Estimation of Waste Volume for Kori # 1 Decontamination Using SP-HyBRID Process

Sang Yoon Park*, Wang Kyu Choi, Seong Byeong Kim, Hui Jun Won, and Man Soo Choi

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

*nsypark@kaeri.re.kr

1. Introduction

Kori # 1, the first pressurized water reactor (PWR) in Korea will permanently shut down in this year. Before decommissioning of shut-downed nuclear power plant, the primary side of the plant should be decontaminated. And it is necessary to review the radioactive waste minimization methods for system decontamination. The CORD process or CITROX process are the chemical decontamination processes currently used due to the low amount of secondary waste produced using in situ decomposition of oxalic acid. Large volume of spent ion-exchange resin, however, is generated because of primary waste such as radioactive materials, corrosion products and residual citric acid/nitric acid etc.

KAERI has been developing a new decontamination process that does not contain any organic chemicals in the decontamination solution and minimizes the use of ion exchange resin in the solution purifying step [1-3]. The process is hydrazine base reductive metal ion decontamination for decommissioning (HyBRID) and consists of N_2H_4, H_2SO_4 and Cu^{2+} ions. A sulfuric acid permanganate process (H_2SO_4 + $KMnO_4$) is used in HyBRID as a pre-oxidative decontamination step. To minimize the waste volume, residual hydrazine is decomposed with hydrogen peroxide and the sulfate ions are precipitated by the addition of $Ba(OH)_2$ or $Sr(OH)_2$ followed by filtration with a candle filter.

In this study, we performed small-scale and bench-scale experiments of hydrazine decomposition, sulfate precipitation and solid-liquid separation. And the waste volume for Kori #1 system decontamination using SP-HyBRID process was calculated and was compared with NP-CITROX or HP-CORD process.

2. Waste Treatment for SP-HyBRID

2.1 On-Line Monitoring of Decontamination Process

Fig. 1 shows the on-line monitoring system to demonstrate the decontamination chemical make-up, the permanganate and hydrazine decomposition, $BaSO_4$ precipitation and process monitoring of SP-HyBRID process.

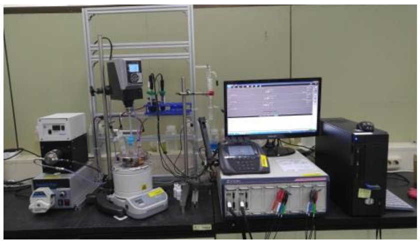

Fig. 1. On-Line Monitoring System.

2.2 Oxidative Step Process

Sulfuric acid permanganate is used in oxidative decontamination step at 95°C with various durations depending on the operating conditions. Typical concentrations of $KMnO_4$ and H_2SO_4 are 6.33 mM and 3.25 mM, respectively. After pre-oxidation treatment, residual permanganate is decomposed with N_2H_4 as follows:

$$4KMnO_4 + 5N_2H_4 + 6H_2SO_4 \rightarrow 4K^+ + 4Mn^{2+} + 5N_2 + 16H_2O + 6SO_4^{2-}$$

The solution after $KMnO_4$ decomposition can be used in the next reductive step with no refill or drain.

2.3 Reductive Step

In reductive decontamination step, 50 mM N_2H_4 + 0.5 mM Cu^{2+} ions + 25 mM H_2SO_4 of solution is used at 95°C for 10 h. After the reductive step, there are several sorts of metal ions, potassium ions and sulfate in the decontamination solution. The necessary concentration of barium hydroxide to precipitate of 28.25 mM sulfate is about 30 mM. Because of the very low value of the solubility product for $BaSO_4$ (i.e., 1.084 x 10^{-10} at 25°C), sulfate ions can be removed from the solution with the addition of the same concentration of barium ions, which is then followed by solid-liquid separation of the precipitated particles. There are several kinds of metal ions in the used solution at the end of the HyBRID process, such as primary wastes (e.g., corrosion products including Fe^{2+}, Ni^{2+}, Cr^{3+}, etc.), secondary wastes (e.g., Mn^{2+}, Cu^{2+}, etc.) and radioactive materials (e.g., Co-60, Co-58, Mn-54, Cr-51, etc.).

3. Results and Discussion

3.1 Process Monitoring

Fig. 2 shows a typical ORP monitoring result for SP-HyBRID process: the oxidative step, decomposition of permanganate, reductive step, decomposition of hydrazine, precipitation of sulfate ions, etc. It is very useful for making the decision to add chemicals or to stop, which is valuable to the waste minimization.

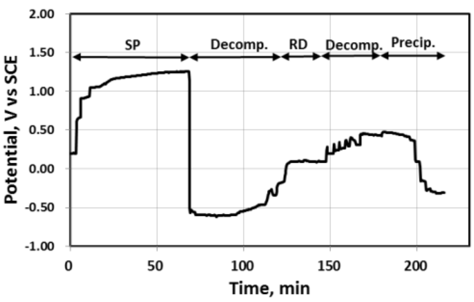

Fig. 2. Typical ORP Monitoring Curve.

3.2 Final Waste Treatment

The simulated decontamination solution was made-up and mixed with $Ba(OH)_2$ solution to remove the sulfate ions in the form of BaSO4 precipitates. After precipitation of sulfate ion, the precipitated particulate should be removed from liquid waste solution. Fig. 3 shows the morphology of the cake made by candle filtration of simulated liquid waste for a 1 cycle SP-HyBRID process. Apparent density of the cake was 2.56 g/cm^3 which will be used to calculate the waste volume for Kori #1 decontamination with the SP-HyBRID process. Before and after precipitation, the chemical concentration in the solution was analyzed with AA and it was conformed that most of sulfate ions and metal ions (higher than 99.5%) were removed from the decontamination solution to solid. It means that only 0.5% of anion and metal ions can be removed by ion-exchange resin.

Fig. 3. Cake Morphology of $BaSO_4$ Precipitates.

4. Conclusion

SP-HyBRID decontamination process can be used to decontamination of Kori # 1 with a minimization of spent ion-exchange resin before decommissioning. The total volume of solid waste can be reduced 1/10 less than that of a commercial process and spent ion-exchange resins can be reduced to 1% of that of a commercial process.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to National Research Foundation of Korea (NRF) for the Future Planning (MSIP) of the Republic of Korea, in support of the authors' work through the Nuclear Research and Development Program (NRF-2012-M2A8A5025655).

REFERENCES

[1] S.B. Kim, H.J. Won, J.K. Moon, and W.K. Choi, Magnetite dissolution using hydrazine-acid solution for chemical decontamination, Transactions of the American Nuclear Society, Vol. 115, Las Vegas, USA (2016).

[2] S.Y. Park, H.J. Won, M.S. Choi, S.B. Kim, W.K. Choi, and J.K. Moon, Waste Minimization of HyBRID Decontamination Process, WM2017 Conference, March 5-9, Phoenix, Arizona, USA (2017).

[3] H.J. Won, W.S. Lee, C.H. Jung, S.Y. Park, W.K. Choi, and J.K. Moon, Asian J. Chem. 25, 5, p. 1327-1330 (2014).