

Development of Chemical and Biological Decontamination Technology for Radioactive Liquid Wastes and Feasibility Study for Application to Liquid Waste Management System in APR1400

액체방사성폐기물에 대한 화학적, 생물학적 제염기술 개발 및 APR1400 액체폐기물관리시스템 적용을 위한 타당성 연구

YoungJu Son¹, Seung Yeop Lee², JaeYeon Jung¹, and Chang-Lak Kim^{1,*}

¹KEPCO International Nuclear Graduate School, 658-91, Haemaji-ro, Seosaeng-myeon, Ulju-gun, Ulsan, Republic of Korea

²Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea

손영주¹, 이승엽², 정재연¹, 김창락^{1,*}

¹한국전력국제원자력대학원대학교, 울산광역시 울주군 서생면 해맞이로 658-91

²한국원자력연구원, 대전광역시 유성구 대덕대로989번길 111

(Received November 5, 2018 / Revised November 27, 2018 / Approved February 20, 2019)

A decontamination technology for radioactive liquid wastes was newly developed and hypothetically applied to the liquid waste management system (LWMS) of the nuclear power plant (NPP) to evaluate its decontamination efficacy for the purpose of the fundamental reduction of spent resins. The basic principle of the developed technology is to convert major radionuclide ions in the liquid wastes into inorganic crystal minerals via chemical or biological techniques. In a laboratory batch experiment, the biological method selectively removed more than 80% of cesium within 24 hours, and the chemical method removed more than 95% of cesium. Other major nuclides (Co, Ni, Fe, Cr, Mn, Eu), which are commonly present in nuclear radioactive liquid wastes, were effectively scavenged by more than 99%. We have designed a module including the new technology that could be hypothetically installed between the reverse osmosis (R/O) package and the organic ion-exchange resin in the LWMS of the APR1400 reactor. From a technical evaluation for the virtual installation, we found that more than 90% of major radionuclides in the radioactive liquid wastes were selectively removed, resulting in a large volume reduction of spent resins. This means that if the new technology is commercialized in the future, it could possibly provide drastic cost reduction and significant extension of the life of resins in the management of spent resins, consequently leading to delay the saturation time of the Wolsong repository.

Keywords: Spent Resins, Radionuclide, Cesium, APR1400, Ion-Exchange Resin

* Corresponding Author.

Chang-Lak Kim, KEPCO International Nuclear Graduate School, E-mail: clkim@kings.ac.kr, Tel: +82-52-712-7333

ORCID

YoungJu Son <http://orcid.org/0000-0002-9282-8096>

JaeYeon Jung <http://orcid.org/0000-0002-4360-2007>

Seung Yeop Lee <http://orcid.org/0000-0002-0388-2315>

Chang-Lak Kim <http://orcid.org/0000-0002-6931-9541>

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited

원자력발전소 운영 과정에서 발생하는 폐기물인 폐수지를 원천적으로 저감하기 위해, 새로운 폐수 정화기술을 개발하고 원전 폐수처리시스템에 가상적으로 적용하여 효용성을 평가하고자 하였다. 본 기술의 기본 원리는 폐수에 존재하는 주요 핵종이온들을 생물학적 혹은 화학적 방법을 통해 무기 결정광물로 바꾸는 방식이다. 실험실에서 폐수를 대상으로 회분식실험을 통해 핵종 제거율을 측정된 결과, 생물학적 방법은 24시간 이내에 세습을 80% 이상 제거하였고, 화학적 방법은 95% 이상 세습을 선택적으로 제거할 수 있었다. 그리고 원전 폐수에 존재하는 다른 주요 핵종들(Co, Ni, Fe, Cr, Mn, Eu)에 대해서도 초기 99% 이상의 높은 제거율을 보여 주었다. 우리는 APR1400 원자력발전소의 폐수처리시스템 공정에서 역삼투압(R/O)과 유기 이온교환수지 모듈 사이에 가상으로 본 기술 모듈을 설치하였다. 가상의 모듈 설치를 통한 기술적 타당성 평가를 통해, 우리는 폐수의 주요 핵종들이 90% 이상 선택적으로 제거되고 폐수지의 발생량이 대폭 감소된다는 결과를 얻을 수 있었다. 이러한 결과가 의미하는 바는 본 기술이 향후 미래에 상용화되었을 경우, 폐수지 관리 비용을 크게 감소시키고 수지 수명도 대폭 연장시킬 수 있어, 결과적으로 월성 방사성폐기물 처분시설의 저장고 포화시점을 최대한 늦출 수 있는 이점이 있다.

중심단어: 폐수지, 방사성핵종, 세습, APR1400, 이온교환수지

1. Introduction

The liquid waste management system (LWMS) is installed and operated in most domestic nuclear power plants (NPPs) including Shin Kori 5&6 that are under construction. Although there are a few different types of LWMS in operation, the LWMS in the APR1400 reactor usually collects, stores, controls, processes, observes and disposes the liquid wastes generated during the normal operation of the NPP including anticipated operational occurrences (AOOs). In the case of APR1400, the LWMS consists of four subsystems including the floor drain subsystem, equipment waste subsystem, chemical waste subsystem, and detergent waste subsystem [1]. Liquid wastes treated by the LWMS are properly managed and discharged obeying the nuclear safety and security commission (NSSC) Notice No. 2017-36 "Radiation protection standards" [2]. Reverse osmosis (R/O) and ion-exchange processes are the main treatment methods used to meet the above discharge criteria for the type and concentration of radionuclides. The ion-exchanger filled with ion-exchange resin is usually positioned after the R/O package to remove the residual radionuclides of liquid waste prior to their final discharge into the sea. In the NPP, there are also some other ion-exchange systems, such as chemical volume

control system (CVCS), spent fuel pool system (SFP), and steam generator blow down system (SGBDS).

In general, the ion-exchange process is reversible and exchanges ions that exist on the insoluble solid surface of resins with other ions dissolved in water. It involves cation exchange and anion exchange depending on the charge of the ions to be exchanged. It is utilized in the industry as a means to purify water or to separate complex ions [3]. Ion-exchange technology is also used extensively in the nuclear power applications to process the raw water and to remove the radionuclides remaining in radioactive liquid wastes.

