

**Chemical Decontamination of a Primary Coolant System Using Hydrazine Based Solutions  
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**ABSTRACT**

For the decontamination of primary coolant system, we have developed a new chemical decontamination process named HYBRID (HYdrazine Based Reductive metal Ion Decontamination) which is not containing organic chelates and organic acids. In the first phase to develop HYBRID process, dissolution tests of magnetite using hydrazine based chemical solutions were carried out in various conditions. We found out the effects of parameters such as the concentration of hydrazine, solution pH, temperature, and the addition of transition metal ions on the dissolution behavior. We suggested the concept of HYBRID process with the dissolution mechanism by the complex formation between hydrazine and copper ions, and the reducing power of the hydrazine copper coordination compound to the ferric ions in magnetite. In the second phase to verify the performance of HYBRID process, the chemical decontamination tests using HYBRID coupled with NP were carried out with radioactive specimen taken from the fuel test loop in which operating conditions are same as those in pressurized water reactor. The contact does rate was greatly decreased after the repetitive application of NP and HYBRID. In addition, the corrosion compatibility of the structural material and the decomposition of hydrazine to reduce the secondary waste have been investigated.

**INTRODUCTION**

Decontamination is conducted for equipment and systems which have been contaminated by the activity build-up with time evolution for maintenance or decommissioning. During the periodic maintenance of nuclear power plant (NPP), the action is mainly focused to reduce the occupational exposure, and additionally to reduce the radioactive waste at the time for decommissioning. Especially, a primary coolant system of NPP after long-term operation has been deposited by radioisotopes which are responsible for the most of the radiation exposure of plant workers. The removal of radioactive isotopes from the primary coolant system takes place with the dissolution of oxide layer in which radioisotopes (e.g. Co-60) are deposited [1]. The dissolution of metal oxides up to the boundary layer of oxide and base metal is ideally required to remove all radioactivities from the target surface. However, too aggressive solution is deemed to cause the undesirable corrosion damage to the base metal as well as generate a large volume of decontamination waste so that relatively mild decontamination solutions have been developed.

Chemical decontamination utilized by oxidation and reduction processes is considered most effective method for system decontamination to date. It is well known that permanganate processes using nitric permanganate (NP), alkaline permanganate (AP), and permanganic acid (HP) have been developed to mainly oxidize chromite oxides. On the other hand, reductive decontamination processes such as CAN-DEREM, CITROX, LOMI, and CORD were developed to dissolve the iron oxides and now widely used in the decontamination of primary system. Acidic solutions such as oxalic acid, vanadous picolinate, citric acid, ethylenediaminetetraacetic acid (EDTA) or mixture of them are mostly used as reducing agents under the pH range of 2 to 3 [2]. Organic chelates are used in most commercial reductive decontamination processes to prevent the precipitation of dissolved metal ion by forming metal-organic acid chelation, which accordingly increases decontamination efficiency compared to the cases with the absence of chelating agents. However, organic chelates such as EDTA in CAN-DEREM or oxalic acid in CORD and CITROX processes are considered detrimental for disposal safety because not only EDTA in the mixed waste may form stable and soluble complexes with radionuclides that can enhance and promote its migration in the subsurface and groundwater but also oxalic acid has the risk of potential release of chemo-toxic substances in the case of accidents of the final repository [3, 4].

To overcome the limited use of organic acids and organic chelating agents, KAERI has developed alternative technologies without using any organic acids or organic chelating agents. Newly developed chemical decontamination processes named HYBRID applicable to primary coolant system were described in this paper.

### **MAGNETITE DISSOLUTION IN HYDRAZINE BASED SOLUTIONS**

The spinel type oxides are formed on the surface of iron-based metals, especially when in contact with the coolant in nuclear power plants so that the dissolution of magnetite as a model oxide was carried out in various conditions using hydrazine which is a potent strong reductive reagent in aqueous solution.

Fig. 1 shows the effect of solution temperature on the dissolution of magnetite in 70 mM  $N_2H_4$  at pH 3 adjusted by the addition of  $HNO_3$ . In the Fig. 1, a significant dissolution reaction was observed at the temperatures greater than  $90^\circ C$  and the dissolution rate increases as the reaction temperature goes higher. Under such a low concentration of  $N_2H_4$ , it was evaluated that the solution temperature above  $120^\circ C$  is required to achieve reasonable dissolution performance.

