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Evaluation of amine emissions from the post-combustion CO₂ capture pilot plant

Koshito Fujita^{a*}, Daigo Muraoka^a, Takashi Ogawa^a,
Hideo Kitamura^b, Kensuke Suzuki^b, Satoshi Saito^b

^aToshiba Corporation, 1 Toshiba-cho, Fuchu-shi, Tokyo183-8511, Japan

^bToshiba Corporation, 2-4 Suehiro-cho, Tsurumi-ku, Yokohama 230-0045, , Japan

Abstract

In this work, we evaluated amine emissions from 10ton-CO₂/day scale pilot plant in Mikawa Power Plant of Sigma Power Co. Ltd. within TS-1 solvent. Firstly, we investigated that how sampling gas flow rate affects measured value of amine concentration in flue gas by using on-line sampling method with PTR-MS analyzer. It was found that the error from an iso-kinetic sampling rises sharply for lower sampling velocities and in the range of higher sample stream velocities, however the error is lower. Secondly, we compared between beginning of operation and 2,800 hours operation in terms of amine emissions at Mikawa pilot plant under one set of conditions. At beginning of operation, there were no degraded amines in TS-1 solution. Thus, there were no amine emissions of degraded amines. However, at 2,800 hours operating, in addition to TS-1 emissions, some quantity of emissions of degraded amines were detected even though degraded amines were much less than TS-1 main amine in TS-1 solution. Toshiba improved operating conditions such as plant system, water wash system to reduce the amount of amine emissions. As a result, the latest tests showed lower emissions of less than 1 ppm(v/v) at 2,800 hours operation. A concentration of degraded amine [D] in TS-1 solution at 2,800 hours operation, which was nearly detection limit, was lower than other degraded amines. Nevertheless, degraded amine [D] accounted for the greater part of amine emissions after water wash was improved. This result suggested that it is crucial to reduce the volatility of emitted degraded amines in order to improve performance of suppression amine emissions further. Then, finally we evaluated effect of addition acid to reduce the volatility of degraded amine [D]. The results in diluted aqueous amines at 40°C showed that effectiveness of acid for reducing amine volatility is in the order: sulfuric acid > oxalic acid ≈ carbonic acid produced by 10%CO₂ > boric acid.

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1. Introduction

Post-combustion carbon dioxide capture is the technique that can be rapidly and safely employed for substantially reducing carbon dioxide emissions from existing and near future power plants. The key question of the absorption/desorption technique for carbon dioxide removal is process economics.

Toshiba is pushing through the post-combustion carbon dioxide capture because it can be employed in rather short period and applied for both retrofit and new thermal power plants.

Toshiba constructed 10ton-CO₂/day scale pilot plant in Mikawa Power Plant of Sigma Power Co. Ltd. in September 2009, and started the test operation using Toshiba solvent(TS-1) to verify the performance of the system with actual flue gas [1]. In the demonstration tests CO₂ capture ratio and captured CO₂ rate exceeded the planning values of 90% and 10t-CO₂/day each during continuous 3,000 hours operation [2]. Moreover, the energy consumption for CO₂ recovery at the stripper had been kept between 3.2 and 3.3 GJ/t-CO₂. These values were much larger than the predicted ones using the thermodynamic simulation. We analyzed the energy flow and the CO₂ loading and compared to the predicted values. After that we modified the pilot plant and found that the energy consumption for CO₂ recovery at the stripper decreased to 2.6GJ/t-CO₂ [3].

On the other hand, CCS plants need not only low heat consumed in the distiller but also near zero amine emissions to the air for two reasons. First, Amine emissions pose serious environmental risks with the resulting by products being potentially more toxic than the parent amines themselves. The photo-oxidation of selected amines by NO_x, HNO₃, O₃ and so on can produce nitrosamines and nitramines which are said to be carcinogenic factor. Second, the make-up costs for lost amines can be quite expensive. Therefore, it is crucial to reduce amine emissions to employ full-scale CCS plants.

