Minimization of Secondary Waste in Chemical Decontamination

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1. Introduction

Because of excessively high costs involved in the radioactive waste disposal, the waste reduction issues of primary side chemical decontamination of nuclear power plants are becoming increasingly important. Various technologies to reduce the secondary waste have been tried in commercialized decontamination methods. The concentration of decontamination reagents has been reduced as low as possible. In CORD process, corrosion products and other metallic ionic materials are continuously removed by a bypass cleanup through ion exchange resins during decontamination process. And at the end of decontamination step the residual chemicals are destroyed to water and carbon dioxide by illuminating the ultraviolet light. So the secondary waste has been reduced remarkably, however, ion exchange resin for the primary waste could not be reduced up to nowadays.

A new oxidative process for removing chromium oxide in primary side of PWR using sulfuric acid and potassium permanganate (SP) was developed and HYBRID (Hydrazine Based Reductive metal Ion Decontamination with sulfuric acid) process for removing iron oxide was also suggested in KAERI[1,2]. These two processes can be used to decontamination of PWR primary surface without rinsing and/or solution exchange with chemical decomposition after each decon step, the process is essentially single stage. The process has several advantages: the sulphate ion can be removed as a precipitation, ion exchange resin generated for removing primary waste is small, and the decon equipment never needs to be drained. The objective of this study is to review the feasibility to minimize of solid waste by the sulphate precipitation and solid-liquid separation.

2. Methods and Results

2.1 One-Stage Decontamination Process

The one-stage process for PWR primary surface decontamination using SP-HYBRID proceeds as follows: SP → decomposition → HYBRID → decomposition. After the final decomposition, liquid and solid separated and the process water can be feedback to the first step without the solution exchange.

In the oxidative step (SP), chromium oxide reacts with permanganate in sulfuric acid solution as follows;

$$Cr_2O_3 + MnO_4^- + H_2O = 2HCrO_4^- + 2MnO_2 \qquad (1)$$

Residual permanganate and manganese dioxide should be decomposed to water and Mn^{2+} ion. In the reductive step (HYBRID), magnetite can be dissolved in sulfuric acid solution as follows [2]:

$$2\,[Cu^+(N_2H_4)] + 4H_2SO_4 + Fe_3O_4$$
$$\rightarrow 3Fe^{2+} + 2[Cu^{2+}(N_2H_4)] + 4H_2O + 4\,SO_4^{2-} \qquad (2)$$

After decontamination, hydrazine will be decomposed with the aid of hydrogen peroxide and sulphate will be precipitated with equivalent content of barium ion or strontium ion. Table 1 shows the typical results of chemical composition after each step of the one-stage process.

Table 1. One-stage decontamination process and chemical composition after each step

Oxide to Dissolve ($0.05NiFe_2O_4$+ $0.002Fe_3O_4$ + 0.0365g/L Cr_2O_3)						
Ni (mM)	Fe (mM)	Cr (mM)				
0.21	0.45	0.48				
Oxidative step (6.33mM $KMnO_4$+3.25mM H_2SO_4)						
Ni (mM)	Fe (mM)	Cr (mM)	K (mM)	Mn(mM)	Cu(mM)	H2SO4(mM)
0.04	0.00	0.39	6.33	6.33	0	3.25
Decomposition N_2H_4 (0.00791+0.05)						
Ni (mM)	Fe (mM)	Cr (mM)	K (mM)	Mn(mM)	Cu(mM)	H2SO4(mM)
0.04	0.00	0.39	6.33	0	0	3.25
Decomposition of MnO_2 H_2SO_4(0.254ml/200ml)						
Ni (mM)	Fe (mM)	Cr (mM)	K (mM)	Mn(mM)	Cu(mM)	H2SO4(mM)
0.04	0.00	0.39	6.33	6.33	0	26.9
HYBRID (0.5mM$CuSO_4$)						
Ni (mM)	Fe (mM)	Cr (mM)	K (mM)	Mn(mM)	Cu(mM)	H2SO4(mM)
0.21	0.37	0.41	6.33	6.33	0.5	27.4
Decomposition of N_2H_4 (H_2O_2)						
Ni (mM)	Fe (mM)	Cr (mM)	K (mM)	Mn(mM)	Cu(mM)	H2SO4(mM)
0.21	0.37	0.41	6.33	6.33	0.5	27.4
Precicipitation of Sulfate $Ba(OH)_2$ 0.027M						
Ni (mM)	Fe (mM)	Cr (mM)	K (mM)	Mn(mM)	Cu(mM)	H2SO4(mM)
0.00	0.00	0.00	6.33	0.00	0.00	0.03

After final precipitation step, primary waste(Ni^{2+}, Fe^{2+}, Cr^{3+} and so on) thought to be co-precipitated in $BaSO_4$ sludge as well as Cu^{2+} ion. This implies there is the possibility of minimization of ion exchange resin usage and total volume of solid waste.

