Comparative Study Using Some Advanced Simulation Methods for Leaching of Cementitious Materials Over Ten Thousands of Years

T. Torichigai*, K. Yokozeki*, T. Ishida**,
K. Nakarai***, D. Sugiyama****
* KAJIMA corporation (JAPAN)
** The university of Tokyo
*** Gunma university
**** Central Research Institute of Electric Power Industry

Background(1/3)

Nuclear power generation covers 30 percents of power generation in Japan.

Method for disposing radioactive waste is very important.

RADIOACTIVE WASTE

○High-level radioactive waste

→Geological disposal

(~-300m)

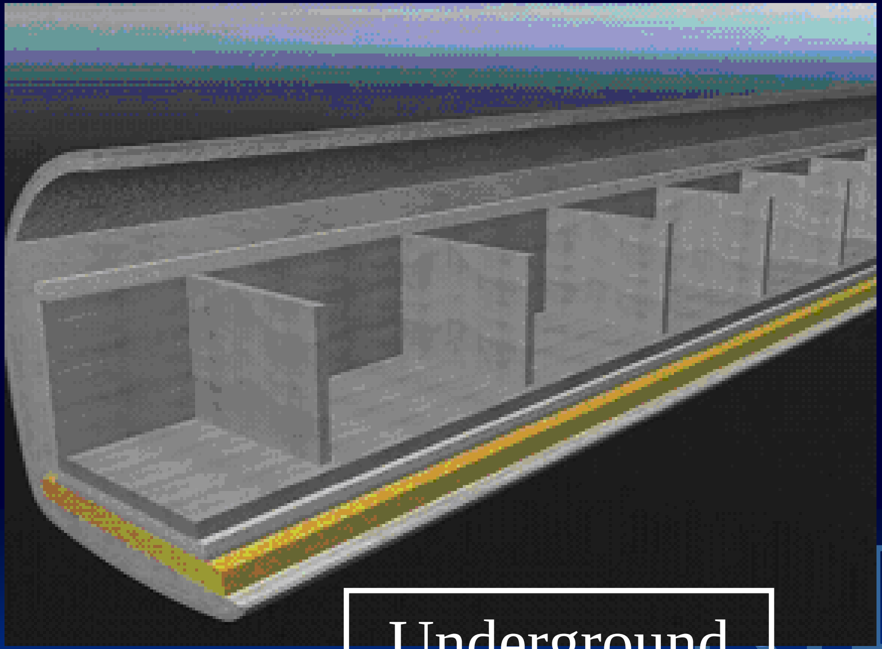
○Low-level radioactive waste

・ Concrete Pit

（ -10 ~ -5m ）

・ Sub-surface Disposal

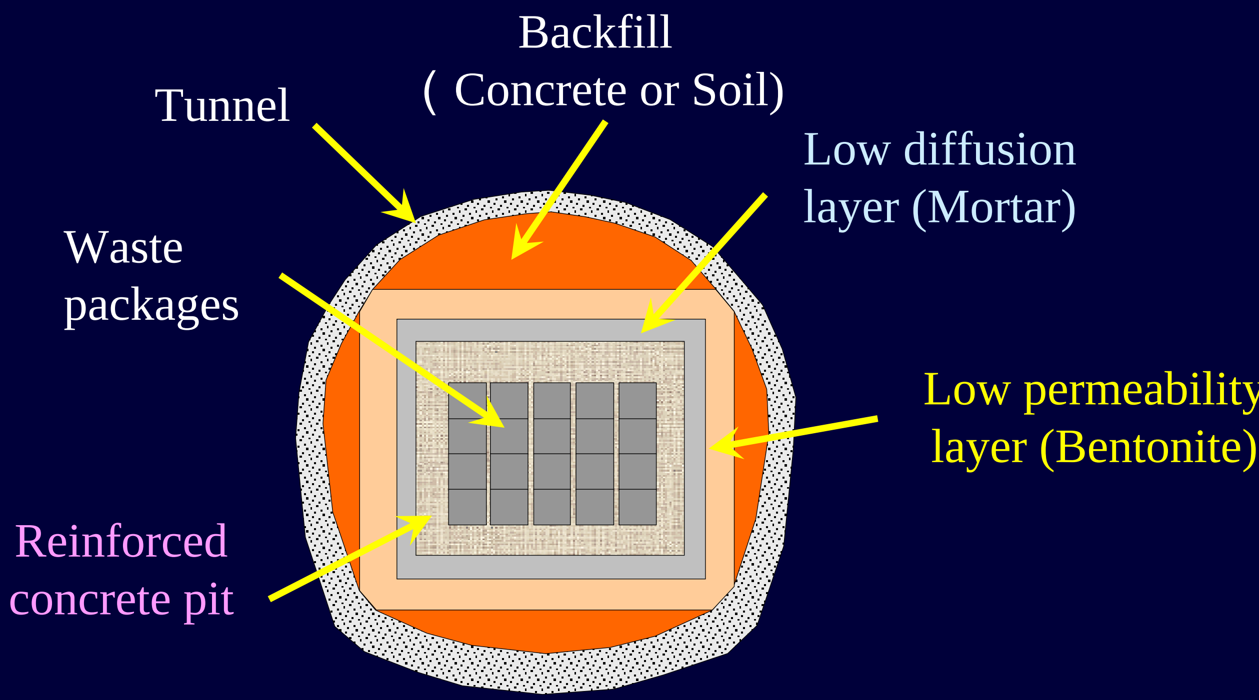
(-100 ~ -50m)



Underground
(-100 ~ -50m)

Background(2/3)

Cross sectional view of sub-surface disposal repository



Concrete pit：Maintaining stability of the repository

Mortar：Preventing radioactive nuclides to leak

Bentonite：Preventing underground water to permeate to the repository

Background(3/3)

