

Modeling of the wet flue gas desulfurization system to utilize low-grade limestone

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Abstract—Wet flue gas desulfurization was simulated to improve gypsum production using low-grade limestone. High-grade limestone with 94 wt% CaCO_3 content is used for producing gypsum with 93 wt% purity, but owing to the resource depletion of high-grade limestone, low-grade limestone should be replaced as an alternative. However, low-grade limestone with CaCO_3 purity of less than 94% contains impurities such as MgCO_3 , Al_2O_3 , and SiO_2 , which reduce gypsum purity. To resolve this issue, a process involving mixing of both low-grade and high-grade limestone was simulated to predict the quantity of low-grade limestone that could be utilized. Many reactions like limestone dissolution, SO_x absorption, and crystallization were considered and were simulated by different models in Aspen plus. For process optimization, the following constraints were set: 93 wt% gypsum purity, 94% desulfurization efficiency, and 3,710 kg/h total limestone usage, which maximized the mass flow of low-grade limestone. The maximum blending quantity of low-grade limestone for 2,100 kg high-grade limestone that satisfied the constraints was ~1,610 kg.

Keywords: Desulfurization, Limestone, Gypsum, Simulation, Flue Gas, Optimization

INTRODUCTION

Since the release of sulfur oxide by thermal power plants is currently considered the main cause of air pollution [1], many thermal power plants have been equipped with flue gas desulfurization (FGD) facilities to reduce sulfur oxide emissions. FGD refers to a technology that removes sulfur oxides from flue gas; it includes many processes such as absorption, adsorption, oxidation, and reduction. The technology can be classified as a wet or dry method depending on the moisture content of the absorbent [2]. Dry FGD is a desulfurization process in which SO_x absorbers are sprayed into a solid-state powder into a combustion chamber to absorb sulfur oxides. This method has the advantages of low equipment cost and low energy consumption but is limited by low desulfurization efficiency due to slower response speed than that of the wet method [3]. More specifically, wet FGD (WFGD) is implemented by many large thermal power plants and is the most common technology because of its high desulfurization efficiency and stability [4,5]. In this method, limestone is crushed by a grinding machine and blended with water to form an alkaline slurry. The resulting solution is then brought into contact with flue gas to absorb SO_2 by a vapor-liquid reaction [6]. At this point, the crystallization of gypsum occurs in the liquid phase in the lower part of the scrubber owing to a solid-liquid reaction [7]. After this reaction, the wastewater is ejected and merchantable gypsum is produced as a byproduct with 93 wt% purity. To obtain gypsum of this quality, high-grade limestone with a CaCO_3 content of ≥ 94 wt% is required [8]. Indeed, low-grade limestone with a CaCO_3 content < 94 wt% is not used due to the presence of

impurities, such as MgCO_3 , SiO_2 , Al_2O_3 , and FeO_3 , which decreases the desulfurization efficiency and the quality of the final gypsum. Although the total reserves of limestone in the Republic of Korea amount to ~10,690 million tons, high-grade limestone reserves account for only 2,142 million tons, constituting 20% of the total. The use of low-grade limestone would, therefore, be desirable due to the ongoing depletion of high-grade limestone reserves. To date, a number of methods have been developed to improve the limestone quality through pretreatment. Kim et al. [9] developed a firing method to improve the quality of low-grade limestone. Following pulverization of the limestone to achieve a suitable particle size for the firing process, the limestone is purified to caustic lime (CaO) upon firing, and the remaining impurities are separated using crushing machines, such as hammer mill, ball mill, or jet mill. In addition, Ahn et al. [10] developed a technology for improving limestone quality based on the separation of magnetic impurities. In this process, the limestone initially undergoes a firing process, after which the magnetic impurities (FeO_3) are removed by magnetic selection. Finally, SiO_2 is removed using the differences in weight through an air distribution system. However, since the above-mentioned methods employ a firing process undertaken for 2-3 h at 900-1,100 °C, they require high energy consumption. Furthermore, due to involvement of firing, grinding, magnetic selection, and air distribution processes, these methods tend not to be cost-effective. Thus, several studies have focused on the use of additives in the WFGD process. Kim et al. [11] tested the byproduct of the adipic acid manufacturing process, dibasic acid (DBA), against other organic acids in the WFGD process. This additive was confirmed to promote buffering action, because it increased the material transfer of SO_2 and thus, the desulfurization efficiency. The gypsum content in the gypsum slurry increased from 22 to 29.7 wt% when adipic acid was employed and to 27.7 wt% when dba was used. the results

