

Empirical Study of Dry Reaction Technology to Remove Acid Gas Emission from Specified Waste Incinerators

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Abstract: *This study aims to remove hazardous gases, sulfur dioxide (SO₂), and hydrogen chloride (HCl) emitted from small- to medium-size incinerators using a dry reaction technology. Actual flue gas from the waste incinerator Unit #1 of company B is applied to design a dry reactor to be installed on the rear of SDR. Two types of highly reactive slaked lime with different physical properties are used to identify and check their acid gas removal efficiency and performance and to propose optimal operation conditions. The result indicates that a dry process outweighs the current semidry one in efficiency for both cost and acid gas removal. When the same condition for operation is given, the highly reactive slaked lime, which has a larger specific surface area and pore volume, shows higher acid gas removal efficiency while contributing to the elimination of dioxins.*

Key words: *Dry reactor, Stoichiometric ratio, Acid gas removal efficiency, Ca(OH)₂, Bag filter, Dioxin, PCDDs/PCDFs*

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I. Introduction

The accelerating urbanization and industrialization led to an increasing amount of household and industrial waste, which has become a serious social issue. [1] In addition, the current increasing number of air quality warning days for PM₁₀ and PM_{2.5} raises great public concern on fine dust emissions from the industrial sector including coal-fired power plants and waste incinerators. A range of studies introduces the risk of fine dust on human health, shedding light on improving polluted air as one of the top social priorities.

The Ministry of Environment of the Republic of Korea established the “Act on the Integration of Environmental Pollution Management.” According to the act, businesses with greater influence on the environment should achieve a transit to the integrated environmental management on a phase-in basis starting from 2017. Moreover, they can apply the Best Available Techniques (BAT), which are economically efficient and achievable when trying to reduce the emissions of air pollutants, thereby reflecting their operating conditions. [2] Waste incinerators in the facility group subject to integrated environmental management are also categorized. In addition, they are required to establish, as early as possible, a management system regarding their environmental permits as well as facility operation and maintenance in an environmentally and economically sustainable way.

In general, incinerators emit organic compounds, heavy metals, acid gases, dioxins, and other hazardous gases. However, their emitted volumes significantly vary depending on diverse factors including the composition of waste for treatment, structure of the incinerator, and incinerating and operating design. In particular, an acidic gas, HCl, shows a sharp change in the resulting concentration by type and volume of the substances to be incinerated, which leads to exceeding the given permissible emission standard.

Compared to CO₂ and NO_x, HCl has a lower emission. However, it allegedly causes damage to combustion furnaces and takes its share in the Deacon reaction and the de novo synthetic reaction, which are mechanisms to produce dioxins. Therefore, the importance of controlling HCl gets highlighted. [3-5] For the appropriate removal of acid gases (SO₂ and HCl), wet and dry methods are applied. The wet method is considered to have a higher removal efficiency but requires a relatively wide area for installation and produces an extra cost for the treatment of waste, which is caused by the use of anti-reaction agents, and the maintenance of equipment corrosion. Compared to wet removal, the dry method has a lower removal efficiency but can be simply applied, and offers additional advantages such as the use of energy from exhausts and the elimination of other compounds including heavy metals. In addition, when it is applied in combination with a filter dust collector, the removal efficiency increases to supplement the different shortcomings of the wet method. [6-10]

Furthermore, the dry method, in most cases, applies a posttreatment technique that uses activated carbon adsorption to remove heavy metals and dioxins, which provides advantages such as cheap costs for the early installation stage and a high removal efficiency. In general, proper dioxin removal is possible only through a process in which a semidry scrubber is connected to a bag filter. However, most of the facilities using

activated carbon absorption at the front of a bag filter are required to satisfy 0.1 ng-TEQ/Nm³ of the permissible emission standard. [11]

Currently, as a response to stricter environmental regulations, waste incineration facilities are tasked to minimize the emissions of air pollutants to secure environmental sustainability. At the same time, they are required to recover the heat generated from the incinerating process and use less chemicals as possible to save on operation costs and secure economic sustainability.

