

MAENGYO OH^{1,2}, KEUNYOUNG LEE^{1*}, RICHARD I. FOSTER^{1,3},
IK-SOO KIM¹, CHANG-HA LEE^{2*}

APPLICABILITY STUDY OF Co AND Eu EXTRACTION USING SOLVENT FROM Ca RICH HCl SOLUTION

This study was conducted to treat radioactive acidic wastewater, which contained radioactive ⁶⁰Co and ¹⁵²Eu. The wastewater can be generated during a decommissioning project to reduce the volume of radioactive concrete waste from nuclear facilities. With a variety of methods for separating the radioactive nuclides available, we evaluated the separation applicability of the solvent extraction method. From our results, Co and Eu could be easily extracted from the Ca rich wastewater using Cyanex301 (Co extraction (%) 99.8, Eu extraction (%) 99.6) without Ca extraction. On the other hand, Eu could be selectively separated by Cyanex272 (Eu extraction (%) 99.1) without Co and Ca extraction at pH 2~3. Therefore, the extraction method can be tailored according to the target radionuclides present in the wastewater and be selectively applied to the overall treatment process. By extracting radioactive Co and Eu from acidic wastewater to below the discharge criteria, treated wastewater could be regarded as non-radioactive industrial waste, to be economically and easily handled. Moreover, it may be possible to reuse separated Co and Eu for research and industrial applications by realizing waste valorization.

Keywords: Solvent extraction; Radioactive wastewater; Waste valorization; Cyanex272; Cyanex301

1. Introduction

Concrete used as the main material for buildings and structures is a mixture of aggregate and hydrated cement. Large volumes of radioactive concrete wastes are generated during the decommissioning of nuclear facilities [1]. This concrete waste has a huge impact on the decommissioning cost, because the cost of disposal of decommissioning wastes is a dominant portion of the total budget. In addition, when radioactive materials and non-polluting materials are effectively separated, the efficiency of waste valorization could be improved [2]. Various studies were conducted to reduce the volume of radioactive decommissioning concrete waste, and recently, a method of effectively reducing the volume of concrete waste by sequentially applying a thermo-mechanical and chemical treatment method has been developed [3]. However, a large amount of secondary acidic radioactive wastewater with a high chloride concentration was generated during the chemical treatment step.

This study was conducted to treat acidic radioactive wastewater, containing ⁶⁰Co and ¹⁵²Eu, which is generated during the volume reduction of radioactive concrete from nuclear facilities

undergoing decommissioning. Separating the radioactive Co and Eu from the wastewater to below the discharge criteria could enable the treated wastewater to be regarded as industrial wastewater, not radioactive wastewater, to be released to the environment under industrial waste guidelines [4]. Furthermore, the volume of radioactive concrete waste requiring long-term disposal could be significantly reduced. With a variety of methods for separating the radioactive nuclides, we evaluated the applicability of solvent extraction as a separation method, which is known to be effective for the selective separation of metal ions.

2. Experimental

The experiment was performed using a simulated acidic solution (HCl), to which reagent grade Co and Eu were added to a concentration of 10 mg L⁻¹ with and without a high Ca concentration (5 wt.%). To select the most suitable extractant for the simulated waste conditions, the extraction behavior of Co and Eu was confirmed by selected cation extractants (D2EHPA, Cyanex272, Cyanex301, PC88A), which were diluted

¹ KOREA ATOMIC ENERGY RESEARCH INSTITUTE (KAERI), DECOMMISSIONING TECHNOLOGY RESEARCH DIVISION, 111, DAEDEOK-DAERO 989 BEON-GIL, YUSEONG-GU, DAEJEON, 34057, REPUBLIC OF KOREA

² YONSEI UNIVERSITY, DEPARTMENT OF CHEMICAL AND BIOMOLECULAR ENGINEERING, 50 YONSEI-RO, SEODAEMUN-GU, SEOUL, 03722, REPUBLIC OF KOREA

³ SEOUL NATIONAL UNIVERSITY, NUCLEAR RESEARCH INSTITUTE FOR FUTURE TECHNOLOGY AND POLICY, 1 GWANAK-RO, GWANAK-GU, SEOUL 08826, REPUBLIC OF KOREA

* Corresponding authors: lky@kaeri.re.kr; leech@yonsei.ac.kr



by n-Dodecane and Kerosene. The changes in concentration of Co and Eu in the aqueous phase were measured using ICP-OES (PQ-9000, Analytik-Jena), and the extraction yield (%) and separation factor (β), as equations 1 and 2, respectively, were calculated to compare each extractant.

