WET OXIDATION CHARACTERISTICS OF METAL CYANIDE COMPLEXES BELOW 423 K

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ABSTRACT

In the present study, the wet oxidation of zinc and copper cyanide complexes (cyanide concentration of 1,000 mg dm^{-3}) was conducted in a hydrothermal reactor, under oxygen atmosphere of which the pressure was set to 1 MPa. The pH of the reaction solution was kept in the range of 11 to 12 and the reaction temperature was changed from 383 K to 423 K. In the experiments, mainly the effect of reaction time on the cyanide decomposition was investigated. As a result, it was found that cyanide decomposition increased with an increase in the temperature and cyanide decompositions of 99.9 % and 96.1 % were achieved after 8 hours at 423 K for $Na_2[Zn(CN)_4]$ and $Na_3[Cu(CN)_4]$, respectively. In the case of $Na_2[Zn(CN)_4]$, mainly $HCOO^-$ and NH_4^+ were identified as the decomposition products. By contrast, in the case of $Na_3[Cu(CN)_4]$, carbon of CN^- was transformed either to H_2CO_3 or $HCOO^-$, and nitrogen was converted to NH_4^+, N_2 or NO_2^-. Based on these results, the decomposition mechanisms of $Na_2[Zn(CN)_4]$ and $Na_3[Cu(CN)_4]$ at a temperature of 423 K and pressure of 1 MPa were discussed.

1. INTRODUCTION

The copper and zinc cyanide complexes are commonly used in the metal finishing industry and are known to be characterized by high toxicity. Therefore, an increasing effort to replace the cyanide plating with less toxic plating method has been observed in the recent years. In the case of zinc plating, alkaline zinc and acidic zinc plating are the promising alternatives, while copper sulfate plating or pyrophosphate plating are being investigated to replace copper cyanide plating. However, the full replacement of cyanide is not to be achieved in the near future, since the cyanide plating still provides the highest cleaning ability as well as the highest effectiveness in keeping metals in solutions during the plating process (Minnesota Office of Waste Management, 1999; Parga and Cocke, 2001). Thus, the effective cyanide removal from rinsing wastewater discharged from plating processes will be still required in the future. Presently, the cyanide decomposition is carried out using various methods such as alkaline chlorination, oxidation with hydrogen peroxide or ozone, biological oxidation etc. (Desai et al., 1998; Sarla et al., 2004; Barriga-Ordonez et al., 2006, Mosher and Figueroa, 1996; White et al., 2000). Among these methods, alkaline chlorination is reported to be well established and the

principle of alkaline chlorination inheres in cyanide oxidation to less toxic cyanate and subsequently to carbon dioxide and nitrogen. However, toxic chlorinated organic compounds can be formed in this treatment (Parga and Cocke, 2001; Desai *et al.*, 1998). The formation of undesirable by-products can be avoided by using cyanide oxidation method with hydrogen peroxide or ozone, but the high costs of the oxidation agents decreases the actual application of hydrogen peroxide or ozone in the cyanide decomposition (Sarla *et al.*, 2004; Barriga-Ordonez *et al.*, 2006).

Therefore, new methods for cyanide decomposition are still being studied and among these new methods, the wet oxidation has attracted many researchers. Generally, the wet oxidation is carried out in a hydrothermal reactor under elevated pressure (3 – 5 MPa) and temperature (473 – 573 K), while oxygen is used as an oxidant. Recently, it has been reported that cyanide decomposition as high as 99.99% was achieved by wet oxidation under such conditions, while the reaction time required varied from about 0.5 hour to about 3.75 hours according to cyanide source, cyanide initial concentration and operation conditions used (Robey, 1983; Kalman *et al.*, 1989). Nevertheless, from a viewpoint of energy savings, the process energy requirements are quite high and therefore further reduction in the operation pressure and temperature is essential to achieve more environmentally friendly system.

