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Project Summary

Mechanisms of Dry SO_2 Control Processes

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This report identifies and evaluates the postulated physical changes, chemical reactions, and reaction mechanisms involved in two dry flue gas desulfurization (FGD) technologies: line spray drying and dry injection of sodium compounds. Topics covered are: (1) chemical reactions and physical changes, (2) proposed reaction mechanisms and mathematical models, (3) process parameters which affect the reactions and rate controlling steps, and (4) needs for additional data to verify the proposed mechanisms and the effects of the various process parameters. The information used in developing this report was obtained from a review of published articles and technical papers.

The reactions involved in lime spray drying are gas-liquid phase reactions. SO_2 removal depends on the moisture content of the drying lime slurry droplet. Initially, the moisture content of the droplet is high and the rate of reaction is controlled by the diffusion of SO_2 to the surface of the slurry droplet. It appears that the greatest amount of SO_2 is removed at this time, and Babcock and Wilcox has mathematically modelled SO_2 removal during this period. As the moisture content of the droplet is reduced by evaporation, the dissolution of $Ca(OH)_2$ into ions becomes the rate limiting factor. SO_2 removal by the spray-dried solids is limited by the dissolution of $Ca(OH)_2$ and by the diffusion of SO_2 through the $CaSO_3 \cdot \frac{1}{2}H_2O$ product that has precipitated on the surface of the lime particle.

The reactions involved in the removal of SO_2 by the dry injection of finely ground sodium compounds are gas-solid phase reactions. Two steps are involved in the removal of SO_2: (1) $NaHCO_3$ is thermally decomposed to Na_2CO_3 (producing small pores in the sorbent particles, which increase the available surface area and the reactivity of the sorbent); and (2) the SO_2 reacts with Na_2CO_3 to produce Na_2SO_3 (beginning at the surface of the particle and moving inward, leaving behind a layer of reacted ash which tends to plug the pores that were formed by thermal decomposition, reducing the reactivity of the sorbent). Therefore, it has been postulated that initially the rate of reaction is controlled by the thermal decomposition of $NaHCO_3$ to Na_2CO_3 and then becomes controlled by the diffusion of SO_2 through the ash layer. Mathematical models describing SO_2 removal for these cases can be derived from the classical unreacted core model.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Summary

This report identifies and evaluates the postulated physical changes, chemical reactions, and reaction mechanisms involved in dry flue gas desulfurization

(FGD). Basically, this work is a review of the available published theories describing the reactions involved in lime spray drying and dry injection of sodium compounds. The topics covered in this report are:

- The physical changes and chemical reactions that occur in the dry scrubbing systems
- Proposed reaction mechanisms and mathematical models.
- Process parameters which affect the reactions and the rate controlling steps
- Additional data needed to verify or expand on the proposed mechanisms and the effects of the various process parameters

The information used in developing this report was obtained from previously published articles and technical papers Much of the information was obtained from papers presented at the October 1980 EPA Symposium on Flue Gas Desulfurization.

The information on spray drying is more complete and consistent than the information on dry injection. Spray drying has been investigated more thoroughly and is presently being applied to commercial-scale units. Dry injection is still being investigated on the pilot scale, although recent tests have been conducted on a system designed to treat 20 MWe equivalent of flue gas.[1]

Note that the term stoichiometry used in this report represents the moles of fresh sorbent introduced to the system divided by the moles of SO_2 entering the system. For lime, the moles of sorbent is based on the equivalent moles of CaO introduced, and for sodium compounds the moles of sorbent is based on the equivalent moles of Na_2O entering the system. This method of describing dry scrubbing stoichiometry is commonly used by system vendors, and the results they report are based on this definition. The conventional FGD definition for stoichiometry in wet systems is the moles of sorbent introduced to the system divided by the moles of SO_2 removed by the system. Compared with the conventional FGD definition of stoichiometry, the definition used by dry scrubbing vendors makes the system look more favorable because it does not account for SO_2 removal efficiency. However, note that the dry scrubbing definition of stoichiometry is the same definition that is conventionally used in chemistry (i.e., the moles of A needed to react completely with B without accounting for efficiency).
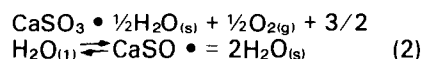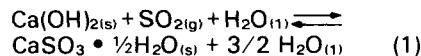
Lime Spray Drying

Spray drying involves contacting SO_2-laden flue gas with an atomized sorbent slurry in a spray dryer The SO_2 is absorbed by the slurry droplets, while the droplets are dried by the hot flue gas. An ESP or fabric filter is used to collect the dried solids exiting the spray dryer.

Information on dry FGD with lime spray drying was evaluated to determine the reactions and reaction mechanisms involved in the removal of SO_2. The results of pilot-scale lime spray drying tests were examined to establish the reaction mechanisms and rate controlling steps. Proposed qualitative and quantitative models describing the spray drying process were also evaluated. Additionally, the important process parameters affecting the spray drying reactions were qualitatively evaluated to determine their influence on the rate controlling steps of the reaction and on the degree of SO_2 removal achievable. Finally, data gaps in published literature were identified. These data gaps prevent complete verification and expansion of the proposed models.

