

## 7. Electrolytic Technique for the Chemical Decontamination Process with Sulfuric Acid-Cerium(IV) for Decommissioning

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### ABSTRACT

An electrolyzer with an ion-exchange membrane as the separator has been used to study the electrolytic redox reaction of  $Ce^{4+}/Ce^{3+}$  in sulfuric acid solution, which is a reagent for predismantling system decontamination.

Influencing factors such as current density, cerium concentration, acidity, electrolyte flow rate, membrane type and electrode material were studied experimentally. The results indicate that the redox can be achieved with high conversion even as the cerium concentration is below 0.005 M. However, the current efficiency strongly depends on the cerium concentration. In addition, the acid content and the electrolyte flow rate show little influence on the redox reaction. Both cation and anion membrane are feasible for this process. Therefore, the operation conditions are widely applicable. Moreover, two different electrode materials, platinized titanium meshes and graphite, were used. The results show that the platinized titanium meshes is preferable to the graphite for higher current efficiency.

### 1. INTRODUCTION

A chemical decontamination process with a high decontamination factor (DF) is requested for decommissioning. Usually, the process should be qualified with the characteristics such as the feasibility of treating large or complicated form waste, the secondary waste should be minimized[1]. The conventional chemical decontamination method using acid or alkaline can clean large or complicated equipment but the decontamination rate and DF are small. Therefore, a powerful technique of redox decontamination has been developed[2-5] and the  $Ce^{4+}/Ce^{3+}$  system is a common choice. A  $H_2SO_4$ - $Ce^{4+}$  solution was developed and applied to the primary system of JPDR in 1987[6]. There are many chemical methods, such as adding  $H_2O_2$  or  $Fe^{2+}$  can fulfill the redox of  $Ce^{4+}/Ce^{3+}$ . Nevertheless, the redox proceeded with electrolytic method is the most convenient way. And the redox decontamination process needs an electrolytic unit to regenerate the  $Ce^{4+}$  solution. Suwa et al.[2] reported that the DF was ca. 33 at 90°

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C for 24 h with 0.25 M  $\text{H}_2\text{SO}_4$ - $5 \times 10^{-3}$   $\text{Ce}^{4+}$  but under electrolytic regeneration of  $\text{Ce}^{4+}$  from  $\text{Ce}^{3+}$  during the decontamination, the DF was raised to 460 even at 80° C for 24 h with 0.25 M  $\text{H}_2\text{SO}_4$ - $1.3 \times 10^{-3}$  M  $\text{Ce}^{4+}$ . Moreover, after the decontamination step the  $\text{Ce}^{4+}$  must be reduced to  $\text{Ce}^{3+}$  for the convenience of the subsequent liquid waste treatment. Fujita et al.[4] reported that the  $\text{Ce}^{4+}$  ions remaining in the spent redox solution were effectively reduced to  $\text{Ce}^{3+}$  ions by electrolysis. Therefore, the electrolytic technique is very important for the redox decontamination process. However, the electrolyser design is not much concerned, it is worthy to have further investigation.

The objectives of this study are to develop the technique of using an ion exchange membrane as cell separator and to find its optimum operation conditions.

## 2. EXPERIMENTAL

The cell depicted in Fig.1 is rectangular in cross section in two halves, and made of plexiglass. The internal dimension of each half was  $21 \times 13 \times 1$  cm<sup>3</sup>. The anode and cathode compartment were separated by an ion exchange membrane (Ionac MA-3475 or MC-3470). The two halves of the cell were bolted together using neoprene gasket with two pieces of bakelite plate in the dimension of  $30.5 \times 21 \times 0.8$  cm<sup>3</sup>. There was a piece of propylene screen in each compartment to enhance the mixing of electrolyte. The electrolyte was pumped into the compartment chamber with a diaphragm metering pump from the reservoir. The outlet electrolyte can be totally recirculated or stored in other reservoir without recycle depending on the selected operation method. Platinized titanium meshes with the dimension  $21 \times 13$  cm<sup>2</sup> and rhombic type hole were used as the electrodes. Graphite plate was also used as cathode. The electrode was bolted on the plexiglass with a titanium rod, and this titanium rod was extended to the outside of the compartment, which was used as the port of current feeder. A 10A-30V DC power supply was used in all runs. Constant current was operated to measure the current efficiency.