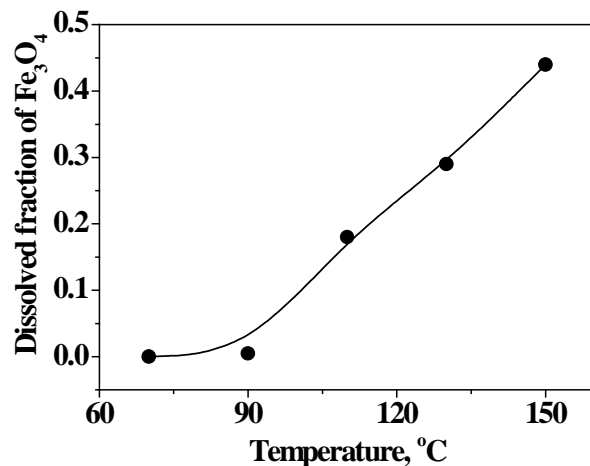


Fig. 1. Effect of temperature on the dissolution of magnetite.

Fig. 2 shows the effect of  $N_2H_4$  concentration on the dissolution of magnetite at 150°C and pH 3. The dissolution rate slowly increases with the increase of hydrazine concentration. The dissolved fraction of magnetite with lower  $N_2H_4$  concentration was too low to be applicable. In other words, to obtain a satisfied dissolution efficiency even in the high solution temperature of 150°C, it was determined that the concentration of hydrazine above 10 mM has to be maintained.

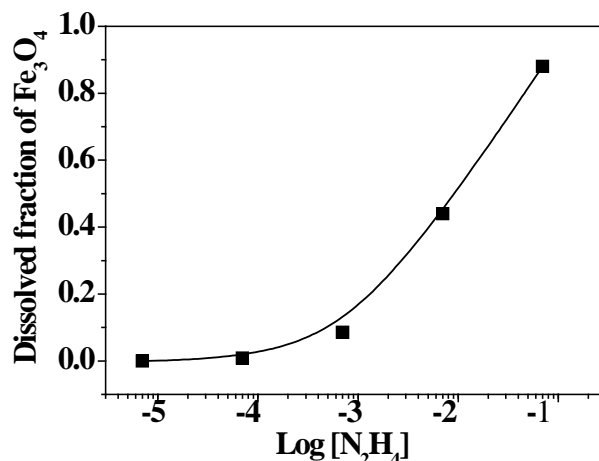


Fig. 2. Effect of hydrazine concentration on the dissolution of magnetite.

Fig. 3 shows the effect of metal ion addition on the dissolution of magnetite in the  $N_2H_4$ - $HNO_3$  system under the condition of 70 mM  $N_2H_4$  and 0.5 mM metal ions, at 95°C and pH 3. After a number of tests with the addition of varied transition metal ions, we found that only copper ions had a remarkable influence to the magnetite dissolution. The dissolution efficiency of magnetite in the case with the addition of Cu ions was improved by 50%, which means the Cu ion can provide more effective reduction path through the coordination with hydrazine. In the previous works, it was reported that transition metal ions form a complex with hydrazine in an aqueous solution or ethanolic solution [5, 6]. Even though the identification of the substitute related Cu ions in the solution is not fully studied, it is assumed potentially as a unidentate, bidentate, or bridging ligands. We also assume that the complex of Cu ion with hydrazine adhered to the ferric

ion site of magnetite, and the complex effectively reduced the ferric ions.

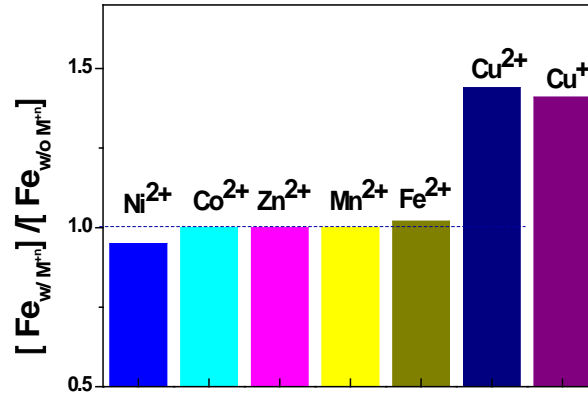
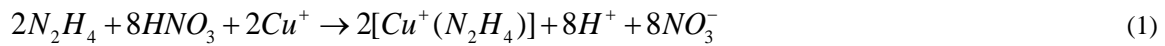


Fig. 3. Effect of metal ion addition on the dissolution of magnetite.