Qualitative and Quantitative Reaction Models for Lime Spray Drying

Models developed for lime spray drying must take into account the simultaneous physical changes and chemical reactions that occur in the spray dryer. The overall chemical reaction takes place between the gaseous SO_2 and the dissolved lime sorbent to form calcium sulfate and sulfite salts:

$$Ca(OH)_{2(s)} + SO_{2(g)} + H_2O_{(l)} \rightleftharpoons$$
$$CaSO_3 \bullet \tfrac{1}{2}H_2O_{(s)} + 3/2\ H_2O_{(l)} \quad (1)$$

$$CaSO_3 \bullet \tfrac{1}{2}H_2O_{(s)} + \tfrac{1}{2}O_{2(g)} + 3/2$$
$$H_2O_{(l)} \rightleftharpoons CaSO \bullet = 2H_2O_{(s)} \quad (2)$$

Simultaneously, the reaction surface is physically changed as the slurry droplet dries.

The reactions that occur are basically gas-liquid phase reactions, because moisture must be present for the reactions to occur. Thus, the moisture content and composition of the slurry droplet during and after drying are extremely important in determining the nature of the rate controlling steps. The slurry droplet is typically composed of many small particles of porous solid lime in an aqueous medium. As the slurry droplet dries, water evaporates from its surface, leaving behind a solid agglomerate composed mainly of sulfite and sulfate product solids and unreacted lime. The dried solids also may contain significant amounts of residual moisture, depending on the length of drying time and the approach to saturation at the dryer outlet.

The most widely accepted qualitative model suggests that the chemical reactions that occur are intimately linked to three stages of droplet drying.[2] These drying stages have been characterized as:

- *Constant rate period.* The greatest amount of water is evaporated from the droplet during this period, and drying is controlled by the rate of diffusion of water vapor from the saturated surface of the droplet.
- *First falling rate period.* During this period, the lime particles in the slurry droplet begin to touch one another due to the loss of moisture, and drying is controlled by the rate of diffusion of water vapor from an unsaturated surface.
- *Second falling rate period.* Drying during this period is controlled by the rate of diffusion of moisture through and around the tightly packed lime particles.

During the constant rate stage of drying, the rate of SO_2 removal appears to be controlled by the diffusion of the SO_2 in the flue gas to the surface of the slurry droplet. The reaction that occurs between the gaseous SO_2 and the water in the droplet is characterized by the following equation:

$$SO_{2(g)} \quad SO_{2(aq)} \quad (3)$$
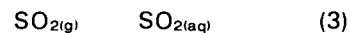
As evaporation proceeds during the two falling rate periods, less water is available for the dissolution of the solid $Ca(OH)_2$ into ions; therefore the dissolution of the $Ca(OH)_2$ becomes the rate limiting factor.[3]

If the spray-dried solids maintain adequate moisture, further reaction may continue in the downstream collection device. This is termed the pseudo-equilibrium period. Reactions during this period are limited by the rate of diffusion of SO_2 through the $CaSO_3 \bullet \tfrac{1}{2} H_2O$ that has formed on the surface of the lime particles and through the pore system of the lime particles.

This qualitative model provides the basis for development of theoretical and

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empirical quantitative (mathematical) models. Once these models have been evaluated and verified against test data, they can be used with confidence to predict SO₂ removal under given conditions

A mathematical model was developed by Babcock and Wilcox (B&W)[4] to characterize the reactions that occur during the constant rate drying period. The qualitative model states that the rate of reaction is controlled by the diffusion of SO₂ to the slurry droplets during this period. From this assumption the following mathematical relationship was developed:

$$E = 1 - \left[\frac{t_p}{Tin\text{-}Tsat}\right]^{0.62} \quad (4)$$

where E = SO₂ removal efficiency, fraction
  Tsat = Adiabatic saturation temperature of the flue gas, °F*
  Tin = Inlet temperature of the flue gas, °F
  t_p = Approach to the adiabatic saturation temperature at the spray dryer outlet (Tout-Tsat), °F
  Tout = Spray dryer outlet temperature of the flue gas, °F

Test data obtained by Buell[2] at the Martin Drake Station seem to show that the model is valid for relatively large spray dryers (greater than 8,500 acfm), but it underpredicted SO₂ removal at B&W's Alliance Research Center 1500 acfm spray dryer.[4] These conflicting results may be due to the different spray dryer designs used by Buell and B&W, or they may be due to "wall effects." These wall effects involve chemical reactions between the SO₂ and the lime that coats the walls of the spray dryer. This coating provides sites for additional SO₂ removal. There is more wall surface area per molecule of gas in a small spray dryer, so that more reaction sites are available per SO₂ molecule. Therefore, under the same test conditions greater SO₂ removal would be expected in a small dryer.

Another mathematical model developed by B&W correlates SO₂ removal efficiency with the stoichiometric ratio The model states that

$$E = 1 - e^{-K \text{ } SR} \quad (5)$$

where: E = SO₂ removal efficiency, fraction
  SR = Stoichiometric ratio =

$$\frac{\text{moles CaO in}}{\text{moles SO}_2 \text{ in}}$$

  K' = Correlation coefficient

The variable K' is a function of the specific surface of the lime (in ft² of surface per lb of lime) and the residence time of the flue gas in the spray dryer. Test data collected by B&W[4] and Buell[2], utilizing a close approach to saturation temperature and SO₂ concentrations less than 2000 ppm, fit the above relationship extremely well. Therefore, it seems that this general correlation can be used to predict SO₂ removal efficiency for these operating conditions.

Process Parameters Affecting the Lime Spray Drying Reactions

It has been postulated that the spray drying reaction rate is controlled initially by the diffusion of SO₂ into the droplet and then becomes controlled by the dissolution of Ca(OH)₂ into ions. The rate of dissolution of Ca(OH)₂ changes as the slurry droplet dries. Initially, Ca⁺⁺ and OH⁻ ions saturate the slurry droplet and are easily dissoluted, but as the droplet dries dissolution becomes limited by the amount of moisture left in the droplet. Therefore, three major processes can be postulated:

1) Gas-phase SO₂ absorption into the slurry droplet.
2) Ca(OH)₂ dissolution in the slurry droplet.
3) Ca(OH)₂ dissolution in the spray-dried solid.

