



## Application of a Modified Electrochemical System for Surface Decontamination of Radioactive Metal Waste

J. H. Lee, Y. K. Lim, H. Y. Yang, S. W. Shin, M. J. Song

Nuclear Environment Technology Institute, Korea Hydro & Nuclear Power Co., Ltd, Korea

### ABSTRACT

In order to develop an effective metal decontamination technique, some experiments were carried out using a modified electrochemical decontamination process. The operational parameters such as current density and reaction time in the electrolytic process were investigated to decide the optimum conditions for the decontamination of the carbon steel generated from nuclear power plants. Decontamination efficiency of the modified electrolytic process, when applied to carbon steel, was much higher than that of the conventional one. In the case of surface contamination, most of the radioactivity is localized within a 10  $\mu\text{m}$  thickness from the surface, in general. Through a series of experiments, 16  $\mu\text{m}$  thickness changes were found in carbon steel with the current density and reaction time as 0.4  $\text{A}/\text{cm}^2$  and 30 minute, respectively. Based on the results of small modified electrochemical experiments, the large lab scale electrochemical decontamination system was designed and manufactured. In particular, it is not necessary to install an extra washing tank because an ultrasonic oscillator is attached to the bottom of the electrolytic decontamination reactor. This system was also designed to decontaminate both sides of the metal waste simultaneously.

**KEY WORD:** modified electrochemical system, radioactive metal waste, current density, electrochemical decontamination, neutral salt electrolyte

### INTRODUCTION

Due to the increase in reactor-years of several nuclear power plants (NPPs) among the 18 operating plants in Korea, a large amount of metal waste has been generated from the maintenance of aged components and equipment in some old NPPs. A considerable portion of the contaminated metal wastes are considered to have radioactive contaminants only on the metal surface, which can be easily removed by applying appropriate decontamination techniques. By reusing the decontaminated metal waste below clearance level, radioactive metal waste amounts from NPPs can be remarkably reduced.<sup>1</sup> The decontamination processes to remove the surface contamination of radioactive metal wastes are physical, chemical and the electrochemical decontamination process. Among these processes, the electrochemical process has a lot of applications for decontamination of radioactive metal wastes because of its fast reaction time and high decontamination efficiency.<sup>2</sup>

Since the conventional electrolytic decontamination system uses the radioactive metal waste as an anode electrode, radiological exposure to workers is a serious problem when the radioactive metal waste is handled after decontamination. It is also difficult to decontaminate various shapes of radioactive metal waste because of its insufficiency in an electrolytic reaction area.<sup>3</sup> Various electrolytes such as sulfuric acid, phosphoric acid and sodium sulfate etc. have been used in the electrochemical decontamination process. Among these, it did not need to neutralize secondary waste and produce the radionuclide deposits that are easily treated by filtration in case using neutral salt electrolyte.

The purpose of this study is to investigate the applicable operational parameters such as current density, reaction time and electrolyte concentration of the modified electrochemical decontamination process, which use the anode and cathode electrodes simultaneously, for decontamination of radioactive metal waste.

### MATERIAL AND METHOD

#### 1. Experimental

Small and large lab-scale electrochemical decontamination setups were designed and manufactured. A small electrochemical decontamination setup consists of a programmable digital DC electronic loader, magnetic stirrer, electrode supporter and ventilation system. This experimental setup is manufactured for use with a 30  $\text{cm}^2$  electrode area and 0.013  $\text{A}/\text{cm}^2$  current density. 5 reactors and 10 electrode supporters were designed for use simultaneously (Fig. 1). Based on the small setups, the large lab scale electrochemical decontamination system was designed and manufactured. This system consists of a waste holding part, ultrasonic-electrochemical decontamination reactor and wastewater circulation parts. In particular, it is not necessary to install an extra washing tank because the ultrasonic oscillator is attached to the bottom of the electrolytic decontamination reactor. This system was also designed to decontaminate both sides of the metal waste by rotation of metal waste. Large lab-scale modified electrochemical decontamination process is showed in Figs. 2. 3.

