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Sodium Sorbents for Dry Injection Control of SO_2 and SO_3

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Outline

- Summary of Dry Sorbent Injection (DSI)
- Sodium sorbents
  - Trona
  - Sodium Bicarbonate
- How effective are sodium sorbents in mitigating SO_2, SO_3, NO_x, HCl, HF and Mercury?
- Parameters that impact the effectiveness of DSI
- Operating concerns and how to address them

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Dry Sorbent Injection

- Dry Sorbent Injection (DSI) is a low capital cost system to control SO_x and other pollutants.
- Requiring only a small footprint and limited operating equipment, DSI is a good fit for plants with limited space or uncertain future.
- DSI systems can be installed with very little service interruption
- Used for more than 20 years at power plants and industrial sites throughout the country, DSI has a long track record of economical compliance
- Good design practice can eliminate potential pitfalls

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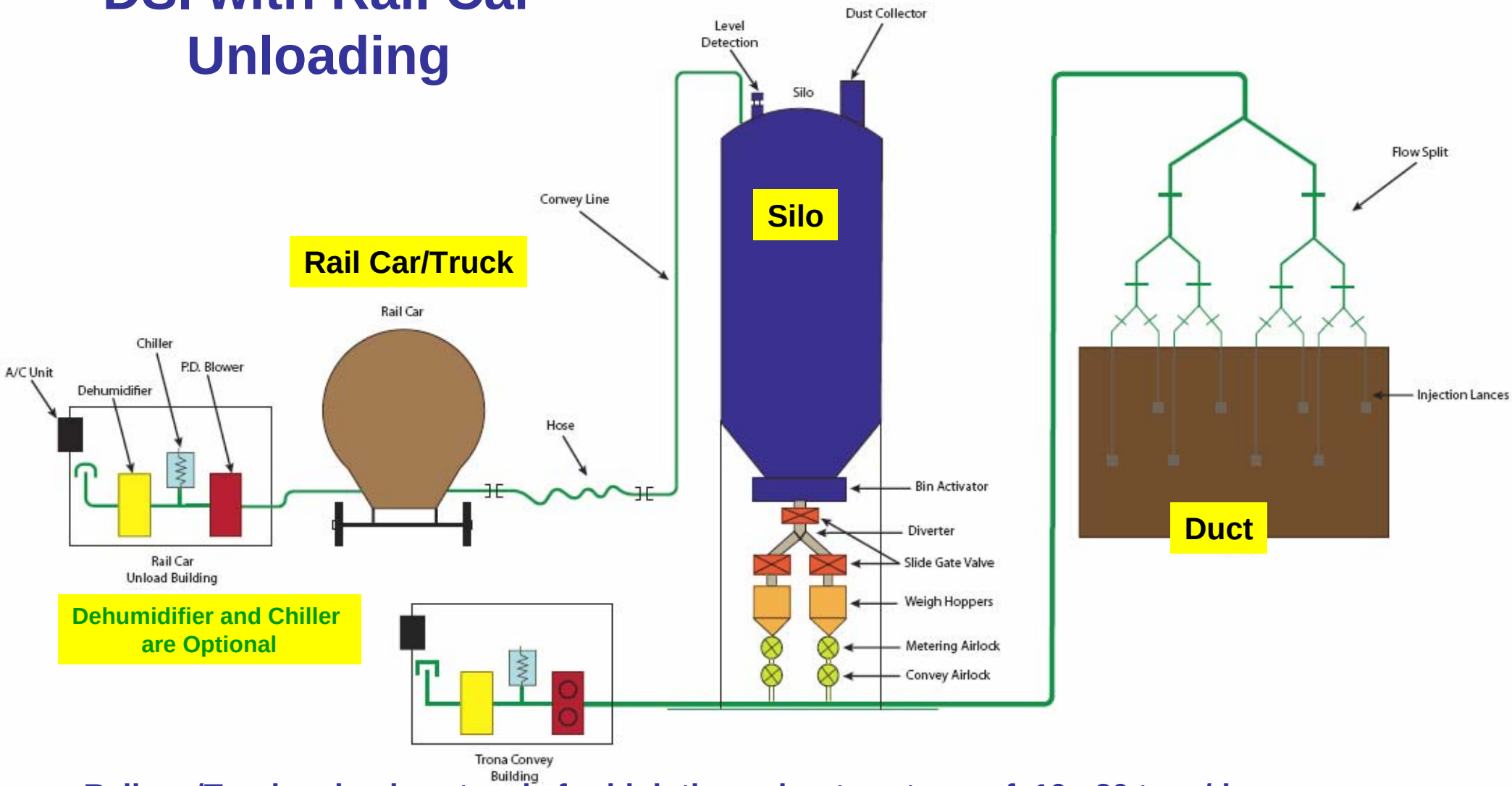
DSI with Rail Car Unloading



