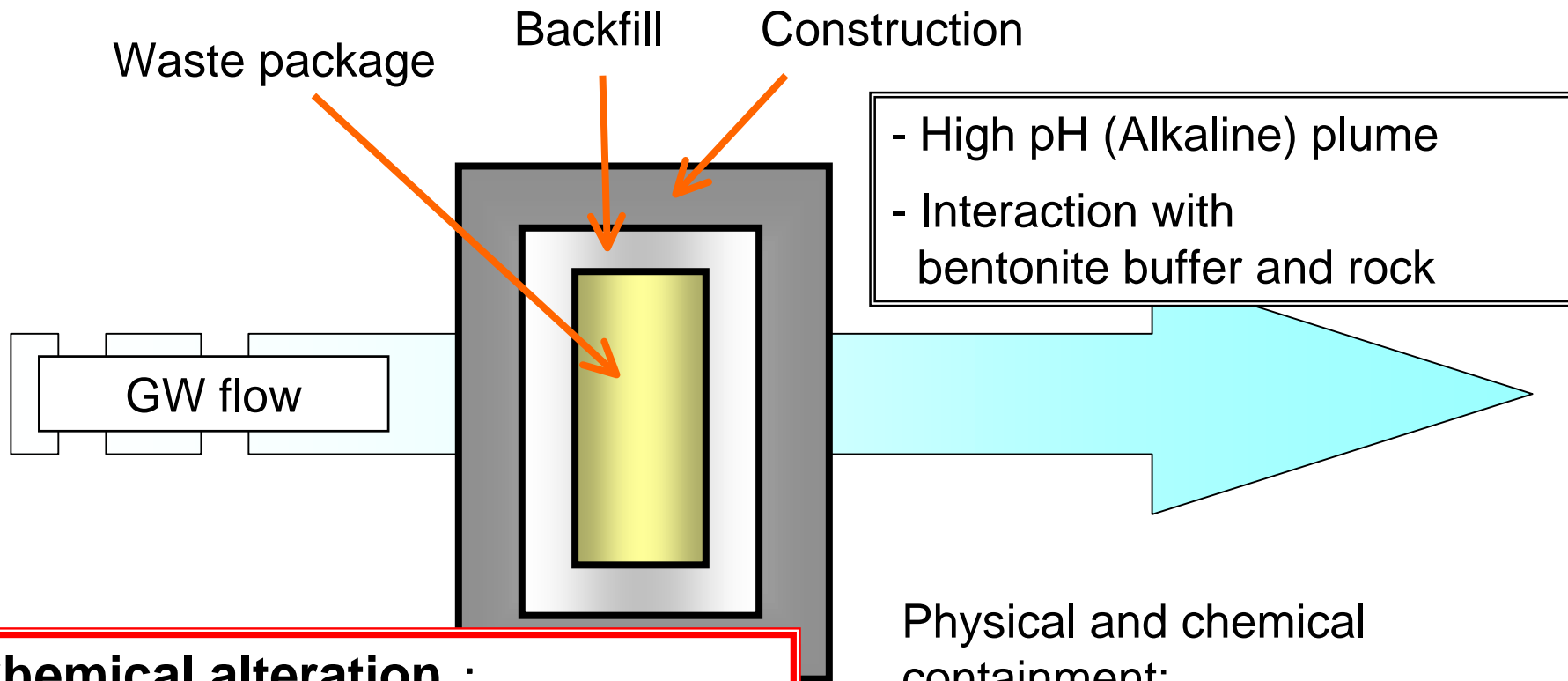


# **Modelling of Chemical Alteration of Cement Materials in Radioactive Waste Repository Environment**

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# Cementitious materials in radwaste repository



## Chemical alteration :

- **Dissolution**
- **Secondary minerals**
- **Crystallization**

for a **LONG TERM**

## Physical and chemical containment:

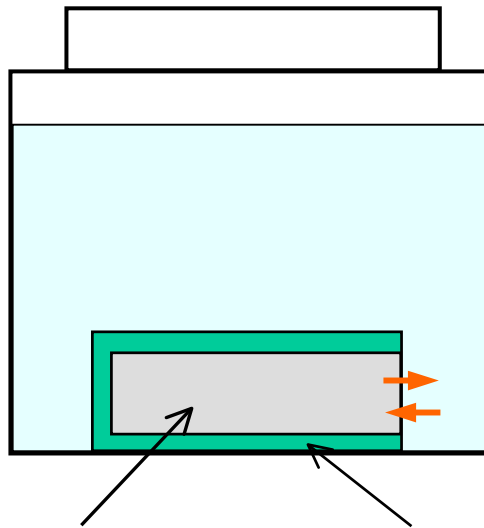
- High pH (low solubility, high sorption)
- Low permeability/diffusivity

# Contents

- 1. Observation of alteration of OPC monolith (Lab. Experimental)**
  - Leaching/precipitation of components in a tank-leaching experiment
  - Effect of surface precipitates ( $\text{CaCO}_3$ ) on alteration
- 2. Development of a reactive transport computational code (CCT-P)**
  - Thermodynamic incongruent dissolution model of C-S-H
  - One-dimensional advection/dispersion/diffusion equation
  - Evolution of the hydraulic properties of the cement solid matrix due to the leaching and precipitation of components
  - Description of precipitation of secondary less-soluble phase acting as a diffusion barrier
- 3. Preliminary calculation of the evolution of the cementitious repository system**
- 4. Summary and conclusions**

# OPC monolith alteration experiments

## A tank-leaching experiment



OPC monolith

Epoxy resin

OPC hydrate monolith:

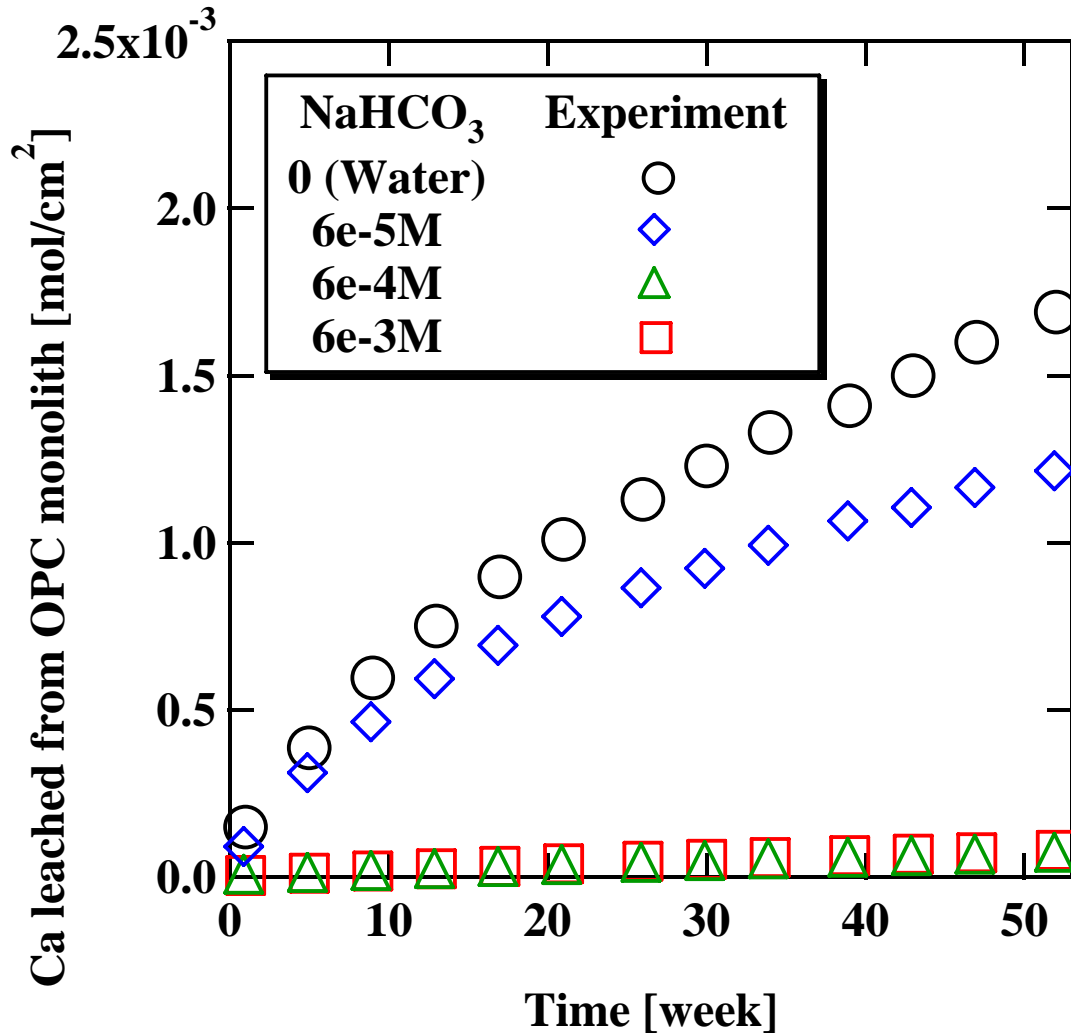
- w/c=0.35, cured in OPC-equilibrated water for 91 days at 50 °C
- 20 x 20 x 70mm
- Only one of the faces of monolith was exposed to the aqueous solution

