REINHOLD ENVIRONMENTAL Ltd.

2014 NOx-Combustion Round Table & Expo Presentations

February 10 & 11, 2014, in Charlotte, NC / Hosted by Duke Energy

Advancing Cleaner Energy

Selenium Mass Balance in Coal-Fired Power Plants

Reinhold NOx Roundtable, February 10-11. 2014

Connie Senior, ADA-ES

Disclaimer

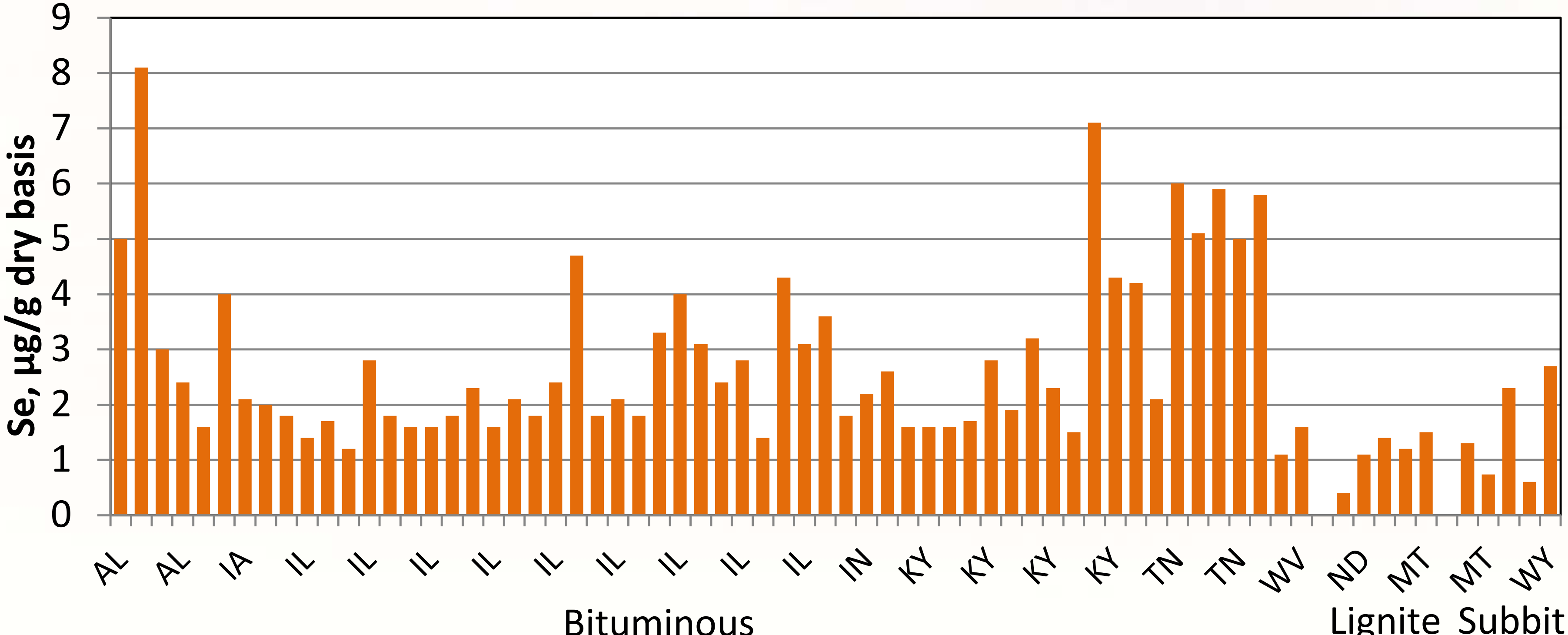
This presentation includes general information on selenium in coal and coal-fired boilers intended for education and illustration purposes only. All information is provided “AS-IS” and without warranty or liability of any kind.

Topics to be Covered

- Se in coal, origins and typical values
- Measurement methods for Se in coal and flue gas
- Se transformations in the flue gas, based on theory and measurements
- Se behavior in APCDs
- Fate of selenium in effluents and byproducts

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



Source: *Illinois State Geological Survey*

Se in Fly Ash

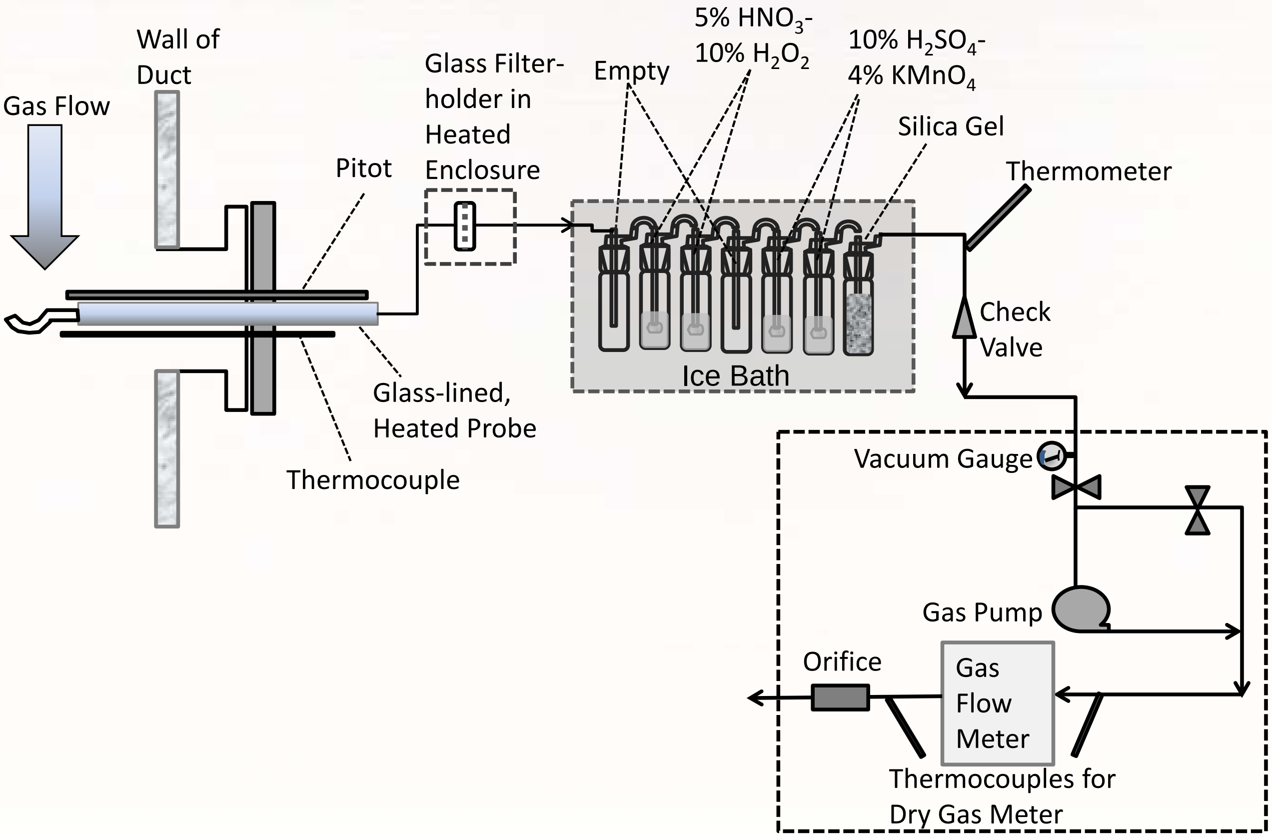
- Examples of measured Se in fly ash from different plants:
  - Instrumental Neutron Activation Analysis (INAA)
  - Inductively Coupled Plasma - Dynamic Reaction Cell - Mass Spectroscopy (ICP-DRC-MS)
- Both methods show good repeatability and low detection limits

Number	Method	Se, µg/g AR	RD of repli-cates	RD: INAA vs. ICP
Plant G(1), “A”	INAA	7.1	1.7%	
Plant G(1), “B”	INAA	6.9		
	Average	7.0		-40.9%
Plant G(1), “C”	ICP-DRC-MS	10.0	1.3%	
Plant G(1), “D”	ICP-DRC-MS	9.8		
	Average	9.9		
Boiler C, “A”	INAA	3.8	4.0%	
Boiler C, “B”	INAA	4.1		
	Average	4.0		-32.1%
Boiler C, “C”	ICP-DRC-MS	5.2	--	
Plant D(1), “A”	INAA	18.3	3.2%	
Plant D(1), “B”	INAA	19.5		
	Average	18.9		-13.8%
Plant D(1), “C”	ICP-DRC-MS	19.3	10.2%	
Plant D(1), “D”	ICP-DRC-MS	23.7		
	Average	21.5		
Boiler E	INAA	182	--	
Boiler E, "A"	ICP-DRC-MS	152	0.7%	15.9%
Boiler E, "B"	ICP-DRC-MS	154		
	Average	153		

Source: Senior et al., Air Quality VIII

Measuring 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

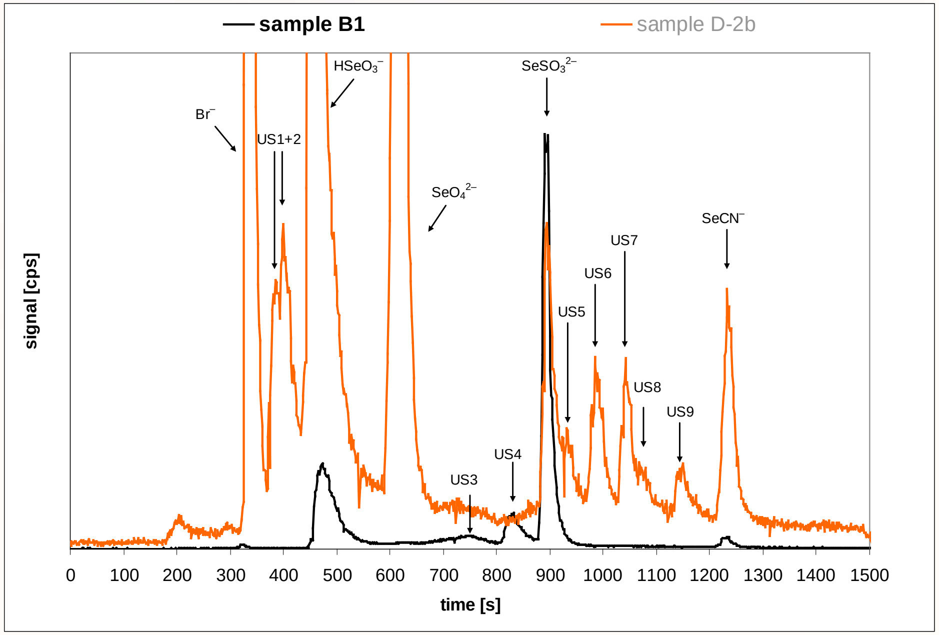


Se in Wet FGD Slurries

- Multiple selenium species have been identified in scrubber 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 in the field and shipped to the analytical laboratory

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

Example for Se Emissions

Ultimate Analysis, wt%	
C	67.70
S	3.60
H_2	4.70
H_2O	3.30
N_2	1.20
O_2	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 µg/g
- Should be able to detect Se in fly ash samples

	----- Se in fly ash, ug/g --------		
		Se in coal, ug/g dry	
Se Removal in ESP	*0.5*	*2*	*4*
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)

