REINHOLD ENVIRONMENTAL Ltd.

2016 APC-Wastewater Round Table & Expo Presentation

July 18 & 19, 2016 in Dearborn, MI / Hosted by DTE Energy

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Advanced Emissions Solutions, Inc.
Advancing Cleaner Energy

How Your APC Choices Affect Wastewater Treatment Options

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Reinhold APC Conference ~ July 18, 2016

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Overview

- Complying with the MATS rule takes care of your air emissions, but how does your air pollution control strategy affect your wastewater and ash disposal?

- The substances you remove with your air pollution control devices have to go somewhere…

- We'll take a holistic look at the fates of important elements such as Hg, Se, As and halogens in a coal-fired power plant and explore options for sequestration

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The Intersection of Rules for Power Plants

- Air emissions from coal-fired boilers and industrial sources are regulated under the federal Clean Air Act as well as under state rules
- These are multi-pollutant rules, which can increase the complexity of finding a compliance solution
- In addition, rules for solid byproducts and residues as well as for water discharges must be considered

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The Intersection of Rules for Power Plants:
Federal Mercury and Air Toxics Standards (MATS)

- What's regulated?
- Mercury (Hg), acid gases (HCl) and particulate matter (PM)

- Who's affected?
- All coal-fired boilers generating > 25 MW electricity

- When?
- Almost all compliance by April 16, 2016

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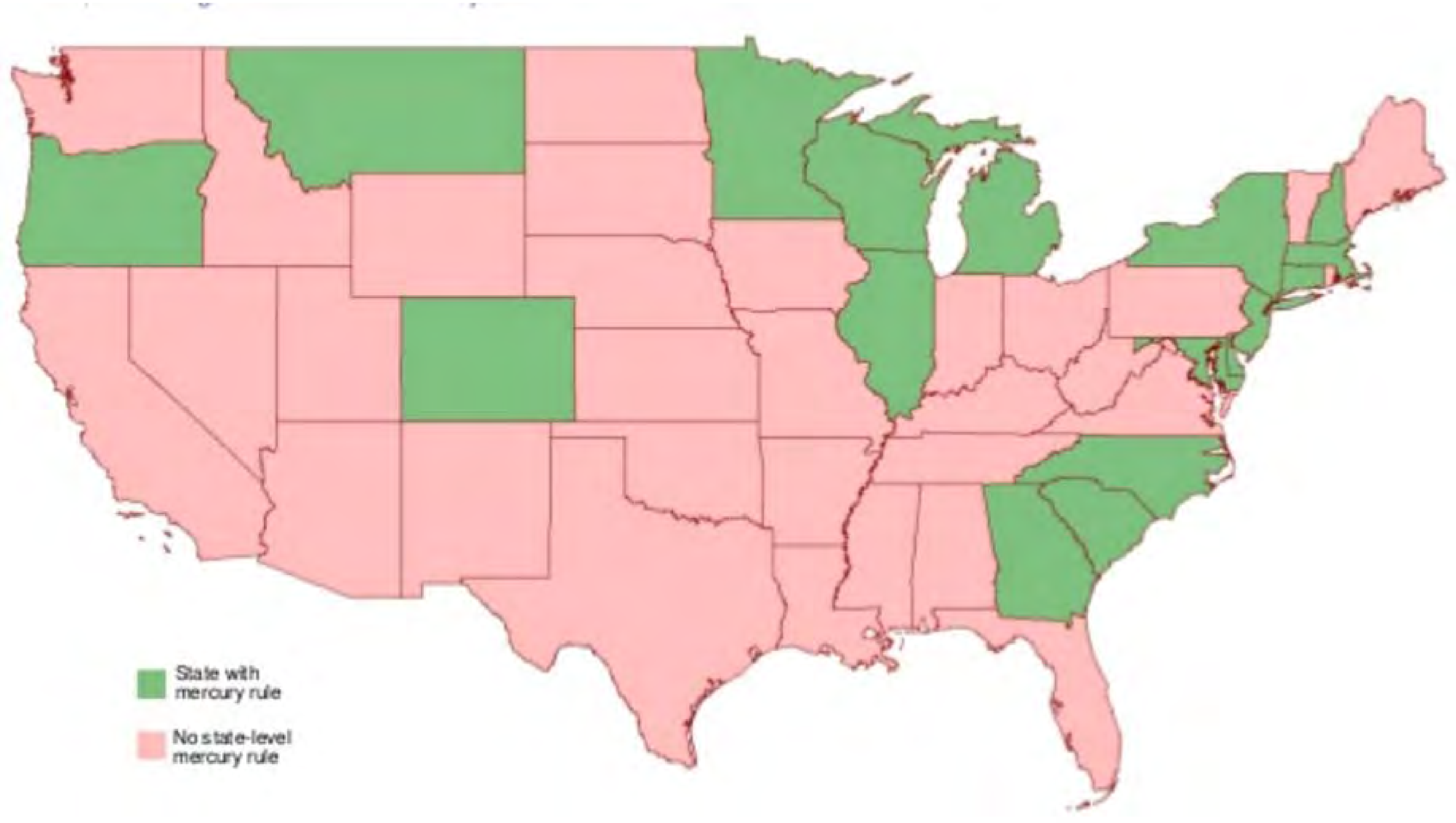
The Intersection of Rules for Power Plants:
State Mercury Rules

- What's regulated?
- Mostly Hg, some rules are multi-pollutant



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The Intersection of Rules for Power Plants:
Cross-State Air Pollution Rule (CSAPR)

- What's regulated?
  - Annual SO_2 emissions
  - Annual or seasonal NOx emissions
- Who's affected?
  - According to EPA, rule affects 3,632 EGUs at 1,074 coal, gas, and oil fired facilities in 27 eastern states and the District of Columbia
- When?
  - In effect January, 2015

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The Intersection of Rules for Power Plants:
National Ambient Air Quality Standards (NAAQS)

- What's regulated?
  - Ambient SO_2
  - …leading to State Implementation Plans (SIPS) to regulate sources
- Who's affected?
  - EPA designated 29 areas in 16 states as Non-attainment Areas per 2010 1-hour SO_2 NAAQS
- When?
  - SIPs in those states by April 4, 2015, showing how they meet the 2010 1-hour SO2 NAAQS by July 15, 2018

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The Intersection of Rules for Power Plants:
Regional Haze Rule

