THE INFLUENCE OF IRON ON AMMONIUM ION GENERATION FROM NITRATE ION IN LIQUID PHASE

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Introduction

Flue gas cleaning using non-thermal plasma process has been intensively studied and we have tried the NO_X and SO_2 removal process using the wet-type plasma reactor[(1)-(4)]. In this system, NO is oxidized to NO_2 and absorbed as NO_3^- while SO_2 is absorbed as SO_3^{2-} and oxidized in the liquid to SO_4^{2-}. But after the reaction, the pH value of the liquid became acidic and the absorption of NO_X and SO_2 was inhibited. Then, alkalization of the liquid was required. We tried the reduction reaction of NO_3^- to NH_4^+ using discharge above the level of the liquid, then the pH value of the liquid changed to alkaline. It has been reported that NO_3^- in liquid phase can be reduced to NH_4^+ using electrolysis [(5)(6)], and the wet-type plasma process can probably be more efficient [(7)(8)]. The objective of this study is to develop an efficient NH_4^+ generation method from NO_3^- to alkalize the liquid. HNO_3 solution was used and the reduction reaction of NO_3^- to NH_4^+ was tested.

Experimental

NH_4^+ generation from NO_3^- using the discharge plasma was tested using HNO_3 solution. Figure 1 shows the reactor for the discharge above the level of the liquid. A metal plate was placed at the bottom of the reactor as the ground electrode. A steel needle was placed 5 mm above the level of the liquid surface as the high voltage electrode and covered with a silicone tube (I.D.:4mm, O.D.:8mm) up to 2mm from the tip of the needle. Streamer discharge was generated between the tip of the needle and the suface of the liquid. It is well known that NO is effectively oxidized to NO_2 by gas phase plasma chemical reaction, and absorbed by water since NO_2 is soluble. This reactor was used because the discharge above the level of the liquid promotes the gas phase plasma chemical reactions, and the radicals generated in the gas or on the liquid surface are absorbed in the liquid to promote chemical reactions in the liquid. The reactor was driven by 250Hz square wave pulsed high voltage. The discharge power and waveform were measured by a digital power meter (HIOKI 3168) and an oscilloscope (TECTRONIX TDS 644A) respectively. NO_3^- and NH_4^+ concentration before and after the experiment were measured using an ion chromatograph (Metrohm Compact IC-731). Fe^{2+} and Fe^{3+} concentration were measured by colorimetric analysis of 1.10 phenanthroline.

Three types of metal plate, aluminum, platinum and iron were tested as ground electrode to investigate the influence of the metal types. Fifty mL of NO_3^- solution was used as the sample solution. The discharge above the level of the liquid was a streamer discharge. Ar gas was introduced into the gas phase of the reactor at a constant rate of 0.5L/min.

We checked the influence of Fe ion (Fe^{2+} and Fe^{3+}) and initial pH values to generate NH_4^+ from NO_3^-. Fifty mL of NO_3^- and Fe^{2+} sulution was prepared by dissolving Fe powder of less than 150 μm of diameter in HNO_3 solution. This solution is then filtered out through a paper that can let out particles less than 5 μm of diameter. The initial pH value of the liquid was adjusted by HNO_3 and KOH solutions. Pt plate was used as the ground electrode.

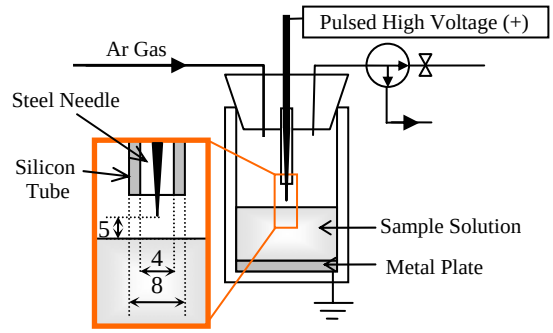

Figure.1 Plasma reactor for discharge above the level of the liquid

Results and Discussion

NO_3^- generation from N_2 and O_2 gas using the discharge above the level of the liquid As the background, NO_3^- generation from N_2 and O_2 gas using the discharge above the level of the liquid was studied. Figure 2 shows the experimental results of the time evolution of NO_3^- and NH_4^+ concentration using the discharge above the level of the liquid. Air at room temperature was used as the gas phase. The platinum plate, which showed low reactivity, was placed as the ground electrode. To remove the dissolved oxigen and nitrogen, 50mL of the pure water was used after 20min of cavitation. The discharge power and the peak voltage were 10W and 10kV respectively. In these conditions, NH_4^+ was not generated and the NO_3^- concentration increased with the time. Because room air was used as the gas phase, NO_3^- might have been generated from N_2 and O_2 gas by the discharge.

