REINHOLD ENVIRONMENTAL Ltd.

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Advanced Emissions Solutions, Inc.
Advancing Cleaner Energy

Selenium Fate and Control in APCDs

Connie Senior
Vice-President of Technology
ADA-ES, Inc.

Reinhold APC Conference ~ July 23, 2018

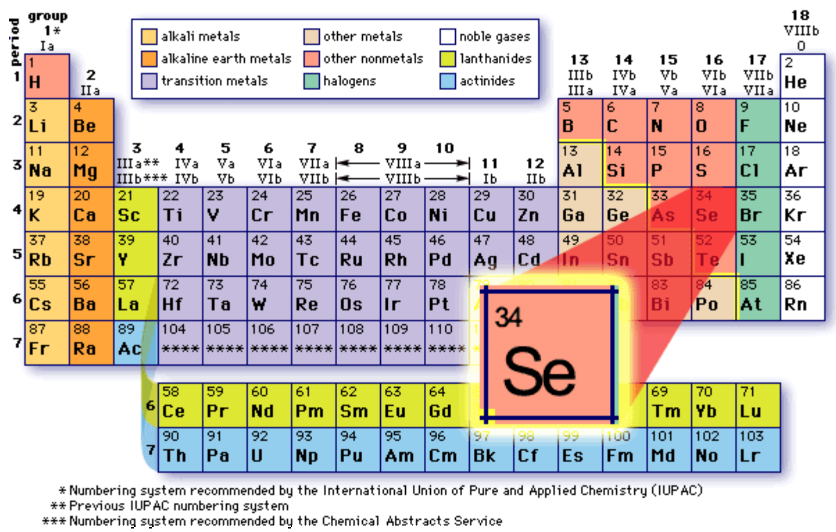
Disclaimer

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

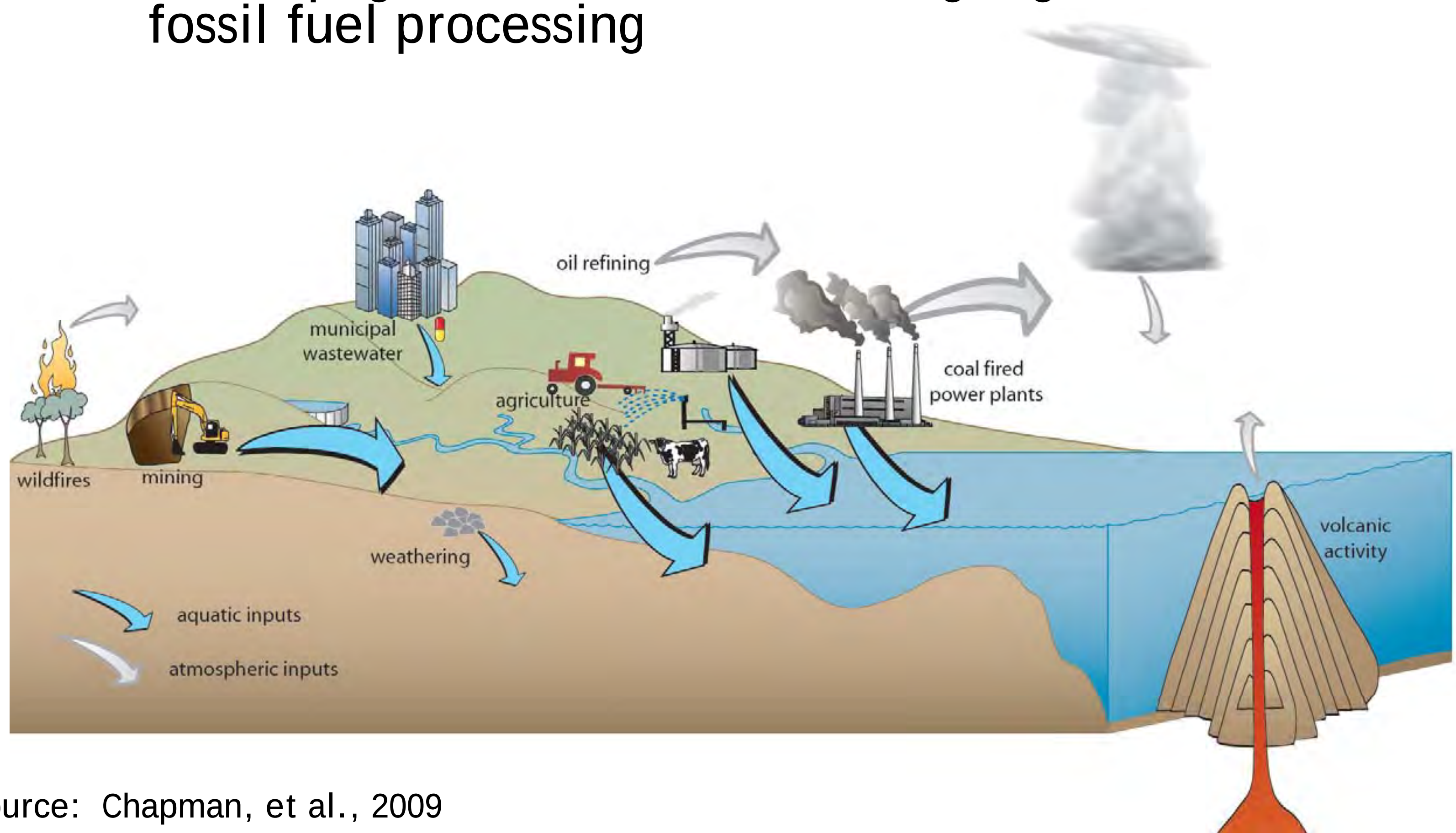


- Selenium can act a lot like sulfur chemically
- …even replacing sulfur in some amino acids

- 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

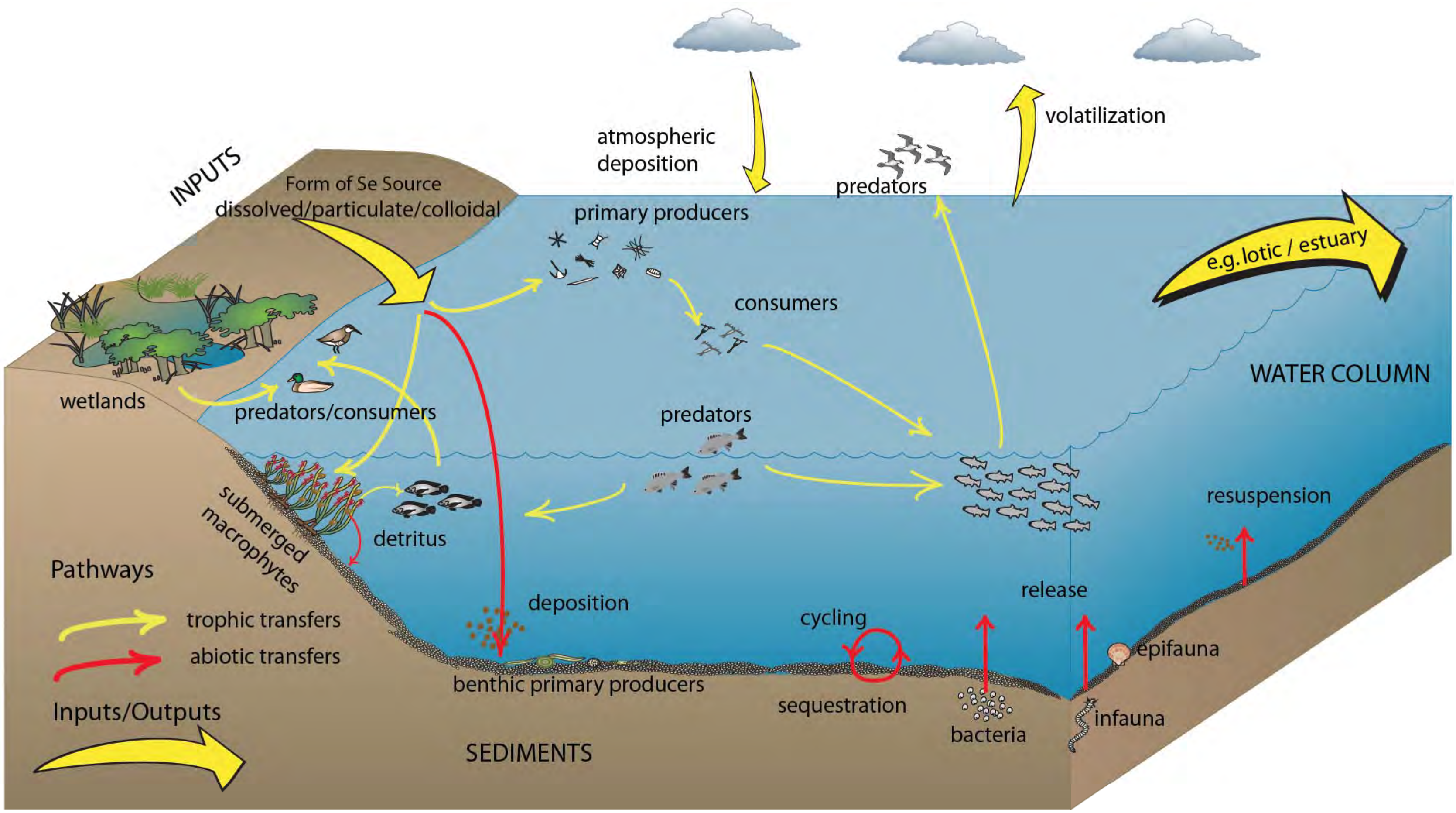
Potential Sources of Se to Aquatic Systems

