Seawater Intrusion Effect on Radioactive Strontium Mobility

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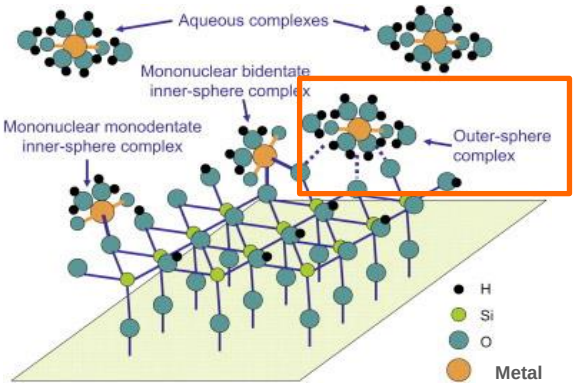
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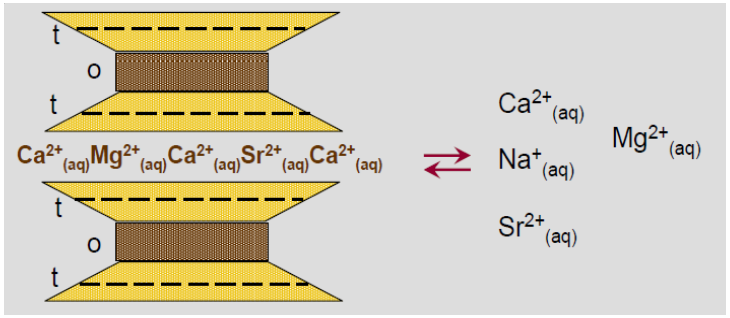
1.1. Rad-Strontium (^{90}Sr)

- Pure β-emitter, $T_{1/2}$ = 28.8 y
- ^{90}Sr migration is controlled by sorption reactions (i.e., ion-exchange).
- In general, ^{90}Sr sorbs on clay / Fe-oxides / other minerals

  → via weakly bound outer-sphere surface complexes
- Degree of sorption
  : depends on factors (e.g. pH / I.S./ solid phase composition/ surface area)

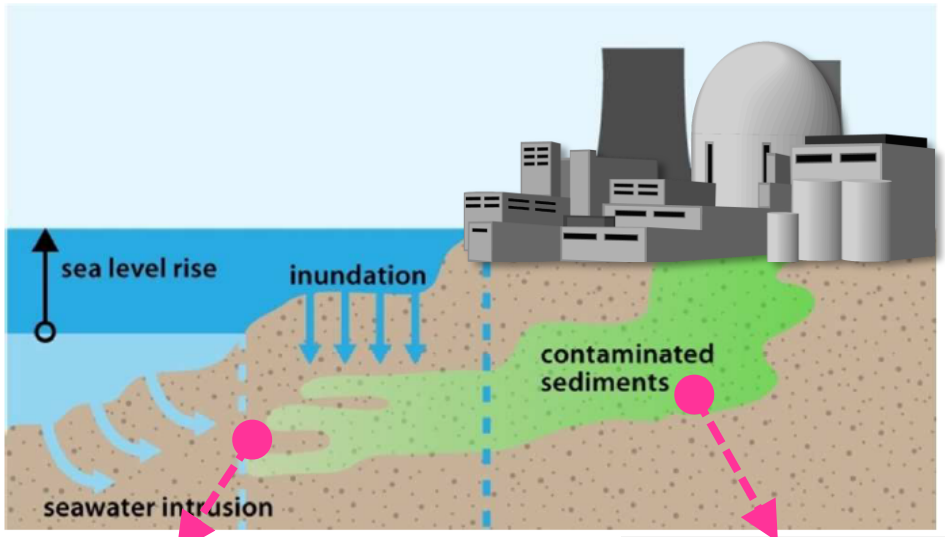


Dan Hawkes, U.S. Department of Energy, 2013



J. P. Mckinley, et. al., 2007

2. Salinization and ^{90}Sr leak scenarios at a NPP site



Jane Eagling, et al., 2012

2) Accelerated radionuclide transport due to the change of subsurface water condition.

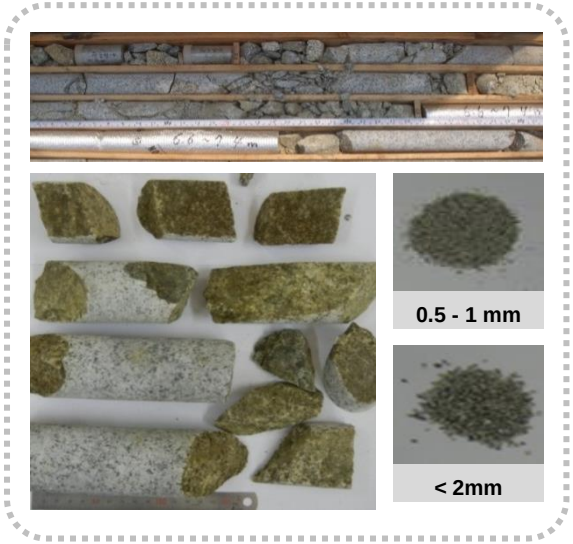
1) Radionuclide transport along the groundwater flow in porous geosphere.