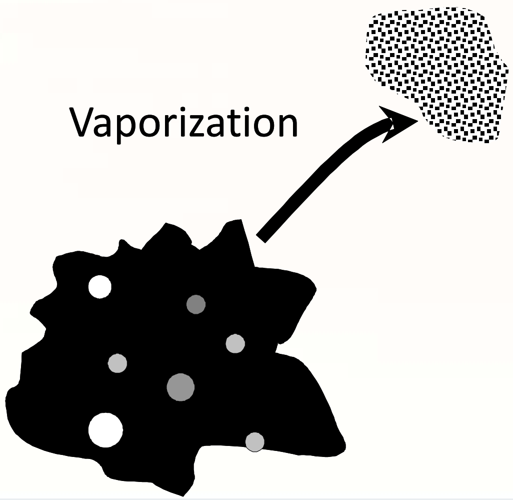
- Except for very high removals in ESP, should be able to detect Se in flue gas post-ESP via M29

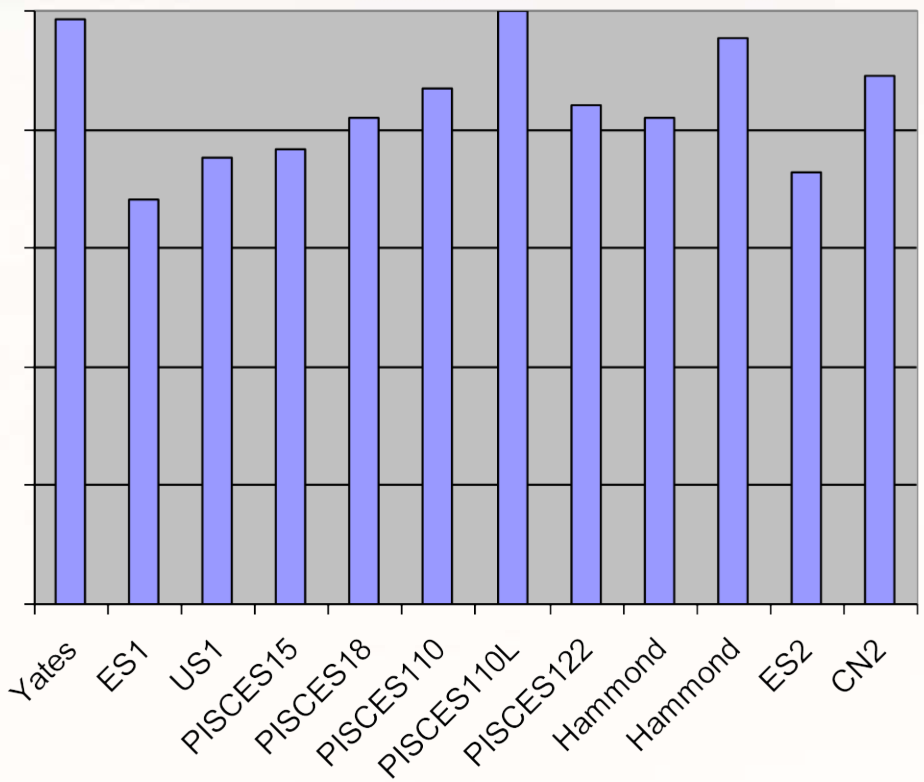
	----- Se in flue gas, lb/TBtu --------				----- Se in flue gas, ug/dscm--------		
		Se in coal, ug/g dry				*Se in coal, ug/g dry*	
Se Removal in ESP	*0.5*	*2*	*4*	Se Removal in ESP	*0.5*	*2*	*4*
10%	33.6	134.4	268.7	10%	42.9	171.8	343.5
25%	28.0	112.0	223.9	25%	35.8	143.1	286.3
50%	18.7	74.7	149.3	50%	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						

CLS 3/2/2010

Vaporization of Se in Coal-Fired Boilers

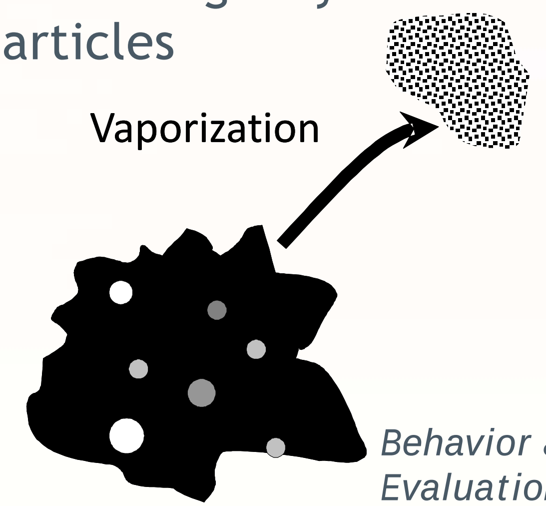
- Data from full-scale campaigns used to calculate vaporization in the combustion zone
- Se vaporization: 70%-100%

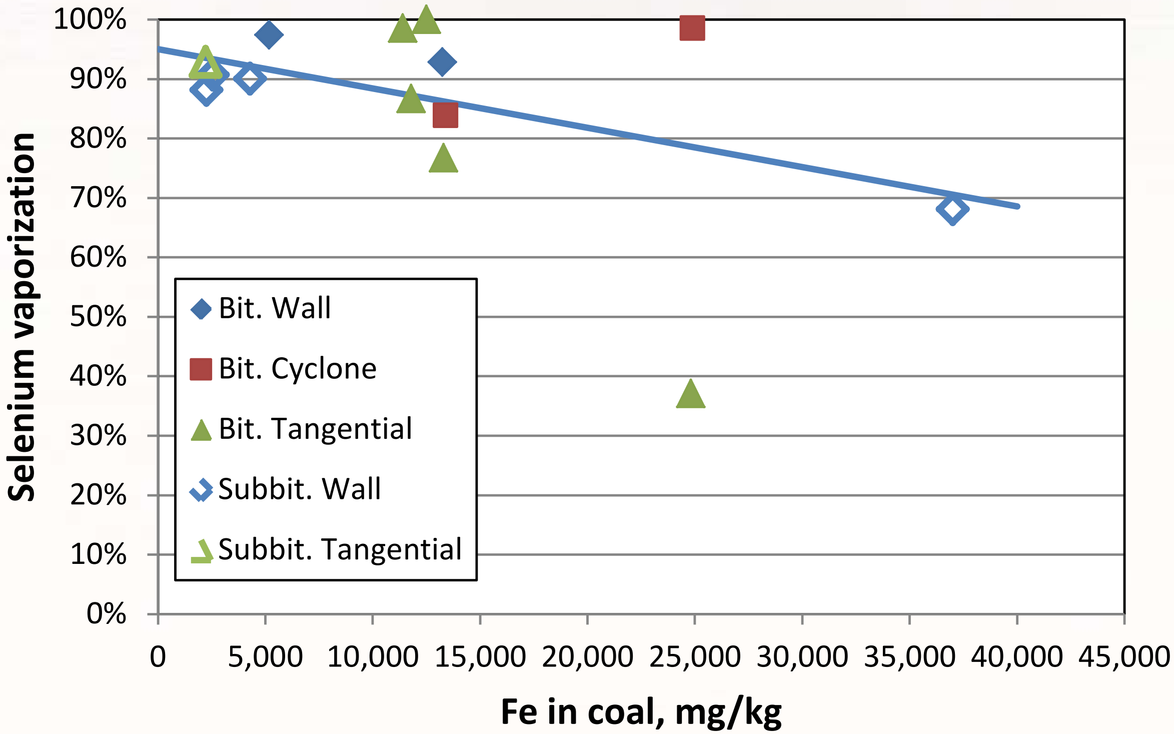




Vaporization of Se in Flame

- Vaporization calculated from bottom ash concentration and coal concentration of Se
- Correlation between vaporization and Fe content of coal may reflect association of Se and Fe in glassy ash particles

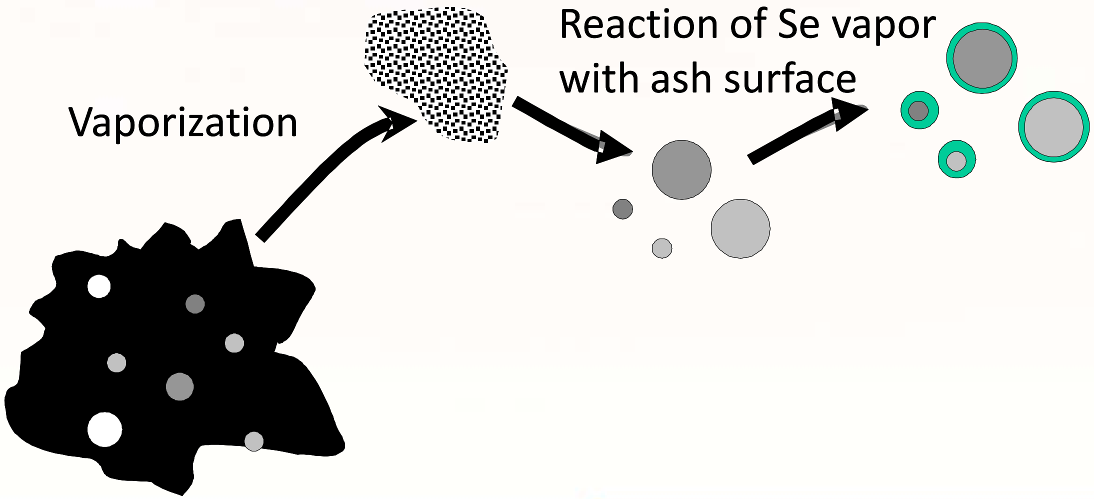




Behavior and Potential Control Strategies for Selenium in Coal-Fired Boilers: Evaluation and Modeling of Full-Scale Data. EPRI, Palo Alto, CA:2010. 1021217

Behavior of Se in Coal-Fired Boilers

- Post-combustion reactions:
  - Iron reacts with selenium at temperatures above 1200ºC/2200ºF (possibly reaction with Fe-Si-Al glasses at sufficiently low viscosity of the ash)
  - Calcium reacts with selenium at temperatures less than 800ºC/1470ºF
  - SO_2 reacts with calcium and iron, but more strongly with calcium



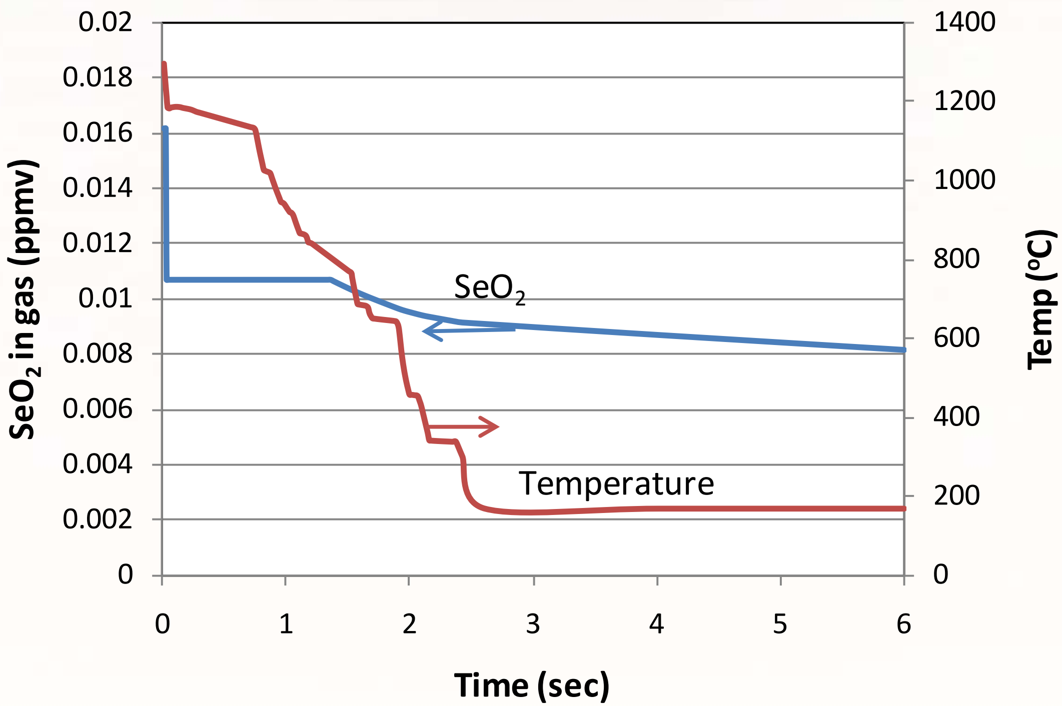
Prediction* of Se Capture by Fly Ash

- Using typical power plant time-temperature history, predict uptake of Se by fly ash from furnace exit to ESP inlet

*Senior, C.; Van Otten, B.; Wendt, J.O.L.; Sarofim, A. Modeling the behavior of selenium in Pulverized-Coal Combustion Systems. *Combust. Flame* **2010**, *157*, 2095-2105.