- 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

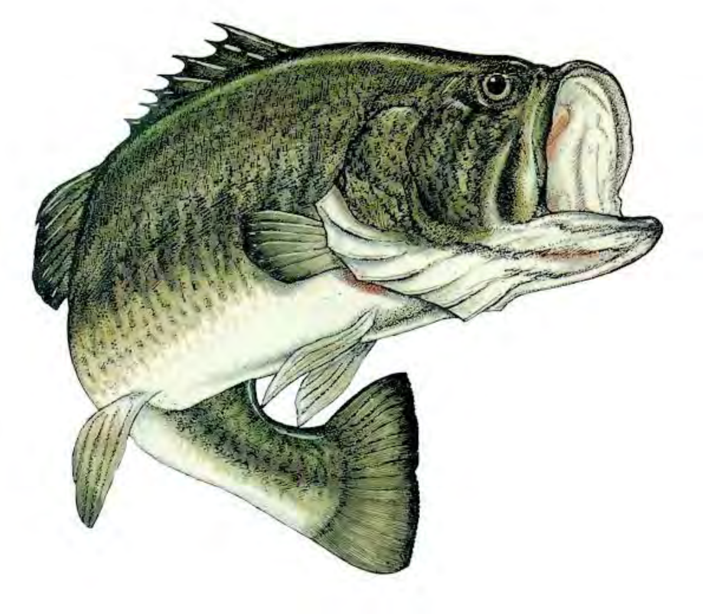
Partitioning of Se in Aquatic Systems



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

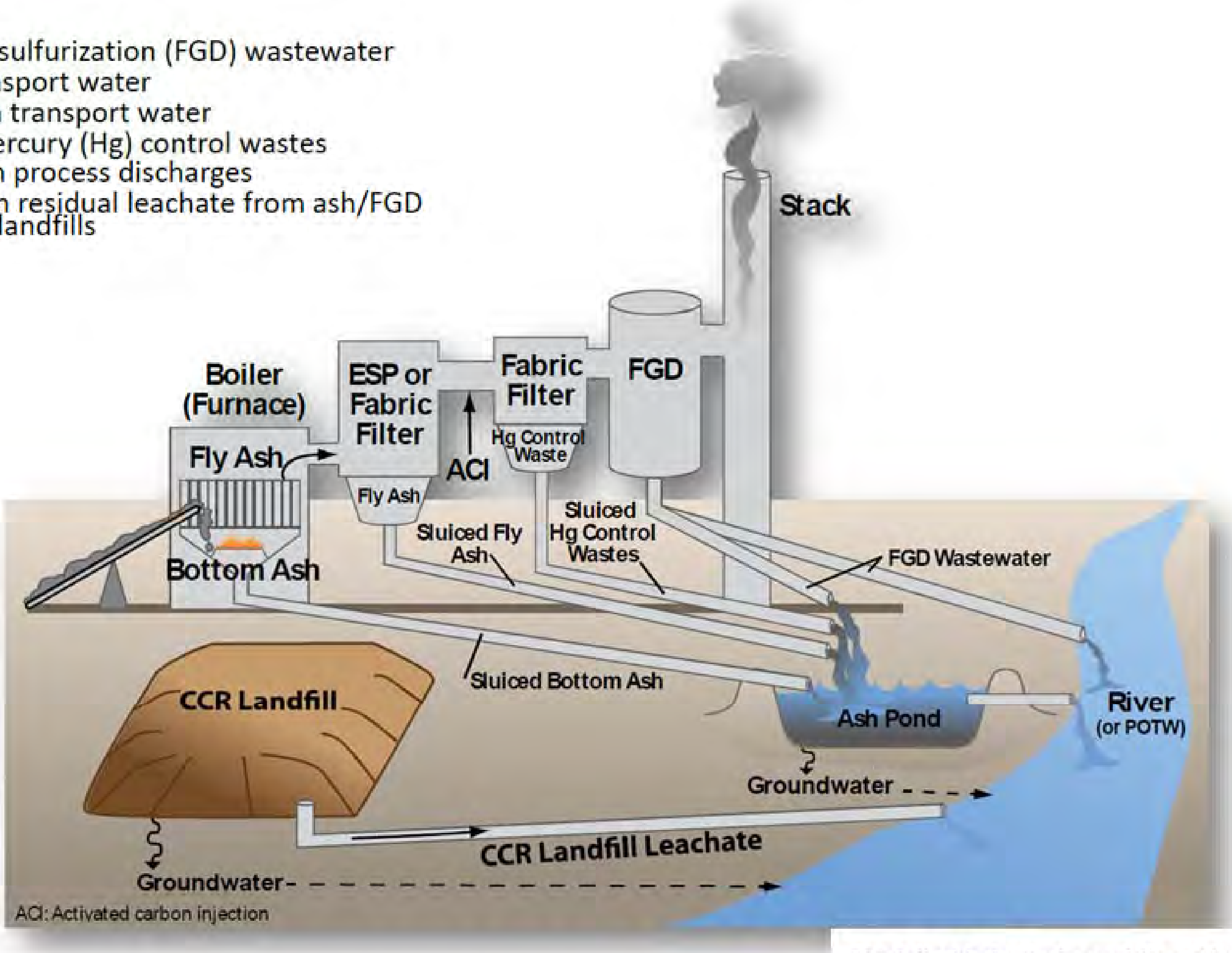
- Belews Lake in North Carolina experienced high influxes of selenium from the nearby power plant ash pond discharges from 1974 to 1985
- Selenium concentrations in the ash pond discharge water were high (150–200 µg Se/L)*
- Deformities and reproductive failure in the fish population decimated nineteen 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)

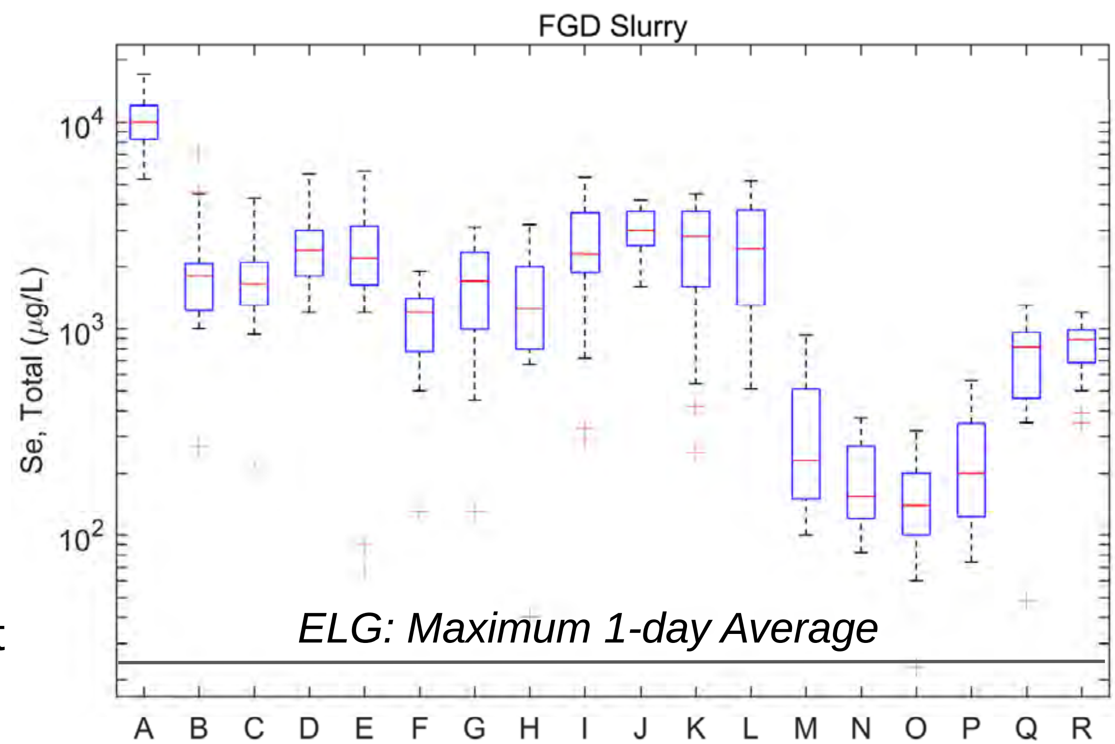
- Flue gas desulfurization (FGD) wastewater
- Fly ash transport water
- Bottom ash transport water
- Flue gas mercury (Hg) control wastes
- Gasification process discharges
- Combustion residual leachate from ash/FGD ponds and landfills



EPA Call with the Institute of Clean Air Companies
June 22, 2016

Se Concentrations in Wet FGD: 2016 SoCo Study

- Se concentrations in scrubber slurries varied from ~100 µg/L (ppb) to ~10,000 µg/L
- Effluent Limitation Guidelines (ELG):*
  - 1-day average Se limit in FGD wastewater discharged = 23 µg/L
  - Monthly average Se limit in FGD wastewater discharged = 12 µg/L



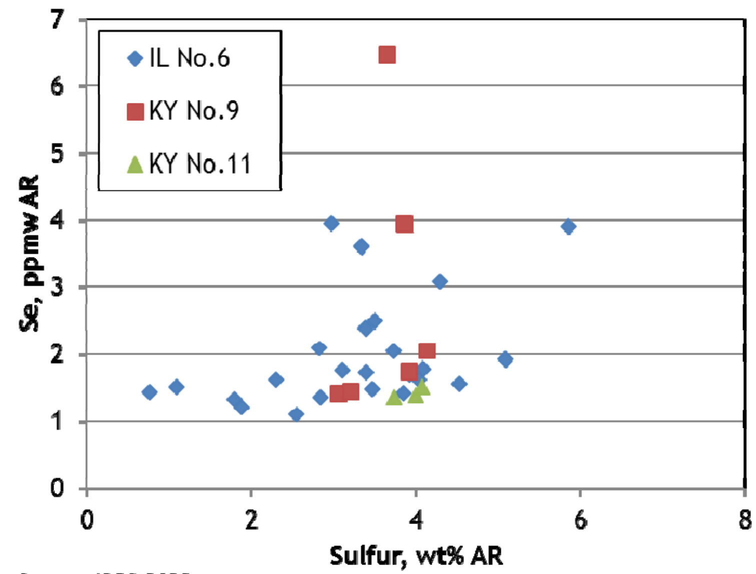
Selenium concentrations in FGD slurries of Southern Company scrubbers

As finalized in 2015, but delayed for two years. EPA is reviewing and may modify in future

Allen, J.O.; Ferens-Foulet, C.K.; Acharya, C.K. 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

Selenium in US Coals

- Selenium is found in coals in trace concentrations
- USGS has reported concentrations in coal as high as 150 µg/g, but 0.5 to 5 µg/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

