

The effect of isosaccharinic acid on the mobility of nickel in the near- and far-field repository conditions

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1. Introduction

There are two important radionuclides of nickel (⁵⁹Ni, ⁶³Ni) that exist in radioactive waste disposal facilities, and they have long half-lives of 76,000 years and 100 years, respectively [1]. Because of this, radioactive nickel is stipulated in the Act as one of the main radionuclides to be determined in order to quantify the total radioactivity in repository [2]. At the low- and intermediate-level radioactive waste (LILW) disposal facility located in Gyeongju, radioactive waste is deposited in a concrete container and stored in a concrete silo. Following the closure of the facility, the environment becomes highly alkaline, which may cause the decomposition of organic waste materials (cotton, tissue, wood etc.) and generate isosaccharinic acid (ISA) within the disposal facility [3]. As the presence of ISA can increase the mobility of radionuclides, it is necessary to investigate the effect of ISA on the mobility of Ni under various repository conditions [4, 5]. Therefore, this study aimed to examine the ISA effect on the sorption and solubility of Ni in both porewater and groundwater conditions to assess its impact on Ni in the near- and far-field conditions of the disposal facility.

2. Methods

Calcium alpha-D-isosaccharinate (Ca(ISA)₂, 98%, Thermo Scientific™) was purchased and used for ISA source. For the sorption experiments, stable Ni(NO₃)₂·6H₂O (97%, Sigma Aldrich) was used, while Ni(OH)₂ (Sigma Aldrich) was used for the solubility experiments, because Ni(OH)₂ has been identified as the solubility-controlling phase in both synthesized groundwater (GW) and porewater (PW). The solution used to simulate the far-field environment was synthesized GW, and for the near-field environment, PW was prepared by the saturated cement with GW. Both GW and PW solutions were used for conducting sorption and solubility experiments.

2.1 Sorption

In the sorption experiment, near-field conditions were simulated using PW and cement, while far-field conditions were simulated using GW and granite. The reactions were maintained in a steady state for more

than three days. There are two types of experiments, one with different concentrations of ISA and another with different initial equilibrium solutions which are shown in Table 1. Polyethylene tubes of 15 mL were filled with medium, nickel, and various concentrations of ISA from 0 to 15mM. The sample tubes were gently shaken using a platform shaker for 7 days and the supernatants were collected after filtering using 0.22um syringe filters. The concentrations of Ni²⁺ were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), and the concentrations of ISA⁻ were analyzed by ion chromatography (IC). The medium was also dried and prepared for scanning electron microscope and energy dispersive spectrometer (SEM-EDS) analysis.

Table 1. Different experimental initial equilibrium solutions with Ni and/or ISA in GW

	① N	② N+I	③ NI	④ I+N
1st saturated condition	Nickel	Nickel	Nickel, ISA	ISA
2nd saturated condition	Nickel	Nickel, ISA	Nickel, ISA	Nickel, ISA

* N: Ni only on sorption experiment; N+I: Ni was spiked first in 1st saturated condition, and then Ni and ISA were added in 2nd saturated condition; NI: Both Ni and ISA were spiked at the same time in both 1st and in 2nd saturated condition; I+N: ISA was spiked first in 1st saturated condition, and then Ni and ISA was added in 2nd saturated condition.

The batch sorption results were used to determine sorption distribution coefficient (K_d) using Eq.1,

$$K_d = \frac{(C_0 - C_w) V_w}{C_w m_s} \quad (\text{Eq.1})$$

where, C_0 (mol/L) represents the initial concentration of Ni²⁺, C_w (mol/L) represents the concentration of Ni²⁺ in solution at equilibrium, V_w (mL) represents volume of solution, and M_s (g) represents mass of solid(medium).

The sorption efficiency was also calculated using the following Eq. (2),

$$R(\%) = \frac{C_0 - C_w}{C_0} \times 100 \quad (\text{Eq.2})$$

where R represents the sorption (%), C_0 (mg/L) represents the initial concentration of Ni²⁺, and C_w (mg/L) represents the concentration of Ni²⁺ in solution at equilibrium.