Rail car/Truck unload system is for high throughput systems of 10 - 20 tons/day or more

SOLVAir® Products
Solvay Chemicals, Inc

- Formed in 2005 to consolidate the activities of Solvay Chemicals in air pollution control
- Solvay Chemicals has sold trona for more than 20 years to the power industry and others for control of SO_2, SO_3, HCl, and HF
- Trona for air pollution control is marketed as SOLVAir® Select 200, formerly known as T-200 and is made in Green River, WY
- Sodium Bicarbonate for air pollution control is marketed as SOLVAir® Select SBC, a product made in Parachute CO, and SOLVAir® Select 300, made in Green River, WY starting in 2010

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What is Trona?

- It is a naturally formed sodium sesquicarbonate rock
  - (Na_2CO_3• $NaHCO_3$•$2H_2O$)
  - The Green River WY deposit is the largest and purest in the world
  - Over 17 MM tons of trona are mined each year in WY – hundreds of years remain
- Solvay processes this rock into a fine, dry powder
  - Average particle size (d_{50}) 30 – 35 microns
- Select 200 is very dry, typically less than 0.03% moisture
  - It is a good idea to keep it dry, wet trona is tough to handle.
  - Contact with water will cause problems.
- Select 200 can compact while stored
  - Often misinterpreted as wet
- Select 200 calcines to form sodium carbonate
  - Trona gives up water when it calcines
  - Calcination is time and temperature dependant, virtually instant at temperatures greater than 280°F

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Sodium Bicarbonate

- Sodium Bicarbonate is baking soda: $NaHCO_3$
- Bicarbonate is a downstream product made from Trona
  - More expensive
  - More reactive with SO_2
- Bicarbonate typically has to be milled prior to use
  - Milling on site to d_{90} less than 20 microns with direct injection gives the best results
  - SOLVAir offers a re-milled material with a d_{90} less than 40 microns
  - Storage and handling issues increase as d_{90} approaches 20 microns
- Used for many years to control acid gases
- For acid gases other than SO_2, trona may the lowest cost option.

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Usage Rates

Molecular Weight

Trona - 226 Bicarbonate - 84

SO_2 - 64 SO_3 – 80

Usage Rates – theoretical, NSR=1

2 moles **Trona** for every 3 moles **SO_2** or 452/192 = **2.35**

2 moles **Trona** for every 3 moles **SO_3** or 452/240 =**1.88**

2 moles **SBC** for every mole of **SO_2** or 168/64 = **2.62**

To calculate the amount of sorbent required, all acid gas must be accounted for.

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Performance Curves

Data generated from dozens of tests and installations with widely varying operating conditions. Field trials recommended to determine performance at any new site. Results higher and lower than shown have been seen -actual results will vary.