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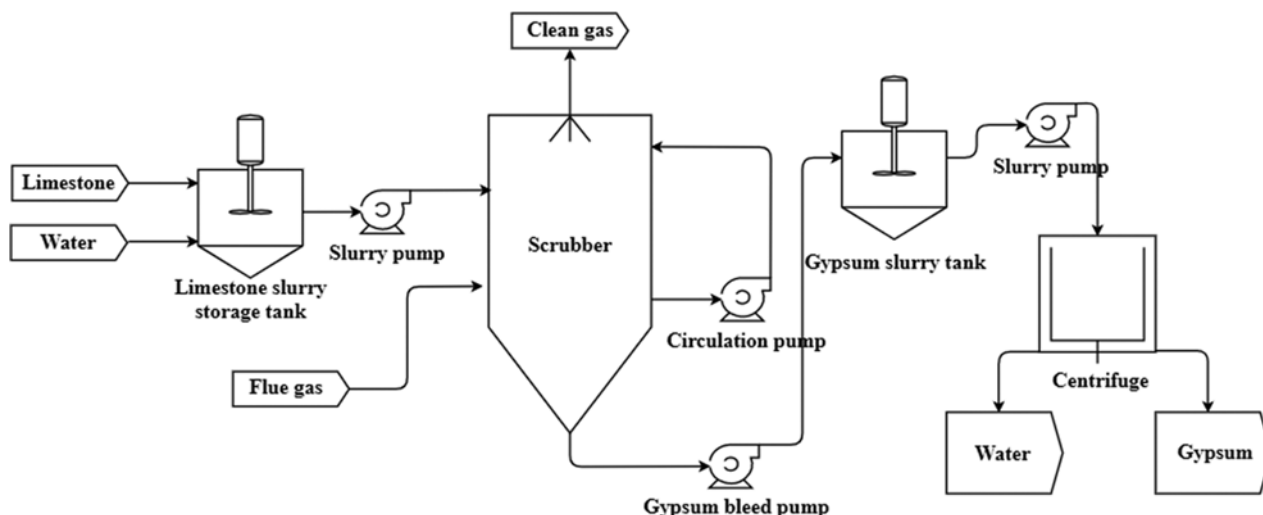


Fig. 1. Workflow of the overall wet flue gas desulfurization process.

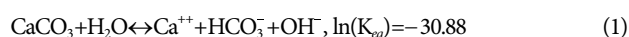
of these experiments confirmed that the use of additives reduced the pH of the slurry and increased the rate of dissolution of limestone, resulting in faster gypsum production. Thus, the use of an additive can speed up the production of gypsum but cannot increase its purity. Thus, herein, we report the development of a model for WFGD using Aspen plus to investigate the feasibility of limestone mixing processes that aims to utilize low-quality limestone without any pretreatment. The development of a model via process simulation can achieve results similar to those obtained in a real process in a relatively short time and at relatively low cost without actually operating a plant, when the physical properties, flow rate, and operating conditions of the actual injected object are known. In addition, although there are a number of variables that cannot be easily predicted or tested in actual plants, the results can be obtained quickly and accurately because these variables can be easily tested by adjusting them in process simulation [12]. Using this model, low-grade limestone can be used, and unlike in the case of improving limestone quality, this model is particularly economical due to the low energy consumption and minimized additional costs. A mixing process is also added to the simulation to ensure that the quantity of low-grade and high-grade limestone can be easily adjusted to obtain the desired gypsum purity. Therefore, this model should provide guidelines for predicting the maximum mixing ratio by utilizing low-quality limestone to achieve the desired gypsum with 93 wt% purity. Utilizing the developed model, a case study was conducted for the Dangjin thermal power plant. For optimization of the conditions, the following constraints are set to maximize the use of low-grade limestone: gypsum purity=93 wt%, desulfurization efficiency=94%, and total limestone usage=3,710 kg/h.

MODEL DEVELOPMENT

1. Process Overview

Fig. 1 shows a workflow chart of the overall WFGD process. Initially, the crushed limestone is dissolved in water in the limestone slurry storage tank prior to spraying of the slurry inside the

scrubber through a slurry pump. Subsequently, the flue gas flows into the scrubber and several reactions such as oxidation and SO_2 absorption occur when the gases and the sprayed alkaline slurry meet. Finally, the clean gas is released from the scrubber. Crystallization takes place in the liquid phase inside the scrubber to produce the desulfurized gypsum, which is the desulfurization product of the wet FGD process in coal-fired power plants and also exists as a liquid slurry at the bottom of the scrubber. Gypsum slurry is then moved to a slurry tank through the gypsum bleed pump prior to separation by centrifugation. Notably, the dissolution of limestone (Eq. (1)) in the limestone slurry storage tank involves the following solid-liquid phase reaction [13], and the equilibrium constant K value is as follows [15].



Other reactions also occur in the scrubber following the dissolution of limestone. Fig. 2 shows a simple schematic of the process undergone in the WFGD scrubber. As shown, the flue gas containing SO_x is absorbed into the scrubber and the limestone slurry

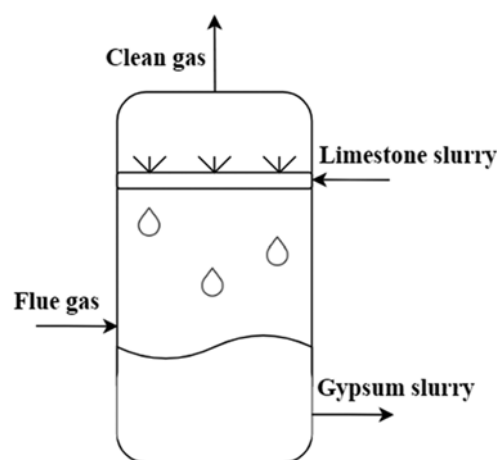
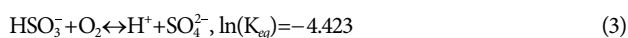
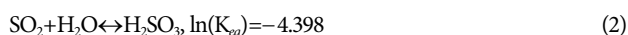


Fig. 2. Simplified schematic representation of the process taking place in the scrubber during WFGD.

