

Article

Full-Scale Industrial Application of Adipic Acid Enhanced Limestone Utilization in Wet Flue Gas Desulfurization Systems

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Featured Application

Using adipic acid in WFGD processes is feasible for reducing limestone consumption by achieving high SO₂ removal efficiency in wet flue gas desulfurization (WFGD) units in coal-fired thermal power plants. This approach can be easily integrated with process modifications in existing WFGD systems, providing plant operators with an effective solution to meet more reliable emission limits and enhance overall operational reliability.

Abstract

Wet flue gas desulfurization (WFGD) is a widely used process for controlling SO₂ emissions in coal-fired power plants. However, the slow dissolution kinetics of limestone (CaCO₃) and the poor dewatering properties of gypsum crystals significantly limit the performance of this process. In this study, the effects of adding adipic acid, an organic acid, at different concentrations (0, 500, 1000, and 1500 ppm) to limestone slurry in the WFGD process were investigated. SO₂ removal performance, limestone consumption, and gypsum quality were evaluated. SO₂ removal efficiency remained unaffected by the addition of adipic acid. The addition of adipic acid reduced limestone consumption by 6.89%, 8.35%, and 9.92% in WFGD, respectively. The moisture content of gypsum decreased from 22.4% to 9.2%. The results revealed that adipic acid accelerates limestone dissolution via a ligand-assisted proton-transfer mechanism and improves the overall efficiency of the WFGD process by controlling gypsum crystallization. The physical quality and structure of gypsum obtained from the WFGD were evaluated by Scanning Electron Microscopy (SEM). Adipic acid led to the development of larger, smoother, and potato-like morphologies in the gypsum crystals and improved dewatering performance. This study demonstrates that using adipic acid in WFGD processes is a significant improvement strategy that enhances process efficiency by accelerating limestone dissolution and controlling gypsum crystallization. Adipic acid addition is an effective optimization strategy for full-scale industrial WFGD systems.

Keywords: adipic acid; gypsum; limestone; organic acid; SO₂; wet flue gas desulfurization (WFGD)



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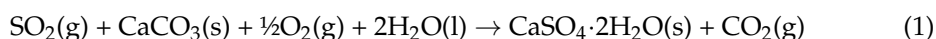
1. Introduction

Coal-fired power plants provide a significant portion of the world's electricity supply. In the modern world, where renewable energy sources are on the agenda, approximately 35% of global electricity production comes from coal. This is because coal has a high energy

capacity potential and is easily accessible in many regions. Sulfur dioxide (SO₂) emitted from coal and oil-fired combustion affects the environment and human health. Also, SO₂ undergoes oxidation pathways in the atmosphere, which are closely linked to the formation of delicate particulate matter (PM_{2.5}), acid deposition, and degradation of visual air quality. Particularly when inhaled or in contact with the skin, SO₂ can cause severe irritation to the nose, throat, and lungs. Therefore, SO₂ emission control has become a crucial necessity in regions with coal-fired power plants [1]. For this reason, FGD technologies are used in coal-fired power plants, and the process can be classified into dry, semi-dry, seawater-based, and wet limestone–gypsum (WFGD) systems. The operational characteristics, advantages, and limitations regarding efficiency, cost, and environmental performance present distinct properties [2–6]. The WFGD process remains the standard technology in large-scale coal-fired power plants. High SO₂ removal efficiencies are obtained from WFGD [7].

Unlike many alternative FGD approaches, the WFGD process produces solid by-product gypsum (CaSO₄·2H₂O). Gypsum can be marketed as a construction material, such as cement and wallboard [8]. The growing global market valuation of gypsum, projected to exceed USD 1.3 billion by 2032, further underscores the commercial appeal of limestone–gypsum systems. These technical and economic advantages mean that WFGD with limestone remains the preferred emission control strategy for utilities seeking both compliance and value recovery from the desulfurization chain [9].

In the conventional WFGD process, SO₂ is absorbed into an aqueous limestone (CaCO₃) slurry, and gypsum (CaSO₄·2H₂O) is formed through acid–base and redox reactions. In the absorber, dissolved SO₂ is hydrated and neutralized to bisulfite/sulfite species, which react with dissolved Ca²⁺ originating from CaCO₃ dissolution; subsequent forced oxidation converts calcium sulfite to gypsum according to the overall stoichiometric reaction in (Equation (1)).