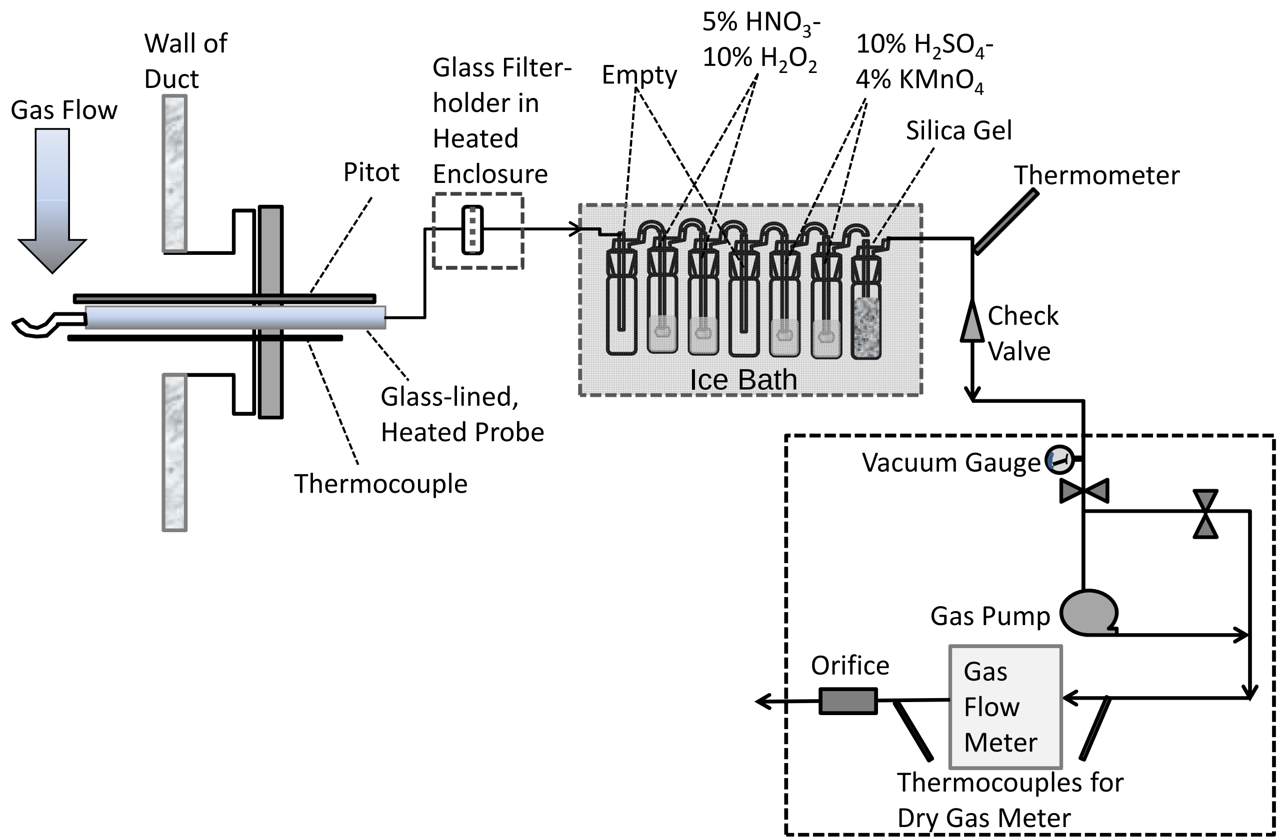
Measurement of Se in Solid Samples

Number	Sample	Method	Se, µg/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		

- 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 Flue Gas

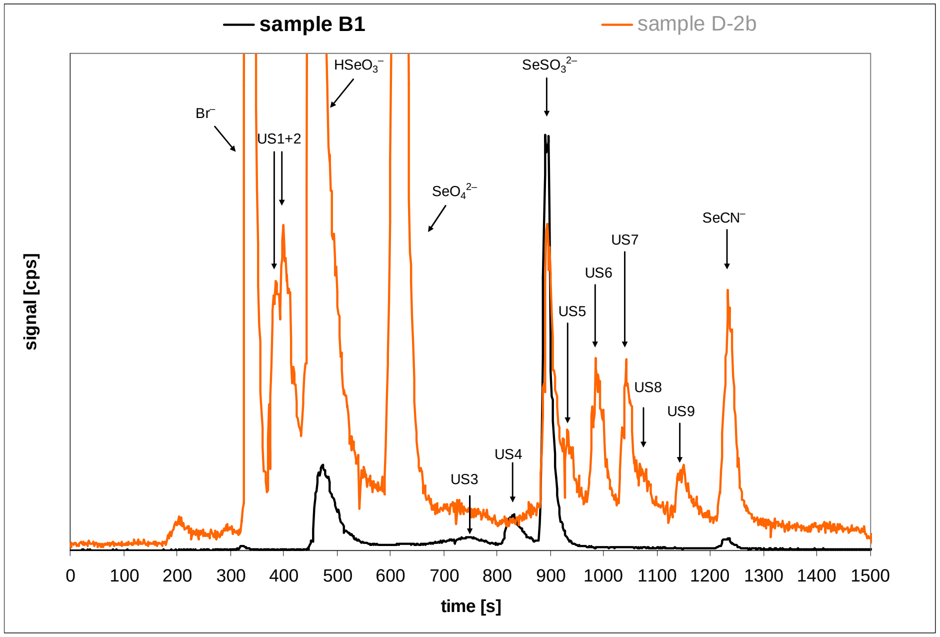
- Sorbent traps offered by Ohio Lumex
- Set-up/equipment similar to Method 30 B
- Isokinetic sample from flue gas
- Sorbent traps analyzed by atomic fluorescence or graphite furnace AA

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 ($SeCN^-$)
  - Selenosulfate – $SeSO_3^{2-}$
  - Dissolved or colloidal Se[0]
  - Unknown Se peaks



Source: P. Chu, EPRI

Developing Se Measurements in Water

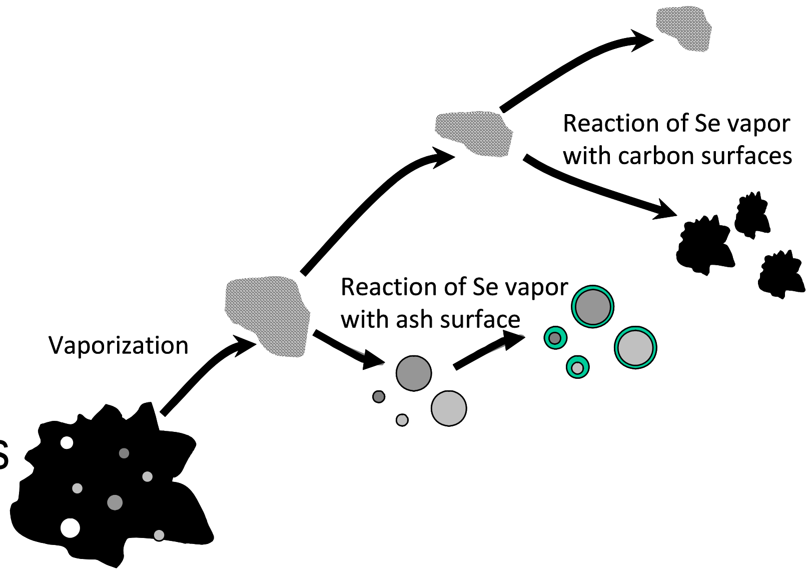
- PSA Analytical
  - Method: generate and detect gaseous hydride
  - Also can measure As
  - Method can only detect selenite in water
  - To measure total selenium, oxidize all Se to Se[VI] and then reduce it back to Se[IV]
  - Sample prep is critical

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

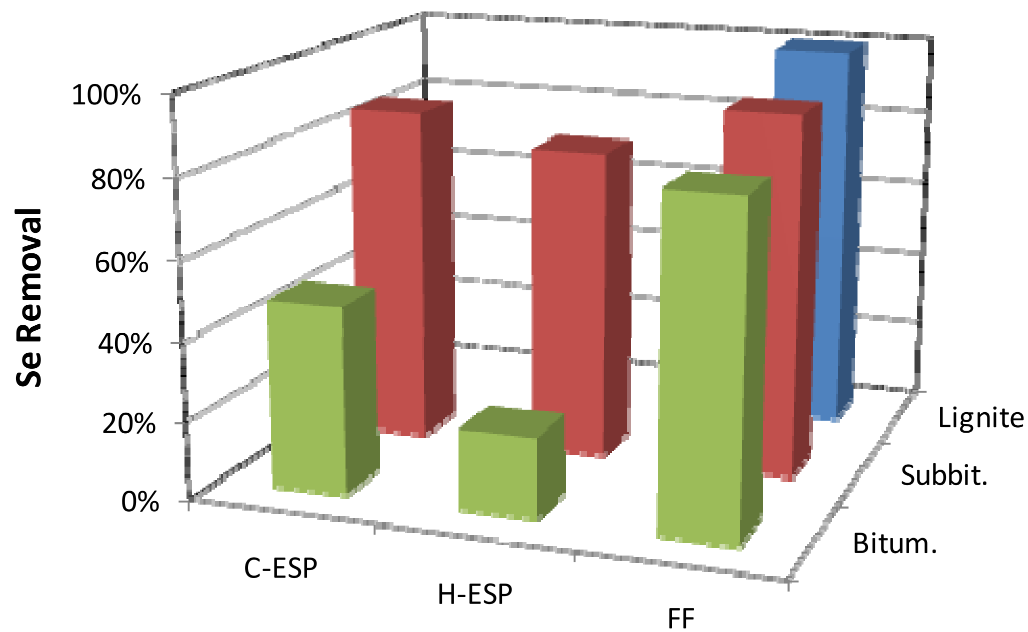
Behavior of Se in Coal-Fired Boilers

- Most coal Se vaporizes in boiler, where gaseous selenium (SeO_2(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
- SeO_2(g) water soluble
  - Some SeO_2(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