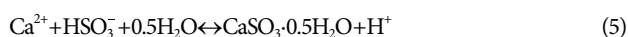
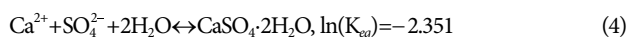
Table 1. Quality standards of desulfurized gypsum

| Component | Standard | Units |
|---|-------------|-------|
| $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | ≥ 93 | wt% |
| CaCO_3 | ≤ 1.5 | wt% |
| $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ | ≤ 0.25 | wt% |
| SiO_2 | ≤ 3.0 | wt% |
| $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ | ≤ 1.5 | wt% |

is introduced by spraying in the form of liquid drops. The resulting contact between the flue gas and the sprayed slurry results in SO_2 absorption (Eq. (2)) and oxidation (Eq. (3)) [7], and the equilibrium constant K value is as follows [16].



Subsequently, hydrated calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is produced in the liquid phase in the lower part of the scrubber and is separated using water and gypsum through centrifugation. During the crystallization process (Eq. (4), (5)), SO_4^{2-} ions absorbed from the flue gas react with ionized Ca^{2+} ions in the limestone as follows:



Finally, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is recycled and commercialized in the form of its anhydrite (CaSO_4) following dehydration. Table 1 lists the quality standards for recyclable desulfurized gypsum obtained in the WFGD process operated in the Dangjin thermal power plant in the Republic of Korea [14].

2. Process Modeling

Fig. 3 illustrates the WFGD process modeled by Aspen plus. In this model, the reactions occur in the liquid phase. Thus, the thermodynamic model employs the electrolytic non-random two liquids (ELECNRTL) property method for the liquid and solid phases using the Redlich-Kwong equation for the gas phase. It can handle a wide range of concentrations when treating water-soluble substances and mixed solvents. Many different parameters of the component such as molecular weight, enthalpy of formation, Gibbs energy of formation, and chemical equilibrium constants were also employed during the modelling process, and they were used to be based on the Aspen Physical Property System Databank. In process modeling, the reactions are divided into four blocks. Initially,

a limestone stream mixer (MIXER) is considered, although this does not exist in the actual process. It mixes the two streams of low-grade (LIME1) and high-grade limestone (LIME2). This stage was added to predict the mixing ratio of limestone that can allow the use of low-grade limestone and high-grade limestone. The second stage involves the slurry storage tank (LIME-DS) where the limestone is dissolved in water. The simulation is conducted using the RSTOIC model inside Aspen plus and includes limestone dissolution in a solid-liquid phase. The RSTOIC model is used when the reaction kinetics are unknown or unimportant, but the stoichiometry is known. It can determine the extent of reaction or the conversion that should be provided as inputs to simulate the RSTOIC unit operation. In this study, the limestone in the slurry tanks was assumed to be ~99% dissolved, which was reflected in the model. Since the maximum solubility of limestone depends on the time and degree of grinding, it was assumed that the dissolution of limestone was complete in the slurry tank. In this model, the reaction of Eq. (1) occurs in the liquid phase. The following step involved the absorption tower (SCRUBBER) shown in Fig. 1, and this was simulated using the RCSTR model, which is used when rigorous simulation of reactors is needed. For a CSTR, two design variables (pressure and temperature or heat duty), specification of the valid phases, and reactor specification are needed. Moreover, two types of reactions presenting the chemistry involved in the ion forming system and general reactions can be defined. When the flue gas (FLUEGAS) and dissolved alkaline slurry (SLURRY) meet, SO_2 absorption and oxidation occur in a liquid-gas phase. Reactions such as SO_2 absorption and oxidation entered in the model are represented by Eqs. (2) and (3). In the actual process, the gypsum crystallizes in the liquid phase at the bottom of the scrubber; however, in process modeling, the crystallizer (GYP-CR) is added in split steps. In the GYP-CR simulated by the RCSTR model, the desulfurized gypsum is produced in a solid-liquid phase. The RCSTR model is used when the reaction kinetics are known and can simultaneously model equilibrium reactions by using rate-based reactions. Each reaction of crystallization is represented by Eqs. (4) and (5). Finally, products such as the purified gas and gypsum are separated using the SEPARATORS model (GAS-SP and GYP-SP). Table 2 lists the operating conditions for the simulation of each block. The operating temperature in the actual limestone slurry storage tank was 30°C , and it took 12-16 h for the limestone to dissolve completely [17]. Therefore, the operating conditions of the LIME-DS were set as 30°C and 14 h, complying with the real data. In the scrubber, the retention time in liquid phase

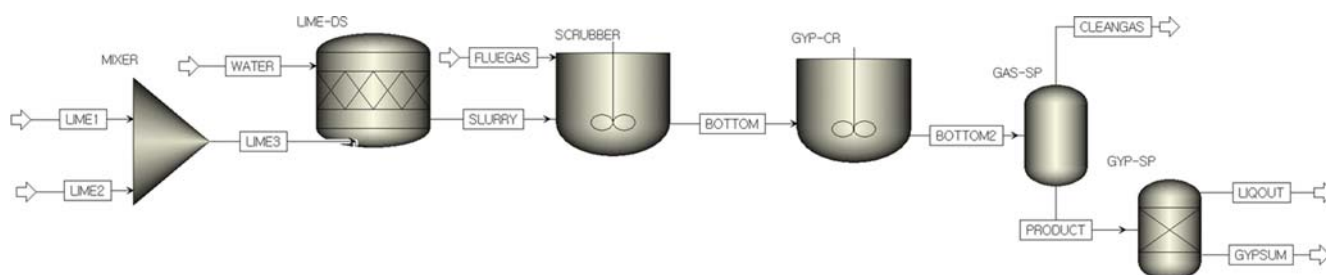
**Fig. 3. Process involved in the desulfurization of wet flue gas.**