Recent studies emphasize that three coupled phenomena critically govern the global desulfurization efficiency:

- (i) Limestone dissolution kinetics, which are hindered under the mildly acidic pH range typical of WFGD and often become rate-controlling, necessitating excess CaCO₃ feed, and can be explained with the ligand-assisted proton transfer mechanism.
- (ii) Gas–liquid mass transfer, where limitations in SO₂ absorption and slurry hydrodynamics can reduce the effective utilization of the absorbent [10–13].
- (iii) Gypsum crystallization and crystal morphology, since poorly developed, needle- or flake-like CaSO₄·2H₂O crystals exhibit low filterability and high residual moisture, undermining by-product quality and increasing operating costs. Kinetic and reactor-scale investigations have demonstrated that particle size, limestone reactivity, and slurry chemistry significantly impact CaCO₃ dissolution and SO₂ uptake.
- (iv) Due to the practical constraints associated with the conventional limestone–gypsum process, recent studies have focused on using chemical additives, including organic dicarboxylic acids, in modern WFGD systems to enhance limestone dissolution, promote mass transfer, and regulate gypsum crystal formation [2,10–14].

A water-soluble limestone slurry (CaCO₃) reacts with SO₂ gas from the flue gas, and bisulfite/sulfite ions are formed in the WFGD process. The efficiency of dissolution reaction kinetics of Ca²⁺ ions determines the dissolution rate of limestone in water and SO₂ diffusion between the gas and liquid phases. This is a critical step in traditional WFGD systems. Therefore, studies on the use of organic acid additives to improve both chemical reactions and mass transfer mechanisms have been reported in the literature. Organic

acids have a buffering effect in the WFGD sludge due to their ionization values (pKa). pKa values lie between those of carbonic and sulfurous acids, ensuring a more stable pH at the gas–liquid interface. Buffering facilitates the dissolution of SO₂ in water and maintains the bisulfite/sulfite equilibrium. This statement concludes that gas–liquid mass transfer is more efficient. The SO₂ removal rate is controlled by the mass transfer resistances imposed by the boundary layers in the gas and liquid phases. The total mass transfer coefficient (K) is expressed as the combination of the gas and liquid phase mass transfer coefficients [15].

Dicarboxylic acids are effective in this buffering region and are preferred in WFGD systems [15]. Organic acid additions accelerate CaCO₃ dissolution. Organic acids promote local proton transfer in the near-surface region, creating a ligand-assisted proton transfer mechanism that improves the dissolution kinetics of Ca²⁺ ions on the CaCO₃ surface and supports the progress of series reactions, thus allowing more calcium ions to react with SO₂. Furthermore, organic acids improve dissolution by forming weak complexes with Ca²⁺ [7,16]. Organic acids significantly increase the SO₂ dissolution rate, with organic acid concentration, solution acidity, and the type of acid used playing critical roles. Organic acid additions not only enhance buffering and limestone dissolution but also improve desulfurization system stability, reduce limestone consumption, and help prevent operational problems such as scaling [16–19]. In these systems, organic acids such as adipic, citric, acetic, succinic, and other dicarboxylic or polycarboxylic acids act via two principal mechanisms: firstly, by providing weak acid protons and chelating Ca²⁺ ions, they enhance the CaCO₃ dissolution rate, increasing the availability of reactive calcium species in the slurry; secondly, by interacting with the surface of growing calcium sulfate dihydrate (gypsum) crystals, they influence nucleation and growth kinetics, steering morphology toward larger, smoother crystals with better dewatering properties. Adipic acid is a significant chemical in the manufacturing of materials such as polyamides, polyurethanes, polyester resins, plasticizers, and lubricants [1,15,18,20–23]. Adipic acid addition increased SO₂ removal efficiency from 83% to 90% and reduced the residual limestone content in the gypsum from 4.6% to 1.4% [15,24,25]. Adipic acid reduces the boundary-layer thickness at the solid–liquid interface, thereby increasing the outer-film mass transfer coefficient. In WFGD systems, the total resistance is primarily determined by boundary-layer resistance, driven by the rapid chemical reaction of SO₂ in the aqueous phase. This effect decreases the overall mass transfer resistance and consequently increases the overall mass transfer coefficient (k) [15].

The sulfur content of feed coal can change suddenly, leading to short-term increases in SO₂ in the WFGD absorption unit. As a result, the pH value temporarily drops, and limestone utilization efficiency decreases. The adipic acid additive has a buffering effect on sudden pH fluctuations that may occur during SO₂ load peaks. This CaCO₃ dissolution and gas–liquid mass transfer can be more effortless with buffering behavior, thereby sustaining SO₂ absorption efficiency even during short-term sulfur fluctuations. Although the system may be temporarily strained by increased SO₂ load, it is expected to exhibit faster recovery than unadded systems thanks to the pH-stabilizing support and calcium ion availability provided by the adipic acid-containing suspension. This indicates that adding adipic acid can improve process stability across varying sulfur inputs. Dynamic modeling studies have shown that SO₂ emissions can overshoot during load cycling when slurry flow rates do not immediately adjust to changing flue gas conditions, highlighting the need for control strategies that accommodate these dynamics in WFGD operation [26].