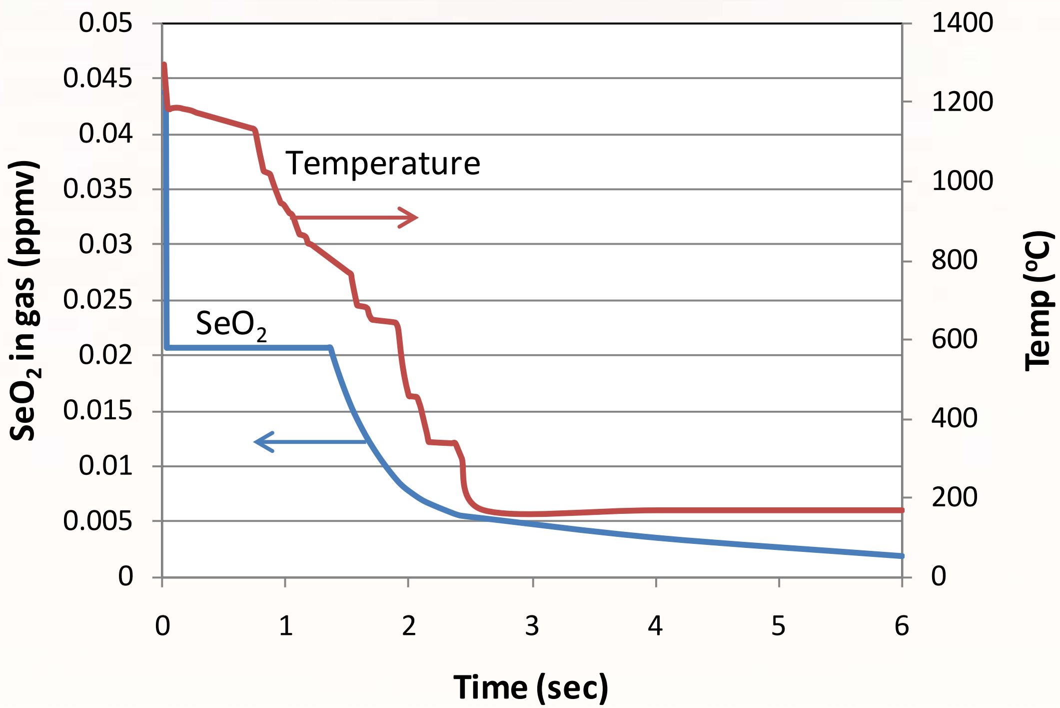
Prediction of Se Capture by Fly Ash

- Using typical power plant time-temperature history, predict uptake of Se by fly ash from furnace exit to ESP inlet
- *Pittsburgh coal*
- High-temperature capture by Fe in ash
- Little capture by Ca in ash
  - Interference from SO_2
- Most Se still in gas at ESP inlet



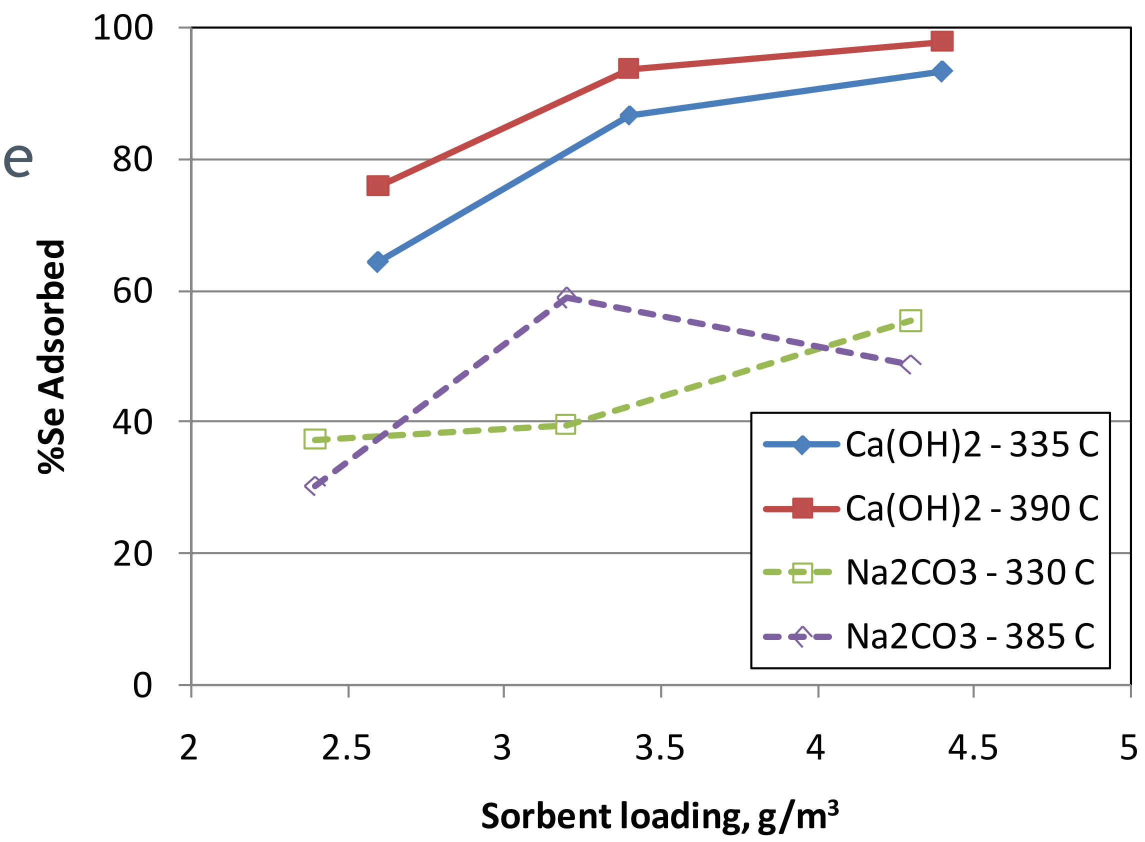
Prediction of Se Capture by Fly Ash

- Using typical power plant time-temperature history, predict uptake of Se by fly ash from furnace exit to ESP inlet
- *Wyodak PRB coal*
- High-temperature capture by Fe in ash
- Remaining Se captured by Ca in ash
- Very high removal of Se by fly ash



Selenium Reacts with Sodium, Too

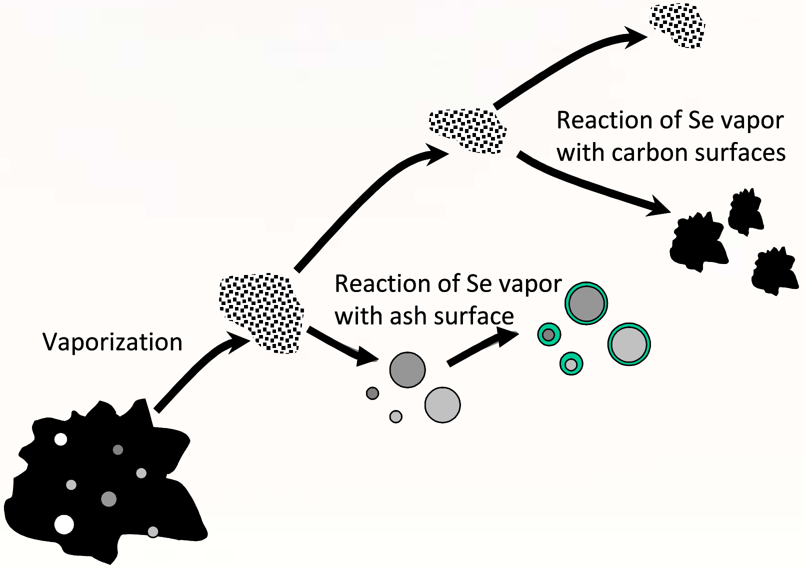
- When sodium or calcium sorbents are injected into coal flue gas, they can react with Se
- Selenium adsorption as a function of sorbent loading for injection of calcium hydroxide or sodium carbonate in the exhaust of glass furnaces



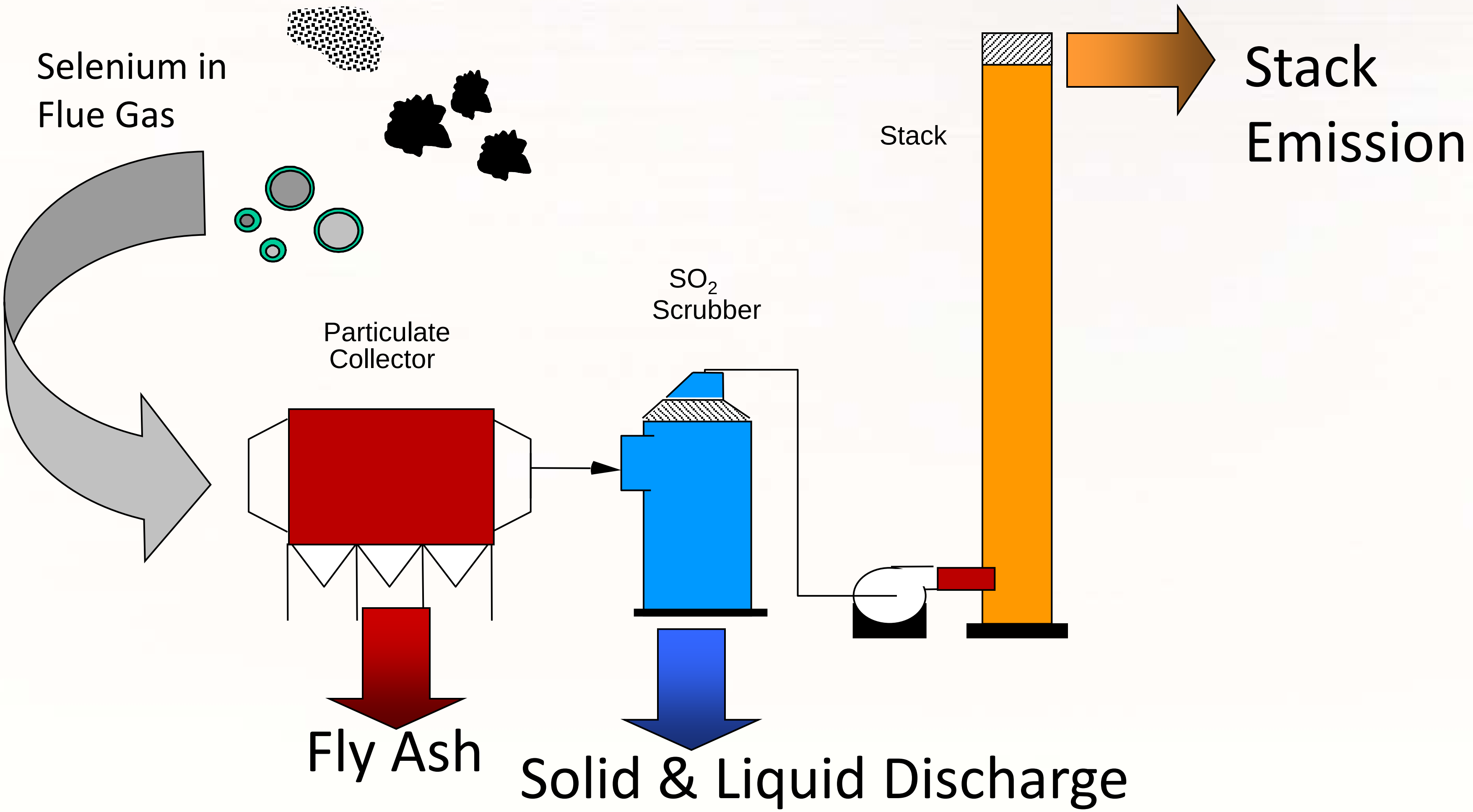
Kircher, U. "Waste Gas Treatment of Soda Lime Silica Glass Furnaces – Investigations with Different Absorption Agents." Ceramic Trans. ***1998****, 82, 75-80.*

