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Operation of the Newly Developed Chemical Decontamination Process for Korean Pressurized Water Reactors

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Abstract

A series of experiments were conducted to establish a total decontaminating process of a newly developed decontaminating agent for decontamination of the primary systems in Korean pressureized water reactors. The newly developed decontamination processes consist of oxidation, reduction, dissolution and decomposition/cleanup processes. Through the operation of a semi-pilot scale equipment based on the results of laboratory scale experiments, the corrosion rate of Inconel 600 was slightly higher than those of SS 304 and 316. And the removal efficiencies of metals (Fe, Cr, Ni, K, Mn) showed 75 % or above, assuming that the radioactivity could be removed from the newly developed decontamination process. In the case of organics, the removal efficiency was slightly low, suggesting that sequential process is need to degrade remaining organics in the process.

1. Introduction

Decontamination is an important means to lower and prevent from spreading and diffusing radioactive materials from all eliminating methods of radioactive contaminants such as decontamination of buildings, equipment, components, system and environment which is excessively exposed to radiation [1,2]. The decontamination methods can be classified into mechanical, electrical and chemical methods. Using decontamination agents, the chemical decontamination is to dissolve cruds and metal oxidizing films on a tube or system. For the effectiveness of the decontamination, it is required to characterize cruds in the system and metal oxide films. Since occasionally the cruds and metal oxide films existing in the primary systems are not available, the simulated cruds, which have a chemical composition and crystalline structure similar to an actual crud without radioactivity, have been considered to estimate the dissolubilities of metal species with respect to decontamination agents.

The newly developed decontamination process, so called KEBA process, is divided into four processes including oxidation, reduction, dissolution and decomposition/cleanup processes, which are analogous with CORD (Chemical Oxidation Reduction Decontamination) process, a regenerative DCD (Dilute concentration decontamination) process. In the KEBA process, an oxidant ($KMnO_4$ in phosphoric acid) dissolves metal oxides in the oxidation. Produced MnO_2 and $HMnO_2$ are reduced by activated carbons with H_2O_2. It is known that organics and metal species are reduced on the surface of activated carbon with H_2O_2 as chemical reaction as well as physical adsorption in the micropore structures of activated carbon. As an actual decontamination step, the chemical reaction for dissolution of metal oxides in chelating agents such as oxalic acid and EDTA. It is noted that the ferric ion from magnetite dissolution is reduced to ferrous ion, which is recovered from activated carbons and cation exchange resins. The dissolution process removes the Mn^{2+} ions produced by reduction of the $HMnO_4$ and cationic metal species such as Fe^{2+}, Ni^{2+}, Co^{2+}, etc. existing as forms of complex with oxalate. As a final process, removal of the oxalic acid and EDTA on anion exchange resin or decomposition by hydrogen peroxide in the decomposition/cleanup process. One characteristic of KEBA process is the decomposition of organic compounds such as oxalic acid and EDTA with a small amount of H_2O_2 and activated carbon [3].

The determined optimal oxidation process was $KMnO_4$ (0.05 %) and H_3PO_4 (0.025 %) at 85 ℃ and 6 hours. And, oxalic acid was considered for the reduction process of oxidants, and then was passed through an activated carbon column with a slow addition of H_2O_2 for 2 hours. In addition, the dissolution process using the newly developed decontaminating agents composed of EDTA, oxalic acid and an additive were performed at 85 ℃ and 6 hours. In the decomposition/cleanup process, organic compounds were degraded by addition of H_2O_2 and then the solution passed through an activated carbon column and ion exchange resin columns.

In this study, semi-scale decontamination equipment was established based on laboratory-scale experiments with the simulated cruds for decontamination of the primary systems in the Korean PWRs. Through the operation, the effects of decontaminating agents on the corrosion behaviors of different materials were investigated. In addition, the removal efficiencies of metal species and organics were investigated using activated carbons combined with H_2O_2 as decomposition step.

2. Experimental

Based on the lab scale test, the newly developed decontamination processes consisting of oxidation process, reduction process, dissolution process and decomposition/cleanup process. The semi-pilot equipment consists of a decontamination tank (about 200 L), an activation carbon tower, cation and anion (or mixed) exchange resin towers, a filter unit, a circulation pump, a chemical injection pump for chemicals such as oxidants and oxalic acid and an electric heater for controlling of solution temperature. The decontamination tank was equipped with an ultrasonic vibrator in order to stir the solution and facilitate the falling of an oxide film as well. As it is important to control in the semi-pilot decontamination system, 2 sets of electric heaters (6 kW) were set up in order to control within 2 ℃ and to prevent the solution from overheating. When pressure difference occurs more than 0.15 mPa during processes, the solution will be circulated through a bypass-line. In addition, the waste is

passed the activated carbon tower, then cation and anion exchange resin.