In this work, we evaluated amine emissions from 10ton-CO₂/day scale pilot plant within TS-1 solvent and measured the volatility of aqueous amines which have been found in TS-1 solvent during continuous 3,000 hours operation. We also investigated effect of addition acids to reduce the volatility of aqueous amines.

2. Experimental Section

2.1. Sampling points

Figure 1 shows Schematic of PCC Pilot Plant in Mikawa Power Plant. Actual flue gas for pilot plant is introduced from the existing coal-fired power plant and captured CO₂ is returned to the Power Plant. Gas and liquid sampling points are also shown in Figure 1. [i] gas sampling point for measuring amine emissions is located at downstream of condenser exit. [ii] liquid sampling point is used to analyze concentrations of degraded amines in TS-1 solvent.

Illustration of measurement site for amine emissions ([i] gas sampling) is presented in Fig.2. We inserted a probe to collect the flue gas containing a mixture of gaseous components, aerosols and droplets at varying sizes. Gas inlet of the probe was set facing gas stream, and center circle of stack pipe. Straight length of inlet section was secured over 20*d_h (diameter of stack: 250mm), and that of outlet section was secured over 10*d_h for appropriate flow path.

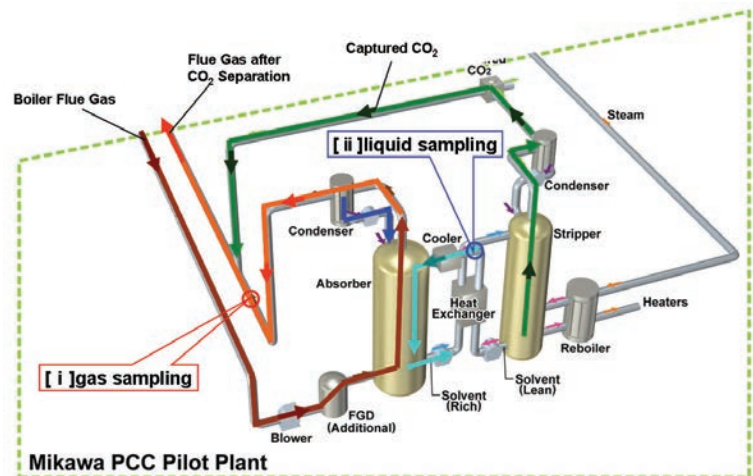


Figure 1 Schematic of PCC Pilot Plant in Mikawa Power Plant

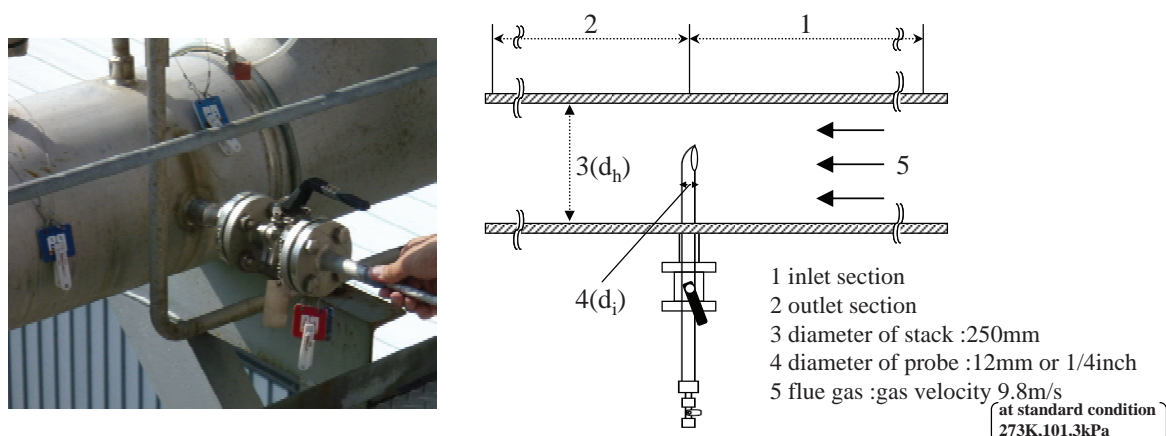


Figure 2 Illustration of measurement site for amine emissions

2.2. On-line analytical method for amine emissions

Amine emissions were measured by using Proton Transfer Reaction-Mass Spectrometry (PTR-MS, Ionicon Analytik GmbH) under on-line operation as shown in Figure 3. The suction pump and the needle valve allow us to adjust the amount of sampling gas, i.e. to set the same velocity as the flue gas in stack pipe. Additionally, Mists and aerosols contained in Sample gas were heated by line heater (150°C) to vaporization, and a part of heated gas was