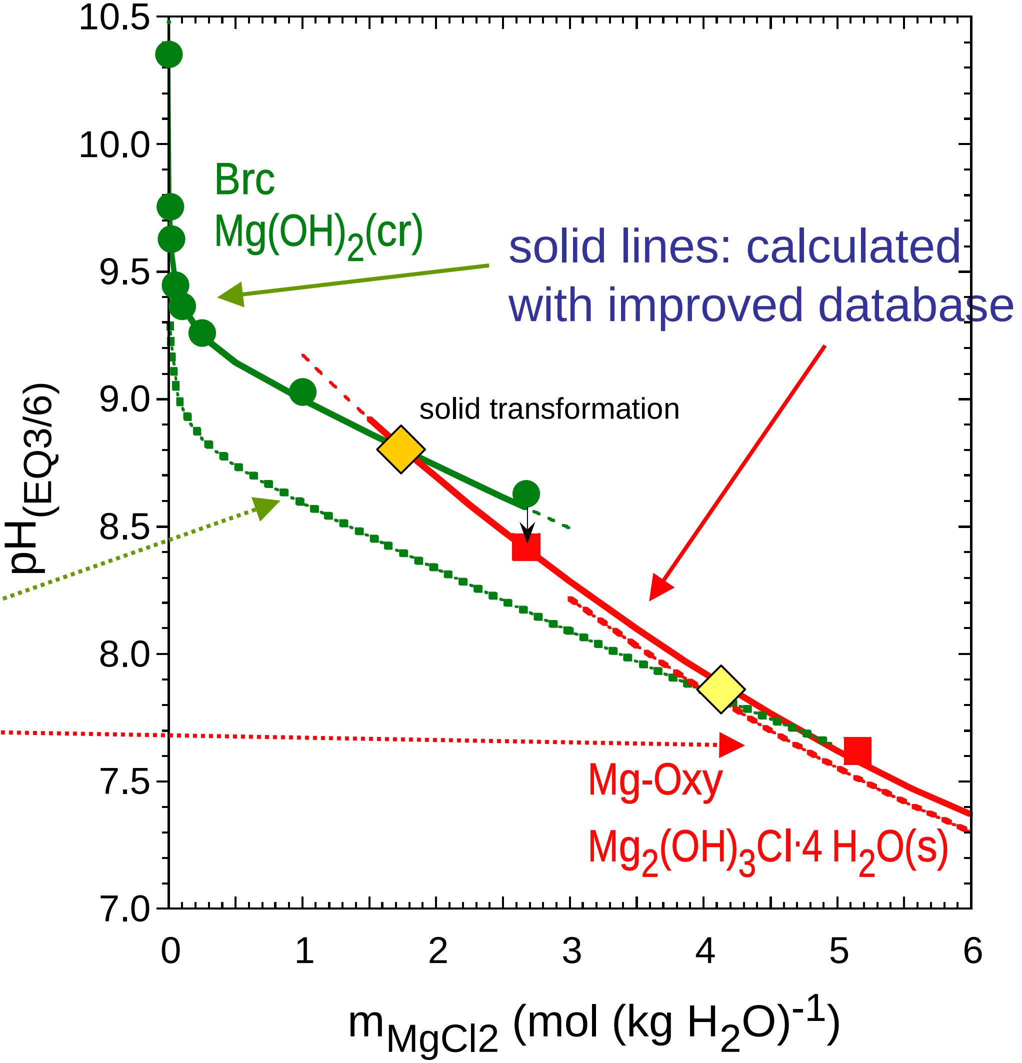
autoclave experiment
Mg-depot in Q-brine
<17 bar CO_2:
formation of magnesite
besides metastable
Mg-hydroxo-carbonates

Improving thermodynamic data for brucite / Mg-oxychloride

Equilibrium $pH_{EQ3/6}$ values in $MgCl_2$ solutions saturated with Brc, Mg-Oxy (25°C)

log $K°_s$(Brc) = 17.1 ± 0.2

log $K°_s$ (Mg-Oxy) = 26.0 ± 0.2

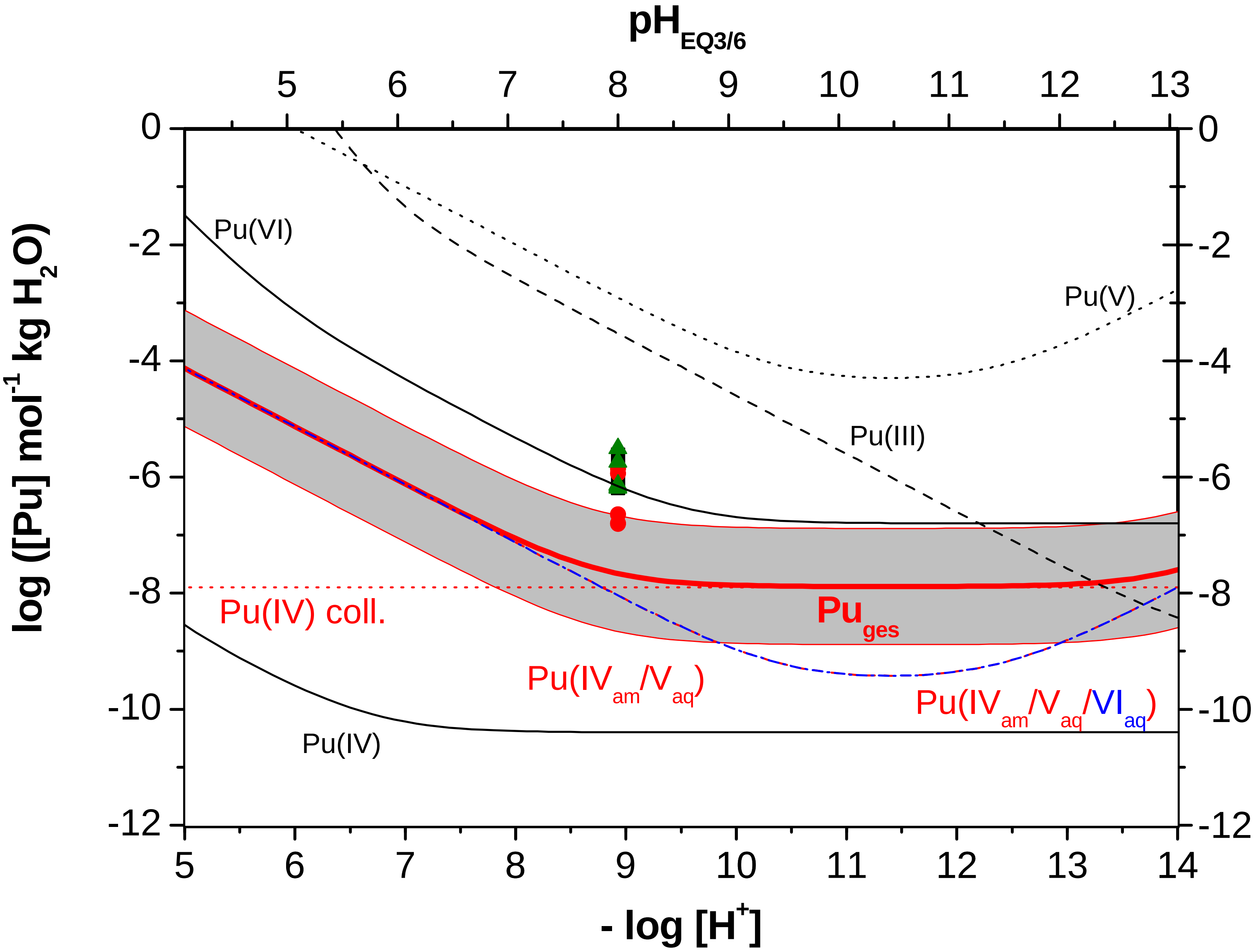


solid lines: calculated with improved database

dotted lines: calculated with thermodynamic data of EQ3/6, GWB, CHESS, SUPCRT92 ... databases

Altmaier, M., Metz, V., Neck, V., Müller, R. & Fanghänel, Th.: *Geochim Cosmochim. Acta* (in press)

Pu solubility



Summary and Conclusions

- ^{14}C load from irradiated zircalloy and spent fuel some from THTR and organic tracers.
- Release during storage of THTR spent fuel by contact with air and gamma radiation generating CO_2.
- In rock salt, dissolved carbonate species sorb onto carbonate containing solids by isotopic exchange.
- In cement dominated systems, high distribution coefficient between DIC and DOC is observed (>1000 ml g^{-1}).
- Interaction of CO_2 gas with Mg bearing material: formation of magnesite and magnesium-hydroxo-carbonate.
- Weak sorption of $^{14}CO_3^{2-}$ onto salt concrete in $MgCl_2$-rich brine. Sorel phases reduce dissolved ^{14}C by more than 100 during 0.5 yr.
- Sorption of methane onto solids could not be verified.

Study on Chemical Behavior of Organic C-14 under Alkaline Condition

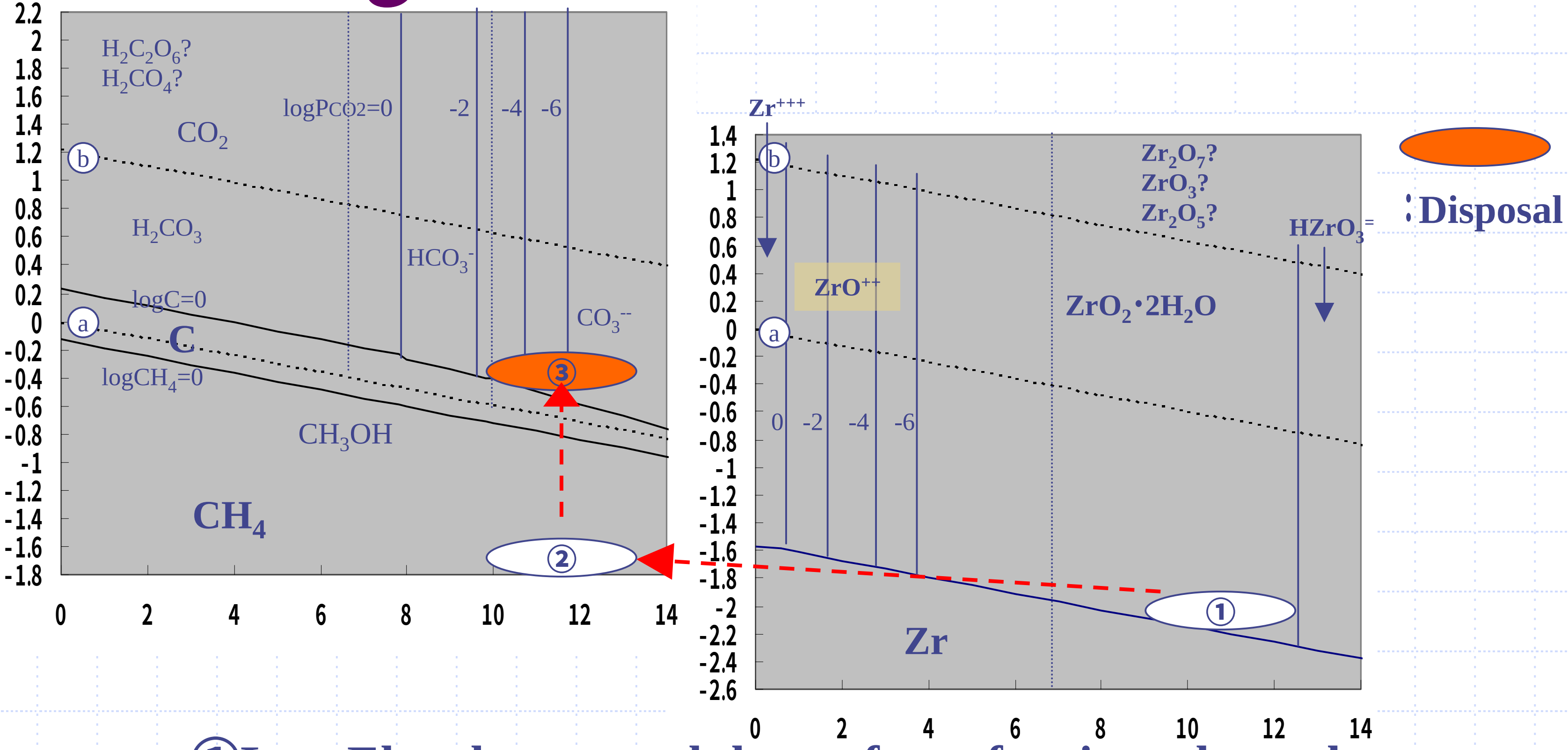
October 27-28, 2003

JNFL
RWMC
TOSHIBA

Contents

1.Background
2.Objective
3.Experimental Procedure
4.Results
5.Summary
6.Future Study

1.Background



①Low Eh value around the surface of activated metals caused corrosion reaction

②In this condition, are organic carbons(C-14:released from metal) stable ?

③In disposal condition, is inorganic carbon stable ?

The Change of C-14 species from activated metals in disposal condition

2.Objective

The study on the change of the chemical forms from activated metals in disposal condition.

-The disposal facility made from cement materials etc.is alkaline and in a reduced condition.

3.Procedure (1／2)

(1) Leaching Test of Organic C-14 from Activated Metal Waste(Test No.1)

The Leaching for Cutting Powder of Activated Metal

The Leaching test

Removal of Co-60

- Leaching
  1 Month

Chemical Form

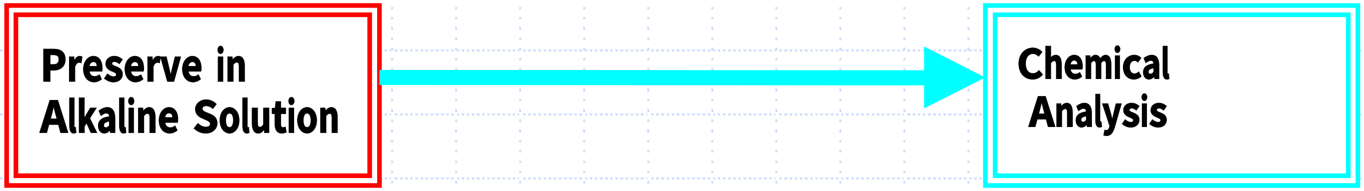
- The Leaching
  - Simulated
  - pH　10
  - Anaerobic
    (3%H_2／97%N_2)
- Leaching
  1 month

- The Cation exchange for removal of Co-60 to avoid the radiolysis
- pH adjustment

- High performance liquid chromatography
- Total organic carbon and inorganic carbon analysis
- Time
  1,3,6,12　Months　after the removal of Co-60

3.Procedure (2／2)

(2) Immersing Test of Organic Compounds in Alkaline Condition(Test No.2)



Preserve in Alkaline Solution

Chemical Analysis

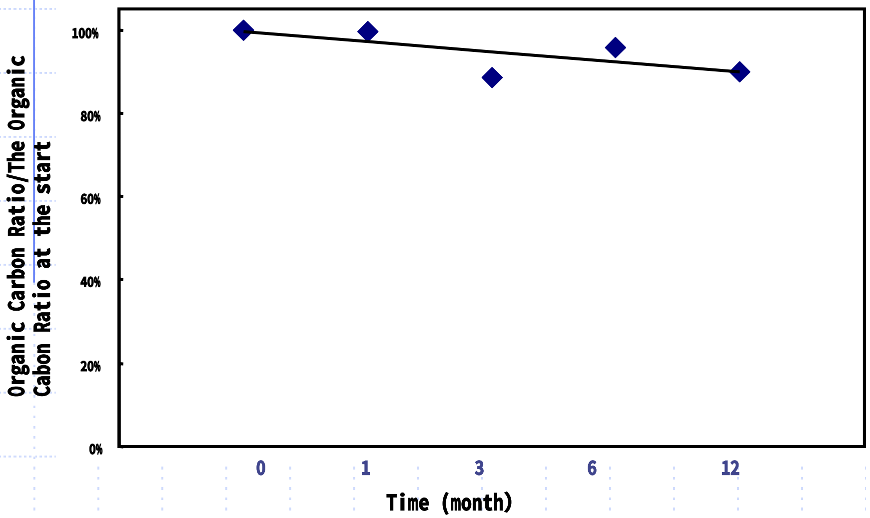
- The Chemicals
  - Formic Acid
  - Acetic Acid
  - Formaldehyde
  - Acetaldehyde
  - Methanol
  - Ethanol
- pH

- Total organic carbon and inorganic carbon analysis

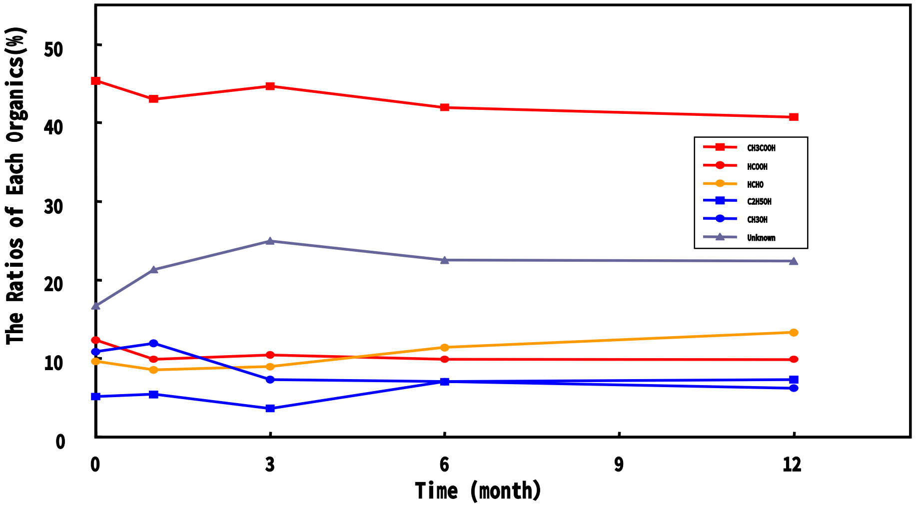
- Time
  - 1～15 months

4.Results (1／2)

(1) Test No.1


The change in the ratio of organic carbon

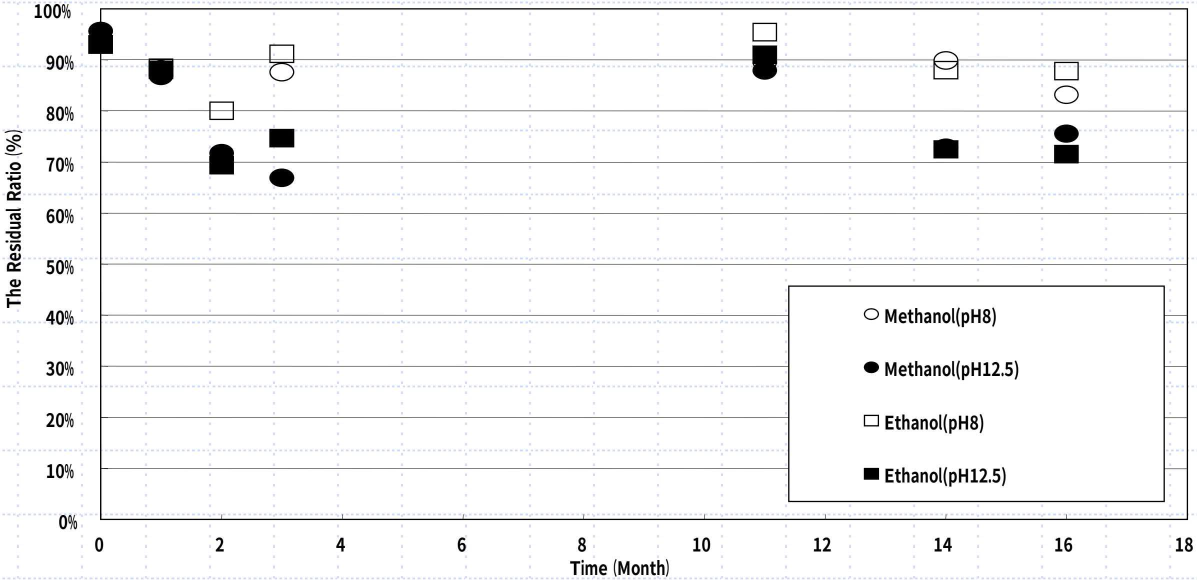
Time	The Ratio of Organics in Total Carbon	
	Data of Measurement	The Data nomalized
0 month	74.9%	100%
1month	74.6%	99.6%
3 month	66.2%	88.4%
6 month	71.6%	95.6%
12 months	67.3%	90.0%


The change in the ratio for each organic to to total organic carbon

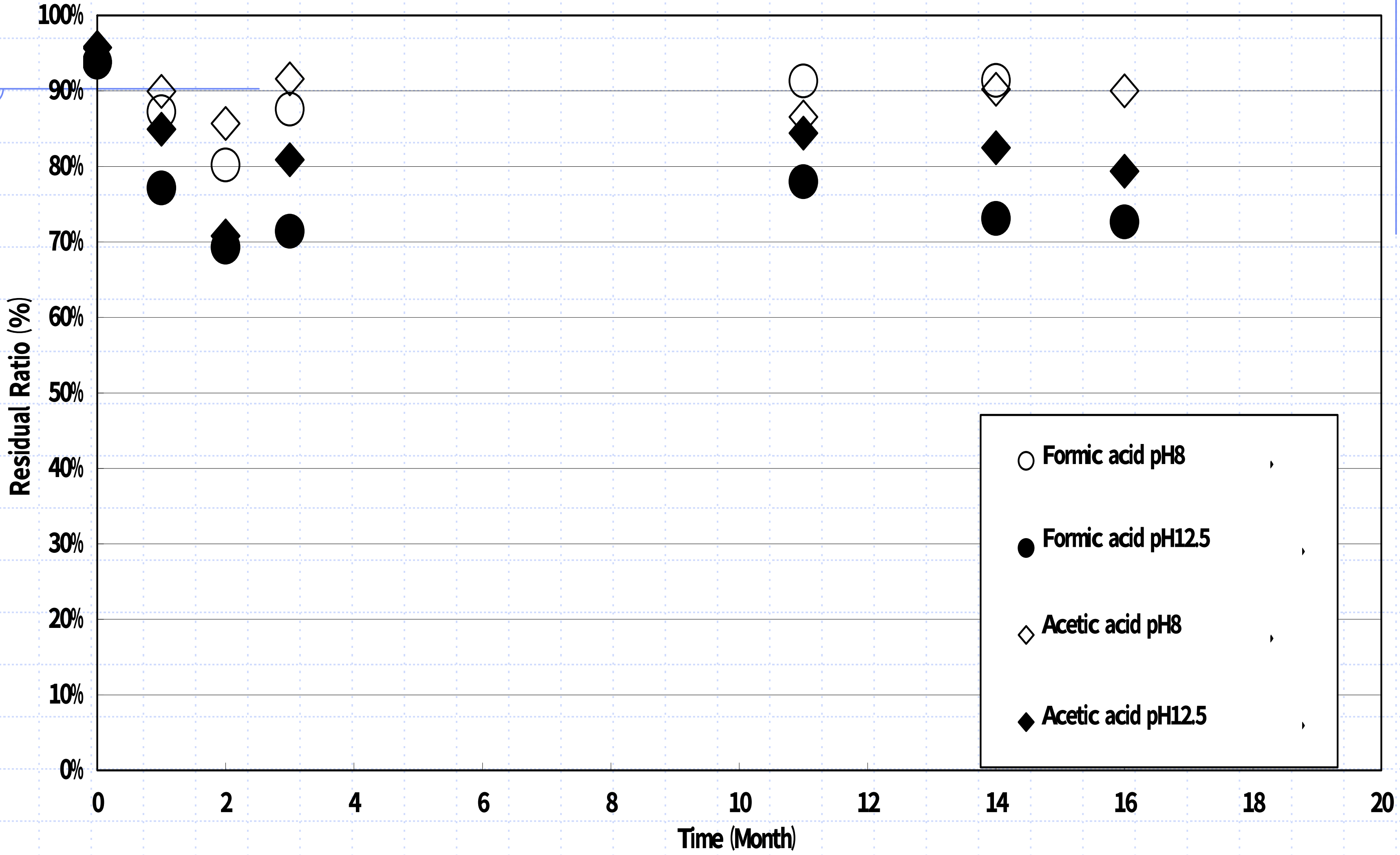
4.Result (2／2)