The solutions were prepared using deionized water and reagent grade chemicals. In each run the volume of catholyte and anolyte was 2 liters respectively. Al samples, each of 3 cm<sup>3</sup>, were taken periodically for analysis. The total cerium concentration was measured with inductive couple plasma (Kontron S35), and the  $\text{Ce}^{4+}$  concentration was determined by the titroprocessor (Metrohm 682). The current efficiency was back calculated from the  $\text{Ce}^{4+}$  concentration change in the electrolyte.

## 3. RESULTS AND DISCUSSION

### 3-1. Effect of current density

The electrochemical reaction rate depends on the applied current. However, as the applied current reaches a value, limiting current, the current efficiency will be drastically decreased if the applied current increases further. The applied current will electrolyze water rather than the cerium species in this case.

Fig.2 shows the effect of applied current on the  $\text{Ce}^{3+}$  oxidation. It indicates that during the same electrolysis cycle

the oxidation percentage increases when the applied current increases from 2 to 5 A. However, when the applied current is over 6 A, the oxidation percentage does not increase further. Fig.3 shows the effect of applied current on the reduction percentage. It can be seen that 4 A is the best, the  $Ce^{4+}$  (0.05 M) are totally reduced to  $Ce^{3+}$  within 10 electrolysis cycle. Comparing Fig.2 and Fig.3, it appears that the electrolytic reduction of  $Ce^{3+}$  from  $Ce^{4+}$  is more effective than that of the electrolytic oxidation of  $Ce^{4+}$  from  $Ce^{3+}$ .

### 3-2. Effect of electrolyte acidity

The acidity of electrolyte will affect the degree of conductivity. The lower acidity is the lower conductivity of the electrolyte. However, the high acidity will induce the evolution of hydrogen at cathode, which would decrease the current efficiency. In addition, the stability of  $Ce^{4+}$  and  $Ce^{3+}$  depends on the acidity too. Therefore, there is a suitable range of acidity for redox decontamination process. The sulfuric acid concentration of sulfuric acid-cerium(IV) solution used in JPDR decontamination experiment was in the range of 0.5-1.0 N[6]. Fujita et al.[4] developed the redox decontamination system with  $HNO_3-Ce^{4+}$  solution and found that 2.0 N  $HNO_3$  was suitable. Therefore, the acidity of  $Ce^{4+}$  solution used in decontamination process is about 0.5-2.0 N.

Fig.4 is the experimental results of the influence of acidity on the electrolytic oxidation of  $Ce^{4+}$  from  $Ce^{3+}$ . It is obvious that the acidity of the electrolyte does not affect the oxidation percentage when the acidity is in the range of 0.5 N to 6.0 N. This result shows that the electrolytic regeneration of  $Ce^{4+}$  is feasible in this acidity range when an ion exchange membrane is used as cell separator. Meanwhile, the electrolytic reduction of  $Ce^{3+}$  from  $Ce^{4+}$  is feasible too in this acidity range, the experimental results are shown in Fig.5. However, it should be noted that the current efficiency will decrease gently due to the problem of  $H_2$  evolution when the acidity is over 8 N. Fortunately, the redox decontamination process is not necessary to use so high acidity.

### 3-3. Effect of electrolyte flow rate

The mixing of electrolyte results from the turbulence of flow for a flow-type electrolyzer. The higher flow rate is the better of mixing. However, the residence time of electrolyte passing through the compartment decreases with increasing flow rate. In addition, high flow rate is energy consumptive.

Fig.6 is the experimental results of the effect of electrolyte flow rate on the  $Ce^{3+}$  oxidation. It indicates that the reaction rate increases with increasing flow rate from 50 to 75  $ml.min^{-1}$  only. The further increasing flow rate does not increase oxidation rate. Therefore, it can be seen that the electrolyte oxidation rate is not limited by the flow rate. Fig.7 shows the experimental results of the influence of flow rate on the  $Ce^{4+}$  reduction. It appears that the reduction percentage are all the same when the flow rates are in the range of 50 to 200  $ml.min^{-1}$ . From Fig.6 and 7, it is clear that the mixing of electrolyte is easy to achieve in this flow-type electrolyzer, the available flow rate is versatile for the demand of whole

decontamination process.