The parameters that affect these processes are presented below

Both the approach to saturation temperatures and the size of the initial slurry droplet affect mass transfer during these three processes and are therefore crucial process variables. The process variables can be categorized as·

1) Variables affecting SO₂ mass transfer into the slurry droplet—
  Approach to saturation temperature.
  Size of the slurry-droplet method of atomization.
  Mixing of the gas and droplets.
  Residence time of flue gas in the dryer.
  Inlet SO₂ concentration.
  Inlet flue gas temperature.

2) Variables affecting Ca⁺⁺ mass transfer in the slurry droplet—
  Stoichiometric ratio.
  Approach to saturation temperature.
  Size of the slurry droplet.
  Residence time of flue gas in the dryer.
3) Variables affecting Ca⁺⁺ mass transfer in the spray-dried solids—
  Approach to saturation temperature.
  Size of the initial slurry droplet.
  Slaking.
  Stoichiometric ratio.
  Off-product recycle.

These variables and their effects are discussed briefly in the following sections.

Approach to Saturation

Operating the spray dryer outlet at a close approach to saturation temperature increases the residual moisture level in the spray-dried solids and affects all three mass transfer processes. The closer the approach to saturation temperature, the cooler and more humid the flue gas becomes. Increased humidity lengthens the evaporation period and also increases the amount of moisture retained by the solids. By reducing the outlet temperature from the spray dryer by 10°F (from a 30°F approach to 20°F), SO₂ removal efficiency can be increased by approximately 10 percent[5].

Slurry Droplet Size - Method of Atomization

The size of the slurry droplets also affects all three mass transfer processes. The spray of slurry droplets must be finely atomized to provide the large surface area required for rapid SO₂ absorption. However, the droplets must be large enough so that they do not dry out before a satisfactory degree of reaction has occurred, the reaction being highly dependent on the presence of water. (The drying time varies with the square of the initial droplet diameter.)[4] Typically, 1 ft³ of reagent properly atomized has a surface area of 18,000 ft².[6] Proper atomization is extremely important for mass transfer during the pseudo-equilibrium period, where the spray-dried solids exit the spray dryer with an equilibrium moisture content, because the size of the final agglomerate is directly related to the initial droplet size.

Residence Time

The effect of residence time is most important during the first two mass transfer processes, SO_2 mass transfer to the slurry droplet and Ca^{++} mass transfer in the slurry droplet, because it determines the amount of time the flue gas and slurry droplets will be in contact in the spray dryer. The flow rate of gas through the absorber must be high enough for efficient mixing of the gas and spray, but not so high that a proper degree of drying cannot occur in the chamber. The residence time, defined as the chamber volume divided by the absorber outlet gas flow volume, must be controlled to an optimum value so that high SO_2 removal rates are obtained. The slower the drying process, the longer surface moisture will exist on the droplet, allowing for more reaction.

Stoichiometric Ratio

The stoichiometric ratio is most important during the last two mass transfer processes, those that involve Ca^{++} mass transfer. The stoichiometry determines the amount of lime that will be present to react with the SO_2 and significantly affects SO_2 removal in spray drying. The relationship between SO_2 removal efficiency and the stoichiometric ratio (SR) is expressed by the proposed mathematical model.[4]

$$E = 1 - e^{-K \, SR} \qquad (5)$$

This model proposes that SO_2 removal is a function of stoichiometric ratio. Pilot spray dryer test data is well correlated to the mathematical model; thus, it would appear that the model is valid for the operating conditions used in these tests.

The obvious method for increasing SO_2 removal would be to increase the lime stoichiometry, but there are several factors which limit the amount of lime which can be added. First of all, the amount of slurry that can be added to the flue gas is set by energy balance considerations to ensure the solids will be properly dried. Secondly, the amount of lime that can be added to the slurry is limited, because an upper limit is reached on the weight percent of lime in the slurry. Finally, the effect of the stoichiometric ratio on SO_2 removal efficiency begins to level off at SR values greater than 3.0

Droplet - Gas Mixing

Mixing of the slurry droplets and the flue gas affects the mass transfer of SO_2 to the droplet. To provide for good contact between the flue gas and the slurry droplets, intimate mixing must be achieved. This requires fine atomization of the slurry droplets, as well as proper gas flow patterns. Some designs rely on gas dispersers placed around the atomizer that impart a swirling downward motion to the gas. These gas dispersers cause the slurry droplets and spray-dried solids to be carried along in the helical pattern of the entering flue gas. This helps to ensure more complete mixing of the slurry droplets and flue gas as it passes through the chamber.[7] Another design also includes a "central gas disperser" that ducts part of the flue gas flow up toward the atomizer

Lime Slaking

The quality of the slaking process determines how large, porous, and reactive the lime particles are. The amount of pore surface area is important for reaction to proceed in the spray-dried solids. Therefore, slaking has the greatest effect on the mass transfer of Ca^{++} in the spray-dried solids. The techniques used in the slaking of lime can significantly affect its reactivity and surface area. Thus, slaking methods are among the first important design considerations in a dry scrubbing system. Slaking involves hydrating the lime to form calcium hydroxide in the presence of excess water, as described by Equation 6.[2]

$$CaO_{(s)} + H_2O_{(1)} \rightarrow Ca(OH)_{2(s)} +$$
$$27,500 \text{ Btu/lb-mole} \qquad (6)$$
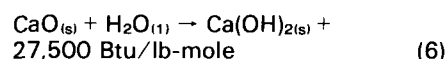
When high calcium, soft-burned pebble lime is slaked with clean water at a water-to-lime ratio of 3:1 or 4:1, the lime pebbles rapidly disintegrate in an explosive, chain-slaking reaction. This produces a slurry of extremely fine (0.5 - 4.0 μm), porous slaked lime particles suspended in water with a large total surface area, which is ideal for use in the spray absorption process.[2] The water used for slaking must be of good quality. The water should not only be softened to prevent scaling problems, but it must be low in sulfates and other chemicals which can cause a reduction in the reactivity of the lime. For best results, slaking should take place at a relatively constant temperature of 190-200°F.[2]

