A Study on Removal of Iodine, Iodide Ion, and Iodate Ion from Radioactive Wastewater

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ABSTRACT

For the two methods to remove iodine, the iodide ion and the iodate ion from radioactive waste water, we proposed previously, the main reactions were experimentally investigated to examine the feasibility of them. One is the reaction of the iodide ion and the iodate ion. In this reaction, it was confirmed that the reaction rate is faster with a pH of less than 2 and, to undergo the reaction faster under the condition of pH 2, an addition of excess iodide ions and iodate ions is necessary. Another is the reduction of the iodate ion and the iodine by pyrite. In the experiment, it was found that when the iodate ion in the solution is in contact with pyrite, it is reduced to iodine on the surface of the pyrite and the produced iodine is consecutively reduced to the iodide ion. The reaction occurred at room temperature under a wide range of pHs. Based on the results of this preliminary study, it is expected that a more substantial method could be prepared for the effective removal of an iodine mixture from radioactive wastewater.

INTRODUCTION

Iodine usually exists in the form of iodine (I_2), an iodide ion (I^-) and an iodate ion (IO_3^-) in an aqueous solution [1]. Due to the various forms of iodine, its removal from radioactive wastewater is difficult by the conventional methods such as an adsorption or ion exchange especially in nuclear power plants and nuclear research institutes. Previously we proposed two new methods to remove a mixture of iodine (I_2), an iodide ion (I^-) and an iodate ion (IO_3^-) in radioactive wastewater [2].

One of the methods to remove the iodine mixture uses the reaction between the iodide ion and the iodate ion. Iodide ion and iodate ion in the mixture are converted to iodine by a reaction

between themselves ($5\ I^- + IO_3^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$). The produced and existing iodine are finally removed by an activated carbon.

Another method uses pyrite to remove the iodine mixture from radioactive wastewater. It was reported that the iodate ion is reduced to iodine and a part of the iodine produced is adsorbed on the surface of the pyrite [3]. If the iodate ion in the wastewater could be reduced to iodine by pyrite, the produced iodine and the iodide ion could be removed by using activated carbon and anion exchange resin.

In this study, as a preliminary step, the main reactions of the methods were experimentally investigated to examine the feasibility of these two methods.

EXPERIMENTALS

Reaction of the Iodide Ion and the Iodate Ion

Solutions containing $2x10^{-3}$ mole/L of the iodide ion and $8x10^{-3}$ mole/L of the iodate ion were prepared by dissolving $NaIO_3$ (Junsei Chem. Co.) and NaI (Merck Co.) respectively in deionized water. By using these solutions, solutions with various concentrations of the iodide ion and the iodate ion were made to examine the reaction of iodide ion and iodate ion. By controlling the pH of the solution and by varying the ratio of iodide ion to iodate ion, the concentration of the produced iodine was measured by colorimetry.

Reduction of the Iodate Ion and Iodine by pyrite

Solutions containing 5~200 mg/L of the iodate ion and 50 mg/L of iodine were prepared by dissolving $NaIO_3$ (Junsei Chem. Co.) and I_2 (AJAX Chem.) respectively in deionized water. Pyrite from the Kangwon-do area in Korea was crushed, sieved (<180μm) and used in the experiment. As the batch test, the pyrite was added into a solution of the iodate ion or the iodine. The sample solution was taken at a certain time and after a filtration using a 0.45μm filter, the concentration of the iodine or the iodide ion was measured. The concentration of the iodine was measured by colorimetry and that of the iodide ion was measured by using an iodide selective electrode.

RESULTS AND DISCUSSION

Reaction of the Iodide Ion and the Iodate Ion

The effect of the pH and the ratio of the iodide ion to the iodate ion were investigated for the following reaction.

$$5\ I^- + IO_3^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$$

First the effect of the pH was evaluated for the reaction of the iodide ion and the iodate ion in the solution. The result is shown in Fig. 1. The reaction was conducted under the condition of a theoretical ratio of the iodide ion and the iodate ion ($I^-:IO_3^-=5:1$). At a pH condition higher than 4, iodine was hardly produced. It was observed that the iodine was produced when the pH of the solution was less than 3. As the pH of the solution decreased, the production rate of the iodine

increased. The reaction of the iodide ion and the iodate ion depends highly on the pH of the solution.