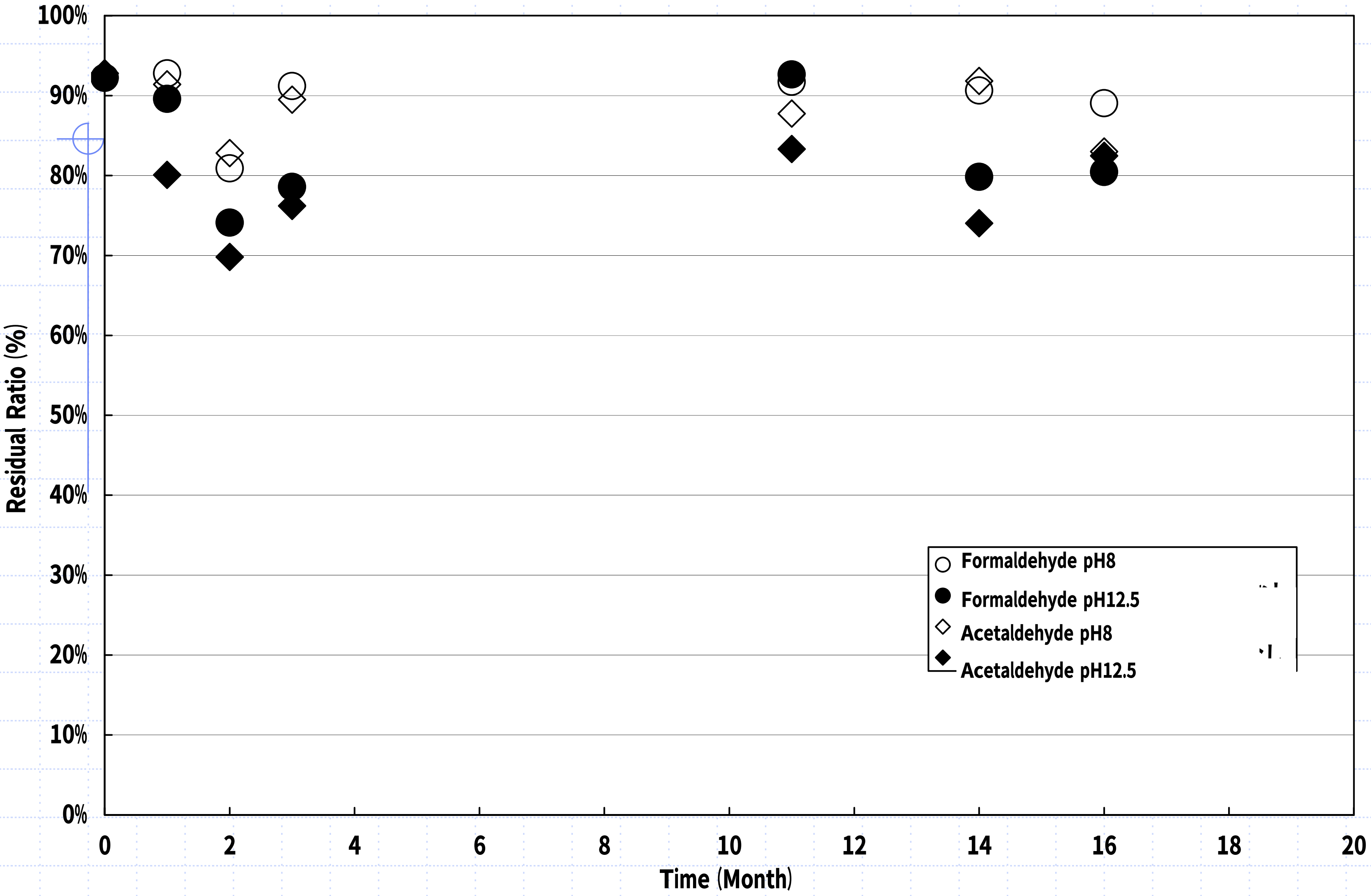
(1) Test No.2

The change in concentration of organics



Added Organics		The Residual Ratio (after 14 months)	
		pH 8	pH 12.5
Carboxylic Acid	Formic Acid	88%	71%
	Acetic Acid	91%	84%
Aldehyde	Formaldehyde	90%	80%
	Acetaldehyde	90%	77%
Alcohol	Methanol	90%	73%
	Ethanol	88%	72%


100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Residual Ratio (%)
0
2
4
6
8
10
12
14
16
18
20
Time (Month)
○ Formic acid pH8
● Formic acid pH12.5
◇ Acetic acid pH8
◆ Acetic acid pH12.5


100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Residual Ratio (%)
0
2
4
6
8
10
12
14
16
18
20
Time (Month)
○ Formaldehyde pH8
● Formaldehyde pH12.5
◇ Acetaldehyde pH8
◆ Acetaldehyde pH12.5

5.Summary

- The organic C-14 released from the activated metals might change to inorganic carbon in the disposal condition (alkaline,reduced)
- In the higher pH Condition, the rate of change to inorganic carbon might be faster.
- The organic carbon might change to inorganic carbon slowly.

6.Future Study

- We are going to study the hydrolysis reaction for organic C-14 in alkaline condition and velocity of this reaction.

- If the hydrolysis of organic C-14 in alkaline condition occurred at a disposal site, it would be possible to rationalize engineering of disposal facility.

Investigations of Distribution Coefficients for C-14 from Activated

October 27-28, 2003

JNFL
RWMC
MHI
NDC
HITACHI Ltd.
TOSHIBA

Contents

1. Objective
2. Experimental Procedure
3. Results
4. Discussion
5. Summary

1. Objective

- Because the C-14 released from the activated metals mainly forms organic compounds that weakly sorb on engineering barriers, effective absorption materials for organic C-14 or oxidation to inorganic C-14 are required for rationalization of engineering for disposal facilities.
- The distribution coefficients of cements for C-14 released from activated metal were measured in this study.

  For other types of materials suitable for engineering barriers, the distribution coefficient experiments were carried out in this study too.

2. Procedure (1/3)

(1) The conditions for the distribution coefficient measurements for C-14 from activated metal

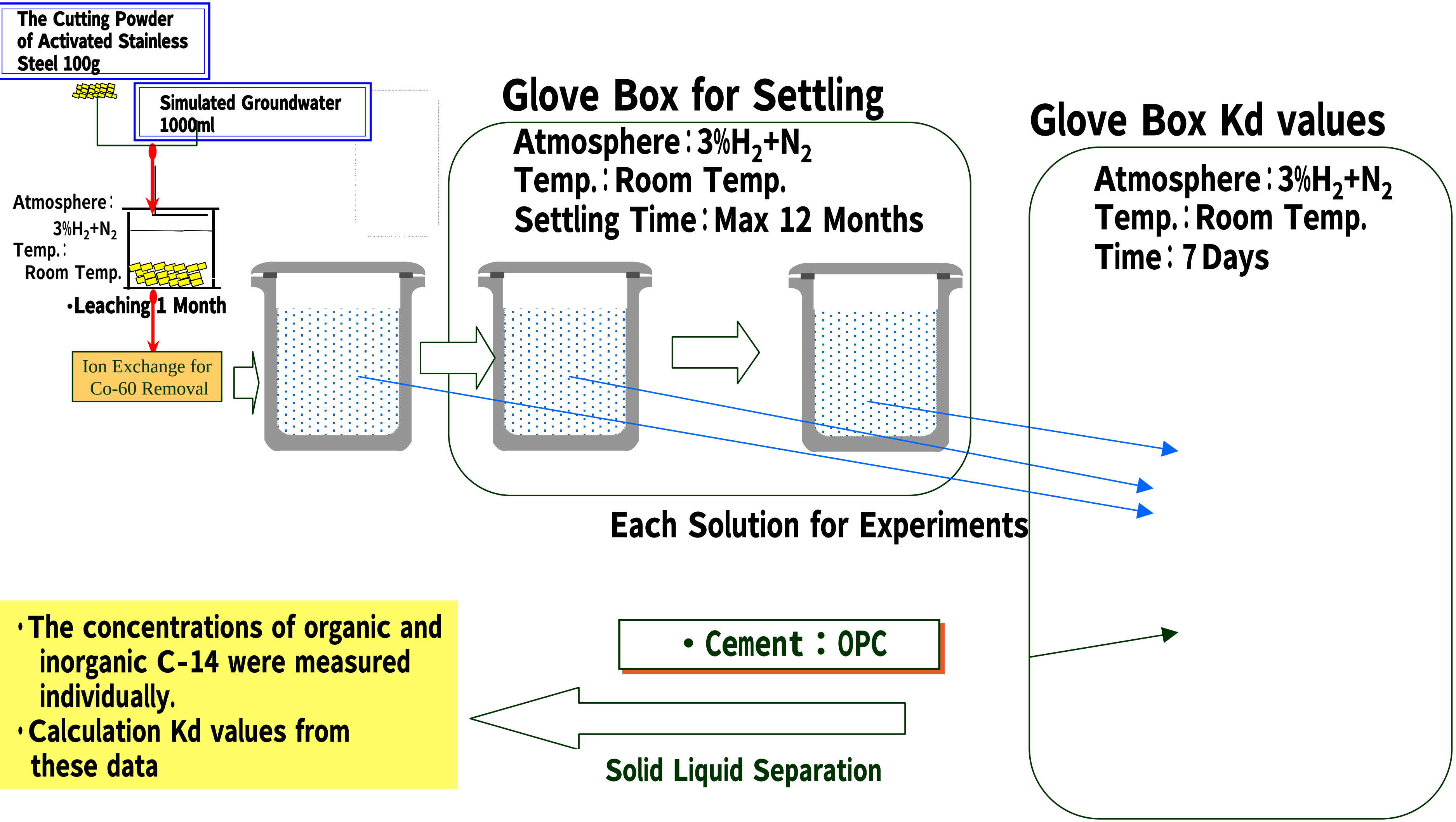
① Activated Materials	(a) Activated Zirconium Alloy (hulls) (Metallic sample and the sample covered with zirconium oxide) (b) Activated stainless steel (without surface oxides)
② Liquid Phase	Simulated Groundwater (Anaerobic alkaline condition)
③ Cement	OPC and mixed cements (OPC:BFS=1/9)
④ Solid Liquid Ratio	1g/10ml

OPC：Ordinary Portland Cement

Mixed Cement ; OPC:BFS=1/9 BFS;Blast Furnace Slag

2. Procedure (2/3)

(2) The Method of the distribution coefficient measurements for C-14 from activated metals



The Cutting Powder of Activated Stainless Steel 100g

Simulated Groundwater 1000ml

Atmosphere: $3\%H_2+N_2$
Temp.: Room Temp.

•Leaching 1 Month

Ion Exchange for Co-60 Removal

Glove Box for Settling

Atmosphere: $3\%H_2+N_2$
Temp.: Room Temp.
Settling Time: Max 12 Months

Glove Box Kd values

Atmosphere: $3\%H_2+N_2$
Temp.: Room Temp.
Time: 7 Days

Each Solution for Experiments

• Cement : OPC

Solid Liquid Separation

- The concentrations of organic and inorganic C-14 were measured individually.
- Calculation Kd values from these data

2．Procedure (3/3)

(3) The Measurements for Kd values of organic C-14 for effective materials

① Materials and Organics

Materials	Organic Carbons	Notes
20 Type	5 types of organic carbon compounds spiked with C-14	* Based on the analysis for activated stainless steel leaching experiment

② Solid Liquid Ratio ：1g/10ml

3. Result (1/4)

(1) The measurements for Kd values of C-14 from activated metals

① Activated Zirconium Alloy "Organic C-14"

(ml/g)

Cement	Run No	Metallic Sample	Sample covered with Zirconium Oxide	Ave.
OPC	1	1.9	5.8	—
	2	4.6	2.5	—
	Ave.	3.3	4.2	3.7
Mixed cement	1	3.6	3.6	—
	2	2.7	8.8	—
	Ave.	3.2	6.2	4.7

The concentration of inorganic C-14 was under the detection limit.

3．Result(2/4)

(1) The measurements for Kd values of C-14 from activated metals

②Activated Stainless Steel

(ml/g)

Item			RUN A	RUN B						Ave.
Leaching Time			11Months	1 Months						-
Settling Time			0 Month	0 Month	1Month	3 Months	6 Months	12 Months	Ave.	-
The Ratio for TOC(C-14)			37%	74.9%	74.6%	66.2%	71.6%	67.3%	-	-
Cement	OPC	Inorg.	580	245	486	1060	873	870	707	686
		Org.	7.5	9.3	5.8	3.5	5.9	2.9	5.5	5.8
		Total	35	15	11	10	12	9.1	11.4	15.4
	Mixed Cement	Inorg.	90	-	-	-	-	-	-	-
		Org.	12	-	-	-	-	-	-	-
		Total	33	-	-	-	-	-	-	-

3． Result(3/4)

(2) The experiments on effective materials for organic C-14 sorption

① selecting materials with high Kd values using acetic acid-C-14

(ml/g)

Materials		Acetic Acid
Minerals in Cement	CSHgel 0.65	0.9
	CSHgel 0.90	0.8
	CSHgel 1.65	0.7
	Ettringite	7.3
	Monosulphate	0.8
	Tobermolite	1
	Hydrotalcite (OH Type)	14.1
Natural Minerals	Illite	5.9
	Acid Clay	39.1
	MgO	1.8
	Al_2O_3	2.1
	TiO_2	0.6
	ZrO_2	1.5
	Fumic Acid	<0.1
	Coal	4.3
Artificial Minerals	Halloysite	64.9
	Ferric Oxides	0.1
	Bismuth Phosphate	0.3
	Charcoal	19.7
	Asphalt	0.2

3． Result(4/4)

(2) The experiments for effective materials for each organic carbon compounds sorption

②Kd values experiments

ml/g

Materials	Oraganic Carbon Compounds				
	Acetic Acid	Formic Acid	Formaldehyde	Methanol	Ethanol
Ettringite	7.3	16	6	0.4	
Hydrotalciteト	14	21	7	0.4	
Illite	5.9	0.1	3.8	1.2	8.4
Japanese Acid Clay	39	7	3.2	0.5	13
Halloysite	65	15	3.8	0.3	12
Charcoal	20	11	43	2.5	17

4. Discussion

① The Kd value of cement for inorganic C-14 released form activated stainless steel is 1060ml/g～245ml/g, and that for organic is 9.3ml/g～3.5ml/g.

② There are no differences between the organic C-14 from the activated zirconium alloy and that from the activated stainless steel.

③ The Kd value of OPC for organic C-14 is the same as that for mixed cement.

④ Several minerals are effective for organic carbon sorption. Regarding their use as engineering barriers, further investigation is required.

5. Summary

- The cement Kd values for C-14 from activated zirconium alloy and activated stainless steel were measured in this study.
- Preparation of a Kd values database for some organic carbons, e.g. carboxylic acids and alcohols, and inorganic carbon would be important for setting up the C-14 in the activated metals.

Migration of C-14 in Activated Metals under Anaerobic Alkaline Condition

October 27-28, 2003

The Kansai Electric Power Co.
Chubu Electric Power Co.
RWMC
TOSHIBA
MHI
NDC

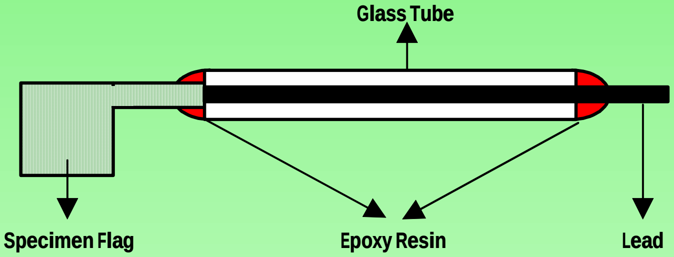
Migration of C-14 in Activated Metals under Anaerobic Alkaline Condition

1. Objective
2. Corrosion Test
3. C-14 Leaching Test
4. Discussion
5. Conclusion

Objective

- For the safety assessment of radionuclide migration, it is necessary to access not excessively conservatively but actually.
- C-14 is considered an important nuclide for the safety assessment of a geological repository facility.
- It is the aim of this investigation to provide data relevant to design the model of C-14 migration mechanism, by dual determinations of leaching rate and corrosion rate.

Corrosion Test -Condition-

Material Of Specimen	• Zirconium Alloy • Stainless Steel • Nickel Alloy
Shape of Specimen	• Plate as Flag 
Surface on Specimen	• Elimination of Oxide-Film by Polishing
Environment of Test	• Anaerobic Alkaline Condition
Method of Measurement	• Polarization Resistance Measurement & Best-fit Curve Calculation

Corrosion Test
-Method of Corrosion Rate Measurement-

- Polarization Resistance Measurement

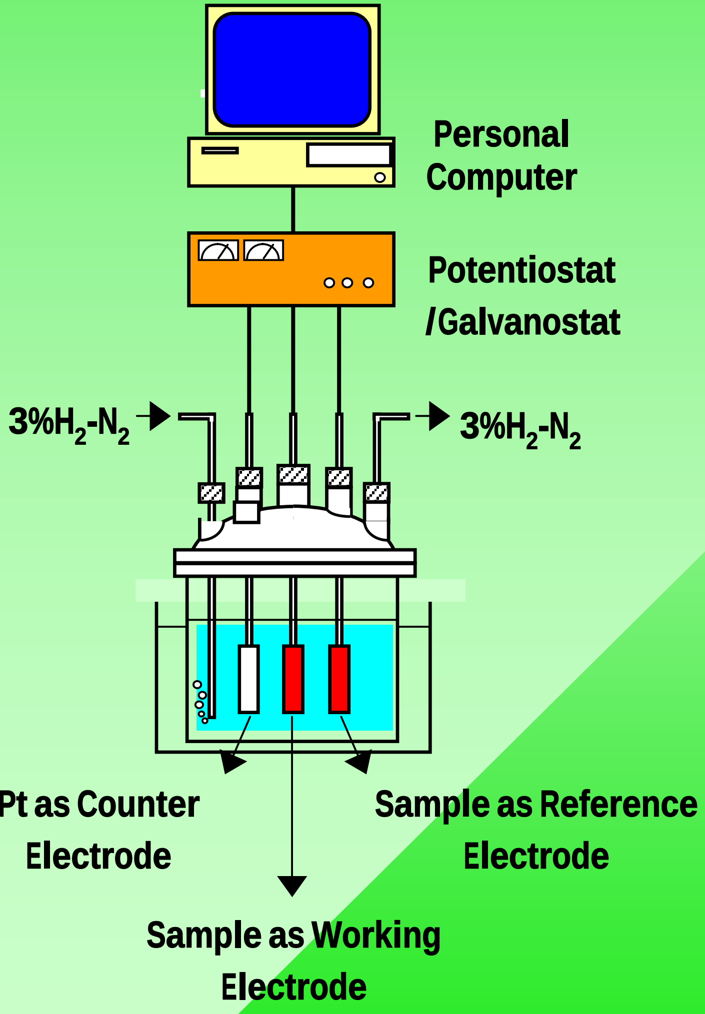
  Possible to measure the small corrosion current over a long period of time

- Best-fit Curve Calculation

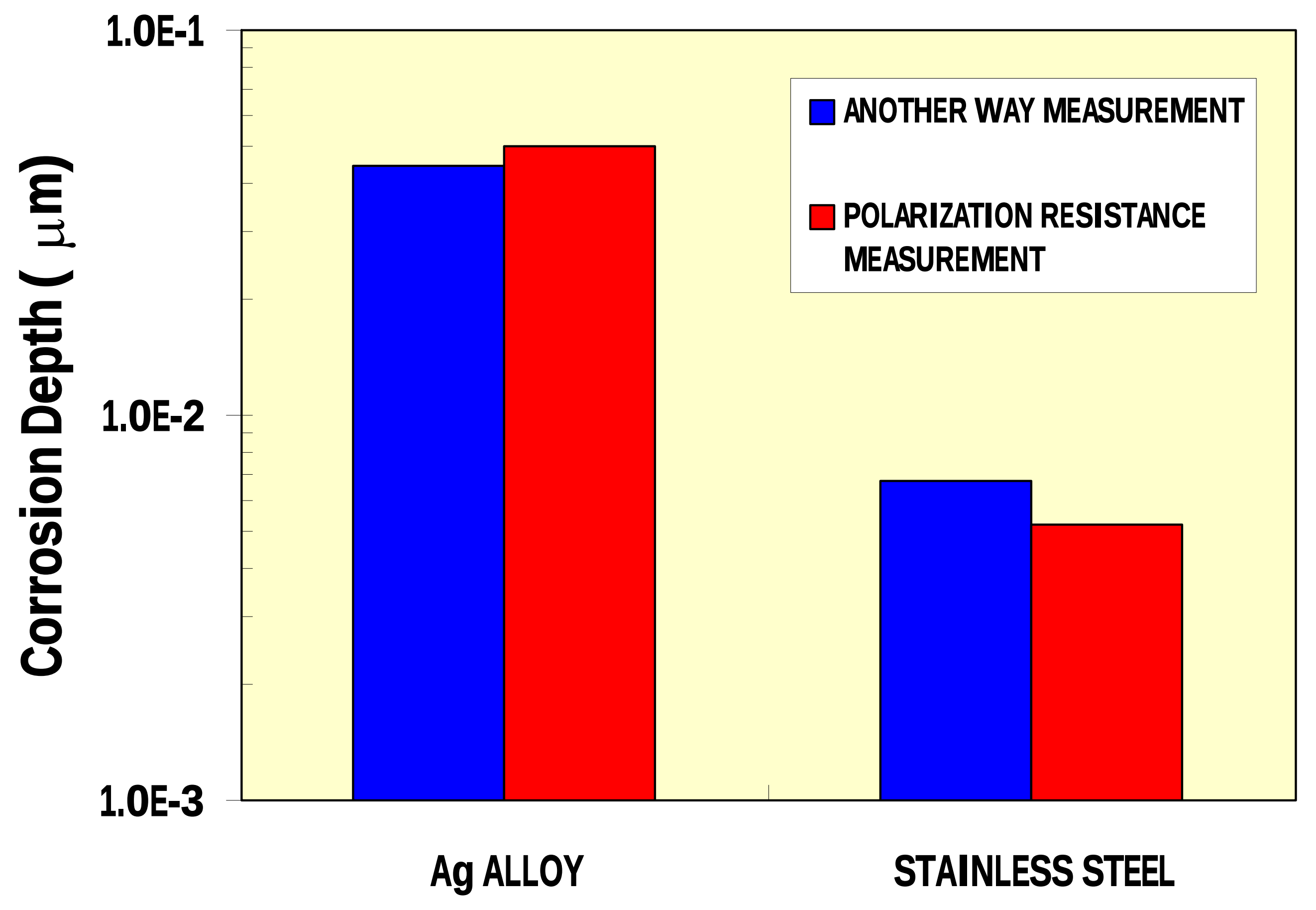
  Possible to obtain the corrosion parameters by graphical analysis of polarization curve