The determined decontamination process was operated with the experimental conditions as shown in Table 1. In the decontamination process, DOWEX 650 C and 550 A were used as cation exchange resin and anion exchange resin, respectively. Using N_2 adsorption at 77 K in a Micrometrics ASAP 2010 gas adsorption surface analyzer, the pore properties of activated carbons were analyzed. The characterized results showed that the activated carbons have the mean pore size of 11.9834 Å. Also, the BET surface area and micropore area were 796.7428 m^2/g and 782.3341 m^2/g, showing that the activated carbons mainly have micropore structures. The concentrations of metal species were analyzed using ICP-AES (Optima 4300 DV, Perkin Elmer). For the organics concentration, TOC analyzer (Mutli N/C 3000, Analytik Jena AG, Germany) was used.

Three plane corrosion specimens of SS 316, SS 304, and Inconel 600 each were prepared to estimate the process effects of determined oxidation and dissolution processes as a simple corrosion test [4,5]. The weight differences between before and after the total decontamination process were measured in the corrosion tests. The corrosion effects of selected base materials were estimated by the corrosion rate (mg/cm^2h) within designated reaction period for the oxidation process and 6 hours for the dissolution process [6,7]. For the simulated crud, 30.3 g of CRUD 10 consisting of 30.5 % Fe, 32.2 % Cr, and 37.3 % Ni was prepared in the decontamination vessel.

3. Results and discussion

With images of SEM, the surfaces of corrosion specimens were observed for SUS 304, SUS 316 and Inconel 600. Three materials did not show significant corrosion effects, which were not shown here. The corrosion tests under the oxidation and the dissolution processes at 85 ^oC were observed and the results were summarized in Table 2. Of materials, SUS 304 showed the lowest corrosion rates of the planar specimens with the range of $0.63\sim0.93\times10^{-3}$ mg/cm^2 hr. In the case of SS 316, the corrosion rate was within 1.26×10^{-3} mg/cm^2 hr and 1.32×10^{-3} mg/cm^2 hr. It is interesting that a nickel alloy, Inconel 600, showed the highest corrosion rate with the range of $2.30\sim4.04\times10^{-3}$ mg/cm^2 hr. It is known that the nickel alloy consisting of 72.0 % Ni (minimum), 8.0 % Fe, 15.5 % Cr and other species is a main material of SG tube in the primary systems. The corrosion results were compared with the previous ones at the lab scale experiments [8,9]. Still, the corrosion rates of Inconel 600 are considered acceptably low. It is concluded through corrosion tests that the newly developed decontamination process gave little effect on base materials.

After decomposition/cleanup step in the decontamination process, the remained crud was measured as 5.3025 g, showing the dissolution efficiency of 82.5 %. Considering the concentrations of Cr and Ni, most of Cr and Ni were dissolved at the early period of the dissolution step using the decontaminating agents consisting of EDTA, Oxalic acid and C-5 organic. Meanwhile, the concentration of iron increased during the dissolution step, implying that the concentration of chemical species should be considered to increase the dissolution rate of Fe (See Fig. 1). Considering the removal efficiencies of metal species, the removal efficiencies of Ni from curd and Mn from oxidant were 99 % as the remaining concentration of 1 mg/L or below. In the case of Fe and K, the removal efficiencies of Fe and K were 74.56 % and 79.01 %, respectively as slightly low efficiencies. The removal efficiencies of

metal species were shown in Fig. 2.

Through decontamination process, 27 L of KEBA solution and 284.6 g of oxalic acid were used as decontaminating agents, as an organic source. Organic concentration at the initial stage of the dissolution step was 57,772 ppmC and reduced to 66.93 % at the final step (anion exchange resin process). The result implies that sequential process for complete oxidation is needy. In this study, the decontamination process contains decomposition step using activated carbon as mentioned before. It is known that organics can be decomposed in the pore structure of activated carbon with a small amount of H_2O_2. The properties of activated carbons little changed after decomposition of oxidant. However, their surface area, micropore area and micropore volume were significantly reduced after decomposition of decontaminating agents. It is considered that the changed properties were due to adsorption of organics and metal species on the surface of the activated carbon. In addition, the adsorption increased pore diameter up to 12.9817 Å. It is concluded that oragnics and metal species were decomposed in the environments of activated carbon and H_2O_2.

4. Conclusions

A semi-scale decontamination equipment was established based on laboratory-scale experiments with the simulated cruds for decontamination of the primary systems in the Korean PWRs. Through the operation, the effects of decontaminating agents on the corrosion behaviors of different materials were investigated. It was found that the corrosion rates of SS 316, SS 394 and Inconel 600 showed somewhat low corrosion rate. As decomposition step, metal species and organics were decomposed in the environments of activated carbon and H2O2. After decomposition of metal species and organics in decontaminating agent the surface area and micropore structures were significantly changed.