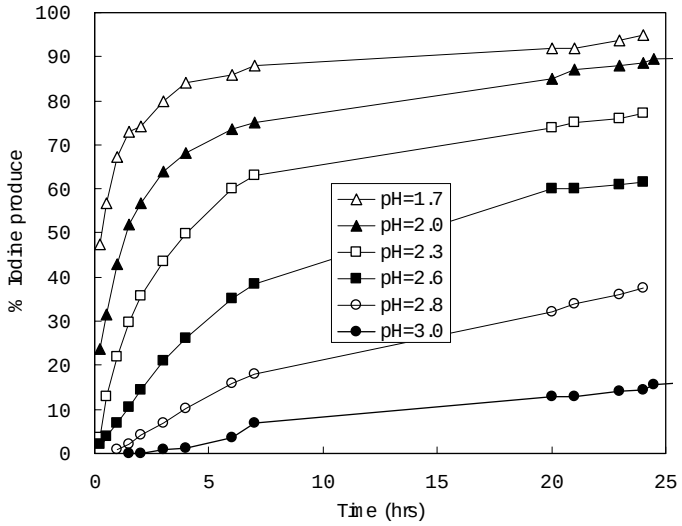

Fig. 1. The changes of the iodine production at various pH values of the solution
- The concentration of the iodide ion in the solution: $5x10^{-5}$ mole/L
- The concentration of the iodate ion: $1x10^{-5}$ mole/L

At the pH value of 2 and a constant concentration of the iodide ion, the effect of an excess of the iodate ion was examined for the reaction rate. The result is shown in Fig. 2. As the iodate ion existed in excess of the theoretical amount, the production rate of the iodine increased. Reversely, at the same pH and a constant concentration of the iodate ion, the effect of an excess of the iodide ion was also observed although it is not shown as the figure. In this case, likewise, when the iodide ion existed in excess of the theoretical amount, the production rate of the iodine increased.

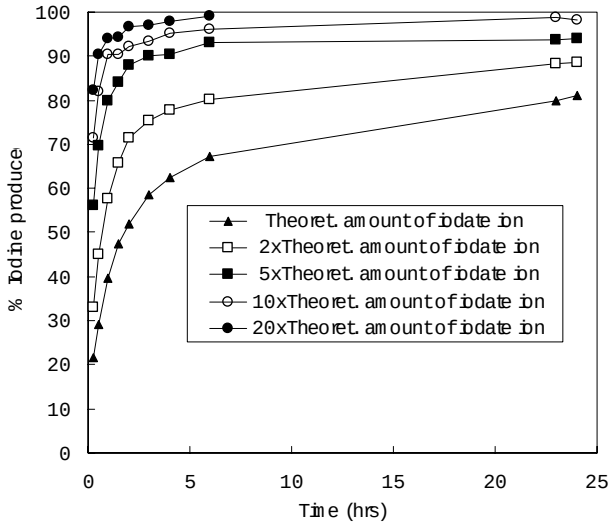

Fig. 2. The changes of the iodine production at the excess of iodate ion in the solution

- The concentration of the iodide ion: $5x10^{-5}$ mole/L
- The pH of the solution: 2

From the experimental results, it was found that the reaction of the iodide ion and the iodate ion is generally slow at a low concentration. To increase the reaction rate, it would be preferable that the pH of a solution be low and an excess of the iodate ion or the iodide ion exists in the solution. However, this is not a simple matter in the process of a wastewater treatment. Therefore, a more substantial investigation must be performed before applying this reaction to the treatment of radioactive wastewater.

