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DRY SORBENT INJECTION
FOR ACID GAS CONTROL:
PROCESS CHEMISTRY, WASTE DISPOSAL
AND PLANT OPERATIONAL IMPACTS

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Dry Sorbent Injection for Acid Gas Control:
Process chemistry, waste disposal and plant operational impacts

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I. Introduction

Dry Sorbent Injection (DSI) refers to the practice of injecting a dry alkaline mineral into a flue gas stream to reduce acid gas emissions (i.e. SO_3/H_2SO_4, HCl, SO_2, and HF). The use of this technology is expanding rapidly as a low capital-cost solution for compliance with evolving environmental control requirements. DSI has advantages in comparison with traditional acid gas scrubber technology, which make DSI an attractive option for both utility and industrial facilities. In addition to lower capital cost, DSI systems have a wide turndown, or range of operation, that allows efficient use of reagent with load changes, fuel changes, and operational cycling.

Hundreds of DSI systems are either installed, in construction/commissioning or in an early planning stage for installation in plants in the US. These DSI systems, available from a multitude of equipment suppliers, come in varying sizes and are being implemented across a wide range of applications. While coal-fired electric utility generators first employed DSI systems for a broad range of acid gas control needs, the use of DSI systems is now expanding to a wide variety of industrial applications. Industries using DSI acid gas control now include: cement plants, pulp and paper mills, coal-fired university boilers producing steam and/or power, coke ovens, brick and tile facilities, smelters, glass plants, medical waste incinerators, waste to energy plants, biomass fired facilities and others. These facilities represent a broad range of acid gas control needs, process conditions, as well as constraints, where DSI systems were successfully installed and are currently operated.

While DSI systems have proven to be effective for a broad range of acid gas pollutants, the use of these sorbents can result in ancillary systems impacts that must be considered when selecting an emission control solution. This paper provides an introduction regarding DSI, the reagents used in these systems, and a review of ancillary impacts to be considered.

II. Basic DSI Chemistry

The chemistry associated with DSI technology is relatively straight forward and well understood. The two primary chemistries being utilized for acid gas control with DSI are based on calcium and sodium-based reagents. The primary calcium reagent being widely utilized is hydrated lime or calcium hydroxide ($Ca(OH)_2$), and the important reactions that result in the capture of the primary acid gases present in industrial flue gas streams are outlined below.

$$Ca(OH)_2 + SO_2 + 0.5O_2 \longrightarrow CaSO_4 + H_2O$$

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$

$$Ca(OH)_2 + 2HF \longrightarrow CaF_2 + 2H_2O$$

Accordingly, the primary reaction products of calcium-based DSI are calcium sulfate, calcium chloride and calcium fluoride. The relative volume of the reaction products is a function of relative initial acid gas concentrations and the capture efficiency for each pollutant. Note that there are other less critical reaction products resulting from interaction with other flue gas constituents, such as CO_2 in the flue gas, but the primary reaction products are those associated with the acid gases present.

The sodium-based chemistry is a bit more complex in that either trona (sodium sesquicarbonate) or sodium bicarbonate can be injected into a gas stream for DSI applications where it thermally decomposes to a more porous sodium carbonate particle upon heating, which then reacts with the acid gases present in the flue gas stream. The basic trona reaction for sulfur capture is outlined below. [1]

$$2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O) \longrightarrow 3Na_2CO_3 + CO_2 + 5H_2O$$

$$Na_2CO_3 + 0.5O_2 + SO_2 \longrightarrow Na_2SO_4 + CO_2$$
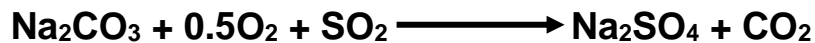
The global hydrogen chloride and hydrogen fluoride capture mechanisms for trona are as follows, respectively, following the trona decomposition step to Na_2CO_3: [1]

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

$$Na_2CO_3 + 2HF \longrightarrow 2NaF + CO_2 + H_2O$$

In the case of the sodium reagents, the primary reaction products are sodium sulfate, sodium fluoride and sodium chloride. Just as with calcium, the relative quantity of the reaction products is a function of both relative initial acid gas concentrations and the capture efficiency for each pollutant. For sodium bicarbonate ($NaHCO_3$) a similar series of reactions occurs in which sodium bicarbonate decomposes upon heating to Na_2CO_3 followed by the reaction with the acid gases present.

DSI chemistry is driven by multiple variables which impact the overall removal efficiency for each application. These variables generally fall into three categories: flue gas properties, reagent properties and DSI system configuration.

1. Flue Gas Properties

- Flue Gas Temperature: Temperature will have a direct effect on the kinetics of the reaction of alkaline sorbents with acid gases. Finding an injection location with an

appropriate flue gas temperature is a function of the overall process conditions and the target pollutant(s).

- Acid Gas Concentrations: The relative amount of all acid gases present should be considered as they impact performance. While temperature at the injection location can impact relative acid gas reactivity, precise selective acid gas removal is not achievable as the alkaline reagents will react with all acid gas species present to some extent. As a result, reactant concentration (overall and local) and reaction kinetics and selectivity play a role in removal dynamics. For example, it has been documented that the relative amount of SO_2 present will impact DSI chemistry for HCl removal due to competitive reactions between these acid gases. [2, 3, 4] The relative reactivity of the various acid gases typically present in flue gas streams is discussed in more detail in the Potential Impacts on Other Airborne Pollutants section of this paper. Therefore, understanding the relative reactivity of each acid gas and how it is impacted by the other factors described herein is important.

- Other Flue Gas Properties: In addition to the non-targeted acid gases present, other flue gas properties including flow distribution, moisture content and carbon dioxide concentration can have a direct effect on overall sorbent performance.