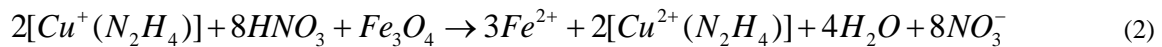
### THE CONCEPT OF HYBRID PROCESS

HYBRID process uses a hydrazine as a strong reducing agent and Cu ion as a catalyst to form a  $\text{Cu}^+(\text{N}_2\text{H}_4)$  coordination compound which transfers an electron from a cuprous ion to a ferric ion to be reduced to a ferrous ion. The formation of  $\text{Cu}^+(\text{N}_2\text{H}_4)$  coordination compound was observed through a single crystal XRD and the complex of nitrogen atom and Cu(I) ion was identified by Far-FTIR analysis. The proposed mechanisms of complex formation and decontamination are as follows.

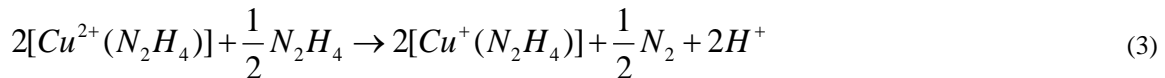
#### Formation of coordination complex



#### Decontamination



#### Regeneration of Cu<sup>+</sup> ion



### DECONTAMINATION PERFORMANCE TEST

Decontamination performance tests of multi-step NP-HYBRID process were carried out using radioactive specimen taken from the fuel test loop (FTL) installed in HANARO, which is a 30 MW open-pool type multi-purpose research reactor in Korea being operated since 1995. Two cycles of NP-HYBRID process were applied with the duration of each decontamination step for 10 hours. Fig. 4 shows the decontamination test results. The initial contact dose rate of the specimen was *ca.* 520  $\mu\text{Sv/h}$  before decontamination and decreased by *ca.* 20  $\mu\text{Sv/h}$  after one cycle of NP-HYBRID process, which means 96 % removal of the initial contact dose rate. After 2nd cycle of the process, dose rate became as low as *ca.* 0.5  $\mu\text{Sv/h}$ , which means 99.9 % removal of the initial dose rate. As shown in Fig. 4, the FTL specimen gradually turns back to the state

before contamination after the application of two cycles of NP-HYBRID process.

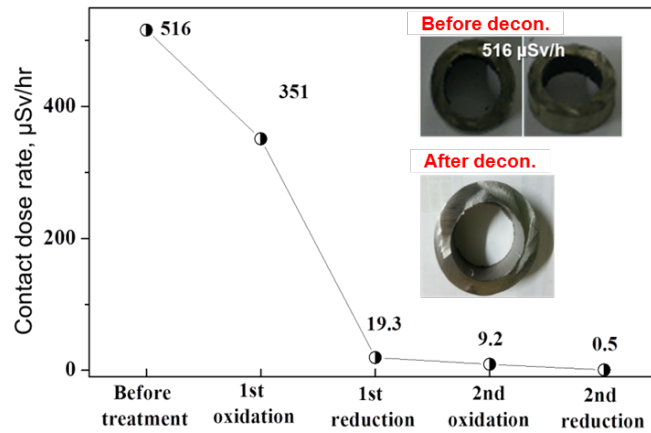


Fig. 4. Decontamination performance test by the application of NP-HYBRID process.

### METAL INTEGRITY TO THE CORROSION IN HYBRID PROCESS

The general corrosion rates of Inconel 600 and 304 SS in HYBRID process were compared with those of typical oxalic acid process as shown in Fig. 5. Significantly low corrosion rates were found on both specimen tested in HYBRID solution. Moreover there was no pitting or IGA on their surfaces in HYBRID solution as given in Fig. 6. From this result, it was confirmed that HYBRID solution has a higher stability against the corrosion on structural metals used in a primary coolant system.

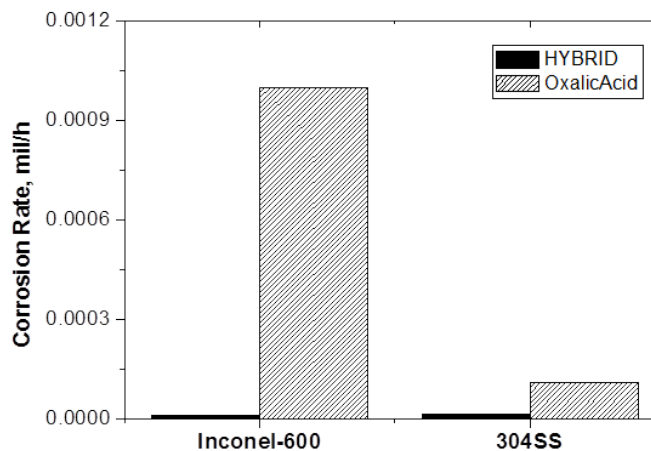


Fig. 5. Comparison of general corrosion rate of Inconel 600 and 304 SS in the HYBRID and typical oxalic acid (2000 ppm) process at 95°C for 20 h.

