# Facile Separation of Sr-90, Fe-55, Nb-94, Ni-59,63 with Large Amount of Ca by Controlled pH Precipitation – 17190

Jung Bo Yoo *, Kyungwon Suh *, Hye Ju Lee *, Hong Joo Ahn *, Kwang Yong Jee *

* Korea Atomic Energy Research Institute

## ABSTRACT

it is important to manage low-and intermediate-level radioactive wastes from nuclear power plants due to a permanent disposal. According to the Nuclear Safety and Security Commission (NSSC), among all the regulatory radionuclides, a few radionuclides from the fission products and corrosion products such as Sr-90, Fe-55, Nb-94, Ni-59,63 which emit low-energy x-ray and beta radiation. Thus, it is necessary to separate beta-emitting nuclides individually. For that reason, KAERI has established analytical procedures which can separate Sr-90, Fe-55, Nb-94, Ni-59,63 from radioactive waste samples. However, when radioactive wastes contain large amount of Ca (above 300 mg), it is not easy to recover the target radionuclides because high concentration of Ca has a strong influence on the effective analyses. In order to combat this problem, there was an attempt to make the precipitate as $CaF_2$ by using hydrofluoric acid. However, this way had a limitation; Fe-55, Nb-94 were precipitated as fluoride compounds as well as Ca. In this study, we have focused on developing a separation procedure stage by stage in the radioactive wastes with Sr-90, Fe-55, Nb-94, Ni-59,63 and large amount of Ca (1500 mg). The detailed steps are described below; (1) Separation of Fe-55, Nb-94, Ni-59,63 as metal hydroxide precipitates: low solubility product constant ($K_{sp}$) between pH 6 and pH 10. (2) Selective elimination of Ca-oxalate complex under strong acidic conditions. Consequently, all the metal sources were sequentially separated and quantitatively recovered by inductively coupled plasma atomic emission spectrometric (ICP-AES) analysis, the recovery is as follows; Sr-90 (3 mg): 89.47±5.48%, Fe-55 (20 mg): 99.80±3.19%, Nb-94 (20 mg): 97.45±2.42%, Ni-59,63 (2 mg): 83.59±15.31%, Ca (1500 mg): 85.32±6.38%, respectively. This methodology will help us separation of radioactive wastes efficiently if apply properly.

## INTRODUCTION

Within the nuclear energy sector in South Korea, a rough categorization divides nuclear waste into low level, intermediate level and high level wastes. High-level radioactive wastes are the highly radioactive materials produced as a byproduct of the reactions that occur inside nuclear reactors. The main sources are as follows; 1) spent reactor fuel when it is accepted for disposal, 2) waste materials remaining after spent fuel is reprocessed. On the other hand, low and intermediate-level radioactive wastes include items that have become contaminated with radioactive material or have become radioactive through exposure to neutron radiation. This waste consists of contaminated protective shoe covers and clothing, wiping filters, papers, gloves, medical tubes, injection needles and other relative materials. Currently, most of low and intermediate-level radioactive wastes are temporarily stored at nuclear power

plants. Except for these sites, Korea Atomic Energy Research Institute (KAERI) is the only place to store the radioactive wastes. KAERI transferred 800 drums (200L per 1 drum) of low and intermediate-level radioactive wastes to Gyeongju which place has the permanent disposal facilities beginning in November 2015 and 800 drums of radioactive wastes per year will be transported to the disposal facilities for the permanent disposal.[1]

When low and intermediate-level radioactive wastes transport to the disposal facilities, it is essential to comply with the safety regulations. According to the Notice No. 2015-04 of the Nuclear Safety and Security Commission (NSSC), it is required to find the identify and clarify radioactivities of representative 10 radionuclides and gross alpha including H-3, C-14, Co-60, Ni-59, Ni-63, Sr-90, Nb-94, Tc-99, I-129 and Cs-137.[2] Especially, Tc-99, Nb-94, Fe-55, Sr-90, Ni-59 and Ni-63 radionuclides should be individually separated not only from a sample matrix but also from co-existing radionuclides in advance of a radioactivity measurement due to their radiochemical properties of low energy beta- and X-ray emitting radionuclides. For this reason, nuclear chemistry research division (NCRD) in KAERI has developed the analytical procedure which can separate Tc-99, Nb-94, Fe-55, Sr-90, Ni-59 and Ni-63 from radioactive waste samples.[3]

However, when radioactive wastes contain large amount of Ca (above 300 mg), it cannot be possible to recover the each nuclides because high concentration of Ca causes an undesirable result. To tackle this matters, there was an attempt to make the precipitate as $CaF_2$ by using hydrofluoric acid (HF). As is well known, HF is readily react with calcium in aqueous solution and to form a $CaF_2$ precipitation with white color. However, this way had a limitation; Nb-94 and Fe-55 radioactive nuclides also readily react with HF.