In this study, the wet oxidation of zinc and copper cyanide complexes (cyanide concentration of 1,000 mg dm^{-3}) was conducted in a hydrothermal reactor, under oxygen atmosphere of which the pressure was set to 1 MPa. The pH of the reaction solution was kept in the range of 11 to 12 and the reaction temperature was changed from 383 K to 423 K. In the experiments, the effect of reaction time on the cyanide decomposition was mainly investigated. The cyanide decomposition was evaluated by determining the residual concentrations of cyanide in the solution after the wet oxidation. Finally, to evaluate the reaction mechanism, the reaction products such as cyanate, ammonium, formic acid, carbonic acid among the others were analyzed.

2. MATERIALS AND METHODS
2.1. Materials
In this study, copper cyanide (CuCN) and zinc cyanide ($Zn(CN)_2$) of reagent grade were used without further purification to prepare cyanide aqueous solutions of $Na_3[Cu(CN)_4]$ and $Na_2[Zn(CN)_4]$ by mixing CuCN with NaCN at a ratio of 1:3, and $Zn(CN)_2$ with NaCN at a ratio of 1:2, respectively. The initial concentration of cyanide complex was adjusted to 1,000 mg dm^{-3} (as CN^- concentration).

2.2. Experimental set-up
The wet oxidation of metal cyanides was carried out in a 200 ml Teflon-coated reactor, shown in Figure 1, at temperatures of 383 K, 403 K and 423 K and oxygen atmosphere (pressure was set to 1.0 MPa). A volume of 100 ml distilled water was poured into the reactor, and air in the reactor was purged by oxygen (purity: 99.9%). Then, the reactor operation temperature was raised to the prescribed temperature, whereupon the wet oxidation experiment was started by injecting a sample solution into the reactor. The reaction period was varied in the range up to 8 hours. At the end of the wet oxidation experiment, the reactor was allowed to cool down. The solution was withdrawn from the reactor and subjected to analyses of residual cyanide, pH, metal concentrations as well as the reaction products.

2.3. Product analysis
The flow chart of experimental and analytical procedures used is shown in Figure 2. After wet oxidation, the sample solutions were filtered using 1 μm pore size filter and the filtrates and filter cakes were subjected to further analyses.

In the determination of residual CN^- concentration and NH_4^+ concentration, the filtrate was distilled (distillation method JIS K0102) and subsequently, the residual CN^- concentration and NH_4^+ concentrations were determined using respective ion selective electrodes (NH_4^+: AE-235, CN^-: CN-125, Ion meter IM-55G, DKK-TOA Corp.). Subsequently, the decomposition of CN^- was determined using Eq. (1).

$$X[\%] = \frac{\text{residual amount of } CN^-}{\text{initial amount of } CN^-} \times 100 \tag{1}$$

The content of organic and inorganic carbon in filtrate was determined using a Total Organic Carbon (TOC) analyzer (TOC-VCSH, Shimadzu). Further, the concentrations of $HCOO^-$, CNO^-, NO_2^- were analyzed using an ion chromatograph (Shimadzu, electroconductivity detector type: CDD-10Avp) equipped with a Tosoh column (TSK gel IC-Anion-PW 6837, 50x4.6 mm I.D), and the concentrations of zinc and copper in the filtrates were determined using ICP (Vista-MPX Simultaneous ICP-OES, Varian, Inc.). The concentration of N_2 in gas phase was analyzed using a gas chromatograph (GC-TCD, GC-14 B, Shimadzu).

