

Equilibrium Concentration of Radionuclides in Cement/Groundwater/Carbon Steel System

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Abstract

Equilibrium concentrations of major elements in an underground repository with a capacity of 100,000 drums have been simulated using the geochemical computer code (EQMOD). The simulation has been carried out at the conditions of pH 12 to 13.5, and Eh 520 and -520 mV.

Solubilities of magnesium and calcium decrease with the increase of pH. The solubility of iron increases with pH at Eh -520 mV of reducing environment, while it almost entirely exists as the precipitate of $\text{Fe}(\text{OH})_3(\text{s})$ at Eh 520 mV of oxidizing environment. All of cobalt and nickel are predicted to be dissolved in the liquid phase regardless of pH since the solubility limit is greater than the total concentration. In the case of cesium and strontium, all forms of both ions are present in the liquid phase because they have negligible sorption capacity on cement and large solubility under disposal atmosphere. And thus the total concentration determines the equilibrium concentration. Adsorbed amounts of iodide and carbonate are dependent on adsorption capacity and adsorption equilibrium constant. Especially, the calcite turns out to be a solubility-limiting phase on the carbonate system.

In order to validate the model, the equilibrium concentrations measured for a number of systems which consist of iron, cement, synthetic groundwater and radionuclides are compared with those predicted by the model. The concentrations between the model and the experiment of nonadsorptive elements - cesium, strontium, cobalt, nickel and iron, are well agreed. It indicates that the assumptions and the thermodynamic data in this work are valid. Using the adsorption equilibrium constant as a free parameter, the experimental data of iodide and carbonate have been fitted to the model. The model is in a good agreement with the experimental data of the iodide system.

1. Introduction

The underground repository for radwaste will be saturated with groundwater after the closure of the repository. As a result, complex reactions are supposed to occur in the repository which consists of cement-based waste containing radionuclides, carbon steel container, and the dissolved constituent of

groundwater. The reactions produce a number of chemical forms and will consequently define the chemical environment in the repository. The chemical condition in the repository is usually assumed to be an equilibrium state due to faster the reaction rate than the diffusion rate.

In the near field of the repository, the solubility (or equilibrium concentration) of radionuclides, in ad-

dition to sorption, may limit the element concentration in the porewater and thereby determines the source-term. The important aspects of repository environment are the pH and the redox conditions of groundwater. Eh and pH in the repository are mainly controlled by the amount of the portlandite in cement and the dissolved oxygen in groundwater. The portlandite keeps pH high and the dissolved oxygen directly influences the Eh value. Because the solubility of oxygen in groundwater is low, and because the oxygen replenishment in subsurface environment is limited, the underground repository maintains the negative value of Eh, that is, reducing environment. At high pH and negative Eh which are the typical conditions of repository, the dissolution of chemical species and the corrosion of metal are suppressed.

The difficulties in handling complex geochemical reactions have essentially required the development of computer codes. The attempt was initiated with the development of codes for the sea water calculations in the 1960's. Since then a large number of codes for various applications have been developed. A few of these, e. g. PHREEQE [1], MINEQL [2], HARPREQ [3], EQMOD [4] and EQ3/6 [5] are extensively used for the treatment of various chemical problems associated with the performance assessments of radwaste repository. The codes are particularly useful to calculate the equilibrium concentration of all chemicals in all phases. Most of the geochemical computer codes are based on the mass action's law and use thermodynamic information as input data. Accordingly, the results from geochemical computer modelling depend almost entirely on the quality of the thermodynamic data used.

The purpose of this work is to predict the equilibrium concentration of major elements under the repository environment using a geochemical computer code, EQMOD, and to validate the model by comparing with the experimental results available. The ions considered are magnesium, calcium, iron, nickel, cobalt, cesium, strontium, iodide and carbonate which are considered to be representative of repository en-

vironment with regard to the abundance.

2. Theory and Calculation

2.1. Assumptions

The repository saturated with groundwater is assumed to be at chemical equilibrium state. Additional assumptions introduced are as follows;

- 1) All chemicals are uniformly distributed throughout the whole system, and can participate in reactions without any restriction.
- 2) Complexation, adsorption, precipitation-dissolution, redox, and acid-base reaction take place simultaneously.
- 3) Only both iron and cobalt take part in redox reaction.
- 4) Sodium, iodide and carbonate take part in adsorption reaction.
- 5) Cesium, iodide and strontium have no solubility limit.

2.2. Input Data

Total concentration of radionuclide elements

For the repository with the capacity of 100,000 drums, the radionuclide inventory [6] is cited to give the total concentration of each element as shown in Table 1. The listed concentrations are based on the unit volume of cement porewater. It has been assumed that the volume of a drum is 200 liter and the cement porosity is 0.2. Although C-14 exists in the waste, it is not incorporated in the total concentration of carbonate due to its small amount.