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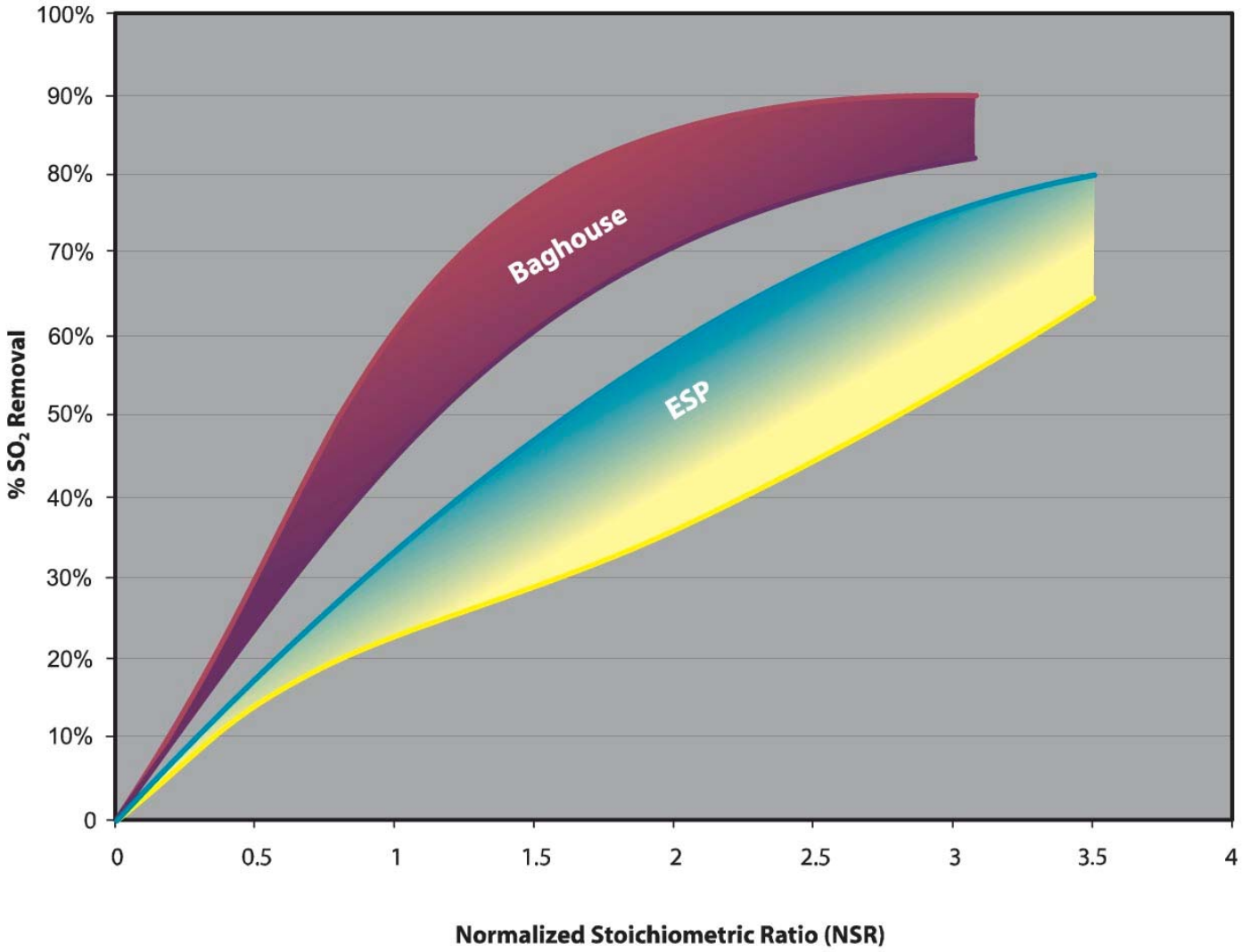
Performance of Trona in SO_2 Mitigation



