

## **Electrochemical and Sludge Dissolution Behavior During a Copper Removal Process for Chemical Cleaning on the Secondary Side of Nuclear Steam Generators**

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**원전 증기발생기 2차측 화학세정을 위한 제동공정중의**

**전기화학적 거동 및 슬러지용해 거동**

**허도행 · 정한섭 · 김우철 · 채성기**

한국원자력연구소

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### **Abstract**

Two major goals for chemical cleaning on the secondary side of nuclear steam generators are to remove sludge effectively and to minimize corrosion of base metals. In this work, electrochemical and sludge dissolution behaviors have been investigated in order to find out which parameters are critical and important during a copper removal process for chemical cleaning and to evaluate safety aspects and effectiveness of two major copper removal processes developed commercially in foreign countries. Hydrogen peroxide is very effective for the process to use EDTA,  $\text{NH}_4\text{OH}$  and EDA at  $38^\circ\text{C}$  to control the potential of copper in a potential range good for copper sludge removal. Corrosion rates for carbon steel SA 285 Gr.C and Alloy 600 are very small during this process if it is controlled properly. However, the corrosion rate of SA 285 Gr.C will be increased greatly if its corrosion potential is maintained below  $-450\text{mV}$ . The process to use EDA and ammonium carbonate is effective at  $60^\circ\text{C}$  to dissolve copper sludge if the corrosion potential of copper can be controlled above  $-200\text{mV}$ . However, it is very difficult to raise the corrosion potential of copper to this range by air blowing and stirring.

### **요 약**

원전 증기발생기 2차측 화학세정시 두가지 주요 목표는 슬러지 제거를 효과적으로 하는 것과 모

재금속의 부식을 최소화하는데 있다. 본 연구에서는 전기화학 실험과 슬러지 용해 실험을 통하여 제동공정 중에 어떤 인자들이 중요한 역할을 하는지 확인하고 외국에서 개발된 두가지 제동공정에 대하여 안전성 측면과 슬러지 제거 효과를 비교, 평가하고자 하였다.

38°C에서 EDTA,  $\text{NH}_4\text{OH}$ , EDA를 사용하는 제동공정에 있어서  $\text{H}_2\text{O}_2$ 는 구리슬러지 제거에 적합한 전위구역으로 구리의 전위를 높여주는데 매우 효과적이었다. 이런 전위구역에서 SA 285 Grade C와 Alloy 600 재료의 부식속도는 매우 작았다. 그러나 전위가 -450 mV 이하로 유지될 때 SA 285 Grade C 재료의 부식속도 증가가 예상된다. 60°C에서 EDA,  $(\text{NH}_4)_2\text{CO}_3$ 를 사용하는 공정은 구리의 부식전위가 -200 mV 이상으로 유지될 때 효과적인 제동이 가능하였으나 전위를 공기주입과 용액교반으로 이 구역으로 올리기는 매우 어려웠다.

## 1. Introduction

Sludge accumulation on the tubesheet in nuclear steam generators can cause local concentration of chemicals in the crevice due to local boiling and provide corrosive environments to steam generator tubing which is part of the pressure boundary between the primary system and the secondary system. In addition, steam generator tubes can be damaged by formation and progression of pitting defects in the presence of copper species in the sludge.

The accumulated sludge can not be removed effectively by mechanical methods such as continuous blow-down or sludge lancing. Therefore, chemical cleaning to remove sludge is one of the methods to retard the propagation rate of defects and to prevent defect formation. Two major generic chemical cleaning processes have been developed<sup>[1-4]</sup> in foreign countries and have been performed at some nuclear power plants<sup>[5,6]</sup>. One of the processes uses EDTA and  $\text{NH}_4\text{OH}$ . pH is finally controlled by EDA and hydrogen peroxide is added after this final pH control. The other process is known to use EDA and  $(\text{NH}_4)_2\text{CO}_3$  as an activator and air is blown during the process. However, some proprietary technical data have not been published and the published data are too limited to evaluate critical parameters, safety aspects and effectiveness of these processes and to modify these generic processes.

In this work, sludge dissolution behavior and electrochemical behavior have been tested to evaluate two major copper removal processes and to find out which parameters are critical and important, with goals to remove sludge effectively and to minimize corrosion of base metals.

## 2. Experimental

### 2.1. Materials and Chemicals

SA 285 Grade C carbon steel, Alloy 600 and Cu rod were machined to have 0.63 cm diameter and 3.0 cm length. These cylindrical specimens were ground with SiC papers down to 600 grade, degreased with acetone and rinsed with distilled water before tests. Sanicro 70 was used as an Alloy 600. Reagent grade EDTA (Ethylenediaminetetraacetic Acid), EDA (Ethylenediamine),  $\text{NH}_4\text{OH}$  and hydrogen peroxide were used. EDTA powder was stirred in distilled water as a  $\text{NH}_4\text{OH}$  solution was added until EDTA was dissolved completely. Final pH was controlled by adding EDA solution. Reagent grade ammonium carbonate was used for the process to use EDA only.