In this regard, this study replaced the sorbent used to enhance the low removal efficiency of the dry method with highly reactive slaked lime and installed a dry reactor for higher reaction, at a demonstration scale, to assess its efficiency and performance.

Specifically, a dry reactor was installed after dismantling wet and semidry scrubbers widely used for specified waste incinerators. Then, two types of highly reactive slaked lime with different physical properties were sprayed, and removal efficiencies for acid gases (SO₂ and HCl) and dioxins were measured. Annual emissions and pollution characteristics were also assessed. This study thus provides basic data for optimal environmental management.

II. Materials and Methodology for the Experiment

2-1. Samples and Materials

Two types of calcium-based, highly reactive slaked lime with different physical properties were used as a dry desulfurizing agent for the experiment. Table 1 shows their chemical and physical characteristics. The element analysis indicated 71.4% and 73.5% of CaO content, respectively, for Ca(OH)₂-TY and Ca(OH)₂-LH. In addition, the study performed analysis with Scanning Electron Microscope (SEM) and Energy Dispersive X-ray spectroscopy (EDS) to identify the other components and characteristics of the two different types of highly reactive slaked lime.

Table 1. Chemical and physical characteristics of fresh sorbents

Sorbent	Elemental Analysis			BET	
	CaO (%)	CaCO ₃ (%)	Others (%)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
Ca(OH) ₂ -TY	71.4	1.21	27.39	36.152	0.152
Ca(OH) ₂ -LH	73.5	0.37	26.13	40.70	0.183

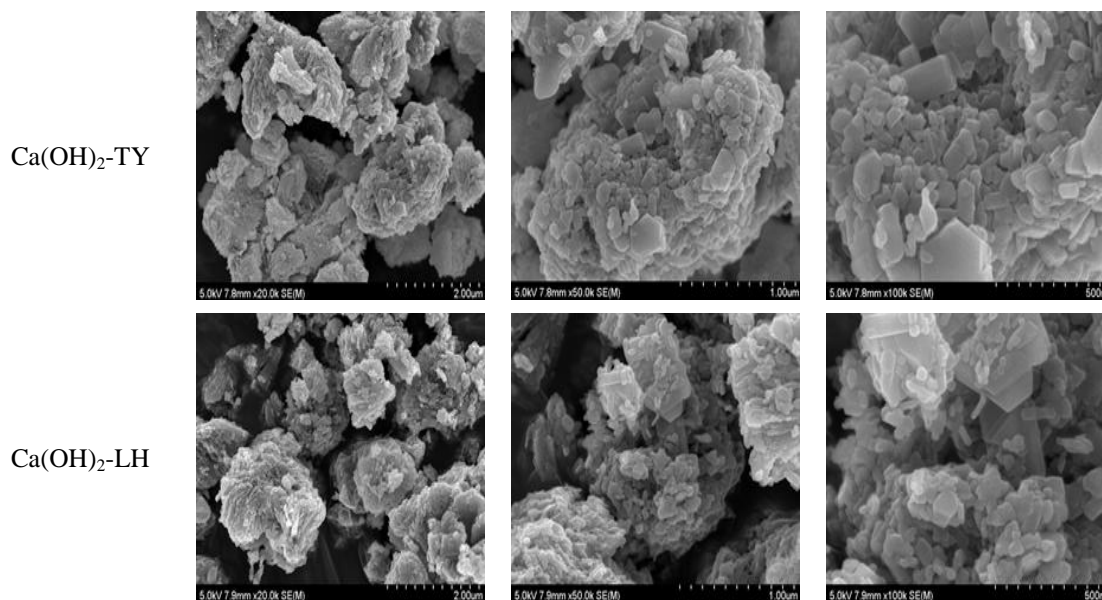


Fig. 1. SEM analysis for fresh sorbents (×20,000, ×50,000, and ×100,000).

