

Improvement of the SO_x Removal by Adding Dibasic Acids into the JBR FGD Processes

Byeong-Kyu Lee*, Sang-Ki Jeon¹⁾ and Seong-Won Cho¹⁾
Department of Civil and Environmental Engineering, University of Ulsan
¹⁾*Ulsan Thermal Power Plant, Korea East-West Power Corporation, Korea*

(Received 28 August 2001; accepted 5 December 2001)

Abstract

Jet Bubbling Reactors (JBRs) were operated for the removal of SO_x in flue gases produced from many electric power plants. However, many JBR flue gas desulfurization (FGD) facility faced a decrease of SO_x removal efficiency and an increase of scale problems with continuous operations. We increased alkalinity of the SO₂ absorbing medium by adding the dibasic acids (DBAs) to solve these problems more effectively. The SO₂ removal efficiency, the purity of CaCO₃ and COD of the wastewater was measured to identify the addition effects of DBAs (150, 200, 250, and 400 ppm) for 2 hr in a day into the JBR attached to the large-scale power plants (400 MW × 3). Addition of the DBAs resulted in the improvement of the SO₂ removal efficiency from 2 to 5% and the purity of the gypsum from 1 to 2%; these improvements were due to the alkalinity increase of the absorbing medium and the reduction of a proportion of un-reacted CaCO₃, respectively. Also, the scale problems formed by un-reacted CaCO₃ inside the reaction zone of the JBR were substantially reduced. Even though the effluent COD of the wastewater slightly increased from 10 ~ 15 to 18 ~ 36 mg/l and the erosion problems in the injection pump and duct occurred, this method of increasing SO₂ removal efficiency by adding the DBAs could be considered as a profitable approach.

Key words : SO_x removal, Flue gas desulfurization, DBAs, CaCO₃, Alkalinity, Solubility

1. INTRODUCTION

A rapid increase of the stationary and mobile sources has accelerated air pollution. The national ambient air quality standards in Korea is getting strict, thus the emission standards of air pollutants at sources will be enforced to reduce total air emissions (KME, 2000). Each power plant, which is one of the huge emission

sources of air pollutants, needs to add new air pollution control (APC) facilities or improve the existing APC facilities to satisfy the strict emission regulations. Especially, many power plants have made significant efforts to reduce the air emissions of SO_x. Many different flue gas desulfurization (FGD) technologies have been developed (Kim *et al.*, 2000; Whang and Lee, 2000; Bong *et al.*, 1998; Song *et al.*, 1998; Wark *et al.*, 1998; Kim, 1993; Lee *et al.*, 1993). The FGD facilities were established in 609 electric power plants which produce total 164,000 MW electricity in 22 countries (KPP,

* Corresponding author.
E-mail : bklee@mail.ulsan.ac.kr

2000; Wojozewicz *et al.*, 1999). Currently, there are 27 FGD facilities established in the electric power plants which use heavy oils as a fuel in Korea and 4 additional new FGDs are under construction in the power plants (KPP, 2000). Recently, Korean government has proposed a new regulation on permissible SO_x emission, which requires satisfying 70 ppm of SO_x emission concentration at the new coal power plants after the year 2004 (KME, 1999). Therefore, the SO_x removal efficiency at the existing FGD facilities should be improved or modified to satisfy the enforced regulation on SO_x emissions at sources. Currently, FGD facilities with JBR have been operated for the removal of SO_x in the flue gases produced from many electric power plants. However, many JBR FGD facilities have faced the decrease of removal efficiency and the increase of scale problem with continuous operations. Various methods to improve SO_2 removal in flue gases in the FGD processes using CaCO_3 have been used (Bejarano and Jia, 2000; Stevens *et al.*, 1993). The improvement methods included the followings: 1) the reactivity improvement through a careful selection and finely pulverizing of reaction materials, 2) the efficiency improvement of the element facilities like absorber (scrubber), and 3) the improvement of the operating conditions like the contact ratios between gas and liquid or pH adjustment. In addition, the improvement in liquid alkalinity of the circulating slurry and in the contact efficiency between gas and liquid in the absorber in the existing FGD processes are also useful for increasing the SO_2 removal efficiency. The liquid alkalinity of the slurry is improved with increasing pH or adding dibasic acids (DBA) into the circulating slurry (Hammack and Gohara, 1997). Increasing pH brings about a rapid increase of a solid phase alkalinity rather than a liquid phase alkalinity. However, the species reacting with the absorbed SO_2 in the absorbing medium are liquid phase alkalinity. Therefore, the actual removal efficiency of SO_2 is reduced compared to the expected efficiency. In order to improve or compensate the reduced SO_2 removal efficiency, the excess addition of CaCO_3 is required. Because of decrease of CaCO_3 utility in the

liquid phase, however, the proportion of the un-reacted CaCO_3 , which is located in the solid phase, will increase. Therefore, the methods to improve the liquid phase alkalinity with keeping a minimum increase of the solid phase alkalinity should be applied to improvement of SO_2 removal efficiency. The addition of the DBA can solve these problems more effectively. From this point of view this study tried to improve the removal efficiency on SO_2 in flue gases by adding the DBAs into the JBR FGD processes of the electric power plants.