In this study, we have focused on developing a separation procedure stage by stage in the radioactive wastes including Tc-99, Nb-94, Fe-55, Sr-90, Ni-59, Ni-63 and large amount of calcium (1500 mg). The two approaches are described below; (1) Separation of Fe-55, Nb-94, Ni-59 and Ni-63 as metal hydroxide precipitates which have low solubility product constant ($K_{sp}$) values between pH 6 and pH 11. (2) Selective elimination of Ca-oxalate complex under strong acidic conditions by using nitric acid. Consequently, all the metal sources were sequentially and quantitatively recovered by inductively coupled plasma atomic emission spectrometric (ICP-AES) analysis, the recovery is as follows; Sr-90 (3 mg): 92.22+5.48%, Fe-55 (20 mg): 99.80+3.19%, Nb-94 (20 mg): 97.45+2.42%, Ni-59,63 (2 mg): 83.59+15.31%, Ca (1500 mg): 85.32+6.38%, respectively. This methodology will help us separation of radioactive wastes efficiently if apply properly.

**METHODS**

**Reagents and solutions**

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. The calcium standard solution with 100,000 mg/L were prepared using a $CaCO_3$(s) powder. In brief, 125 g of $CaCO_3$ power, 200 mL of 0.5M $HNO_3$ and 300 mL of c-$HNO_3$ solution were added to a 2,000 mL glass beaker, and the solution was stirred for 1 h. Synthetic radioactive waste solutions of Nb (20 mg), Fe (20 mg), Sr (3 mg) and Ni (2 mg) were prepared by diluting and combining calibrated standard solutions for the ICP-AES analysis or metal salt solutions to the appropriate concentrations due to the lack of similar certified reference materials for reliability evaluation of the separation procedure confirmed in the study.

**Equipment**

A radiation shielded ICP-AES system (Thermo Jarrell Ash, USA) composed of an ICP-AES and a stainless steel glove box was employed for the analysis of the radioactive waste samples. DI-water was used a Milli-Q plus Ultra-Pure Water System (Millipore).

**DISCUSSION**

**Sequential separation of Fe, Nb and Ni from large amount of Ca**

The standard solutions of Sr (3 mg), Fe (20 mg), Nb (20 mg), Ni (2 mg) and large amount of Ca (1500 mg) were loaded into the 50 mL centrifuge tube with 20 mL of 0.5 M $HNO_3$ solution. After the solution was stirred for 15 min, 10% $NH_4OH$ was dropped into the solution to adjust pH range between 6.0 and 11.0. Brown precipitate formed and was separated from the solution by centrifugation (4,000 rpm, 5 min). To verify the amount of elements, ICP-AES analysis was performed.
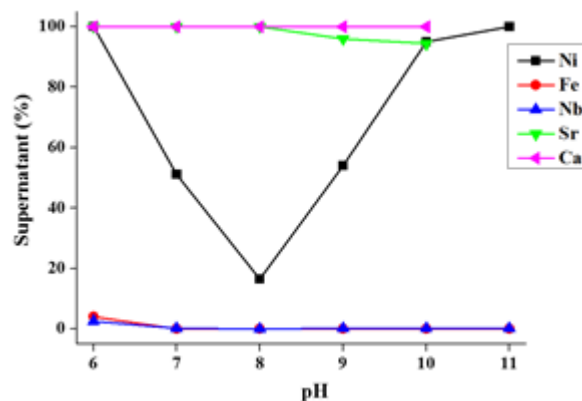


**Fig. 1** pH-induced precipitation behavior of Sr, Fe, Nb, Ni and large amount of Ca

Fig.1 shows the pH-induced precipitation behavior of Sr, Fe, Nb, Ni and large amount of Ca. Ca and Sr elements show the distinctive behavior in comparison with Fe, Nb and Ni elements. These two elements have lower solubility product constant than Fe, Nb and Ni; $Sr(OH)_2$: $3.2 \times 10^{-4}$, $Ca(OH)_2$: $1.3 \times 10^{-6}$, $Fe(OH)_2$: $1.8 \times 10^{-15}$, $Ni(OH)_2$: $1.6 \times 10^{-16}$. Thus, Ca and Sr elements have no precipitate products between pH 6.0

and pH 11.0. Whereas Fe, Nb and Ni elements were totally precipitated because of the high solubility product constant values. Thus, the experimental results correspond to the $K_{sp}$ values. Also notable is the fact that Ni element showed the distinct behavior compare to Fe, Nb in spite of high $K_{sp}$ value. The solubility of Ni was decreased up to pH 8 but the solubility was increased above pH 8. It suggests that the optimize pH range to precipitate Fe, Nb and Ni was near pH 8.0.