The use of organic acid additives in WFGD affects mercury chemistry and re-emission behavior. Mercury originates from the natural composition of coal used in power plants. The oxidized mercury compounds (Hg²⁺) can be retained in the liquid phase along with SO₂ in WFGD. This can negatively affect dissolution efficiency and increase environmental

loads. Dissolved Hg^{2+} species can be re-emitted into the gas phase as elemental mercury (Hg^0) in a reactive medium. The adipic acid increases the Hg^0 re-emission rate, particularly at high sulfate concentrations, by reducing Hg^{2+} to Hg^0 . This effect stems from organic acids acting as more potent reducing agents. The fundamental reason for this behavior is that the reducing character of sulfate (SO_3^{2-}) species in the solution prepares organic acid anions to more readily accept electrons in Hg^{2+} complexes. The conversion of Hg^{2+} species back to Hg^0 facilitates their re-decomposition into the gas phase under redox conditions [27,28].

Organic acids have significant potential for pilot-scale and industrial applications beyond laboratory studies. In Europe, organic acid additives in limestone have been well established in industrial WFGD applications. The use of organic additives such as adipic acid and carboxylic acid mixtures (DBA) in full-scale WFGD plants increases SO_2 removal efficiency, improves limestone dissolution kinetics, and reduces limestone consumption per unit of SO_2 removal in German power plants. [20,29]. In Poland and the Czech Republic, the use of different chemical additives in WFGD systems operating in coal- and lignite-fired thermal power plants is reported as a standard practice; these additives are said to increase process stability and improve pollutant removal performance [30]. Full-scale applications of additives in European countries such as Poland, the Czech Republic, and Germany are summarized in Table 1.

Table 1. The full-scale applications of chemical additives in the WFGD system.

Country	Organization	Additives	Industrial Benefits
Germany	Utility-operated coal-fired power plants	Adipic acid, DBA (dicarboxylic acids)	Improved SO_2 removal efficiency, enhanced limestone dissolution, reduced limestone consumption, improved absorber stability, and lower operating costs [20,29].
Poland	Coal-fired power plants with limestone WFGD systems	Chemical additives (organic and inorganic)	Enhanced desulfurization efficiency and improved operational stability [30].
Czech Republic	Lignite-fired power plants equipped with WFGD	Chemical additives in slurry systems	Improved pollutant removal efficiency under real operating conditions [30]

Laboratory and pilot-scale studies in the literature have shown that adding organic acids, such as adipic acid, to wet flue gas desulfurization (WFGD) processes improves SO_2 removal performance. However, comprehensive evaluations conducted under full-scale industrial operating conditions are limited. Considering these limitations, the present study investigated the effects of different adipic acid concentrations on SO_2 removal efficiency in a full-scale WFGD system at a coal-fired thermal power plant. This study fills a significant gap in the literature by demonstrating the effects of adipic acid doping on WFGD performance via a ligand-assisted proton transfer mechanism in a full-scale thermal power plant. This is a novel finding compared to previous studies.

2. Materials and Methods

2.1. Materials

The bituminous coal was used as steam coal and supplied from Colombia. The fundamental proximate analyses (moisture, ash, volatile matter, and carbon content) were determined in accordance with American Society for Testing and Materials (ASTM) standards. Total moisture content was determined according to ASTM D3302 [31], Ash, and volatile matter analyses were performed according to ASTM D7582 [32], and the amount of bound carbon was calculated indirectly according to ASTM D7582. Elemental analyses (ultimate analysis) of the coal were conducted to determine its total carbon, hydrogen, and nitrogen content according to ASTM D5373 [33]. Hydrogen analyses were reported both including and excluding moisture. Total sulfur content was determined using ASTM D4239 [34]. The gross and net calorific values were measured according to ASTM D5865 [35] using isothermal bomb calorimetry. The chemical properties of steam (bituminous) coal are shown in Table 2. AR Grade adipic acid, used to increase desulfurization efficiency, was supplied from China. The physicochemical properties of adipic acid were obtained from the manufacturer's technical datasheet and are summarized in Table 3. Limestone was supplied from Sariseki Limestone Mine in İskenderun, Turkey. The chemical composition of the limestone was determined via X-ray fluorescence spectroscopy (XRF) using an Arl OptimX 177 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Limestone samples were dried at 105 °C, sieved, and homogenized. There was approximately 0.6 g of limestone powder, as shown in Table 4.

Table 2. Proximate analysis of steam (bituminous) coal.