introduced to “PTR-MS” automatically. A major part of heated gas was cooled by water cooler to atmosphere temperature to meet the specification of the mass flow meter. This method can detect amine emissions to less than 10ppb(v/v)*. The system normally operated at a sampling gas flow rate of 8.8NL/min with probe of 1/4inch diameter, which provides a same gas velocity as the flue gas in stack pipe.

*In this paper, concentrations of amines in flue gas expressed in ppm(v/v) or ppb(v/v). This expression means number of moles of amines respectively in both gas phase (vapor) and liquid phase (mist and aerosols) relative to the total number of moles of all substances in the gas phase.

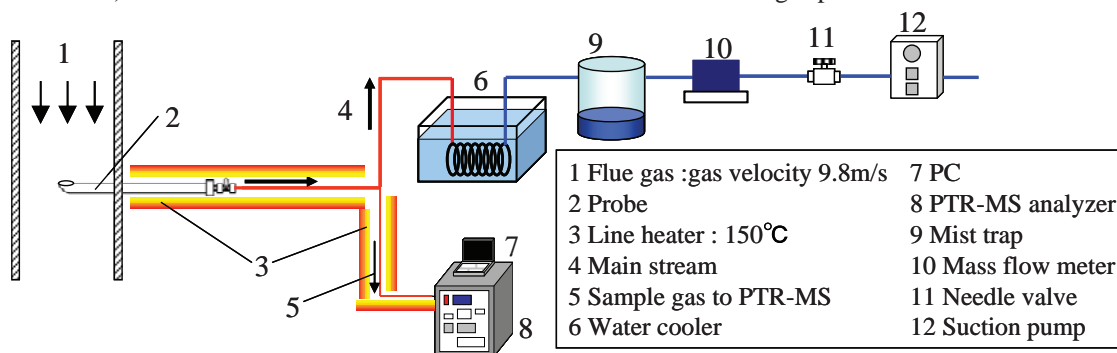


Figure 3 On-line analytical method with PTR-MS

2.3. Batch (manual) analytical method for amine emissions

Schematic drawing of batch (manual) analytical method is presented in Figure 4. Flue gas was sampled by bubbling through the reagent in two impingers catching vapor and mist amines for approximately an hour, which provided enough time for accumulating amines that allowed us to detect amines to less than 0.2 ppm(v/v) by GC/MS (5975, Agilent Technology) and LC/MS (HP1100, Agilent

Technology). As the amount of second impinger capturing amine was much less than a-tenth that of first impinger, it is thought that two impingers can catch almost all amines in flue gas. The method for estimating the concentration of amine in flue gas is given in equation 1 and 2.

$$C_1 [\text{mg} / \text{Nm}^3] = A \times 20 [\text{ml}] / \left(G_{\text{total}} \times \frac{273}{273 + t} \right) \quad (1)$$

$$C_2 [\text{ppm}(\text{v} / \text{v})] = \frac{C_1}{M} \times 22.4 \quad (2)$$

C_1 : concentration of amine [mg/Nm^3]

C_2 : concentration of amine [ppm]

20[ml]: total amount of reagent in an impinger

A: concentration of amine in the reagent [$\mu\text{g}/\text{ml}$]

G_{total} : total amount of bubbling gas

t: bubbling gas temperature [$^{\circ}\text{C}$]