Total concentration of ions in groundwater

Total concentrations of ions in groundwater [7] are summarized in Table 2. The data are of the groundwater sampled at the seabed of Baltic Sea. It is noticeable that the concentration of sodium and chloride is considerably higher than those in usual

Table 1. Inventory and Concentration of Radionuclides Used in Calculation

R/N	Inventory ¹⁾ (Ci)	half life (yrs)	g/Ci	concentration (mole/l)
Cs-137	3825.6	30.0	1.146×10^{-2}	8.0×10^{-8}
Sr-90	73.3	28.1	7.050×10^{-3}	1.4×10^{-9}
Co-60	7553.1	5.3	8.793×10^{-4}	2.8×10^{-8}
Ni-63 ²⁾	1902.9	92.0	1.607×10^{-2}	1.2×10^{-7}
C-14	109.3	5,730.0	2.239×10^{-1}	4.4×10^{-7}
I-129	0.3	1.7×10^7	6.115×10^3	3.6×10^{-6}

1) It is calculated on the basis of 100,000 drums capacity

2) Inventory of Ni-63 is including that of Ni-59

Table 2. Composition of Groundwater Used in Calculation

Ion	mg/l	mole/l
Ca	1,000	0.0250
Na	2,500	0.1087
Mg	300	0.0123
Cl	5,000	0.141
SO ₄	500	0.0052
CO ₃	100	0.0016

granitic groundwater.

Total concentration of iron

Major source of iron is the waste container which is made of carbon steel. The contents of iron in carbon steel is known to be about 99 % by weight [8] and the weight of a carbon steel container is assumed to be 10 kg. Thereby the equivalent total concentration of iron is reduced to 4.4 mole/l for the repository porewater.

Total concentration of calcium

The most likely source of calcium is the cement which is the main component of waste. There is also the calcium in groundwater, however, its amount is very low comparing with that in the cement. It is known that the cement of 1 liter contains about 210g CaO [7], and thus the total concentration of calcium is assumed to be 18.7 mole/l for the repository porewater.

Table 3. Chemical Species and Reaction Equilibrium Constant

Chemical form	Log K	Chemical form	Log K
Component Species(15)			
Fe ⁺⁺⁺	0	HSO ₄ ⁻	1.99
Mg ⁺⁺	0	HCO ₃ ⁻	10.33
Ca ⁺⁺	0	H ₂ CO ₃	16.67
Na ⁺	0	Fe ⁺⁺	13.01
Cs ⁺	0	FeSO ₄	15.31
Sr ⁺⁺	0	FeCL ⁺	13.91
Ni ⁺⁺	0	FeOH ⁺	3.51
Co ⁺⁺⁺	0	Fe(OH) ₂	-7.59
Cl ⁻	0	Fe(OH) ₃ ⁻	-17.99
SO ₄ ⁻⁻	0	Fe(OH) ₄ ⁻⁻	-32.99
I ⁻	0	Co ⁺⁺	30.59
CO ₃ ⁻⁻	0	HCoO ₂ ⁻	-1.10
H ⁺	0	HNiO ₂ ⁻	-30.40
e ⁻	0		
SOH	0	Adsorbed Species (5)	
		SO ⁻	-11.50
		SOH ₂ ⁺	5.70
Complex Species (30)			
OH ⁻	-13.99	SONa	-9.20
FeSO ₄ ⁺	4.20	SOH ₂ I	18.00
FeCl ⁺⁺	1.40	SOH ₂ CO ₃ ⁻	20.00
FeOH ⁺⁺	-2.19		
Fe(OH) ₂ ⁺	-5.67	Precipitated/Dissolved Species (12)	
Mg(OH) ⁺	-11.52	Fe(OH) ₂ (S)	0.91
MgHCO ₃ ⁺	10.52	Fe(OH) ₃ (S)	-2.60
MgCO ₃	2.88	MgCO ₃ (S)	-7.46
MgSO ₄	2.23	Mg(OH) ₂ (S)	-16.84
CaOH ⁺	-12.85	Ca(OH) ₂ (S)	-22.00
CaCO ₃	3.15	CaCO ₃ (S)	8.42
CaSO ₄	2.31	CaSO ₄ (S)	4.38
CaHCO ₃ ⁺	11.33	NiCO ₃ (S)	6.89
NaSO ₄ ⁻	0.70	Ni(OH) ₂ (S)	-12.18
NaHCO ₃	10.03	CoCO ₃ (S)	10.00
NaCO ₃ ⁻	1.30	Co(OH) ₂ (S)	18.00
Na ₂ CO ₃	0.77	Co(OH) ₃ (S)	1.05

tory porewater.

