

SO₂ & NO_x 동시 제거 반응에서 ClO₂ 공급 속도에 따른 영향진동섭, 박보령, 조항대, 최원길, Bal Raj Deshwal¹, 박영성², 이형근*

한국에너지기술연구원 청정에너지연구부,

¹인도 A. I. J. H. M. 대학 화학과,²대전대학교 환경공학과

(hklee@kier.re.kr*)

Effect of ClO₂ Feeding Rate on Simultaneous Reaction of SO₂ & NO_x Removal by ClO₂Dong-Seop Jin, Bo-Ryoung Park, Hang-Dae Cho, Won-Kil Choi, Bal Raj Deshwal¹,
Young-Seong Park², and Hyung-Keun Lee*

Clean Energy Research Department, Korea Institute of Energy Research,

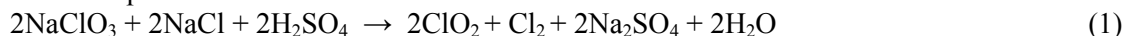
¹Department of Chemistry, A. I. J. H. M. College, India,²Department of Environmental Engineering, Daejeon University

(hklee@kier.re.kr*)

1. Introduction

Since 19th century industry revolution, about 85% of the world energy has been dependent on fossil fuels including a coal, petroleum and natural gas etc. and also it will remain as one of the major sources of energy forever. Toxic emissions like SO_x, NO_x, CO and HC are formed by combustion of the fossil fuel from incinerators, boilers, power plants and so on. Particularly, SO_x and NO_x are the major pollutants. Recently, it has become dire need to remove NO_x, because NO_x is increasing significantly. The emission of SO_x and NO_x is a major environmental concern because of their hazardous effects on human health such as respiratory problems and the ecosystems such as acid rain. Nitrogen oxides are also responsible for stratospheric ozone layers ruin, smog and visibility problems. So the effective reduction of NO_x emissions from both stationary and mobile sources poses a major challenge.

Chlorine-dioxide is yellowish green gas which has emerged as highly efficient chemical agent for bleaching, oxidation and disinfection. In this experiment, Chlorine-dioxide has been generated by reduction of chlorate with sodium chloride in a relatively concentrated acid solution in the manner described by Deshwal and Lee [2004] and Hong et al. [1967]. The general stiochiometry of this reaction can be expressed as follows:



Since sodium chlorate is very stable and does not decompose even in 10 to 12N sulfuric acid solution, so a solution of sodium chlorate in relatively concentrated acid is filled first in the reactor. Solid NaClO₃ can also be added directly into 10 to 12N sulfuric acid solution. Thereafter, NaCl solution is injected continuously at a suitable rate with the help of syringe pump or peristaltic pump. Chlorine-dioxide formation starts immediately on addition of sodium chloride. So chlorine-dioxide generation can be controlled by NaCl injection rate. The object of the present study is to know the effect of ClO₂ feeding rate in the simultaneous removal of SO₂ and NO_x.

2. Experimental Section

The experimental system is divided into two parts i.e. chlorine dioxide generation unit and flue gas treatment unit. Chlorine dioxide generation unit is composed of a reactor which is a well stirred sealed vessel having total volume of 2.5L. Concentrated sodium chloride solution (1M) was continuously injected into reactor at suitable flow rates (0.5, 0.8, 1 or 2 ml/min) by syringe pump. The reactor was filled with 1.5L solution of sodium chlorate (0.2M) in a relatively concentrated sulfuric acid (~12N). Continuous stirring was provided by a mechanical agitator. Temperature of the reaction vessel was controlled within 45±0.1°C by water thermostat. The reactor was wrapped with an

aluminium foil to avoid any photo-dissociation of chlorine dioxide. Nitrogen gas was purged through the reaction mixture using a bubbling device at a flow rate of 2L/min. Chlorine-dioxide carried by N₂ gas was further introduced into bubbling reactor.