Solution:

- Deionised water
- NaHCO<sub>3</sub> solution (6e-5, 6e-4, 6e-3 M)

- The solution and solid samples were separated and the monolith samples were recontacted with fresh deionised water or NaHCO<sub>3</sub> solution after 1, 5, 9, 13, 17, 21, 26, 30, 34, 39, 43, 47 and 52 weeks.
- All experiments were carried out in an nitrogen-filled glovebox.

# Results(1): Calcium leaching



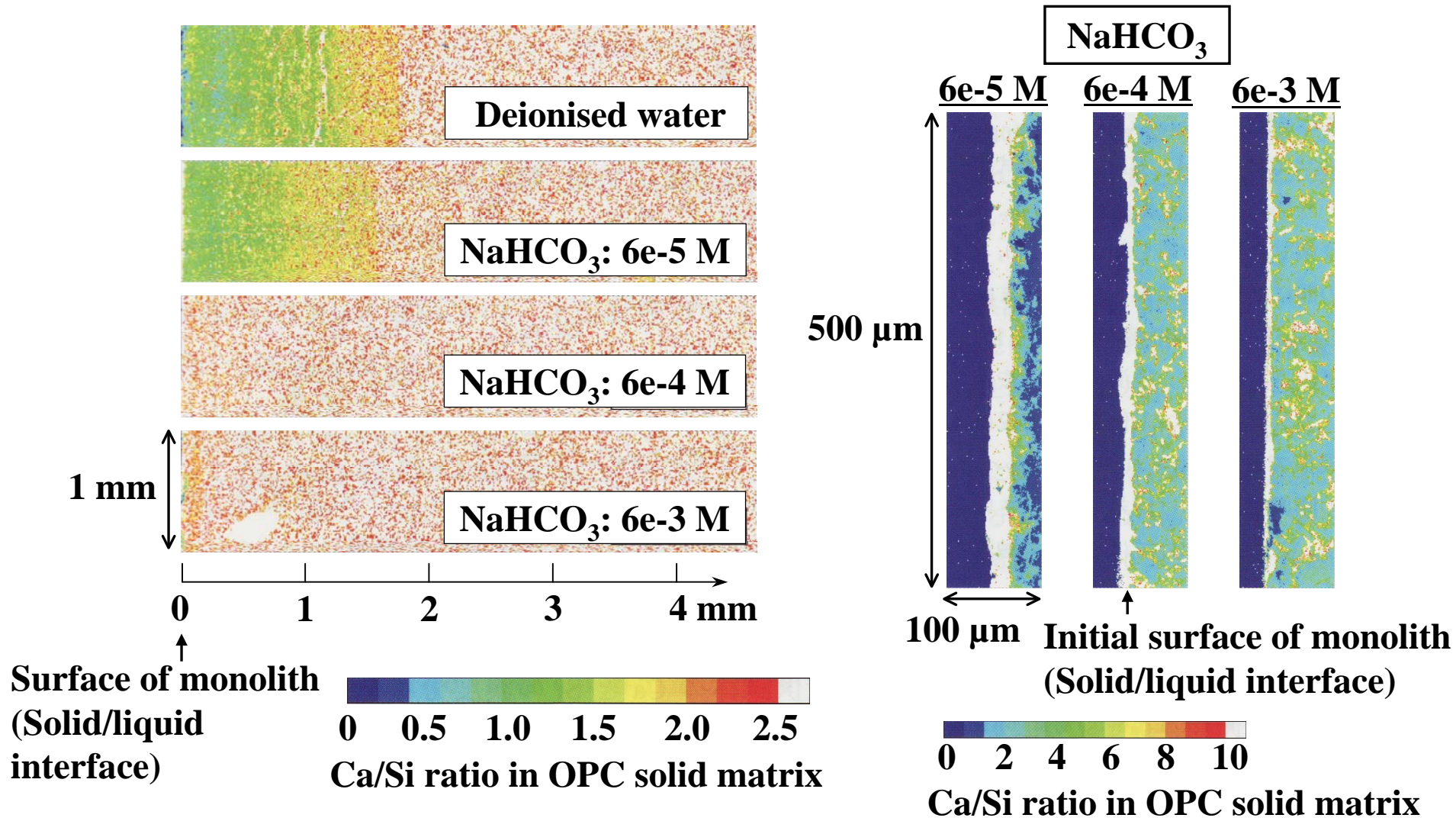
In Deionised water :

The dissolution of  $\text{Ca}(\text{OH})_2$  dominated the leaching of calcium in the early stage, then the incongruent dissolution of C-S-H gel in the altered surface region dominated the calcium leaching.

In  $\text{NaHCO}_3$  solution :