- What's regulated?
  - Visibility in national parks and wilderness areas
  - …leading to controls on NOx, SO_2, PM from sources
- Who's affected?
  - Sources near certain national parks and wilderness areas
- When?
  - States must meet requirements in their Regionals Haze Plan prior to 2018, with equipment typically installed by 2017

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The Intersection of Rules for Power Plants:
Coal Combustion Residual (CCR) Rule

- What's regulated?
  - Disposal of coal combustion residuals (CCR) as a solid waste
- Who's affected?
  - Landfills and surface impoundments at coal-burning electric utility sites that are still producing electricity as of October 19, 2015
- When?
  - Effective October 19, 2015, phased in over a multi-year period

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The Intersection of Rules for Power Plants:
Effluent Limitation Guidelines(ELGs)

- What's regulated?
  - Discharges of pollutants to surface waters: Hg, Se, As, nitrates
- Who's affected?
  - Fossil- steam electric generating units greater than 50 MW that
    - Have wet FGDs and discharge their wastewater
    - Use wet ash transport and discharge ash transport water
- When?
  - "As soon as possible" beginning November 1, 2018 – no later than December 31, 2023

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What Does It All Mean?

- Many plants have new processes for controlling one or more of these air emissions:
  - Hg, HCl, SO_2, SO_3
- Plus all the previous air pollution control!
- New rules are coming for discharge of As, Se, Hg in FGD wastewater
- Taking these pollutants out of the flue gas means putting them somewhere else: fly ash, FGD discharges or byproducts
- Is your plant making the right choices?

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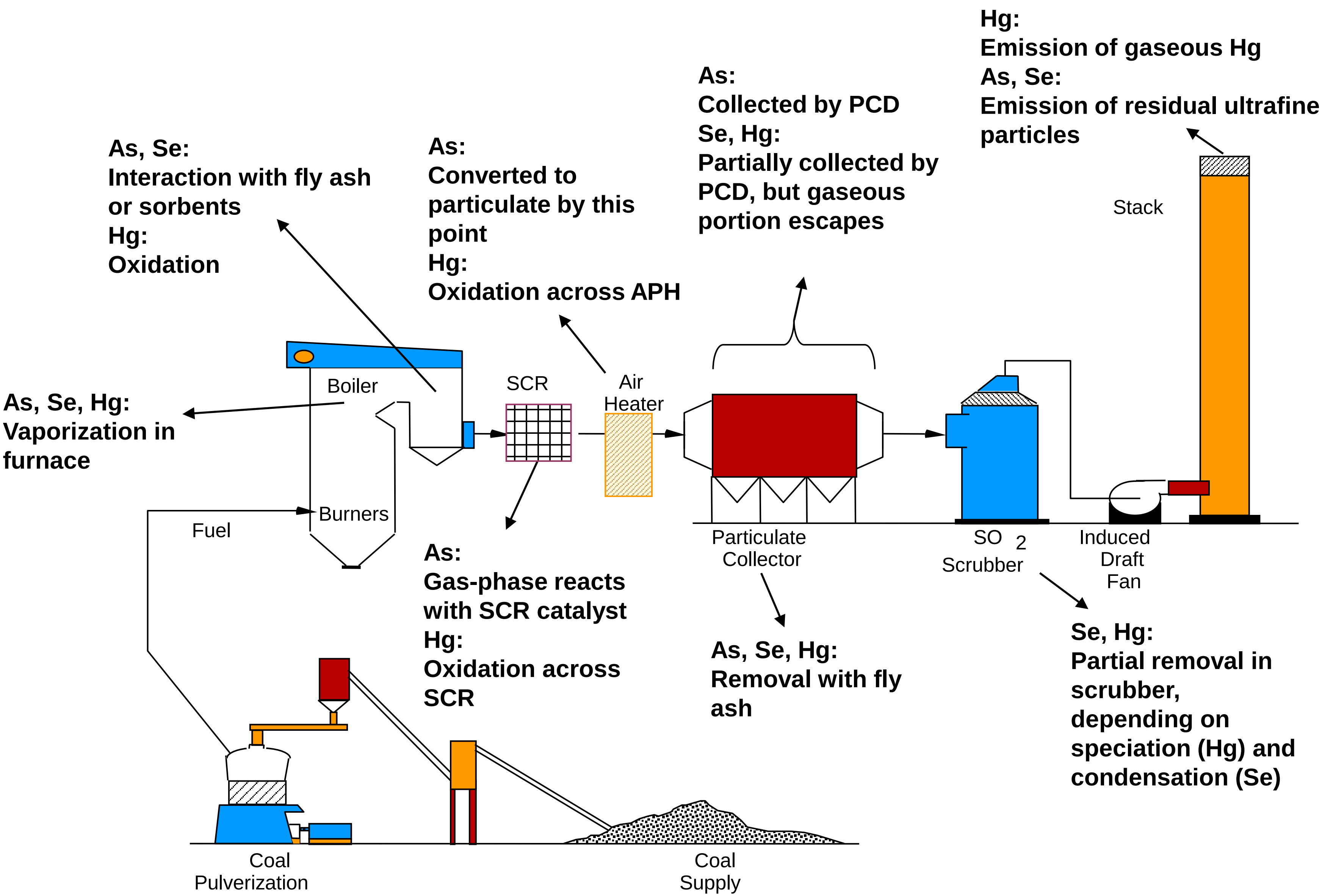
Fate of Selected HAP Metals



