Reduction of S02 in Flue Gas and Applications of Fly Ash: A Review

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Reduction of SO₂ in Flue Gas and Applications of Fly Ash: A Review

Ling Li, Maohong Fan, Robert Clinton Brown, Jacek Adam Koziel, and J. (Hans) van Leeuwen

ABSTRACT

Flue gas and fly ash are the two most important wastes from power plants. This review focuses on technologies for SO₂ removal from emissions and on properties and applications of fly ash. It predominantly focuses on the non-European situation; in Europe, flue gas desulfurization and ash utilization have been extensively practiced during several decades. Flue gas desulfurization (FGD) technologies are the most commonly used methods in the removal of SO₂ in flue gas. Factors influencing SO₂ removal efficiency and optimal operation conditions are considered. Physical and chemical properties of fly ash make it useable in various fields, such as cement production, concrete admixtures, soil amendment, as a low-cost adsorbent of certain types of contaminants in wastewater, and in the production of effective wastewater coagulants.

INTRODUCTION

All fossil fuels contain a certain amount of sulfur, ranging from 0.1–5 % [1]; consequently, significant amounts of SO₂ are emitted from power plants following oxidation during combustion. Emission of SO₂ from fossil fuels is the major contributor to acid rain, which causes material damage and acidification of natural water bodies and soil. Such acidification could be a disaster for many aquatic life forms, soil fertility and plant diversity. SO₂ can undergo complex photochemical reactions to form light-scattering aerosols, the main concern of which is the impairment of visibility. Investigations estimate that 0.1 mL · m⁻³ (ppm) SO₂ with 50 % relative humidity could reduce the visibility to 8 km [2].

Legislation to control SO₂ emissions, desulfurization of power plant flue gases and removal of sulfur from crude oil and coal has contributed to the decline of SO₂ emissions over the past 30 years. However, SO₂ emissions still totaled over 60 · 10⁶ t in 2000 worldwide [3]. In the United States, although the emission of SO₂ has been decreased by one-third over the past 30 years, the amount was still more than 20 · 10⁶ t in 2000, 75–80 % of which was released during fuel combustion [4]. Since fuel-fired power plants are responsible for most of the SO₂ emissions, it is expedient to reduce SO₂ concentrations in these flue gases.

Another important waste from power plants is fly ash, which is a fine particulate material that is produced by the combustion of pulverized coal and carried out by flue gas. Coal-fired power plants produce significant amounts of fly ash each year. According to American Coal Ash Association (ACAA) data, combustion of coal in the United States alone produced approximately 68 million tons of fly ash in 2001 [5]. Fly ash primarily contains oxides of Si, Al, Fe and Ca, with smaller concentrations of Na, K, Mg, Ti, sulfate and various trace elements. The chemical properties of fly ash make it useful in various fields, such as cement production, concrete admixtures, soil amendment, as a low-cost adsorbent of certain types of contaminants in wastewater, and in the production of effective wastewater coagulants.

SO₂ REMOVAL TECHNOLOGIES

Possible measures that may be used to control SO₂ emissions from fuel combustion include burning low-sulfur fuels, reducing sulfur content in the fuel, and emission control technologies. Low-sulfur fuels such as natural gas, low-sulfur oil and low-sulfur gas are not easily available and are relatively expensive. Therefore, these fuels may
not be economically viable alternatives. For high-sulfur coals, blending with low-sulfur coals can reduce the total sulfur content to meet the limit of SO$_2$ emissions [7–9]. There are different models predicting the appropriate blending quantities of coals with different sulfur contents [10–13]. Although a number of linear or non-linear models can be used to determine the predicted sulfur content, it is still difficult to optimize the combustion conditions simply based on the model. In addition to sulfur content, many other characteristic parameters, such as heating value, ignition temperature, burnout efficiency, and ash content, also need to be considered [7]. Due to its complexity, it is difficult to optimize each parameter in a blended coal. Therefore, a case-by-case investigation is needed in order to determine suitable blending conditions. Considering the cost of low-sulfur coals, a reasonable ratio of coal price to sulfur content needs to be introduced.

The most commonly accepted SO$_2$ emission control method is flue gas desulfurization (FGD). There are mainly two categories of FGD systems: dry and wet FGD systems, which are defined simply by whether or not the active reagent is added in liquid slurry.