Table 2. Reactions and operation conditions of the blocks employed in the simulation

| Block | Reaction | Ref. temp. | Operating condition |
|----------|---|------------|--|
| MIXER | - | - | Pressure: 1 bar Valid Phase: solid only |
| LIME-DS | $\text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$ | 20 °C | Temperature: 30 °C Pressure: 1 bar Valid Phase: liquid only Residence time: 14 h |
| SCRUBBER | $\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HSO}_3^-$ $\text{HSO}_3^- + \text{O}_2 \leftrightarrow \text{H}^+ + \text{SO}_4^{2-}$ | 25 °C | Temperature: 60 °C Pressure: 1 bar Valid Phase: liquid-vapor Residence time: 15 min |
| GYP-CR | $\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{HSO}_3^- + 0.5\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + \text{H}^+$ | 20 °C | Temperature: 60 °C Pressure: 1 bar Valid Phase: liquid-vapor Residence time: 15 min |
| GAS-SP | - | - | Temperature: 60 °C Pressure: 1 bar |
| GYP-SP | - | - | - |

Table 3. Process conditions employed at the Dangjin thermal power plant

| Category | Stream name | Permissible value | Unit |
|-----------------------|-------------|-------------------|-------------------|
| Water consumption | WATER | ≤92,200 | kg/h |
| Limestone consumption | LIME1+LIME2 | ≤3,710 | kg/h |
| Amount of exhaust gas | FLUEGAS | 1,523,144 | m ³ /h |

Table 4. Composition of the different limestone samples

| Component | LIME1 (low-grade) | LIME2 (high-grade) | Unit |
|--------------------------------|-------------------|--------------------|------|
| CaCO ₃ | 91.7 | 94.2 | wt% |
| MgCO ₃ | 5.88 | 2.97 | wt% |
| SiO ₂ | 1.07 | 1.72 | wt% |
| Al ₂ O ₃ | 1.35 | 1.11 | wt% |

Table 5. Composition of the flue gas

| Component | Molar fraction |
|------------------|----------------|
| SO ₂ | 0.03832 |
| H ₂ O | 9.433 |
| CO ₂ | 9.384 |
| N ₂ | 76.25 |
| O ₂ | 4.896 |

was 8–15 min and the operating temperature was 60 °C. Thus, the operating conditions were set as 60 °C and 15 min for SCRUBBER [18]. In this model, the crystallization of gypsum was divided into stages and GYP-CR was subjected to the operating conditions identical to those of the SCRUBBER because in the real process, the reaction takes place at the same place. In the final step of the GAS-SP, the clean gas was separated and the components corresponding to the quality standard were separated at GYP-SP.

In this study, the conditions employed at the Dangjin thermal power plant were considered for simulation and optimization. Table 3 lists the process conditions, which were set at their corresponding maximum values in this model.

The composition of low-grade and high-grade limestone (LIME1 and LIME2, respectively) was input by referring to the composition of limestone samples supplied by different mines [8]. Table 4 shows the composition of each sample.

The composition of the flue gas (FLUEGAS) was assumed using the absorption factor (Ca/S ratio). The Ca/S ratio is expressed as a

percentage by dividing the actual amount of limestone consumed by the theoretical limestone consumption and generally lies in the range 0.7–2.7 [19]. In this model, the Ca/S ratio was set at 1.5, and Table 5 shows the composition of flue gas.

3. Simulation Results

Conducting simulations using this model involved two cases according to the process conditions. Based on the conditions listed in Table 3, Case 1 is the situation that used low-grade limestone (LIME1) and Case 2 is that used high-grade limestone (LIME2). The simulation results indicated that the desulfurization efficiency was satisfied in both cases, but the purity of desulfurized gypsum was not satisfied according to the quality standard in Case 1. The purity was reduced mainly by the MgCO₃ impurity. In Case 2, the results satisfied all the quality standards as well as the desulfurization efficiency requirements. The obtained results confirmed that the presence of impurities in low-grade limestone affects the purity of the obtained desulfurized gypsum. Table 6 shows the simulation results.

Table 6. Results of the simulation

| Category | Quality standard | Case 1 | Case 2 | Unit |
|--|------------------|--------|------------------------|------|
| Desulfurization efficiency | ≥94 | 99 | 99 | % |
| CaSO ₄ ·2H ₂ O | ≥93 | 91.8 | 93.9 | wt% |
| CaCO ₃ | ≤1.5 | 0.811 | 0.852 | wt% |
| CaSO ₃ ·1/2H ₂ O | ≤0.25 | 0 | 3.59×10 ⁻¹³ | wt% |
| SiO ₂ | ≤3.0 | 0.947 | 1.56 | wt% |
| Al ₂ O ₃ +Fe ₂ O ₃ | ≤1.5 | 1.19 | 1.00 | wt% |
| MgCO ₃ | - | 5.20 | 2.69 | wt% |

OPTIMIZATION

1. Optimization Conditions

Optimization comprises a series of algorithms to determine the optimal value of the process for variables that have not been determined [20]. In this study, process optimization was conducted using the sequential quadratic programming (SQP) algorithm built into Aspen plus, using the following settings: Maximize: LIME1; subject to the constraints: purity (GYPSUM) ≥0.93, desulfurization efficiency ≥0.94, and mass flow (LIME3)=3,710. In general, the algorithms of optimization require extensive analysis, sensitivity evaluation, and frequent calculations according to the objective function and the constraints. In addition, increasing the design variable is computationally difficult and requires considerable time when the optimal solution starts at a distance from the starting point. However, through the SQP algorithm, a solution can be achieved by approximating a nonlinear equation with multiple variables and calculation time can be considerably reduced. In this study, the optimization was carried out on the basis of the initial operating conditions of the Dangjin thermal power plant. However, in the case of other plants, fast calculation is crucial; thus, the SQP algorithm was used in this model. The mass flows of low-grade limestone (LIME1) and high-grade limestone (LIME2) were used as variables for optimization. The objective was to maximize LIME1 keeping in mind economic requirements and resource utilization within the constraints. In terms of the constraints, the gypsum purity was set at ≥93%, considering the quality standard for the desulfurized gypsum. The total use of limestone (LIME3) was set at 3,710 kg/h considering the total limestone consumed in the real process. Table 7 shows the optimization constraints and Table 8 lists the optimization variables.

