Waste Minimization of HyBRID Decontamination Process – 17060

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ABSTRACT

The Korea Atomic Energy Research Institute (KAERI) developed a Hydrazine base reductive metal ion decontamination (HyBRID) and related pre-oxidation techniques for use in decommissioning a nuclear facility. Inorganic chemicals were used to increase the integrity of the radioactive waste in a repository. Decomposition and precipitation of residual reagents with inorganic chemicals were introduced to minimize the final waste volume. The waste volume was calculated theoretically and demonstrated in a small-scale waste treatment system and bench-scale candle filtration system. The total waste volume of the HyBRID process was less than 1/10 of that of commercial processes, and spent ion-exchange resins were significantly reduced to 5% of that of commercial processes.

INTRODUCTION

The important factors for selecting chemical decontamination for decommissioning a nuclear facility are the decontamination factor (DF), the amount of waste and appropriate type of waste to disposal. There are many chemical decontamination techniques that use organic acids, such as oxalic acid, citric acid, nitrilo triacetic acid (NTA), and ethylenediaminetetraacetc acid (EDTA) [1-3]. However, such organic acids and chelating ligands are often problematic for the safety of radioactive wastes. In particular, a metal EDAT complex in a repository potentially forms a complex with radionuclides, which increases the mobility of radionuclides and consequently increases the probability of the radioactive contamination of groundwater [4].

The CORD UV process is one of the chemical decontamination processes commonly used due to the high DF and the low amount of secondary waste produced using in situ decomposition of organic acid by UV. Its strong corrosiveness, however unnecessarily generates inactive corrosion products that are loaded in ion exchange resins with the active corrosion products [3]. Furthermore, in Korea, spent ion exchange resins are considered to be problematic waste that requires special approaches, and to date, there is no proper solidifying method to meet the acceptable repository criteria [4].

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 [5]. The process is hydrazine base reductive metal ion decontamination for decommissioning (HyBRID) and consists of N_2H_4, H_2SO_4 and Cu^+ 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.

Our study was concerned with the feasibility of volume reduction using the HyBRID process. We performed small-scale and bench-scale experiments of hydrazine decomposition, sulfate precipitation and solid-liquid separation. The co-precipitation properties of metal ions (e.g., Fe^{2+}, Ni^{2+}, Cr^{3+}, Mn^{2+}) during the barium sulfate precipitation were also evaluated.

WASTE TREATMENT FOR the HyBRID PROCESS

The waste treatment process of HyBRID for PWR decontamination is as follows:
- Oxidative decontamination step with sulfuric acid permanganate;
- Decomposition of residual permanganate with hydrazine;
- HyBRID step;
- Precipitation of sulfate with barium hydroxide;
- Decomposition of residual hydrazine with hydrogen peroxide;

The following sections describe the typical concentration of chemicals and the procedure for waste treatment in HyBRID.

Oxidative Step and Decomposition of Residual Permanganate

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 (1g/L) and 3.25 mM, respectively. After pre-oxidation treatment, residual permanganate is decomposed with N_2H_4 as follows:

$4KMnO_4^- + 5N_2H_4 + 6H_2SO_4 \rightarrow 4K^+ + 4Mn^{2+} + 5N_2 + 16H_2O + 6SO_4^{2-}$ (Eq. 1)

The amount of N_2H_4 necessary to decompose 6.33 mM of $KMnO_4$ is 7.9 mM. The solution after $KMnO_4$ decomposition can be used in the next reductive step with no refill or drain.

