Asian Journal of Chemistry; Vol. 29, No. 7 (2017), 1506-1508

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20542

Measurement of Ce(IV) Concentration and Oxidation of Ce(III) in Foam Decontaminant

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Received: 25 January 2017; *Accepted*: 26 April 2017; *Published online*: 13 May 2017; AJC-18383

In order to regenerate Ce(III) to Ce(IV) in nanoparticle-based foam decontaminant containing tetrapropylenebenzene sulfonate (TBS) surfactant, it is necessary to determine the optimal conditions for ozonation treatment. The research was carried out to determine whether the potentiometric titration method can be used for an analysis of Ce(IV) concentration in nanoparticle-based foam decontaminant. Potentiometric titration with Fe(II) is able to effectively analyze the concentration of Ce(IV) in nanoparticle-based foam decontaminant containing a surfactant regenerated through ozonation treatment. The oxidation conversion rate of Ce(III) was increased with an increase in the flow rate of the gas mixture and ozone injection amount. The oxidation time for 100 % oxidation conversion of Ce(III) at an ozone injection amount of 9.0 and 7.5 g/h was 6.0 h and 7.0 h, respectively. The time required for 100 % oxidation conversion of Ce(III) to Ce(IV) at a specific ozone injection amount can be predicted from these experimental data.

Keywords: Foam, Decontamination, Cerium, Ozone, Oxidation, TBS surfactant.

INTRODUCTION

Facilities that handle radioactive materials deteriorate with age after a long period of operation. Consequently, a decontamination technology has been developed to prevent the proliferation of radioactive materials and reduce the radiation exposure of operators while at work. In particular, foam decontamination technology can significantly reduce the radioactive waste produced after decontamination for large equipment or facilities, because more than 90 % of the decontaminating materials used with this technology consist of gases [1-3]. To improve the stability of the foam, surfactants and inorganic materials such as nanoparticles can be added.

A nanoparticle-based foam decontaminant is composed of a surfactant and nanoparticles for the generation and maintenance of foam and a chemical decontamination agent made of Ce(IV) dissolved in nitric acid. Cerium(IV) will be reduced to Ce(III) through the decontamination process. Oxidizing the cerium(III) can be reused as a decontamination agent, Ce(IV). Oxidation treatment technology by ozone uses its strong oxidizing power [4]. It can be regarded as an environmentally friendly process, because ozone cannot be stored and transported like other industrial gases (because it quickly decays into diatomic oxygen) and must therefore be produced on site and used ozone can immediately begin to decompose [5]. A concentration analysis of Ce(IV) in foam decontaminant containing a surfactant is necessary prior to the derivation of optimal conditions for the regeneration of Ce(III) through ozonation treatment.

A UV spectrometric method using the absorbance or potentiometric method with a potential difference in Ce(III)/Ce(IV), or a potentiometric titration method using Fe(II), can be used for analysis of Ce(IV) concentration. A UV spectrometric method has a problem receiving the influence of the surfactant and a potentiometric method is difficult to use because of the problem of an insignificant change in the potential difference value of the Ce(III)/Ce(IV).

The study was undertaken to determine whether the potentiometric titration method can be used for an analysis of the Ce(IV) concentration in nanoparticle-based foam decontaminant containing a surfactant. A further study was then carried out to determine the optimal conditions for ozonation treatment in the regeneration of Ce(III) to Ce(IV) in the nanoparticle-based foam decontaminant containing surfactant.

EXPERIMENTAL

Measurement of Ce(IV) concentration: The potential change appears as a titration with a 0.1 M Fe(II) solution (ammonium ferrous sulfate, 99 %, Aldrich) of a mixture of 2 M sulfuric acid (or 2 M nitric acid) and 0.1 M Ce(IV) (cerium(IV) ammonium nitrate, 99.5 %, Alfa Aesar), which were measured using an ORP electrode (Epoxy Low Mainte-

nance ORP/ATC Triode No. 9179 BNMD) and were analyzed for the concentration of Ce(IV).

The potential change was measured according to the variation of surfactant concentration in the range of 0.5-1.5 % in order to determine whether the potentiometric titration method is valid for the analysis of Ce(IV) concentration in nanoparticle-based foam decontaminant containing anionic fluorosurfactant Zonyl TBS (Dupont). This was compared with the case in which TBS was not used.