2. Reagent Properties

- Reagent Properties: Reagent properties, such as reactivity, surface area, pore volume, purity, and particle size, all impact the performance of that reagent within a DSI system. Research and development aimed at understanding critical sorbent properties has advanced understanding of how manipulating these properties will influence DSI chemistry. Advanced calcium-based reagents have been introduced into the US industry in recent years, which provide improved acid gas removal and/or reduced reagent consumption requirements. Advancements in milling technologies have improved sodium-based reagent performance based on reducing particle size distribution.

3. DSI System Configuration

- Particulate Control Device: Whether the injected reagent and subsequent reaction products are collected from the flue gas stream via an electrostatic precipitator, fabric filter or other technology will impact the DSI acid gas removal efficiency. This will be discussed in greater detail later within this paper.

- Residence Time: Generally speaking, more in-flight residence time for the reagent particles in the flue gas will result in improved reagent utilization.

- Sorbent-to-Gas Mixing: Ensuring that the target pollutant(s) comes into direct contact with the alkaline reagents within the flue gas stream is critical to maximizing reagent utilization and ensuring the desired acid gas removal efficiency

is achieved. Reagents are introduced into the flue gas stream via injection port(s) or injection lances. Recent advances have resulted in new injection lance designs and other mixing technologies to improve sorbent utilization and reduce sorbent consumption while achieving the necessary emission targets.

III. Typical DSI System Configuration

DSI systems are mechanically simple and consist of much fewer moving parts and ancillary systems compared to other scrubbing technologies such as wet scrubbers, spray dryer absorbers and circulating dry scrubbers. The fundamental DSI system can be broken down to a storage and metering system, conveying air system, milling system (for sodium sorbents only) and conveying piping / injection grid. The following flow diagram is a general representation of a typical DSI system.[5]
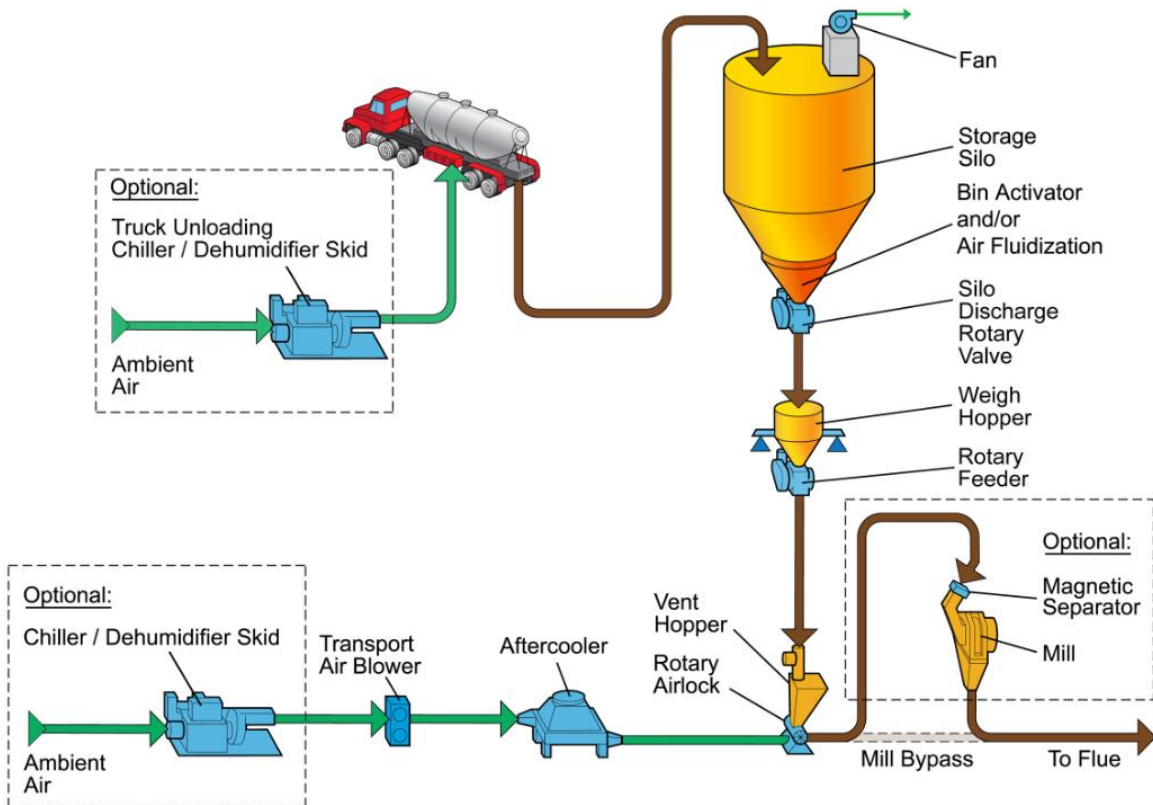

Figure 1. Typical DSI System Flow Diagram [5]

The conveying air system consists of a motive air source, typically a positive displacement blower, which uses ambient air as the transport medium for carrying the reagent from the metering system to the flue gas stream. Since trona is hydroscopic, these systems should have limited exposure to high humidity as well as high temperatures, which can drive off bound moisture. Accordingly, systems designed to handle trona should include dehumidification as well as air cooling to minimize exposure to those potentially

troublesome conditions. This recommendation is applicable to both the reagent unloading system as well as the conveying system.

It is common, but not always necessary, to condition the conveying air used for hydrated lime systems by reducing the conveying air moisture and temperature prior to reagent transportation by utilizing chillers, dehumidifiers and/or after-coolers or some combination of these components. Whether using sodium or calcium based reagents, DSI system operating experience has found that conditioning the conveying air has had positive effects in reducing build-up and scaling within the metering system components as well as the conveying piping.