Long-term durability (over 10,000 years) is demanded for this repository

Evaluating long-term durability of concrete is necessary

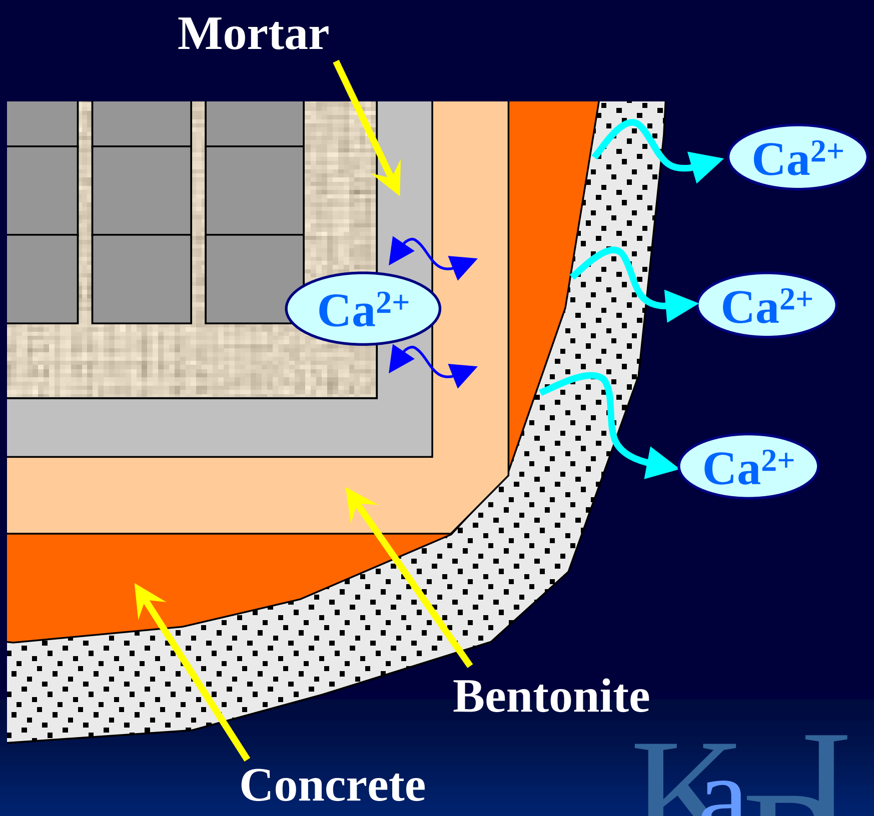
Issues for cementitious material

*Crack

*Chemical degradation

*Calcium leaching to underground water

*Chemical reaction between mortar and bentonite



Target of this study

Simulation-code for evaluating calcium leaching

for example… DuCOM, LIFE D.N.A., CCT-P

※Method of simulation is different.

Evaluating calcium leaching of cement hydrates by 3 codes.

- What kind of deterioration will occur in sub-surface disposal repository?
- How fast is the deterioration speed?

Evaluating method for calcium leaching

Numerical Simulations

Dissolution/Precipitation of Hydrates

- Thermodynamic database
- Solid-liquid equilibrium for calcium

& **Mass Transfer**

- Advection
- Diffusion
- Electrical potential

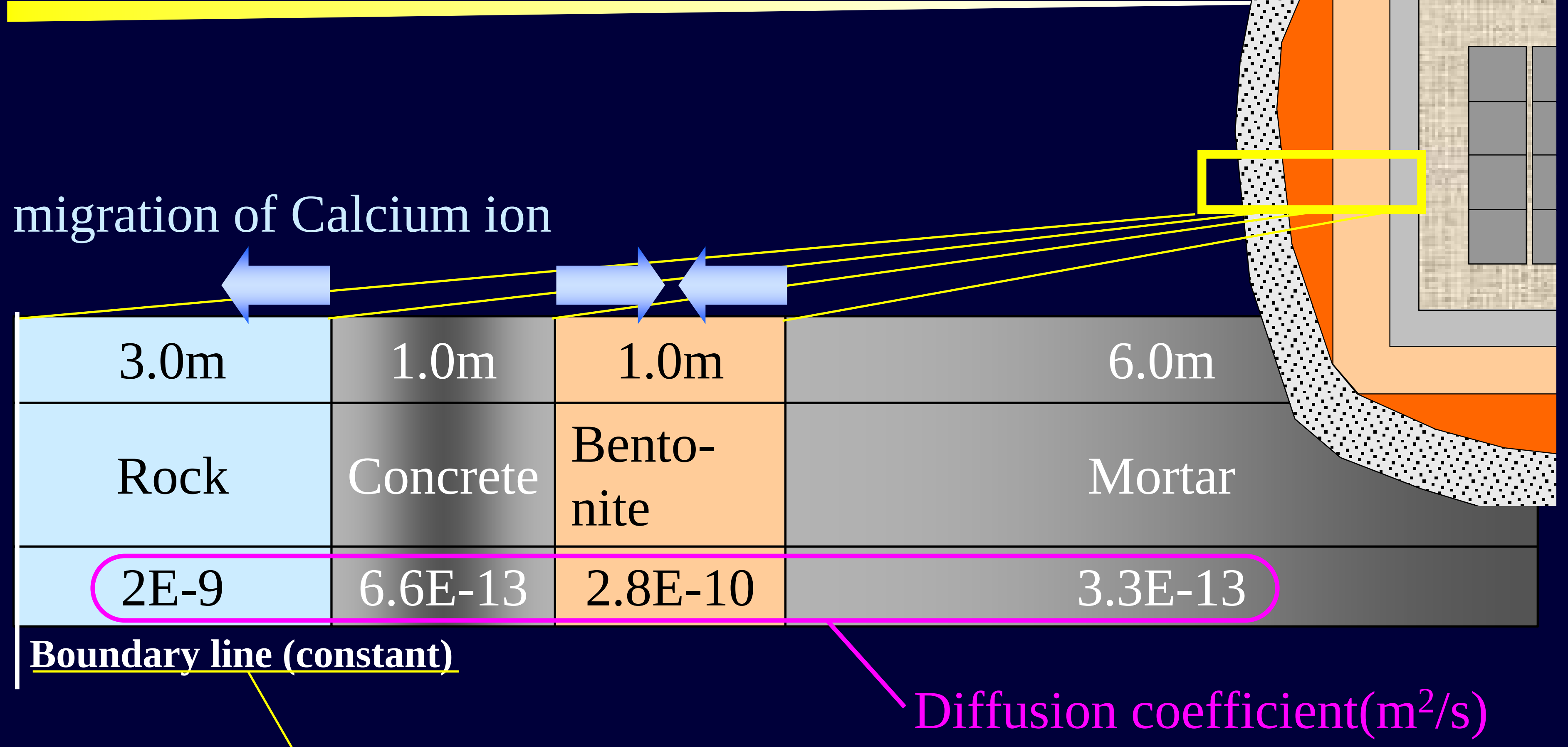
Experimental Models

$L = a \times t^{1/n}$ n ; parameter (generally n=2)
a ; constant parameter

Comparison of 3 codes

Code	Model of diffusion coefficient	Chemical reactions	
		Cementitious material	Bentonite
DuCOM	$D_{eff} = \frac{\phi \cdot S}{\Omega} \cdot \delta \cdot D_{ion}$	* Solid/liquid equilibrium for calcium	Absorption of Ca ions
LIFE D.N.A.	$D_{eff}^{i} = \eta \cdot \beta \cdot f(\phi) \cdot D_{\mathbf{0}}^{i}$	* Solid/liquid equilibrium for calcium (considering with Na, K) * precipitation of $CaCO_3$,$Mg(OH)_2$, Friedel's salt.	Absorption of Ca ions
CCT-P	$D(t) = D(0) \cdot \left(\frac{\phi(t)}{\phi(0)} \right)^n$	* Thermodynamic database * Incongruent dissolution of C-S-H * Dissolution/ precipitation of $CaCO_3$	Ion exchange reactions of Na, K, Ca and Mg

