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ARTICLE

Development of treatment method for analytical waste solutions in STRAD project - Role of trace chloride ion in ammonium ion oxidation with the presence of Co(II) ion

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Radioactive liquid wastes are generated and accumulated in nuclear research facilities, and their disposal or treatment procedures have not been established due to their complicated compositions. Radioactive liquid waste generated mainly from analysis of reprocessing process contains ammonium salt, which poses a risk of forming ammonium nitrate. We focused on the NH_4^+ ozonation with Co^{2+} as a treatment method below 373 K and at ordinary pressure. NH_4^+ oxidation by O_3 was performed with Co^{2+} at different Cl^- concentrations. NH_2Cl was formed when $Cl^-/NH_4^+ = 1$, while further chlorination of NH_2Cl hardly proceeded when excess Cl^- was present in the solution. Notably, however, NH_4^+ oxidation proceeded even when Cl^- concentration was lower than NH_4^+ concentration. It is suggesting that formed NH_2Cl underwent decomposition into NO_3^- or N_2, thus releasing Cl^- to the reaction solution, therefore small amount of Cl^- was needed to decompose NH_4^+.

Keywords: radioactive liquid waste; ammonium ion; ozone oxidation; STRAD project

1. Introduction

Most radioactive liquid wastes generated in nuclear facilities contains nuclear or radioactive materials. A wide variety of materials and reagents are used in experimental operations, bringing diversity of type and composition of the radioactive liquid wastes. As treatment procedures of these radioactive liquid wastes, various methods have been reported so far ([1-4]). Unfortunately, the applicability of these methods is limited, and there are still many radioactive liquid waste for which treatment methods have not been established, thus they have been reluctantly accumulated in the facilities as legacy wastes. Since long-term storage of radioactive liquid wastes containing reactive materials poses a risk to the facilities, it is keenly desired to develop treatment technologies for disposal of the radioactive liquid wastes.

STRAD (Systematic Treatments of Radioactive liquid wastes for Decommissioning) project was launched by Japan Atomic Energy Agency (JAEA) in collaboration with several universities and companies to develop a treatment technology for radioactive liquid waste with highly reactive substances [5]. In this project, Chemical Processing Facility (CPF) of JAEA is taken as a model case of the facilities that conducts research and development using nuclear materials. CPF is a facility that conducts research and development on fast reactor fuel reprocessing and vitrification. The facility also analyzes contaminated water generated at the Fukushima Daiichi Nuclear Power Plant. Most radioactive liquid wastes generated in CPF comes from analysis operations, for which ammonium salts are often used. Long-stay of ammonium salts in nitric acid solution potentially forms explosive ammonium nitrate, bringing high risk to the facility. Thus, ammonium salts, especially ammonium ion (NH_4^+), in radioactive liquid waste must be safely decomposed to reduce the risk on the facilities.

Ammonium salts are common reagents and are produced in various places and situations. Thus, methods for the treatment of water containing ammonium ion or ammonia have been developed, e.g., breakpoint chlorination, in which excess hypochlorous acid is used to decompose ammonium ion [6-8]; microbial treatment, in which ammonia is nitrified by microorganisms and then nitrate is reduced to dinitrogen ([9,10]); ammonia stripping, in which ammonia is transferred into gas phase by blowing air ([11-13]); catalytic wet air oxidation (CWAO), in which ammonia is combusted by the reaction with air (O_2) in the presence of catalysts [14-17]; and advanced oxidation process (AOP), in which some methods producing hydroxyl radical such as oxidation with ozone (ozonation), UV irradiation, and hydrogen peroxide oxidation are combined to effectively decompose ammonia ([18-20]). In nuclear facilities like CPF, since treatment of the radioactive liquid wastes must be performed in a concrete cell or grove box, complex operations cannot be adopted, and only limited reagents can be used. In addition, safety is top priority in the treatment, and waste generation by the treatment should be suppressed as low as possible.