<Objectives>

- To determine K_d and R depending on different ionic strength degrees in solution
- To model quantitatively the amount of sorption affinity of ^{90}Sr as a function of the corresponding activities in solution
- To compare the exchange convention for describing the data set

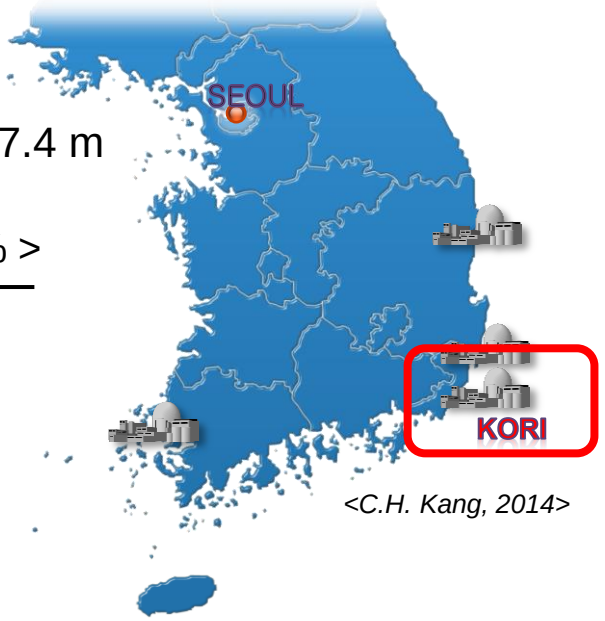
3.1. Materials

- Study area : Shin-Gori 3-4 reactor site in Koera
- Solid samples : core rock (shattered zone), GL(-) 6.6 – 7.4 m



< Mineral composition, % >

Quartz	**22.20**
Albite	**39.00**
Orthoclase	19.00
Muscovite	6.00
Biotite	3.00
Chlorite	6.00
Actinolite	4.80
Total	100.00



<C.H. Kang, 2014>

- Cation exchange capacity

Methods	Fraction size	CEC [μeq/g]
NH_4-OA_c (pH 7)	0.5 – 1 mm	**23.11**
1 M of $NaNO_3$ / KNO_3 (pH 7)	< 2 mm	**24.21**

- Solution samples

	pH	I.S. [M]
GW	7.70	**0.005**
SW	8.08	**0.770**

3.2. Batch & Column exp.

<Batch adsorption>

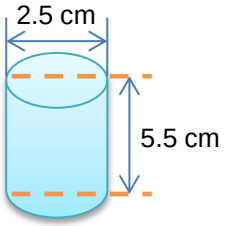
- < 1 mm size solid, adsorbent (0.5 g/ 10 mL)
- ^{90}Sr 10 Bq/mL, reaction time 10 d
- Experimental procedure
  - initial concentration : ^{90}Sr 10 Bq/mL



<Column>

- 0.5 – 1 mm fractionated solid
- Stable Sr (ICP-OES analysis)
- Injected Br / Sr: 10071 and 0.175 mg/L
- Column set-up condition