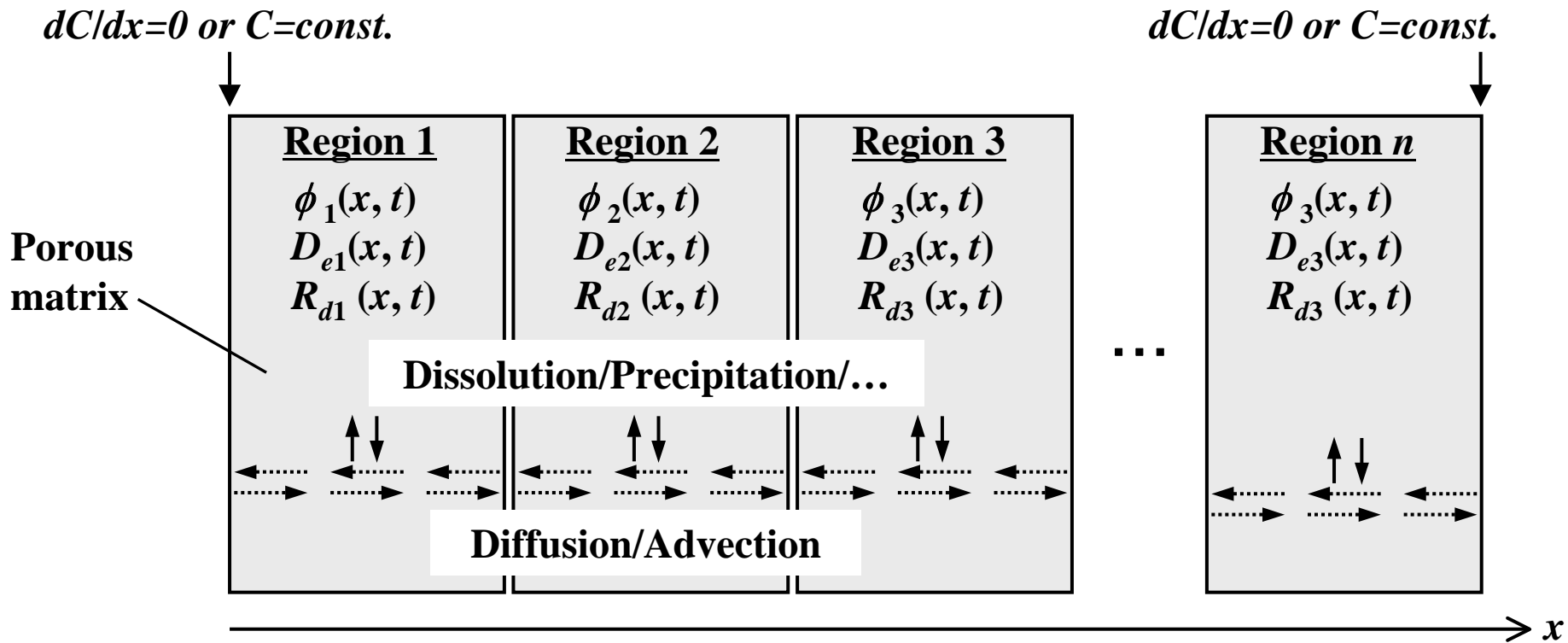
The leaching of calcium was inhibited, significantly at the  $\text{NaHCO}_3$  concentrations of 6e-4 and 6e-3 M.

# Results(2): Calcium concentration in solid



In  $6 \times 10^{-4}$  and  $6 \times 10^{-3}$  M sodium bicarbonate solutions, little calcium was leached and a layer of calcite precipitation formed.

# CCT-P : A coupling transport and chemical equilibrium calculation code



$$\frac{\partial}{\partial x} \left\{ D_e(x,t) \cdot \frac{\partial C(x,t)}{\partial x} \right\} - V_d \cdot \frac{\partial C(x,t)}{\partial x} = \frac{\partial \{ \phi(x,t) \cdot R_d(x,t) \cdot C(x,t) \}}{\partial t} - S_{eq}(x,t)$$

$C$ : concentration of aqueous species,

$t$ : time,  $\phi$ : porosity,

$V_d$ : velocity of flow in matrix,

$D_e$ : effective diffusion constant in matrix,

$S_{eq}$ : source term given by chemical equilibrium calculation within matrix,

$R_d$ : retardation factor ( $R_d(t) = 1 + \rho \cdot K_d \cdot \left( \frac{1 - \phi(t)}{\phi(t)} \right)$ ),  $\rho$ : density,  $K_d$ : distribution coefficient.

# The evolution of the hydraulic properties of the solid

In CCT-P, the diffusion coefficient in the altered region of the solid matrix can be described as a function of porosity;

$$D(t) = \left( D(0) \cdot \frac{\phi(t)}{\phi(0)} \right)^n \quad (n = 2 \text{ in this study})$$

The porosity of the solid matrix increases or decreases as the component minerals are dissolved and leached or precipitated, respectively;

$$\phi(t) = 1 - (1 - \phi(0)) \cdot \frac{V_{solid}(t)}{V_{solid}(0)}$$

$$V_{solid}(t) = \sum_{i:solid} CS_i(t) \cdot v_{mol_i} + V_{solid,static}$$

$V_{solid}$ : volume of solid phase,

$CS$ : molarity of component mineral,

$v_{mol}$ : molar volume of component mineral

$$v_{mol \text{ Ca(OH)}_2} = 0.0331 \text{ dm}^3 \text{ mol}^{-1},$$

$$v_{mol \text{ SiO}_2} = 0.0273 \text{ dm}^3 \text{ mol}^{-1},$$

$$v_{mol \text{ CaCO}_3} = 0.0369 \text{ dm}^3 \text{ mol}^{-1},$$

$V_{solid,static}$ : volume of insoluble residual solid phase.



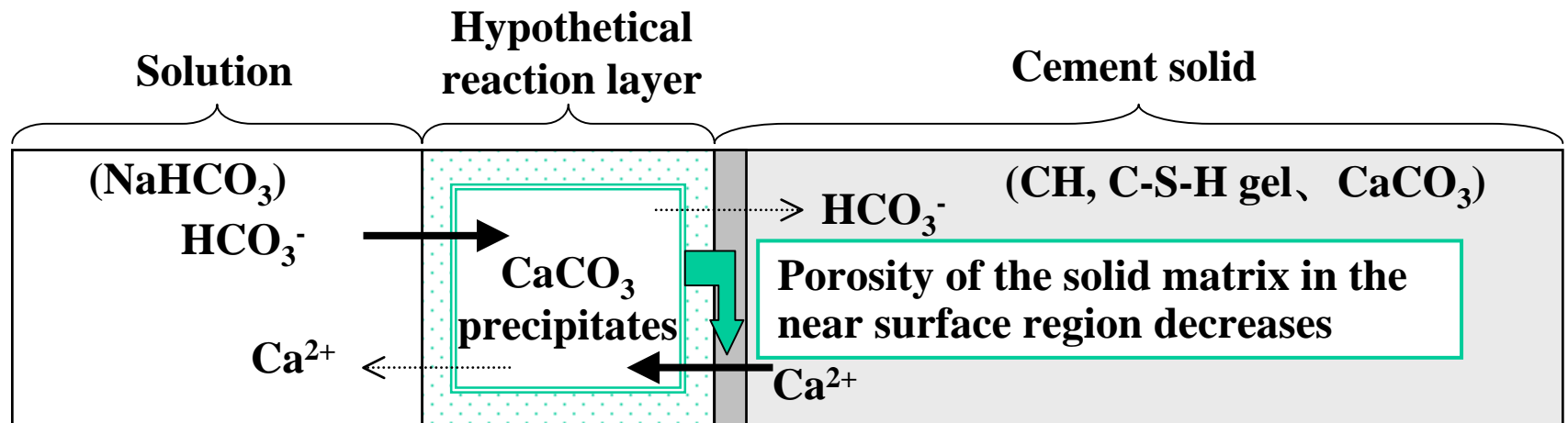
# A hypothetical reaction layer model

At the boundaries of the regions, the advection/dispersion/diffusion equations in adjacent regions are connected as follows:

$$-D_e(x,t)_{upper} \cdot \frac{\partial C(x,t)}{\partial x} \Big|_{upper} + V_{d_{upper}} \cdot C(x,t)_{boundary} = -D_e(x,t)_{lower} \cdot \frac{\partial C(x,t)}{\partial x} \Big|_{lower} + V_{d_{lower}} \cdot C(x,t)_{boundary},$$

A hypothetical reaction layer model is introduced when a less-soluble or insoluble phase is precipitated:

$$-D_e(x,t)_{cement} \cdot \frac{\partial C(x,t)}{\partial x} \Big|_{cement} = \left( \frac{\phi(t)}{\phi(0)} \right)_{surface} \cdot \left\{ -D_e(x,t)_{HRL} \cdot \frac{\partial C(x,t)}{\partial x} \Big|_{HRL} \right\}$$



# Incongruent C-S-H dissolution/precipitation model

- C-S-H is described as a binary nonideal solid solution of  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$ .
- The notable features of the model are its good continuity and simplicity, so that the model predicts well the equilibria of the incongruent precipitation/dissolution of cementitious materials accompanying the change of Ca/Si ratio by iterative numerical calculations.