- Reference Electrode use same Material for Working Electrode

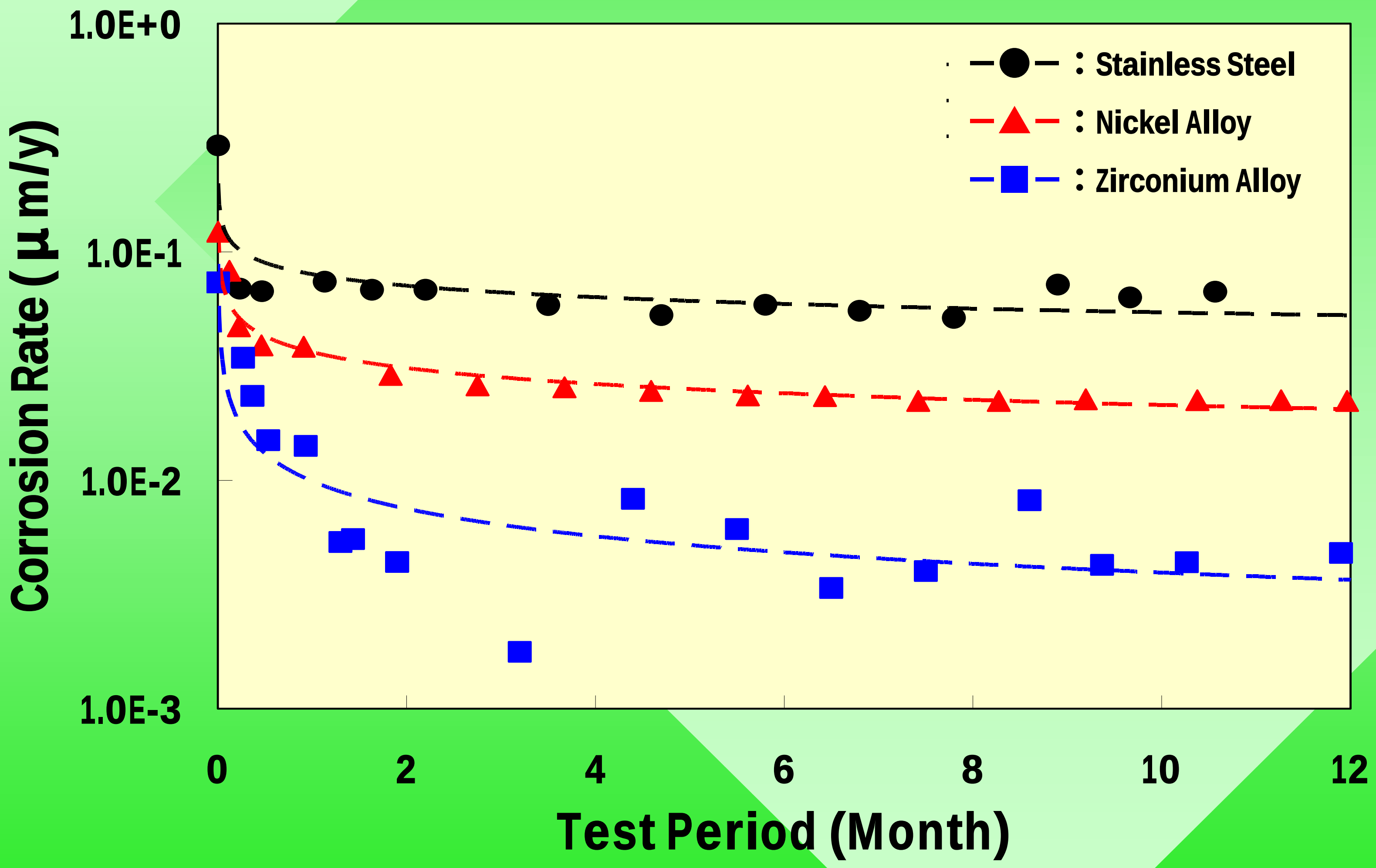
  Possible to keep the experiment condition easy by using a simple experimental setup



Corrosion Test
-Comparison with Alternate Methods-



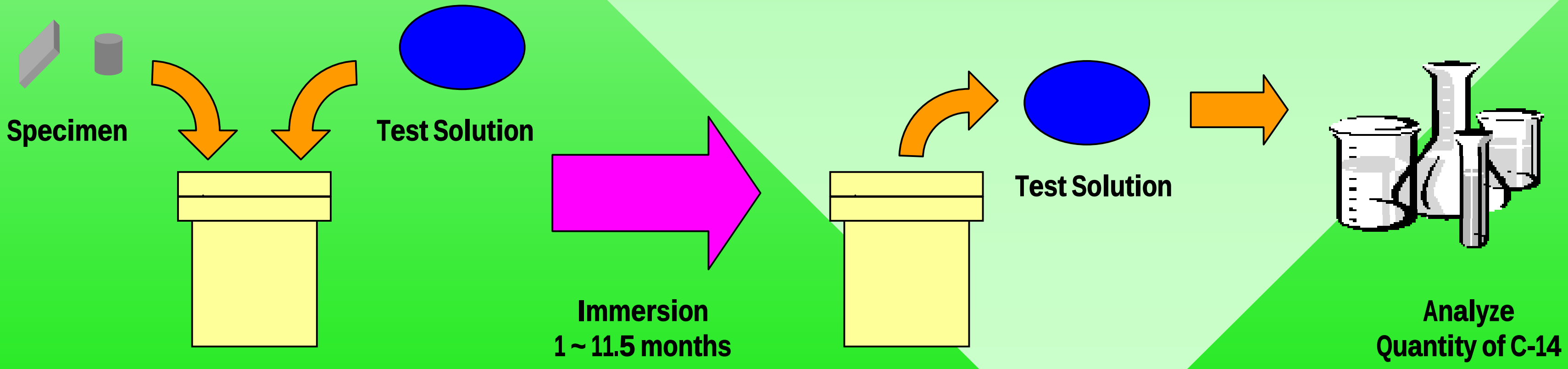
Corrosion Test -Results : Corrosion Rate-



NAGRA / RWMC Workshop on C-14

C-14 Leaching Test -Condition-

Material of Specimen	• Activated Zirconium Alloy • Activated Stainless Steel • Activated Nickel Alloy
Shape of Specimen	• Activated Zirconium Alloy Tube • Activated Stainless Steel / Activated Nickel Alloy Plate
Surface on Specimen	• Elimination of Oxide-Film by Polishing
Environment of Test	• Anaerobic Alkaline Condition



C-14 Leaching Test -Results-

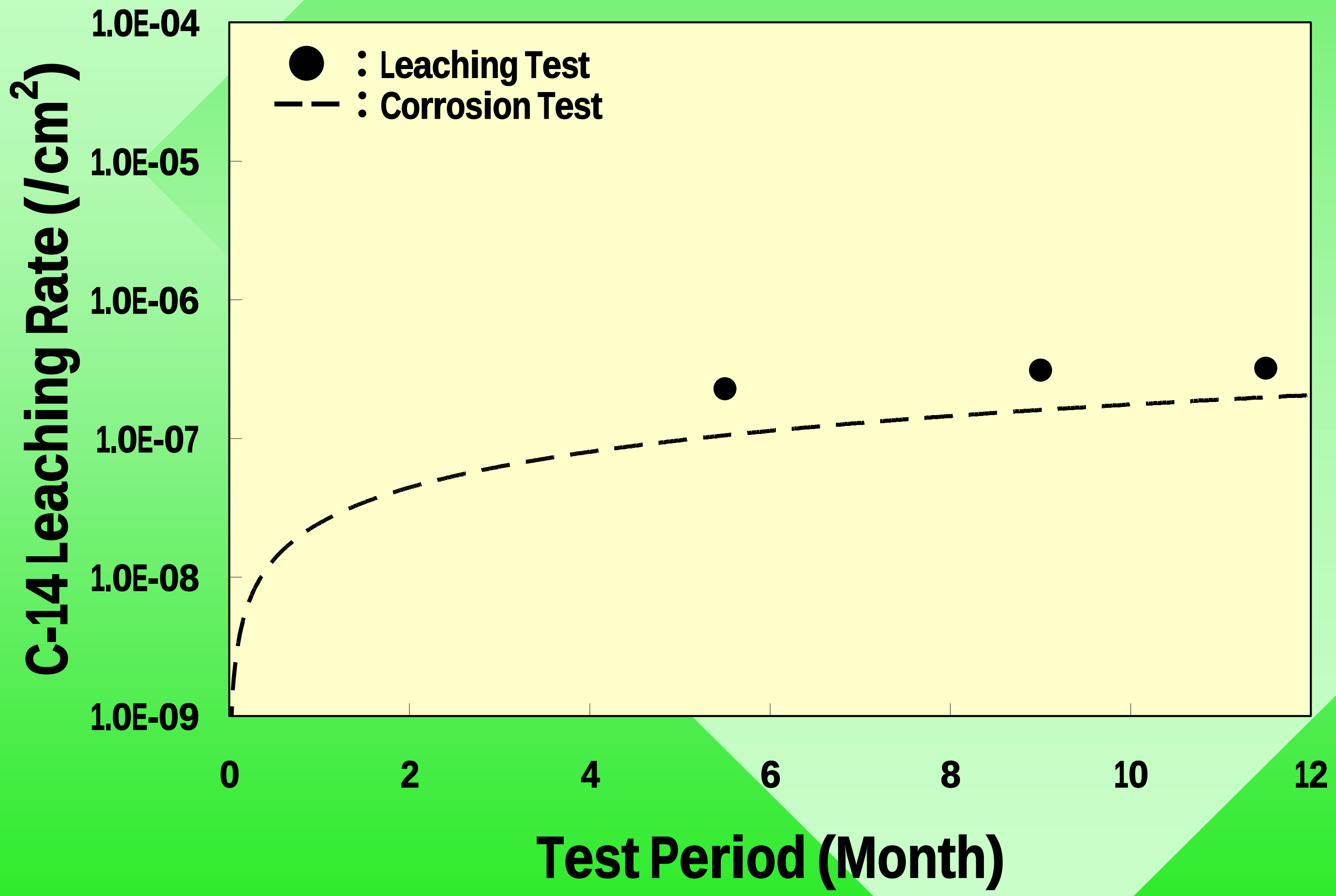
Activated Zirconium Alloy				Bq/Unit
Test Period (Month)	5.5	9	11.5	
-	1.1×10^{1}	1.5×10^{1}	1.6×10^{1}	

Activated Stainless Steel				Bq/Unit
Test Period (Month)	1	3	6	
High Irradiated	8.7×10^{-1}	7.9×10^{-1}	1.9×10^{0}	
Low Irradiated	4.3×10^{-1}	2.0×10^{0}	ND	

Activated Nickel Alloy				Bq/Unit
Test Period (Month)	1	3	6	11
-	ND	ND	ND	2.9×10^{-1}

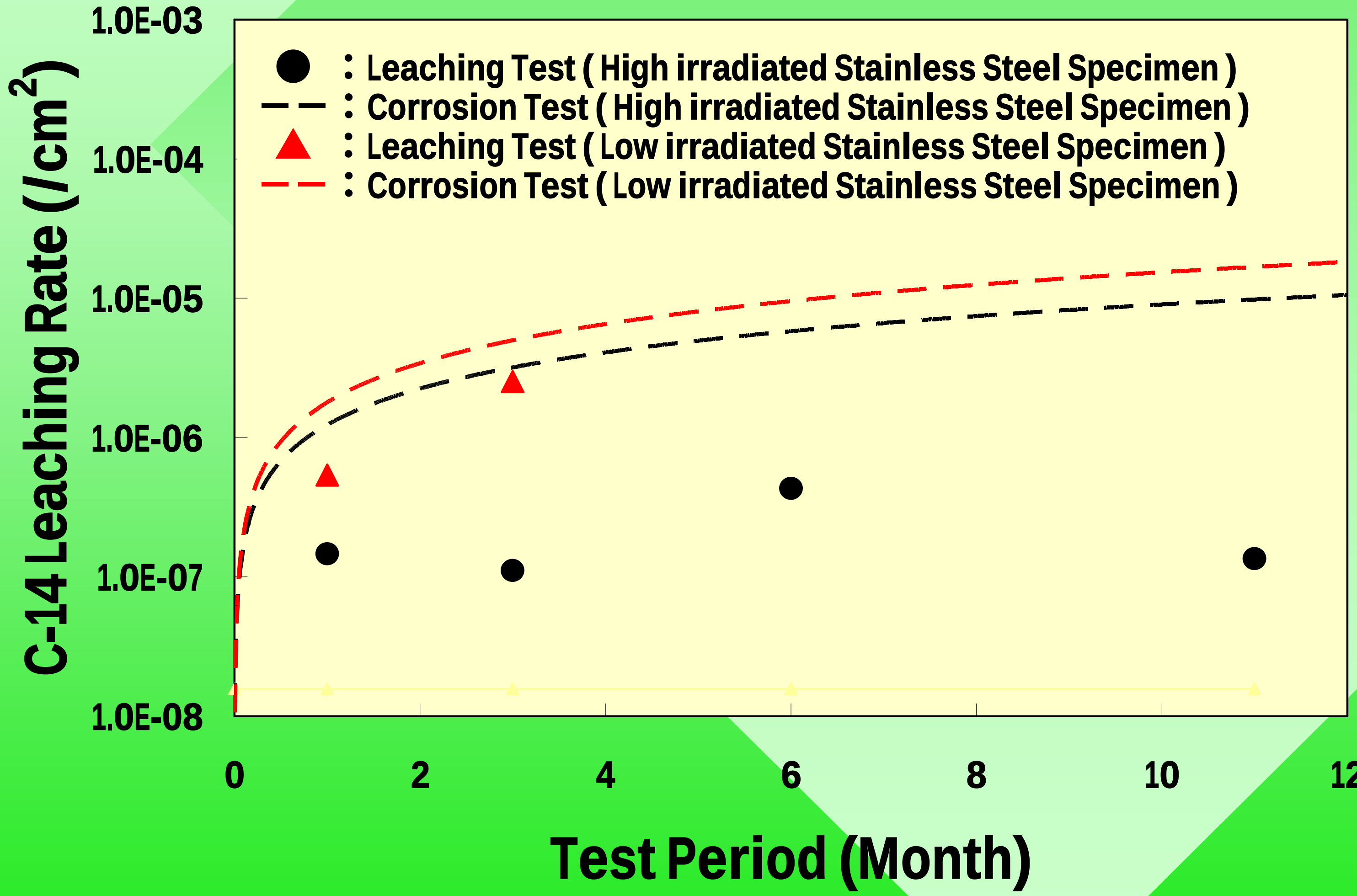
Discussion -Zirconium Alloy-

Leaching Test Result ≈ Calculated value from Corrosion Test Results



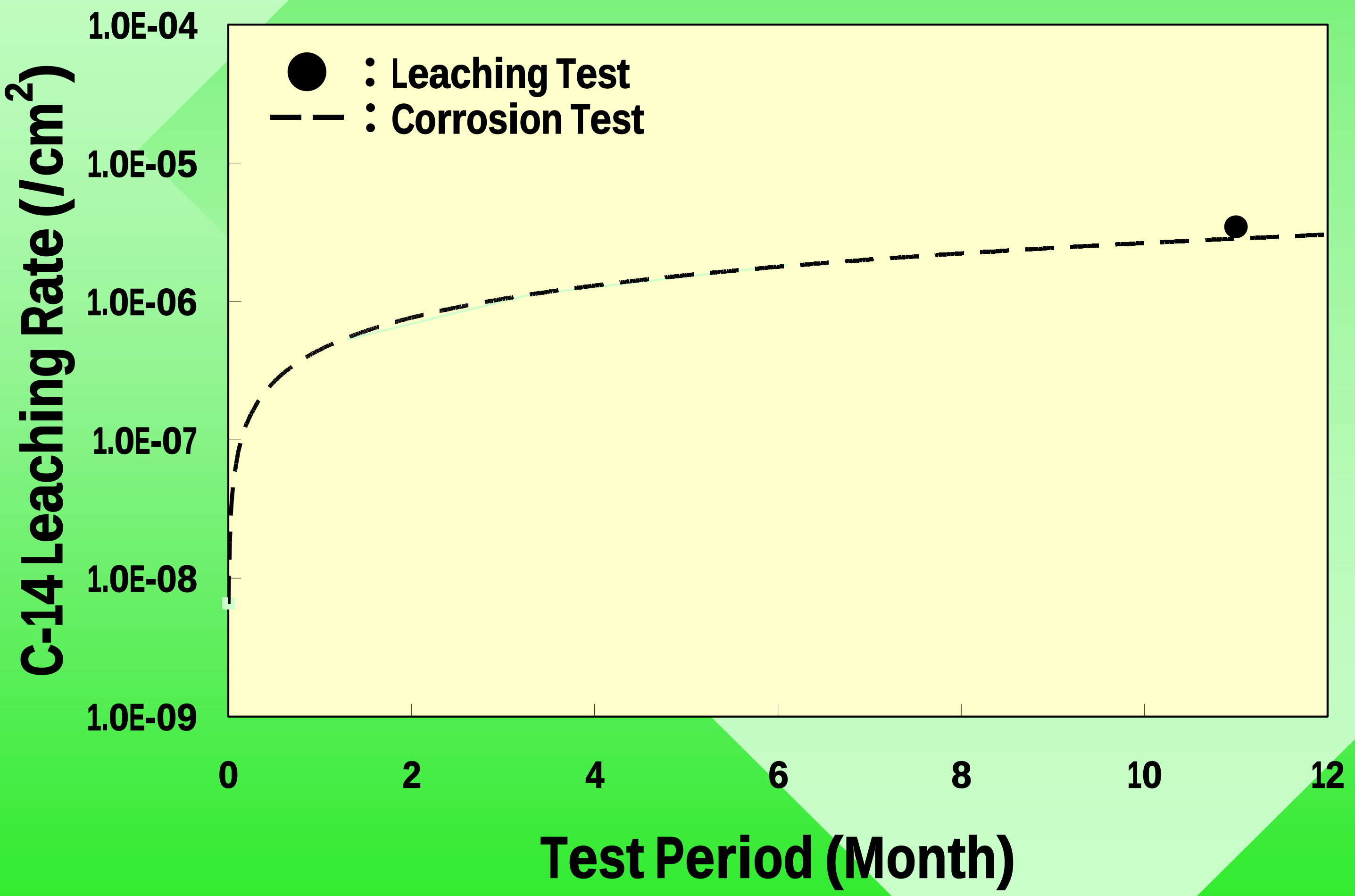
Discussion -Stainless Steel-

Low Irradiated : Leaching Test Result ≈ Calculated value from Corrosion Test Results
High Irradiated : Leaching Test Result < Calculated value from Corrosion Test Results



Discussion -Nickel Alloy-

Leaching Test Result ≈ Calculated value from Corrosion Test Results



Conclusion

The C-14 leaching test and the corrosion test have been carried out to design the model of C-14 migration mechanism.

- The C-14 leaching test results coincide approximately with the leaching rate calculated from corrosion rates.

Our plans for the near future are:

- The estimation about the influence of fluctuation in disposal environment parameters for C-14 migration behavior.

BNFL

Modelling the Partitioning and Transport of C-14 in a Microbially Active LLW Site

Joe Small

Nuclear Sciences and Technology Services (NSTS)

NAGRA C-14 Workshop 28th October, 2003

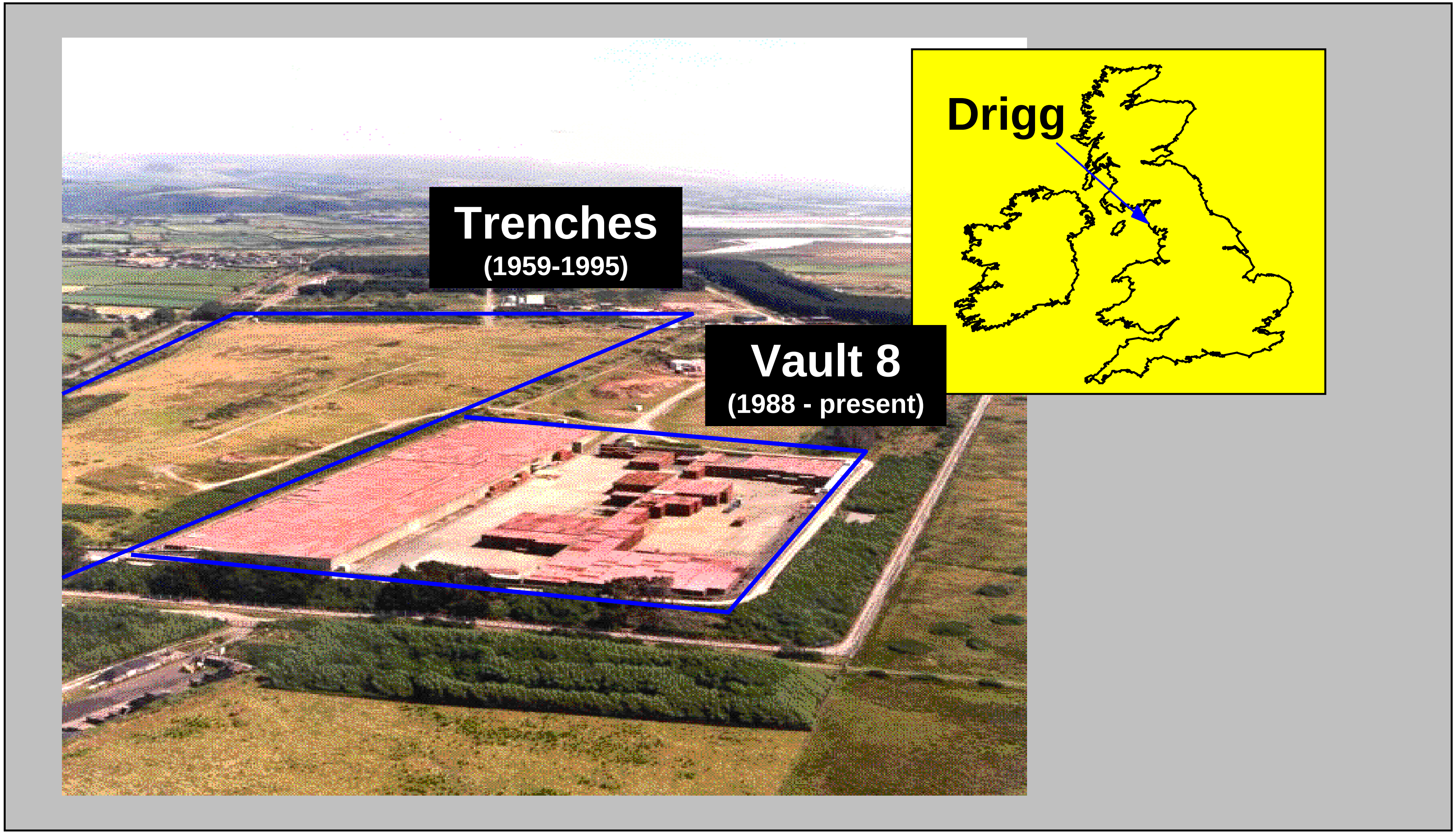
Introduction

- Carbon is a key reactive element in LLW resulting from its organic content and the microbiological and geochemical processes that occur in the surface and near-surface.
- Realistic assessment of C-14 release from LLW requires consideration of the various organic and inorganic reactions that occur in the near-field that involve carbon.

Aims

- Presentation of a mechanistic based modelling approach to consider the partitioning of C-14 among reactive carbon species.
- Discussion of isotope fractionation effects.
- Discuss how such models are used in performance assessment calculation of the Drigg LLW site, UK.

The Drigg site



Drigg LLW & C-14

- Drigg LLW comprises organic (cellulosic) and iron waste and has the potential for gas generation and generation of anaerobic conditions.
- The form of the C-14 inventory in LLW is, in general, poorly constrained and may be distributed among activation products in steel and concrete and graphite as well as being associated with reactive cellulose waste.
- For the Drigg PCSC it is assumed, conservatively, to consider C-14 present in the form of cellulose.

Fate of C-14 in LLW

Through processes of LLW waste degradation C-14 has the potential to be redistributed to various phases e.g.

