Study of the Sulfur Trioxide Generation Mechanism and Control Method Using Wet Solution

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Abstract: *In coal fired power plant, especially using sulfur content fossil fuels, much attention in recently paid to sulfur trioxide and sulfuric acid mist emission, because conventional desulfurization system should not be removed, which is installed to meet air quality standard for sulfur dioxide. Sulfur trioxide is highly reactive with water vapor and generally convert to sulfuric acid mist in atmosphere. Sulfuric acid is very fine under-sub-micron sized particulate matter or droplets. Recently sulfur trioxide cause air pollution and public health, discussion comes out, especially in the United States and Japan, that regulations and guideline should be enlarge the sulfur dioxide to sulfur trioxide and sulfuric acid. Moreover most countries reinforce sulfur oxides emission regulations or guidelines from coal-fired power plant. In this study, focusing that how to control the sulfur trioxide and sulfuric acid mist. Sulfuric acid mist found depending on the flue gas temperature. Generation and conversion rate of sulfur trioxide were measured according to temperature. The absorbent was selected to remove sulfur trioxide and sulfuric acid using wet type desulfurization system which the most proven technology at this moment.*
Keywords: *Absorbent, Control method, Flue gas Desulfurization system (FGD), Sulfur trioxide, Sulfuric acid*

I. Introduction

Petroleum cokes is a product made by forming refuse-derived fuel from dust particles remaining at the very last phase in the process of refining crude oil. This contains around 8,500 ~ 9,000 kcal/kg of calories, which can be used as an alternative fuel such as for cement plants or thermoelectric power plants requiring high consumption of fossil fuel. Recently, cogeneration power plants and power plants generating a large amount of steam are gradually changing their fuel. The world's Petroleum cokes output is estimated to be on or over 100 million tons as of 2011, and is expected to increase to nearly approximately 170 million tons by 2016.[1, 2]

In the flue gas processing system of general coal thermal power plants, some of the representative pollutants included in the flue gas emitted from boilers are dust particles, sulfur oxides compounds (SOx), nitrogenous compounds (NOx), and COx, and a small amount of heavy metals are also included. As methods to satisfy the sulfur oxides emission regulations, methods such as converting fuel into low-sulfur fuel and installing flue gas desulfurizing equipment are used. The current flue gas desulfurization can remove 90% of SO_2, however, is unable to process SO_3 and results in releasing SO_3, which may incur new environmental problems. At the rear part of flue gas desulfurizing equipment (FGD) installed in large power plants, H_2SO_4 mist and SO_3 are not removed from the flue gas desulfurizing equipment but are released, which cause corrosion of the equipment installed at the rear part. When H_2SO_4 exists within the final gas discharged, a flue gas exhibiting bluish light is released, which is known to be released in a concentration reaching a maximum of approximately 50ppm. [1, 3]

In particular, because the recent trend of power plants is to install the SCR device at the rear part of the economizer, due to the additional conversion of SO_2 into SO_3 caused by the catalyst, the increase of troubles and corrosion in the duct and gas-gas heater (GGH), which is at the rear part of the wet flue gas desulfurizing system, are known to form further risks factors in the operation of the equipment. A report announced the result that the SO_3 concentration improves dust collection efficiency.[4] The resistibility of dust is reduced when SO_3 absorbs fly ash. This brings the result where the ESP's ability to remove ash from the gas flow is improved. Nevertheless, the acid concentration remaining in the flue gas causes the corrosion of Electric Static Precipitator (ESP) components. [5, 6]

As the method of processing sulfur oxides within flue gas, the wet, dry, semi-dry, and electric precipitation technologies are generally used. One recent method of reducing sulfur oxides during combustion is to apply suppression to fundamentally prevent the occurrence of sulfur compounds by injecting MgO within the interior through combustion.[7, 8] This can be said to be the most efficient method without disturbing the combustion. However, some studies report the phenomenon where combustion efficiency is reduced, and there is a problem of having to readjust the combustion condition of boilers.[5, 9] The method by which a desulfurizing agent and sulfur oxides within the gas react to be removed as particulate matters is the most

general method, and the calcium family and sodium family are used most widely as the desulfurizing agents.[10] The method mostly used for processing sulfur oxides included inside flue gas after combustion is the wet or dry (or semi-dry) flue gas desulfurizing process.[11] The method of removing solid substance formed after absorbing sulfur oxides while allowing the contact of limestone (CaCO3) or magnesium hydroxide aqueous solution with flue gas by using a scrubber is the method currently most widely applied in industrial fields for the flue gas desulfurizing process.[12, 13] This method allows to obtain high desulfurizing removal efficiency and enables enlargement, which is why it is selected by large-sized facilities including power plants, however, water processing issues arise as an ancillary issue due to using aqueous solution and large-sized facilities are required, thus, this method is difficult to apply to medium and small-sized emission sources. [14]