Table 2. EDS analysis for fresh sorbents (Ca(OH)₂-TY and Ca(OH)₂-LH)

Ca(OH) ₂ -TY		Ca(OH) ₂ -LH	
Element	Weight (%)	Element	Weight (%)
O	57.91	O	46.98

Mg	1.39	Mg	0.62
Ca	40.70	Ca	52.40
Total	100.00	Total	100.00

Figure 1 and Table 2 shows the SEM and EDX analysis result of the sorbents used for the experiment. The main ingredients were C, O, and Ca, with a small amount of Mg.

To identify the activated areas of the sorbents, BET analysis was conducted with the ASAP 2010 model of Micromeritics. For adsorptive gas, N₂ with a measured temperature of 77.3 K was used. As shown in Table 1, for the analysis result, the respective specific surface area and pore volumes were 36.152 m²/g and 0.152 cm³/g for Ca(OH)₂-TY and 40.70 m²/g and 0.183 cm³/g for Ca(OH)₂-LH.

2-2. Device and Methodology for the Experiment

Figure 2 shows a conceptual diagram and an actual image of the dry sorbent reactor used for this study. The dry reactor is composed of different parts: the inlet of flue gas, which is a mixture of hazardous acid gases and particulate matters; a zone for mixing the flue gas flowing inside with a highly reactive slaked lime (Ca(OH)₂); an internal circulating zone for highly reactive slaked lime and flue gas; and an outlet of reaction product and clean gas. The acid gas that flows into the dry reactor undergoes a gas–solid reaction with the highly reactive slaked lime injected in the diffusive zone for the first removal. The remaining acid gas and slaked lime that have been removed in the first process are reacted again in the internal circulation zone of the upper part of the reactor for the second removal. This two-step design aims to maintain high acid gas removal efficiency.

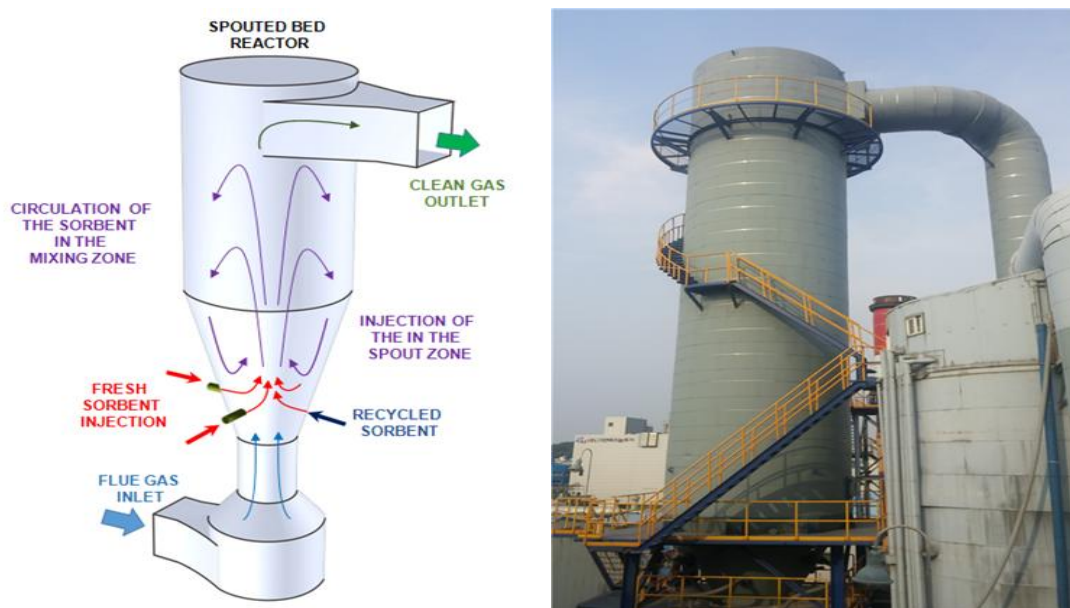


Fig. 2. Photograph and structure of the dry sorbent reaction accelerator (SRx)

As shown in Table 3, the dry reactor is designed with a structure of 4,200 mm for the internal diameter (ID) and 16,500 mm for the height, and has a retention time of 8 s. Acid gas removal is carried out by injecting highly reactive slaked lime in a spout zone with high-pressure, dual-fluid spraying.