Behavior of Se in Coal-Fired Boilers

- 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
- Possible low-temperature reactions, such as
  - Se-halogen reactions
  - Se-carbon reactions
  - Formation of H_2SeO_3

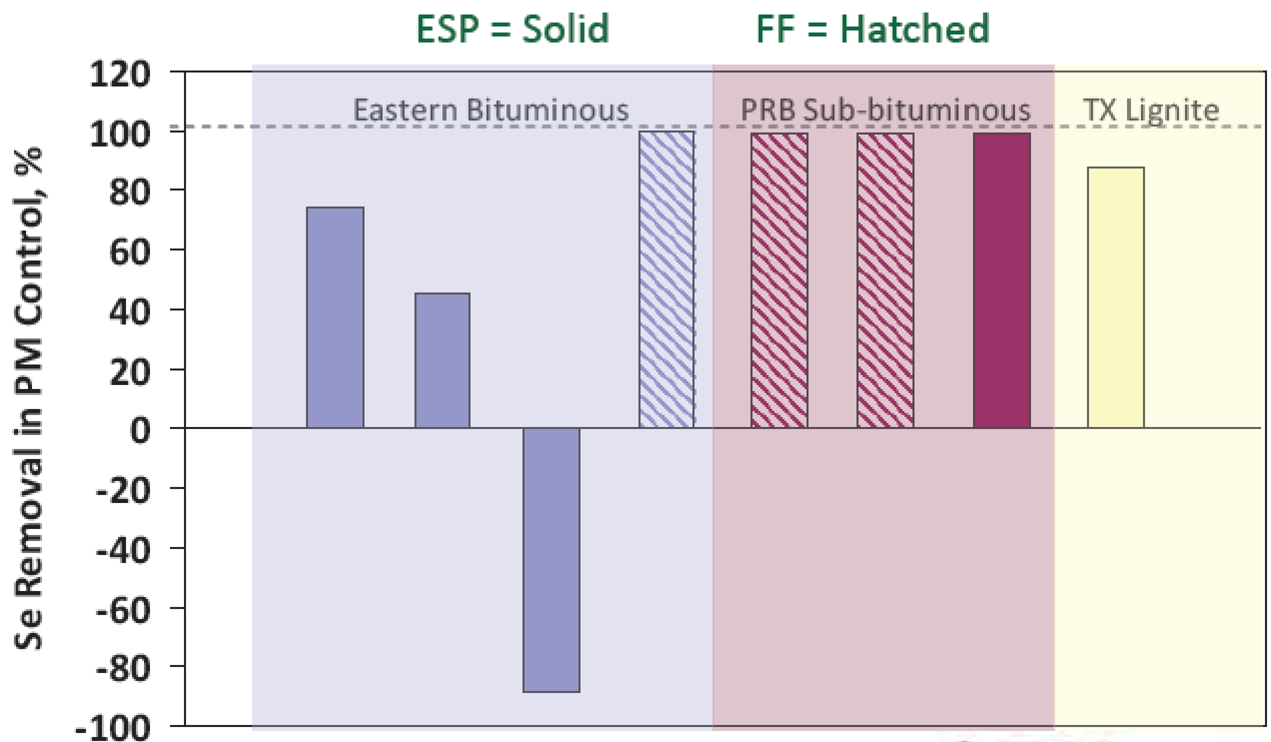


Fate of Selenium in APCDs



Fate of Se in PM Control Devices: Pilot Data

- Pilot-testing at EPA's multi-pollutant research facility:
  - 4 MMBtu/hr (1,000 cfm flue gas flow)
  - Capable of firing all ranks of coal
  - Representative time-temperature history
  - ESP or FF can be used



Source: Hutson, US EPA, 2010

Fate of Se in PM Control Devices: Pilot Data

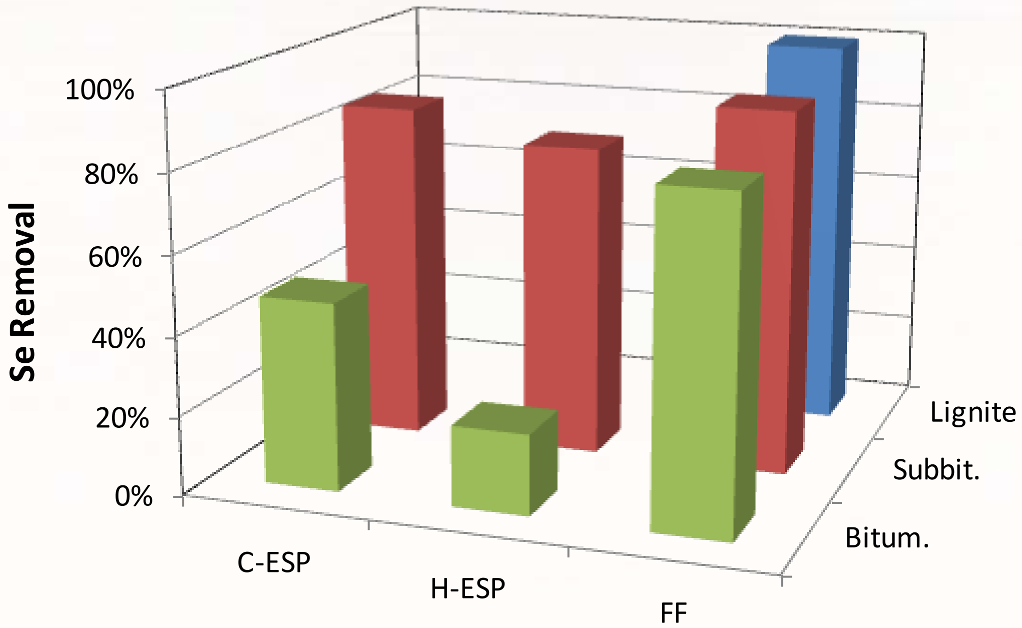
- Observations in-line with SeO_2-ash interaction model:
  - Se removal by fly ash lower in bituminous case than low rank case (ESP tests)
- Additional capture occurs across FF with bituminous

Source: Hutson, US EPA, 2010

EPA United States Environmental Protection Agency

Fate of Se in PM Control Devices: Utility ICR Data

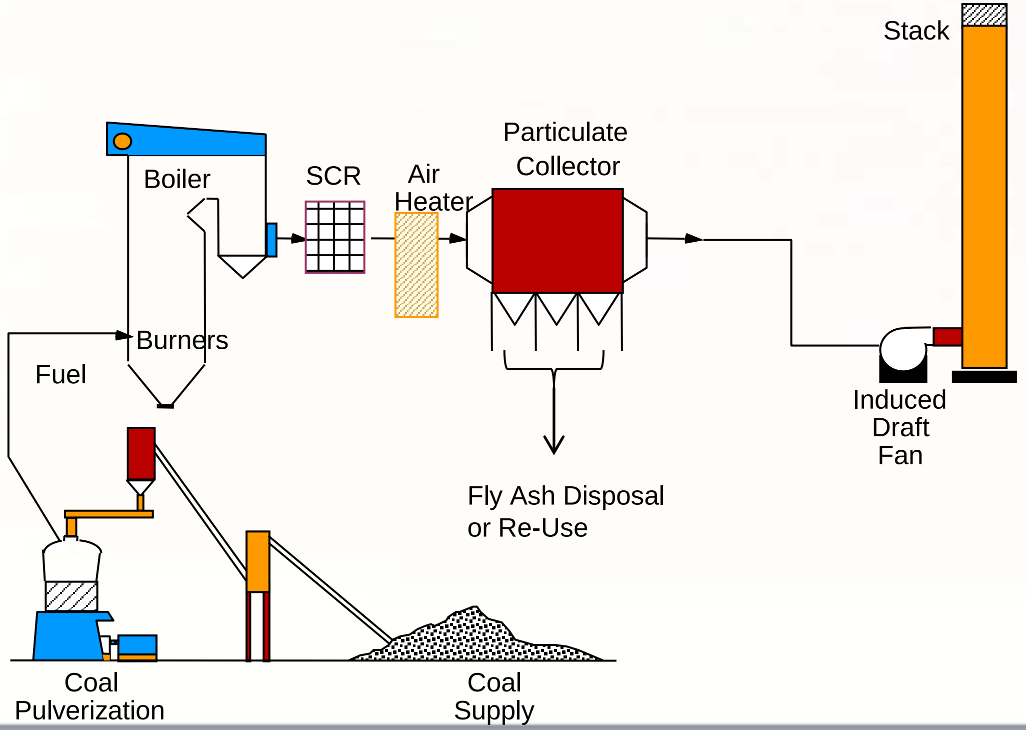
- Average Se removal
- Plants with ***only particulate control devices***
- Se removal across C-ESPs, 40% to >90%
  - Higher removal for low-rank coals
- FFs show higher removal, all ranks