In addition, a mixture of a 0.1 M Ce(IV) solution and a 2 M nitric acid solution was tested in accordance with the potential value changes to examine whether the potentiometric titration method is effective with an acid medium change. It was compared with the behaviour in a 2 M sulfuric acid medium.

Oxidation of Ce(III): A mixture of 0.5 M Ce(III) (cerium(III) nitrate, 99.5 %, Alfa Aesar) and 1 % anionic fluorosurfactant Zonyl TBS (Dupont) in 2 M nitric acid) was prepared and used for the regeneration of Ce(III) through ozonation treatment.

The potentiometric titration method was used for an analysis of the Ce(IV) concentration in the nanoparticle-based foam decontaminant [6]. Ozone was supplied by an ozone generator (Ozonetech lab-1). The oxidation reaction of Ce(III) to Ce(IV) is as follows:

$$2Ce^{3+} + O_3 + 2H^+ \longrightarrow 2Ce^{4+} + O_2 + H_2O$$

RESULTS AND DISCUSSION

Determination of Ce(IV) concentration: It was investigated whether the potentiometric titration method can be used for an analysis of the Ce(IV) concentration, since the analysis on the concentration of Ce(IV) present in the surfactant is difficult by conventional methods such as a UV colorimetric or potentiometric method. In this case, the reaction of Ce(IV) and Fe(II) is as follows:

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$

The potential change in value was measured in a surfactant concentration range of 0.5 to 1.5 % in order to search whether the potentiometric titration method is valid for an analysis of Ce(IV) concentration in nanoparticle-based foam decontaminant containing a TBS surfactant.

As shown in Fig. 1, the same inflection point in the potential appeared at the point at which 20 mL of a Fe(II) solution was added, regardless of the concentration of TBS. These results were the same as in the case of a non-addition of TBS. Therefore, it was found that the TBS surfactant has no effect on an analysis of Ce(IV) concentration by the potentiometric titration method using Fe(II).

Ce(IV) and Fe(II) are present at their most stable state in 1-2 M sulfuric acid. Because the nanoparticle-based foam decontaminant used in this study is made up of 2 M nitric acid, it was examined whether the potentiometric titration method in a 2 M nitric acid medium is effective for an analysis of Ce(IV) concentration. The results show that the same inflection point appeared in the potential at which 20 mL of a Fe(II) solution was added, in both 2 M nitric acid and 2 M sulfuric acid medium. Thus, it is possible to determine the Ce(IV) concentration using the potentiometric titration method with Fe(II) in a 2 M nitric acid medium.

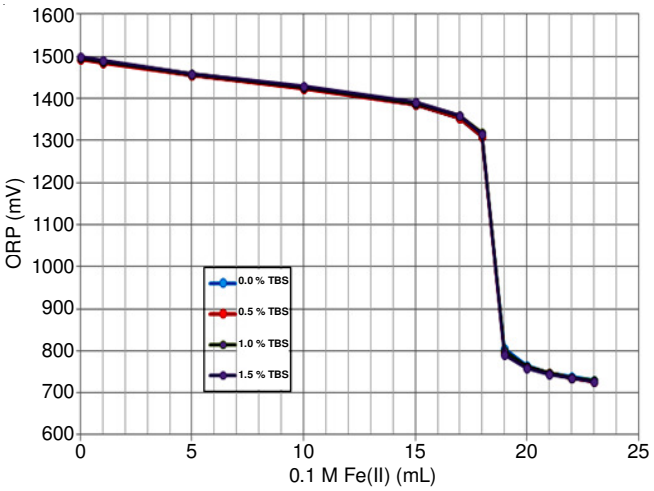

Fig. 1. Potentiometric titration curves using Fe(II) according to TBS concentration of 0-1.5 % in 1M sulfuric acid solution

Nanoparticle-based foam decontaminant used for this study contains TBS surfactant of 1 % in 2 M nitric acid medium. Therefore the effect of TBS surfactant on the potential change for an analysis of Ce(IV) in 2 M nitric acid solution was investigated. As shown in Fig. 2, the same inflection point in the potential appeared at the point at which 20 mL of a Fe(II) solution was added, in both 2 M nitric acid and 2 M nitric acid containing 1 % TBS. It was found that potentiometric titration with Fe(II) can be used for the analysis the concentration of Ce(IV) in nanoparticle-based foam decontaminant containing 1 % TBS surfactant in 2M nitric acid solution.

