REINHOLD ENVIRONMENTAL Ltd.

2019 REINHOLD Round Table Presentation

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Impact of Air Pollution Controls on Selenium in FGD and Wastewater Treatment Systems

2019 Reinhold Round Table

Workshop 30

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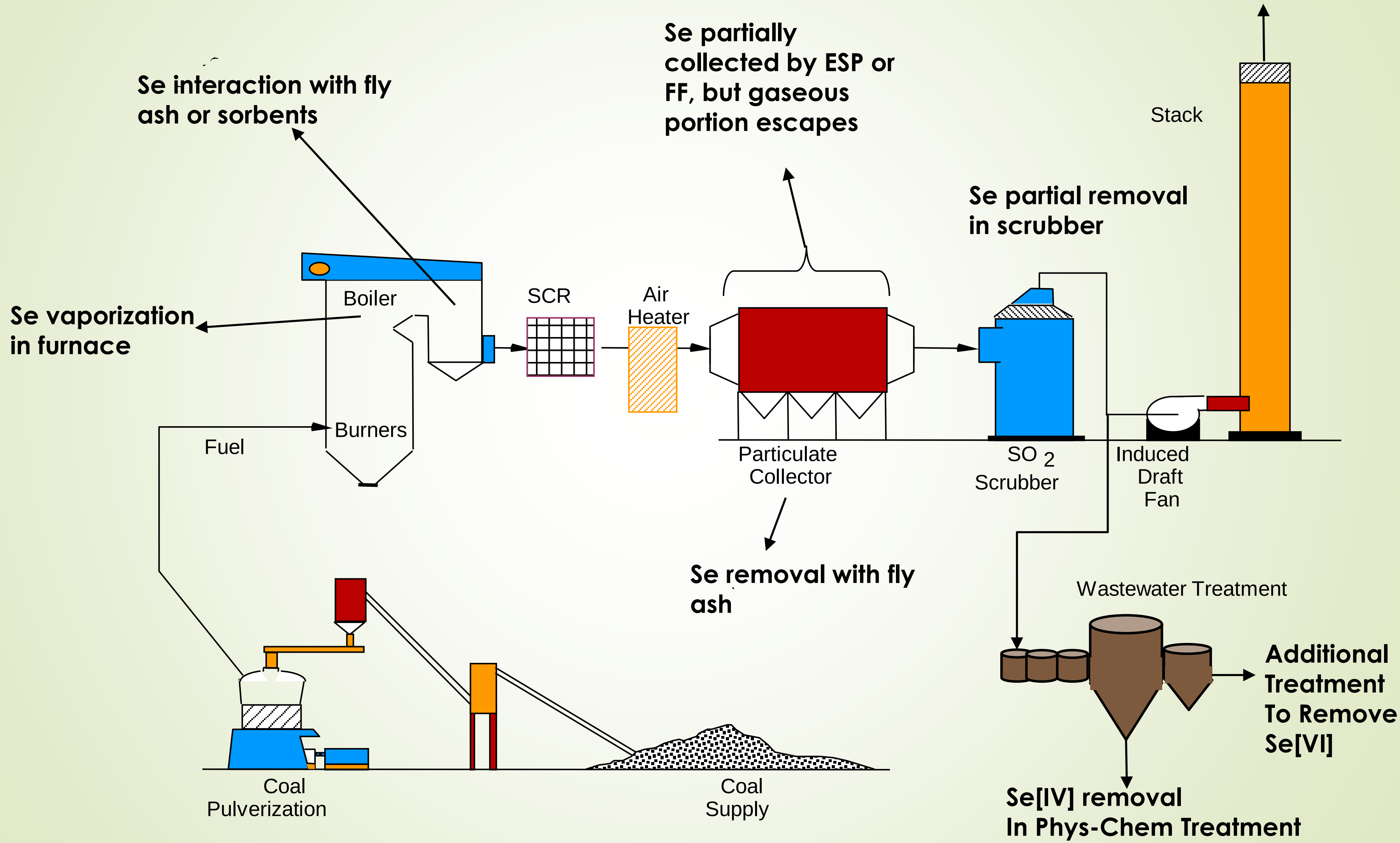
General information on coal and coal-fired boilers intended for education and illustration purposes only. All information is provided "AS-IS" and without warranty or liability of any kind.

Questions to Answer

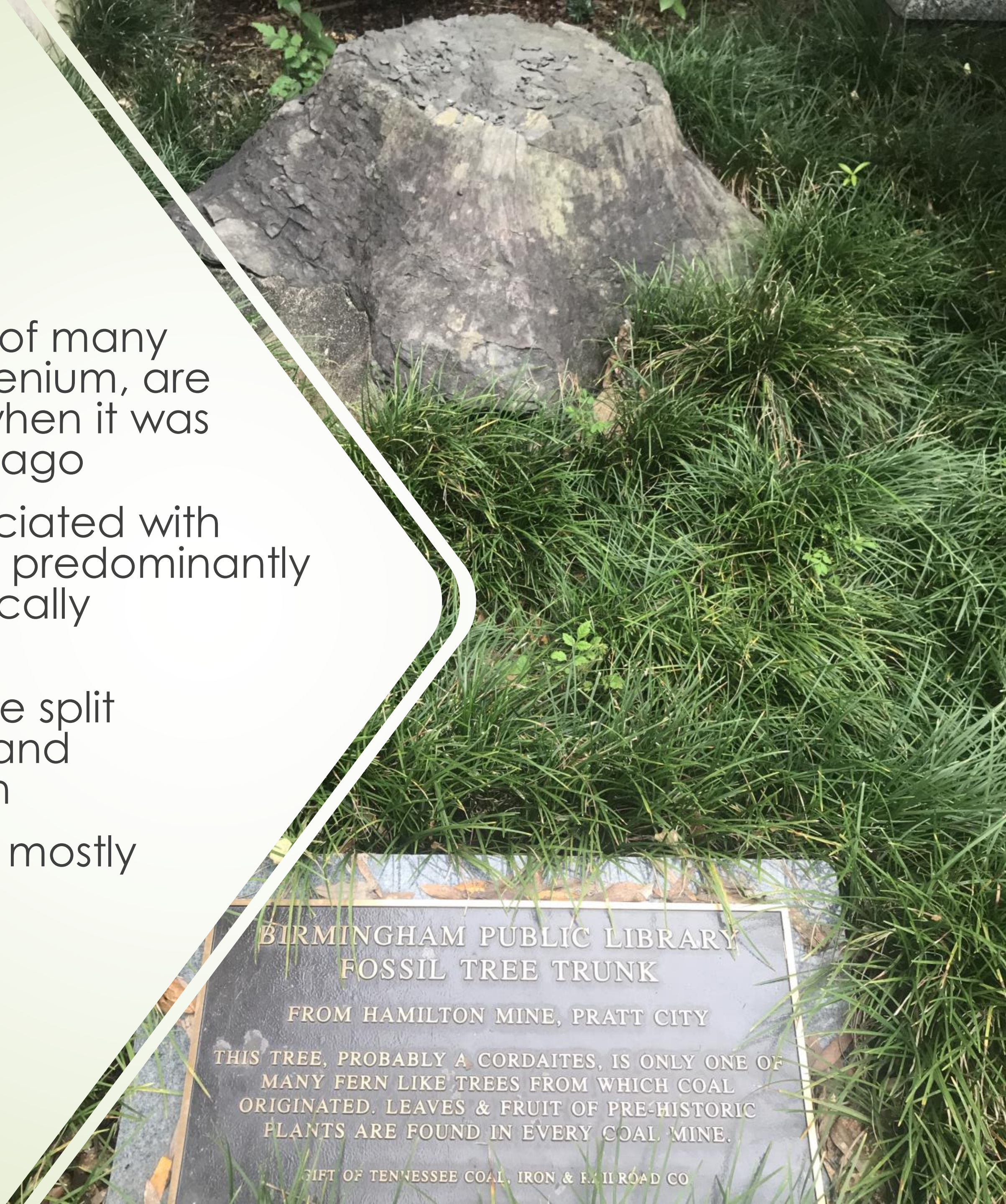
- How much selenium is in coal?
- What happens to selenium in the combustion process?
- How effective are particulate control devices at removing selenium?
- What happens to selenium in flue gas desulfurization systems?
- How much, and what form, of selenium is in FGD discharge, and how difficult is it to remove in wastewater treatment systems?