Table 3. Basic specification of a dry-type spout bed circulating reactor

Parameter	Range
Gas treatment capacity	Maximum of 42,000 Nm ³ /hr
Flue gas temperature	180°C~200°C
Functional role	Removal of SO _x and HCl

Geometric dimension	Diameter: 4,200 mm, Height: 16,500 mm
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Figure 3 shows the general flow diagram of an air pollution prevention facility for the specified waste incinerator Unit #1 of Company B. Acid gas was measured at the front, rear, and stack of the dry reactor for comparison. An FTIR gas analyzer, GASMET Dx-4000, was used for real-time consecutive measurement.

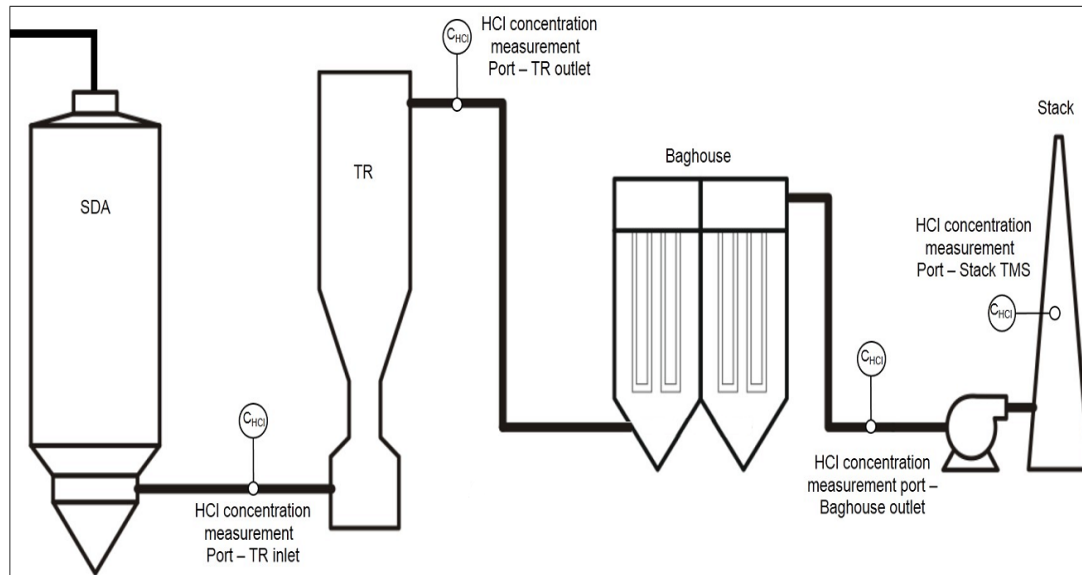


Fig. 3. Flow diagram and the HCl measurement ports

Figure 4 shows images for each subunit of the air pollution prevention facility installed in the waste incinerator Unit #1 of Vinotech Co., Ltd. The facility includes an incinerator, waste heat boiler, semidry scrubber, dry reactor, bag filter, and stack when listed in order of location. After the dry reactor was installed to start its independent operation, the semi-dry scrubber stopped the operation.



Fig. 4. Functional units of the air pollution prevention facility of the municipal waste incinerator

2-3. Measurement

Figure 5 shows the measurement by GASMET, an FTIR type of gas analysis. GASMET Dx-4000 is used for the consecutive measurement of optimal quality and quantity within the shortest time. The analyzer extracts acid gas, which has characteristics of wet and strong corrosiveness, in a hot-wet manner at an isothermal condition of 180°C. At this time, moisture exists in the form of saturated vapor, and dust are eliminated progressively at two zones. Then, a comparison analysis at the upper layer is conducted for the spectrometer of each molecule with the Reference Library and Background by ingredient.