When the radioactive liquid wastes are treated by the ion-exchange process, the byproduct, which is a spent ion-exchange resin, can be classified as intermediate or low level waste [4]. Unlike spent ion-exchange resins used in non-nuclear industries, those used in the NPPs must be permanently disposed without regeneration. The annual production amounts of spent resins based on the final safety analysis reports (FSAR) for four domestic NPPs are shown in Table 1. The data show that the ion-exchange resins are being heavily used for the decontamination of radioactive liquid wastes.

In Korean NPPs, the ion-exchange resins are commonly used to remove radioactive nuclides, and there are

Table 1. Annual production of spent resins based on the Final Safety Analysis Report (FSAR)

Nuclear Power Plants	Volume (L·yr ⁻¹)
Shin Kori 3&4 [5]	71,360
Shin Wolsong 1&2 [6]	44,500
Yonggwang 5&6 [7]	55,640
Ulchin 5&6 [8]	55,640

currently no other substances (adsorbents) to replace them. From the wide use of the resins in Korea, however, there are some problems to resolve urgently. First, most resins are imported from foreign countries [9, 10], and the costs are high. Second, due to the wide use of resin in NPPs, secondary radioactive wastes are annually produced in large volume. Therefore, some efforts have been made to develop techniques to reduce the waste volumes of spent resins [9-12]. Third, the cost for the radioactive waste disposal in Korea is very high. The overall disposal cost for intermediate and low level radioactive wastes including spent resin is approximately ₩15 million per 200 L drum (including management cost and commission fee) and it continues to increase [13]. In addition, the Wolsong low and intermediate level radioactive wastes disposal center (WLDC) in Gyeong-Ju, the only radioactive waste repository in Korea, has a limited storage capacity.

The current techniques developed for the volume reduction of spent resins are as follows: acid/desorption stripping [9, 11], wet oxidation [10], ultrasonic [12], incineration [14], and vitrification [15]. Recently, a blending method has been suggested to reduce high radioactive waste by simply mixing it with low radioactive waste [16, 17]. However, no technology has been proposed to remove the major radionuclides remaining in the liquid waste, a method that would improve the ion-exchange resin method without a secondary waste volume increase.

We currently developed a new technology that uses some underground bacteria to remove cesium as a compact mineral, pautovite (CsFe₂S₃) [18]. The biotechnology was

basically derived from a previous technique that controls dissolved uranium by using microorganisms [19]. Through this biological technique, we have effectively removed some radioactive nuclides such as uranium, iodine, and strontium as crystalline solids [19-21]. For the mineralization of radionuclides, an abiotic technique has been also currently studied for application to the liquid wastes together with the biotic technology.

In this study, we applied the new technology to the NPP system and checked its merits and potential. The full scale adoption study was performed by hypothetically installing the technology in the current LWMS of APR1400. From a virtual simulation, a simple and assumptive economic evaluation was also carried out for the new LWMS operation based on our small scale experiments.

2. Experiments

2.1 Biological Method

Sulfate reducing bacteria (SRB) were used to biologically remove cesium in our system. The SRB were cultured prior to interacting with radionuclides. The culture medium was produced as follows: 1 L of solution was prepared with 2.5 g of sodium bicarbonate (NaHCO₃), 1.0 g of ammonium chloride (NH₄Cl), 0.5 g of potassium hydrogen phosphate (K₂HPO₄), 2.0 g of magnesium sulfate (MgSO₄), 1.0 g of calcium sulfate (CaSO₄), 5.0 g of sodium citrate (Na₃C₆H₅O₇), 3.5 g of sodium lactate (C₃H₅NaO₃), and 1.0 g of yeast extract [20]. The culture medium solution was distributed into 100 mL serum bottles. Then, the medium was purged with N₂ gas for 40 min, sealed with butyl rubber septa, capped and crimped with aluminum seals, and pressurized with ultra-pure N₂. After the serum bottle was autoclaved, 2 mL of 5% ferrous ammonium sulfate was aseptically added by syringe and needle into the medium and then the SRB were added and cultured for 24 hours at 30°C.

The cesium removal experiment was performed in a batch type. 125 mL serum bottles were filled with 2 mM of iron(II) chloride, 6 mM of sodium lactate as an electron donor, and 1 mL of cultured SRB. 3 mM of NaHCO_3 and 3 mM of Na_2SO_4 as an electron acceptor were added to reach 100 mL total solution. Prior to the addition of cesium, a cesium stock solution (1,000 ppm) was prepared by dissolving a known amount of inactive CsCl (Aldrich) in a distilled water. From the cesium stock solution, $0.01\sim 10\text{ mg}\cdot\text{L}^{-1}$ of cesium chloride was aseptically added to the serum bottles containing the previously injected reactants. Finally, cells were injected into the serum bottles to provide ca. $1\text{ mg}\cdot\text{L}^{-1}$ cell protein. The cell suspensions were incubated at 30°C in the dark unless otherwise noted. Solution samples of 5 mL were regularly collected and filtered through $0.2\ \mu\text{m}$ filter, and cesium concentration was analyzed by inductively coupled plasma mass spectrometry (ICP-MS). A solid sample (1 ml) suspended in the serum bottle was frequently removed by syringe and needle, and then it was trapped by $0.2\ \mu\text{m}$ filter and dried at room temperature for several hours. The solid sample trapped on the filter was investigated by scanning electron microscope (SEM).

A 10 L container with radioactive liquid waste of $1,000\text{ Bq}\cdot\text{L}^{-1}$ of ^{137}Cs was used as a small trial reaction tank, which was set up in our laboratory. The experimental reaction was performed for 7 days. After the reaction, the supernatant was collected with syringe. We determined the removal quantity of ^{137}Cs from the liquid waste by measuring the remaining ^{137}Cs radioactivity by using the γ -ray analyzer (Canberra).

2.2 Chemical Method

2.2.1 Removal of Cesium

Another batch test was also performed by using a chemical method without microorganisms to effectively remove cesium from solution. The chemical method was fundamentally based on the biological mechanisms observed in the microbial Cs removal experiment. The basic mechanism in their methods is to convert cesium ions into the cesium

mineral (pautovite), which is a stable and precipitable solid, via a biological or chemical reaction process that sulfate is reduced to sulfide in the presence of iron component.