Flue gas cleansing unit composed of simulated flue gas supply system, bubbling reactor, pH control system, ClO₂ absorber, data acquisition system, and sampling cum analysis system. The simulated flue gas was obtained by controlled mixing of SO₂, NO, N₂ and O₂ using mass flow controllers. Continuous stirring was provided by mechanical agitator with a speed of 250rpm. Temperature of the reaction vessel was controlled within 45±0.1°C. The pH of reaction solution was controlled at 3.5 by using an auto-pH control system by continuous addition of NaOH (0.2M) solution with the help of peristalsis pump. The chlorine dioxide absorber (2L vessel) consisted of ca. 2% carbonate buffered potassium iodide solution (1.5L). Samples from reactor and absorber were analyzed using either ion chromatograph (IC) or iodometrically with the help of auto-titrator (Metrohm-Swiss). The SO₂ and NO_x concentrations of inflow gas were analyzed using the gas analyzers (Ultramat 23, Siemens, Germany and Model: 42C, Thermo Environmental Instruments Inc., USA) after removing its moisture in the sample conditioner.

3. Results and discussion

Experiments were carried out at input SO₂ concentration of 500ppm, input NO concentration of 350ppm, pH of 3.5 and fixed temperature of 45°C to investigate the simultaneous removal of sulfur dioxide and nitric oxide using chlorine-dioxide. Concentrated sodium chloride solution (1M) was injected continuously into reactor at 0.5, 0.8, 1 and 2ml/min respectively with the help of syringe pump. Chlorine-dioxide formation started immediately on addition of concentrated sodium chloride. Thereafter, generated chlorine-dioxide came in bubbling reactor by using nitrogen gas (2L/min) as a carrier gas for further removal of SO₂ and NO_x.

3.1. Rate of chlorine-dioxide generation with injection rate of sodium chloride

The rate of chlorine-dioxide generation depends on several factors like molar concentration of sulfuric acid, molar concentration of sodium chlorate, molar concentration of sodium chloride, volume of the reaction solution and injection rate, temperature and quantity of sodium chloride and so on. In this experiment, chlorine-dioxide generation rate was investigated with the injection rate of sodium chloride solution. Fig. 1 shows the generated chlorine-dioxide with time at various injection rates of sodium chloride solution. Here, generated chlorine-dioxide indicates the inflow concentration of ClO₂ into the bubbling reactor. Inflow concentration of ClO₂ was determined at various injection rate of sodium chloride i.e 0.5, 0.8, 1 and 2ml/min. Supply of ClO₂ was stabilized after about 20 minute of ClO₂ generation. The rate of ClO₂ generation can be determines at any time from the equation that fits the curve best.

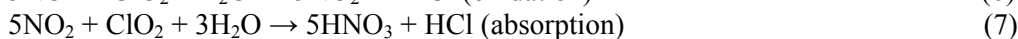
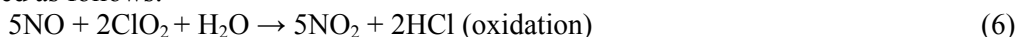
3.2. Simultaneous removal of sulfur dioxide and nitric oxide

Simultaneous removal of SO₂ and NO was also studied at input SO₂ and NO concentration of 500 and 350ppm respectively at pH of 3.5 at 45°C. SO₂ and NO_x removal efficiencies are plotted with time on the various feeding rate of ClO₂ in Fig. 2. Sulfur dioxide was removed about 95% by using NaOH and force air as oxidizing agent. When ClO₂ is passed into bubbling reactor, removal efficiency of SO₂ was increased to about 99%. The reaction between chlorine-dioxide and SO₂ can be expressed as [Sada, and Kumazawa, 1978]:

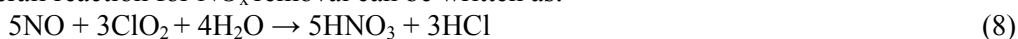


NO_x removal starts only after achieving 100% SO₂ removal. It is of course due to more reactivity of SO₂ compared to NO_x. The NO_x removal efficiency at various ClO₂ feeding rate is plotted in Fig. 3. Almost no NO_x removal has noticed at the feeding rate of ClO₂ from 0 to 0.5mmol/min.

