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Advanced Emissions Solutions, Inc.  
Advancing **Cleaner** Energy

# Selenium Fate and Control in APCDs

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# Disclaimer

This presentation includes general information on coal and coal-fired boilers intended for education and illustration purposes only. All information is provided “AS-IS” and without warranty or liability of any kind.

# Questions to Answer

- ▶ What does selenium do in the environment?
- ▶ How does selenium get into coal-fired boilers?
- ▶ How is selenium measured?
- ▶ What happens to selenium in the combustion process?
- ▶ What happens to selenium in air pollution control devices?
- ▶ What happens to selenium in coal combustion byproducts?

# Selenium In the Environment

group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1a	2a	3a**	4a	5a	6a	7a	8a	9a	10a	11a	12a	IIIb	IVb	Vb	VIb	VIIb	VIIIb
1	H												B	C	N	O	F	Ne
2	Li	Be											Al	Si	P	S	Cl	Ar
3	Na	Mg	IIIa**	IVa	Va	VIa	VIIa	VIIIa	VIIIb				Ga	Ge	As	Se	Br	Kr
4	K	Ca	IIIb***	IVb	Vb	Vb	Vb	Vb	Vb				In	Sn	Sb	Te	I	Xe
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt								
7	Fr	Ra	Ac															
			58	59	60	61	62	63	64				69	70	71			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd				Tm	Yb	Lu			
			90	91	92	93	94	95	96	97	98	99	100	101	102	103		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

\* Numbering system recommended by the International Union of Pure and Applied Chemistry (IUPAC)  
 \*\* Previous IUPAC numbering system  
 \*\*\* Numbering system recommended by the Chemical Abstracts Service

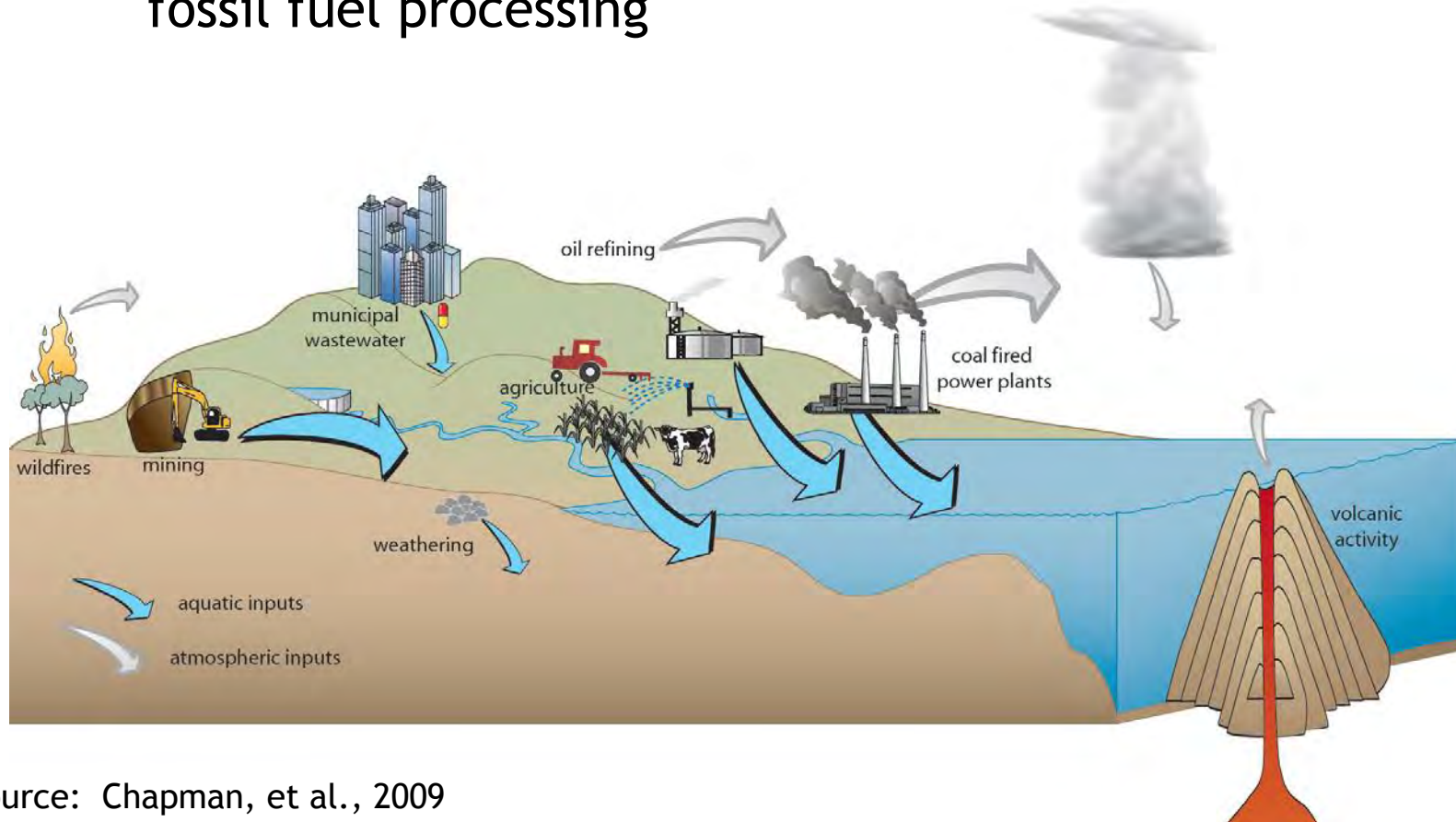
- ▶ Selenium can act a lot like sulfur chemically
- ▶ ...even replacing sulfur in some amino acids

- ▶ We all need a little: Selenium is an essential micronutrient for animals and some plants
- ▶ At high concentrations, selenium can be toxic, especially to aquatic life



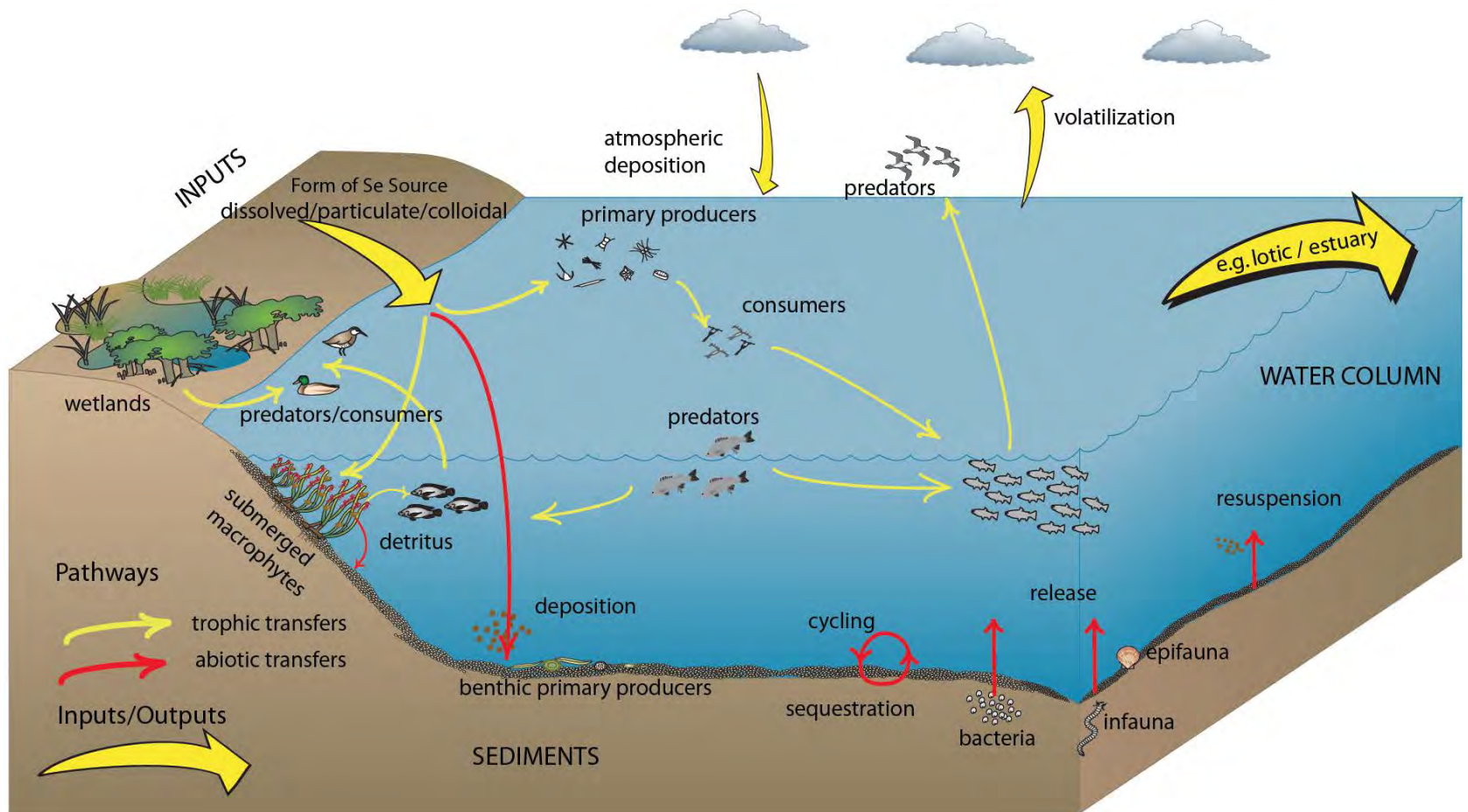
# Potential Sources of Se to Aquatic Systems

- ▶ How does selenium get into aquatic systems?
  - ▶ Natural sources like weathering of shales
  - ▶ Anthropogenic sources like mining, agricultural run-off and fossil fuel processing



Source: Chapman, et al., 2009

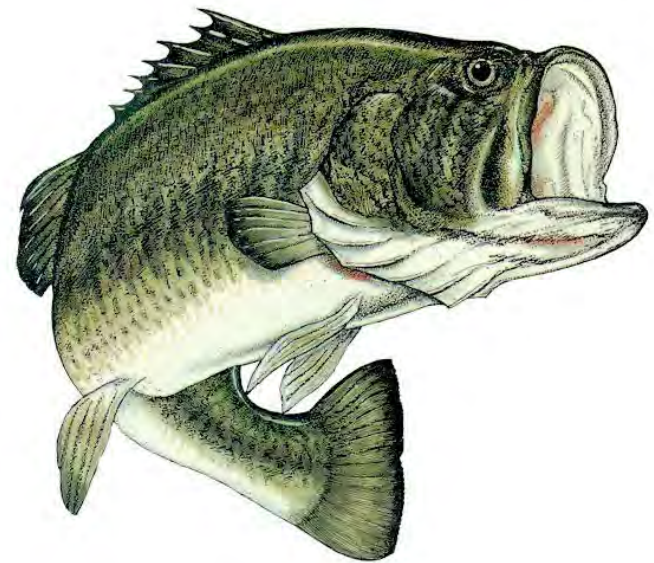
# Partitioning of Se in Aquatic Systems



Source: Chapman, et al., 2009

# Se Impact on Aquatic Life

- ▶ Primary exposure route in aquatic ecosystems is diet
- ▶ Bioaccumulation of selenium happens in the food chain, starting with algae, phytoplankton, etc.
- ▶ The concentration range between essential nutrient and toxicity is narrow
- ▶ Mammals aren't as sensitive to dietary exposure as fish or birds
- ▶ What are the effects of selenium toxicity?
  - ▶ In fish larvae, mutations and developmental abnormalities
  - ▶ In birds, embryo mortality



# Example of Se Impact on Aquatic Life

- ▶ Belews Lake in North Carolina experienced high influxes of selenium from the nearby power plant ash pond discharges from 1974 to 1985
- ▶ Selenium concentrations in the ash pond discharge water were high (150-200  $\mu\text{g Se/L}$ )\*
- ▶ Deformities and reproductive failure in the fish population decimated nineteen of twenty species of fish in the lake
- ▶ In 1986, the discharges were eliminated to the lake and fish populations recovered
- ▶ Selenium concentrations in the lake's biota were reduced by 85-95% after ten years, although elevated selenium concentrations in the sediments still posed a risk to fish

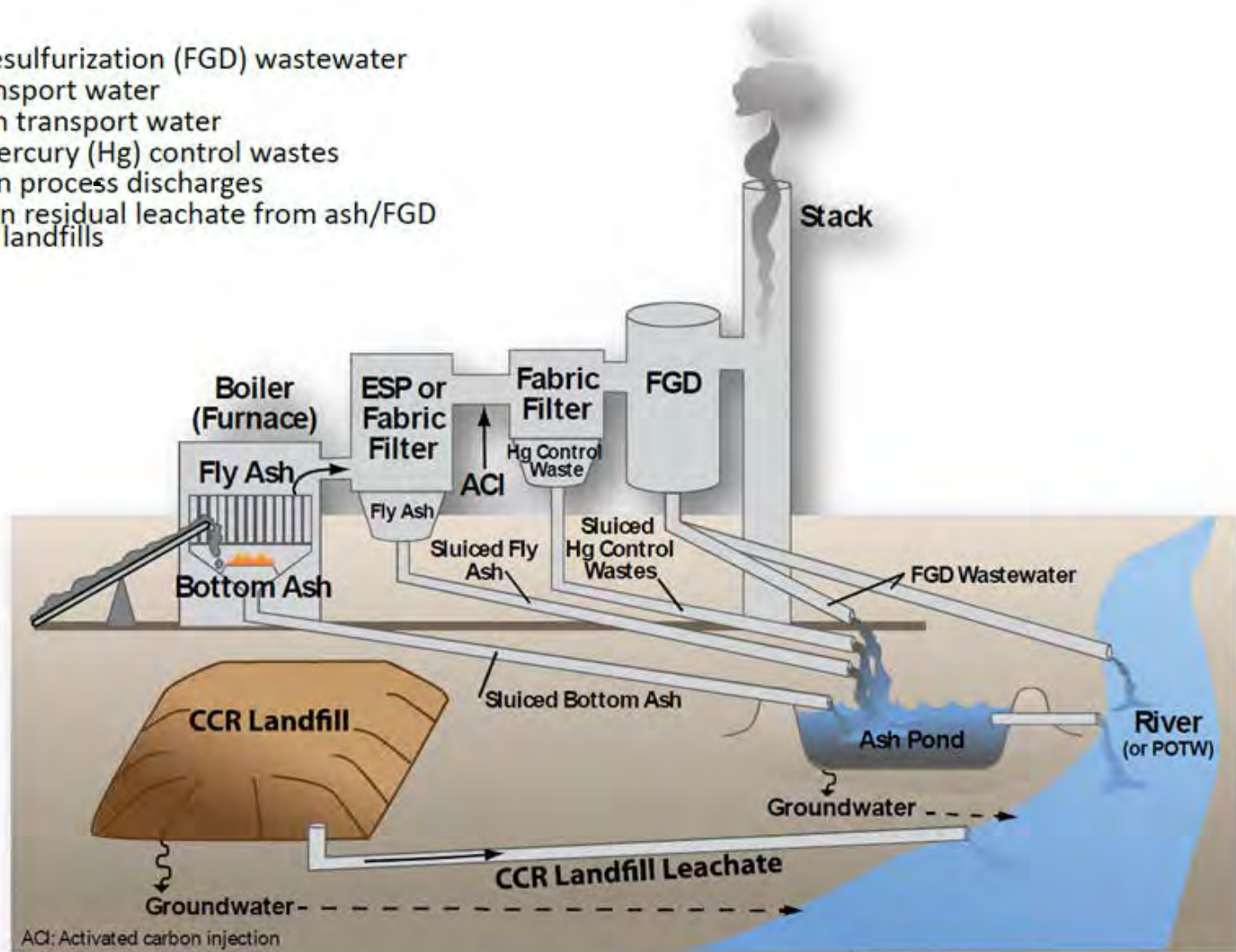


<http://www.northcarolinasportsman.com>

\*Lemly, A.D. Ecosystem Recovery Following Selenium Contamination in a Freshwater Reservoir. *Ecotoxicology* 1997, 36, 275-281.

