Far-field assessment of radioactive Co transport with polycarboxylic ester (PCE) cement admixture from the LILW disposal facility

Donghun Pak[1], Nara Jeong[1], Soojeong Ji[1], Wooyong Um[1,2]

1 Division of Advanced Nuclear Engineering, POSTECH, Pohang, South Korea

2 Division of Environmental Science & Engineering, POSTECH, Pohang, South Korea

donghun@postech.ac.kr, wooyongum@postech.ac.kr

*Keywords : Radioactive Waste, Polycarboxylic ester, Portland Cement, Carbonation

1. Introduction

Engineered barriers in radioactive waste repositories play an important role in ensuring the high safety of the system [1]. The most widely used material for these barriers is Portland Type I cement, a well-known material with good compressive strength. When using cement, the ratio of water to cement has a significant impact on the compressive strength and the flowabilty, which are important factors to consider. In this case, superplasticizers, organic chemical admixture are used by cement manufacturers to improve the dispersion, hydration, and workability properties of concrete [2-5]. However, in the context of radioactive waste disposal, the interaction of organic materials with radioactive materials is an important issue [6]. Cobalt ions are of particular interest in this study. Cobalt-60 is a radioactive isotope which is one of the main sources of gamma-ray emissions from radioactive waste [7]. Previous studies have shown that cobalt ions bind strongly to cement through ion exchange with M^{2+} site in the crystal structure, while it also possibility to sorb onto CSH gel [8-9]. However, it is important to investigate how the interaction with organic additives released from the cement affects the sorption and mobility of cobalt ions. Furthermore, understanding the effect of reaction between Co and additive is expected to provide insight into the mobility of other radionuclides present in repository. In this study, we investigated the changes in sorption, desorption, and solubility of Co in two different types of hydrated cement under varying the mixing ratios of cement admixtures. By understanding the interactions between radionuclides and cement materials, these results contribute to a more thorough safety assessment and long-term performance evaluation of nuclear waste repositories.

2. Methods

Ordinary Portland Cement (OPC) purchased from SsangYong Industrial Co, was used in this study as a material for immobilizing Cobalt. And commercial cement superplasticizer Polycarboxylic-ester (PCE) polymer was used for cement admixture source from H.B.Technology. For the Co sorption experiments, 0.0042 mmol of $CoCl_2$ (97 %, Sigma Aldrich) was used to react the prepared cement powder (size: 75 ~150 µm).

For the desorption experiment, 0.019 mmol of $Ca(NO_3)_2 \cdot 4H_2O$ (ACS reagent, 99.0 %, Sigma Aldrich) was chosen as the competing ions. After Co sorption, the cement paste was fully dried and used for the desorption experiments with a liquid-to-solid ratio of 1:100. Furthermore, for the solubility experiments, a range of pH buffers (pH 7, 10, and 12) and groundwater (GW) samples from the vicinity of the disposal site, along with the prepared groundwater cement leachates (GWCL), were employed to conduct the Co solubility experiments.

2.1 Hydration of cement

In this study, Portland cement and deionized water were mixed at two different water-cement ratios, 0.3 and 0.55. Additionally, PCE was mixed at various weight ratios (0.0, 0.1, 2.0, and 5.0) relative to the total weight (wt %) of cement cylinders (5 cm x 10 cm) to investigate their effects on cement properties. The prepared cement pastes were cast in a paper mold with a diameter of 50 mm and a height of 100 mm under room temperature conditions (T: 20-23 °C, RH: above 80%). To simulate the real environment of a disposal facility, a weathering effect was also represented by CO_2 purging. The hydrated cement was prepared by sieving into particle sizes ranging from 75 µm to 150 µm and then mixed with deionized water at a solid-liquid ratio of 1:100 for giving the weathering effect. During this process, CO_2 was injected at a rate of approximately 100 cc/min for approximately 2 hours.

2.2 Sorption

To investigate the behavior of the cement structures under far-field conditions, sorption experiments were performed to compare their performance with normal and weathered cement. 0.0042 mmol of cobalt was introduced. The major cement components prepared with PCE content were characterized using X-ray fluorescence (XRF) and shown in Table 1. Sample tubes with a solid-liquid ratio set at 1:100 was gently shaken using a platform shaker for 3 days, filtered using a 0.20 µm syringe filter, and the supernatant collected. The concentration of Co was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

Table 1. XRF results for hydrated cement samples containing different PCE admixture (weight %)

Sample	CaO	SiO$_2$	CO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	K$_2$O	SO$_3$
PCE 0.0	60.0	14.8	9.3	4.06	3.14	3.04	2.18
PCE 0.1	59.9	15	9.49	4.09	3.22	2.83	2.1
PCE 2.0	58.9	14.6	10.4	4.17	3.23	2.22	3.09

*Less than 1.0 % of component were ignored.