Selenium: Coal to Effluents



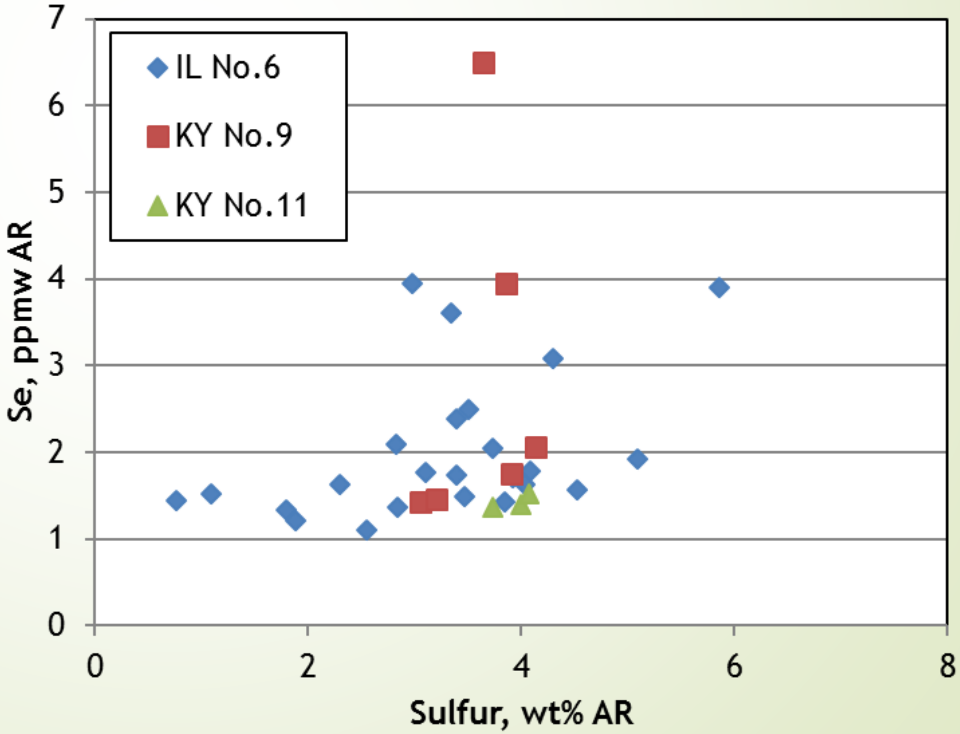
Coal

- Trace concentrations of many minerals, including selenium, are present in coal from when it was formed ~ 300 M years ago
- Selenium is often associated with metal sulfide minerals, predominantly pyrite, or as an organically associated element
  - Bituminous coals: Se split between organic and mineral association
  - Low-rank coals: Se mostly organically bound



Selenium in US Coals

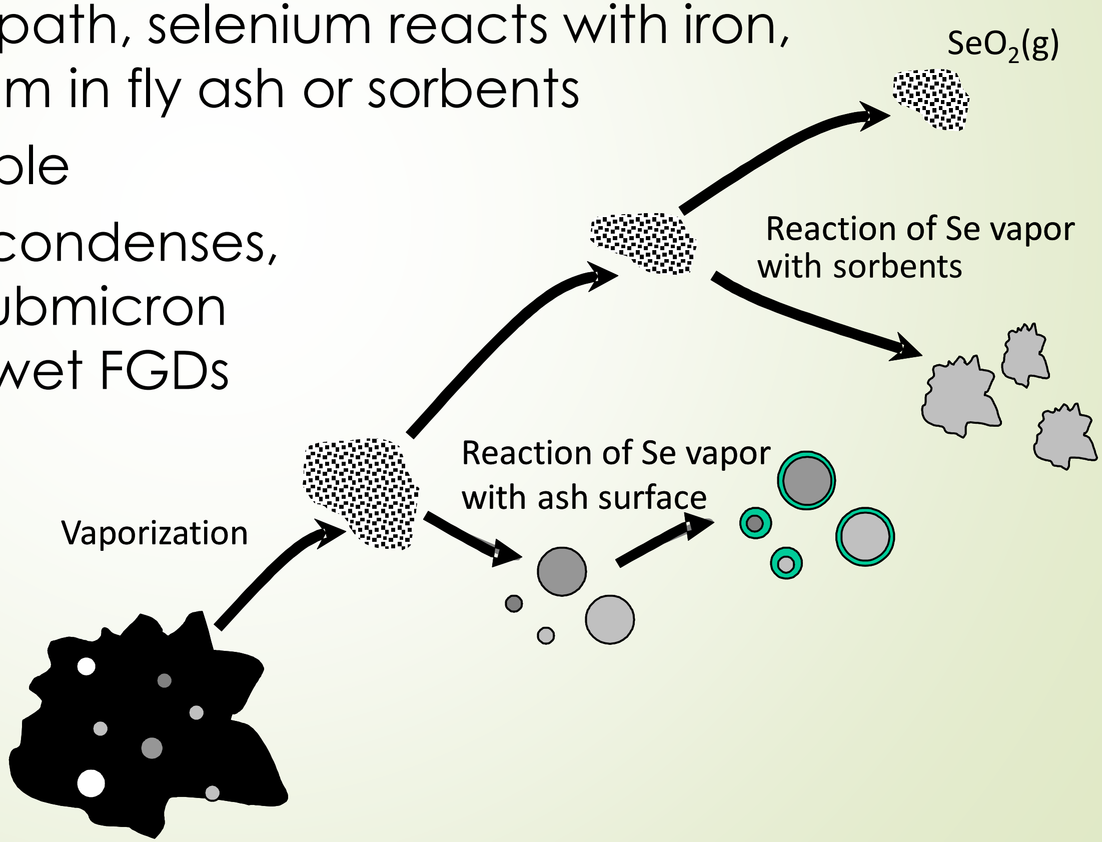
- Selenium is found in coals in trace concentrations
- USGS data: typical Se concentrations in US coals 0.5 to 5 µg/g, as high as 150 µg/g measured



Source: ISGS C499

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 & Control

- Unlike most HAP metals, Se can be gaseous (SeO_2) at temperatures in air pollution control devices
- Se can be captured by fly ash, but not always removed with high efficiency by particulate control devices
  - Low-rank (high calcium) ash more effective at capturing Se than bituminous ash
  - Fabric Filters more effective than ESPs
  - Some other control processes (e.g., dry sorbent injection) affect the split between gas-phase selenium and particulate-phase selenium at the inlet to the particulate control device
- Some Se enters FGD in gas-phase and a portion is captured in the scrubber
- If wastewater is discharged, secondary wastewater treatment may be required

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

Wastewater Treatment Options

FGD Wastewater Treatment

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

→ Surface Water Discharge

ZLD

Wastewater Volume Reduction

- Evaporation
- Advanced Membranes

→ Clean Water for Re-Use

→ Concentrated Brine

→ Solidification/ Stabilization Process

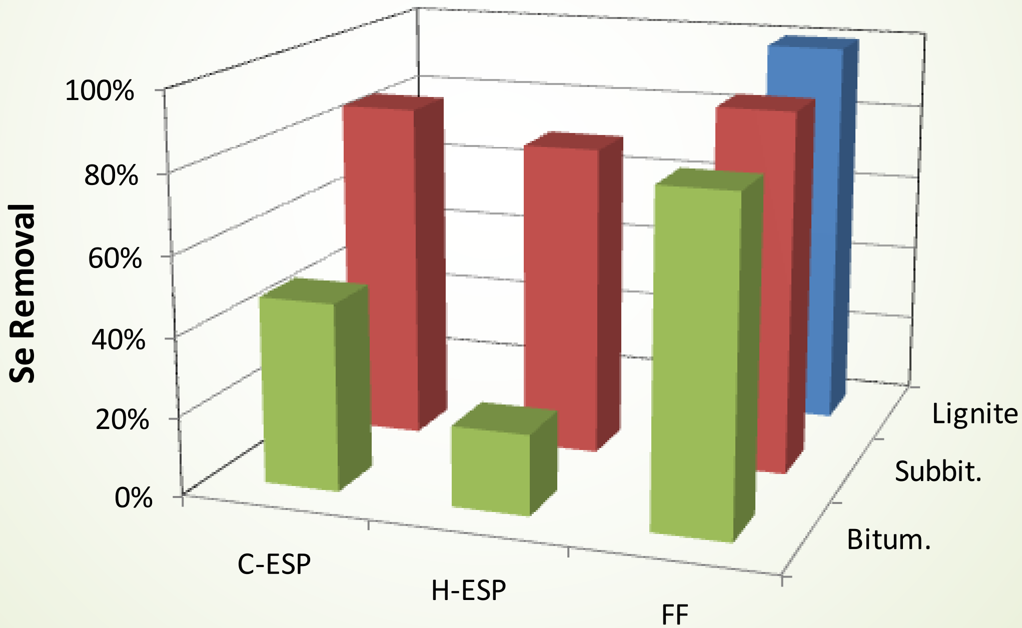
→ Solid to Landfill

Non-ZLD WWT Options

- Physical-chemical precipitation
  - Removes solids and most metals
  - **Does NOT remove all selenium, only Se[IV]/Selenite**
- Secondary treatment
  - **MAY be required to remove Se[VI]/Selenate**
  - Biological reactors most established technology
  - Other technologies under development, e.g., zero-valent iron (ZVI)
- ***Which leads us to ask:***
  - *How much selenium gets into the wet FGD?*
  - *How much selenium will end up in the wastewater?*
  - *Will the selenium in the wastewater be primarily selenite/Se[IV] or selenate/Se[VI]?*