2.2 Review of the Sludge Separation Method

As showed in previous section, waste minimization in the one-stage process relies on the effective solid-liquid separation (SLS) methods. There are several techniques for SLS in the one-stage process, e.g., filtration with screw press, decanting centrifuges, etc. The particle size distribution of barium sulphate plays a critical role in the SLS. Fig.1 shows the filtration methods and the particle size can be filtered. The use of reverse osmosis membrane can be removed very fine particles, but it needs high cost to apply in one-stage process. The use of microfiltration can be easily applied in the process, however, it cannot remove the smaller than 0.05 μm particles as showed in Fig.1.

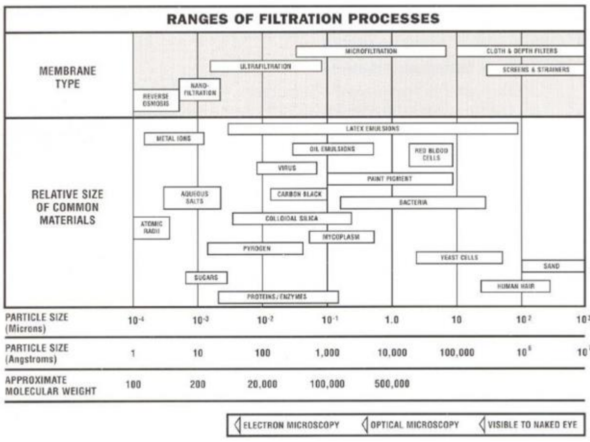

Fig. 1. The filtration methods and the particle size can be filtered

The performance of decanting centrifuge in SLS for barium sulphate containing solution depends on sludge concentration, liquid viscosity, specific gravity, and particle size distribution. And the sludge separation ratio is in the range of 95 ~ 99% according to physical and chemical properties of the sludge. For the SLS of produced sludge in the one-stage decontamination process, particle size distribution and particle shape are most important parameters. Fig. 2 shows the particle shape of $BaSO_4$ precipitation prepared in semi-batch system [3] and T-type mixer [4]. The particle made in T-type mixer was regular in shape and in size which is advantageous for SLS using the decanting centrifuge. The important factors affected to particle size distribution and particle shape are pH of the reactant solution, supersaturation ratio, and mixing effect, sampling time and so on. In the one-stage process, however, the chemical conditions are fixed; the physical conditions are important and variable. The batch or semi-batch systems are suitable to make a large particle but the particle shape and size are irregular. T-type or Y-type mixer is suitable to control particle shape and size [3,4].

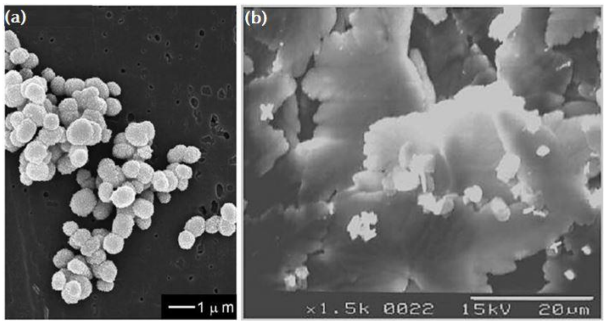

Fig. 2. Particle morphologies of $BaSO_4$ made in (a) T-shape mixer [3] and (b) semi-batch type reactor [4]

3. Conclusions

The feasibility to minimize of solid waste by the sulphate precipitation and solid-liquid separation in the one-stage decontamination of SP-HYBRID process was reviewed. In the small batch test, the possibility of minimizing the ion exchange resin volume was suggested and the valuable solid-liquid separation techniques in the engineering scale were reviewed. The optimized technologies and conditions were tested in further studies.

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