**Dry Flue Gas Desulfurization (Dry FGD)**

**Dry FGD procedure**  Dry powdered sorbent is injected into the furnace in conjunction with pulverized coal or combustion gas in the dry FGD systems. In general, the SO$_2$ removal efficiency of dry FGD is in the range of 40–60%. It is known that CaCO$_3$ decomposes rapidly at 800 °C, and the produced CaO can react with SO$_2$ to form CaSO$_3$ and CaSO$_4$, resulting in the reduction of SO$_2$. Therefore, lime or limestone is usually blended with the coal as a SO$_2$ sorbent [11,14]. In conventional furnaces, the combustion temperature is usually higher than 1200 °C. At such a high temperature, the thermal instability of sulfate products has to be considered in the control of SO$_2$ removal efficiency. In addition, the short residence time of SO$_2$ and/or H$_2$S in the coal bed makes it an inefficient contact between the gas phase and the solid sorbent [7]. Studies have shown that simply blending limestone or lime with pulverized coal results in the removal of only 15–20% of sulfur in conventional furnaces. This would not meet the SO$_2$ removal requirement of at least 70% to achieve a SO$_2$ emission rate less than 0.26 · 10$^{-6}$ kg·kJ$^{-1}$ (0.6 lb/10$^8$ BTU) or 90% to achieve a SO$_2$ emission rate less than 0.52 · 10$^{-6}$ kg·kJ$^{-1}$ (1.2 lb/10$^8$ BTU) [15,16]. Injecting the sorbents into the combustion gas can achieve a higher SO$_2$ removal efficiency [17–19]. Generally, SO$_2$ removal efficiency by this method is about 40–60% [7]. Further investigations demonstrated that blending CaCO$_3$ with pulverized coal was only able to remove 26.8% SO$_2$; however, injecting it directly with the combustion gas improved the SO$_2$ removal efficiency to 56.8% [20]. A two-stage desulfurization process showed that combining sorbents with feed coal and injecting them into combustion gas could improve SO$_2$ removal efficiency to about 75% [21]. An application of the combined two-stage desulfurization process gave an in-furnace SO$_2$ removal of 75–77% and a total SO$_2$ removal of 85–90% [22,23]. Figure 1 shows the schematic flow diagram of a dry FGD system.

![Figure 1: Schematic flow diagram of dry flue gas desulfurization (dry FGD).](image-url)
Factors influencing dry FGD

Factors that control sulfur removal efficiency in the sorbent injection process include Ca/S ratio, injection location, particle size and structure of the sorbents, and temperature. The optimal molar ratio of Ca/S is 2 and it is suggested that this be maintained in a very limited range [7]. A further increase in the Ca/S ratio has little benefit. Studies on the influence of the Ca/S ratio on SO₂ removal showed that when the molar ratio of Ca/S was increased from 2 to 6, the SO₂ removal efficiency was improved from 23 % to 24 % only [21]. The SO₂ removal efficiency was reported to increase as the sorbent particle sizes decrease in a certain range [7]. At a Ca/S ratio of 2, a decrease in sorbent particle size from 10 µm to 1 µm improved SO₂ removal from 40 % to 50 % [24]. Ultrafine sorbent particles (diameter < 1 µm) can be beneficial in increasing the reaction rate of the combustion process. However, grinding cost, destruction of pore volume and increase of diffusion resistance inside the particles should be considered. Therefore, the optimal sorbent particle size in an injection process is suggested to be approximately 5 µm [7].

The porosity structure of the sorbent particles has an important impact on SO₂ removal in the limestone injection process. Suitable pore size distribution is reported to be effective in providing more surface area, which contributes higher sorbent reactivity and higher CaO conversion [25]. It has been reported that for sorbents with particle sizes in the range of 1-5 µm, pore diameters of 5-30 nm are desirable [26].

Temperature also affects SO₂ removal. A limestone sorbent can effectively capture SO₂ at 700-800 °C, but it has a low efficiency in absorbing SO₂ at lower temperatures. At high temperatures, the thermal instability of sulfate products can be a big concern in the removal of SO₂ [7].

Improvements in dry FGD

Some studies have shown that by adding proper amounts of clay minerals, including silicates, together with limestone into the blended coal, the desulfurization efficiency of limestone can be improved in a certain temperature range [27,28]. Although certain kinds of clay minerals can improve the SO₂ removal efficiency, other clay minerals such as bentonite and zeolite have very little effect on improving sulfur removal [29]. Further investigation on zeolites found that it emits sulfur volatile organic compounds (VOCs), which could have an adverse effect on SO₂ removal [30].