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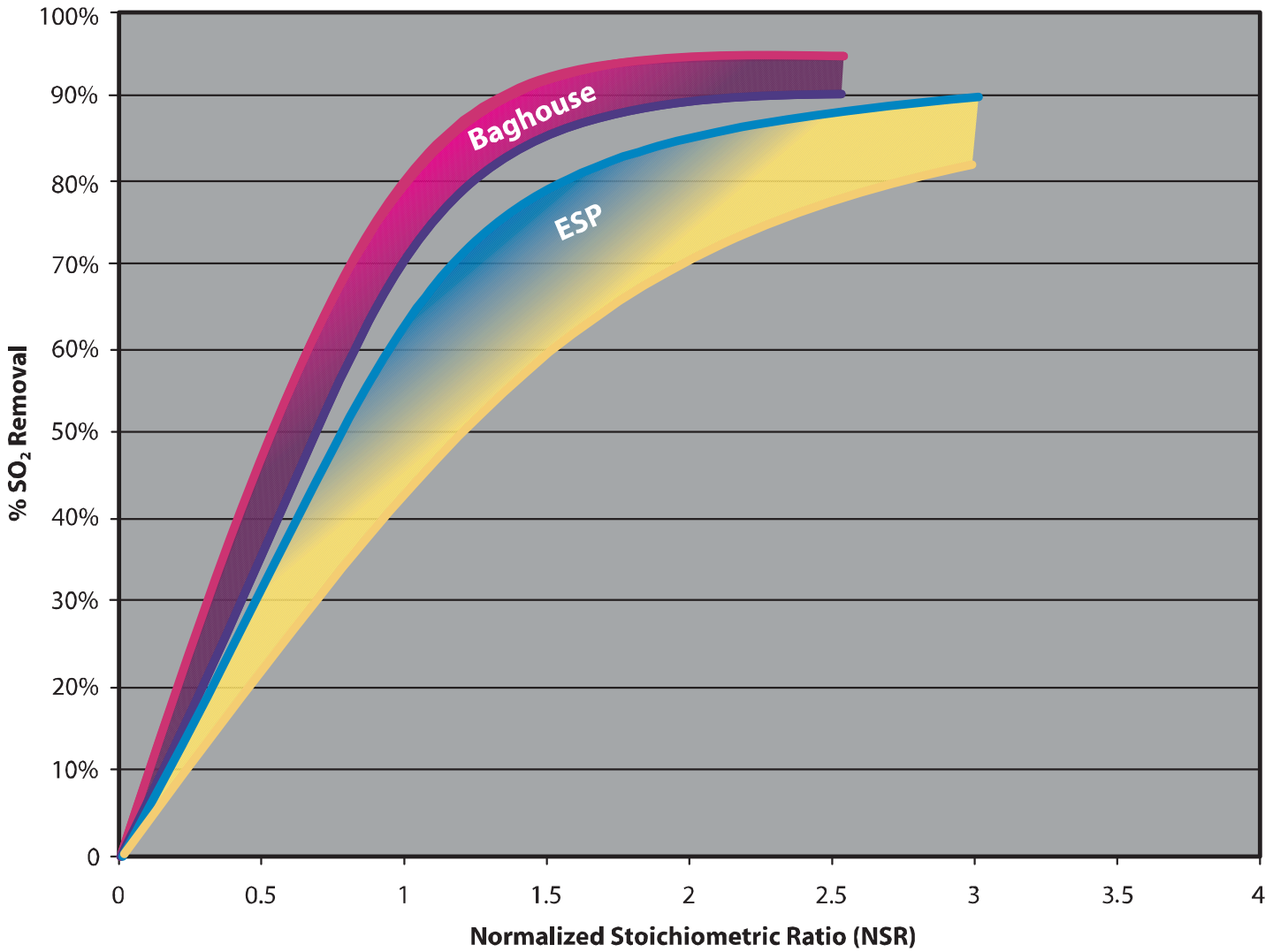
Performance of Sodium Bicarbonate in SO_2 Mitigation