Fate of Selenium in APCDs

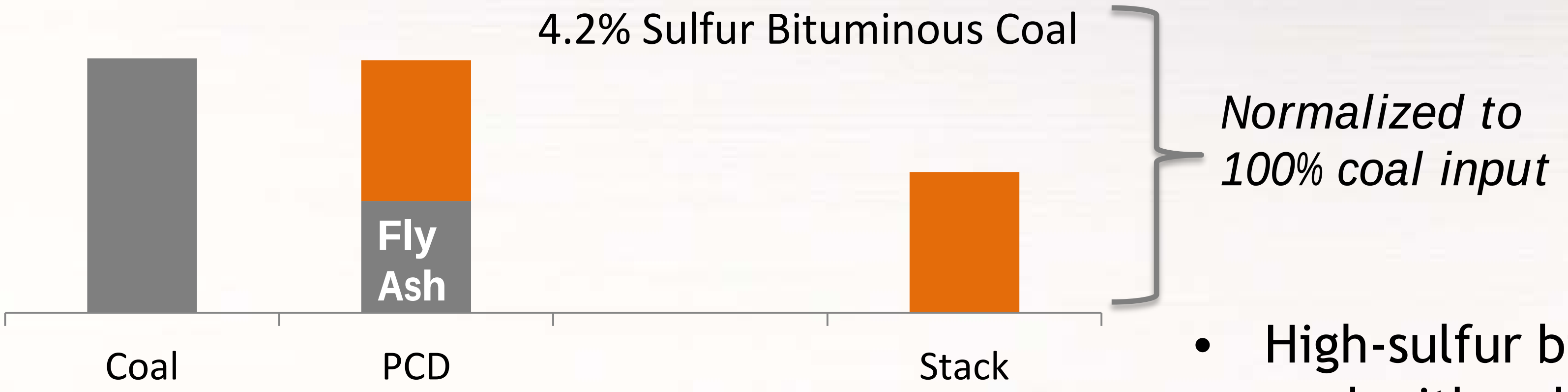
1.5% Sulfur Bituminous Coal

Normalized to 100% coal input

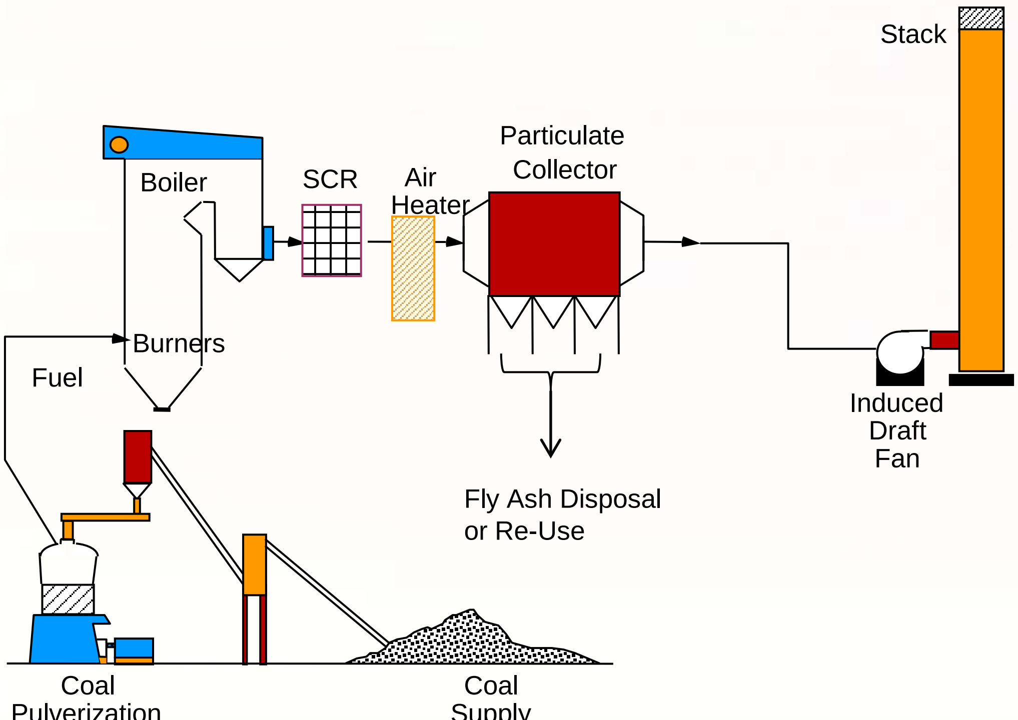


- Low-sulfur bituminous coal with only cold-side ESP
- Most Se removed in fly ash
- 24% of Se in coal emitted to the stack
- *Example based on measured field data*

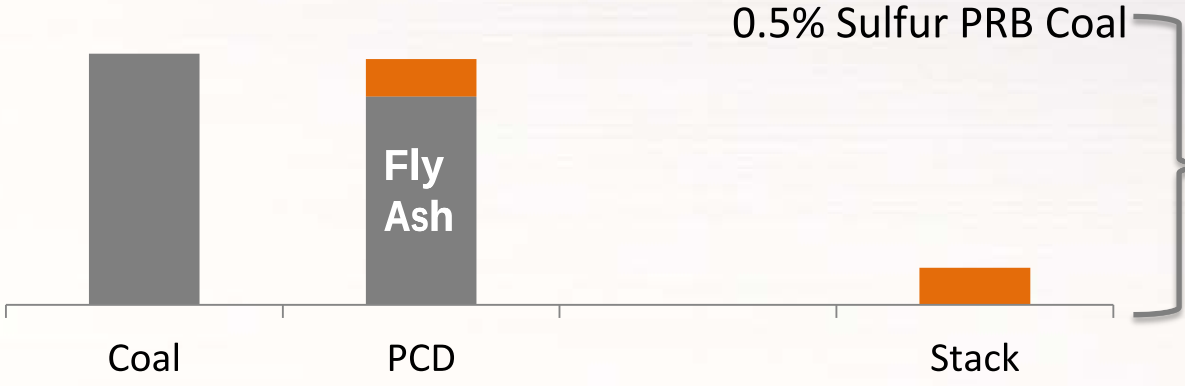
Fate of Selenium in APCDs



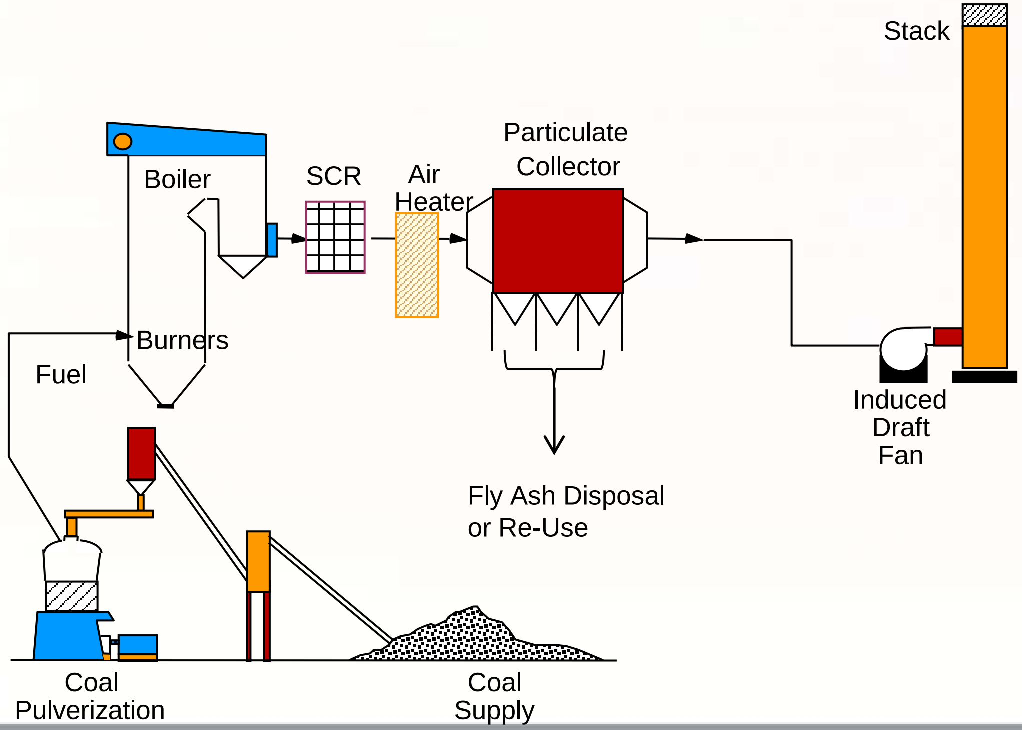
- High-sulfur bituminous coal with only cold-side ESP
- Fly ash does not remove most Se
- 55% of Se in coal emitted to the stack
- *Example based on measured data*



Fate of Selenium in APCDs



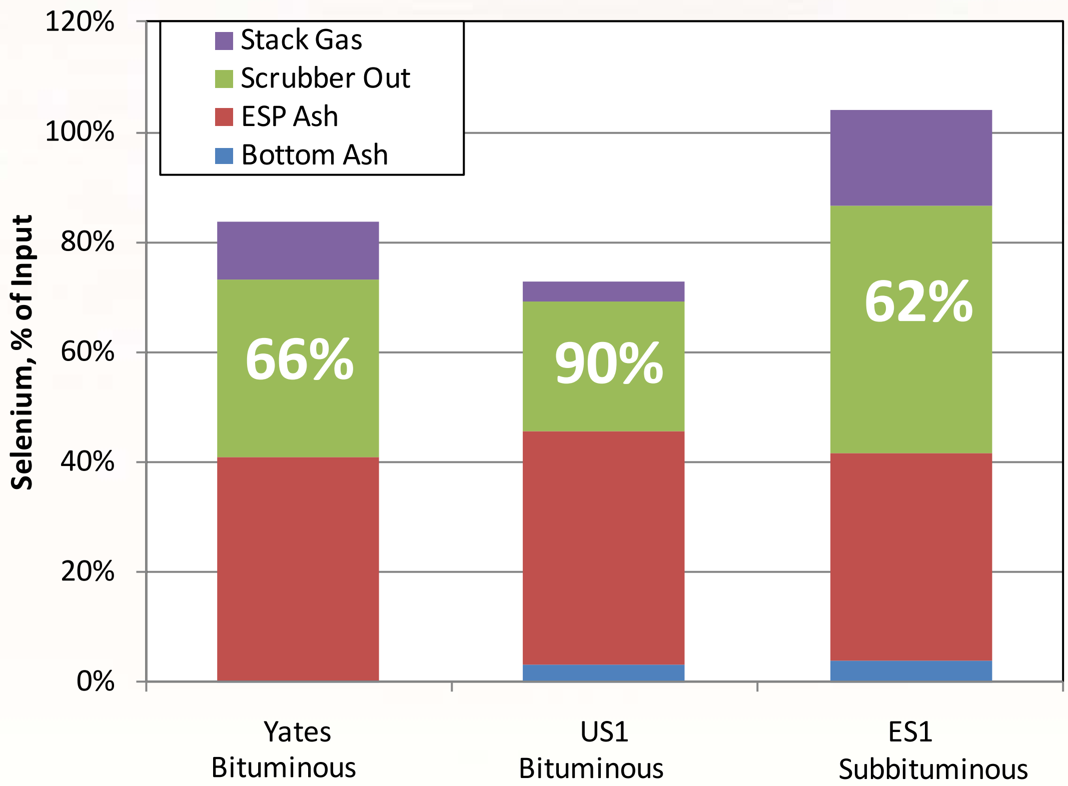
Normalized to 100% coal input



- Low-sulfur PRB subbituminous coal with only cold-side ESP
- Fly ash removes 83% Se
- 15% of Se in coal emitted to the stack
- *Example based on measured data*