Table 7. Constraints for the optimization process

| Name in model | Specification | Unit |
|---------------|---------------|------|
| GYPSUM | ≥93 | wt% |
| LIME3 | 3,710 | kg/h |

Table 8. Optimization variables

| Variables | Low limit | Upper limit | Step size | Unit |
|-----------|-----------|-------------|-----------|------|
| LIME1 | 1 | 4,000 | 0.05 | kg/h |
| LIME2 | 1 | 4,000 | 0.05 | kg/h |

Table 9. Results of optimization 1

| Variable | Initial value | Final value | Unit |
|----------------------------|---------------|-------------|------|
| LIME1 mass flow | 0 | 1,610 | kg/h |
| LIME2 mass flow | 3,710 | 2,100 | kg/h |
| GYPSUM purity | 93.90 | 93.00 | wt% |
| Desulfurization efficiency | 99.99 | 99.99 | % |

Table 10. Results of optimization 2

| Category | Quality standard | Initial value | Final value | Unit |
|--|------------------|------------------------|-------------|------|
| Desulfurization efficiency | ≥94 | 99 | 99 | % |
| CaSO ₄ ·2H ₂ O | ≥93 | 93.9 | 93 | wt% |
| CaCO ₃ | ≤1.5 | 0.852 | 0.834 | wt% |
| CaSO ₃ ·1/2H ₂ O | ≤0.25 | 3.59×10 ⁻¹³ | 0 | wt% |
| SiO ₂ | ≤3.0 | 1.56 | 1.29 | wt% |
| Al ₂ O ₃ +Fe ₂ O ₃ | ≤1.5 | 1.00 | 1.09 | wt% |
| MgCO ₃ | - | 2.69 | 3.79 | wt% |

2. Optimization Results

To compare the initial value with the optimization results, the initial value was set to Case 2, which uses only high-grade limestone. In meeting the constraints, the optimization results confirmed that 1,610 kg of low-grade limestone could be mixed with up to 2,100 kg of high-grade limestone without any pre-treatment. The desulfurization efficiency of the initial and optimized values was 99% in both cases, meeting the required quality standard. The total impurity content was slightly higher, but the purity of the gypsum was 93%, which met the quality standard. The optimization results confirmed the maximum mixing ratio of low-grade to high-grade limestone. Tables 9 and 10 display the results of the optimization. Notably, the initial value refers to the value obtained using only high-grade limestone, while the final value indicates the optimization result. This optimization result indicates that only high-quality limestone, which suffers from resource depletion, used a consumption rate of 3,710 kg/h to satisfy the purity available for sale at the Dangjin Thermal Power plant but 1,610 kg/h of low-grade limestone can be replaced with high-grade limestone. Thus, an approach that resolves the problem of using scarce high-grade limestone and that enhances the utilization of low-grade limestone has been proposed.

SENSITIVITY ANALYSIS

Optimization is a method that maximizes or minimizes the objective function under the given constraints. For this optimization design, the impact of each input variable on the objective function must be analyzed: sensitivity analysis. There are two factors governing the purity of gypsum when the developed model is applied to the WFGD process. The first is the use of limestone, which depends on the deposits of limestone and the degree of mining. If the amount of low-grade limestone is higher than that of mixed limestone calculated by the model, the purity of limestone may be reduced. The second factor is the solubility of lime-

stone. In this study, it was assumed that the limestone in the slurry storage tanks was completely dissolved. Limestone tends to exhibit different solubility depending on the degree of grinding and operating time, but in general, it requires 12-16 h to dissolve completely. However, in the actual process, limestone is not completely dissolved due to the different degree of solubility. Therefore, the purity of gypsum was analyzed in terms of the two factors. Initially, sensitivity analysis was performed for the mass flows of LIME1 and LIME2 as

the input variables, and the purity of GYPSUM as the result variable. Table 11 lists the input conditions for the sensitivity analysis.

Table 11. Conditions for sensitivity analysis

| Variable | Starting point | End point | Unit |
|----------|----------------|-----------|------|
| LIME 1 | 1,410 | 1,810 | kg/h |
| LIME 2 | 2,300 | 1,900 | kg/h |