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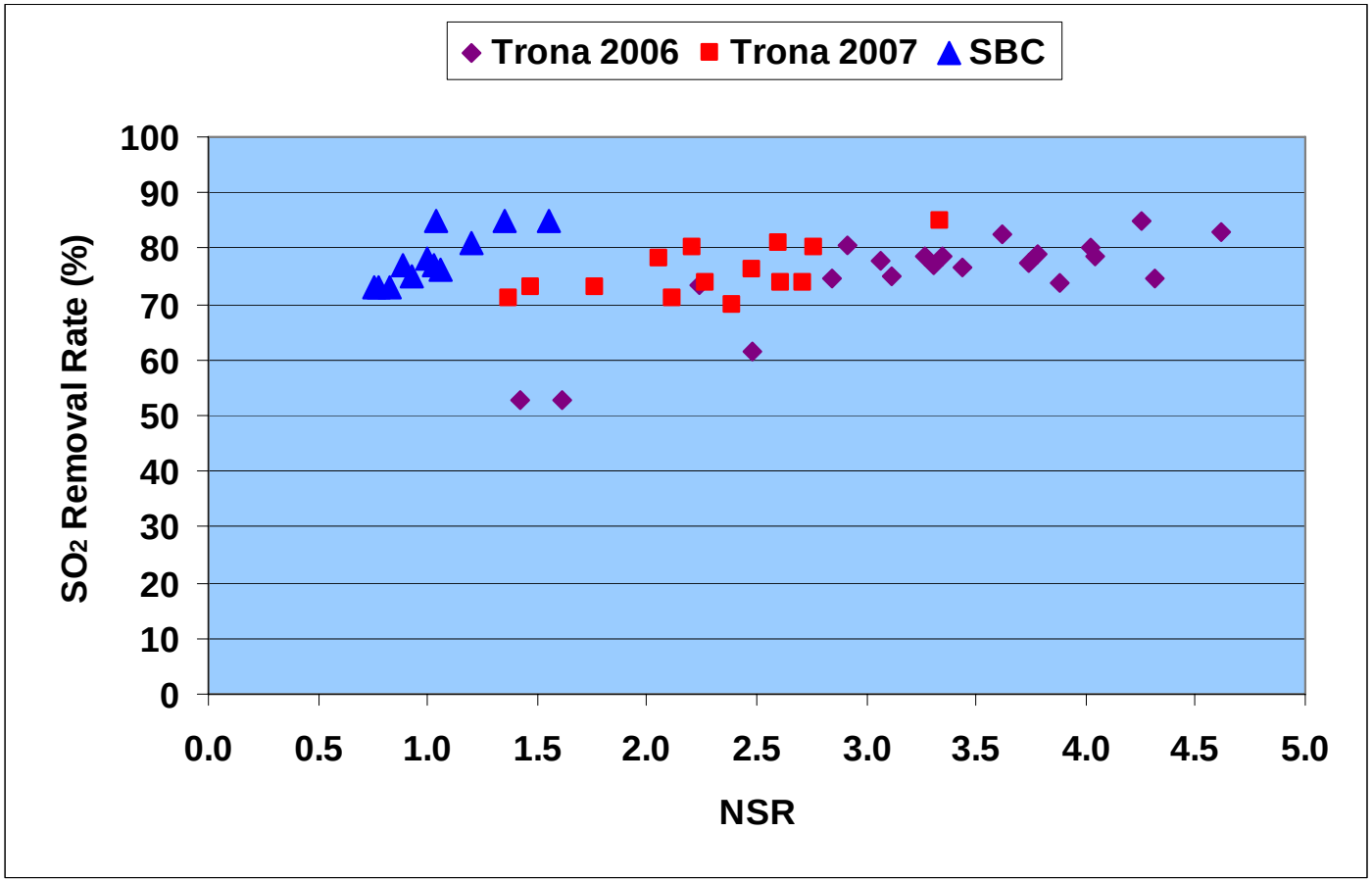
Comparison of SO2 Removal Rates with Trona (unmilled) and Sodium Bicarbonate (SBC) (milled)



- The 2006 data was obtained during a test using a temporary set up.
- The 2007 trona data was generated from a permanent installation
- Unmilled trona: d_{90} = 140 µm; milled SBC: d_{90} < 40 µm

