

# **INVISTA DBA Dibasic Acid**

For Flue Gas Desulfurization November 17, 2010



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- Subsidiaries of Koch Industries, Inc. acquired INVISTA from DuPont in 2004 and combined it with KoSa



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# Role of INVISTA DBA in flue gas desulfurization (FGD)

- Organic acid additives have been successfully used in coal-burning power plant wet scrubbers since the 1980's
- Drivers for the use of DBA in FGD Systems
  - Regulatory compliance
  - Reduce cost (maintenance, energy, capital)
  - Flexible fuel strategy
- Organic acid additives such DBA offer:
  - Improved scrubbing efficiency & operational flexibility
  - Improved reliability
  - Reduced operating cost



### Utility of DBA additive in FGD systems

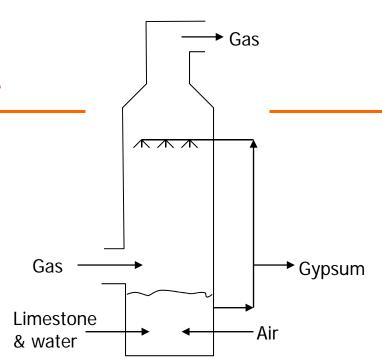
- **Retrofit** to existing wet scrubbers
  - Improve performance
  - Overcome design limitation
  - Increase operational flexibility
  - Technology of choice for retrofit applications
- Original equipment for new wet scrubbers
  - Reduce capital cost (minimize the amount of overdesign necessary to ensure meeting SO<sub>2</sub>-removal requirements)
  - Increase SO<sub>2</sub> removal efficiency (95% +)
  - Increase limestone utilization or use lower-grade limestone
  - Reduce coal cost
  - Reduce maintenance cost
  - Contingency planning for spray header or recirculation pump problems



# Limitations of wet limestone scrubbers

- Dissolved limestone provides liquid-phase neutralizing capability (LOW solubility)
- At high pH, SO<sub>2</sub> dissolves and is rapidly neutralized
  - Neutralization of SO<sub>2</sub> consumes liquid-phase neutralizing capability
- Rapid depletion of neutralizing capacity at surface of droplet
  - Replenished more slowly by diffusion of dissolved reagent from interior of droplet to the surface
- Depletion of dissolved reagent from interior
  - Limited replenishment due to low solubility of limestone and slow dissolution rate
- When dissolution of limestone cannot keep up with consumption of liquidphase neutralizing capacity, pH drops and SO<sub>2</sub> adsorption slows





### Chemistry of wet limestone scrubbers (simplified)

#### Without DBA

 CaCO<sub>3</sub> (limestone) is virtually insoluble, but dissolves to provide a small amount of SO<sub>2</sub>-neutralizing capacity

 $CaCO_3(solid) \implies CaCO_3(aq)$ 

 $SO_2(g) \implies SO_2(aq)$ 

 $SO_2(aq) + H_2O \implies H_2SO_3$ 

$$H_2SO_3 + CaCO_3 \longrightarrow CaSO_3 + H_2O + CO_2$$

CaSO3 + Air → CaSO4

- Liquid-phase neutralizing capacity is depleted by SO<sub>2</sub> neutralization
- Rate of replenishment depends on limestone dissolution
- When LS dissolution cannot keep up with SO<sub>2</sub> neutralization, pH drops and SO<sub>2</sub> scrubbing stops

#### With **DBA**

- DBA "predissolves" limestone.
- CaDBA is soluble and provides much more SO<sub>2</sub>-neutralizing capacity than limestone alone