### 2.2. Sludge Dissolution Test

Reagent grade Cu powder was used by 40g/L and the solution was stirred in a glass container by an external device. Copper concentrations were

analyzed by an Atomic Absorption Spectrophotometer.

### 2.3. Electrochemical Test

A Princeton Applied Research Model 173 Potentiostat, Model 376 Logarithmic Current Converter, Model 175 Universal Programmer, Model 379 Digital Coulometer and X-Y recorder were used for electrochemical tests. Each cylindrical specimen was screwed and connected to an Alloy 600 rod with 3 mm diameter shielded by Teflon and it was used as a working electrode for electrochemical tests. Galvanic corrosion was prevented for this working electrode. A Calomel electrode and a graphite electrode were used as a reference electrode and a counter electrode, respectively. Single anodic scanning was used at a scanning rate 30mV/min to obtain polarization

curves.

## 3. Results and Discussion

### 3.1. Sludge Dissolution Tests

The effect of hydrogen peroxide concentration on copper sludge dissolution was tested at 38°C with copper powder in the solution in Figure 1. This solution was prepared as described previously and stirred during the test. Copper concentration in the solution increases much as the concentration of hydrogen peroxide increases from 1% to 2% and copper concentration increases slightly as the concentration of hydrogen peroxide increases from 2% to 3%.

Temperature dependence on copper sludge removal was investigated in Figure 2. Copper concentration increases slightly as temperature in-

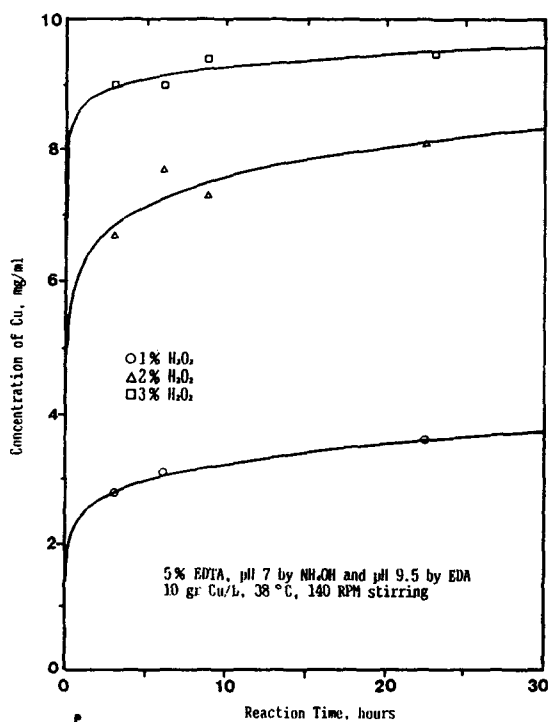


Fig. 1. The effect of H<sub>2</sub>O<sub>2</sub> concentration on Cu dissolution

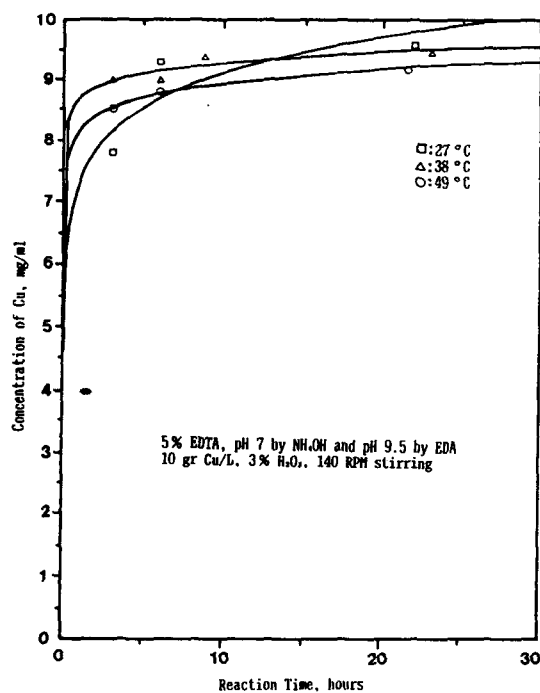


Fig. 2. The effect of temperature on Cu dissolution

creases from 27°C to 49°C in 6 hours. However, the difference is small. And there is a temperature limit since hydrogen peroxide is getting unstable as the temperature increases, especially with the presence of sludge.