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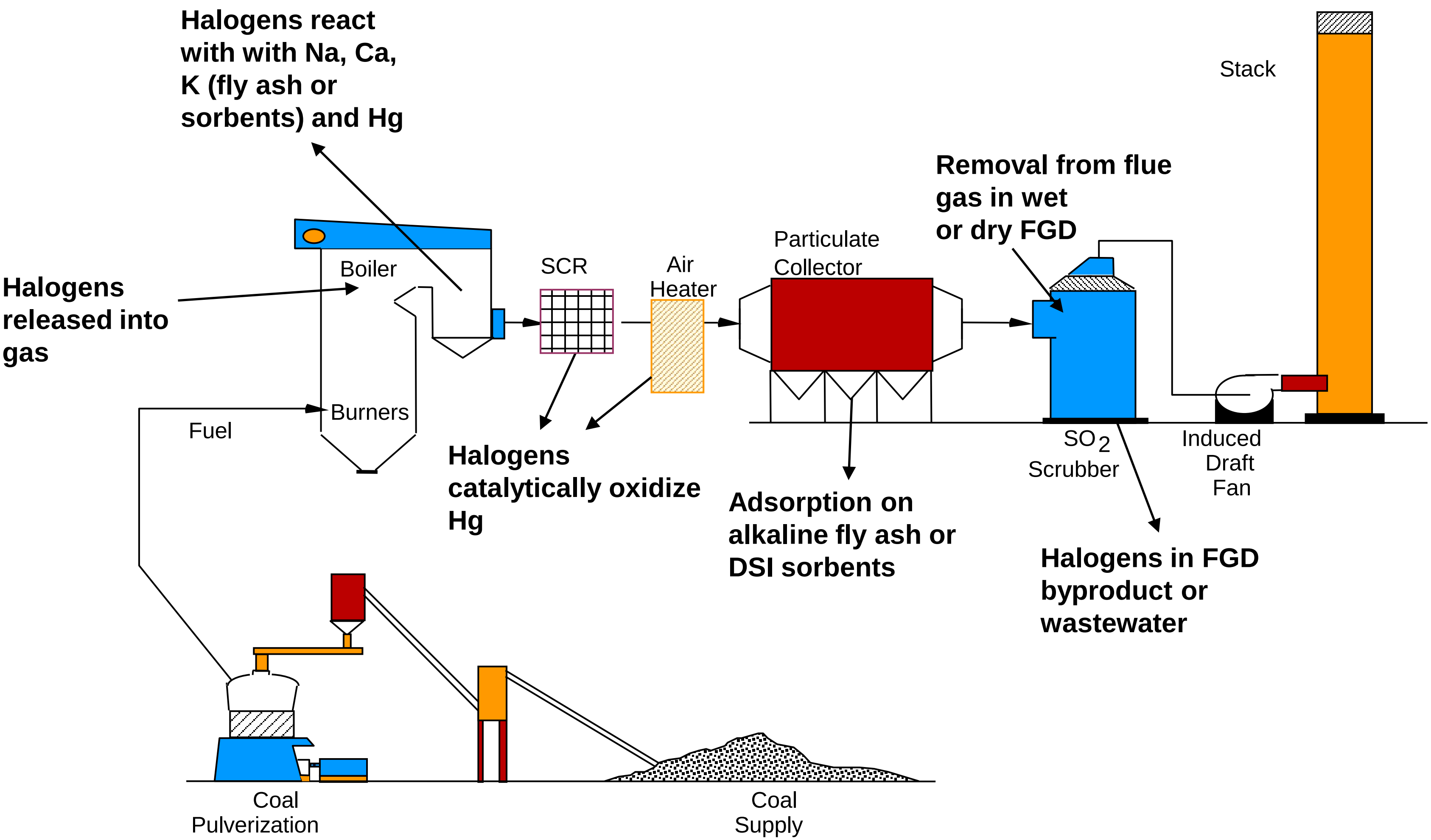
Fate of Halogens



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Compliance with Air Rules Means Choices for Air Pollution Control

Mercury Control

- Three main strategies for Hg air emissions control
  - Activated carbon injection (ACI)
  - Coal halogen injection (CHI)
  - Wet or dry FGDs
- These may be combined (e.g., ACI+CHI, CHI+FGD, ACI+FGD, etc.)
- Hg control can have an impact on halogens and selenium in flue gas, ash, and water

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How Does Hg Control Affect As and Se?

- Arsenic
  - Arsenic condenses at temperatures above typical PAC injection temperatures
  - No known reactions with added halogens
- Selenium
  - 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

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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*

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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*

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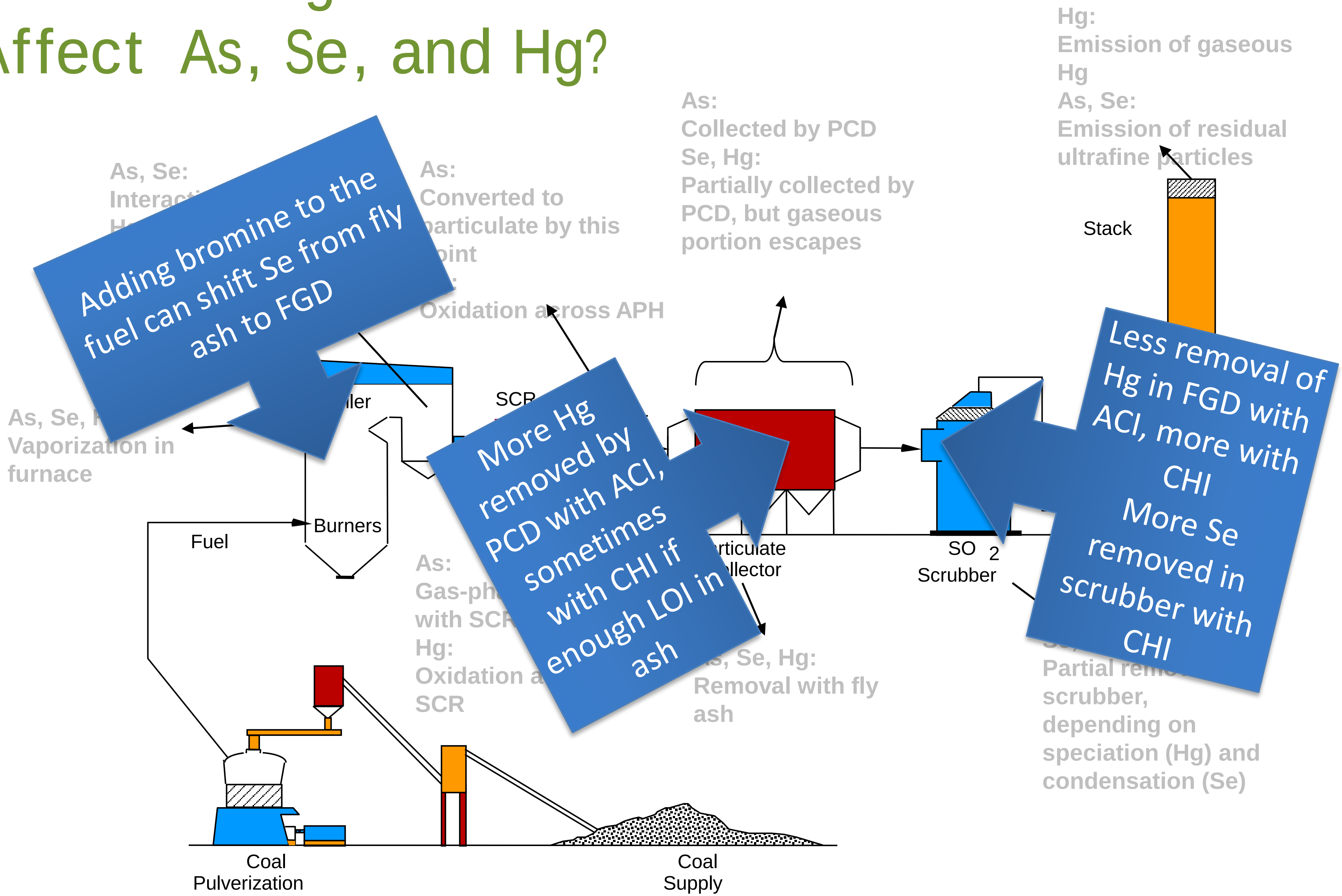
How Does Hg Control Affect As, Se, and Hg?