We designed a new chemical method by initially preparing a mixture of anaerobic carbonate and sulfate solution (5 mM of sodium bicarbonate and 3 mM of iron(II) sulfate) with 100 ml in a 125 ml serum bottle, which was autoclaved and used as a basic solution in our experiment. The medium in the serum bottle was sealed with butyl rubber septa, capped and crimped with aluminum seals. A concentrated anaerobic stock solution of iron(II) chloride (10 mM) was also prepared by purging it with N_2 gas for 40 min and then was added as 2 mM to the serum bottle. Another stock solution of sodium sulfide (10 mM) was anaerobically prepared and injected as 2 mM by using syringe and needle. Finally, $0.1\sim 1.0\text{ mg}\cdot\text{L}^{-1}$ of cesium chloride from an anaerobic cesium stock solution (1,000 ppm) was added to the serum bottles containing the previously injected reactants. The serum bottles were shaken with 100 rpm at 30°C for 7 days. The liquid samples were frequently collected and passed through $0.2\ \mu\text{m}$ filter by using syringe and needle and analyzed by ICP-MS. The solid sample that was suspended in the serum bottle was frequently collected by syringe and needle and trapped by $0.2\ \mu\text{m}$ filter and investigated by using SEM.

2.2.2 Removal of Major Nuclides

We conducted a study to determine if it is possible without using ion exchange resins, to remove the principal radionuclides such as cobalt (Co), nickel (Ni), iron (Fe), manganese (Mn), chromium (Cr), and europium (Eu) found in the radioactive liquid wastes of NPPs. The experimental conditions were the same as the method for Cs removal in this study. To reflect the typical radioactive liquid wastes in the NPP, $0\sim 1,000$ ppm of boric acid was added to the experimental solution. The initial concentrations of principal radionuclides (Co, Ni, Fe, Mn, Cr, Eu) were set to be 1.0 ppm. Generally, the radioactivity of principal radionuclides in the domestic liquid wastes of NPP has been known to be

Table 2. The stepwise decreases of dissolved cesium from its initial concentrations during the biological reaction process in liquid wastes

Initial Cesium Concentrations (ppm)	1st Day	2nd Day	4th Day	7th Day
0.01	0.002 (± 0.001)	N.D.*	N.D.	N.D.
0.1	0.055 (± 0.004)	0.010 (± 0.001)	0.005	0.005
1.0	0.806 (± 0.017)	0.579 (± 0.002)	0.539 (± 0.003)	0.530 (± 0.004)
10	9.085 (± 0.142)	8.693 (± 0.057)	8.524 (± 0.077)	8.358 (± 0.012)

*N.D.: not detected to the detection limit of 0.001 ppm

< 0.01~0.1 ppm concentration. All prepared serum bottles were shaken, and 5 mL samples were regularly collected with a syringe, filtered through 0.2 μm filter, and analyzed by ICP-MS to measure the concentration of nuclides.

2.3 Analytical Method

Solid samples containing nuclides that were precipitated from solution were examined with a Field Emission Scanning Electron Microscope (FE-SEM) S-4700 (Hitachi). The samples were prepared by centrifuging them at 10,000 rpm for 10 minutes and washing them with anaerobic distilled water multiple times. The samples were dried in a glove box filled with N_2 gas. After drying, the samples were evenly smeared onto carbon tape attached to a holder and osmium tetroxide (OsO_4) was sprayed over the sample to coat it to about 10 nm thickness under vacuum condition. The size and shape of the samples were investigated and an Energy Dispersive Spectrometer (EDS) was used to analyze its chemical composition.

3. Results

3.1 Characteristics of Cesium Removal

Characteristic dissolved cesium decreases by the biological method for solutions with various cesium concentrations are presented in Table 2. The data interestingly

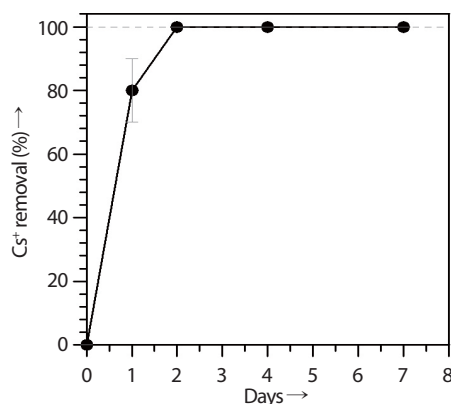


Fig. 1. The selective cesium removal from a liquid waste with 0.01 ppm Cs concentration by a biological method.

show that as initial Cs concentrations are lower, Cs removal efficiencies are higher in the system. In general, however, the removal efficiency of a solute by using adsorbents decreases if its dissolved concentration is initially lower, due to the relative increase of other competitive ions that coexist in solution.

Interestingly, our biological method selectively removed around 80% cesium from the solution with 0.01 ppm Cs at the first day, and then most of remaining cesium ions were scavenged over time (Fig. 1). It has been known that the actual radioactivity of cesium in the domestic liquid waste of NPP is measured to be less than ppb (1/1,000 ppm) as converted to ionic concentration. In our experiment, cesium ions in low concentration of 0.01 ppm were easily removed by being precipitated as mineral particle forms without using any adsorbents such as the ion exchange