2. MATERIALS AND METHODS

The Jet Bubbling Reactor (JBR: CHIYODA Co. Ltd.) used in this study directly sprays the flue gases including SO_2 into the absorbing medium (pulverized CaCO_3 passed (90%) through 200 mesh) using the gas sparger. Four reactions including the absorption of SO_2 , the oxidation of acid sulfite to acid sulfate, the neutralization of acid sulfate, and the growth of gypsum crystal simultaneously occur in the JBR. These reactions are started in the jet bubbling zone and completed in the reaction zone of the JBR. In the jet bubbling zone the interfacial area between gas and liquid is formed, thus SO_2 in the flue gases is dissolved into the liquid film on the bubble surface. The bubble sizes are ranged from 3 to 20 mm and the liquid droplets smaller than the bubbles are sometimes formed within the gas bubbles. Limestone slurry is fed into the reaction zone located in the bottom part of the jet bubbling zone. The reaction zone is designed to maintain the slurry residence time longer than 20 hrs. Thus the JBR can have much longer residence time than that of a spray type. In general, the removal efficiency on SO_2 of the JBR might be better than other SO_2 control devices. This is because the JBR has more effective contact zones between gas and liquid and a longer residence time in the reactor than the other types. The SO_2 removal efficiency of the JBR is given as a function of the depth of the sparger submergence, in general, ranging the depth

of 100 (150 mm). The depth of the sparger submergence is adjusted by controlling the pressure difference between the inlet and the outlet by providing raw water and filtrate water into the gas cooling section. The main power to remove SO₂ comes from not the slurry recirculation pump like a spray type but the booster fan. The JBR is designed to be operated in the pH range, 4.5~5.5. This pH value is very low compared to a spray type, and thus the JBR has some other advantages: a rapid dissolution of CaCO₃, a small proportion of unreacted CaCO₃, an accumulation prevention of alkali species in the absorber, a rapid and complete oxidation of sulfite to sulfate, and a better removal efficiency on SO₂.

In order to improve the SO_x removal efficiency and to solve the scale problems occurred within the JBR FGD facilities, this study employed a method to increase alkalinity of the absorbing medium by adding dibasic acids (DBAs) which are obtained as by-products generated from plants synthesizing adipic acid. The DBA solution, which consisted of 3% of adipic acid, 4% of succinic acid, and 12.4% of glutaric acid, was injected into the filtrate pump suction line by a pump. In order to maintain constant DBA concentration of 19.4% in the absorber, the gypsum slurry concentration in the absorber decreased down to 15% before the experiment started. Also, the constant DBA concentration (analyzed by HPLC) was maintained by stopping the emission of the gypsum slurry in the absorber during the experiment of the DBA addition. Also, the amount of changes in the removal efficiency of SO₂, the purity of CaCO₃, and COD of the wastewater, by adding DBAs for 2 hours in a day into the JBR attached to the large-scale power plants (400 MW × 3), were measured. The SO₂ removal effect was measured by an in-situ type SO₂ analyzer (Thermo Environmental Co.) that measures a change of UV absorbance depending upon SO₂ concentration. The efficiency change of SO₂ removal at the JBR inlet and outlet was evaluated as a function of DBA addition concentrations that are 150, 200, 250, and 400 ppm.

3. RESULTS AND DISCUSSION

In the reaction slurry of the JBR both the absorption of SO₂ and the dissolution of CaCO₃ simultaneously occur. In the previous experience of the JBR operation the pH decrease in the interface between gas and liquid decreased the solubility and absorption rate of SO₂. Thus the SO₂ removal efficiency decreased with a continuous operation of the JBR. Also, the pH increase in the interface between solid and liquid decreased the solubility and dissolution rate of CaCO₃. Thus, in order to keep the constant SO₂ removal efficiency, it was necessary to put more CaCO₃ into the reaction zone, and thus it produced scale accumulation problems due to unreacted or undissolved CaCO₃ inside the reaction zone. Therefore, pH conditions in reaction slurry should be controlled with optimum conditions to improve both the solubility and absorption rate of SO₂ and the solubility and dissolution rate of CaCO₃.