Finally, the filter cake/precipitate was dried and then subjected to an X-ray powder diffraction analysis (XRD) with scanning mode of *2θ/θ*, under the condition of 50 kV/100 mA (RINT-2500 TTR, Rigaku Model).
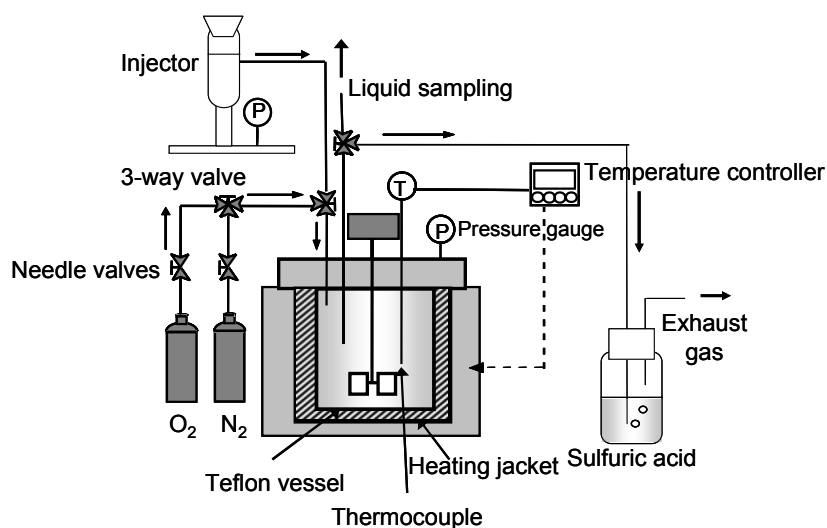
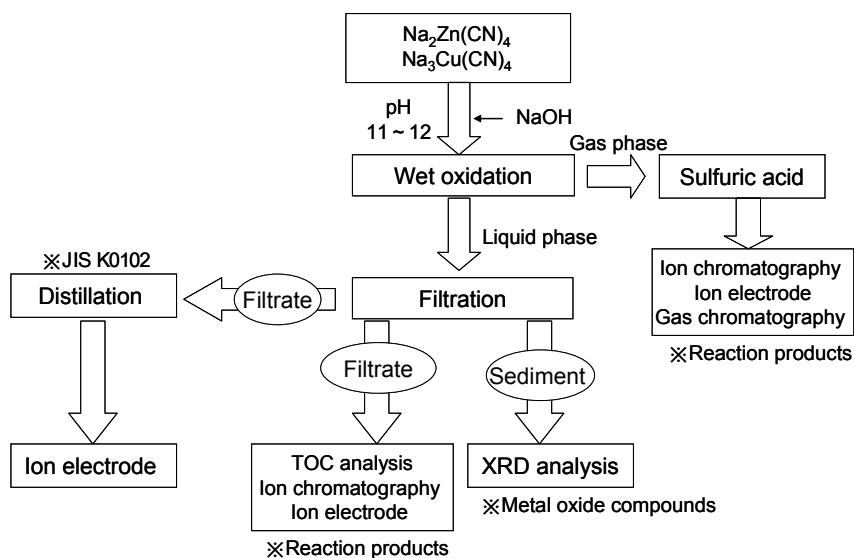

Figure 1. Experimental apparatus

Figure 2. Flow chart of experimental and analytical procedures

3. RESULTS AND DISCUSSION

The wet oxidation experiments of copper and zinc cyanide complexes were carried out at a temperature range of 383 K to 423 K. Figure 3 shows the results of cyanide decomposition obtained and it can be seen that the cyanide decomposition significantly increased with an increase in the temperature.
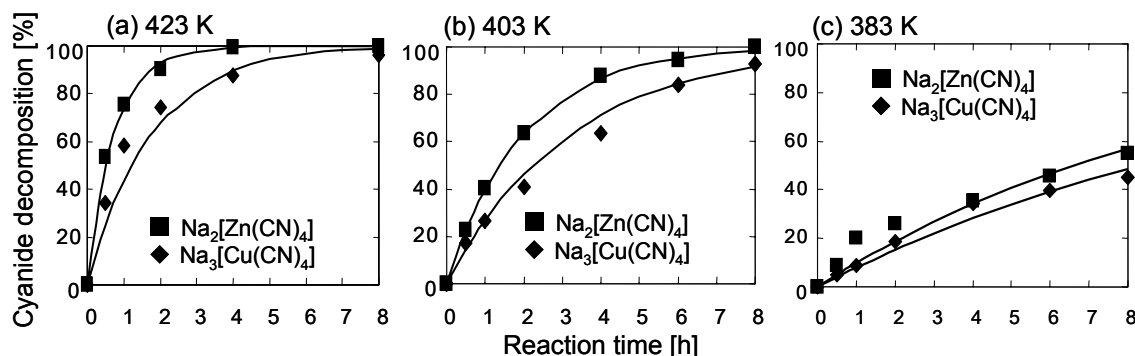
Figure 3. Decomposition of $Na_2[Zn(CN)_4]$ and $Na_3[Cu(CN)_4]$ at different temperatures