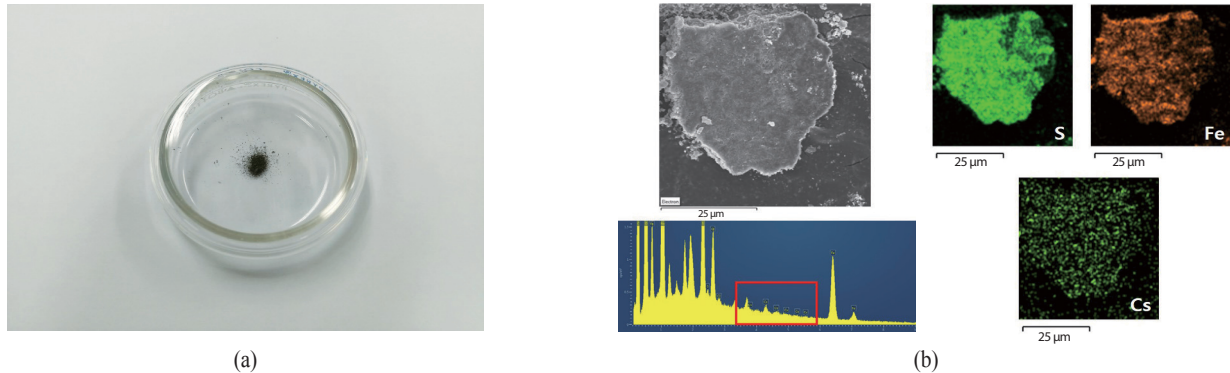


Fig. 2. (a) A characteristic dark and solid precipitate from the treated liquid waste by the biological method, (b) SEM image, elemental mapping, and EDS analysis of the solid sample that shows Cs element present in the crystalline form.

resin (Fig. 1). Fig. 2(a) shows an image of cesium minerals, which is a cluster form of dark and inorganic crystals. The amount of the precipitated mineral sludge was just 0.02 g per 100 mL. The solid sample was analyzed by SEM (Fig. 2(b)). The solid sample was found to be a sulfide mineral with $> 1 \mu\text{m}$ sizes. The elemental mapping showed that it was mainly composed of iron (Fe) and sulfide (S) with cesium that was fixed in the mineral structure. As shown in EDS spectrum, the removal of cesium was very selective even in the lower concentration of Cs than the other dissolved ions in the liquid waste.

The selective removal of cesium was practically tested on a radioactive liquid waste containing highly radioactive ^{137}Cs (Fig. 3). A small trial reaction tank of 10 L with $1,000 \text{ Bq}\cdot\text{L}^{-1}$ of ^{137}Cs was set up. The experimental result showed that ^{137}Cs was selectively removed from the liquid waste, finally exhibiting about 97% removal of ^{137}Cs . The removal efficiency for ^{137}Cs was as good as the one for the inactive cesium that was used previously.

A chemical method was also applied to remove cesium instead of the biological method. With the chemical method, the removal of cesium ions was remarkable with high efficiency as presented in Table 3. The experimental result shows that $> 99\%$ of cesium ions were removed from the liquid waste (initially 0.1 ppm Cs) following 95% cesium removal within 24 hours (Fig. 4). Furthermore, the final solid sludge produced



Fig. 3. Practical performance for the selective removal of radioactive ^{137}Cs from a radioactive liquid waste containing ^{137}Cs .

was as small as 0.015 g per 100 mL liquid waste. As a result, it seems that the chemical method is more effective than the biological method to remove cesium, exhibiting its higher Cs selectivity and lower waste production.

3.2 Characteristics of Major Nuclides Removal

There are several kinds of radionuclides including cesium in radioactive liquid wastes, so we conducted another experiment to remove them with the same chemical method previously adopted to cesium removal. The nuclides

Table 3. The stepwise decreases of dissolved cesium from its initial concentrations during the chemical reaction process in liquid wastes

Initial Cesium Concentrations (ppm)	1st Day	2nd Day	4th Day	7th Day
0.1	0.005 (± 0.004)	N.D.*	N.D.	N.D.
1.0	0.494	0.485	0.480	0.476

*N.D.: not detected to the detection limit of 0.001 ppm

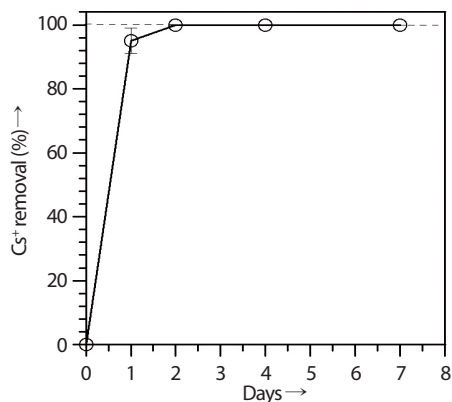


Fig. 4. The selective cesium removal from a liquid waste with 0.1 ppm Cs concentration by a chemical method.

Table 4. The stepwise decreases of dissolved metal nuclides from their initial 1.0 ppm concentration during the chemical reaction process in liquid wastes with boric acids

Metal Nuclides	1st Day	2nd Day	4th Day	7th Day
Co	0.018 (± 0.004)	0.004 (± 0.001)	N.D.*	N.D.
Fe	0.015 (± 0.003)	0.007 (± 0.002)	0.007 (± 0.002)	0.006 (± 0.001)
Ni	0.010 (± 0.002)	0.004 (± 0.002)	N.D.	N.D.
Cr	0.005 (± 0.001)	0.003 (± 0.001)	0.003 (± 0.001)	0.003 (± 0.001)
Eu	0.004 (± 0.001)	0.003 (± 0.001)	0.003 (± 0.001)	0.003 (± 0.001)
Mn**	0.044 (± 0.014)	0.025 (± 0.009)	0.023 (± 0.009)	0.020 (± 0.008)
Mn***	0.471 (± 0.005)	0.460 (± 0.005)	0.457 (± 0.006)	0.455 (± 0.005)
Mn****	0.581 (± 0.018)	0.562 (± 0.014)	0.558 (± 0.010)	0.554 (± 0.010)

*N.D.: not detected to the detection limit of 0.001 ppm

**Boric acid 10 ppm included

***Boric acid 100 ppm included

****Boric acid 1,000 ppm included

selected for the experiment were Co, Fe, Ni, Cr, Mn, Eu which are commonly found in the radioactive liquid wastes of NPPs [17]. With the chemical method, the removal of

metal nuclides was remarkable with high efficiency as presented in Table 4. The experimental result shows that all of those inactive nuclides were removed by 99% except Mn as

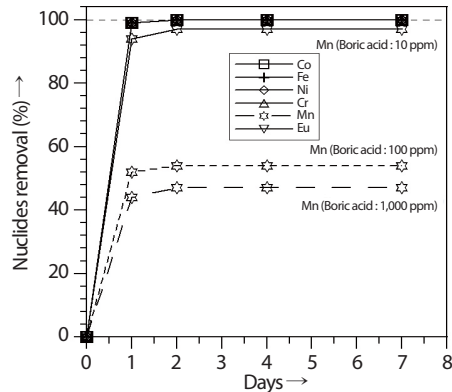


Fig. 5. The effective removal of principal nuclides that are usually found in the liquid waste of NPP by the chemical method.