Inlet SO_2 Concentration

The concentration of SO_2 in the flue gas that enters the spray dryer affects the mass transfer of SO_2 to the slurry droplet. The inlet SO_2 concentration has only a moderate affect on SO_2 removal over the range of concentrations which have been investigated and for which data are available.

Flue Gas Inlet Temperature

The inlet temperature of the flue gas affects SO_2 diffusion and, therefore, influences the mass transfer of SO_2 to the slurry droplet. Contradicting results have been obtained regarding the effect of the flue gas inlet temperature on SO_2 removal efficiency. In a test performed by Babcock and Wilcox, the inlet temperature was reduced from 280°F to 230°F at a constant approach to saturation of 20°F.[5] The decrease in temperature resulted in a 10-percent decrease in SO_2 removal efficiency. However, a series of tests performed by Buell indicate that the inlet gas temperature has a negligible effect on SO_2 removal.[2]

The mathematical model developed by B&W,

$$E = 1 - \left[\frac{t_p}{T_{in} - T_{sat}} \right]^{0.62} \qquad (4)$$

predicts that higher flue gas inlet temperature will result in higher SO_2 removal efficiency. An attempt was made to numerically evaluate the effect of changing the inlet flue gas temperature by using this mathematical model. Since it is difficult to assess the adiabatic saturation temperature without knowing the flue gas humidity, this temperature was assumed to be 125°F. A reduction in the flue gas inlet temperature from 280 to 230°F, at a constant approach of 20°F, results in a decrease in SO_2 removal efficiency of 8 percent. This seems to support the results of the test performed by B&W. Further testing may be required to clarify the effect of inlet flue gas temperature on SO_2 collection efficiency.

Spray-Dried Off-Product Recycle

The use of off-product (reacted and unreacted sorbent and fly ash) recycle may provide more available lime surface which allows for increased mass transfer of Ca^{++} in the spray-dried solids. Recycling of the spray dryer off-product permits the reuse of unreacted lime reagent, and if the fly ash is high in available alkalinity, it may reduce the amount of required lime by substituting fly ash alkalinity for lime.[6] Fly ash recycle may improve spray dryer performance in two ways: (1) by providing

available alkalinity, and (2) by acting as a surface catalyst to enhance the lime-SO_2 reaction. The fly ash acts as a surface catalyst by providing an alternate site for $CaSO_3$ to precipitate, thus decreasing the solid deposits on the lime particles which cause increased resistance to mass transfer.

Since making additional alkaline material available for reaction with SO_2 is the primary objective of recycling part of the off-product, care must be taken in the design of the recycle system so that the maximum benefit is realized. The pH of the slurry to which the recycle material is added must be sufficiently low so that a reasonable amount of the recycle alkali will go into solution. Tests performed by Buell showed that if off-product was added to the lime slurry, which was saturated with $Ca(OH)_2$ at a pH of 12, no measurable benefit resulted, regardless of the amount of process off-product added. When a separate slurry of process off-product and water alone was prepared in a separate tank and mixed with the lime slurry at the point of injection to the absorber, however, considerable benefit resulted.[2]

Fabric Filter versus ESP Particulate Collection

For the spray drying system either an ESP or a fabric filter can be used to remove particulates from the spray dryer exhaust to meet environmental emission requirements The type of particulate collection device used will influence mass transfer in the spray-dried solids. Some tests have shown that the downstream collection device can increase the total system SO_2 removal by approximately 10 percent.[8]

Initially, it was felt that a fabric filter would provide better SO_2 removal than an ESP,[6] and only one commercial system purchased to date uses an ESP; the rest use fabric filters. As the fabric filter operates, a cake of the spray-dried solids builds up on the filter. If this cake contains unreacted sorbent, it can act to remove SO_2 as the flue gas passes through the filter. However, test results obtained by B&W at the Jim Bridger Station have shown that both ESPs and fabric filters provide about the same degree of SO_2 removal.[5]

One of the advantages of using an ESP instead of a fabric filter is that the ESP allows the spray dryer to be operated at a closer approach to the saturation temperature without causing maintenance problems in the collection

device. A closer approach to the saturation temperature will provide greater SO_2 removal in the spray dryer. ESPs have been found to perform very well in collecting the particulates from the spray dryer exhaust. The spray-dried product does not build up on the discharge and collecting electrodes. Due to the humidity of the flue gas, the fly ash becomes conditioned, which results in higher particulate migration velocities than would be expected. Also, the low outlet temperature from the spray dryer reduces the resistivity of the fly ash. In addition, ESPs can be operated at lower system pressure drops than fabric filters.