Species and reaction equilibrium constant

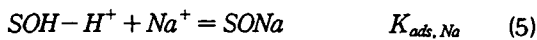
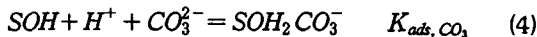
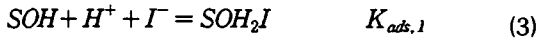
This work employs the chemical species of total 62; 14 component species, 1 adsorbent (cement particle), 30 complex species, 5 adsorbed species, and

12 precipitates. The chemical formula and their logarithmic reaction equilibrium constant used in this work are given in Table 3, and extracted from literatures [4, 9]. We can classify the chemicals listed in the table into four groups; 1) Fe, Ca, Mg, Ni, Co and SO_4 in the liquid phase and in precipitates, 2) Cs, Sr and Cl in the liquid phase, 3) Na and I in the liquid and adsorbed phase, and 4) CO_3 in all phases.

In the first group, solubility is likely to be a major variable controlling the equilibrium concentration, and in the third adsorption capacity is, and in the fourth both solubility and adsorption capacity are.

2.3. Adsorption

The following five sorption mechanisms which are based on the simple surface complexation model are assumed.



Here, SO^- , SOH and SOH_2^+ represent negatively charged, neutral and positively charged surface hydroxyl groups (sorption sites), respectively. K_{ads} is the adsorption equilibrium constant. The adsorption capacity is the sum of the concentration of all adsorbed ions. Let the adsorption capacity be $(\text{SO})_{\text{total}}$, then the following relationship is satisfied.

$$(\text{SO})_{\text{total}} = (\text{SOH}) + (\text{SO}^-) + (\text{SOH}_2^+) + (\text{SOH}_2\text{I}) + (\text{SOH}_2\text{CO}_3^-) + (\text{SONa}) \quad (6)$$

Using the equilibrium relations of the reactions (1) through (5), and Eq. (6), we have the adsorbed amount of ion i as

$$(\text{SO}i) = \frac{(\text{SO})_{\text{total}} K_{\text{ads},i}^a (i) \nu_i}{1 + \sum_i K_{\text{ads},i}^a (i) \nu_i}, \quad i = \text{I}^-, \text{CO}_3^{2-}, \text{Na}^+ \quad (7)$$

where

$$K_{\text{ads},\text{Na}}^a = \frac{K_{\text{ads},\text{Na}}}{[\text{H}^+] + K_{\text{ads},o} + K_{\text{ads},H} [\text{H}^+]^2} \quad (8)$$

$$K_{\text{ads},I}^a = \frac{K_{\text{ads},I} [\text{H}^+]^2}{[\text{H}^+] + K_{\text{ads},o} + K_{\text{ads},H} [\text{H}^+]^2} \quad (9)$$

$$K_{\text{ads},\text{CO}_3}^a = \frac{K_{\text{ads},\text{CO}_3} [\text{H}^+]^2}{[\text{H}^+] + K_{\text{ads},o} + K_{\text{ads},H} [\text{H}^+]^2} \quad (10)$$

$K_{\text{ads},i}^a$ is the apparent adsorption equilibrium constant of ion i , and ν_i the activity coefficient of ion i . The parenthesis means the liquid phase concentration. $[\text{H}^+]$ is the activity of hydrogen ion. Eq. (7) is a typical multicomponent Langmuir isotherm.

Eq. (7) to (10) show that the adsorbed amount is a function of pH, adsorption capacity, activity coefficient, and the liquid phase concentration of adsorptive component. The adsorbed amount of cation (SONa) increases with pH, while that of anions (SOH_2I , $\text{SOH}_2\text{CO}_3^-$) decrease with the increase of pH. On the other hand, the activity coefficient is a function of the ionic strength [9] which is proportional to the liquid phase concentration of all ions, and consequently the adsorbed amount is also a function of the liquid phase concentration of non-adsorptive ions. When nonadsorptive ion reacts with adsorptive one to form a complex or precipitate in the liquid phase, the reaction will have influence on the adsorbed amount. In this work, since the adsorptive ions are presumed not to take part in the redox reaction, the adsorbed amount will be independent of Eh value.

What is called a distribution coefficient is often used to account for the retardation effect in the repository safety assessment. In the system where the ratio of liquid phase volume to adsorbent weight is V/W , the distribution coefficient of ion i , K_{di} , with dimensions of $[\text{L}^3/\text{M}]$ is estimated by

$$K_{di}^a = \frac{(\text{SO}i) + \sum (\text{Precipitate of } i)}{(i) + \sum (\text{Complex of } i)} \cdot \frac{V}{W} \quad (11)$$

$$= \frac{\text{Total conc. of } i - \text{Liquid phase conc. of } i}{\text{Liquid Phase conc. of } i} \cdot \frac{V}{W}$$

The value reflects the removal of chemical from the liquid phase by both precipitation and adsorption.