Application of a fluidized bed together with dry scrubbing could increase SO₂ removal efficiency greatly. Investigation has shown that dry scrubbing with limestone in a fluidized bed removed more than 90 % of SO₂ from the original concentration of 8 000 mg · kg⁻¹ [31].

In some FGD processes, the flue gas is contacted with a fine mist of sorbent slurry. These processes are sometimes referred to as semi-dry or wet-dry scrubbing. Since the fly ash in such systems is not removed prior to the scrubber, the flue gas leaving the scrubber contains both fly ash and sorbent particles. Therefore, a particulate collection system such as a baghouse or fabric filter is needed. The removal efficiency of SO₂ in a semi-dry system can be as high as 80 % when a sufficient amount of sorbent is injected. In addition, when a fabric filter is applied, SO₂ removal efficiency can be improved to over 90 % [1]. In semi-dry FGD systems, ammonia can also be used instead of the lime or limestone used in dry FGD systems. Both bench-scale and pilot-plant tests have shown that reduction with NH₃ can remove SO₂ from flue gas effectively [32,33]. However, SO₂ removal efficiency is sensitive to the NH₃/SO₂ ratio and reaction temperatures [33,34]. It was reported that over 95 % SO₂ removal was achieved when NH₃ was injected into the combustion gas at a NH₃/SO₂ molar ratio of slightly less than 2 and at a temperature range of 64–85 °C [35].

The amount of solid waste produced in dry FGD systems is a serious concern. A 1 000 MW power plant using a fluidized bed dry scrubbing system could produce 800 000 t of solid particles each year to be disposed of [1].

Wet Flue Gas Desulfurization (Wet FGD)

Wet FGD process and influencing factors

Wet FGD has been considered as the most cost effective SO₂ control technology since the early 1970s [36]. Wet FGD is also increasingly recognized as a multi-pollutant control method. It can achieve high removal efficiency of acid gases, including SO₂, fine particulate matter and heavy metals, such as mercury. The flue gas containing SO₂ enters a spray tower or absorber, where it is in contact with lime or limestone slurry. Figure 2 shows the schematic flow diagram of a wet FGD system.

![Figure 2: Schematic flow diagram of wet flue gas desulfurization (wet FGD).](image-url)
Lime or limestone in the slurry reacts with SO₂ to form insoluble calcium sulfite. In order to make commercially valuable calcium sulfate (gypsum) from a wet FGD process, compressed air is bubbled through the slurry to oxidize sulfite to sulfate. This procedure is known as forced oxidation. Both lime and limestone wet scrubbing can achieve over 90 % SO₂ removal efficiency for both high and low sulfur coals, some of them as high as 99 % [37]. Considering the cost of the material, limestone is more popular for large FGD systems since it is cheaper than lime [38]. Under given operation conditions, SO₂ removal efficiency depends on the limestone content in the slurry and limestone characteristics. It has been reported that limestone with smaller particle sizes performed better in SO₂ removal. This is because smaller particles can be slurried more easily, resulting in increased reactivity of the limestone [38]. Studies on using coarse granular limestone as sorbent in the wet FGD process showed that the slurry consumption was much higher than when using fine particle limestone [39]. Further analysis of limestone structures by scanning electron microscopy (SEM) and X-ray diffraction (XRD) showed that limestone with higher purity had a better dissolution rate [38]. The ratio of the recycled slurry used to absorb flue gas to the flue gas flow rate (L/G) and pH of the slurry have great impacts on SO₂ removal and operation cost. A good design could minimize the L/G ratio, thus minimizing slurry and power consumption. The optimum pH value is suggested to range from 5.5 to 5.7 and the Ca/S ratio to range from 1.03 to 1.05 in wet FGD systems [40].