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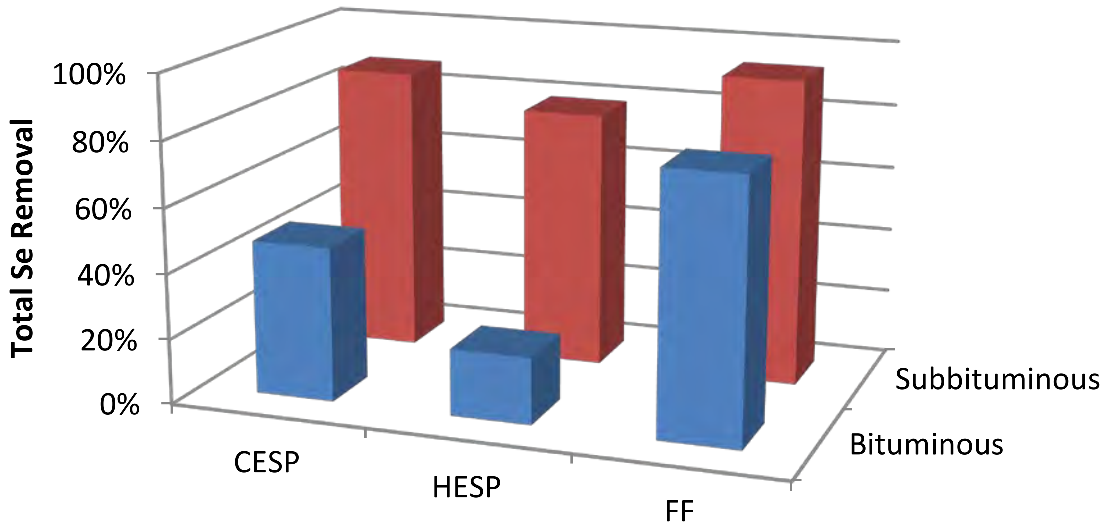
Compliance with Air Rules Means Choices for Air Pollution Control

Particulate Matter Control

- PM control can have an impact on selenium in flue gas, ash, and water
- High Ca in ash and low SO_2 in flue gas (low-rank coals) beneficial for Se capture by fly ash
- FFs capture more Se than ESPs



Source: 2010 ICR

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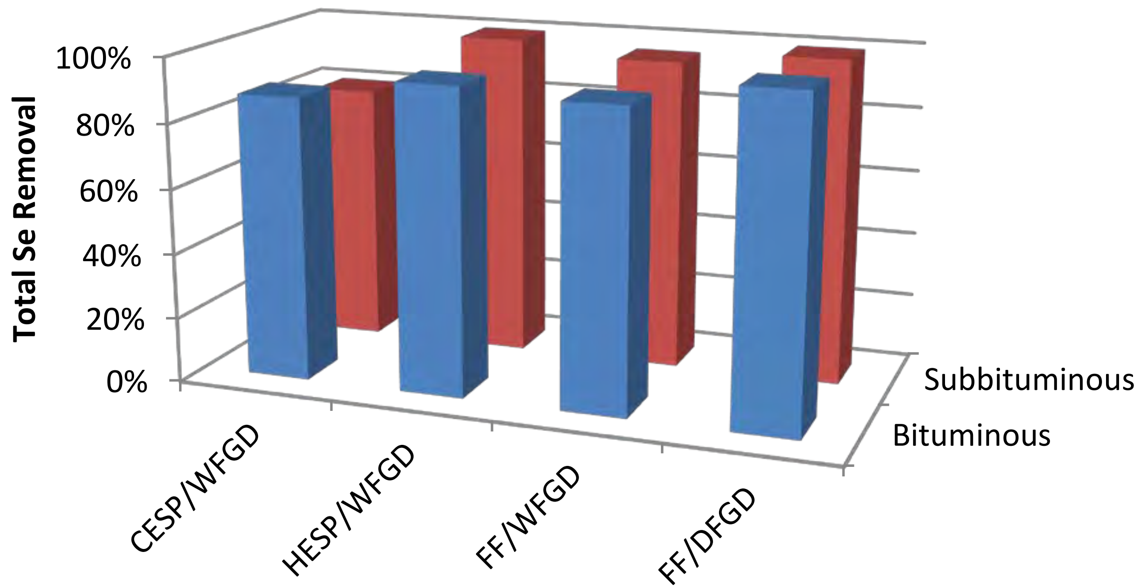
Compliance with Air Rules Means Choices for Air Pollution Control

Acid Gas Control

- Combination of FGDs and PM devices have very high removal for Se
- As shown earlier, partitioning between fly ash and FGD byproducts depends on type of coal and type of PM control
- What about DSI?