Effect of final pH of the solution on the copper sludge dissolution was tested at 38°C in Figure 3. Final pH was controlled by adding EDA. As the pH decreases from 9.5 to 9.0, copper concentration increases. However, corrosion of other base metals should be considered in this case.

Copper sludge dissolution behavior was tested in 2% EDA and  $(\text{NH}_4)_2\text{CO}_3$  at 60°C with 200cc/min air blowing during the process and the test results were shown in Figure 4. 10.8 g Cu powder per 1 liter of solution was charged for this test. As the  $(\text{NH}_4)_2\text{CO}_3$  concentration increases from 5.6 to 56.4 g/L, copper concentration in-

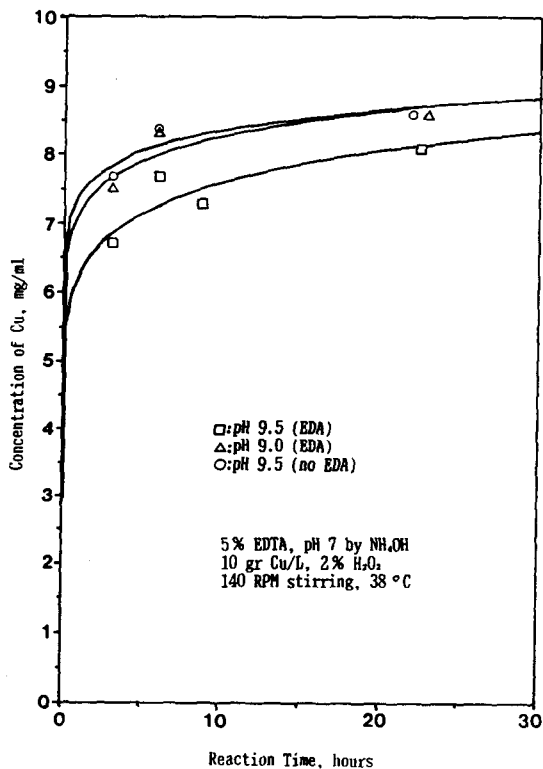


Fig. 3. The effect of pH adjustment on Cu dissolution

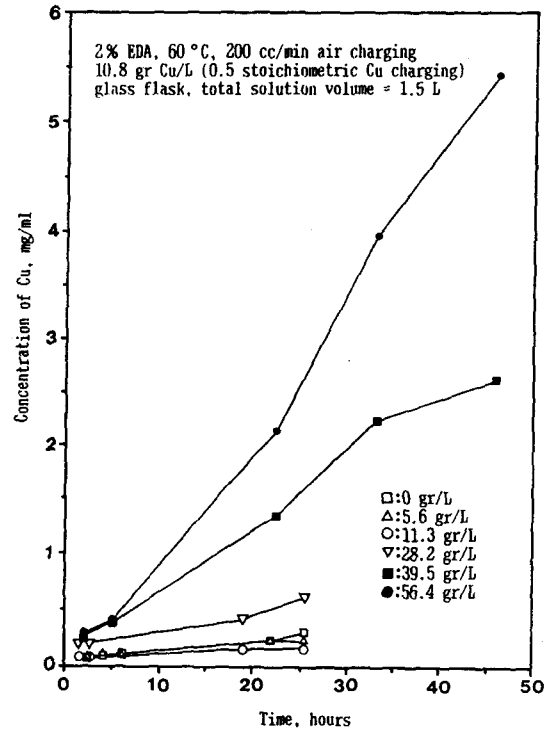


Fig. 4. The effect of  $(\text{NH}_4)_2\text{CO}_3$  concentration on Cu dissolution

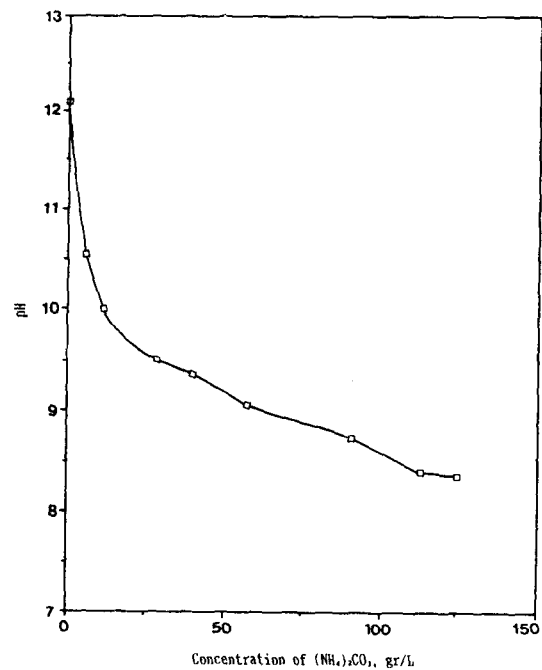


Fig. 5. pH variation of 2% EDA solution vs. ammonium carbonate concentration

creases from 0.2 to 1.9 mg/ml in 20 hours which is a typical period with this process. However, this Cu concentration value is much lower than the values by the process with hydrogen peroxide in Figure 1. Figure 5 shows corresponding pH values when  $(\text{NH}_4)_2\text{CO}_3$  is added.