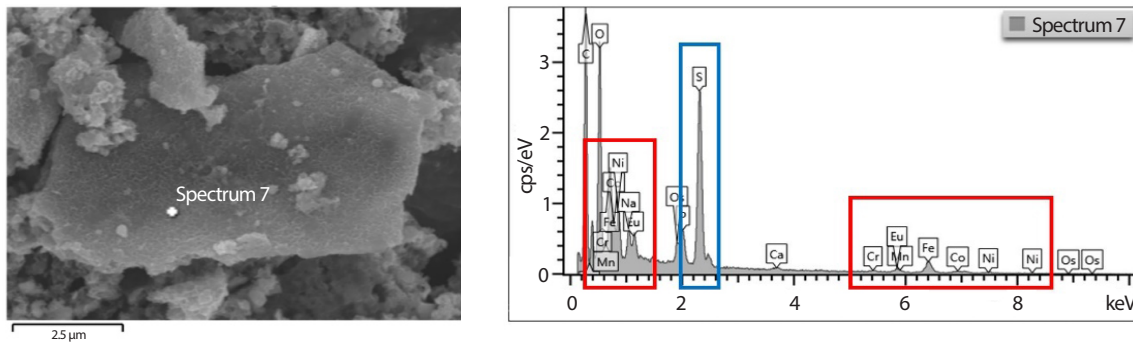


Fig. 6. SEM image and EDS spectrum of the crystalline sample with principal nuclides precipitated from liquid waste by the chemical method.

shown in Fig. 5. The removal efficiency was very high even though the experiment was performed with the same conditions used for cesium removal. For manganese, the boric acid in the liquid waste significantly affected Mn removal rate, just removing 50% of Mn in the presence of 1,000 ppm of boric acid. However, the removal amount of Mn increased to 95% as the boric acid concentration dropped to 10 ppm. Except Mn, the removal of other nuclides was not significantly affected by the boric acid.

Fig. 6 shows SEM image of a solid sample precipitated from the liquid waste containing various cationic nuclides. The sample was found as aggregated particles to have more than μm sizes, which mostly formed with inorganic crystals. When the sample was analyzed by EDS, it was identified as

a sulfide mineral, in which most nuclides were incorporated and fixed stably.

4. Discussion

4.1 Removal Efficiency of Cesium and Major Nuclides

In this study, we adopted the chemical or biological (chem or bio) decontamination process module to the current LWMS of NPPs, where most radionuclides in the radioactive liquid wastes are currently removed by R/O package and organic ion-exchange resin bed. The new module proposed here may improve some difficult issues and make

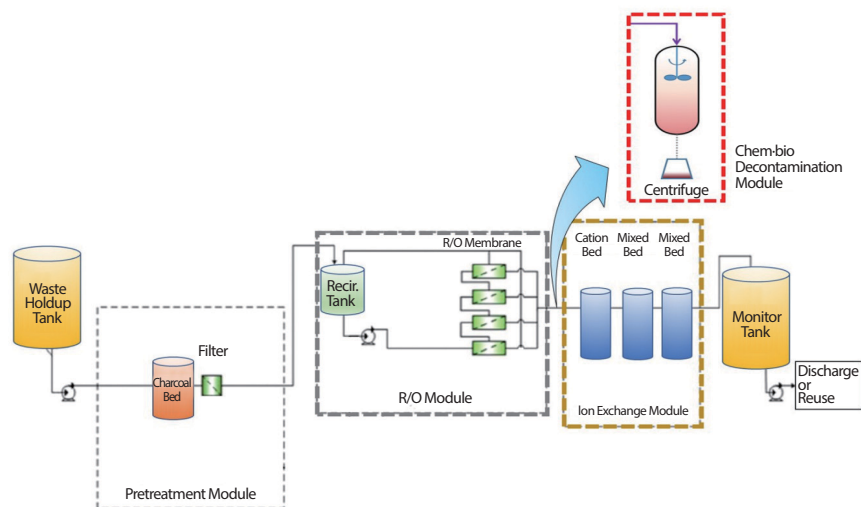


Fig. 7. Schematics of the modified LWMS of Shin Kori 3&4 (APR1400) [24].

the LWMS system more effective. For example, if we add the new module that can selectively remove principal radionuclides to the LWMS, it may reduce a large volume of ion-exchange resins by enhancing the efficiency of LWMS.

The chemical and biological experiments conducted in this study demonstrated that the advanced technique can remove more than 80~95% of cesium ions in solution within 24 hours. In particular, the chemical technique was more effective than the biological one for removing cesium (Fig. 4) and other nuclides (Co, Fe, Ni, Cr, Mn, Eu) (Fig. 5). In addition, the sludge produced from the chemical technique is wholly inorganic minerals, which are more favorable to be disposed in the repository. While the organic ion-exchange resins that are widely used in the NPP are weak and unstable in radiation and heat and difficult to manage, the final sludge produced by our technique is very stable and does not produce any gas due to the intrinsic nature of inorganic components. Furthermore, while the resin just weakly adsorbs radionuclides onto its outer surface, the mineral sludge can fix them into its crystal structure to prevent their possible desorption and evaporation during the long-term period of disposal. Due to such merits of the waste form, it is desirable that the new

technology developed here could be used in the LWMS as well as in the decontamination and decommissioning (D&D) projects. Fortunately, most radionuclides of interest in D&D projects [22, 23] are almost the same ones that were tested in our study.