# 2015 Effluent Limitation Guidelines (ELG)

- Flue gas desulfurization (FGD) wastewater
- Fly ash transport water
- Bottom ash transport water
- Flue gas mercury (Hg) control wastes
- Gasification process discharges
- Combustion residual leachate from ash/FGD ponds and landfills



EPA Call with the Institute of Clean Air Companies

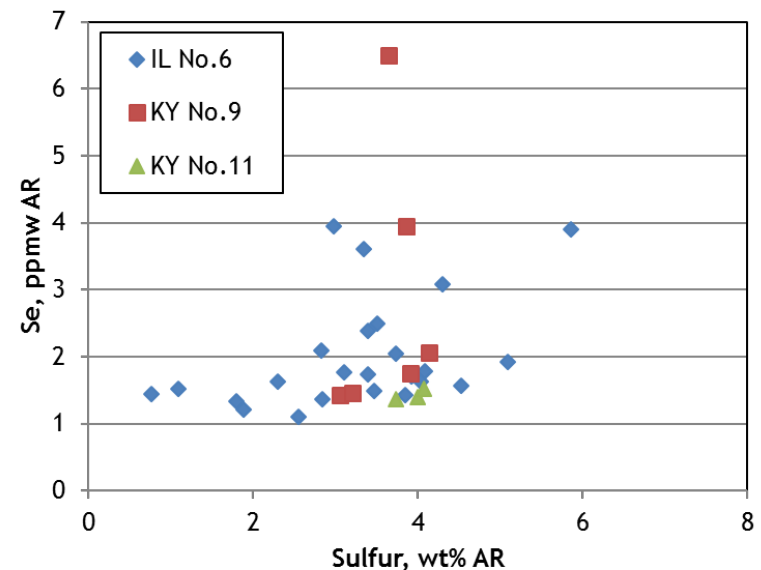
June 22, 2016

# FGD Wastewater in 2015 ELG

- ▶ FGD wastewater includes scrubber blowdown and wastewater from solids separation and dewatering processes
- ▶ 1982 Rule
  - ▶ Regulated as “low volume waste”
  - ▶ Existing and new sources
    - ▶ Effluent limits: TSS, Oil & Grease
    - ▶ Technology basis: impoundment
- ▶ 2015 Rule
  - ▶ Established as a waste stream separate from “low volume waste”
  - ▶ Existing sources
    - ▶ Effluent limits: As, Se, Hg,  $\text{NO}_2+\text{NO}_3$
    - ▶ Technology basis: chemical precipitation plus biological treatment
  - ▶ New sources
    - ▶ Effluent limits: As, Se, Hg, TDS
    - ▶ Technology basis: chemical precipitation plus evaporation

# Selenium in US Coals

- ▶ Selenium is found in coals in trace concentrations
- ▶ USGS has reported concentrations in coal as high as 150  $\mu\text{g}/\text{g}$ , but 0.5 to 5  $\mu\text{g}/\text{g}$  is a more typical range for US coals
- ▶ Selenium is often found in coal either associated with metal sulfide minerals, predominantly pyrite, or as an organically associated element
- ▶ In low-rank coals, selenium is mostly organically bound, but in bituminous coals the element is split between organic and mineral association



Source: ISGS C499

# Estimate for Se Emissions

Ultimate Analysis, wt%	
C	67.70
S	3.60
H <sub>2</sub>	4.70
H <sub>2</sub> O	3.30
N <sub>2</sub>	1.20
O <sub>2</sub>	9.20
Ash	10.30
Total	100.00

- ▶ Example: Illinois Bituminous coal
- ▶ Measured Se for this coal was 2.2 µg/g
- ▶ Vary Se from 0.5 to 4 µg/g to estimate Se emissions and Se concentration in fly ash

# Estimate of Se in Fly Ash

- ▶ Detection limits for Se in fly ash are 0.1-0.2  $\mu\text{g/g}$
- ▶ Should be able to detect Se in fly ash samples

Se Removal in ESP	----- Se in fly ash, ug/g -----		
		<i>Se in coal, ug/g dry</i>	
	<i>0.5</i>	<i>2</i>	<i>4</i>
10%	0.5	1.8	3.6
25%	1.1	4.5	8.9
50%	2.2	8.9	17.8
98%	4.4	17.5	35.0

# Estimate of Se in Flue Gas (Post ESP)

- ▶ Except for very high removals in ESP, should be able to detect Se via M29

Se Removal in ESP	----- Se in flue gas, lb/TBtu -----			Se Removal in ESP	----- Se in flue gas, ug/dscm-----		
	<i>Se in coal, ug/g dry</i>				<i>Se in coal, ug/g dry</i>		
	0.5	2	4		0.5	2	4
10%	33.6	134.4	268.7	10%	42.9	171.8	343.5
25%	28.0	112.0	223.9	25%	35.8	143.1	286.3
50%	18.7	74.7	149.3	50%	23.9	95.4	190.8
98%	0.8	3.0	6.0	98%	1.0	3.8	7.6
Shaded areas might be below detection limit for M29							

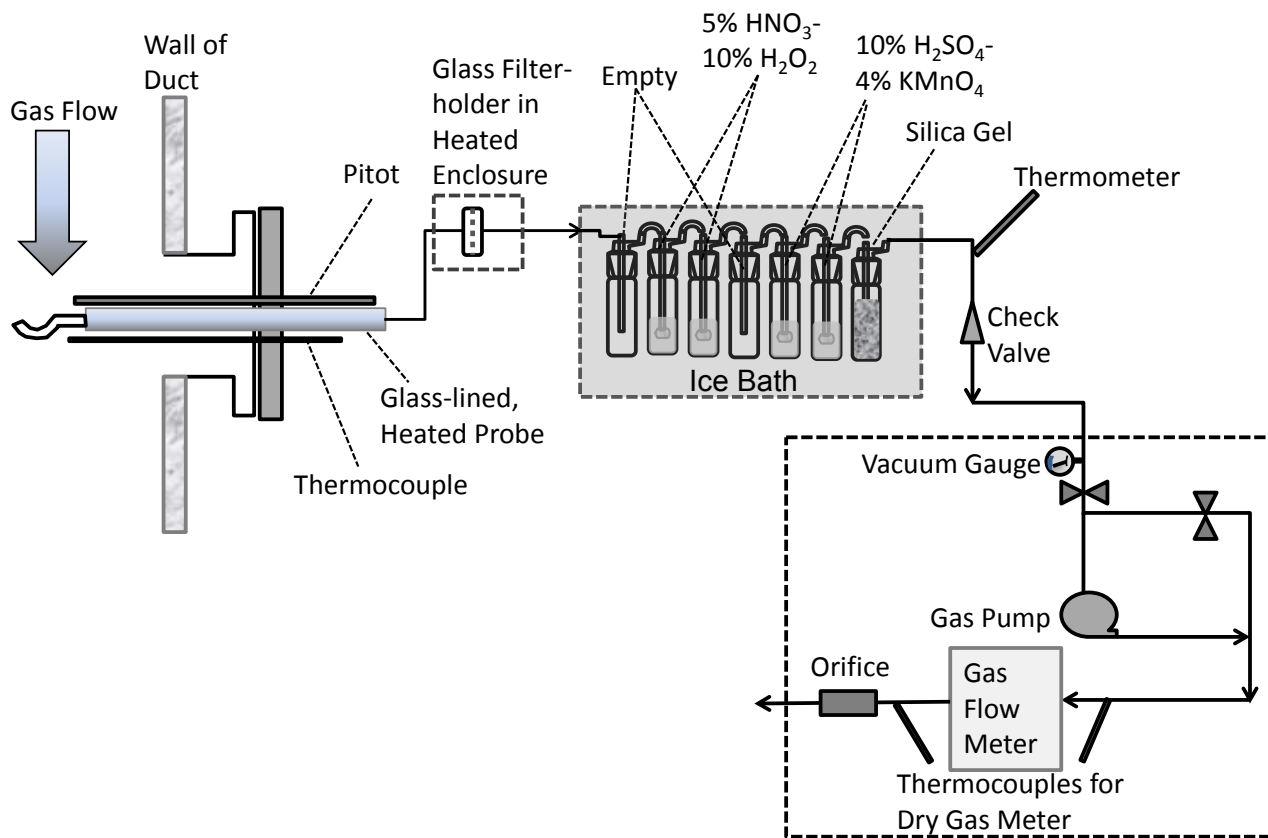
Number	Sample	Method	Se, $\mu\text{g/g AR}$	RD of replicates	RD: INAA vs. ICP
Plant B(1), "A"	Coal	INAA	4.56	1.3%	
Plant B(1), "B"	Coal	INAA	4.44		
		Average	4.50		-8.4%
Plant B(1), "C"	Coal	ICP-DRC-MS	4.94	1.2%	
Plant B(1), "D"	Coal	ICP-DRC-MS	4.82		
		Average	4.88		
Boiler F, "A"	Coal	INAA	1.71	29.1%	
Boiler F, "B"	Coal	INAA	0.94		
		Average	1.33		46.4%
Boiler F, "C"	Coal	ICP-DRC-MS	0.71		
Plant G(1), "A"	Fly ash	INAA	7.13	1.7%	
Plant G(1), "B"	Fly ash	INAA	6.89		
		Average	7.01		-40.9%
Plant G(1), "C"	Fly ash	ICP-DRC-MS	10.00	1.3%	
Plant G(1), "D"	Fly ash	ICP-DRC-MS	9.75		
		Average	9.88		
Boiler C, "A"	Fly ash	INAA	3.80	4.0%	
Boiler C, "B"	Fly ash	INAA	4.12		
		Average	3.96		-32.1%
Boiler C, "C"	Fly ash	ICP-DRC-MS	5.23	--	
Plant D(1), "A"	Fly ash	INAA	18.30	3.2%	
Plant D(1), "B"	Fly ash	INAA	19.50		
		Average	18.90		-13.8%
Plant D(1), "C"	Fly ash	ICP-DRC-MS	19.30	10.2%	
Plant D(1), "D"	Fly ash	ICP-DRC-MS	23.70		
		Average	21.50		
Boiler E	Fly ash	INAA	182	--	
Boiler E, "A"	Fly ash	ICP-DRC-MS	152	0.7%	15.9%
Boiler E, "B"	Fly ash	ICP-DRC-MS	154		
		Average	153		

## Measurement of Se in Solid Samples

- ▶ Instrumental Neutron Activation Analysis (INAA)
- ▶ Inductively Coupled Plasma - Dynamic Reaction Cell - Mass Spectroscopy (ICP-DRC-MS)
- ▶ Both methods show good repeatability
- ▶ Agreement between methods good to fair

# Measurement of Se in Flue Gas

- ▶ Method 29 measures the particulate and gaseous emissions of mercury and 16 other trace elements including Se
- ▶ Gas-phase metals and mercury are collected in two impingers in series containing an acidified peroxide solution
- ▶ Elemental mercury collected in two impingers in series containing acidified permanganate





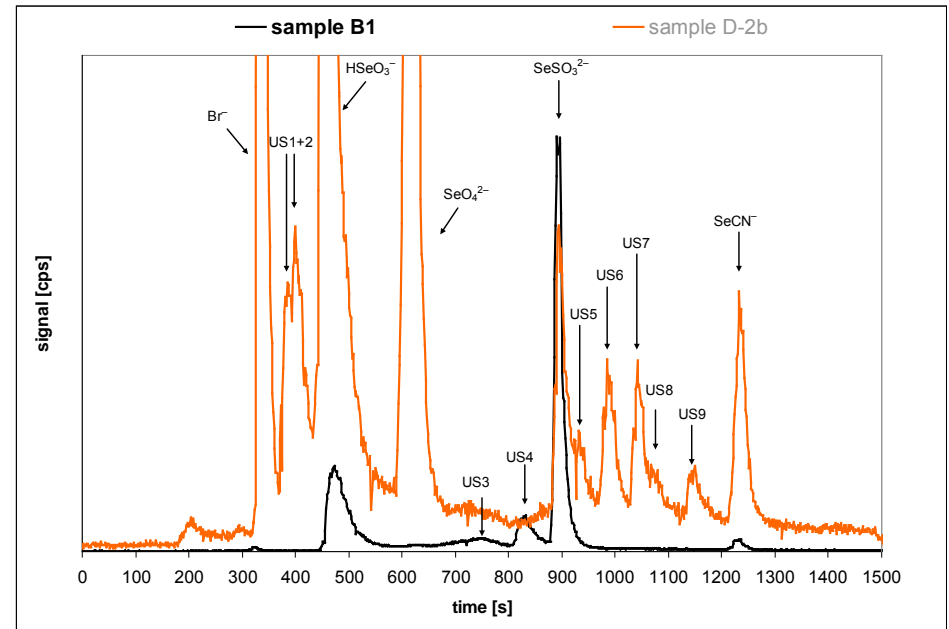
# Measurement of Se in Wet FGD Slurries

- ▶ Sample preservation techniques in the field important for making selenium speciation measurements
- ▶ Preservation techniques include
  - Cryo-freezing (rapidly freezing with liquid nitrogen)
  - Acidification
- ▶ Solid and liquid phases separated after the samples received at the analytical laboratory