Table 1 shows the effects on SO₂ removal and gypsum purity by addition of DBA in the JBR FGD processes in the oil-fired power plants. When the concentration of the DBA added in the JBR FGD increases up to 250 or 400 ppm, the SO₂ removal efficiency and the gypsum purity were slightly improved compared to that prior to the addition of the DBAs. The highest SO₂ removal effect was observed at the highest addition concentration of the DBAs.

The DBAs used in this study was a mixture of dicarboxylic acids that have two pK_a values, e.g., adipic acid has two pK_a of 4.5 and 5.5, and thus they provided a buffering effect in the process of the JBR FGD. The DBA ions composed of adipate, succinate, and glutarate promote absorption of SO₂ into the absorbing medium. The increase of the liquid phase alkalinity by addition of the DBA could improve the conversion of SO₂ gas to liquid phase SO₂, one of the rate controlling steps, on the bubble film surface in the jet bubbling zone of the JBR. Then the reaction of the DBA ions with SO₂ produces acids in the limestone slurry and then the acids promote the solubility of CaCO₃. Therefore, the

Table 1. Effects on SO_x removal and gypsum purity by addition of DBA in the JBR FGD.

Power plant	DBA injection status	DBA injection (ppm)	Load (MW)	SO _x (ppm)		Removal efficiency (%)	Gypsum purity (%)	COD (mg/l)
				Inlet	Outlet			
A	Before injection	–	338	1,285	106	91.7	95.4	10 ~ 15
	After injection	150	341	1,301	103	92.0	96.8	18 ~ 35
		200	370	1,340	98	92.7	96.5	
		250	380	1,386	96	93.0	96.7	
B	Before injection	–	296	1,194	121	89.9	95.4	10 ~ 15
	After injection	150	373	1,315	128	90.4	96.8	18 ~ 36
		200	380	1,319	125	90.5	96.8	
		250	380	1,322	115	91.3	96.7	
		400	380	1,289	77	94.0	96.8	

increases in solubility of SO₂ and dissolution of CaCO₃ in the absorbing medium promote SO₂ removal effects. That is, the SO₂ removal efficiency is improved by both the increase of the liquid phase alkalinity by the DBA addition and the acids produced in the DBA addition process. In fact, the reversible process of DBAs can occur depending upon pH of the reaction medium and thus DBAs can role as a kind of buffer materials without consumption. Therefore, the consumption rate of the DBAs in FGD fields is not calculated by a simple material balance equation but it is dependent upon the following operating conditions: SO₂ input concentration (determined by a sulfur content in a fuel), DBA addition concentration (determined by SO₂ removal efficiency) and pH. In general, DBAs are not materials consumed in the SO₂ removal reaction with CaCO₃ except for operation losses. Thus just making up the amount lost in operation like a solution loss and a non-solution loss is enough to keep the system effectively. Also, it does not have to add continuously or constantly the DBAs and it is enough to add the amount required for the day from a storage tank for 1 or 2 hours in a day.

Increase on SO₂ removal efficiency could decrease the amounts of CaCO₃ added into the reaction zone of the JBR. Thus the proportion of un-reacted CaCO₃ resulting from insufficient solubility of CaCO₃ could reduce and then the purity of gypsum increased. This truth implies that we could overcome the scale pro-

blems formed by un-reacted CaCO₃ inside the reaction zone of the JBR.

One of the identified disadvantages by addition of DBAs in the JBR was increase on chemical oxygen demand (COD) of the effluent water. For example, the COD in the outlet of the JBR and the COD of the effluent water before the DBA addition was 250 and 18 mg/l, respectively. However, the COD in the outlet of the JBR and the COD of the effluent water after the DBA addition was 640 and 36 mg/l, respectively. Since the permissible emission standard on a COD value in the effluent water is currently 90 mg/l, the COD value in the effluent water by the DBA addition was still a very safe range. However, in this study, the result of the COD value in the effluent water is still uncertain. This is because this study was performed only up to the addition the DBA of 400 ppm. In general, the JBR process has advantages there are almost no COD causing materials in the slurry. This COD increase might be due to the bleeding water contained DBAs, however, the COD increase mechanisms not clear yet. In a continuous increase of the addition concentration of the DBA more than 400 ppm for further improvement on the SO₂ removal efficiency, higher COD value could be observed. Therefore, further experiments to check the effects of SO₂ removal and COD value with increase of DBA concentration are highly required. Another disadvantage of the DBA addition is the erosion problems occurred in the injection pump and duct. This

erosion was due to strong corrosive 5% of HNO₃ contained in the DBA components. Thus it was identified a bad pumping and some leakage at the injection facilities.