More precisely, at the reaction temperature of 423 K, it was found that the cyanide decomposition rapidly proceeded for the first 2 hours and the values of cyanide decomposition obtained were 74.5% and 90.5% for $Na_3[Cu(CN)_4]$ and $Na_2[Zn(CN)_4]$, respectively. Further, when the reaction time was extended up to 8 hours, the decomposition increased to 96.1% for $Na_3[Cu(CN)_4]$ and 99.9% for $Na_2[Zn(CN)_4]$. Generally, it can be seen that the decomposition of $Na_2[Zn(CN)_4]$ was higher than that of $Na_3[Cu(CN)_4]$, irrespective of reaction temperature, which was attributed to a higher stability of $Na_3[Cu(CN)_4]$ complex. The complex stability constants of $Zn(CN)_4$ and $Cu(CN)_4$ are reported to be $10^{19.6}$ and $10^{23.1}$, respectively (The Chemical Society of Japan, 1993).

Further, the results of the analysis of reaction by-products obtained after 2 hours at different temperatures are shown in Figures 4 and 5 for zinc cyanide complex and copper cyanide complex, respectively. In the case of $Na_2[Zn(CN)_4]$, $HCOO^-$ and NH_4^+ were mainly formed as reaction by-products, irrespective of reaction temperature. Then, regarding the decomposition of $Na_3[Cu(CN)_4]$, carbon of CN^- was transformed to H_2CO_3 and $HCOO^-$, while the nitrogen of CN^- was converted to NH_4^+ and N_2.
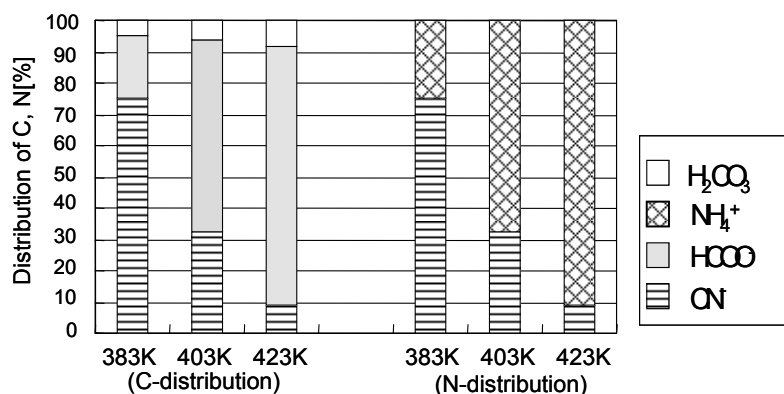

Figure 4. Distribution of C, N elements during wet oxidation of zinc cyanide complex (Pressure: 1 MPa; O_2 atmosphere; pH: 11 ~ 12; Cyanide initial concentration: 1000 mg dm^{-3}; Reaction time: 2 hours)