4.2 Applicability to Liquid Waste Management System (LWMS)

In the current LWMS of APR1400, radioactive liquid wastes are sequentially passed through a charcoal bed, filter, R/O package and ion-exchanger as shown in Fig. 7. This system step by step removes floating matter and radioactive ions remaining in the radioactive liquid wastes. The radioactivity of radionuclides is usually monitored at the end of the system. At a monitoring tank, the liquid wastes satisfying the discharge criteria can be released into the sea, but those that exceed the criteria must be recirculated through the R/O package. Recirculation is frequently required because of the excess presence of ^{58}Co , ^{134}Cs , and ^{137}Cs radionuclides that are incompletely removed by the current ion-exchanger. Therefore, if the chem or bio decontamination process is available in the current LWMS,



Fig. 8. Operational concept for the chem or bio decontamination process.

Table 5. Annual radioactivity of principal radionuclides dissolved in the liquid waste of Shin Kori 3&4

No.	Radionuclide	LWMS [5] (Bq·yr ⁻¹)	After R/O package (Bq·yr ⁻¹)*	Target Nuclides of Chem or Bio Decontamination
1	⁵⁵ Fe	1.66×10 ⁶	1.66×10 ⁵	O
2	⁶⁰ Co	7.36×10 ⁵	7.36×10 ⁴	O
3	⁶³ Ni	0	0	O
4	⁹⁰ Sr	1.67×10 ⁴	1.67×10 ³	X
5	¹³⁷ Cs	7.14×10 ⁷	7.14×10 ⁶	O
	Total	6.81×10 ⁸	7.38×10 ⁶	

*Decontamination Factor of R/O package: 10 [5]

recirculation may not be necessary. By adopting the new process, we could also reduce manpower and operation time. The new process that we propose here could be retrofitted to the LWMS without a significant modification to its original design and equipment (Fig. 7). The new decontamination module is adequate to be placed between the R/O package and the ion-exchanger.

The virtual operational concept of the chem or bio decontamination process is shown in Fig. 8. The new process mainly consists of two storage tanks (including level sensors, temperature control, pH control), one columnar chem or bio reaction mixer (including reagent & reagent injectors), dehydration equipment, and other pumps and piping lines. The detail specifications for the equipment type, quality, and quantity in the new process would be established through further investigation and study. If the chem or bio decontamination process is very effective to remove radionuclides, no recirculation of liquid waste in the LWMS would be required. In addition, it is expected that the spent resin generation rate would be greatly

reduced by a significant extension of replacement cycle.

4.3 Feasibility Study on Full Scale Waste Reduction

For the APR1400 model, 7 NPPs (BNPP123&4 in United Arab Emirates (UAE), Shin Hanul 1&2, and Shin Kori 4) are currently under construction. Since Shin Kori 3 only started the commercial operation in December 2016, it is impossible to collect long term reliable data on the annual resin consumption in LWMS. As a result, based on the amount of spent resins being reported from the FSAR document of Shin Kori 3&4 [5], we tried to evaluate the validity and feasibility of the new technology in an assumed and modified process of LWMS.

We conducted an assumptive calculation on operating costs for two options:

- Option 1: only LWMS
- Option 2: LWMS + chemical decontamination process (except biological method)

Table 6. Target rates and decontamination rates of the various liquid wastes of Shin Kori 3&4 as the chemical decontamination process is applied

System	Target Rates of Chemical Process (%) [*]	Decontamination Rates (%) ^{**}
Primary Bleed Waste	100	95.00
Liquid Waste System	99.98	94.98
Steam Generator Blow Down Waste	99.89	94.89
Turbine Building Drains	99.91	94.92
Adjusted Total ^{***}	99.90	94.91
Detergent Waste	99.97	94.97
Wastes Total ^{****}	99.94	94.94

^{*}For 4 major radionuclides: ¹³⁷Cs, ⁶⁰Co, ⁵⁵Fe, ⁶³Ni

^{**}Decontamination Efficiency: 95%

^{***}Adjusted total is subtotal value that is adjusted to include 5.92×10^9 Bq·yr⁻¹ attributable to operational occurrences that result in unplanned releases [26]

^{****}Adjusted total + Detergent waste

To compare Option 2 with Option 1, there are some assumptions as follows:

- Based on the discussion in section 4.2, it is assumed that the chemical decontamination process would be installed between R/O package and ion-exchanger in Shin Kori 3&4.
- The chemical decontamination process is assumed to be applicable in full scale.
- It is assumed that the data and results from our small scale experiments could be directly employable to a full scale operation.
- It is assumed to be possible to commercialize Option 2 in full scale.

First, we selected some specific radionuclides from the viewpoint of the waste acceptance criteria (WAC) of the nuclear waste disposal facility. Through the selection process, 13 identified radionuclides (³H, ¹⁴C, ⁵⁵Fe, ⁵⁸Co, ⁶⁰Co, ⁵⁹Ni, ⁶³Ni, ⁹⁰Sr, ⁹⁴Nb, ⁹⁹Tc, ¹²⁹I, ¹³⁷Cs, ¹⁴⁴Ce) in the NSSC Notice No. 2017-60 “Regulation in delivery of intermediate level and low level radioactive waste” [25] are specified. Considering the temporary storage period of waste at the NPP

site, only radionuclides with more than one year of half-life were sorted separately. Second, we referred to the annual liquid release source terms (Total 54 radionuclides including all others [5]) of liquid radioactive materials from the FSAR of Shin Kori 3&4. By narrowing the candidate radionuclides, we finally selected five radionuclides (⁵⁵Fe, ⁶⁰Co, ⁶³Ni, ⁹⁰Sr, ¹³⁷Cs) as major ones. Among them, ⁵⁵Fe, ⁶⁰Co, ⁶³Ni, and ¹³⁷Cs will be target radionuclides of our chemical decontamination process.

We have calculated the emission radioactivity for the five chosen major radionuclides. Table 5 shows calculation values for radioactive emission at the end of the R/O package based on the Annual Liquid Release Source Terms of FSAR [5]. The decontamination rates for the chemical decontamination process were calculated based on the data from 0.1 ppm Cs in Table 3. A decontamination rate of 95% was conservatively chosen from the 95~99% range of decontamination rates for the four target nuclides. This rate was used in Eq. (1). As a result of calculation using Eq. (1), the decontamination rate of the chemical decontamination process in the modified LWMS was 94.98%.

$$\left(\frac{\text{Sum of Activities from 4 Radionuclides } (^{55}\text{Fe}, ^{60}\text{Co}, ^{63}\text{Ni}, ^{137}\text{Cs})}{\text{Total Activities of 5 Radionuclides}} \right) \times 100 \times 0.95 \quad (1)$$

Table 6 shows the resulting target rates for the 4 major radionuclides and decontamination rates in radioactive liquid wastes. All types of radioactive liquid wastes evaluated by the procedure show an average decontamination rate of about 95%. Considering the conservative engineering margin, we reduced the chemical decontamination rate to 90%.