M: mol weight of amine [kg/kmol]

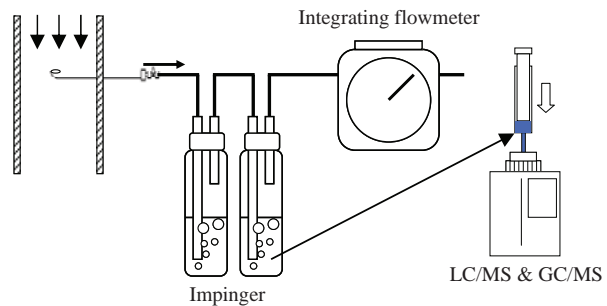


Figure 4 Schematic drawing of batch analytical method

2.4. Measurement of amine volatility

Amine volatility was measured in a 100 cc glass reactor with 50 cc of aqueous amine at 20 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$, and 60 $^{\circ}\text{C}$, as shown in Figure 5. 100% N_2 or 10% CO_2 gas (N_2 base) was bubbled through the aqueous amine from 0.5 to 1.0 NL/min at atmospheric pressure. Moreover, the exhaust gas from the reactor was cooled and condensed to trap amine vapor into the reagent, which was analyzed by GC/MS and LC/MS. Thus, volatility of amines was estimated by amounts of both the bubbled gas volumes and amine concentration in the reagent, given in equation 1 and 2.

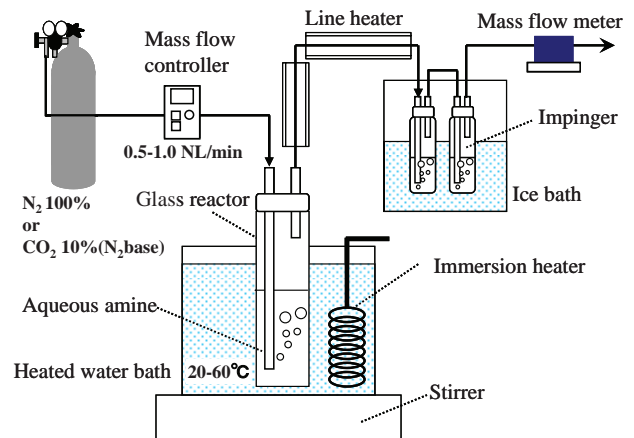


Figure 5 Illustration of measurement of amine volatility

3. Results and discussion

3.1. Effect of sampling gas flow rate

We investigated that how sampling gas flow rate affects measured value of amine concentration in flue gas by using on-line sampling method (Figure 3). Amine concentration in flue gas consists of a gaseous component (vapor), non-gaseous component such as aerosol and droplet at varying sizes. It is generally agreed that it is necessary to remove the sample stream at the same velocity as the main stream of flue gas at the point of sampling for collecting a representative sample which is correct with respect to non-gaseous circumstance. Sampling gas flow with droplets can be broadly divided into three cases regarding sampling velocity, as shown in Figure 6. In the iso-kinetic case ($V_s = V_0$), the amount of

particles entering probe is same as the circumstance in flue gas. If the sample taking velocity is too low ($V_s < V_o$), heavy particles can enter the probe even if the gas flow line on which they were located passes by the probe. As the result, too many large particles are collected. On the other hand, if the sample taking velocity is too high ($V_s > V_o$), heavy particles fail to follow the gas flow lines and end up bypassing the probe. Thus, it is thought that too few large particles are collected.