 $CaCO_3 + DBA \implies CaDBA + CO_2 + H_2O$ 

 $SO_2(g) \implies SO_2(aq)$ 

 $SO_2(aq) + H_2O \implies H_2SO_3$ 

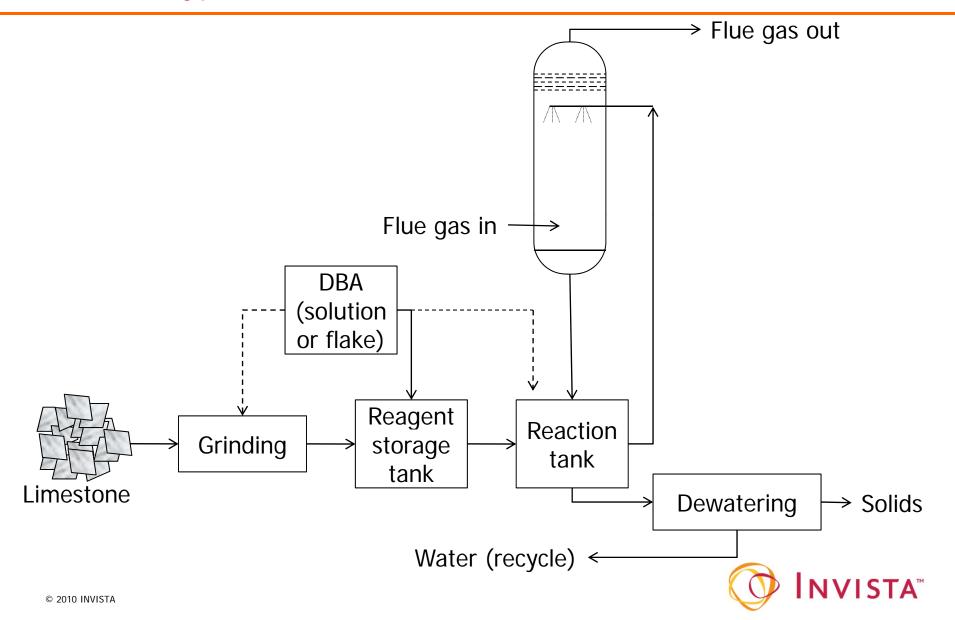
 $H_2SO_3 + CaDBA \longrightarrow CaSO_3 + DBA$ 

 $CaSO_3 + Air \longrightarrow CaSO_4$ 

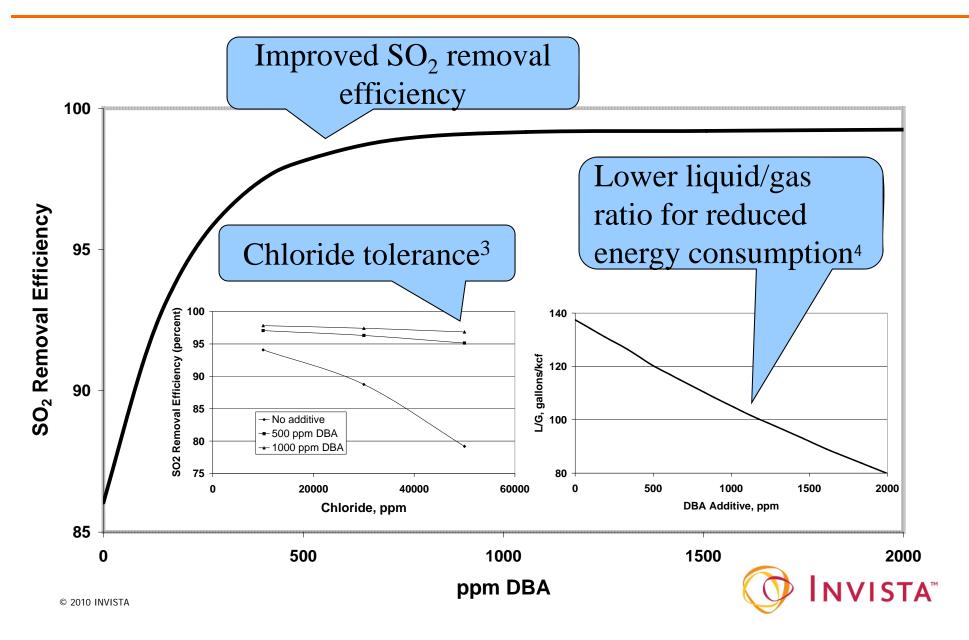
- More liquid-phase neutralizing capacity is available for SO<sub>2</sub> neutralization
- Rate of replenishment is increased
- pH does not drop as much, so SO<sub>2</sub> scrubbing efficiency is improved