- Carbonate phases (primarily associated with cement grout)
- Residual organic matter (microbial biomass)
- Gases CO_2, CH_4
- Aqueous species HCO_3^-, CH_3COO^-, complex organics

Modelling the Drigg near-field

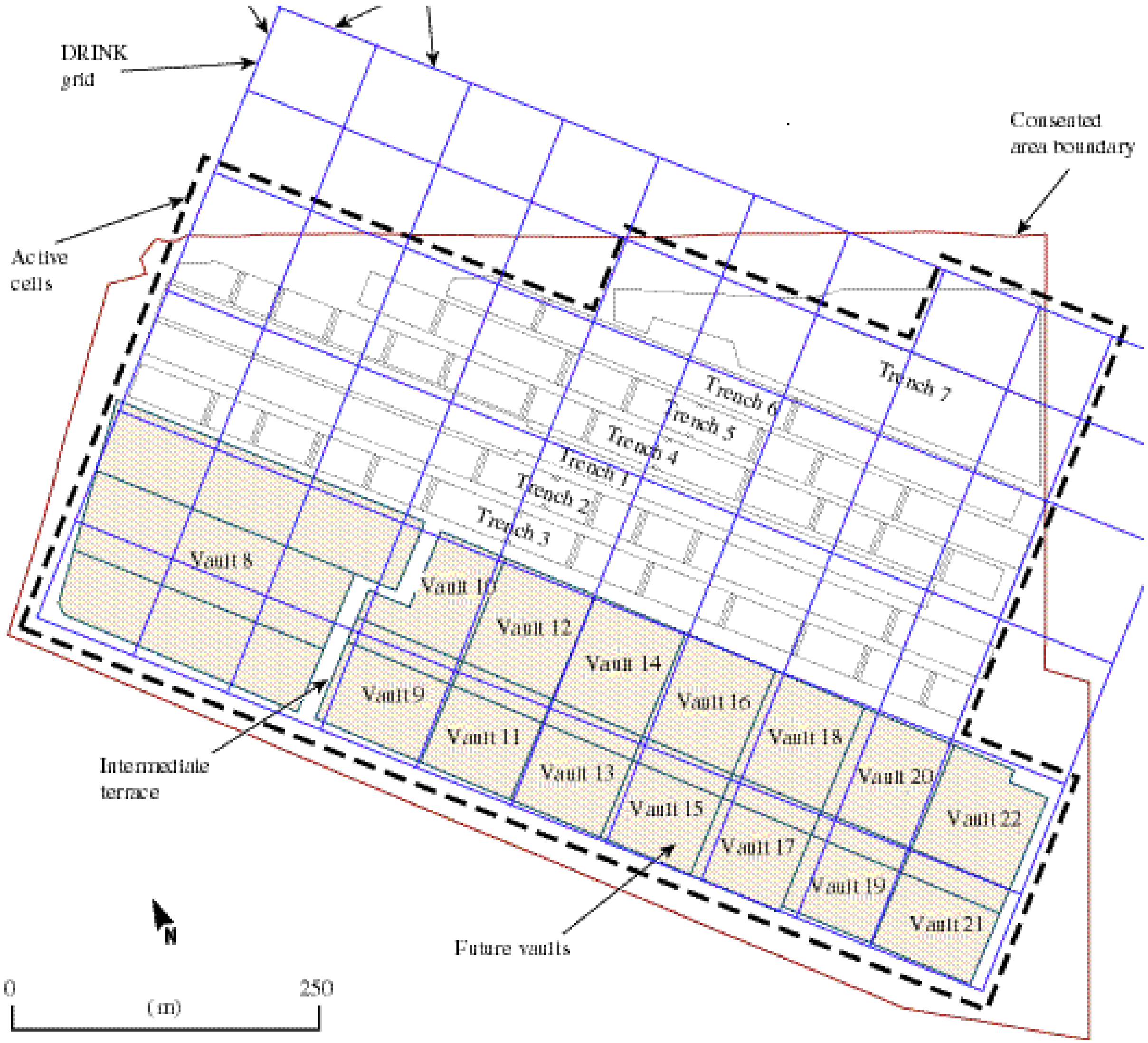
BNFL-NSTS has developed the GRM reactive-transport code to model biogeochemical processes of LLW degradation.

The GRM code couples various process:

- Microbial processes of organic degradation and mediation of redox reactions
- Metal corrosion
- Chemical speciation, mineral precipitation and dissolution
- Gas exchange and reaction
- Radionuclide sorption
- Radioactive decay
- Groundwater flow

The GRM code includes specific subroutines that follow the reaction and transport of C-14

The GRM-DRINK model

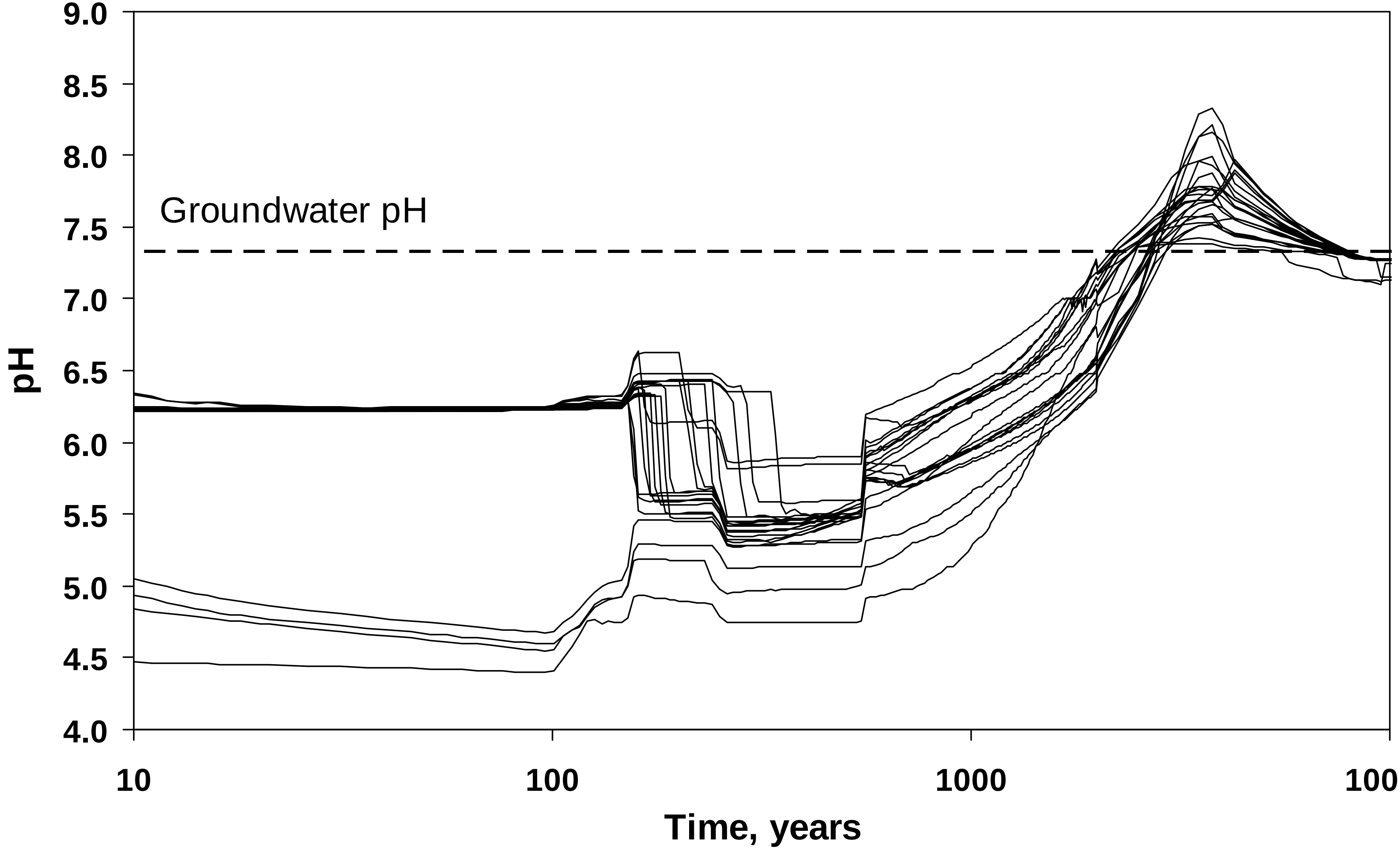


Reaction-transport calculation are performed using a finite difference grid

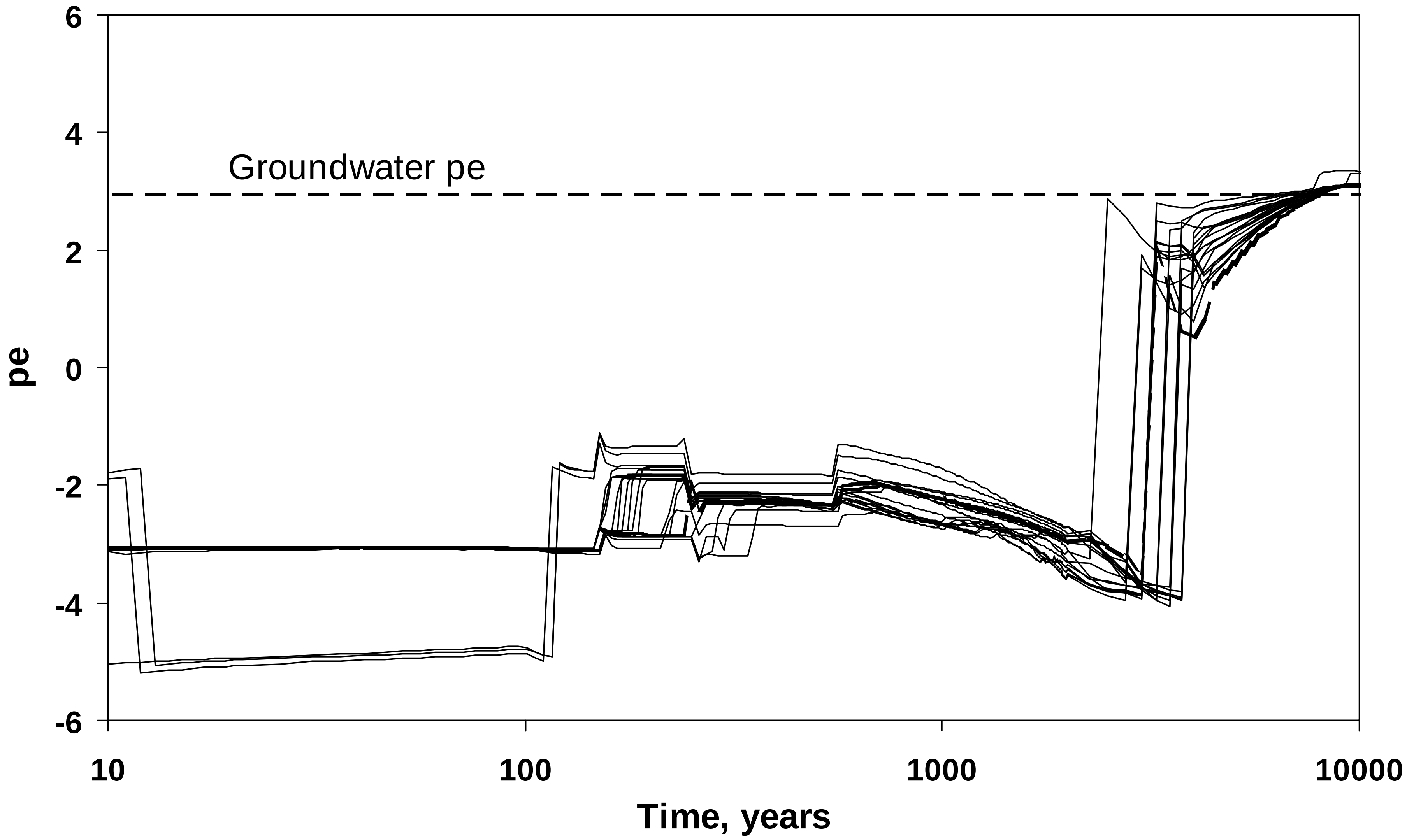
Reactive calculations are performed in a each of the 63 cells representing the Trenches and Vaults to determine chemical conditions

The model outputs an aqueous and gaseous source term of radionuclides including C-14

Model Results:
pH variation - trench cells

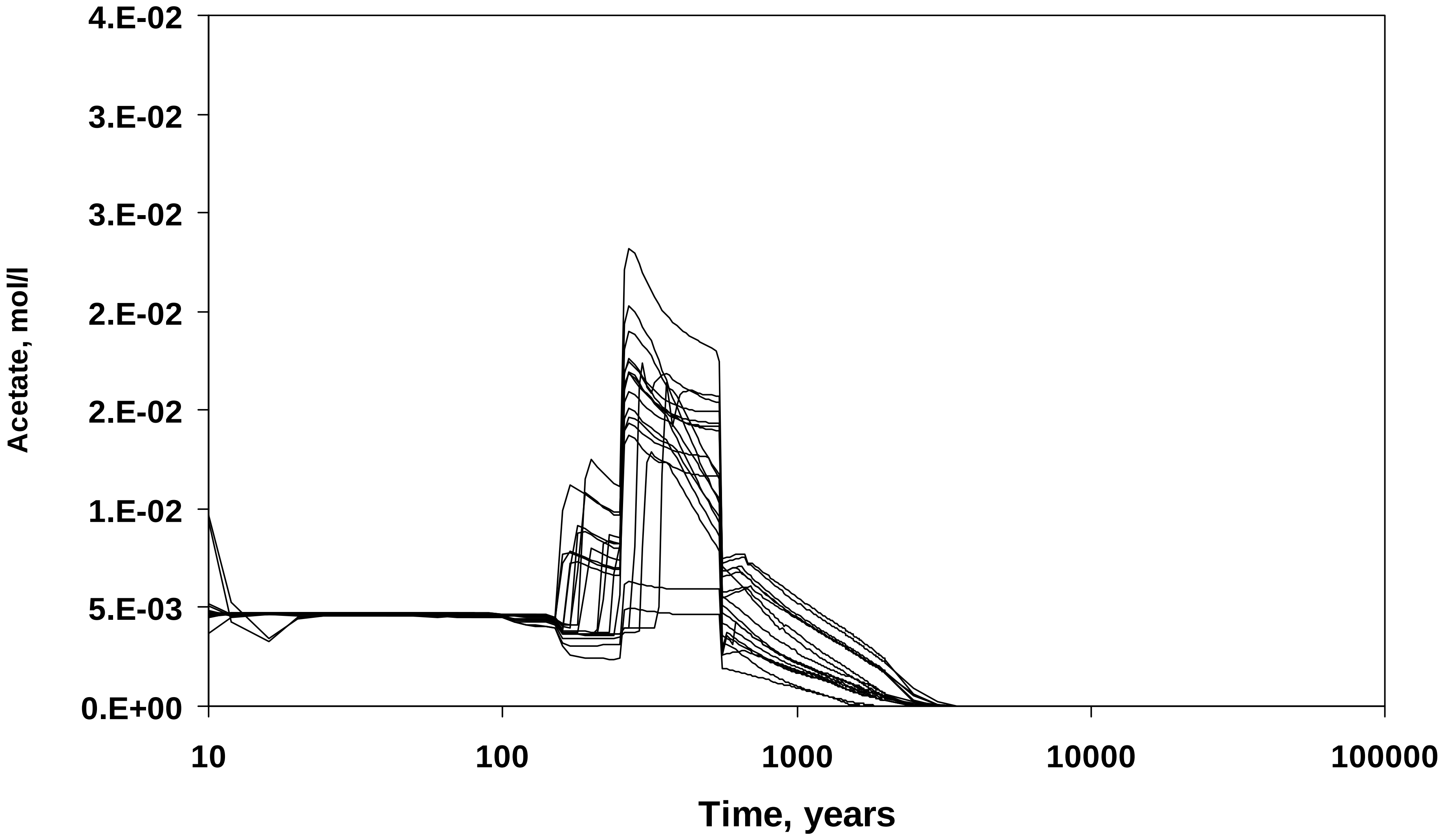


Model Results:
Redox variation - trench cells

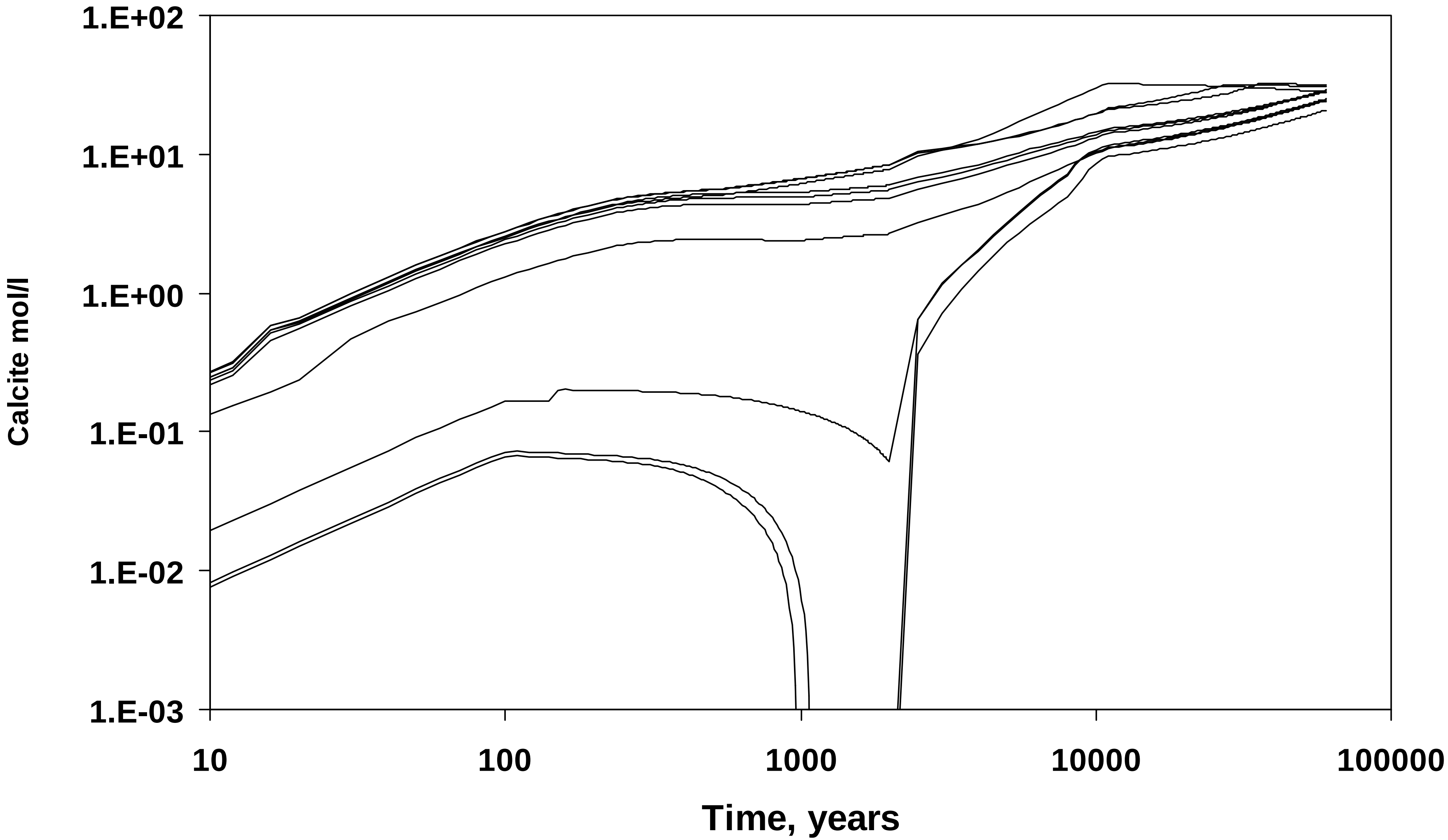


File ref:

Model Results:
acetate - trench cells



Model Results:
Calcite - vault cells

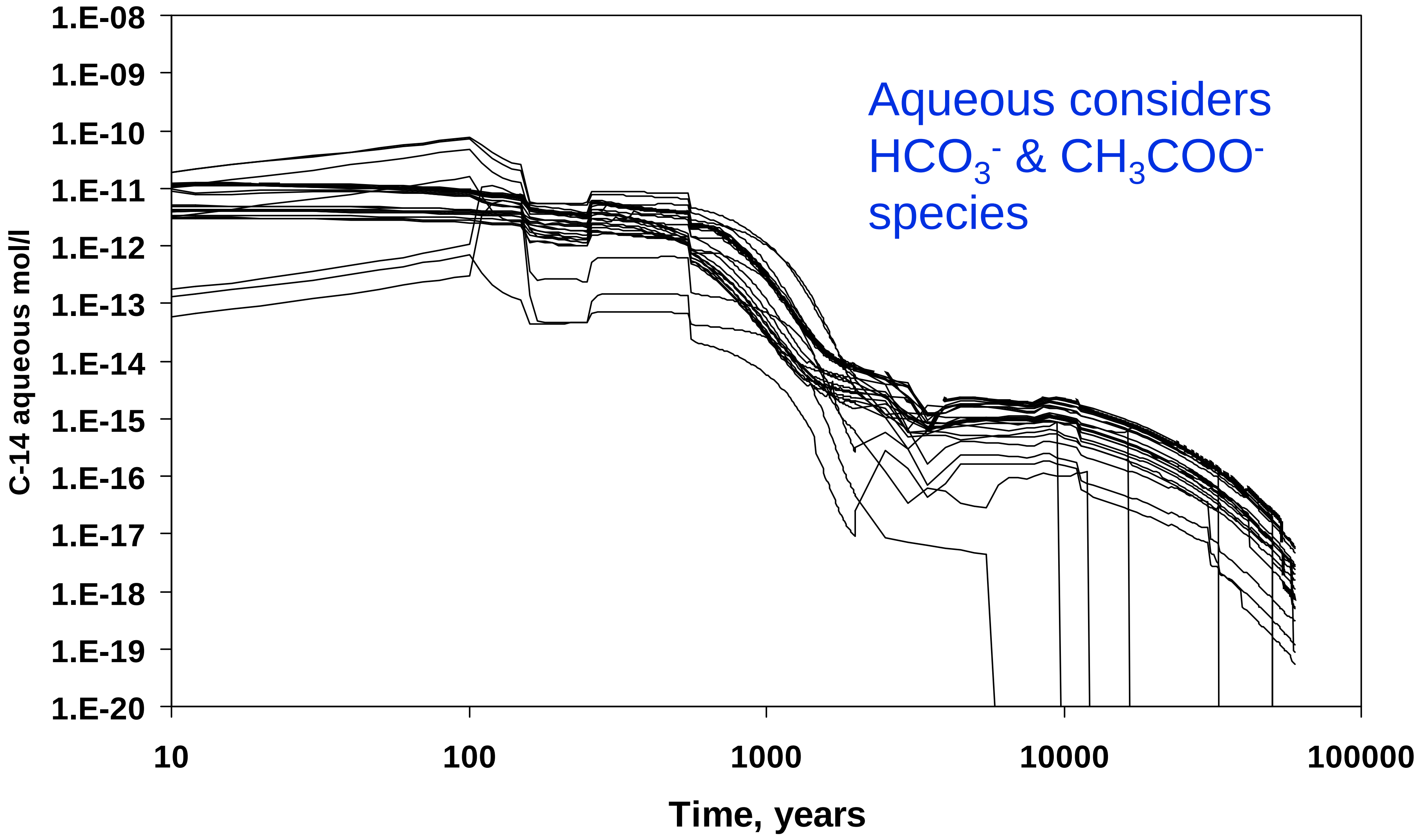


C-14 partitioning

For each reaction involving carbon, C-14 released from the reactants is redistributed into the product species.