**Separation of Ca-oxalate with under acidic condition**
After eliminating Fe, Nb and Ni as metal hydroxide precipitates from Sr, Fe, Nb, Ni and large amount of Ca, c-HNO$_3$ solution and oxalic acid were added into the 50 mL centrifuge tube which have Ca and Sr supernatants. White precipitate formed and was separated from the solution by centrifugation (4,000 rpm, 5 min). To verify the amount of elements, ICP-AES analysis was performed.
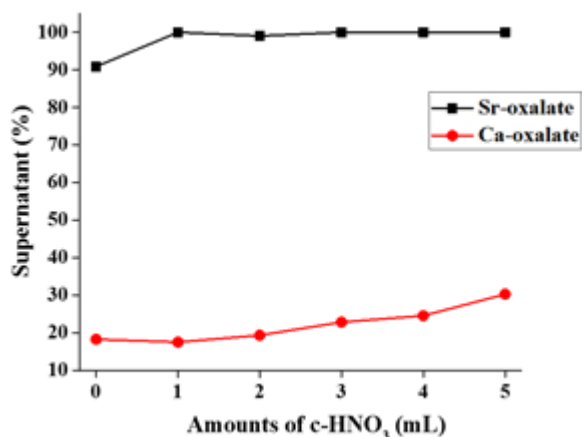


**Fig. 2** The effects of adding nitric acid in oxalic acid medium to precipitate Ca and Sr as an oxalate complex

Fig.2 shows the effects of adding nitric acid in oxalic acid medium to precipitate Ca and Sr as an oxalate complex. In the acidic media, Ca-oxalate complex was favorable. On the other hand, Sr-oxalate complex was unfavorable. It suggests that the role of c-HNO$_3$ is to provide the acidic conditions for separating Ca from the supernatants. In fact, it is well-known that Ca can precipitate with oxalic acid as a Ca-oxalate complex below pH 6.0 and Sr cannot precipitate with oxalic acid as a Sr-oxalate complex below pH 3.0. The experimental results were well-matched with the pH-induced precipitation behavior.

**CONCLUSIONS**
We developed a separation procedure in the radioactive wastes including Tc-99, Nb-94, Fe-55, Sr-90, Ni-59, Ni-63 and large amount of Ca. We tried to separate target materials by using two outstanding strategies and the details are described below; (1) Separation of Fe-55, Nb-94, Ni-59 and Ni-63 as metal hydroxide precipitates which have low solubility product constant ($K_{sp}$) values between pH 6 and pH 11. (2) Selective elimination of Ca-oxalate complex under strong acidic conditions by using nitric acid. Consequently, all the metal sources were sequentially and quantitatively

recovered by inductively coupled plasma atomic emission spectrometric (ICP-AES) analysis, the recovery is as follows; Sr-90 (3 mg): 92.22+5.48%, Fe-55 (20 mg): 99.80+3.19%, Nb-94 (20 mg): 97.45+2.42%, Ni-59,63 (2 mg): 83.59+15.31%, Ca (1500 mg): 85.32+6.38%, respectively. This methodology will help us separation of radioactive wastes efficiently if apply properly.

**REFERENCES**

[1] C. H. Lee, M. Y. Suh, K. Y. Jee, W. H. Kim, "Sequential separation of 99Tc, 94Nb, 55Fe, 90Sr and 59/63Ni from radioactive wastes", J. Radioanal. Nucl. Chem., 272, 187, (2007)

[2] C. H. Lee, M. H. Lee, S. H. Han, Y-K Ha, K-S, "Systematic radiochemical separation for the 99Tc, 90Sr, 55Fe, 94Nb and 59,63Ni in low-and-intermediate level radioactive waste samples", J. Radioanal. Nucl. Chem., 288, 319, (2011)

[3] C. H. Lee, H. J. Ahn, J. Lee, Y-K. Ha, J-Y Kim, "Rapid separation of 99Tc, 90Sr, 55Fe, 94Nb and 59,63Ni in radioactive waste samples", J. Radioanal. Nucl. Chem., 308, 809, (2016)