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Under such situation, we though that the oxidation of ammonium ion with ozone in the presence of a catalyst is the most suitable method for the treatment of the radioactive liquid waste. This method does not require high temperature and high-pressure conditions because the reaction proceeds under the conditions that can be handled with liquid (lower than 373 K) and at ordinary pressure, and thus, is safe and does not require large and complex equipment. Furthermore, ozone is clean oxidizer that does not generate secondary waste because it decomposes into oxygen, and the catalyst is used in small quantities. These are significant advantages, as it is very important to control the amount of secondary waste generated.

Previous studies demonstrate that ammonium ion in water was decomposed by ozonation under ordinary pressure in the presence of heterogenous catalysts, and Co_3O_4 was the most effective one ([21-23]). Furthermore, we found that the decomposition of ammonium ion proceeded in the presence of cobalt ion (Co^{2+}) ([24]), which acted as a homogeneous catalyst. Generally, homogeneous catalysts like Co^{2+} are not suitable for the treatment of liquid waste though the high catalytic activity is attractive, because the catalyst itself causes secondary pollution, which makes it difficult to release the treated liquid waste to the environment. However, it is not a problem for radioactive liquid waste, because the treated radioactive liquid waste is not released to the environment. In the previous study ([24]), we demonstrated that both Co^{2+} and chloride ion (Cl^-) in the solution were indispensable for effective decomposition of ammonium ion by ozonation, and monochloramine (NH_2Cl) was a main product under the conditions. Cl^- is an additive that less amount is preferable, though the behavior of Cl^- under low Cl^- concentration is not clear. Therefore, in the present study, to examine the behavior of Cl^- in low concentration, we investigated influence of the concentration of Cl^- on the oxidation of ammonium ion with ozone in the presence of Co^{2+} and proposed a reaction scheme for the reaction based on the obtained results.

2. Experimental method

2.1. Preparation of test solutions

Test solutions containing Co^{2+}, NH_4^+ and Cl^- were prepared from $(NH_4)_2SO_4$, $Co(NO_3)_2{\cdot}6H_2O$, and NaCl (FUJIFILM Wako Pure Chemicals Co.), respectively. The concentrations of Co^{2+} and NH_4^+ were fixed at 4.5×10^{-3} and 5.0×10^{-2} mol L^{-1}, respectively, while that of Cl^- was changed from 0 to 1.1×10^{-1} mol L^{-1} ($[Cl^-]_0$=0, 5.0×10^{-4}, 5.0×10^{-3}, 1.0×10^{-2}, 3.0×10^{-2}, 5.0×10^{-2}, 8.0×10^{-2}, and 1.1×10^{-1} mol L^{-1}). pH of the test solution was adjusted to 4 by the addition of dilute nitric acid.

2.2. Oxidation of ammonium ion with ozone

Oxidation of NH_4^+ with ozone was performed in a three-necked separable flask with a condenser. Downstream of the condenser, three trap bottles were placed in series, where pure water was put in the first and second one and KI solution (1 mol L^{-1}) was done in the last one. Ozone (O_3) was generated from O_2 using an ozone generator and O_3/O_2 mixture was flown to the flask. The total flow rate of the O_3/O_2 mixture was 21.6 L h^{-1} and the amount of O_3 generated was 1.45×10^{-2} mol h^{-1}, which was determined by redox titration with KI and sodium thiosulfate solutions.

The test solution (200 mL) and a stirrer bar were put in the flask. The temperature of the solution was increased to 333 K in a flow of O_2, and when it reached to 333 K, O_3 was generated to start the reaction (t = 0). A small portion of the test solution was taken at t = 0, 1, 3, and 5 h to determine pH, and the concentrations of NH_4^+, NO_3^-, Cl^- and dissolved Co ion. pH was measured by a pH meter (Standard ToupH electrode 9615S-10D, Horiba). The concentrations of NH_4^+, NO_3^-, and Cl^- were measured by ion chromatographs (ICS-1100, Dionex; and CS16 and AS20 columns for cation and anion analyses, respectively) and that of dissolved Co ion was done by ICP-AES (SPS3520UV, Seiko Instruments Inc.).