### 3.2. Electrochemical Tests

Figure 6 shows polarization curves for SA 285 Gr.C carbon steel, Cu and Alloy 600 in the mixed solution of 5% EDTA,  $\text{NH}_4\text{OH}$  and EDA at  $38^\circ\text{C}$ . pH was controlled to 9.5 in case of Cu, there is a large anodic current density peak from potential  $-0.5$  to  $+0.4$  volt. SA 285 Gr.C shows an anodic current density peak around  $-0.7$  volt. Alloy 600 has very low current density values from  $-0.5$  to

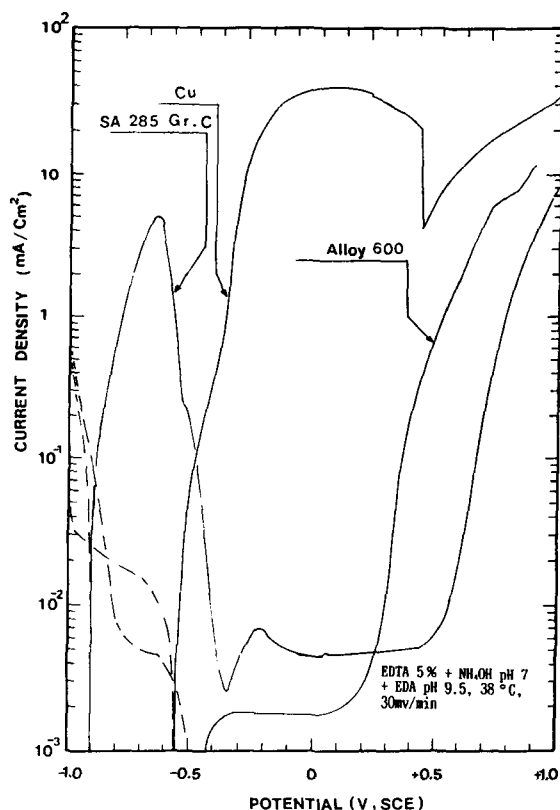


Fig. 6. Polarization curves for SA 285 Gr.C, Cu and Alloy 600 in 5% EDTA +  $\text{NH}_4\text{OH}$  + EDA solution with pH 9.5 at  $38^\circ\text{C}$

+0.2 volt. Corrosion potentials were measured with SA 285 Gr.C, Cu and Alloy 600 in Figure 7. When  $\text{H}_2\text{O}_2$  was added to 3%, corrosion potentials were increased to about +0.1 volt. The effect of  $\text{H}_2\text{O}_2$  concentration on the corrosion potential of Cu was investigated in Figure 8. The corrosion potential of Cu was increased from  $-0.56$  to  $-0.32$  volt by the addition of 1%  $\text{H}_2\text{O}_2$  and it was increased to +0.05 volt at 2%  $\text{H}_2\text{O}_2$  concentration after 4 hour tests. Similar corrosion potentials around +0.1 volt were measured at 3% and 5%  $\text{H}_2\text{O}_2$  concentrations. From these data, the following results can be obtained.

- $\text{H}_2\text{O}_2$  is very effective to increase the corrosion potential of Cu and to remove copper content in sludge
- $\text{H}_2\text{O}_2$  concentration is not enough at 1% to control corrosion potential in an optimum range for copper removal.  $\text{H}_2\text{O}_2$  concentration more than 2% is sufficient and the corrosion potential is increased slightly in an optimum range at 5%.
- If the corrosion potential of carbon steel SA 285 Gr.C is controlled from  $-0.6$  to  $-0.8$  volt inadequately during a copper removal process, considerable amount of Fe corrosion will be expected.
- The corrosion rate of Alloy 600 is very small during a copper removal step.