2.2 Solubility

For the solubility experiment, multiple sets of samples were prepared by mixing 100 mg of Ni(OH)₂(s) with 100 mL of 0, 1, 10, or 20 mM ISA concentration. One sample, called PN, was made by adding 100 mg of Ni(OH)₂(s) to 50 mL PW. On the 14th day, 50 mL of ISA 20 mM was added to the PN sample. The sample collection period was 3 hours, 1, 3, 14, 28, 56, 84, and 120 days. The resulting mixture was sampled and filtered using 0.22 filters, and the supernatant was analyzed using ICP-MS and IC for Ni²⁺ and ISA⁻ concentration, respectively. After solubility experiments, the solid phase was characterized using X-ray diffraction (XRD) and SEM analyses.

3. Results and Discussion

3.1 Sorption

The results of sorption experiments in different concentrations of ISA are shown in Figure 1. The Ni sorption to granite decreases as the concentration of ISA increases. How Ni binds to ISA and affects the Ni K_ds are shown in Eq. 3. Sorption experiment data in Table 2 also shows that the Ni K_d values decrease with increasing concentration of ISA. This can be explained by the equilibrium reaction, since the formation of NiISA⁺ complex can reduce the availability of Ni for sorption on granite. This means that the sorption capacity of granite to Ni decreases with increasing concentration of ISA, which is reflected in the decreasing trend of Ni sorption K_d values.

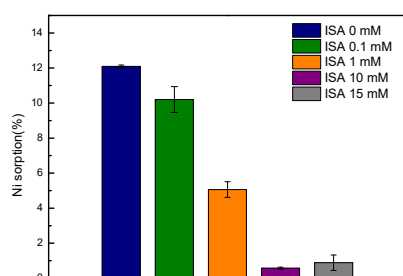


Fig. 1. Ni sorption (%) with different ISA concentrations in GW (pH ≃ 8.05).

Table 2. Ni K_d values with different ISA concentrations in GW

ISA (mM)	K _d (m ³ /kg)
0	0.069 ± 0.0005
0.1	0.057 ± 0.0046
1	0.027 ± 0.0025
10	0.003 ± 0.0003
15	0.007 ± 0.0022

Sorption experiment results in different initial equilibrium solutions are shown in Table 3. N is the case without ISA, and the remaining three (N+I, NI, and I+N) are to confirm the sorption effect of Ni on granite according to the initial equilibrium solution. The N+I samples were subjected to an injection of Ni and ISA subsequent to the adsorption of Ni onto the granite. This suggests that the Ni, which had already been adsorbed onto the granite, became dissociated from granite and formed a complex with ISA (NiISA⁺). NI seems to be similar to the case of I+N. I+N samples were first dissolved with ISA and then injected with Ni and ISA. ISA was already dissolved in the solution and the added Ni formed a complex with ISA, making it difficult for Ni to adsorb on the granite surface. As a result, the amount of Ni adsorbed on the granite was the smallest. Therefore, considering that the K_d values of NI and I+N are lower than those of N+I, it can be seen that Ni sorption to granite is advantageous when Ni reacts first on granite surfaces.

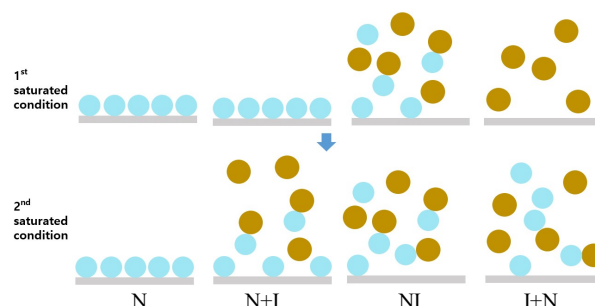


Fig. 2. Mechanism of Ni (blue circle) and/or ISA (brown circle) sorption in different initial equilibrium solutions on granite.