Fate of Se in Particulate Control Devices

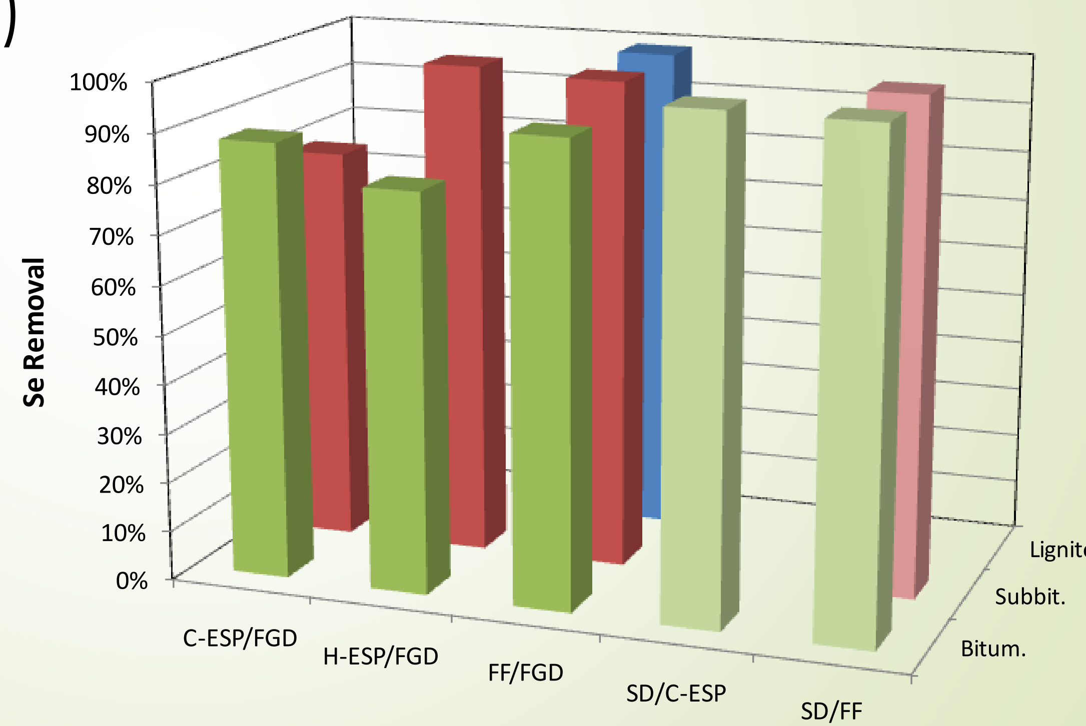
- Se removal across C-ESPs, 40% to >90%
  - Higher removal for low-rank coals
- FFs show higher removal, all ranks



Plants with only particulate control devices (no FGD)
2011 Utility ICR Data

Fate of Se in Units with FGDs

- Se removal greater across boilers with SO_2 control
- Spray dryers appear to have average higher removal than FGDs (with FF or C-ESP)



Plants with spray dryer (SD) or wet FGD
2011 Utility ICR Data

How Does Hg Control Affect Se?

- Interactions between activated carbon and vapor-phase Se not clearly demonstrated
- Bromine addition to fuel has been shown to reduce Se removal with fly ash
  - *which means more gaseous Se leaves particulate control device and may be captured in FGD*

Interaction between ACI and Se

- Conclusions from EPRI-sponsored study* on activated carbon injection (ACI) and Se emissions:
  - Bituminous-fired boilers with ACI: Insufficient data from 2010 ICR
  - Subbituminous-fired boilers: No clear positive effect of ACI
    - Operational differences between plants and low baseline Se emissions may have compounded results
  - Analysis of 9 ACI test sites (2004-2009) with and without ACI at same site:
    - 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:

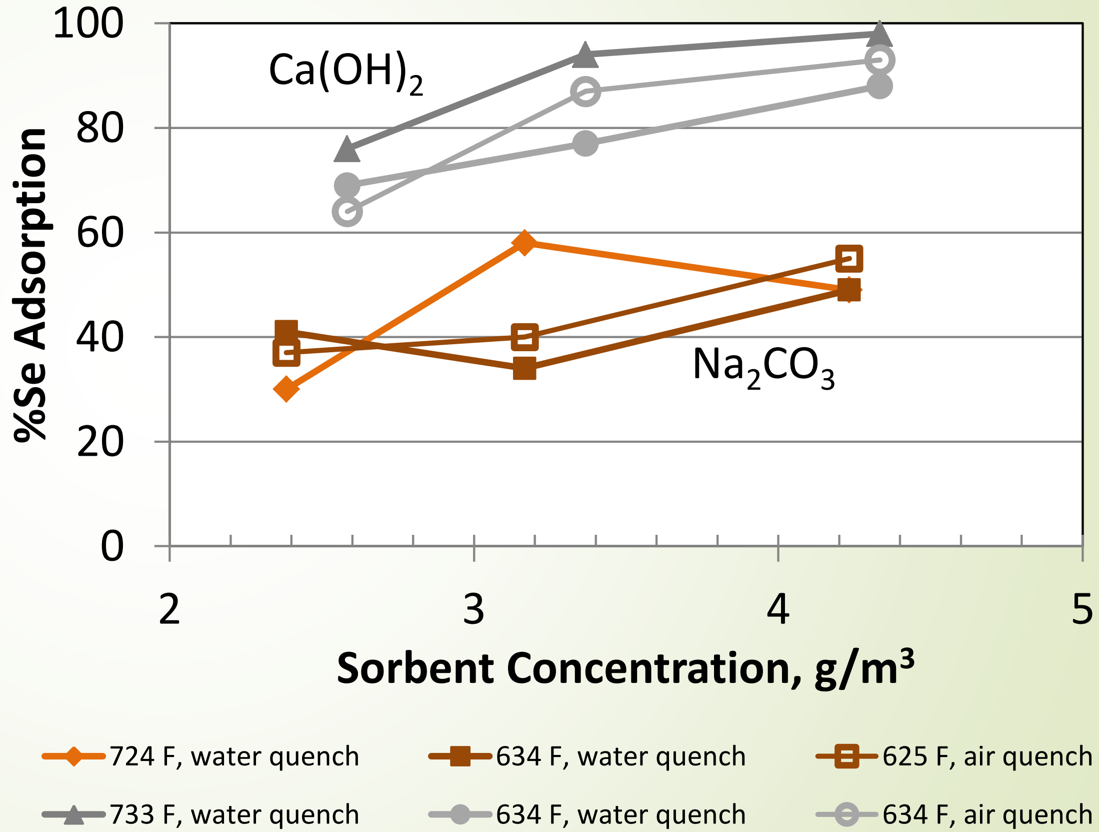
Condition	Se in Fly Ash, µg/g	%Se Capture by Fly Ash	Se in FGD Liquor, µ/L
Baseline	24	70%	300
Br Addition	10	20%	4,900

  - 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

How Do DSI Sorbents Affect Se?

- When sodium or calcium sorbents are injected into coal flue gas, they can react with Se

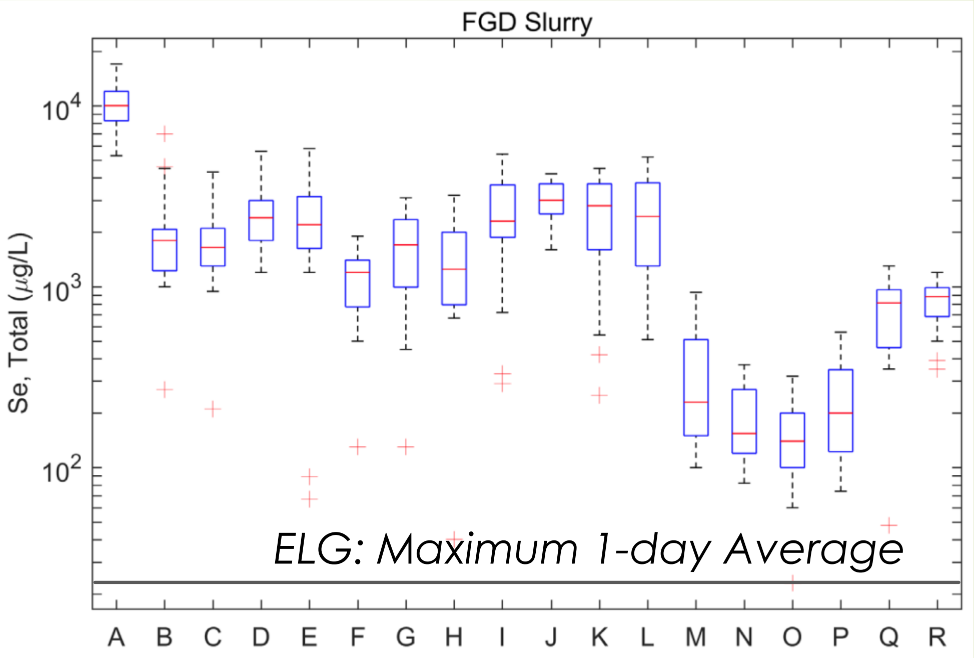


Kircher, U. "Waste Gas Treatment of Soda Lime Silica Glass Furnaces – Investigations with Different Absorption Agents." Ceramic Trans. ***1998****, 82, 75-80.*

Should Plants be Concerned?
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