Source: 2010 ICR

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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*

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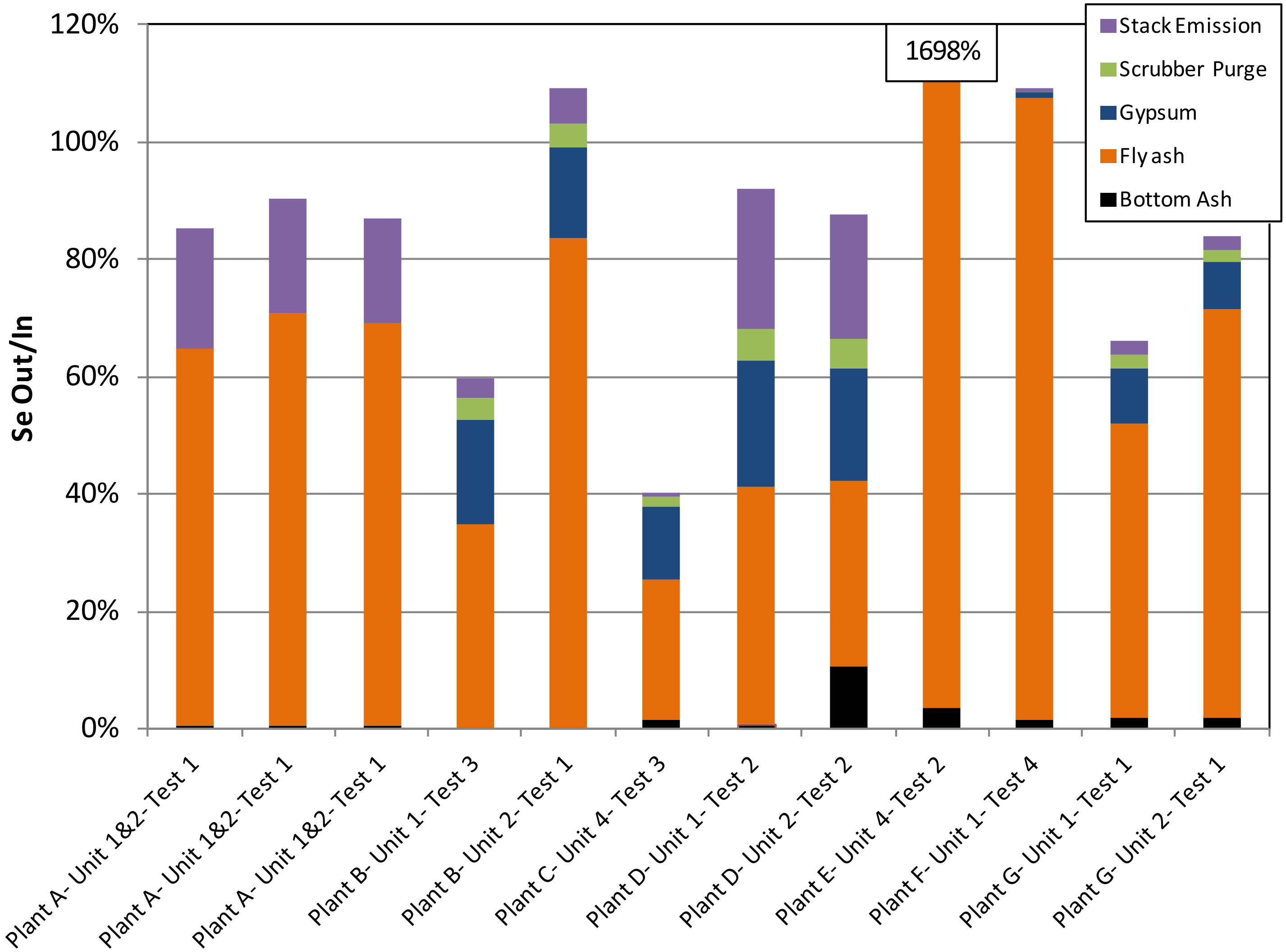
Selenium Mass Balance



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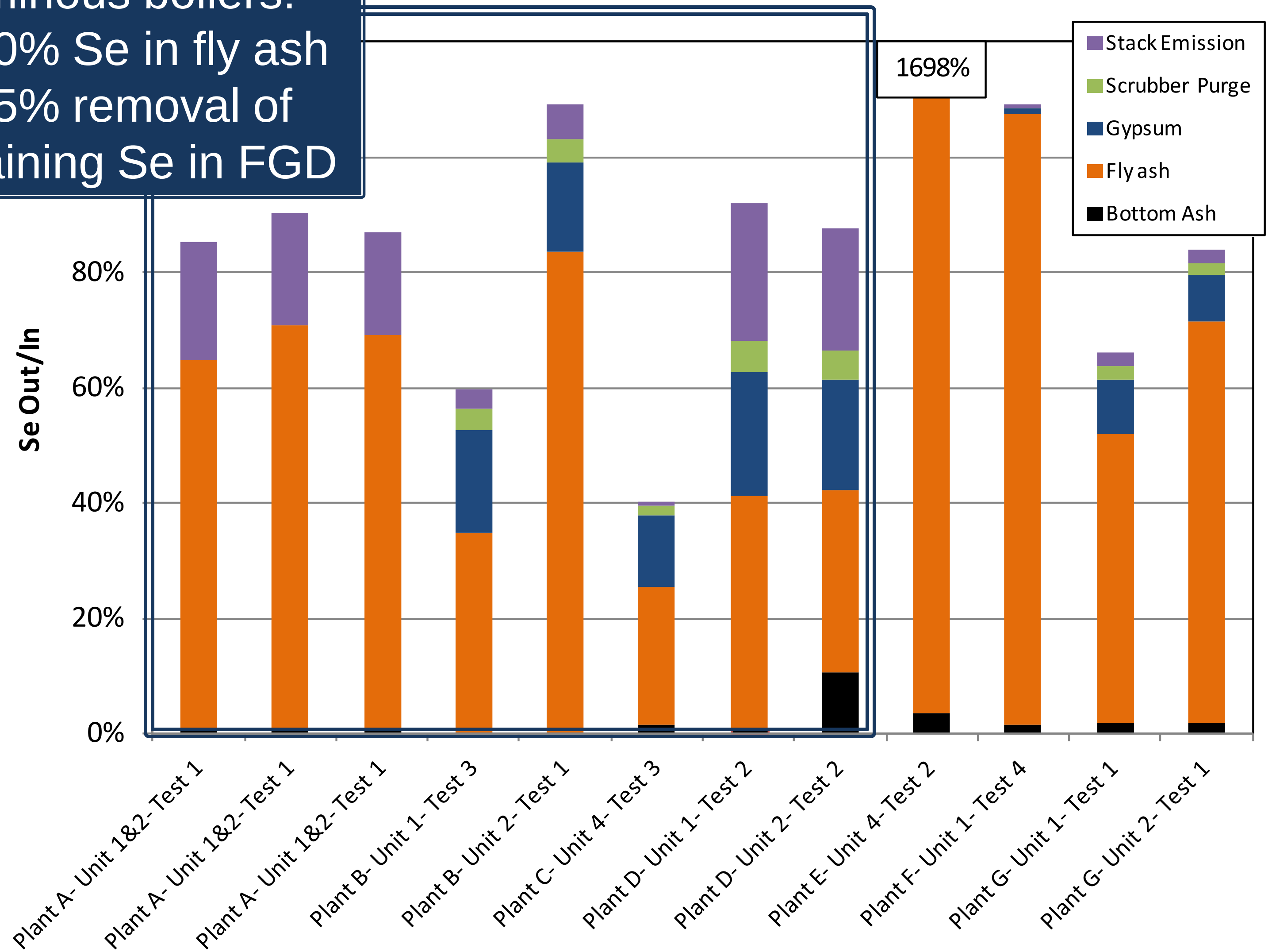
Selenium Mass Balance