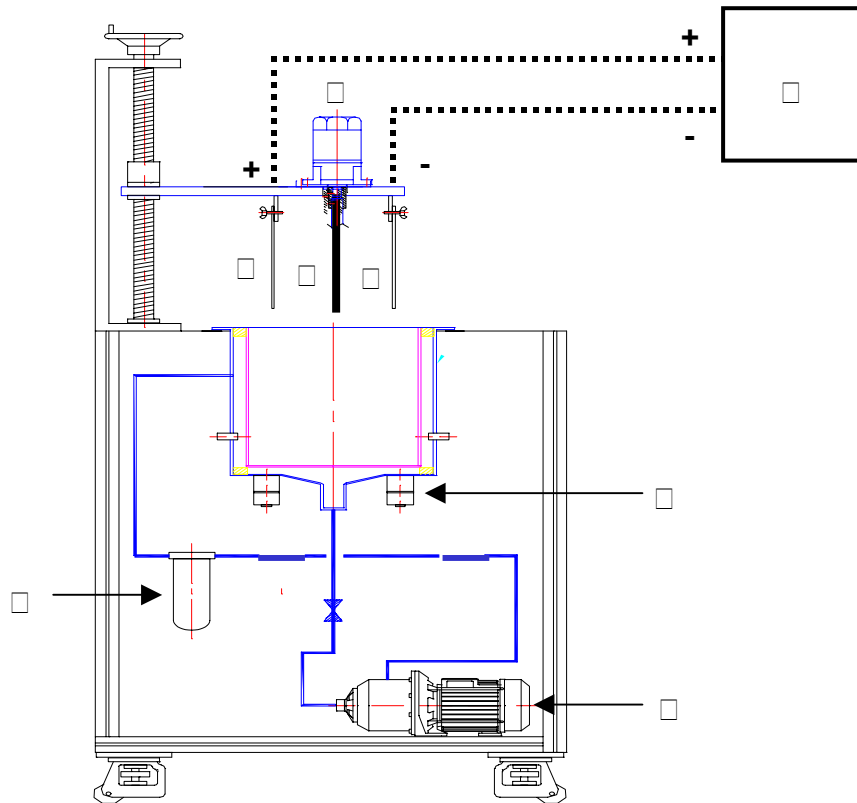


Fig. 1. small electrochemical decontamination setups

Fig. 2. Large lab-scale modified electrochemical decontamination system

## 2. Experimental Methods and Analyses

Carbon steel was used as the simulated metal wastes with dimensions of 30×70×2mm in the small system and 100×200×3mm in the large lab-scale modified electrochemical system. The conventional process used simulated metal wastes as the anode and titanium as the cathode. On the other hand, the modified process used inconel and Hastelloy



(1) Anode (2) Metal Waste (3) Cathode (4) ultrasonic oscillator  
(5) Pump (6) Filter (7) Power Supply System (8) Rotating Motor

Fig. 3. Schematic diagram on large lab-scale modified electrochemical decontamination system

as the anode and titanium as the cathode and installed carbon steel in the middle of both electrodes. Sodium sulfate solution was prepared with a range from 0.5 to 1.7 M. The experiments were performed from 10 to 60 min at room temperature with the current density ranging from 0.06 to 0.41A/cm<sup>2</sup>. The analyses were performed for characteristics such as weight loss and thickness change of the metal wastes after decontamination.

## RESULTS

### 1. Effects on electrochemical decontamination methods

The Conventional and modified electrolytic decontamination experiments were performed in a 1.7 M solution of sodium sulfate with a 0.3 A/m<sup>2</sup> current density. The experimental conditions are summarized in table 1. Fig. 4 and fig. 5 show the weight losses and thickness changes of the simulated metal wastes after conventional and modified electrochemical decontamination. Metal waste in the modified electrolytic decontamination system showed a weight loss of 7.7mg/m<sup>2</sup> and thickness change of 9.8 μm while they reacted up to 2.9mg/m<sup>2</sup> and 3.7μm in the conventional system with a 0.3 A/m<sup>2</sup> current density and 1.7 M sodium sulfate.

Table 1. Experimental conditions on conventional and modified electrochemical decontamination

Electrolyte	Na <sub>2</sub> SO <sub>4</sub> 1.7 mol/L
Simulated metal waste	Carbon Steel (SS41)
Dimension of metal waste	70 ×30 ×2 mm modified system 150 ×70 ×2 mm conventional system
Material of Electrode	Inconel-600, Titanium
Dimension of Electrode	150 ×30 ×2 mm
Current Density	0.3 A/cm <sup>2</sup>
Temperature	Room Temp.
Distance of each Electrode	50 mm
Reaction Time	1 hr

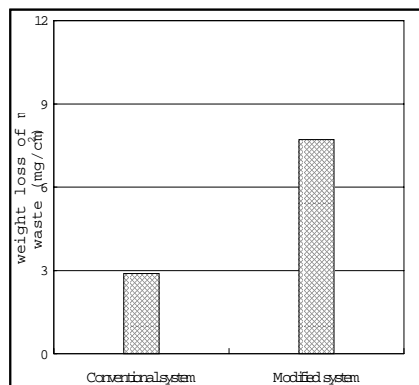


Fig. 4. Weight losses of simulated metal wastes after conventional and modified electrochemical decontamination