The batch sorption results were used to determine Co sorption capacity (q$_e$) at equilibrium using Eq.1,

$$q_e = \frac{(C_i - C_e) \times V}{m} \quad \text{(Eq.1)}$$

, where C$_i$ (mol/L) represents the initial concentration of Co, C$_e$ (mol/L) represents the equilibrium concentration of Co in solution, V (mL) represents volume of solution, and m (g) represents mass of solid (cement).

2.3 Desorption

There are two primary approaches for conducting desorption experiments, involving physical and chemical methods. First, the physical desorption method is explained. A solid-to-liquid ratio of 50 mL of deionized water (DIW) to 0.5 g of cement sample with sorbed cobalt is selected, and the mixture is agitated for 1 hour at 150 rpm. Subsequently, the solid and supernatant are separated through centrifugation at 10,000 rpm. This separation process is repeated iteratively until the concentration of cobalt ions in the supernatant is reduced to 0.2% or less of the Co initial concentration. This experimental procedure is conducted four times.

Next, 0.019 mmol of calcium was used as a competing ion for chemical desorption. A shaker operating at 150 rpm was used in the stirring process using the same solid-liquid ratio of 1:100, and sampling was performed at various intervals from 3, 6, 9, and 12 hours, 1, 3, 5, 7, 14, and 28 days. The supernatant generated from the stirring process was then used to assess the residual concentration of cobalt (or released Co concentrations). This assessment was performed using both ICP-MS and total organic carbon (TOC) analysis.

2.4 Solubility

For the solubility experiments, the Solubility Limited Solid Phase (SLSP) of cobalt ions was determined by Geochemist's Workbench Modeling (GWB), and several sets of samples were prepared by mixing with 0.0, 0.1, and 2.0 wt% of PCE. In each sample, 0.3 g and 0.5 g of Spherocobaltite (CoCO$_3$) or Cobalt Oxide (Co$_3$O$_4$) were added to 100 mL of pH buffer solution (pH 7, 10, and 12), GW (Gyeongju Wolseong EN-01 pond shown in Table 2), and GWCL. The GWCL was prepared using the crushed cement (size fraction between 150 and 300 μm) made with PCE (0.0, 0.1, and 2.0 wt%) reacting with GW at a fixed solid/liquid ratio of 10 g/L for 30 days. The prepared solubility samples collection period

were 3 hours, 1, 3, 7, 14, 21, 28, 50, and 90 days. The resulting mixture was sampled and filtered using 0.20 μm filters, and the supernatant was analyzed using ICP-MS. In addition, after solubility experiments the remaining solid phase was characterized using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) analyses.

Table 2. Groundwater compositions used in this study

Species	pH	Eh (mV)	Mg^{2+} (ppb)	Na$^+$ (ppb)	K$^+$ (ppb)	Ca^{2+} (ppb)	Li$^+$ (ppb)
Conc	7.7	334	68276	52358	9233	18355	1579

Species	Ba^{2+} (ppb)	Sr^{2+} (ppb)	Mn^{2+} (ppb)	Zn^{2+} (ppb)	Si^{2+} (ppb)	Cl$^-$ (ppm)	SO$_4^{2-}$ (ppm)
Conc	11.47	1143	1731	1234	15813	1226.9	781.8

3. Results and Discussion

3.1 Sorption and Desorption

The results of the sorption experiments conducted in the presence of PCE are presented in Table 2. Regardless of the content of the cement additive, most of the cobalt ions (approximately 99.5 %) were sorbed in the cement. M^{2+} divalent ions, such as cobalt ions, are commonly recognized for their propensity to form outer- or inner-sphere bonds with the C-S-H structure [8-9], the primary component of cement. Moreover, considering the target sorbed cobalt ion concentration of 0.0042 mmol, it can be inferred that a substantial portion of the target concentration was indeed adsorbed. This is attributed to the inherent characteristics of cement, allowing higher Co concentrations to be readily adsorbed.

