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**2013 APC Round Table  
& Expo Presentation**

**July 8-9, 2013, in St. Louis, MO / Hosted by Ameren**

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Advancing **Cleaner** Energy

# Dry Sorbent Injection Impacts on Hazardous Air Pollutant Metals

Connie Senior

Air Pollution Control Conference  
July 8-9, 2013  
St. Louis, Missouri

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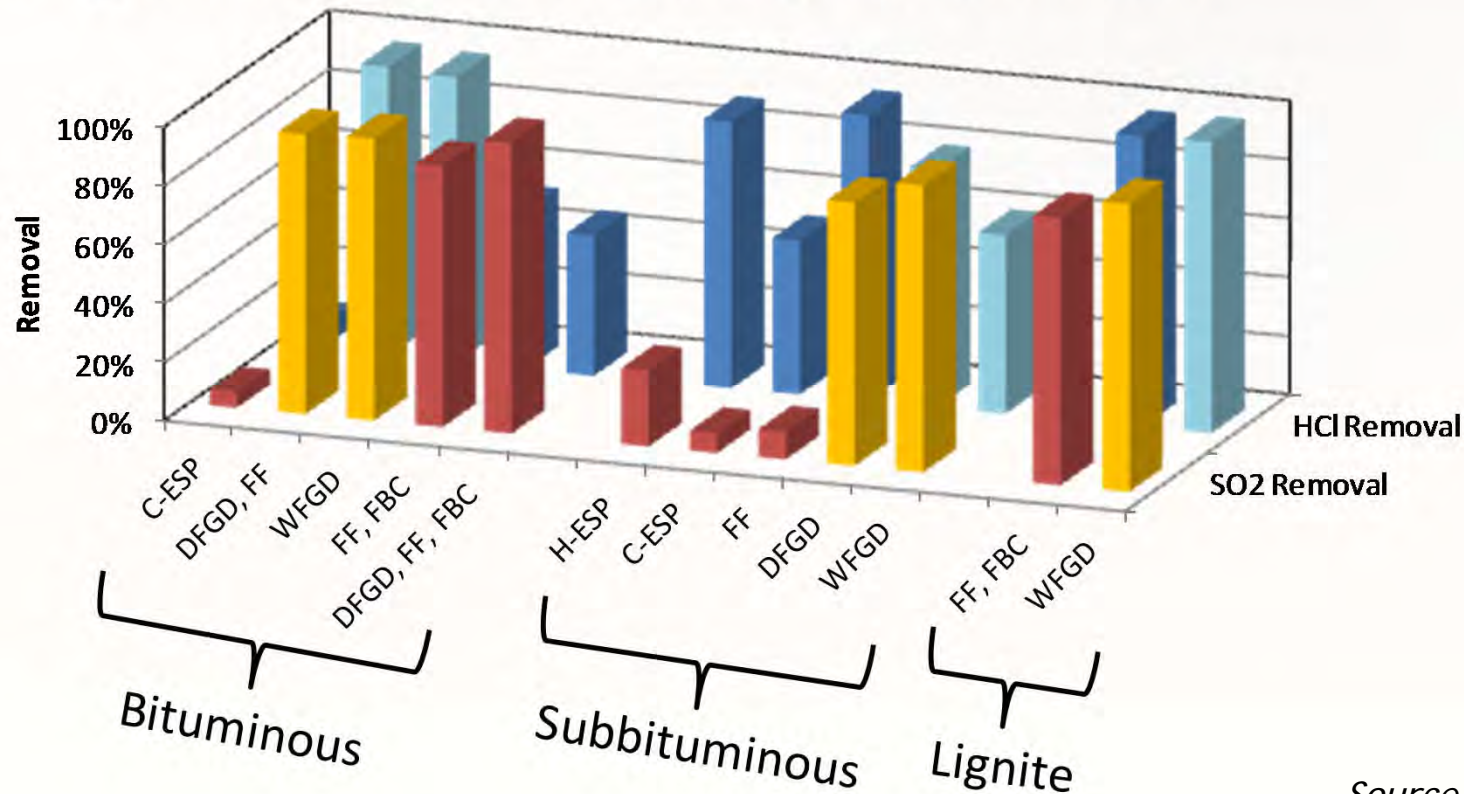
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## Workshop Outline

- ▶ What is DSI?
  - A brief process overview
  - Sorbents used
- ▶ Fate of certain metals in coal combustion boilers
  - Focus on mercury, arsenic, and selenium
- ▶ Interaction between selected metals and DSI sorbents
- ▶ Leaching of metals from DSI-fly ash mixtures
- ▶ Summary

# Control of Acid Gases

- ▶ Wet or dry scrubbers remove SO<sub>2</sub> and HCl with high efficiency
- ▶ SO<sub>3</sub> not removed efficiently by wet FGDs



Source: 2010 ICR data

# Control of Acid Gases

- ▶ Wet or dry scrubbers removal  $\text{SO}_2$  and  $\text{HCl}$  with high efficiency
- ▶  $\text{SO}_3$  not removed efficiently by wet FGDs
- ▶ Scrubbers are not always the answer, e.g.,
  - Older, smaller boilers can't afford to install high-capital cost equipment for  $\text{SO}_2$  control
  - If a scrubber is not needed for  $\text{SO}_2$  removal, adding one for  $\text{HCl}$  control is an expensive option
  - $\text{SO}_3$  isn't removed efficiently by wet FGDs, causing persistent and visible plumes
  - Too much  $\text{SO}_3$  in flue gas upstream of particulate control device interferes with ACI

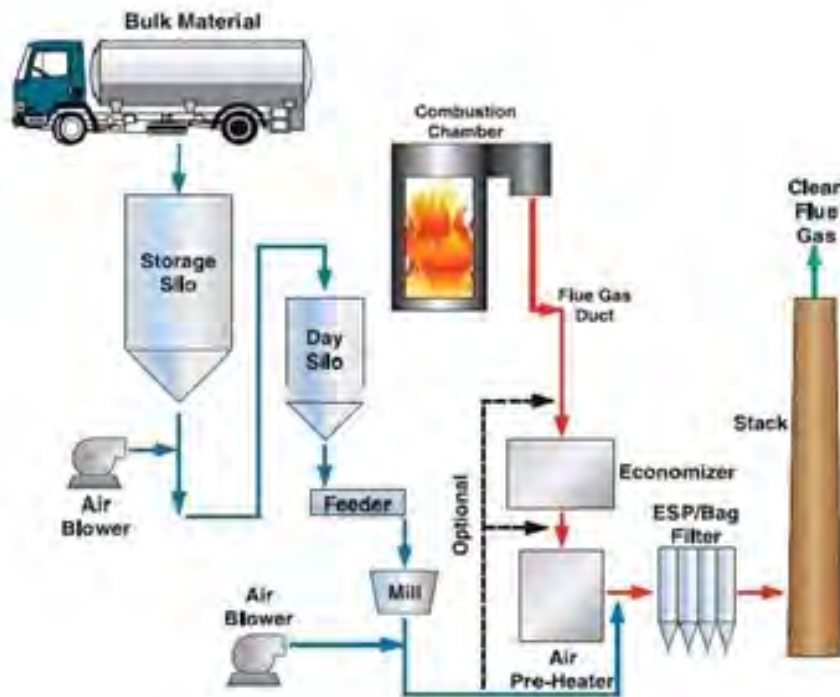
# Control of Acid Gases

- ▶ When adding a scrubber is not an option, Dry Sorbent Injection (DSI) may be considered
- ▶ What do we mean by DSI?
  - Injection of alkaline sorbent into the flue gas, anywhere from SCR inlet to scrubber inlet
- ▶ Various alkaline sorbents have been used
- ▶ Sorbent properties and sorbent dispersion critical to achieving high utilization of the sorbents

# DSI Injection System

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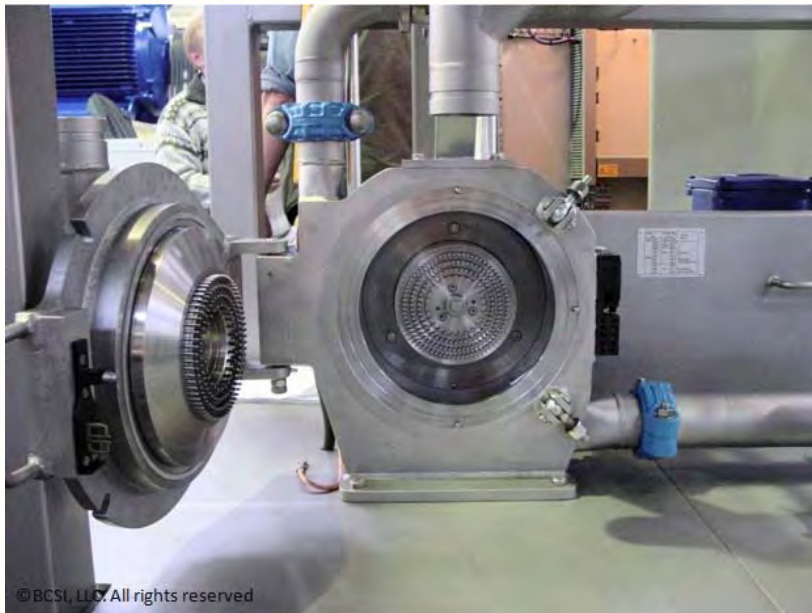
Typical Dry Sorbent Injection System



- ▶ Solids Island
  - Storage Silo
  - Feeder
  - Milling (optional)
- ▶ Air Island
  - Motive Air
  - Conditioning System
- ▶ Distribution System
  - Piping
  - Distribution Manifold and Lances