2.4. Computer Code

Geochemical computer code, EQMOD [4], has been used to simulate the equilibrium concentration. The code had been designed to solve geochemical equilibrium problems that include simultaneous processes of aqueous complexation, adsorption, ion exchange, precipitation-dissolution, redox, and acid-base reactions. The code is numerical model using full pivoting to solve the matrix equation, and Newton Raphson iteration for fast convergency. It adopts the surface complexation model for the treatment of adsorption and Davies' equation [9] for the activity coefficient calculation.

Equilibrium concentrations have been calculated at pH 12, 13 and 13.5 which are expected to be the conditions of a sealed repository. The Eh values of 520 mV and -520 mV are adapted in the calculation to see the effect of redox potential.

3. Results and Discussion

3.1. Effect of pH and Adsorption on Ionic Strength

Adsorption process causes the change in ionic strength and consequently influences the liquid phase concentration of nonadsorptive ions. Fig. 1 shows the activity coefficient as a function of the ionic strength for varying computational conditions. At pH 12 and 13, the ionic strength ranges from 0.15 to 0.2, and at pH 13.5 it varies between 0.25 and 0.3. At constant pH, the higher the adsorption capacity is, the smaller the ionic strength becomes. Because the adsorbed amount increases with the adsorption capacity, the lower liquid phase concen-

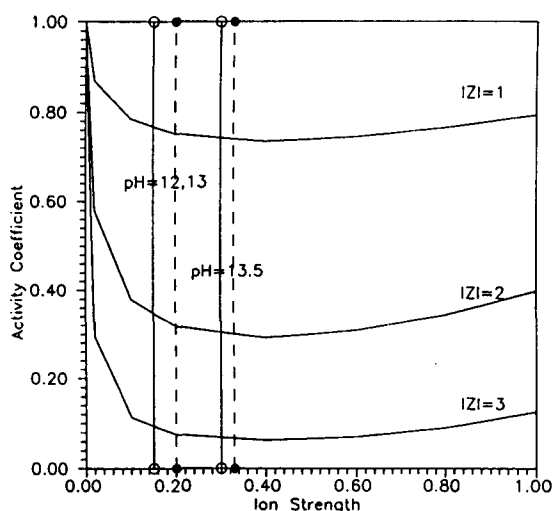


Fig. 1. Activity Coefficient with Ionic Strength and its Value in Calculation Conditions (○-○ : $(S_o)_{total} = 2 \times 10^{-1}$ mole/l, ●-● : $(S_o)_{total} = 2 \times 10^{-6}$ mole/l)

tration of ions and the lower ionic strength will result from the higher adsorption capacity. Nevertheless, the change of ionic strength according to adsorption capacity seems to be negligible due to the low total concentration of adsorptive ions. In other words, the total concentration of iodide and carbonate participating in the adsorption reactions are respectively 3.6×10^{-6} and 1.6×10^{-3} mole/l. These values are 2 to 5 orders of magnitude less than the ionic strength. It means that the variation of ionic strength by the adsorption is negligible. Therefore we expect that the presence of iodide and carbonate would not affect the liquid phase concentration of nonadsorptive ions.

3.2. Magnesium, Calcium, Iron and Chloride

The decrease of pH leads to the dissolution of $Mg(OH)_2(s)$ and $Ca(OH)_2(s)$, resulting in the increase of the liquid phase concentration of magnesium and calcium as shown in Fig. 2. Main solid phase of magnesium and calcium is hydroxide precipitate. Calcite, $CaCO_3(s)$, is also formed under the condition of high carbonate concentration. Magnesium and calcium are presumed not to participate in the redox reaction, in

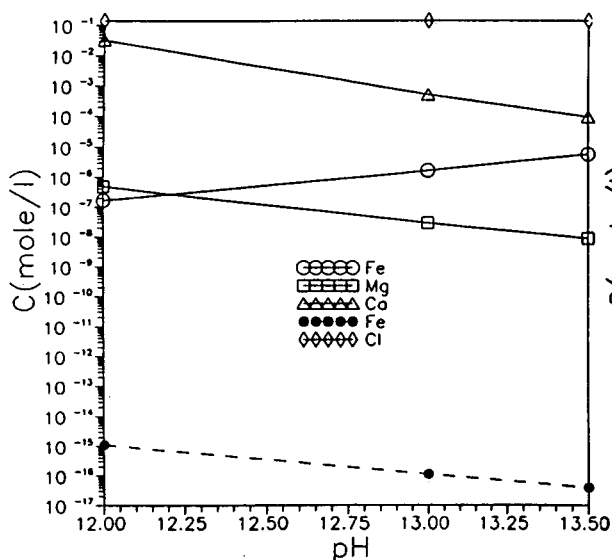


Fig. 2. Effect of pH on Concentration of Iron, Magnesium, Calcium and Chloride (—: Eh = -520 mV, ---: Eh = 520 mV)

other words they are independent of the Eh value.