Extraction yield (%)

$$\left(1 - \frac{\text{Residual concentration of target element}_{(aq)}}{\text{Initial concentration of target element}_{(aq)}} \right) \times 100 \quad (1)$$

Separation factor ($\beta_{A/B}$)

$$\beta_{A/B} = \frac{D_A}{D_B},$$

$$\left(D_{A \text{ or } B} = \frac{\text{Extraction yield of A or B}(\%)}{(100 - \text{Extraction yield of A or B}(\%))} \right) \quad (2)$$

D_A – Distribution coefficient of target element A,

D_B – Distribution coefficient of non-target element B.

3. Results and discussion

The extraction ability of the extractants were evaluated by comparing the extraction yield (%) and separation factor (β) under pH 6, because the initial pH of the actual wastewater is expected to be acidic [3]. The separation factor, the ratio of distribution coefficients, is a parameter describing the selectivity of the extractant for the target elements, and the selectivity of the target element for the extractant is proportional to the separation factor [5,6].

Fig. 1 shows the extraction yield (%) of Co or Eu in a single-component system as a function of initial pH. After extraction, the pH of the aqueous solution was found to consistently be over pH 3, regardless of the target element (Cyanex301: pH 2.38, D2EHPA: pH 3.07, PC88A: pH 2.62, Cyanex272: pH 2.9). In the case of Co, the extraction yield (%) was generally low, apart from Cyanex301 which exhibited complete extraction regardless of the initial pH. In addition, the extraction yield (%) by D2EHPA increased, when the pH is higher than 2, but complete extraction was never achieved. This trend can be explained by considering the acid dissociation constant value (pK_a) of each extractant (TABLE 1), because the extraction yield (%) of Co is highly dependent on the pK_a [7]. The extraction of Eu did not have a large difference of extraction yield (%) between extractants under the pH 2 condition, however, the extraction yield (%) of D2EHPA was significantly decreased, when the pH was higher than 2. In other words, the extraction of Eu is not highly dependent on the pK_a of each extractant based on our experimental results, except for D2EHPA. This is because D2EHPA and Eu reaction was derived of equation 3 and had an inverse third-power dependency on the HCl concentration of the aqueous solution [8].

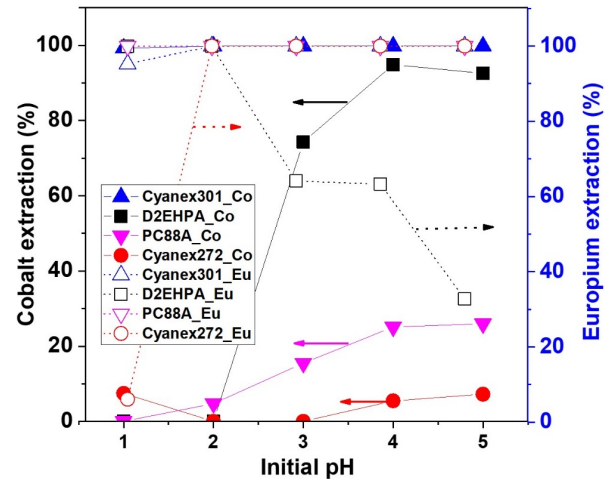
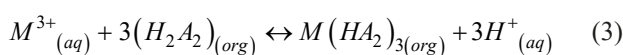


Fig. 1. Extraction yield of single component system Co or Eu with different initial pH