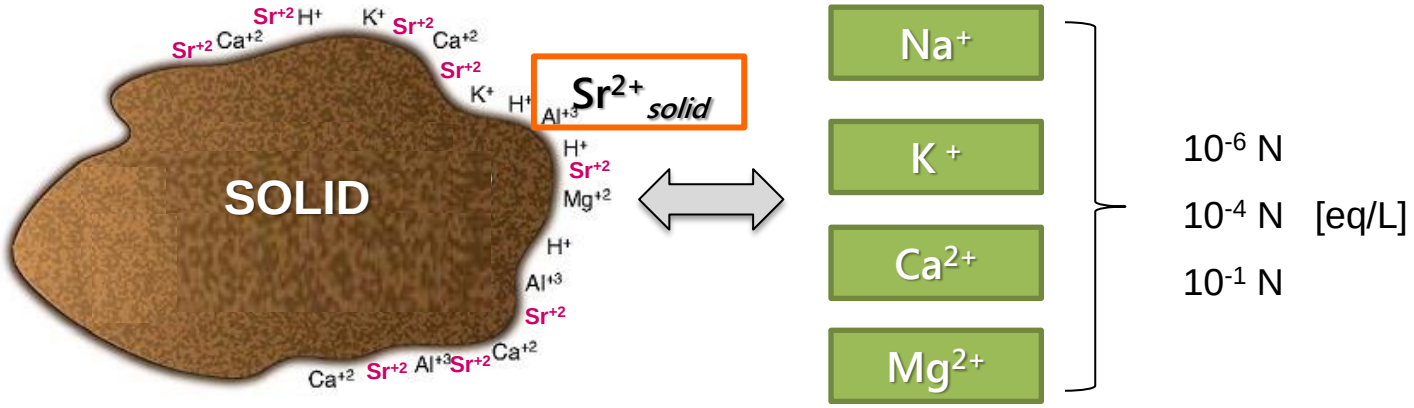




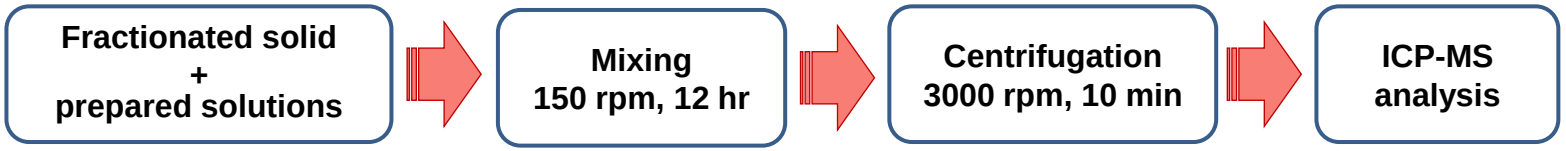
No.	Type fluids	I.S. [M]	Porosity (θ)	Bulk density [g/cm^3]	Pore vol. [cm^3]	Flow rate [mL/min]
1	**GW**	**0.005**	0.42	1.43	11.73	
2	**GW+SW (50 : 50)**	**0.388**	0.40	1.55	11.00	0.03
3	**SW**	**0.770**	0.41	1.49	11.33	

3.3. Binary ion-exchange exp.

- 75 - 150 μm fractionated solid (non pretreated)
- Reaction time: 12 h (0.5 g /10 mL)
- Initial pH of solutions: pH 7
- Chemical reagent: $NaNO_3$, KNO_3, $Ca(NO_3)_2 \cdot 4H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$



- Experimental procedure



- Selectivity coefficient, $K_{selectivity}$

  - indicate the adsorption affinity to the solid materials

    : dependence on pH, I.S., sorbent heterogeneity, specific adsorption, or variation of the activity of the adsorbed species

- Mole fraction

$$x_{Sr} = q_{Sr}/(qSr + qM)$$

- Equivalent fraction

$$y_{Sr} = q_{Sr}/(2qSr + qA)$$

$$y_{Sr} = q_{Sr}/(2qSr + 2qB)$$

M: competing cation (Na^+, K^+, Ca^{2+}, Mg^{2+})
A: monovalent cation (Na^+, K^+)
B: divalent cation (Ca^{2+}, Mg^{2+})
q: amount of bound cations
a: activities in solution
$SrX, AX\ and\ BX$: exchanger phase with -1 charge
$SrY, AY\ and\ BY$: exchanger phase with -2 charge

- X (surface site) = '-1'

$$SrX_2 + 2A^+ = A_2X_2 + Sr^{2+}$$ <hetero-exchange>

$$SrX_2 + B^{2+} = BX_2 + Sr^{2+}$$ <homo-exchange>

$$K_{Vanselow} = \frac{a_{Sr}x^2A}{a^2A\,x_{Sr}} \text{ or } = \frac{a_{Sr}xB}{aB\,xSr}$$

$$K_{Gaines_Thomas} = \frac{a_{Sr}y^2A}{a^2A\,y_{Sr}} \text{ or } = \frac{a_{Sr}yB}{aB\,y_{Sr}}$$

- Y (surface site) = '-2'

$$SrY + 2A^+ = A_2Y + Sr^{2+}$$ <hetero-exchange>

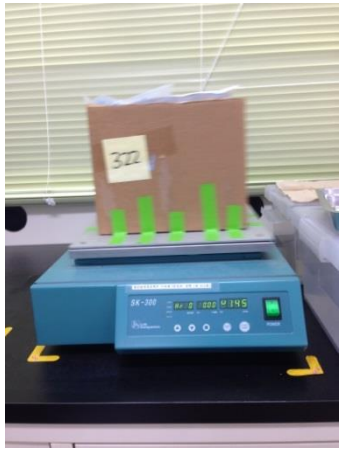
$$SrX_2 + B^{2+} = By + Sr^{2+}$$ <homo-exchange>

$$K_{Cernik} = \frac{a_{Sr}yA}{a^2A\,y_{Sr}} \text{ or } = \frac{a_{Sr}yB}{aB\,y_{Sr}}$$