# Measurement of Se in Wet FGD Slurries

- ▶ Se typically measured by ion chromatography + ICP-MS
- ▶ Oxidation states:
  - Selenite - Se[IV]
  - Selenate - Se[VI]
  - Elemental - Se[0]
- ▶ Compounds:
  - Selenocyanate ( $\text{SeCN}^-$ )
  - Selenosulfate -  $\text{SeSO}_3^{2-}$
  - Dissolved or colloidal Se[0]
  - Unknown Se peaks



Source: P. Chu, EPRI

# Developing Se Measurements in Water

## ► PSA Analytical

- Method: generate and detect gaseous hydride
- Also can measure As
- Method can only detect selenite in water
- To measure total selenium, oxidize all Se to Se[VI] and then reduce it back to Se[IV]
- Sample prep is critical



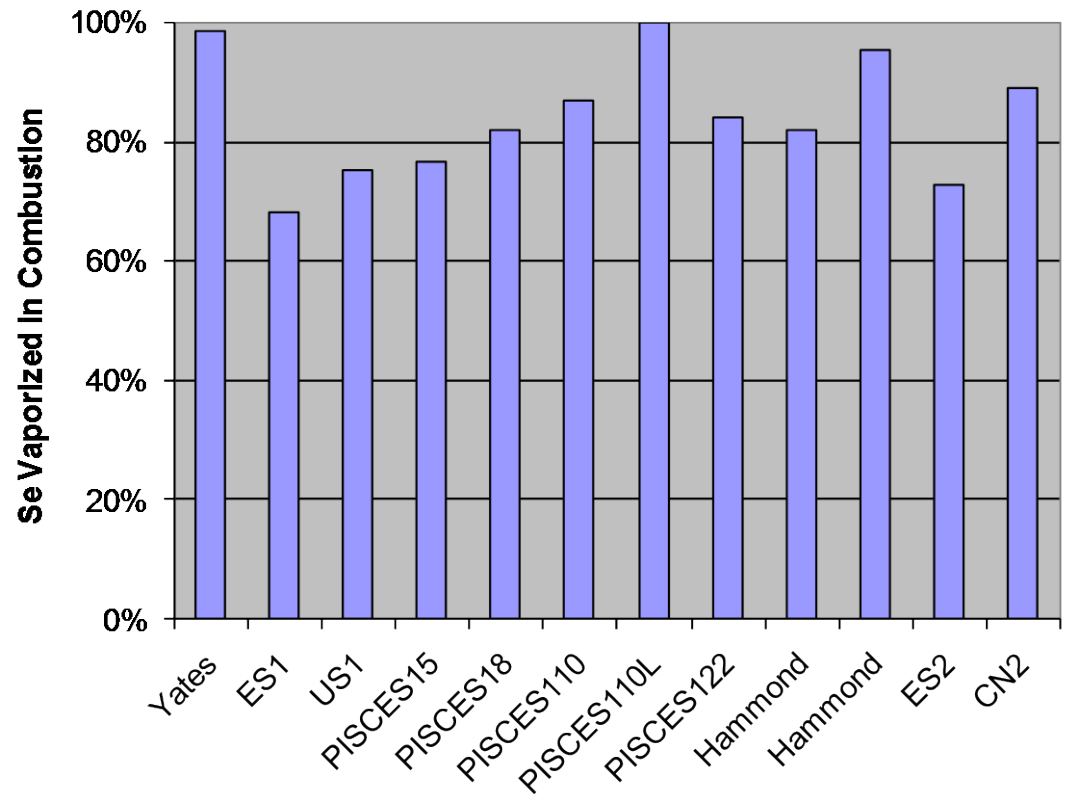
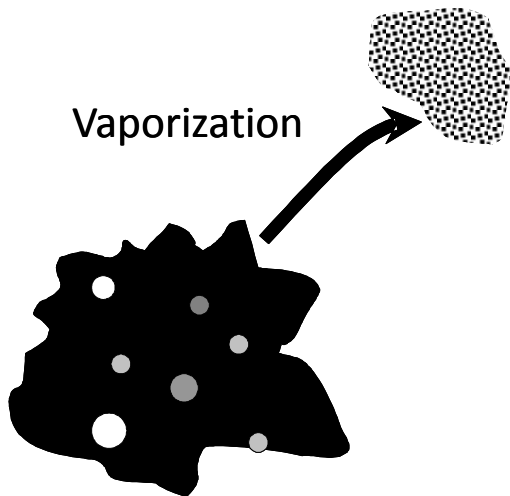
# Developing Se Measurements in Water



- ▶ Aqua Metrology Systems
  - Method: cathodic stripping voltammetry (CSV)
  - Method can only detect selenite in water
  - To measure total selenium, oxidize all Se to Se[VI] and then reduce it back to Se[IV]
  - Method is highly selective for selenium, sample prep is critical
  - Se can be measured down to 1 ppb in water

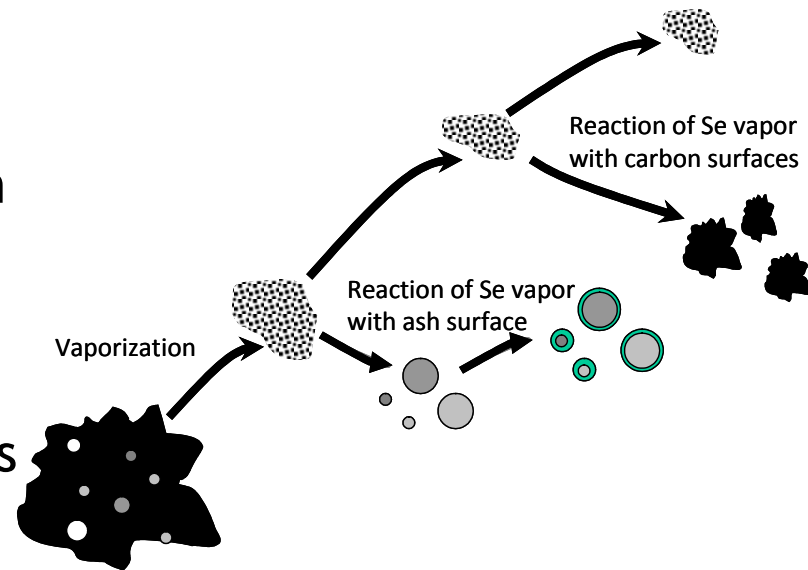
# Behavior of Se in Coal-Fired Boilers

- ▶ Data from full-scale campaigns used to calculate vaporization in the combustion zone
- ▶ Almost all selenium vaporizes in combustion



# Behavior of Se in Coal-Fired Boilers

- Gaseous selenium ( $\text{SeO}_2(\text{g})$ ) can exist in flue gas from combustion zone to 160°F
- Along the flue gas path, selenium reacts with iron, calcium, and sodium in fly ash or sorbents
- $\text{SeO}_2(\text{g})$  water soluble
  - Some  $\text{SeO}_2(\text{g})$  condenses, converted to submicron aerosol across wet FGDs
- Implications for emissions and control
  - Efficient capture of Se by fly ash in boilers firing subbituminous and lignites
  - Poor capture of Se by fly ash in boilers firing high-sulfur bituminous
  - Wet FGDs may not efficiently remove Se



# Selenium-Iron Interactions

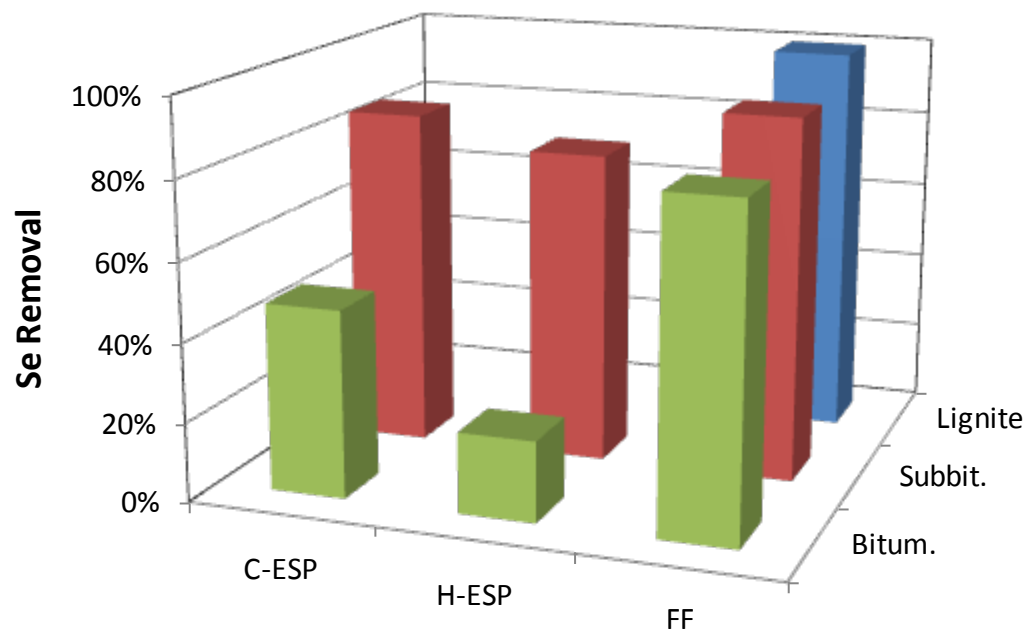
- ▶ Addition of iron compounds to combustion zone can reduce gas-phase Se at stack
- ▶ Studies by B&W (Mitagent 95 additive) at PRB-fired boiler with SCR, C-ESP and wet FGD

Stack Sampling Date	Test ID	Gas phase Hg Emission Rate (lb/ Tbtu)	Gas Phase Se Emission (lb/ Tbtu)	Gas Phase P Emission (lb/ Tbtu)
1/10	With BPAC injection	0.7	0.41	8.1
1/11	Baseline	3.6	0.27	7.9
1/12	With 300 ppm Cl addition	1.4	0.49	7.6
1/13	30 ppm Br addition	1.0	0.57	8.2
1/14	30 ppm of bromine in form of Mitagent™ 95 additive	1.1	0.14	4.5

Source: Gadgil, et al., APC Roundtable, 2013

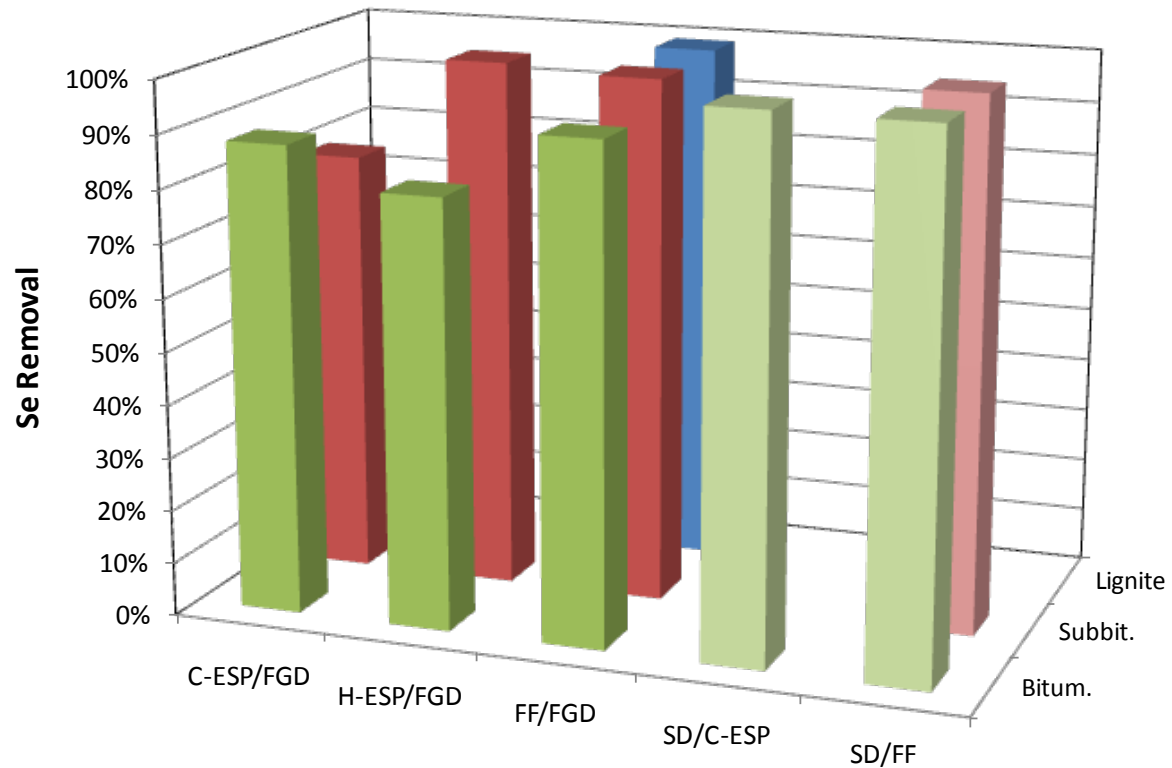
# Fate of Se in Particulate Control Devices: 2011 Utility ICR Data

- Average Se removal
- Plants with **only particulate control devices**
- Se removal across C-ESPs, 40% to >90%
  - Higher removal for low-rank coals
- FFs show higher removal, all ranks



# Fate of Se in Flue Gas Desulfurization: 2011 Utility ICR Data

- Average Se removal
- Plants with spray dryer (SD) or wet FGD
- Se removal greater across boilers with SO<sub>2</sub> control
- Spray dryers appear to have average higher removal than FGDs (with FF or C-ESP)



# How Does Hg Control Affect Se?

- ▶ Interactions between activated carbon and vapor-phase Se not clearly demonstrated
- ▶ Wet FGDs remove gaseous Se
- ▶ Bromine addition to fuel has been shown to reduce Se removal with fly ash => which means more gaseous Se leaves PCD and can be collected in wet FGD, if present