TABLE 1

Acidic dissociation constant of extractants [9,10]

	D2EHPA	Cyanex272	Cyanex301	PC88A
pK_a	3.24	6.37	2.61	4.51

Following the single component experiment, we performed the experiment in a dual-component system with different initial pH, for which almost identical trends are observed for both Co and Eu between the single and dual-component systems. The separation factor (β), representing the selectivity of Co and Eu, was calculated based on the above results and shown in Fig. 2. The separation factor for Co ($\beta_{Co/Eu}$) of Cyanex301 slightly decreased between pH 1 and 2 before maintaining a value of $\sim 10^{-1}$ regardless of pH, thus indicating that the selectivity of Co vs Eu was very low. Considering the results presented in Fig. 1 and Fig. 2, Cyanex301 is effective for the extraction of Co and Eu from solution simultaneously, but it was very difficult to extract them separately. The reason for this is related to the structural characteristics of Cyanex301, which contains sulfur donor atoms in its functional group [10]. In the dual system, Co, intermediate cation, is well binding with sulfur donor, while the Eu, hard acid cations, was hardly reacted with sulfur donor following the HSAB (hard soft acid base) principle [6]. However, the sulfur donor with Eu such as lanthanides was sp^3 hybridized to form a sigma bonding and the d orbital overlap with the π orbital, it could be extracted the Eu by Cyanex301 [11]. Therefore, the Co and Eu were extracted spontaneously by Cyanex301. The separation factor for Co ($\beta_{Co/Eu}$) of D2EHPA was very low ($\sim 10^{-6}$) under pH 2, but greatly increased to 10^1 at pH 3, and maintained the value even when the pH was further increased. This means that the selectivity of D2EHPA was dependent on the initial pH of the aqueous solution, which could be utilized to selectively extract Co from Eu with adequate pH manipulation. The separation factor of Cyanex301 for Co is lower than D2EHPA above the pH 3 range. Because Cyanex301 has no selectivity for Co and Eu, but D2EHPA could extract only Co selectively above the pH 3. Both PC88A and Cyanex272 exhibit very high separation

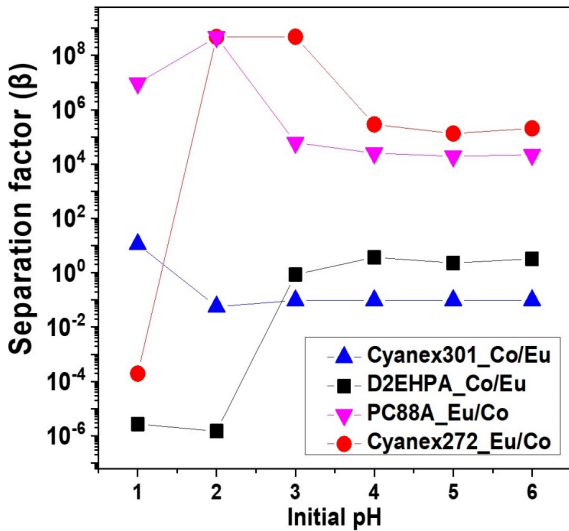


Fig. 2. Separation factor of Co and Eu in dual component system with different initial pH

factors for Eu ($\beta_{Eu/Co}$) regardless of initial pH, with the exception of Cyanex272 at pH 1. Furthermore, both extractants have higher selectivity for Eu compared to Cyanex301 and D2EHPA. When these two extractants were combined sequentially with Cyanex301 or D2EHPA, they could effectively separate Eu from Co. In other words, Co and Eu could be selectively extracted by using different extractants in a stepwise combination or controlling the initial pH of the aqueous wastewater.

Fig. 3 shows the extraction yield (%) of each component from a multi-component system containing Ca (5 wt%) and variation of pH, which is consistent with the actual wastewater [3]. In the case of Cyanex301, Ca was not extracted while both Co and Eu were effectively extracted regardless of initial pH depending on the separation factor in TABLE 2. Furthermore, selective extraction of Eu by Cyanex272 was successful with Cyanex272 showing no affinity for Ca or Co in the multi component system (TABLE 2). In other words, it is possible to separate both Co and Eu from the Ca-rich condition using Cyanex301, or in-turn from each other via a stepwise process by combination of Cyanex272(Eu) followed by Cyanex301(Co).