3.1. Mechanism of zinc cyanide complex decomposition at 423 K

Figure 6 shows the results of analysis of cyanide decomposition by-products and it can be seen that 86.3% of carbon of CN^- was converted to $HCOO^-$ within first 2 hours and this value increased to 100% after 8 hours of wet oxidation. Meanwhile, 89.6% of nitrogen of CN^- was converted to NH_4^+ within the first 2 hours and the value increased to 100% after 8 hours.
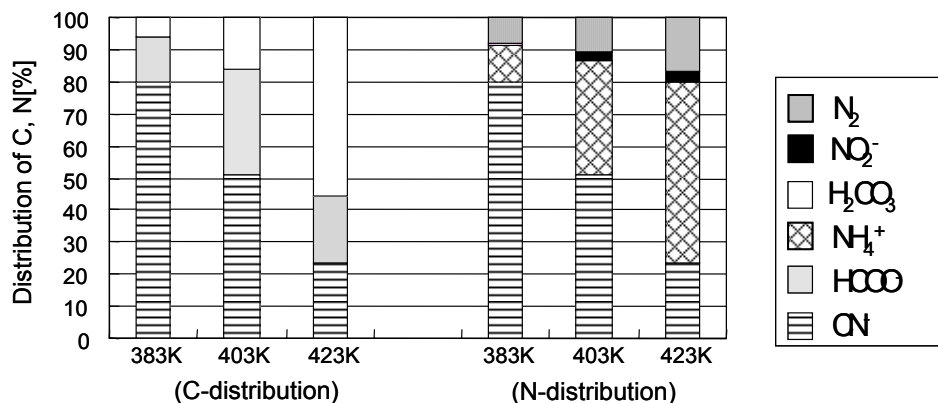
Figure 5. Distribution of C, N elements during wet oxidation of copper cyanide complex
(Pressure: 1 MPa; O_2 atmosphere; pH: 11 ~ 12; Cyanide initial concentration: 1000 mg dm^{-3};
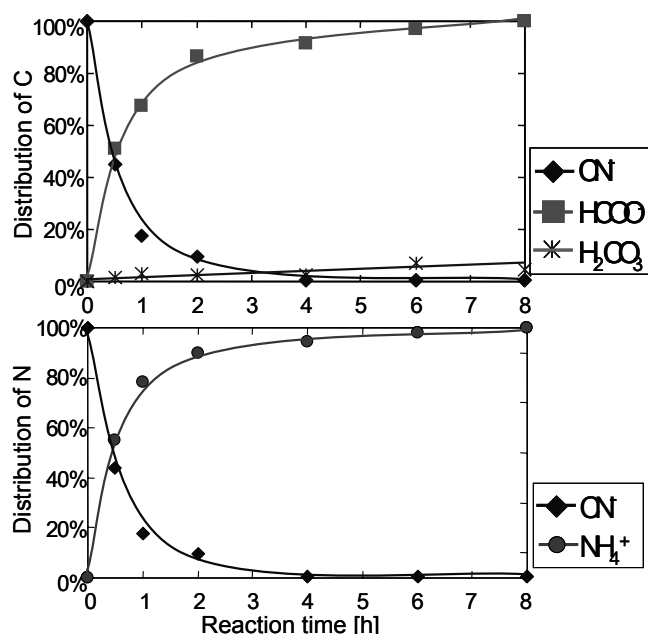Reaction time: 2 hours)

Figure 6. Carbon and nitrogen distribution after wet oxidation of zinc cyanide
(Temperature: 423 K; Pressure: 1 MPa; O_2 atmosphere; pH: 11 ~ 12;
Cyanide initial concentration: 1000 mg dm^{-3})

In consideration of reaction mechanism, it was assumed that zinc cyanide complex of $Na_2[Zn(CN)_4]$ was mainly decomposed to ammonia and sodium formate. Further, based on the XRD analysis of the reaction precipitate, it was concluded that, in alkaline pH range, the Zn^{2+} ions were precipitated as ZnO. The overall reaction mechanism of cyanide decomposition is expressed by Eq. (2). Subsequently, formic acid is supposed to be gradually converted to carbonic acid as shown in Eq. (3).

$$Na_2[Zn(CN)_4] + 2NaOH + 7H_2O \rightarrow 4NH_3 + 4HCOONa + ZnO \qquad (2)$$

$$HCOOH + 1/2O_2 \rightarrow H_2CO_3 \qquad (3)$$

3.2. Mechanism of copper cyanide complex decomposition at 423 K

Figure 7 shows the results of analysis of cyanide decomposition by-products and it can be seen that 58.0% of carbon of CN^- was transformed to H_2CO_3 and the remaining carbon was distributed among $HCOO^-$ and un-decomposed CN^-, within the wet oxidation for 8 hours. Meanwhile, the nitrogen of CN^- was converted to NH_4^+ (76.3%) and to N_2 (19.9%) within the
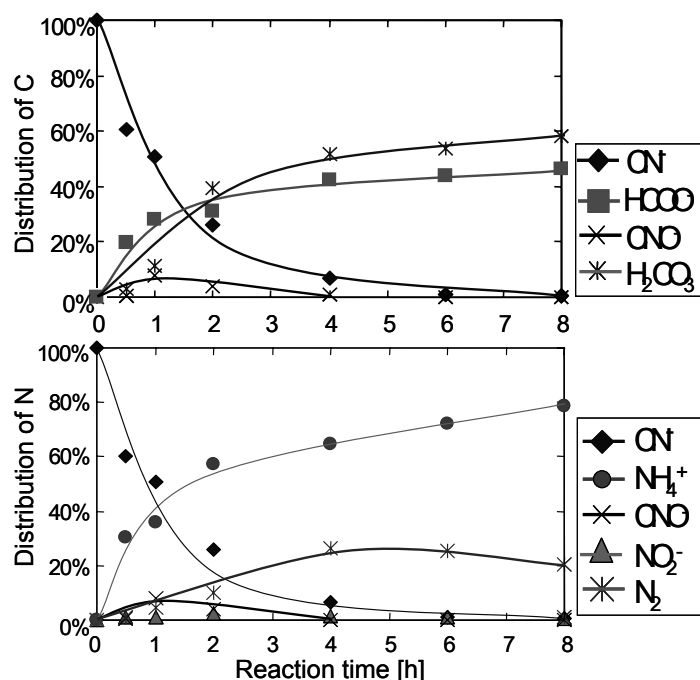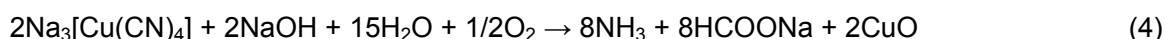
same period.

