Regeneration of Ce(Ⅲ) in sulfuric-cerium decontamination spent solution

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1. Introduction

Sulfuric-Cerium (S-C) decontamination method has been reviewed as a promising one for the preliminary decontamination of large scale metallic waste such as a retired steam generator. In this process, a regeneration of Ce ion, which is a decontamination reagent, is very important for ensuring process performances. In this study, therefore, regeneration of the spent decontamination solution was performed by using ozone.

The ORP (Oxidation Reduction Potential), which are used to measure the concentration of Ce^{3+} and Ce^{4+} in the Ce regeneration process, was used. In order to evaluate the regeneration of Ce^{3+}, the injected mass of ozone with time was calculated through S-C decontamination waste solution. Furthermore, according to the experiment on S-C decontamination with the simulated sample of SUS and Inconel, the variation of Ce^{4+} concentration, which measured the ratio of $[Ce^{4+}]/[Ce^{3+}]$ from the value of the ORP, and the removal efficiency of metal oxide layer was compared.

2. Materials and method

2.1. Working curve of $[Ce^{4+}]/[Ce^{3+}]$ vs. ORP

The concentration of standard with 10 mM of Ce concentration were made into various ratio of $[Ce^{4+}]/[Ce^{3+}]$ (0.01, 0.05, 0.11, 0.25, 1, 4, 9, 19). And the values of ORP were measured in each standard solution by ORP meter (Table-type ORP meter, Denver Ins.). Finally, standard working curve was plotted through the values of ORP.

2.2. Ce (Ⅲ) regeneration by ozone

The reaction of Ce^{3+} regeneration by ozone is below.

$$2Ce^{3+} + O_3(g) + 2H^+ \rightarrow 2Ce^{4+} + H_2O + O_2(g)\uparrow \quad (1)$$

Ozone was generated with 5 % (v/v, O_2 base) from ozone generator (LAB-1, Ozonetech co.) and was injected into 1.2 L of waste solution (total Ce conc. = 10 mM, sulfuric acid conc. = 0.25M) of S-C decontamination with 1.0 L/min of flow rate. The value of ORP with time was measured when contacted ozone mass is increased. Ce^{4+} concentration was also calculated using ORP value by standard working curve of $[Ce^{4+}]/[Ce^{3+}]$ vs. ORP value.

2.3. Variation of Ce concentration during S-C decontamination process

ORP value with time was measured during S-C decontamination process for the simulated metal oxide of 304 SUS and Inconel 600. Ce^{4+} concentration was also evaluated when metal oxide layer was removed from the surface of 304 SUS and Inconel 600.

3. Results and discussions

Standard working curve of $[Ce^{4+}]/[Ce^{3+}]$ ratio vs. ORP value was shown in Fig. 1. Ce^{4+} concentration could be calculated from this curve by measuring ORP value.

Ce^{4+} concentration change during ozone regeneration process of S-C decontamination waste solution was shown in Fig. 2. Ce^{3+} was regenerated to Ce^{4+} until about 92 % when ozone was supplied for 15 minute (38.2 mmol of ozone).

Fig. 3. shows the variation of Ce^{4+} concentration and weight loss of metal oxide with decontamination time. Metal oxides in SUS and Inconel were completely removed within 2 hrs and 4 hrs, respectively. After the S-C decontamination process, Ce^{4+}, which was remained in the waste solution, was calculated to 13.9 % (1.4 mM) in SUS and 7.0 % (0.7 mM) in Inconel. During 1 hr decontamination, Ce^{4+} conc. was decreased into 25.9 % (2.6 mM) in SUS and 30.6 % (3.1 mM) in Inconel. It is shown that Ce^{4+} was quickly consumed in the initial time of decontamination, resulting in the prompt removal of metal oxide.

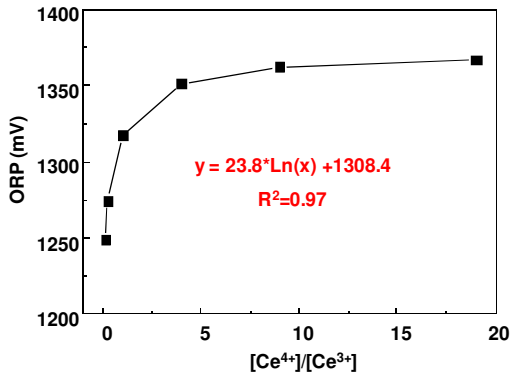


Fig. 1. Standard working curve of $[Ce^{4+}]/[Ce^{3+}]$ ratio vs. ORP value (ORP = 23.8*Ln{$[Ce^{4+}]/[Ce^{3+}]$} + 1308.4, R^2=0.97)

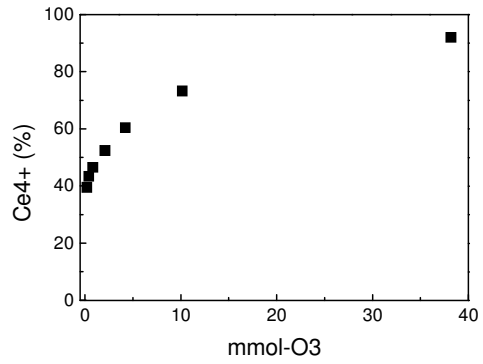
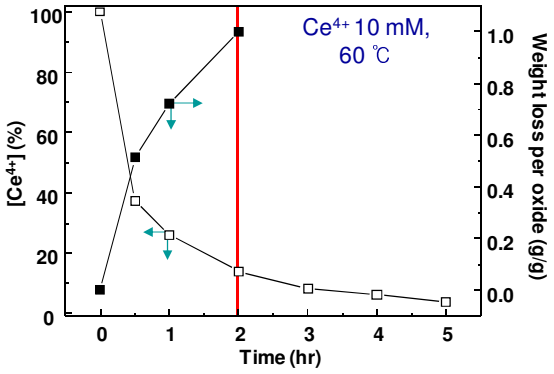
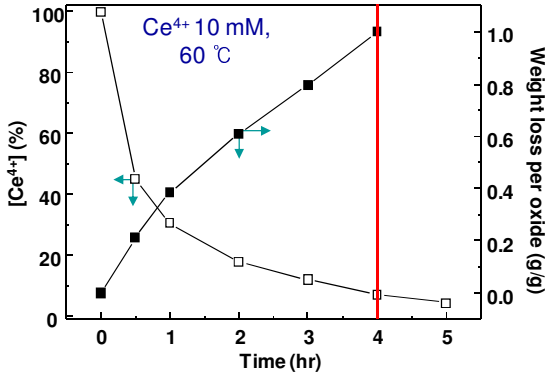


Fig. 2. Ce^{4+} concentration change during ozone regeneration process of S-C decontamination waste solution



(a) SUS



(b) Inconel

Fig. 3. Variation of Ce^{4+} concentration and weight loss of metal oxide with decontamination time (60℃, total Ce conc. = 10 mM)

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