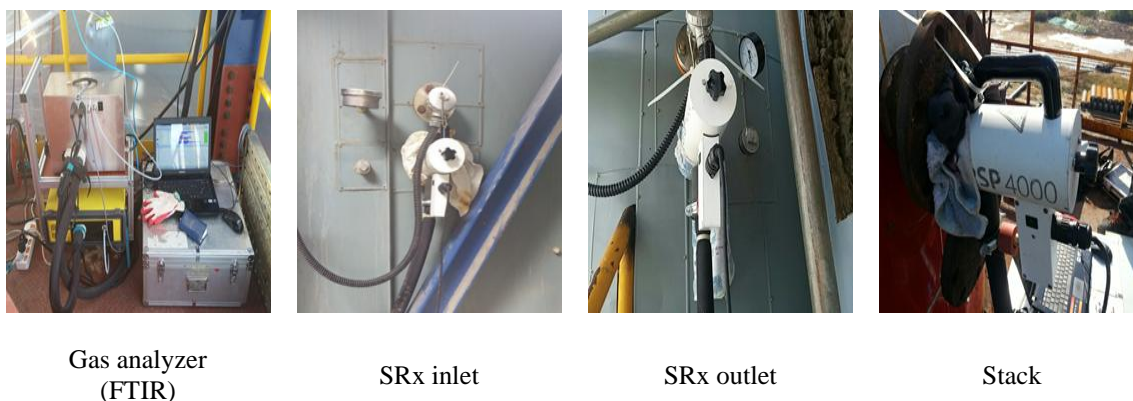


Fig. 5. Method for measuring HCl concentration (GASMET Dx-4000)

2-4. Conditions for the Experiment

Table 4 shows the conditions for the experiment of the dry reactor. For desulfurizing agents, there are two types of highly reactive slaked lime with different specific surface areas and pore volumes. The temperature and flow rate conditions for the experiment were 170°C and 42,000 Nm³/hr, respectively, which is the same as those for the actual operation of waste incinerators. HIC concentrations were measured for a week at the front of the reactor with GASMET Dx-4000, and the result was 550 ppm on average. The highly reactive slaked lime was injected for 90 kg/hr on average, with a molar ratio of 2.

Table 4. Experimental conditions

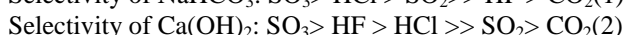
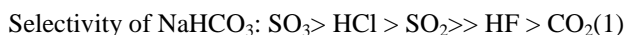
Variables [Unit]	Range
Test unit [-]	SRx and bag filter
Test sorbent [-]	Ca(OH) ₂ -TY and Ca(OH) ₂ -LH
Flue gas temperature [°C]	170
Gas flow rate [Nm ³ /min]	42,000
Superficial gas velocity [Nm/s]	2
HCl inlet concentration [ppm]	500
Stoichiometric ratio [-]	2.0
Ca(OH) ₂ feed rate [kg/hr]	67.5

III. Theoretical Review

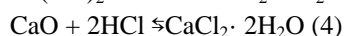
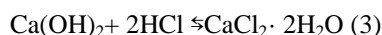
3-1. Principle of Ca(OH)₂ and HCl Reaction

Calcium- and sodium-based dry reaction agents are widely used for acid gas removal. Among them, Ca(OH)₂ has been reported as an optimal sorbent to remove HF and HCl from the combustion of waste. Ca(OH)₂ has the most efficient performance for absorption at a combustion temperature ranging from 240°C to 350°C.