Fabric filters have also been found to collect the spray-dried solids very well. The main advantage of a baghouse is that it is a bulk collection device whereas an ESP is a percentage collector. Tests on recirculation have at times produced dust loading as high as 25 gr/ft³ as an extreme condition. If environmental restrictions were to call for a maximum outlet loading of 0.01 gr/ft³, the precipitation efficiency would have to be 99.96 percent - a number that may be difficult to achieve consistently with a precipitator in a power plant. Properly designed baghouses, on the other hand, should be able to meet a 0.01 gr/ft³ outlet emission regardless of inlet loading. In addition, the cost of an ESP for the above duty could be far more than the comparable baghouse, and the baghouse will generally be more reliable in producing low opacity.[6]

Data Gaps in Literature

To test the proposed mathematical models and the effects of the variables listed above, detailed test data are required. Much of the published test data lack detailed and complete information on inlet SO_2 concentration, stoichiometric ratio, or approach to saturation.

There is a particular lack of information on spray dryer performance when the SO_2 concentration exceeds 2500 - 3000 ppm SO_2. This information is necessary to test the applicability of lime spray drying for use in units firing coals containing more than 3 percent sulfur. Additional analysis might also be required to resolve conflicting theories on the effects of certain variables (e g., inlet gas temperature, off-product recycle) on SO_2 removal efficiency.
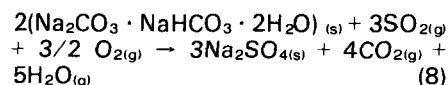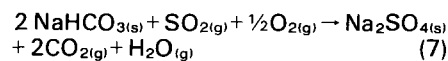
Dry Injection of Sodium Compounds

Dry injection involves contacting SO_2-laden flue gas with a dry sorbent. The sorbent is pneumatically injected into the duct carrying the flue gas and/or precoated on fabric filter bags. The SO_2 is removed from the flue gas by adsorption by the sorbent.

Information on dry injection of sodium compounds was evaluated to characterize the reactions and reaction mechanisms involved in the desulfurization process. The sodium sorbents that were investigated were nahcolite ore (predominantly $NaHCO_3$) and trona ore ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). The results of laboratory- and pilot-scale dry injection tests were evaluated to establish the reaction mechanism and rate controlling steps. There was a great deal of inconsistency in the experimental results, which made it difficult to draw conclusions about the dry injection process However, qualitative and quantitative models describing the dry injection process have been proposed[7,9] and are presented in this report. In addition, important process parameters which influence the dry injection reactions were qualitatively evaluated. Finally, data gaps and conflicting results identified in published literature are discussed to identify areas that may require further investigation.

Qualitative and Quantitative Reaction Models for Sodium Compound Dry Injection

The dry injection reactions that occur when the SO_2 is contacted with the sorbent are strictly gas-solid phase reactions. The overall chemical reactions that occur during dry injection for nahcolite and trona, respectively, are:

$$2\,NaHCO_{3(s)} + SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow Na_2SO_{4(s)} + 2CO_{2(g)} + H_2O_{(g)} \quad (7)$$

$$2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O)_{(s)} + 3SO_{2(g)} + 3/2\,O_{2(g)} \rightarrow 3Na_2SO_{4(s)} + 4CO_{2(g)} + 5H_2O_{(g)} \quad (8)$$

These reactions do not occur in the single steps written above, but instead involve a series of three steps: (1) thermal decomposition of $NaHCO_3$ to Na_2CO_3, (2) reaction between Na_2CO_3 and SO_2 to form Na_2SO_3, and (3) oxidation of Na_2SO_3 to Na_2SO_4 Several changes in the physical characteristics of the sorbent accompany these reactions.

When the $NaHCO_3$ is thermally decomposed to Na_2CO_3, small pores (approximately 0.3 μm in diameter) develop in the sorbent particle as H_2O and CO_2 gas are evolved. These pores provide an increased surface area for chemical reaction, thus increasing the reactivity of the sorbent. The rate of decomposition of $NaHCO_3$ is extremely temperature dependent, and temperatures between 300 and 600°F are required for adequate pore development.

Test results have shown that trona is less reactive than nahcolite.[10] It is postulated that trona is less reactive because it already contains 1 mole of Na_2CO_3 for every mole of $NaHCO_3$ present. Therefore, trona does not contain as much $NaHCO_3$ as nahcolite, and the decomposition of the sorbent does not generate as much pore volume per particle of trona. It has been found that the sorbent with the greatest amount of sodium bicarbonate ($NaHCO_3$) parts for total sodium parts present will generally be the most effective for SO_2 removal.

The reaction of the SO_2 with the sodium sorbent proceeds from the exterior of the sorbent particle inward, leaving behind an inert layer of Na_2SO_4 on the surface of the sorbent particle. The molar volume of this reacted Na_2SO_4 layer is approximately 26 percent greater than the molar volume of the unreacted Na_2CO_3.[7] This increase in the molar volume tends to plug the internal pores that were generated by the decomposition of the sorbent. The plugging of the pores tends to reduce the reactivity of the sorbent. Scanning electron micrographs (SEMs) of halved sorbent particles recovered after reaction with SO_2 showed a surface zone of Na_2SO_4, an intermediate reaction zone, and a central unreacted core of Na_2CO_3.

The SEMs of the reacted sorbent particles warrant the application of the classical unreacted-core model. This model proposes three major steps involved in the reaction of SO_2 with the sorbent:

1) Diffusion of gaseous SO_2 to the surface of the sorbent particle through the stagnant gas film surrounding the particle.
2) Penetration and diffusion of gaseous SO_2 through the Na_2SO_4 ash layer to the unreacted core.
3) Chemical reaction of gaseous SO_2 with the sorbent at the reaction surface

Each of these steps has a different resistance to the rate of reaction, but the step with the highest resistance is considered to be rate controlling. Test results indicate that the diffusion of gaseous SO_2 through the stagnant gas film is not a rate controlling step.[9] It has been proposed[9] that initially the rate of reaction is controlled by chemical reaction, and as the ash layer builds up, the rate of reaction becomes controlled by the diffusion of SO_2 through the ash layer.