Simulation model



Composition of underground water

(mmol/l)

Ca^{2+}	Na^{+}	K^{+}	Mg^{2+}	SO_4^{2-}	Cl^{-}	CO_3^{2-}	pH
0.13	0.77	0.03	0.16	0.14	0.44	0.62	8.6

Conditions

Mix proportions of concrete and mortar

	W/B (%)	Air (%)	Unit Quantity (kg/m^3)					
			W	LPC	FA	LSP	S	G
Concrete	**45**	**2.5**	**160**	**249**	**107**	**249**	**832**	**786**
Mortar	**45**	**2.5**	**230**	**358**	**153**	**307**	**1223**	**-**

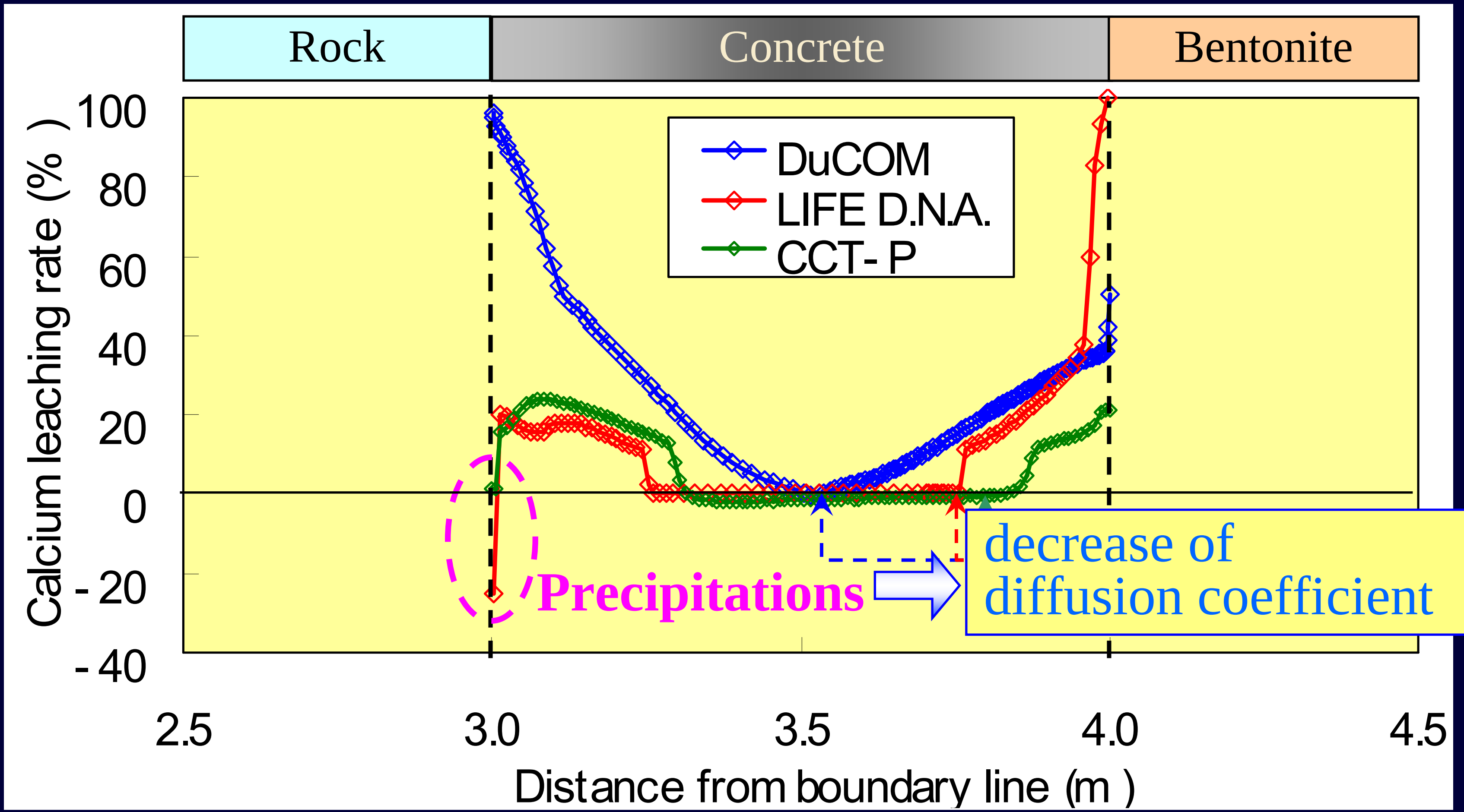
Cement hydrates using in calculation