# DSI Injection System

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  - Milling (optional)



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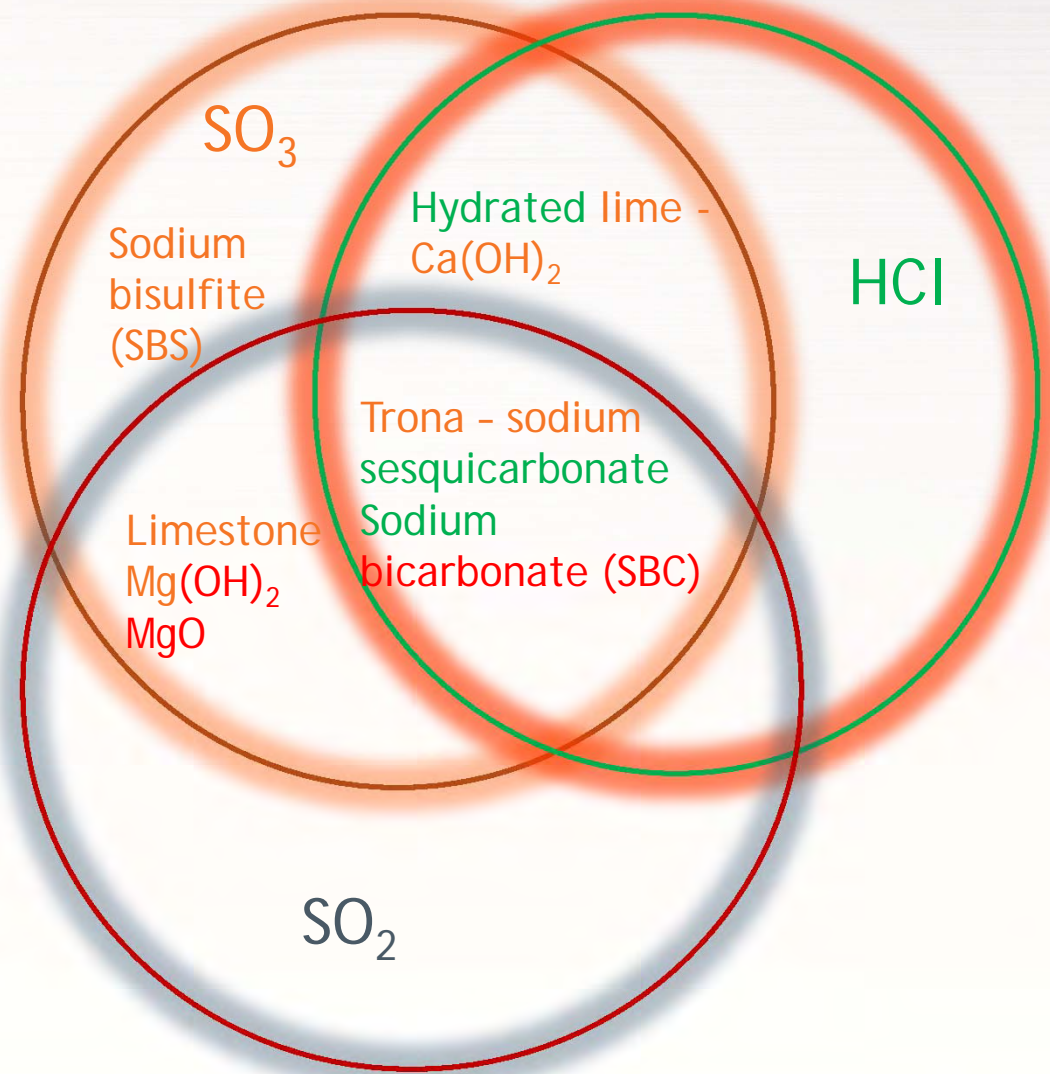


# DSI Injection System

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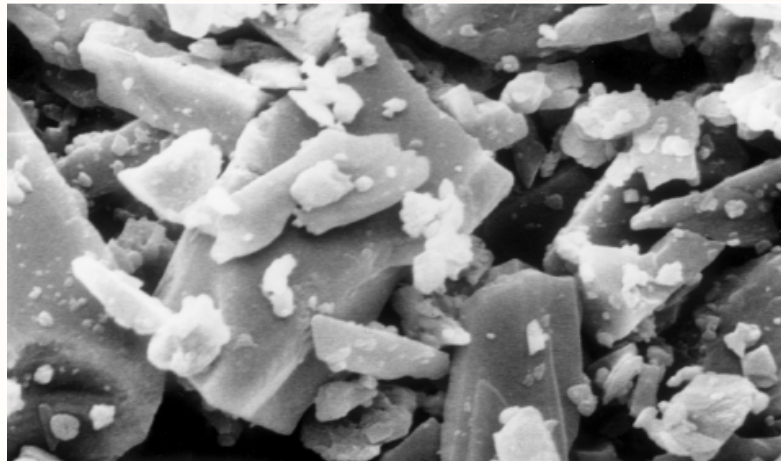
# Sorbents for Acid Gas Control



# Sorbents for Acid Gas Control

## ▶ Trona

- Trona is naturally formed sodium sesquicarbonate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ )
- The Green River WY deposit is the largest and purest in the world
- Over 17 million tons of trona are mined each year in WY
- Processed into a fine, dry powder, typical mean particle size (D50): 30 - 35  $\mu\text{m}$

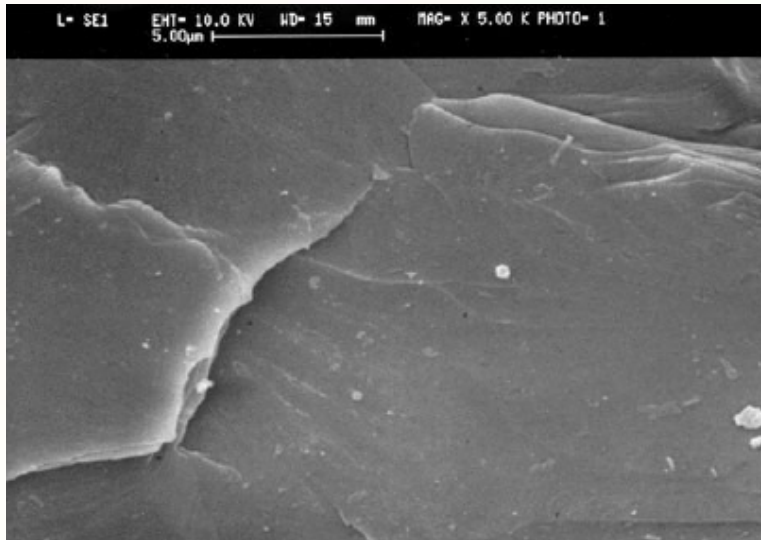


Source: Kong et al., 2009

# Sorbents for Acid Gas Control

## ▶ Sodium Bicarbonate

- $\text{NaHCO}_3$  - Baking soda or sodium bicarbonate (SBC)
- Solvay Chemicals manufactures SBC in Parachute, CO and Green River, WY
- Solvay's SBC products are coarse powders (D50 ~ 100  $\mu\text{m}$ ) that require milling prior to use



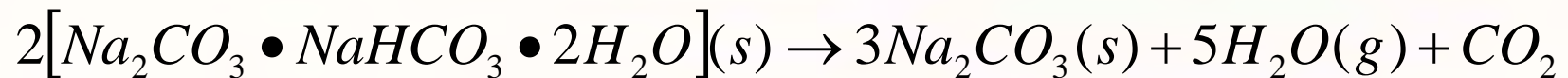
Source: Kong et al., 2009

# Sorbents for Acid Gas Control

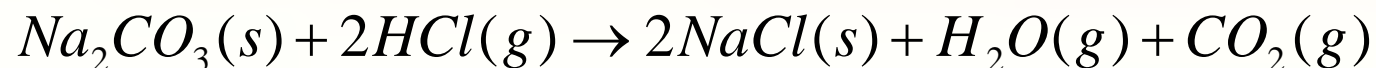
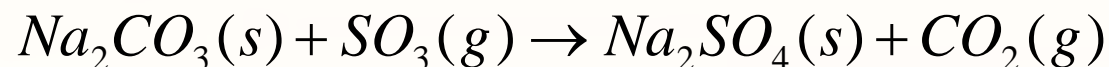
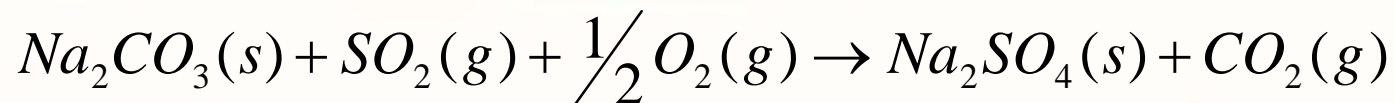
- ▶ Sodium Sorbents
- ▶ Acid gas control chemistry
  - Trona decomposition



- SBC decomposition

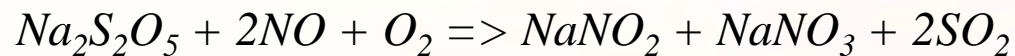
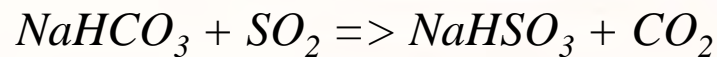