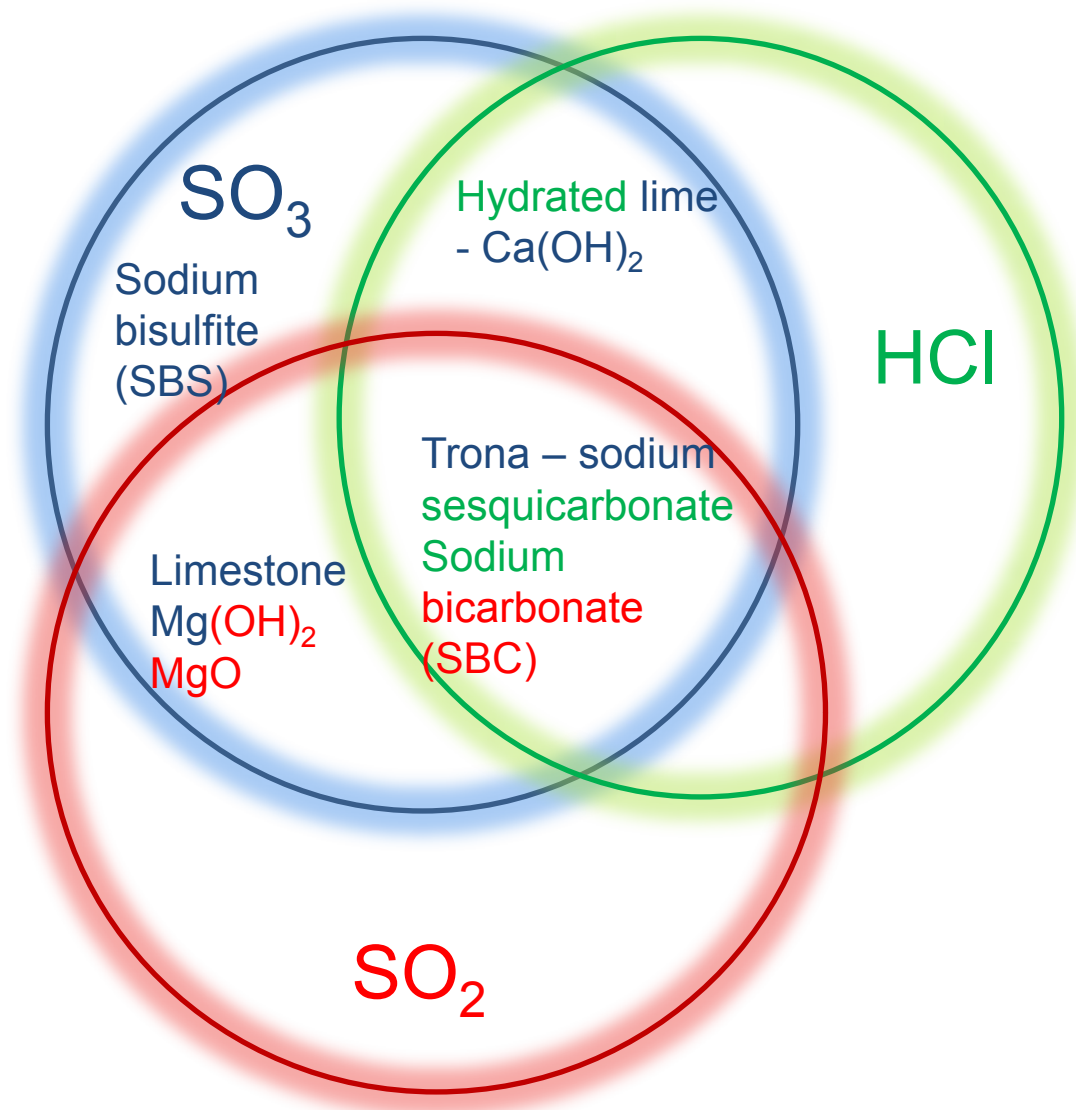


# Interaction between ACI and Se

- ▶ EPRI-sponsored study\* looked at the effect of activated carbon injection (ACI) on Se emissions and concluded that
  - Insufficient data from 2010 ICR on bituminous-fired boilers with ACI
  - 2010 ICR data for subbituminous-fired boilers with ACI showed no clear positive effect of ACI on Se stack emissions
    - ▶ Operational differences between plants and low baseline Se emissions may have compounded results
  - EPRI analysis of 9 ACI test sites (2004-2009) with and without ACI at same site:
    - ▶ Suggested a possibility for increased Se removal with ACI
    - ▶ Four sites showed increase in Se with ACI; five sites did not

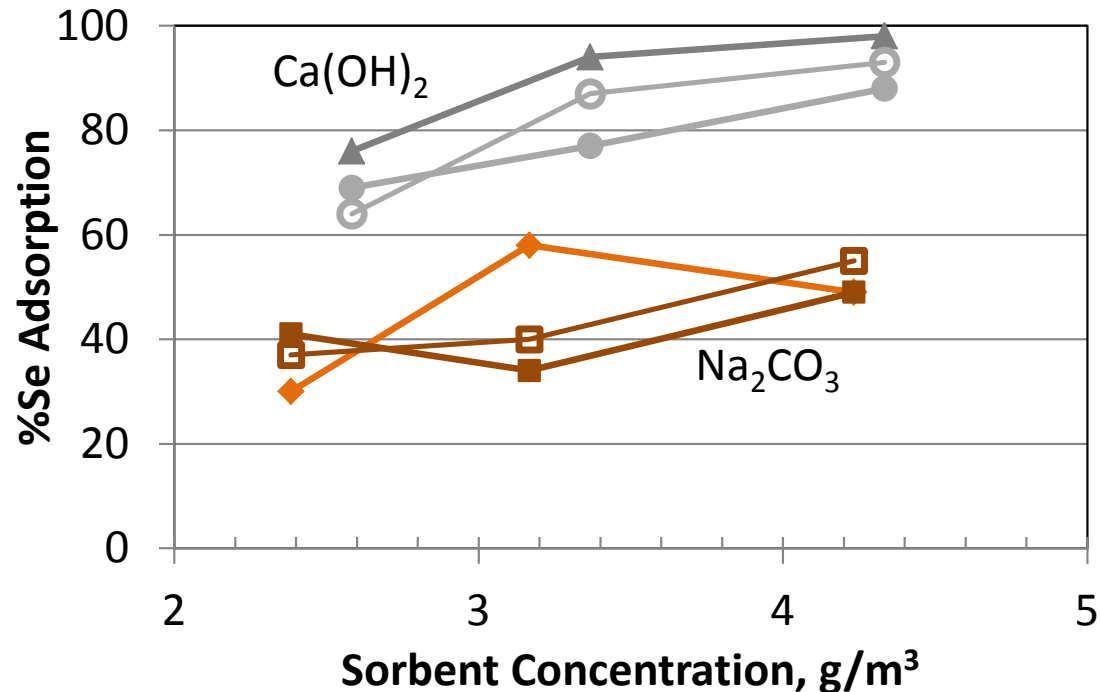
\*Dombrowski et al., Air Quality VIII Conference, 2011

# What About DSI?



# How Does Injecting DSI Sorbents Affect Se?

- ▶ 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



◆ 724 F, water quench    
 ■ 634 F, water quench    
 ▣ 625 F, air quench  
▲ 733 F, water quench    
 ● 634 F, water quench    
 ○ 634 F, air quench

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

# Interaction between Bromine and Se

- ▶ Adding bromine to the fuel can shift Se from fly ash to wet FGD
- ▶ EPRI study\* noted data from three test sites showing an increase in Se concentration in FGD liquor during bromine addition to fuel
- ▶ For example, at one bituminous-fired boiler bromine was added for 10 days:

Condition	Se in Fly Ash, $\mu\text{g/g}$	%Se Capture by Fly Ash	Se in FGD Liquor, $\mu\text{/L}$
Baseline	24	70%	300
Br Addition	10	20%	4,900

- ▶ Test at a subbituminous-fired boiler\*\* with SCR, ESP and wet FGD showed 110% increase in gas-phase Se at wet FGD inlet: 30 ppmw Br addition compared to baseline

\*Dombrowski et al., Air Quality VIII Conference, 2011

\*\*Gadgil et al., APC Roundtable, 2013

# Plant Wansley Study\*: Mechanisms for Removal Across Wet FGD

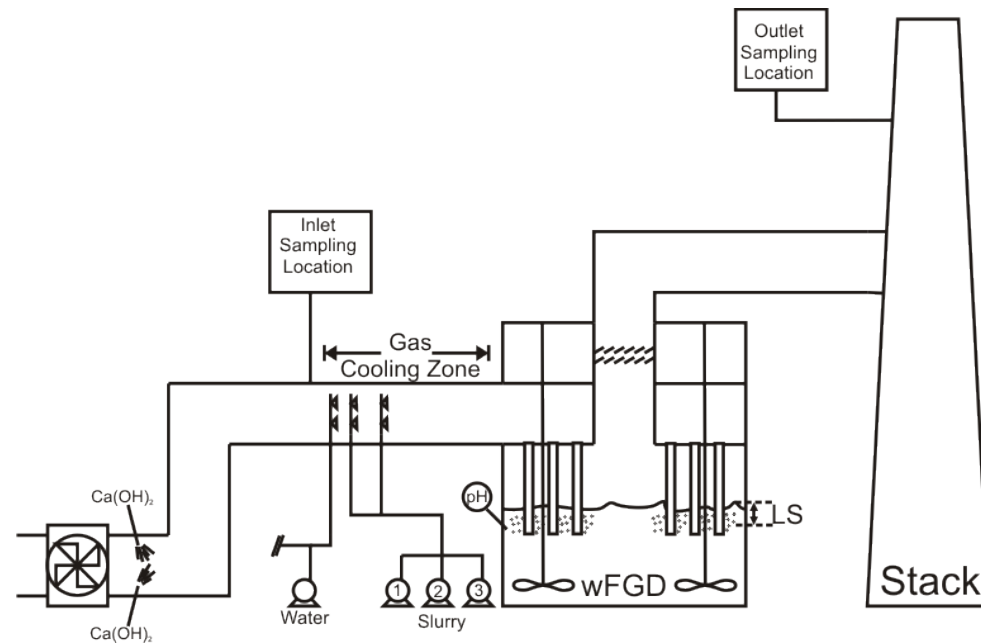
- ▶ Determine removal of Se across full-scale wet scrubber in a low-sulfur bituminous-fired boiler
  - ▶ 900 MW boiler, burning Eastern bituminous coal
  - ▶ APCD: cold-side ESP, MHI Chiyoda scrubber
  - ▶ Hydrated lime injection between ESP and FGD for SO<sub>3</sub> control
- ▶ Obtain better understanding of Se behavior across wet scrubbers

\*Senior, C.L.; Tyree, C.A.; Meeks, N.D.; Acharya, C.; McCain, J.D.; Cushing, K.M. Selenium Partitioning and Removal Across a Wet FGD Scrubber at a Coal-Fired Power Plant. *Env. Sci. Technol.* 2015, 49, 14376-14382.

# Measurement Methods

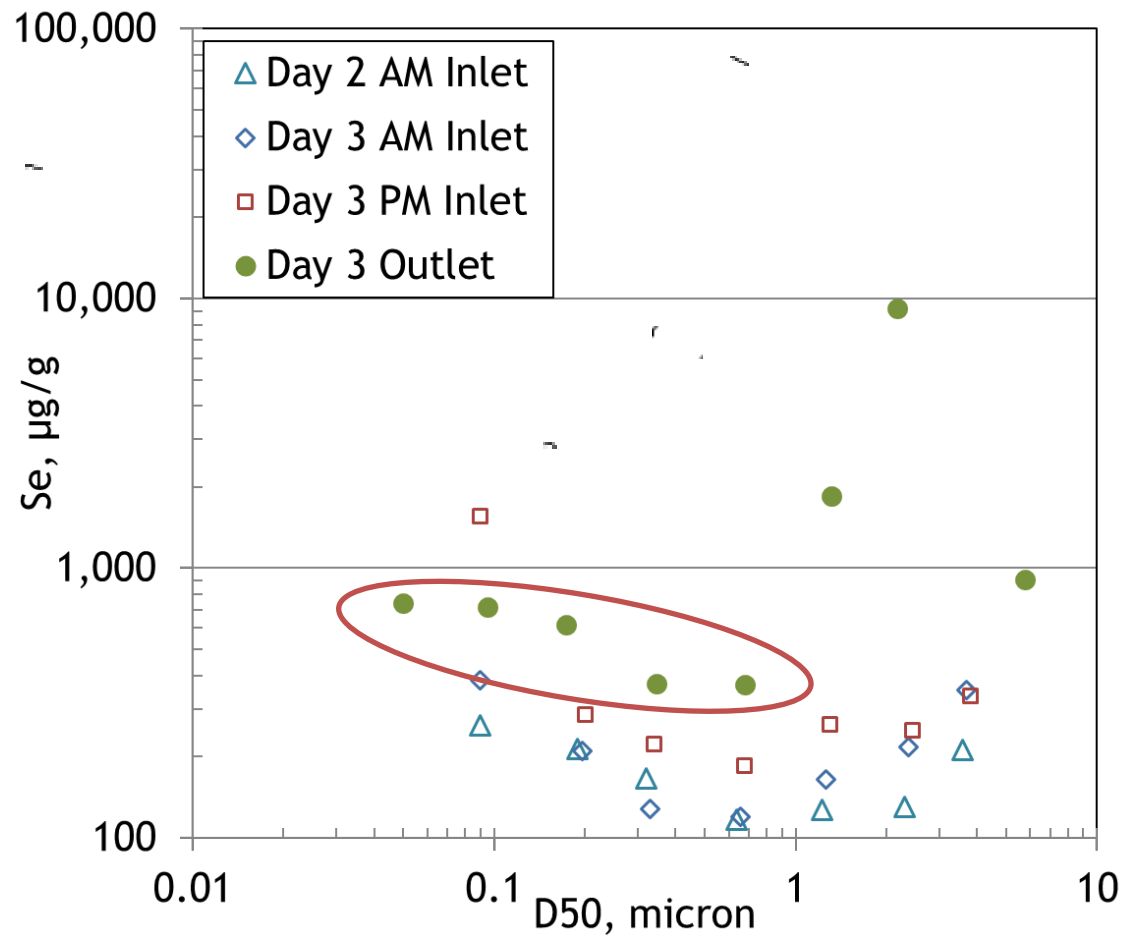
- ▶ Samples taken at inlet and outlet of scrubber: gaseous Se and size-segregated fly ash
- ▶ FGD inlet sample taken after  $\text{Ca}(\text{OH})_2$  injection