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



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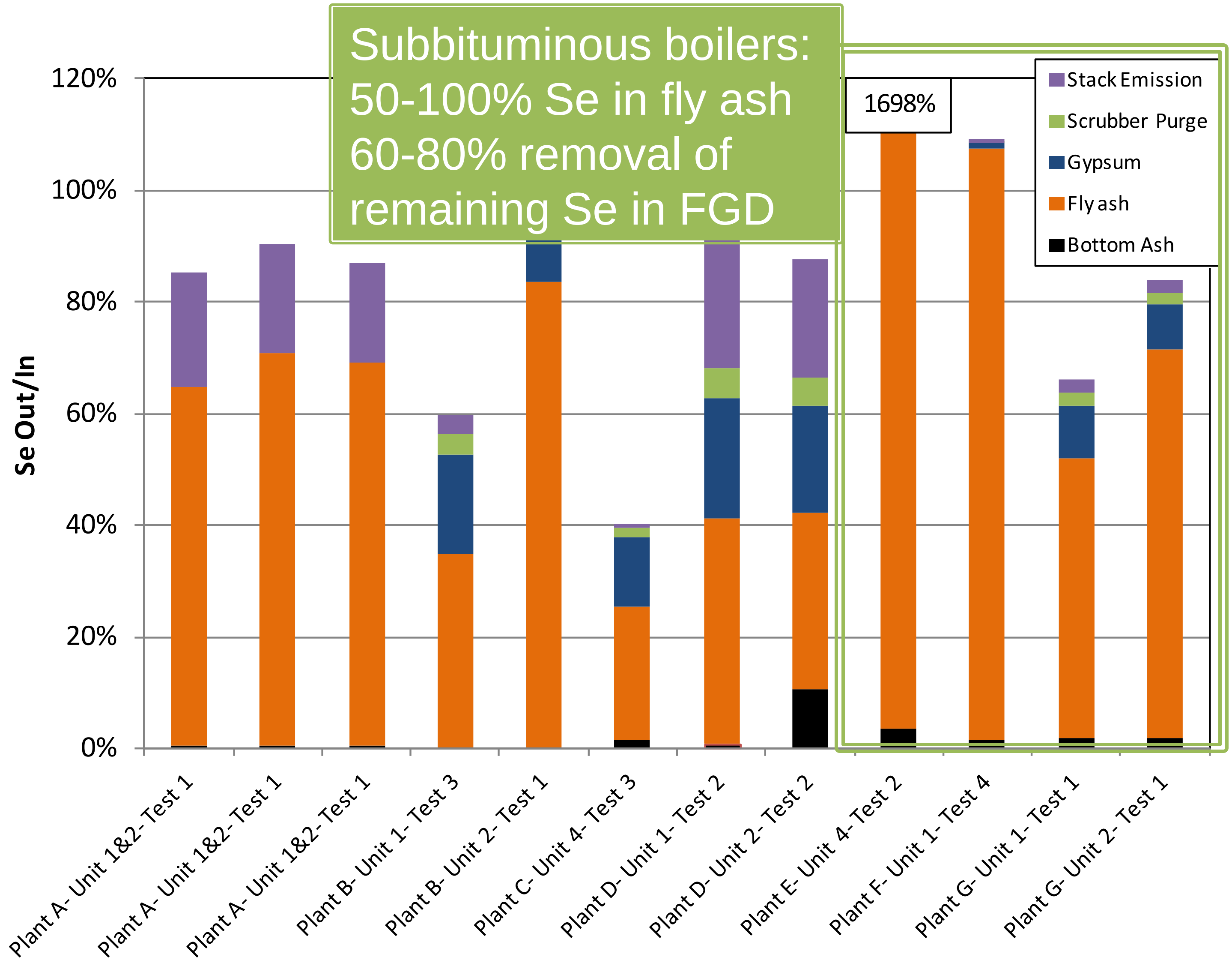
Selenium Mass Balance