Taking part in redox reaction, iron shows some other trend depending on Eh value. At Eh of -520 mV, the oxidation state of iron is +II, and with the increase of pH $\text{Fe}(\text{OH})_2(\text{s})(+II)$ is dissociated to $\text{HFeO}_2^-(+II)$ to give higher solubility. In contrast, at Eh of 520 mV, iron is almost of $\text{Fe}(\text{OH})_3(\text{s})(+III)$ form that does not dissociate to $\text{Fe}(\text{OH})_2^+(+III)$. The results appear also in the Eh-pH diagram given by Pourbaix [10].

Through reacting with air trapped in the repository, a protective iron oxide, $\text{Fe}_2\text{O}_3(\text{s})$, is formed on steel surface. In high alkaline environment (pH > 12), the oxide film which passivates the steel is hardly broken up and adheres tightly to the surface so that the contact of bare iron with oxygen is disturbed. Lowering pH in the porewater (pH < 9) makes the passive layer less stable. Break up of the layer can also be caused by the ingress of chloride at high concentration. However, such a corrosion goes on continuously over thousands years. Therefore we exclude the redox reactions involving chloride since our interest is only in the equilibrium concentration dur-

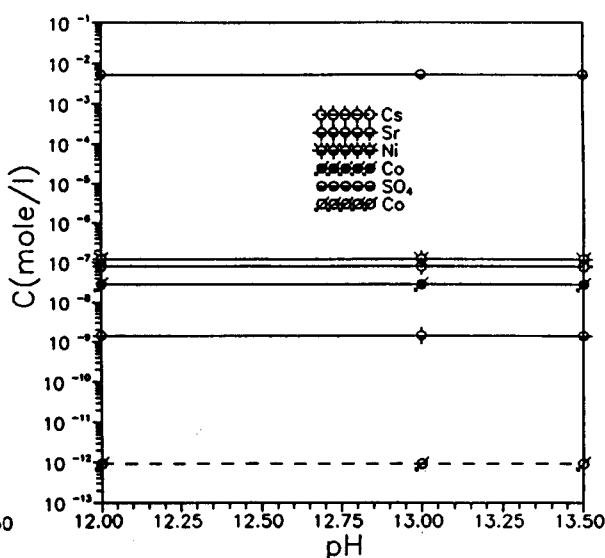


Fig. 3. Effect of pH on Concentration of Cesium, Strontium, Cobalt, Nickel and Sulphate (—: Eh = -520 mV, ---: Eh = 520 mV)

ing the short-term prospect after closure. As the chloride is assumed not to take part in the precipitation as well as in the adsorption reaction, all chloride is present in the liquid phase. In this case, the initial total concentration determines the equilibrium concentration.

3.3. Cobalt and Nickel

Cobalt is involved in the redox reaction. At the reducing condition of Eh -520 mV, cobalt maintains the equilibrium concentration of 2.8×10^{-8} mole/l which is equivalent to its total concentration (see Fig. 3). In the range of pH 12 to 13.5, the maximum solubility of cobalt at Eh -520 mV is higher than the present total concentration (see Fig. 4). It means that the amount of cobalt is still too low to form a solid phase. If the total concentration exceeds solubility limit, then the solubility equilibrium is attained. In such a case, cobalt will dissolve in the liquid phase as much as the level of solubility limit, and the excess amount over the solubility limit will be precipitated as $\text{Co}(\text{OH})_2(\text{s})(II)$. At the range of pH 12 to 13.5, the sol-

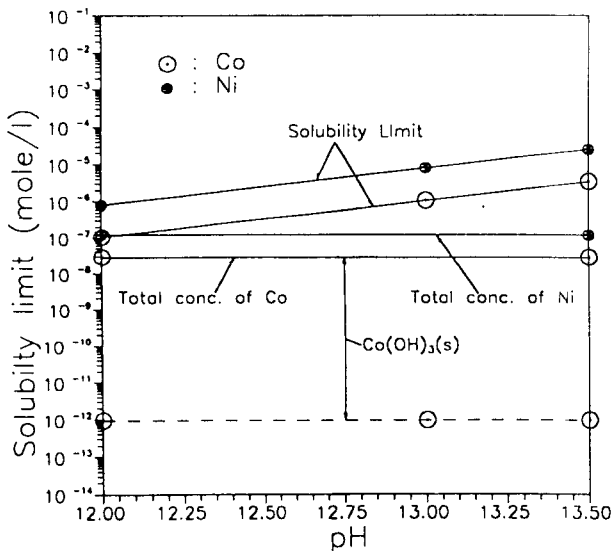


Fig. 4. Solubility Limit of Cobalt and Nickel with pH

ubility limit increases with pH because $\text{Co(OH)}_2(\text{s})$ (II) dissolves into HCoO_2^- (II). At Eh 520 mV, cobalt is seldom dissolved and mainly exists as the precipitate of $\text{Co(OH)}_3(\text{s})$ (III).