Next, the waste disposal costs were calculated. We conservatively added a 10% margin to the disposal cost based on the MOTIE Notice No. 2017-195 “Regulation on calculation criteria for radioactive waste management costs and spent fuel management fees” [13] and set the disposal cost per 200 L drums at ₩15,804,300. The disposal cost per one domestic high-integrity container (HIC) was estimated at ₩87,177,200 [27]. The annual waste amount generated

Table 7. Estimated waste production from the chemical decontamination process in Shin Kori 3&4

	Unit: ₩1,000,000
Liquid waste production (L·day ⁻¹)*	11,092.4
Unit production of solid waste from liquid waste (kg·L ⁻¹)**	0.00015
Annual solid waste production (kg·yr ⁻¹)***	605.90
Processing capacity per Unit HIC (L)****	818
No. of HIC consumed per year	1

*Clean waste + Dirty Waste [5]

**Data derived from experiments

***Solid waste 1 kg ≅ 1 L

****Data from domestic High-Integrity Container (PC HIC): 818 L [27]

Table 8. Estimated annual costs to dispose the spent resin wastes via two options in Shin Kori 3&4

	Option 1*		Option 2**		Waste from Chemical Process
Spent Resin Waste Streams	High Activity Spent Resin	Low Activity Spent Resin	High Activity Spent Resin	Low Activity Spent Resin	
Volume from FSAR (L·yr ⁻¹)	17,060	54,300	1,706	5,430	-
Projected Volume (L·yr ⁻¹)	2,075	6,600	207.5	660	605.90
Processing Capacity per Unit HIC/Drum [27]	818 L	187 L	818 L	187 L	818 L
No. of Containers /Drums	3	36	1	4	1
Disposal Cost per Containers/Drums (₩)	87.18	15.80	87.18	15.80	87.18
Disposal Cost (₩)	261.54	568.80	87.18	63.20	87.18
Total Disposal Cost (₩)	830.34		237.56		

*Only LWMS [17]

**LWMS + chemical decontamination process

by the introduction of the new chemical process is about 605.90 L, which is disposable in one HIC (Table 7).

Table 8 shows the results of disposal cost for the two options (Option 1: only LWMS [17], Option 2: LWMS + Chemical decontamination process) evaluated based on the above calculation. It presumes that the chemical decontamination process achieves a decontamination rate of 90% and thus reduces the burden of post-stage resin process by

a factor of 10. Based on this result, it is calculated that the resin life increases 10 times and the amount of spent resin generated per year is reduced by a factor of 10. As a result of comparing Option 1 with Option 2, the annual amount of spent resins decreased from 3 to 2 for HICs and from 36 to 4 for 200 L drums. If the number of disposal containers is converted to disposal costs, it is estimated that the annual disposal cost would decrease from about ₩800 million to

Table 9. Total costs to use resins or chemical technology and to polymerize and dispose their wastes that will be produced for 40 years operation of Shin Kori 3&4

		Unit: ₩1,000,000	
Item		Option 1*	Option 2**
	Facility Purchase Cost	-	1,000.00***
Operation Cost of Ion-exchange Resins/Chemical Process (₩)	Electric Cost	-	-
	Manpower Cost	-	-
	Material Cost	14,233.95****	2,883.40****
Polymerization Cost (₩)*****		11,534.40	1,281.60
Disposal Cost (₩)		33,213.60	9,502.40
Total Waste Management Cost (₩)		58,981.95	14,667.40

*Only LWMS [17]

**LWMS + chemical decontamination process

***Values derived from experiments (material cost = reactant cost + reduced spent resin cost)

****Cost of Resin (IRN-170): 4.45 \$/L, Currency: 1,120.60 ₩/\$

*****Only applied to Low Activity Resin

₩200 million (about 71% reduction) per year.

In addition, if the chemical decontamination process is operated for 40 years for Shin Kori 3&4, the total spent resin management cost is estimated to be lower as follows: -79.74% for material cost, -88.89% for polymerization cost, -71.39% for disposal cost (Table 9). Finally, if the LWMS is operated for 40 years by adopting the chemical decontamination processes, the total cost saving in waste management for spent resin would be 75.13% (about ₩44.31 billion) for only two units, Shin Kori 3&4.

5. Conclusion

It is difficult and costly to manage the radioactive wastes produced from domestic NPPs, where radioactive liquid wastes are primarily treated by resins. We have attempted to improve the current LWMS by adopting a new technology that enhances the radionuclide removal efficiency and reduces the spent resin volume. The biological or chemical method proposed here is a new technology that can effectively remove cesium by > 80~95% as well as

major nuclides (Co, Ni, Fe) by > 99% without any addition of adsorbents. It was estimated that such an effective radionuclide removal technology could significantly reduce spent resins, if it is used in the LWMS.

Although we did not actually conduct the above test in the full scale LWMS of NPP, it seems to be meaningful to check if the new system would have some merits as joined in the current one. Based on the results from our lab scale experiment and full scale simulation, we have performed a feasibility study on the possible application of the new system. To evaluate its potential for commercialization, however, it should require further study and research on it from a practical point of view. We thus are planning a full scale test in the LWMS of NPP later, strictly evaluating its efficiency and costs including logistics-relevant details such as installation space, maintenance, and worker radiation exposure.

Acknowledgement

This research was supported by the Nuclear Safety Research Program through the Korea Foundation of Nuclear

Safety (KOFONS), granted financial resource from the Nuclear Safety and Security Commission (NSSC), Republic of Korea (No. 1605008).