The storage system consists of a cylindrical silo which is sized to provide a desired reagent storage capacity based on expected consumption rates specific to each plant. These silos consist of level monitoring instrumentation, dust collection equipment to maintain very low fugitive dust emissions as well as fluidization equipment, such as air pads and/or bin activators, to promote reagent flow from the silo by minimizing reagent "rat-holing" and bridging in the silo cone. For DSI systems that inject small dosages of reagent, it is possible to receive reagent by super-sacks; therefore, there is no need for a silo system as the reagents are fed directly from the super-sacks into the metering system.

The storage silos are typically skirted and enclose the metering system within the skirt below the silo.   Metering systems can be designed to feed the sorbent either gravimetrically or volumetrically. When using a gravimetric design, the metering system generally consists of weigh hoppers and rotary valves and/or screw feeders to direct reagent from the storage system into the conveying system piping. It is common for weigh hoppers to be mounted on load cells to enable the DSI system to provide a loss-in-weight gravimetric reading on the injection rates, meaning the reagent dosing rates are measured by the change in reagent mass in the weigh hoppers over measured time increments.   In the volumetric approach, the DSI system does not have load cells installed, but rather uses a calibration curve and a screw or rotary valve speed to measure the reagent injection rates.

Once the reagent is metered into the conveying air stream for transport, it is then delivered through the conveying piping to the injection grid system. However, if sodium-based reagents are used, then the reagent may be milled in-line just prior to injection to reduce the reagent particle size distribution to improve the acid gas removal efficacy and sorbent performance. Air classifying mills, pin mills, jet mills and turbine/cutting block mills have all been used on DSI systems. A mill with an integrated air classifier allows the user to adjust the final particle size distribution by varying the speed of the air classifying wheel.[6] Pin mills consist of a series of stationary and rotating pins each mounted on discs in which centrifugal forces cause the reagent particles to accelerate toward the edge of the discs and pass through the pins. The reagent particle size distribution is reduced via impaction on the pins as it passes through pins and subsequently discharged from the pin mill into the discharge cone. Pin mills can be in a horizontal or vertical orientation based on pin orientation.[7] Jet mills use compressed air to impact the particles on themselves, thereby

breaking them into smaller pieces. Although they are capable of producing very fine particle sizes, compressed air consumption is high. Finally, the in-line turbine/cutting block mills use a rotating turbine to "throw" the particles against cutting blocks, which creates smaller particles that exit through specifically sized slots. The primary advantage of this design is to create small particles without overheating the sodium sorbents.

The design of the conveying system piping that transports the reagent from the silo to the injection locations is critical for successful operation. A poorly designed pipe run and improper elbow design can lead to build-up and scaling within the conveying piping, which would then require cleaning to prevent shutting down the DSI system. As previously mentioned, the conveying air properties can directly impact the scaling and build-up potential within the conveying piping just as the conveying piping design itself can. The conveying piping can also consist of flow splitters used to split the reagent feed to multiple injection ports.

The injection grid is an important component to the DSI system, as it will dictate how well the reagent is dispersed into the flue gas stream, thereby contacting and reacting with acid gases present. The injection grid can consist of a single injection port or several injection ports depending on the DSI system design and the cross sectional area of the ductwork in which the flue gas stream is transported. The injection lances are typically steel pipes that are inserted directly into the flue gas stream where the reagents will disperse from the open end of each lance. Depending on site-specific conditions, injection grids can consist of injection lances of one length or multiple lengths based on the design and necessity for ample reagent distribution into the flue gas stream. In some cases (typically industrial applications), no injection lances are used at all and the conveying piping attaches to the injection port and the reagent is blown directly into the flue gas stream via the injection port.

The injection grid can be optimized to increase particle dispersion in the duct, which in turn reduces the quantity of sorbent needed, as well as providing better pollutant removal performance. Computational Fluid Dynamics (CFD) modeling is often conducted to help choose the best injection location as well as the number and length of the lances in order to achieve the optimal sorbent dispersion. A number of DSI system providers and commercial CFD modeling firms can perform CFD modeling. Depending on the duct, the use of CFD modeling could result in a design that provides sorbent savings that far outweigh the cost of the modeling. CFD modeling may also be essential for difficult ducts with low residence time or complicated configurations. Sorbent dispersion can also be optimized through advanced injection lance design or duct mixing devices that are designed to ensure complete dispersion in as much of the duct as possible.

It is typical that a plant installing a DSI system maximizes its overall flexibility by having the ability to inject either calcium or sodium-based reagent. While there are some fundamental differences in these reagents, systems for calcium or sodium-based reagents are fundamentally the same. However, there are a few considerations to keep in mind. Sodium-based reagents have approximately twice the bulk density as compared to that of calcium-based reagents; therefore, a specific DSI storage silo can hold

approximately twice the mass of sodium-based reagents as compared to that for calcium-based reagents. Keeping this difference in bulk density in mind is important when considering the DSI system design and the desired on-site storage capacity. Another fundamental difference between calcium and sodium-based reagents is that sodium-based reagents typically require on-site milling to reduce particle size to improve acid gas removal efficiency.[8] Calcium-based reagents do not require any on-site processing. Sodium reagent performance improvement associated with on-site milling is typically weighed against the additional capital expense as well as the operation and maintenance costs required for the on-site milling system to determine if an on-site milling system should be installed. Regardless of the sorbent used, many facilities are now beginning to evaluate various technologies that provide improved reagent-to-gas mixing within the ductwork as it has been shown to reduce reagent consumption and reduce the DSI system operating costs. Such technologies include improved injection lance designs,[9] lance-less boosted air designs[10] and in-duct static mixers[11] to name a few.

IV. Reagents

The two sodium based DSI reagents are sodium bicarbonate and trona. The primary calcium based DSI reagent is calcium hydroxide.