Anisokinetic sampling result with the 1/4 inch diameter probe in Mikawa pilot plant under one set of conditions is shown in Figure 7. The horizontal axis shows the velocity ratio of sample stream/main stream (in flue gas) and the vertical axis shows the ratio of measuring result/true value (iso-kinetic sampling) regarding TS-1 concentration containing both vapor and droplet (non-gaseous component). Obviously the error at equal velocities is zero, and TS-1 emissions under the iso-kinetic sampling was approximately 10ppm(v/v). In addition, in our study with the method Figure 5 shows, The volatility of TS-1 component amine in TS-1 at 40°C is much less than a-tenth of 10ppm(v/v). Therefore, it can be thought that droplet accounts for almost all part of TS-1 emissions under this experimental condition of pilot plant. In this study, it was found that the error from an iso-kinetic sampling rises sharply for lower sampling velocities and in the range of higher sample stream velocities, however the error is lower. The error is thought to be resulted mainly due to the particle inertia. The effect of particle inertia is typically characterized by the Stokes number. It is well-known that Davies model with Stokes number considered agrees very well with anisokinetic dust sampling, is given in equation 3 and 4. In addition, the Calculation results by Davies model depending on particle size are also shown in Figure 7. As the result, Davies model calculated at 10µm agreed very well with the experimental result. This result implies that nearly 10µm particle, corresponding to (volume×number) of particle, accounts for major part of TS-1 concentration under this condition. The result was found to be in harmony with that the droplets from absorber are eliminated by the demisters which show trapping efficiency is 99.6% against upper 10µm particles.

$$\frac{C_s}{C_o} = \frac{S_r}{0.5 + S_r} \frac{V_o}{V_s} + \frac{0.5}{0.5 + S_i} \tag{3}$$

$$S_i = \frac{Dp^2 \rho_p V_o}{9\mu D_n} \tag{4}$$

C_o : Particle concentration of flue gas under iso-kinetic sampling [mg/m^3]

C_s : Particle concentration of flue gas under anisokinetic sampling [mg/m^3]

V_o : Velocity of flue gas main stream [m/s]

V_s : Sampling velocity at probe entrance [m/s]

S_r : Stokes number [-]

Dp : Particle diameter [cm]

ρ_p : Density of particle [g/cm^3]

μ : Coefficient of viscosity of gas [$\text{g}/\text{cm}\cdot\text{s}$]

D_n : Diameter of probe entrance [cm]

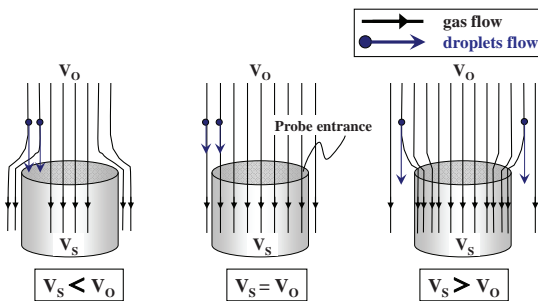


Figure 6 Sampling gas flow with droplets

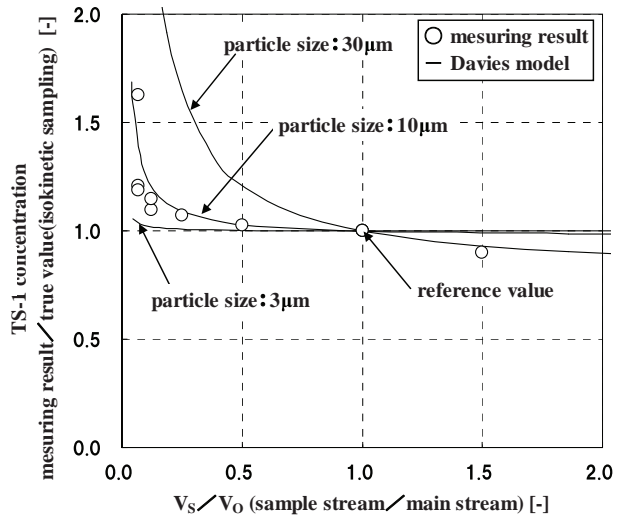


Figure 7 Anisokinetic sampling with the 1/4 inch probe

3.2. Comparison between batch analysis and on-line analysis

If sampling is iso-kinetic, there is no particle loss at the inlet of sampling probe, regardless of particle size or inertia. However, on-line analysis can not allow us to identify amine components specifically because of mass spectrometry by “PTR-MS” revealing only mass information. On the other hand, batch analysis enables us to identify amine components by GC/MS and easily to use. Therefore, in this work we use batch analysis method mainly. To compensate, we experimentally compared batch analysis with on-line analysis at iso-kinetic condition by measuring TS-1 concentration at Mikawa pilot plant under one set of conditions, as shown in Figure 8. As a beginning, Figure 8 shows amine concentrations in flue gas from absorber tend to vary considerably. Hence it follows the measured result of batch analysis is obtained the average value of variable concentrations of amine.