- Acid gas mitigation reactions:  $SO_3 > HCl \gg SO_2$



# Sorbents for Acid Gas Control

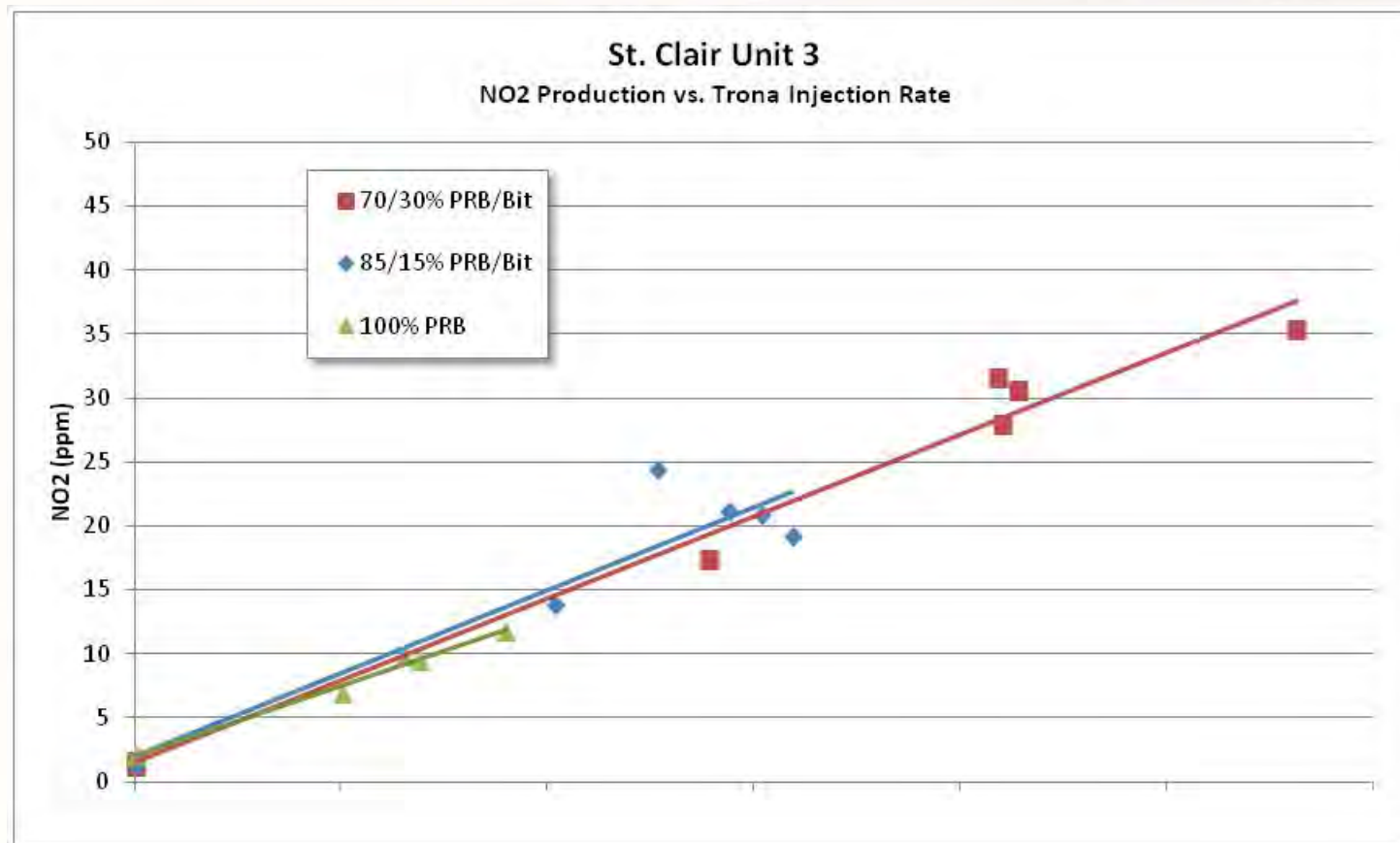
- ▶ Sodium Sorbents
- ▶ Side reaction: NO removal/NO<sub>2</sub> formation



- NO<sub>2</sub> is assumed to be formed by the decomposition of sodium nitrite (NaNO<sub>2</sub>)
- More NO<sub>2</sub> formation with SBC than with trona
- For both sorbents, increasing the reaction temperature increases the NO<sub>x</sub> reduction but also increases the amount of NO<sub>2</sub> formed

# Sodium Sorbents: NO<sub>2</sub> Production with Trona Injection

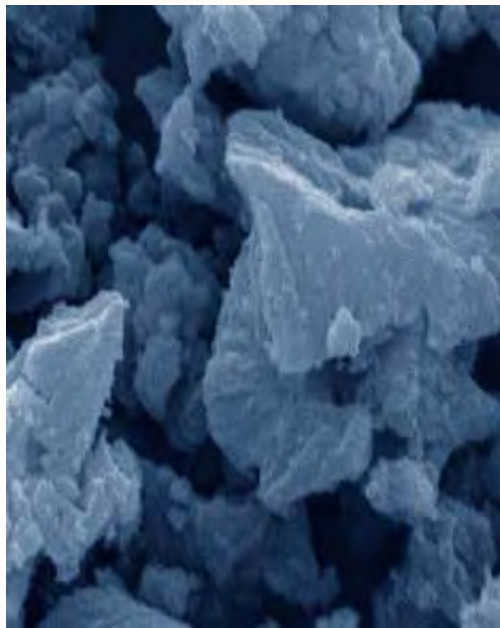
- ▶ Sodium-based DSI can increase flue gas NO<sub>2</sub>



*Results from Testing at DTE St. Clair Unit 3  
W. Rogers, EUEC 2013*

# Sorbents for Acid Gas Control

▶ Hydrated Lime



Standard  
Hydrated lime

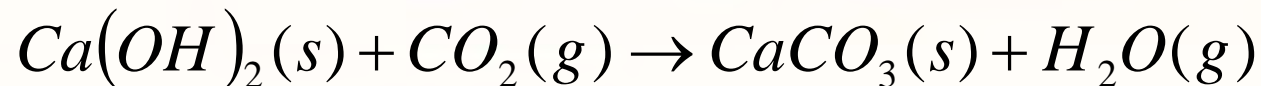
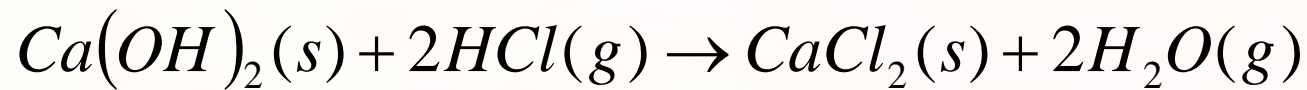
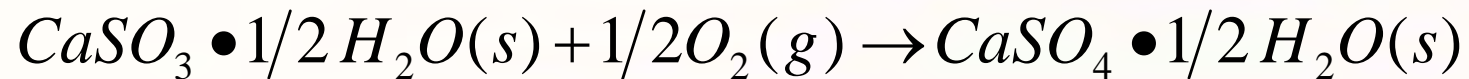


