Comparative study of thermodynamic database (TDB) for estimation of radionuclide solubility in KURT conditions

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1. Introduction

As groundwater infiltrates into the deep geological disposal repository, it has the potential to corrode the canister and dissolve the radionuclides until they reach their solubility. Therefore, it is important to estimate the solubility of radionuclides in groundwater condition to evaluate the deep geological disposal safety assessment. The estimation of radionuclide solubility is dependent on the chemical composition of the solution, the thermodynamic database (TDB), and solubility limiting solid phase (SLSP) [1]. To ensure reliable solubility modeling results, it is crucial to have the high quality of TDB, which includes internally consistent thermodynamic data and comprehensiveness of the chemical components and species [2]. Therefore, this study aims to predict the radionuclides solubility under oxidizing conditions in the KAERI Underground Research Tunnel (KURT) site using various TDBs (NEA, Thermochimie, PSI/Nargra), and the predicted solubility will be compared with actual solubility measurement data.

2. Material and Method

2.1. Thermodynamic database

The detailed information of TDB are shown in Table 1. The NEA TDB has been updated using Chemical Thermodynamics Volume 14 (2020). ThermoChimie developed by ANDRA has been upgraded to version 12a. The latest PSI/Nagra version published in 2020 is used in this study.

Table 1. Comparison of TDB used in this study

	NEA (2021)	ThermoChimie (2023)	PSI/Nagra (2020)
Activity model	SIT		
Elements	49	68	56
Basis species	55	69	60
Redox couples	34	35	41
Aqueous species	445	1421	992
Minerals+Oxides	182	911	396
Gases	58	13	8
Virial coefficients	380	606	1273

2.2. Geochemical modeling

Geochemical modeling was performed using the Geochemist's Workbench (GWB) with NEA(2021), Thermochimie(2023), and PSI/Nagra(2020) TDB. Solubility modeling was evaluated with KURT groundwater and the detailed chemical composition is represented in Table 2. The Eh value of KURT groundwater is set as +100 mV to simulate oxidizing conditions at the beginning of the disposal system.

Table 2. The chemical composition of KURT groundwater

pH		9.05
Eh	[mV]	100~200
Na^+	[mg/L]	37.9
Ca^{2+}	[mg/L]	5.7
K^+	[mg/L]	0.33
Mg^{2+}	[mg/L]	0.29
SiO_2	[mg/L]	7.5
HCO_3^-	[mg/L]	79.3
Cl^-	[mg/L]	1.79
SO_4^{2-}	[mg/L]	5.8
NO_3^-	[mg/L]	0.68
F^-	[mg/L]	8.1

2.3. Solubility experiments

The solubilities of radionuclides in KURT synthetic groundwater were measured using the undersaturation method. Briefly, excess amounts of SLSP were added to the solution, and the concentration of the solution was periodically measured to confirm that individual nuclides reached to the equilibrium.

3. Results and discussion

3.1. Nickel

The SLSP of nickel in KURT condition appears differently depending on the TDB. According to NEA TDB, it appears as $NiCO_3$, while Thermochimie reports $NiSiO_3$, and PSI/Nagra reports $Ni(OH)_2$ (Figure 1). However, it should be noted that $NiSiO_3$ is highly unstable at 1 atmosphere condition, and there is no information available on the X-ray diffraction pattern for pure $NiSiO_3$ [3]. Therefore, $NiSiO_3$ was excluded from the Thermochimie TDB, and modeling was reperformed, and $Ni(OH)_2$ came out as SLSP (Figure 1(c)).

The experimental values of Ni solubility and the calculated values of Ni solubility using each TDB are given in Table 3. As a result of the experiment, the solubility value of $Ni(OH)_2$ was found to be 5.623×10^{-5} M, which was 18 to 525 times higher than the modeling value.

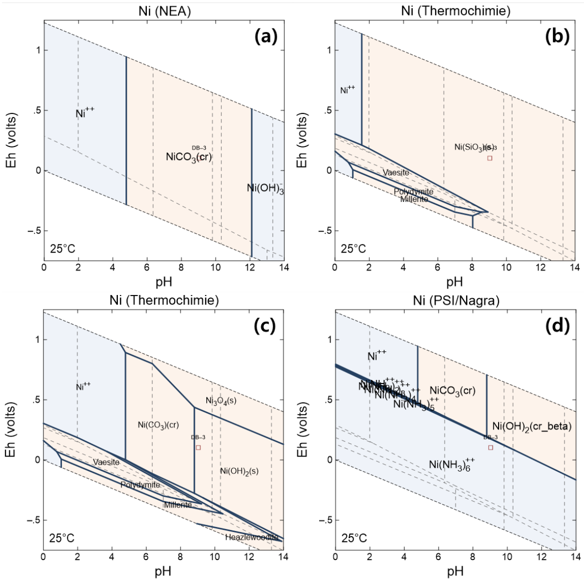

Figure 1. Nickel pH-Eh diagram (a) NEA TDB, (b) Thermochimie TDB, (c) Thermochimie TDB suppress $Ni(SiO_3)$, (d) PSI/Nagra TDB

Table 3. The chemical composition of KURT groundwater

	Experimental Data	NEA	Thermochimie	PSI/Nagra
SLSP	$Ni(OH)_2$	$NiCO_3$(cr)	$Ni(OH)_2$	$Ni(OH)_2$ (cr_beta)
Solubility [M]	5.623×10^{-5}	1.614×10^{-7}	1.072×10^{-7}	3.205×10^{-6}

4. Conclusion

In this study, different TDBs were used to predict the SLSP and solubility values in the deep geological disposal environment and compared with experimental values. Solubility modeling results showed the differences in Ni SLSP and solubility values depending on the TDB, and there were significant disparities observed compared to measured solubility values. When evaluating the deep geological disposal safety assessment, it is crucial to supplement modeling with experimental measurements to determine solubility values.

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