3. Results and Discussion

3.1. Oxidation of ammonium ion in the test solution with low Cl^- concentration

Appearances of the test solution with low Cl^- concentration ($[Cl^-]_0$=5.0×10^{-4} mol L^{-1}) before and after O_3 blowing for 5 h are shown in **Figure 1**. Before O_3 blowing (Figure 1a), the test solution showed pale red, which was due to Co^{2+} dissolving in the solution, because

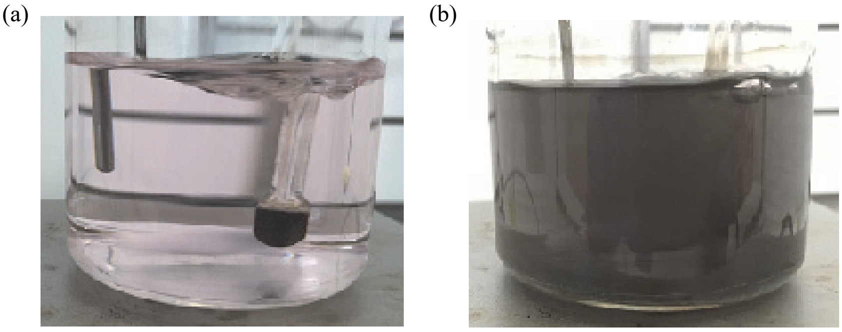

Figure 1. Appearance of the test solutions (a) before and (b) after O_3 blowing for 5 h. Initial concentrations of Co^{2+}, NH_4^+ and Cl^- in the test solution were 4.5×10^{-3}, 5.0×10^{-2} and 5.0×10^{-4} mol L^{-1}, respectively. The black part in (a) is the filter of the gas dispersion tube, which is not visible in (b) due to the turbidity of the liquid.

the solution without Co^{2+} was colorless transparent ([24]). However, after O_3 blowing (Fig. 1b), the solution turned black and cloudy. The resulting black and cloudy suspension was filtered, and black solid (mainly cobalt oxyhydroxide) and pare red filtrate were obtained, indicating that some of Co^{2+} remained in the solution. As we reported in the previous paper ([24], the black solid was not formed in the test solution containing 5.0×10^{-2} mol L^{-1} of Cl^-.

Therefore, suppression of the formation of cobalt precipitate is one of the functions of Cl^-. In the test solutions with Cl^- concentration of 5.0×10^{-3} mol L^{-1} or higher, no change in the appearance of the solutions was observed after O_3 blowing. Because formation of the cobalt precipitate decreased the concentration of dissolved Co ion in the test solution, the suppression effect by Cl^- is beneficial for the oxidation of NH_4^+ with O_3.

Figure 2 shows time courses in the concentrations of NH_4^+, NO_3^-, Cl^-, and dissolved Co ion for the reactions with different Cl^- concentrations ($[Cl^-]_0$=1.1×10^{-1}, 3.0×10^{-2}, 5.0×10^{-4}, and 0 mol L^{-1}). The pH after 5 h was 3~4. For NO_3^-, changes in the concentration ($\Delta[NO_3^-]$) instead of absolute one are shown in Figure 2, because the test solutions originally contained 4.5×10^{-3} mol L^{-1} of NO_3^- from the cobalt salt ($Co(NO_3)_2{\cdot}6H_2O$). Concentrations of NO_2^- are also detectable by ion chromatography, but they are not shown in the figures because no significant concentrations were present in any of the test solutions. For the reaction with conditions of high Cl^- concentrations ($[Cl^-]_0$=1.1×10^{-1} and 3.0×10^{-2} mol L^{-1}, Figures 2a and b, respectively), the decrease in Cl^- concentration was almost the same as that in NH_4^+ concentration, demonstrating the formation of NH_2Cl as eq. 1 under the reaction conditions as we previously reported ([20]).

$$NH_4^+ + HClO \rightarrow NH_2Cl + H_3O^+ \qquad (1)$$

In addition, the decrease rate of NH_4^+ concentration, of course that of Cl^- concentration, was independent of Cl^- concentration for the reaction with Cl^- concentrations more than 3.0×10^{-2} mol L^{-1}. The concentration of dissolved Co ion was constant throughout the reaction time, indicating no formation of cobalt precipitate.