Sorbacal<sup>®</sup> SP

*Source: L'Hoist, 2011*

# Sorbents for Acid Gas Control

- ▶ Hydrated Lime
- ▶ Acid gas control chemistry

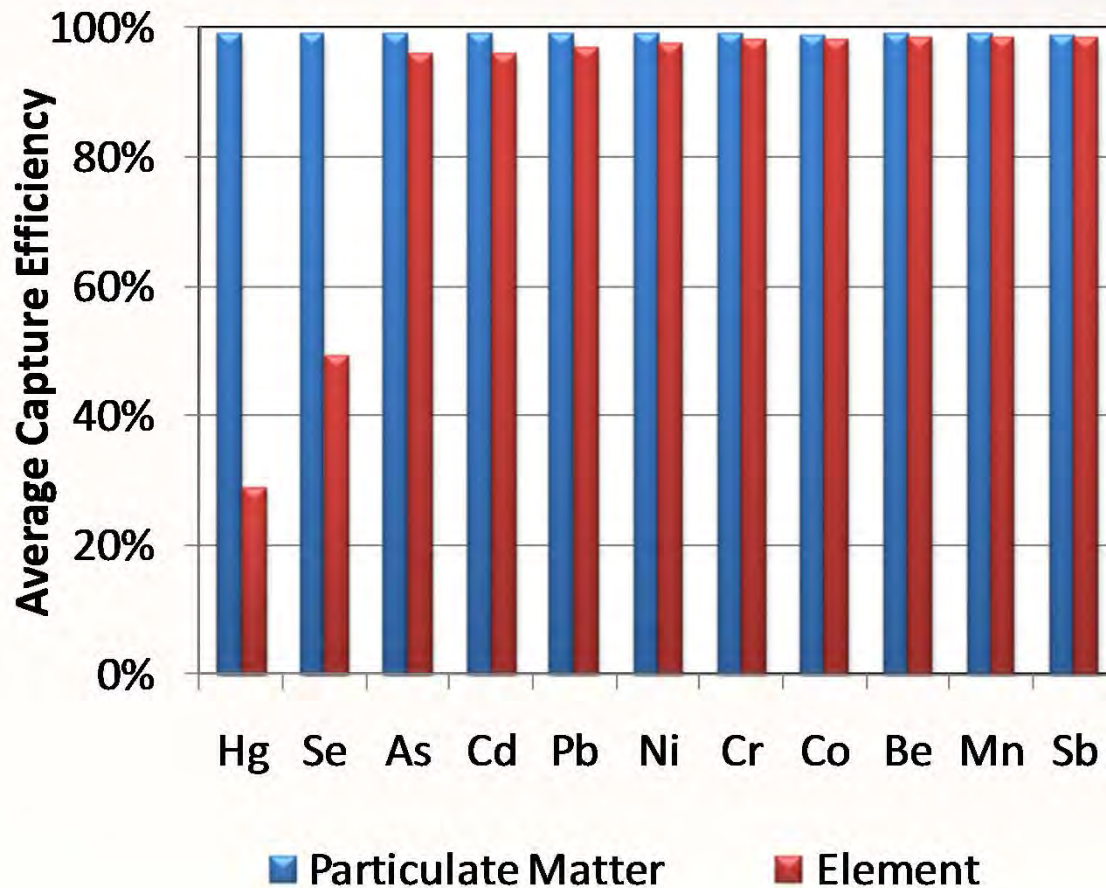


- ▶ Carbonation reaction competes for sites, but is slower than other reactions

# Hazardous Air Pollutant Metals

- CAA Section 112 specifies Hazardous Air Pollutants (HAPs), including metals:
  - ▶ Antimony Compounds
  - ▶ Arsenic Compounds (inorganic including arsine)
  - ▶ Beryllium Compounds
  - ▶ Cadmium Compounds
  - ▶ Chromium Compounds
  - ▶ Cobalt Compounds
  - ▶ Lead Compounds
  - ▶ Manganese Compounds
  - ▶ Mercury Compounds
  - ▶ Nickel Compounds
  - ▶ Radionuclides (including radon)
  - ▶ Selenium Compounds

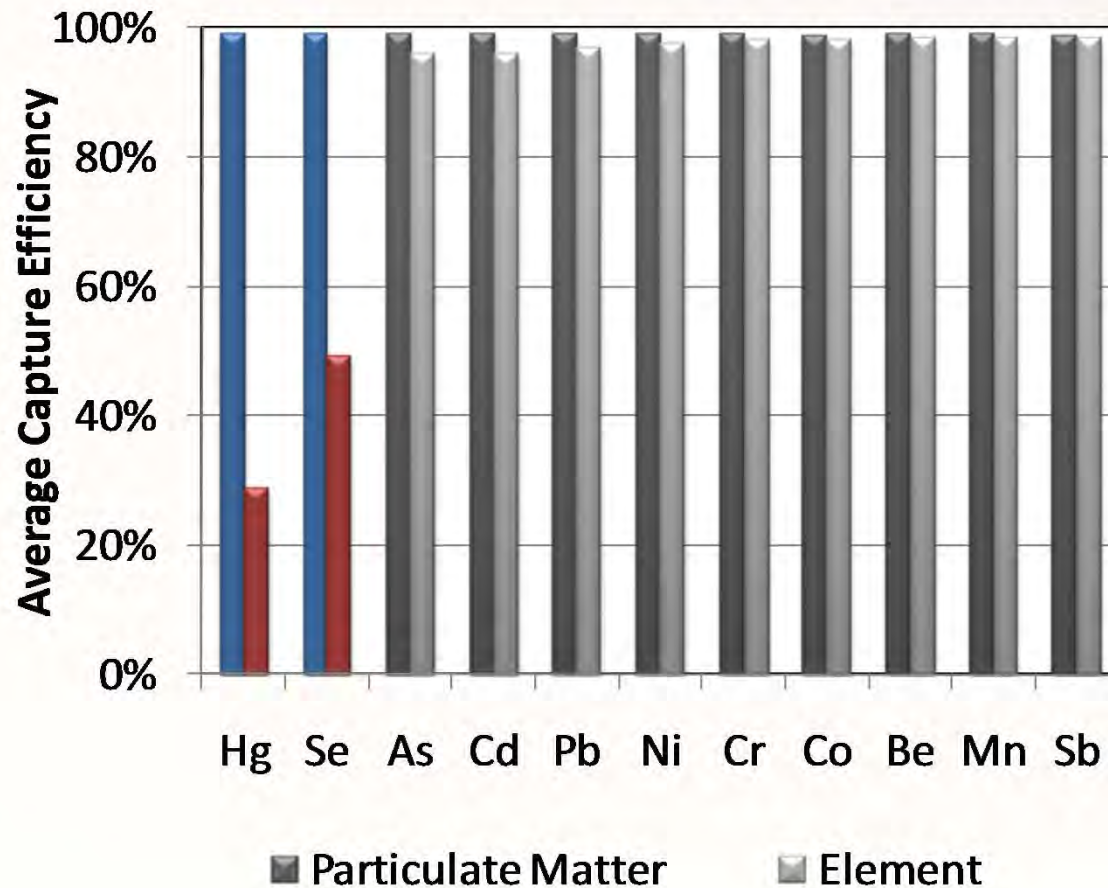
# Fate of HAP Metals: Capture Efficiency in ESPs



- ▶ PISCES/DOE field data
- ▶ Most HAP metals have the same capture efficiency as PM, *which means most metals are in the particulate (not gas) phase at the PCD inlet*

Source: Helble, 2000

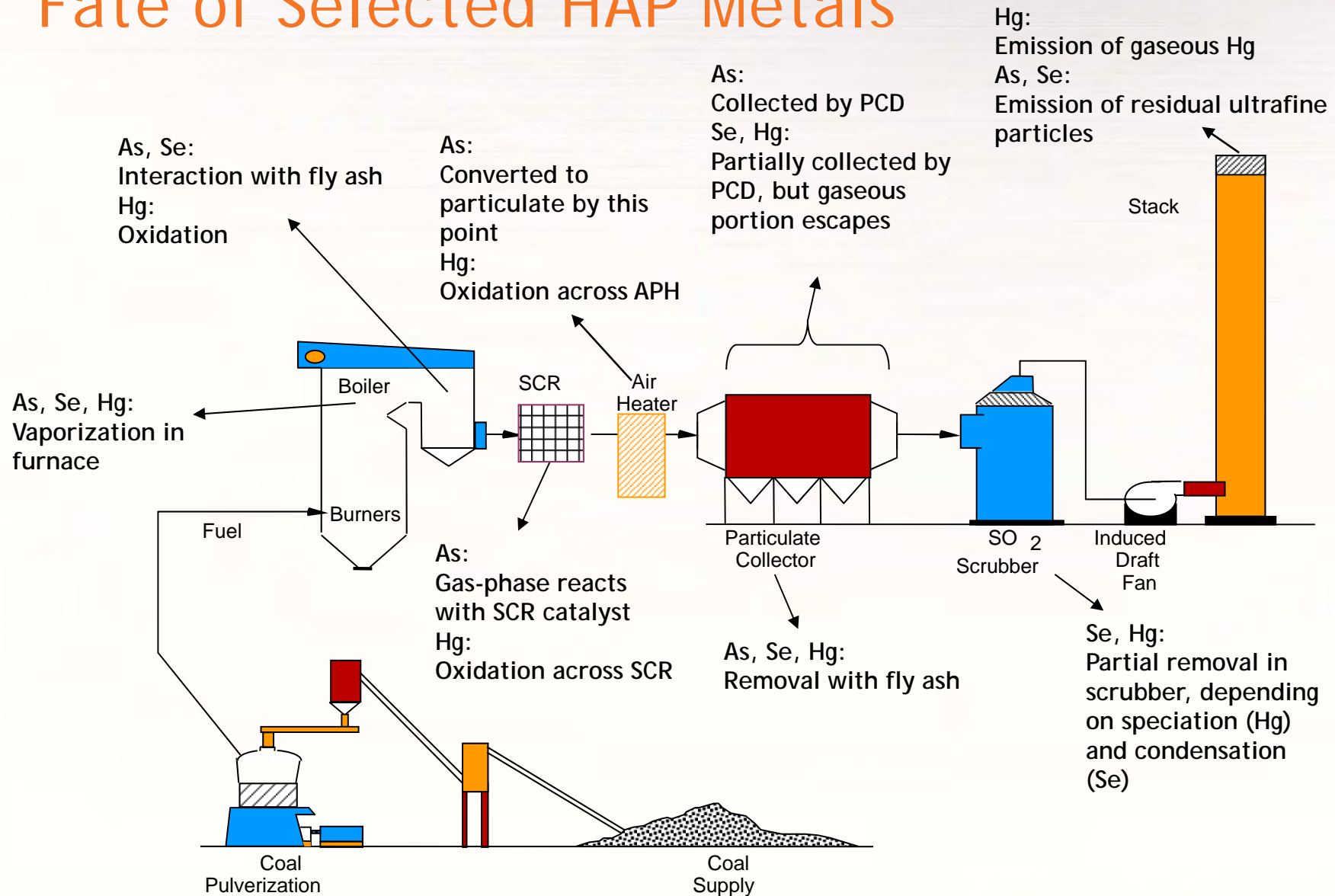
# Fate of HAP Metals: Capture Efficiency in ESPs



- ▶ The exceptions:
  - Mercury
  - Selenium
- ▶ These HAPs can be in the gas phase at PCD temperatures *and have potential to interact with DSI sorbents*

Source: Helble, 2000

# Fate of Selected HAP Metals



# How Does Injecting DSI Sorbents Affect As, Se, and Hg?

## ▶ Mercury

- Potential reaction of  $\text{HgCl}_2(\text{g})$  with alkaline sorbents
- Alkaline sorbent injected upstream of air preheater removes  $\text{HCl}$ , which can result in less oxidized Hg in the flue gas
- Removal of  $\text{SO}_3$  by DSI sorbent enhances Hg capture by unburned carbon or activated carbon
- Production of  $\text{NO}_2$  by sodium DSI sorbent can reduce effectiveness of activated carbon for Hg capture