Some researchers have performed sulfur trioxide removal tests from actual flue gas in power plants, and as a result, reported that 70~90% of the sulfur could be eliminated from coal-burning flue gas. This research reported that among the sodium family desulfurizing agents, bicarbonate sodium could obtain the highest efficiency when used at $120 \sim 175℃$. [15, 16]

This article seeks to find the conditions in which sulfur trioxide is generated and to deduct the conditions allowing to effectively control sulfur trioxide. Studies on why sulfur trioxide occurs due to which mechanism allows to form a condition preventing the generation of sulfur trioxide. Moreover, a method of overcoming the limits of the existing FGD has been studied by developing a wet scrubber solution. A desulfurizing solution with high sulfur trioxide removal efficiency has been selected and applied to the existing wet scrubber process.

II. Materials And Methods

2.1 Materials

In order to study the SO_3 generation mechanism, a sulfur trioxide generation device in the size of a laboratory has been produced. The main part of the SO_3 generation device was composed of the SO_2 gas entrance, assist gas entrance, and catalyst reacting part. The variables for the generation of SO_3 was set as SO_2 gas and 99.999% high purity oxygen gas (O_2), 99.999% high purity nitrogen gas (N_2), and moisture (H_2O mist) etc. The condition in which SO_3 may be generated, thus, an oxidizing agent, was used, and the SO_2 and the oxidant reacted, inducing sulfur dioxide to convert into sulfur trioxide. For the catalyst, 95% of vanadium pentoxide (V_2O_5) was used.[17, 18] A condition of 300~ 450°C was formed to induce reaction. The size of the reaction flask was set by using a reacting area of 100 mm × 100 mm × 100 mm ~ 200 mm × 155 mm × 300 mm, and the catalytic amount per reaction area was adjusted to use the reacting dose and reaction time as the variables. Sodium hydroxide solution(NaOH), Magnesium sulfate heptahydrate($MgSO_4 \cdot 7H_2O$), Sodium bicarbonate($NaHCO_3$), Sodium surfate(Na_2SO_4), Iron sulfate($FeSO_4$) were purchased from Aldrich(USA) and were used without further purification.

2.2 Methods

The part reacting when sulfur trioxide is generated is the catalyst part. Once the sulfurous acid gas creates an adequate environment regarding temperature, humidity, and concentration, it becomes oxidized and is converted into sulfur trioxide. However, the reacting temperature is 300 ~ 450 ℃, reacting in high temperature, thus, the material of the reaction flask was designed in a material that does not melt in high temperature. The catalyst part was produced with the Duplex material, which has outstanding resistance to heat, compared to the SUS 316 material.

This study focused on experimenting sulfur trioxide generated upon combustion of Petroleum cokes, and the related specific experimental variables are shown in Table 1. The experiment was conducted by using a flow regulator and ID fan to supply the gas pressure in a consistent flow into the reaction flask. The quantity of the absorbing solution was produced by using distilled water and reagent in a consistent quantity per experiment.

Table 1. SO_3 removal solution selection experiment conditions

Category	Type	
Absorbent	NaOH, Mg(OH)$_2$, NaHCO$_3$, Na$_2$SO$_4$	
Temperature	SCR rear	200 ~ 250 ℃
	WET EP rear	30~50 ℃
Absorbent concentration	2, 3, 5, 6.2, 8, 10 mol/L	
Sulfur trioxide (SO$_3$) concentration	20, 30, 50 mg/L	
L/G ratio (L/m^3)	2, 4, 6, 8, 10	
Flow	10 m^3/min	
Absorbent injection speed	40, 80, 120, 160, 200 ml/min	