For the reactions with conditions of high Cl^- concentrations, even though the amount of Cl^- in the test solution was only centesimal of that of NH_4^+ ($[NH_4^+]_0$=5.0×10^{-2} mol L^{-1}). The concentration of dissolved Co ion was slightly decreased with rection time, indicating formation of the cobalt precipitate, which was consistent with the change in the appearance of the test solution by O_3 blowing (Figure 1b). The reaction behavior with low Cl^-

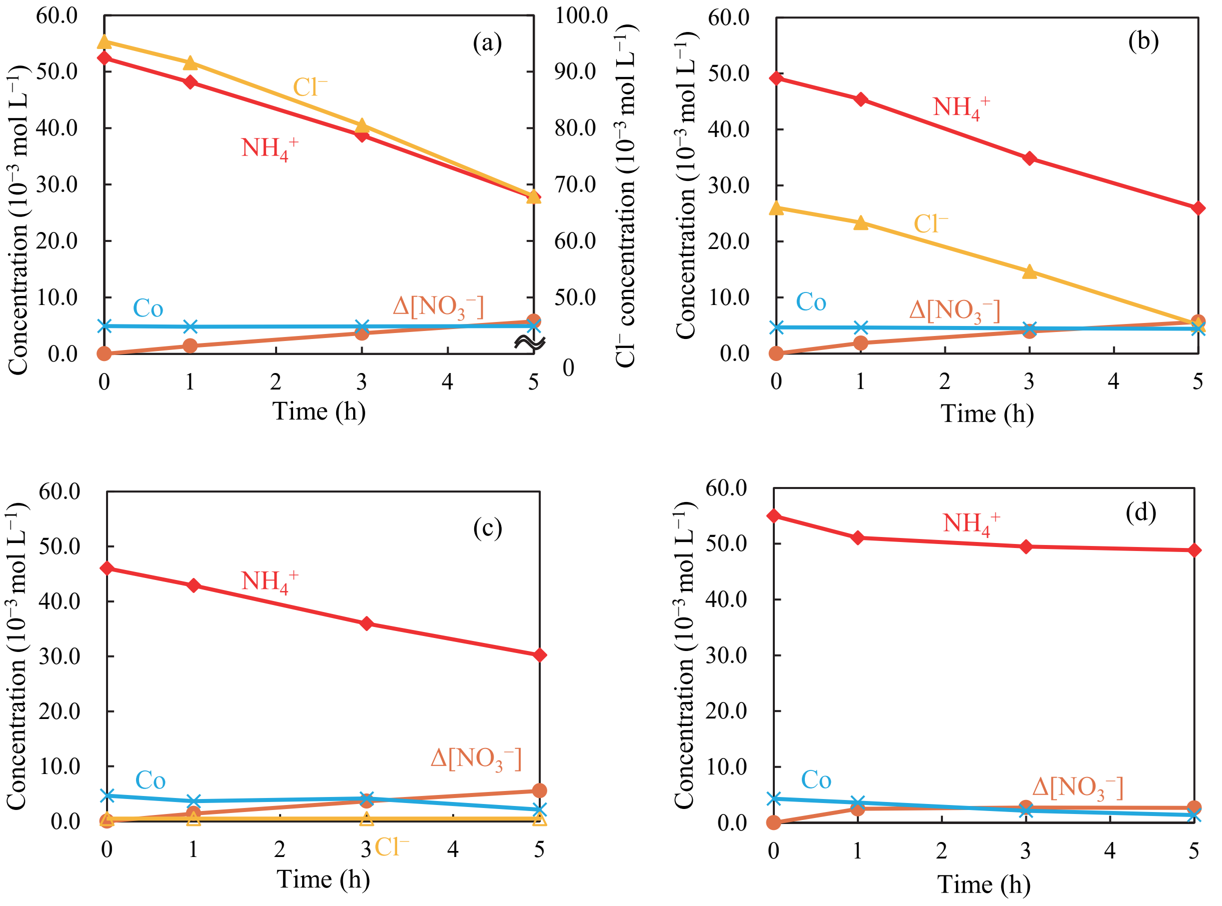

Figure 2. Time courses in the concentrations of (◆) NH_4^+, (●) $\Delta[NO_3^-]$, (▲) Cl^-, and (×) dissolved Co ion for the oxidation of NH_4^+ with O_3 in the presence and absence of Cl^-. $[Cl^-]_0$ = (a) 1.1×10^{-1} mol L^{-1}, (b) 3.0×10^{-2} mol L^{-1}, (c) 5.0×10^{-4} mol L^{-1}, and (d) without Cl^-. Open symbols represent the value lower than the determination limit.