Parameter	Value	Dry Basis	Air Dry Basis
Total Moisture (%)	15.71%	-	-
Residual Moisture (%)	-	-	8.20
Moisture Lost with Air-Drying (%)	-	-	-
Ash (%)	11.15%	13.22	12.14
Volatile Matter (%)	31.89%	37.83	34.73
Fixed Carbon (%)	41.25%	48.94	44.93
Total Carbon (%)	58.11%	68.94	63.29
Total Sulfur (%)	0.47%	0.56	0.51
Hydrogen (%)	5.84%	4.84	5.36
Hydrogen (Exclude Moisture) (%)	-	4.08	-
Nitrogen (%)	1.29%	1.53	1.40
Gross Calorific Value (kcal/kg)	5679 kcal/kg	6737	6185
Net Calorific Value (kcal/kg)	5379 kcal/kg	6490	5910

Table 3. Physical and chemical properties of adipic acid.

Parameter	Value
Purity (m/m)	99.89%
Crystalline	White crystalline powder
Colour (Pt-Co)	1.47
Melting Point (°C)	152.5
Water Content (m/m)	0.09%
Nitric Acid Content (mg/kg)	1.23
Iron Content (mg/kg)	0.16
Ash Content (mg/kg)	2.5
Purity (m/m)	99.89%
Crystalline	White crystalline powder
Colour (Pt-Co)	1.47
Melting Point (°C)	152.5

Table 4. The content of limestone.

Parameter	Value
CaO (%)	51.22
MgO (%)	3.00
SiO ₂ (%)	1.02

2.2. Methods

2.2.1. Preparation of Limestone Slurry

For limestone slurry, crushed limestone was fed into the ball mill. Water was added to the ball mill to create a wet grinding environment. As the mill rotated, the balls tumbled and ground. The limestone is ground into a fine powder (typical particle size: 90–95% passing through a 325-mesh screen, or ~44 microns). When ground limestone and water were combined, a limestone slurry formed. Slurry concentration is typically around 30–35% solids by weight for wet Flue Gas Desulfurization (FGD) systems. This balance ensures proper flowability and reaction efficiency with SO₂. The slurry exited the ball mill and was collected in a slurry tank. Agitators in the tank keep the particles suspended. From there, it was pumped to the WFGD absorber as needed.

2.2.2. Preparation of Adipic Acid Solution

To prepare the adipic acid solution, solid adipic acid was added to the adipic acid preparation tank, along with pure water. The solution was then continuously stirred in the tank using the stirrer. Since adipic acid has low solubility in water at room temperature [36], a heater is used in the tank to maintain a solution temperature of around 50–60 °C. The prepared adipic acid solution is then dosed into the limestone slurry tank.

2.2.3. Wet Flue Gas Desulphurization (WFGD) Process

The power plant has a 600 MW pulverized-coal-fired boiler operating at base load. At full load, the flue gas flow rate is approximately 2,071,140 Nm³·hour^{−1}, and the average flue gas temperature at the boiler outlet is 350 °C. The sulfur content of the coal used varies between 0.25% and 0.8% (by weight), depending on fuel supply conditions. The WFGD system operates at a pH range of 5.3–5.6, with an approximate liquid/gas ratio of 10.35 L·m^{−3}, and the limestone sludge concentration is maintained at 25–27.5% (by weight). The system is designed to achieve a SO₂ removal efficiency of over 93.4% under standard operating conditions. The absorber tower was fed adipic acid at 0, 500, 1000, and 1500 ppm. Limestone slurry was sprayed through nozzles with circulation pumps to wash away the SO₂-containing flue gas, during which CaCO₃ reacted with SO₂ to form CaSO₃. Calcium sulfide was converted to gypsum (CaSO₄·2H₂O) with oxidation air.

Flue gas SO₂ concentrations are measured continuously and in real time using a gas analyzer based on the Non-Dispersive Infrared (NDIR) principle via a Continuous Emission Monitoring System (CEMS) (Ultramat 23, Siemens AG, Munich, Germany) installed in the power plant chimney, in accordance with international emission monitoring standards. According to the manufacturer's specifications and EN 15267 [37] requirements, the analyzer's measurement uncertainty is within ±2% of the measured value (expanded uncertainty, k = 2) under stable operating conditions. The SO₂ concentrations before and after FGD absorber application were determined from measurements at different sampling points using the same CEMS. The SO₂ concentration was measured using a sampling line located upstream of the FGD unit at the absorber inlet. These measurements are of the flue gas entering the absorber directly. The WFGD flowchart is shown in Figure 1.