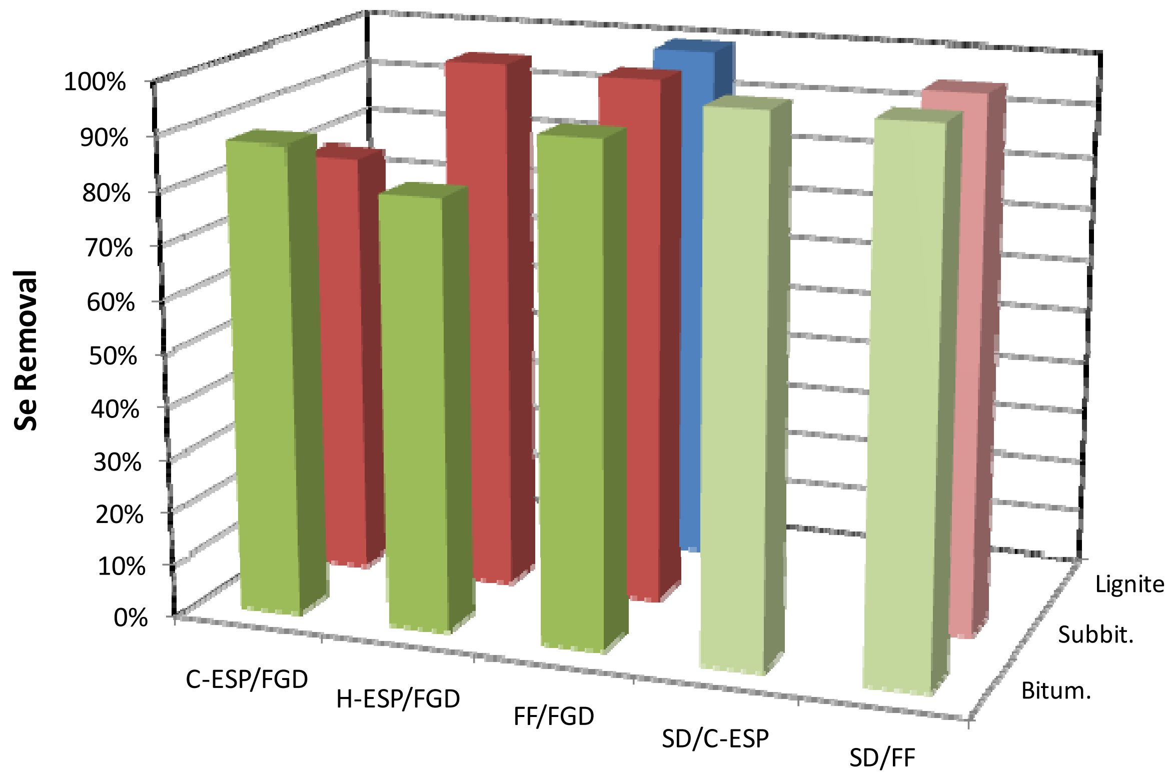
Fate of Se in Particulate Control Devices: 2011 Utility ICR Data

- 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_2 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*

Interaction between Bromine and Se

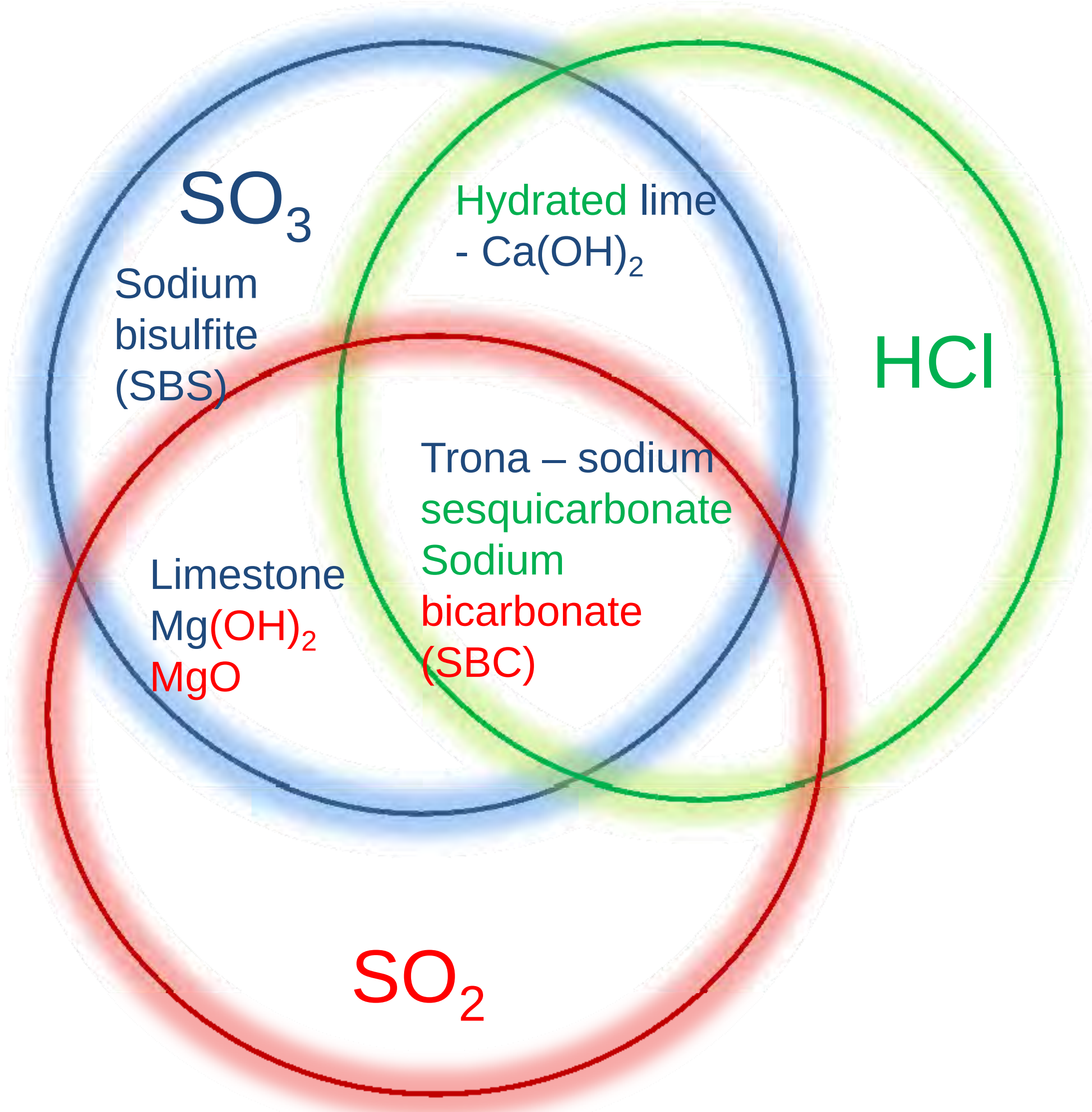
- Adding bromine to the fuel can shift Se from fly ash to wet FGD
- EPRI study* noted data from three test sites showing an increase in Se concentration in FGD liquor during bromine addition to fuel
- For example, at one bituminous-fired boiler bromine was added for 10 days:

Condition	Se in Fly Ash, µg/g	%Se Capture by Fly Ash	Se in FGD Liquor, µ/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

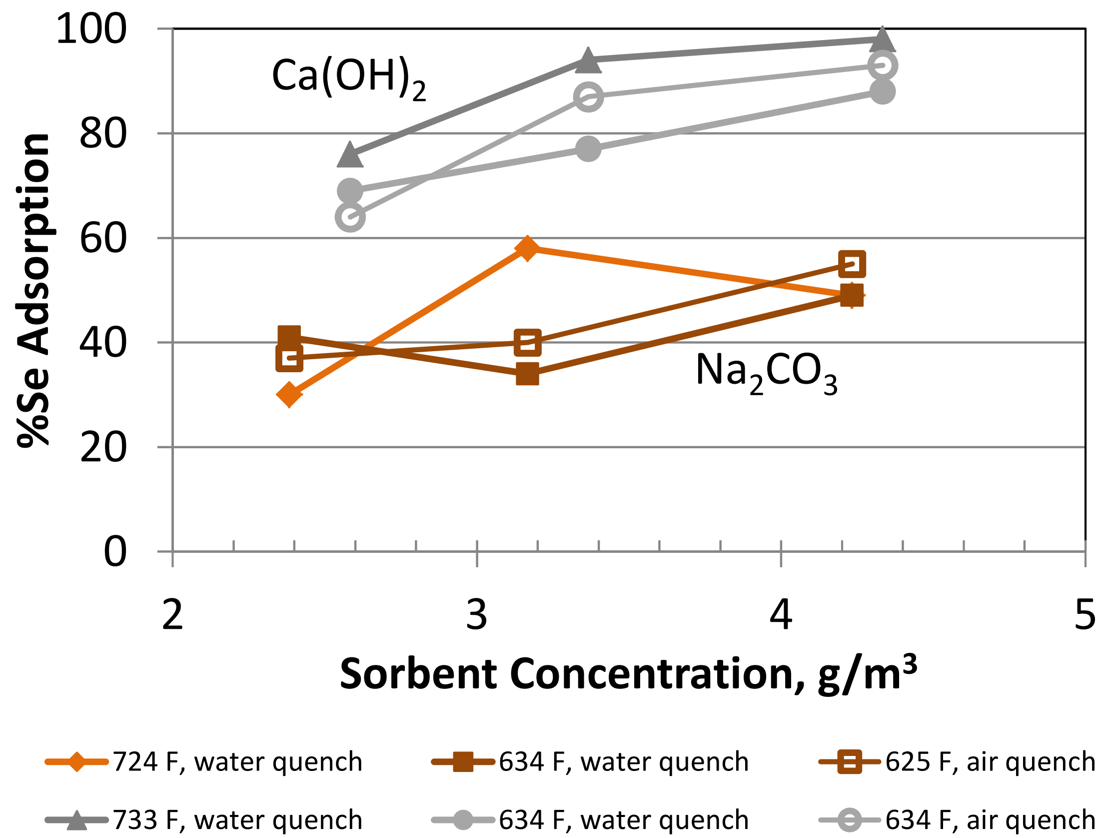
**Dombrowski et al., Air Quality VIII Conference, 2011*
***Gadgil et al., APC Roundtable, 2013*

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



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

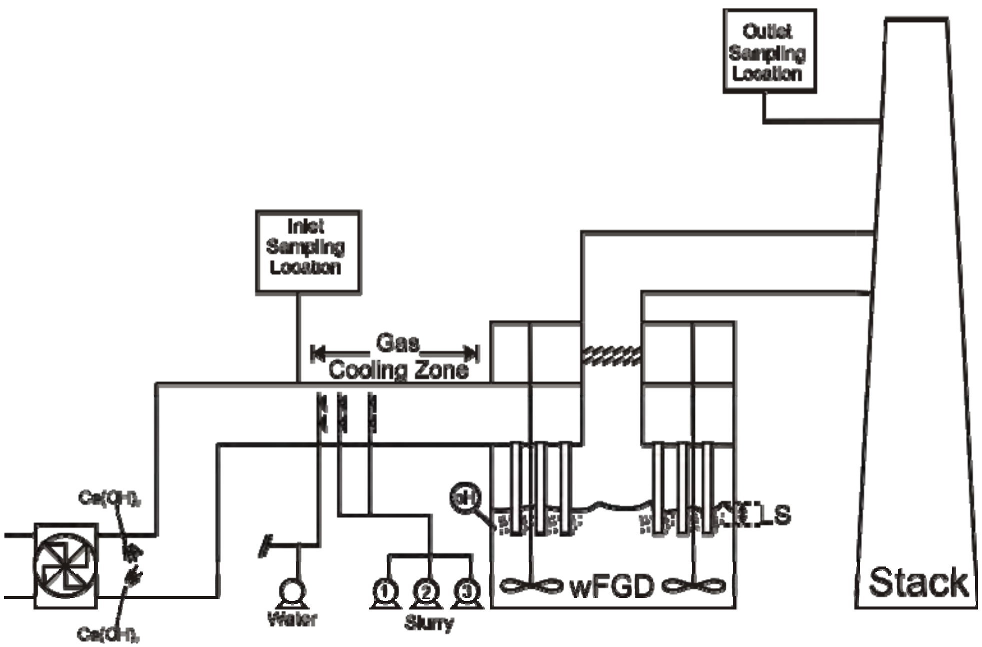
Plant Wansley Study*: Mechanisms for Removal Across Wet FGD