DuCOM ; Portlandite, C-S-H

LIFE D.N.A. ; Portrandite, C-S-H, Calcite, Brucite, Friedel's salt, NaOH, KOH

CCT-P ; All hydrates in database

Simulation result of calcium leaching rate at 50,000 years



Faced to Bentonite

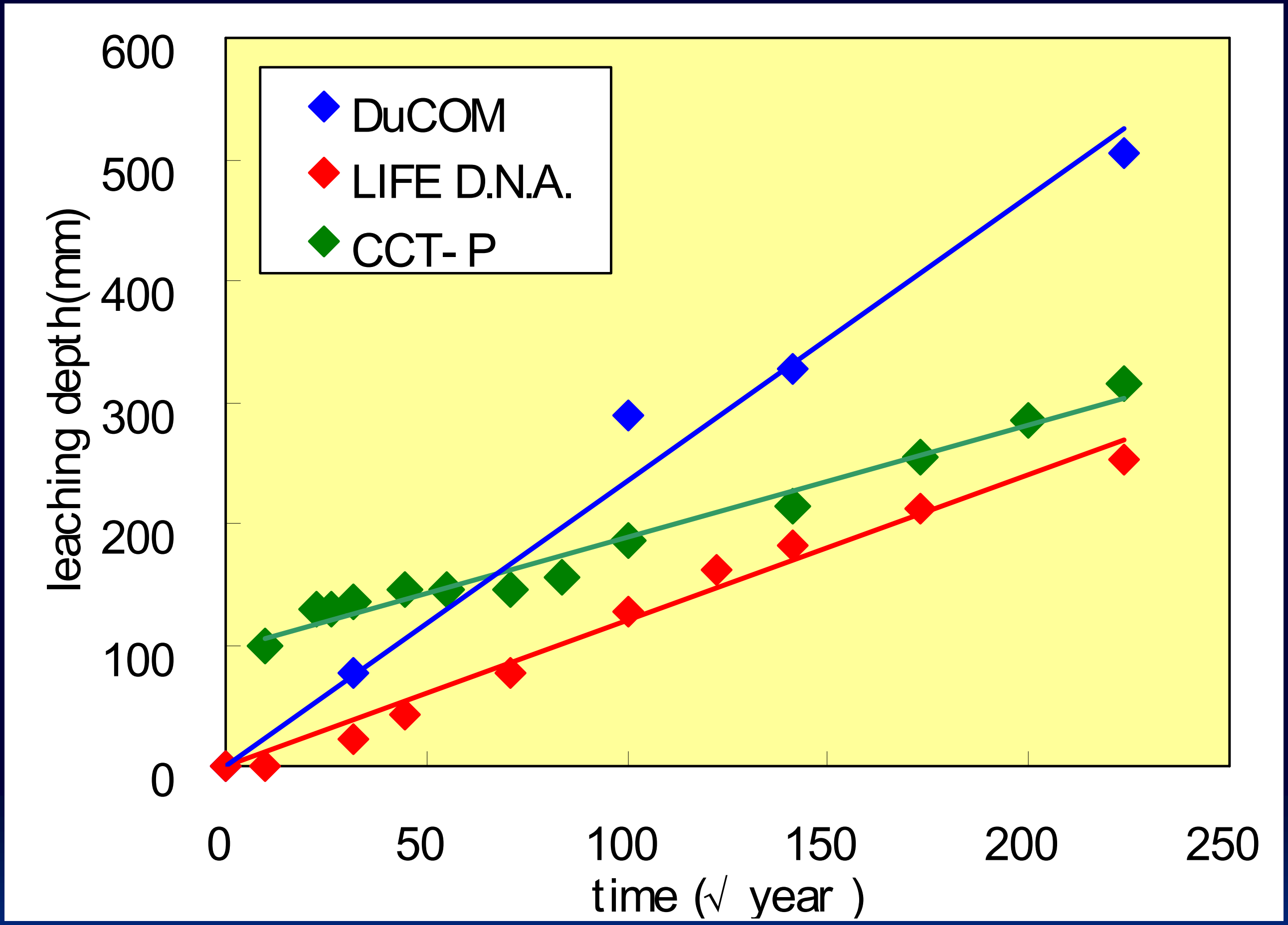
Leaching depth：DuCOM > LIFE D.N.A. > CCT-P

Faced to Rock

Leaching depth：DuCOM > CCT-P > LIFE D.N.A.

Evaluating for calcium leaching speed

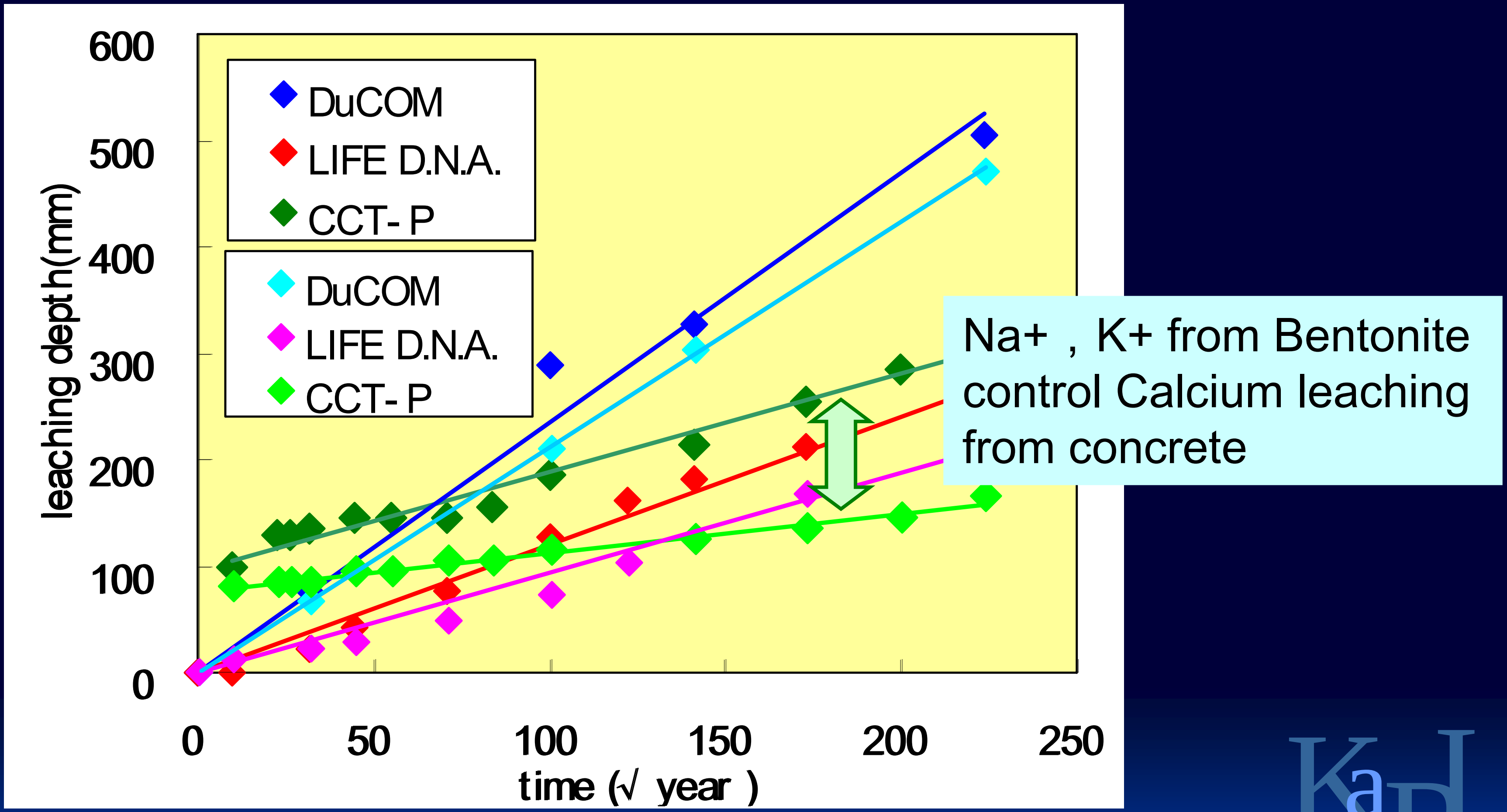
Calcium leaching speed of concrete (faced to rock)