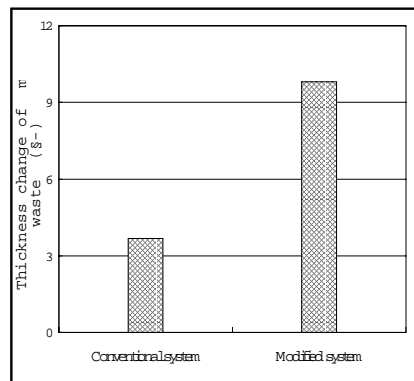


Fig. 5. Thickness changes of simulated metal wastes after conventional and modified electrochemical decontamination

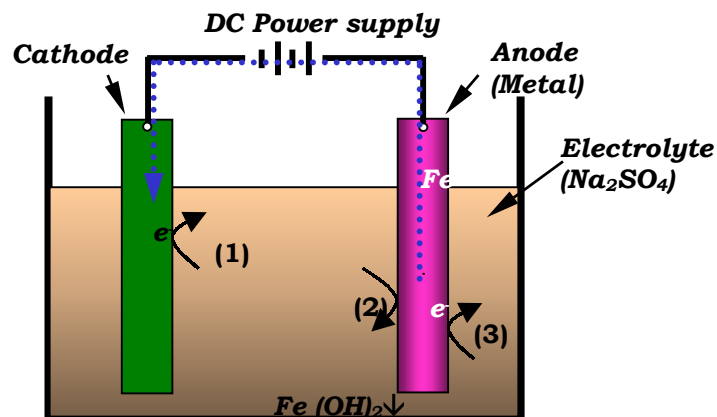


Fig. 6. Schematic diagram of the conventional electrochemical decontamination process

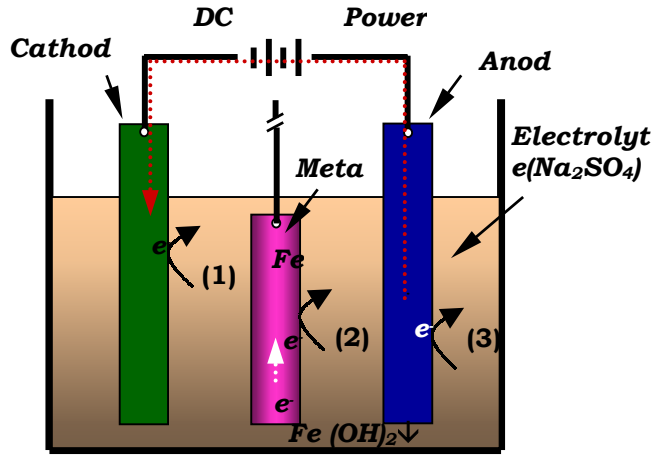


Fig. 7. Schematic diagram of the modified electrochemical decontamination process

The surface of the simulated metal waste(M) is dissolved by the following reaction in the case of applying both the conventional and modified electrochemical decontamination<sup>4</sup>.

- a) conventional electrochemical decontamination (Fig. 6)
- cathode  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (1)
- anode  $\text{M} \rightarrow \text{M}^{n+} + \text{ne}^- \rightarrow \text{M}(\text{OH})_n$  (2)
- anode  $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 1/2 \text{O}_2 + 2\text{e}^-$  (3)
- b) Modified electrochemical decontamination (Fig. 7)
- cathode  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (1)
- Metal waste  $\text{M} \rightarrow \text{M}^{n+} + \text{ne}^- \rightarrow \text{M}(\text{OH})_n$  (2)
- anode  $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 1/2 \text{O}_2 + 2\text{e}^-$  (3)

The simulated metal waste can be decontaminated by the above electrochemical decontamination mechanism. As for the results of this research, in a condition of 0.3 A/cm<sup>2</sup> current density and 1.7 M sodium sulfate, the modified electrochemical decontamination process can decontaminate more effectively than the conventional decontamination process because of the different anode material which causes higher induced electro-motive forces.

## 2. Effects on reaction time

Modified electrolytic decontamination experiments were performed to investigate the optimum decontamination time. An anode and cathode were used with Hastelloy and titanium respectively, and the simulated metal waste was located in the middle between the anode and cathode. The experimental conditions are summarized in table 2 and the results are as follows.

Table 2. Experimental conditions for the decontamination effect on reaction time.