### 3-4. Electrode materials

The redox decontamination technique is one of the oxidative dissolution decontamination methods, so the used electrode materials should be corrosion resistive. Fujita et al.[4] measured the corrosion rate for platinum, gold, titanium, niobium, Hastelloy-C and Zircaloy-2 in the  $Ce^{4+}$ - $HNO_3$  solutions and found that the platinum, gold and titanium were not corroded. In this study, we choose platinized titanium meshes as anode, and platinized titanium meshes or graphite plate as cathode.

Fig.8 is the electrolytic reduction rate comparison between platinized titanium meshes and graphite plate which are used as cathode. The result shown in Fig.8 demonstrates that reduction rate is faster using platinized titanium meshes than that of using graphite plate. Furthermore, the cell voltage of using platinized titanium meshes is lower than that of using graphite. From other investigators' experiences and our own experimental results, it is obvious that the platinized titanium material is a good choice as electrode for  $Ce^{4+}/Ce^{3+}$  redox reaction.

### 3-5. Type of ion exchange membrane

Using ion exchange membrane as cell separator has many advantages such as prevention of reverse reaction of redox, free choice of the ions transferred across the membrane. Generally, there are two types of ion exchange membrane, which are anion and cation membrane. After the pretreatment with sulfuric acid solution, the anion membrane can transfer  $SO_4^{2-}$  ions and the cation membrane can transfer  $H^+$  ions. Therefore, during the electrolysis with cation membrane the  $H^+$  ions are transferred from anode compartment to cathode compartment due to the electric field. On the other hand, the  $SO_4^{2-}$  ions are transferred from cathode compartment to anode compartment if the anion membrane is used as cell separator.

Fig.9 is the results of using different membranes in electrolytic reduction of  $Ce^{4+}$  from  $Ce^{3+}$ . Both anion and cation membrane as separator can achieve 100% reduction, but it seems that the anion membrane is better than cation membrane in this operation condition. In the beforementioned discussion, we know that electrolyte acidity does not drastically affect the redox performance using anion membrane as cell separator. However, the acidity of electrolyte will affect the transfer of  $H^+$  across the membrane when the cation membrane is used. Fig.10 shows that the average current efficiency of  $Ce^{4+}$  reduction increases with increasing electrolyte acidity, but the average current efficiency markedly decreases when the acidity is over 5 N. The phenomenon shown in Fig.10 can be explained as follows. In the beginning, since the electrolyte conductivity and  $H^+$  ions transfer rate depend on the  $[H^+]$ , the average current efficiency of  $Ce^{4+}$  reduction increases as the acidity of electrolyte is from 0.25 to 3 N. However, the increasing  $[H^+]$  both from the initial addition and transferred from anode compartment will enhance the opportunity of evolution of  $H_2$ , so the current efficiency decreases when the acidity is over 5 N. In the meantime, since the acidity does not affect the evolution of  $O_2$  at anode, the acidity of electrolyte would have less influence on oxidation.

### 3-6. Effect of cerium concentration

Although different concentration of cerium solutions all can obtain high conversion in redox reaction, the current efficiency drastically depends on the cerium concentration.

Fig.11 shows that the average current efficiency of  $Ce^{3+}$  oxidation increases linearly with increasing  $Ce^{3+}$  concentration. Fig.12 indicates the same tendency for the  $Ce^{4+}$  reduction. Since we have shown in above that the electrolyte flow rate does not affect the redox rate when the flow rate is over  $70 \text{ ml}\cdot\text{min}^{-1}$ , it seems that redox rate is controlled by the  $Ce^{4+}$  or  $Ce^{3+}$  diffusion rate from the diffusion layer to electrode surface.