$$\log K_s = \frac{1}{1+y} \cdot \log K_{s0} - \frac{1}{1+y} \cdot \log \frac{1}{1+y} + \frac{y}{(1+y)^2} \cdot [A'_{s0} + A'_{s1} \left(\frac{1-y}{1+y}\right) + A'_{s2} \left(\frac{1-y}{1+y}\right)^2]$$

$$\log K_c = \frac{y}{1+y} \cdot \log K_{c0} - \frac{y}{1+y} \cdot \log \frac{y}{1+y} + \frac{y}{(1+y)^2} \cdot [A'_{c0} + A'_{c1} \left(\frac{1-y}{1+y}\right) + A'_{c2} \left(\frac{1-y}{1+y}\right)^2]$$

( y = Ca/Si of C-S-H )

End member	SiO <sub>2</sub>			Ca(OH) <sub>2</sub>		
	A <sub>s0</sub>	A <sub>s1</sub>	A <sub>s2</sub>	A <sub>c0</sub>	A <sub>c1</sub>	A <sub>c2</sub>
Ca/Si ≤ 0.833	-18.908	57.821	-58.779	36.902	-37.015	163.21
Ca/Si > 0.833	-18.933	49.633	24.582	36.923	-7.8143	-50.323

at Ca/Si ≤ 0.400  
at 1.686 ≤ Ca/Si

SiO<sub>2</sub>: logK<sub>s</sub> = logK<sub>s0</sub> - log(1+y)

SiO<sub>2</sub>: logK<sub>s</sub> = -7.835

Ca(OH)<sub>2</sub> : logK<sub>c</sub> = 22.71 (= log K<sub>c0</sub>)

logK<sub>s0</sub> = -2.639

logK<sub>c0</sub> = 22.71

(JNC-TDB)

Refs: D. Sugiyama and T. Fujita, Cem Concr Res 36 (2006) 227-237.

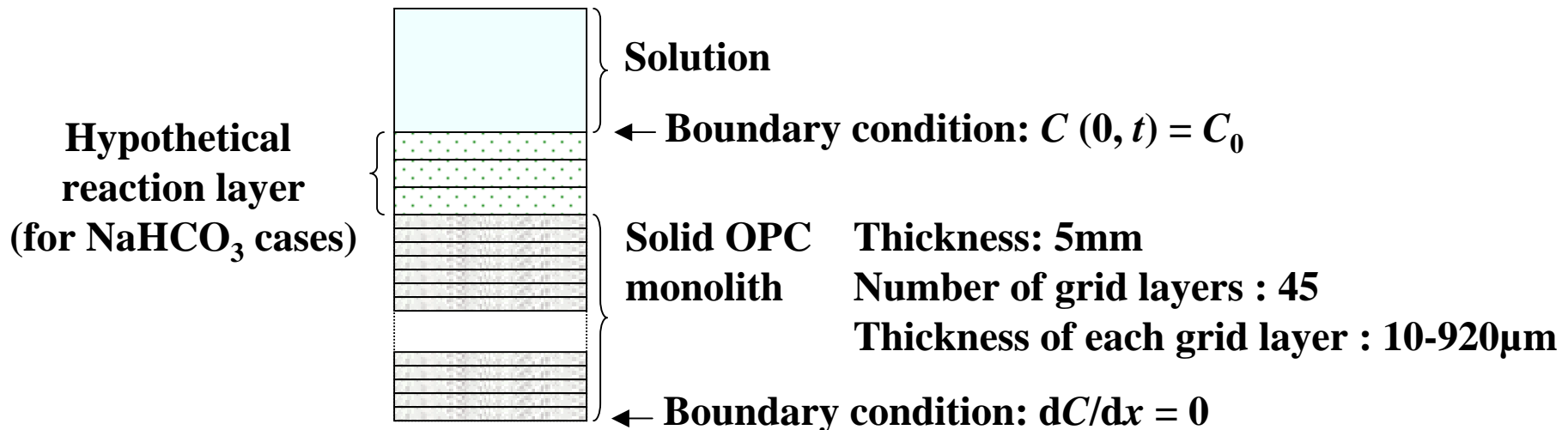


# Modelling of the OPC experiment

## Calculated mineral composition in OPC hydrate

[mol/kg]

Ettringite	Ca(OH) <sub>2</sub>	C-S-H gel (Ca/Si = 1.686)	NaOH	KOH
0.31	2.5	2.7	0.052	0.064