Table 3. The Ni K_ds of different initial equilibrium solutions in GW ([Ni]=10 μg/L, [ISA]=10 mM).

Sample	K _d (m ³ /kg)
N	0.099 ± 0.005
N+I	0.037 ± 0.009
NI	0.019 ± 0.002
I+N	0.017 ± 0.002

3.2 Solubility

The results of the solubility experiment in PW are shown in Figure 3. The solubility of Ni was relatively similar both in the absence of ISA and with the addition of 1 mL of ISA. However, a significant increase in Ni solubility occurred when ISA concentration exceeded 10 mM. There are two samples in which a 10 mM ISA solution is used as a solvent. The first sample (P10) has this concentration of ISA (10 mM) from the beginning, but the second sample (PN) had no ISA at the beginning and additional 10 mM concentration of ISA was added on the 14th day sample. The P10 sample with 10 mM

ISA from the beginning showed higher Ni solubility compared to PN. Both P10 and PN samples have high pHs (~12.5). It appears that the solubility of Ni(OH)₂(s) in P10 increased by forming Ni(OH)₃ISA²⁻ complexes from the beginning, following the Eq. 4. In contrast, in PN, Ni(OH)₃⁻ anionic species was formed first before reacting with the ISA anion (Eq. 5). Therefore, it seems that the solubility of PN is different from P10 as it does not form as many Ni-ISA complexes.

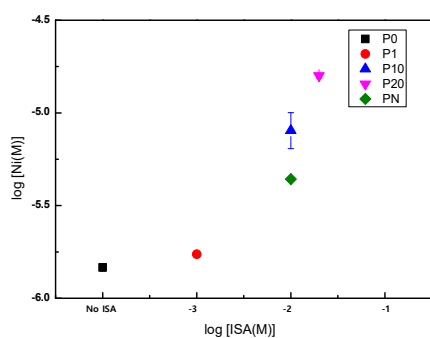
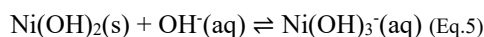
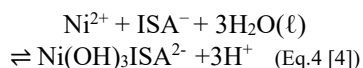


Fig. 3. The Ni solubility with different ISA concentrations in PW (pH ≈ 12.5) on 56day.

The solubility of Ni in GW also increased with increasing ISA concentration (Fig. 4). In GW, similar to PW, Ni solubility greatly increased by adding the ISA concentration of 10 mM or higher. In addition, Ni has a higher solubility in GW (pH ≈ 8.5) than in PW (pH=12.5), attributed to the impact of pH leading to the precipitation of Ni(OH)₂(s) in PW and therefore lowering its solubility. Conversely, in PW, ISA undergoes deprotonation at high pH levels, resulting in the formation of ISA⁻. This leads to increased complexes with Ni and ISA. Comparatively, the impact of ISA on Ni solubility is more pronounced in PW compared to GW.

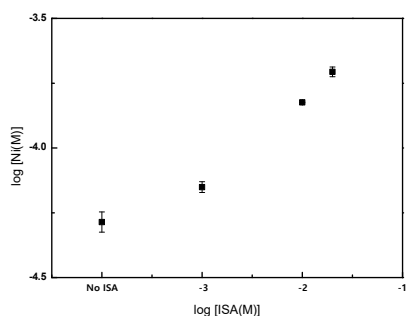


Fig. 4. The Ni solubility with different concentrations ISA in GW (pH ≈ 8.5) on 84day.

3. Conclusion

The results of the sorption experiments indicate that the presence of ISA decreased the sorption of Ni on the granite and cement. Furthermore, the Ni solubility showed an increase in the presence of ISA, with a marked increase observed at ISA concentrations of 10 mM or higher in both GW and PW. This finding confirms that complexation between Ni and ISA can lead to the increased mobility of Ni in both near and far-field environments.

4. Acknowledgments

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