Both sodium bicarbonate and trona are available from a variety of suppliers in the U.S. Delivery of these reagents is available both by truck and rail-direct if the receiving facility has rail access. The following properties are typical for sodium sorbents:

- Sodium Bicarbonate
    - Bulk Density 63 lb/ft^3
    - D_{50} 150 – 230 microns
    - D_{90} 255 – 385 microns

- Trona
    - Bulk Density 78 lb/ft^3
    - Assay >95%
    - D_{50} <46 microns
    - Percent free moisture <0.07

Calcium-based reagents are available from a multitude of suppliers all across the US.[12] The primary calcium reagent, calcium hydroxide, is available in supersacks or bulk loads with delivery by truck or rail-direct if the receiving facility has rail access. For DSI applications a standard hydrated lime product is available from a majority of calcium-based reagent suppliers which consists of the following properties,

- Specific Surface Area ≈ 15 – 20 m^2/g
- Pore Volume ≈ 0.07 – 0.08 cm^3/g
- Available $Ca(OH)_2$ > 90%
- D_{50} Particle Size ≈ 3 – 12 microns
- Free Moisture ≈ 0.5 – 1.5%

However, multiple calcium-based reagent suppliers also produce enhanced hydrated lime products which provide improved acid gas removal efficacy. These enhanced hydrated lime reagents are engineered to optimize these reagent properties to improve reagent performance which, in turn, results in lower reagent consumption when compared to standard hydrated lime products. Reducing the reagent consumption also provides the following benefits:

- reduced dust loading to the particulate control device and ash handling systems,
- less fly ash / byproducts required for disposal,
- additional DSI silo storage capacity when retrofitted to existing silo using standard hydrated lime,
- and fewer truck deliveries required.

Enhanced hydrated lime products typically reduce the amount of reagent required for a given acid gas control requirement by 30-50%. It is also possible to obtain an optimized hydrated lime product that is blended with powder activated carbon (PAC) to provide simultaneous acid gas and mercury control using a single injection skid.

V. Particulate Matter (PM) Control Impacts

DSI reaction products, as well as unreacted sorbent, are typically collected in a particulate control device. The most common particulate control devices used are electrostatic precipitators (ESPs) and baghouses. With injection of DSI sorbents, the quantity of particulate will increase and the composition of particulate collected in the particulate control device will change from just fly ash to a mixture of fly ash, sorbents and reaction products. This increased dust loading and new particulate matter (PM) composition may impact operation of the ESP or baghouse in a variety of ways as discussed later in this section. The composition of the collected byproduct may be altered in such a way that an alternative way to dispose of this byproduct may be required. The most common way to understand how a DSI system may impact the particulate control device is to run a DSI trial to confirm pollutant mitigation and to observe and record changes to the particulate control device and the byproduct handling and disposal. Potential impacts for baghouses, ESPs and ash handling systems are discussed below.

1. Potential Baghouse Impacts
A baghouse, or fabric filter, is a device that separates and collects filterable particulate matter from a flue gas stream.[13] Flue gas flows through the filter bags and the filterable particulate is collected on the outside of the filter bags for a pulse jet type fabric filter or inside the filter bags for a reverse air baghouse.

With the addition of DSI, particulate loading will increase and particulate composition will change. The impact to baghouse systems are described below.

Baghouse particulate emission limits are usually not affected. Since baghouses are designed based on air-to-cloth ratios, increased loading usually will not affect emissions.

If PM emissions increase, this is an indication that leakage across some filter bags already exists and the increased emissions are a direct result of that leakage.

Baghouse pressure drop or cleaning frequency will increase with the additional PM loading from DSI. If the bag cleaning controls are set on a timer, then the pressure drop will increase. If cleaning events are under pressure drop control, then the cleaning frequency will increase. It will be up to the plant to decide which method is the more appropriate control based on actual baghouse operation; however, no change may be necessary.

Corrosion in the back-end of the system and in the baghouse will usually be reduced when injecting calcium and sodium-based sorbents for acid gas mitigation. This also applies when injecting a halogenated activated carbon with a calcium or sodium-based sorbent and/or with a high calcium oxide fly ash.

Filter cake formation on the bags will be different depending upon the concentration of DSI sorbents and reaction products in relation to the existing fly ash. Collecting and testing samples during a DSI trial will help to evaluate if the filter bags experience properties that could affect long term operation.

Under normal circumstances, filter bag replacement should not be more frequent with DSI addition. The exception will be if very fine particles are produced which can blind the bags. This is usually associated with condensable particulate being formed such as ammonium bisulfate and is not typical with DSI.

Given that the filter cake properties and the DSI sorbent concentration within the filter cake will provide additional acid gas removal, optimization of the baghouse operation may have a direct impact on the overall DSI performance and subsequently the sorbent consumption. Such baghouse optimizations have been shown to reduce sorbent consumption when utilized in conjunction with DSI; for example, increasing the pressure drop cleaning set-point to increase time between each cleaning cycle, or in the case of reverse air baghouses, limiting cleaning cycles to one compartment per cleaning rather than all compartments. Reducing sorbent consumption via baghouse optimizations typically results in an operating cost savings. Studies have shown that sorbent consumption has been reduced by up to approximately 33% via baghouse optimizations which optimize filter cake duration on filter bags.[14,15]

2. Potential ESP Impacts

A dry ESP is a particulate control device used to capture particulate by charging the particles as they enter the ESP and collecting them on a grounded plate. The plates are cleaned by rapping on a timed basis.[13]

With the addition of DSI, particulate loading will increase and particulate composition will change. The impacts to ESP systems are described below.