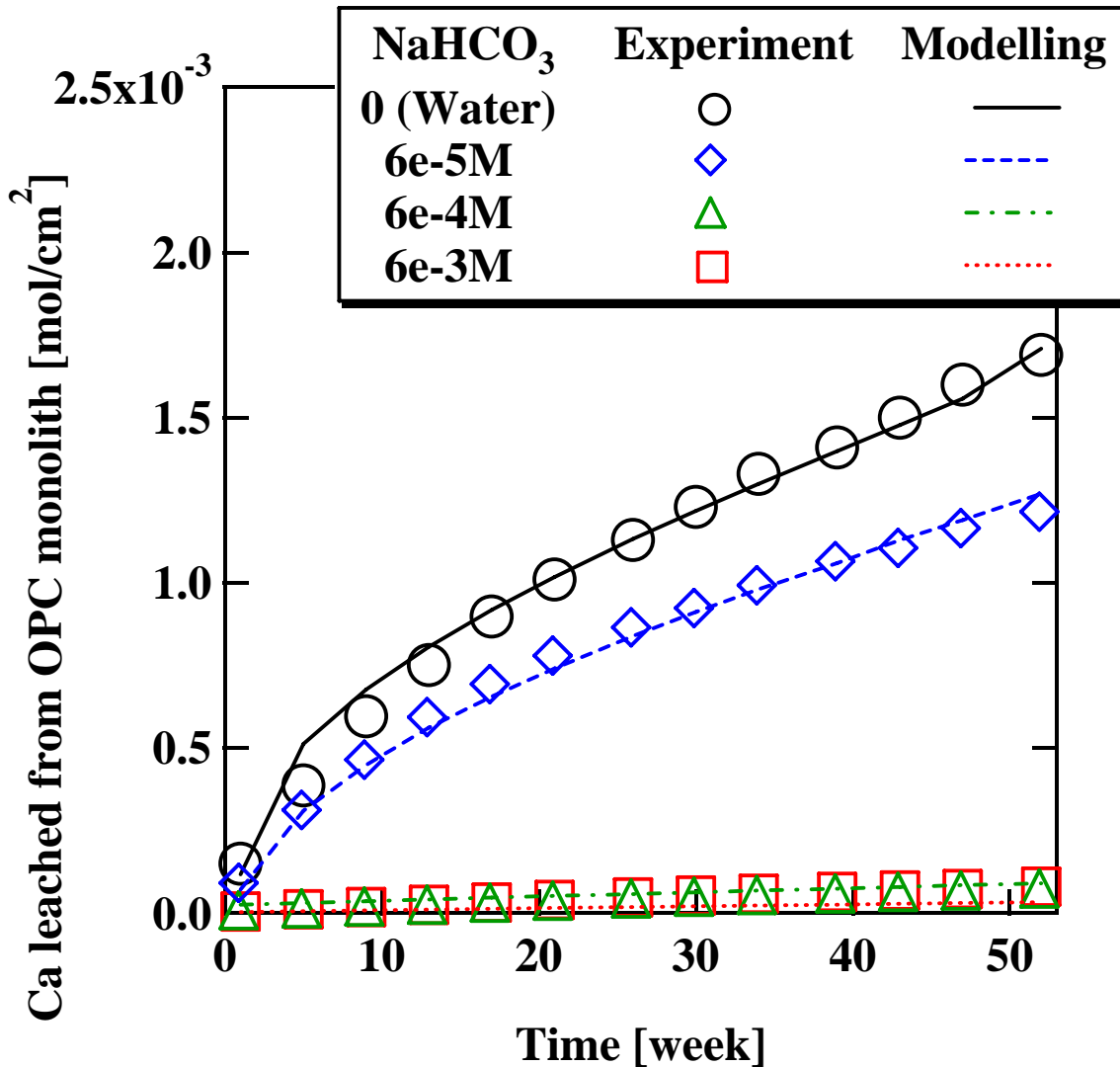


$$D_e(0) = 7.8e-12 \text{ [m}^2\text{/s] within the initial solid matrix}$$

# Calculation parameters for OPC modelling

Solution		Deionised water	$6 \times 10^{-5}$ mol $\text{dm}^{-3}$ $\text{NaHCO}_3$	$6 \times 10^{-4}$ mol $\text{dm}^{-3}$ $\text{NaHCO}_3$	$6 \times 10^{-3}$ mol $\text{dm}^{-3}$ $\text{NaHCO}_3$
Hypothetical reaction layer	Thickness of region [mm]	—	0.6	0.6	0.6
	Number of grid layers	—	3	3	3
	Thickness of each grid layer [mm]	—	0.2	0.2	0.2
	Initial $D_e^*$ [ $\text{m}^2 \text{s}^{-1}$ ]	—	$8.0 \times 10^{-10}$	$8.0 \times 10^{-10}$	$8.0 \times 10^{-10}$
	Initial porosity	—	1	1	1
Vicinity of the surface of OPC monolith	Thickness of region [mm]	2.7	2.7	0.4	0.4
	Number of grid layers	40	40	40	40
	Thickness of each grid layer [mm]	0.0675	0.0675	0.01	0.01
	Initial $D_e$ [ $\text{m}^2 \text{s}^{-1}$ ]	$7.8 \times 10^{-12}$	$7.8 \times 10^{-12}$	$7.8 \times 10^{-12}$	$7.8 \times 10^{-12}$
	Initial porosity	0.138	0.138	0.138	0.138
Matrix of OPC monolith	Thickness of region [mm]	2.3	2.3	4.6	4.6
	Number of grid layers	5	5	5	5
	Thickness of each grid layer [mm]	0.460	0.460	0.92	0.92
	Initial $D_e$ [ $\text{m}^2 \text{s}^{-1}$ ]	$7.8 \times 10^{-12}$	$7.8 \times 10^{-12}$	$7.8 \times 10^{-12}$	$7.8 \times 10^{-12}$
	Initial porosity	0.138	0.138	0.138	0.138

# Modelling Results(1): Calcium leaching

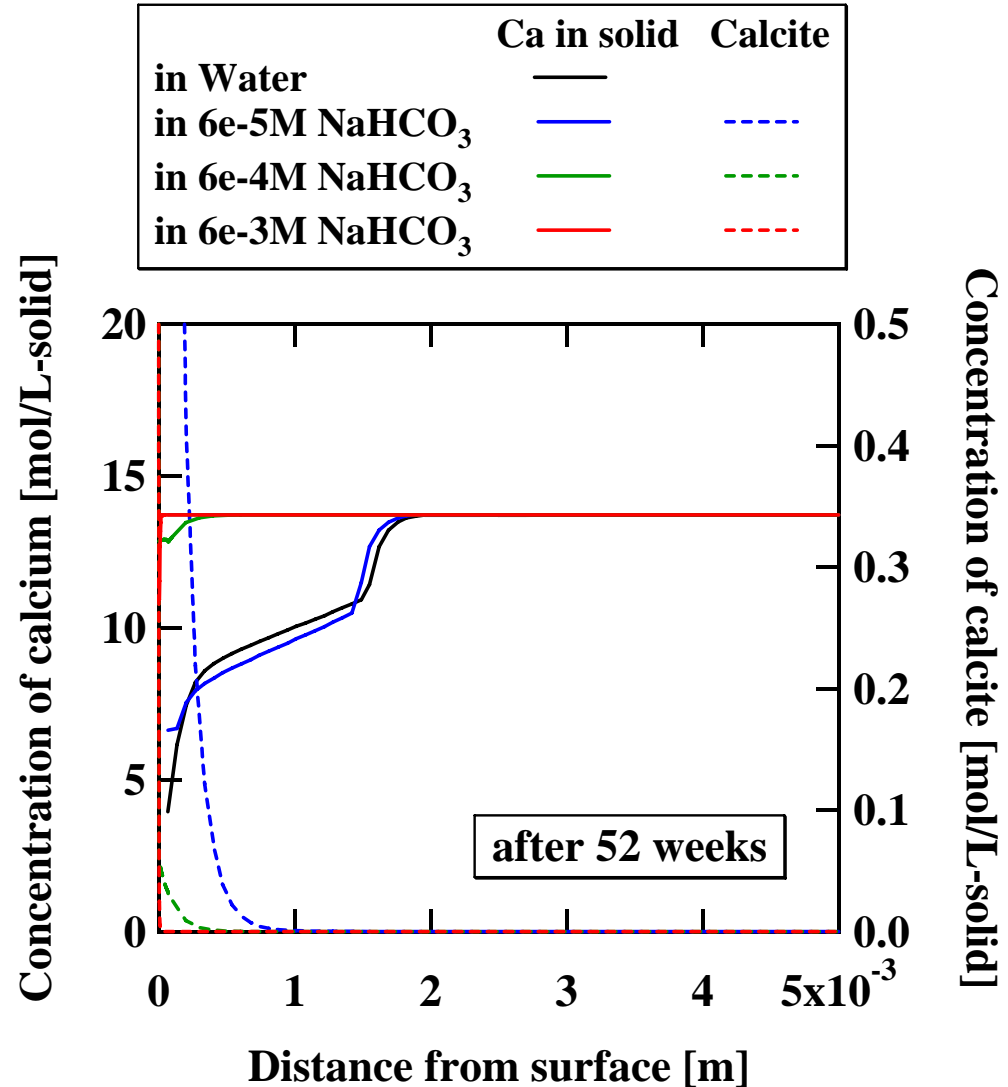
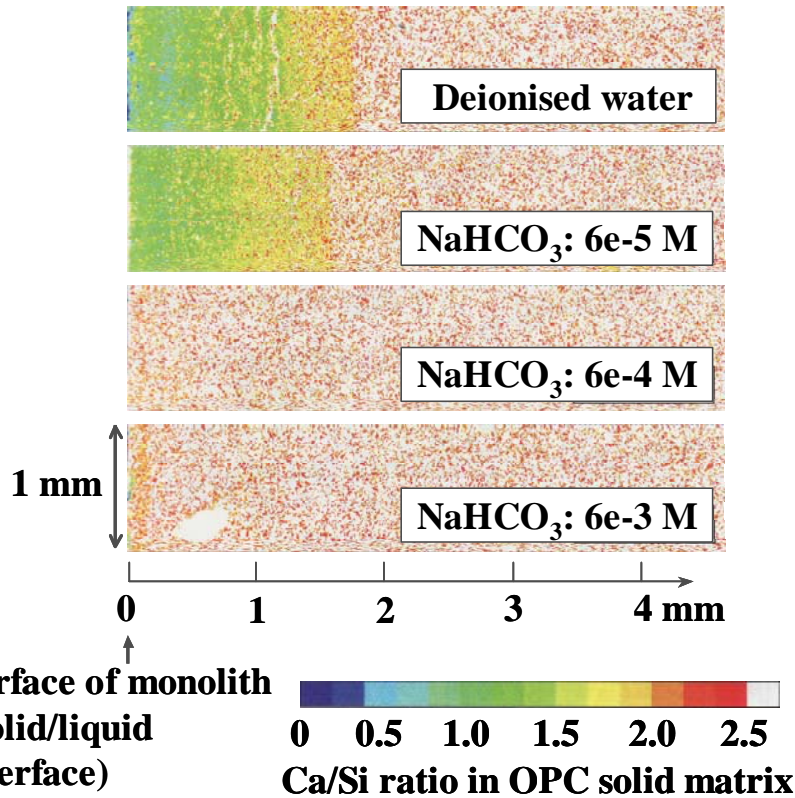