### 3-7. Feasibility of simultaneous redox in the same electrolyzer

In the common redox decontamination process, the regeneration of  $Ce^{4+}$  from  $Ce^{3+}$  needs an electrolyzer in which the working electrode is anode. Moreover, the electrolytic reduction of  $Ce^{3+}$  from  $Ce^{4+}$  for the purpose of subsequent wastewater treatment needs another electrolyzer in which the working electrode is cathode. If these two separated steps can be combined into one step,  $Ce^{4+}$  reduction happens in cathode compartment and the  $Ce^{3+}$  oxidation occurs in anode compartment at the same time, then the redox decontamination process can be improved. The electrolyzer using ion exchange membrane as cell separator is suitable for this requirement.

Fig.13 is the performance of simultaneous  $Ce^{4+}/Ce^{3+}$  redox reaction in the same electrolyzer but different compartment with anion membrane as cell separator. It appears that both reduction and oxidation can achieve near 100% conversion in 2 h electrolysis. Experimental result also shows good performance when using cation membrane as cell separator. Therefore, it can conclude that the simultaneous redox of  $Ce^{4+}/Ce^{3+}$  in the same electrolyzer is feasible. This result is encouraging for the improvement of redox decontamination process.

## 4. CONCLUSIONS

An electrolyzer separated with ion exchange membrane is suitable for the redox decontamination process. The experimental results show its widely applicable operation conditions. The available acidity and electrolyte flow rate are versatile for the choice to fit the process requirement. In addition, both anion and cation membrane can be used in  $Ce^{4+}/Ce^{3+}$  redox reaction. The platinized titanium meshes is good material as anode and cathode. Although the current efficiency drastically depends on the cerium concentration, even very diluted cerium solution can achieve high redox conversion within limited electrolysis time. Finally, the most important result is that the simultaneous  $Ce^{4+}/Ce^{3+}$  redox with the same electrolyzer in different compartment can proceed with good performance. And this advantage can be used to improve the redox decontamination process.

## 5. REFERENCES

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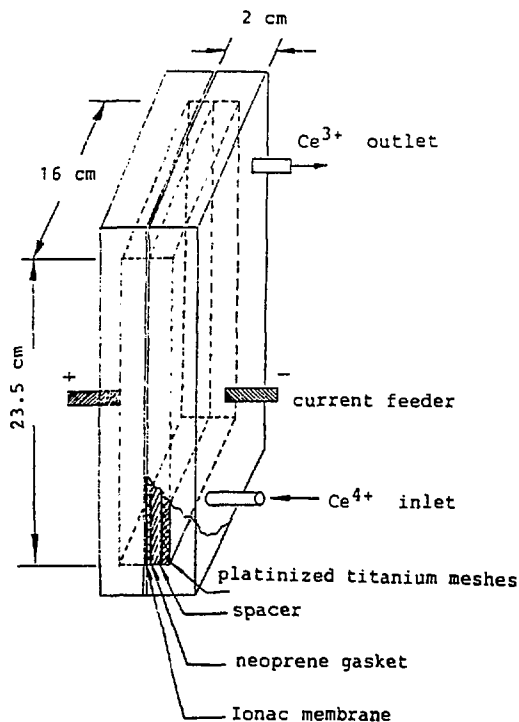
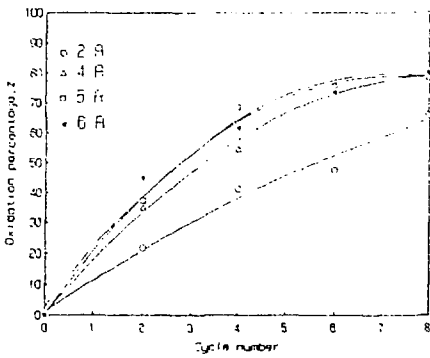


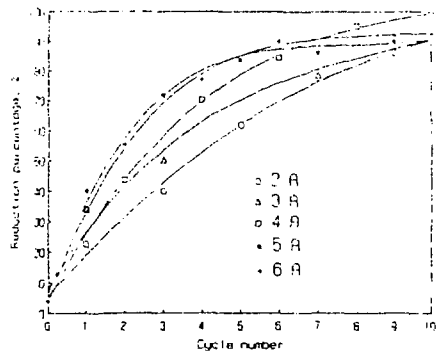
Figure 1. Schematic diagram of electrolyzer used in this experiment.