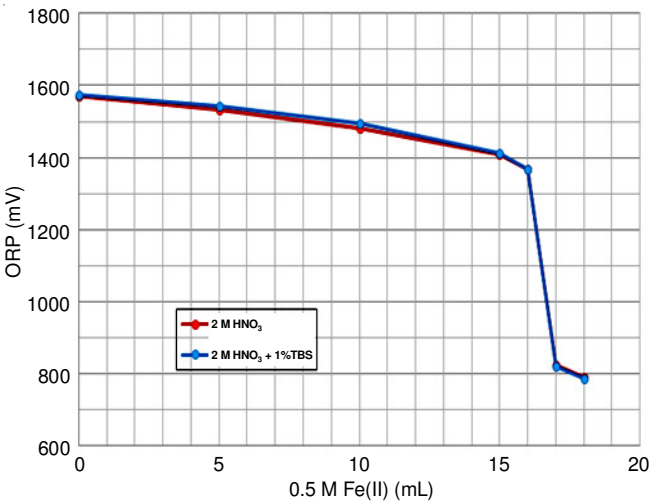

Fig. 2. Effect of TBS surfactant on the measurement of Ce(IV) conc. in 2 M nitric acid solution by potentiometric titrations

Oxidation of Ce(III): The parameters to be considered are the Ce(III) concentration, regeneration temperature and ozone injection volume to derive the optimal conditions for the regeneration of Ce(III) through ozonation treatment. However, the parameter that can be changed is limited by the ozone injection volume, since the Ce(III) concentration and regeneration temperature were fixed. Therefore the oxidation conversion rate of Ce(III) to Ce(IV) over time was examined by changing the flow rate of the gas mixture (air and ozone) corresponding to the amount of ozone desired. The flow rate of the gas mixture was in the range of 0.5-3.0 LPM.

As shown in Fig. 3, the oxidation conversion rate of Ce(III) to Ce(IV) was increased with an increase in the flow rate of the gas mixture during the oxidation time of 7.5 h and the oxidation conversion rate at a flow rate of 2.0 and 3.0 LPM was 55 and 100 %, respectively.

From this result, it was possible to derive the ozone injection amount required for 100 % oxidation conversion of Ce(III).

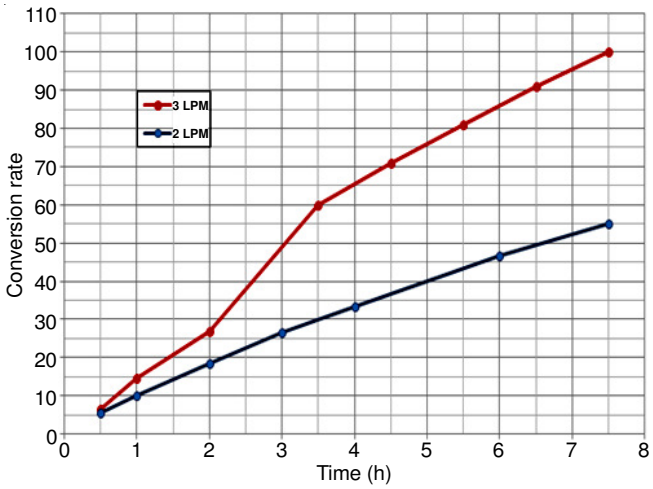

Fig. 3. Ce(III) conversion rate on the variation of the mixed gas flow rate

The effect of TBS surfactant on the oxidation behaviour of Ce(III) to Ce(IV) were investigated. Simillar oxidation behaviours of Ce(III) were as shown in Fig. 4, regardless of the presence of a surfactant TBS. Therefore, it was found that the oxidation of Ce(III) with ozone is effective in nanoparticle based foam decontaminant containing a TBS surfactant.

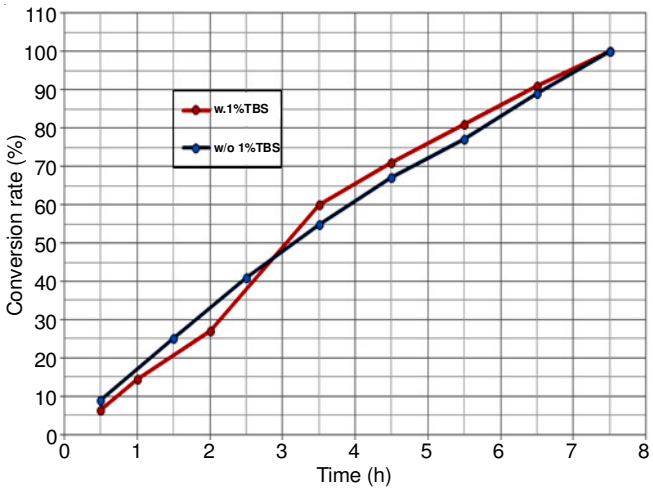

Fig. 4. Effect of TBS surfactant on the Ce(III) conversion rate at a mixed gas flow rate of 3 LPM