The effective diffusion coefficient within the initial solid matrix was estimated by a series of sensitivity analyses to fit the measured amount of leached calcium in deionised water.

$$D_e(0) = 7.8e-12 \text{ [m}^2\text{/s]}$$

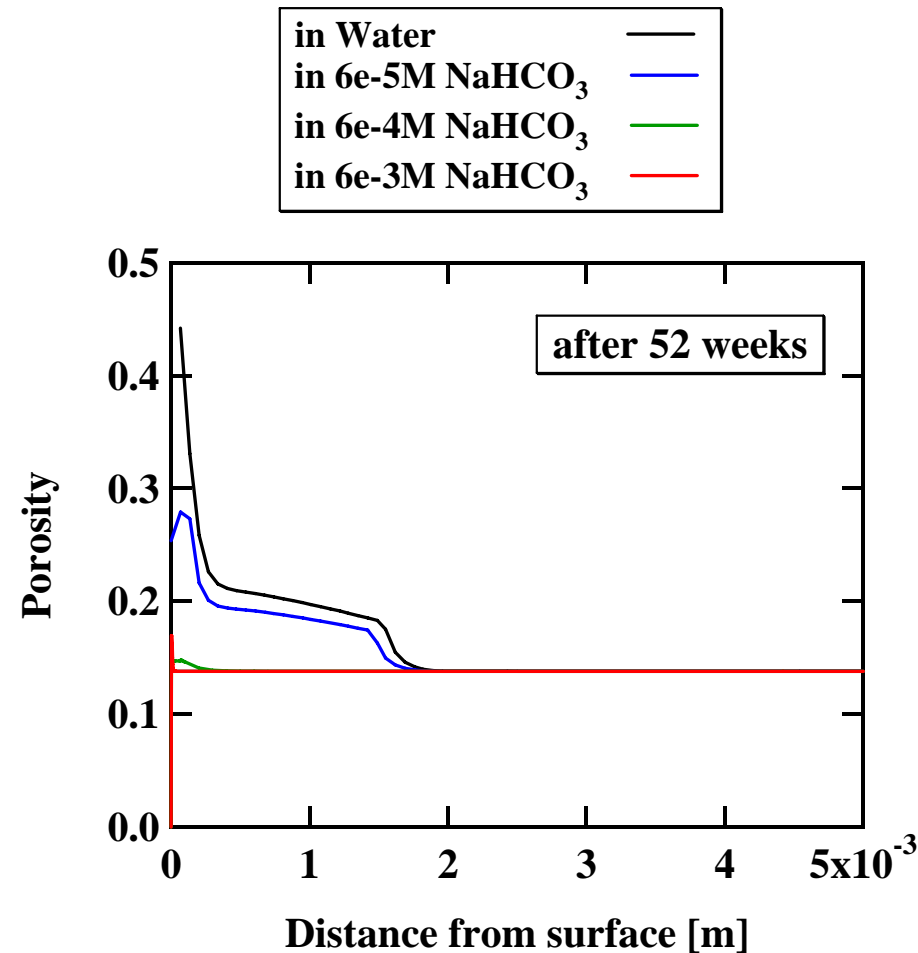
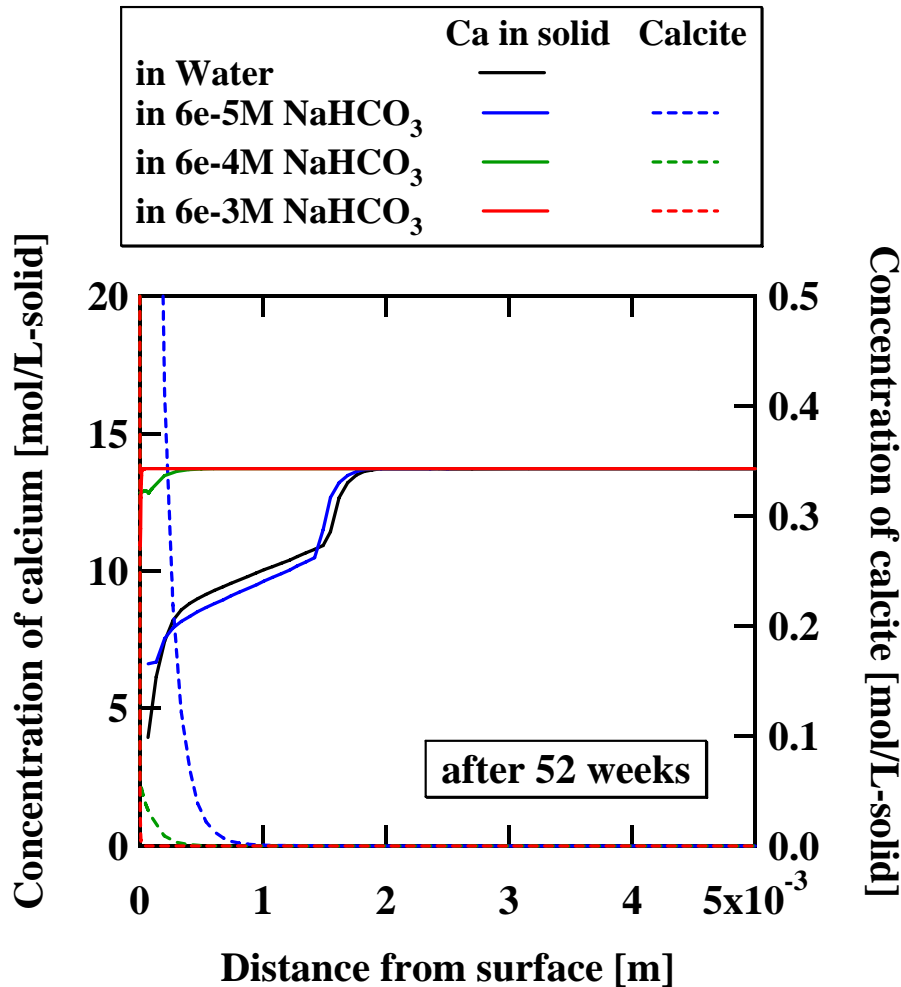
**The modelling calculations very accurately quantitatively predicted the experimental results for the leaching of calcium.**

# Modelling Results(2): Calcium in solid



The modelling calculations quantitatively predicted the experimental results.

