# 2–6 Migration of Radionuclides from Radioactive Wastes of Reactor Core Structures in Underground Environments

## —Modeling Niobium Sorption onto Clay Minerals in the Presence of Calcium—

- Nb sorption was described by complexation of aqueous species and surface hydroxyl groups (surf_OH) of clay minerals.
- Only Nb-OH complexes were considered by Ervanne et al.

➡ Our model deals with Ca-Nb-OH complexes.

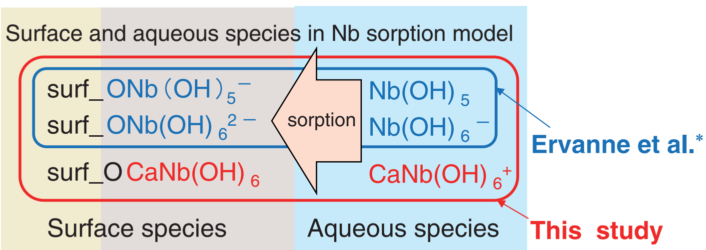


**Fig.2-17 Conceptual drawing of Nb sorption model**
The proposed sorption model includes the aqueous species ($CaNb(OH)_6^+$), which was confirmed to form in the solubility experiments in addition to aqueous $Nb(OH)_5$, aqueous $Nb(OH)_6^-$, and surface_$OCaNb(OH)_6$ (surf_$OCaNb(OH)_6$).

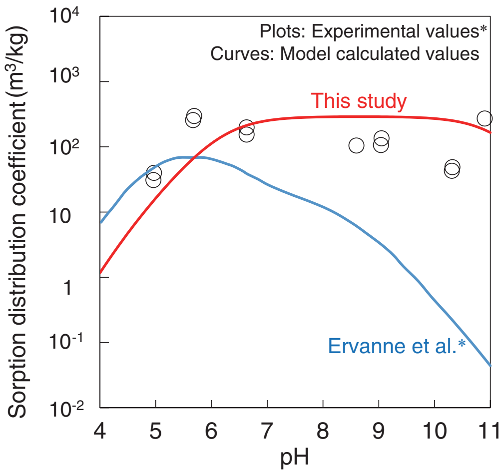


**Fig.2-18 Model results for Nb sorption onto illite in 0.1 M $Ca(ClO_4)_2$ solution**
The proposed model can explain the tendency of the experimental data provided by Ervanne et al.* in the presence of Ca. The sorption distribution coefficient is the ratio of the concentration of Nb adsorbed on the solid phase to that in solution; the higher the value, the higher the sorption property.

Radioactive waste from activated reactor core internals is classified as relatively higher radioactive waste, which is a category of low-level waste. As these wastes contain long-lived radionuclides and must be kept away from the biosphere long-term, it is planned to be disposed of underground in Japan. Safety assessments of radioactive waste disposal must analyze the capacity of radionuclides leached from waste forms to migrate through the bedrock to the biosphere, where humans can be exposed to the waste. The migration of radionuclides is expected to be slowed by sorption onto rock-forming minerals. This process is affected by coexisting ions in groundwater, the compositions which may change according to the long-term disposal environment. Therefore, a reliable model must be developed to estimate the sorption properties of radionuclides onto rock-forming minerals.

Niobium-94 ($^{94}Nb$) is a long-lived radionuclide (half-life: 20300 y) contained in the wastes of reactor core internals and important in the safety assessment of waste disposal because of its contribution to radiation doses. However, few researchers have examined the sorption of Nb onto minerals. Ervanne et al.* examined the effect of sodium (Na) and calcium (Ca) on Nb sorption onto illite, which is a type of rock-forming clay mineral with a high specific surface area (i.e., high sorption capacity). In the presence of Na, the experimental sorption data were reproduced by their proposed model, which assumed aqueous and surface species of Nb hydroxide complexes ($Nb_x(OH)_y^{5x-y}$). However, their model did not agree with the data obtained in the presence of Ca.

Therefore, we developed a Nb sorption model to resolve this divergence by assuming the existence of Nb complexes with $OH^-$ and $Ca^{2+}$ (Ca-Nb-OH complex), which had not been considered before. In order to confirm the formation of aqueous Ca-Nb-OH complexes, solubility experiments of Nb were performed under various Ca concentrations and pH. The experimental results showed that $CaNb(OH)_6^+$ was formed as the dominant aqueous species, in addition to $Nb(OH)_6^-$ and $Nb(OH)_7^{2-}$. Additionally, Ca-Nb-OH complexes containing surface $OH^-$ groups (surf_OH) were assumed to be formed and follow the sorption reaction: surf_$O^-$ + $CaNb(OH)_6^+$ = surf_$OCaNb(OH)_6$. In this reaction, we excluded $H^+$ because no pH dependence was observed in the sorption data. Therefore, $CaNb(OH)_6^+$ and surf_$OCaNb(OH)_6$ were added to each species in the developed model (Fig.2-17). The Nb sorption onto illite in a 0.1 M $Ca(ClO_4)_2$ solution was then calculated using the geochemical calculation code (PHREEQC) with thermodynamic $CaNb(OH)_6^+$ data determined from the solubility experiments. The model results represented trends in the experimental data obtained by Ervanne et al.* that could not be explained by the previous model, as shown in Fig.2-18.

The results of this study will be used as a scientific basis for highly reliable evaluation of the sorption property of $^{94}Nb$ to rock in the future disposal of the wastes from reactor core internals.

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* Ervanne, H. et al., Modelling of Niobium Sorption on Clay Minerals in Sodium and Calcium Perchlorate Solutions, Radiochimica Acta, vol.102, issue 9, 2014, p.839–847.


**Reference**

Yamaguchi, T., Ohira, S. et al., Consideration on Modeling of Nb Sorption onto Clay Minerals, Radiochimica Acta, vol.108, issue 11, 2020, p.873–877.