**As finalized in 2015, but delayed. EPA is reviewing and may modify in future*



Selenium concentrations in FGD slurries of Southern Company scrubbers

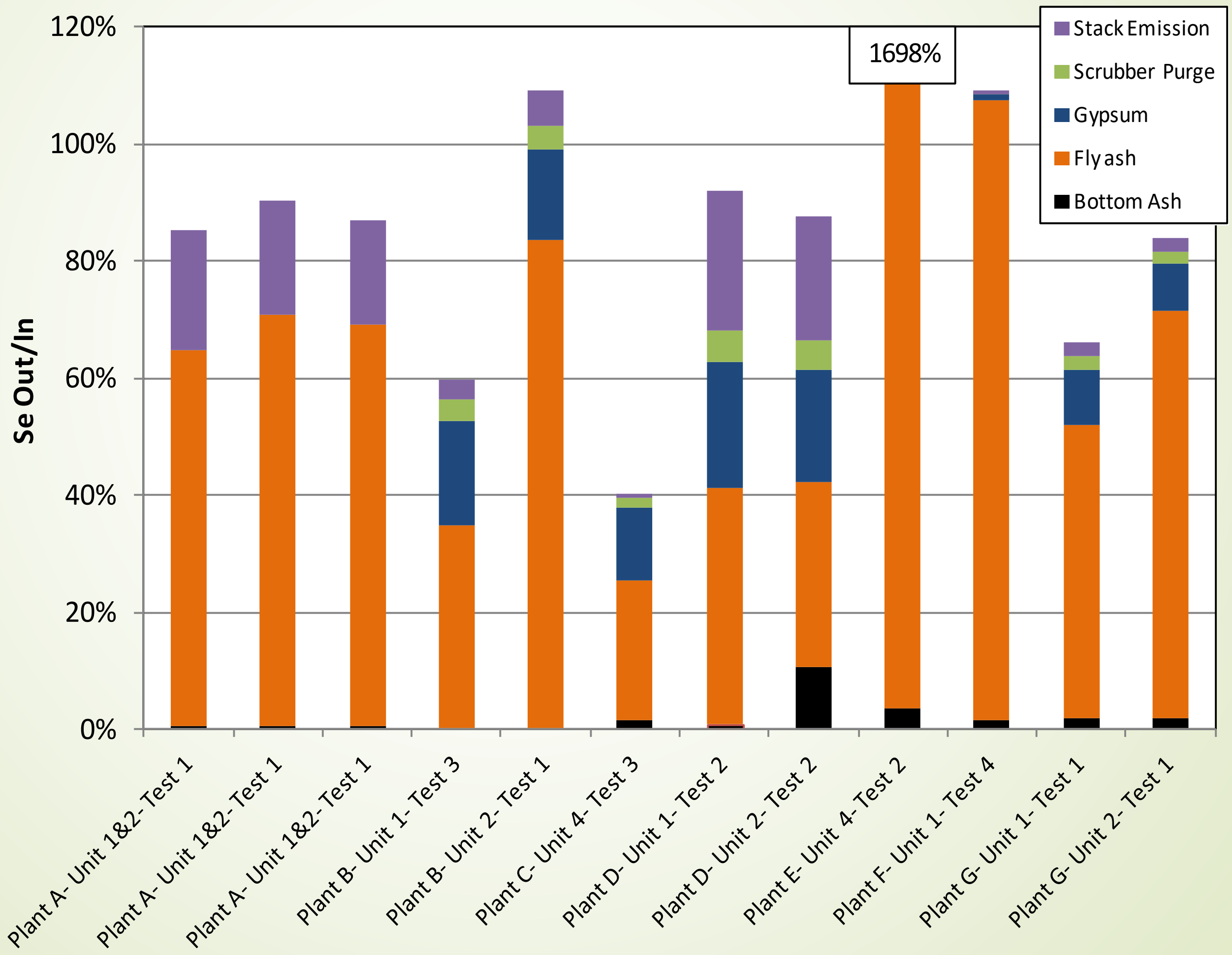
Allen, J.O.; Ferens-Foulet, C.K.; Acharya, C.K. Effluent Trace Metals Survey and Related Plant Operations at 18 Flagship Units. Presented at Power Plant Pollutant Control and Carbon Management "Mega" Symposium, Baltimore, MD, August 16-19, 2016

Selenium 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

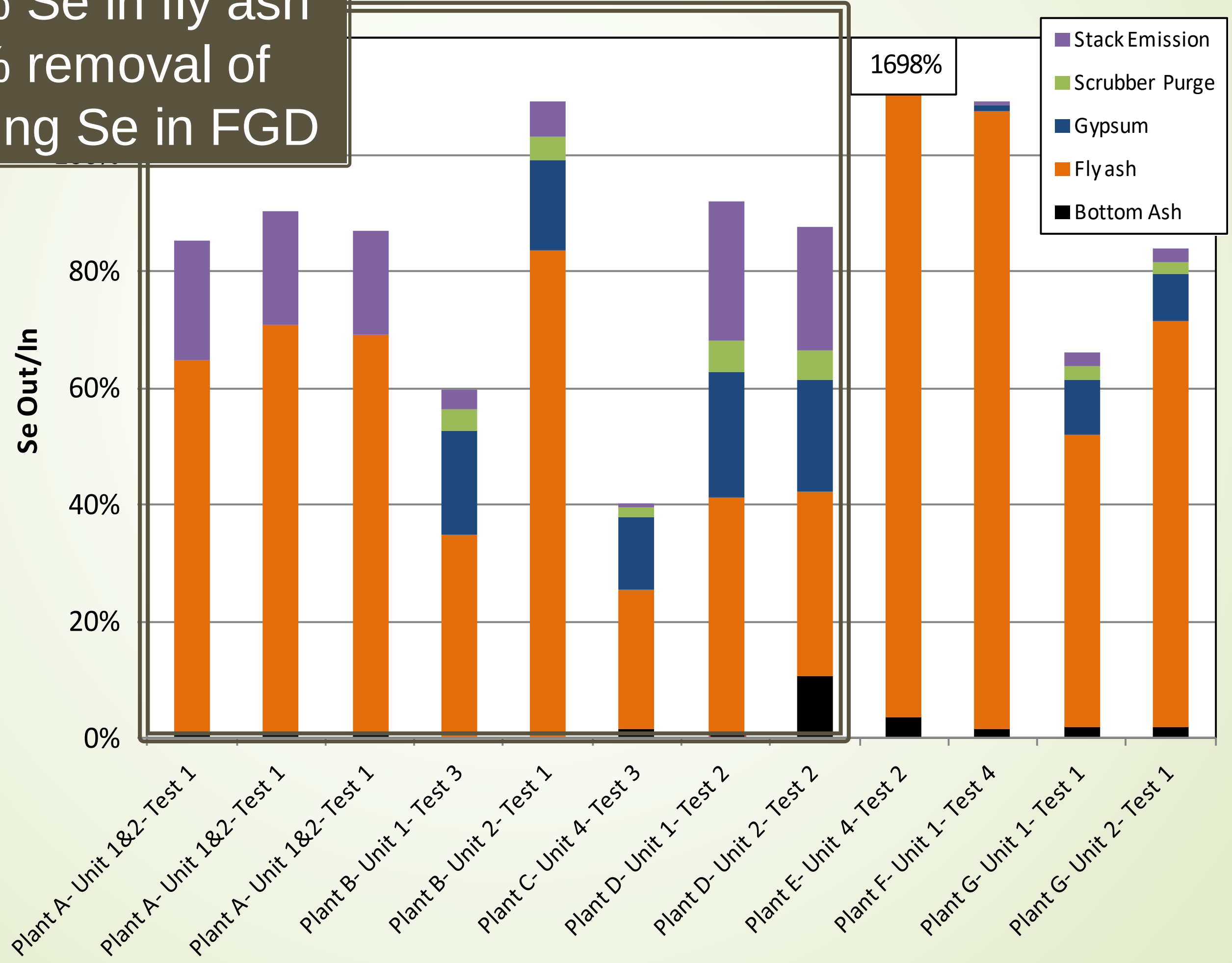
**Senior et al., AQVIII Conference, 2011*