3.4. Salinity effect on exchangeable Sr

- 75 - 150 μm fractionated solid (non pretreated)
- original GW and SW
- 0.5 g / 10 mL^{-1}
- Reaction time: 1, 4, 12 h and 1, 3, 7, 14, 30 d
- Solution types

Name	GW : SW [%]	I.S. [M]	pH	Sr [mg/L]
SET 1	**100 : 0**	**0.01**	7.81	**0.23**
SET 2	**70 : 30**	**0.24**	7.90	**2.09**
SET 3	**50 : 50**	**0.39**	8.00	**3.33**
SET 4	**30 : 70**	**0.54**	8.01	**4.65**
SET 5	**0 : 100**	**0.77**	8.10	**6.50**



4.1. Batch & Column experimental Results

<Results of batch adsorption>

- Sorption distribution coefficient (K_d) of ^{90}Sr

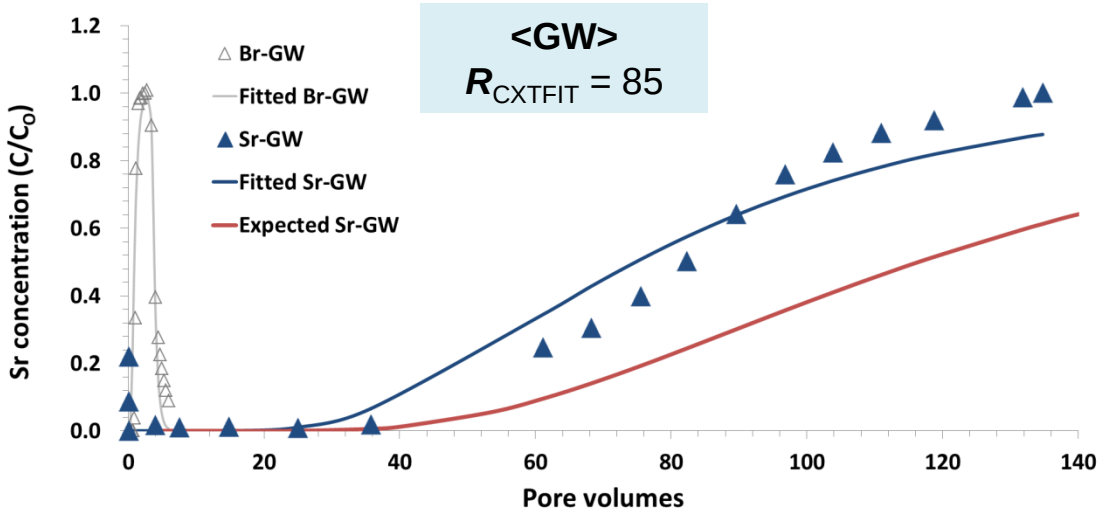
No.	Fluid type	I.S. [M]	pH	K_d [mL/g]
1	GW	0.005	7.81	**39.0**
2	GW+SW (50 : 50)	0.388	8.00	**26.2**
3	SW	0.770	8.10	**13.4**