5. References

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Table 1 Outlines of experimental conditions for the KEBA decontamination process

Process step		Experimental conditions
Oxidation		$KMnO_4$ 70.2 g H_3PO_4 63 mL Crud 30.3 g
Oxidant decomposition		Activated carbon 5 L H_2O_2 70 mL
Decontaminating agents supply		KEBA solution 27 L Oxalic acid 284.6 g
Decontaminating agents decomposition		Activated carbon 5 L H_2O_2 70 mL
Cleanup	Cation exchange	DOWEX 650 C 5 L
	Anion exchange	DOWEX 550 A 5 L

Table 2 Corrosion rates of materials in the decontamination experiments

	Minimum ($x10^{-3}$) mg/cm^2 h	Maximum ($x10^{-3}$) mg/cm^2 h	Average ($x10^{-3}$) mg/cm^2 h
SS 304	0.63	0.91	0.77
SS 316	1.26	1.32	1.29
Inconel 600	2.30	4.04	3.17

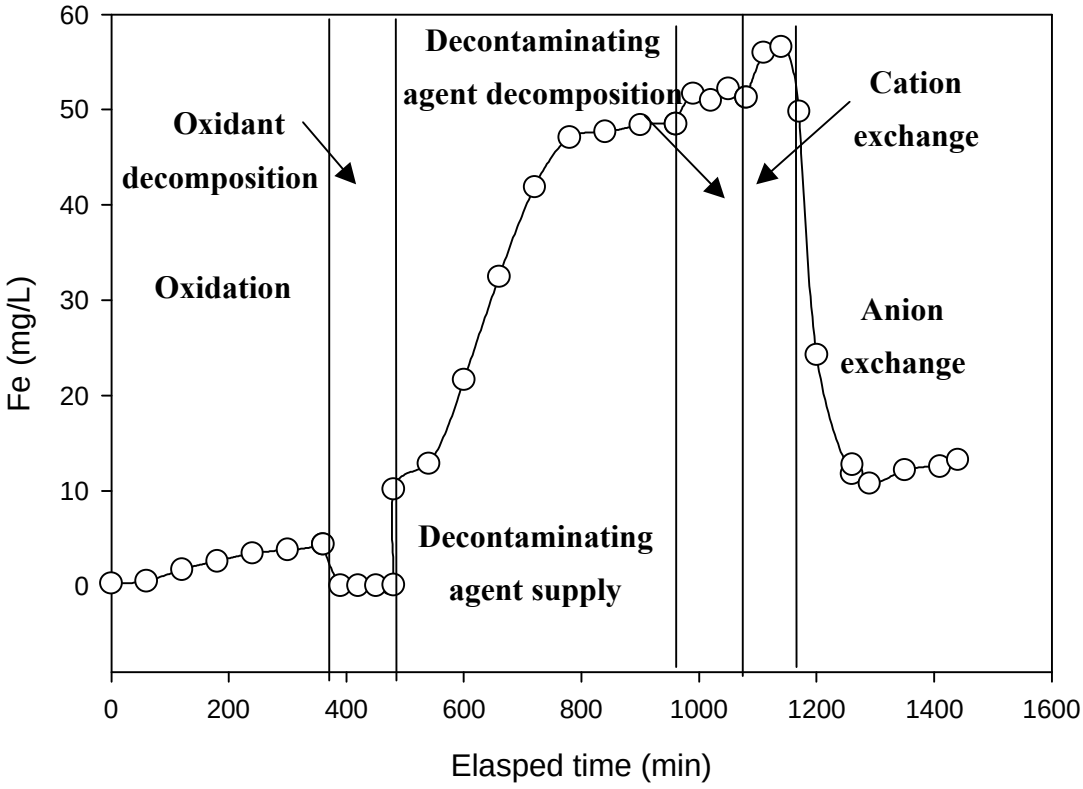

Fig. 1. Dissolution of Fe according to time during decontamination experiment.

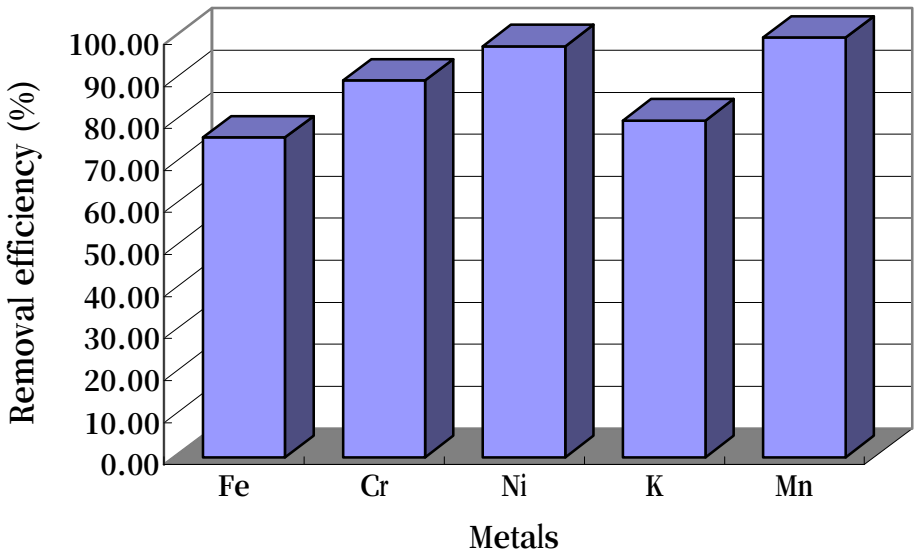

Fig. 2. Removal efficiencies of metal species in the decontaminating experiment.