Despite low sampling gas velocity of batch analysis, TS-1 concentration of batch analysis was less than that of on-line analysis. The result suggests that there was particle loss due to attaching the probe, and it was confirmed that batch analysis indicates approximately 80% value of on-line analysis, considered true value.

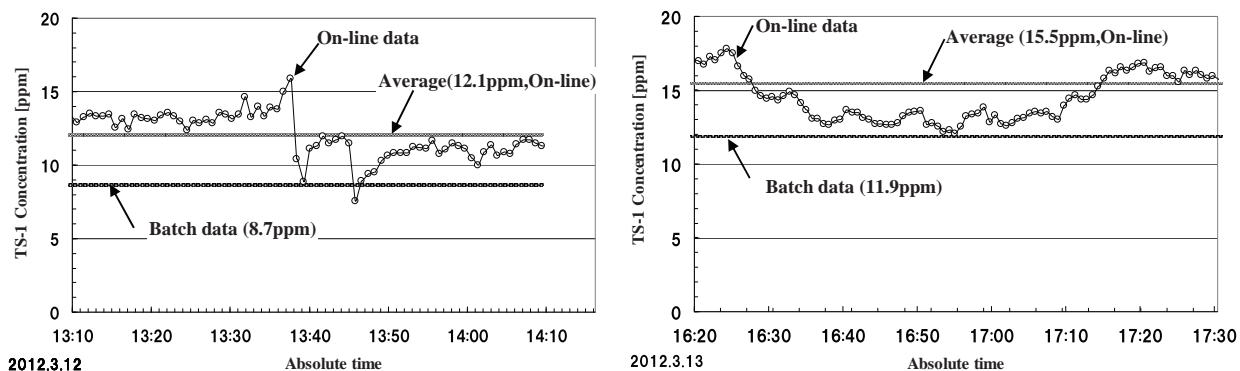


Figure 8 Comparison between batch analysis and on-line analysis

3.3. Measurement of amine emissions

While pilot plant was operated for 3,000 hours, our system had been realizing good performance and not degraded in terms of both CO₂ capture ratio (90%) and captured CO₂ rate (10 t-CO₂/day) [2]. However, degraded amines were accumulated in TS-1 solution during 3,000 hours operation. Over 20 degraded amines were identified after 3,000 hours operation in TS-1 solvent, wash water scrubbing flue gas, and flue gas by using GC/MS and LC/MS. It was found that “5” degraded amines were especially large in quantity in above described 3 places. Figure 9 shows that the concentrations of 4 degraded amines ([A],[B],[C],[D], except [E] because of under detection limit) in TS-1 solution had been increasing linearly depending on operation time due to oxygen, SO_x, NO_x, heat and so on. It was found that amounts of degraded amines in TS-1 solvent were [A], [B], [C] and [D] in that order.

Figure 10 shows comparison between beginning of operation and 2,800 hours operation in terms of amine emissions at Mikawa pilot plant under one set of conditions. At beginning of operation, there were no degraded amines in TS-1 solution. Thus, there were no amine emissions of degraded amines. However, at 2,800 hours operating, in addition to TS-1 emissions, some quantity of emissions of degraded amines were detected even though degraded amines were much less than TS-1 main amine in TS-1 solution. Additionally, degraded amine [A] was not detected despite the largest amount in TS-1 solution.