Selenium Mass Balance



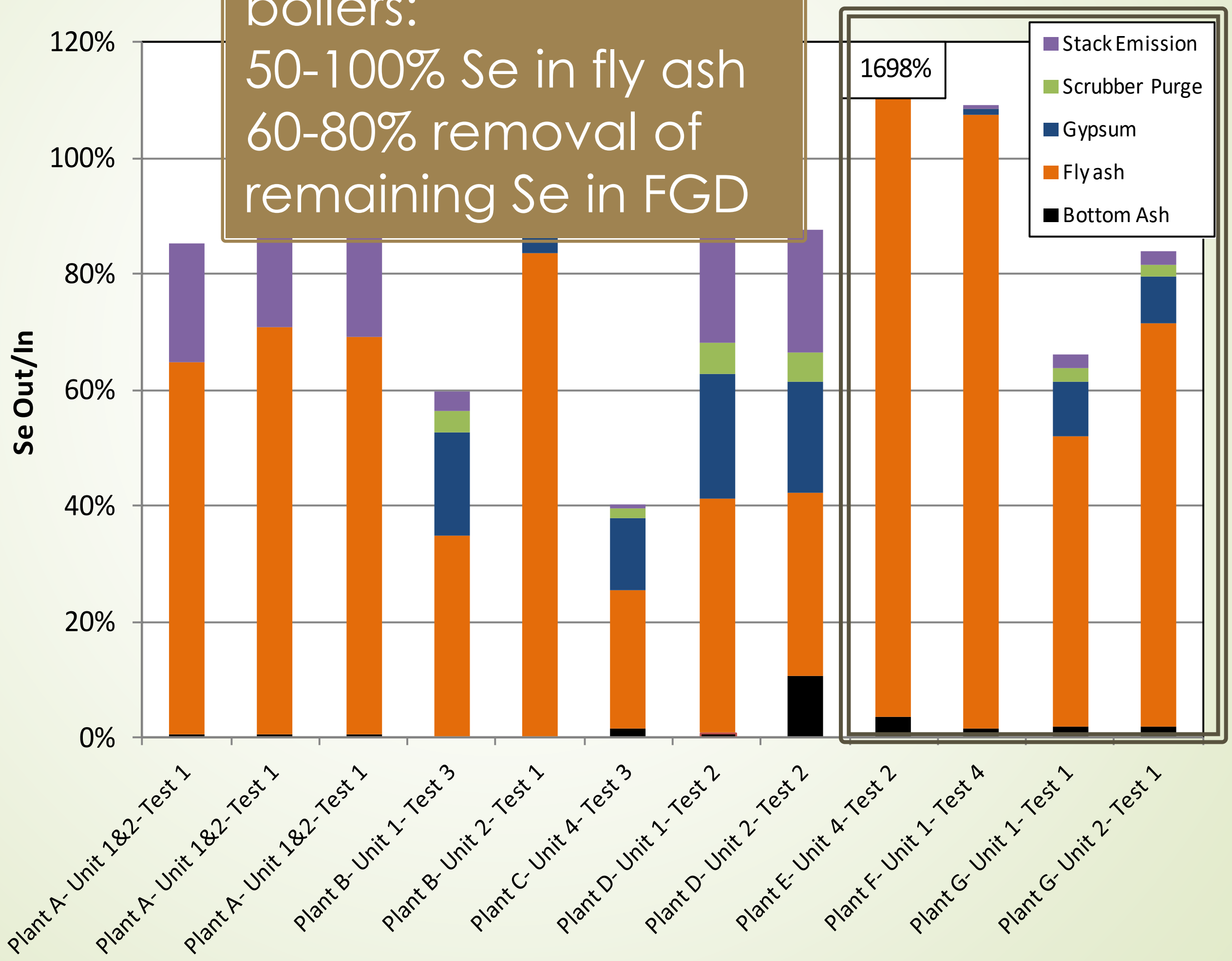
Selenium Mass Balance

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



Selenium Mass Balance

Subbituminous boilers:
50-100% Se in fly ash
60-80% removal of remaining Se in FGD



Se Mass Balance: 2010 EPRI Study

- 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.
- Note that four boilers in the dataset, which had more complete data, show:
  - 2-4% of bituminous coal selenium reports to scrubber purge
  - ~ 0% of subbituminous coal selenium reports to scrubber purge

						Se mass balance (% of input)					
Boiler	Coal	Coal S, wt% dry	Firing System	Coal S, wt% dry	APCD	Mass Balance Closure	Bottom Ash	Fly ash	Gypsum	Scrubber Purge or Effluent	Stack Emission
B1	Bit.	1.61	Front wall	1.61	SCR/CSE/wFGD	60%	0%	35%	18%	4%	3%
B2	Bit.	1.15	Front wall	1.15	SCR/CSE/wFGD	109%	0%	84%	16%	4%	6%
C	Bit.	4.02	Wall	4.02	SCR/ACI/FF/wFGD/WESP	40%	1%	24%	13%	2%	1%
F1	Subbit.	0.77	Tangent.	0.77	FF/wFGD	109%	2%	106%	1%	0%	1%

**Behavior and Potential Control Strategies for Selenium in Coal-Fired Boilers: Evaluation and Modeling of Full-Scale Data.* EPRI, Palo Alto, CA:2010. 1021217.

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

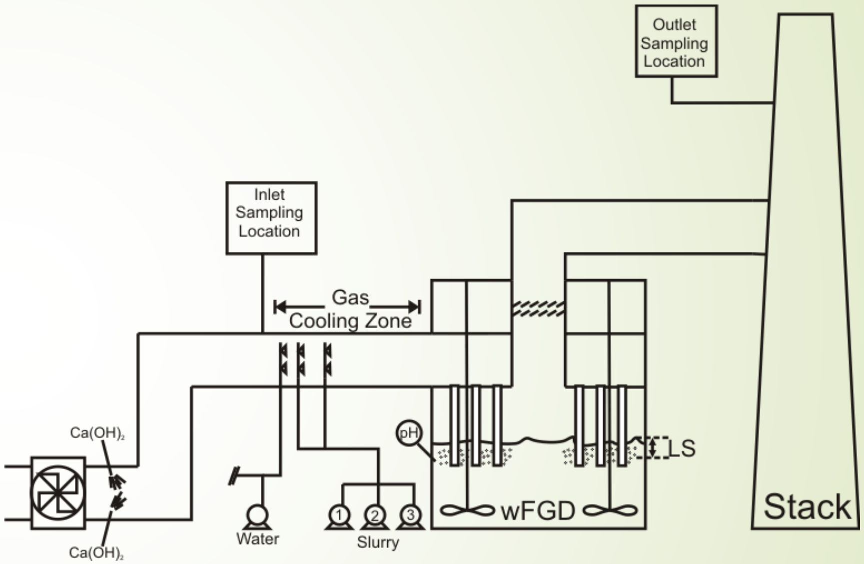
- Determine removal of Se across full-scale wet scrubber in a low-sulfur bituminous-fired boiler
  - 900 MW boiler, burning Eastern bituminous coal
  - APCD: cold-side ESP, MHI Chiyoda scrubber
  - Hydrated lime injection between ESP and FGD for SO_3 control
- Obtain better understanding of Se behavior 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.

Note that Plant Wansley is not representative of other Southern Company plants

Plant Wansley Study*

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



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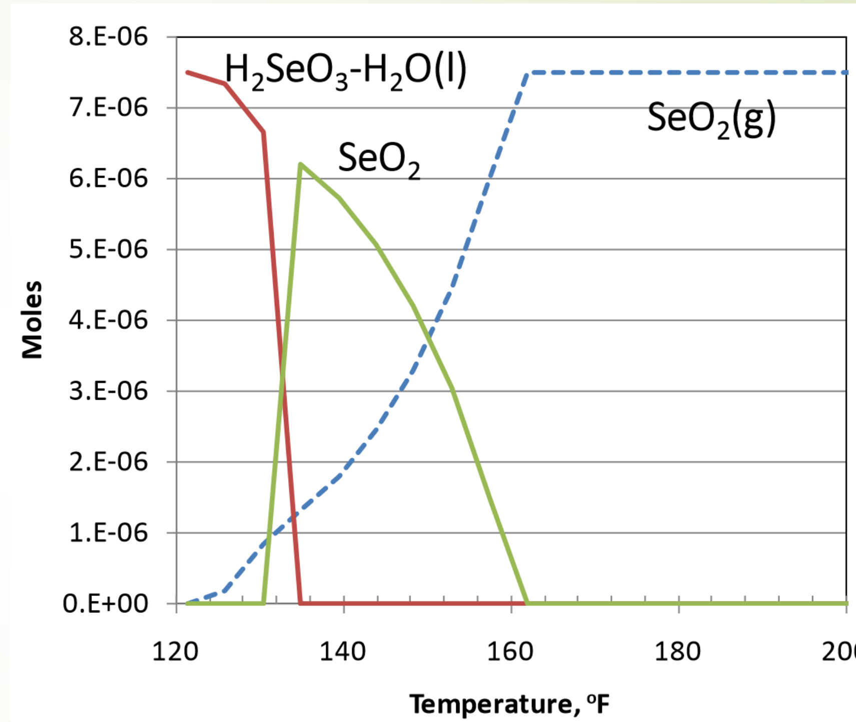
*Senior, C.L.; Tyree, C.A.; Meeks, N.D.; Acharya, C.; McCain, J.D.; Cushing, K.M. Selenium Partitioning and Removal Across a Wet FGD Scrubber at a Coal-Fired Power Plant. Env. Sci. Technol. 2015, 49, 14376-14382.

Gas-to-Particle Conversion

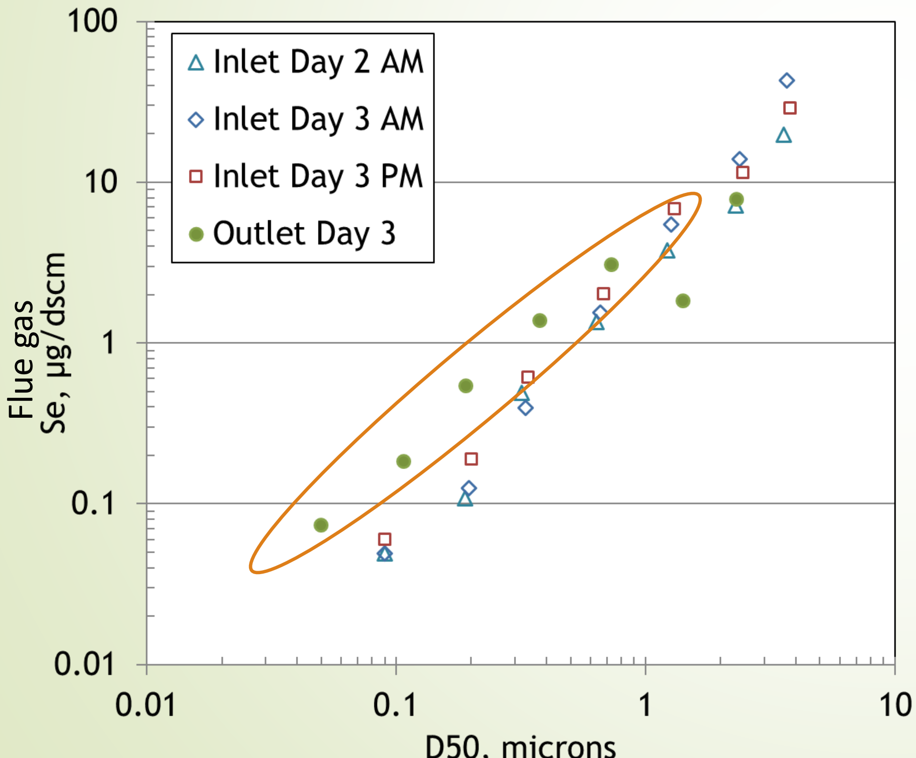
- Equilibrium calculations using typical flue gas compositions
- Condensation of SeO_2 at temperatures below 160°F