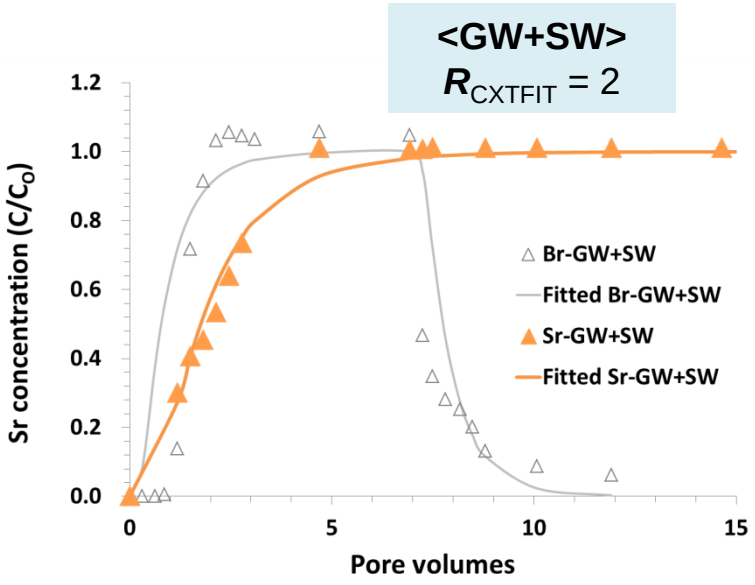
<Results of column – Br tracer>

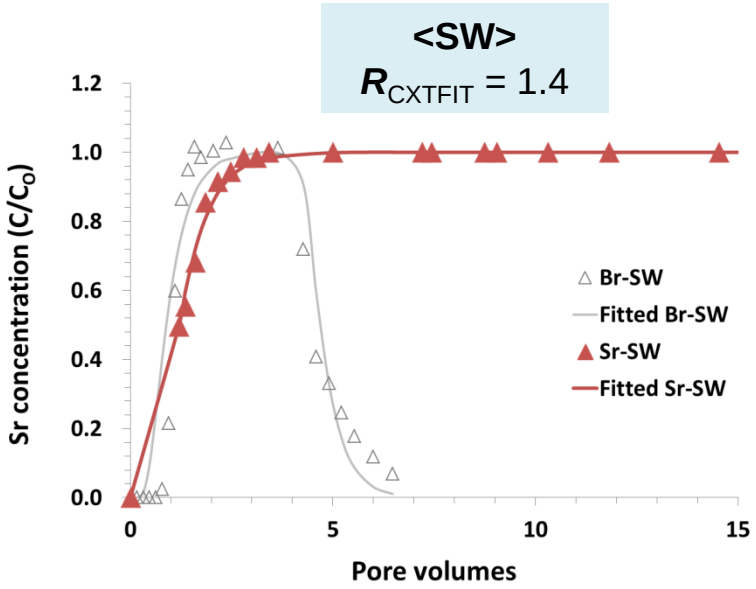
- Dispersion coefficient ***(D)*** from CXTFIT equilibrium model fit

No.	Fluid type	I.S. [M]	*R*	*D* [cm^2/min]
1	GW	0.005	1	**0.01**
2	GW+SW (50 : 50)	0.389	1	**0.01**
3	SW	0.770	1	**0.02**

<Results of Sr transport>







4.2. Binary ion-exchange exp.

- Sr_{Solid} - Na^{+}

log I.S. [M]	log $Sr_{extracted}$ [M]	log K_{G-T}
-3.6	-7.87	**3.59**
-2.7	-7.38	**2.65**
0.2	-6.16	**1.60**

- Sr_{Solid} - K^{+}

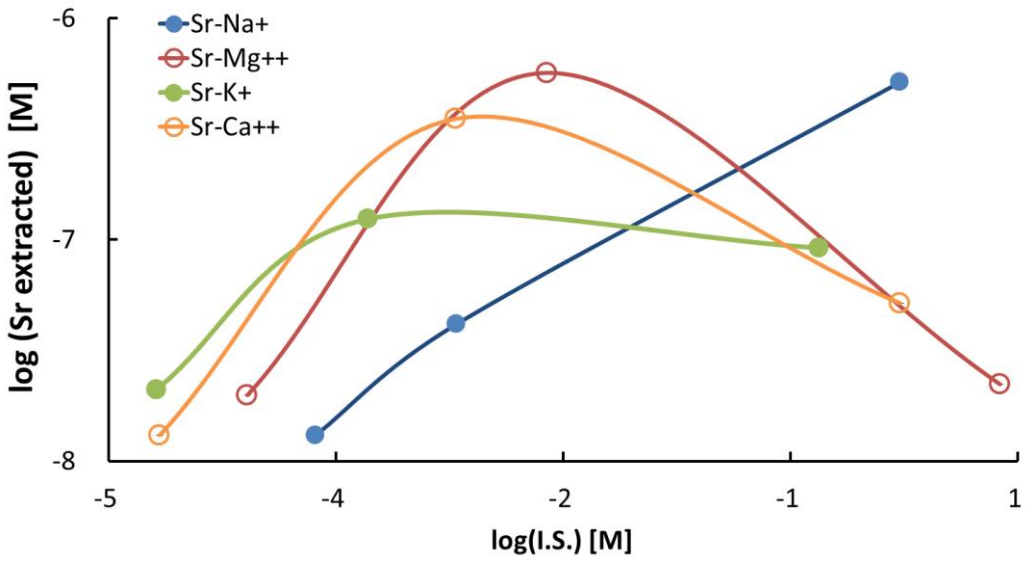
log I.S. [M]	log $Sr_{extracted}$ [M]	log K_{G-T}
-4.7	-7.66	**3.89**
-3.3	-6.86	**3.08**
-0.3	-6.42	**0.13**

- Sr_{Solid} – Ca^{2+}

log I.S. [M]	log $Sr_{extracted}$ [M]	K_{G-T}
-4.7	-7.87	**1.00**
-2.7	-6.37	**0.99**
0.2	-6.59	**0.84**