Reductive Step and Precipitation of sulfate in the Spent Solution

In a typical reductive decontamination step, 50 mM N_2H_4 + 0.5 mM Cu^{2+} ions + 25 mM H_2SO_4 (pH control) 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. The precipitation reaction of sulfate with a barium hydroxide is as follows:

$$H_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2H_2O \qquad \text{(Eq. 2)}$$

Because of the very low value of the solubility product for $BaSO_4$ (i.e., 1.084×10^{-10} at $25\,^{\circ}C$), 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.). All these metallic ions can be co-precipitated during a precipitation of $BaSO_4$ as follows:

$$M^{n+} + nOH^- \rightarrow M(OH)_n \qquad \text{(Eq. 3)}$$

Most of the radioactive material and metal ions can be precipitated at higher pH values (>8.5)[6]. Moreover, the pH value of the HyBRID solution after addition of $Ba(OH)_2$ is as high as pH 11-12, which enables fast precipitation and accordingly complete removal of those ions from the solution.

Solid-Liquid Separation of Precipitates

Waste minimization in the HyBRID process relies on the effective solid-liquid separation (SLS) method. There are several techniques for SLS in a one-stage process, e.g., filtration with a screw press, decanting centrifuges, etc. The particle size distribution of barium sulfate plays a critical role in the SLS. $BaSO_4$ particle size distribution made in the process is less than 5 µm, so candle filtration was considered to be an appropriate SLS method in the HyBRID process.

Decomposition of Hydrazine

There is a high concentration of hydrazine in used HyBRID solution. To reuse the solution for the next oxidation step, it is necessary to decompose the residual hydrazine. The residual hydrazine is decomposed with the addition of hydrogen peroxide as follows:

$$N_2H_4 + 2H_2O_2 \rightarrow N_2 + 4H_2O \qquad \text{(Eq. 4)}$$

The decomposition rate of hydrazine can be varied by the temperature and pH of the solution.
We found that hydrazine is perfectly decomposed by the addition hydrogen peroxide. The amount of hydrogen peroxide that was necessary to decompose hydrazine, however, was three times the stoichiometric amount due to the self-decomposition in the presence of sulfuric acid [5].

PERFORMANCE TESTS FOR WASTE MINIZATION

Demonstration of Precipitation and Filtration

Fig. 1 shows small-scale of waste treatment system (left) to demonstrate the decontamination chemical make-up, the permanganate and hydrazine decomposition, and $BaSO_4$ precipitation and the bench-scale candle filtration system (right) to separate the precipitate from the waste solution. The simulated decontamination solution was made-up and mixed with $Ba(OH)_2$ solution to remove the sulfate ions in the form of $BaSO_4$ precipitates. The system was equipped with an ORP electrode, a pH electrode and a conductivity sensor for on-line system monitoring.

Fig. 1 Picture of small-scale waste treatment system and bench-scale SLS system

Fig.2(a) shows an on-line monitoring result(ORP) for the HyBRID process: the pre-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(b) shows the detail of hydrazine decomposition process. Hydrogen peroxide was added six times in 1L of simulated waste solution. The ORP curve was very sensitive to addition of hydrogen peroxide. Each ORP peak means that the decomposition reaction was very fast and it is confirmed by showing a vigorous gas evolution during the formation of each peak.
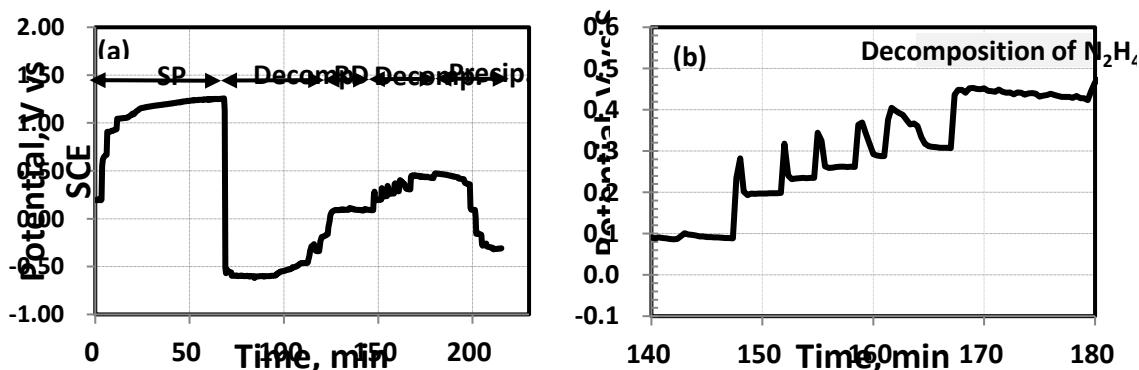