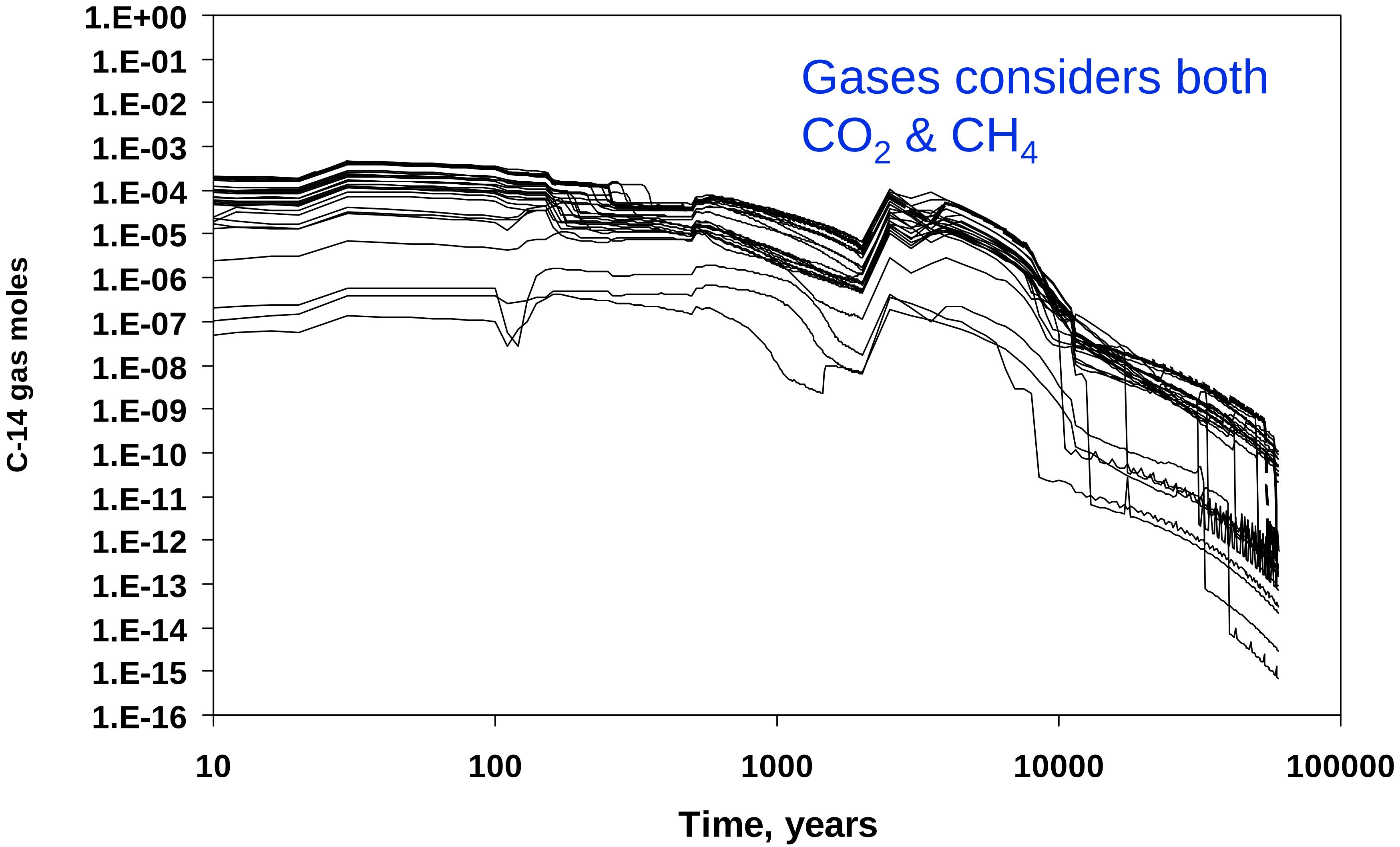
- The C-14 content of each species is followed as a fraction of the total moles of carbon present in that species.
- The C-14 fraction of each product species is recalculated at each reaction as a average for that species in each calculation cell

Model Results:
C-14 aqueous - trench cells

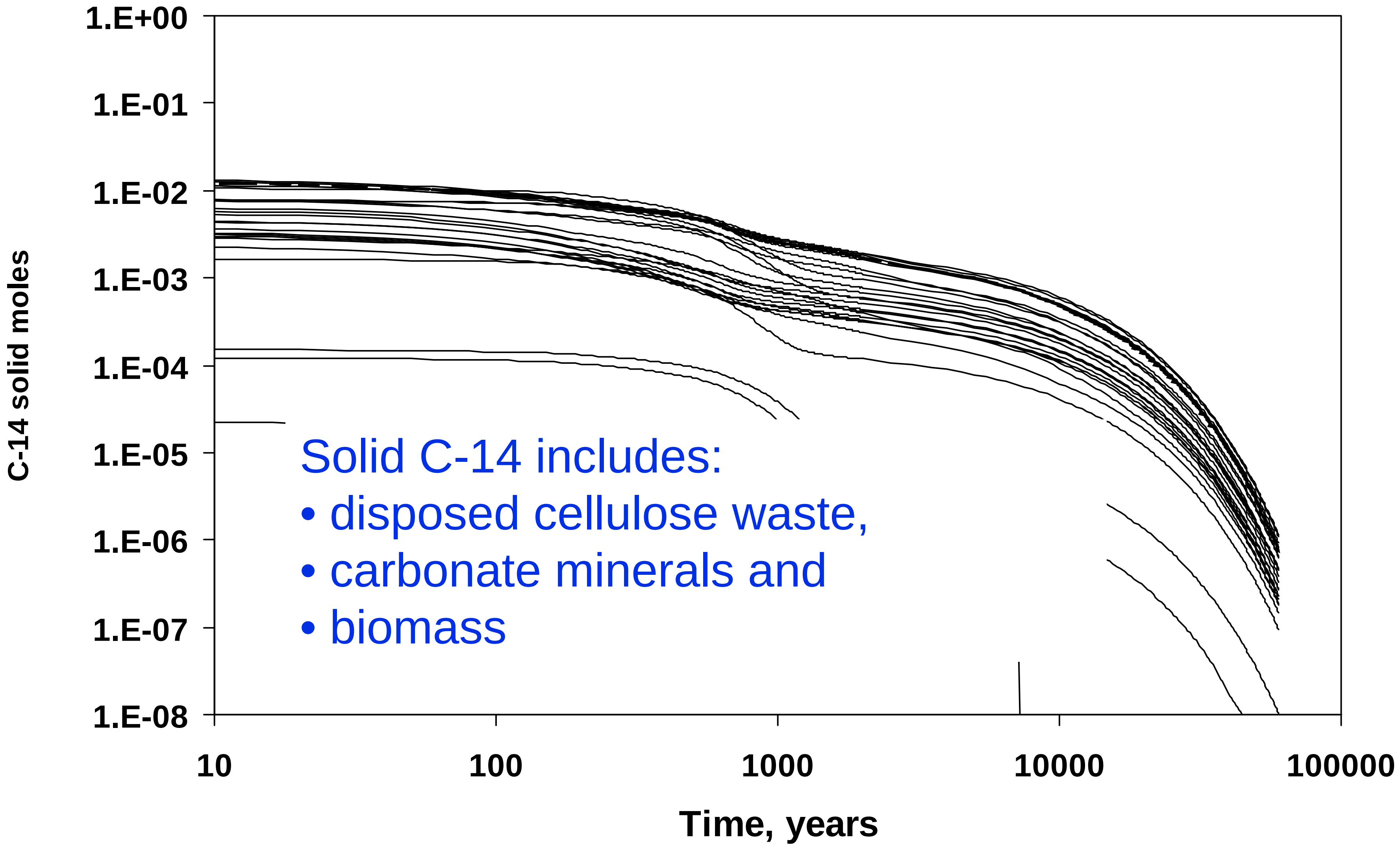


Aqueous considers HCO_3^- & CH_3COO^- species

Model Results:
C-14 gaseous - trench cells



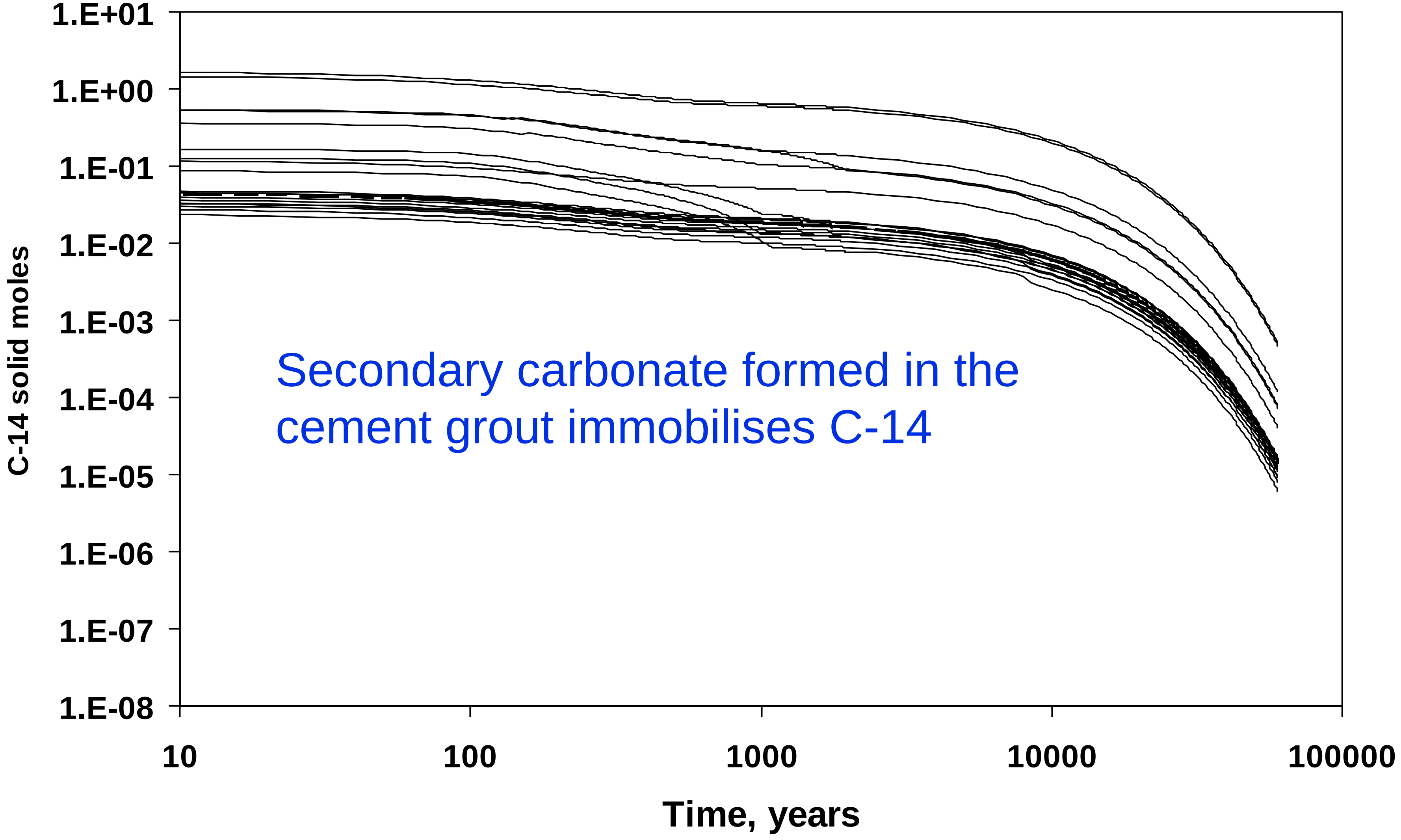
Model Results:
C-14 solid - trench cells



Solid C-14 includes:

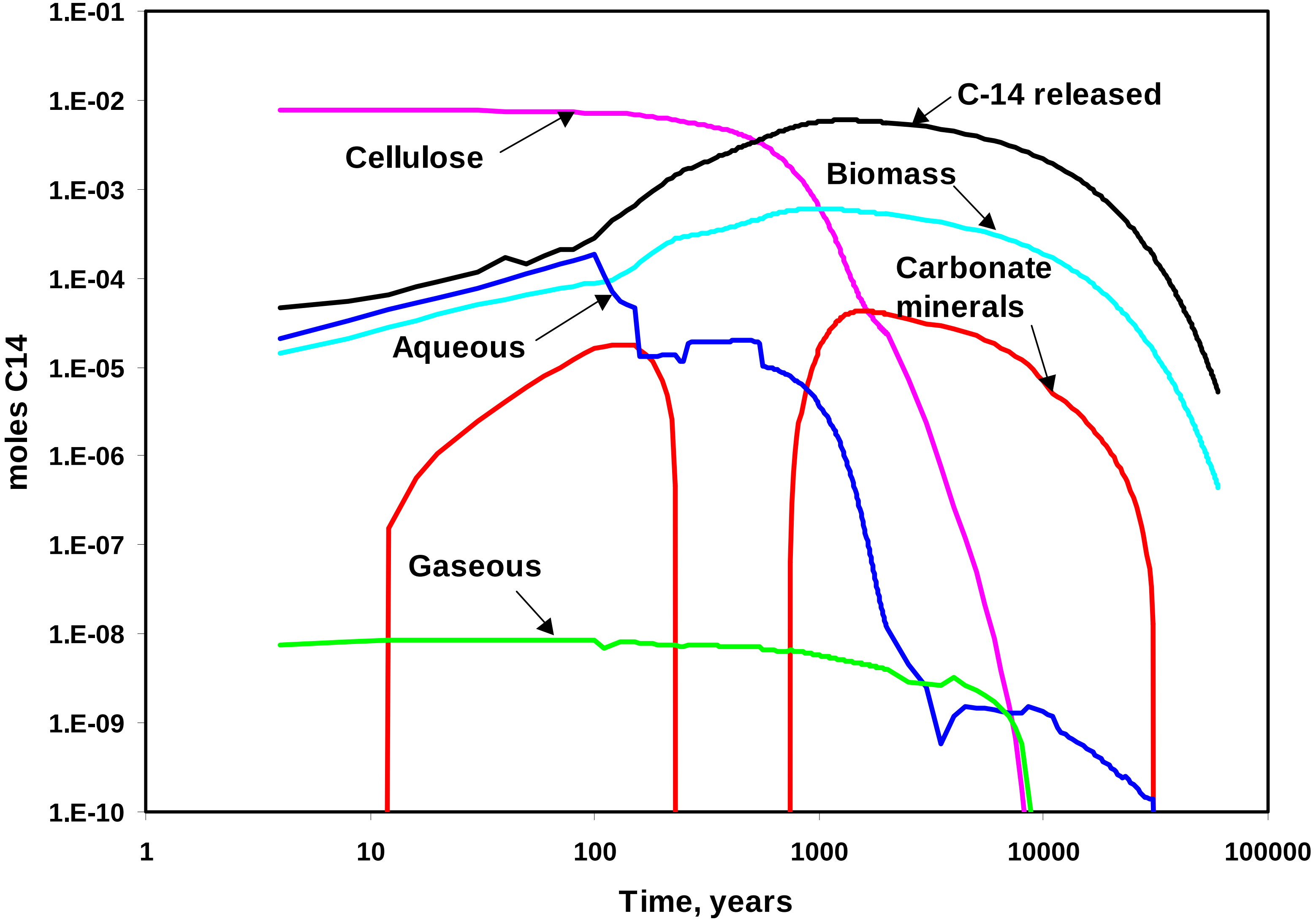
- disposed cellulose waste,
- carbonate minerals and
- biomass

Model Results:
C-14 solid - vault cells

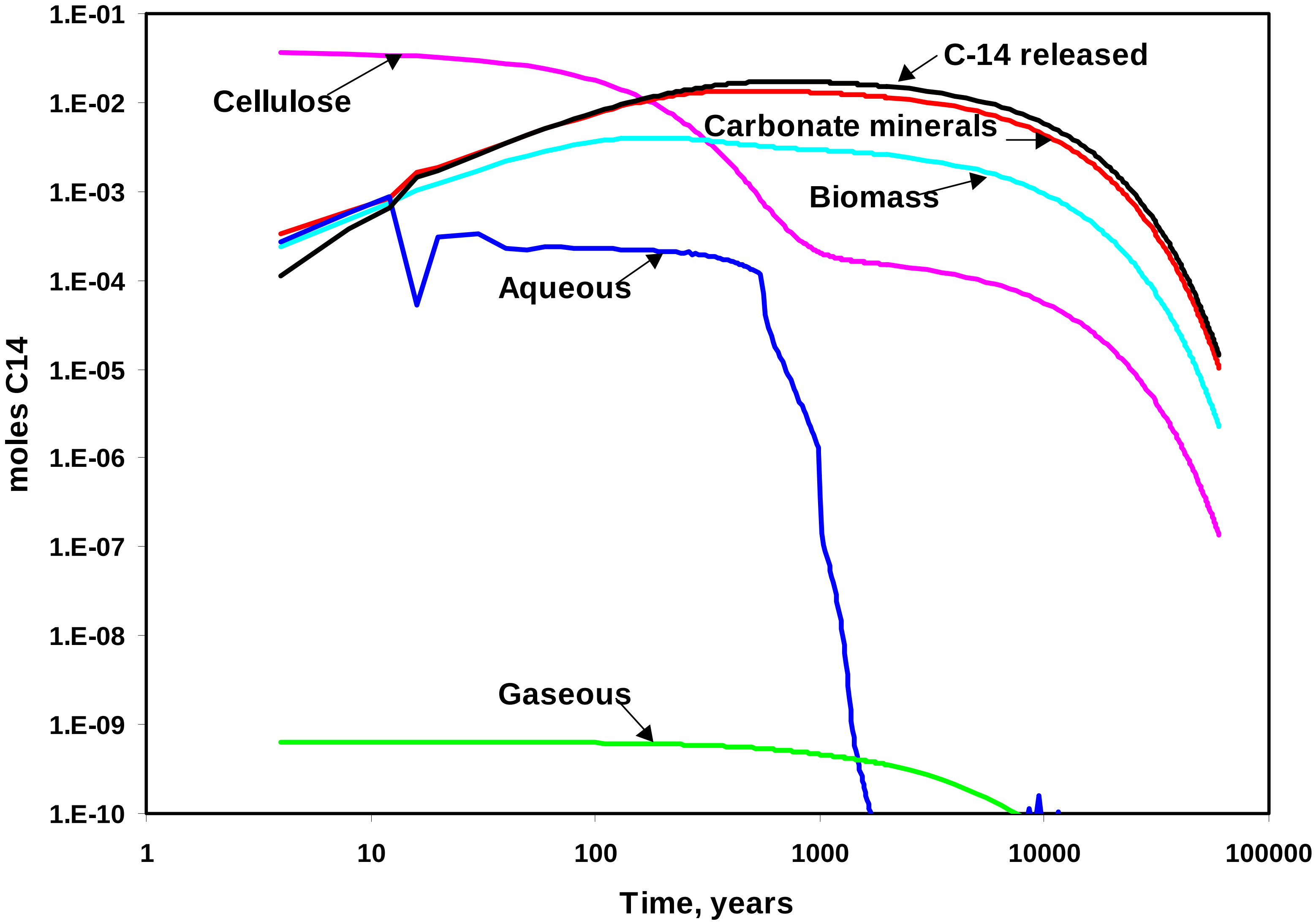


Secondary carbonate formed in the cement grout immobilises C-14

C-14 modelled redistribution - single trench cell



C-14 modelled redistribution - single vault cell



Isotope fractionation

The fractionation of C-14 and C-12 during biogeochemical processes has the potential to influence the partitioning of C-14 during waste degradation.

C-13/C-12 fractionation is extensively researched and is an important geochemical tool. Fractionation results from slight differences in the strength of chemical bonds of C-12, C-13 and C-14.

Fractionation affects both inorganic and biological processes and there is the potential to deplete or enrich C-14 in products of LLW degradation.

Consideration of isotope fractionation

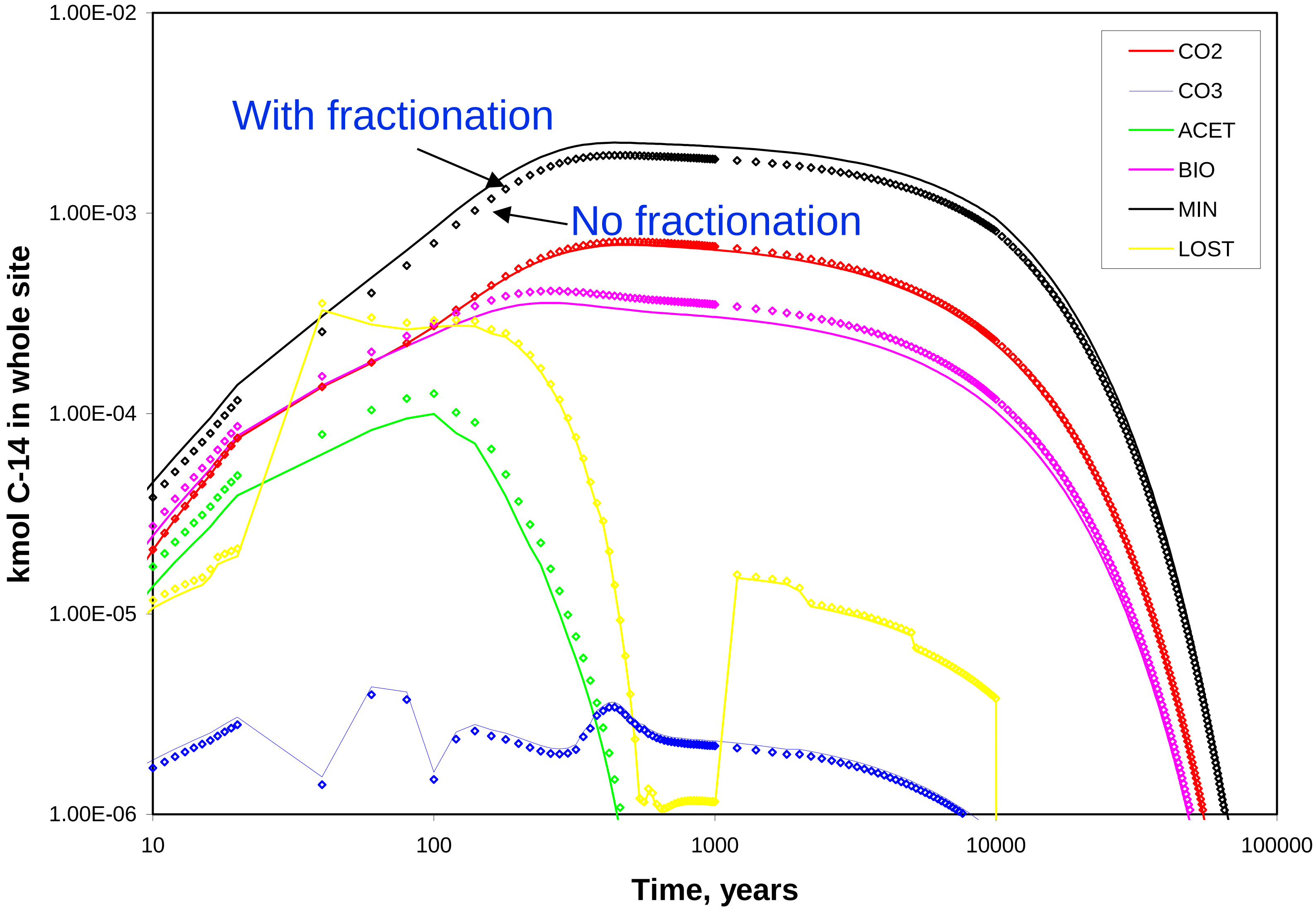
The extent of isotopic fractionation between two phases (A&B) is given by the fractionation factor α.

$$\alpha_{A-B} = \frac{{}^{13}C_A / {}^{12}C_A}{{}^{13}C_B / {}^{12}C_B}$$

Phase	***Fractionation Factor (α)***
CO_2 gas (reference)	1.0
Dissolved Carbonate	1.1
Acetate	0.8
Microbial Biomass	0.9
Carbonate Minerals	1.2

Estimated values of α for C-14/C-12 for reactions between species in the GRM model

Effect of fractionation



Summary

- In LLW microbial and geochemical processes influence the reactions of carbon and hence the release and transport of C-14

- A modelling approach has been developed to examine the partitioning and release of C-14 from LLW through the gaseous and aqueous pathways

- Isotope fractionation effects have been considered and have been shown to be insignificant

- The model has been used to provide a cautious-realistic assessment of C-14 release for the Drigg safety case which shows that around 80% of the C-14 inventory is immobilised by chemical processes within the near-field

Modelling the generation of C-14 containing gases

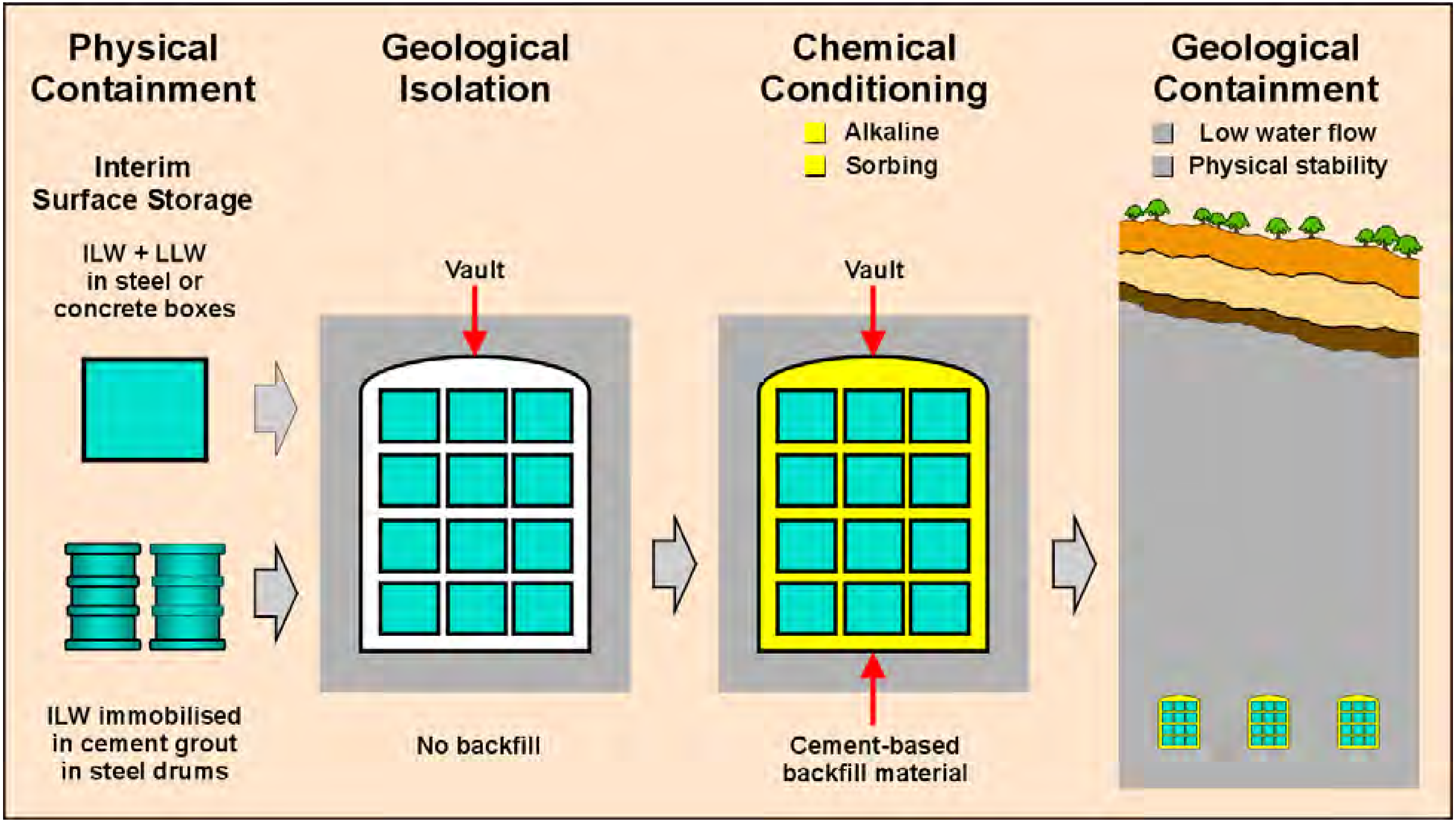
Sarah Vines

October 2003

Nirex

Nirex is the UK waste management organisation, providing options for the long-term management of radioactive materials