- Sr_{Solid} – Mg^{2+}

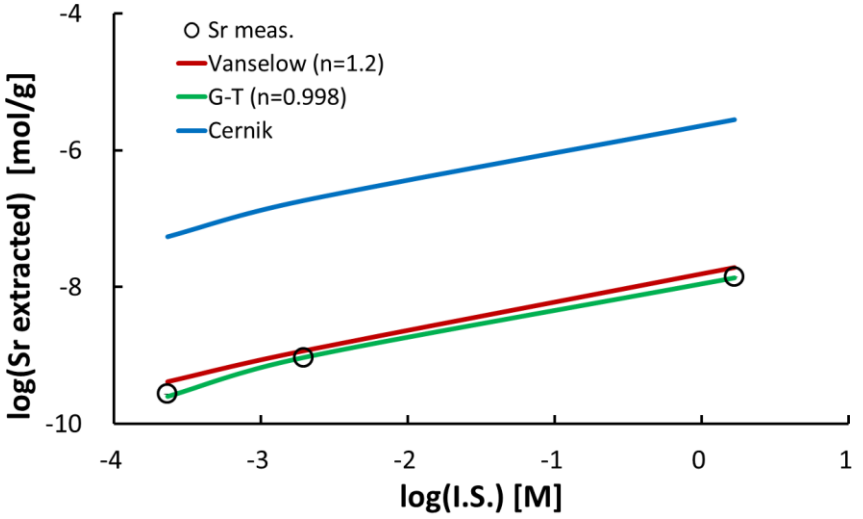
log I.S. [M]	log $Sr_{extracted}$ [M]	log K_{G-T}
-4.1	-7.68	**0.99**
-2.1	-6.09	**0.97**
0.9	-6.86	**0.52**



<hetero-exchange isotherm>

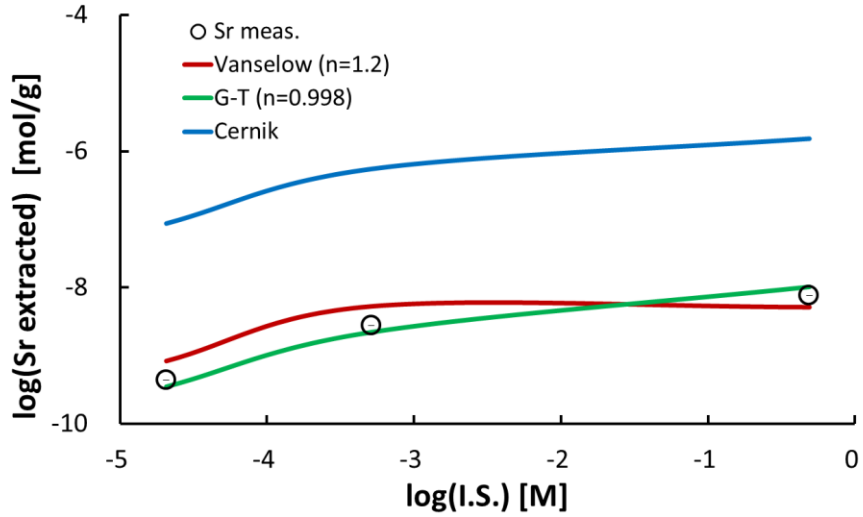
- Sr_{Solid} - Na^+

log I.S. [M]	log $Sr_{extracted}$ [M]	log $K_{Vanselow}$	log K_{G-T}	log K_{Cernik}
-3.6	-7.87	**3.89**	**3.59**	**3.58**
-2.7	-7.38	**2.95**	**2.65**	**2.64**
0.2	-6.16	**1.90**	**1.60**	**1.60**



- Sr_{Solid} - K^+

log I.S. [M]	log $Sr_{extracted}$ [M]	log $K_{Vanselow}$	log K_{G-T}	log K_{Cernik}
-4.7	-7.66	**4.19**	**3.89**	**3.89**
-3.3	-6.86	**3.38**	**3.08**	**3.08**
-0.3	-6.42	**0.43**	**0.13**	**0.13**