#### Typical FGD unit with DBA addition



#### Typical benefits of DBA on FGD scrubber



# Potential DBA benefits to FGD (on Large Utility Boilers)

Parameter	Wet Scrubber on Large Utility Boilers <i>without DBA</i>	Wet Scrubber on Large Utility Boiler <i>with DBA</i>
SO <sub>2</sub> Removal efficiency	80-90% (typical)	<b>90-98%</b> <sup>1</sup>
Limestone consumption	Increasing limestone feed to improve SO <sub>2</sub> removal may result in poor limestone utilization.	Improved SO <sub>2</sub> removal may reduce the need for excess limestone and improve limestone utilization.
Gypsum quality	Standard FGD solids	Higher purity at no additional cost
Solids disposal (non-gypsum producers)	Typical FGD solids	Less solids and lower disposal cost due to better limestone utilization
Slurry recirculation energy	Increasing liquid/gas ratio to improve SO <sub>2</sub> removal may increase energy use.	Improved SO <sub>2</sub> removal may allow operation at lower liquid/gas ratio, reducing energy use
Scaling and plugging	Scaling and plugging may cause downtime and reduced removal efficiency.	Reduced scaling and plugging may result in less downtime and improved removal efficiency
Chloride inhibition	Buildup of chloride reduces limestone utilization and scrubbing efficiency	Higher efficiency even at high chloride
Fuel (i.e. coal) selection	Choice of fuel may be limited by emission constraints	Improved SO <sub>2</sub> removal may allow wider range of fuel options

The DBA benefits described above are a general summary of modeling and industry experience. Actual benefits will vary with individual scrubber and operational parameters.

1 – Percent reduction will depend upon FGD scrubber design and individual unit operational parameters. © 2010 INVISTA



### **DBA** consumption

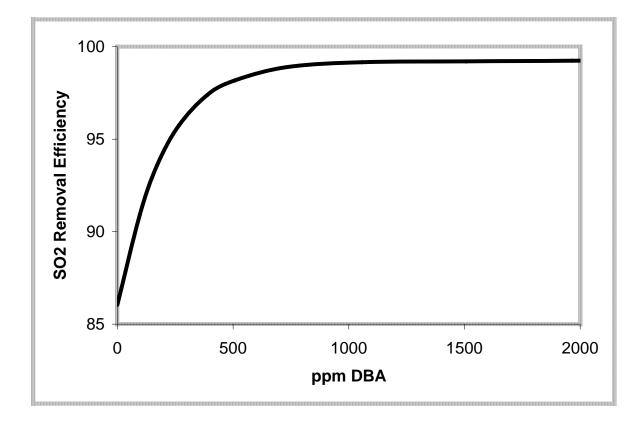
#### DBA is slowly depleted through several different mechanisms:

- Slow oxidation (chemical degradation)
  - Oxidation and decarboxylation
  - Some oxidation products remain functional
- System purges (blow down)
- Co-precipitation with solids in natural or inhibited oxidation scrubbers
  - Not significant with forced oxidation
- Solution losses (process liquor entrained with solids)

The dominant mechanism(s) will be determined by mode of operation of the FGD unit



### Testing DBA in FGD scrubbers



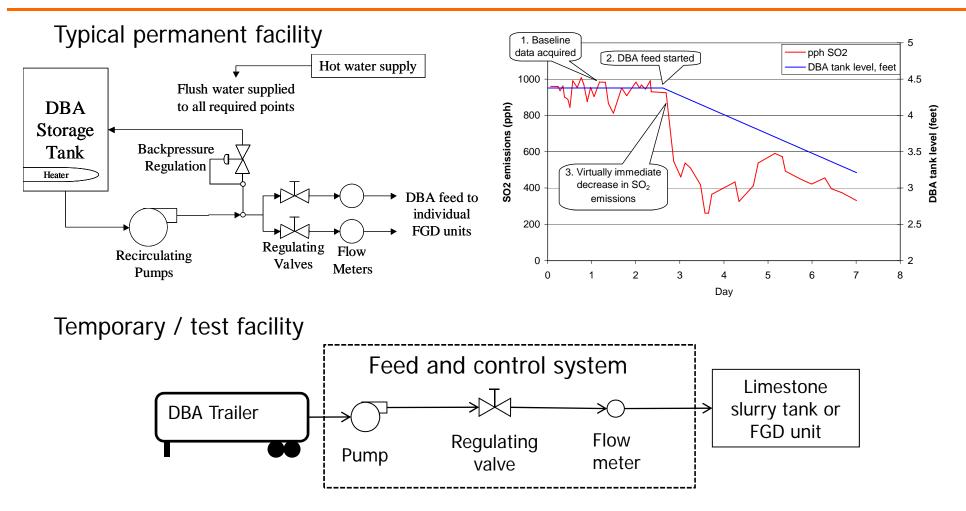
The shape and curve will be unique for each scrubber and must be determined by testing.



