Development of Low-contaminated Sludge Separation Technology

HeeJin Ahn^{*}, MiHyun Lee, and KangOk Cho

Korea Hydro & Nuclear Power Co., Ltd Central Research Institute, 70, Daedeok-daero 1312beon-gil,

Yuseong-gu, Daejeon, Republic of Korea

*cowahn61@khnp.co.kr

1. Introduction

When nuclear power plants are dismantled, radioactive waste of various kinds and levels such as metal, concrete, and soil is generated in a very short period of time. If the appropriate waste management plan is not applied from the beginning of the decommissioning project, it will cause enormous hindrance to the decommissioning business such as increase of the disposal cost. In particular, disposal alternatives are not available due to insufficient treatment technology for disposal unsuitable wastes generated during decommissioning of nuclear power plants such as sludge wastes.

As a part of the development of radioactive waste disposal technology and special waste treatment technology, we conducted a survey on the status of low - contaminated sludge and the case of sludge separation technology at Hanbit 3 power plant. In addition, samples of low - contaminated sludge from Hanbit 3 power plant, radionuclide analysis and chemical characteristics analysis were performed.

2. Survey of low-contaminated sludge and sludge separation technology

2.1 Survey on the status of low-contaminated sludge

A large amount of radioactive waste was generated at the sewage treatment plant due to the contamination of demineralized water supply system of Hanbit Unit 5. It was collected and stored in 220 pieces of 1 ton reinforced plastic cylinders. The contaminants on the upper part of the slurry were dried and stored in a bag of 40 kg. The sludge on the floor is stored in a 689 sack bag of 40 kg capacity and is located 147 feet from the radioactive waste disposal facility. It is expected that the pollution degree of the sludge and the filter material collected at the wastewater treatment plant is very low. Therefore, it is necessary to take measures to properly dispose of these radioactive wastes below the disposal limit in accordance with legal procedures, rather than drum-disposing them.

2.2 Sludge separation technology case study

The main purpose of the sludge separation technology is to minimize the radiation effects. The key to the treatment technology is separation and concentration. Radioactive waste, which has become very low in concentration through separation, is disposed of itself, and enriched is isolated from the living environment through solidification treatment after volume reduction for efficient storage and management. The method of treatment of radioactive waste should be selected according to the radioactive level of radioactive waste, physical and chemical conditions, kinds of radionuclides contained in radioactive waste, and so on. As a result of the survey, the radioactive sludge generated from the nuclear power plant was partially treated for solidification, but no radioactive material was removed through the separation of nuclides. However, related research is ongoing in the United States and Japan [1].

3. Sampling of low-contaminated sludge, analysis of radionuclides and chemical characterization

3.1 Results of low-contamination sludge radionuclide analysis

Radionuclides of low - contaminated sludge were analyzed. As a result, the radionuclides above the reference concentration were Mn-54, Co-58, Co-60, Cs-137 and Nb-94.

The Concentrations of nuclides in waste types were up to 17 times higher than that of Co-60, but other nuclides were $2 \sim 3$ times higher than self-disposal concentration or slightly higher than the reference value. Table 1 shows the nuclide analysis results for self-disposal evaluation.

4. Nuclide removal experiment of lowcontaminated sludge

4.1. Washing treatment and ultrasonic treatment

Experiments were conducted to remove the nuclides above self-disposal standards.

As a method of removing nuclides, a washing treatment method and an ultrasonic treatment method were used. In the washing process, 250 cc sample was placed in a 500 cc sample bottle, and 250 cc of deionized water was filled in the sample bottle, followed by washing and ultrasonic treatment. As a result of the nuclides removal treatment, Cs-137 was completely removed. Co-60 was removed to about 1/2 to 1/5 level. This suggests that it was moved to a pH alkaline area by OH- ions present on the surface of sludge. And radioactive cobalt that must be leached are present as sediment in Co(OH)₂ and were not leached.