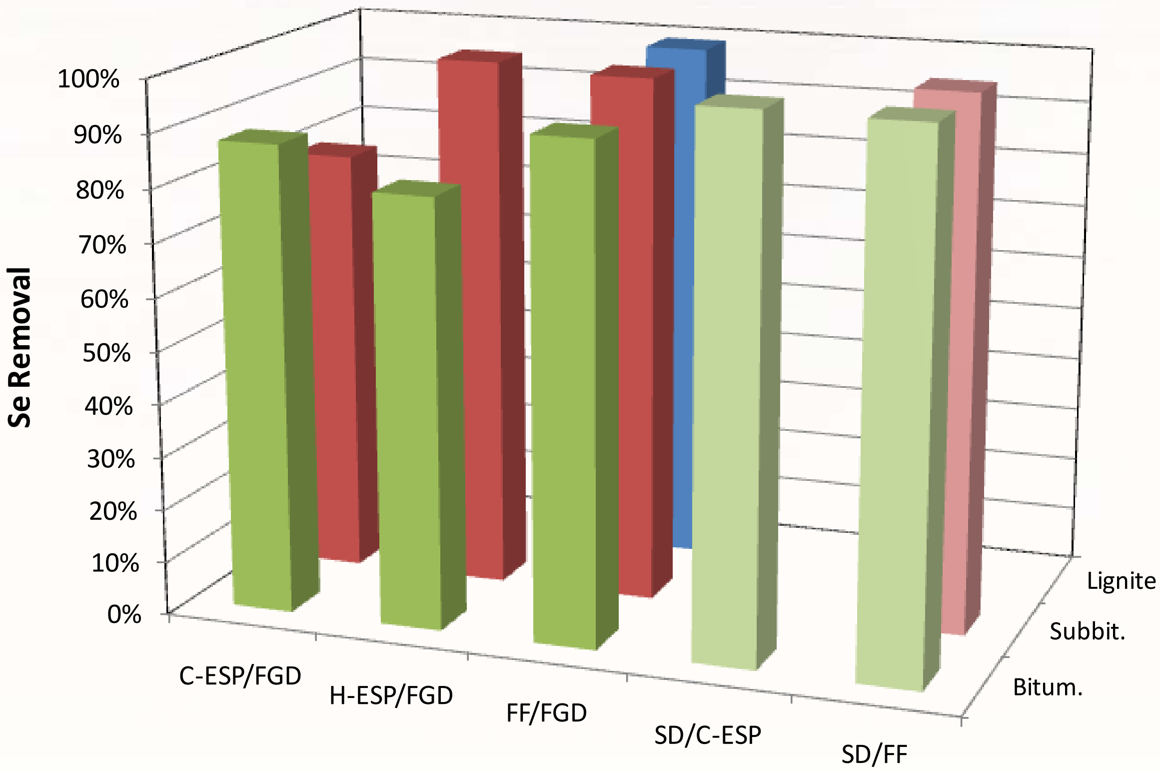
Fate of Se in Scrubbers: Literature Data

- How effective are wet scrubbers in removing gas-phase SeO_2?
- Limited data suggest removal of SeO_2 < SO_2
- Why?
  - SeO_2 solubility similar to SO_2



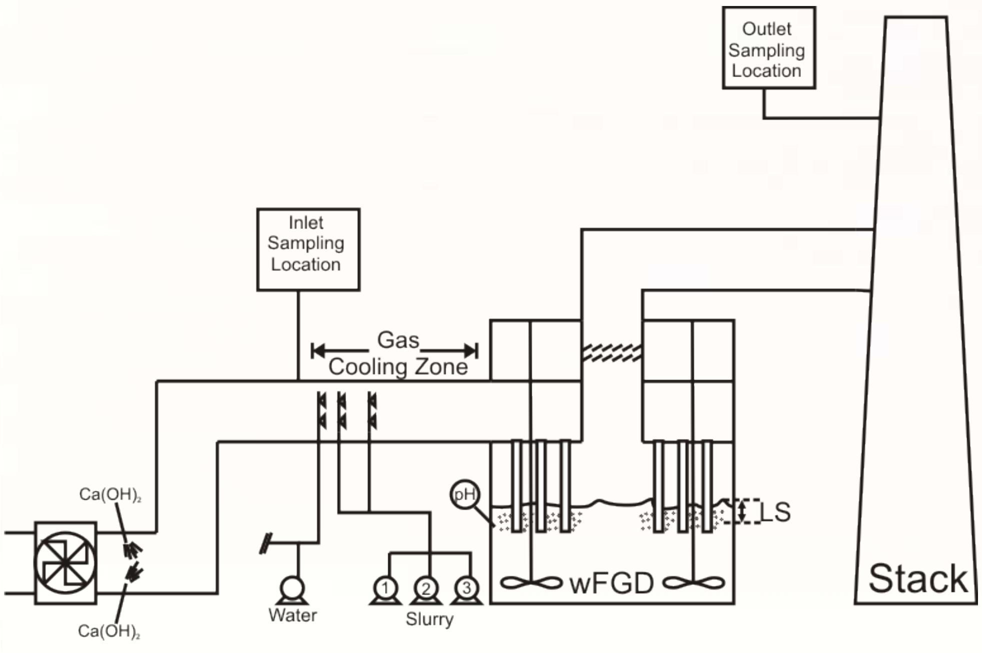
Fate of Se in Scrubbers: Utility ICR Data

- 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)



Fate of Se in Scrubber: 900 MW Plant

- Samples taken at inlet and outlet of scrubber: gaseous Se and size-segregated fly ash
- Hydrated lime injection between ESP and FGD for SO_3 control



- 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

Source: Tyree & Senior, EUEC 2011

Total Removal of Se Across FGD

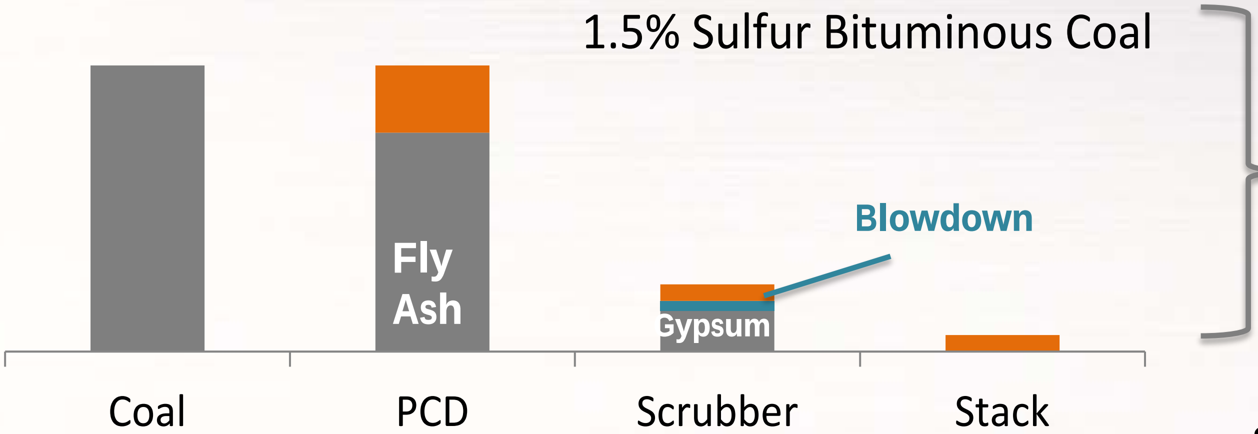
- Total removal ~70% when hydrated lime injected and ~60% without lime injection
- Se removal across FGD consistent with literature data and less than SO_2 removal

Date	Solid	Gas	Total
11/3/09 AM	80%	35%	70%
11/3/09 PM	86%	49%	73%
11/4/09 AM	39%	22%	26%
11/4/09 PM	84%	45%	71%
11/5/09 AM	67%	65%	66%
11/5/09 PM	55%	57%	57%

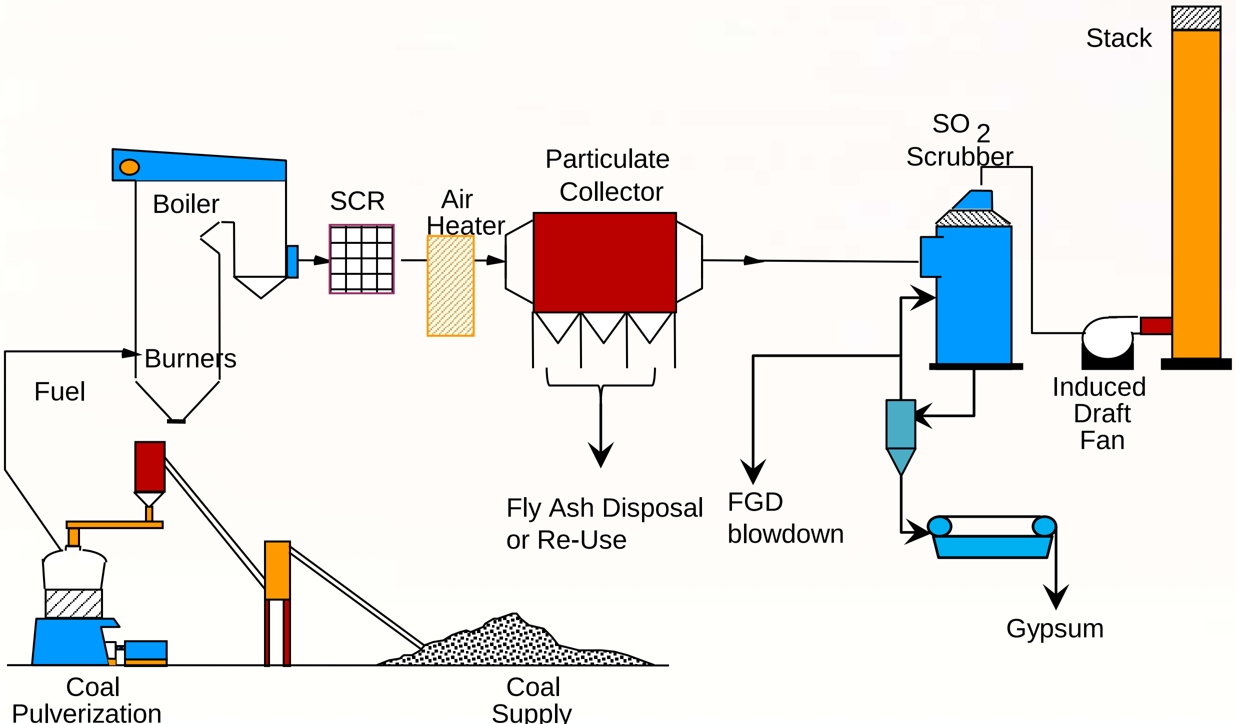
Conclusions from 900 MW Study

- Hydrated lime, injected between ESP and FGD, captured a significant amount of gas-phase Se before the scrubber
- Total removal of Se (gas plus particle-bound) 61% average
  - In line with observations at other boilers
- Gas-to-particle conversion of Se across FGD could limit removal of Se across FGD