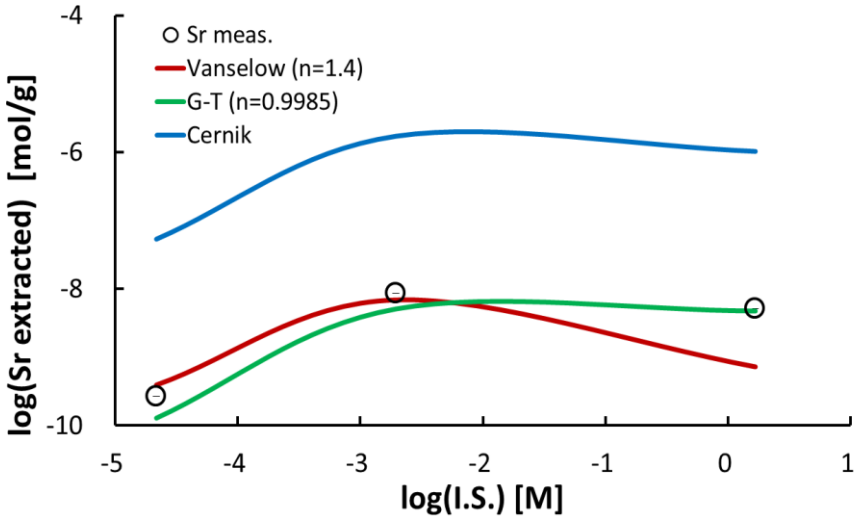
<homo-exchange isotherm>

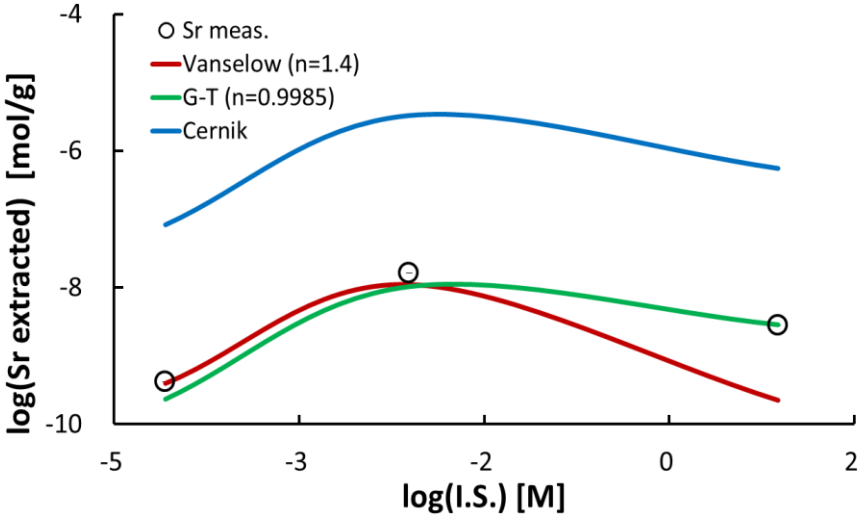
- $Sr_{Solid} - Ca2^{+}$

log I.S. [M]	log $Sr_{extracted}$ [M]	$K_{Vanselow}$	K_{G-T}	K_{Cernik}
-4.7	-7.87	**1.00**	**1.00**	**1.00**
-2.7	-6.37	**0.99**	**0.99**	**0.99**
0.2	-6.59	**0.84**	**0.84**	**0.84**

- $Sr_{Solid} - Mg2^{+}$

log I.S. [M]	log $Sr_{extracted}$ [M]	$K_{Vanselow}$	K_{G-T}	K_{Cernik}
-4.1	-7.68	**0.99**	**0.99**	**0.99**
-2.1	-6.09	**0.97**	**0.97**	**0.97**
0.9	-6.86	**0.52**	**0.52**	**0.52**