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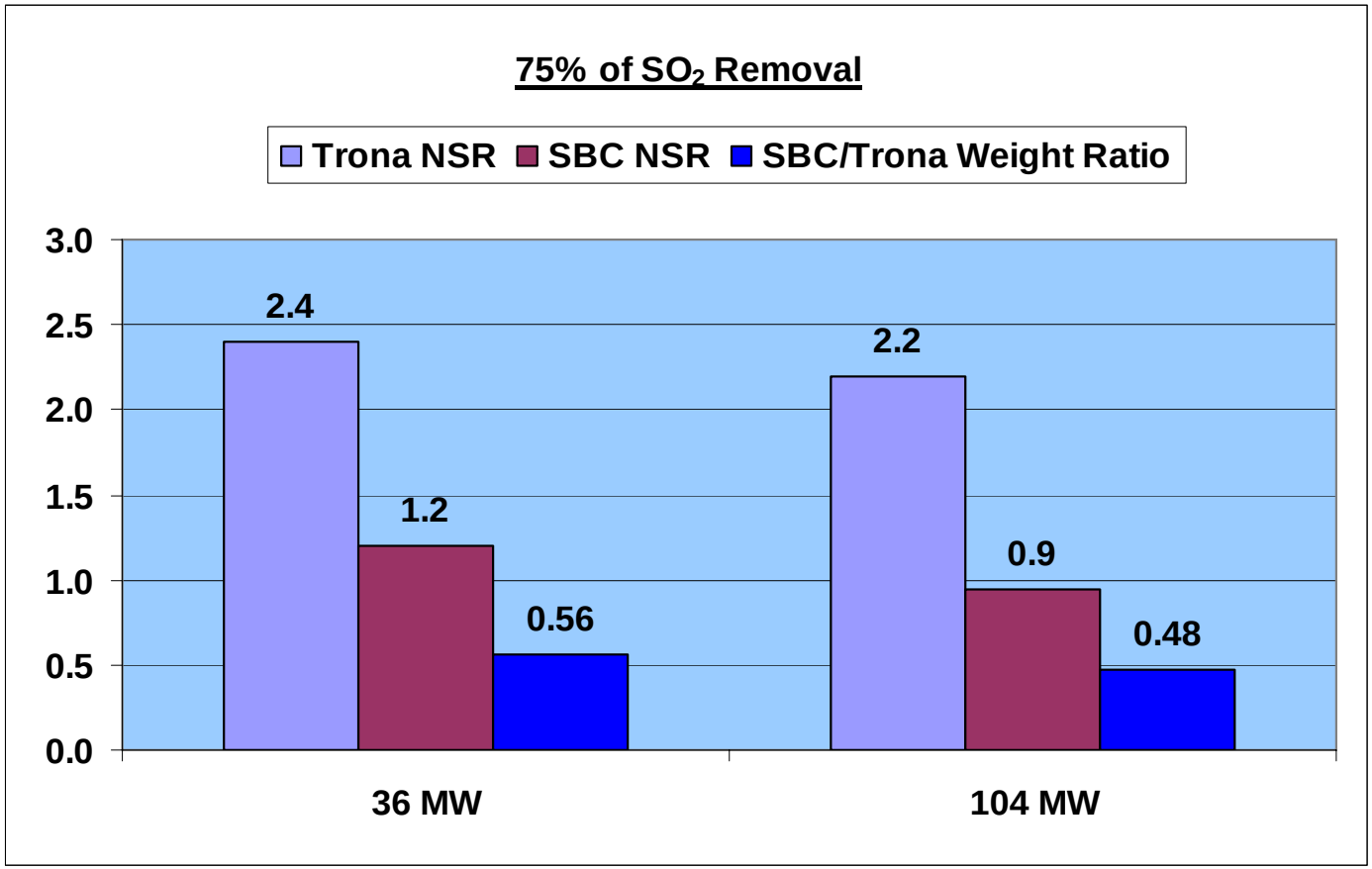
Comparison between Trona and SBC* at Different Loads