Since the absorption of SO₂ in the sorbent slurry is the dominating procedure in wet FGD, researchers have been investigating models of SO₂ absorption into lime or limestone suspensions since the 1980s [41,42]. Early models of SO₂ absorption into aqueous solutions were derived by using penetration theory [43]. In the lime/limestone desulfurization procedure, the sorbent suspension contains particles of sorbent, sulfites and sulfates. Therefore, the absorption of SO₂ into the sorbent slurry is more complicated. Proper models of SO₂ absorption and sorbent dissolution are important for choosing the optimal design and operation parameters of wet FGD systems. Uchida and Ariga derived a two-reaction zone model using assumptions of instantaneous reaction in the liquid phase and a three-region mass transfer on the gas-liquid interface [44]. Other researchers have applied the film theory in describing SO₂ absorption into Ca(OH)₂, CaSO₄ and CaCO₃ slurries. These models have been successfully used in estimating the rate of SO₂ absorption into slurry [45-47]. The sorbent dissolution rate is another important factor to be considered in wet FGD design and operations. It has been found that particle size distribution has a great impact on the dissolution rate of limestone at certain pH values [38,48,49]. The mass transfer model of limestone dissolution derived by Toprac and Rochelle was able to predict the dissolution rate with a good approximation considering the impact of particle size distribution [48]. Brogren and Karlsson developed a model predicting limestone dissolution in wet FGD and introduced a factor describing the variation of the flux of calcium ions from the limestone surface [36]. Their results showed that changes in the flux were caused by the presence of sulfite, which had a significant impact on the limestone dissolution. The model accurately predicted the impact of particle size distribution on the limestone dissolution rate, and was in good agreement with the measured values in a continuously stirred tank reactor. Warych and Szymankowski considered a complete procedure in wet FGD, including SO₂ absorption and oxidation, limestone dissolution and gypsum crystallization [60]. The model was used in the analysis of cost optimization in wet FGD systems and was in good agreement with data from a FGD system at a power plant in Poland.

Improvements in wet FGD Earlier studies found that organic acids with buffering capacity would enhance the dissolution of limestone in the acidic slurry [51]. Further investigations showed that certain types of dibasic organic acids, including adipic acid, glutaric acid, and succinic acid, are capable of providing good buffering and forced oxidation [52]. It is important to maintain the pH value in the optimum range in wet FGD systems. Since the concentration of SO₂ in the spray tower or absorber changes as the reaction goes on, the pH fluctuates accordingly. Therefore, adding organic acids with good buffering capacity can help in maintaining the pH in the optimal range for SO₂ absorption. A recent study showed that adding acetic acid greatly improved SO₂ removal efficiency. When granular limestone was used directly as the sorbent, only 60.7 % SO₂ was removed. However, when 10 mmol·L⁻¹ acetic acid was added, the removal efficiency of SO₂ was improved to 87 % under the same operational conditions [53].

One problem of wet FGD with lime or limestone is that scaling occurs inside the scrubber and reduces SO₂ removal efficiency. The addition of MgSO₄ and MgSO₃ could not only reduce scaling, but also increase SO₂ removal efficiency [54]. Wet FGD systems also have disposal problems with the slurry since the by-products are of low market value and need to be disposed of in a landfill.

In some coastal power plants, seawater has been used successfully to absorb SO₂. Because seawater is alkaline in nature, it has some neutralizing capacity with respect to the acidification caused by the absorption of SO₂. After SO₂ absorption in seawater, the effluent flow is aerated to oxidize sulfide to sulfate, which is a natural ingredient in seawater. When the seawater containing sulfate is returned to the sea, the increase of sulfate is within natural variation. In addition, with the active sulfur bacteria, sulfates in seawater are converted to sulfides, which can be fixed into organic materials [55]. In seawater FGD systems, no solid waste is produced, but this advantage is only available in power plants along the coast.

Table 1 summarizes dry and wet FGD systems by SO₂ removal efficiency and influencing factors.
that the 'dielectric barrier discharge technology was the non-uniformity of the oxidizing radicals (400 are two disadvantages: the high-energy requirement and the non-uniformity of the oxidizing radicals produced [60].

Table 1:
Summary of dry and wet flue gas desulfurization (FGD) systems.