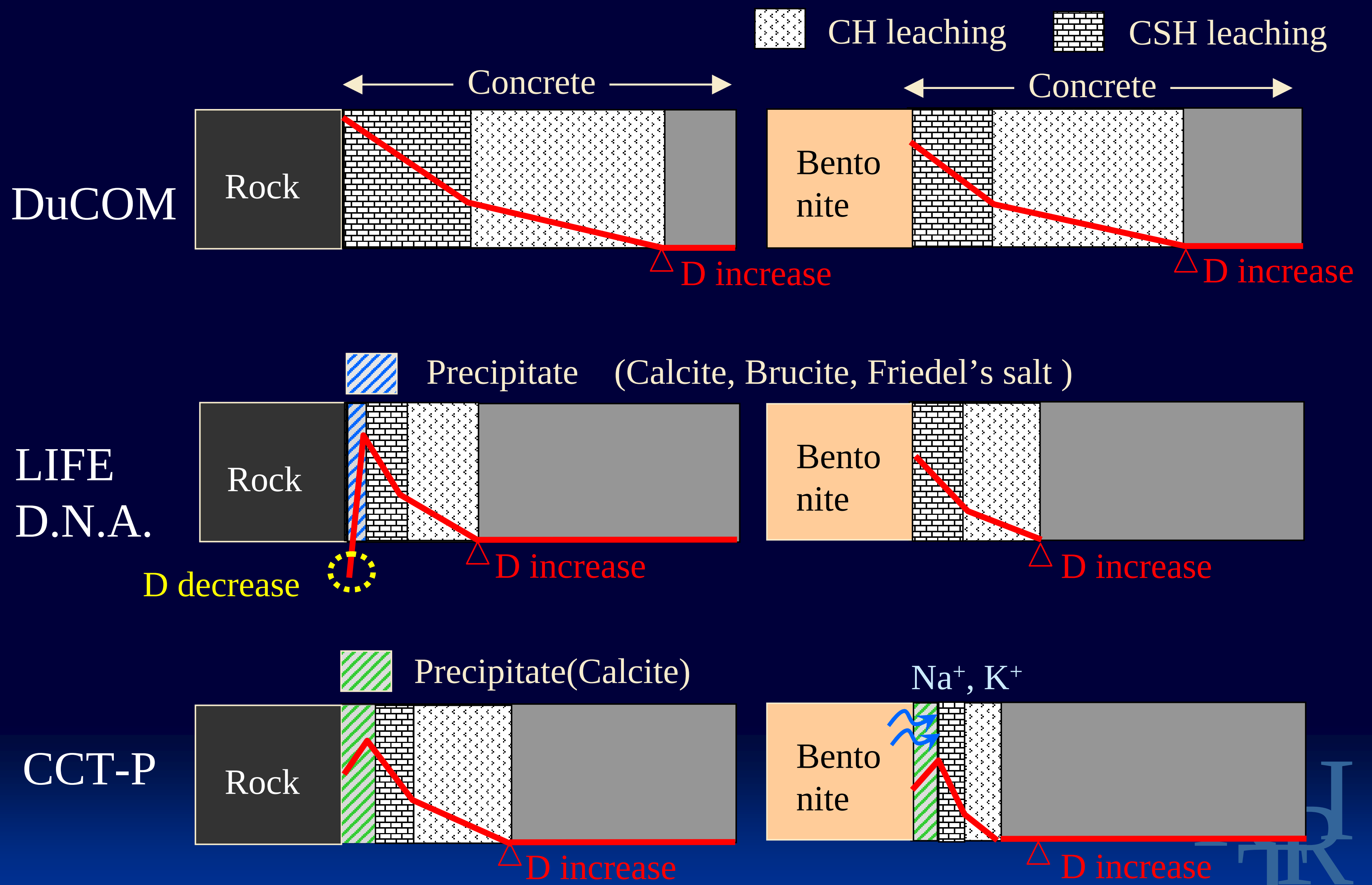
Leaching speed：DuCOM > LIFE D.N.A. > CCT-P

Evaluating for calcium leaching speed

Calcium leaching speed of concrete (faced to rock & bentonite)