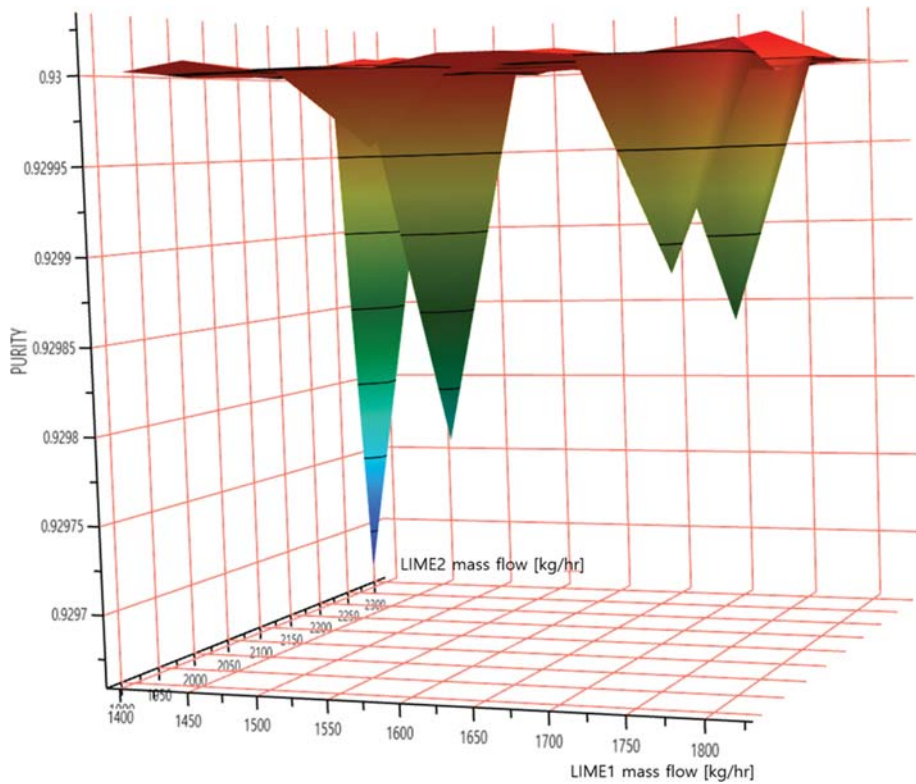


Fig. 4. 3D surface plot obtained from sensitivity analysis.

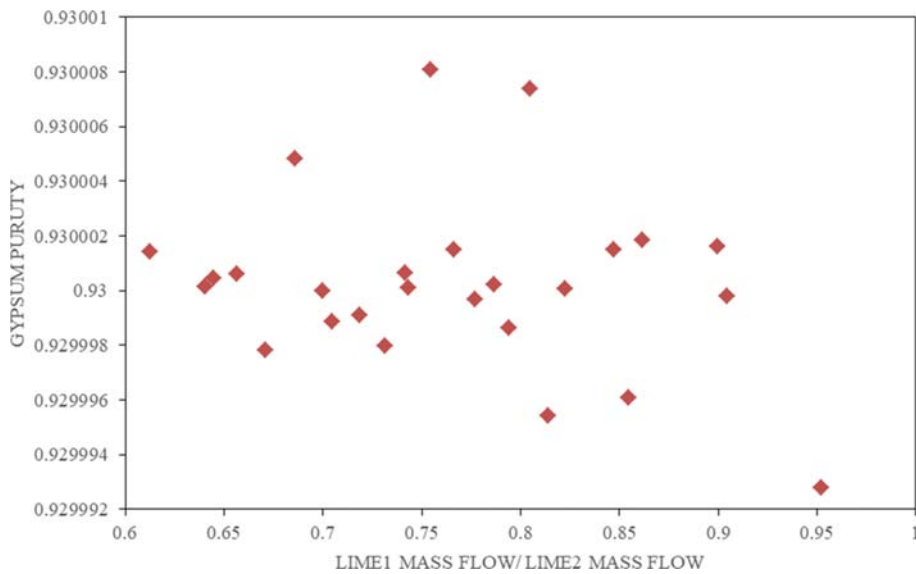


Fig. 5. Gypsum purity as a function of limestone blending ratio.

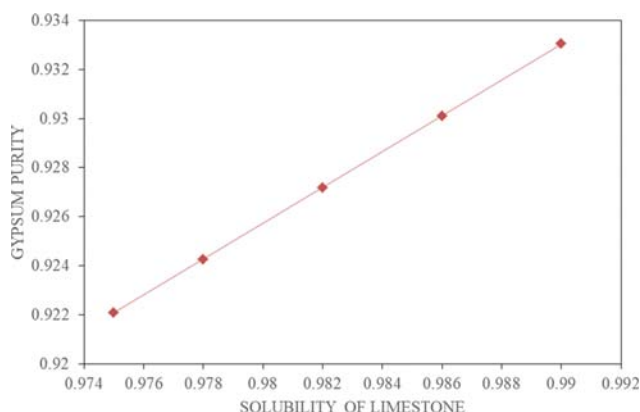


Fig. 6. Gypsum purity as a function of limestone solubility.

At the Dangjin thermal power plant, the total use of limestone is maintained below 3,710 kg/h. However, the actual process can lead to errors in the use of limestone due to factors like the amount of limestone mined. Sensitivity analysis was therefore performed with a margin of error of 200 kg based on the maximum mixing ratio obtained from the optimization results. The results of sensitivity analysis (Fig. 4) showed that within the studied range, the gypsum purity was 0.92968–0.93002 wt%.

Fig. 5 shows the relationship between limestone mixing ratio and the resulting gypsum purity. Indeed, this plot confirms that the gypsum purity satisfied the quality standard with high probability.

Secondly, based on the sensitivity analysis results, an additional sensitivity analysis was performed with the solubility of limestone as the input variable and the purity of gypsum as the result variable. The solubility of the input variable was set in the range 97.5–99%, because limestone solubility <97.5% would mean that the gypsum will fail the quality standard due to the presence of unreacted CaCO_3 . Fig. 6 shows the results obtained for sensitivity analysis, where it can be seen that at least 98.6% of the limestone must be dissolved to meet the quality standard.