<table>
<thead>
<tr>
<th>FGD Process</th>
<th>SO₂ removal [%]</th>
<th>Optimal values of operating parameters</th>
<th>Ref.</th>
<th>Improvements and benefits</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry FGD</td>
<td>40-60</td>
<td>Ca/S ratio: 2</td>
<td>7, 21</td>
<td>Two-stage dry FGD: increases SO₂ removal to 85-90 %</td>
<td>22, 23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sorbent particle size: 1-5 µm</td>
<td>7, 25, 26</td>
<td>Fluidized bed: increases SO₂ removal to over 90 %</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sorbent pore diameter: 5-30 µm</td>
<td>26</td>
<td>NH₃ injection: increases SO₂ removal to over 95 % and reduces slurry production in semi-dry FGD systems</td>
<td>32-35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature: 700-800 °C</td>
<td>7</td>
<td>Buffer with certain kinds of organic acids: helps in maintaining pH in the optimal range</td>
<td>41-43</td>
</tr>
<tr>
<td>Wet FGD</td>
<td>&gt; 90</td>
<td>L/G ratio: minimized</td>
<td>40</td>
<td>Addition of MgSO₄ and MgSO₃ helps in reducing scaling problems</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca/S ratio: 1.03-1.05</td>
<td>40</td>
<td>Sea water absorption: no solid waste is produced</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH: 5.5-5.7</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Other Flue Gas Desulfurization Technologies
The circulating fluidized-bed absorber (CFBA) is another SO₂ removal technology. In CFBA systems, the humidified flue gas flows through the fluidized bed containing sorbent particles, typically slaked lime. The CFBA unit is usually followed by particulate collection equipment [56]. Ollero et al. conducted a pilot-plant study at a 500 MW power plant. The SO₂ concentration in the flue gas was 350-3 000 mg · m⁻³. Their results showed that high SO₂ removal efficiency (95 to 97 %) and high sorbent utilization can be reached under suitable operating conditions.

Pulsed corona and dielectric barrier discharges are plasma-based SO₂ removal technologies aimed at oxidizing SO₂ in the gas phase. In plasma-based SO₂ removal systems, SO₂ is oxidized to SO₃ or H₂SO₃ by either free O or OH radicals, which are dissociated from SO₂ itself or from moisture by plasma [57,58]. Experimental investigations have shown that SO₂ removal efficiency can be greater than 80 % for a simulated flue gas stream containing 1 000 mg · kg⁻¹ SO₂ [57]. Sun et al. [59] proved further that the dielectric barrier discharge technology was capable of removing up to 99 % SO₂ under low concentrations (400 mg · kg⁻¹) and suitable moisture content. Although pulsed corona discharge is effective in removing SO₂, there are two disadvantages: the high-energy requirement and the non-uniformity of the oxidizing radicals produced [60].

When SO₂ is present in the air, it is a pollutant that needs to be removed; SO₂ can, however, be used as an important raw material in industry. SO₂ can be converted to sulfuric acid by oxidation. Sulfuric acid has wide application in producing sulfur-containing fertilizers, such as superphosphate of lime and ammonium sulfate, or sodium sulfate, which is an important chemical in the soap, paper and glass industries [61,62]. Shi et al. used SO₂ in acetic acid and lactic acid recovery from calcium acetate and calcium lactate solutions. Their investigation demonstrated that the recovery processes of acetic acid and lactic acid by SO₂ at room temperature are applicable [63,64]. Fan et al. developed an effective SO₂ removal method aimed at producing polymeric ferric sulfate (PFS), a commonly used water treatment coagulant, at the same time [65,66].

PROPERTIES AND APPLICATIONS OF FLY ASH
Fly Ash Properties
Physical properties of fly ash Fly ash is a fine particulate material that is produced by the combustion of pulverized coal and carried out by flue gas. The characteristics of fly ash can vary widely depending on combustion methods, coal sources, and particle shape. The color of fly
ash varies from tan to dark gray, depending on the chemical components. Light colored fly ash typically indicates high lime content. Reddish or brownish color is associated with iron content and dark gray colored fly ash usually has unburned carbon contents, as measured by the loss on ignition (LOI). Normally, fly ash particles are of spherical shape and exhibit smooth surface texture. Giere et al. [67] investigated the micro- and nano-chemistry of fly ash particles and found that the single fly ash particles are either hollow or filled with a series of smaller particles. The size of most fly ash particles is in the range of 0.01 to 0.1 mm. This size range and the spherical shape improve the fly ash fluidity, which contributes to a cementing effect (pozzolanic activity), meaning that it will react with free lime and water to produce cementitious compounds. The American Society of Testing Materials (ASTM) classifies fly ash as Class C or Class F mainly based on calcium oxide content. Class C is generally produced from sub-bituminous coal and contains more than 20 % CaO, and Class F is usually derived from bituminous and anthracite coals and has less than 10 % CaO [5]. Class C is self-cementing since it contains enough CaO. For Class F fly ash, additional lime is usually added if it is used in producing cements [68]. Fly ash usually has a bulk density of 1.01-1.43 g · cm⁻³, and a specific gravity of 1.6-3.1 g · cm⁻³. Investigations on 23 fly ashes from across the United States showed that the pH range was from 4.2 to 11.8 [5]. The pH of fly ash depends largely on the sulfur content of the parent coal. Eastern coals in the U.S. contain high sulfur contents and produce acidic fly ashes, and western coals are low in sulfur, producing alkaline fly ashes [69].