Degradation process of cement hydrates



D;diffusion coefficient

Changing in diffusion coefficient

Dissolution/precipitation of cement hydrates

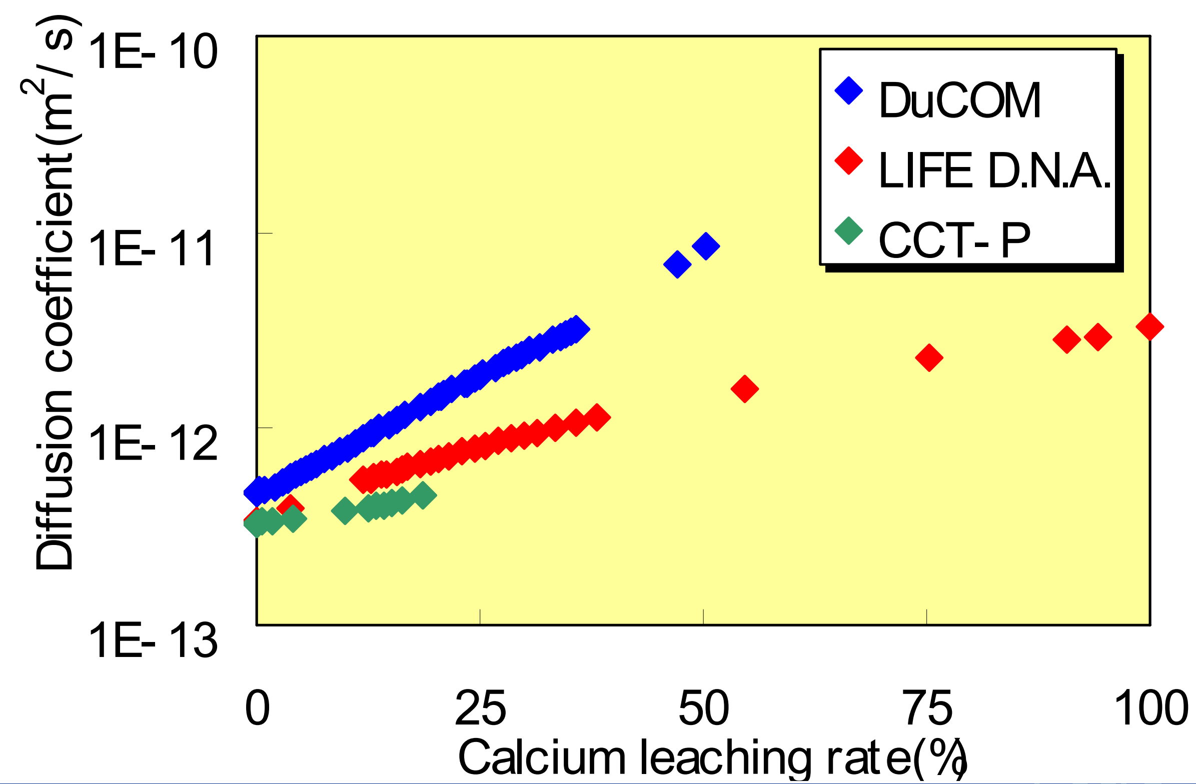
... Porosity increase/decrease

... Diffusion coefficient increase/decrease

$$D_{eff} = \frac{\phi \cdot S}{\Omega} \cdot \delta \cdot D_{ion}$$

$$D_{eff}^{i} = \eta \cdot \beta \cdot f(\phi) \cdot D_{0}^{i}$$

$$D(t) = D(0) \cdot \left(\frac{\phi(t)}{\phi(0)} \right)^{n}$$



Influential factor for Calcium leaching

- Changing in diffusion coefficient
- Chemical reaction (especially, precipitation)

⇓

- Degradation process of cement hydrate is different
- Calcium leaching speed is different

Conclusions

Evaluating calcium leaching of cement hydrates by 3 codes.

- What kind of deterioration will occur in sub-surface disposal repository?
  - Portlandite & C-S-H leach from cementitious material
  - Secondary minerals would precipitate
  - Degradation process is different in 3 codes

- How fast is the deterioration speed?
  - Calcium leaching speed is DuCOM > LIFE D.N.A.>CCT-P
  - Calcium leaching depth at 50,000 years are 130~500mm
  - The reason why simulation result is different…

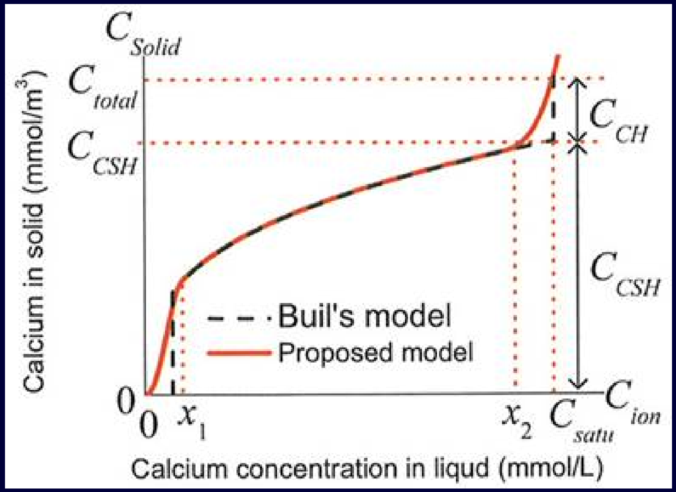
    Changing in diffusion coefficient

    Chemical reaction (especially, precipitation)