The results obtained for the limestone solubility were derived for each case by using the developed model. The analysis was conducted by assuming the solubility of the limestone. However, when the model was applied to the actual process, it was necessary to obtain the limestone solubility experimentally, because the grinding of limestone and the operating times differed. As the RSTOIC model was used in the modeling, the solubility of the limestone could be adjusted, rendering it easier to represent the results of the experiment at a later point. The maximum mixing ratio was obtained based on the conditions implemented at the Dangjin thermal power plant, which was the focus of the case study. However, in many other plants, the amount of limestone used and the solubility of limestone encountered are different. Using the developed model, the maximum mixing ratio of low-grade and high-grade limestone can be calculated for each situation by adjusting the conditions and carrying out optimization.

ECONOMIC ANALYSIS

A mixed blending model, a guideline for utilizing low-grade lime-

stone, can lead to economic benefits and increased resource utilization. Low-grade limestone is less expensive than high-grade limestone because it contains other species mixed with the limestone and therefore there is currently little demand for it. The distribution price of the Korea Institute of Applied Statistics is updated to the price of high-grade limestone at 13,000 won/ton, which equates to ~\$11 per ton. However, low-grade limestone has low demand, and thus has no distribution price assigned to it. According to a previous survey by Jeon [21], low-grade limestone is sold at approximately half the price of high-grade samples; based on this, it was estimated at \$5.5 per ton to calculate the annual savings made by the optimized process proposed herein. Although the capital expenditure (CAPEX), the cost used to acquire or upgrade material assets like equipment, land, and buildings, should be considered, it was not addressed herein because only the mixing ratio of limestones was changed in the same process. In contrast, the operating expense (OPEX) refers to the costs of running an already available infrastructure, including the mining, transportation, labor, operating, maintenance, and raw material costs of limestone. The costs of mining, transportation, and the limestone itself all differed from those of the existing process. The mining cost of limestone was expected to be reduced because it was not necessary to selectively mine for high-grade limestone. In addition, transportation costs were reduced owing to the development of mines close to the process location. However, the actual calculation of these costs was limited by a number of variables, and thus, for simplification, the analysis was conducted for only the raw material cost. Therefore, the raw material cost should be reduced upon using low-grade limestone to give the results listed in Table 12. In this table, the initial costs of the raw materials and that of the raw materials after optimization are provided; the cost was reduced by approximately \$77,473 per year.

The total annual costs can then be calculated as follows:

$$\text{Annual Cost} = \text{Sales rate} \times \text{variable cost} (1 + \text{Market growth rate}) (n-1) + \text{fixed cost}; (n = \text{year number})$$

The sales rate and annual fixed costs were assumed to be the same as those of the existing process. The variable costs were assumed only for the raw material cost. The market growth rate refers to the sales of goods or services in a particular market compared to the total sales in the previous year; it represents the difference as a percentage. Table 13 lists the amount of gypsum sold at the Dangjin thermal power plant between 2014 and 2018.

As indicated, the latest market growth rate (2017 and 2018) de-

Table 12. Comparison of initial and final material costs

| Category | Value | Unit |
|---------------------------|---------|---------|
| Initial raw material cost | 357,496 | \$/year |
| Final raw material cost | 280,022 | \$/year |

Table 13. Sale volume of gypsum at the Dangjin thermal power plant between 2014 and 2018

| Base year | Unit | 2014 | 2015 | 2016 | 2017 | 2018 |
|-------------|------|---------|---------|---------|---------|---------|
| Sale volume | ton | 389,000 | 420,000 | 363,000 | 382,000 | 379,000 |

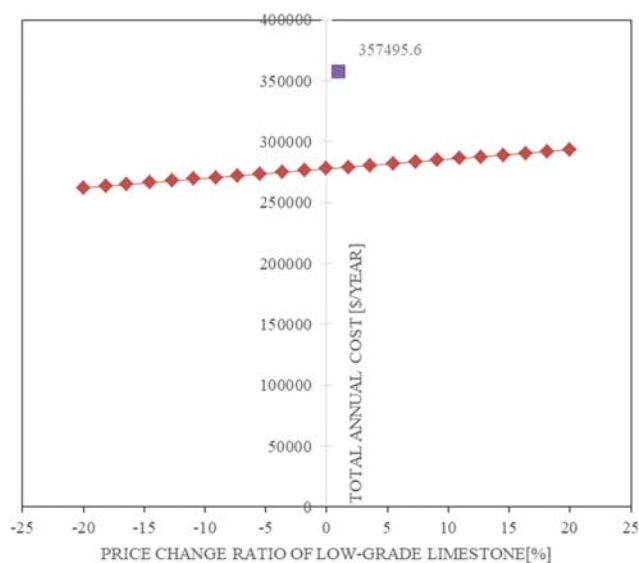


Fig. 7. Total annual cost according to the price change ratio of low-grade limestone.

creased slightly to -0.8% . Based on this market growth rate, the annual cost reduction was calculated to be approximately \$76,853. However, this value may be erroneous because the assumed price of low-grade limestone was not the actual price. Sensitivity analysis was therefore performed with 20% variation in the assumed price. Fig. 7 plots the total annual cost against the price change ratio of low-grade limestone, and it is apparent that the annual cost was reduced in the range \$61,464–92,243.