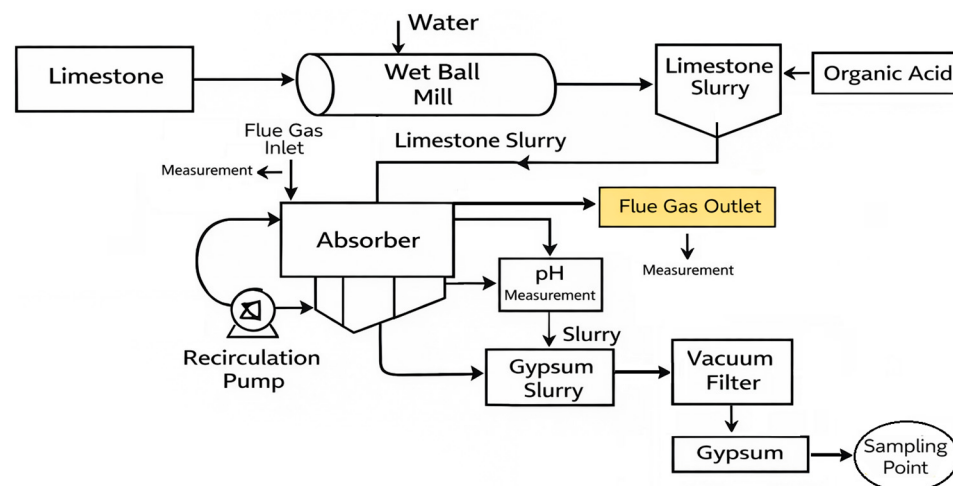


Figure 1. The WFGD system flow chart.

The inlet and outlet SO_2 concentration in the flue gas was measured using the CEMS. When the SO_2 level reached approximately 200 Nm^{-3} , the absorber was initially fed with a limestone slurry without adipic acid. Slurry feeding was continued until the SO_2 concentration at the absorber outlet dropped to approximately 50 Nm^{-3} . The feeding start time is given as 00:15 in Table 5. When the SO_2 concentration reached 50 mg/Nm^3 , feeding was stopped, and the feeding time was recorded. This process was repeated three times on the same day at approximately 3 h intervals, with an average limestone slurry feeding time of 12 min. Subsequently, the same procedure was followed, and limestone slurry containing 500 ppm adipic acid was fed into the absorber. Feeding began when the inlet SO_2 concentration was approximately 200 mg/Nm^3 and ended when the outlet SO_2 concentration dropped to 50 Mg/Nm^3 . The feeding time for this condition was 22:00. Experiments were performed three times at approximately 3-h intervals on the same day, and the average feeding time was 17 min.

Table 5. Desulphurization performance of limestone slurry enriched with different concentrations of adipic acid.

Parameter	Initial	500 ppm	1000 ppm	1500 ppm
Limestone Slurry Feeding Time	00:15	22:00	21:57	21:55
Limestone Slurry Feeding Time (min)	12	17	10	18
Removed SO_2 tonnes/hour	2.67	2.81	3.20	3.49
SO_2 Inlet Avg mg/Nm^3	695	695	765	792
SO_2 Outlet Avg mg/Nm^3	55	50	82	58
R-SO_2^1	4.81	4.48	4.44	4.00
Limestone Consumption Reducing (%)	-	6.85	8.35	9.92

¹ Amount of limestone slurry required for 1 ton SO_2 removal (tonnes).

The same experimental approach was also applied to limestone slurries containing 1000 ppm and 1500 ppm of adipic acid; the average feeding times for these concentrations were determined as 10 and 18 min, respectively. Experiments with both adipic acid-free and adipic acid-containing concentrations were conducted at one-week intervals. The WFGD system was operated with only limestone slurry, and with limestone slurry enriched with 500 ppm, 1000 ppm, and 1500 ppm adipic acid. The amount of limestone slurry consumed per ton of removed SO_2 was compared, along with gypsum quality. The quality and shape of gypsum were characterized by SEM analysis.

2.2.4. Characterization

The characterization of gypsum, the final product of the desulfurization process, was performed using Scanning Electron Microscopy (SEM) TÜBİTAK Marmara Research Center (MAM), Gebze, Kocaeli, Turkey. Gypsum samples were collected from the underflow of the dewatering unit after steady-state operation of the WFGD system at each adipic acid dosage (0, 500, 1000, and 1500 ppm). For each operating condition, representative slurry samples were collected, filtered, and gently washed with deionized water to remove residual soluble salts. The solids were then dried in an oven at 40–50 °C until constant mass was achieved and lightly disaggregated with a mortar and pestle to avoid breaking individual crystals. A small amount of dried powder was mounted on aluminum stubs using double-sided conductive carbon tape. To prevent charging under the electron beam, the samples were sputter-coated with a thin Au–Pd layer ($\approx 5\text{--}10\text{ nm}$). SEM observations were performed at an accelerating voltage of 10–15 kV and a working distance of 8–12 mm. Images were acquired at various magnifications to evaluate particle shape, surface texture, and crystal aggregation.