## ▶ Arsenic

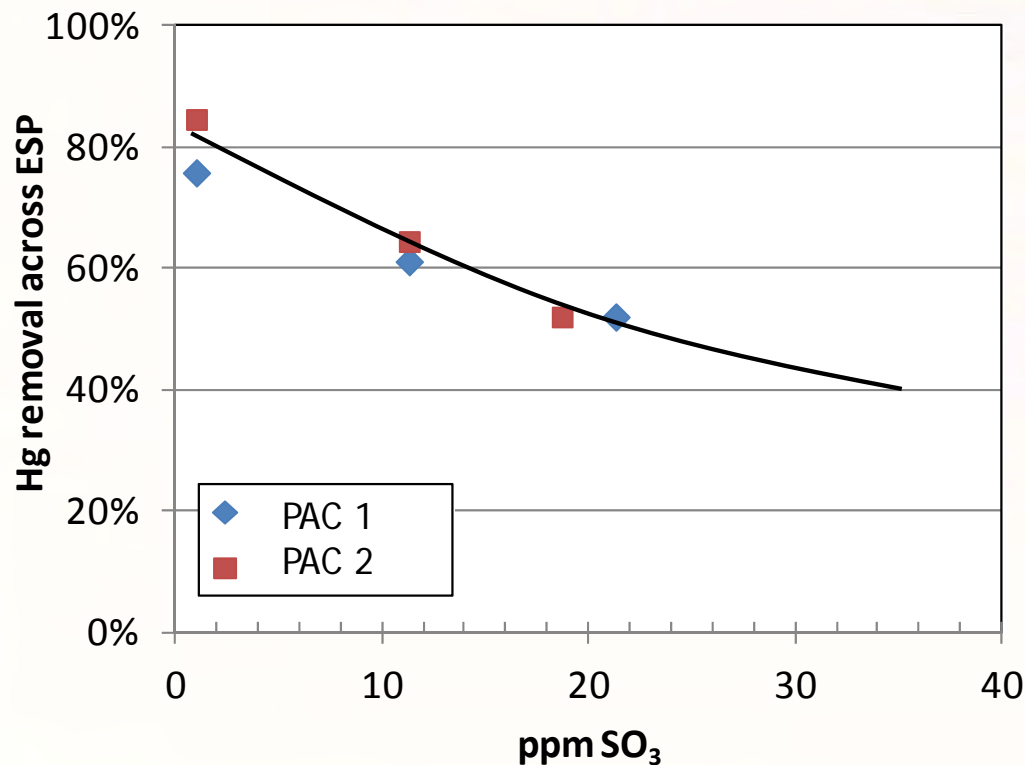
- High temperature reaction with calcium sorbent (possibly sodium sorbent) removes  $\text{As}_2\text{O}_3$  from gas pre-APH, but doesn't change ultimate fate of arsenic

## ▶ Selenium

-

# SO<sub>3</sub> and ACI Performance

MRC Results: 10 lb/MMacf, injection upstream of APH  
 APH Inlet: 627 F; APH outlet: 300 F (assume 1 ppm baseline SO<sub>3</sub>)

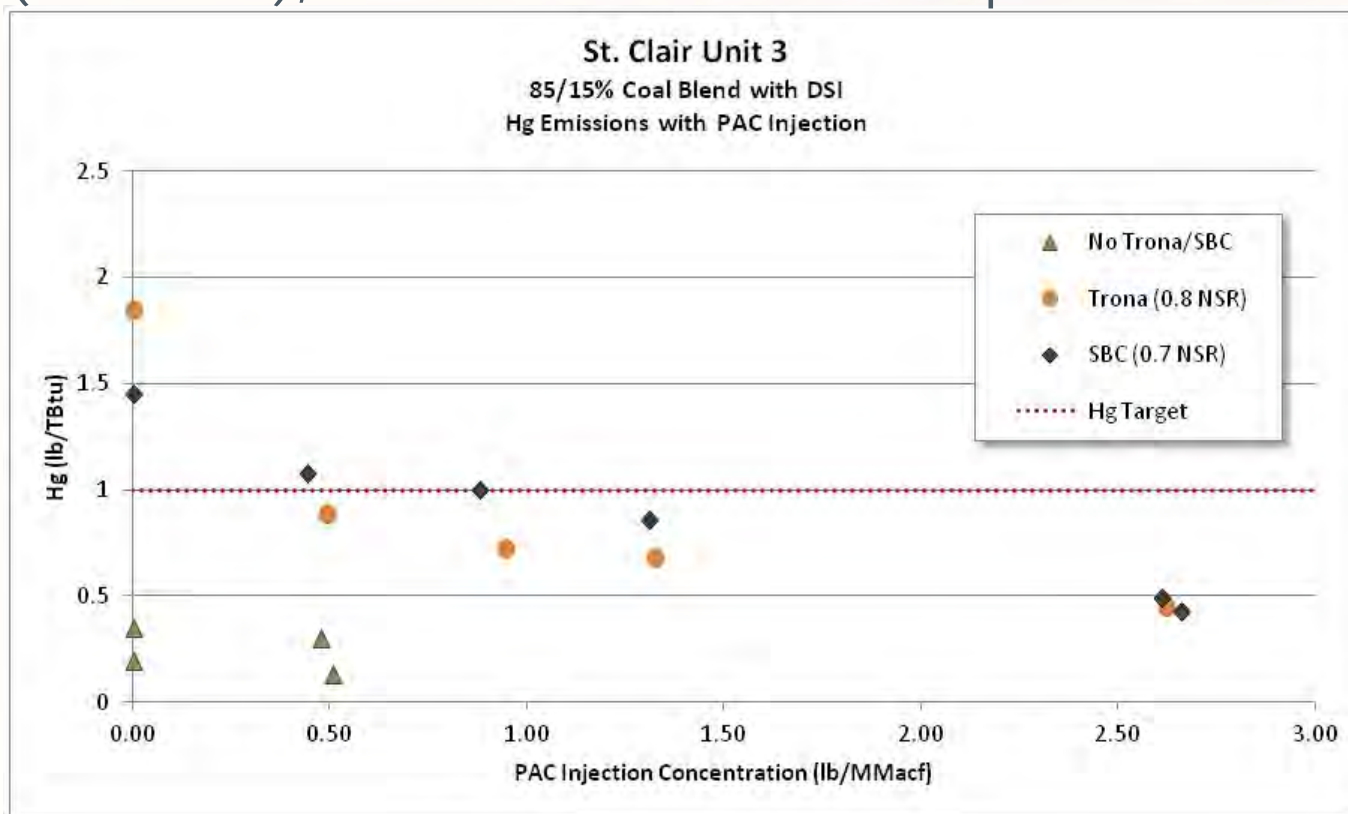


- ▶ Any SO<sub>3</sub> in gas phase appears to affect Hg capture by activated carbon
- ▶ Removal of SO<sub>3</sub> by DSI sorbent enhances Hg capture by unburned carbon or activated carbon

Source: Pollack, Air Quality VII, 2009

## Impacts of NO<sub>2</sub> on PAC

- ▶ Production of NO<sub>2</sub> by sodium DSI sorbent can reduce effectiveness of activated carbon for Hg capture
- ▶ Production of NO<sub>2</sub> doesn't happen at every installation: kinetics, PCD (ESP vs. FF), and baseline NO<sub>x</sub> levels important factors



Results from Testing at DTE St. Clair Unit 3, W. Rogers, EUEC 2013

# How Does Injecting DSI Sorbents Affect As, Se, and Hg?

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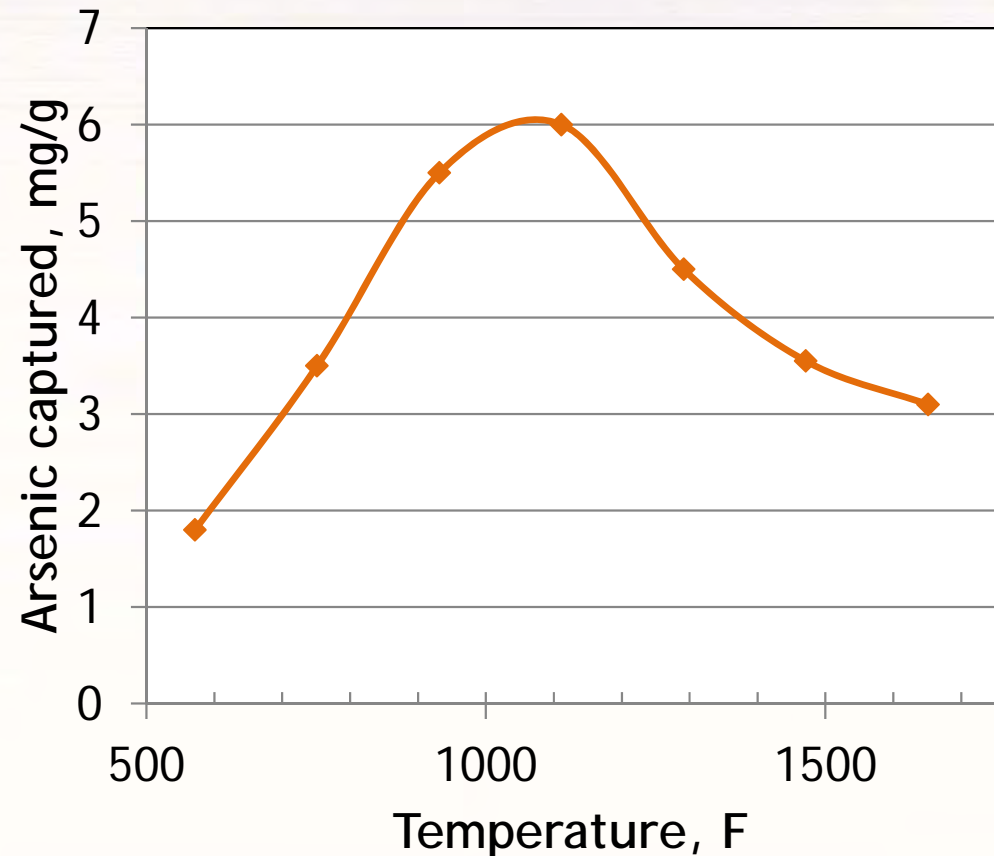
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## ▶ Selenium