TABLE 2

Separation factor for Co and Eu vs Ca in multi component system with Cyanex extractants

Initial pH	Cyanex272		Cyanex301	
	$\beta_{Co/Ca}$	$\beta_{Eu/Ca}$	$\beta_{Co/Ca}$	$\beta_{Eu/Ca}$
1	1.00×10^0	8.74×10^2	2.21×10^6	1.07×10^5
2	1.00×10^0	1.04×10^6	1.00×10^8	8.81×10^5
3	1.00×10^0	1.00×10^8	1.00×10^8	1.74×10^6
4	1.00×10^0	1.00×10^8	1.00×10^8	2.22×10^6
5	1.00×10^0	1.00×10^8	1.00×10^8	2.48×10^6
6	1.00×10^0	1.00×10^8	1.00×10^8	2.61×10^6

On the other hand, both D2EHPA and PC88A show varying degrees of Ca removal at approximately 5 and 20%, respectively;

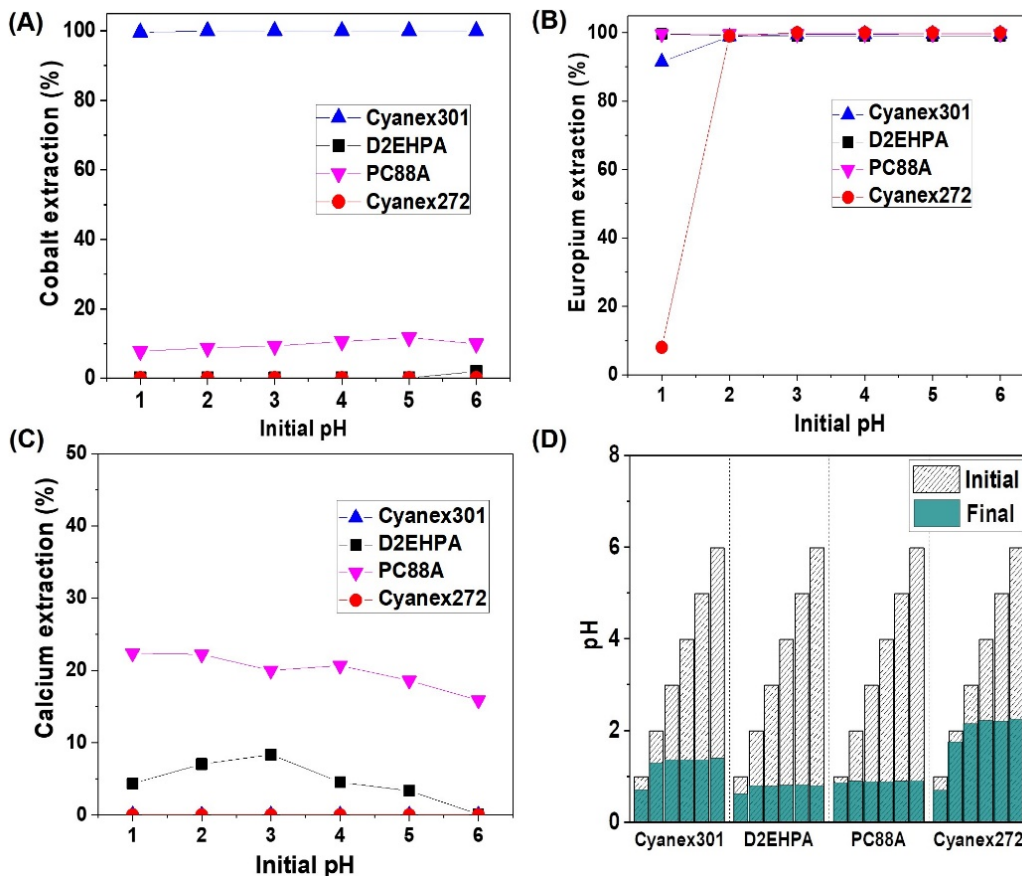


Fig. 3. Extraction yield of (A) Co; (B) Eu; (C) Ca; and (D) variation of pH in multi component (Ca-rich) system with different initial pH