concentration (Figure 2c, d) was different to that for the reaction with high Cl^- concentrations (Figure 2a, 2b), suggesting that the reaction different to that occurring with high Cl^- concentration proceeded in the low Cl^- concentration, which will be discussed in detail later.

For the reaction without Cl^- (Figure 2d), initially NH_4^+ was also decomposed but the reaction was almost stopped after 1 h. In addition, the initial reaction rate of NH_4^+ decomposition was much lower than those for the reaction in the presence of Cl^-. It is known that hydroxyl radical is formed by the reaction of Co^{2+} with O_3 and H_2O (Eq. 2) ([25] [26]) and hydroxyl radical can oxidize ammonia mainly into NO_3^-. In this reaction, Co^{2+} was oxidized and the valence of Co ion changed from divalent to trivalent. The chemical species of Co(III) could not be determined, but $Co(OH)^{2+}$ was assumed to be suitable for the reaction.

$$Co^{2+} + O_3 + H_2O \rightarrow Co(OH)^{2+} + O_2 + OH\cdot \qquad (2)$$

However, the reaction of Eq. 2 does not proceed catalytically, namely stoichiometric reaction, and thus, only a small amount of NH_4^+ almost equivalent to the amount of Co^{2+} ($=4.5 \times 10^{-3}$ mol L^{-1}) could be oxidized. Anyway, the reaction occurring in the presence of trace amount of Cl^- (Fig. 1c) was quite different to that in the absence of Cl^-.

To know the reaction order for NH_4^+ decomposition with respect to Cl^-, common logarithm of the initial rate ($t = 0 \sim 1$ h) of NH_4^+ decomposition (log r) is plotted as a function of that of $[Cl^-]_0$ in **Figure 3a**. Of course, the data for the reaction without Cl^- is not plotted in the figure. As Figure 3a shows, the reaction rate for NH_4^+ decomposition was almost independent of $[Cl^-]_0$, meaning a zero-order reaction. To further investigate especially changes in the reaction behavior with respect to $[Cl^-]_0$, we calculated the amounts of consumed Cl^- and NH_4^+ for 5 h, which are denote to $\Delta[Cl^-]$ and $\Delta[NH_4^+]$, respectively, and the ratio ($\Delta[Cl^-]/\Delta[NH_4^+]$) is plotted as a function of common logarithm of $[Cl^-]_0$ in **Figure 3b**. For the reaction with high Cl^- concentrations ($[Cl^-]_0 \geqslant 3.0 \times 10^{-2}$ mol L^{-1}), the ratio was almost 1 regardless of $[Cl^-]_0$, indicating that the formation of NH_2Cl was predominant. In addition, it should be noted that the result suggested that NH_2Cl formation by chlorination of NH_4^+ took priority over successive chlorination of NH_2Cl to dichloramine ($NHCl_2$) even when excess Cl^- over NH_4^+ was present in the test solution like $[Cl^-]_0 = 1.1 \times 10^{-1}$ mol L^{-1}.