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



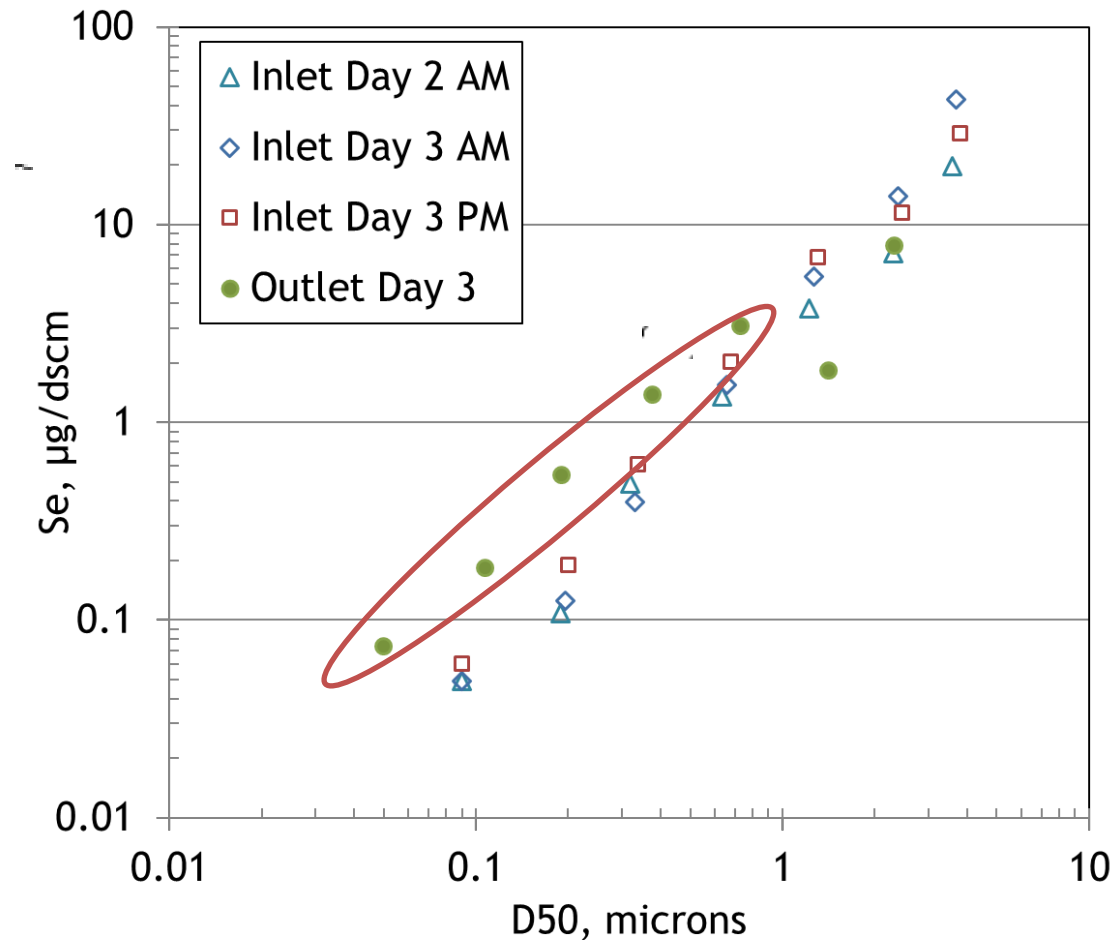
# Gas-to-Particle Conversion

- ▶ Concentration of selenium in submicron particles increases from FGD inlet to FGD outlet

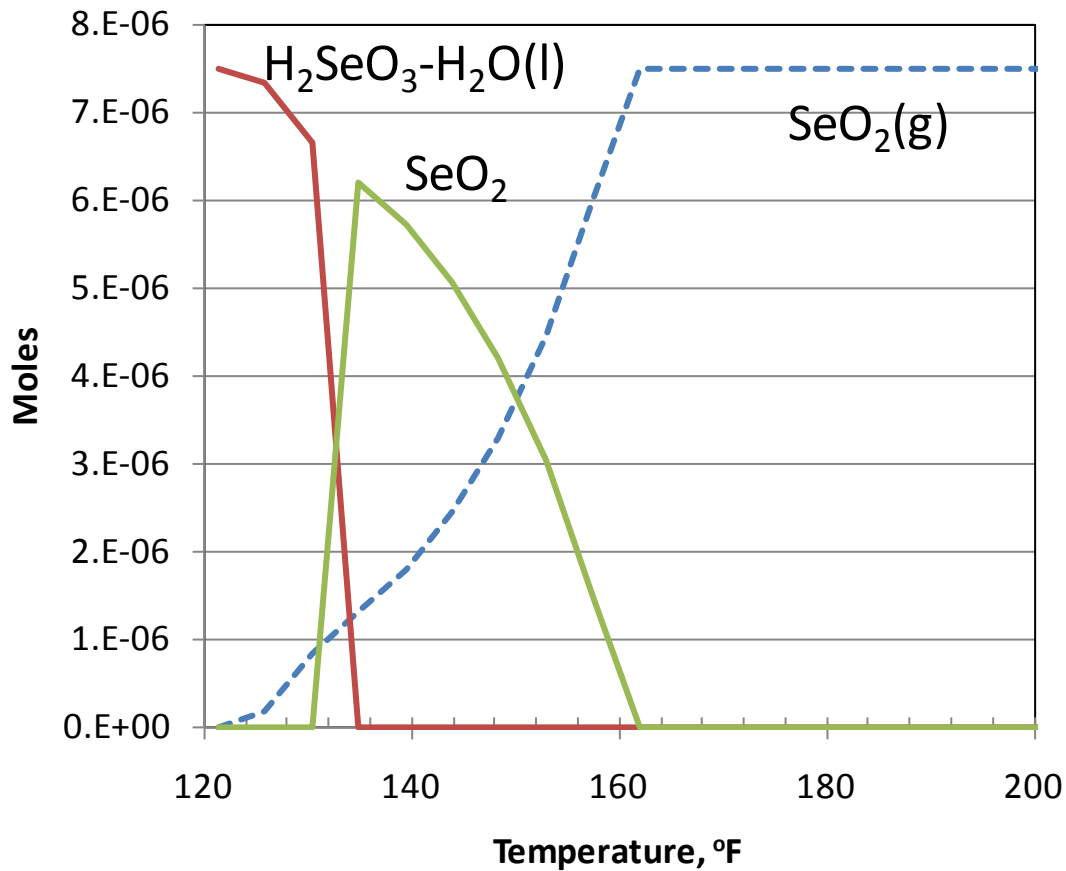


# Gas-to-Particle Conversion

- ▶ Concentration of selenium in submicron particles increases from FGD inlet to FGD outlet
- ▶ AND concentration of submicron Se in the flue gas increases across the scrubber
- ▶ What could be going on?

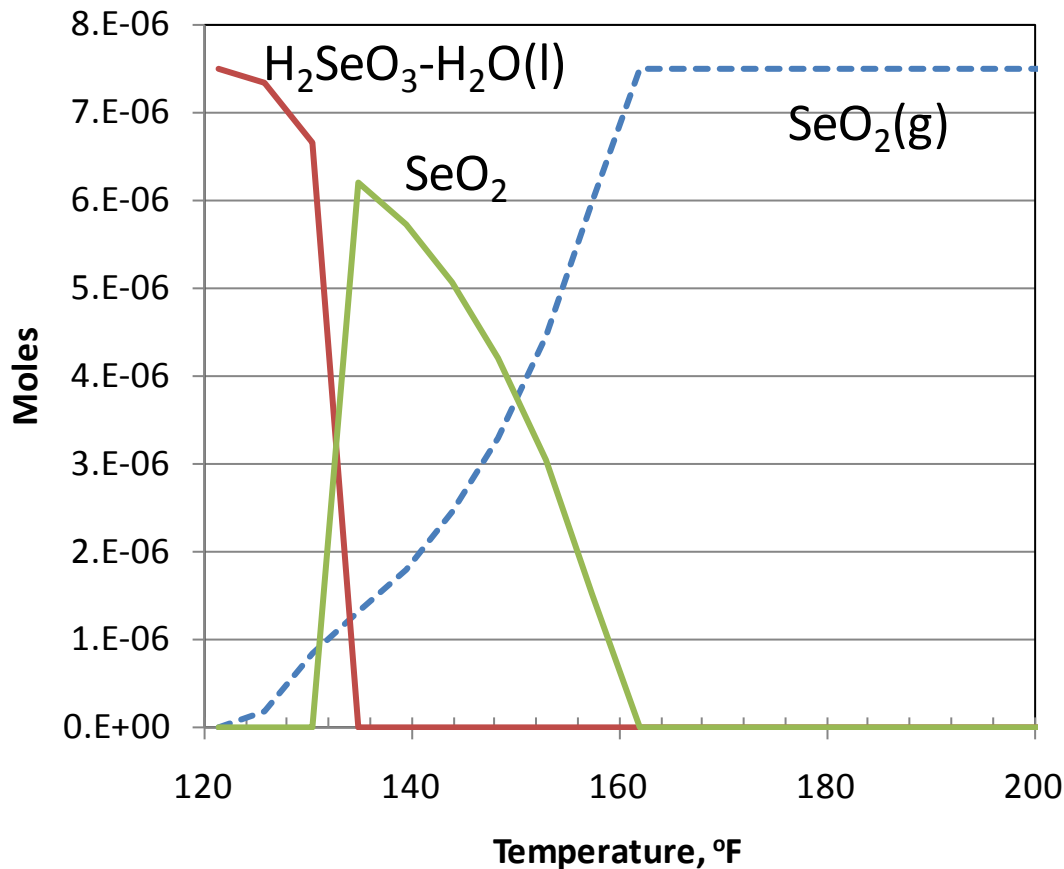


# Gas-to-Particle Conversion



- ▶ Equilibrium calculations using typical flue gas compositions
- ▶ Condensation of  $\text{SeO}_2$  at temperatures below 160°F

# Gas-to-Particle Conversion



- ▶ Rapid quench in scrubber could convert gaseous SeO<sub>2</sub> to H<sub>2</sub>SeO<sub>3</sub> aerosol or SeO<sub>2</sub> condensed on fly ash
- ▶ Preferential condensation would be on submicron particles (higher surface area)

# Conclusions from Wansley Study

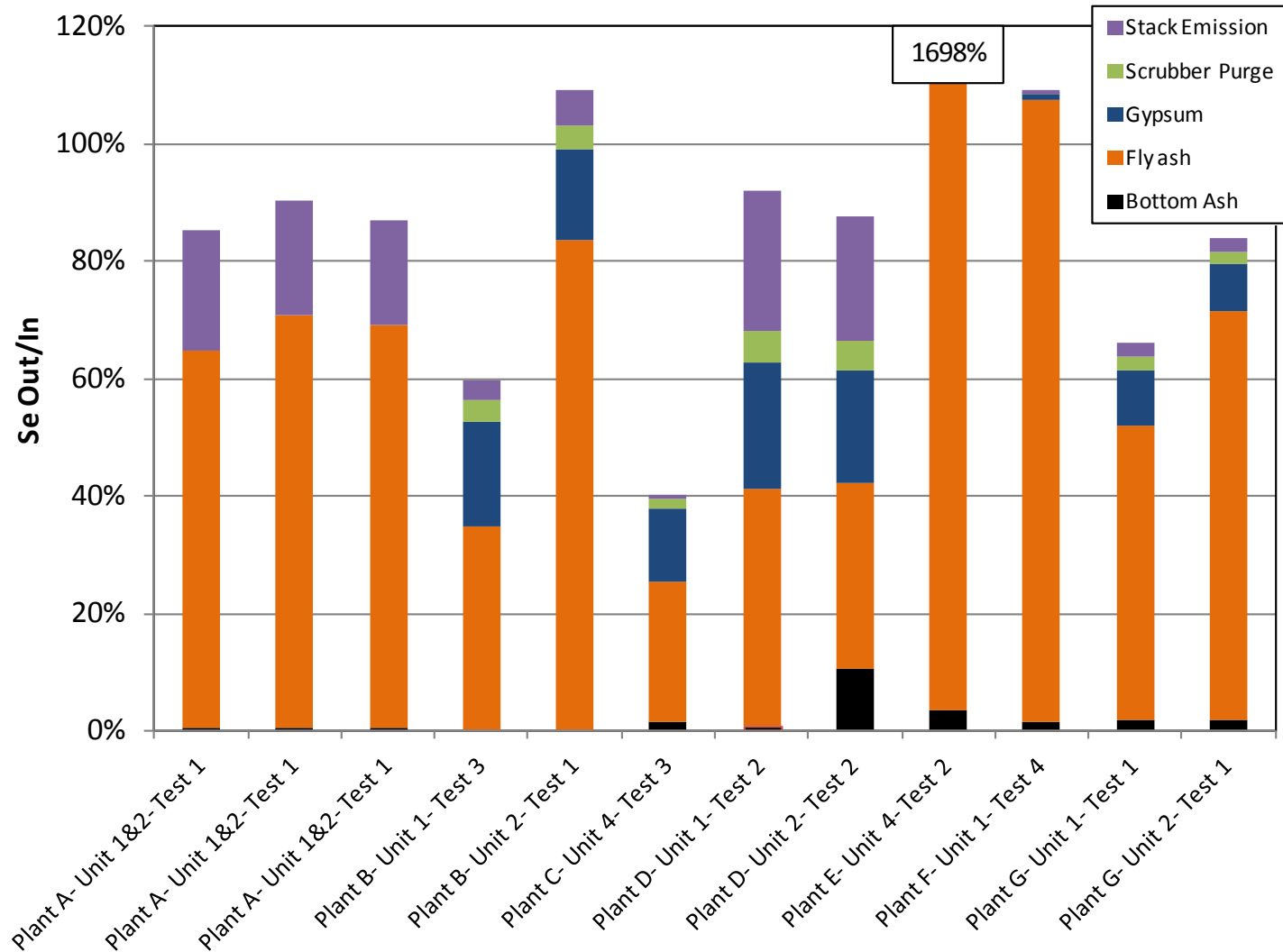
- ▶ Total removal Se (gas plus particle-bound) across FGD averaged 61% even though SO<sub>2</sub> removal was >97%
  - ▶ In line with observations at other boilers
- ▶ Gas-to-particle conversion of Se across FGD could limit removal of Se across FGD