Electrolyte	Na <sub>2</sub> SO <sub>4</sub> 1.5 M
Specimens	Carbon Steel
Specimen Size	70 ×30 ×2 mm
Electrode Material	Hastelloy(+), Ti(-)
Electrode Size	150 ×30 ×2 mm
Current Density	0.4 A/cm <sup>2</sup>
Operation Temp.	Room Temp.
Electrode Distance	50 mm
Reaction Time	10 ~ 60 minutes

Fig. 8 shows the thickness change of the simulated metal wastes for the above conditions. Metal wastes showed thickness changes of 5.2 to 30.5 mm with an increasing reaction time ranged from 10 to 60 min. 30 min is considered to be an applicable reaction time which showed a 16 mm of surface etching on the metal waste. T. IZUMIDA et al.<sup>5</sup> reported that most radioactivity is assumed to be localized within a 10 mm from the surface. In this research, 30 min is considered to be an applicable reaction time which showed a 16 mm of surface etching on the metal waste. It is expected to decontaminate most radioactive metal wastes which are contaminated on the surface below the level for their unrestricted release into the environment by this modified electrolytic decontamination system.

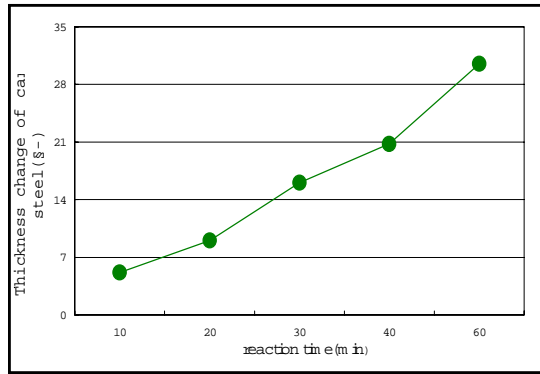


Fig. 8. Plot of etching thickness vs. reaction time.

### 3. Effects on current density and electrolytes concentration

To find an optimum concentration of neutral electrolyte and current density, a modified electrolytic decontamination experiment was performed in a sodium sulfate solution from 0.5 to 1.7 M with a current density ranging from 0.06 to 0.41 A/cm<sup>2</sup>. The experimental conditions are summarized in table 3.

Table 3. Experimental conditions for selection of current density and electrolyte concentration

Electrolyte	Na <sub>2</sub> SO <sub>4</sub> 0.5 ~ 1.7 M
Specimen Material	Carbon Steel
Specimen Size	70 × 30 × 2 mm
Electrode Material	Hastelloy(+), Ti(-)
Electrode Size	150 × 30 × 2 mm
Current Density	0.06 ~ 0.41 A/cm <sup>2</sup>
Operation Temp.	Room Temp.
Electrode Distance	50 mm
Reaction Time	30 minutes

Fig. 9 shows the different thickness changes of the simulated metal wastes for the above conditions. Metal wastes showed thickness changes from 0.4 to 15.8 g by increasing the concentration of the sodium sulfate from 0.5 to 1.7M and current density ranging from 0.06 to 0.41 A/cm<sup>2</sup>. The condition of 0.4 A/cm<sup>2</sup> current density and 1.5 M sodium sulfate showed a 15.8 g of surface etching on the metal waste and are considered to be the applicable current density and electrolyte concentration.

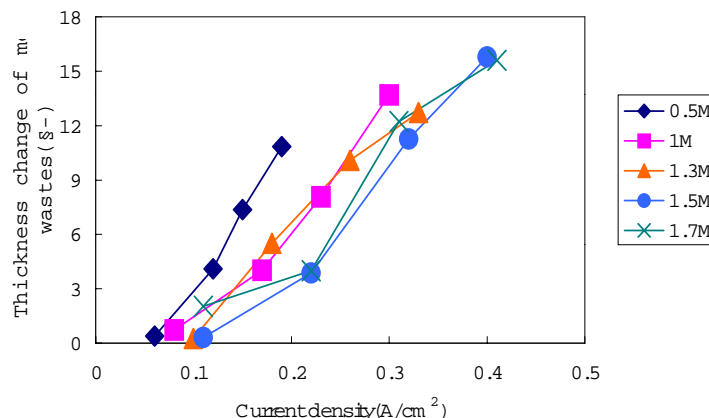


Fig. 9 Plot of thickness change of metal Waste vs. current density for the various concentration of electrolyte

Generally, the relation between the amounts of mass transport, ( $W$ ) and electricity ( $it$ ), is represented by the following expression.

$$W = \frac{M}{nF} it$$

where  $i$  is the current,  $t$  is the time,  $M$  is molecular weight,  $n$  is the number of electron and  $F$  is Faraday constant. Current density ( $I$ ) can be represented by rearranging above expression as follows.

$$I = \frac{i}{A} = nF \left( \frac{W}{M} \right) \left( \frac{1}{t} \right) \left( \frac{1}{A} \right) = nFv$$

where  $A$  is electrode area and  $v$  is electrochemical reaction rate<sup>6</sup>. It indicates that current density is proportional to the electrochemical reaction rate. Thus, as for the results of this research, the decontamination efficiency is increased in proportion to the current density ranging from 0.06 to 0.41A/cm<sup>2</sup>.