Chemical properties of fly ash  

The chemical composition of fly ash depends greatly on the mineral chemistry of the coal sources, additives used in the combustion or post-combustion processes, and the pollution control technologies [5]. Fly ash primarily contains oxides of Si, Al, Fe and Ca, with smaller concentrations of Na, K, Mg, Ti, sulfate and various trace elements. Table 2 gives a normal range of chemical compositions of fly ash produced from different coal sources.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bituminous</th>
<th>Sub-Bituminous</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20-60</td>
<td>20-30</td>
<td>15-45</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5-35</td>
<td>5-30</td>
<td>10-25</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10-40</td>
<td>4-10</td>
<td>4-15</td>
</tr>
<tr>
<td>O₂</td>
<td>1-12</td>
<td>5-30</td>
<td>15-40</td>
</tr>
<tr>
<td>MgO</td>
<td>0-5</td>
<td>1-6</td>
<td>3-10</td>
</tr>
<tr>
<td>SO₃</td>
<td>0-4</td>
<td>0-2</td>
<td>0-10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0-4</td>
<td>0-2</td>
<td>0-6</td>
</tr>
<tr>
<td>K₂O</td>
<td>0-3</td>
<td>0-4</td>
<td>0-4</td>
</tr>
<tr>
<td>LOI</td>
<td>0-15</td>
<td>0-3</td>
<td>0-5</td>
</tr>
</tbody>
</table>

Table 2: Normal percent range of chemical composition of fly ash [7].

LOI = loss on ignition

Applications of Fly Ash

Coal-fired power plants produce significant amounts of fly ash each year. According to the ACAA data, combustion of coal in the United States alone produced approximately 68 · 10⁶ t of fly ash in 2001 [5].

Some European countries, such as Germany and the Netherlands, utilize fly ash to almost 100 % [71]. The United States uses considerably less: about 70 to 75 % of fly ash generated is disposed of in landfills. However, considering landfill space limitations and transportation cost, landfilling is a poor solution to fly ash disposal. In addition, the transportation and disposal of fly ash will increase particulate material concerns in the air during windy days. Moreover, much of the fly ash is capable of being reused; it may find application in highway and building construction, and agriculture. Currently, over 20 million tons of fly ash is used annually in the United States [5]. Of the fly ash produced in 2001 as an example, 22 · 10⁶ t, or about 30 % of the total fly ash production, was used, and over 60 % of this in producing cement and concrete [5].

Application of fly ash in cement and construction

Fly ash is rich in siliceous or silicious and aluminous materials, which could react with Ca(OH)₂ at ordinary temperatures to produce cementitious compounds in the presence of water. There are specific criteria for fly ash suitability in cement/concrete applications. First of all, fly ash has to meet the fineness requirement, since the rate of pozzolanic activity and the workability of the concrete are affected greatly by the fly ash particle size. A minimum of 66 % passing the 0.044 mm sieve is required by the American Coal Ash Association [5]. Chemical composition is also important. Since the chemical composition of fly ash varies from site to site, the reactive aluminosilicate and calcium aluminosilicate (represented as SiO₂, Al₂O₃ and CaO) components should be checked regularly to meet the criteria. The content of SO₃ should be limited to 5 % and available alkalis should not exceed 1.5 % [5]. High loss on ignition (unburned carbon) is not desired. Traditionally, Class C or high calcium fly ash is added into Portland cement to improve some of the cementitious properties, such as increased ultimate strength, durability, and chemical resistance, and reduced permeability [57,72]. The Environmental Protection Agency (EPA) headquarters in Washington D.C. was constructed with cement containing fly ash. Fly ash concrete has been used in severe exposure applications such as the decks and piers of the Sunshine Skyway Bridge in Tampa Bay, Florida.
Recent research has shown considerable interest in converting fly ash into cementitious materials without Portland cement. Rostami and Brendley used low carbon Class F fly ash, sand, and gravel, which were mixed together with sodium hydroxide and sodium silicate solutions, to make concrete [72]. Their results showed that compared to Portland cement, the fly ash-based cement had higher ultimate strength, better acid resistance, and better freeze-thaw durability. A variety of new technologies have been developed for manufacturing fly ash-based cement, in which fly ash, a calcium (or magnesium) reinforcing solution, and a modifier are used as the raw materials [73–77].