3. Results

The performance of a full-scale WFGD system was analyzed to quantitatively and qualitatively evaluate it under different adipic acid concentrations. The results are presented based on SO₂ removal performance, limestone consumption per unit of SO₂ removal, and the physical properties of the resulting gypsum (moisture content and crystal morphology). All measurements and data were performed under operating conditions.

The WFGD system was operated with only limestone slurry, as well as limestone slurry enriched with 500 ppm, 1000 ppm, and 1500 ppm adipic acid. The gypsum quality and the amount of limestone slurry consumed per ton of SO₂ removed were measured. During the desulfurization process, the absorber inlet and outlet SO₂ concentrations were measured using a Continuous Emission Monitoring System (CEMS) installed in the plant's chimney. Measurements were performed continuously and in real time using a Siemens Ultramat 23 NDIR analyzer, in accordance with relevant national and international standards. The Desulphurization performance of limestone slurry enriched with different concentrations of adipic acid is presented in Table 5. The limestone consumption and moisture were evaluated. The gypsum formed after the sulfur removal process was sent to a hydrocyclone via a gypsum slurry pump to separate it from the limestone. The gypsum slurry was separated from the limestone using a hydrocyclone and sent to a vacuum belt filter. In the vacuum belt filter, the water in the gypsum slurry was removed via vacuum. The quality and shape of gypsum were characterized by SEM analysis, and the images are presented in Figure 2.

As shown in Table 5, 4.81 tons of limestone slurry were used for 1 ton of SO₂ without using adipic acid, and 4.48 tons, 4.44 tons, and 4.00 tons of limestone slurry were consumed to remove 1 ton of SO₂ in the use of limestone slurry enriched with 500 ppm, 1000 ppm, and 1500 ppm adipic acid, respectively. The limestone slurry consumption efficiency increased by 6.89%, 8.35%, and 9.92%, respectively. The moisture content of the gypsum, a product of the desulfurization process, was 22.4%, 11.6%, 10.3%, and 9.2%, respectively.

The SEM images in Figure 2 reveal that gypsum crystals grew, became smoother, and took a potato-like shape as the use of adipic acid increased. This situation increased the dewatering efficiency on the vacuum belt. As shown in Figure 2a, gypsum crystals not treated with adipic acid have a flaky and fragmented appearance. Flake-like morphologies with rough surfaces indicate rapid nucleation and limited crystal growth. This implies a high moisture content in the gypsum. This is thought to cause problems with removing moist crystals from the vacuum line during processing, as they will adhere to the vacuum

cloth. This also prevents moisture from being removed from the system due to poor dewatering performance [33].

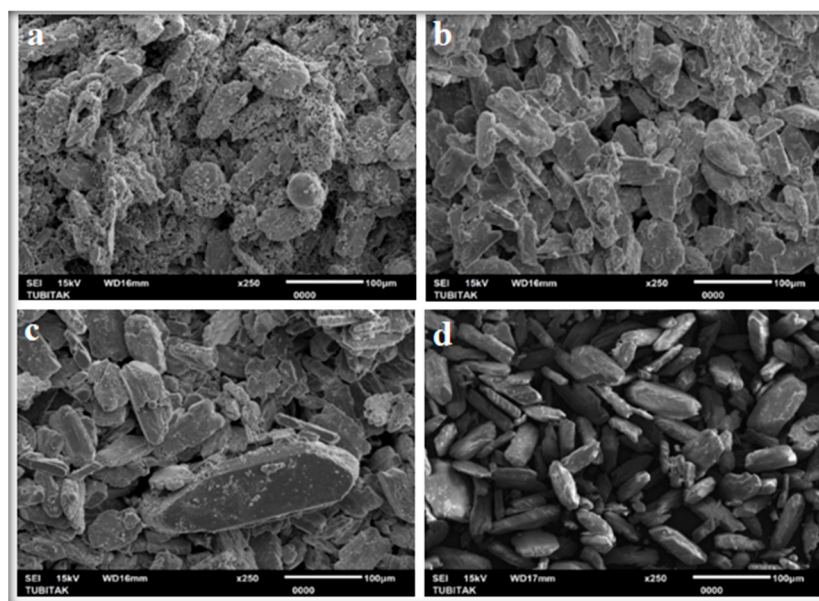


Figure 2. The SEM images of gypsum after desulphurization processes in different adipic acid concentrations, (a) before adipic acid, (b) after 500 ppm adipic acid, (c) after 1000 ppm adipic acid, and (d) after 1500 ppm adipic acid.