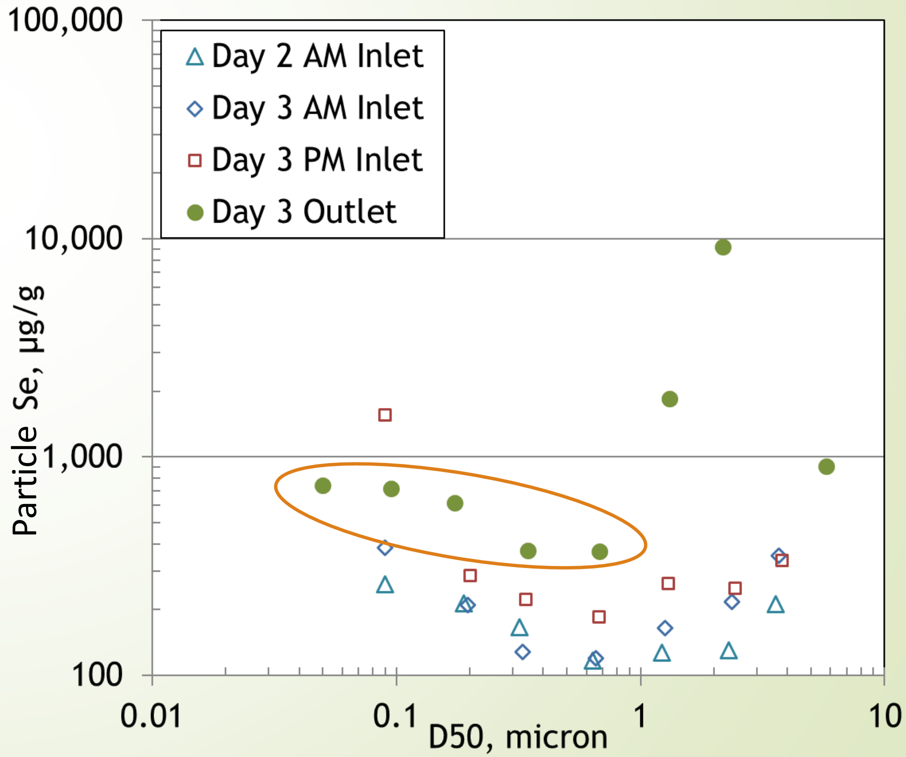
Gas-to-Particle Conversion

- Rapid quench in scrubber could convert gaseous SeO_2 to H_2SeO_3 aerosol or SeO_2 condensed on fly ash

- Flue gas concentration of submicron particle-bound Se increases across FGD



- Selenium concentration in submicron particles increases across FGD



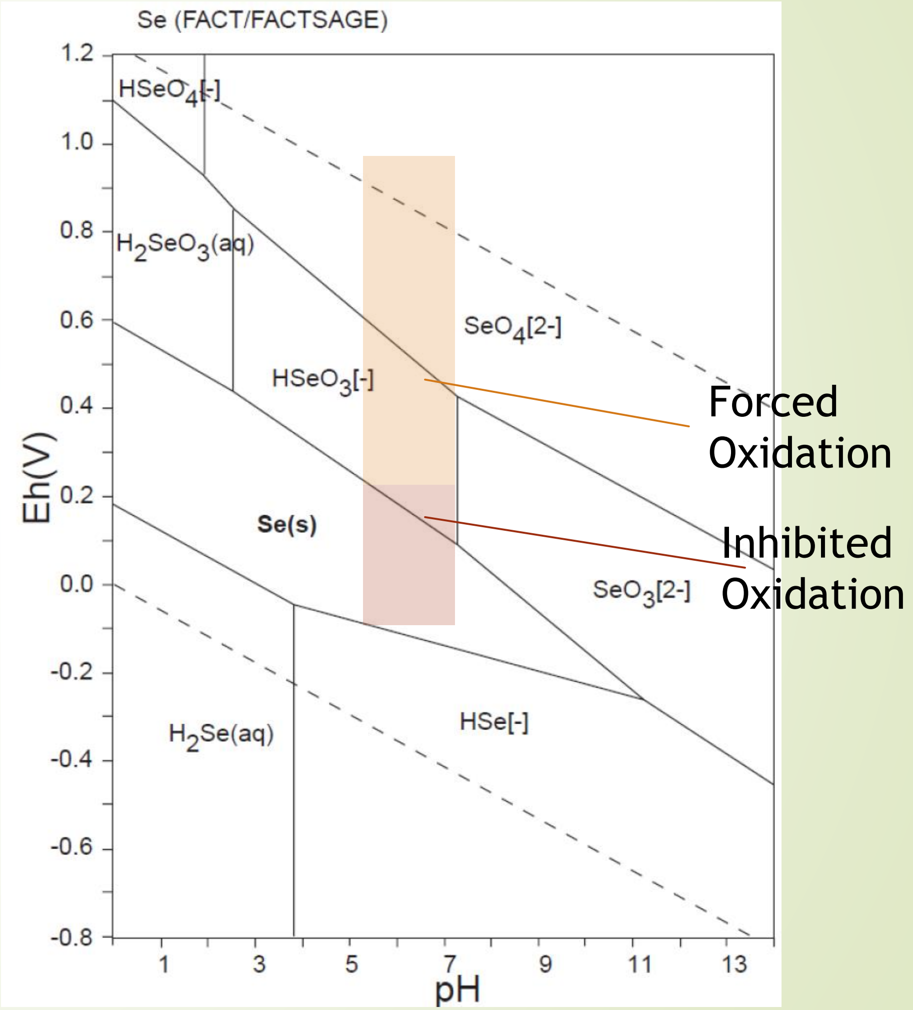
Preferential condensation would be on submicron particles (higher surface area)

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 Speciation in Wet FGDs

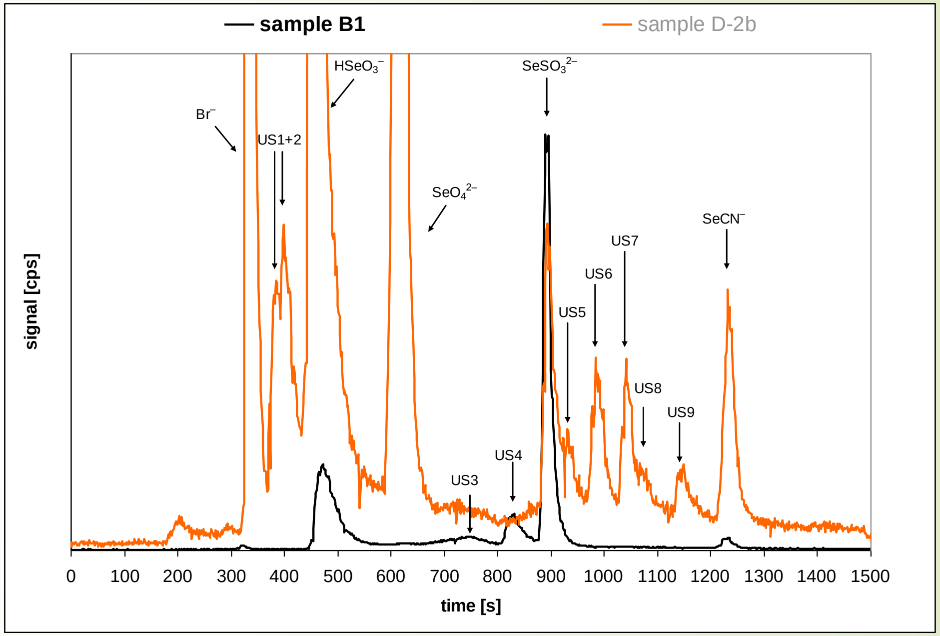
- Selenium can exist in aqueous phase or solid phase in wet FGD slurry
- A range of different Se species are expected in wet FGD slurries
- Speciation of selenium in the scrubber varies with pH and ORP, affected by, for example
  - Scrubber design
  - Transition metals in slurry
  - Scrubber additives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