In contrast to the reaction with high Cl^- concentrations, $\Delta[Cl^-]/\Delta[NH_4^+]$ was far below 1 for the reaction with low Cl^- concentrations ($[Cl^-]_0 \leqslant 1.0 \times 10^{-2}$ mol L^{-1}). As mentioned above, Cl^- was indispensable to promote NH_4^+ decomposition even when the concentration was lower than that of NH_4^+. To further investigate the reaction under low Cl^- concentration conditions, the reaction with $[Cl^-]_0 = 1.0 \times 10^{-2}$ mol L^{-1} was performed up to 10 h and we investigated how far the Cl^- concentration was decreased during the reaction. In this experiment, the taken test solution was not diluted for ion chromatography analysis to precisely determine the low concentration Cl^-. The result is shown in **Figure 4a**. Concentration of Cl^- was decreased with reaction time and was 1.5×10^{-4} mol L^{-1} at 5 h. At 7 h, a trace amount of Cl^- (7.0×10^{-5} mol L^{-1}) was still detected and then the concentration became below the detection limit (1.0×10^{-5} mol L^{-1}) at 10 h. On the other hand, concentration of NH_4^+ was also decreased up to 7 h but did not do after 7 h, indicating that the NH_4^+ oxidation almost stopped at 7 h. This timing matched with that when Cl^- was no longer detected in the test solution, strongly suggesting necessity of Cl^- for NH_4^+ oxidation even in trace amount.

To follow the changes in the reaction behavior at each reaction time in the reaction shown in Figure 4a, the amounts of consumed NH_4^+ and Cl^-, which are denoted to $\Delta[NH_4^+]_t$ and $\Delta[Cl^-]_t$, respectively, were calculated for each reaction time period, namely Δt = 0~1, 1~2, 2~3, 3~4, 4~5, 5~7, and 7~10 h, and the ratio ($\Delta[NH_4^+]_t/\Delta[Cl^-]_t$) is plotted as a function of reaction time in **Figure 4b** (note that the denominator and numerator in Figure 4b is opposite to that in Figure 3b.). Until 3 h, the ratio was about 1~2, but increased sharply after 4 h, reaching 36 ($=\Delta[NH_4^+]_t/\Delta[Cl^-]_t$) at 7 h. This result clearly indicated that until 3 h, at which concentration of Cl^- was above 1.0×10^{-3} mol L^{-1}, NH_2Cl formation predominantly proceeded as the reaction with high Cl^- concentrations, but after 5 h, where the concentration of Cl^- was below 1.0×10^{-3} mol L^{-1}, reactions other than NH_2Cl formation occurred,

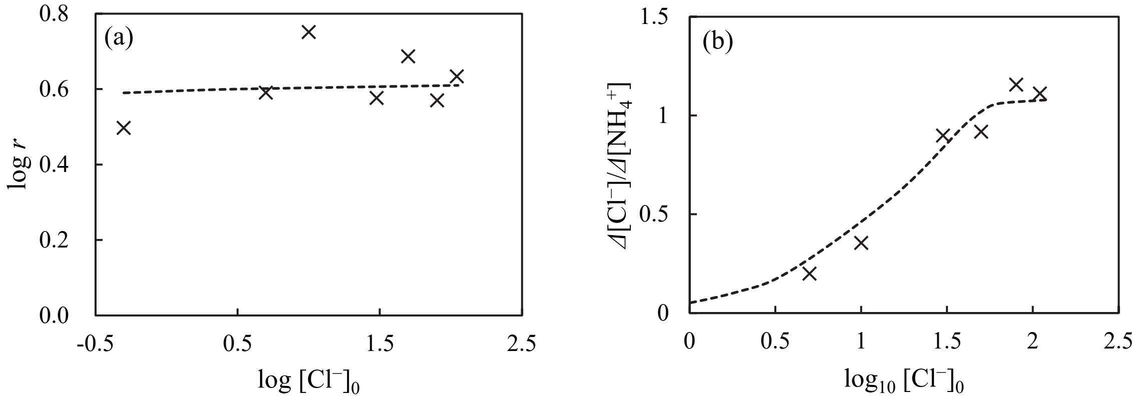

Figure 3. (a) log–log plot of $[Cl^-]_0$ vs. initial rates of NH_4^+ decomposition, and (b) the ratio of consumed Cl^- to NH_4^+ ($\Delta[Cl^-]/\Delta[NH_4^+]$) with respect to log of $[Cl^-]_0$.