When reviewing the impact of DSI on ESP outlet emissions, both the increased particulate loading and the new fly ash composition must be evaluated together. The ESP may be impacted by changes in particulate loading, particle resistivity, sulfuric acid inlet concentration and particle size distribution (PSD) changes experienced when injecting alkaline reagents with a DSI system.

DSI for acid gas control uses calcium or sodium-based sorbents. In general, calcium-based sorbents will increase the resistivity of the fly ash making the ash more difficult to charge and capture while sodium sorbents decrease the resistivity of the fly ash making the ash easier to charge and collect. The degree of change is directly related to the amount of sorbent injected. Additionally, in solid or liquid fuel combustion applications where fuel has significant sulfur content and low alkali content, most ESPs are expected to have significant free sulfuric acid vapor in the flue gas stream, which reduces the resistivity of the fly ash entering the ESP. Once the fly ash is less resistive, it is easier to remove from the flue gas stream. But, when DSI is applied for acid gas control, most, if not all, the sulfuric acid is removed.

Typically, sodium sorbents can compensate for the reduction in sulfuric acid by increasing the conductive sodium content of the ash, and thus not seriously affecting ESP operation. But calcium sorbents do not compensate for the loss of sulfuric acid, and, in the absence of offsetting quantities of any other conductive species such as conductive sodium sulfate, the increased CaO, $Ca(OH)_2$ and $CaSO_4$ content of the fly ash increases the ash resistivity. With the increased fly ash resistivity, the use of calcium sorbents may make the ESP operate less efficiently. The gross impact on particulate emissions will depend on the size of the ESP. For example, an ESP with a specific collection area (SCA) of 150 ft^2/1000 acfm at 12" gas passage spacing may experience problems, but an ESP with an SCA of 600 ft^2/1000 acfm at 12" gas passage spacing would not be seriously degraded.

Predictions of ESP performance can be made with DSI provided good baseline data on existing ESP design, fly ash resistivity, power, secondary current and voltage for each transformer-rectifier (T/R) set and ESP efficiency is known. This data, in combination with the expected new fly ash resistivity and the expected sulfuric acid concentration, is required. Typically, DSI trials are done to confirm if the ESP operation will be impacted. On industrial applications, it is even more important to consider trials, since predictive tools for fly ash resistivity and particle size distribution are not as well developed for combustion systems utilizing various coals as fuel or utilizing other solid fuels such as biomass.

If it is determined that the fly ash resistivity increases significantly and/or back corona occurs with the addition of DSI, then potentially the ESP power supplies can be upgraded to improve performance. Single-phase T/R sets can be upgraded to include the latest versions of automatic voltage controllers (AVC) with intermittent energization (IE) capability to manage the quenching of back corona. For handling higher ash resistivity, increased rapping will also assist in keeping the plates cleaner, and total useful power to ESP can be increased before back corona effects set in.

Alternatively, if the fly ash resistivity decreases using sodium-based reagents, and there is a need for greater PM removal, larger power supplies can be installed to increase ESP efficiency.

Depending on the DSI injection rate, the rapping frequency and high voltage sectionalization may need to be increased to keep the collecting and high voltage system components clean.

Corrosion in the system is similar to the baghouse and it would usually be reduced when injecting calcium and sodium-based sorbents for acid gas mitigation.

3. <u>Potential Ash Handling System Impacts</u>

Ash or byproduct handling systems may also be impacted by the use of DSI. It should be confirmed that the byproduct handling system, including the pump for fan pressures and capacities, can handle the additional loading associated with the DSI injection. Additionally, the composition of the collected particulate matter will change. The byproduct system supplier should be contacted and advised of the new composition to confirm the material used is appropriate. For example, is the hopper design appropriate for the new particulate characteristics? Is a heater needed? Is additional rapping or addition air required? Are the vacuum system fans capable of unloading the extra solids?

VI. Performance Impacts Related to the Capture of Non-Targeted Acid Gases

The Industrial Boiler MACT rule is a multi-pollutant standard. Acid gases are regulated under the Boiler MACT; HCl is the surrogate pollutant that must be measured to demonstrate compliance. SO_2 emissions may be regulated as a result of the Regional Haze Rule, the National Ambient Air Quality Standards (NAAQS) or even due to a consent order. SO_3 (H_2SO_4) emissions are not regulated at the federal level. However, some states have imposed standards on condensable particulate matter – largely sulfuric acid mist (SAM). Even though SO_3 emissions are not widely regulated, controlling SO_3 is often necessary. Fine H_2SO_4 aerosols scatter light efficiently. Low concentrations of SAM (5-10 ppmv) can be visible as a persistent plume, which is visible to the public. In addition, SO_3 in the flue gas reduces the effectiveness of activated carbon for Hg control, as discussed below.

As previously noted, the reactivity of the sorbents toward specific acid gases varies, but the following relationship is generally accepted: SO_3 > HCl/HF >> SO_2. The relative removals are different for different sorbents and, in fact, relative removals are also impacted by the specific conditions at the injection location.

As an example, enhanced hydrated lime products have demonstrated the capability to achieve greater than 95% SO_2 removal on industrial baghouse applications and greater than 80% SO_2 removal on utility ESP applications. [16,17] However, hydrated lime is less efficient at removing SO_2 at lower temperature injection locations. Accordingly, the amount of reagent required to capture a given acid gas will also be impacted by the reactions with other acid gases and the specific conditions at the injection location.