Measurement of Se in Wet FGD Slurries

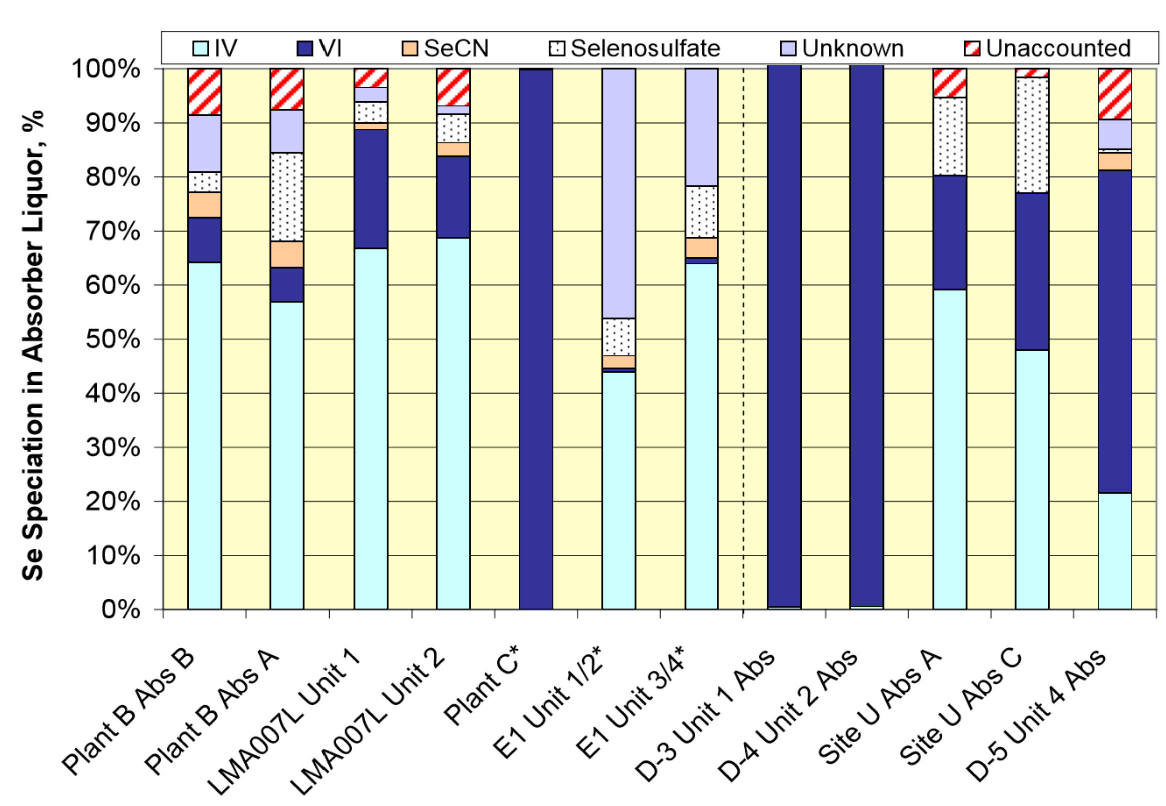
- Se typically measured by ion chromatography + ICP-MS
- Oxidation states:
  - Selenite (SeO_3^{2-}), Se[IV]
  - Selenate (SeO_4^{2-}), Se[VI]
  - Elemental, Se[0]
- Compounds:
  - Selenocyanate ($SeCN^-$)
  - Selenosulfate ($SeSO_3^{2-}$)
  - Dissolved or colloidal Se[0]
  - Unknown Se peaks



Source: P. Chu, EPRI

Se Speciation in Wet FGD: 2010 EPRI Study

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



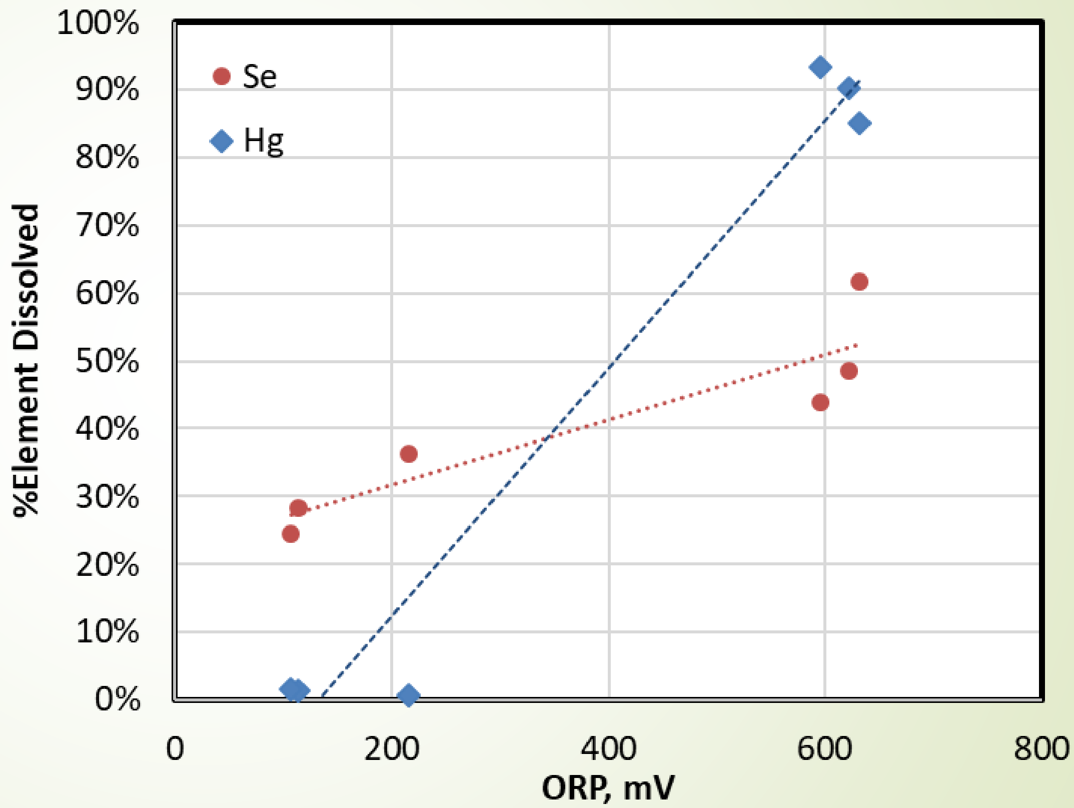
Impact of Wet FGD Design and Operations on Selenium Speciation: 2010 Update. EPRI, Palo Alto, CA: 2010. 1019870.

Se Oxidation to Selenate: Potential Contributing Factors

- APC equipment upstream of FGD (SCR, SO_3 control, etc.)
- Liquor residence time in absorber/reaction tank
- Cycles of concentration in the FGD liquor (impacts many times FGD liquor gets recycled back into the absorber loop before discharge)
- FGD operating temperature, which impacts oxidation reaction rates
- Concentrations of precipitated metals in the absorber slurry, such as iron hydroxides, which can absorb or co-precipitate selenite
- Concentrations of dissolved metals in the absorber liquor, which can serve as catalysts for oxidation reactions

Partitioning in Wet FGD: 2010 EPRI Study

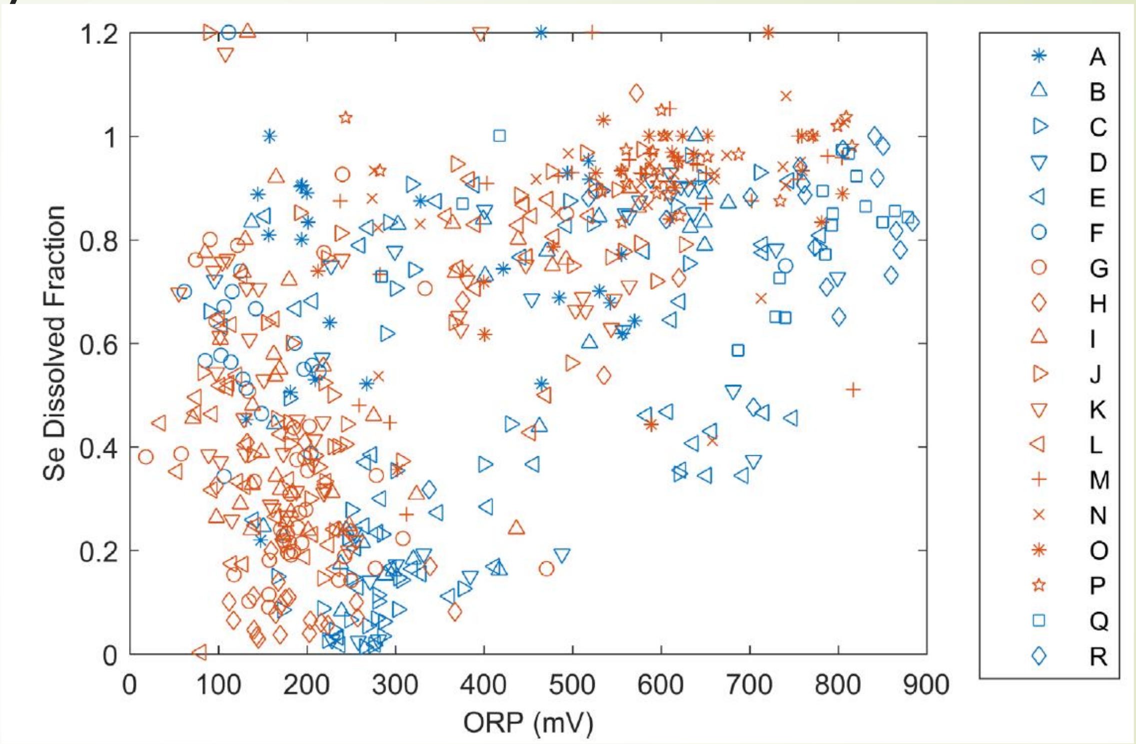
- Fraction of both Se and Hg dissolved in FGD slurry increases with increasing ORP
  - Limestone forced oxidation (LSFO) scrubbers



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

- 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
- Much scatter in the data