Equations (1) and (2) show the reactivity of NaHCO₃ and Ca(OH)₂ with acid gas in the flue gas at the waste incinerator. [12]



Studies on the reaction mechanism of HCl gas and calcium-based sorbent reported that Ca(OH)₂, CaO, and CaCO₃ had a calcination response as shown in Equations (3)–(5), and the produced CaO had more pores and a larger surface area compared to its raw material. [13]



It was also reported that under a low-temperature condition of 150°C or lower, an increasing H₂O content led to a stronger binding power, and when a consistent relative humidity was given, the equilibrium moisture content significantly increased with the higher temperature. Under a lower temperature ranging from 60°C to 150°C, the lime change rate was sharply raised with the higher relative humidity. Under a temperature of 100°C or higher, the influence of relative humidity became weaker, while under a temperature of 200°C or higher, there was no influence of relative humidity reported. Under a temperature of 150°C or lower, the H₂O contents enhanced the binding power. Reportedly, the increase in the lime change rate at a lower temperature and a higher relative humidity was attributed to the disconnected crystal grids of lime reactants and the formation of saturated aqueous (water) substance. [14]

3-2. Reactant Amount for Injection

To define a reactant amount, the theoretical stoichiometric ratio (SR) by an acid gas concentration was calculated before the injection. The reaction occurs for Ca(OH)₂ at a mole, and the SR can be expressed as follows.

$$\text{Total acid SR} = \frac{\text{Actual sorbent flowrate}}{\frac{\text{HCl flowrate}}{36.5 \times 2} + \frac{\text{SO}_2 \text{ flowrate}}{64}} \quad (6)$$

IV. Results and Discussion

4-1. Experiment of the Acid Gas Removal Performance of the Dry Reactor

Figures 6 and 7 show the results of TMS real-time measurement from 2012 to February 2018. For 2012 to August 2014, September 2014 to February 2016, and March 2016 to the present, liquefied slaked lime (Ca(OH)₂-TY), highly reactive slaked lime (Ca(OH)₂-TY), and highly reactive slaked lime (Ca(OH)₂-LH) were used, respectively, for acid gas removal. When using liquefied slaked lime, HCl and SO₂ were 12 ppm and 6 ppm, respectively. For the highly reactive slaked lime (Ca(OH)₂-TY), HCl and SO₂ were 5 ppm. For the same type of slaked lime (Ca(OH)₂-LH), HCl and SO₂ were 5 ppm and 1 ppm, respectively.

As such, the high efficiency of acid gas removal was observed when replacing an old semidry scrubber with a dry reactor. This is because the latter caused the decreasing flow rate and the increasing retention time of flue gas to result in more time for acid gas to contact with the highly reactive slaked lime and, therefore, more time for gas–solid contact. In addition, as the highly reactive slaked lime has a larger specific surface area and a higher pore volume compared to the liquefied one, it enhanced its own reaction rate with the acid gas. A bag filter was also installed on the rear of the dry reactor and cooperated to attach remaining high reactive slaked lime, which did not react at the first removal stage, to the surface of the filter for the second reaction. This is considered as further increasing the efficiency of acid gas removal.

The comparison analysis between Ca(OH)₂-TY and Ca(OH)₂-LH identified that the use of the latter led to a more enhanced removal rate, with the SO₂ concentration maintained at 1 ppm or lower. This is because Ca(OH)₂-LH has a higher CaO content and a larger or higher specific surface area and pore volume than Ca(OH)₂-TY. Therefore, when the reactant contacts with the acid gas, the concentrations of the Ca⁺ ion and the 2OH⁻ ion increased, and more active reactions occur not just with HCl, which has the original characteristic of a stronger reaction, but also with SO₂, thereby accelerating the removal.