As an example, if targeting capture of either HCl or HF with hydrated lime, injecting at a lower temperature (such as 300-400 degree F) will limit the amount of reagent consumed by the reaction with SO_2 while still capturing high levels of HCl and HF as hydrated limes (both standard grade and enhanced hydrated limes) have demonstrated the ability to achieve greater than 90% HCl and HF removal in coal-fired applications.[18] Full-scale DSI testing on high HCl concentration application (i.e. medical waste incineration), in which enhanced hydrated lime was injected, demonstrated the capability to achieve over 99% HCl removal.[19] However, if targeting SO_2 in conjunction with HCl and/or HF with hydrated lime, injecting at a higher temperature would result in higher SO_2 capture performance. Hydrated lime has been shown capable of achieving greater than 95% SO_2 removal on some industrial applications.[19]

Sodium-based reagents have various injection temperature profiles. Sodium bicarbonate can be injected at temperatures similar to the favored hydrated calcium temperature profile. Trona is effective at injection temperatures up to 1,000 °F.

Sodium sorbents have the potential for high levels of SO_2 removal with sodium bicarbonate being somewhat more reactive than trona with respect to SO_2. Sodium bicarbonate has been shown to achieve greater than 97% SO_2 removal. Trona has been shown to achieve as high as 95% SO_2 removal.[20] Thus, if sodium sorbents are used for removal of HCl, higher levels of SO_2 reduction might be expected as compared to the use of hydrated lime for HCl removal. On the other hand, if high levels of SO_2 reduction are desired using DSI, sodium-based sorbents have been typically used. Recently, lime manufacturers have developed enhanced products, which are intended to have the ability to remove higher percentages of SO_2 than in the past.

In summary, the sorbents commonly used for acid gas control using DSI (trona, SBC, and hydrated lime) remove multiple acid gases from the flue gas (SO_2, SO_3, HCl, HF). Understanding all the acid gas constituents of the flue gas, and not just the targeted acid gases, is critical to determining the effectiveness of a DSI application.

VII. Potential Impacts of DSI Reagents on Capture of Mercury

Dry sorbents used for acid gas control can be beneficial or harmful to the mercury control effectiveness of emissions control processes. A harmful effect can occur when halogens in the flue gas are relied upon for oxidation of mercury. Either calcium or sodium-based sorbents can strip out or neutralize the halogens and thereby degrade or eliminate the oxidation of mercury.   This can have adverse effects on mercury control by particulate collectors, scrubbers, or activated carbons in which no oxidation capability has been designed (non-halogenated PAC). In addition, two acid gases have been observed to have adverse impacts on mercury capture by particulate collectors with or without standard PACs: SO_3 and NO_2. Where DSI removes SO_3 upstream of PAC, it can also preserve or enhance mercury capture effectiveness.[21] Where DSI is sodium-based and generates NO_2, it can adversely impact mercury capture effectiveness.[22] These adverse effects have been documented as described in the paragraphs below, and solutions have

been developed through both a PAC sorbent development approach and through design and placement of injection systems, as also described below.
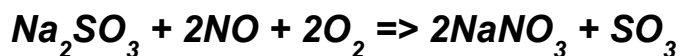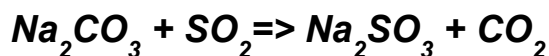
1. Halogen Scavenging

The ability to remove mercury from combustion gas is significantly impacted by the presence of halide gases like hydrogen chloride (HCl) and hydrogen bromide (HBr). The halogen component of these acid gases promotes oxidation of elemental Hg (Hg^0) to its divalent state (Hg^{2+}), which can then be easily removed with the injection of powdered activated carbon (PAC) into the flue gas stream. PAC can also be impregnated with halides as part of its formulation, having the same effect of oxidizing and then securely capturing the mercury. Some higher rank fuels inherently have high halogen concentrations, providing relatively high, averaging 80%, Hg oxidation in the boiler and downstream ductwork. Alternatively, lower rank coals can be deficient in native halogens, driving addition of supplemental additives onto the fuel prior to combustion or introduction of halogens directly at the point of capture, which is typically achieved by impregnation onto the PAC. Regardless of the halogen source, when DSI is introduced for acid gas control, the alkaline sorbents, whether calcium or sodium-based, will dramatically reduce the halogen content. Using halogenated PAC can solve this problem, and depending on the DSI configuration, may be sufficient to regain the needed mercury control.

2. Acid Gas Interactions

A second adverse impact is sometimes observed with sodium-based DSI sorbents. This impact has been attributed to NO_2 in the flue gas acting as an interference agent on the surface of the activated carbon, blocking mercury interactions and reducing sorbent effectiveness for mercury control.

There is a side reaction of sodium-based sorbents that can reduce concentrations of nitrogen oxide (NO) in the flue gas, but increase concentrations of NO_2. The result can be a small (less than 10%) reduction in total nitrogen oxides (NOx). After decomposition of SBC or trona to Na_2CO_3, Na_2CO_3 reacts with SO_2 to form sodium sulfite (Na_2SO_3). Nitrogen oxide (NO) reacts with sodium sulfite (Na_2SO_3) at temperatures less than 500°F. NO_2 is formed by the decomposition of sodium nitrate ($NaNO_3$).

$$Na_2CO_3 + SO_2 => Na_2SO_3 + CO_2$$

$$Na_2SO_3 + 2NO + 2O_2 => 2NaNO_3 + SO_3$$

$$2NaNO_3 + SO_2 => Na_2SO_4 + 2NO_2$$

The temperature range for this reaction pathway is 300°F to 500°F.[23]

Production of NO_2 by sodium sorbents doesn't happen at every DSI installation at a coal-fired boiler. Reaction kinetics, type of particulate control device (ESP vs. FF), and baseline NOx levels are important factors. One recent example, however, shows that NO_2 production with the injection of trona or sodium bicarbonate can interfere with Hg capture by PAC. Figure 2 shows NO_2 production at St. Clair Power Plant Unit 3 in which trona or SBC was injected upstream of the air preheater to control HCl emissions. The unit burned mixtures of Powder River Basin (PRB) subbituminous coal and Eastern

bituminous coal and had a cold-side ESP. The normal stoichiometric ratio (NSR) is relative to SO_2 in the untreated flue gas; that is, NSR represents the ratio of moles of Na_2 (from trona) to moles of SO_2.