Figure 7. Carbon and nitrogen distribution after wet oxidation of copper cyanide
(Temperature: 423 K; Pressure: 1 MPa; O_2 atmosphere; pH: 11 ~ 12;
Cyanide initial concentration: 1000 mg dm^{-3})

The presence of various decomposition by-products suggested more difficult decomposition mechanism of $Na_3[Cu(CN)_4]$ than that proposed for $Na_2[Zn(CN)_4]$ and it was considered that $Na_3[Cu(CN)_4]$ decomposition proceeded via two sets of simultaneous reactions. The first set of reactions is given by Eqs. (4) and (5) and it was considered that $Na_3[Cu(CN)_4]$ was decomposed to ammonia and sodium formate (the mechanism is similar to that of $Na_2[Zn(CN)_4]$) and formic acid formed was partially converted to carbonic acid in the subsequent step. The metal ion of Cu^+ was oxidized to Cu^{2+} and subsequently precipitated as CuO.

$$2Na_3[Cu(CN)_4] + 2NaOH + 15H_2O + 1/2O_2 \rightarrow 8NH_3 + 8HCOONa + 2CuO \quad (4)$$

$$HCOOH + 1/2O_2 \rightarrow H_2CO_3 \quad (5)$$

The second set of reactions, expressed by Eqs. (6)-(8), involves an intermediate product of CNO^-, which was subsequently oxidized to H_2CO_3 and NO_2^-. The NO_2^- ions then supposedly reacted with NH_4^+ to form N_2 detected by gas chromatography.

$$2CN^- + O_2 \rightarrow 2CNO^- \quad (6)$$

$$2CNO^- + 3O_2 + 2H_2O \rightarrow 2H_2CO_3 + 2NO_2^- \quad (7)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (8)$$

4. CONCLUSIONS

The decomposition of $Na_2[Zn(CN)_4]$ and $Na_3[Cu(CN)_4]$ was carried out in a hydrothermal reactor at a temperature of 423 K, under oxygen atmosphere (pressure of 1.0 MPa). As a result, 99.9% decomposition of $Na_2[Zn(CN)_4]$ was obtained after wet oxidation for 8 hours. In the case of $Na_3[Cu(CN)_4]$, the decomposition of 96.1% was obtained at the same period.
Then, based on the analysis of decomposition by-products, the decomposition mechanisms of these cyanide complexes were proposed. In the case of zinc cyanide, $Na_2[Zn(CN)_4]$ was considered to be mainly decomposed to ammonia and sodium formate, while Zn^{2+} ions were precipitated as ZnO. As for the copper cyanide, two simultaneous decomposition mechanisms were proposed. The first decomposition mechanism involved $Na_3[Cu(CN)_4]$ decomposition to ammonia and sodium formate (the mechanism is similar to that of $Na_2[Zn(CN)_4]$),

accompanied by precipitation of copper ions as CuO. Meanwhile, the second decomposition mechanism was considered to proceed through an intermediate product of CNO^-, which was subsequently oxidized to H_2CO_3 and NO_2^-. The NO_2^- ions then supposedly reacted with NH_4^+ to form N_2.

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