- 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_3 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

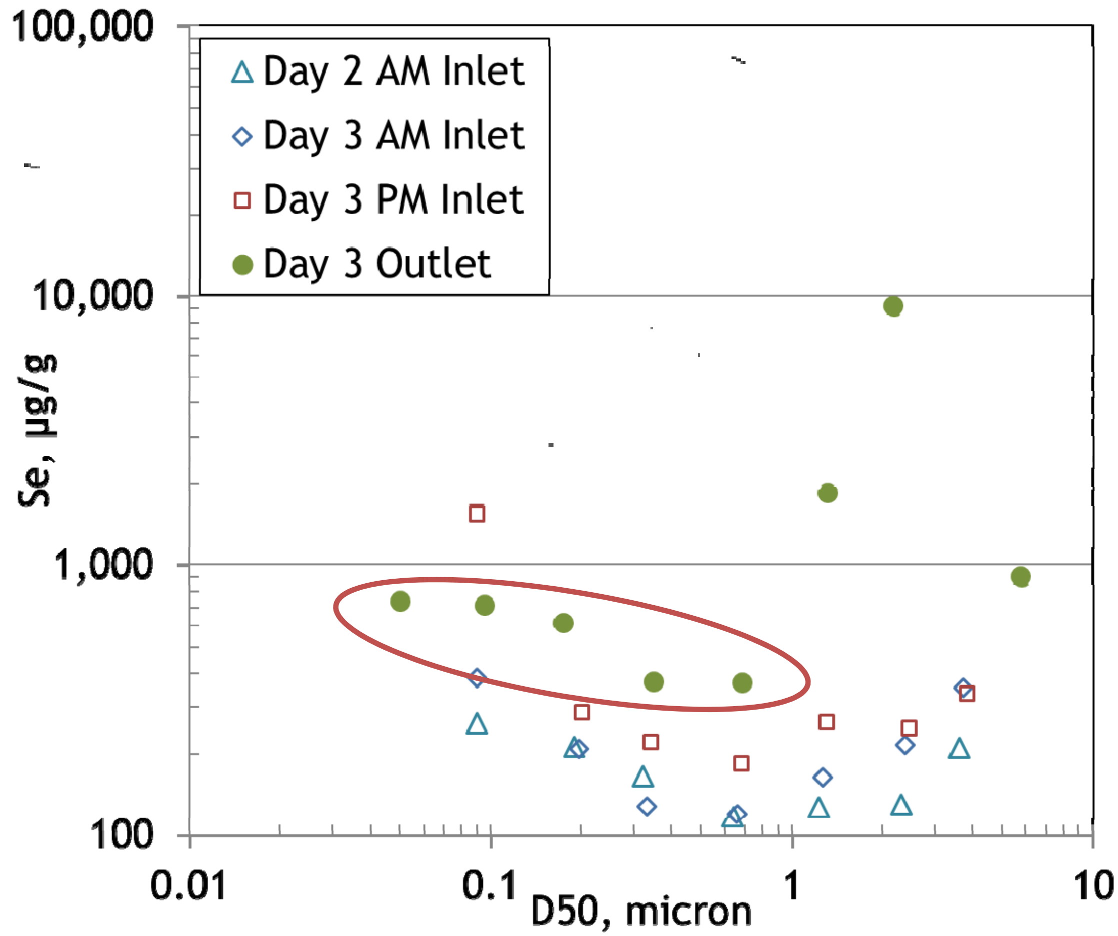
- Samples taken at inlet and outlet of scrubber: gaseous Se and size-segregated fly ash
- FGD inlet sample taken after $Ca(OH)_2$ injection



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

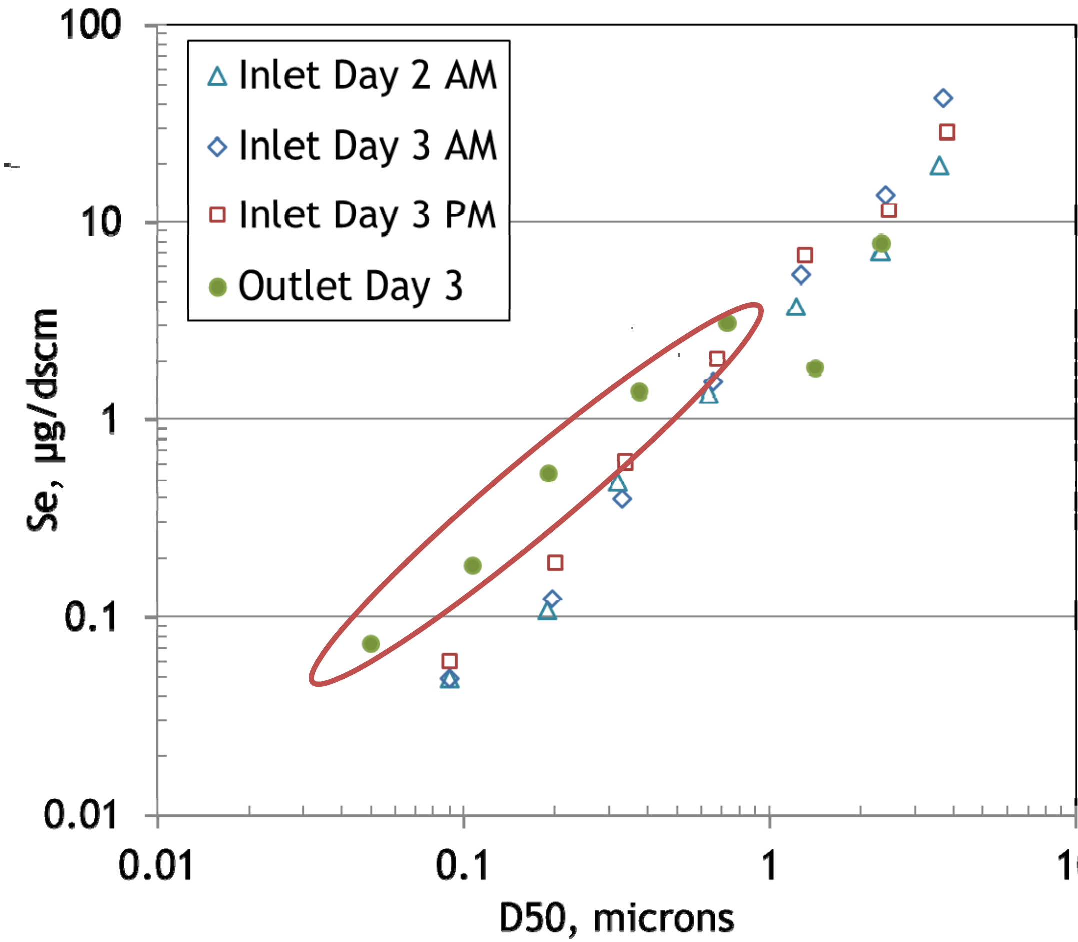
Gas-to-Particle Conversion

- 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
- Rapid quench in scrubber could convert gaseous SeO_2 to H_2SeO_3 aerosol or SeO_2 condensed on fly ash
- Preferential condensation would be on submicron particles (higher surface area)



Conclusions from Wansley Study

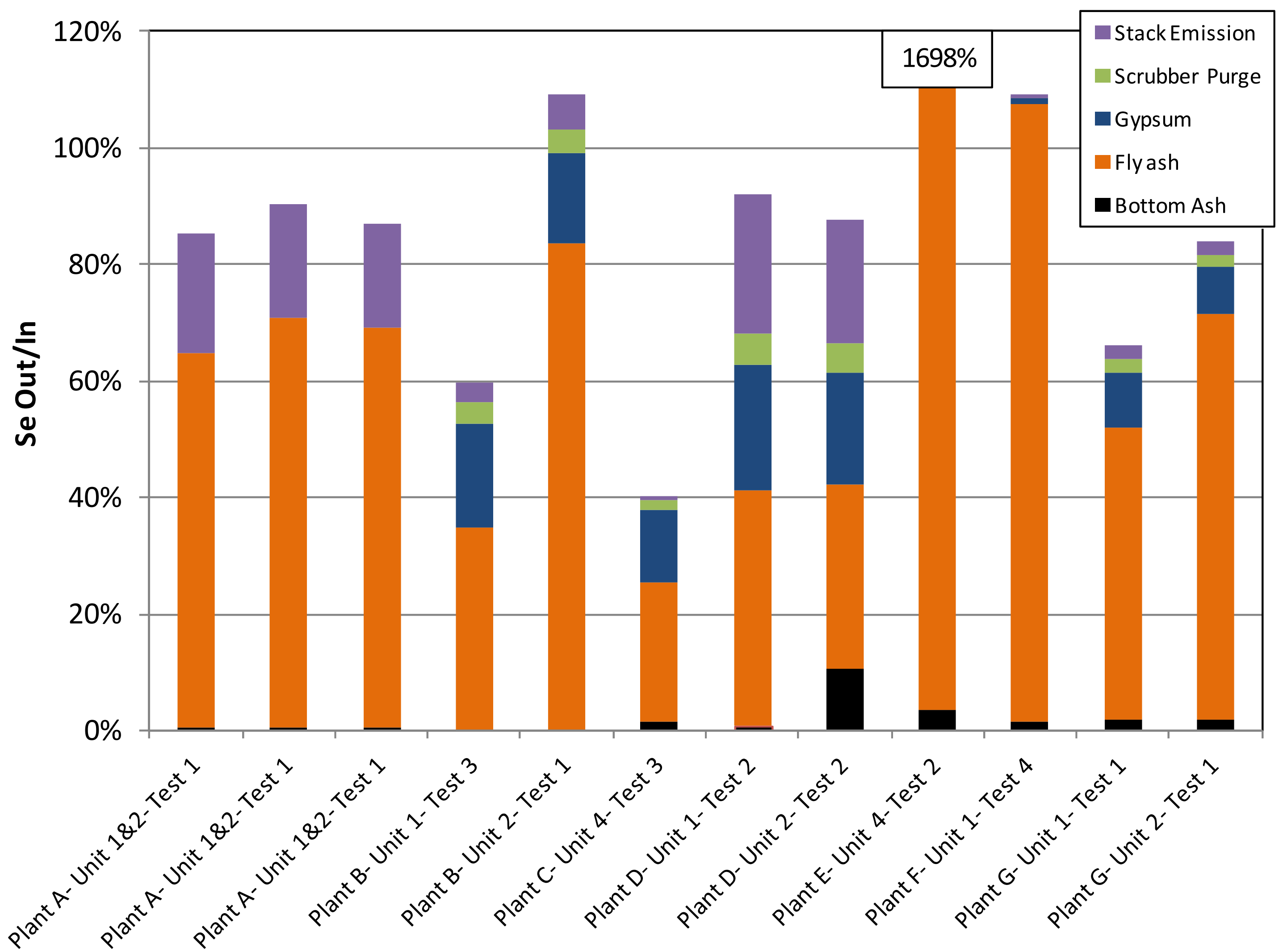
- Total removal Se (gas plus particle-bound) across FGD averaged 61% even though SO_2 removal was >97%
  - In line with observations at other boilers
- Gas-to-particle conversion of Se across FGD could limit removal of Se across FGD