Nickel also maintains the equilibrium concentration of 1.2×10^{-7} mole/l which is the same level as its total concentration since the total concentration is less than the solubility limit under the given pH range. Accordingly, all nickel ions must be present in the liquid phase like cobalt. In this work, the redox reaction of nickel has not been considered since it is known that nickel almost entirely exists as Ni^{++} (II) or HNiO_2^- (II) in the liquid phase [10].

3.4. Cesium, Strontium and Sulphate

Whereas the solubility of cesium and strontium is very high, the solubility limit of both ions is usually not considered at the repository conditions [11]. Eh and pH do not affect the solubility of cesium and strontium. Sulphate has been involved in the precipitation reaction to form $\text{CaSO}_4(\text{s})$, however the precipitate is not produced due to the small presence of sulphate. Therefore all the above three ions should be fully present in the liquid phase. In this case, the

equilibrium concentration is determined by the total concentration.

3.5. Iodide and Carbonate

The adsorption characteristics of iodide and carbonate have been qualitatively studied for the adsorption capacity range of 2×10^{-5} to 2×10^{-1} mole/l.

Under groundwater conditions, iodine will be present as iodide. Fig. 5 shows the liquid phase and the adsorbed phase concentrations of iodide. The adsorbed amount increases with the adsorption capacity and the adsorption equilibrium constant. Iodide that are not adsorbed on cement will be present in the liquid phase. Therefore the liquid phase concentration is entirely associated with the adsorption capacity. Referring to the definition of Eq. (11), we infer the distribution coefficient of iodide to be increased with the adsorption capacity and the adsorption equilibrium constant.

The equilibrium characteristics of carbonate are given in Fig. 6. Most important features of carbonate system are that the precipitate is formed and that the liquid phase concentration is restricted within the sol-

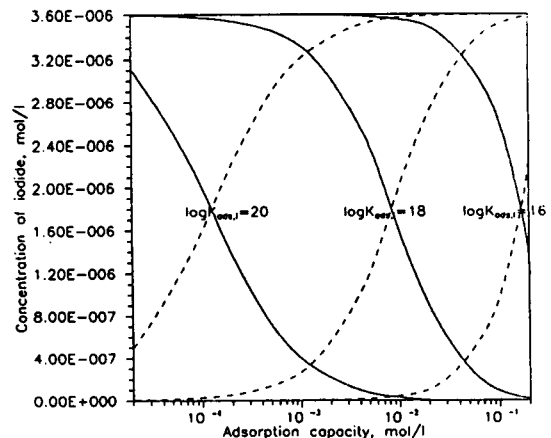


Fig. 5. Liquid Phase (—) and Adsorbed Phase (---) Concentration of Iodide Depending on Adsorption Capacity and Adsorption Equilibrium Constant (pH=13, Total Concentration= 3.6×10^{-6} mol/l)

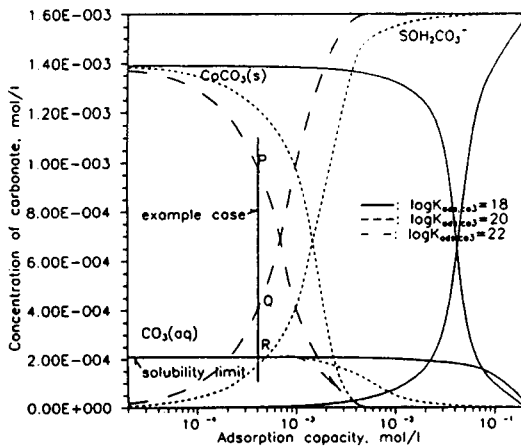


Fig. 6. Liquid Phase($\text{CO}_3(\text{aq})$), Adsorbed Phase (SOH_2CO_3) Concentration of Carbonate Depending on Adsorption Capacity and Adsorption Equilibrium Constant ($\text{pH}=13$, Total Concentration= 1.6×10^{-3} mol/l)

ubility limit, even though the carbonate is abundant. The solubility limiting phase is calcite, $\text{CaCO}_3(\text{s})$. Especially, when the liquid phase concentration is equal to the solubility limit at a given pH, the value of distribution coefficient is at the minimum. An ion can be adsorbed as much as its adsorption capacity (SOH_2CO_3) when its adsorption is very strong and its total concentration is higher than the adsorption capacity. For example, let us consider the carbonate of the following case (vertical line PQR in Fig. 6); $\log K_{\text{ads},\text{co}_3}=22$, $(\text{SO})_{\text{total}}: 4 \times 10^{-4}$ mole/l and total concentration: 1.6×10^{-3} mole/l. For this case, the adsorbed amount is 4×10^{-4} mole/l which is corresponding to the adsorption capacity (point Q), and the liquid phase concentration is the point R corresponding to the solubility limit, and the precipitated concentration is the point P.