REFERENCES

- [1] Korea Electric Power Corporation and Korea Hydro & Nuclear Power Co. Ltd., APR1400 Design Control Document Tier 2, Chapter 1 - Introduction and General Description of The Plant, APR1400-k-X-FS-14002-NP Rev. 0 (2014).
- [2] Nuclear Safety and Security Commission, Radiation Protection Standards, NSSC Notice No. 2017-36 (2017).
- [3] D. Hendricks, Fundamentals of Water Treatment Unit Processes: Physical, Chemical, and Biological, 1st Ed., 512-513, CRC Press, Florida (2010).
- [4] D.H. Shin, K.W. Ju, S.I. Cheong, and J.W. Rhim, "Removal of Radioactive Ions from Contaminated Water by Ion Exchange Resin", Appl. Chem. Eng., 27(6), 633-638 (2016).
- [5] Korea Hydro & Nuclear Power Co. Ltd., Final Safety Analysis Report for Shin Kori 3&4 (2010).
- [6] Korea Hydro & Nuclear Power Co. Ltd., Final Safety Analysis Report for Shin Wolsong 1&2 (2011).
- [7] Korea Hydro & Nuclear Power Co. Ltd., Final Safety Analysis Report for Yonggwang 5&6 (2001).
- [8] Korea Hydro & Nuclear Power Co. Ltd., Final Safety Analysis Report for Ulchin 5&6 (2003).
- [9] H.Y. Yang, J.S. Won, Y.K. Choi, G.I. Park, I.T. Kim, K.W. Kim, K.C. Song, and H.S. Park, "Ion Adsorption Characteristics of IRN-150 Mixed Resin and Removal Behavior of ^{14}C Radionuclide from Spent Resin by Stripping Solutions", J. Korean Radioact. Waste Soc., 4(4), 373-384 (2006).
- [10] K.S. Kim, S.H. Son, K.M. Song, J.H. Han, K.D. Han, and S.H. Do, "Treatment of Spent Ion-Exchange Resins from NPP by Supercritical Water Oxidation (SCWO) Process", J. Korean Radioact. Waste Soc., 7(3), 175-182 (2009).
- [11] Y.K. Choi, S.G. An, D.H. Kim, J.H. Cho, H.S. Park, and H.J. Ahn " ^{14}C Removal Technology for the Treatment of Spent Resin from Nuclear Power Plants: A Review", Transactions of the Korean Nuclear Society Autumn Meeting, October 30-31, 2014, Pyeongchang, Republic of Korea.
- [12] G.H. Sung, "Research and Development for Decontamination System of Spent Resin in Hanbit Nuclear Power Plant", J. Radiat. Ind., 9(4), 217-221 (2015).
- [13] Ministry of Trade, Industry and Energy, Regulation on Calculation Criteria for Radioactive Waste Management Costs and Spent Fuel Management Fees, MOTIE Notice No. 2017-195 (2017).
- [14] S.W. Long, The Incineration of Low-level Radioactive Waste: A Report for the Advisory Committee on Nuclear Waste, U.S. Nuclear Regulatory Commission, NUREG-1393, Washington, D.C. (1990).
- [15] C.M. Jantzen, D.K. Peeler, and C.A. Cicero, Vitriification of Ion-exchange (IEX) Resins: Advantages and Technical Challenges, Westinghouse Savannah River Co., WSRC-MS-95-0518 (1995).
- [16] D.S. Kessel and C.L. Kim, "US Policy and Current Practices for Blending Low-Level Radioactive Waste for Disposal", J. Nucl. Fuel Cycle Waste Technol., 14(3), 235-243 (2016).
- [17] N.S. Kamaruzaman, D.S. Kessel, and C.L. Kim, "Management of Spent Ion-Exchange Resins from Nuclear Power Plant by Blending Method", J. Nucl. Fuel Cycle Waste Technol., 16(1), 65-82 (2018).
- [18] S.Y. Lee, J.H. Hwang, M.H. Baik, B.K. Seo, and M. Lee. Biomineralogical Method and Apparatus for Removing Cesium Ions, Korea Atomic Energy Research Institute, KR Patent No. 10-1754790 (2017).
- [19] S.Y. Lee, M.H. Baik, and J.W. Choi, "Biogenic Formation and Growth of Uraninite (UO_2)", Environ. Sci. Technol., 44(22), 8409-8414 (2010).
- [20] S.Y. Lee, J.Y. Lee, J.H. Min, S.S. Kim, M.H. Baik, S.Y. Chung, M. Lee, and Y. Lee, "Microbial Copper

- Reduction Method to Scavenge Anthropogenic Radioiodine”, *Scientific Reports*, 6, 28113 (2016).
- [21] S.Y. Lee, K.H. Jung, J.E. Lee, K.A. Lee, S.H. Lee, J.Y. Lee, J.K. Lee, J.T. Jeong, and S.Y. Lee, “Photosynthetic Biomineralization of Radioactive Sr via Microalgal CO₂ Absorption”, *Bioresour. Technol.*, 172, 449-452 (2014).
- [22] K.J. Lee, H.S. Kim, S.W. Shin, M.J. Song, and Y.K. Lee, “Preliminary Estimation of Activation Products Inventory in Reactor Components for Kori Unit 1 Decommissioning”, *J. Radiat. Prot. Res.*, 28(2), 109-116 (2003).
- [23] J.S. Song, H.M. Kim, and S.H. Lee, “A Study on Radioactive Source-term Assessment Method for Decommissioning PWR Primary System”, *J. Nucl. Fuel Cycle Waste Technol.*, 12(2), 153-164 (2014).
- [24] J.M. Kim and C.L. Kim, “Performance Improvement of Liquid Waste Management System for APR1400”, *Prog. Nucl. Energy*, 100, 93-102 (2017).
- [25] Nuclear Safety and Security Commission, Regulation in Delivery of Intermediate Level and Low Level Radioactive Waste, NSSC Notice No. 2017-60 (2017).
- [26] U.S. National Regulatory Commission, Calculation of Releases of Radioactive Materials in Gaseous and Liquid Effluents from Pressurized Water Reactors, U.S. NRC, NUREG-0017, Washington, D.C. (1985).
- [27] Korea Electric Power Corporation Engineering and Construction Company, Economic Evaluation Report for Disposal Method of Wet Solid Radioactive Waste, KWQ11-00670 (2011).