Based on these test results, we had found the improved operating conditions such as plant system, water wash system, to reduce the amount of amine emissions, as shown in Figure 11. Firstly we

strengthened lean cooler at the entrance of absorber. Amine emissions were reduced to 5.6ppm(v/v) by cooling lean temperature which did not disturb the normal function of absorbing CO₂. Secondly we had improved operating condition of water wash system. As a result, the latest tests showed lower emission of less than 1 ppm(v/v) at 2,800 hours operation.

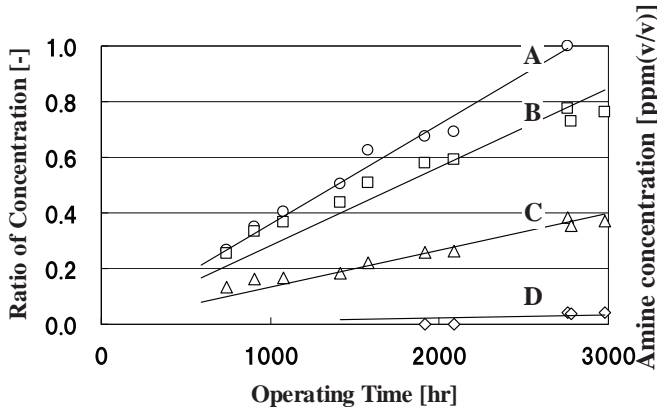


Figure 9 Concentration of degraded amines

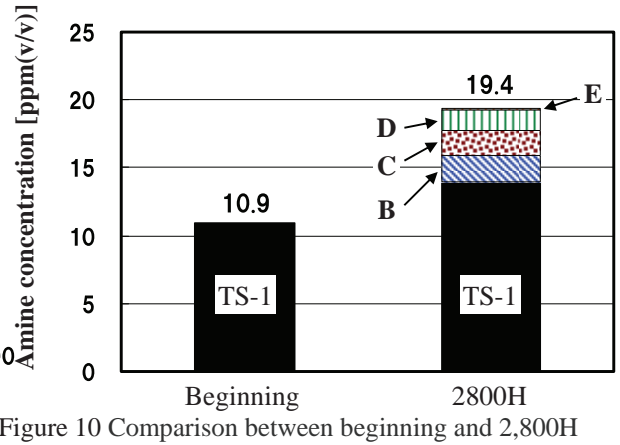


Figure 10 Comparison between beginning and 2,800H

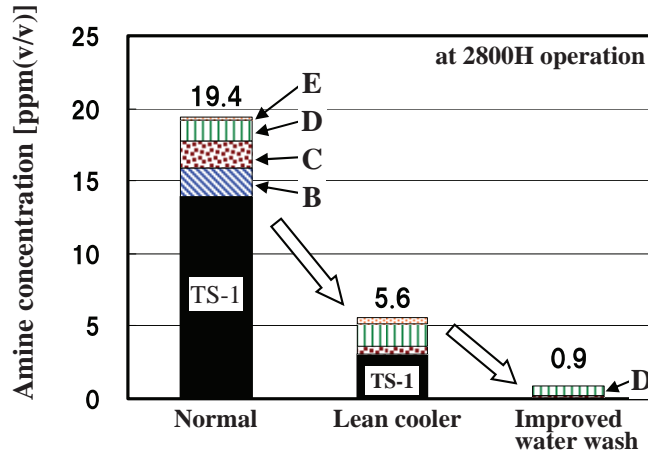


Figure 11 Reduction process of amine emissions at 10ton-CO₂/day scale pilot plant

3.4. Volatility of aqueous amine

A concentration of amine [D] in TS-1 solution at 2,800 hours operation, which was nearly detection limit, was lower than other degraded amines. Nevertheless, amine [D] accounted for the greater part of amine emissions after water wash was improved. Because it was considered that amine [D] has high volatility, we measured the gas phase composition of degraded amines include [D] in diluted aqueous amines at 40°C using Figure 5 method. Figure 12 shows Vapor-liquid equilibrium (VLE) of degraded amines, [B], [C], [D], and [E] respectively. It was found that the volatility of degraded amine in diluted aqueous amines was ranked in the order: [D] > [E] > [C] > [B] >> [A]. This result suggests that it is crucial to reduce the volatility of emitted amine in order to improve performance of amine emissions further.