Table 3. Sorption of Co in (un)weathered hydrated cement (W/C = 0.55)

Sorbents	PCE (wt%)	q$_e$ (mg/g)	sorption (%)
(B) OPC	0.0	479.0	99.19
	0.1	479.8	99.36
	2.0	479.2	99.24
(A) OPC	0.0	490.6	99.80
	0.1	489.2	99.51
	2.0	489.3	99.52

* (B): Before-weathered hydrated cement
** (A): After weathered hydrated cement

The physical desorption rate as a function of the number of washes with DIW is shown in Fig 1. After undergoing four wash cycles, the cobalt concentration was found to be less than 0.2 % of the initial Co concentration, suggesting that no significant proportion of the cobalt initially sorbed within the cement particles underwent through physical desorption.
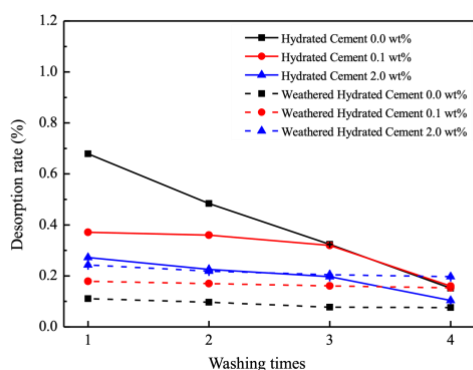
Fig 1. Co removal by weathered status and the number of washes (Line: Before weathering, Dash: After weathering)

The sorbed sample was dried and subjected to chemical desorption using the competing ion, calcium. The results of the chemical desorption experiments are shown in Figure 2.
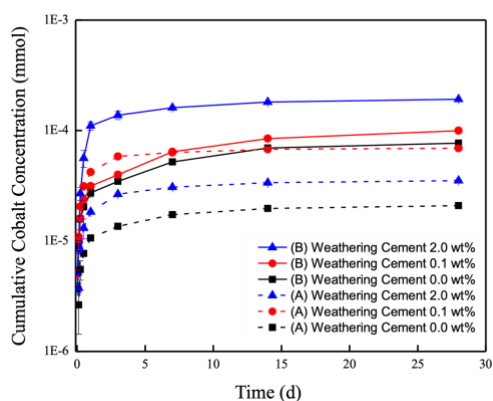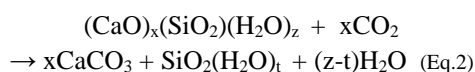

Fig 2. Cumulative desorption of cobalt concentration from before or after weathered hydrated cement with varying PCE content. Initial cobalt concentration: 0.0042 mmol, (Line: hydrated cemet, Dash: after weathered cement, Square: 0.0 wt%, Circle: 0.1 wt%, Triangle: 2.0 wt% of PCE).

$$(CaO)_x(SiO_2)(H_2O)_z + xCO_2$$
$$\rightarrow xCaCO_3 + SiO_2(H_2O)_t + (z-t)H_2O \quad \text{(Eq.2)}$$

The results of the chemical desorption experiments are shown in Figure 2. The results are presented considering the influence of weathering and varying PCE contents. In the case of the unweathered sample, higher PCE content led to greater desorption of cobalt ions. However, lower cobalt desorption was noted in the samples subjected to weathering rather than un-weathered cement samples. As demonstrated by Eq. 2, the formation of calcite contributed to the decrease of the cement pore network and cement matrix permeability, potentially leading to intensified inner-sphere bonding of cobalt ions [10].

Furthermore, the weathered samples exhibited an intriguing phenomenon. Lower desorption of cobalt ions was observed in samples containing 2.0 wt% PCE

admixture. The reasons, in the context of high molar weight of polymers such as PCE, these substances tend to form a positively charged surface film of a few nanometers on cement particles, inducing an attractive force between them [11]. Nevertheless, during the hydration process, these PCE films break down, resulting in a more robust binding between cement particles. During this stage, it is inferred that as carbonation progresses to a certain level, the structure of cement particles becomes denser, therefore limiting the release of Co.

3.2 Solubility

The results of the Co solubility experiment in GW is shown in Figure 3. The solubility of Co exhibited a strong correlation with the PCE content: a significant solubility increase was observed at both 0.1 and 2.0 wt% content levels, albeit not proportionally. The samples without PCE and with 0.1 wt% PCE showed relatively stable Co solubility during the initial 7 days, followed by a slight increase that amounted increment by 50 days. However, with the addition of 2.0 wt% PCE, the solubility consistently exceeded the original level throughout this study's period, resulting in high solubility result. This result can be attributed to Co and polymer electrolyte adsorption [12-13]. This complexation reaction elucidates the delayed cement hydration and the observed zeta potential shift, influencing the ionization of divalent ions while prominently elevating solubility in aqueous solutions.
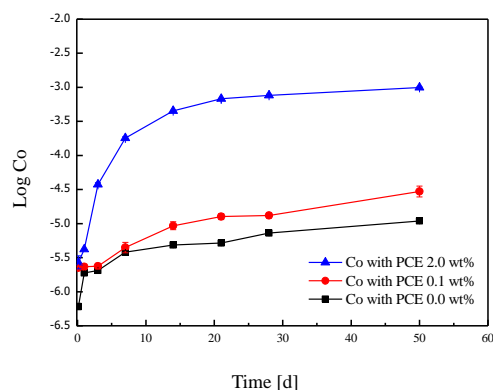