Reduction of the Iodate Ion and Iodine by Pyrite

The reduction of the iodate ion and iodine by pyrite was investigated. First the iodate ion in the solution was contacted with pyrite in the slurry. The result is shown in Fig. 3. As Fuhrmann had already reported [3], it was observed that an iodine production occurred and disappeared in the solution. They explained that the production of iodine is due to the reduction of the iodate ion on the surface of the pyrite and assumed that the decrease of the iodine may be caused by an adsorption of the iodine in the solution on the surface of the pyrite.

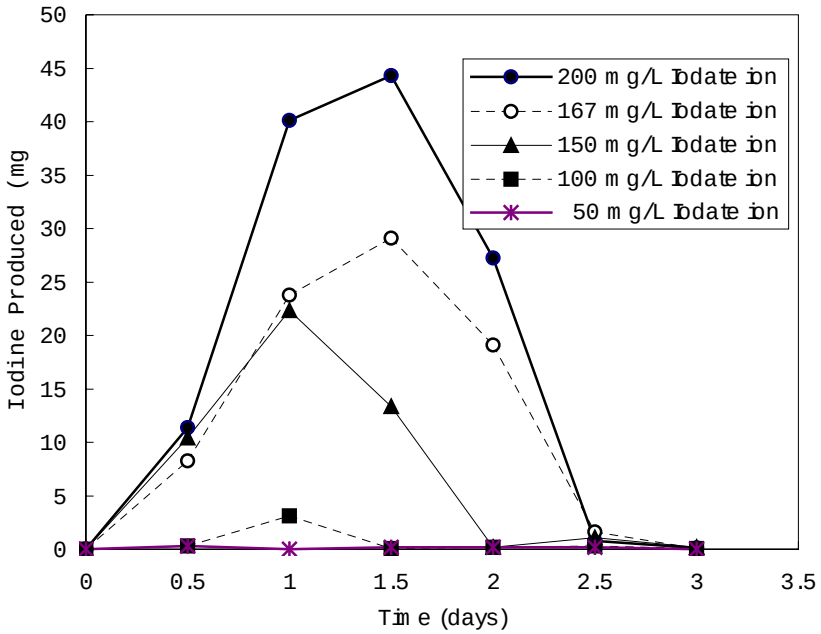

Fig. 3. The changes of the concentration of iodine in the solution containing the iodate ion and pyrite(The amount of pyrite in the solution: 0.3 wt%)

However, it is questionable how a large amount of iodine could be adsorbed on the surface of pyrite. As a way to trace the cause of the disappearance of the iodine, a solution containing the iodate ion and pyrite was prepared to measure the concentration of the iodide ion that didn't exist in the original solution. The result is shown in Fig. 4. The occurrence of the iodide ion was observed from the initial stage of the reaction of the iodate ion and pyrite. As time went by, the concentration of the iodide ion increased. A decrease of the concentration of the iodide was not

observed unlike in the case of the iodine. And it was estimated that the iodine produced from the reduction of the iodate ion by pyrite may be consecutively reduced to the iodide ion by pyrite. Also it was found that the concentration of the iodide ion increased while that of the iodine decreased when pyrite was added to the solution in which the iodine was dissolved. This is the evidence that supports the reduction of iodine by pyrite.