The rate of chemical reaction may be controlled by either the rate of thermal decomposition of $NaHCO_3$ to Na_2CO_3 or the rate of uptake of SO_2 by the Na_2CO_3 to form Na_2SO_3. However, most experimental results [7,9,10] seem to indicate that thermal decomposition is the rate controlling chemical reaction.

Mathematical relationships have been developed[11] for the case where each of the three reaction steps (gas film diffusion, ash layer diffusion, and chemical reaction) controls the rate of reaction. However, for the dry injection process the rate of SO_2 removal is controlled by either the rate of chemical reaction or diffusion through the ash layer. Expressions describing SO_2 removal efficiency as a function of reaction time for these two cases are:

Ash Layer Diffusion Controls

$$\frac{t}{\tau} = 1 - 3(1-E/SR)^{2/3} + 2(1-E/SR) \qquad (9)$$

where: $$\tau = \frac{\rho R^2}{6 D_v C_{SO_2}\text{-}g(MW)} \qquad (10)$$

(The above equation cannot be solved directly for E.)

Chemical Reaction Controls

where: $$E = \left[1 - \left[1 - \frac{t}{\tau} \right]^3 \right] SR \qquad (11)$$

$$\tau = \frac{\rho R}{k_s C_{SO}\text{-}g(MW)} \qquad (12)$$

The variables included in these equations are defined as:

t	= Time, sec
τ	= Time needed for complete conversion of the sorbent, sec
E	= SO_2 removal efficiency,

$$\frac{\text{mole } SO_2 \text{ removed}}{\text{mole } SO_2 \text{ in flue gas}}$$

SR = Stoichiometric ratio,

$$\frac{\text{mole } Na_2 O \text{ injected}}{\text{mole } SO_2 \text{ in flue gas}}$$

R	= Initial particle radius, ft
ρ	= Density of the sorbent, lb/ft^3
$C_{SO}\text{-}g$	= Concentration of SO_2 in the gas phase, $lb\text{-}mole/ft^3$
(MW)	= Molecular weight of sorbent, $lb/lb\text{-}mole$
D_v	= Mass diffusivity of SO_2 through the ash layer, ft^2/sec
k_s	= First-order rate constant for chemical reaction, ft/sec

These mathematical models were not evaluated because test data published thus far have been incomplete, and many of the variables required for the determination of τ (i.e., D_v, k_s, R, and ρ) were not provided and could not be easily estimated from the available literature.

Process Parameters Affecting the Dry Injection Process

Many process parameters affect SO_2 removal efficiency in the dry injection process. These parameters were evaluated and were ranked in the approximate order of their relative importance.

In general, the parameters that may affect SO_2 removal in dry injection are those that affect the diffusion of SO_2 to the surface of the sorbent particle, diffusion of SO_2 through the inert ash layer on the particle surface, or chemical reaction. Parameters that influence these three reaction steps are characterized below.

1) Variables affecting SO_2 mass transfer to the sorbent particles:
   Particle size.
   Residence time of the reactants in the duct.
   Inlet SO_2 concentration.
   Gas velocity and air-to-cloth ratio.
   Mode of sorbent injection.
   Gas temperature.
2) Variables affecting SO_2 mass transfer through the inert ash layer:
   Sorbent preparation.
   Particle size.
   Residence time of the reactants in the duct.
   Filter cleaning intervals.
   Stoichiometric ratio.
3) Variables affecting chemical reaction:
   Sorbent type.
   Sorbent preparation.
   Temperature.
   Stoichiometric ratio.

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These variables and their effects are discussed briefly in the following sections.

Sorbent Type

The type of sorbent used for dry injection will directly affect the chemical reactions that occur. Tests with a wide variety of sorbents have shown that only sodium compounds produce significant SO_2 removal at typical air preheater outlet temperatures (approximately 300°F). Lime and limestone have been demonstrated to achieve SO_2 removal only at much higher gas temperatures (600°F+).[1] Sorbents that have been shown to have good potential for SO_2 removal are sodium bicarbonate, nahcolite ore, and trona ore. Nahcolite ore is a naturally occurring mineral which typically contains 70 - 90 percent sodium bicarbonate. Trona ore is also a naturally occurring mineral which contains approximately 40 - 50 percent sodium carbonate (Na_2CO_3) and 20 -30 percent sodium bicarbonate ($NaHCO_3$).

Experimental results from tests using sodium carbonates and sodium bicarbonates indicate that the bicarbonate form is much more reactive. The increased reactivity of $NaHCO_3$ is thought to result from the pores that develop when $NaHCO_3$ particles are thermally decomposed to Na_2CO_3. In general, the sorbent with the highest percentage of "bicarbonate parts" for "total sodium parts" present would be expected to perform the best.[10]

Sorbent Preparation

Treatment of the sorbent prior to injection influences both the chemical composition and porosity of the sorbent. Any changes in porosity will influence the ability of SO_2 to diffuse through the ash layer that surrounds the sorbent particles, and changes in chemical composition will affect the rate of chemical reaction. Sorbent preparation generally involves grinding the particles to increase the surface area available for reaction and heating to thermally decompose the $NaHCO_3$ to Na_2CO_3, causing an increase in the pore volume of the particles. The effects of thermal decomposition will be discussed in this section; particle size effects are discussed in the following section.