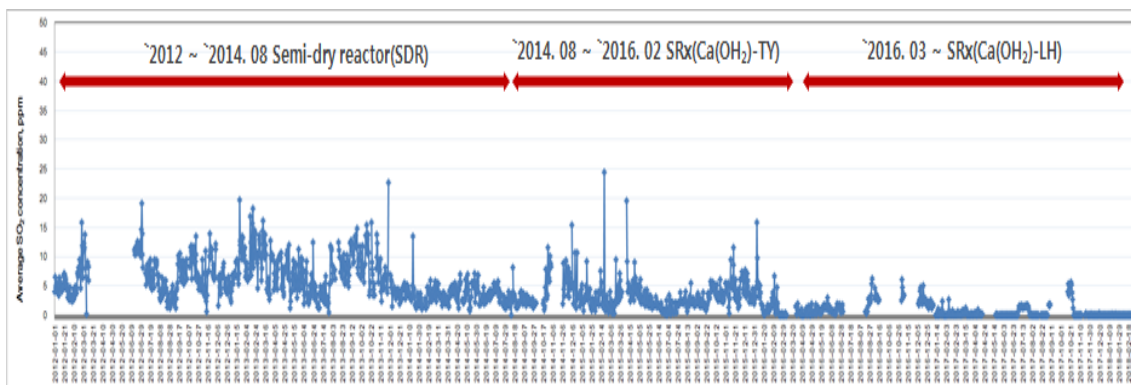


Fig. 6. Average SO₂ concentration at TMS

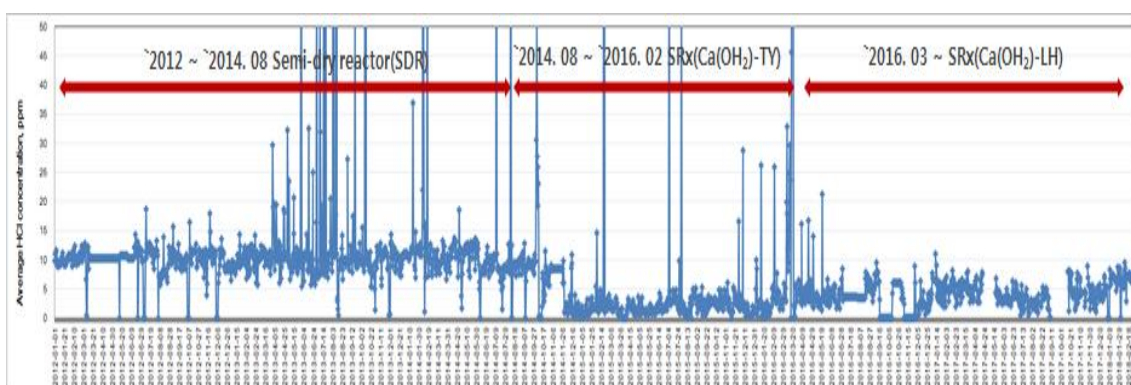


Fig. 7. Average HCl concentration at TMS

An SEM was used to identify the crystal structure of fly ashes, while an EDS was used to analyze the samples with X-ray wavelength to measure their elements and contents. Figure 9 shows the SEM images of the ashes collected from the bag filter, with a magnification of $\times 5,000$, $\times 10,000$, and $\times 20,000$. In general, fly ashes are arranged in a wide range of disproportionate forms on a porous surface. Table 5 summarizes the characteristics of the fly ashes that were measured with EDS. They were mainly composed of C, O, Na, Mg, Al, Si, S, Cl, K, and Ca, with higher shares of C, O, Cl, and Ca.

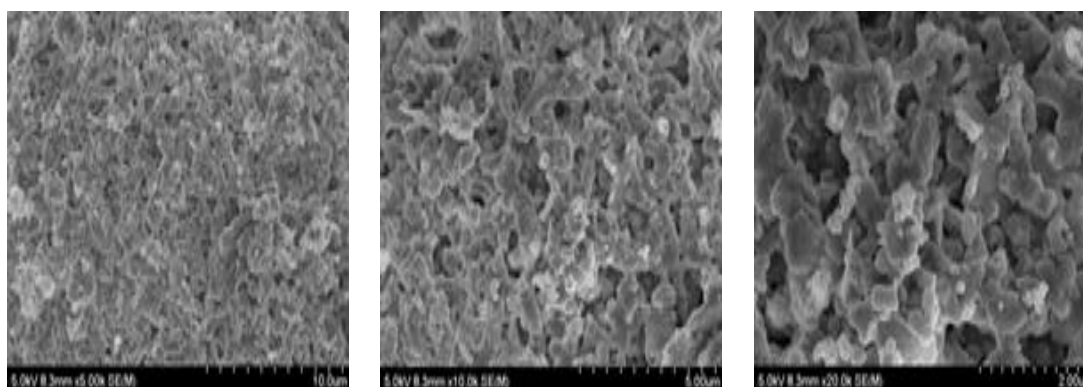


Fig. 8. SEM analysis for fly ashes ($\times 5,000$, $\times 10,000$, and $\times 20,000$)