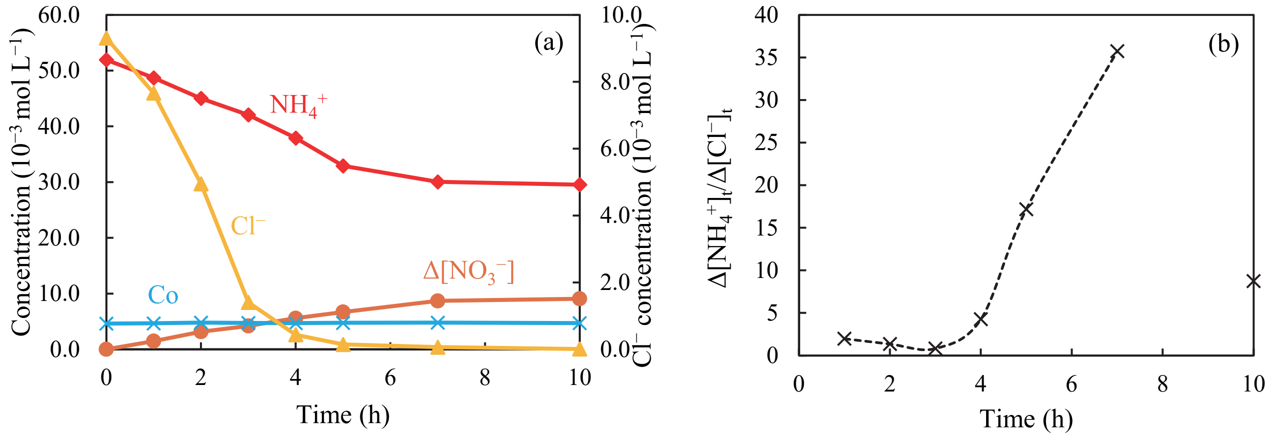

Figure 4. (a) Time courses in the concentrations of (◆) NH_4^+, (●) NO_3^-, (▲) Cl^-, and (×) dissolved Co ion for the oxidation of NH_4^+ with O_3 for 10 h, and (b) the ratio of consumed NH_4^+ to Cl^- to ($\varDelta[NH_4^+]/\varDelta[Cl^-]$) with respect to reaction time. Initial concentrations of Co^{2+}, NH_4^+ and Cl^- in the test solution were 4.5×10^{-3}, 5.0×10^{-2} and 1.0×10^{-3} mol L^{-1}, respectively. Open symbols represent the value lower than the determination limit.

because of very large value of $\varDelta[NH_4^+]_t/\varDelta[Cl^-]_t$. The reactions occurring under such low Cl^- concentration conditions will be discussed in 3.2.

3.2. NH_4^+ oxidation under low Cl^- concentration conditions

As mentioned in 3.1, Cl^- was necessary to promote NH_4^+ oxidation even at very low concentration than NH_4^+. This fact suggests the involvement of reactions that releases Cl^- once it is incorporated into the products, making a reaction cycle with Cl^-, and thus Cl^- was not apparently consumed in that reaction cycle. The reactions that produce Cl^- from the plausible products would be the following two.

$$NH_2Cl + 3O_3 \rightarrow NO_3^- + 2H^+ + Cl^- + 3O_2 \tag{3}$$
$$NHCl_2 + NH_2Cl \rightarrow N_2 + 3H^+ + 3Cl^- \tag{4}$$

In the former reaction (Eq. 3), formed NH_2Cl is further oxidized with O_3 to form NO_3^- and Cl^- ([27]). While NH_2Cl cannot be detected by ion chromatography, it must be present in the test solution after all Cl^- was consumed. In the latter reaction (Eq. 4), $NHCl_2$ was reacted with NH_2Cl to form Cl^- along with N_2 ([8,28]). As discussed in 3.1, since further chlorination of NH_2Cl to $NHCl_2$ was slow comparing with chlorination of NH_4^+ to NH_2Cl, the reaction of Eq. 4 might be a minor route to release Cl^-. Anyway, released Cl^- was again oxidized by $Co(OH)^{2+}$ to HClO as Eq. 5 ([24]) and formed HClO oxidized NH_4^+ to NH_2Cl (Eq. 1).

$$2Co(OH)^{2+} + Cl^- + 2H^+ \rightarrow 2Co^{2+} + HClO + H_2O \tag{5}$$

As a result, the oxidation of NH_4^+ continued to progress. Because the nitrogen-containing products formed by the reactions of Eqs. 3 and 4 are NO_3^- and N_2, respectively, concentration of NH_4^+ did not increased with the release of Cl^-.