# Selenium Removal in Wet FGDs

- ▶ In 2010, ~200 boilers chosen by EPA for stack sampling of metal emissions in ICR
- ▶ In EPRI-sponsored study,\* additional samples collected at eleven boilers:
  - ▶ Coal (a split of the ICR sample, if possible)
  - ▶ Bottom ash & Economizer ash (if available)
  - ▶ Fly ash from the particulate control device hopper
  - ▶ From FGD (all limestone forced oxidation):
    - ▶ Limestone
    - ▶ Make-up water
    - ▶ Gypsum product
    - ▶ Scrubber purge stream

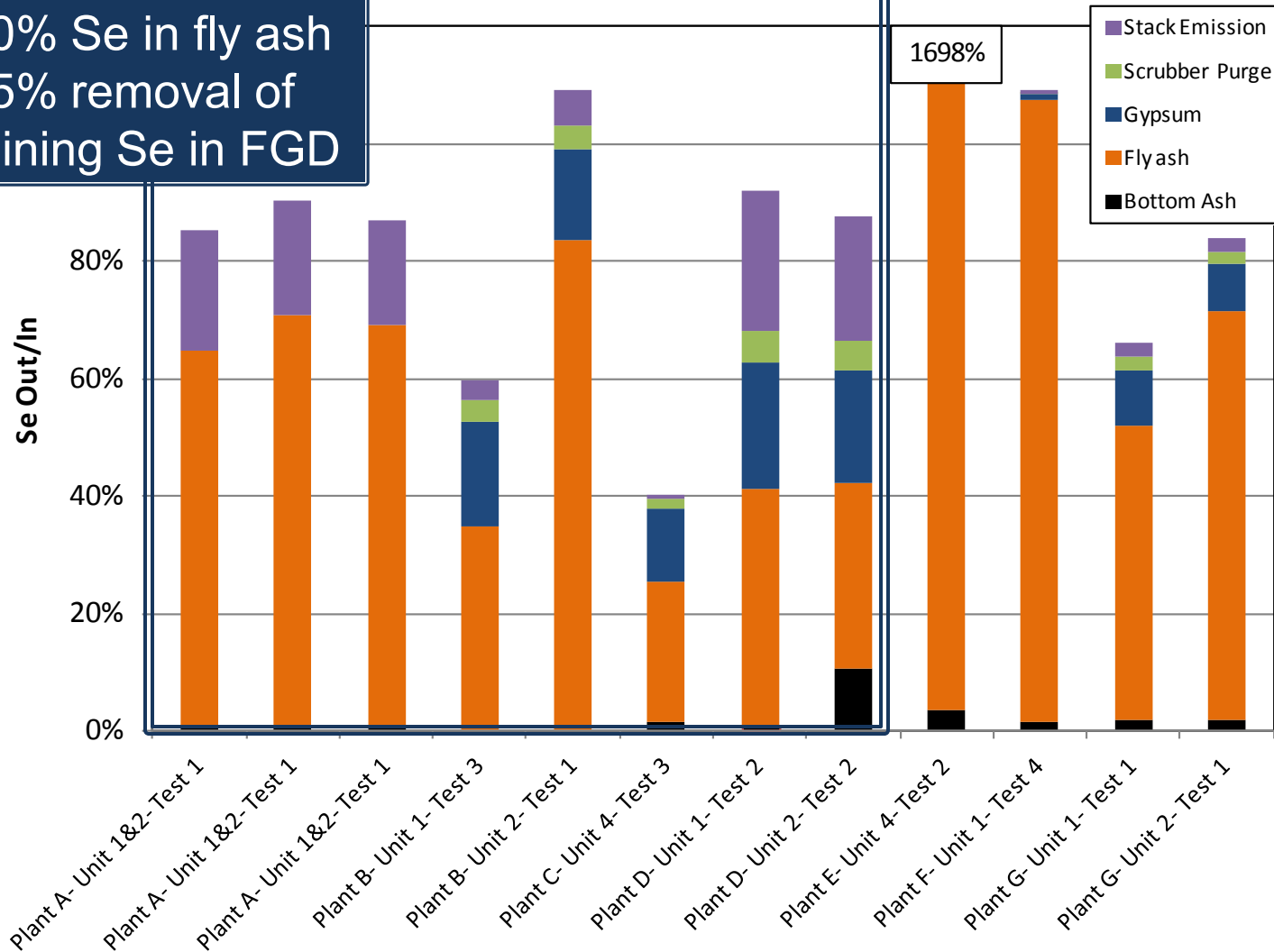
\*Senior et al., AQVIII Conference, 2011

# Selenium Mass Balance

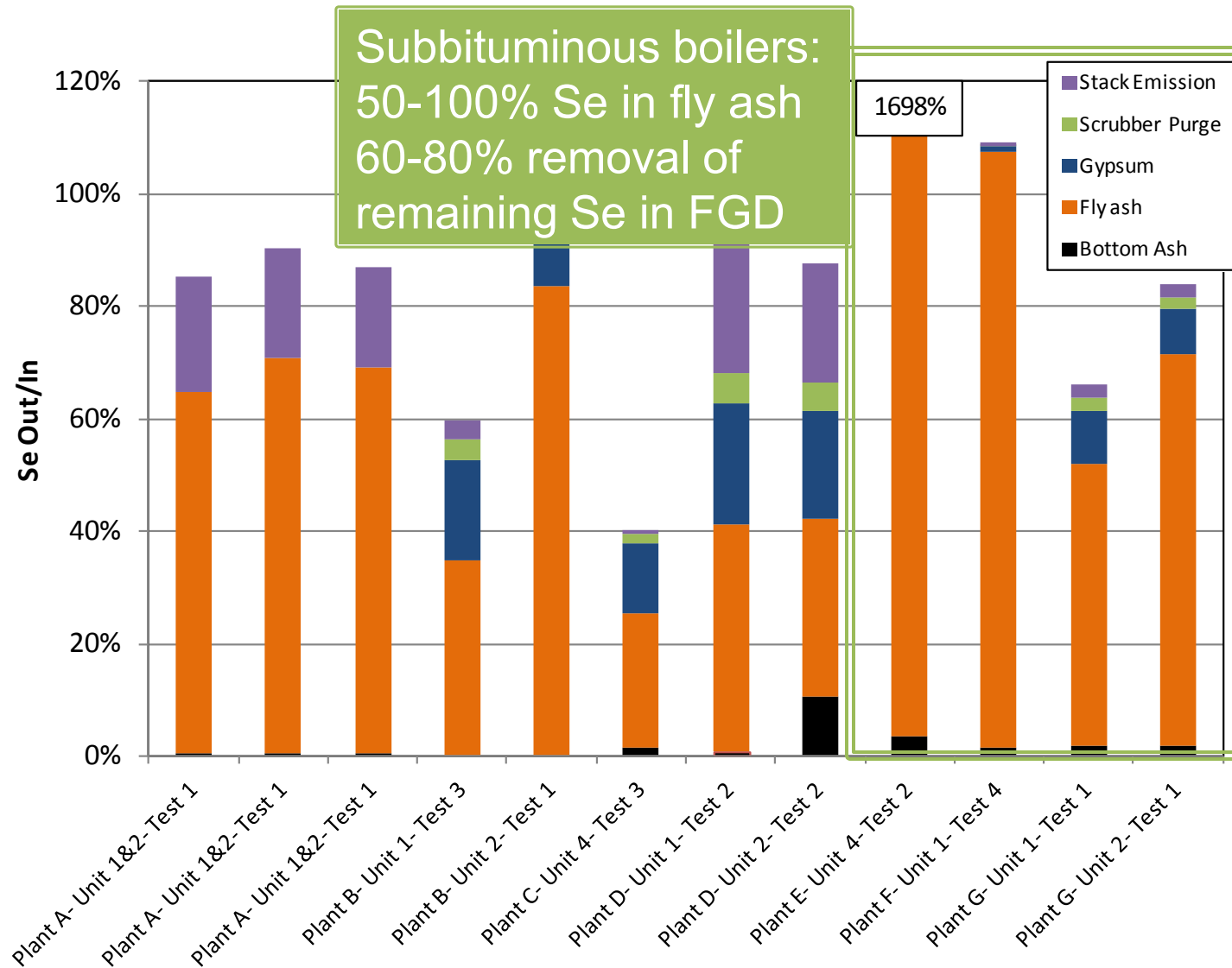


# Selenium Mass Balance

Bituminous boilers:  
25-80% Se in fly ash  
50-95% removal of  
remaining Se in FGD

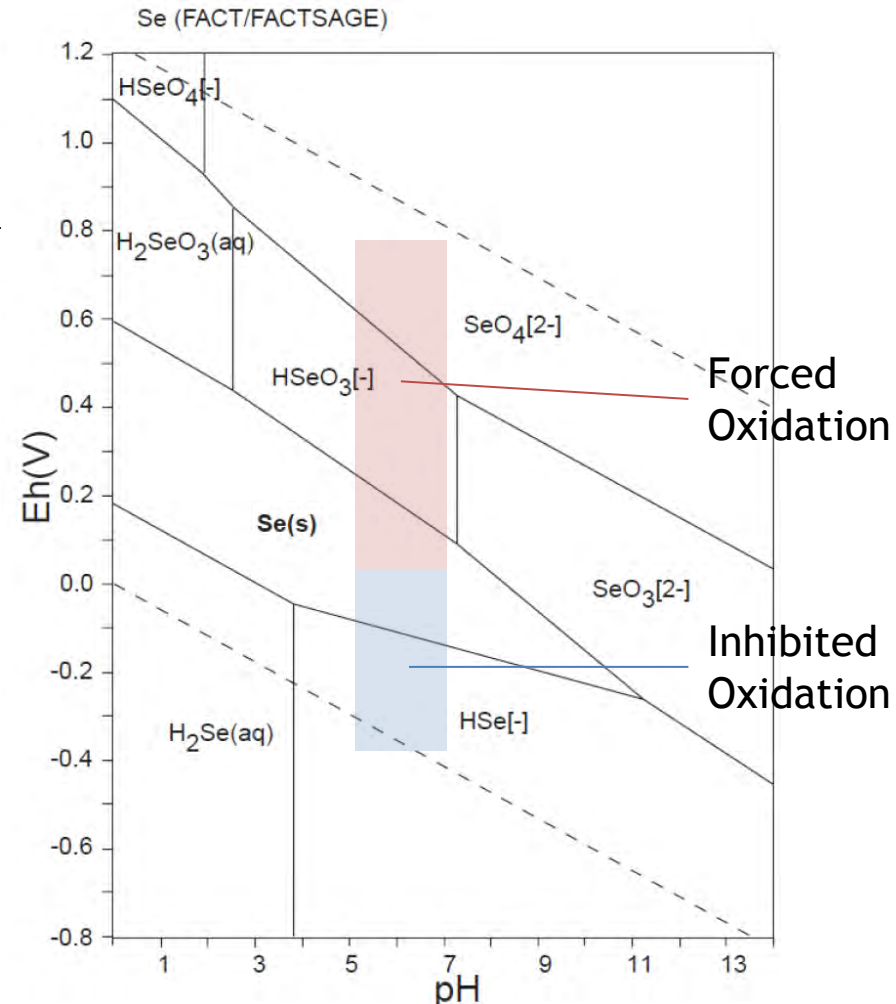


# Selenium Mass Balance



# Selenium Speciation in Wet FGDs

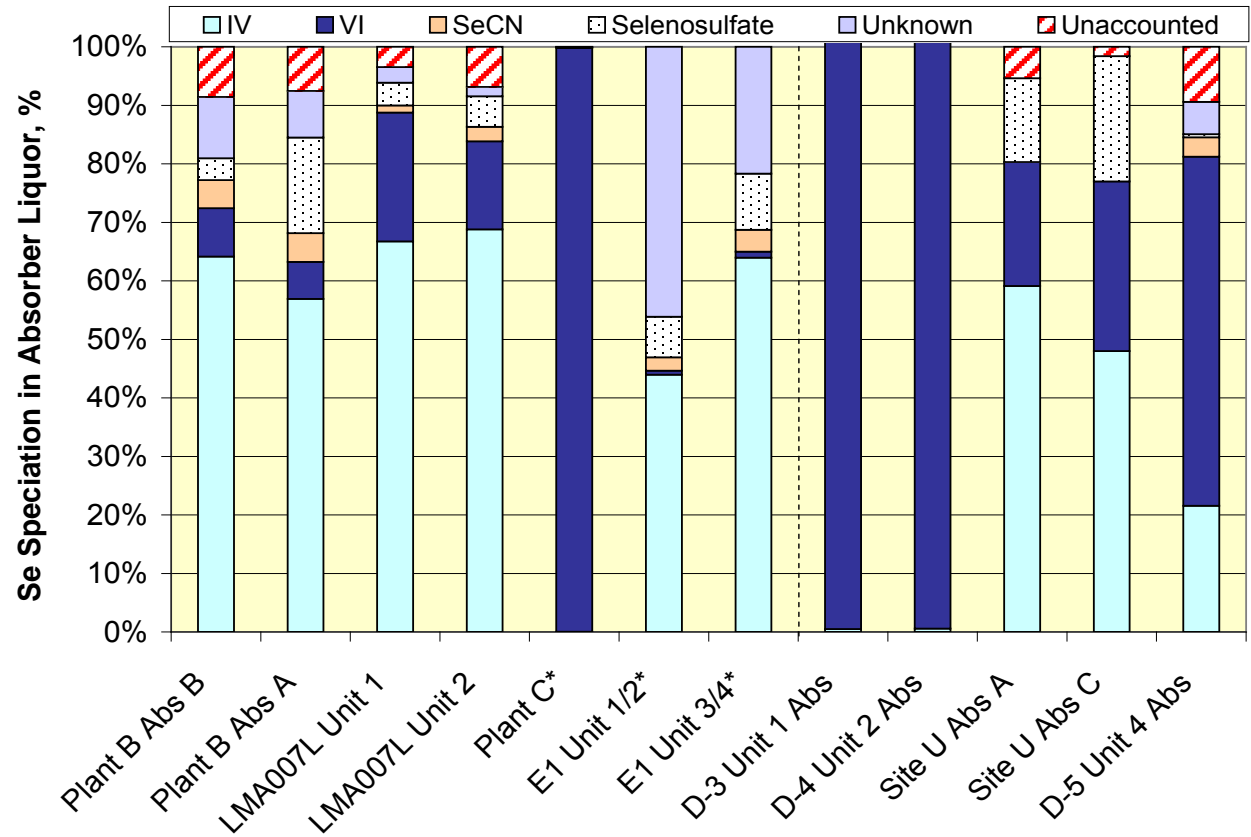
- ▶ Selenium can exist in aqueous phase or solid phase in wet FGD slurry
- ▶ A range of different Se species are expected in wet FGD slurries
- ▶ Speciation of selenium in the scrubber varies with pH and ORP, affected by, for example
  - ▶ Scrubber design
  - ▶ Transition metals in slurry
  - ▶ Scrubber additives
- ▶ Implications for downstream wastewater treatment