Then, we evaluated effect of addition acid to reduce the volatility of amine [D]. Figure 13 shows ratio of amine [D] volatility in diluted aqueous amine at 40°C, when acids such as boric acid, carbonic acid,

oxalic acid, and sulfuric acid, were added respectively. The means by which 10%CO₂ gas (N₂ base) is bubbled through the aqueous amine was adapted for adding carbonic acid into diluted aqueous amine [D]. Every acid except carbonic acid was added to molar equivalent against amine [D], and we also evaluated additive amount of acid in terms of difference between molar equivalent and one quarter of that among sulfuric acid.

In this study, on one hand, effectiveness of acid for reducing amine volatility is in the order: sulfuric acid > oxalic acid ≈ carbonic acid produced by 10%CO₂ gas > boric acid. On the other hand, it was suggested that over molar equivalent of acid is necessary for sufficient performance. These results suggest that toshiba could reduce amine emissions to nearly 0.01ppm(v/v) (1ppm×0.01) by utilizing sulfuric acid appropriately.

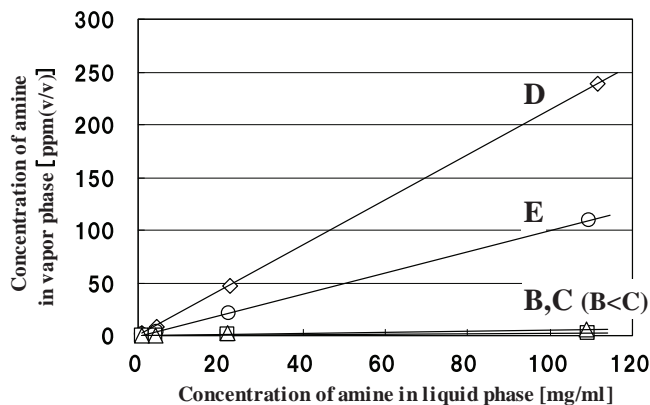


Figure 12 VLE of degraded amine at 40°C

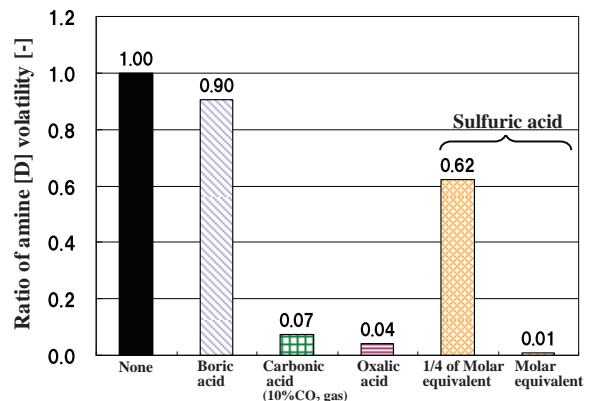


Figure 13 Effect of acid for reducing amine volatility

4. Conclusion

We evaluated amine emissions from 10ton-CO₂/day scale pilot plant in Mikawa Power Plant of Sigma Power Co. Ltd. within TS-1 solvent. Toshiba improved operating conditions such as plant system, water wash system, to reduce the amount of amine emissions. As a result, the latest tests showed lower amine emissions of less than 1 ppm(v/v) at 2,800 hours operation. We also evaluated effect of addition acid to reduce the volatility of degraded amines. The experimental results in diluted aqueous amine at 40°C showed that effectiveness of acid for reducing amine volatility is in the order: sulfuric acid > oxalic acid ≈ carbonic acid produced by 10%CO₂ gas > boric acid. In addition, it was suggested that over molar equivalent of acid is necessary for sufficient performance. Toshiba will utilize the results of these studies to further improve and optimize the performance of suppression amine emissions.

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