CONCLUSION

To use untreated low-grade limestone in the wet flue gas desulfurization process for gypsum production, a blending model using Aspen plus was developed to predict the maximum mixing ratio of low-grade and high-grade limestone. Using this developed model, a case study was conducted for the Dangjin thermal power plant in the Republic of Korea. The simulation results showed that the quality standards of desulfurized gypsum were not met because of the numerous impurities present in low-grade limestone. Optimization performed using the model under specific constraints revealed that 1,610 kg of low-grade limestone could be mixed with up to 2,100 kg of high-grade limestone. This result shows that low-grade limestone itself can be used in gypsum production without any pretreatment. This will overcome the issue related to the resource depletion of high-grade limestone, thus facilitating a very efficient alternative to the existing methods of improving the quality of low-grade limestone, which require combustion at high temperatures and additional processes such as magnetic selection and air distribution. Therefore, these existing methods are not commercialized because of the high operation cost. The results of this study are, thus, expected to be considerably useful because low-grade limestone can be used without any prior treatment, additional process installation is not required, and only the proportion of raw materials will change as a result. A sensitivity analysis was also performed with a margin of error of 200 kg for the use of limestone

based on the optimized mixing ratio, revealing that the purity of the gypsum met the quality standard with high probability. Therefore, the model could be successfully applied to an actual process. Furthermore, the blending model developed herein offers a guideline for determining an appropriate mixing ratio for the utilization of low-grade limestone, which should offer economic advantages and compensate for the depletion of high-grade resources. For this study, it was assumed that $\sim 99\%$ of the limestone in the slurry storage tank had dissolved, which was reflected in the model. However, in the actual process, the degree of grinding and the operating time were different; thus, the resulting limestone solubility also differs. The solubility of limestone was therefore specified to be in the range 97.5–99% when estimating the gypsum purity. However, for an actual process, the solubility should be obtained experimentally. Since the RSTOIC model was employed here, the limestone solubility could be directly adjusted, making it easier to reflect the results of the actual experiment at a later point. In terms of economic analysis, the price of high-grade limestone was set at \$11 per ton, and that of low-grade limestone was considered half of this at \$5.5 per ton. The initial annual costs were then compared with the results obtained after optimization, and annual savings for the variable costs of raw materials and market growth rates was calculated to be approximately \$76,853 per year. The model also included a stream mixer to allow the streams of low-grade limestone and high-grade limestone to be mixed; however, the actual process simply changes the proportion of raw materials. Therefore, installation of additional processes is not required. In addition, because the operating conditions can be applied without modification, the total cost and annual production cost of low-grade limestone will be very low compared to those of the existing methods for improving quality of low-grade limestone. In this study, it was assumed that only the impurities present in the low-grade limestone affected the purity of the final gypsum product. However, in a real system, the physical and chemical reactions of these impurities can also deteriorate the product purity. An experimental study on the effects of impurities will therefore be conducted and incorporated into this model in future.

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REFERENCES

1. G. Cheng and C. X. Zhang, *Pol. J. Environ. Stud.*, **27**, 481 (2018).
2. M. A. Gostomczyk and W. Kordylewski, *ARCH COMBUST*, **30**, 15 (2010).
3. E. K. Oh, *J. Korea Society of Environmental Administration*, **9**, 187 (2003).
4. C. Carletti, C. Blasio, E. Mäkilä, J. Salonen and T. Westerlund, *Ind.*

- Eng. Chem. Res.*, **54**, 9783 (2015).
5. T. Recelj and J. Golob, *Process Saf. Environ. Prot.*, **82**, 371 (2004).
6. R. Krzyżyńska and Y. Zhao, *Polish J. Environ. Stud.*, **19**, 1255 (2010).
7. L. E. Kallinikos, E. I. Farsari, D. N. Spartinos and N. G. Papayannakos, *Fuel Process. Technol.*, **91**, 1794 (2010).
8. S. S. Park, H. S. Ahn, K. H. Kim, S. W. Yun and K. K. Park, *J. Korea Soc. Waste Manag.*, **2010**, 125 (2010).
9. H. S. Kim, Korea Patent, 10-2012-0018757 (2012).
10. J. H. Ahn, Korea Patent, 10-2015-0061150 (2015).
11. H. S. Kim, Y. I. Yun, H. K. Li and S. H. Kim, *J. Korean Ind. Eng. Chem.*, **13**, 468 (2002).
12. J. H. Kim, K. J. Tak and I. Moon, *Ind. Eng. Chem. Res.*, **51**, 10191 (2012).
13. V. Russo, T. Salmi, C. Carletti, D. Murzin, T. Westerlund, R. Tesser and H. Grénman, *Ind. Eng. Chem. Res.*, **56**, 13254 (2017).
14. S. Gu, B. Fu, T. Fujita and J. W. Ahn, *Appl. Sci.*, **9**, 2262 (2019).
15. Y. Yin, *Q. J. R. Meteorol. Soc.*, **131**, 221 (2005).
16. S. S. Park, J. P. Hong, Y. M. Ahn, S. Y. Park and H. M. Uhm, *J. Korean Soc. Environ. Eng.*, **22**, 1407 (2000).
17. B. N. Kim, *Trans. Korean Soc. Mech. Eng.*, **A**, 97 (2003).
18. J. Katolicky and M. Jicha, *Heat Transf. Eng.*, **KJ3**, 57 (2007).
19. X. Ma, T. Kaneko, T. Tashimo, T. Yoshida and K. Kato, *Chem. Eng. Sci.*, **55**, 4643 (2000).
20. K. J. Tak, I. K. Lee, H. E. Kwon, J. H. Kim, D. H. Ko and I. Moon, *Ind. Eng. Chem. Res.*, **54**, 9992 (2015).
21. H. Jo, D. S. Uh, U. M. Choi and M. W. Han, *Korean Chem. Eng. Res.*, **50**, 270 (2012).