The absorbent under development in this research not only is specialized for the use of absorbing sulfur trioxide(SO_3) gas, but also has a multi-purpose character that can be used universally. The sulfur trioxide

removal experiment is currently almost at its initial stage, thus, there was difficulty in selecting the solution due to lack of reference materials. Because Flue Gas Desulfurization(FGD) removing sulfurous acid gas, that has a similar character to sulfur trioxide, is used, this study selected and used the solution used in the existing Flue Gas Desulfurization(FGD) as the base solution. The L/G ratio was fixed by adjusting the flow with a liquid pump by controlling the absorbent sprayed with the nozzle on the upper side, depending on the experiment variable, once gas entered inside the reaction flask, the gas-liquid contact was made to be smooth with the condition of injecting a one inch pall ring filler inside the reaction flask, and the filler and inside of the reaction flask was cleansed with distilled water in every experiment, to reduce the error of the removal rate pursuant to the character of the absorbent. The sulfur trioxide removal efficiency was tested by measuring the concentration of flue gas inflow and outflow by using Lancom 200 of Land Company. Before measuring the SO_3 concentration, a scrubber was used after substituting the air inside the reaction flask into SO_3 gas, with the same partial pressure under the experimental conditions, and the SO_3 concentration removed through the absorption was measured. Moreover, the pH was measured by collecting a sample of the absorbent every certain hours from the storage flask during the circulation of the absorbent.

III. Results And Discussion

3.1 Generation Mechanism of Sulfur Trioxide Gas

Among flue gas, sulfur changes depending on the reaction condition and form of sulfur during combustion. The ingredients containing sulfur appearing in combustion are extremely diverse, from simple forms such as H_2S to organic-sulfur species having a complex structure.[17] During the early stage of combustion, sulfur species in gas convert into a simple sulfur ingredient such as SO_2, H_2S, or S_2. Deoxidated sulfur species exist in an extremely stable condition where oxygen is extremely lacking, however, most of the sulfur ingredients in the gas exist in a SO_2 form even in a deoxidized condition in a form preferring sulfur oxides. In an excess air combustion condition, most of the sulfur is completely oxidized into sulfur oxides where SO_2 is the main ingredient, and a small amount of SO_3 is generated. Based on the research results until present, the sulfur trioxide generation volume is reported to be affected by numerous variables, such as the sulfur content, ash's content and ingredient, convection area to combustion, temperature distribution, excess air quantity, and existence of catalyst, however, the exact generation mechanism has not been investigated. [19]

3.1.1 Generation of SO_3 Pursuant to Catalyst Temperature

Fig. 1 shows the temperature difference per flue gas process. Generally, the temperature of the brazier increases up to or over 1,800℃ for facilities operating a boiler to produce steam. The driving temperature value per process has been realized by using a device in the size of the laboratory. The sulfurous acid gas was released by 2,000ppm and the temperature was increased up to 1,050℃, however, SO_3 gas was not generated. Some research results report that oxidation reaction happens when the high temperature within the brazier and material containing sulfur meet in a condition of on or over 1,000℃, however, it is difficult to confirm the exact temperature conditions. As a result of going through a sulfur trioxide generation experiment for five consecutive times near the SCR outlet, which includes the catalyst, it was confirmed that sulfur trioxide gas could be generated due to a catalyst.
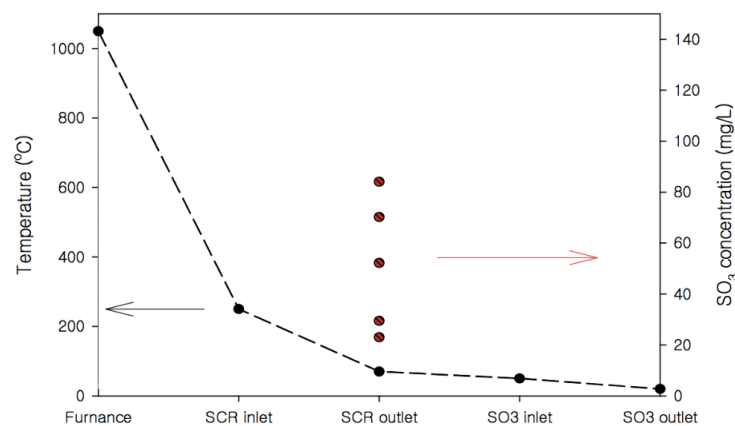