* Unmilled trona: d90 = 140 µm; milled SBC: d90 < 40 µm

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SO_2 Control
Bicarbonate vs. Trona

- **Trona and Sodium Bicarbonate are effective at removing SO_2**
- **Sodium bicarbonate may be more economical to use for SO_2 than trona when the following situations exist**
  - An ESP is the particulate control device
  - Higher SO_2 removals are required
  - Injection is after the air heater
    - Bicarbonate needs less than 800ºF
  - On site milling is available
  - Freight costs are high
  - Fly ash disposal costs are high
- **Use of sodium sorbents results in higher sodium content in the fly ash.. In most cases, the use of sodium for SO_2 control precludes the beneficial use of fly ash. The customers should check the fly ash properties before determining appropriate applications or disposal**

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Control of SO_3, HCl, HF, NO_x

- Sodium sorbents are very effective in the control of SO_3, HCl, HF
- Trona is very effective and normally is used for SO_3 control
- SBC may be used for HCl or HF if very high removal rates are required
- Byproducts are non-corrosive and easy to handle
- SO_3, HCl, HF react faster than SO_2 and as such, are typically eliminated first. Stoichiometric ratios of 1 – 1.5 are the norm
- It is possible to control SO_3 without reacting much with SO_2 making sodium sorbents ideal for eliminating the blue plume that can occur after SCR installation
- Removal rates of over 98% of HCl and HF have been demonstrated
- Reduction of 10 – 20% of NO_x is typically seen as a side benefit when SO_2 removals are at a high rate. Sodium sorbents are not considered a treatment system for NO_x

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Mercury Control

- It is well documented that the presence of SO_3 interferes with mercury capture, native or with PAC injection
- Trona eliminates SO_3
- Removal rates of up to 80% Hg have been seen with trona injection alone
- Trona injection can enhance performance of PAC
- Depending on the injection point, BPAC may have to be used if additional Hg must be captured

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The Bisulfate Concern

- In a sodium starved environment, trona may not completely react to sodium sulfate and instead sodium bisulfate could be formed. This may be seen when controlling SO_3 in a high SO_2 environment
- Sodium bisulfate, if formed, may condense in the air heater and can lead to pluggage problems
- Increasing trona dose decreases the amount of sodium bisulfate formed as the reaction is no longer sodium starved
- Proper dosing into the duct to avoid localized distribution problems is important
- Trona can be added at higher temperatures to avoid bisulfate formation

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Se and As

- Sodium sorbents have an affinity for Se and As
- If present in the coal in significant amounts, Se and As may be captured when using sodium sorbents
- The more sodium that is used, the higher the likelihood of capture
- If Se or As is captured from the flue gas, it will land in the fly ash, which may cause permit limits to be exceeded
- More representative sampling of the fly ash will discern if there is a problem
- More efficient application of the sodium will result in lower Se or As
  - **Mill the sorbent to reduce the usage**
  - **Improve the distribution system in the duct**
  - **Switch from trona to sodium bicarbonate**

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Fly Ash Considerations

- Higher sodium content in the fly ash.
- Ashes from SO_2 treatment typically not suitable for applications in concrete or structural fill
- When used for SO_3 control, the amount of sodium added may not be a significant amount to affect the fly ash
- Solubility of sodium compounds in the fly ash (i.e. Na_2SO_4, Na_2CO_3)
- Disposal issues should be investigated early in the process.
- Customers encouraged to check properties and work closely with their fly ash marketers.