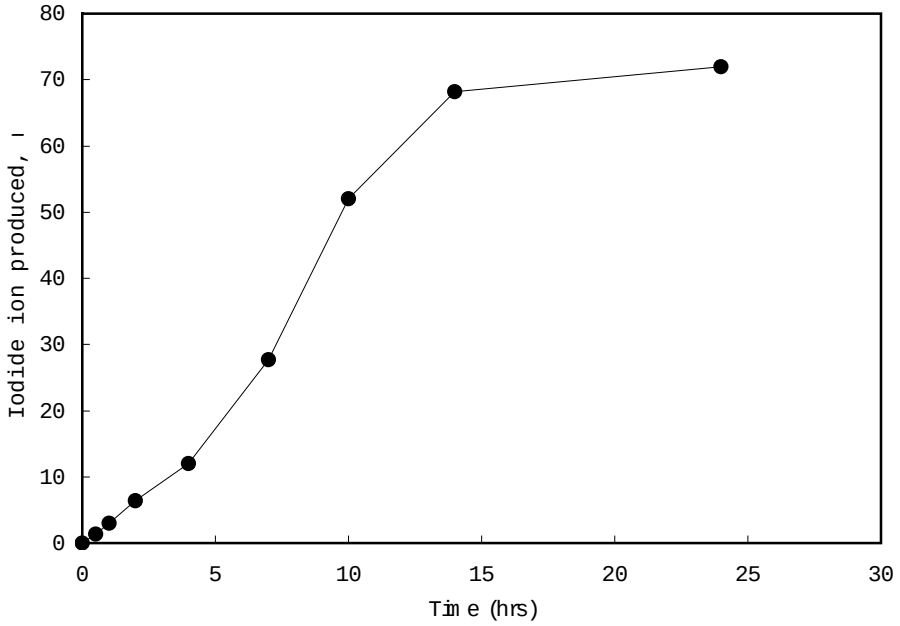

Fig. 4. The changes of the concentration of the iodide ion in the solution containing the iodate ion and pyrite (The amount of pyrite in the solution : 0.3 wt%)

Accordingly it was concluded that the iodate ion in the solution is eventually reduced to the iodide ion through the iodine by pyrite. This reaction could be applied to the treatment of radioactive wastewater containing an iodine mixture. If the mixture of iodine in the wastewater could be reduced to the iodide ion by using pyrite, the removal of the iodide ion from wastewater could be relatively easier than that of a mixture of iodine from the wastewater.

SUMMARY

Previously we proposed two new methods to remove iodine (I_2), an iodide ion (I^-) and an iodate ion (IO_3^-) in radioactive wastewater. One method to remove the iodine mixture uses the reaction between the iodide ion and the iodate ion ($5\ I^- + IO_3^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$). In this method, the iodide ion and the iodate ion in the mixture are converted to iodine by a reaction between themselves. The produced and existing iodine are finally removed by an activated carbon. Another method uses pyrite to remove the iodine mixture from the radioactive wastewater. In this study, as a preliminary step, the main reactions of the methods were experimentally investigated to examine the feasibility of these two methods.

As a result of the experiments on the reaction between the iodide ion and iodate ion for the former method, it was confirmed that the reaction rate is faster with a pH of less than 2 and, to undergo the reaction faster, under the condition of pH 2, an addition of an excess of the iodide ion and the iodate ion is necessary. However, because the reaction rate is relatively slow at a low concentration, a more substantial method must be prepared to apply this reaction to the treatment of radioactive wastewater.

For the latter method, the reduction of the iodate ion by pyrite has been investigated in detail. In this experiment, it was found that iodate ion is eventually reduced to the iodide ion through the iodine by pyrite. When the iodate ion in the solution is in contact with pyrite, it is reduced to iodine on the surface of the pyrite. And the iodine produced is consecutively reduced to the iodide ion. This reaction has occurred at room temperature under a wide range of pHs. By using this reaction, an iodate ion and iodine from radioactive wastewater could be converted into the iodide ion and all of the iodide ions could be simply removed by an ion exchange method.

Base on these results, it is expected that a more effective method could be developed to remove an iodine mixture from radioactive wastewater.

REFERENCES

1. Silen, L.G. (1961). The physical chemistry of seawater. In *Oceanography*, ed. M.Seer. American Association for the Advancement of Science (Washington D.C.)
2. KAERI, *A study on the Removal of Iodine, Iodide Ion and Iodate Ion from Radioactive Wastewater*, KAERI/RR-2509/2004 (in Korean)
3. Fuhrmann, M., Bajt and Schoonen M.A.A (1998). Sorption of iodide on minerals investigated by X-ray absorption near edge structure (XANES) and I-125 tracer sorption experiments, *Applied Geochemistry, 13: 127-141*