Ferrous Oxalate Precipitation Behavior Depending on Ferrous Concentration and Temperature for Reductive Chemical Decontamination of Nuclear Power Plant

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1. Introduction

Chemical decontamination is the way to dissolve the magnetite of the radioactive corrosion oxide film inside of nuclear plant with ferrous ion using oxalic acid. The main chemical reactions are as follows.

$$Fe_3O_4 + 8H^+ \rightarrow 2Fe^{3+} + Fe^{2+} + 4H_2O$$
 (1)

$$Fe_3O_4 + H_2C_2O_4 + 6H \to 3Fe^{2+} + 2CO_2 + 4H_2O \qquad (2)$$

However, Fe ions increase above the certain concentration range, precipitation reaction is occurred by oxalic acid as follows.

$$Fe^{2+} + C_2 O_4^{2-} \to FeC_2 O_4$$
 (3)

These precipitations hinder in removing Fe ions and effective decontaminating by forming foreign substances in inner wall of treatment process. Therefore, this study was researched the behavior of precipitation reaction of ferrous ions and oxalic acid by varying ferrous ion concentrations, reaction time and temperature conditions.

2. Experimental details

Materials of this experiment were used $FeCl_2$ and oxalic acid dehydrate (DAEJUNG, Korea). All experiments were used in 500 mL volume.

To determine the effect of ferrous ion

concentration on Fe-oxalate precipitate formation, experiments were performed in the 1, 2, 4 and 8 mM ferrous ions at 95 $^{\circ}$ C.

Effect of temperature on the formation of Feoxalate precipitate was evaluated at 40 and 60 $^{\circ}$ C with initial concentration of oxalic acid of 8 mM. The times of sample extraction were the same as other experiment.

3. Results and discussion

At Fig. 1, we can see that precipitation behavior was observed at over 1 mM. And it needs almost 1 hour for precipitation reaction to occur. The slopes at 25 $^{\circ}$ C became gentle between 40 and 60 min. After 60 min, the precipitate amount seems to be constant.

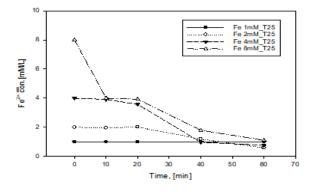


Fig. 1. Ferrous oxalate precipitation behavior depending on $FeCl_2 \mbox{ concentration [mM] at 25 \ }^{\circ}C.$

At Fig. 2, precipitate behavior was not observed at 1 and 2 mM.. After 90 min, ferrous ions are constant at 4 and 8 mM. It means that precipitation reaction seems to have been completed between 40 and 60 min.

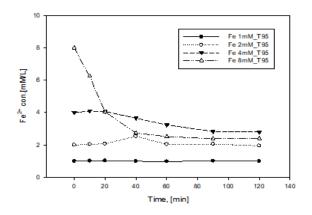


Fig. 2. Ferrous oxalate precipitation behavior depending on FeCl₂ concentration [mM] at 95 $^{\circ}$ C.

In other words, precipitation reaction is dependent on temperature. Therefore, the optimal conditions of the decontamination seem to high temperature and low concentration.

4. Conclusion

The following conclusions were obtained regarding the ferrous oxalate precipitation behavior depending on the ferrous concentration and temperature which is necessary to control the excess ferrous concentration by a cation ion exchange during the reductive chemical decontamination:

1. During the reductive chemical decontamination around the temperature of 95 $^{\circ}$ C, the ferrous ion concentration should be maintained below 2 mM to prevent from precipitation, while during decomposition of the oxalate at the room temperature, the ferrous oxalate precipitation is taken place above 1 mM.

2. The rate of ferrous oxalate precipitation is relatively slow and it takes time about 40 minutes, so that it should be taken into consideration to control the ferrous concentration during the reductive chemical decontamination.

5. Acknowledgement

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