4.2 Chemical elution and substitution

4.2.1 Radiochemical properties of Co-60. Cobalt has oxidation states of 0, +2 and +3, and Co²⁺ & Co³⁺

coexist in a stable state as Co^{2+} ion in aqueous solution. The Cobalt chemical species are absorbed into small particles in the water, settled down to rocks or sand, or are directly absorbed into materials such as sand and gravel [2].

This degree of adsorption depends on the pH, the oxidation-reduction atmosphere, and the concentration of dissolved organic matter. When a strong oxidizing agent is present in the aqueous solution, the cobalt ions are present in the oxidized state of Co^{3+} and exist in the form of a precipitate of $Co(OH)_3$ over the acidic and alkaline regions. In the absence of oxidant, cobalt ions exist in the form of Co^{2+} , and exist in the form of precipitates of $Co(OH)_2$ from alkaline near neutral to strongly alkaline.

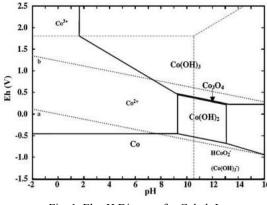


Fig. 1. Eh-pH Diagram for Cobalt Ion.

4.2.2 Co-60 elution experiment using strong acid. It is believed that the Co-60 are absorbed onto their surfaces due to the presence of large amounts of iron and manganese in the sludge contents, to remove the co-60 that is absorbed on the surface, use acid solutions such as HCl, HCl+HNO₃, HCl+H₂SO₄, HCl+HClO₄ to dissolve iron or manganese[3]. In this experiment, 0.5 M HCI was used, and three kinds of reducing agent such as oxalic acid (C₂H₂O₄), chloride tin (SnCl₂), and hydroxyl amine (NH₂OH·HC) were used for elution of Co-60[4].

$$\operatorname{Co}^{2+}(\operatorname{aq}) + 3\operatorname{Ox}^{2-}(\operatorname{aq}) \rightleftharpoons [\operatorname{Co}(\operatorname{Ox})_3]^{4-}(\operatorname{aq}) \qquad (1)$$

In particular, chloride annotations $(SnCl_2)$ were used to replace eluted Co-60 with Sn. To check the time effect of elution and substitution, stirred it for 10 minutes, 1 hour, 6 hour and 24 hours, respectively.

5. Conclusion

In order to reduce the amount of radioactive waste generated due to contamination of the desalination water supply system of Hanbit Unit 5, a self-disposal plan was sought. The types of wastes were ground sludge of sedimentation tank, gravel used as filtration media, sand, activated carbon anthracite. As a result of the analysis of radionuclides in low-contaminated radioactive wastes, radionuclides exceeding the selfdisposal standard values were analyzed as Mn-54, Co-58, Co-60, Cs-137 and Nb-94. Concentrations of nuclides in waste types were up to 17 times higher than that of Co-60, but other nuclides were $2 \sim 3$ times higher than self-disposal concentration or slightly higher than the reference value. In order to confirm the possibility of self-disposal of radioactive waste, a nuclide elimination experiment in radioactive waste was conducted.



Fig. 2. Co-60 activity in Sludge after treating nuclide removal.

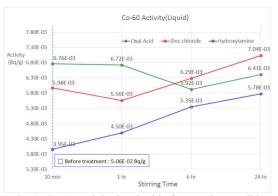


Fig. 3. Co-60 activity in Liquid after treating nuclide removal.

The biggest effect of removing nuclide was in case of chloride annotations were treated as reductants when the analysis of sludge nuclides after treating nuclide removal.

The elimination rate of nuclide was treated up to about 20%, which is equivalent to 1/10 of the criteria for self-disposal and, it is sufficient level self-disposal.

REFERENCES

- [1] ANDRA, "National Inventory of Radioactive Materials and Waste", 2012.
- [2] M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", National Association of Corrosion Engineers, Houston, Texas, USA, p. 325. 1974.
- [3] Sahuquillo et al, Analytica Chimica Acta, 382(3), 317 ~ 327, 1999.
- [4] McLaren et al., Journal of Soil Science, 37(2), 223 ~ 234, 1986.