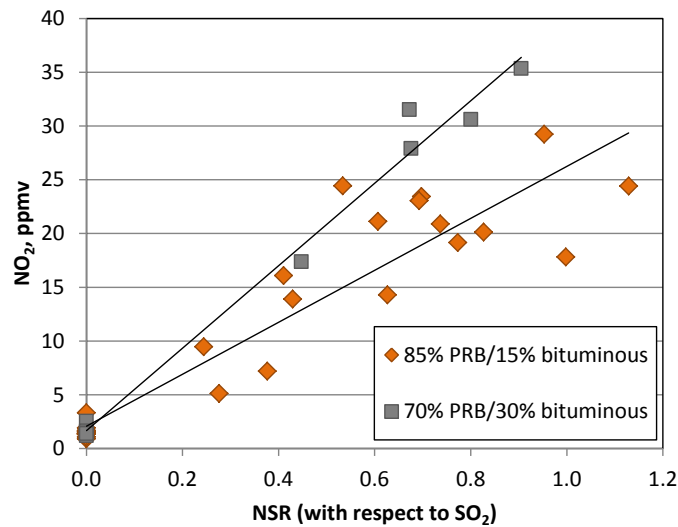**Figure 2. NO$_2$ measured in the stack as a function of NSR with respect to SO$_2$.[22]**

The potential reduction of NOx is small enough to be insignificant. However, the potential production of NO_2 can have a large impact on the performance of powdered activated carbon (PAC) for mercury control, as discussed in the section below.

Figure 3 shows data, also taken from St. Clair Unit 3, on stack mercury emissions. Non-brominated PAC was injected downstream of the air preheater, while sodium sorbent was injected upstream of the air preheater. Bromine was also added to the coal in these tests. When either trona or SBC was injected, mercury stack emissions increased significantly. Additionally, the NO_2 formed has the potential to create a visible brown plume.[24, 25]
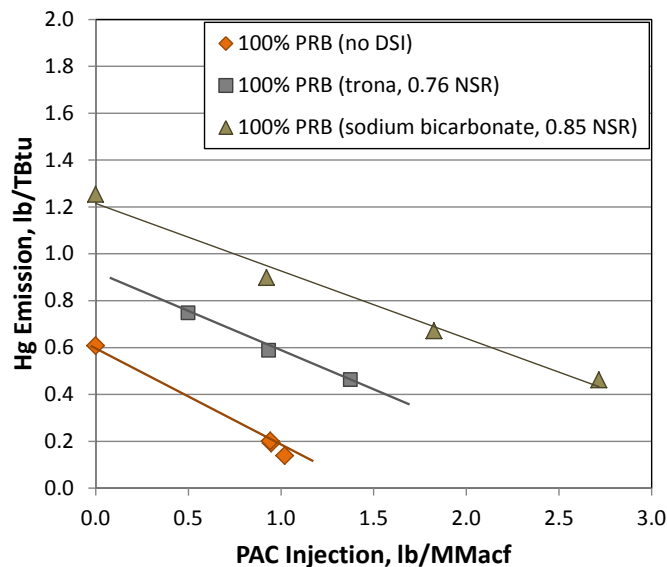

Figure 3. Mercury emissions as a function of non-brominated PAC injection rate with and without sodium DSI sorbents.[22]

This impact on non-brominated PAC performance has been seen at other sites with sodium-based DSI as well. One approach to improve the performance has been to modify injection locations and/or equipment design and another has been to modify the PAC formulation. Recent studies have demonstrated improved performance in the presence of sodium DSI by Generation 4 PACs.[26] For plants that require both DSI and ACI, the choice of where to inject the alkaline sorbent and the PAC depends on the specific configuration and fuel in use. Some considerations include: type of DSI sorbent used; uncontrolled SO_3 concentration in the flue gas; flue gas temperature at the particulate control device; and available residence time before the particulate control device. Manufacturers of sorbents and sorbent injection equipment should be consulted to find the best injection locations for specific sorbents.

The second acid gas interaction is with SO_3. In the presence of high levels of flue gas SO_3, interference with PAC mercury control effectiveness has been observed.[21,27] However, this can be mitigated by DSI when it removes the SO_3 upstream of the PAC injection location. Another approach is to utilize advanced PAC formulations designed for SO_3 tolerance. Successful testing of these technologies has brought performance back to required levels.[26, 28]

VIII. Potential Impacts on Process Byproducts

It is inevitable that the addition of DSI reagents will impact any process byproduct from your system in that the material will now be co-mingled with unreacted DSI reagents as well as with reaction compounds from the interaction with acid gases as outlined above in the DSI chemistry section. Whether these materials are currently being disposed or marketed, these impacts need to be considered.

In the case of calcium DSI reagents, the use of DSI will result in the byproduct containing $CaSO_4$, $CaCl_2$ and CaF_2 to the extent these acid gases are present in a given flue gas stream. When a sodium compound is utilized as the DSI reagent, the reaction compounds present include Na_2SO_4, $NaCl$ and NaF, in concentrations that depend on the acids present in the flue gas.

While there are other reaction products that can be formed, the reaction products above tend to dominate the behavior of the byproduct material produced. Experience suggests that the two primary properties impacted by the addition of unreacted DSI reagent and reaction products are solubility and metal leaching potential. These changed properties can impact the manner in which the resulting byproduct material can be utilized or responsibly disposed. A given facility should evaluate this impact on any byproduct material they produce. The general impact on each of these properties is discussed below.

1. Solubility Impacts
The solubility of a byproduct material is a critical parameter for materials destined for reuse or disposal. Accordingly, it is import to understand the relative solubility of the

reaction compounds. Below is a summary table of reaction product compounds as reflected in the CRC Handbook of Chemistry and Physics.