# Modelling Results(3): Porosity in solid



**In deionised water:**

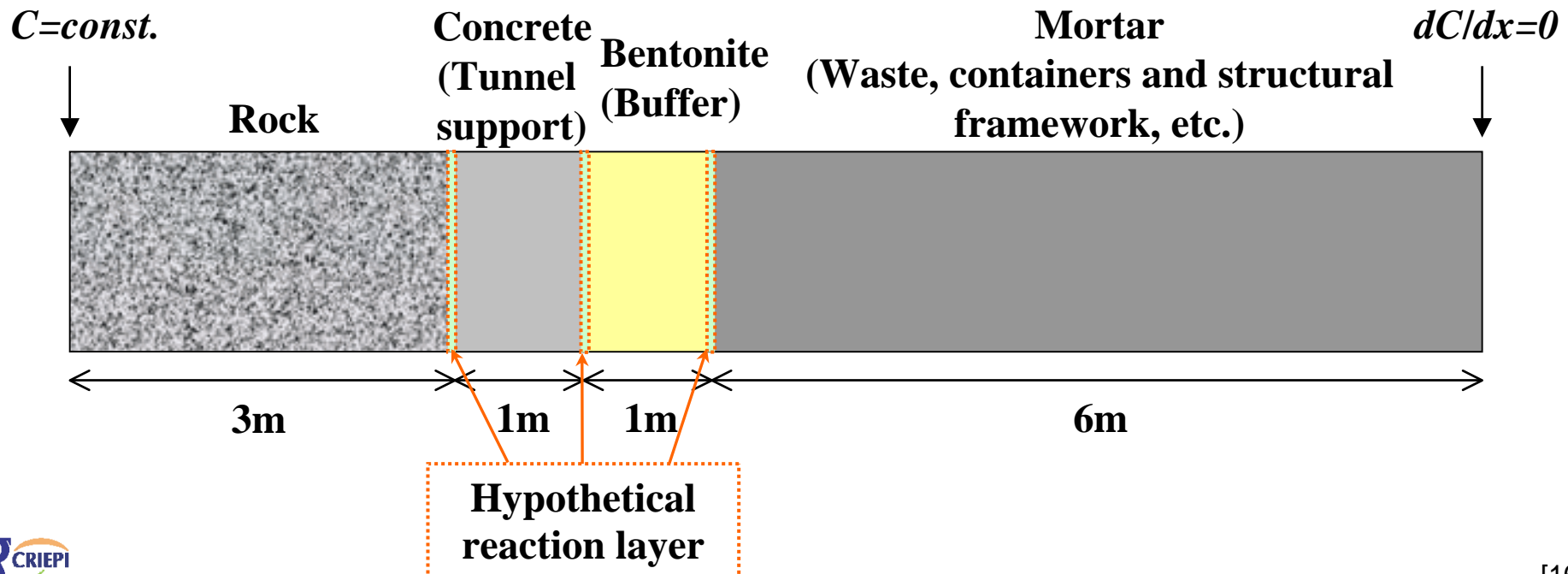
The porosity in the altered region (<1.8 mm from the surface) increased.

**In NaHCO<sub>3</sub> solution :**

The porosity decreased at the surface in 6e-5 M NaHCO<sub>3</sub>, and a reduction of the porosity to ~ 0 was predicted for 6e-4 and 6e-3 M NaHCO<sub>3</sub> solutions.

# Preliminary calculation of the evolution of the cementitious repository system

- Groundwater in the near-field of the repository contains various chemical species which may precipitate secondary minerals in the cementitious materials.
- Calcite precipitation and the effect of clogging on the long-term alteration of the cementitious repository system is preliminarily discussed (**with and without the hypothetical reaction layer**).





# Calculation parameters for Cementitious repository modelling (1)

Mineral composition of cement materials (OPC):

[mol/kg]

Mineral	Ettringite	Ca(OH) <sub>2</sub>	C-S-H gel (Ca/Si = 1.686)	NaOH	KOH
Mortar	0.081	0.97	0.91	0.018	0.021
Concrete	0.047	0.56	0.53	0.010	0.012

Composition of bentonite material:

	Ion-exchange reaction	[meq/100g]
Na- montmorillonite	-	51.4
Ca- montmorillonite	2ZNa-Z <sub>2</sub> Ca, log K <sub>G&amp;T</sub> = 0.69	7.4
K- montmorillonite	ZNa-ZK, log K <sub>G&amp;T</sub> = 0.42	0.6
Mg- montmorillonite	2ZNa-Z <sub>2</sub> Mg, log K <sub>G&amp;T</sub> = 0.67	0.7

# Calculation parameters for Cementitious repository modelling (2)

Solution composition:

Concentration [mol/L]

	Precipitated groundwater (FRHP)	Bentonite pore solution
$\text{Na}^+$	3.6 E-3	2.8 E-2
$\text{Ca}^{2+}$	1.1 E-4	5.3 E-5
$\text{K}^+$	6.2 E-5	1.2 E-4
$\text{Mg}^{2+}$	5.0 E-5	4.2 E-6
C ( $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ )	3.5 E-3	1.1 E-4
$\text{SO}_4^{2-}$	1.1 E-4	1.6 E-2
$\text{Cl}^-$	1.5 E-5	1.5 E-5

The parameters of the physical properties of the barrier materials and the composition of groundwater were extracted from the literatures:

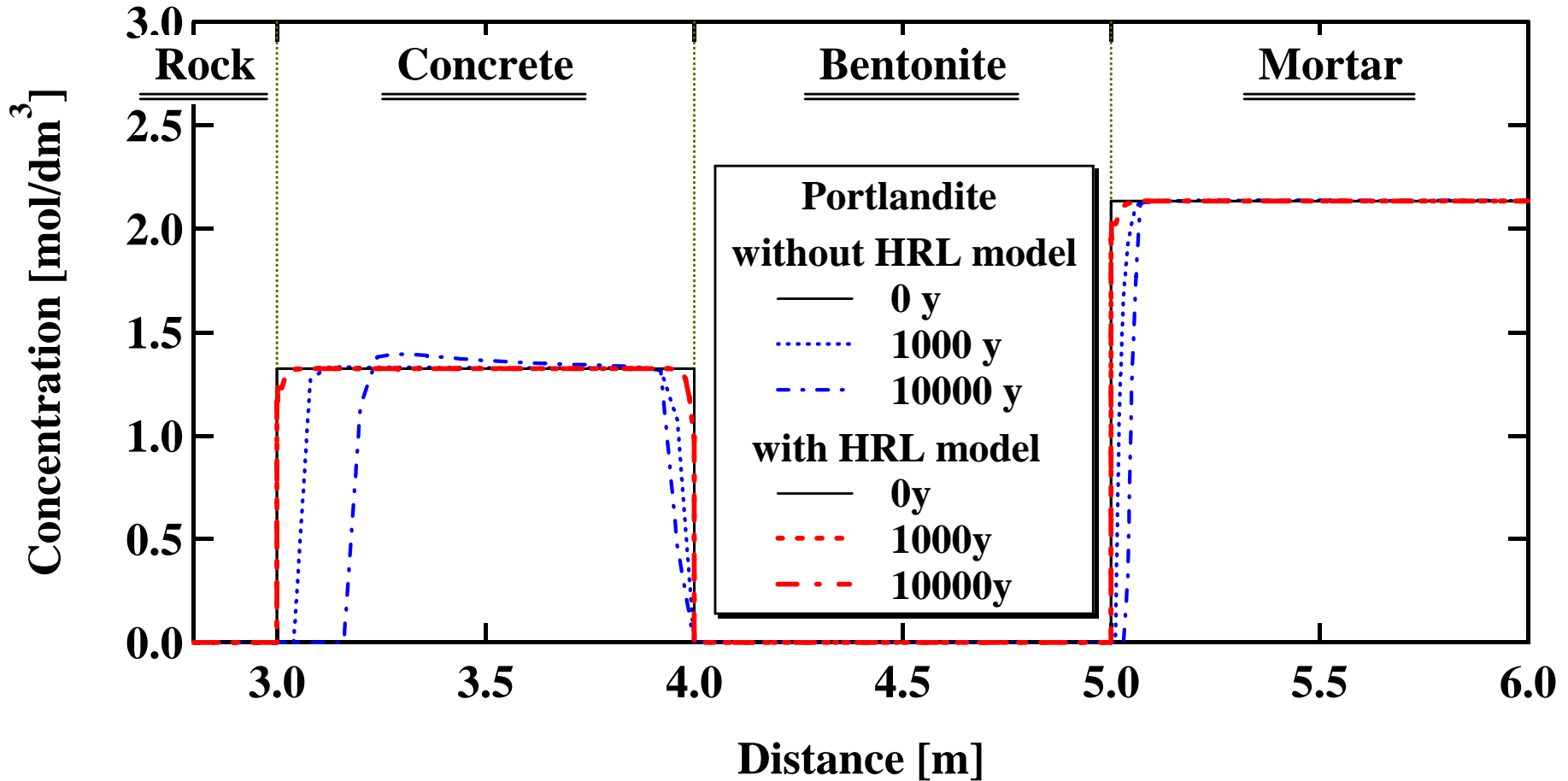
JNC, H12: Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, Supporting Report 3, JNC TN1410 2000-004, April 2000.