4. Discussion

In this study, the performance of a full-scale WFGD system was analyzed to quantitatively and qualitatively evaluate it under different adipic acid concentrations. The results show that adipic acid accelerates CaCO_3 dissolution on the limestone surface via a ligand-assisted proton-transfer mechanism, thereby enabling more efficient Ca^{2+} release. It also promotes the controlled growth of gypsum crystals by regulating the supersaturation conditions in the solution. This mechanism plays a dual role in reducing limestone consumption and improving gypsum quality for full-scale WFGD systems. The adipic acid simultaneously enhances process efficiency and byproduct quality [16,20]. Figure 3 schematically illustrates the ligand-assisted proton transfer mechanism underlying the improved limestone utilization observed in this study. Figure 3 provides a mechanistic framework linking adipic acid addition to both improved sorbent utilization and byproduct quality under full-scale operating conditions. Table 6 presents a literature review showing that the addition of adipic acid increases SO_2 removal efficiency and reduces limestone consumption at both the laboratory and industrial scales.

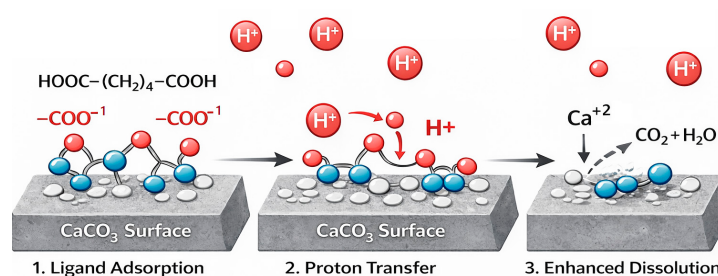


Figure 3. The Ligand-Assisted Proton Transfer Mechanism for reducing limestone consumption.

Table 6. Comparative literature review on the effect of adipic acid addition in WFGD systems.

Scale & Additive	Reference	Findings	Support
Full-scale WFGD (Pilot/Industrial) & Adipic acid	Mobley & Chang (1981) [20]	Accelerated limestone dissolution by buffering effect Enhanced SO ₂ removal efficiency Reduced sorbent (limestone) consumption No adverse impact on byproduct (gypsum) quality	Reduced limestone consumption Improved overall process efficiency Consistent with the observed decrease in SO ₂ levels in the present study.
Full-scale WFGD (Industrial) & Adipic acid (~2200 ppm)	Clarke et al. (1982) [38]	SO ₂ removal efficiency increased from ~55% to >90% with adipic acid addition Stable industrial operation was maintained	Confirms safe application of adipic acid in full-scale WFGD systems Demonstrates significant performance enhancement
Full-scale WFGD (Industrial) & Adipic acid	Ostroff et al. (1983) [39]	Accelerates CaCO ₃ dissolution via a ligand-assisted proton transfer mechanism Occurs at the solid–liquid interface without changing the bulk slurry pH	Provides strong theoretical support for the ligand-assisted proton transfer mechanism proposed in Figure 3 of the present study
Laboratory Adipic acid and other organic acids	Liu et al. (2012) [16]	Enhanced CaCO ₃ dissolution with organic acid additives Increased SO ₂ absorption efficiency	Demonstrates consistency between laboratory-scale results and full-scale performance trends
Pilot/Laboratory & Adipic acid, citric acid, and organic acids	Lv (2021) [25]	Improved SO ₂ removal efficiency with organic additives Enhanced gypsum crystal morphology and filterability	Consistent with SEM observations of improved crystal integrity and reduced moisture content in the present study
Laboratory Modeling & Organic acids	Jeong et al. (2023) [18]	Organic acids significantly influence Ca ²⁺ release during desulfurization Affect crystal growth behavior	Supports the conclusion that adipic acid regulates gypsum crystal growth Leads to the formation of larger and smoother gypsum crystals

Table 6. Cont.

Scale & Additive	Reference	Findings	Support
Full-scale WFGD (Industrial) & Adipic acid	Present Study	Limestone consumption reduced by 6.9–9.9% Gypsum moisture content decreased from 22.4% to 9.2% SEM analyses revealed smoother, more compact, and “potato-like” gypsum crystal morphologies	SO ₂ removal efficiency, sorbent utilization, gypsum morphology, moisture content, and filtration performance were quantitatively evaluated together (Unlike previous studies) Comprehensive evaluation conducted in a full-scale WFGD system.

Surface-bound ligands facilitate the localized transfer of protons from the general solution to reactive carbonate sites. This does not alter the solution’s pH and accelerates CaCO₃ dissolution. Experimentally, increasing the concentration of adipic acid reduces limestone consumption. This is due to improvements in interfacial properties that affect dissolution kinetics. Furthermore, the controlled release of Ca²⁺ ions from the limestone surface stabilizes supersaturation conditions during gypsum precipitation, thereby promoting the formation of larger, smoother gypsum crystals and improving dewatering performance in the WFGD system [39].