Table 1. Solubility in water of selected compounds.[29]

Reaction Compound	Cold H_2O Solubility*
Na_2SO_4	100
$CaSO_4$	0.21
NaCl	35.7
$CaCl_2$	74.5

*Grams per 100 cc H_2O

In the case of flue gas streams with chlorides as the primary acid gas, it would be expected that the use of sodium would result in somewhat less soluble byproduct materials as the solubility of NaCl is lower than that of $CaCl_2$. However, if there is sulfur in the flue gas stream, it would be expected that the solubility of byproducts impacted by sodium DSI reagents would be significantly higher than the byproduct alone or byproducts impacted by calcium reagent products since Na_2SO_4 is two orders of magnitude more soluble than Ca_2SO_4. Indeed, significantly higher solubility potential in the form of elevated total dissolved solids (TDS) at ground water monitoring wells has been noted by utilities using sodium DSI reagents.

2. Metals Leaching Potential
For most metals, leaching from byproducts is a function of pH. The addition of alkaline DSI reagents to a given byproduct material has the potential to increase the leaching of metals from a given byproduct material. While both calcium and sodium are strong alkaline materials and likely have this impact on metals leaching potential of byproducts, there is another mechanism in play with calcium reagents that impacts metals leaching potential. This additional mechanism is the pozzolanic reaction of the byproduct material driven by the addition of calcium.

Many byproducts, such as coal combustion residues (CCR), are pozzolans, which by definition are finely divided siliceous compounds that react with water and calcium hydroxide to form compounds that exhibit cementitious properties. Accordingly, when calcium hydroxide is used as a DSI reagent, some of the reagent that does not react with acid gases in the flue gas stream reacts with the pozzolan in the flue gas stream resulting in some metals being encapsulated in the process. In some cases, this cementing mechanism can offset the impact of the increased pH of the DSI material and reduce the metals leaching potential of some byproduct materials. An example of this behavior is illustrated in Figure 4 below where the 15% addition of $Ca(OH)_2$ does not increase the leaching of arsenic despite the increase in alkalinity. As sodium does not have the potential to drive this cementitious mechanism, metals leaching potential is inevitably increased when sodium DSI reagents are utilized. It should be noted that this effect of

pH impact will be different for every fly ash and, accordingly, it is recommended that a site specific evaluation be performed to determine the impact of DSI reagents on metals leachability for a given byproduct material.
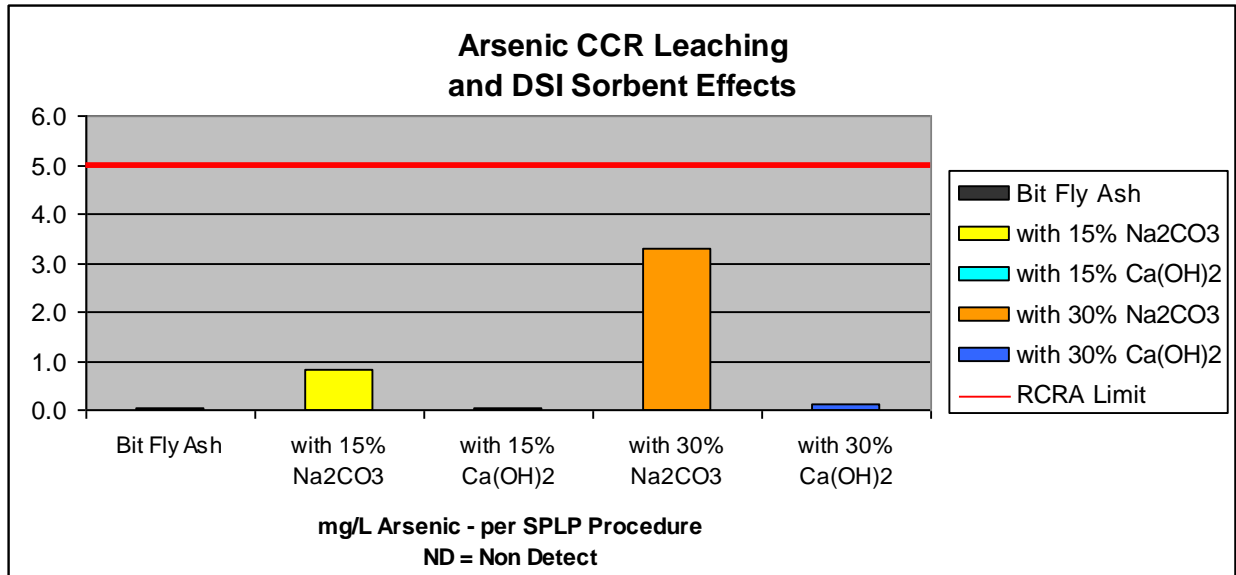
Arsenic CCR Leaching and DSI Sorbent Effects

Figure 4. Arsenic leaching from bituminous fly ash combined with DSI Reagents.[30]

In short, the impact of the use on any DSI reagent on an industrial process residue can have significant impacts on the overall cost of using a given control technology and should be considered. Many of these impacts can be assessed by taking samples of the residue during a technology trial and performing the appropriate analysis.

IX. Conclusion

DSI provides a low-capital-cost, resilient and flexible solution for control of primary acid gases, trace acid gases, and even enhanced mercury capture in some applications. It provides the significant advantage of effective turn-up and turn-down with actual unit load, fuel changes, and operational cycles. Like any air pollution control technology retrofit, careful consideration of many design parameters and the unit's specific operating profile and goals need to be taken into account during the design, installation and startup/optimization processes. There are excellent resources, including many ICAC companies, to assist with evaluating, implementing and optimizing DSI applications.

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