- People and time (motivated site advocate, support services)
- Regulatory (e.g. potential impact on air and water permits)
- Aversion to change (potential disruption to operations, concern about gypsum quality, new chemical, uncertainty about DBA benefits)
- Cost (of testing, equipment and additive)
- Misalignment of corporate and site objectives (e.g. corporate goal to minimize overall SO<sub>2</sub> compliance costs vs. site goal to minimize site operating expenses)
- Implementation lack of physical facilities to store and meter DBA into system
- Lack of large scale testing facilities (i.e. no DBA storage tank)



# DBA addition and testing concepts

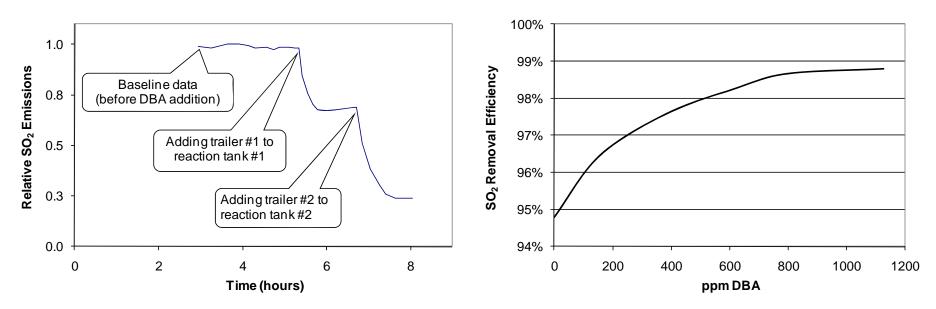


• Transfer lines electrically heated to prevent DBA crystallization



### Temporary facility for testing DBA

- DBA added directly from trailer to two scrubber reaction tanks to obtain a concentration of approximately 1200 ppm in scrubber
- The response was immediate. Performance was monitored as DBA concentration declined to develop efficiency curve



\*\* As each scrubber is unique, it is important to run a test to determine scrubber performance as a function of DBA concentration in the scrubber



#### Wastewater issues<sup>6,7</sup>

#### • Highly site specific

- Some sites are "zero discharge" no issue
- Others have varying outfall requirements (BOD, aquatic tox., etc.)
- DBA is an organic diacid and contributes toward BOD / COD
  - DBA is "readily biodegradable" the most easily degradable class
  - Some degradation occurs in the scrubber and downstream equipment
  - Activated sludge, ponds, wetlands are all effective bio-oxidizers to varying degrees
- Studies to date show no adverse effect on Se removal by biotreatment at DBA levels up to 2000 ppm in the waste water<sup>7</sup>
- Several specialized firms can assist with wastewater treatment issues



# INVISTA DBA supply update

- September 2008
  - Hurricane IKE hits Texas gulf coast near Galveston
  - Extensive flooding forces shutdown and damages INVISTA's Orange, TX facility
- 2009-2010
  - INVISTA repositions global adipic acid business for world-class competitiveness and growth
- First quarter 2011
  - INVISTA anticipates re-start of the Orange, TX adipic acid facility



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### INVISTA DBA

- INVISTA can provide free trial quantities of DBA solution contact us for details
- Technical documents available on request include:
  - DBA shipping and handling guidelines for flue gas desulfurization
  - Measurement of buffer capacity of FGD scrubber liquid
  - Testing INVISTA dibasic acid (DBA) in wet scrubbers
  - DBA in FGD brochure
- If you face any hurdles planning your trial, please call us. INVISTA may be able to help!

Contact Us: 1-800-231-0998 www.dba.invista.com





#### References

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- 7. ABMet Biological Selenium Removal from FGD Wastewater. Jill Sonstegard, Tim Pickett, Zenon Environmental (includes the former Applied Biosciences Corp) Official Proceedings - International Water Conference (2005), 66th, IWC.05.72/1-IWC.05.72/5. Available from www.eswp.com.