decreasing as initial pH increased (Fig. 3-(C)). This impacted the removal efficiencies of Co and Eu. Cobalt was not extracted at all by D2EHPA, regardless of the initial pH change. However, D2EHPA showed excellent extraction yields for Eu, even at elevated pH, unlike in the single and dual-component systems. Because the pH of the aqueous phase was strongly decreased by extracting the Ca following the Fig. 3-(D), which could increase the extraction yield of Eu [12]. In addition to, the extractant PC88A removed most of the Eu under pH 6 and appears to be unaffected by the presence of Ca, but co-extraction of Ca occurred at approximately 20%. Interference from Ca during the extraction of Co and Eu using D2EHPA and PC88A significantly reduces them efficiently to the point of exclusion for use as extractants for the target wastewater. Methods for effectively separating Co and Eu from Ca in the multi-component system could be conducted as two options. First, Cyanex301 could be used to extract both Co and Eu simultaneously from the wastewater without distinction, which is then disposed of as radioactive waste. Conversely, as a method of recovering the elements for reuse, Cyanex272 is first used to separate Eu from the wastewater, and then Co is separated using Cyanex301.

4. Conclusions

It has been confirmed that extraction of Co and Eu without Ca from the target wastewater was possible by solvent extraction using Cyanex301 and 272. Furthermore, selective separation of Co from Eu was also achieved by using a stepwise combined extractant and pH-controlled process. It has been shown that Co and Eu could be separated effectively from the simulated solution, thus reducing the large volume of the radioactive wastewater. In addition, it may be possible to reuse the separated Co and Eu for research and industrial applications to realize waste valorization after optimizing the stripping method in the future [9]. The described method could be applied to similar target wastewaters containing Co and Eu.

Acknowledgments

This work was supported by the National Research Foundation of Korea grant (No. RS-2022-00155421) funded by the Ministry of Science and ICT.

REFERENCES

- [1] International Atomic Energy Agency, *Managing Low Radioactivity Material from the Decommissioning of Nuclear Facilities*, Vienna 2008.
- [2] International Atomic Energy Agency, *Application of the Concepts of Exclusion, Exemption and Clearance*, Vienna 2004.
- [3] M. Oh, K. Lee, R.I. Foster, C.H. Lee, *J. Environ. Chem. Eng.* **9** (4), 105742 (2021).
- [4] International Atomic Energy Agency, *Setting Authorized Limits for Radioactive Discharges: Practical Issues to Consider*, Vienna 2010.
- [5] T. Goto, M. Smutz, *J. Inorg. and Nucl. Chem.* **27** (6), 1369-1379 (1965).
- [6] J. Rydberg, *Solvent Extraction Principles and Practice Revised and Expanded* (2nd ed.), CRC Press 2004.
- [7] K. Omelchuk, P. Szczepański, A. Shrotre, M. Haddad, A. Chagnes, *RSC Adv.* **7**, 5660 (2017).
- [8] D. Peppard, W. Driscoll, R. Sirobien, S. Mccarty, *J. Inorg. Nucl. Chem.* **4**, 326-333 (1957).
- [9] H.S. Moon, S.J. Song, T.T. Tran, M. Lee, *Resources Recycling* **29** (5), 55-63 (2020).
- [10] V.N.H. Nguyen, T.H. Nguyen, M. Lee, *Metals* **10** (8), 1105 (2020).
- [11] K.C. Sole, J.B. Hiskey, *Hydrometallurgy* **37**, 129-147(1995).
- [12] C. Bourget, B. Jakovljevic, D. Nucciarone, *Hydrometallurgy* **77** (3-4), 203-218 (2005).