Figure 2.



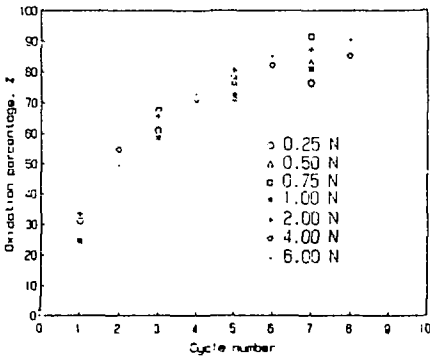
Effect of operation current on the oxidation percentage (initial [Ce<sup>3+</sup>]=0.05 M; [H<sup>+</sup>]=1 N; 1 N H<sub>2</sub>SO<sub>4</sub> solution as catholyte)

Figure 3.



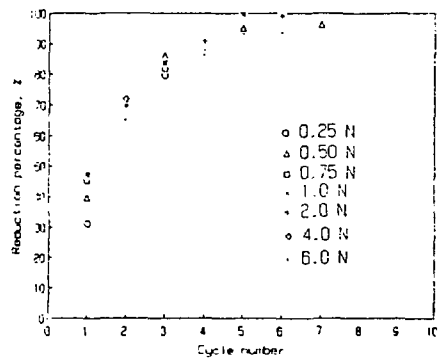
Effect of operation current on the reduction percentage (initial [Ce<sup>4+</sup>]=0.05 M; [H<sup>+</sup>]=1 N; 1 N H<sub>2</sub>SO<sub>4</sub> solution as anolyte)

Figure 4.



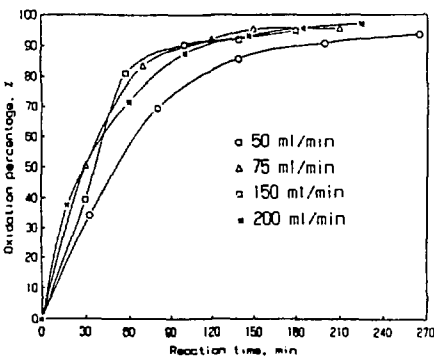
Effect of anolyte acidity on Ce<sup>3+</sup> oxidation with platinumized titanium meshes anode and anion membrane as cell separator([Ce<sup>3+</sup>]=0.0025 M)

Figure 5.



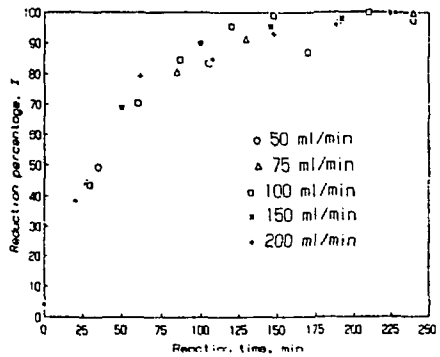
Effect of catholyte acidity on Ce<sup>4+</sup> reduction with platinumized titanium meshes cathode and anion membrane as cell separator(initial [Ce<sup>4+</sup>]=0.0025 M)

Figure 6.



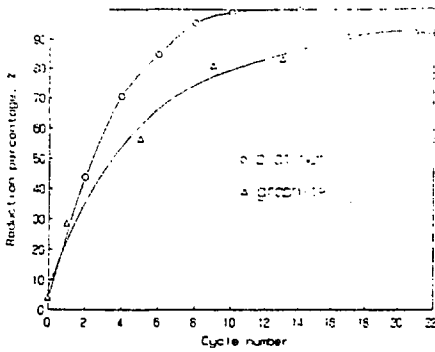
Effect of electrolyte flow rate on Ce<sup>3+</sup> oxidation (operation current=4 A; initial [Ce<sup>3+</sup>]=0.05 M)

Figure 7.