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

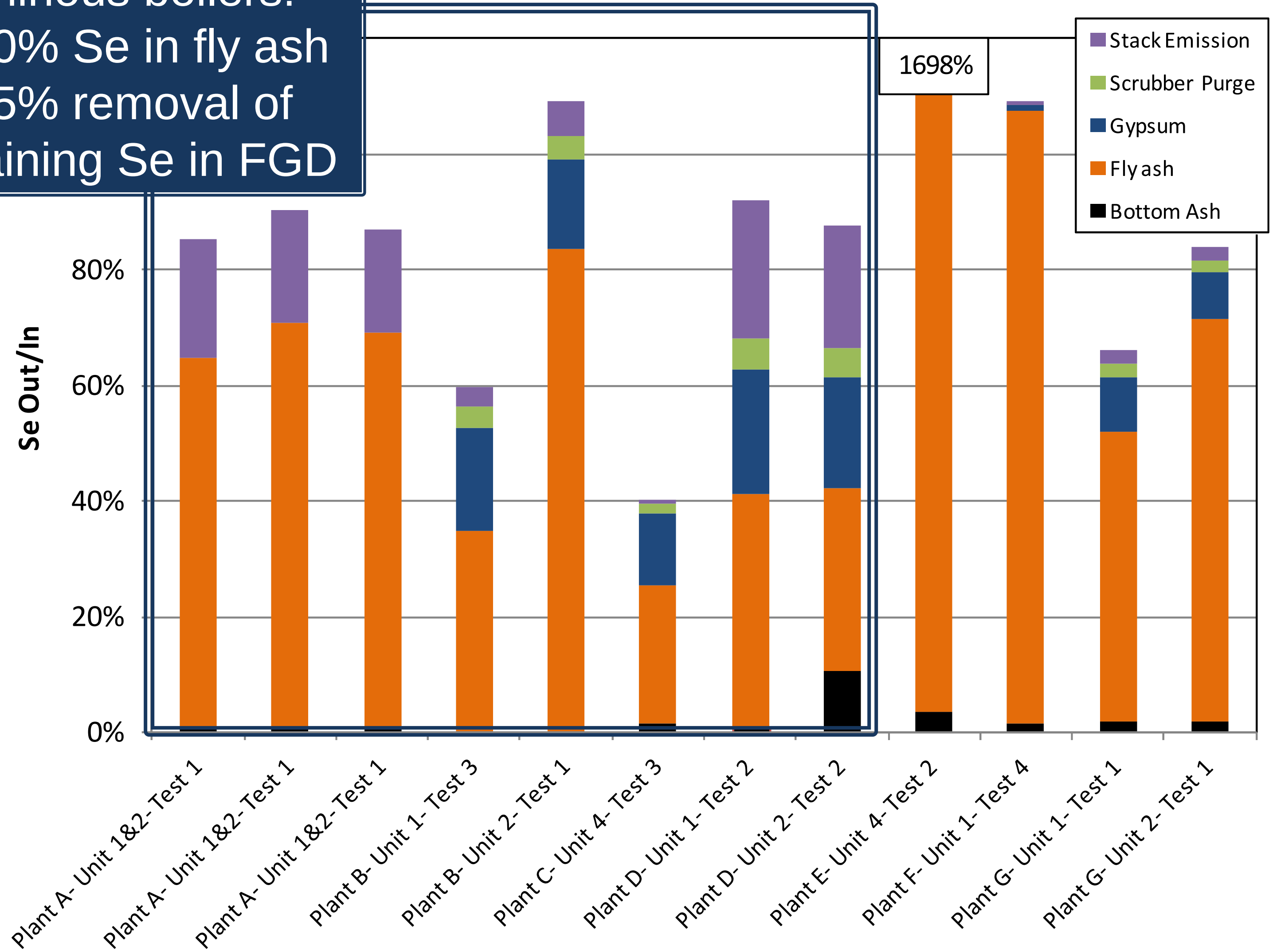
**Senior et al., AQVIII Conference, 2011*