The thermal decomposition of $NaHCO_3$ to Na_2CO_3 increases the porosity of the sorbent, which increases the surface area available for contact with SO_2. Howatson[12] investigated the pore development of nahcolite at 300°F with a

scanning electron microscope (SEM) and found scattered development of 0.1 - 0.7 μm pores after 10 minutes. After 20 minutes the surface was completely covered with pores averaging about 0.3 μm. The Na_2CO_3 particles produced in this manner have a much larger void space than the parent $NaHCO_3$ particle.[13] These pores provide a greater surface area for chemical reaction and a greater volume for SO_2 diffusion. The reactivity of the sorbent particles has been found to increase by up to a factor of 60 because of thermal decomposition.[14]

Investigations have been conducted[15,16] to determine if decomposition of the sorbent prior to injection enhances SO_2 removal and to determine the optimum decomposition temperature. These experiments have often produced conflicting results. However, a majority of the tests show that predecomposition of the sorbent at high temperatures reduces SO_2 removal efficiency. Carson[15] reported that predecomposition of $NaHCO_3$ to Na_2CO_3 significantly reduced the desulfurization capacity of the sorbent, however, the decomposition temperature was not specified. A bench-scale study by Genco et al.[14] with a fluidized-bed reactor also showed a reduction in SO_2 removal with nahcolite that had been predecomposed at 600°F.

Particle Size

The size of the sorbent particles affects the mass transfer of SO_2 through the gas film that surrounds the particle, because it determines the surface area through which the SO_2 must diffuse. Particle size also influences diffusion through the inert ash layer because the rate of decomposition of $NaHCO_3$ to Na_2CO_3 is somewhat dependent on particle size, and the decomposition rate influences the porosity of the sorbent particle. Results characterizing the role of particle size in SO_2 removal efficiency are often conflicting. However, the general consensus is that better removal is obtained with smaller particles.

Temperature

The temperature of the flue gas influences the diffusivity of the SO_2 molecules and the mass transfer of SO_2 to the sorbent particles. However, SO_2 mass transfer properties will vary only slightly in the typical flue gas temperature range (300° - 400°F). The temperature at which the sorbent is injected into the flue gas affects the thermal decomposition of $NaHCO_3$ to Na_2CO_3. This in turn influences the reactivity of

the sorbent. Many tests have been performed trying to characterize the effect of temperature on SO_2 removal. Again, these tests have yielded conflicting results. However, it appears that the best SO_2 removal occurs when the sorbent is injected into the duct at approximately 600°F, and the baghouse is operated at approximately 300°F. The high injection temperature allows for rapid decomposition of $NaHCO_3$ to Na_2CO_3, and a temperature of 300°F is optimum for the reaction between Na_2CO_3 and SO_2 to form Na_2SO_3.

Two methods of elevating the flue gas temperature above air preheater outlet temperatures have been employed in pilot-scale systems. One method involves using a stream of hot flue gas which bypasses the air preheater; the other method utilizes heaters or heat exchangers at the air preheater outlet duct.

Stoichiometric Ratio

Since the stoichiometric ratio determines the quantity of sodium available to react with a given quantity of SO_2, it affects the chemical utilization of the sorbent particles and the degree of completion of the chemical reaction. Also, at lower stoichiometries the utilization of the sorbent should be greater than at higher stoichiometries. That is, the individual sorbent particles will be more highly reacted at lower stoichiometries because fewer particles are injected into the flue gas. Therefore, at low stoichiometries the ash layer surrounding the particles should be thicker and tend to limit SO_2 mass transfer.

The stoichiometric ratio in dry injection is defined as.

$$SR = Me/MSO_2 \qquad (13)$$

where: Me = Mole equivalent of Na_2O in the sorbent

MSO_2 = Moles of SO_2 in the inlet flue gas

Work by several organizations (EPRI, University of Tennessee, Battelle-Columbus, Air Preheater, American Air Filter, Wheelabrator-Frye, and Buell) has shown an increase in SO_2 removal with increased stoichiometric ratio.

Mode of Injection

The mode of sorbent injection affects the external mass transfer of SO_2 to the entrained sorbent particles in the ductwork and through the filter cake in the fabric filter. The sorbent can be injected into the system in three ways:

1) *Continuous.* After the bag is cleaned, sorbent is continuously supplied to the flue gas from injection points in the ductwork, upstream of the baghouse. The sorbent them accumulates on the bags to produce a filter cake.

2) *Batch.* After the bag is cleaned, all sorbent is added to the bag as a precoat before flue gas is resumed.

3) *Semi-batch.* This feeding method is a combination of methods 1 and 2. After bag cleaning, some sorbent is precoated onto the bags and the remainder is added continuously upstream.

In a typical semi-batch system, 20 percent of the ground ore is used to precoat the filter bags. The additional sorbent is added continuously in the duct. A maximum grain loading of 10 gr/acf for continuous injection was used by Genco et al. to prevent particle settling in the duct.[14]

The effects of precoat on SO_2 removal have been analyzed by KVB for EPRI. They found that precoating the bags with nahcolite increased SO_2 removal from 42 to 66 percent, with all other conditions held constant.[13]

Tests have also been conducted in an attempt to characterize where SO_2 removal occurs, in the ductwork or in the filter. These tests indicate that SO_2 removal in the ductwork is variable and is a strong function of the flue gas temperature in the duct. In general, very little SO_2 removal will occur in the duct at temperatures around 300°F; however, substantial SO_2 removal will be achieved in the duct at temperatures around 600°F.