Appendix

Dissolution/Precipitation of Hydrates

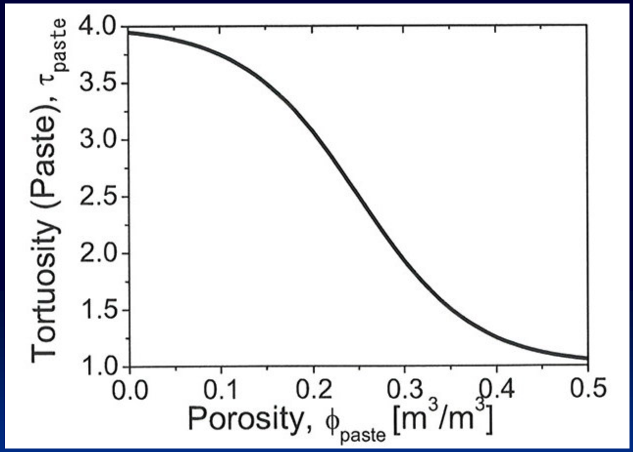
Calcium liquid/Solid equilibrium

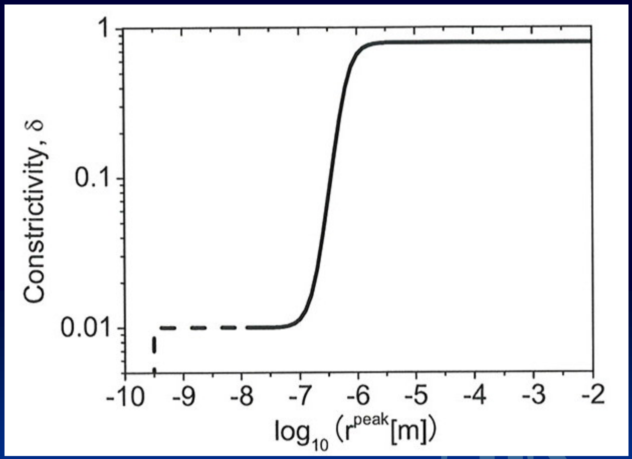


Mass Transfer

- Transport by solution flow
- Transport by diffusion

$$D_{eff} = \frac{\phi \cdot S}{\Omega} \cdot \delta \cdot D_{ion}$$

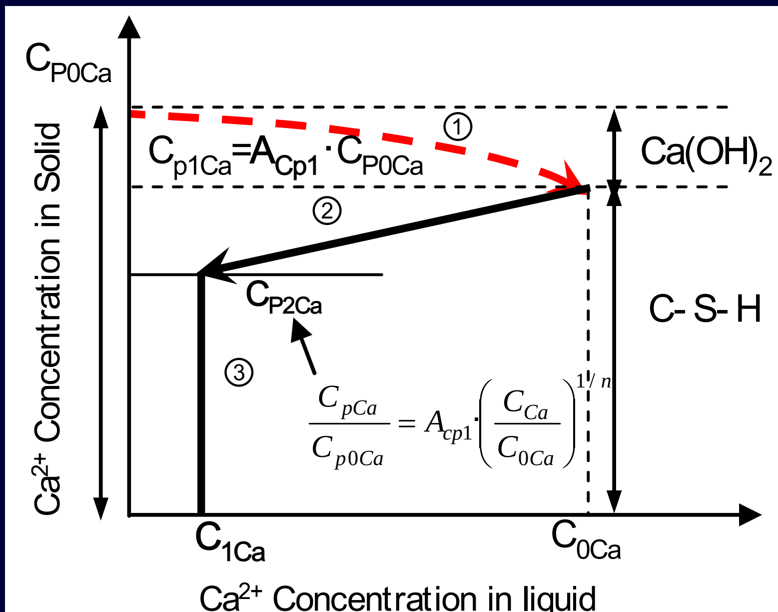




Calcium leaching = Porosity increase = D increase

Dissolution/Precipitation of Hydrates

Calcium liquid/Solid equilibrium



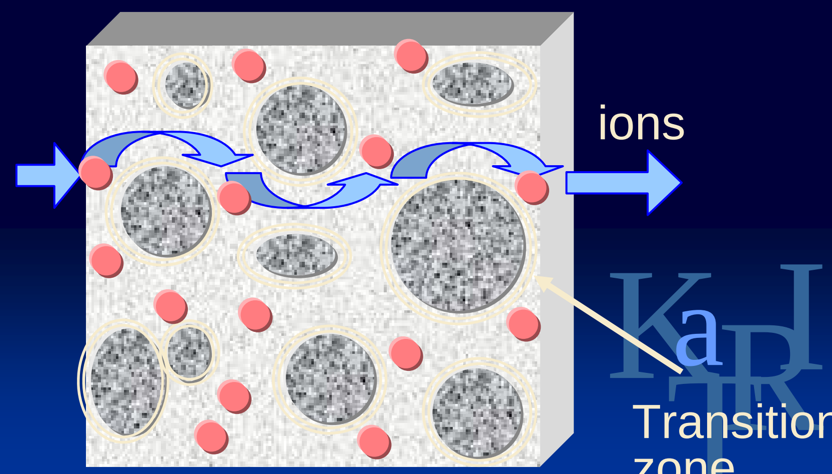
$$f(\phi) = 0.001 + 0.07\phi^2\{1.8(\phi - 0.18)\cdot \mathrm{H}(\phi - 0.18)$$

$$\beta = \frac{1 - c \cdot G_{vol}}{1 - d \cdot S_{vol}} \cdot P_{vol}$$

Mass Transfer

- Transport by solution flow
- Transport by diffusion
- Electric force

$$D_{eff}^{i} = \eta \cdot \beta \cdot f(\phi) \cdot D_{\mathbf{0}}^{i}$$



CCT-P

Dissolution/Precipitation of Hydrates

- the thermodynamic database (Chemical reaction code HARPHRQ)
- Incongruent dissolution of C-S-H

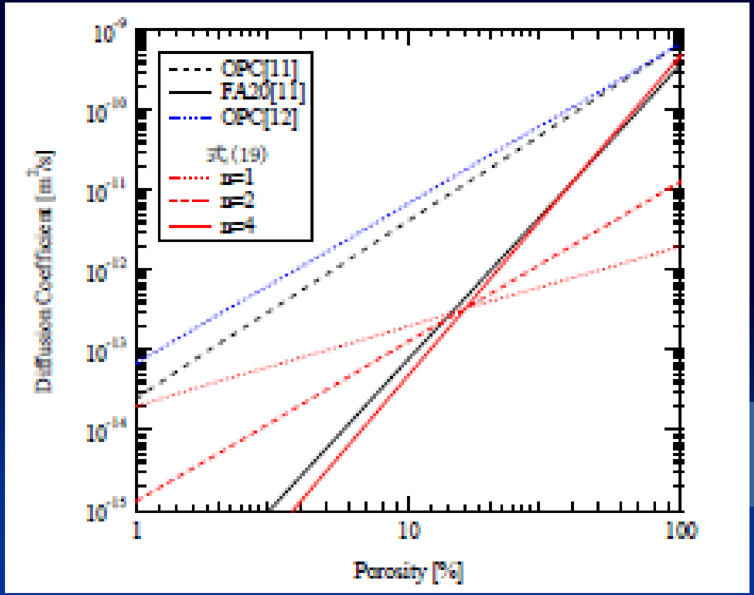
$$\log K_i = \frac{x^{i-1}}{1+x}\log K_{0i} - \frac{x^{i-1}}{1+x}\log\left(\frac{x^{i-1}}{1+x}\right) + \frac{x}{(1+x)^2}\left\{A_{0i} + A_{1i}\frac{1-x}{1+x} + A_{2i}\left(\frac{1-x}{1+x}\right)^2\right\}$$