Even though the slightly higher COD value and some erosions are expected with an addition of higher DBA concentration, the DBA addition in the JBR is sufficiently profitable. That is, even though a slight increase, 2~5%, of the SO₂ removal efficiency is obtained by adding DBAs into FDG facilities with JBR, the total saving is substantial. This is because very expensive costs are necessary to even a slight increase of the SO₂ removal efficiency of the system. Also, because of decrease of the consumption of the CaCO₃ in the JBR FGD processes, the purchasing costs of CaCO₃ will reduce. The sale price of the gypsum owing to the increase in the gypsum quality or purity could be more profitable. In addition, since the DBA is obtained as by-products in Korea, the DBA is very stably provided from the domestic markets and the purchasing cost is also very low.

4. CONCLUSIONS

The dibasic acids (DBAs) were added into the flue gas desulfurization (FGD) processes with Jet Bubbling Reactor (JBR) to improve the removal efficiency on SO₂ in flue gases in the electric power plants. Increase of liquid alkalinity of the absorbing medium by addition of the DBAs caused the improvement in the SO₂ removal efficiency of 2~5%. The acids produced from the reactions between SO₂ and DBAs increased the dissolution of CaCO₃ in the slurry. This increase of the dissolution of CaCO₃ improved the reactions between the SO₂ and CaCO₃, thus resulted in increasing the SO₂ removal efficiency. The proportion of the un-reacted CaCO₃ was also reduced and it resulted in improvement of the purity of the gypsum of 1~2%. In addition, the scale problems formed due to the un-reacted CaCO₃ inside the reaction zone of the JBR was substantially reduced. However, the effluent COD of the

wastewater produced from the SO₂ removal facilities increased from 10~15 mg/l to 18~36 mg/l. However, the erosion problems occurred in the injection pump and duct. As an overall evaluation, however, this method adding DBAs into the FGD facilities with JBR could be considered as a profitable approach to improve SO₂ removal.

REFERENCES

- Bejarano, C. and C.Q. Jia (2000) Developing a Coke-based Sulfur-Producing Flue Gas Desulfurization (SP-FGD) Process. In: *Proceedings of 93rd Annual Conference & Exhibition of AWMA*, Salt Lake City, Utah, USA, June 18-22, AE-1d 00-185.
- Bong, C.K., M.J. Boo, J.H. Kim, J.J. Lee, and S.D. Kim (1998) The characteristics of the treatment of pollutants (SO₂, NO_x) using surface discharge induced plasma chemical process, *J. KAPRA*, 14(4), 333-341.
- Chung, J.S. (1993) Recent Technologies for control of SO₂ emission from stationary sources, *J.KAPRA*, 9(1), 25-32.
- Hammack, D.L. and W.F. Gohara (1997) Use of stack emissions to control DBA enhanced FGD systems burning fuel highly variable in sulfur content, presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium, Washington, DC.
- Kim, B.J., S.H. Chung, W.S. Hong, J.H. Kim, C.Y. Park, D.H. Ha, and B.H. Ham (2000) Experiment of back corona in electrostatic precipitator. In: *Proceedings of 31st Meeting of KOSAE*, Kyungseong Univ., November 10-11, EB5.
- KME (Korean Ministry of Environment) (2000) Designation and management of areas required special measures for air protection, *Environmental white book in Korea*, 306-308.
- KME (Korean Ministry of Environment) (1999) Amendment proposal on the permissible emission standards of air pollutants.
- KPP (Korea Power Plant Co. Ltd.) (2000) Improvements on desulfurization efficiency. In: *Proceedings of seminar on desulfurization technologies*, 53-85.
- Lee, H.K., I.H. Baek, and S.H. Kim (1993) Disposal of sludge produced from flue gas desulfurization by wet

- process, In: *Study of technologies for recovering energy from specified wastes*, KE-93012B, 253-267.
- Song, H.C., Y.K. Lee, and J.W. Park (1998) A study on SO₂ removal in flue gas by semidry flue gas desulfurization method, *J. KAPRA*, 14(4), 273-280.
- Stevens, G.E., W.M. Horton, O.W. Hargrove, and D.R. Owens (1993) Evaluation of high SO₂ removal efficiency upgrade options: EPRI high sulfur test center, presented at the 1993 SO₂ Symposium, Boston, MA.
- Wark, K., C.F. Warner, and W.T. Davis (1998) Control of sulfur oxides and other acid gases. In: *Air pollution: its origin and control*, 3rd Edn., Addison Wesley, 400-429.
- Whang, S.K. and S.K. Lee (2000) An experimental study of the combined removal SO₂ and HCl in a dry lime injection scrubber. In : *Proceedings of 31st Meeting of KOSAE*, Kyungsoong Univ., November 10-11, EA4.
- Wojozewicz, W., R. Singer, K. Srivastava, and P.E. Tsirigotis (1999) Status of SO₂ scrubbing technologies, presented at EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium, Vol. 1, Atlanta, GA.