Analysis of SEM images revealed that adipic acid produced smooth, uniformly sized gypsum crystals, thereby significantly improving selectivity and permeability and reducing moisture. Regarding the chelating and surface modification behavior of organic dicarboxylic acids, adipic acid plays a dual role as both a dissolution accelerator and a morphology controller. The evaluation of gypsum quality, together with SO₂ removal efficiency and limestone consumption data, did not provide any indication of degradation byproduct formation resulting from the addition of adipic acid. SEM images show that the addition of adipic acid not only increases the chemical solubility of CaCO₃ but also improves the physical quality of the gypsum byproduct, producing industrially viable crystals with lower water retention capacity and higher purity. Adipic acid partially dissociates in the slurry, adsorbing onto the CaCO₃ surface via carboxylate groups and forming transient calcium-organic surface complexes, as shown in Figure 3 [18].

The crystal structure appears more integrated and contains more clusters in Figure 2b. The partial flattening of limestone crystals is due to the binding of adipic acid molecules to active growth sites. This leads to supersaturation, slowing down the nucleation process. At 1000 ppm (Figure 2c), it was observed that the structural integrity of the gypsum particles was further improved and transformed into more homogeneous and rounded crystals. The “potato-like” shapes are consistent with the well-surfaced CaSO₄·2H₂O crystals in Figure 2d, which support rapid liquid drainage during filtration. The most pronounced transformation was observed at 1500 ppm adipic acid, where the crystals appeared compact, with smooth surfaces, uniform dimensions, and minimal surface irregularities. Adipic acid effectively controls the crystal structure and growth kinetics of limestone in the WFGD process. It also demonstrates the ability to sustain a stable supersaturation regime, thereby increasing both crystal size and mechanical stability. Consequently, it is thought that this will facilitate the filtration of larger, smoother crystals by reducing the proportion of larger particles [10,18].

After vacuum filtration, the gypsum's moisture content decreased from 22.4% to 9.2%. Filter morphology is crucial for dewatering performance in belt filters. If finer, needle-like, or more tightly packed flaky crystals form and cannot be filtered sufficiently, the cake structure becomes clumpier, increasing resistance to vacuum filtration. This leads to lower dewatering efficiency and higher outlet moisture content in band filters. However, more ordered crystal structures of adipic acid improve vacuum filtration performance in filters, allowing a higher percentage of water to be removed from the structure [40]. Controlled crystal growth and increased structural integrity indicate significant improvements in the filterability and water-retention behavior of the gypsum. These properties are directly consistent with the essential quality criteria for gypsum in building material applications.

5. Conclusions

This study primarily aims to investigate the effects of adipic acid, an organic acid, when used as an additive in full-scale WFGD systems. Based on the survey, SO₂ removal performance, limestone consumption per unit of SO₂ removal, and the physical properties of the resulting gypsum (moisture content and crystal morphology) were evaluated. All measurements and data were performed under operating conditions. The WFGD system was operated with only limestone slurry, as well as limestone slurry enriched with 500 ppm, 1000 ppm, and 1500 ppm adipic acid. The gypsum quality and the amount of limestone slurry consumed per ton of SO₂ removed were measured. The results demonstrate that adding organic acids, such as adipic acid, to limestone slurry in full-scale WFGD systems enhances SO₂ removal efficiency while simultaneously reducing limestone consumption and improving gypsum quality. Among the tested concentrations, adipic acid dosages in the range of 1000–1500 ppm yielded the most effective performance. In particular, the addition of 1500 ppm adipic acid reduced limestone consumption by up to 9.92%, indicating a significant potential for cost reduction in continuous industrial WFGD operations. The novelty of this study lies in its being one of the few that comprehensively evaluate the use of adipic acid in limestone-based WFGD systems under full-scale industrial conditions in a real coal-fired thermal power plant. This research demonstrated that adipic acid accelerates limestone dissolution via a ligand-assisted proton-transfer mechanism without significantly altering slurry pH; it also improves gypsum crystal morphology and dewatering performance. The combined evaluation of SO₂ removal efficiency, limestone consumption, and byproduct gypsum quality constitutes the main contribution of this study to the literature. Such studies will enable the development of large-scale, sustainable industrial applications of organic acid-assisted WFGD systems.

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Abbreviations

The following abbreviations are used in this manuscript:

ASTM	American Society for Testing and Materials
CaO	Calciumoxide
CaSO ₄ 2H ₂ O	Gypsum
CaCO ₃	Limestone
CEMS	Continuous Emission Measurement System
DBA	Dicarbocyclic scif
FDG	Flue gas desulfurization
MgO	Magnesiumoxide
NDIR	Non-Dispersive Infrared
SEM	Scanning Electron Microscope
SO ₂	Sulphurdioxide
SiO ₂	Siliciumdioxide
Pka	Ionization Value
XRF	X-ray fluorescence spectroscopy
WFDG	Wet flue gas desulfurization

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