Yoon and Yun introduced a new method to produce a glass-ceramic from fly ash and waste glass. Proper mixing ratio and temperature will generate practical glass-ceramic with good mechanical strength and bending strength [78]. Mohanty and Chugh developed a new method of making automotive brake lining using fly ash and other ingredients. In their research, the brake lining raw material contains more than 50% fly ash. The fly-ash-based brake lining is 50 to 60% lighter in weight than current commercial materials for similar friction [79].

**Application of fly ash in soil modification** Although applications of fly ash in soil modification and agriculture are not very popular yet, it has been proven that fly ash can be used to improve the physical and chemical properties of coarse or sandy soils [68,80–83]. Since fly ash is comprised mostly of silt-sized particles, it can be used to improve coarse-textured soils and increase the soil moisture holding capacity, which is helpful in increasing plant growth. Pathan et al. investigated the changes in the properties of soils when admixing different amounts of fly ash. Their results showed that with a properly fly ash to soil ratio, the water holding capacity was increased three times, which could increase plant growth [83]. Depending on its pH, fly ash can be either acidic or alkaline, which makes it useful in modifying the pH of soils [82,85]. This is especially useful when alkaline fly ash is added to neutralize acidic soils [81]. Beside oxides of Si, Al, Ca and Fe, fly ash also contains smaller amounts of P, N, K, Na, Mg, which makes it potentially useful as a fertilizer supplement [85]. A 4-month greenhouse experiment showed that application of 20% and 40% fly ash with soil increased the yield of rice significantly [86]. Another two-year field experiment found that when fly ash was combined with chemical fertilizer, the uptake of N, P, K and other nutrients was higher, resulting in higher crop yield [85]. An investigation of fly ash as a soil amendment and fertilizer conducted by Kaira et al. showed similar results [70]. The most important concern of using fly ash as a soil amendment is the possible release of trace elements. The toxicity characteristic leaching procedure (TCLP) experiments indicated that the potential for release of harmful trace elements was below U.S. EPA regulatory levels and did not prove to impose adverse effects on plant growth [68,83]. However, since the composition of fly ash varies from site to site, laboratory evaluation of physical and chemical properties should be conducted prior to the use of fly ash for soil amendment.

**Application of fly ash in environmental remediation**

Fly ash has been used as a low-cost adsorbent in the removal of dyes in industrial wastewater [87–90]. Mohan et al. investigated the effects of different factors, such as temperature, pH value, fly ash particle sizes, and adsorbent doses on the adsorption of dyes. Their findings showed that the absorption of the dye increased with increasing temperature and was inversely proportional to the particle size of the fly ash [88]. Dyeing effluents from the textile industry impose great threats to the environment since they contain highly toxic metal complexes [89]. Chatterjee et al. investigated the absorption and photocatalysis of dye removal from textile wastewater using fly ash and sunlight. Their results revealed that the capacity of fly ash absorption of dyes was very good and Fe(III) in the fly ash acted as a photocatalyst in breaking down dye molecules to non-hazardous products [90]. Ravikumar et al. used a mixture of 1:1 carbon and fly ash in the absorption of dyes and found that under optimum conditions, complete removal was achieved [91]. Alkaline fly ash can also be used in improving phosphate removal in wastewater sand filtration systems [92]. The fly ash used in this research contained high calcium concentration, to precipitate calcium phosphate. Moreno et al. [93] used fly ashes from power plants to synthesize zeolites, which were successfully used in purifying acid mine waters.

The U.S. EPA confirms that fly ash from coal combustion does not need to be regulated as a hazardous waste. However, it may still impose some environmental concerns since fly ash from different sources may contain different trace elements, such as Ni, V, As, Be, Cd, Ba, Cr, Cu, Mo, Zn, Pb, Se and Ra. Though these elements are usually found in extremely low concentrations, their presence should be considered in the fly ash applications.