There is an equilibrium reaction between HClO and Cl_2 in aqueous solution (Eq. 6).

$$HClO + H^+ + Cl^- \rightleftarrows Cl_2 + H_2O \tag{6}$$

The equilibrium of Eq. 6 shifts to the right when the solution is acidic. Cl_2 in the solution can migrate to gas phase, leading to decrease of Cl^- concentration in the test solution. Eventually, the concentration of NH_2Cl became too low to release enough amount of Cl^-, resulting in the stop of NH_4^+ oxidation.

Based on the discussion so far, the reaction scheme for NH_4^+ oxidation under the conditions with low Cl^- concentrations is proposed as **Figure 5**. As demonstrated in our previous study ([24]), Co^{2+} dissolved in the test solution was first oxidized by O_3 and formed $Co(OH)^{2+}$ oxidized Cl^- to HClO. Then, HClO reacted with NH_4^+ to form NH_2Cl, which was a predominant product by the reaction with high Cl^- concentration. A part of HClO migrated to gas phase as Cl_2 during the reaction. A small part of NH_2Cl was further chlorinated to $NHCl_2$ by the reaction with HClO.

Under the conditions with low Cl^- concentration, formed NH_2Cl was oxidized with O_3 to form NO_3^- and at the time Cl^- was regenerated in the test solution. The reaction of NH_2Cl with $NHCl_2$ also gave Cl^-. By such reactions, Cl^- was regenerated and thus NH_4^+ oxidation continued to progress even in the presence of small amount of Cl^-. To confirm this reaction scheme, we have to detect chloramines including $NHCl_2$ and $NHCl_2$, and investigate how those are reacted. Unfortunately, however, since chloramines are unstable and quantitative analytical methods especially for low concentration chloramines have not been established, those have not been done yet and is an issue for the future.

4. Conclusion

NH_4^+ oxidation by O_3 in the presence of Co^{2+} was performed at different Cl^- concentrations. NH_2Cl was

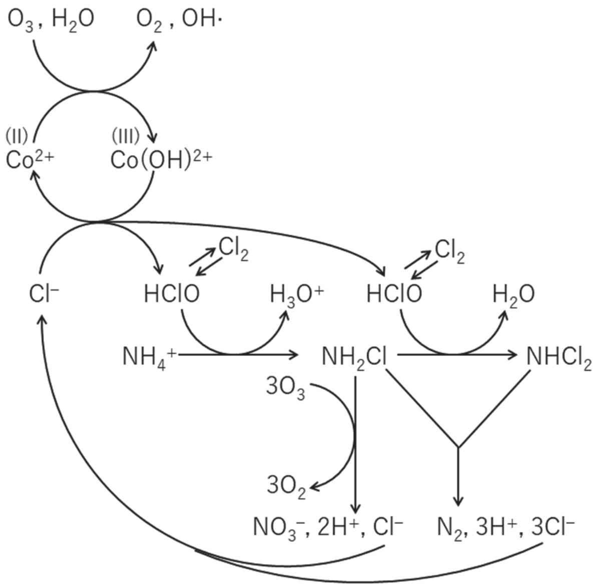

Figure 5. Reaction scheme for NH_4^+ oxidation with O_3 in the presence of Co^{2+} under low Cl^- concentration conditions.

predominantly formed by the reaction of NH_4^+ with HClO generated from Cl^- in the test solution with high concentration Cl^-. However, the NH_4^+ decomposition hardly proceeded in the absence of Cl^-, but it did when it was present even trace amount. A reaction scheme that the release of Cl^- by the decomposition of NH_2Cl into NO_3^- or N_2 explained the absence of an apparent decrease in Cl^- concentration was proposed. Since the reaction proceeded even with a small amount of Cl^-, this is a safety and simple NH_4^+ decomposition method that reduces equipment burden.

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