-

# Arsenic Reacts with Calcium

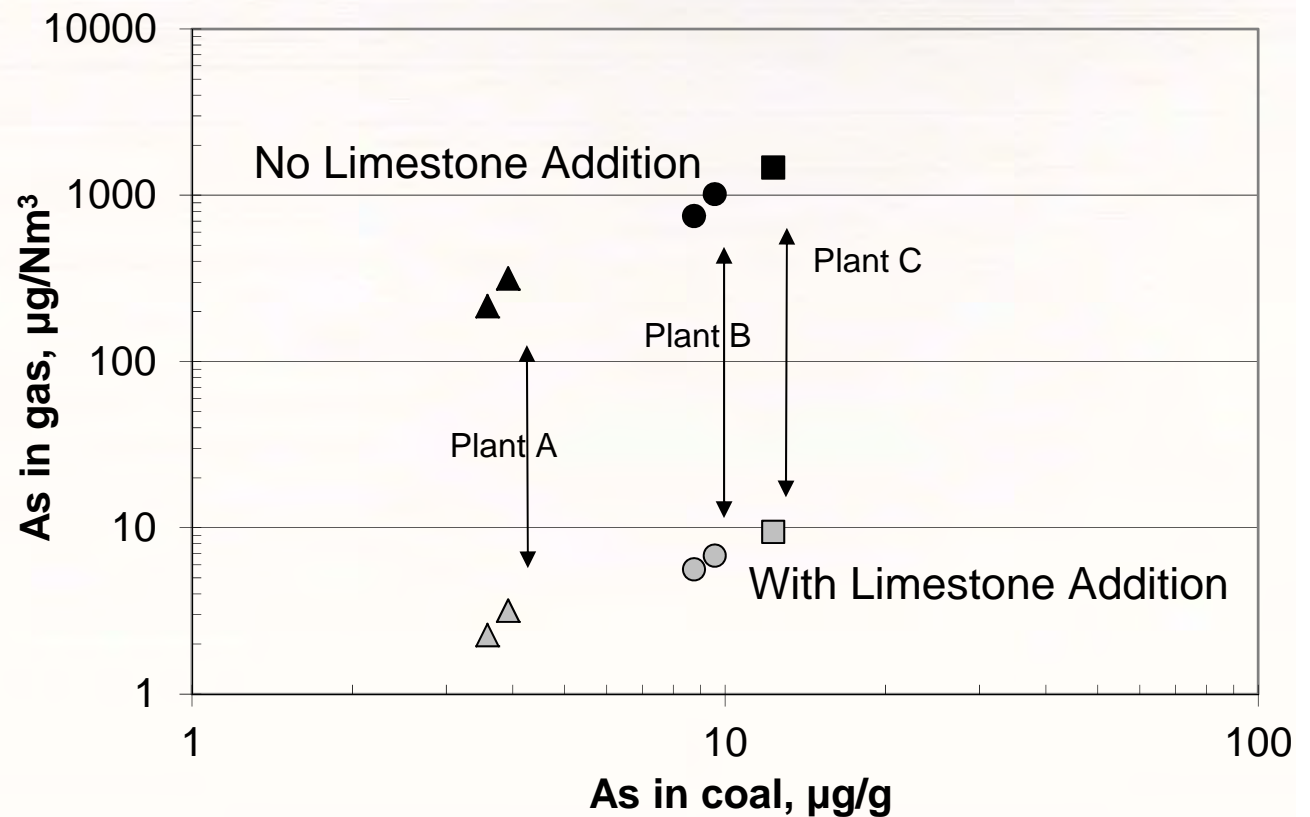
- ▶ Lab-scale study of reaction between  $\text{As}_2\text{O}_3(\text{g})$  and lime
- ▶ Peak temperature corresponds to economizer outlet



*Jadhav, R.A.; Fan, L.S. Capture of Gas-Phase Arsenic Oxide by Lime: Kinetic and Mechanistic Studies. Environ. Sci. Technol. 2001, 35, 794-799.*

# Arsenic Reacts with Calcium

- ▶ Full-scale data
- ▶ Arsenic can be in gas phase at SCR temperatures (650-750°F), but not at APH outlet temperatures



*Data of Pritchard et al. (1995) for wet-bottom boilers with 100% fly ash recycle, with and without limestone injection for three different plants.*

# How Does Injecting DSI Sorbents Affect As, Se, and Hg?

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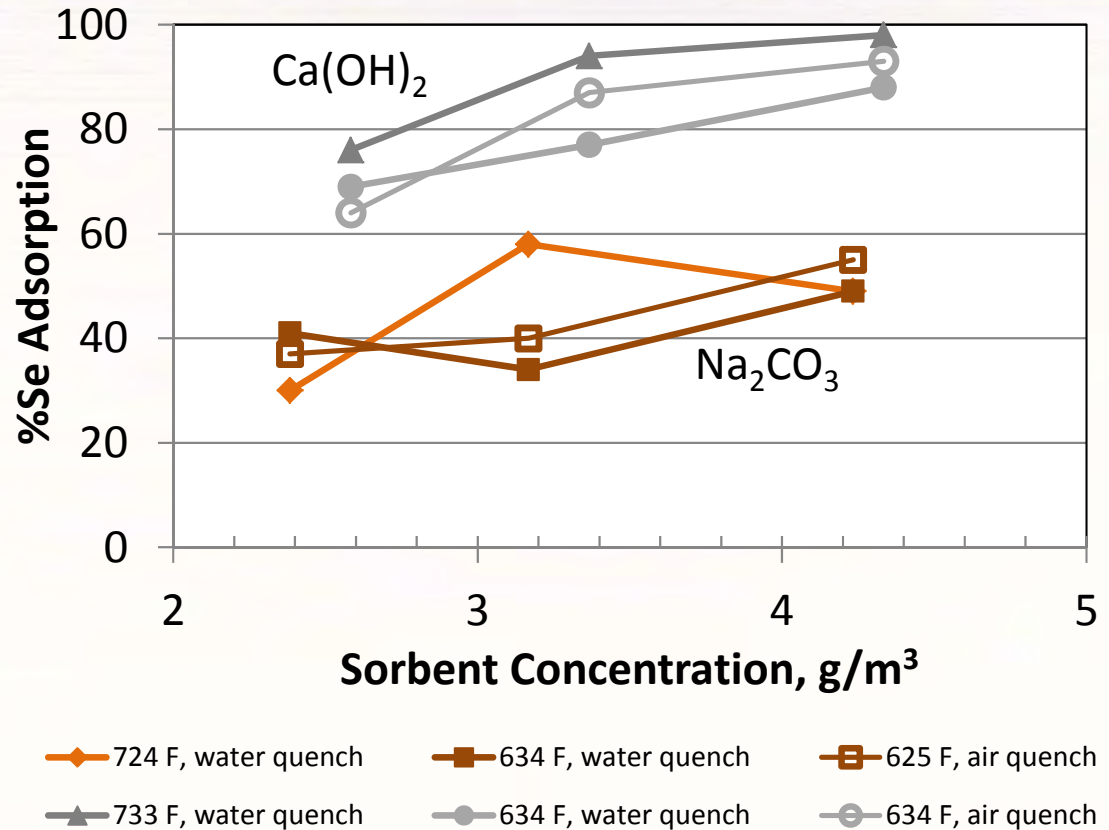
## ▶ Selenium

- Reacts with sodium or calcium sorbents: potential to shift Se from scrubber to fly ash