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Equipment Design

Silo – trona, milled sodium bicarbonate

- 70º Cone on the silo if no external force used
- Vibrating bottom desirable
- Any pulsed air jets or air pads must use instrument quality air
- Avoid protrusions inside the silo, bolted silos are not recommended

Silo – unmilled sodium bicarbonate

- Sodium bicarbonate, is relatively free-flowing
- Vibrating bottom desirable

Transfer system

- Conditioned air for unloading can be helpful but not required
- Avoid sharp turns - elbows preferable designed with 10 - 12 pipe diameters in radius.
- Ideal relative humidity is below 40% for transfer to storage - not important at injection
- Temperature of transfer air should be kept below 140ºF especially if transfer line and contact time is long

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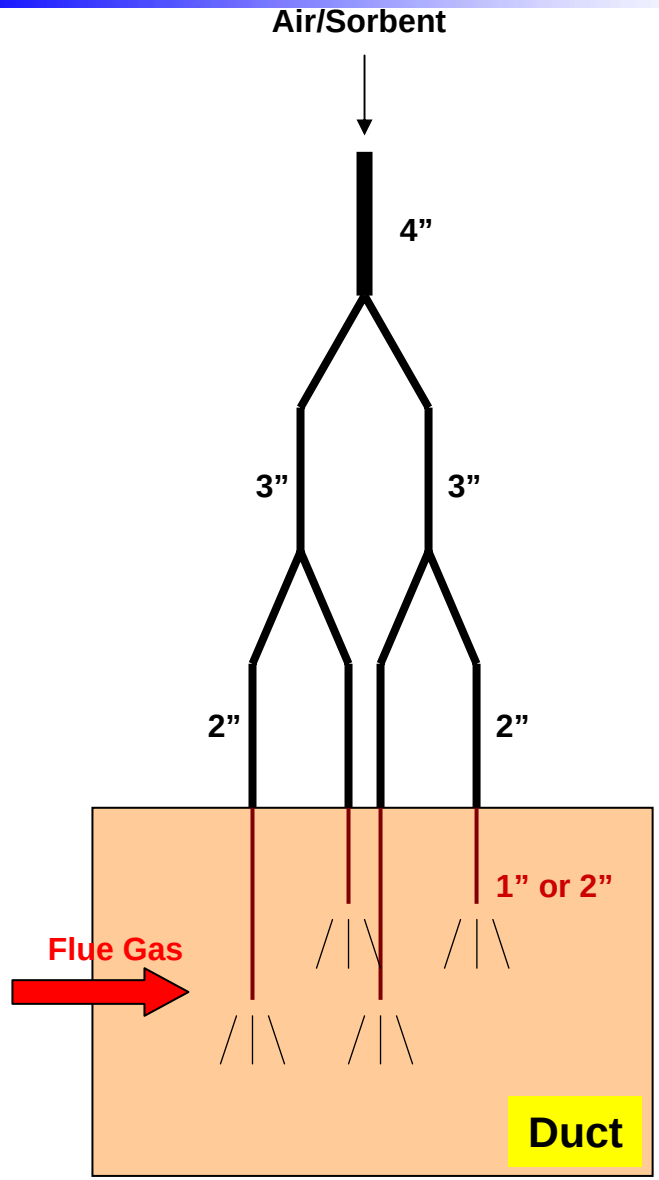
Injection System

- Injection lance assembly should distribute sorbent evenly across the duct.
- If more than 8 – 10 injection points are required, a second convey system should be considered.
- A CFD analysis of the proposed duct injection point will indicate the best possible lance layout.
- Lances can be designed to penetrate the duct to different depths, and can also have a staggered arrangement.
- Lances should be stainless to hold up to acid gas corrosion.
- Ceramic nozzles can give longer resistance to wear and corrosion but are not necessary.



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Summary

- **Dry Sorbent Injection of trona or sodium bicarbonate is a cost effective way to mitigate acid gas emissions.**
  - Low capital
  - Compatible with ESP and Baghouses. Because of the positive effect sodium has on the resistivity of particles, trona or sodium bicarbonate can actually enhance ESP performance.
  - Effective over a wide temperature range (275^0F - 1500^0F)
- **Sodium bicarbonate is more effective than trona in mitigating SO_2, especially in the case of high removal requirements using a cold side ESP**
- **Pluggage and handling issues can be avoided with proper design**
- **Use of sodium sorbents results in higher sodium content in the fly ash.**
- **Additional information and case studies can be found at www.solvair.us**

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Thank You

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