Figure 1. Sulfur trioxide generation point and temperature relationships

Fig. 2 shows a graph on the relationship between the temperature and concentration of sulfur trioxide gas. Unlike the temperature scope, which is measured to be between 257.7~259℃, the concentration of sulfur

trioxide gas showed a huge change. This shows that a factor other than temperature and catalyst exists regarding the generation of sulfur trioxide gas.
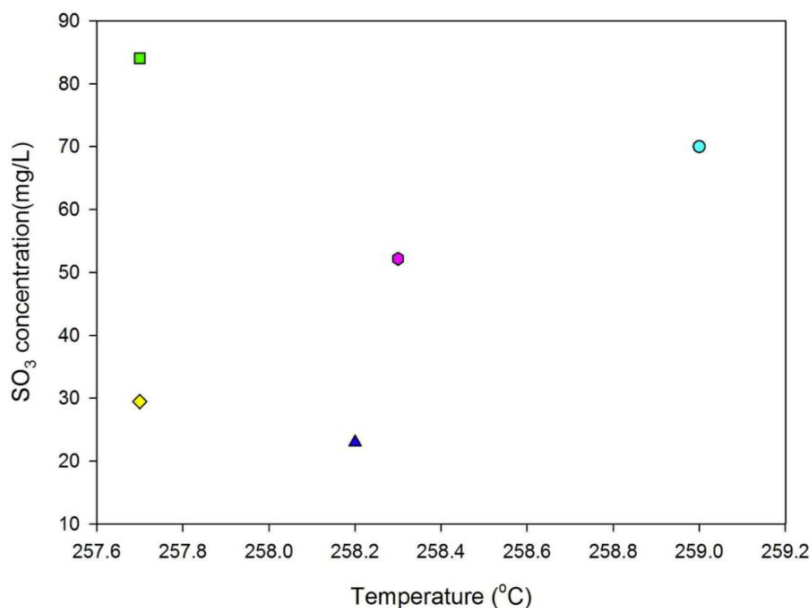

Figure 2. Sulfur trioxide concentration in various temperature

3.1.2 Conversion Ration from SO$_2$ to SO$_3$

Fig. 3 shows the conversion rate of sulfurous acid gas to sulfur trioxide gas. Each of the experiment conditions were set at 2,000mg/L for the concentration of the inflowing SO$_2$ gas, 3g for the catalyst volume of vanadium pentoxide, and 10 minutes for catalyst reacting time, and the SO$_3$ concentration was generated through five random experiments. Through each of the experiments, it was confirmed that a low conversion rate was shown with the conversion rate of SO$_2$ to SO$_3$ being 0.53~1.94. This is a different result from some of the other articles reported, as there is a report that states that the conversion rate from SO$_3$ to SO$_3$ is nearly 99%. This phenomenon may have occurred because the experiment conditions for each experiment is not clear, and also because there may be issues reproducing the experiment results.
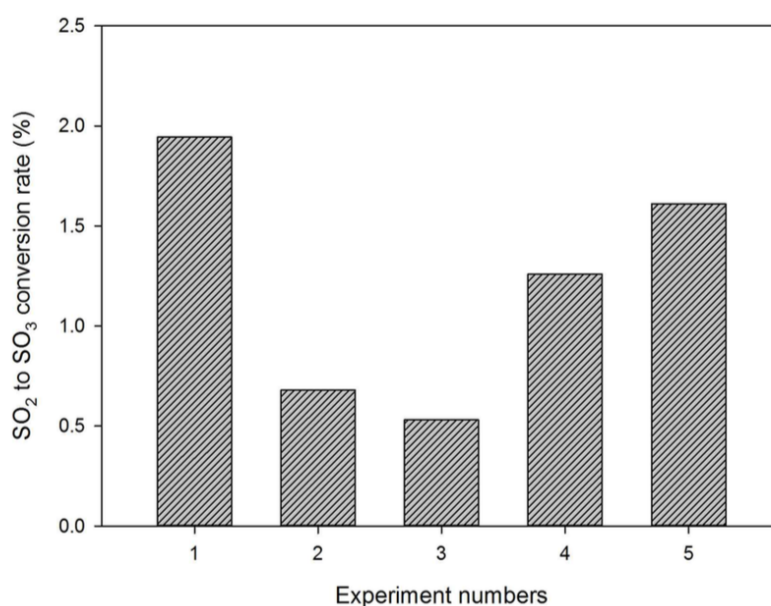

Figure 3. Sulfur trioxide conversion ratio from sulfur dioxide

3.2 Selection of Sulfur Trioxide Removal Solution

Fig. 4 generally uses desulfurizing agents in the calcium family and sodium family, however, a result comparing the desulfurizing performance at 250 ℃, which is the temperature of the front part of the precipitator,