# Selenium Reacts with Ca and Na at Pre-APH Temperatures



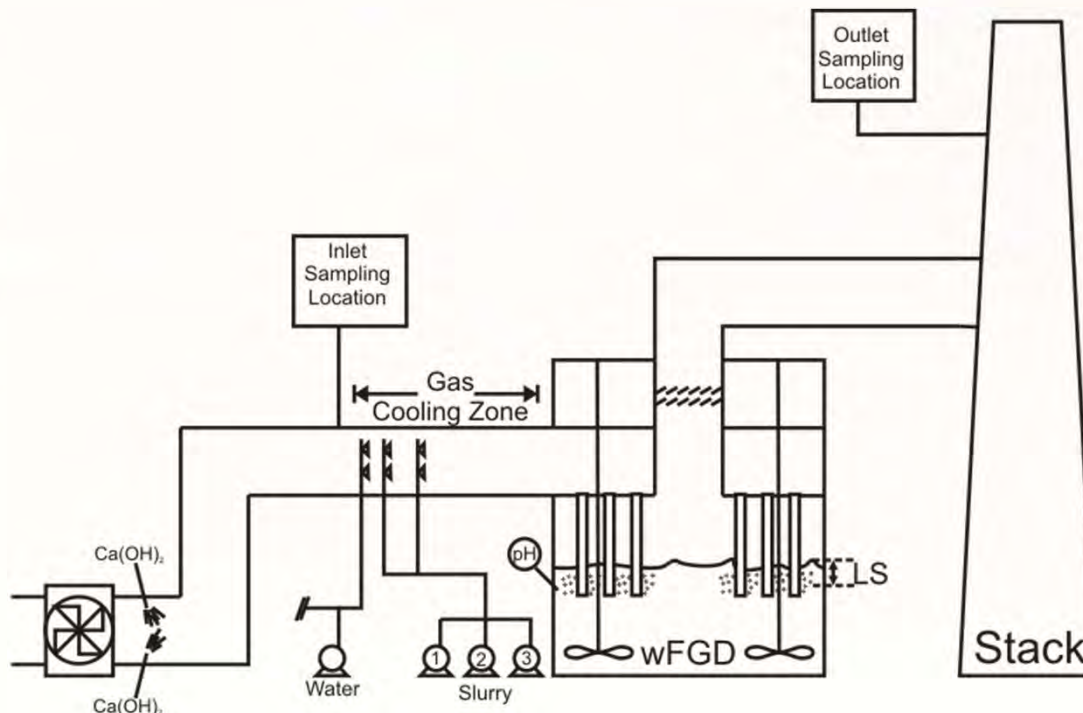
- ▶ When sodium or calcium sorbents are injected into coal flue gas, they can react with Se
- ▶ Selenium adsorption as a function of sorbent loading for injection of calcium hydroxide or sodium carbonate in the exhaust of glass furnaces



Kircher, U. "Waste Gas Treatment of Soda Lime Silica Glass Furnaces - Investigations with Different Absorption Agents." *Ceramic Trans.* 1998, 82, 75-80.

# Selenium Reaction at Post-APH Temperatures

- ▶ Measurement at 900 MW bituminous-fired boiler
- ▶ Samples taken at inlet and outlet of scrubber: gaseous Se and size-segregated fly ash
- ▶ FGD inlet sample taken after  $\text{Ca}(\text{OH})_2$  injection



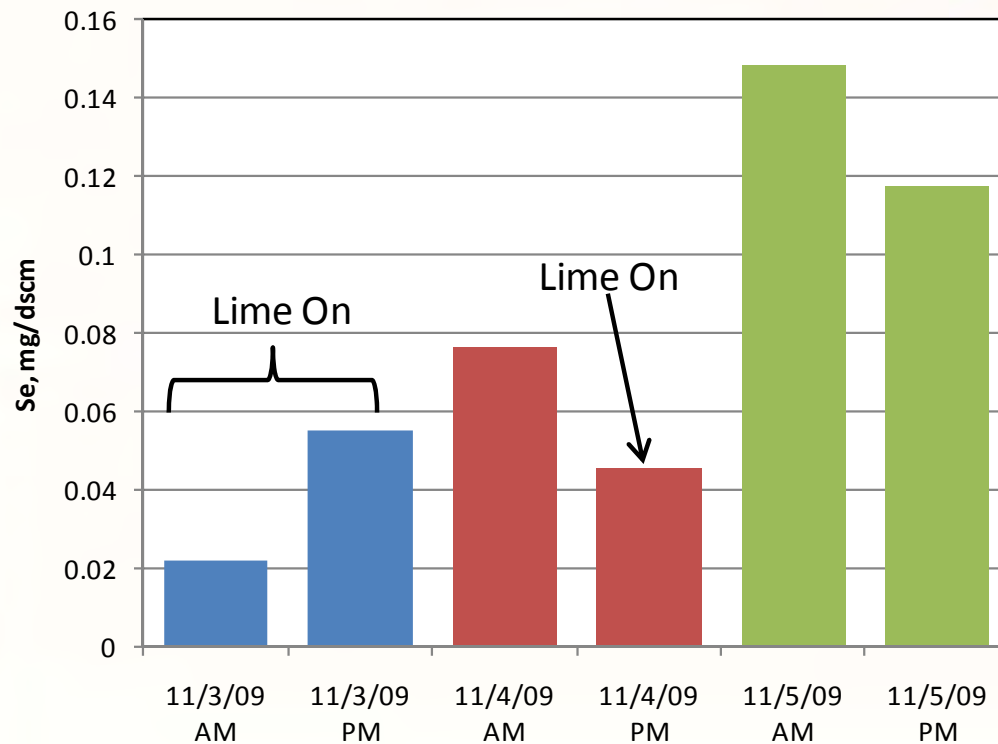
- Gaseous Se sampled with modified Method 29
  - Inertial separator instead of filter
- Size-segregated ash collected with cascade impactor

Source: Tyree, et al., EUEC 2011

# Selenium Reaction at Post-APH Temperatures



- ▶ Lower gas-phase Se at scrubber inlet when hydrated lime injected because of reaction with sorbent



- ▶ Se might also react with sodium sorbents post-APH, but no data to show

Source: Tyree, et al., EUEC 2011

# How Does Injecting DSI Sorbents Affect As, Se, and Hg?

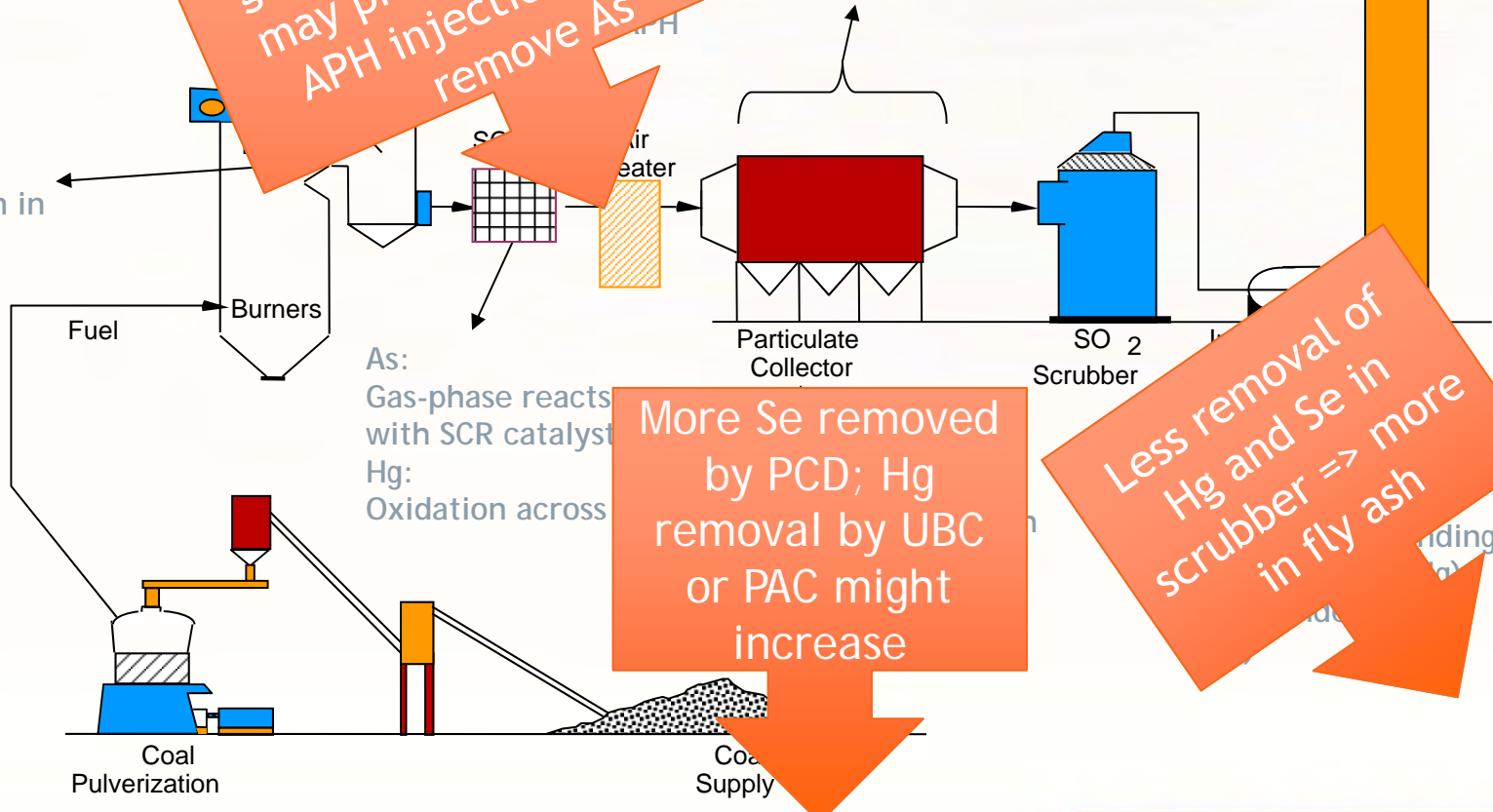
Hg:  
Emission of gaseous Hg  
As, Se:  
Emission of residual ultrafine particles

As, Se:  
Interaction with fly ash  
Hg:  
Oxidation

Injection pre-APH removes gaseous As, Se, SO<sub>3</sub>, but may produce NO<sub>2</sub>; post-APH injection doesn't remove As

As:  
Collected by PCD  
Hg:  
Partially collected by PCD but gaseous Hg escapes

As, Se, Hg:  
Vaporization in furnace



As:  
Gas-phase reacts with SCR catalyst  
Hg:  
Oxidation across

More Se removed by PCD; Hg removal by UBC or PAC might increase

Less removal of Hg and Se in scrubber => more in fly ash

# Leaching of Metals from DSI-Fly Ash Mixtures



- ▶ DSI sorbents might increase the amounts of Se and Hg in the fly ash
- ▶ What is the fate of these metals in fly ash?