Fig. 2 On-line monitoring curve for the total HyBRID process (a) and hydrazine decomposition step (b)

Fig. 3 (left) shows the morphology of the cake made by candle filtration of simulated liquid waste for a 1 cycle HyBRID process and Fig. 3 (right) shows a typical SEM photograph of the particle morphology of $BaSO_4$ precipitates before the filtration process. M21U002 filter media with an average pore size of 1.08 μm was used in the candle filtration. Candle filtration test results were as follows:

- Volume of cake = 41.16 cm^3
- Mass of cake before drying = 105.31 g
- Mass of cake after drying = 35.6 g
- Content of water = 35.6%
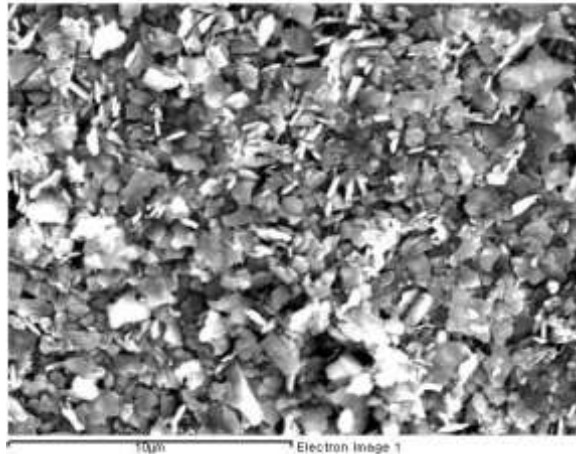- Apparent cake density =2.56 g/cm^3 (Theoretical density = 4.5g/cm^3)

Fig. 3 Cake and particle morphology of $BaSO_4$ precipitates after candle filtration

Decomposition of Chemicals

TABLE I shows the chemical concentration of the simulated liquid waste before and after precipitation with $Ba(OH)_2$ solution. The initial solution before precipitation was simulated so that the typical liquid waste produced during 1 cycle of the HyBRID process, that is, oxidative step → decomposition of permanganate → reductive step → decomposition of hydrazine → precipitation of sulfate, dissolved a $Ni_{0.6}Fe_{1.2}Cr_{1.2}O_4$ oxide layer. The content of Ba was not from the decontamination solution but from the barium hydroxide added after decontamination to precipitate sulfate. A total of four runs of tests were performed using the same solution. Most of the metal (> 99.8%) ions and sulfate anions were removed from the decontamination solution to sludge. Higher than 99.9% of residual hydrazine was decomposed by the addition of hydrogen peroxide. This result means that the use of spent ion-exchange resin in the HyBRID process can be minimized by the decomposition and filtration treatment.

TABLE I Chemical concentration of simulated liquid waste before and after precipitation treatment

		Concentration, ppm								
		Fe	Cr	Ni	Cu	Ba	K	Mn	SO$_4$	N$_2$H$_4$
Before Treatment		24	24	12	32	5819	247	348	3500	1440
After precipitation	1	0.003	0.007	0.003	0.034	23	109	0.172	4	0.592
	2	0.001	0.001	0.001	0.005	103	119	0.104	4	0.89
	3	0.001	0.008	0.003	0.007	35	140	0.012	4	0.862
	4	0.001	0.001	0.001	0.005	40	120	0.021	8	0.72
Average		0.002	0.004	0.002	0.013	50.25	122	0.077	5	0.766
Removal Rate, %		99.99	99.98	99.98	99.96	99.14	50.51	99.98	99.86	99.95