The copper removal process with EDA and air blowing uses  $(\text{NH}_4)_2\text{CO}_3$  as an activator. Effect of  $(\text{NH}_4)_2\text{CO}_3$  on polarization curves was tested for the copper removal process with EDTA,  $\text{NH}_4\text{OH}$ , EDA and  $\text{H}_2\text{O}_2$  in Figure 9. The anodic current density for Cu was not increased by adding 1%  $(\text{NH}_4)_2\text{CO}_3$  in the controlled potential range by  $\text{H}_2\text{O}_2$  injection for copper removal. However, it can eliminate a current density drop at +0.4 volt, which was shown without  $(\text{NH}_4)_2\text{CO}_3$ . What reaction is involved in this potential range has not been investigated yet. From these data, it is shown that  $(\text{NH}_4)_2\text{CO}_3$  is not effective for the process

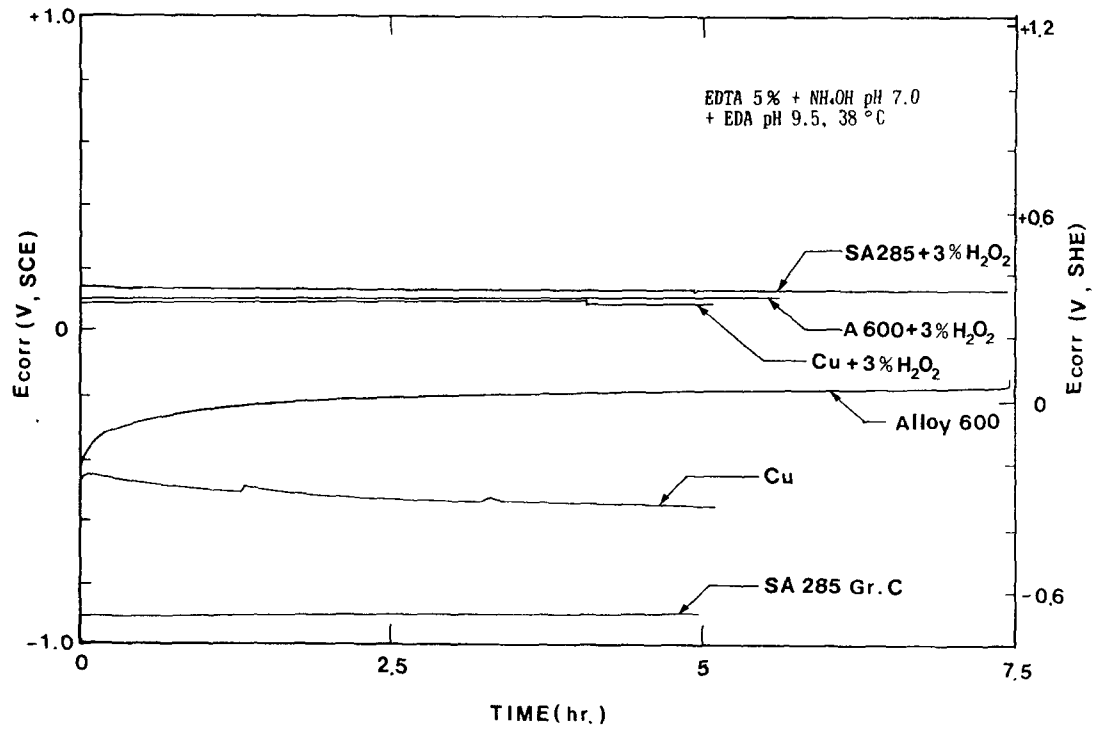


Fig. 7. Corrosion potentials for SA 285 Gr.C, Cu and Alloy 600 with or without 3%  $\text{H}_2\text{O}_2$