JAEA and FEPC, The Federation of Electric Power Companies of Japan, Second Progress Report on Research and Development for TRU Waste Disposal in Japan, JAEA-Review 2007-010, FEPC TRU-TR2-2007-01, March 2007.

# Calculation parameters for Cementitious repository modelling (3)

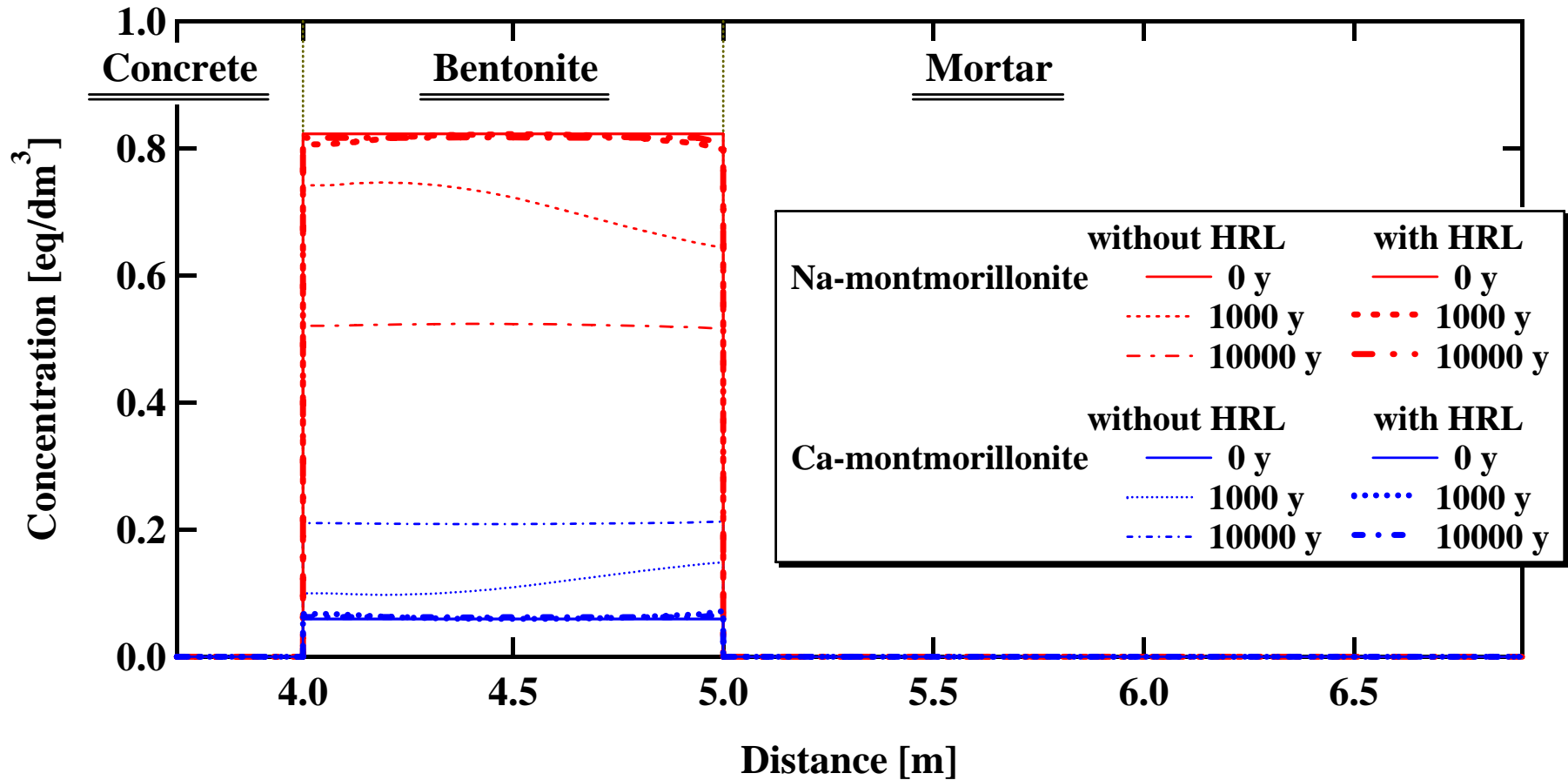
Model		With the hypothetical reaction layer model				Without the hypothetical reaction layer model					
Region		Thickness of region [mm]	Number of grid layers	Thickness of each grid layer [mm]	Initial $D_e$ [ $\text{m}^2 \text{s}^{-1}$ ]	Initial porosity	Thickness of region [mm]	Number of grid layers	Thickness of each grid layer [mm]	Initial $D_e$ [ $\text{m}^2 \text{s}^{-1}$ ]	Initial porosity
Rock		3000	16	187.5	$8.0 \times 10^{-10}$	0.5	3000	16	187.5	$8.0 \times 10^{-10}$	0.5
Concrete	Hypothetical reaction layer	6	3	2	$8.0 \times 10^{-10}$	1.0	-	-	-	-	-
	Vicinity of the solid surface	1	100	0.01	$4.5 \times 10^{-12}$	0.13	-	-	-	$4.5 \times 10^{-12}$	0.13
	Bulk matrix of solid	998	100	9.98			1000	25	40		
	Vicinity of the solid surface	1	100	0.01			-	-	-		
	Hypothetical reaction layer	6	3	2	$2.8 \times 10^{-10}$	1.0	-	-	-	-	-
Bentonite		1000	16	62.5	$2.8 \times 10^{-10}$	0.415	1000	16	62.5	$2.8 \times 10^{-10}$	0.415
Mortar	Hypothetical reaction layer	6	3	2	$2.8 \times 10^{-10}$	1.0	-	-	-	-	-
	Vicinity of the solid surface	1	100	0.01	$1.4 \times 10^{-11}$	0.19	-	-	-	$1.4 \times 10^{-11}$	0.19
	Bulk matrix of solid	300	30	10			1500	150	10		
		5699	10	570			4500	10	450		

# Modelling Results(1): Calcium leaching



The leaching of calcium was predicted to be significantly inhibited by the calcite precipitate layer in the case with the hypothetical reaction layer.

# Modelling Results(2): Bentonite alteration



The alteration of the bentonite buffer was suggested to be reduced if the calcite layer acted as a diffusion barrier at the interface between the cement and bentonite.

# Summary and Conclusions

- **A reactive transport computational code CCT-P, in which a geochemical model including the thermodynamic incongruent dissolution model of C-S-H is coupled with the advection-diffusion/dispersion equation, was developed.**
- **The code can consider the evolution of the hydraulic properties of the solid cement matrix due to the leaching and precipitation of components and the clogging effect by insoluble secondary phase precipitation that may inhibit the alteration of cement materials.**
- **A preliminary modelling calculation predicted that the evolution of the cementitious repository system would be significantly reduced under certain groundwater conditions by insoluble secondary minerals being precipitated on the cement materials.**