Pourbaix diagram for  $10^{-10}$  M Se in water, Cited in Allen et al., 2016 Mega Symposium

# Se Speciation in Wet FGD: 2010 EPRI Study

- ▶ Absorber sample selenium speciation percentages
- ▶ Large variation in Se speciation from scrubber to scrubber



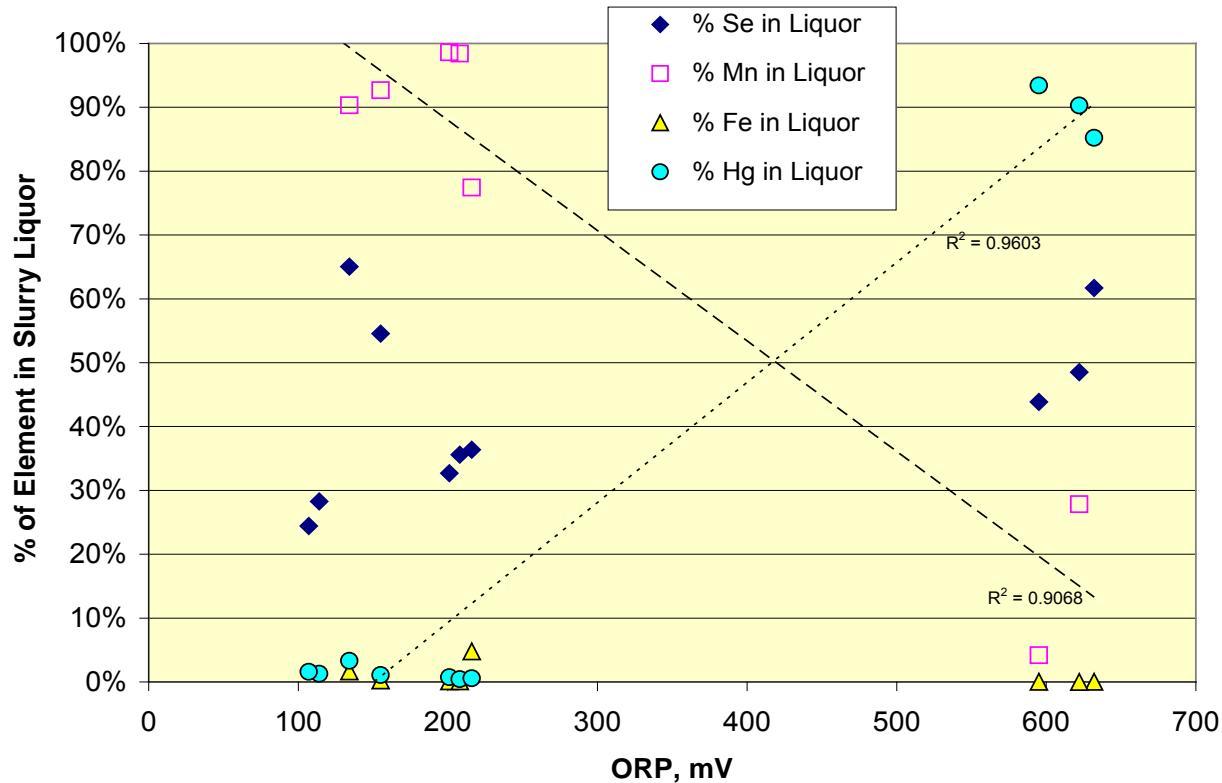
*Impact of Wet FGD Design and Operations on Selenium Speciation: 2010 Update.* EPRI, Palo Alto, CA: 2010. 1019870.

# Se Speciation in Wet FGD: 2010 EPRI Study

- ▶ No clear trends with ORP for total dissolved Se

- ▶ Highly soluble  $Mn^{2+}$  form at lower ORP, but at higher ORP the relatively insoluble  $MnO_2$  ( $Mn^{4+}$ ) favored

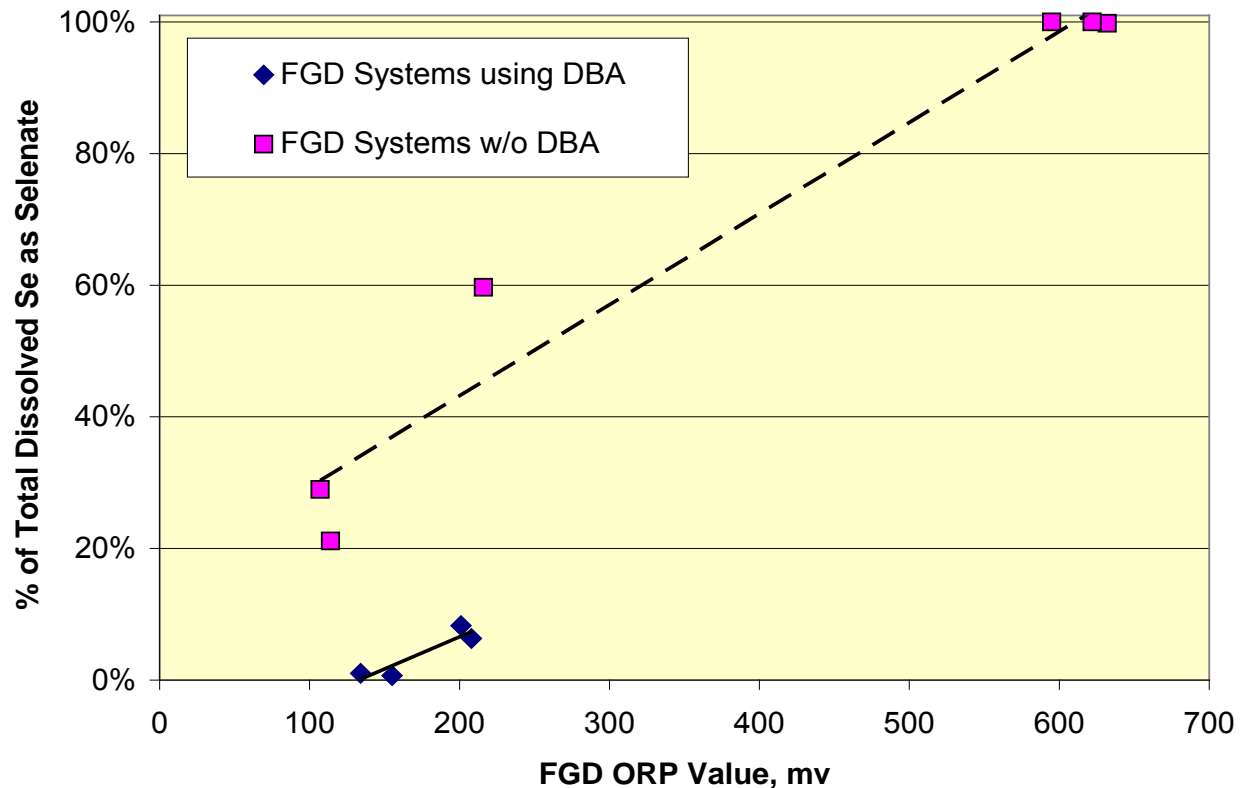
- ▶ At lower ORP nearly all of the mercury adsorbed on solids in the FGD slurry, while at high ORP (~600 mV or greater) most of the mercury remains in the liquor



*Impact of Wet FGD Design and Operations on Selenium Speciation: 2010 Update.*  
EPRI, Palo Alto, CA: 2010. 1019870.

# Se Speciation in Wet FGD: 2010 EPRI Study

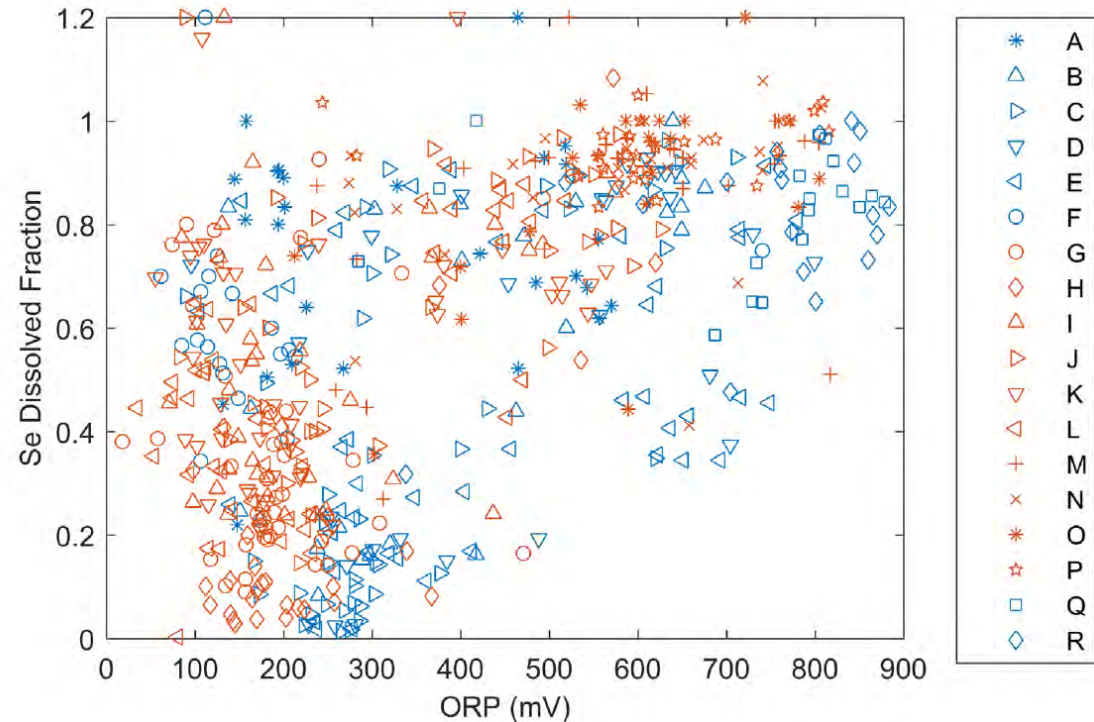
- ▶ ORP values for the FGD systems that do not use DBA as a performance additive appear to correlate well with the selenate percentages in the corresponding absorber samples



*Impact of Wet FGD Design and Operations on Selenium Speciation: 2010 Update.*  
EPRI, Palo Alto, CA: 2010. 1019870.

# Se Partitioning in Wet FGD: 2016 SoCo Study

- ▶ Much scatter for ORP vs total dissolved Se
- ▶ At lower ORP <50% of the selenium adsorbed on solids in the FGD slurry, while at high ORP (~400 mV or greater) most of the selenium remains in the liquor

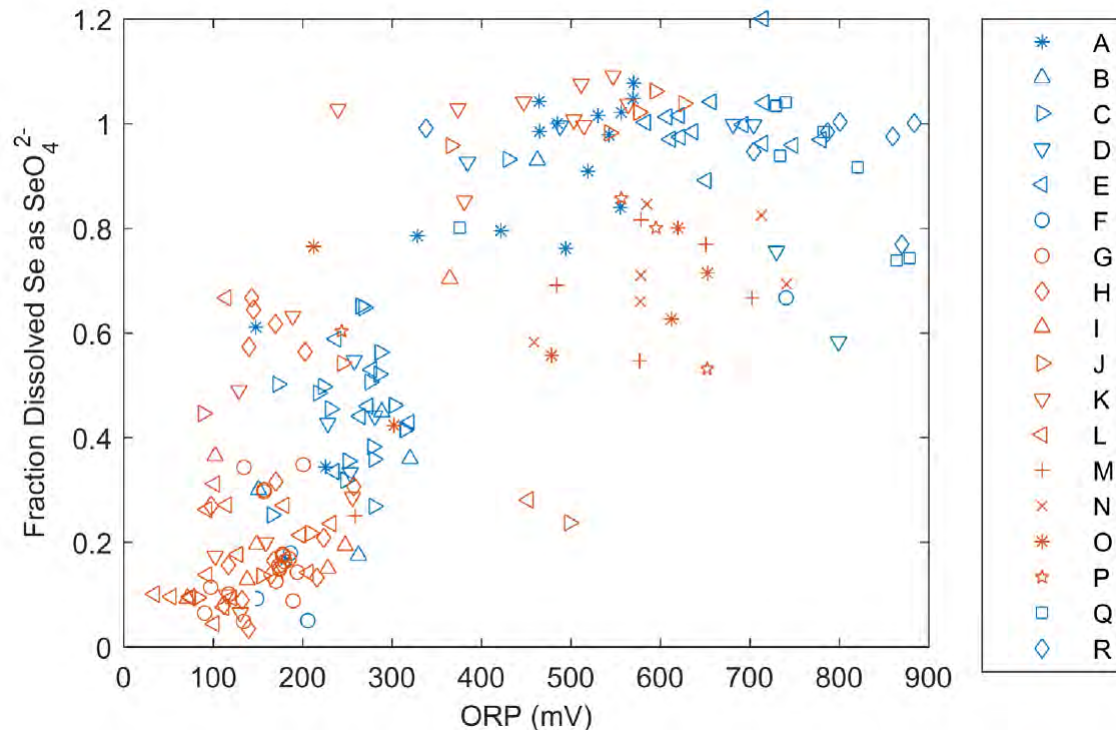


Dissolved Se fraction in FGD slurries  
(Red, ADVATECH; Blue, Chiyoda)