Selenium Mass Balance

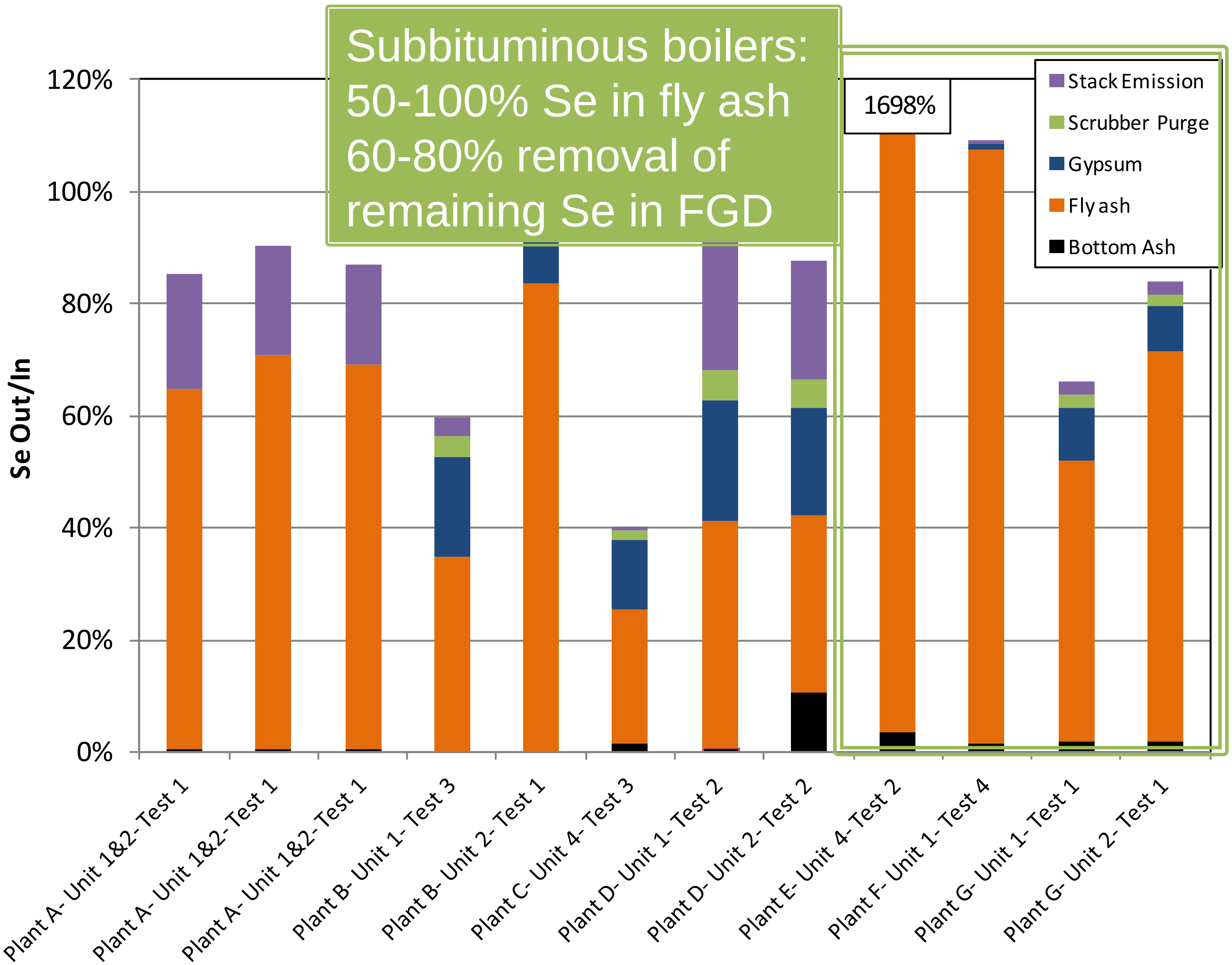


Selenium Mass Balance

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

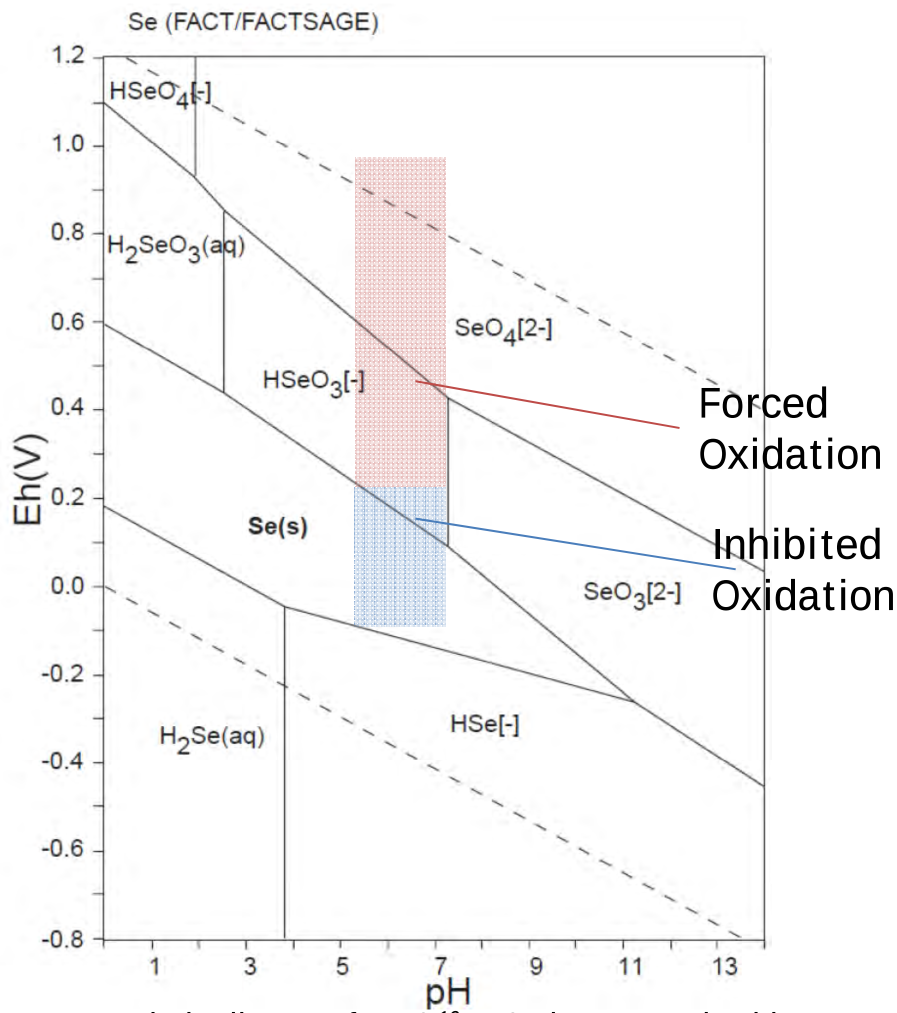


Selenium Mass Balance



Selenium Speciation in Wet FGDs

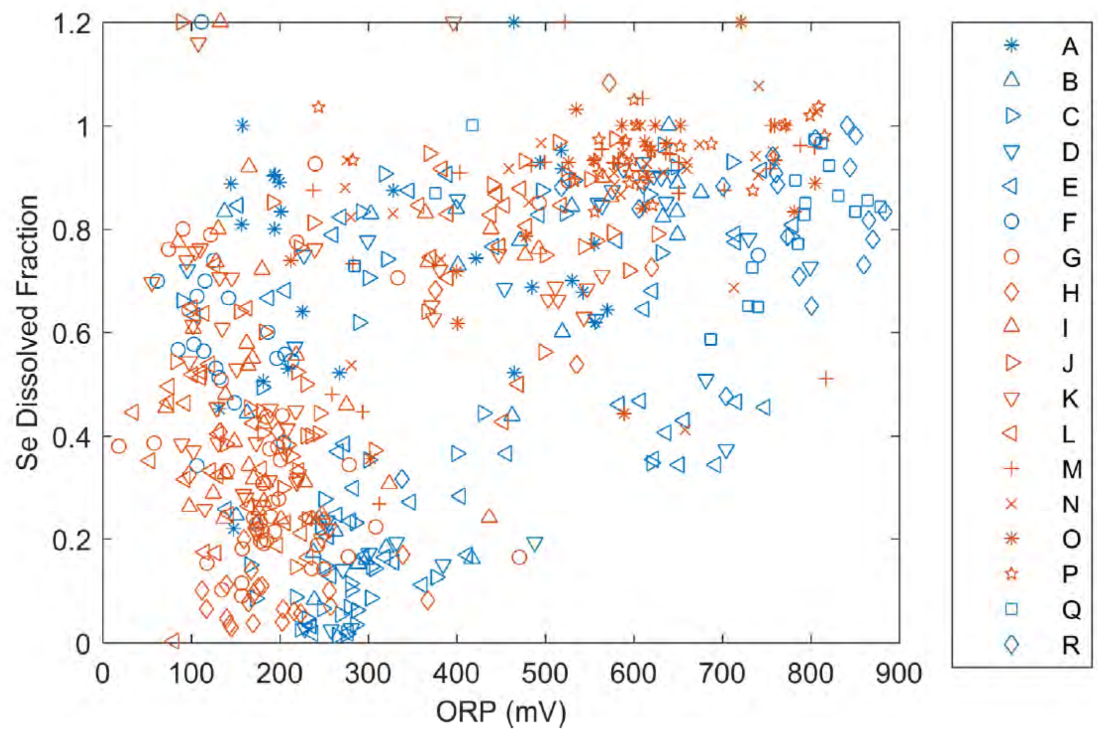
- Selenium can exist in aqueous phase or solid phase in wet FGD slurry
- A range of different Se species are expected in wet FGD slurries
- Speciation of selenium in the scrubber varies with pH and ORP, affected by, for example
  - Scrubber design
  - Transition metals in slurry
  - Scrubber additives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



Pourbaix diagram for 10^{-10} M Se in water, cited in Allen et al., 2016 Mega Symposium [Note 0 mV ORP (Ag/AgCl) = 200 mV Eh]

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

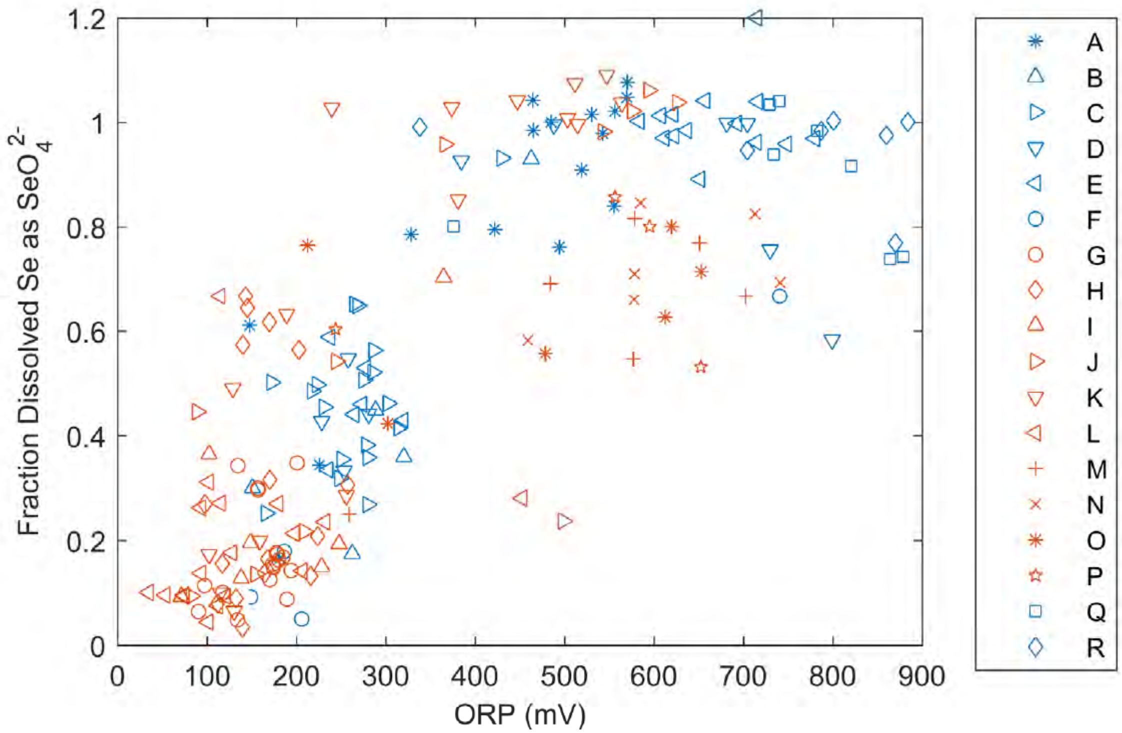


Dissolved Se fraction in FGD slurries (Red, ADVATECH; Blue, Chiyoda)

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

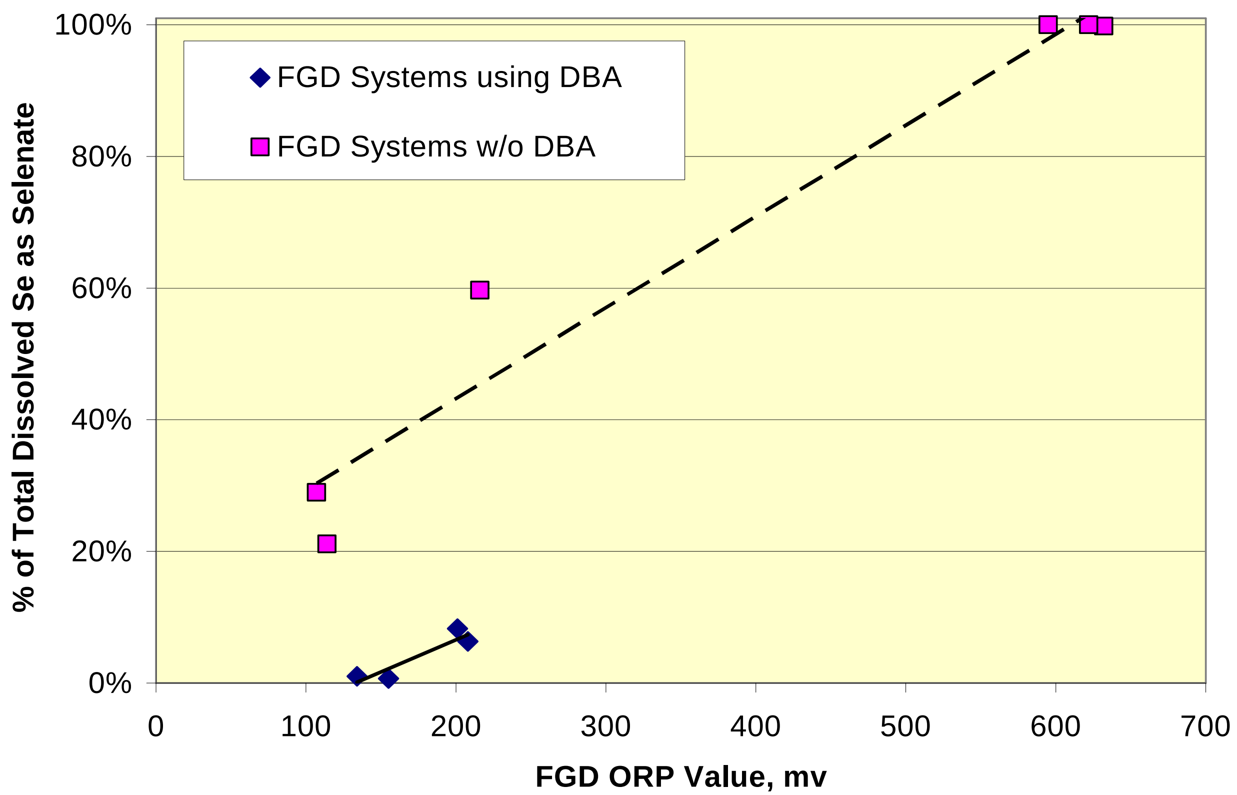


Fraction of dissolved Se as SeO_4^{2-} in FGD slurries (Red, ADVATECH; Blue, Chiyoda)