However, NO_x removal was around 50% at ClO₂ feeding rate of 0.73mmol/minute and it increased to around 70% at ClO₂ feeding rate of 1.11mmol/min. When ClO₂ feeding rate was further increased to 2.03mmol/min, removal efficiency of NO_x didn't show any significant improvement. In Fig. 3, the output concentrations of NO_x are plotted against the various ClO₂ feeding rates. NO oxidation increased with increasing ClO₂ feeding rate and it has been found that ClO₂ can oxidize NO into NO₂ completely if it has sufficient concentration. The consistent and reproducible NO₂ absorption efficiency of about 70% is maintained during the course of experiment. NO_x removal by ClO₂ can be expressed as follows:



The overall reaction for NO_x removal can be written as:



3.3. Utilization of chlorine-dioxide for removal of SO₂ & NO_x

Fig. 4 shows the utilization of chlorine-dioxide at various feeding rate of ClO₂. Utilization of ClO₂ was calculated from difference between input ClO₂ and output ClO₂. In case of 0.55mmol/min ClO₂, it was found that there was about 99% utilization because ClO₂ evolved from the reactor is negligible. However, utilization of ClO₂ decreased with increasing feeding rate of ClO₂ as indicated by increasing output ClO₂.

3.4. Analysis of ion in the reactor after removal of SO₂ & NO_x

Formation of sulfate, nitrate and chloride as suggested above in the equations 2 to 8 is confirmed by analyzing the sample from bubbling reactor using ion chromatograph and variation of ion concentration with time is presented in Fig 5. And also, relation between calculated SO₄²⁻ and experimental SO₄²⁻ is plotted in Fig 6.

4. Conclusions

Effect of ClO₂ feeding rate on SO₂ and NO_x removal

Chlorine dioxide has several advantages for simultaneous removal of SO₂ and NO. The effect of feeding rate of chlorine dioxide can be summarized as:

- The ClO₂ generation rate depends on injection rate of NaCl,
- 99% SO₂ removal efficiency, 100% NO oxidation and about 70% NO_x removal efficiency has been achieved at optimum conditions.
- Removal efficiency of NO_x increased up to ClO₂ feeding rate of 1.11mmol/min and became constant thereafter.
- Utilization of ClO₂ decreased with increasing ClO₂ feeding rate.
- Calculated SO₄²⁻ has been found equal to the experimental SO₄²⁻ proving the mass balance.

References

- Deshwal, B.R., Lee, H.-K., "Kinetics and mechanism of chloride based chlorine dioxide generation process from acidic sodium chlorate", J. Hazard. Mater. **B108**, 173-182 (2004).
- Deshwal, B.R., Lee, H.-K., "Variation in ClO₂/Cl₂ Ratio in Chloride-Chlorate Process under Different Conditions", Journal of Industrial and Engineering Chemistry, 10, **4**, 667-673(2004).
- Hong, C.C., Lenzi, F., Rapson, W.H., "The kinetics and mechanism of the chloride-chlorate reaction", Can. J. Chem. Eng. **45**, 349-355 (1967).
- Hwang, Taek-Sung., Kim, Young-Su., Park, Jin-Won and Lee, Hyung-Keun., "Adsorption Properties of NO on PAN-based Fibrous Ion Exchanger and Its Potential for Air Purification", Journal of Industrial and Engineering Chemistry, 10, **4**, 504-510(2004).
- Sada, E., and Kumazawa, H., "Absorption of Lean NO in Aqueous Slurries of Ca(OH)₂ with NaClO₂ or Mg(OH)₂ with NaClO₂", Chem. Eng. Sci., **34**, 719-724 (1978).

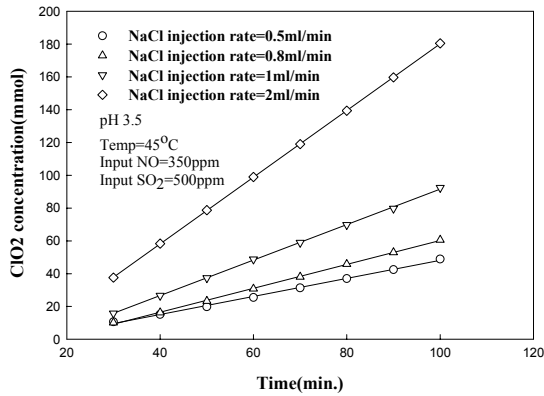


Fig. 1. Rate of chlorine dioxide generation with time.