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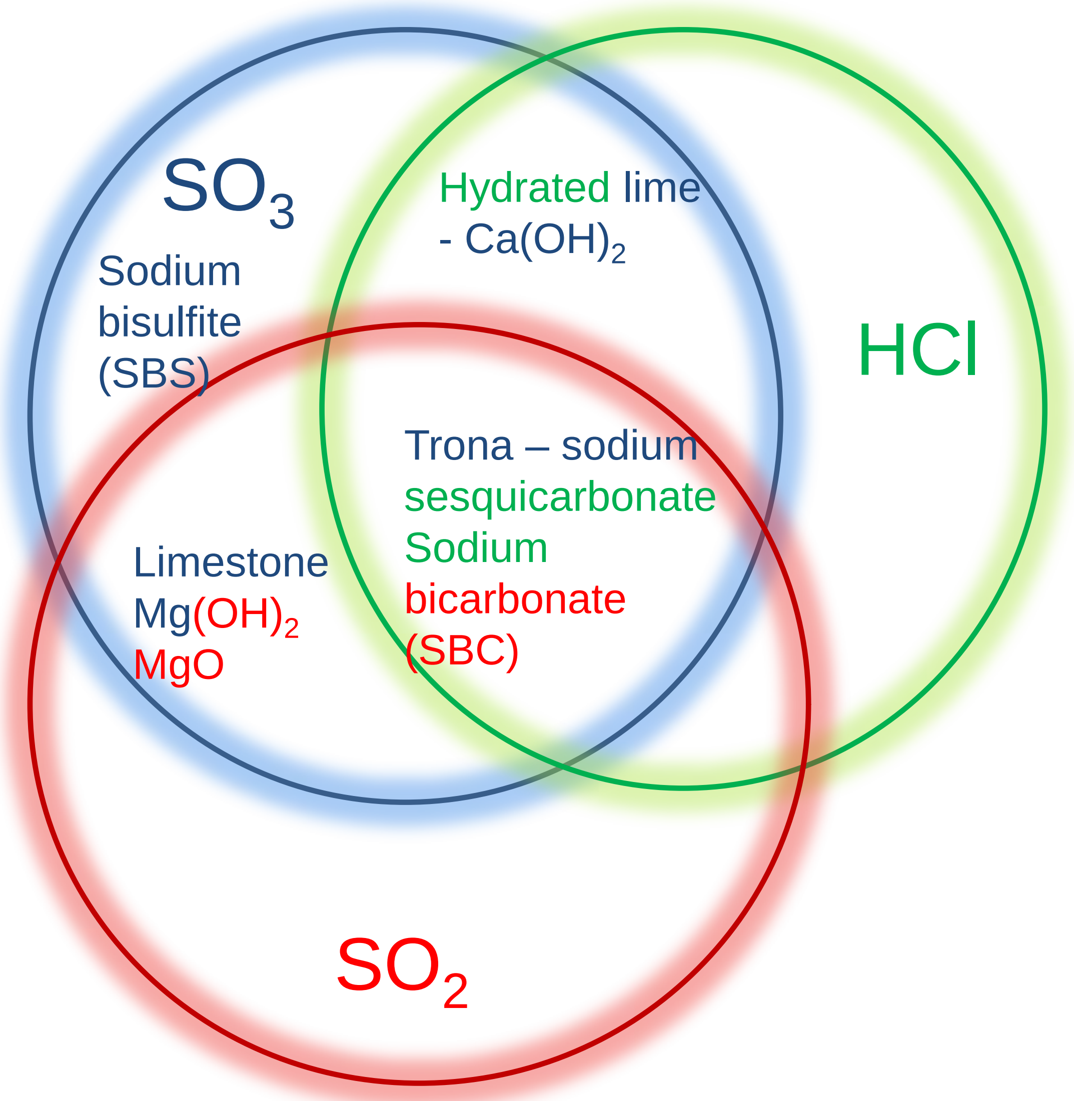
What About DSI?



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

- **Mercury**
  - Potential reaction of $HgCl_2$(g) with alkaline sorbents
  - Alkaline sorbent injected upstream of air preheater removes HCl, which can result in less oxidized Hg in the flue gas
  - Removal of SO_3 by DSI sorbent enhances Hg capture by unburned carbon or activated carbon
  - Production of NO_2 by sodium DSI sorbent can reduce effectiveness of activated carbon for Hg capture
- **Arsenic**
  - High temperature reaction with calcium sorbent (possibly sodium sorbent) removes As_2O_3 from gas pre-APH, but doesn't change ultimate fate of arsenic
- **Selenium**
  - Reacts with sodium or calcium sorbents: potential to shift Se from scrubber to fly ash

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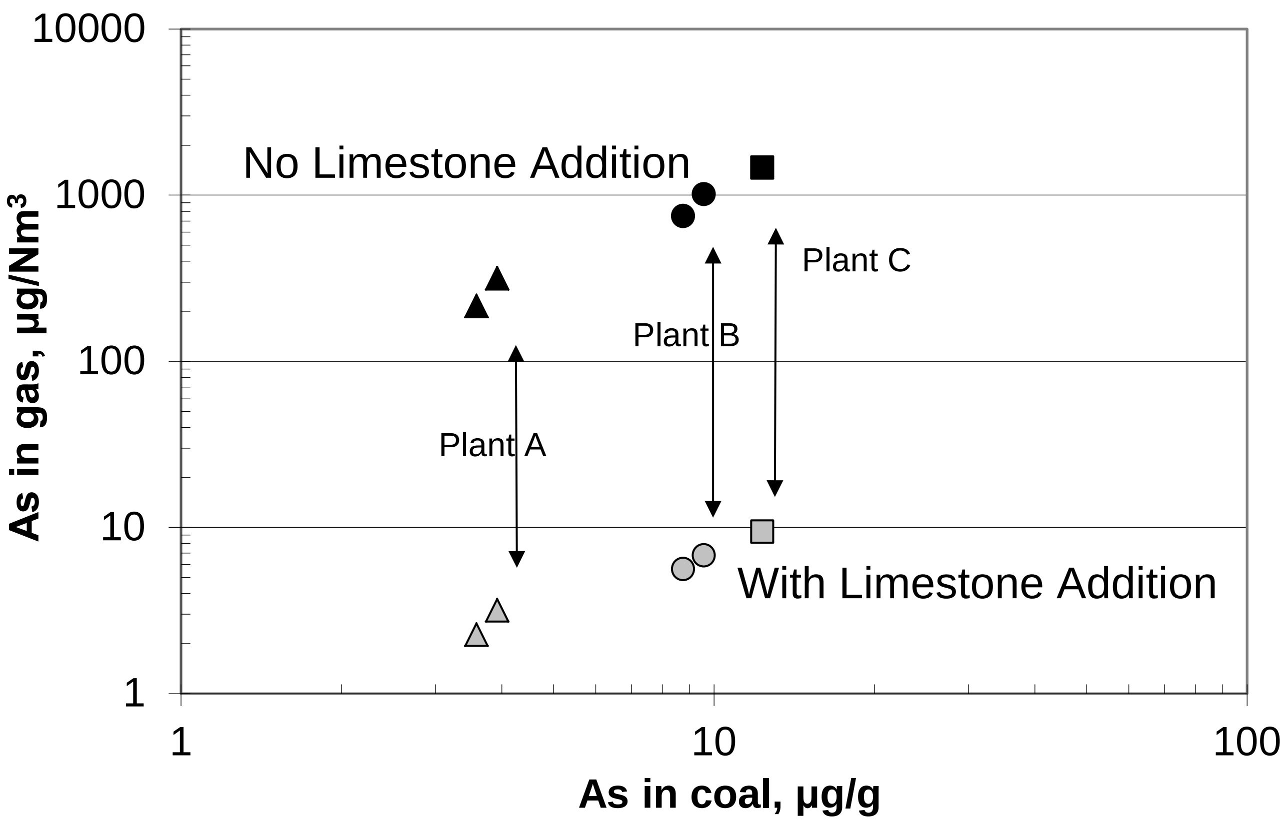
Arsenic Reacts with Calcium at Pre-APH Temperatures