Estimation of Final Waste Volume

TABLE II shows the calculated results of the total waste and ion-exchange (IX) resin volume generated during one-through decontamination with 1000 L of processing water. To compare the waste volume, the H$_2$SO$_4$/KMnO$_4$+HyBRID process and HNO$_3$/KMnO$_4$+ CITROX process were selected and calculated. The total waste for the KMnO$_4$+HyBRID process without precipitation was 85.0 L, which was not much less than the waste generated from the KMnO$_4$+CITROX process. After BaSO$_4$ precipitation, however, the total waste of the KMnO$_4$+HyBRID process was reduced to less than 1/10 and the volume of spent IX resin was greatly minimized to 1/20 that of the KMnO$_4$+CITROX process.
Fig. 4 shows a comparison of the total waste and spent IX volume calculated in a way similar to that in TABLE II for the various types of decontamination processes: KMnO$_4$-CITROX, HMnO$_4$-2000 ppm oxalic acid(OA), KMnO$_4$-HyBRID and HMnO$_4$-HyBRID. It is clear that to minimize the waste, the HMnO$_4$-HyBRID process is the best option.
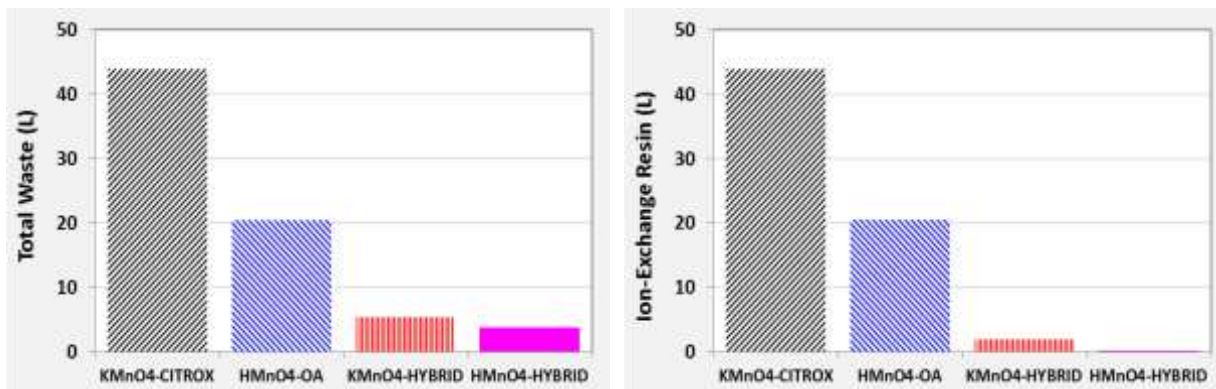

Fig. 4 Comparison of the total waste and ion-exchange resin for the various decontamination processes

TABLE II Comparison of the final solid waste between the KMnO$_4$+HyBRID process and the KMnO$_4$+Citrox process for the Korean style RCP internal surface decontamination