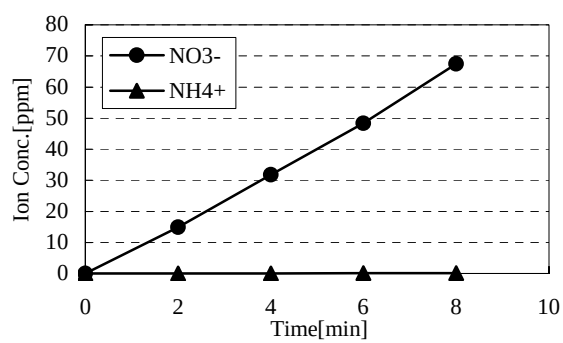

Figure 2. NO_3^- generation using discharge above the level of the liquid (Ground electrode: platinum, Gas phase: Room Air Batch, 10W, 10kV)

Discharge above the level of the liquid using Ar gas flow To eliminate the possibility of NO_3^- generation from N_2 and O_2 gas, Ar gas was fed to the reactor instead of room air. The reactor was filled with Ar gas flowing for few minutes before starting each experiment. Figures 3 and 4 show the NH_4^+ concentration and the pH value for different initial pH values. The discharge power and the peak voltage were 10W and 10kV respectively. NH_4^+ was generated using the discharge with Fe plate as the ground electrode for all the initial pH values (4, 7 and 10). The acidic condition was more effective for the NH_4^+ generation, better than neutral and alkaline conditions. But when aluminum and platinum plate were used, NH_4^+ was not generated for any initial pH values. When NH_4^+ was generated, the

pH value decreased. On the other hand, when the plasma discharge was not applied, NH_4^+ was not generated for none of all the types of electrodes. These results suggested that NH_4^+ was generated from NO_3^- in the case of discharge plasma and Fe plate as the ground electrode with the consequent alkalization of the solution.

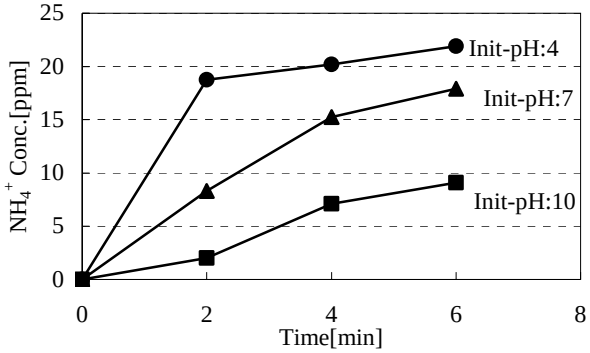

Figure 3. NH_4^+ generation using discharge above the level of the liquid for different initial pH values (GND: Fe plate, Gas: Ar flow 0.5L/min, 10W, 10kV)

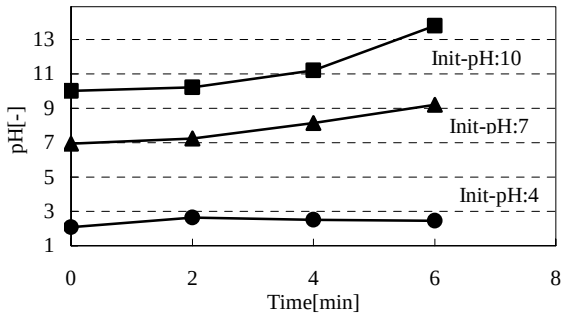

Figure 4. pH values using discharge above the level of the liquid (GND:Fe plate, Gas phase: Ar flow 0.5L/min, 10W, 10kV)