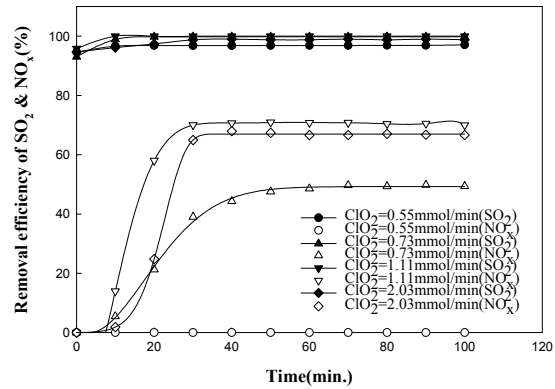


Fig.2. Removal efficiency of SO₂ & NO_x with time at various feeding rates of chlorine-dioxide.

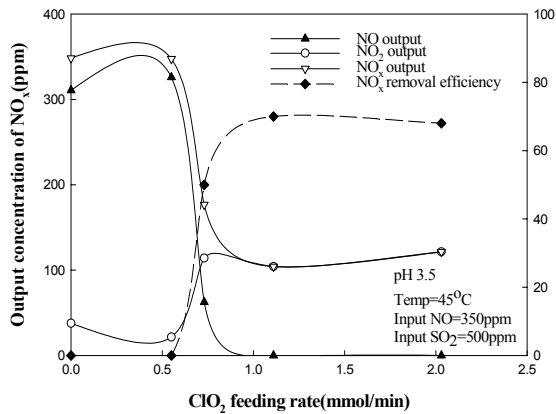


Fig. 3. Output concentration & removal efficiency of NO_x at various ClO₂ feeding rates.

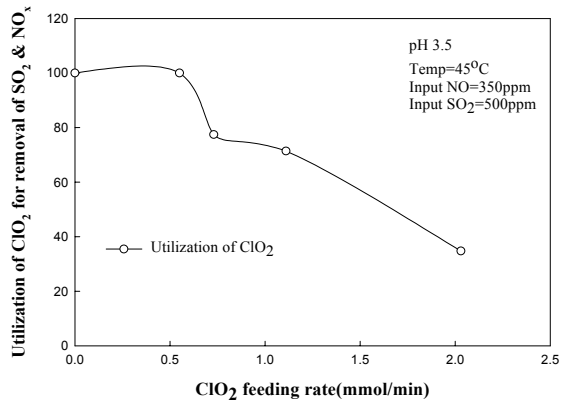


Fig.4. Utilization of chlorine-dioxide at various ClO₂ feeding rates.

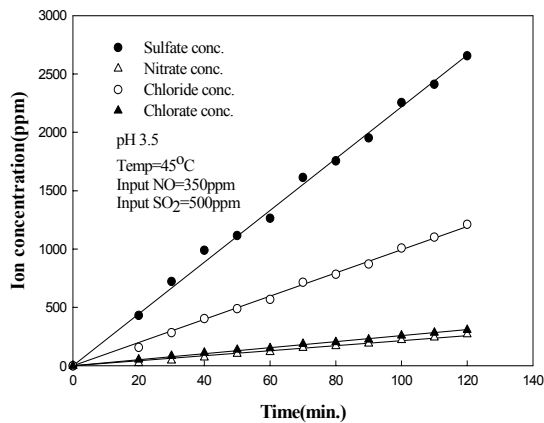


Fig. 5. Variation in ion concentration on passing ClO₂ in the simultaneous removal SO₂ and NO_x.

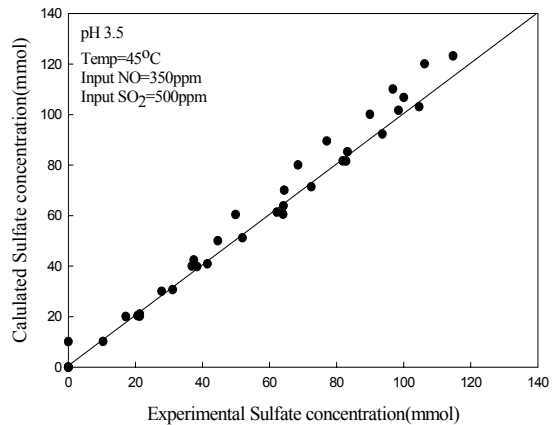


Fig. 6 Comparison between calculated and experimental sulfate