Fate of Selenium in APCDs

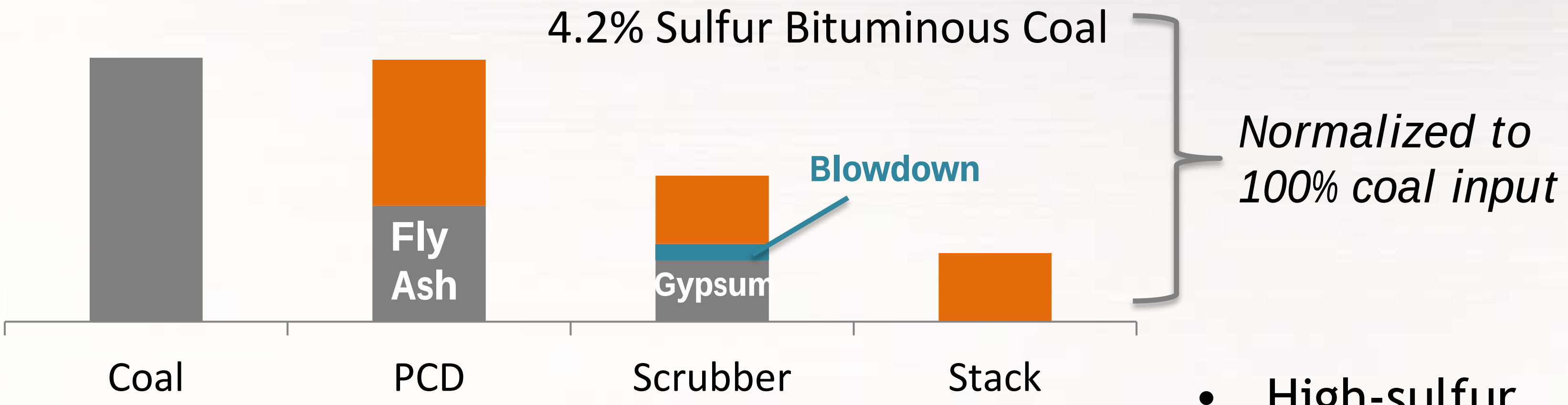


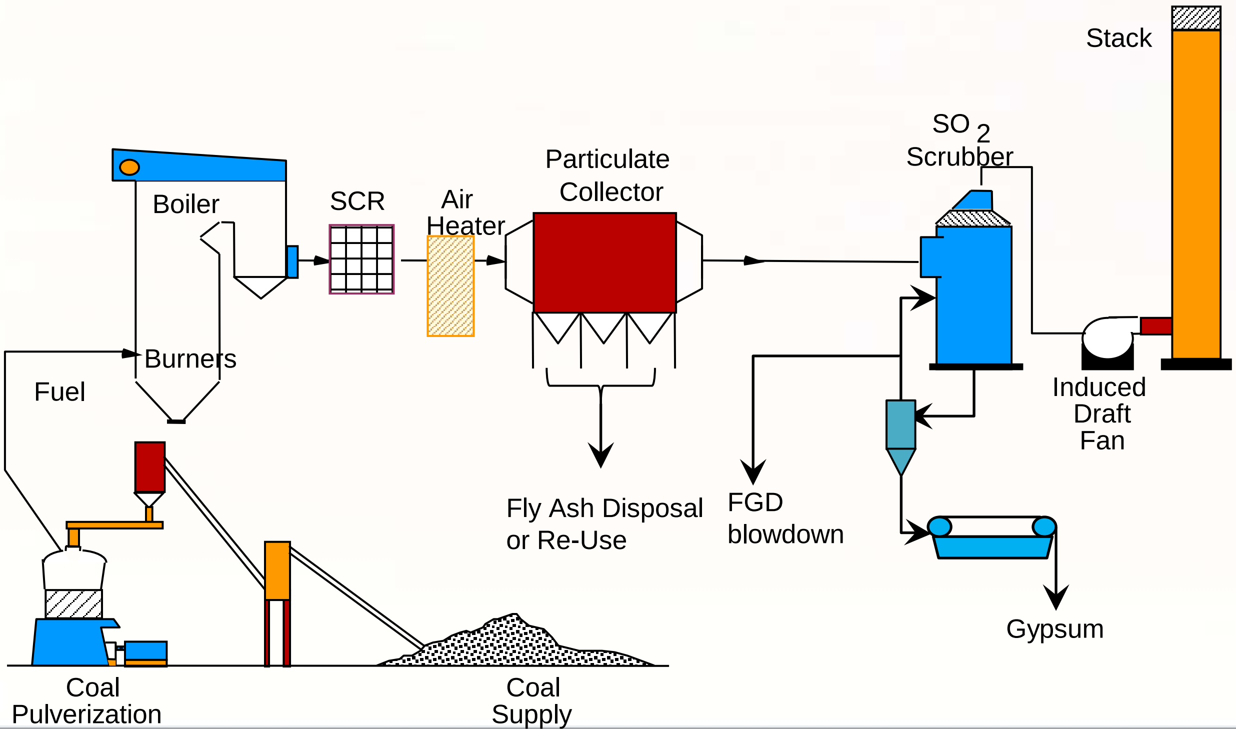
Normalized to 100% coal input



- Low-sulfur bituminous coal with cold-side ESP & wet FGD
- In FGD, most of Se removed with gypsum
- *Example based on measured data*

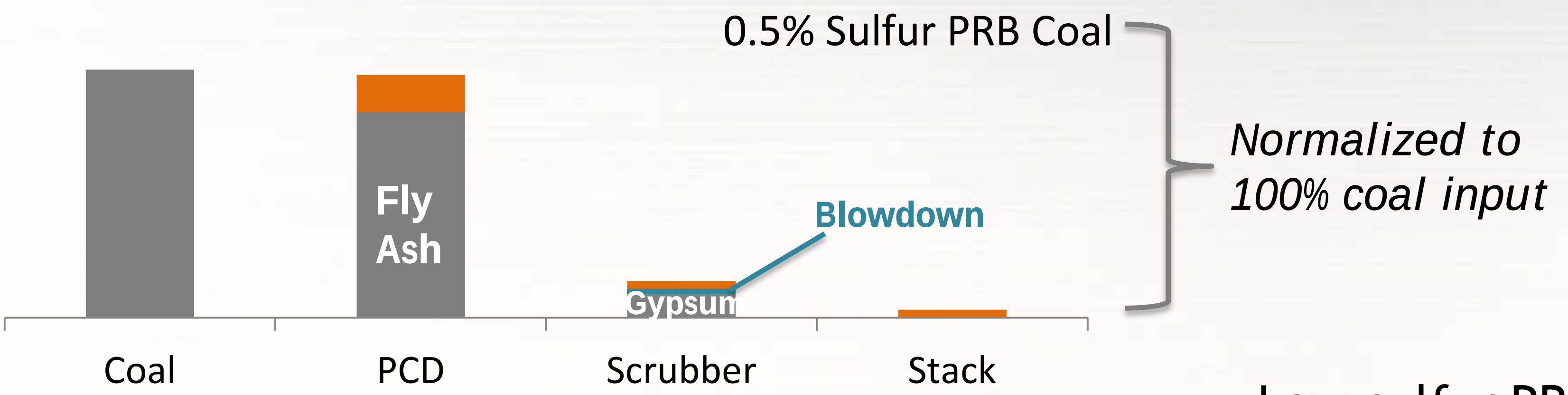
Fate of Selenium in APCDs

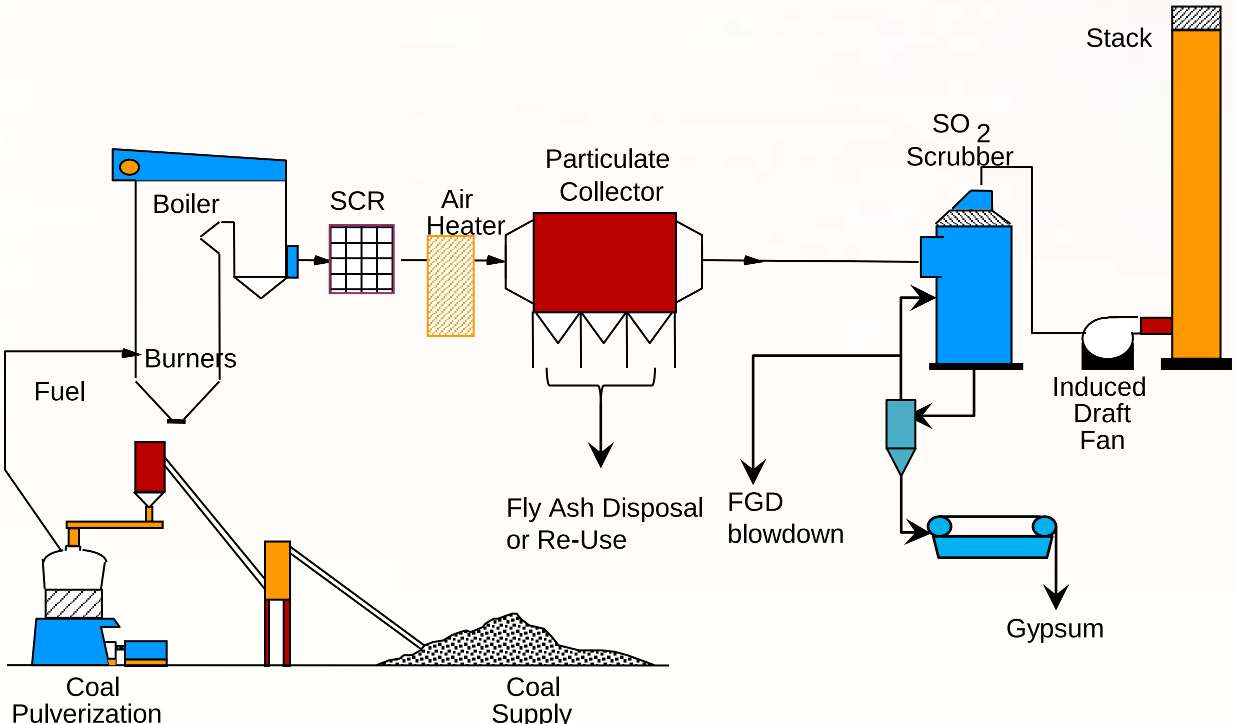




- High-sulfur bituminous coal with cold-side ESP & wet FGD
- About half of Se removed in scrubber (mostly to gypsum)
- *Example based on measured data*

Fate of Selenium in APCDs





- Low-sulfur PRB subbituminous coal
- Little gas-phase Se enters FGD, and most removed with gypsum
- *Example based on measured data*

Advancing Cleaner Energy

Se in APCDs: 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

Se in APCDs: 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 wet FGDs less than removal of SO_2 (60%-90%)
- Selenium in scrubbers can report to gypsum (LSFO) or purge stream
- Selenium removed across wet FGDs could become an issue in wastewater discharge

Fate of Selenium in Effluents & Byproducts

Solubility of Se in Fly Ash

- 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

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
$Na_2SeO_3 = 2Na^+ + SeO_3^{2-}$	3.51
$CaSeO_3 = Ca^{2+} + SeO_3^{2-}$	7.65
$CaSeO_4 = Ca^{2+} + SeO_4^{2-}$	4.77
$FeSeO_3 = Fe^{2+} + SeO_3^{2-}$	9.99
$FeSeO_4 = Fe^{2+} + SeO_4^{2-}$	6.52
$Fe_2(SeO_4)_3 = 2Fe^{3+} + 3SeO_4^{2-}$	23.19

Leaching from Fly 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 Fly Ash-Trona Mixtures: Bituminous Ash