Influence of Fe ion (Fe^{2+} and Fe^{3+}) In the previous experiments, NH_4^+ was only generated when using Fe plate and the discharge above the level of the liquid, then, we checked the influence of Fe ion (Fe^{2+} and Fe^{3+}) to generate NH_4^+ from NO_3^-. Figure 5 shows Fe^{2+} and Fe^{3+} concentration in the acidic solution conditions when NH_4^+ was generated using the discharge above the level of the liquid. The discharge power and the peak voltage were 10W and 10kV respectively. When Fe^{2+} was present in the liquid, NH_4^+ was generated and Fe^{2+} was oxidized to Fe^{3+}. When only Fe^{3+} was present in the liquid, NH_4^+ was not generated and Fe^{3+} concentration did not change. The results showed that the reduction of NO_3^- to NH_4^+ was associated to the oxidation of Fe^{2+} to Fe^{3+}. Fe^{2+} was required to generate NH_4^+ from NO_3^-, and the pH value of the liquid is an important parameter. So the effect of the initial pH value was also tested. The pH value was set in 4, 7 and 10 and controlled by the addition of KOH solution. NH_4^+ was generated for all the pH conditions and Fe^{2+} was oxidized to Fe^{3+}. The pH value always increased after the discharge for all the initial pH values.

Conclusions

From the experimental study of the discharge above the level of the liquid, the following conclusions were obtained:

(1) NH_4^+ can be generated from NO_3^- conversion using the discharge in the presence of Fe in liquid solution. When platinum and aluminum plate were used as ground electrode, NH_4^+ was not generated.

(2) NH_4^+ generation from NO_3^- is related to the oxidation of Fe^{2+} to Fe^{3+}.

(3) The discharge converts NO_3^- to NH_4^+ changing the pH to alkaline levels.

These results suggest that the alkalized reaction by the discharge above the level of the liquid is possible and the wet type plasma reactor is effective for NO_X and SO_2 removal with the minimum consumption of water.

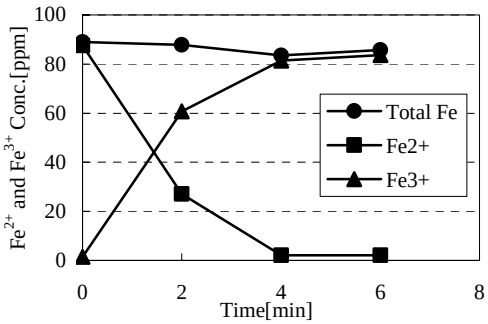

Figure 5. Fe^{2+} and Fe^{3+} concentration using discharge above the level of the liquid (GND: Platinum plate, Gas phase: Ar flow 0.5L/min, 10W, 10kV)

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References

(1) Akira Mizuno, J. S. Clements, and R.H.Davis, “Method for the removal of sulfur dioxide from exhaust gas utilizing pulsed streamer corona for electron energization”, IEEE Trans. Ind. Appl, Vol.22, pp.516-522, May/June 1986.

(2) R.Hackam and H.Akiyama, “Air Pollution Control by Electrical Discharges”, IEEE Trans.on Dielectrics and Electrical Insulation, Vol.7, No.5, pp.654-683, 2000.

(3) Akira Mizuno, Kazuo Shimizu, Tsutomu Matsuoka and Satoshi Furuta, "Reactive Absorption of NOx Using Wet Discharge Plasma Reactor", IEEE Trans. Ind. Appl, Vol.31, pp1463-1468, 1995.

(4) Hyun-Ha Kim, Chunxi Wu, Youhei Kinoshita, Kazunori Takashima, Shinji Katsura and Akira Mizuno, “The Influence of Reaction Condition on SO_2 Oxidation In a Discharge Plasma Reactor”, IEEE Trans. Ind. Appl, vol.37, pp.480-487, March/ April, 2001.

(5) Tsuyoshi Matsumura, Naohiro Goto, Hong-Ying Hu, Koichi Fujie and Toshiaki Tsubone, "Electrolytic Treatment of Nitrate in Wastewater" Journal of Japan Society on Water Environment, No.33, p.260, 1999.

(6) Tsuyoshi Matsumura, Mitsuru Iwasaki, Hong-Ying Hu and Koichi Fujie, ”Removal of Nitrite in Wastewater Using Metal Iron as Reductant”, Journal of Japan Society on Water Environment, No.32, p.84, 1998.

(7) Masato Kurahashi and Akira Mizuno, "Basic study of ammonia synthesis by discharge inside bubbles in solution", Journal of the Institute of Electrostatics Japan, pp.195-198, 1996.

(8) Keita Saito, Youhei Kinoshita, Naoki Okumura, Kazunori Takashima, Shinji Katsura and Akira Mizuno, "Reduction of NO_3^- on Wet Type Plasma Reactor Using Fe Electrode " Journal of the Institute of Electrostatics Japan, pp.117-118, 2002.