Fig. 3. The Co solubility with different presence of PCE concentrations in GW (pH $\approx$ 7.7) on 50 days.

3. Conclusion

The results of the desorption experiments indicate that the presence of PCE increased the desorption of Co on the weathered cement. However, the overall desorption rates were negligible with and without the cement admixture (up to 2.0 wt%). Furthermore, Co solubility was found to increase in the presence of PCE, with a significant increase observed at 2.0 wt% of PCE at both pH 7-12 and GW conditions. Based on these findings, it

can be inferred that the engineered barriers employing cement mixtures can provide substantial capacity in near-field environment of LILW repository. However, the impacts of PCE on radionuclide mobility beyond the barrier should be monitored with care under far-field conditions.

4. Acknowledgments

REFERENCES

[1] International Atomic Energy Agency. (2001). Performance of Engineered Barrier Materials in Near Surface Disposal Facilities for Radioactive Waste: Results of a Co-ordinated Research Project. International Atomic Energy Agency.

[2] Ouyang, X., Qiu, X., & Chen, P. (2006). Physicochemical characterization of calcium lignosulfonate—A potentially useful water reducer. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 282, 489-497.

[3] Russo, A., Schorer, A., Rentsch, M., Nese, G., Montagnaro, F., & Santoro, L. (2017). Use of Non-Purified Polycarboxylate Ether (PCE) as Superplasticizer-Structural Determination and PCE/Cement Interaction. Recent Innovations in Chemical Engineering (Formerly Recent Patents on Chemical Engineering), 10(1), 27-47.

[4] Chen, G., Lei, J., Du, Y., Du, X., & Chen, X. (2018). A polycarboxylate as a superplasticizer for montmorillonite clay in cement: Adsorption and tolerance studies. Arabian journal of chemistry, 11(6), 747-755.

[5] Yi, S. T., Heo, G., Choi, H. S., Lee, S. W., & Kim, J. K. (2008, September). Experimental study on the setting time of cement paste mixed accelerating admixtures. In Creep, shrinkage and durability mechanics of concrete and concrete structures, two volume set: Proceedings of the CONCREEP 8 conference held in Ise-Shima, Japan (Vol. 1, p. 403).

[6] Hakanen, M., & Ervanne, H. (2006). The influence of organic cement additives on radionuclide mobility. A literature survey.

[7] Centers for Disease Control and Prevention. (2018, April 4). CDC radiation emergencies. Centers for Disease Control and Prevention. https://www.cdc.gov/nceh/radiation/emergencies/isotopes/cobalt.htm

[8] Bonen, D., & Sarkar, S. L. (1994). Environmental attack on concrete. In Proc 16th Eng Found Conf, Am Soc Civil Eng New York (pp. 11-23).

[9] Noshita, K., Nishi, T., & Matsuda, M. (1998). Improved sorption ability for radionuclides by cementitious materials. WM, 98, 1880-1886.

[10] Park, S. M., & Jang, J. G. (2018). Carbonation-induced weathering effect on cesium retention of cement paste. Journal of Nuclear Materials, 505, 159-164.

[11] Javadi, A., Jamil, T., Abouzari-Lotf, E., Soucek, M. D., & Heinz, H. (2021). Working mechanisms and design principles of comb-like polycarboxylate ether superplasticizers in cement hydration: quantitative insights for a series of well-defined copolymers. ACS Sustainable Chemistry & Engineering, 9(25), 8354-8371.

[12] Glaus, M. A., & Van Loon, L. R. (2004). A generic procedure for the assessment of the effect of concrete admixtures on the retention behaviour of cement for radionuclides: Concept and case studies (No. NTB--03-09). Paul Scherrer Institute (PSI).

[13] Iriya, K., Kubo, H., Kato, T., & Fujita, H. (2001). Study on evolution of disposal environment due to alteration of cement. Commission work report (No. JNC-TJ--8400-2001-034). Japan Nuclear Cycle Development Inst.