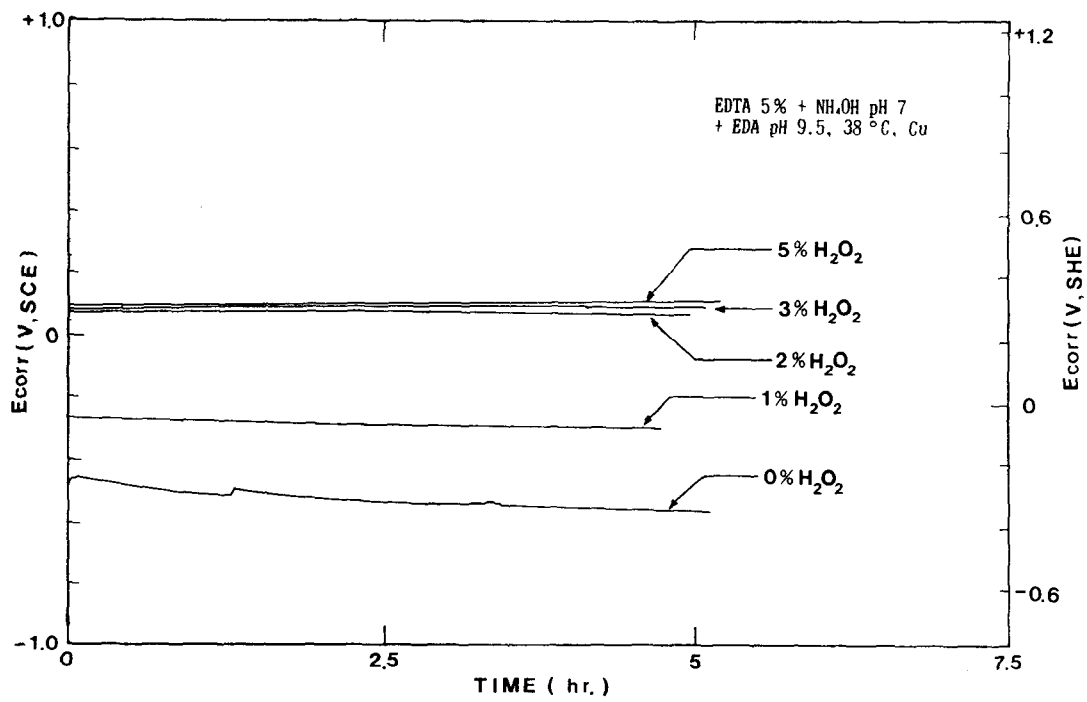


Fig. 8. Effect of  $\text{H}_2\text{O}_2$  concentration on corrosion potential for Cu

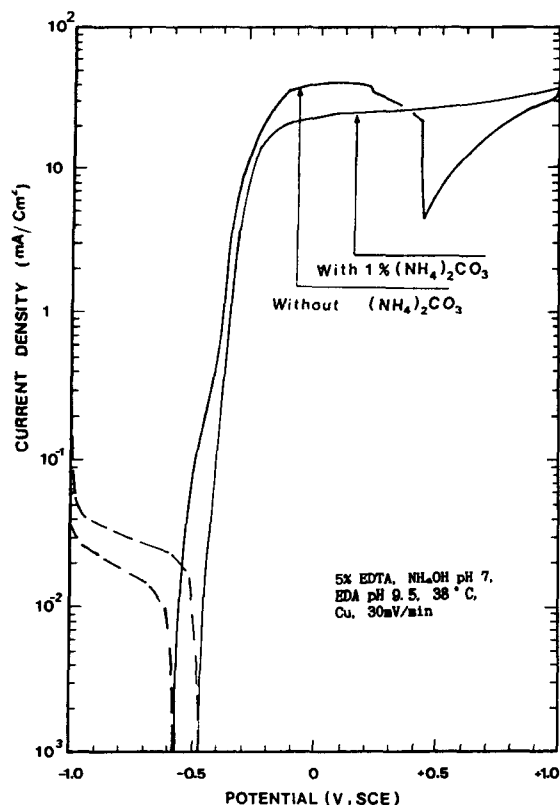


Fig. 9. Polarization curves for Cu in 5% EDTA +  $\text{NH}_4\text{OH}$  + EDA with pH 9.5 at 38°C with or without 1%  $(\text{NH}_4)_2\text{CO}_3$

using EDTA,  $\text{NH}_4\text{OH}$ , EDA and  $\text{H}_2\text{O}_2$ .

Polarization curves were obtained for Cu in 2% EDA + 1%  $(\text{NH}_4)_2\text{CO}_3$  and in 4% EDA + 1%  $(\text{NH}_4)_2\text{CO}_3$  at 60°C in Figure 10. The anodic current density increased much at the potentials above -0.5 volt. Corrosion potentials for Cu were measured in 2% EDA + 1%  $(\text{NH}_4)_2\text{CO}_3$  at 60°C by air blowing and without aeration in Figure 11. The corrosion potential for Cu was -0.55 volt after 5 hour test without aeration. The corrosion potential for Cu was increased to -0.5 volt by 200 cc/min air blowing and it was not increased by changing air blowing rate to 500 cc/min and by stirring later. Therefore, the potential change was only about 50mV by air blowing and it was not so effective as  $\text{H}_2\text{O}_2$ . Since  $\text{H}_2\text{O}_2$  is unstable at elevated temperatures, it is not recommended