The time required for 90-100 % oxidation conversion of Ce(III) was examined by changing the ozone injection amount. Fig. 5 shows the typical results on the oxidation conversion rate of Ce(III) with a variation of ozone injection amount at a gas mixture flow rate of 2.0 LPM. The oxidation conversion rate of Ce(III) to Ce(IV) was increased when increasing the ozone injection amount and the oxidation time for 100 % oxidation conversion of Ce(III) at an ozone injection amount of 9.0 and 7.5 g/h was 6 and 7 h, respectively.

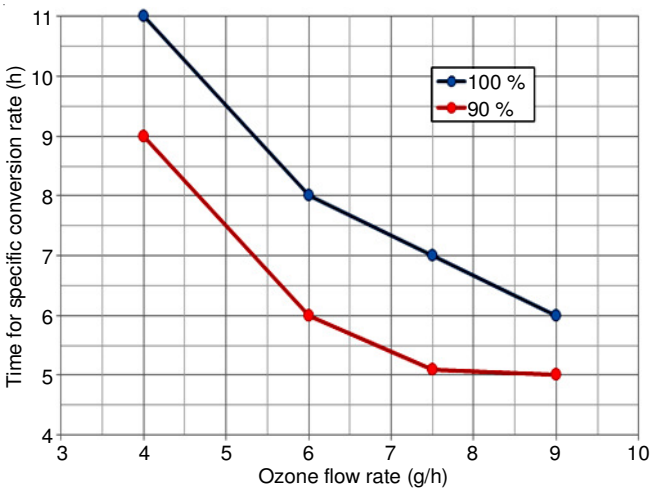

Fig. 5. Oxidation time for specific Ce(III) conversion rate on the variation of ozone flow rate

Conclusions

This study was undertaken to determine the optimal conditions for ozonation treatment in the regeneration of Ce(III) to Ce(IV) in nanoparticle-based foam decontaminant containing a TBS surfactant.

• Potentiometric titration with Fe(II) was able to effectively analyze the concentration of Ce(IV) in nanoparticle-based foam decontaminant containing a surfactant regenerated through ozonation treatment. In addition, it was confirmed that a Ce(IV) concentration analysis is valid using this potentiometric titration method because it exhibits the same behaviour in a different acid medium. Therefore, it will be effectively used for a Ce(IV) concentration measurement, in relation to the subsequent research on the derivation of optimal conditions for the regeneration of Ce(III) through ozonation treatment.

• The oxidation conversion rate of Ce(III) was increased with an increase in the flow rate of the gas mixture and ozone injection amount. The time required for 100 % oxidation conversion of Ce(III) to Ce(IV) at a specific ozone injection amount can be predicted from these experimental data.

ACKNOWLEDGEMENTS

This work has been carried out under the Nuclear R&D Program (2012M2A8A5025655) funded by Ministry of Science, ICT & Future planning.

REFERENCES

1. J. Penfold, I. Tucker, R.K. Thomas and J. Zhang, *Langmuir*, **21**, 10061 (2005); https://doi.org/10.1021/la0505014.
2. B. Fournel, S. Angot and P. Joyer, Decontamination of Phebus Experimental Target Chember using Sprayed Foam, ICONE 10, Arlington, USA (2002).
3. J.P. Turchet, B. Fournel and G. Estienne, Pipe Decontamination Involving String-Foam Circulation, Icone 10, Arlington, USA (2002).
4. V.P. Shilov and A.M. Fedoseev, Role of Peroxynitrite in Oxidation of *f*-Element Ions in Solutions, Frumkin Institute of Physical Chemistry and Electrochemistry (2013).
5. K. Shishido, S. Muromachi and R. Ohmura, *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.*, **7**, 111 (2013).
6. C.H. Jung, H.B. Yang *et al.*, Measurement of Ce(IV) Concentration in Foam Decontaminant Containing Fluorosurfactant, Transactions of the Korean Nuclear Society, Spring Meeting, Jeju, Korea, May 12-13 (2016).