and the thermal stability of desulfurizing agents was reported in Japan, and this study group implemented an experiment verifying the result. As a result of proceeding with a thermo-gravimetric analysis experiment at 60 ℃, which is a temperature disabling pyrolyze from proceeding, regarding sodium bicarbonate, weight change due to the absorption of SO_3 could not be observed, and in the thermo-gravimetric analysis implemented at 250 ℃, sodium carbonate was found to absorb SO_3 pertaining to 35% of the weight of the desulfurizing agent, while quicklime appeared to be able to absorb SO_3 up to 15.6% and slaked lime up to 6.5%. When comparing the initial reaction speed at 250 ℃, the calcium family desulfurizing agents showed an initial non-reaction time, while the sodium family desulfurizing agents reacted more quickly with SO_3 compared to the reactant of the calcium family.
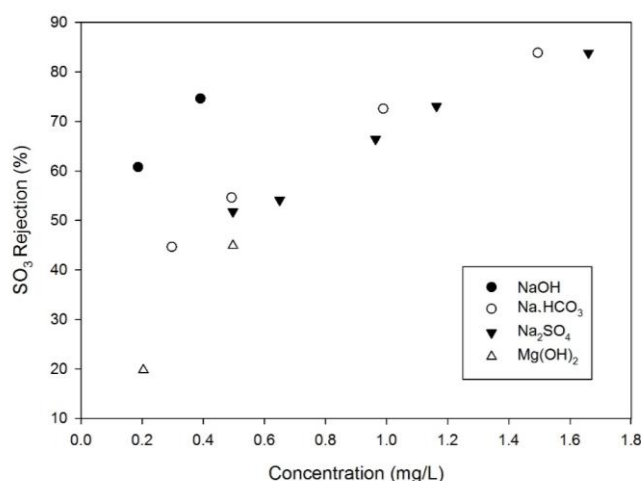

Figure 4. Absorbing solution and rejection to remove sulfur trioxide

In the temperature-programmed desorption experiment implemented in room temperature, the slaked lime in the calcium family appeared to have absorbed more SO_3 than sodium carbonate, which is in the sodium family. Thus, it was confirmed that slaked lime in the calcium family is a more adequate desulfurizing agent in low temperature while sodium carbonate in the sodium family is a more adequate desulfurizing agent in high temperature.

3.3 Sulfur Trioxide Removal Efficiency Pursuant to Removal Solution
Fig. 5 is the result that removal efficiency depend on concentration of magnesium hydroxide solution. As can be seen in the experiment result, the SO_3 removal efficiency appeared to increase as the concentration of the absorbent increases.
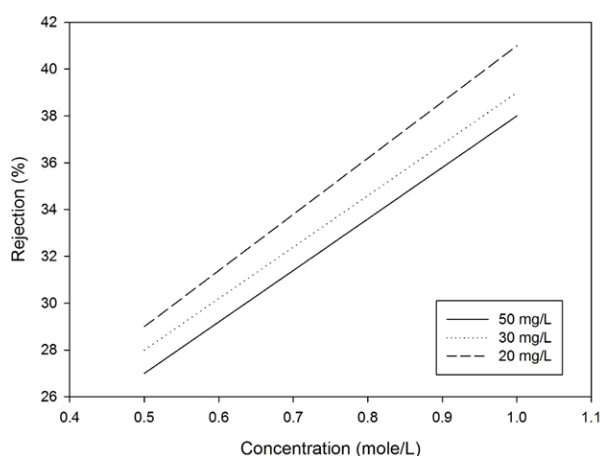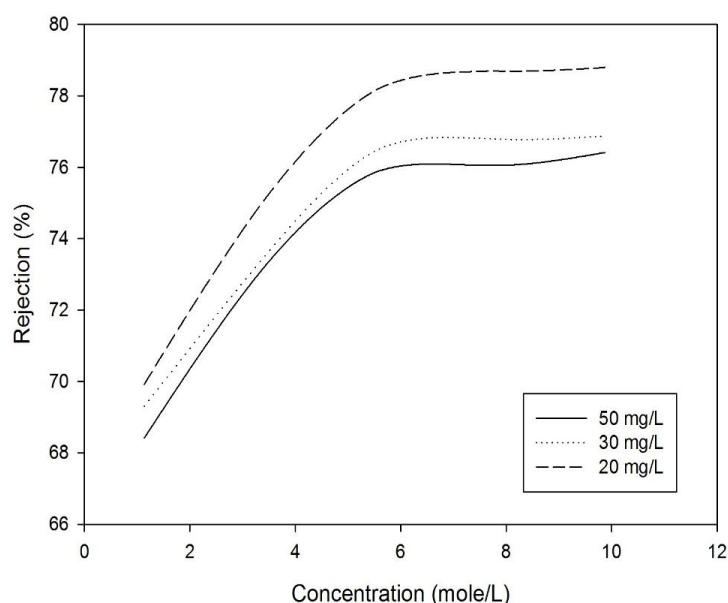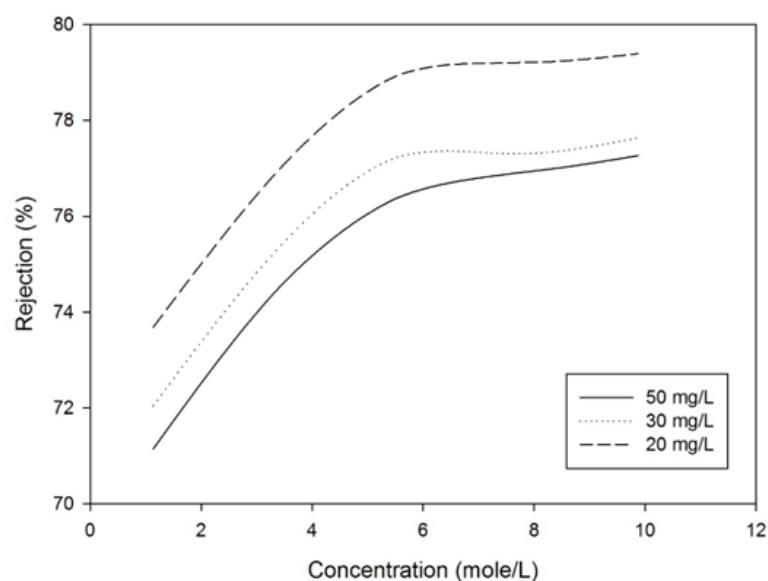