Process	Chemical	Initial Concentration in 1000 L		After Decomposition		After Precipitation	
		ppm	mM	ppm	mM	ppm	mM
H$_2$SO$_4$ KMnO$_4$ + HyBRID Process	K$^+$	256	6.5	256	6.5	128	3.25
	Mn^{2+}	348	6.3	348	6.3	0.3	0.01
	N$_2$H$_4$	1850	57.8	1.9	0.06	1.9	0.06
	SO$_4^{2-}$	3500	36.4			3.5	0.04
	Fe^{3+}	24	0.4			0.02	0.00
	Cr^{3+}	24	0.5			0.02	0.00
	Ni^{2+}	12	0.2			0.01	0.00
	Cu^{2+}	32	0.5			0.03	0.00
	Ba^{2+}			5000	36.4	5	0.04
	BaSO$_4$					8500	36.4
	MnO$_2$					565	6.5
	Fe(OH)$_3$					43	0.4
	Cr(OH)$_3$					52	0.5
	Ni(OH)$_2$					19	0.2
	Cu(OH)$_2$					49	0.5
	Cation IX	23.21 eq.	**12.2 L**			3.27 eq.	**1.72L**
	Anion IX	72.80 eq.	**72.8 L**			0.07 eq.	**0.13L**
	Cake					9223 g	**3.6 L**
	Total		**85.0 L**				**5.5 L**
HNO$_3$ KMnO$_4$ + CITROX Process	K$^+$	256	6.5	256	6.5		
	Mn^{2+}	348	6.3	348	6.3		
	C$_2$O$_4^{2-}$	1954	22.2	0	0.0		
	C$_6$H$_5$O$_7^{3-}$	1287	6.7	1287	6.7		
	NO$_3^-$	785	12.7	35	12.7		
	Fe^{3+}	24	0.4	24	0.4		
	Cr^{3+}	24	0.5	24	0.5		
	Ni^{2+}	12	0.2	12	0.2		
	Cation IX	22.23 eq.	11.7 L	22.23 eq.	**11.7 L**		
	Anion IX	57.06 eq.	77.2 L	12.66 eq.	**32.8 L**		
	Total				**44.5 L**		

Small-Scale Decontamination Test

A small-scale decontamination test of the $KMnO_4$-HyBRID process was performed with a Korean PWR (HANUL #3) primary side specimen with an outer diameter of 2.5 cm and length of 60 cm. Before the decontamination, the maximum contact dose was 560 µSv/h. TABLE III shows the radioisotope and activity of the 1 cycle decontaminated liquid waste before and after precipitation. Most of the radioactivity (>99.9%) was removed from the solution to sludge. These results were consistent with the removal rate of metal ions in TABLE I. The minimization of waste volume in the HyBRID process critically relies on the sulfate precipitation and filtration performance.

TABLE III Comparison of radioactivity between before precipitation and after precipitation during the HyBRID process for the decontamination of the HANUL#4 primary side specimen

Radionuclide	Before Precipitation (Bq/g)	After Precipitation (Bq/g)	Removal Rate (%)
Mn-54	183.25	ND	100
Co-57	15.43	ND	100
Co-58	1,508.00	0.68	>99.9
Fe-59	4.38	ND	100
Co-60	308.06	ND	100
Zn-65	3.57	ND	100

CONCLUSION

We developed the HyBRID process, which is one-through decontamination for use in decommissioning a nuclear facility. Dilute inorganic chemicals were used to increase the integrity of the radioactive waste in a repository. Decomposition and precipitation of residual reagents with inorganic chemicals were introduced to minimize the final waste volume. Most of the metal ions, radioactivity and chemicals (secondary waste) were removed from the liquid waste to precipitates that were simply separated from liquid to cake by means of a candle filtration system. The total volume of the solid waste of the HyBRID process was 1/10 that of a commercial process and spent ion-exchange resins were 5% of that of a commercial process.

REFERENCES

1. C.J. Wood, "A Review of the Application of Chemical Decontamination Technology in United States", Progress in Nuclear Energy, 23(1), p.35-80 (1990)
2. D. Bradbury, "A Review of Decontamination Technology Development 1977-2000", Water Chemistry of Nuclear Reactor Systems 8, BNES, p.173-178, (2000)
3. R. Riess, S. Odar, and J. Kysela, "Decontamination and Steam Generator Chemical Cleaning" LCC5 Special Topic Report, ANT International, Krongjutarvagen 2C, SE-730 50 Skultuna, Sweden (2009)
4. 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)
5. 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)
6. IAEA, "Chemical Precipitation Processes for the Treatment of Aqueous Radioactive Waste" IAEA Technical Report Series No.337, IAEA, Vienna (1992)

ACKNOWLEDGEMENTS