# Solubility of Se in Fly Ash

Sample	% water-soluble Se	%Se[IV] in water-soluble fraction
1	11.6	100.0
2	2.7	83.8
3	11.4	100.0
4	1.2	--
5	0.0	--
6	11.5	100.0
7	3.6	--
8	38.6	100.0
9	0.0	41.9
10	51.6	100.0
11	0.3	100.0
12	13.8	100.0
13	13.7	100.0
14	1.9	37.1
15	11.4	92.2
16	13.0	91.3
17	63.0	93.2
18	15.1	80.5
19	0.7	100.0
20	2.8	100.0
21	27.4	100.0
22	63.5	100.0
23	23.1	100.0

- ▶ Water-soluble fraction of Se in fly ash varies from 0% to 100%
  - Not readily correlated with pH of solution, as with most other trace metals
- ▶ Speciation of Se in fly ash may be important

*Jackson, B.P.; Miller, W.P. Arsenic and selenium speciation in coal fly ash extracts by ion chromatography-inductively coupled plasma mass spectrometry. J. Anal. Atom. Spectr. 1998, 13, 1107-1112.*

# Solubility of Se in Fly Ash

- ▶ Selenate (Se(VI)) more soluble in water than selenite (Se(IV))
- ▶ For a given oxidation state, the cation associated with the selenium oxyanion also affects the solubility: in terms of solubility, Na > Ca > Fe
- ▶ Example, solubility product constants for selenites at 298 K:
  - Values of pK closer to zero in the table mean that the reactant is more likely to dissolve

Reaction	pK
$\text{Na}_2\text{SeO}_3 = 2\text{Na}^+ + \text{SeO}_3^{2-}$	3.51
$\text{CaSeO}_3 = \text{Ca}^{2+} + \text{SeO}_3^{2-}$	7.65
$\text{CaSeO}_4 = \text{Ca}^{2+} + \text{SeO}_4^{2-}$	4.77
$\text{FeSeO}_3 = \text{Fe}^{2+} + \text{SeO}_3^{2-}$	9.99
$\text{FeSeO}_4 = \text{Fe}^{2+} + \text{SeO}_4^{2-}$	6.52
$\text{Fe}_2(\text{SeO}_4)_3 = 2\text{Fe}^{3+} + 3\text{SeO}_4^{2-}$	23.19

# Leaching from Ash-Hydrated Lime Mixtures: Bituminous Ash



- ▶ Pilot-scale hydrated lime injection tests (bituminous coal)
- ▶ Samples of ash with and without hydrated lime injection subject to TCLP leaching
- ▶ Se leaching approximately doubled with hydrated lime injection
- ▶ Other RCRA metals showed little or no increase in leaching

Leached Metal	TCLP Results	
	Baseline Ash, mg/L	Ash with HL, mg/L
As	<0.005	0.008
Se	0.054	0.096
Hg	0.011	0.013
Ba	0.477	0.225
Cr	0.024	<0.005
Pb	0.07	<0.005
Ag	<0.005	<0.005
Cd	<0.005	<0.005

*Dickerman, J.; Fitzgerald, H. HCl control by dry sorbent injection (DSI) with hydrated lime. Presented at Air Quality VIII, Arlington, VA, October 23-27, 2011.*

# Leaching from Ash-Trona Mixtures: Bituminous Ash



- ▶ Set of paired fly ash samples collected from H-ESP at a full-scale power plant that burned bituminous coal: control ash collected before trona injection and a trona ash collected during trona injection test
- ▶ Batch leaching experiments conducted using DI water under unadjusted pH conditions at L/S ratios of 10:1 and 5:1
- ▶ Effects of the liquid/solid (L/S) ratio, pH, dry storage time, and leaching time on As and Se leaching and speciation examined

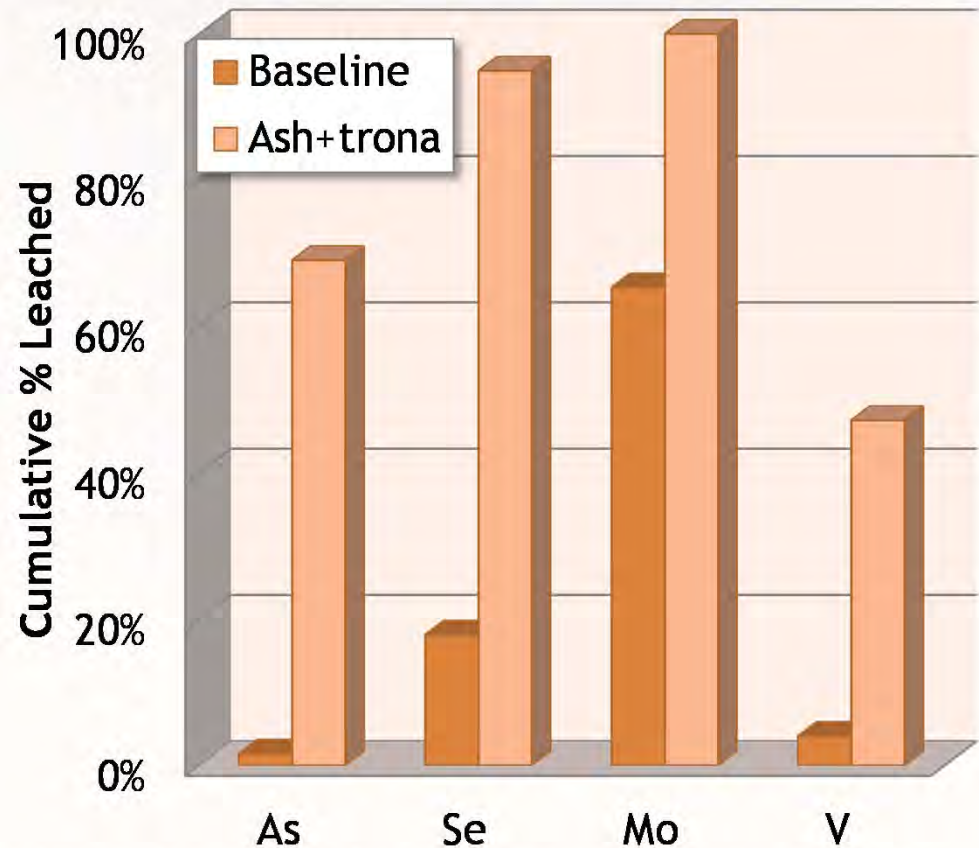
			Cl	Na	SO <sub>4</sub> <sup>-2</sup>	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
	Ash L/S	pH	(mg/L)	(mg/L)	(mg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)
Control Ash	5:1	7.5	1.2	8.9	345	0.3	88	300	3.5	1.1	5.3	0.1	4.6
Ash+Trona	5:1	11.1	252	5456	9970	2.2	6321	478	4.5	87.8	6.4	3.2	3109
Control Ash	10:1	7.6	1.2	5.1	159	0.3	94	396	1.9	2	5.7	0.1	4.8
Ash+Trona	10:1	11	131	2837	4700	0.8	3319	341	2	69.3	5.4	1.9	1611

*Su, T; Shi, H.; Wang, J. Impact of Trona-Based SO<sub>2</sub> Control on the Elemental Leaching Behavior of Fly Ash. Energy Fuels 2011, 25, 3514-3521.*

# Leaching from Ash-Trona Mixtures: Subbituminous Ash



- ▶ Set of paired fly ash samples collected from C-ESP at a full-scale power plant that burned subbituminous coal: control ash collected before trona injection and a trona ash collected during trona injection test
- ▶ Batch leaching experiments (24 hours) conducted using DI water under unadjusted pH conditions at L/S ratio of 10:1



Dan, Y.; Zimmerman, C.; Liu, K.; Shi, H.; Wang, J. Increased Leaching of As, Se, Mo, and V from High Calcium Coal Ash Containing Trona Reaction Products. *Energy Fuels*, 2013, doi/10.1021/ef3020469.

# Summary



# How Does Injecting DSI Sorbents Affect As, Se, and Hg?

## ▶ Mercury

- Potential reaction of  $\text{HgCl}_2(\text{g})$  with alkaline sorbents
- Alkaline sorbent injected upstream of air preheater removes  $\text{HCl}$ , which can result in less oxidized Hg in the flue gas
- Removal of  $\text{SO}_3$  by DSI sorbent enhances Hg capture by unburned carbon or activated carbon
- Production of  $\text{NO}_2$  by sodium DSI sorbent can reduce effectiveness of activated carbon for Hg capture

## ▶ Arsenic

- High temperature reaction with calcium sorbent (possibly sodium sorbent) removes  $\text{As}_2\text{O}_3$  from gas pre-APH, but doesn't change ultimate fate of arsenic

## ▶ Selenium

- Reacts with sodium or calcium sorbents: potential to shift Se from scrubber to fly ash

# Leaching from Ash-Sorbent Mixtures



## ▶ Trona injection

- Significantly enhanced leaching of major anions of concern, including Se, As, Cr, and V but not Hg
- With trona addition, distribution of these anions shifted to the soluble trona fraction of the ash
- pH of bituminous ash leachate increased from ~7.5 to ~11 with addition of trona

## ▶ Hydrated lime injection

- Limited pilot data available
- Some increase in Se leaching (no other metals of concern), but small enhancement compared to trona

# Questions?

- ▶ If you have any questions, please contact Connie Senior:
  - [connies@adaes.com](mailto:connies@adaes.com)
  - 303-962-1959