Phased Geological Long-term Management Concept



Physical Containment

Interim
Surface Storage

ILW + LLW
in steel or
concrete boxes

ILW immobilised
in cement grout
in steel drums

Geological Isolation

Vault

No backfill

Chemical Conditioning

- 🟨 Alkaline
- 🟨 Sorbing

Vault

Cement-based
backfill material

Geological Containment

- ◼ Low water flow
- ◼ Physical stability

nirex

Assessments of gas generation for

- Providing packaging advice to waste producers
- Modelling the operational period of a repository
- Modelling the post-closure period of a repository

C-14

C-14 has the potential to be a key radionuclide in the gas pathway

So far only C-14 in organic waste considered in gas assessments

Wastes containing C-14 in the 1998 UK inventory

- Irradiated steel, 1670 TBq (Hydrocarbons?)
- Irradiated Zircaloy, 21 TBq ("Organic form"?)
- Irradiated Magnox, 29 TBq (acetylene?)
- Irradiated uranium, 4.7 TBq (methane etc?)
- Irradiated aluminium, <7 TBq (methane?)
- Irradiated graphite, 1800 TBq (dissolved CO_2?)
- Barium carbonate, 205 TBq (no gas release)
- Organic molecules, 670 TBq (CO_2 or CH_4)

Further work on sources of C-14

- Graphite experiments ongoing
  - Alkaline leaching of graphite, with gas measurement
- Metal carbides
  - Data presented here?
  - Monitoring of Magnox wastes during packaging

New model of gas generation (SMOGG)

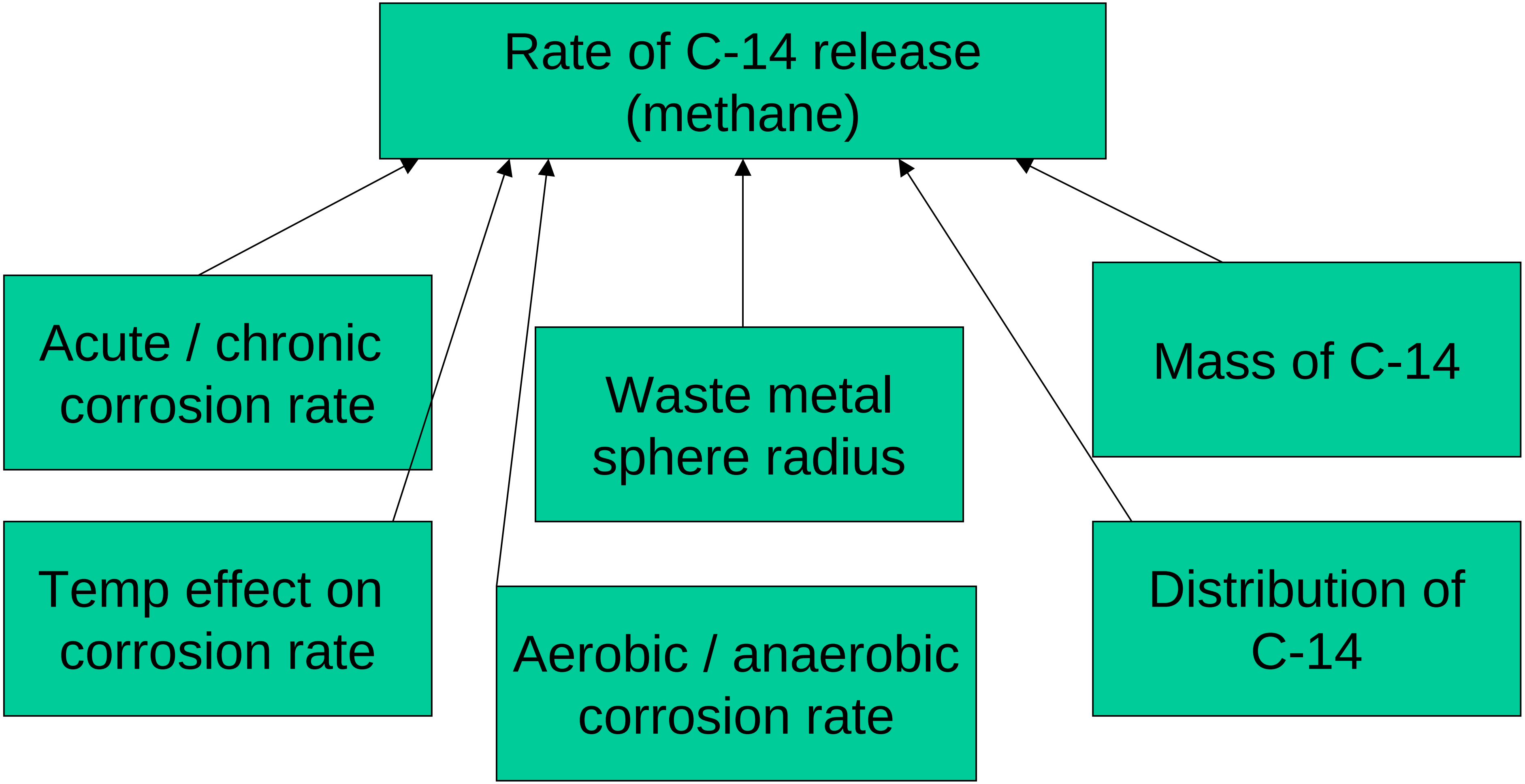
Considers release of C-14 in gas from

- Corrosion of irradiated metal
- Leaching of irradiated graphite
- Microbial degradation of organic molecules

Conditions

- Water
  - Initial amount specified by the user
  - Additional water from diffusion & resaturation
  - Eventually becomes unlimited
- Oxygen
  - aerobic during transport and storage
  - becoming anaerobic post closure
- Temperature
  - Profile set by the user

Corrosion



Rate of C-14 release (methane)

Acute / chronic corrosion rate

Temp effect on corrosion rate

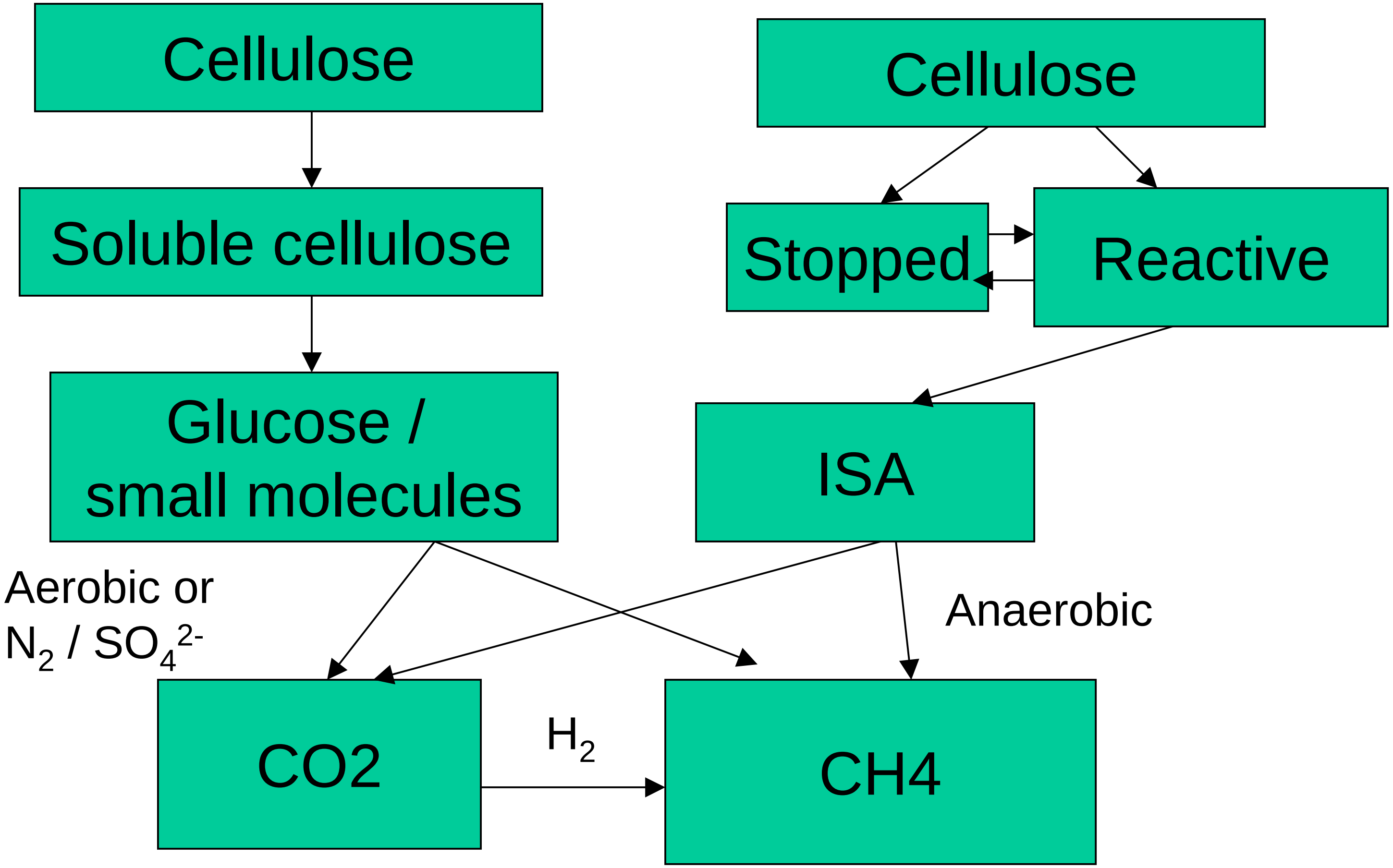
Waste metal sphere radius

Aerobic / anaerobic corrosion rate

Mass of C-14

Distribution of C-14

Microbial degradation of organic waste - Reaction scheme



Cellulose

Soluble cellulose

Glucose / small molecules

Cellulose

Stopped

Reactive

ISA

Aerobic or N_2 / SO_4^{2-}

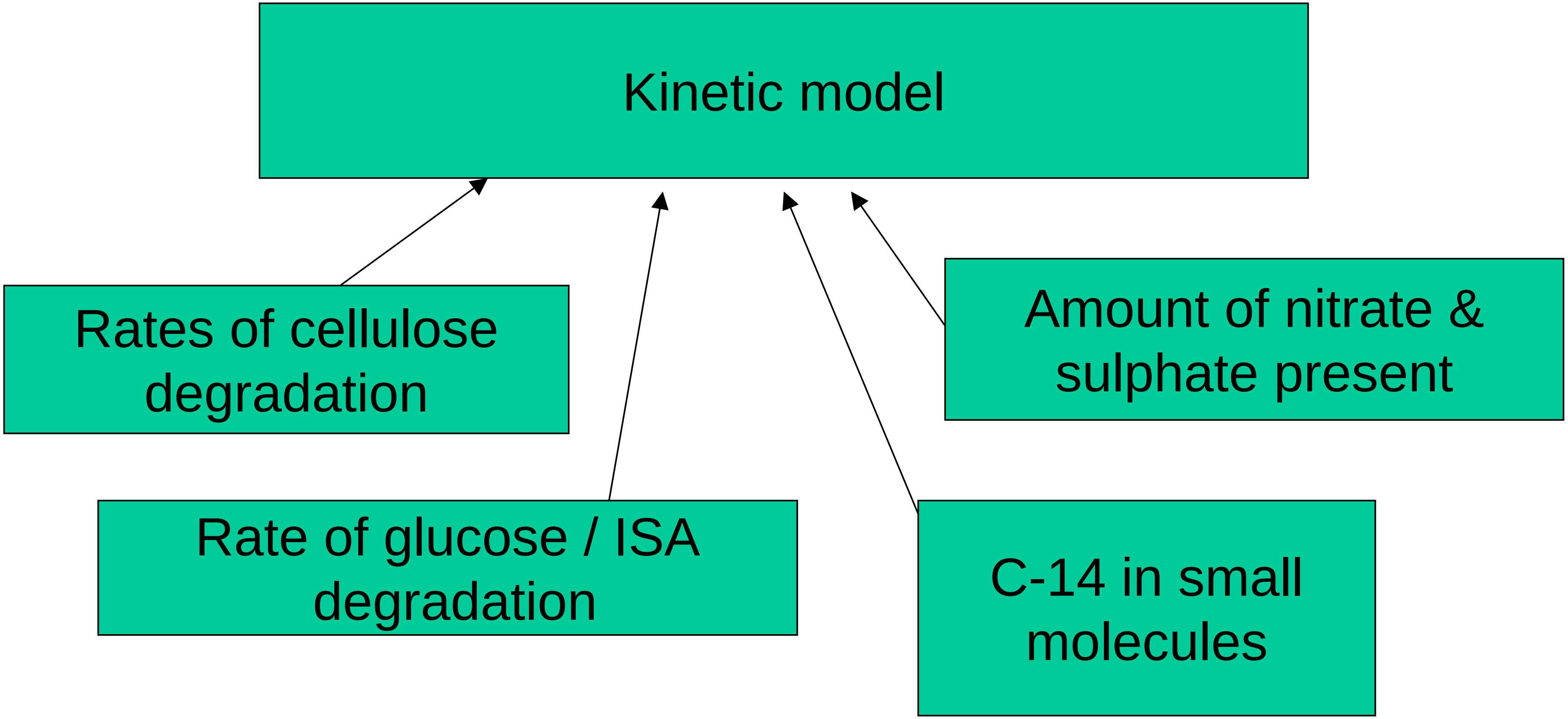
Anaerobic

CO2

H_2

CH4

Microbial degradation (2)



Kinetic model

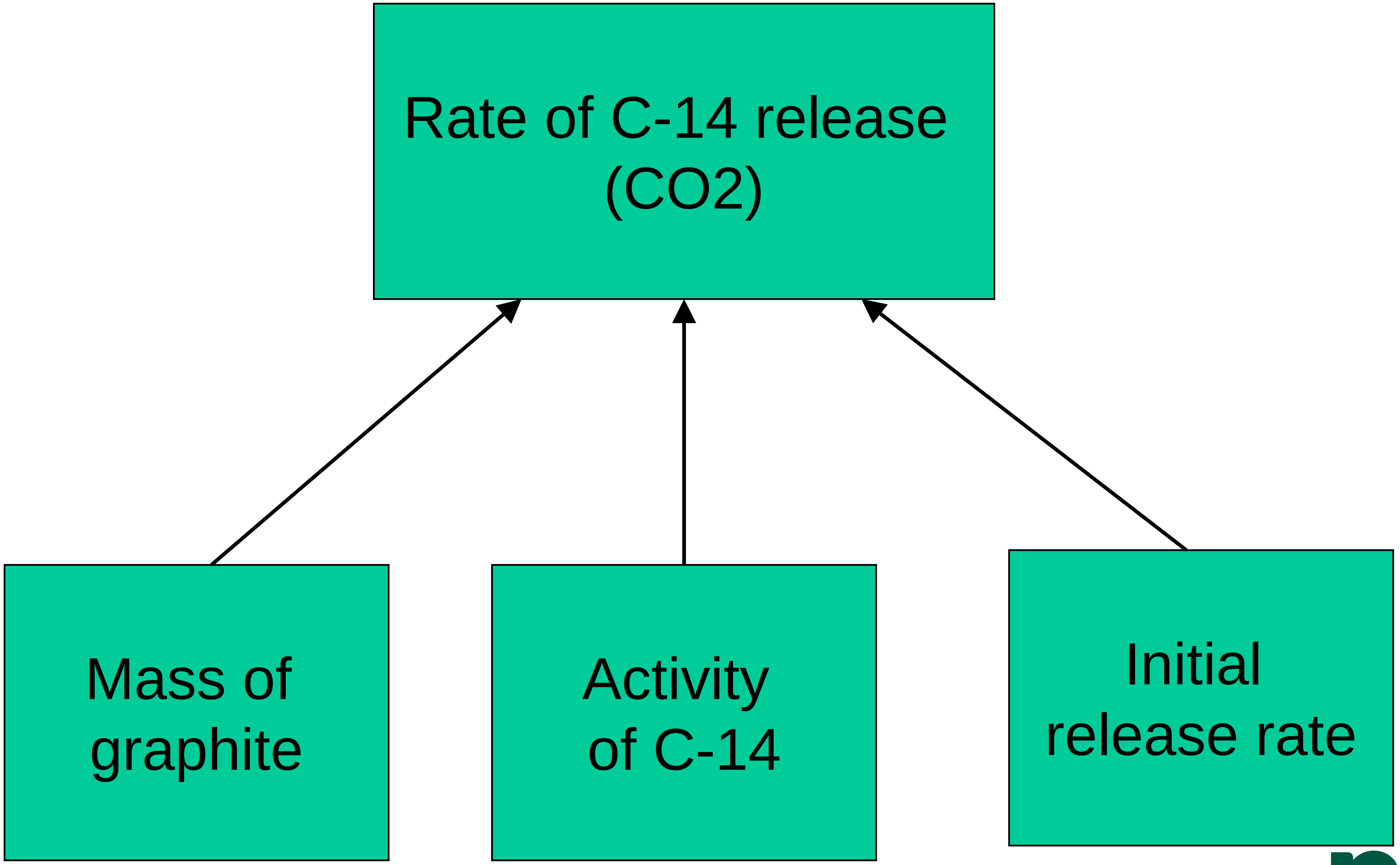
Rates of cellulose degradation

Rate of glucose / ISA degradation

C-14 in small molecules

Amount of nitrate & sulphate present

Graphite leaching



Rate of C-14 release (CO2)

Mass of graphite

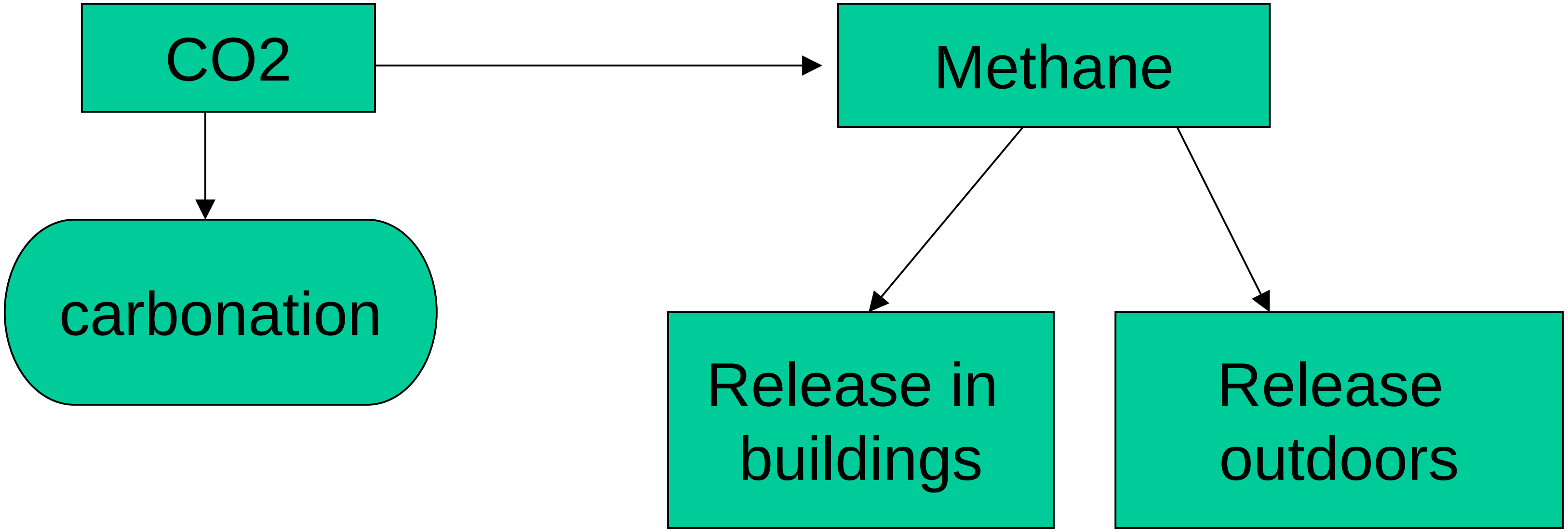
Activity of C-14

Initial release rate

Carbonation

Fraction of CO_2 removed
by carbonation

Radiological consequences



CO2

carbonation

Methane

Release in buildings

Release outdoors

Risk depends on:
Release area
Consumption by microbes in soil
Tolerable release rate is 2.4 10^{-3} TBq/year,
to surface area 10,000m^3

Comparison with GAMMON

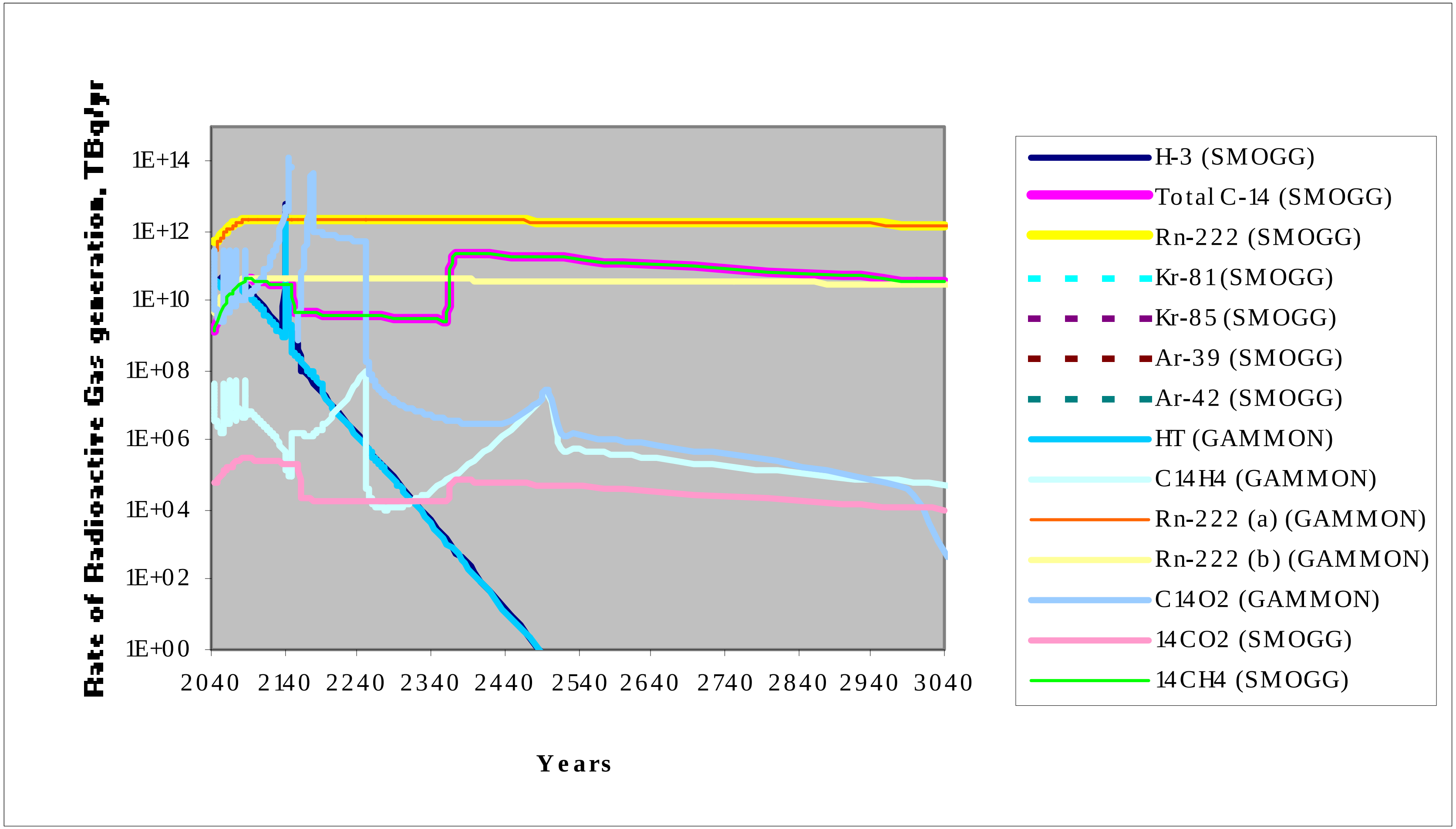
- Comparison of new model with GAMMON
- GAMMON represents complex microbial reactions - difficult to validate
- C-14 from microbial degradation only (both GAMMON and SMOGG)
- SMOGG calculates more CH_4 and less CO_2

Repository Operation and Closure Timing and Conditions, GAMMON & SMOGG Models

Stage	Year	Temp (^oC)	Water availability	Oxygen availability
Emplacement	2040 - 2090	35	Pore space in containers initially water filled	Aerobic
Care and maintenance	2090 - 2140	35	Continue	Aerobic
Backfilling and closure	2140-2150	80 for 5 years 50 for 5 years	Continue	Aerobic
Post-closure	2150 -	50 for 100 years 35 subsequently	Resaturates all pore space	Oxygen present at closure is consumed

nirex

Comparison of SMOGG and GAMMON Active Gas Generation Rates, on Basis of Unshielded Intermediate Level Waste Inventory from 2003 Update of Generic Documents



Summary & Key issues

- Potential sources of C-14 have been identified
- A model has been developed, which can calculate a source term
- Key unresolved issues
  - C-14 release from irradiated materials
  - Carbonation
  - Data
  - Differences in software output

添付資料 3

T.Yamaguchi, S.Tanuma, H.Tanabe,
et al.,
“A Study on Chemical Forms and
Migration Behavior of Radio
nuclides　in Hull wastes,”
Radioactive Waste Management and
Environmental Remediation
(ICEM 1999),
Nagoya, Japan, (1999).