#### 4. Effects on scale up of experimental setups

Based on the operational parameters in the small modified decontamination experiment, the experiments were performed to find the decontamination efficiency of the scale up effects. The experimental conditions are shown in table 4.

Table 4. Experimental conditions for scale up study

	Small experimental setup	Large lab-scale experimental setups
Electrolyte	Na <sub>2</sub> SO <sub>4</sub> 0.5 mol/L	Na <sub>2</sub> SO <sub>4</sub> 0.5 mol/L
Specimen Material	Carbon steel,	Carbon steel,
Size	70×30×2 mm	200×100×3 mm
Electrode Material	Inconel(+), Titanium(-)	Inconel(+), Titanium(-)
Electrical Currents	0.4 A/cm <sup>2</sup>	0.4 A/cm <sup>2</sup>
Temp	25	25
Distance of Electrode	15 mm	15 mm
Reaction Time	60 min	60 min

Fig. 10 shows the different thickness changes of the simulated metal wastes for the above conditions. The thickness change of carbon steel was 12 μm in the small experiment and 11.4 μm in the lab-scale experiment which means size increase does not create adverse effects for the decontamination reaction.

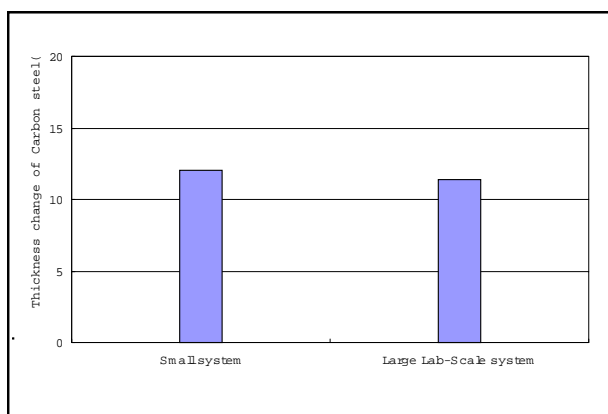


Fig. 10 Thickness change of carbon steel after decontamination by small and large lab-scale electrochemical decontamination.

#### CONCLUSION

Conventional and modified electrolytic decontamination experiments were performed in a solution of sodium sulfate for the decontamination of carbon steel as the simulated metal wastes which are generated in large amounts from nuclear power plants. The effect of reaction time, current density and concentration of electrolytes in the modified electrolytic decontamination system were examined to remove the surface contamination of the simulated radioactive metal wastes. As for the results of this research, the modified electrochemical decontamination process can

decontaminate more effectively than the conventional decontamination process by applying different anode material which causes higher induced electro-motive forces. When 0.5 M sodium sulfate, 0.4 A/cm<sup>2</sup> current density and 30 minutes reaction time were applied in the modified process, a 16 • thickness change that is expected to remove most surface contamination in radioactive metal wastes was achieved on carbon steel which is the main material of radioactive metal waste in nuclear power plants. The decontamination efficiency of metal waste showed similar results with the small and large lab-scale modified electrochemical system. The application of this modified electrolytic decontamination system is expected to play a considerable role for decontamination of radioactive metal waste in nuclear power plants in the near future.

## REFERENCE

1. OECD/NEA. *Decontamination Techniques Used in Decommissioning Activities*, Report by the NEA Task Group on Decontamination, 1996.
2. *Radioactive Metal Waste Recycling Technology Development.*: Korea Atomic Research Institute, 1997, KAERI/AR-474/97.
3. *Development of Metal Surface Decontamination Technology for the Volume Reduction of Radwaste.*: Nuclear Environment Technology Institute, 2001, TM.P2001.3.
4. *Decontamination Method of Radioactive Metal Waste*, Japan Patent Book, Research No. 2064(C), pp.37 ~ 44, 1994.
5. T. Izumida et al., "Electrolytic Decontamination of Surface Contaminated Metal by Alternating Electrolysis Using Square Wave Current in a Neutral Salt Electrolyte", *Nuclear Technology*, Vol.70, Aug., p.249~253, 1985.
6. Junyoung ,Kim. *Recent Electrochemistry and Industry*. Seoul National University, 1985, pp117 ~ 121.