

Surface Complexation Modeling of Nickel Sorption Under Varying Geochemical Conditions at the Wolsong Repository Site.

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1. Introduction

Radioactive nickels (^{59}Ni , ^{63}Ni) are one of the significant radionuclides, because they have relatively long half-life (76,000 and 96 years, respectively) and show high portion of radioactive wastes generated from nuclear power plants (NPPs). Nickel is an important constituent in a wide range of corrosion-resistant metal alloys including stainless steels, inconels, and monels, which are mainly used as structural materials in nuclear power reactor. Radioactive nickel isotopes are produced by neutron activation of these materials, resulting in a major part of radioactive wastes generated during the operation and decommissioning of the NPP.

Low-and-intermediate-level (LILW) radioactive wastes generated from NPPs will be disposed in the Wolsong repository site in Gyeongju, which has been built as underground concrete silo type and operated since 2015. For a long-term safety assessment of the repository, reactive transport models utilize the distribution coefficient (constant- K_d) modeling approach to describe the mobility of radionuclides in the subsurface environments. However, K_d values are very sensitive to the varying environmental conditions, specially by different pH conditions due to the reaction between groundwater (pH: ~8) and cement (pH: ~12). Wolsong repository utilizes lots of cementitious materials by engineered barrier system, backfill, and solidified materials. After closure of repository, these cementitious materials will interact with groundwater, then will buffer the pH to hyper-alkaline conditions (pH 10.5-13.1) [1].

In contrast to the constant- K_d approach, surface complexation models (SCM) can describe changes in nickel's sorption onto minerals as environmental

conditions vary. A lot of literatures on SCM indicated that the SCM approach has been successfully applied to predict sorption of contaminants (metal and radionuclide ions) on soils and sediments.

Therefore, in this study, nickel sorption onto minerals was studied in batch experiments as a function of pHs and different initial nickel concentrations. Then, in order to enable further predictive simulations, the experimental data were used to develop the surface complexation models.

2. Materials and Methods

2.1 Groundwater and mineral samples preparation

The mineral sample was collected from Wolsong repository site taking into account the location of the silos and the direction of groundwater flow. Specific surface area was determined by N_2 -BET method.

Artificial groundwater was synthesized to simulate the major ion compositions of the repository groundwater.

2.2 Batch sorption experiments

Three different initial concentrations of non-radioactive nickel (10, 50 and 100 ppb) were spiked into artificial groundwater. The pH range of solution was adjusted from pH 4 to pH 12 using HNO_3 (1M) or NaOH (1M). After 24 hours of reaction, supernatants were separated using a syringe filter (0.45 μm) and sampled for nickel concentration measurements using ICP-MS.

2.3 Surface complexation model (SCM)

A generalized composite surface complexation model (GC-SCM) was used to fit nickel sorption data using FITEQL 4.0 software. For simplicity, a non-electrostatic model (NEM) was used, which do not consider electric double layer (EDL).

3. Results and discussion

3.1 Nickel speciation in disposal condition

Ni^{2+} , NiOH^+ and $\text{Ni}(\text{OH})_{2\text{aq}}$ are the main nickel species in acidic and neutral pH conditions. However, above pH 12, the negatively charged complex $\text{Ni}(\text{OH})_3^-$ and $\text{Ni}(\text{OH})_4^{2-}$ are becoming more dominant species (Fig. 1).

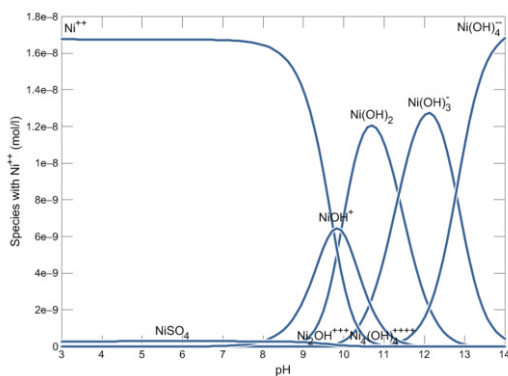


Fig. 1. Nickel speciation distribution in different pHs.

3.2 Nickel sorption experiment results

The sorption of nickel (or K_d value) is strongly influenced by the variable pH conditions. As expected, the amount of nickel sorption increased with increasing pH. However, although the surface of the mineral is negatively charged at high pH and negatively charged nickel species prevail, almost 100% of nickel sorption occurred (Fig.2a) at high pH (>8.0). Considering the solubility modeling result, these high sorption removals at hyper-alkaline condition is expected to result from $\text{Ni}_2\text{SiO}_4(\text{s})$ precipitation.

A non-electrostatic GC-SCM approach simulated the measured nickel sorption data very well as well as predicted the sorption at high pH (Fig. 2b).

Without SCM model prediction, simple batch sorption tests may mislead the nickel sorption removal, especially at high pH condition.

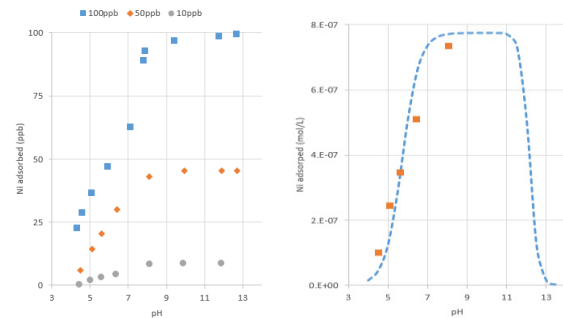


Fig. 2. a) Nickel sorption as a function of pHs at three different initial concentrations. b) SCM result.

4. Conclusion

The sorption of nickel is strongly influenced by the variable pH conditions. GC-SCM (NEM) approach simulates the experimental data very well, therefore it can be also applied to predict sorption behavior of nickel as disposal conditions vary.

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