A STUDY ON CHEMICAL FORMS AND MIGRATION BEHAVIOR OF RADIONUCLIDES IN HULL WASTES

Takashi Yamaguchi and Susumu Tanuma
Kansai Electric Power Co.

Isamu Yasutomi, Tadashi Nakayama and Hiromi Tanabe
Radioactive Waste Management Center

Kiyomichi Katsurai, Wataru Kawamura and Kazuto Maeda
Mitsubishi Heavy Industries Ltd.

Hideo Kitao and Moriyuki Saigusa
Nuclear Development Co.

ABSTRACT

A hot test using real hull was conducted, to evaluate chemical forms, migration behavior and other properties of C-14 and nuclides in the hull waste, with large contributions to a dose equivalent to TRU waste disposal. As a result of hull specimen without oxide film radioactive inventory analysis, the inventory of C-14 was 9.9 x 10^4Bq/35mm sample (3.0 x 10^4 Bq/g), roughly matching ORIGEN 2 calculation results. The leaching test results showed that the chemical forms of C-14 leached from the hull are organic and that the oxide film influences leaching speed. A study of a C-14 leaching model, based on leaching test results and reference data show a possibility of leaching from the oxide film diffusing out. There is also a possibility of film formation after corrosion and diffusion inside the film for the leaching from base material. On the basis of this leaching scenario, an evaluation of the leaching period of C-14 was conducted.

Keywords: TRU waste disposal, hull waste, C-14, chemical form, inventory, distribution coefficient.

INTRODUCTION

In TRU waste disposal, C-14 and Cl-36 in hull waste are considered nuclides which contribute substantially to radiation exposure. C-14 in particular, is considered an important nuclide with considerable influence on disposal notion, and stability and economy in disposal.

However, observational data on the leaching rate of C-14 in hull waste and its distribution coefficient in barrier material have not been obtained, resulting in a rather conservative parameter setting in safety evaluation. For this reason, the possibility of C-14 or Cl-36 becoming a dominant nuclide in safety assessment and exerting influence on the current disposal concept is now being examined.

The purpose of this study was to contribute to the establishment of an optimum disposal concept by obtaining and evaluating data on hull waste radiation, its leaching behavior and the distribution coefficient for cement which is an engineered barrier material.

TEST DESCRIPTIONS

Fabrication of Hull Specimens

Most of C-14 in zircaloy is generated as an activation product of nitrogen, contained as an impurity in zircaloy. [^{14}N (n,p) ^{14}C] There is no difference in this generation mechanism according to the type of light water reactor, so the hull specimen for the hot test in this research was prepared from PWR spent fuel (burn-up: 47.9GWd/t).

In our hull specimen preparation method, the treatment method of spent fuel was similar to the one in a reprocessing plant, but there was no dissolution of fuel pellet, which was first eliminated by a mechanical process, followed by the dissolution and cleaning of a small amount of attached pellet powder in the same dissolution conditions as in a reprocessing plant.

In this study, the following three types of specimen, were prepared to examine differences in radioactive inventory and leaching behavior between zircaloy base material and oxide film: 1) Hull specimen 2) Hull specimen without oxide film 3) Oxide film (separation treatment from hull specimen) The hull specimen without oxide film was prepared by mechanical scraping, and the oxide film was prepared by compressing the hull specimen.

Radioactive Inventory Analysis

For conducting the analysis of radioactive inventory in hull, the whole hull specimen was dissolved by acid, and an analysis of nuclides in the solution and the off-gas was carried out. The following three types of specimen were analyzed: 1) Hull specimen 2) Hull specimen without oxide film 3) Oxide film. After the solution undergoes refining treatment and sodium hydrate, which is the off-gas trap, the measurement of C-14 and Cl-36 is conducted by beta liquid scintillation counting. The measurement of gamma-ray nuclide was conducted by a gamma spectrometry of the solution.

Leaching Test of C-14 in an Environment Simulating a Disposal Environment

For the C-14 leaching test, the following two types of tests were planned: 1) Short-term test focusing on grasping the leached C-14 chemical form, and 2) Long-term test focusing on leached volume. The composition of the test solution was decided from the calculation results using the geochemical calculation code PHREEQE (2, 3) by assuming a reaction between concrete and sea-water-derived groundwater, which is considered to provide conditions for the most advanced corrosion of hull. In the short-term test, the specimen was compressed in order to increase the surface area to volume ratio with the purpose of accelerating the leaching process. This was based on the prediction that the nuclide leaching behavior from the hull waste differs from the leaching from oxide film and the leaching from hull base material. A test was conducted on two types of specimen, the hull specimen and hull specimen without oxide film. The test conditions are shown in Table I.

TABLE I

Test Parameters of the Leaching Test

Item	Test specimen and test solution / batch					Test period
	Specimen form	Specimen volume used	Test solution characteristics	Test solution volume	Specimen surface area per unit volume	
Short-term test	Hull specimen (compressed)	35mm x 2	Cement equilibrium simulated groundwater	1 liter	40cm^2 / liter	3 months 5.5 months
Long-term test	Hull specimen	35mm x 5	Cement equilibrium simulated groundwater	10 liters	10cm^2 / liter	5.5 months 9 months 11.5 months
	Hull specimen without oxide film	35mm x 5	Cement equilibrium simulated groundwater	10 liters	10cm^2 / liter	5.5 months 9 months 11.5 months

Figure 1 shows the conceptual plan of the leaching test. A stainless steel container was placed in a hot cell and the hull specimen was put in the test container. After displacement by argon was conducted in the test container, reductant cement equilibrium simulated groundwater prepared outside the hot cell was poured into the test container through a tube. With the conditions of the immersion environment simulating those of groundwater environment, the test container was left to stand and stored for a certain period of time.

From reference (4) and (5) concerning the chemical forms of C-14 released from zircaloy, there is a possibility that the leached C-14 may exist in the chemical forms of CO_2 and CO/CH_4 in gas phase. Therefore, a wet analysis was conducted to judge whether the C-14 in liquid phase is organic or inorganic, as shown in the analysis flow in Fig. 2.

In this method of analysis, inorganic carbon in the sample solution is brought into contact with inorganic acid to form carbon dioxide and discharged for a measurement as inorganic carbon. Next, oxidizing agent is added to the remaining sample to oxidize and discharge all carbon as carbon dioxide for its measurement as organic carbon. For the C-14 in gas phase, the following method was employed for separation and recovery. C-14 in CO_2 form is first absorbed into sodium hydroxide solution, then C-14 in CO form is converted into CO_2 by a catalyst and is absorbed into a sodium hydroxide solution. Finally, C-14 in CH_4 form is burned for conversion into CO_2 and absorbed into the sodium hydroxide solution.

Obtaining Test of the Barrier Material's Distribution Coefficient

To examine the migration behavior of leached C-14 in engineered material, an obtaining test of the distribution coefficient for two types of cement barrier material using the leached solution obtained in the leaching test was conducted. In order to simulate the disposal environment, the test was conducted inside a glove box controlled by argon gas-displaced atmosphere. 1L leaching solutions were poured into polypropylene bottles, and after the oxidation-reduction potential was lowered by iron powder, 100g of material was added and the solutions were left to stand for 7 days. After the immersing test, the solids and liquids were separated by filtering, and an analysis of C-14 in the filtered liquid was conducted using wet analysis. The test conditions are shown in Table II.

TEST RESULTS

Radioactive Inventory

Table III shows the inventory analysis results. The volume of C-14 in the hull specimen was 1.2 x 10^5Bq/35mm sample (3.2 x 10^4Bq/g), which matched the total of the volumes separately analyzed for the hull specimen without oxide film and the oxide film, thus achieving mass balance. The C-14 volume in the oxide film was approximately 17%.

Cl-36 was detected with a concentration lower than that of C-14 by three digits. Among other radionuclides, the gamma nuclides of Co-60, Cs-134, Cs-137, Eu-154, Ru-106/Rh-106 and Sb-125 were detected.

Leaching Test of C-14 in a Simulated Disposal Environment

Table IV shows the results of the short-term leaching test. The leached C-14 was not detected in the chemical form of CO_2, CO or CH_4 in the gas phase, most of it in organic forms were detected in the liquid phase. Thus, most of the leached C-14 must was presumed as organic compounds in the liquid phase. Filtering the leached liquid with an anion filter showed that most of the C-14 exists in the filtered liquid and that, as a result of this, there is a possibility of C-14 existing as a substance other than organic acid. However, the concentration of the leached C-14 was too small, with 0.1 Bq/ml, to identify the chemical species.

Figure 3 shows the results of the long-term leaching test with the volume of C-14 leached against time. Similar to the short-term test, C-14 was detected in the liquid phase not in the gas phase and, most of it in organic forms. The volume of C-14 leached from a hull specimen without oxide film was one digit less compared to C-14 leached from the hull specimen, showing an obvious difference of the existence or absence of oxide film. The rate at which the volume was leached decreased with time. The leached nuclides that were detected included Co-60, Cs-134, Cs-137, Eu-154, Ru-106/Rh-106 and Sb-125 aside from C-14, but Cl-36 was not detected.

Conducting a Measurement Test for the Distribution Coefficient of Material

Table V shows the concentration of C-14 in the solutions before and after the test and the distribution coefficient obtained from the result. The distribution coefficient is expressed in the following equation.

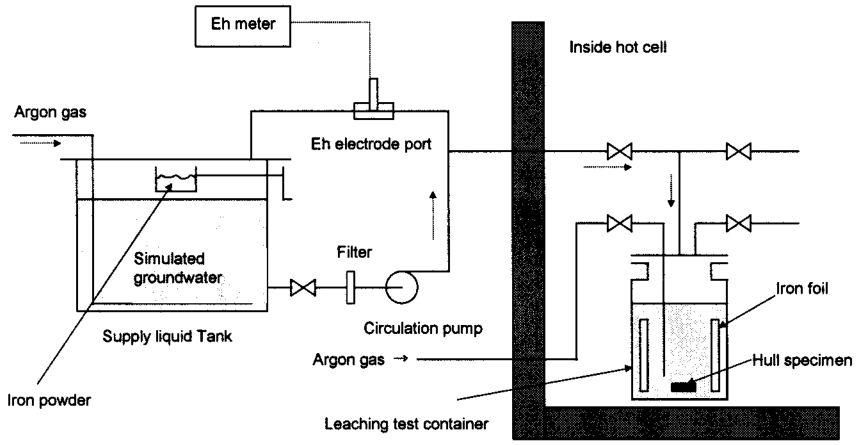


Fig. 1. Leaching test outline diagram.

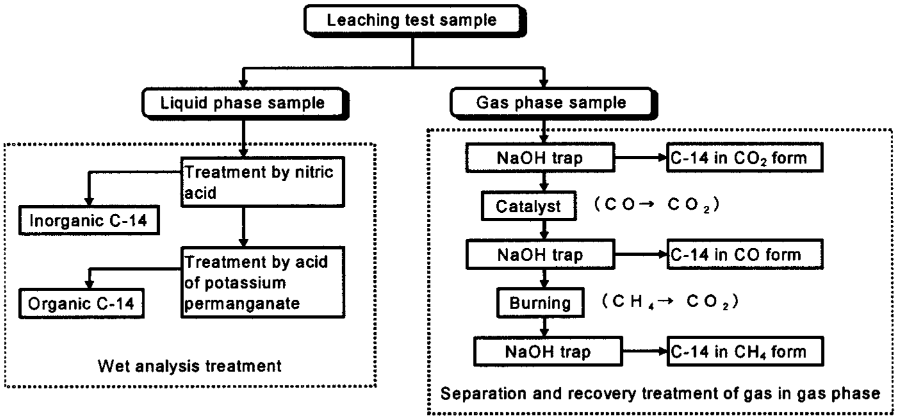


Fig. 2. Leaching test sample analysis flow.

TABLE II

Test Conditions for Obtaining Distribution Coefficient Data

Item	Conditions
Barrier material	(1)OPC (2)1/9 cement (OPC/BFS)
Test solution	Leached liquid obtained from the leaching test
Solid-to-liquid ratio	1 : 10
Test period	1 week
Test temperature	Room temperature

$$Kd=(Co/Ce-1)\ V/W$$

The symbols stand for the following:

Kd	: distribution coefficient
Co	: initial concentration of C-14 (Bq/ml)
Ce	: concentration of C-14 after the test (Bq/ml)
V	: test solution volume (ml)
W	: barrier weight (g)

For the distribution coefficient of C-14 for material, values were in the range of 1.9~8.8 ml/g. There was no significant difference in distribution coefficient according to the type of material between OPC cement and 1/9 (OPC/BFS) cement. There was also no significant difference in the liquid leached from the hull specimen and the hull specimen without the oxide film.

DISCUSSION

C-14 Inventory

Table VI shows the C-14 analysis values obtained as a result of inventory analysis and C-14 calculation results by ORIGEN-2. In the ORIGEN-2 calculation, the value of the impurity nitrogen, from which C-14 was generated, was calculated by the nitrogen concentration according to JIS chemical composition standard (6) of zircaloy. It value is considered to be the maximum value of nitrogen. As a result, the values calculated from JIS chemical composition standard values were approximately two times as much as the inventory analysis values, and can be considered as conservative values in the inventory evaluation of C-14 in hull. If the analysis value of nitrogen in zircaloy is used to ORIGEN-2 calculation, it is estmated that the calculation result more match the inventory result.

TABLE III

Inventory Analysis Results

	Hull specimen	Hull specimen without oxide film	Oxide film
C-14 (Bq/35mm length)	1.2×10^5	9.9×10^4	2.0×10^4
Cl-36 (Bq/35 mm length)	2.7×10^2	2.1×10^2	1.1×10^1

TABLE IV

Results of the Short-term Test

No.	Test period	Liquid phase		Gas phase			Total
		Inorganic C-14	Organic C-14	CO_2	CO	CH_4	
RUN-1	3 months	<0.1 Bq (0.1%)	102.2 Bq (100%)	<0.1 Bq (0.1%)	<0.1 Bq (0.1%)	<0.1 Bq (0.1%)	102.2 Bq
RUN-2	5.5 months	18.5 Bq (21.1%)	69.5 Bq (78.9%)	<0.1 Bq (0.1%)	<0.1 Bq (0.1%)	<0.1 Bq (0.1%)	87.5 Bq

*The specimen is a compressed hull with oxide film.

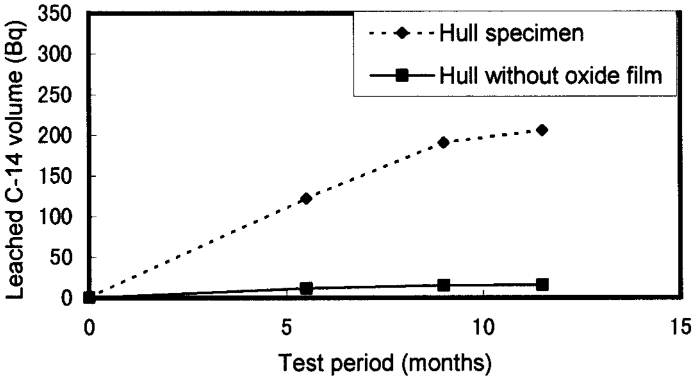


Fig. 3. Change of C-14 depending on time in the long-term leaching test.

TABLE V

Results of the Distribution Coefficient Measurement Test

Barrier material	Test solution	C-14 concentration (Bq/ml)		Distribution coefficient (ml/g)
		Before test	After test	
OPC	Leached liquid from hull specimen	1.9×10^{-2} 1.9×10^{-2}	1.6×10^{-2} 1.3×10^{-2}	1.9 4.6
	Leached liquid from hull without oxide film	1.5×10^{-3} 1.5×10^{-3}	9.5×10^{-4} 1.2×10^{-3}	5.8 2.5
1/9 cement (OPC/BFS)	Leached liquid from hull specimen	1.9×10^{-2} 1.9×10^{-2}	1.4×10^{-2} 1.5×10^{-2}	3.6 2.7
	Leached liquid from hull without oxide film	1.5×10^{-3} 1.5×10^{-3}	1.1×10^{-3} 8.0×10^{-4}	3.6 8.8

Chemical forms of C-14 in the Leached Liquid

The results of the leaching test, confirmed that most of the C-14 released from the hull and existing in the leached liquid are in organic forms. From a thermodynamic viewpoint, the disposal environment has reduction atmosphere conditions with oxidation-reduction potential at approximately -300mV, further it is estimated that the oxidation-reduction potential is even lower in the phase boundary in which the corrosion of zircaloy occurs, a region where methane and methanol exist in stable forms according to the Pourbaix chart (7). Adding to this condition, there is much hydrogen generated from reduction condition corrosion of Zr (i.e. Zr + 2H$_2$) → ZrO$_2$ + 2H$_2$). The ratio of the released number of atoms of C to H from one atom of Zr may be estimated to be about 1 : 10^3 if the concentration of C in zircaloy metal is 270ppm according to JIS specification. Thus, there is a high possibility that the released C-14 exist as those organic matters.

TABLE VI

Comparison of Analysis Results with ORIGEN-2 Calculation Results

	Inventory analysis results [a]	ORIGEN-2 calculation results [b]
C-14 (Bq/g)	3.0×10^4	6.3×10^4

a) The unit is converted from inventory analysis results of hull specimen without oxide film.

b) Nitrogen content : 80ppm (JIS specication)

The chemical forms of C-14 in the hull is not clear, there is a possibility that it may exist in graphite or carbon compounds forms including ZrC (zircaloy carbide). These forms are generally stable. However, there is a report that hydrocarbon compounds linking multiple carbon atoms are generated from iron carbide in an iron / water system containing carbon (8), which implies the possibility of carbon compounds that are contained in a metal becoming organic matters when released from the metal in a metal / water system.

The chemical forms of C-14 leached from the hull is important in determining the retention functions of the nuclide in the barrier material.

Although the chemical species of the leached C-14 could not be identified due to its low concentration, obtaining data concerning the identification of its chemical species, generation mechanism and migration in a disposal environment is considered important for the near future.

Study of the Concept of the Leaching Model

From the long-term leaching test results, the rates of leaching were evaluated for C-14 and other nuclides, resulting in a grasp of the leaching trend of each nuclide. Figures 4 show the change depending on time of the rate of leaching from hull specimen and from hull specimen without oxide film for each nuclide.

The leaching rate of each nuclide is defined as follows:

$$R=A_1/A_0$$

R : leaching rate (-)

A_1 : leached nuclide (Bq)

A_0 : nuclide in hull (Bq)

Although no major difference is observed in the leaching rate for each nuclide, leaching rate values are different for each nuclide, which is true in hull specimen and hull specimen without oxide film alike. Fission products (FP nuclides) such as Cs-134 and Cs-137 show a higher leaching rate than C-14, which can be attributed to the uneven distribution due to implantation of FP nuclides into the hull or the dissolution of nuclides attached on oxide film. On the other hand, leaching rates are lower for activation products (AP nuclides) such as Co-60 or Sb-125 than for C-14. Their incorporation into the film of zirconium oxide generated with corrosion of zircaloy is a possible cause for this.

Because there were differences in leaching behavior, the 'scenario' of C-14 from its existence inside the hull to leaching was sorted out by identifying processes including the following as individual scenarios: 1) diffusion in base material 2) diffusion in oxide film 3) congruent dissolution with oxide film 4) corrosion of base material → formation of oxide film 5) desorption of attached substances From these scenarios, the leaching scenario

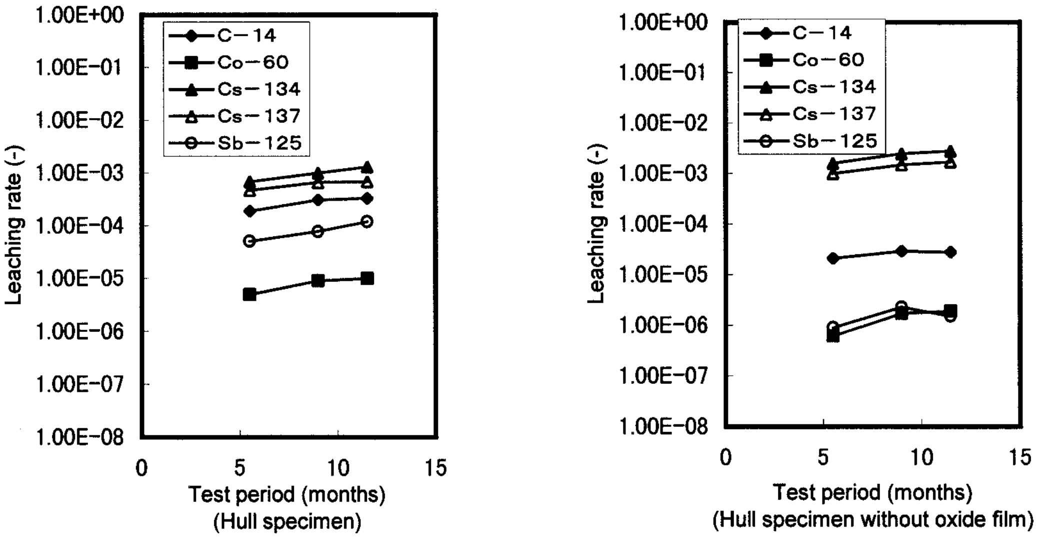


Fig. 4. Change depending on time of the leaching rate.

of C-14 was examined, with the oxide film and base material as the source for generation.

Using reference data (9), (10), (11) and (12), a trial calculation of the leaching volumes in these scenarios was performed and the calculation results were compared with the long-term leaching test results, to evaluate the validity of these scenarios. For the diffusion coefficient, temperature correction was made to reference data for conversion to values at room temperature. Table VII shows the results of studying the validity of the leaching scenario. For the hull specimen, the degree of corrosion influence was small, implying a possibility of the influence of diffusion and attached substances. The evaluation using diffusion coefficients from the reference materials by Smith, et al. (9) matched well with the test results. For the hull specimen without oxide film, it became clear that the influence of the corrosion scenario is extensive.