Allen, J.O.; Ferens-Foulet, C.K.; Acharya, CK. Effluent Trace Metals Survey and Related Plant Operations at 18 Flagship Units. Presented at Power Plant Pollutant Control and Carbon Management “Mega” Symposium, Baltimore, MD, August 16-19, 2016

# Se Speciation in Wet FGD: 2016 SoCo Study

▶ As expected from theory, ORP has significant influence on speciation of Se in liquid phase of FGD slurries



■ Fraction of dissolved Se as  $\text{SeO}_4^{2-}$  in FGD slurries (Red, ADVATECH; Blue, Chiyoda)

Allen, J.O.; Ferens-Foulet, C.K.; Acharya, CK. Effluent Trace Metals Survey and Related Plant Operations at 18 Flagship Units. Presented at Power Plant Pollutant Control and Carbon Management “Mega” Symposium, Baltimore, MD, August 16-19, 2016

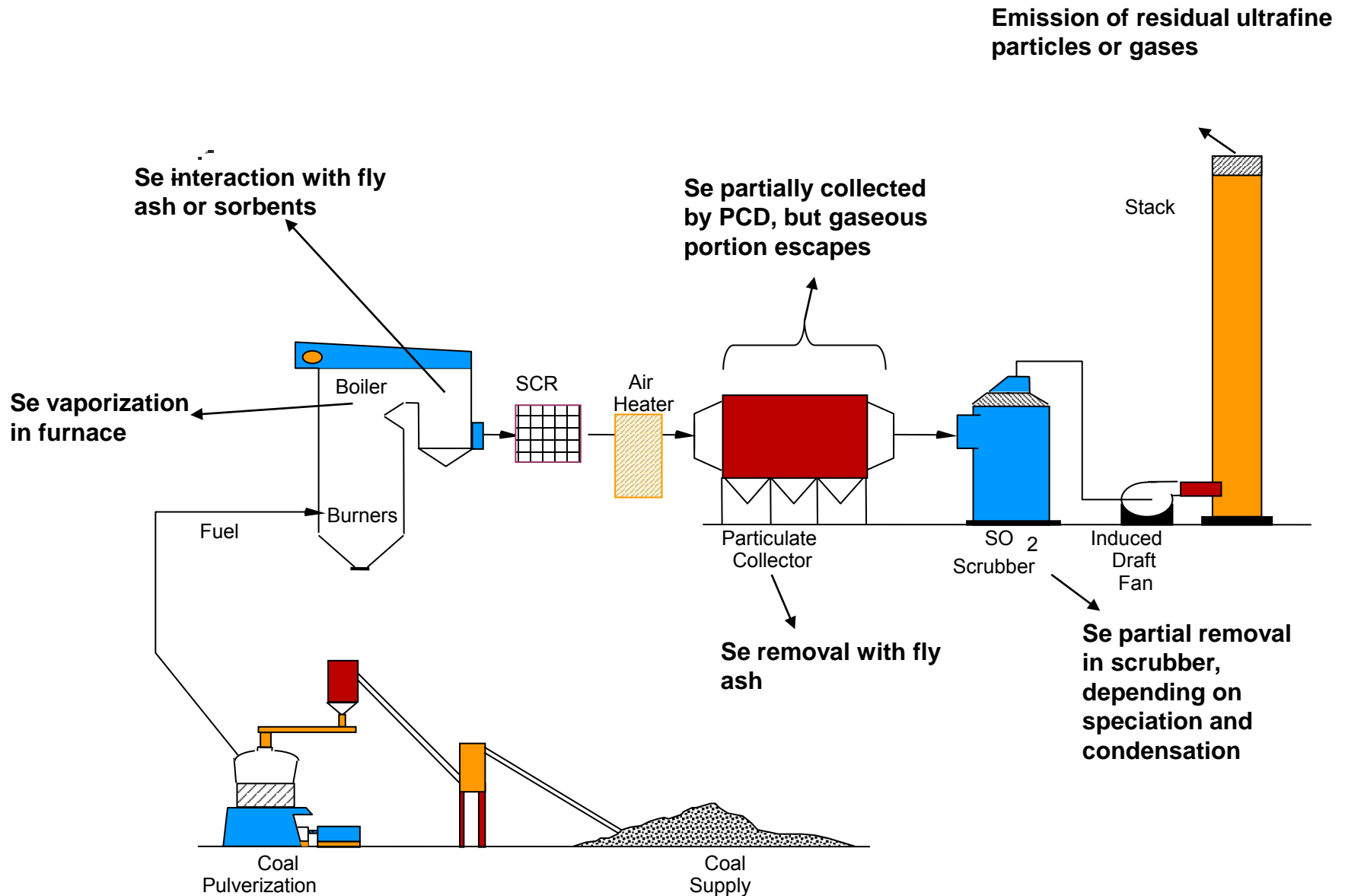
# Conclusions from Speciation Studies

- ▶ ORP is significant in influencing partitioning and speciation, but other factors appear to be at work, too
- ▶ Selenite and selenosulfate appear to dominate in inhibited oxidation FGD systems
- ▶ Selenate is most prevalent for in situ forced oxidation FGD systems
  - ▶ But, range of conversion to selenosulfate is large
  - ▶ Factor that control range remain unclear
- ▶ Unknown and unaccounted-for Se species appear to be more prevalent, on average, in systems that use organic acid buffers
  - ▶ Again, the range is wide and factors controlling are unknown

# Factors that May Control Se Oxidation to the Selenate Form, Total Se in FGD Liquor

- ▶ Liquor residence time in absorber/reaction tank loop
- ▶ Cycles of concentration in the FGD liquor (impacts how many times FGD liquor gets recycled back to the absorber loop before discharge)
- ▶ FGD operating temperature, which impacts oxidation reaction rates
- ▶ Concentrations of dissolved metals in the absorber liquor, which can serve as catalysts for oxidation reactions
- ▶ Concentrations of precipitated metals in the absorber slurry, such as iron hydroxides which can adsorb or co-precipitate selenite
- ▶ Se concentration in the coal
- ▶ The type of particulate control device upstream of the FGD system
- ▶ Composition of the coal ash (e.g., ash alkalinity)
- ▶ Other APC equipment upstream of FGD (SCR, SO<sub>3</sub> control, etc.)

# Fate of Selenium



# Implications for Emissions and Control

- ▶ Unlike most HAP metals, Se can be gaseous ( $\text{SeO}_2$ ) at temperatures in APCDs
- ▶ Se can be captured by fly ash, but not always removed with high efficiency by PCDs
  - ▶ Low-rank ash more effective at capturing Se than bituminous ash =>
  - ▶ FFs more effective than ESPs

# Implications for Emissions and Control

- ▶ Significant portion of Se can enter FGD in gas-phase
  - ▶ Combination of PCD+scrubber removes >85% Se
- ▶ Removal of  $\text{SeO}_2$  across FGDs (60%-90%) less than removal of  $\text{SO}_2$
- ▶ Selenium absorbed in FGDs could become an issue for wastewater treatment systems, if Se in liquid is predominantly  $\text{SeO}_4^{2-}$  / Se[VI]

# Fate of Selenium in Effluents & Byproducts

# Leaching of Metals from DSI-Fly Ash Mixtures

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



# Solubility of Selenium Compounds

- ▶ Selenate (Se(VI) or  $\text{SeO}_4^{2-}$ ) more soluble in water than selenite (Se(IV) or  $\text{SeO}_3^{2-}$ )
- ▶ For a given oxidation state, the cation associated with the selenium oxyanion also affects the solubility: in terms of solubility,  $\text{Na} > \text{Ca} > \text{Fe}$
- Example, solubility product constants for selected compounds 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
$\text{CaSeO}_4 = \text{Ca}^{2+} + \text{SeO}_4^{2-}$	4.77
$\text{FeSeO}_4 = \text{Fe}^{2+} + \text{SeO}_4^{2-}$	6.52
$\text{CaSeO}_3 = \text{Ca}^{2+} + \text{SeO}_3^{2-}$	7.65
$\text{FeSeO}_3 = \text{Fe}^{2+} + \text{SeO}_3^{2-}$	9.99



# Solubility of Selenium in Fly Ash

## ▶ Pilot-scale data from Seames:

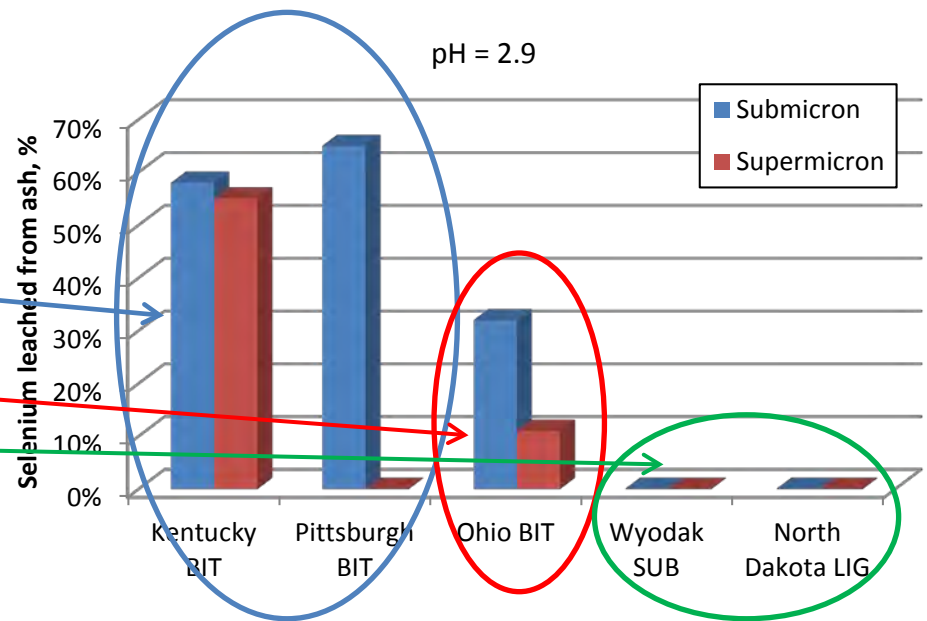
- ▶ Fly ash from different coals collected at ~1000°F
- ▶ Size-segregated with cascade impactor
- ▶ Leaching of submicron ash vs. supermicron ash

- According to Seames, Se speciation in ash varied from predominantly

- $\text{FeSeO}_4$
- $\text{SeO}_2$
- $\text{CaSeO}_3$

- Leaching trends follow expected solubilities

- Se leached more easily from submicron fly ash



*Leaching at pH=2.9 of Selenium from Size-Segregated Fly Ash Samples from Pilot-Scale Combustor [Seames, 2000]*

# 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

# 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

TCLP Results		
Leached Metal	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

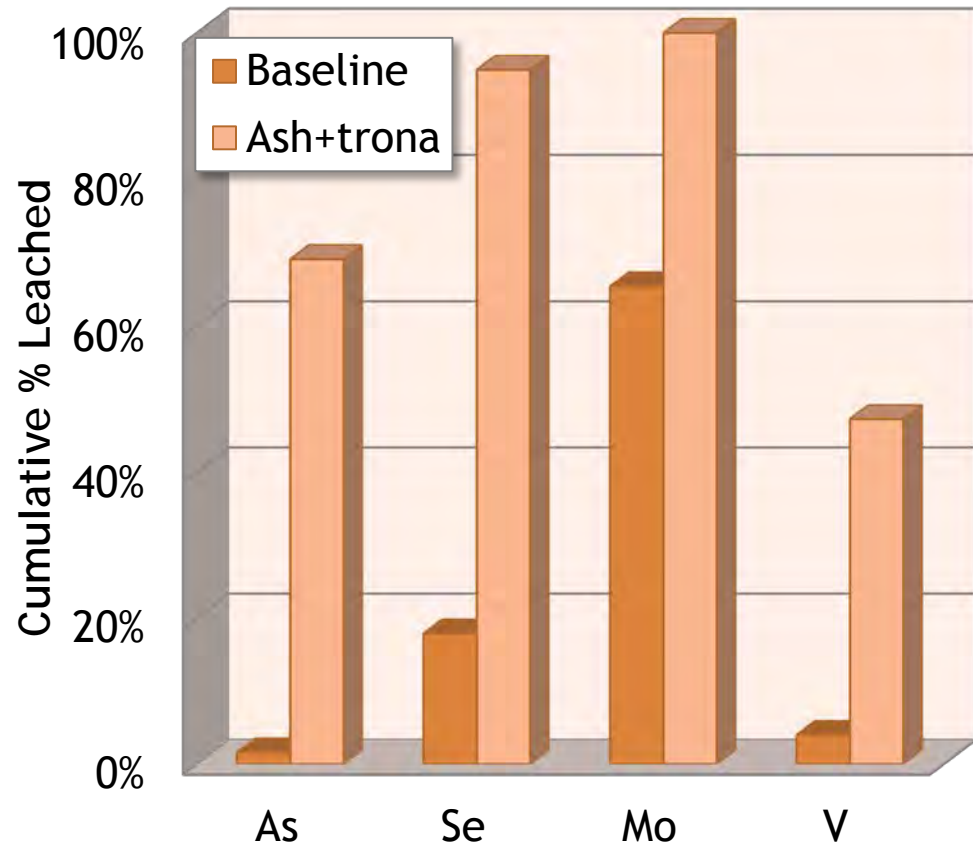
- ▶ Set of paired fly ash samples collected from H-ESP at a full-scale power plant that burned bituminous coal: control ash collected before trona injection and a trona ash collected during trona injection test
- ▶ Batch leaching experiments conducted using DI water under unadjusted pH conditions at 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.

# Take a Deep Breath and Summarize

- ▶ Unlike most HAP metals, Se can be gaseous ( $\text{SeO}_2$ ) at temperatures in APCDs
- ▶ Se can be captured by fly ash, but not always removed with high efficiency by PCDs
  - ▶ Low-rank ash more effective at capturing Se than bituminous ash
  - ▶ FFs more effective than ESPs
  - ▶ Leachability of Se from fly ash is an issue



- ▶ Significant portion of Se can enter FGD in gas-phase
  - ▶ Combination of PCD+scrubber removes >85% Se
- ▶ Removal of  $\text{SeO}_2$  across FGDs (60%-90%) less than removal of  $\text{SO}_2$
- ▶ Selenium removed by FGDs could become an issue in WWT

QUESTIONS? →

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