Residence Time of the Reactants in the Duct

The residence time determines the amount of time that the flue gas and sorbent will be in contact in the duct. Therefore, it affects the extent of mass transfer through both the gas film and the ash layer that surround the sorbent particles. Residence time is defined as the volume of the duct divided by the volumetric flow of gas through the duct and is normally expressed in seconds. In general, SO_2 removal in the duct increases with increased residence time [7]

Filter Cleaning Intervals

The longer the baghouse operates between cleanings, the greater the sorbent utilization. An increase in sorbent utilization causes the ash layer surrounding the particles to become thicker. This increase in ash layer thickness decreases the mass transfer of SO_2 through the ash. When the sorbent being used is nahcolite, the filter cells should be operated for at least 40 minutes between cleanings, because it takes 40 minutes to achieve maximum steady state SO_2 removal with nahcolite.[1] However, maximum steady state removal with trona is achieved very rapidly.[1] Genco et al. operated the filter cells for approximately 70 minutes between cleanings for a nahcolite sorbent.[14] The filter cleaning interval must be balanced against the rate of SO_2 removal. After a certain amount of sorbent has been utilized, the rate of SO_2 removal begins to level off, and a longer filter cleaning interval will result in very little additional SO_2 removal.

Inlet SO_2 Concentration

The inlet SO_2 concentration affects the mass transfer of SO_2 to the sorbent particles, because it determines the driving force for SO_2 mass transfer to the particle surface. Several studies measuring the effect of SO_2 concentration on removal efficiency showed that the inlet SO_2 concentration had only a small effect on removal for a given stoichiometric ratio. Work by Wheelabrator-Frye, with a nahcolite sorbent and inlet SO_2 concentrations of 800 - 2800 ppm, showed that removal was slightly higher for higher inlet SO_2 levels. It was felt that the slight increase in removal resulted from a higher driving force for the diffusion of SO_2 from the bulk gas to the solid particle. However, the increase in removal was somewhat offset because at higher inlet SO_2 concentrations more nahcolite had to be fed to maintain stoichiometric ratios, which necessitated more frequent bag cleaning and resulted in lower nahcolite residence time in the system.[1] Note that Wheelabrator-Frye's reasoning is not consistent with reaction models developed in this report, because the diffusion of SO_2 from the gas to the particle was not considered to be a rate controlling step.

The dry injection system has not been tested with SO_2 concentrations greater than approximately 3500 ppm. Therefore the applicability of dry injection with coals containing greater than 3.5 percent sulfur is not known.

Gas Velocity and Air-to-Cloth Ratio

The velocity of the flue gas relative to the sorbent particles affects the mass transfer of SO_2 through the stagnant gas film to the surface of the sorbent particle. Gas velocity affects the diffusional properties of the SO_2 and the time the sorbent and flue gas are in contact. The lower the velocity of the flue gas, the longer it remains in the dry injection system to react with the sorbent. However, studies by several sources (Buell, EPRI, American Air Filter, University of Tennessee, and Wheelabrator-Frye) showed that the velocity of the gas had no significant effect on SO_2 removal. The air-to-cloth ratio, which represents the velocity of the gas through the filter cloth and is described as the volumetric flow of the gas through a specified filter area, was varied from 1.4 to 5.0 ft/min with no observable effect on SO_2 removal.[10,14,1]

Data Gaps in Literature

It is proposed that the unreacted core model can be applied to the reactions that occur during dry injection.[10] However, this model was not evaluated against experimental data; therefore, it may not be valid.

To evaluate the applicability of the unreacted core model, experimental data describing sorbent conversion versus time will be required. The mechanism by which the desulfurization reaction

$$Na_2CO_{3(s)} + SO_{2(g)} \rightarrow Na_2SO_{3(s)} + CO_{2(g)} \quad (14)$$
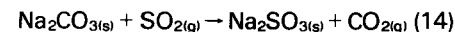
proceeds also needs to be established, and the influence of the flue gas moisture content on desulfurization should be examined.

It would be useful to characterize SO_2 removal at inlet SO_2 concentrations greater than 2000 ppm to determine if dry injection is applicable to systems that burn coal with a higher sulfur content In addition, parametric testing should be performed to clear up conflicting experimental results concerning the effects of particle size, injection temperature, and thermal predecomposition of the sorbent on SO_2 removal. Finally, it may be beneficial to test dry injection on a flue gas produced from combustion under low excess air conditions. Minimizing the oxygen content of the flue gas could reduce the oxidation of Na_2SO_3 to Na_2SO_4. If in fact the oxidation of Na_2SO_3 causes the pores in the sorbent particle to plug, then a reduction in the amount of Na_2SO_4

generated should reduce plugging and allow for better SO_2 removal.

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Appendix

Conversion Factors

British	Metric
1 ft	= 0.3048m
1 lb	= 0.454 kg
1000 cfm	= 0.5 m^3/s
1 gal./1000 ft	= 0.13 liters/m
1 Btu	= 1.055 kJ
1 gal	= 3.79 liters
1 ft^3	= 28.32 liters
1 lb-mole	= 453.6 g-mole
1 atm	= 1.013 x 10^5 Pa
$1 \dfrac{Btu}{ft^2\text{-}hr\text{-}°F}$	$= 5.678 \dfrac{J}{m^2\text{-}s\text{-}K}$
$1 \dfrac{Btu}{lb\text{-}°F}$	$= 4.187 \times 10^3 \dfrac{J}{kg\text{-}K}$
$1 \dfrac{ft^2}{sec}$	$= 9.29 \times 10^{-2} \dfrac{m^2}{s}$
$1 \dfrac{lb}{ft^3}$	$= 16.018 \dfrac{kg}{m^3}$
$1 \dfrac{lb}{ft\text{-}hr}$	$= 4.133 \times 10^{-4}$ Pa-s

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(Order No. PB 82-196 924; Cost: $13.50, subject to change) will be available
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