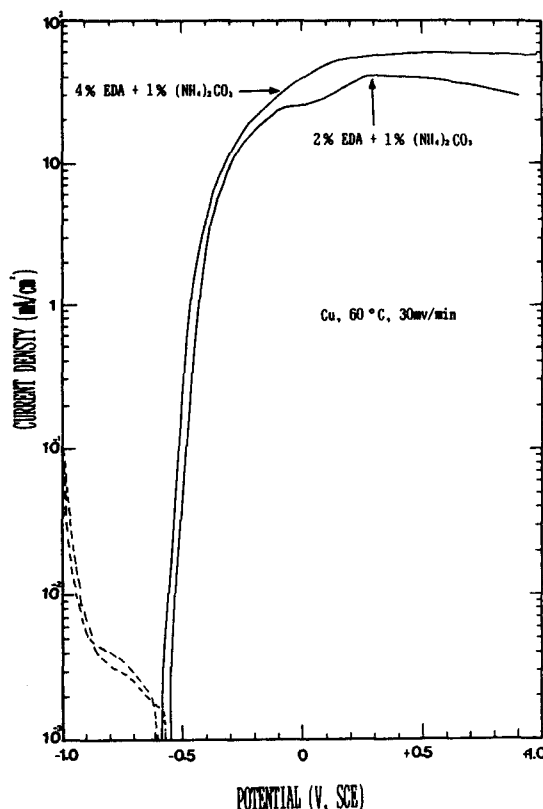


Fig. 10. Polarization curves for Cu in 2% EDA + 1%  $(\text{NH}_4)_2\text{CO}_3$  and 4% EDA + 1%  $(\text{NH}_4)_2\text{CO}_3$  at 60°C

to be used for the process at 60°C.

Anodic current density and total anodic charge data were measured as a function of time for the processes using EDA +  $(\text{NH}_4)_2\text{CO}_3$  at 60°C and EDTA +  $\text{NH}_4\text{OH}$  + EDA at 38°C in Figure 12. Typical corrosion potentials are -500 mV for the process with air blowing and +80mV for the process with  $\text{H}_2\text{O}_2$  injection. Even though the  $\text{H}_2\text{O}_2$  concentration will be decreased gradually with sludge by its decomposition, the copper removal by this process will be effective if the corrosion potential is maintained above -300 mV by the proper control of  $\text{H}_2\text{O}_2$  concentration as shown in Figure 6. The process using air blowing will be satisfactory if the corrosion potential is kept above -200 mV as shown in Figure 10. However, the corrosion potential could be raised up to -500mV