Figure 5. Rejection efficiency depend on concentration of sulfur trioxide using $Mg(OH)_2$

Fig. 6 is the result that removal efficiency depend on concentration of sodium bicarbonate solution. Which showed a generally similar condition with Fig 5, and the removal efficiency of 6 M NaOH aqueous solution appeared to be 77.7%, which is a 0.9% increase compared to the SO_3 50 ppm condition.

Figure 6. Rejection efficiency depend on concentration of sulfur trioxide using $NaHCO_3$

Fig. 7 is the result that removal efficiency depend on concentration of sodium hydroxide and the removal efficiency of SO_3 increased as the absorbent concentration increased as in the experiment result of Fig. 5 and Fig. 6. Moreover, the 50 ppm SO_3 in Fig. 7 appeared to have a removal efficiency regarding NaOH aqueous solution that is 0.5~1% higher than 20 ppm SO_3, and appeared to have a 0.2~0.5% higher efficiency than 30 ppm SO_3.

Figure 7. Rejection efficiency depend on concentration of sulfur trioxide using NaOH

Mg(OH)$_2$ was expected to show the highest removal efficiency theoretically, however, while pollution of the aqueous solution inside the circulating water storage flank and scaling phenomenon of the nozzle and packing occurred while forming calcium sulfite ($CaSO_3$) or calcium sulfate ($CaSO_4$), regarding $NaHCO_3$ and NaOH, the above problem did not occur as Na_2SO_4 are all aqueous solutions, showing a relatively higher removal efficiency. The reason is probably because the reaction speed and neutralization with SO_3 is the lowest because the alkalinity was relatively low when the pKa value of NaOH, $NaHCO_3$, and $Ca(OH)_2$ was respectively 13, 13, and 12.4.

IV. Conclusions

Through this experiment, the absorbent with the highest absorption efficiency appeared to be $NaHCO_3$, and NaOH showed a similar efficiency level, and when considering the efficiency and economic feasibility

based on the fact that it has two times higher unit cost than NaOH and has high corrosion, NaOH seems to be the most suitable absorbent to control SO_3.

1. The removal efficiency was expected to increase when the absorption speed of SO_3 that is absorbed to the absorbent increases pursuant to the increase of SO_3 concentration, however, in reality, the removal efficiency was higher under the conditions of 20ppm and 30ppm SO3 compared to 50ppm SO_3, nevertheless, the increase range was minimal, thus, a huge difference did not appear.

2. The removal efficiency did not appear to have a huge difference under the SO_3 condition of 10~50 ppm, but rather, the removal efficiency appeared to have a decreasing trend in the SO_3 concentration condition on or over 50 ppm. This shows the same trend as the results of Mitsubishi of Japan and EPA of the United States. Thus, the experiment in this study was implemented by setting the scope of sulfur trioxide concentration as 10 ~ 50 ppm, and this did not have a huge effect on the volume of SO_3 absorbed to the absorbent.

Acknowledgments

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