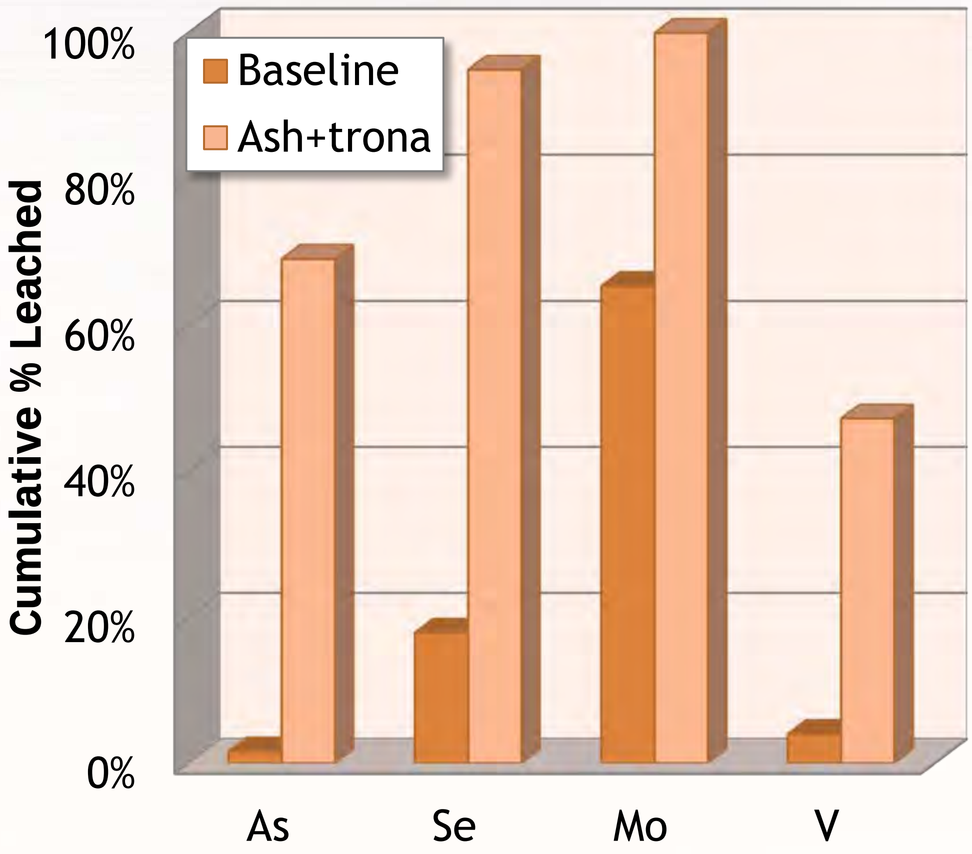
- Set of paired fly ash samples collected from H-ESP at a full-scale power plant that burned bituminous coal: control ash collected before trona injection and a trona ash collected during trona injection test
- Batch leaching experiments conducted using DI water under unadjusted pH conditions at L/S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

Chemistry of Se in Scrubbers

- SeO_2(g) removed from gas as selenite in the ionic form, can be oxidized to the selenate form (Se(VI)), and/or can form other species
- Absorbed selenium can report to the solid phase by mechanisms such as adsorption or co-precipitation with iron hydroxide fines
- Selenite (Se(IV)) predominant form of aqueous-phase selenium in low-sulfite-oxidation FGD systems
- Selenium is more difficult to oxidize to the +6 state than sulfur, and correspondingly a mixture of selenite and selenate is often found in forced oxidation systems
- Se(IV) difficult to precipitate and ends up in blowdown stream

Se Fate in Wet FGD: 2010 EPRI Study

- Eight boilers had wet FGDs on line during testing

Plant	Unit	Unit Type	MWe	Fuel	PM Control	NOx Control	SO_2 Control	SO_3 Ctrl
Plant A	Unit 1[1]	PC, front wall	48	bit.	C-ESP	--	--	--
Plant A	Unit 2[1]	PC, front wall	48	bit.	C-ESP	--	--	--
Plant B	Unit 1	PC, front wall	208	bit.	C-ESP	SCR	Wet FGD (Spray and Tray)	--
Plant B	Unit 2	PC, front wall	203	bit.	C-ESP	SCR	Wet FGD (Spray and Tray)	--
Boiler C	Unit 4	PC, wall	175	bit.	FF (pulse)	SCR	Wet FGD (Spray and Tray)	Wet ESP
Plant D	Unit 1[2]	Cyclone	151	bit., petcoke	C-ESP	SCR	Wet FGD (Spray type)	--
Plant D	Unit 2[2]	PC, tangential	261	bit., petcoke	C-ESP	SNCR	Wet FGD (Spray type)	--
Boiler E	Unit 4	PC, opposed wall	708	subbit.	C-ESP	SCR	Wet FGD (Spray type)[3]	--
Boiler F	Unit 1	PC, tangential	566	subbit.	FF (reverse gas)	--	Wet FGD (Spray type)	--
Plant G	Unit 1	PC, opposed wall	449	subbit.	FF (pulse)	--	Wet FGD (Spray type)	--
Plant G	Unit 2	PC, opposed wall	440	subbit.	FF (pulse)	--	Wet FGD (Spray type)	--

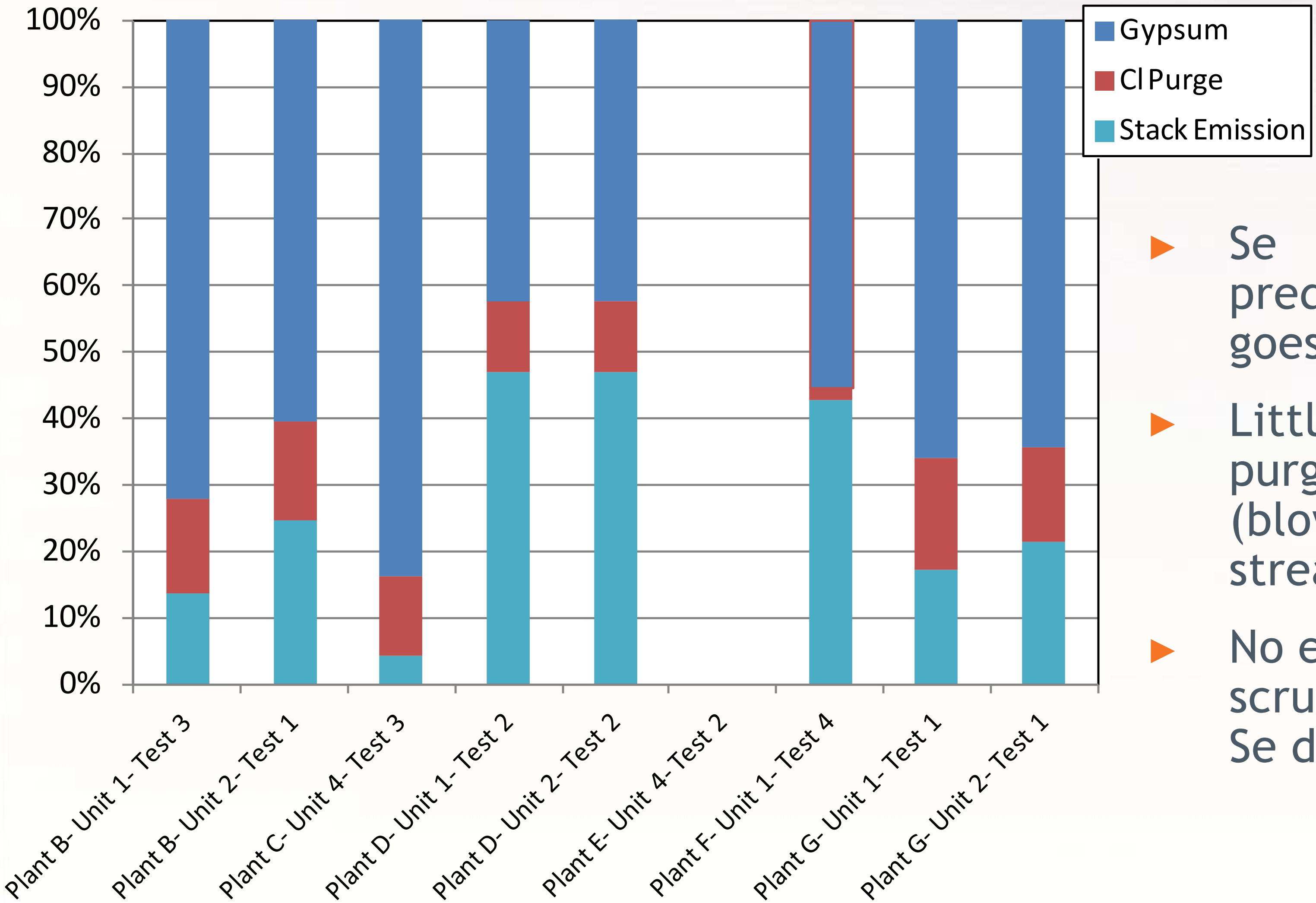
[1]Unit 1 and 2 had combined stack

[2]Unit 1 and 2 shared scrubber and stack

[3]Scrubber was off-line during metals testing

Senior, C.; Blythe, G.; Chu, P. Multi-Media Emissions of Selenium from Coal-Fired Electric Utility Boilers. Presented at Air Quality VIII, Arlington, VA, October 23-27, 2011.

Output of Se from Scrubbers: 2010 EPRI Study



Normalized to 100% of output

- Se predominantly goes into gypsum
- Little Se into Cl purge (blowdown) stream
- No effect of scrubber type on Se distribution

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_3 control, etc.)

Effluent Limitations Guidelines for Steam Electric Plants

- Process changes including new air pollution controls have created waste streams that are not adequately treated
- FGD and other wet processes have proliferated, creating major increases in volume discharge.
- Power plants now make up the majority of toxic releases to U.S. surface waters

EPA proposed different options, some of which for the first time set limits on discharge of As, Hg and Se

ELG for Steam Electric Plants: Proposed Options

ELG Regulatory Options by Wastestream

Option/ Wastestream	***1***	***3a***	***2***	***3b***	***3***	***4a***	***4***	***5***
FGD Wastewater	Chemical Precipitation	BPJ Determination	Chemical Precipitation + Bio Treat	Chemical Precip. + Bio Treat for >2000 MW/facility: BPJ for <2000 MW/facility	Chemical Precipitation + Bio Treat	Chemical Precipitation + Bio Treat	Chemical Precipitation + Bio Treat	Chemical Precipitation + Evaporation
Fly Ash Transport Water	Impoundment (equal to BPT)	Dry handling	Impoundment (equal to BPT)	Dry handling	Dry handling	Dry handling	Dry handling	Dry handling
Bottom Ash Transport Water	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Dry handling/closed loop for units >400 MW; Impoundment (equal to BPT) for units<400 MW	Dry handling/closed loop	Dry handling/closed loop
Combustion Residual Leachate	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Impoundment (equal to BPT)	Chemical Precipitation	Chemical Precipitation
FGMC Wastwater (Hg control)	Impoundment (equal to BPT)	Dry handling	Impoundment (equal to BPT)	Dry handling	Dry handling	Dry handling	Dry handling	Dry handling
Gasification Wastewater	Evaporation	Evaporation	Evaporation	Evaporation	Evaporation	Evaporation	Evaporation	Evaporation
Metal Cleaning	Chemical Precipitation	Chemical Precipitation	Chemical Precipitation	Chemical Precipitation	Chemical Precipitation	Chemical Precipitation	Chemical Precipitation	Chemical Precipitation

BAT = Best Available Control Technology Currently Available

BPJ = Best Professional Judgement Determination

BPT = Best Practicable Control Technology Currently Available

EPA Preferred Options

More Stringent

ELG Timeline

- EPA to propose final rule (2014?)
- ELG's apply as soon in the permit cycle after July 1, 2017 as possible (3 years+)
- All facilities to be in compliance by 2022 (8 years)
- Case-by-case special needs considered via permitting process
- Voluntary provisions could extend time to compliance for up to <u>5 years</u>

Summary: 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
  - Leachability of Se from fly ash is an issue

Summary:
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 wet FGDs less than removal of SO_2 (60%-90%)
- Selenium in scrubbers can report to gypsum (LSFO) or purge stream
- Selenium removed across wet FGDs could become an issue in wastewater discharge

Questions?

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