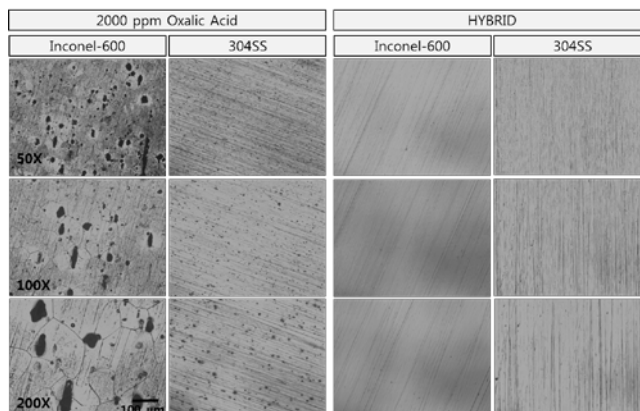


Fig. 6. Surface morphology of Inconel 600 and 304 SS corroded in the HYBRID and typical oxalic acid (2000 ppm) process at 95°C for 20 h.

### CHEMICAL DECOMPOSITION OF HYDRAZINE

In terms of secondary waste generation after the completion of chemical decontamination, decomposition tests of hydrazine were conducted. It was reported that the oxidation of hydrazine in the presence of copper ion as a catalyst is closely related to the decomposition of hydrogen peroxide as follows [7].



The higher cupric ion concentration is, the faster the decomposition reaction of hydrazine goes. When the temperature and the solution pH increased, the decomposition reaction rate of hydrazine also increased. Whereas one step excess injection of hydrogen peroxide could not decompose the hydrazine efficiently, the decomposed portion of hydrazine, on the other hand, could be increased by the repetitive continual injection of hydrogen peroxide as shown in Fig. 7. It was found that hydrazine in HYBRID solution was completely decomposed into water and nitrogen by the oxidation with hydrogen peroxide.

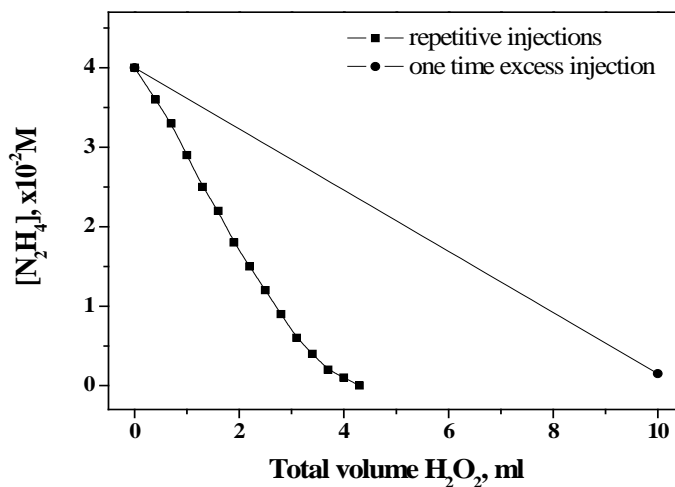


Fig. 7. Effect of injection volume of H<sub>2</sub>O<sub>2</sub> on the decomposition of N<sub>2</sub>H<sub>4</sub>.

## CONCLUSIONS

A chemical decontamination for the reactor coolant system in the phases of maintenance and repair, periodic safety assessment, and decommissioning of NPPs is quite important to mitigate the occupational exposure and improve the work safety. Along this line, KAERI has developed the unique HYBRID decontamination process to complement or improve the performance, environmental friendliness, and process safety through the basic tests on the dissolution of magnetite and the decontamination performance tests using radioactive specimen obtained from the FTL.

The plausible decontamination mechanism in HYBRID process was suggested based on the formation of a Cu<sup>+</sup>(N<sub>2</sub>H<sub>4</sub>) coordination compound which plays an important part in the dissolution of magnetite.

Decontamination performance in NP-HYBRID process using FTL specimen contaminated mainly with Co-60 was proved to be good as much as 99.9% radioactivity is removed by the application of 2 cycles of oxidative and reductive process.

The integrity of base metal to the corrosion in HYBRID process was considerably excellent compared with that in typical oxalic acid based reductive chemical decontamination processes and it is expected that the amount of secondary wastes can be reduced by the chemical decomposition of hydrazine as a main decontamination reagent in HYBRID solution resulting water and nitrogen.

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