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

Se Speciation in Wet FGD: 2010 EPRI Study

- Selenate (Se[VI]) fraction in the liquid increases with increasing ORP
- Use of scrubber additive DBA affects Se speciation in the liquid



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

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

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 SeO_4^{2-}) more soluble in water than selenite (Se(IV) or SeO_3^{2-})
- 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 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
$Na_2SeO_3 = 2Na^+ + SeO_3^{2-}$	3.51
$CaSeO_4 = Ca^{2+} + SeO_4^{2-}$	4.77
$FeSeO_4 = Fe^{2+} + SeO_4^{2-}$	6.52
$CaSeO_3 = Ca^{2+} + SeO_3^{2-}$	7.65
$FeSeO_3 = Fe^{2+} + SeO_3^{2-}$	9.99

More Soluble

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

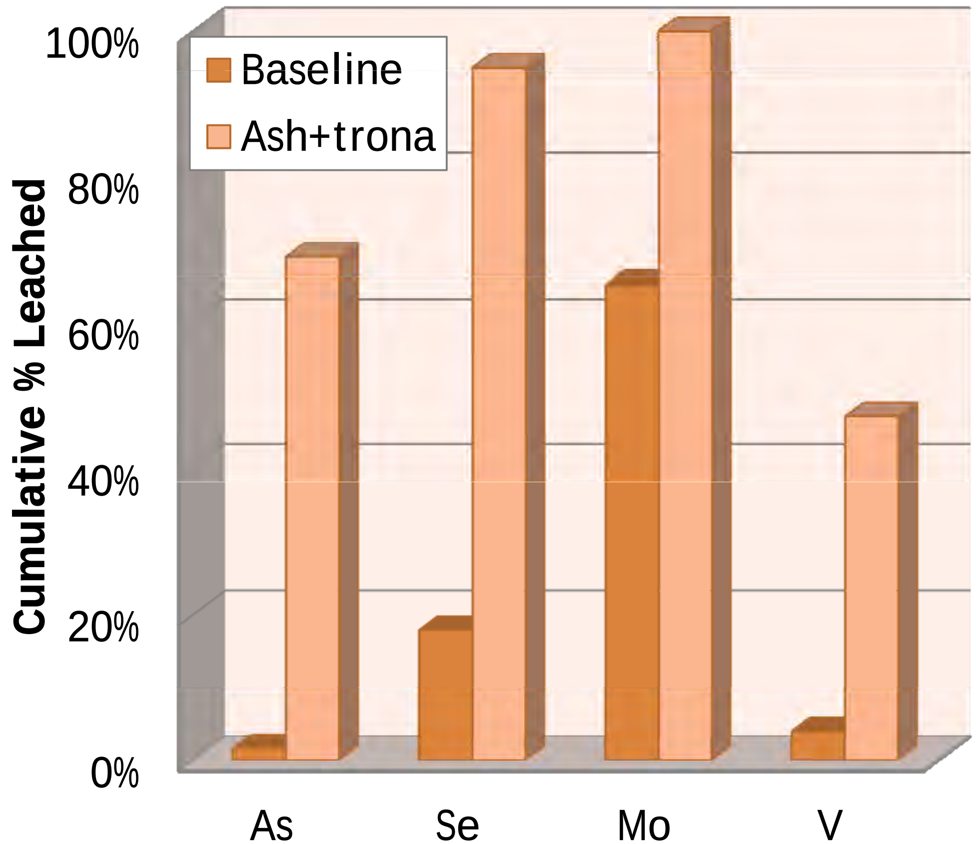
- Set of paired fly ash samples collected from H-ESP at a full-scale power plant that burned bituminous coal: control ash collected before trona injection and a trona ash collected during trona injection test
- Batch leaching experiments conducted using DI water under unadjusted pH conditions at L/S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

Ash	L/S	pH	Cl (mg/L)	Na (mg/L)	SO_4^{-2} (mg/L)	Ag (µg/L)	As (µg/L)	Ba (µg/L)	Cd (µg/L)	Cr (µg/L)	Hg (µg/L)	Pb (µg/L)	Se (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_2 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*.

Wastewater Treatment Options

FGD Wastewater

FGD Wastewater Treatment
- Physical-chemical precipitation
- Secondary treatment, e.g.
  - Biological reduction
  - Thermal evaporation
  - Zero-valent iron

→ Surface Water Discharge

Wastewater Volume Reduction
- Evaporation
- Advanced Membranes

→ Clean Water for Re-Use

→ Concentrated Brine → Solidification/ Stabilization Process → Solid to Landfill

Wastewater Treatment Options

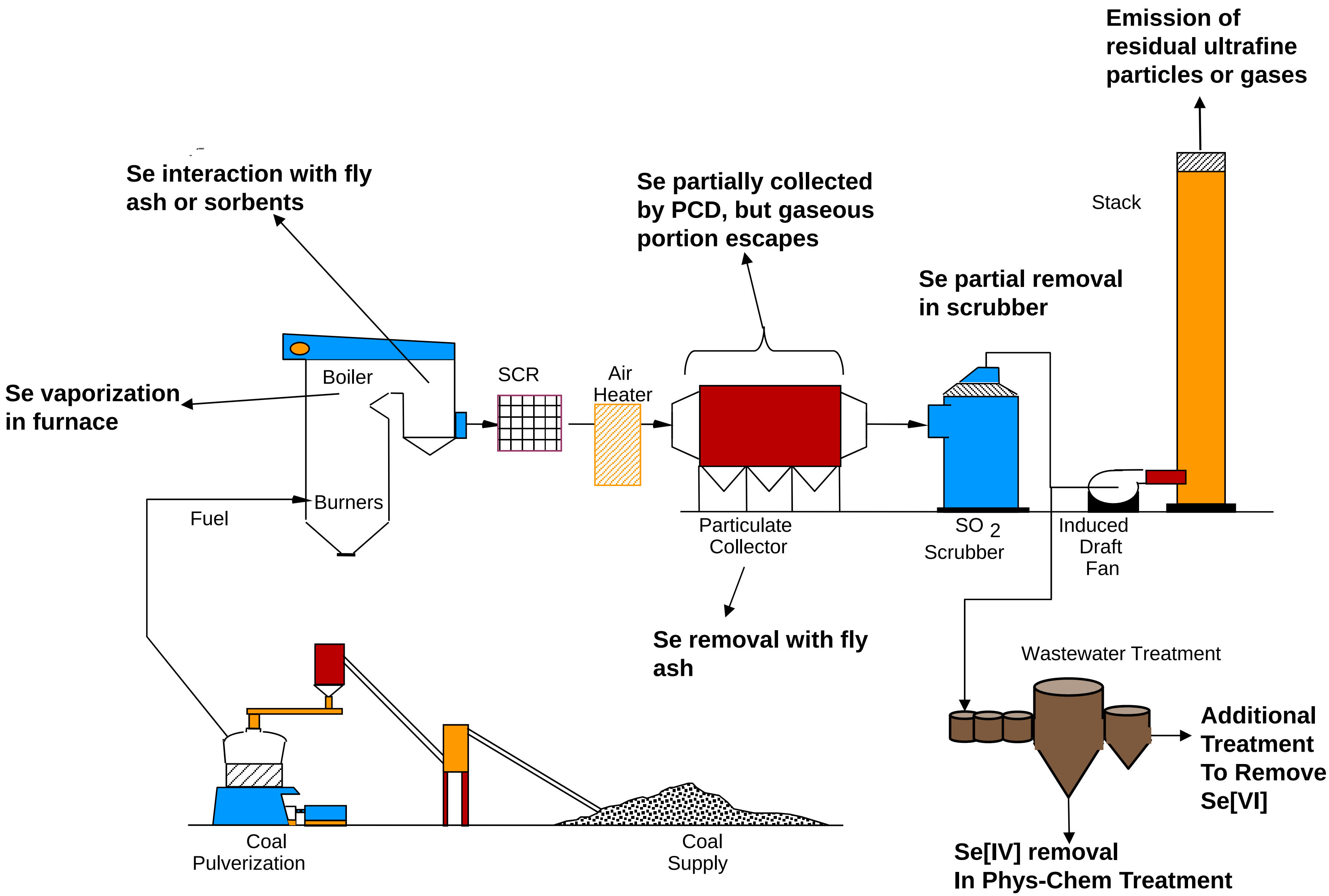
FGD Wastewater

FGD Wastewater Treatment
- Physical-chemical precipitation
- Secondary treatment, e.g.
  - Biological reduction
  - Thermal Evaporation
  - Zero-valent iron

Surface Water Discharge

- Physical-chemical precipitation
  - Removes solids and most metals
  - Does NOT remove all selenium, only Se[IV]/Selenite
  - Does NOT removal nitrite/nitrate
- Secondary treatment
  - MAY be required to remove Se[VI]/Selenate and nitrite/nitrate
  - Biological reactors most established
  - Other technologies under development, e.g., zero-valent iron (ZVI)

Se Fate: Coal Pile to Emissions



Implications for Emissions and Control

- Unlike most HAP metals, Se can be gaseous (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 SeO_2 across FGDs (60%-90%) less than removal of SO_2
- Selenium absorbed in FGDs could become an issue for wastewater treatment systems, if Se in liquid is predominantly SeO_4^{2-}/Se[VI]

Take a Deep Breath and Summarize

- Unlike most HAP metals, Se can be gaseous (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 SeO_2 across FGDs (60%-90%) less than removal of SO_2
- Selenium removed by FGDs could become an issue in WWT

QUESTIONS?

connies@adaes.com