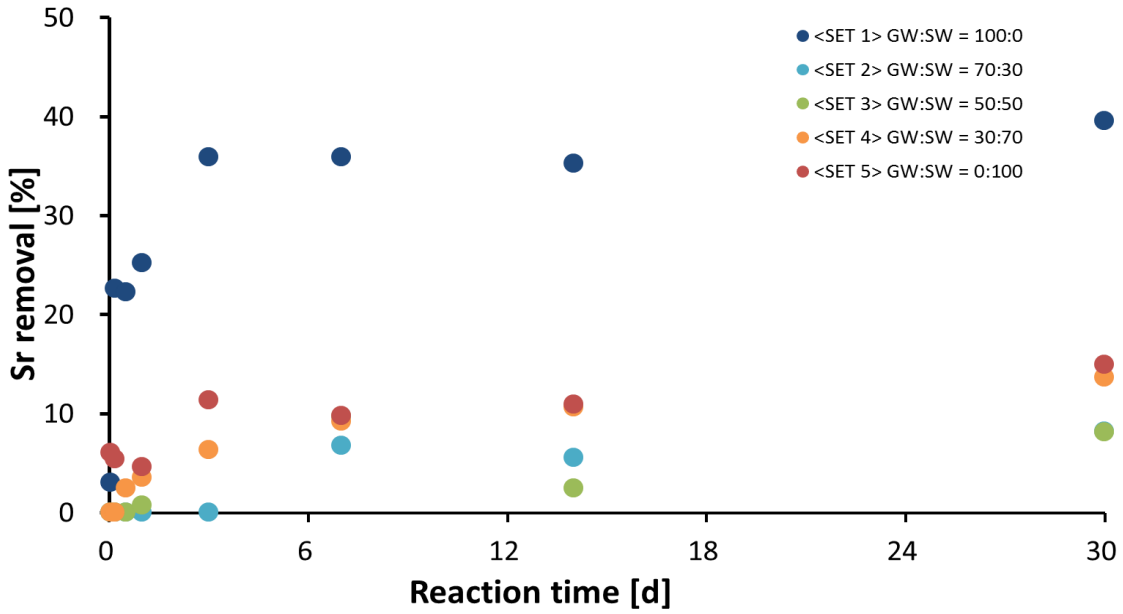




4.3. Salinity effect on exchangeable Sr

- Sr removal efficiencies in solution

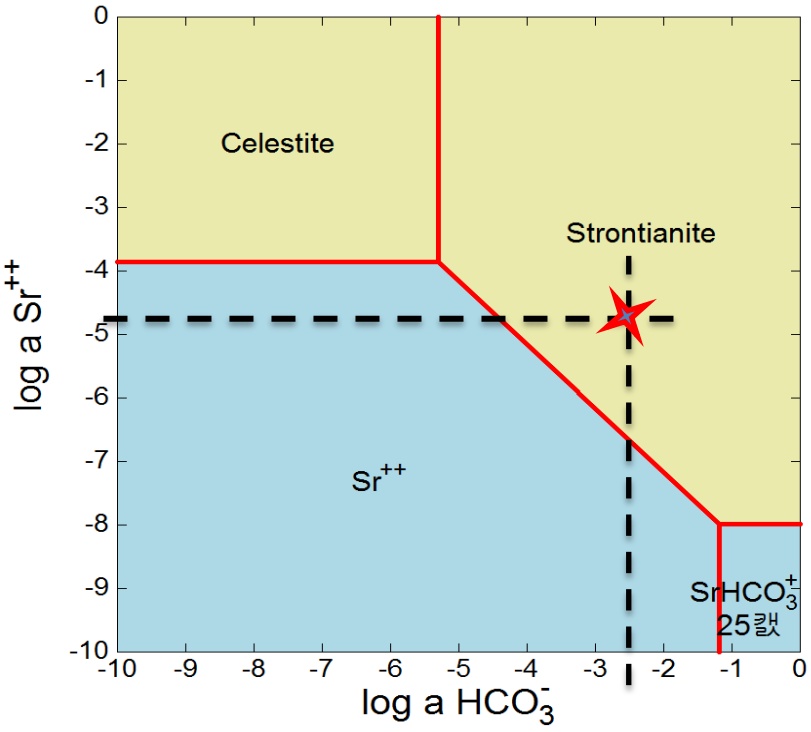
Name	GW : SW [%]	I.S. [M]	$Sr_{initial}$ [mg/L]	$Sr_{after\ reaction}$ [mg/L]	Max. $Sr_{solution}$ removal [%]
SET 1	100 : 0	0.01	0.23	0.14	39.5
SET 2	70 : 30	0.24	2.08	1.91	8.18
SET 3	50 : 50	0.39	3.33	3.06	8.11
SET 4	30 : 70	0.54	4.65	4.02	13.7
SET 5	0 : 100	0.77	6.49	5.52	15.0



4.3. Salinity effect by kinetic reaction

- Sr removal efficiencies in solution

Name	GW : SW [%]	I.S. [M]	$Sr_{solution}$ removal [%]
SET 1	**100 : 0**	**0.01**	39.5
SET 2	**70 : 30**	**0.24**	8.18
SET 3	**50 : 50**	**0.39**	8.11
SET 4	**30 : 70**	**0.54**	13.7
SET 5	**0 : 100**	**0.77**	15.0



→ Precipitation as 'Strontianite'

$$Sr^{2+} + HCO^{3-} \rightarrow SrCO_3(s) \downarrow + H^+$$

(log Q/K = 1.3010 s/sat)

5. Conclusions

- Sr sorption distribution coefficient (K_d) decreased by increasing I.S.
  : Sr sorption affinity in groundwater decreased with the seawater intrusion

- The mobility of Sr decreased in groundwater column
  : higher Sr sorption affinity in groundwater condition than seawater due to low amounts of competing cations.

- Sr-Na exchange showed linear isotherm
  : Sr ion-exchange reaction affected by divalent cations at low I.S. condition, however, Na^+ ion should be more affected factor at high I.S. condition.

- Vanselow and Gains-Thomas conventions well described Sr hetero-exchange reaction, while Gains-Thomas showed better homo-exchange isotherm under low I.S. condition.

- Strontianite precipitation occurs at high concentration of Sr in seawater solution.

<Future study> The additional model parameters have to be optimized to improve the model fit and to handle the variability of $K_{selectivity}$ for Sr transport model.

Acknowledgement

This research work was supported by World Class University (WCU) (R31-30005) Program and is supporting by Basic research support project (4.0010363.01) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology. The authors also acknowledge the KEPCO/ENC and Dong-A consulting company for the sample collection.

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