$\log K_{sp}$ of C-S-H gel depend on the rate of Ca/Si

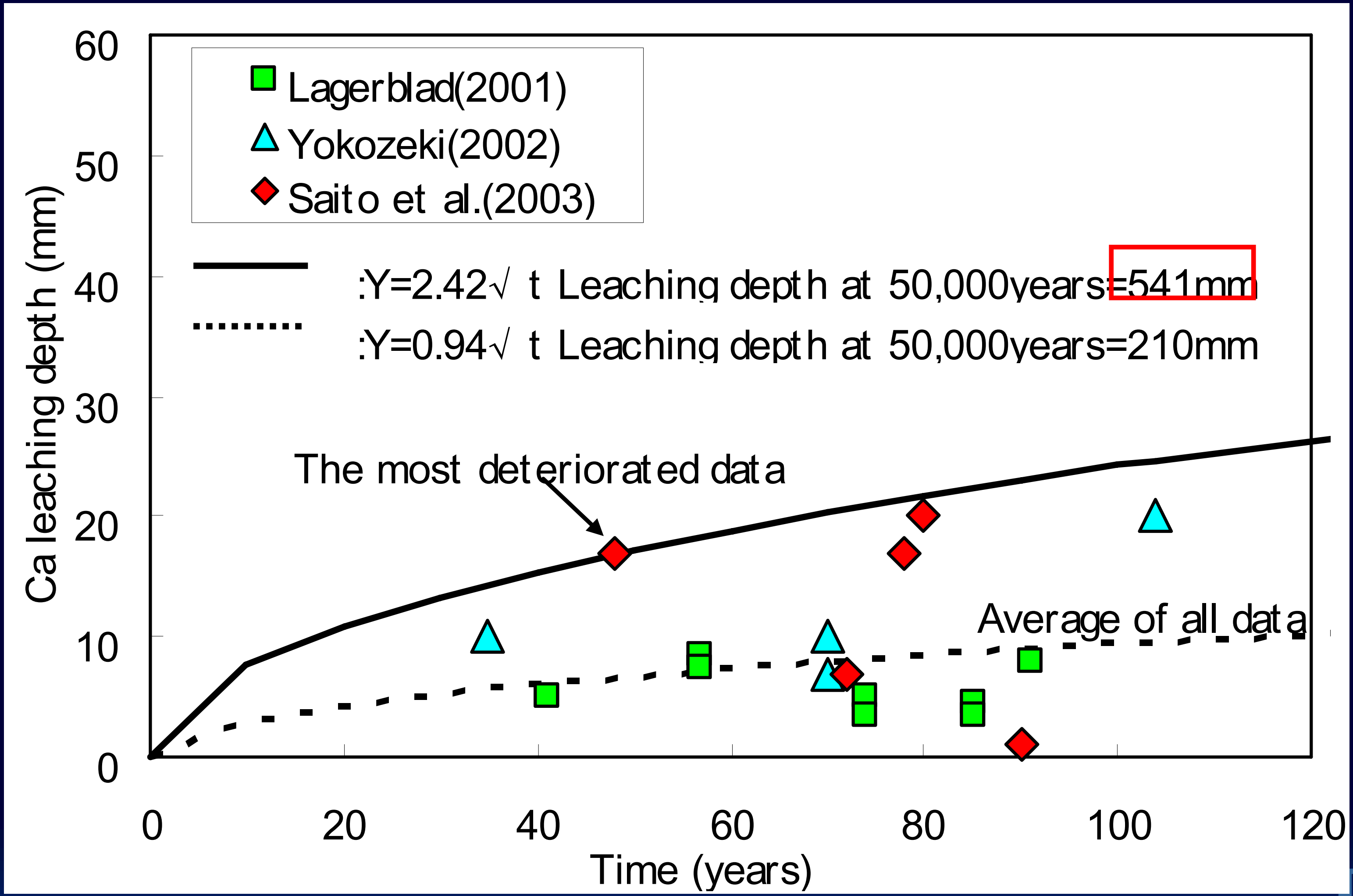
Mass Transfer

- Transport by solution flow
- Transport by diffusion

$$D(t) = D(0)\cdot\left(\frac{\phi(t)}{\phi(0)}\right)^n$$

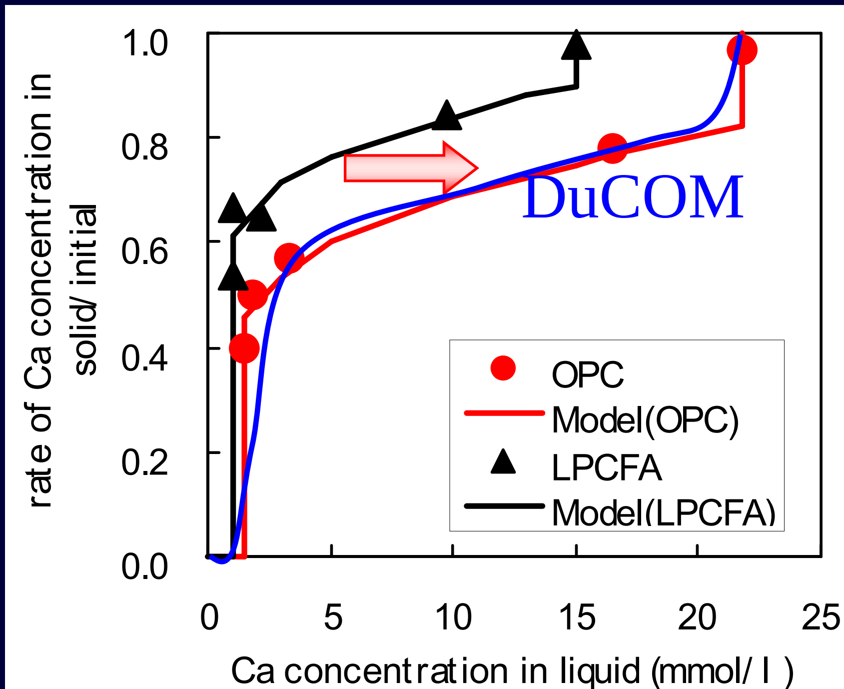


Investigation result of the old structures

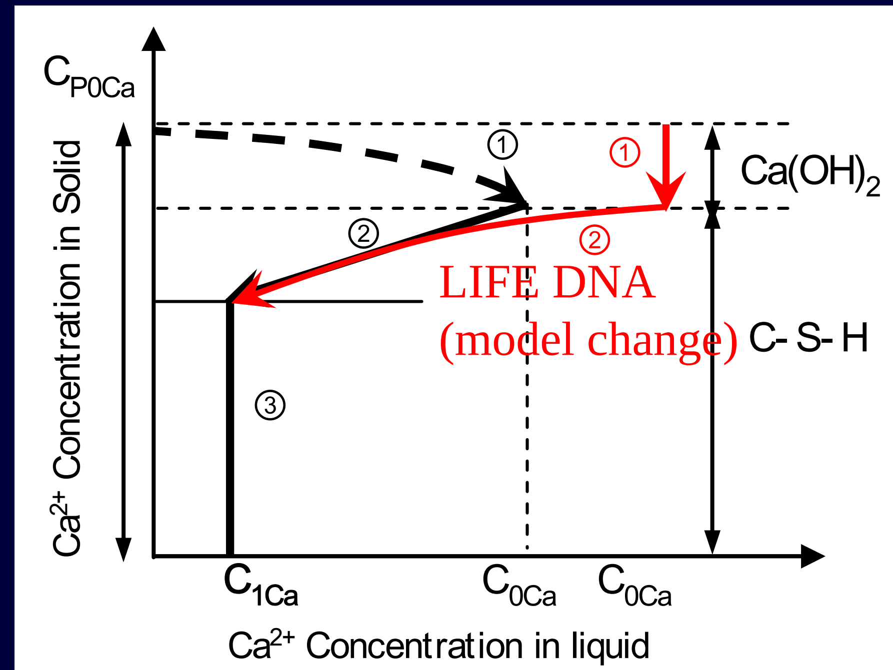


Simulation results = 130 ~ 500mm at 50,000 years

Comparison DuCOM to LIFE D.N.A.



<Different type of cement>



<affect Na ions & K ions>