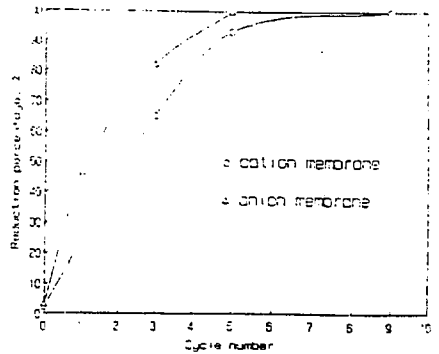
Effect of electrolyte flow rate on Ce<sup>4+</sup> reduction (operation current=4 A; initial [Ce<sup>4+</sup>]=0.05 M)

Figure 8.



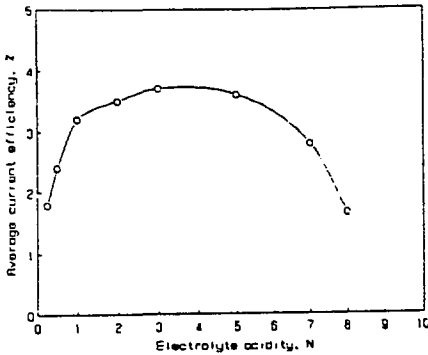
Comparing the reduction performance between the platinumized titanium meshes and graphite as cathode (operation current=4 A; initial  $[Ce^{4+}] = 0.05 M$ )

Figure 9.



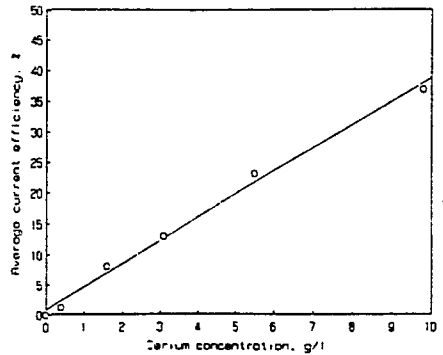
Comparison of  $Ce^{4+}$  reduction percentage between the different type of membrane used as cell separator (initial  $[Ce^{4+}] = 0.05 M$ ;  $[H^+] = 1 N$ )

Figure 10.



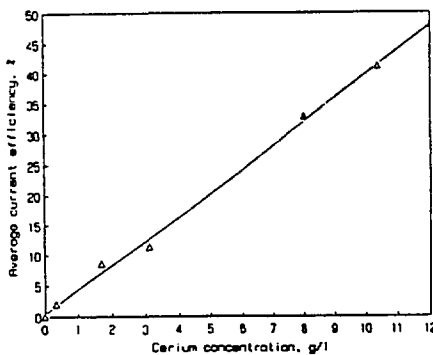
Effect of catholyte acidity on the average  $Ce^{4+}$  reduction current efficiency with platinumized titanium meshes cathode and cation membrane as cell separator (operation current=4 A; initial  $[Ce^{4+}] = 0.005 M$ )

Figure 11.



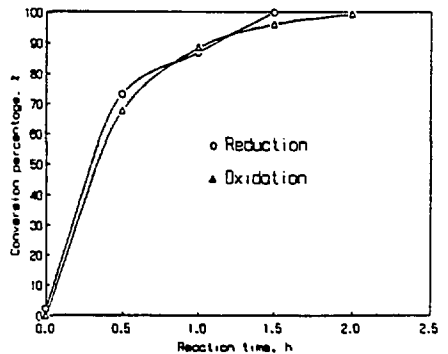
Effect of  $Ce^{3+}$  concentration on the average oxidation current efficiency calculated on the basis of 85% conversion (operation current=4 A;  $[H^+] = 1 N$ )

Figure 12.



Effect of  $Ce^{4+}$  concentration on the average reduction current efficiency calculated on the basis of 90% conversion (operation current=4 A;  $[H^+] = 1 N$ )

Figure 13.



Performance of simultaneous  $Ce^{4+}/Ce^{3+}$  redox reaction in the same electrolyzer but different compartment with anion membrane as cell separator (operation current=6 A; initial  $[Ce^{4+}] = 0.015 M$ ; initial  $[Ce^{3+}] = 0.015 M$ ;  $[H^+] = 6 N$ )