Based on the fact that fly ash is rich in aluminum and iron oxides, which are essential raw materials for the production of water and wastewater treatment coagulants, and sulfur dioxide can be oxidized to sulfur trioxide, which can be used in making sulfuric acid, our research group conducted a project aimed at the removal of sulfur dioxide with fly ash and sodium chloride as an oxidant with production of a wastewater treatment coagulant. The results showed that the produced coagulant containing both polymeric ferric sulfates (PFS) and polymeric aluminum sulfates (PAS) performed well in the removal of total suspended solids (TSS) and turbidity. At the same time, SO2 was effectively removed by reacting with sodium chloride in the fly ash slurry [94]. This investigation provided a possible application of the two important power plant wastes, fly ash and flue gas.
CONCLUSIONS

This review deals with the most recent SO₂ removal technologies for flue gas and applications of fly ash from power plants. Dry and wet FGD systems are the most commonly accepted SO₂ emission control methods. In dry FGD systems, dry powdered lime or limestone is injected directly with pulverized coal or into the combustions gas. Although the desulfurization system is relatively simple, dry FGD is only able to remove 40 to 60% of SO₂. Only a small part of the sorbent can be utilized due to the thermal instability of sulfate products at high temperatures and the low reaction rate of the combustion procedure. The Ca/S ratio, sorbent particle size and pore size distribution of the sorbent particles also play important roles in the removal of SO₂. Suitable values for the Ca/S ratio and particle size of the sorbent are 2:1 and 5 µm, respectively. Increasing the Ca/S ratio beyond this has very limited benefits for the removal of SO₂. In wet FGD systems, the equipment cost is relatively high because a spray tower or an absorber is needed. However, over 90% of the SO₂ can be removed for both lime and limestone sorbent. The ratio of the recycled slurry to the flue gas flow rate (L/G) and the pH of the slurry are the most important impact factors on SO₂ removal and operation cost. A minimum L/G ratio is desired to minimize slurry and power consumption. Optimum pH value is suggested to be 5.5 to 5.7 and Ca/S ratio is 1.03 to 1.05. Certain kinds of dibasic organic acids are helpful in increasing SO₂ removal under certain operation conditions. Main problems caused by wet FGD include scaling and disposal of the low market value slurry. Circulating fluidized-bed absorber (CFBA) and plasma-based SO₂ removal technologies are also available on the market. These new technologies are able to remove SO₂ up to 99%. However, energy consumption and equipment cost should be considered. It was reported that SO₂ can also be used as the raw material to produce sulfuric acid, sulfur-containing fertilizers, and polymeric ferric sulfate, a wastewater treatment coagulant. It also can be used in the recovery of acetic acid and lactic acid from calcium acetate and calcium lactate solutions.

Most fly ash is disposed of in landfilling in the United States. However, fly ash can find applications in many fields due to the complicated physical and chemical properties. In general, fly ash is rich in oxides of Si, Al, Fe and Ca, with smaller concentrations of Na, K, Mg, Ti and sulfate. The siliceous or siliceous and aluminous components in fly ash can be converted to Ca(OH)₂ to produce cementitious compounds in the presence of water. Studies have shown that fly-ash-based cements and ceramic materials have better performance in various applications. Particle size and chemical composition are the two most important factors impacting the production of fly-ash-based cementitious materials. Because of the silt-sized particles and minor nutrient compounds such as P, N, K, Na, and Mg, fly ash can also be used as soil modification and fertilizer supplements to improve the physical and chemical properties of coarse or sandy soils. The proper fly ash to soil ratio needs to be considered under all circumstances. In addition, case-by-case tests are recommended due to the complexity of fly ash properties. Fly ash can also be used as a low-cost adsorbent to remove dyes from textile wastewaters. It can also be used as the raw material to produce complex coagulants containing both PFS and PAS. Although fly ash is not regulated as a hazardous waste, some fly ashes may contain trace amounts of heavy metals, which may have adverse impacts on the environment. Therefore, experimental studies and governmental regulatory actions are still needed.

REFERENCES


Reduction of SO₂ in Flue Gas and Applications of Fly Ash: A Review


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Ling Li (M.S., Chemical Engineering, Tianjin University, Tianjin, China, Ph.D., Environmental Engineering, Iowa State University, Ames, IA, U.S.A.) has worked on the production of a new wastewater treatment coagulant from fly ash with concomitant removal of SO₂ from flue gas. Her research focuses on the evaluation of the performance of the produced coagulant in wastewater treatment, reaction kinetics and mass transfer in the production procedure.

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