4. Validation of the Model

In order to validate the model, the experimental data measured for five systems, 1) cement+synthetic groundwater (SGW), 2) cement+SGW+pure iron, 3) cement+SGW+pure iron+completely oxidized

Table 4. Comparison Between Model and Experiment for the Liquid Phase Concentration of Cobalt, Calcium and Iron

Experiment									Model	
System No.	pH	Eh (mv)	Co ^{II}	Ca	Fe	Co	Ca	Fe		
1	12.59	224	<0.02ppm	267ppm	ND	0.023	101	10 ⁻¹⁰ ppm<		
2	12.69	63	-	281	-	0.030	67	-		
3	12.68	59	-	320	-	0.028	70	-		
4	12.63	46	-	354	-	0.025	85	-		
5	12.68	63	-	300	-	0.028	70	-		

1) Initial concentration of Co : 20 ppma

Table 5. Comparison Between Model and Experiment for the Liquid Phase Concentration of Nickel, Calcium and Iron

			Experiment			Model		
System	pH	Eh	Ni ^{II}	Ca	Fe	Co	Ca	Fe
No.		(mV)						
1	12.68	221	<0.02ppm	254ppm	ND	0.218	70	10 ⁻¹⁰ ppm<
2	12.69	213	•	256	•	0.223	67	•
3	12.65	220	•	329	•	0.203	79	•
4	12.63	198	•	343	•	0.194	85	•
5	12.67	14	•	292	•	0.213	73	•

1) Initial concentration of Ni : 20 ppm

iron, 4) cement+SGW+completely oxidized iron, and 5) cement+SGW+partially oxidized iron, are compared with those predicted by the model with the input data associated with the experimental conditions. The data [12] were measured by batch method at temperature 25°C and V/W ratio of 5.

In Tables 4 and 5, the predicted and the experimental concentrations for cobalt and nickel are summarized. The Eh and pH values shown are the measured one for each system. On the whole, the systems including iron (system 2 to 5) tend to have less Eh value than the system without iron (system 1). Corrosive reaction of iron promotes the consumption of oxygen in the system since the oxygen alone is likely to be an oxidizing agent in SGW. The origin of oxygen is presumed to be the air dissolved in water in

the process of SGW generation. From Eh values, it is suggested that the systems be still under oxidizing environment. As expected, Eh values for the cobalt system are smaller than those for the nickel system because cobalt participates in redox reaction but nickel does not.

The concentration of cobalt is detected to be less than 0.02 ppm in the experiment, which is almost coincident with the model prediction. The liquid phase concentration of iron is undetectable, and also it agrees well with the predicted one. The liquid phase concentration of iron in both experiment and model is very small and it means that the iron exists mainly as the undissolved $\text{Fe}(\text{OH})_3(\text{s})$ (III) in the liquid phase at oxidizing condition. Calcium is predicted to have two or three factors lower concentration than the experimental data. It may be caused by the over-saturation of water with respect to calcium.

The concentration of nickel is predicted to be as high as about tenfold of the experimental value although its absolute value is very much small. Pourbaix [10] showed that the solubility of nickel ranged from 0.06 to 0.6 ppm in the pure water at around pH 12.5. The values predicted by the present model are well within the range of Pourbaix. The discrepancy between the experiment and the model may be attributed to the experimental error. Also, the nickel adsorption on cement or iron precipitates can be considered as a cause of the difference.

In this work, it is assumed that cesium and strontium have no solubility limit and their adsorption on cement is insignificant [13]. It suggests that both ions be present in the liquid phase. As expected, the liquid phase concentration of both ions are well agreed with their initial total concentration (see Table 6). This result confirms the above assumptions for cesium and strontium.