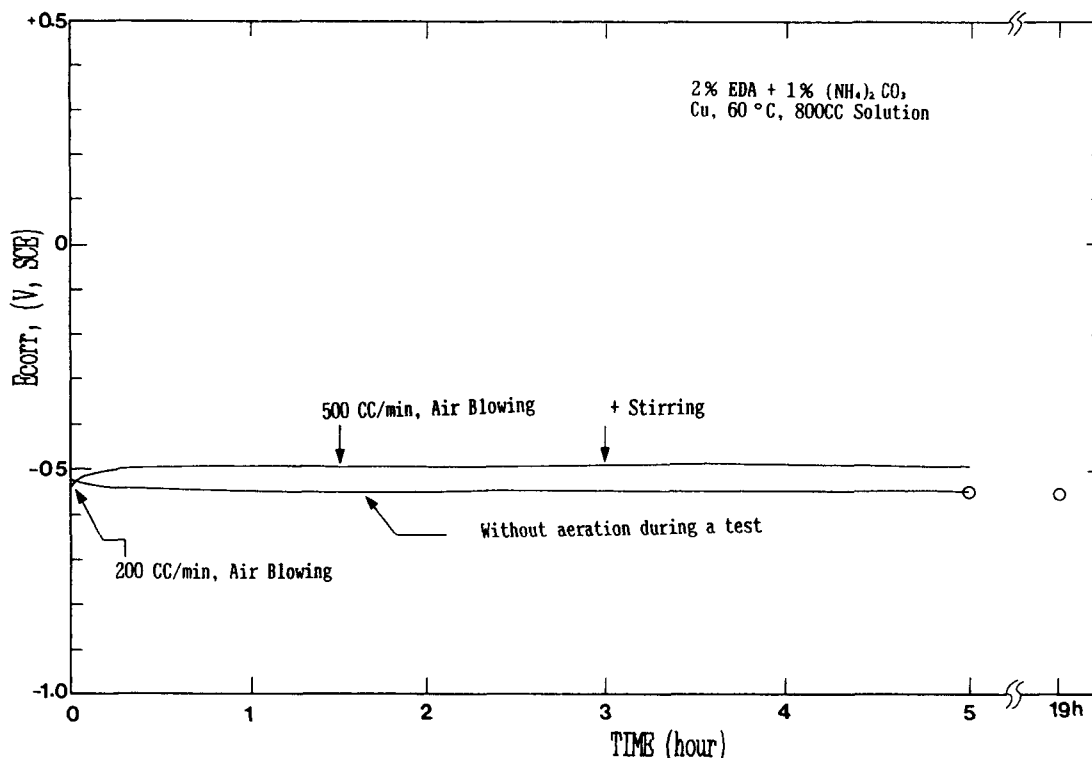


Fig. 11. Effect of air blowing and stirring on the corrosion potential of Cu

by air blowing and stirring. From these data, the process using EDA and  $(\text{NH}_4)_2\text{CO}_3$  at 60°C is fine from a polarization stand point of view. However, it is very difficult to control corrosion potential by air blowing in the optimum range for copper removal. The process using EDTA,  $\text{NH}_4\text{OH}$  and EDA at 38°C is very effective to dissolve copper species by the good control of  $\text{H}_2\text{O}_2$  concentration.

The work performed here by sludge dissolution and electrochemical tests, can be used to evaluate the copper removal processes and to provide technical data base for the application of a recommended copper removal process and to modify the process in the future.

#### 4. Conclusions

1. Hydrogen peroxide is very effective for the process to use EDTA,  $\text{NH}_4\text{OH}$  and EDA at 38°C

to control potential of copper in a potential range from -200mV to +200mV good for copper sludge removal.

2. Corrosion potentials of SA 285 Gr.C, copper and Alloy 600 are increased to about +100 mV by addition of 3% hydrogen peroxide. Corrosion potential of copper is too low to dissolve copper sludge if a hydrogen peroxide concentration is less than 1%.
3. Copper sludge will be dissolved effectively when the corrosion potential of copper is kept from -200mV to +200mV and current density values for SA 285 Gr.C and Alloy 600 are  $5 \mu\text{A}/\text{cm}^2$  and  $2 \mu\text{A}/\text{cm}^2$  in polarization curves at +100 mV, respectively, while the current density for copper is  $40\text{mA}/\text{cm}^2$ . This indicates that corrosion rates for carbon steel SA 285 Gr.C and Alloy 600 are very small during a copper sludge removal process if it is well controlled.

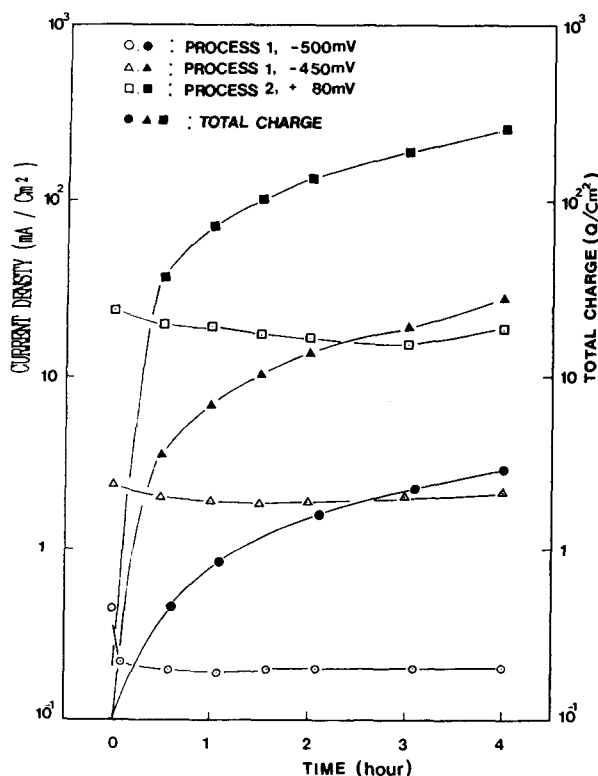


Fig. 12. Comparison of current density and total charge data by Cu removal processes (PROCESS 1: 4% EDA+1%  $(\text{NH}_4)_2\text{CO}_3$ , 60°C PROCESS 2: 5% EDTA,  $\text{NH}_4\text{OH}$  pH 7, EDA pH 9.5, 38°C)

4. However, the corrosion rate of SA 285 Gr.C will be increased greatly if hydrogen peroxide is greatly depleted or SA 285 Gr.C contacts the solution for a certain period before addition of hydrogen peroxide.
5. Ammonium carbonate is not effective for the process to use EDTA,  $\text{NH}_4\text{OH}$  and EDA while it is used as an activator for the process to use EDA for copper sludge removal. But it eliminates a current density drop at +400mV.
6. The process to use EDA and ammonium carbonate is good enough at 60°C to dissolve copper sludge effectively if the corrosion potential of copper can be controlled above -200mV. However, it is very difficult to raise the corrosion potential of copper to this range and its potential

is -500mV when air blowing is applied and the solution is stirred. Hydrogen peroxide is not recommended at 60°C since it is unstable at elevated temperatures.

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