Inventory analysis results confirmed that the C-14 volume had the same concentration as in the base material that exists in the oxide film, there is a possibility of a mechanism in which C-14 is not released immediately by corrosion but is incorporated into the film and released by diffusion.

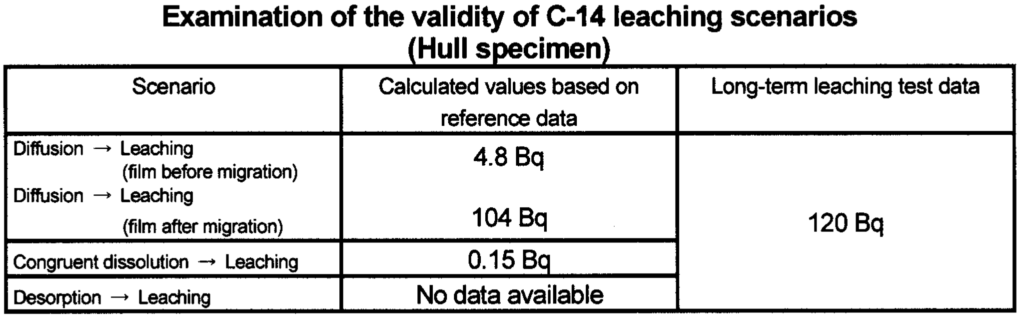
Based on the results of the long-term leaching test and a study of the leaching model, the period required for all the C-14 in hull to be leached out was calculated. The results of the long-term leaching test were classified, according to the leaching value curve, to initial and at-equilibrium states for the purpose of evaluation. From the leaching model, it was assumed that leaching conforms with 1/2 square-law of time for an evaluation of the base material and oxide film. From these results, it was evaluated that a minimum period of 20,000 years or longer is required for all of C-14 to be released from the hull. As C-14 has a half-life of 5,730 years, it became clear that there is a possibility that introducing the hull leaching model may reduce the dose equivalent of C-14. The challenge for the near future includes obtaining test data for establishing the C-14 leaching model for leaching from the hull.

SUMMARY OF THE RESULTS AND CONCLUSION

1) Hull specimen was prepared from spent fuel to conduct inventory analysis of C-14 and C1-36 and to immerse the hull specimen in the test solution simulating groundwater for a measurement of the leaching rate and chemical forms of C-14. By using the leached solution, an abtaining test of distribution coeffieient was carried out.
2) Results of the inventory analysis of C-14 showed that C-14 volume in hull specimen was 1.2 x 10^5 Bq/35mm sample (3.2 x 10^4 Bq/g) and C-14 volume in oxide film was 17%.
3) Two types of leaching tests were conducted. The short-term leaching test and the long-term leaching test. Most of the leached C-14 detected in the leached solution is in organic form, pointing to the need for future research to understand its generating mechanism and migration in barrier material. The results of the long-term leaching test made it clear that the existence or absence of oxide film has a considerable influence on leached volume.
4) By a comparison of the leaching test results data and the leached volume calculated from reference data, it was assumed, as the scenarios of C-14 leaching from the hull, that there is a possibility of diffusion for the leaching from oxide film and a possibility of film formation after corrosion and diffusion inside the film for the leaching from base material.

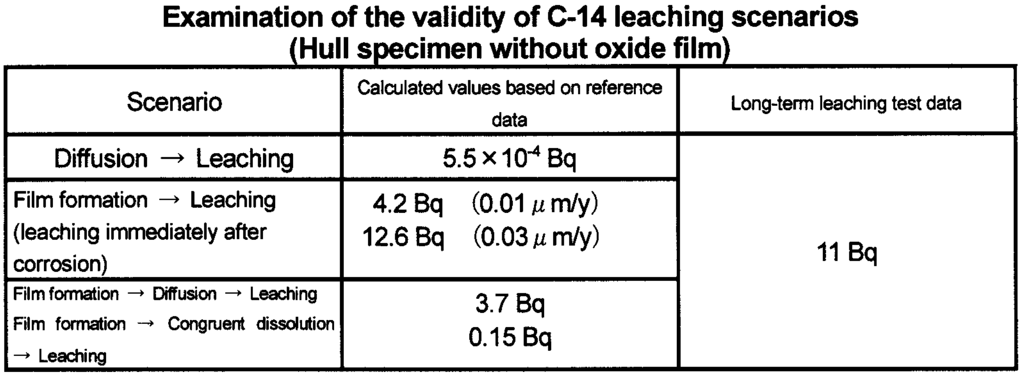
TABLE VII

Examination of the Validity of C-14 Leaching Scenarios



Examination of the validity of C-14 leaching scenarios (Hull specimen)

Scenario	Calculated values based on reference data	Long-term leaching test data
Diffusion → Leaching (film before migration)	4.8 Bq	120 Bq
Diffusion → Leaching (film after migration)	104 Bq	
Congruent dissolution → Leaching	0.15 Bq	
Desorption → Leaching	No data available	



Examination of the validity of C-14 leaching scenarios (Hull specimen without oxide film)

Scenario	Calculated values based on reference data	Long-term leaching test data
Diffusion → Leaching	5.5×10^{-4} Bq	11 Bq
Film formation → Leaching (leaching immediately after corrosion)	4.2 Bq (0.01 μm/y) 12.6 Bq (0.03 μm/y)	
Film formation → Diffusion → Leaching Film formation → Congruent dissolution → Leaching	3.7 Bq 0.15 Bq	

5) Based on this leaching model, it was calculated that the period required to leaching all the C-14 from the hull waste is 20,000 years or longer. This made clear the possibility that by introducing a leaching model, a dose equivalent of C-14 in hull waste may be reduced.

ACKNOWLEDGEMENT

This research was funded by the Japanese electric utilities and Japan Nuclear Fuel Limited.

REFERENCES

1. PNC, ‘Technical Report of Research and Development in High-Level Waste Geological Disposal, 1991 Report’
2. A. ATKINSON et al., ‘Evolution of pH in a Rodwaste Repository: Experimental Simulation of Cement Leaching,’ DOE/RW/89/025
3. E.J. REARDON, ‘Problems and Approaches to the Prediction of the Chemical Composition in Cement/Water System’
4. LOIS et al., ‘Investigations Into the Chemical Status of C-14 After Leaching of Cladding Material From Spent PWR and BWR Fuel Rods in a Salt Solution,’ SIEMENS U9414/88/001 (Apr.1988)
5. JAERI-M, 83-035
6. JIS H 4751 (1990)
7. MARCEL POURBAIX, ‘Atlas of Electrochemical Equilibria in Aqueous Solutions’
8. BAOLIN DENG et al., ‘Hydrocarbon Formation in Metallic Iron/Water System,’ Environ.Sc.Technol., 1997, 31.1185-1190
9. H.D. SMITH et al., ‘An Investigation of Thermal Release of Carbon 14 From PWR Zircaloy Spent Fuel Cladding,’ Journal of Nuclear Materials, 200(1993) 128-137
10. Japan Metal Society, ‘Metal Data Book,’ 1984
11. C.M. HANSSON, ‘The Corrosion of Zircaloy — 2 in Anaerobic Synthetic Cement Pore Solution,’ SKB/KBS Technical Report, 84-13 (Dec.1984)
12. G. PLANTE et al., ‘Etudes de Corrosion des Materiaux de Conteneuers Pour le Stockage des Dechets Radioactifs en Sites Granitiques,’ Communautes Europeennes, EUR-8762FR (1984)

添付資料 4

S.Kaneko, H.Tanabe, M.sasoh, et al., “A Study on the Chemical Forms and Migration Behavior of Carbon-14 Leached from the Simulated Hull Waste in the Underground condition,” Mat. Res. Soc. Symp. Proc. Vol.757, p.621-p.626, (2003).

2002 MRS FALL MEETING
December 2-6 BOSTON, MA

A Study on the Chemical Forms and Migration Behavior of Carbon-14 Leached from the Simulated Hull Waste in the Underground condition

Satoru Kaneko*, Hiromi Tanabe*, Michitaka Sasoh**, Ryota Takahashi**, Takayuki Shibano**, Shinji Tateyama**
*Radioactive Waste Management Funding and Research Center, 2-8-10 Toranomon Minato-ku, Tokyo 204-0001, JAPAN
**Toshiba Corporation, 4-1 Ukishima-cho Kawasaki-ku, Kawasaki, 210, JAPAN

ABSTRACT

The chemical forms of carbon leaching from carbon-containing Zr and Fe-based metallic materials have been investigated to improve the estimation of the contribution of C-14 in the performance assessment of TRU waste disposal. Both organic and inorganic carbons were identified in the leached solution with carbon containing zirconium and steel, and the concentrations of total carbon (organic plus inorganic) in the leached solutions increased with time. The carbon concentrations in the leached solution for both metallic samples were higher at higher pH. With High Performance Liquid Chromatography (HPLC), organic carbons were identified to be low-molecular weight alcohols, carboxylic acids and aldehydes.

To explore the chemical state of carbon in the matrix materials, the leaching experiments were carried out also for ZrC, Fe_3C, the powder mixtures of carbon and zirconium, and of carbon and iron. The low-molecular weight organic carbons were detected only in the case of carbides (ZrC and Fe_3C). The chemical forms of carbon in the zirconium alloy were suggested to be carbide or carbon by H.D.Smith[1]. The present result suggests that the chemical forms of carbon in zirconium or iron are mainly in the form of carbide.

In the interest of performance assessment, the distribution coefficients of the organic carbon species identified in the leached solution for cement were obtained. As expected, some of them were shown to be larger than the values assumed in the performance assessment of Progress Report on Disposal Concept for TRU Waste in Japan[2].

INTRODUCTION

In the performance assessment of transuranic (TRU) waste disposal, from the Nuclear Fuel Reprocessing Facility, carbon-14 (C-14) in the hull (zircaloy cladding waste) and end pieces has been so far estimated to considerably contribute to the radiation exposure to the public[2]. In this performance assessment, however, the estimation is based on the fairly conservatively selected parameters for C-14, since the chemical forms of C-14 leaching from the hull are unknown[3]. For the performance assessment to be more realistic, the chemical forms of C-14 leaching from the hull should be identified. For example, the distribution coefficients of C-14 for barrier materials, example cement, bentonite and so on, would be low, if the form of C-14 is mainly organic. Thus, the chemical forms of carbon leaching from carbon-containing Zr and Fe-based metallic materials have been investigated to improve the estimation of the contribution of C-14 in the performance assessment of TRU waste disposal. To support the discussion for the speciation of C-14 in the leached solution, the leaching experiments were also carried out for ZrC, Fe_3C, the powder mixtures of carbon and zirconium, and of carbon and iron. Based on this result, the distribution coefficients of some organic carbon species identified in the leached solution for cement were carried out in this study.

EXPERIMENT

Table 1: HPLC measurement System

Measurement conditions	
Column	Rspax KC-811*2
Mobile phase	1mM $HClO_4$
Flow rate	0.8ml/min
Column temperature	40℃
UV detector	
Wavelength	210nm
Response	SLOW
Output	0.001AU/mV
RI detector	
Polarity	+
Response	SLOW
Output	0.5*10-6RIU/10mV
Injection	100μl

Leaching experiment

In the leaching experiments, zirconium powder (carbon content: 0.02wt.%) and carbon steel cutting powder (carbon content: 0.12wt.%) were used to simulate hull and end pieces[4]. These kinds of metallic powder were immersed in solutions of the pH adjusted to 8 or 12.5 using NaOH (sodium hydroxide) solution. The liquid-to-solid ratio of experimental samples is 1ml/g. These samples were kept in a glove box under reducing atmosphere. Sampling of the solutions was conducted at regular intervals, and the concentrations of total carbon, organic carbon and inorganic carbon were measured using a continuous total organic carbon analyzer (TOC analyzer SHIMADZU Co. Ltd. Model 5000 A)[5]. High performance liquid chromatography (HPLC) was also carried out for the solution samples to identify the organic carbon compounds. The conditions and the equipments for the HPLC analysis are shown in Table 1.

To examine the mechanism of the releasing process of carbon compounds from zircaloy and steel, the leaching experiments were also conducted with using ZrC, Fe_3C, the mixture of carbon powder and Zr powder, the mixture of carbon powder and Fe powder as the solid phase. The experimental conditions, pH and liquid-to-solid ratio and the surrounding atmosphere were the same as in the leaching experiment for metallic powder.

Sorption Experiment

Hydrated ordinary portland cement was used in the experiment to obtain the sorption distribution coefficeints of the organic carbon species identified in the leached solution for cement. After pH of the solution was adjusted to around 12.5 with sodium hydroxide, the solutions were contacted with the powdered hydrated cement (<250 micrometer) at a ratio of 40 cm^3 to 4 g. After 100 days the solutions were filtered through 0.45-micrometer filter. All operations for this experiment were performed inside glovebox. The detailed parameters for the experimental condition are listed in Table 2.

Table 2: Measurement conditions of distribution coefficient values

Solid phase	OPC
Liquid phase	Purified water
Solid particle diameter	250 micrometer or less
Liquid-to-solid ratio	10ml/g
The organic materials covered	Methanol、Ethanol、Formaldehyde、Formic acid、Acetic acid
Concentration of organic materials	10ppm
Temperature	Room temperature
Atmosphere	Reducing atmosphere (in a glove box of 3%nitrogen-hydrogen)

RESUTS & DISCUSSION

The changes over time in the concentration of organic and inorganic carbon in the leaching experiments for carbon steel and zirconium powder are shown in Figures 1 and 2 respectively. It is clear from these figures that the carbon concentration became constant for after approximately five months of leaching in the solution. In both leaching experiments of carbon steel and zirconium, the existence of inorganic carbon species were confirmed as well as organic carbon. Also, regarding the leaching tendency of carbon, it was discovered that the higher the pH, the greater the amount of carbon leached into solution.

Figure 3 shows the changes over time in carbon concentration, total organic carbon concentration and inorganic carbon concentration for ZrC and Fe_3C.

Similarly to the cases of carbon steel and zirconium, the results indicate that the inorganic carbon exists as well as organic carbon, and that the amount of carbon leached into solution is greater at higher pH.

In the Liquid Chromatograms(HPLC), organic carbon species were identified as low-molecular weight alcohols, carboxylic acids and aldehydes. The identified carboxylic acids were formic acid (HCOOH) and acetic acid (CH_3COOH) from HPLC, and the aldehyde was formaldehyde (HCHO). Methanol (CH_3OH) and ethanol (C_2H_5OH) were confirmed.

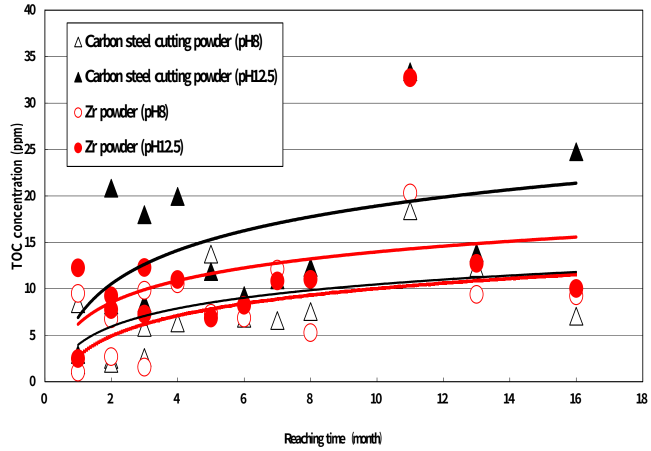


Figure1: The total organic carbon concentration leached from Zr and Carbon steel

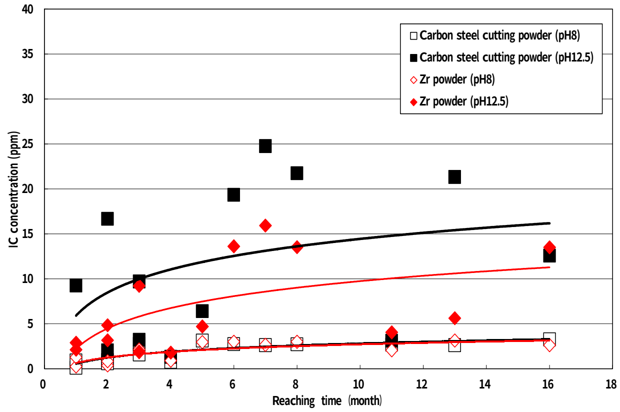
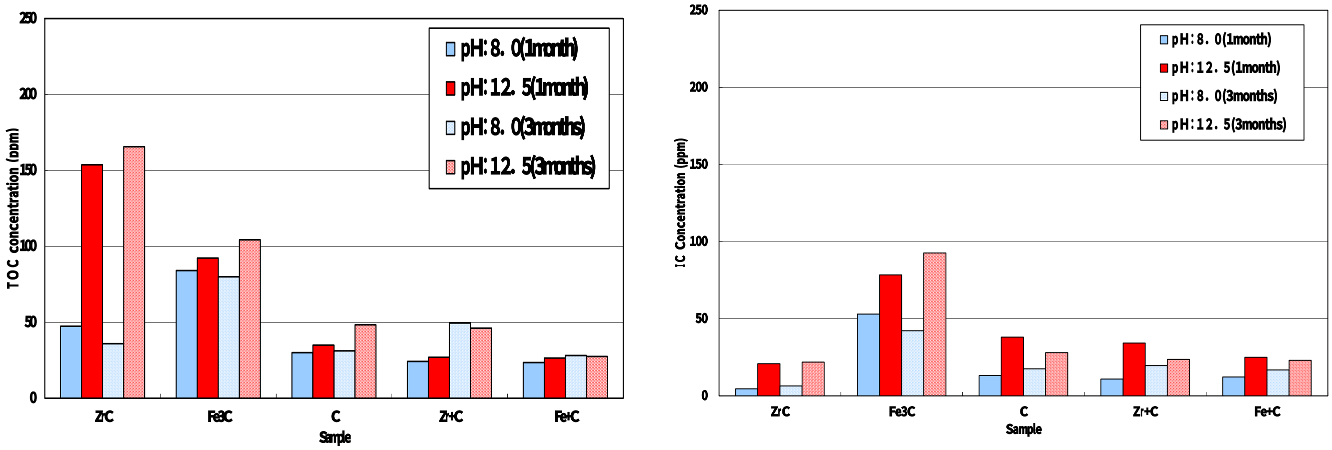


Figure2:The inorganic carbon concentration leached from Zr and Carbon steel



Total organic carbon concentaration from carbaides

Inorganic carbon concentaration from carbaides

Figure 3: The carbon concentration leached from carbides

From the leaching experiments for ZrC, Fe_3C, the mixture of carbon powder and Zr powder, the mixture of carbon powder and Fe powder, the low molecular weight organic carbon was detected only in the case of carbide (ZrC and Fe_3C). Figure 4 and 5 show the results of identification by HPLC for leaching experiments of metallic powders and carbides. These figures confirm that most of the organic carbon obtained from the leaching tests of the metal samples and carbides were carboxylic acids.

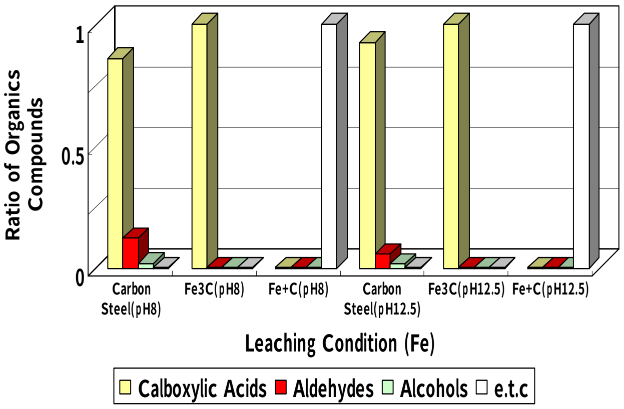


Figure 4: The Ratio of Organics Compounds in Leaching Solution for Carbon Steel, Fe3C and the mixture of Iron and Carbon

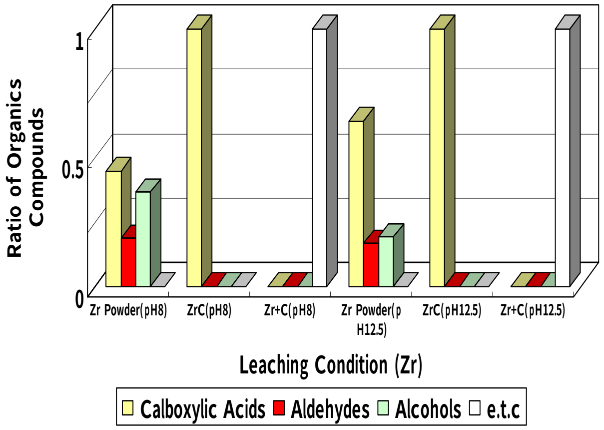


Figure5: The Ratio of Organics Compounds in Leaching Solution for Zirconium ,ZrC and The Mixture of Zirconium and Carbon

Although the chemical forms of the carbon contained in metals are still unknown, H. D. Smith et al. suggested that carbon exists in the form of carbides or atomic carbon in zircaloy. If the carbon in metallic matrix is carbide, it is thought that the generation of organics in the leaching solution causes from carbides reaction with water such as hydrolysis of zirconium carbide. In the case of atomic carbon, the organic carbon species should result from the reduction of carbon with oxidizing metal to its oxides. In the present study, when considering the fact that the main organic carbon compounds obtained from the leaching experiments of metal samples are carboxylic acids and that most of the organic carbon compounds whose existence is confirmed in the leaching experiments of carbides are carboxylic acids, it is implied that one of the chemical forms of carbon in metals could be carbide.

Sorption experiment was conducted for some organics to cement materials. We used the five organic carbon compounds (methanol, ethanol, formaldehyde, formic acid and acetic acid) from the leaching experiments. The distribution coefficients of the organic compounds for cement are shown in Table 3. The distribution coefficient is calculated using the following formula.

The distribution coefficient =$(C_0-C_f)/C_f)\cdot V/m$

C_0 : The concentration of organic compound in initial liquid phase

C_f : The concentration of organic compound in fainal liquid phase m：Solid quantity〔g〕、V：Liquid volume〔L〕

These distribution coefficient values of around 10ml/g for the distribution coefficients of organic carbon compounds are larger than the values used in the performance assessment in the Progress Report on the Disposal Concept of TRU Waste in Japan, where the conservative values were selected due to the insufficient knowledge on the carbon speciation.

Table 3: The Distribution coefficient values of Organic Compounds for Ordinary Portland Cement

Organic Compound	Distribution coefficient (ml/g)
Methanol	7.2
Ethanol	12
Formaldehyde	10
ormic acid	4.1
Acetic acid	9.5

CONCLUSIONS

The leaching experiments of C-14 with carbon-containing Zr and Fe-based metallic materials have been carried out under reducing condition. Main compounds of the organic carbon leached from metals are carboxylic acids. According to the comparison of the result with those observed in the leaching experiment with ZrC, Fe_3C, the powder mixtures of carbon and zirconium, and of carbon and iron, the chemical form of carbon in the metal matrices may be mainly carbides. Furthermore, it was confirmed that the cement distribution coefficients of the organic carbon compounds identified in the leached solutions from the metals were confirmed to be higher than those currently used in the Japanese performance assessment of TRU waste disposal

REFERENCES

1. H.D.Smith, D.L.Baldwin, An Investigation of Thermal Release of Carbon-14 from PWR Zircaloy Spent Fuel Cladding, Journal of Nuclear Material 200(1993)128-137
2. JNC.FEPC, Progress Report on Disposal Concept for TRU Waste in Japan, (Mar.2000)
3. T.Yamaguchi, S.Tanuma, A Study on Chemical forms and Migration Behavior of

Radionuclides in HULL Waste, ISEM1999

4. Methods for determination of carbon in zirconium and zirconium alloys, JIS,H1663,1988
5. Testing methods for total organic carbon in highly purified water, JIS,K0551,1994

【問合せ先】
〒１０５－０００１　東京都港区虎ノ門２丁目８番１０号（第１５森ビル４階）
　　財団法人　原子力環境整備促進・資金管理センター（原環センター）
　　電話 03-3504-1081　ファックス 03-3504-1297

Radioactive Waste Management Funding and Research Center(RWMC)
No.15. Mori Bldg, 2-8-10, Toranomon, Minato-ku, Tokyo, 105-0001, Japan