In the case of iodide and carbonate, the distribution coefficient can be used to check the model validity. The distribution coefficient is a function of both the adsorption capacity and the adsorption equilibrium constant. At present, the distribution co-

Table 6. Comparison Between Model and Experiment for the Liquid Phase Concentration of Strontium and Cesium

System No.	Sr ⁽¹⁾		Cs ⁽²⁾	
	Experiment ⁽³⁾	Model	Experiment	Model
1	26.3ppm	20.01ppm	19.56ppm	20.98ppm
2	26.6	-	19.37	-
3	28.0	-	18.18	-
4	27.1	-	20.94	-
5	27.3	-	20.94	-

1) Initial concentration of Sr : 20.01ppm

2) Initial concentration of Cs : 20.98ppm

3) Measured concentration higher than initial one is caused by release of Sr in cement

Table 7. Comparison Between Model and Experiment for the Adsorption Reaction Constant of Iodide

System No.	pH	Experiment ⁽¹⁾			Model		
		Eh (mV)	$K_{d,exp}$ (dm ³ /kg)	$(\text{SO})_{\text{total}} = 0.2 \text{ mole/l}$	$(\text{SO})_{\text{total}} = 0.05 \text{ mole/l}$	K_d	$\log K_{ads,l}$
1	12.66	207	16.9	13.8	15.1	13.7	15.7
2	12.67	182	32.3	33.2	15.5	32.8	16.1
3	12.62	164	10.9	13.1	15.0	13.0	15.6
4	12.56	169	7.7	8.6	14.7	8.5	15.3
5	12.73	223	36.4	40.1	15.7	39.7	16.3

1) Initial concentration of I : 19.44ppm

efficient can not be predicted since adsorption data are absent. Instead, using the adsorption equilibrium constant as a free parameter, we have calculated the distribution coefficients by the best fitting to the experimental value.

Some examples of the calculated results for iodide are shown in Table 7. The logarithmic adsorption equilibrium constant ($\log K_{ads,l}$) is around 15 at the adsorption capacity of 0.2 mole/l, while it is around 16 at 0.05 mole/l. The value itself might be meaningless, for it is not based on the exact adsorption data. However, the qualitative trend encourages the extended application of the model with the proper thermodynamic data.

It is known that the carbonate is very strongly

Table 8. Comparison Between Model and Experimenta for the Adsorption Reaction Constant of Carbonate

System No.	pH	Eh (mV)	Experiment ¹⁾		Model
			$K_{d,exp}^a$ (dm ³ /kg)	(SO) _{total} = $2 \times 10^{-5} \sim 2 \times 10^{-1}$ mole/l K_d^b (dm ³ /kg)	$\log K_{ads,CO_3}^c$
1	12.75	224	49.6	448>	—
2	12.70	202	25.8	549>	—
3	12.69	46	44.9	571>	—
4	12.67	23	28.4	617>	—
5	12.70	18	42.6	550>	—

1) Initial concentration of carbonate : 42.13ppm

adsorbed on cement and its equilibrium distribution coefficient is usually 10^4 ml/g and above [14]. In this work, the values obtained by the experiment are at least one order lower than the minimum value that can be obtained by the model (see Table 8), and furthermore, two orders lower than the values in literatures. Thus, we could not attain a proper adsorption equilibrium constant to fit the experimental data to the model. Further studies including a more detailed experiment of the carbonate system may be required to identify more specific explanation. On the other hand, when the adsorbed amount of carbonate can be neglected compared with the precipitated amount, the calcite, the solubility-limiting phase, will control the distribution coefficient (the distribution coefficient is minimum at the given pH). In this case, the solubility of carbonate is only dependent on pH. Lowering pH leads to weaker dissolution of calcite, resulting in higher distribution coefficient (see the K_d value by model in Table 8.).

5. Conclusions

In the safety assessment for radwaste disposal, the equilibrium concentrations of chemicals at around the disposal location are significant to determine the source-term of repository. Using the geochemical code, EQMOD, we have simulated the equilibrium

concentrations of major elements under the disposal atmosphere, and the major concluding remarks are as follows;

- Equilibrium concentrations of nonadsorptive ions are almost independent of the adsorbed amount of adsorptive ions.
- Solubilities of magnesium and calcium decrease with the increase of pH.
- The solubility of iron increases with pH at reducing condition, while it exists as the precipitate of $Fe(OH)_3(s)$ (III) at oxidizing condition.
- All of both cobalt and nickel are predicted to be dissolved in the liquid phase regardless of pH due to their low total concentration.
- In the case of cesium and strontium, all of both ions are present in the liquid phase because they have negligible sorption capacity on cement and large solubility under disposal atmosphere.
- The distribution coefficient of iodide is predicted to be increased with the adsorption capacity and the adsorption equilibrium constant.
- In carbonate system, the liquid phase concentration is restricted within the solubility limit, even though the carbonate is abundant, and the solubility limiting phase is calcite, $CaCO_3(s)$.

In order to validate the model, the experimental data for five systems are compared with the model prediction with the input data associated with the experimental conditions. The model predicts well the experimental data of nonadsorptive ions. It means that the assumptions and thermodynamic data in this work are valid. The unknown adsorption properties of adsorptive ions make it impossible to predict the meaningful equilibrium concentration. However, the qualitative trend encourages the extended application of the model with the proper thermodynamic data.

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