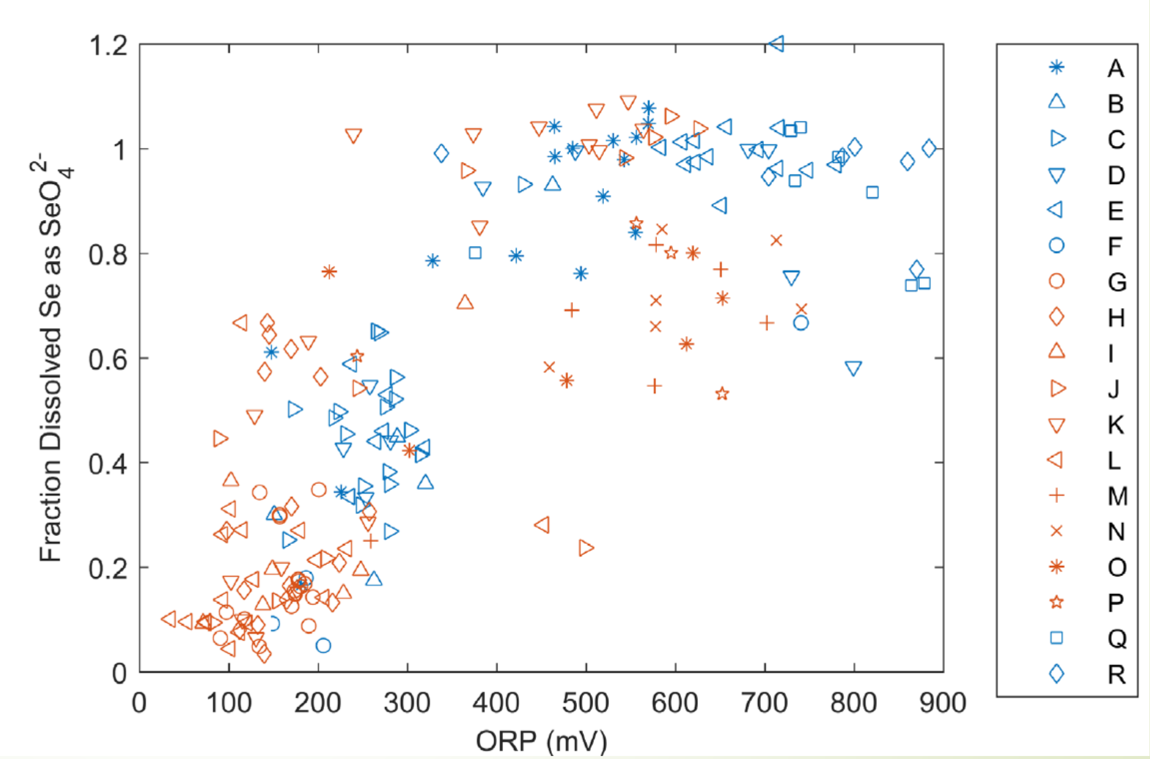
Dissolved Se fraction in FGD slurries (Red, ADVATECH; Blue, Chiyoda)

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
- Typically 50% to 100% selenate at ORP > ~ 350 mv

Dissolved Selenate

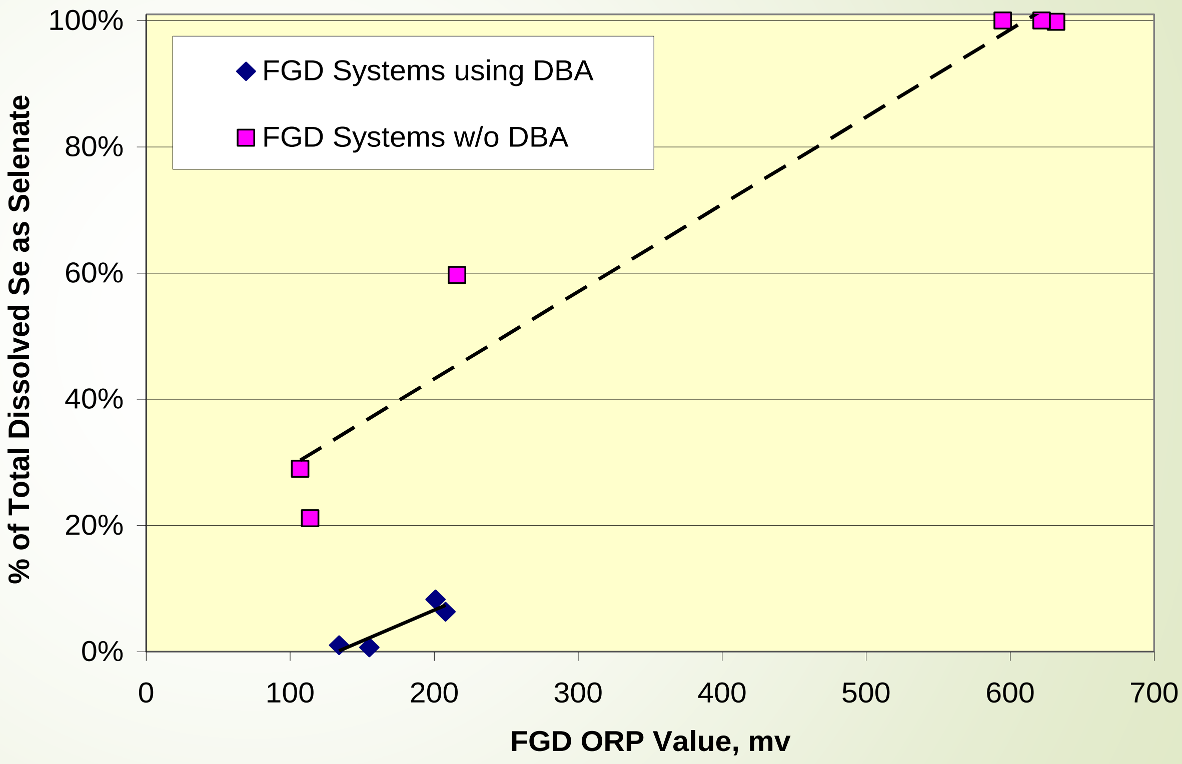


Fraction of dissolved Se as SeO_4^{2-} in FGD slurries (Red, ADVATECH; Blue, Chiyoda)

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
  - Factors 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

FGD Operation and Selenium:
Decreasing FGD Chloride Purge Flow Rate

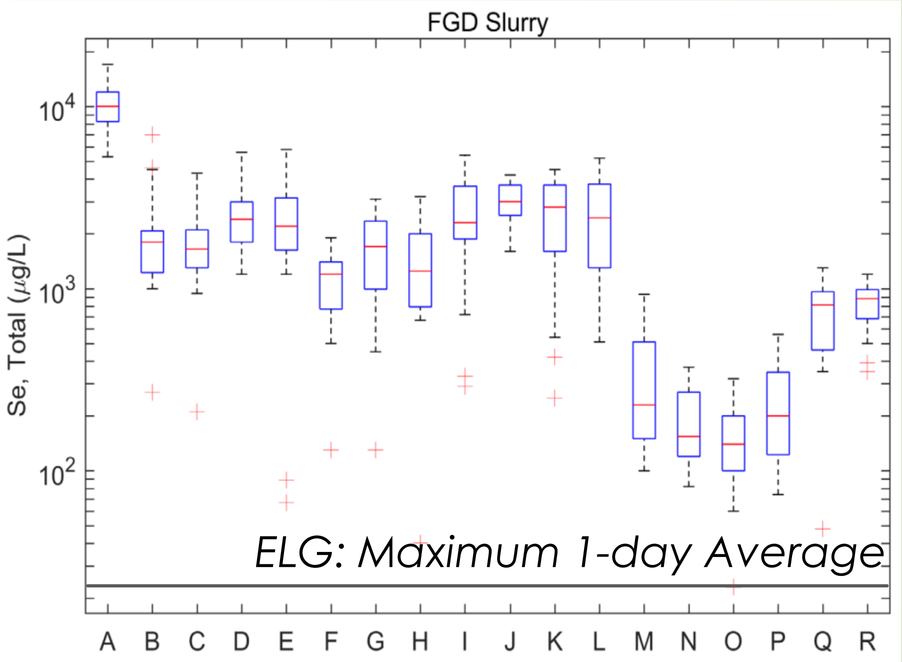
- Some plants "cycle up" wet FGDs to reduce the amount of water being discharged in the chloride purge stream
- This reduces the cost of wastewater treatment by reducing the volume of water to be treated
- Reducing the volume of FGD wastewater discharge concentrates Se in the wastewater discharge

Managing Unit Operation to Minimize Secondary Treatment:
Shifting Se from Liquid to Solid Phase in FGD

- We know that the ORP of a wet FGD affects what fraction of Se is in the liquid vs. solid
  - Typicaly < ~ 350 mv
  - Conditions in which Se is mostly in solid phase in FGDs often mean predominantly selenite (Se[IV]), which is easier to remove in WWT
- Shifting Se in the FGD slurry from liquid phase to solid phase reduces concentration of Se in the chloride purge stream (which would go to waste water treatment)
- **Can speciation of Se in discharge be controlled sufficiently to eliminate the need for biological treatment?**

Managing Unit Operation to Minimize Secondary Treatment:
Removing Se Upstream of FGD

- Extremely high levels of upstream selenium removal (>>90%) may be required to render concentrations of Se in FGD discharge close to original ELG limits
- High concentrations of selenium in wet FGD discharge could require an expensive secondary treatment system
- **Speciation of Se in discharge will also influence need for secondary treatment**



Selenium concentrations in FGD slurries of Southern Company scrubbers. Allen, J.O "Mega" Symposium, 2016

Key Points to Remember: Selenium and FGDs

- Unlike most HAP metals, Se can be gaseous (SeO_2) at temperatures in ESPs and fabric filters
- Significant portion of Se can enter FGD in gas-phase
  - Se can be captured by fly ash, but not always removed by particulate control devices with sufficiently high efficiency to eliminate need for downstream treatment
- Not all selenium is removed in the FGD
  - Overall Se removal across FGD is much lower than for SO_2
- FGD operation can minimize discharge of difficult-to-treat forms of selenium
- **Typical bituminous coal-fired boilers with wet FGDs will need >>90% Se removal upstream of FGD to avoid need for secondary WWT, based on original ELG limits**

QUESTIONS?

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