Table 5. EDS analysis of the fly ashes collected from the bag filter

Element	Weight%	Atomic%
C K	6.25	12.89
O K	25.55	39.58
Na K	3.82	4.12
Al K	0.46	0.42

Si K	1.38	1.22
S K	1.67	1.29
Cl K	34.79	24.32
K K	1.74	1.10
Ca K	24.34	15.05
Total	100.00	

4-2. Experiment of the Dioxin Removal Performance of Highly Reactive Slaked Lime

Dioxins are known as a by-product generated from combustion or the organo-hydrochloric chemical manufacturing process. South Korea needs to pay particular attention to this substance because the country is highly dependent on incineration for waste treatment. As a result, Korea has observed the high contribution of waste incineration to the dioxin level, and is thus required to identify how dioxins are formed and restrict their generation. The dioxin samples for this experiment were taken from emissions in stacks for twice a year and underwent pretreatment before analyzed with HRGC/MS, as guided by the Official Test Method on Air Pollution.

Table 6 shows the dioxin (PCDDs/PCDFs) concentrations measured for six years from 2012 to 2017. Compared to 2012 and 2013, the year 2014 saw lower dioxin concentrations at 0.1 ng-TEQ/Sm³ or less. This is considered attributable to the pore structures of highly reactive slaked lime, such as the specific surface area and pore volume, which accelerate the absorption of isomers, chlorinated dioxins (PCDDs), and chlorinated furans (PCDFs).

Table 6. PCDDs/PCDFs concentration in stacks

(Unit: ng-TEQ/Sm³)

	2012	2013	2014	2015	2016	2017
First	0.164	0.234	0.051	0.055	0.017	0.012
Second	0.294	0.198	0.053	0.031	0.133	0.009

V. Conclusions

The acid gas (SO₂, HCl) removal technique that uses a desulfurizing agent causes the reaction of acid gases in combusted flue gas with the agent for gas–solid reaction to collect the gases in a solid form and to reduce their concentration in the emissions.

The study developed a dry reactor to enhance the rate of reaction with acid gases and apply it to a waste incinerator at a demonstration level. The study used two types of highly reactive slaked lime with different physical characteristics as a desulfurizing agent and conducted a comparison analysis for changes in the concentrations of acid gases and dioxins. The results are as follows.

1. The removal rates of the highly reactive slaked limes were measured at the dry reactor with the following actual operating conditions: 170°C internal temperature, 8 s retention time, and 2 SR. It was identified that the liquefied slaked lime and the highly reactive slaked lime had increased acid gas removal rates with a smaller particle size, and a larger particle surface area and pore size under the same temperature.

2. When using the two types of highly reactive slaked limes with different physical properties, the study found that the one with a larger specific surface area and pore volume contained higher concentrations of Ca⁺ ion and 2OH⁻ ion in the pores to lead an active reaction with acid gases.

3. For the analysis of the emission characteristics of dioxins (PCDDs/PCDFs), it was identified that the concentrations of PCDDs/PCDFs in the stacks decreased by 90% or more from 0.164 and 0.294 ng-TEQ/Sm³ for 2012 to 0.012 and 0.009 ng-TEQ/Sm³ for 2017. This is considered attributable to the pore structures of highly reactive slaked lime such as the specific surface area and pore volume that accelerate the absorption of isomers, PCDDs, and PCDFs.

As a result, a dry reactor can be an effective and economical technique to respond to stricter environmental regulations and to replace the wet and semidry techniques currently used for most coal-fired power plants, steel mills, and waste incinerators.

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