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



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

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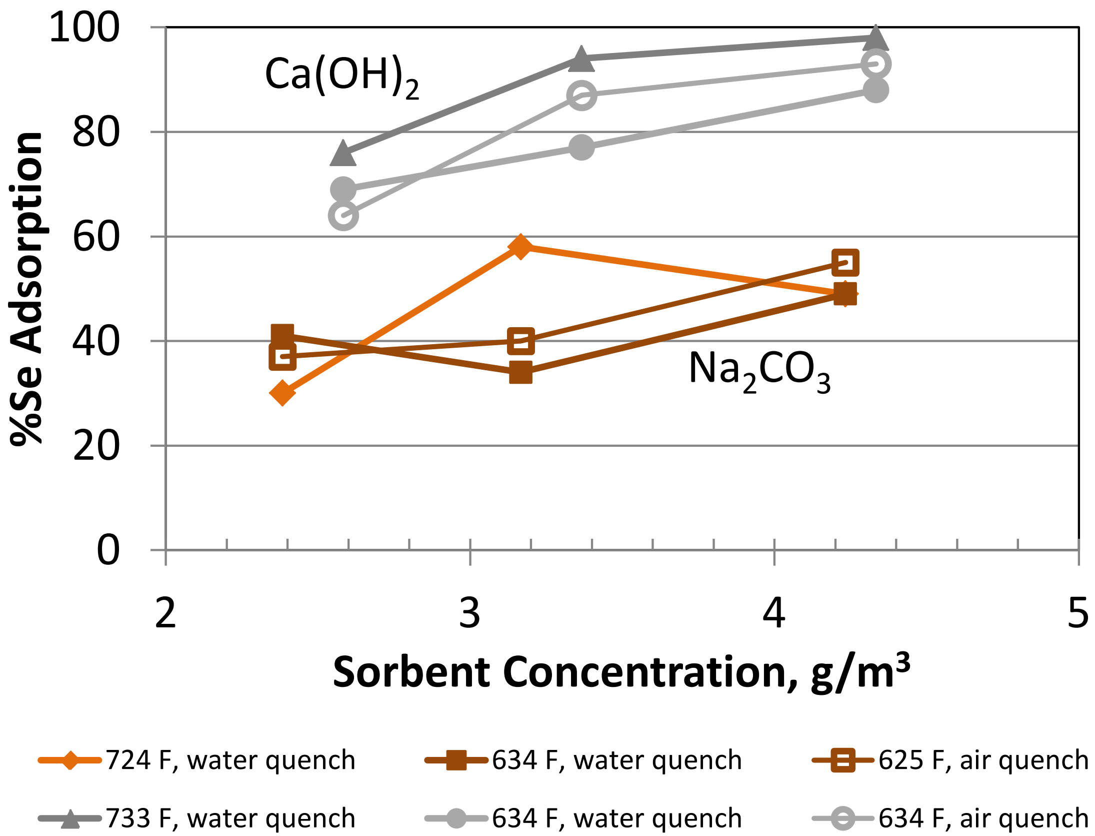
Selenium Reacts with Ca and Na at Pre-APH Temperatures

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



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

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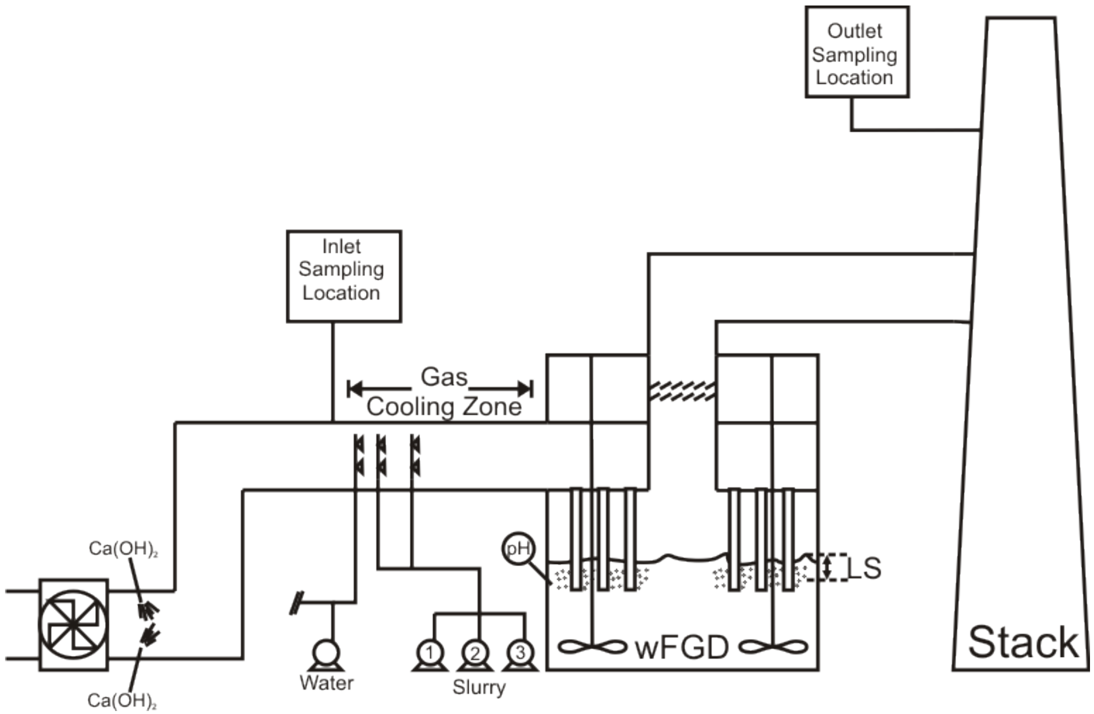
Selenium Reaction at Post-APH Temperatures

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



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

Source: Senior et al., 2016

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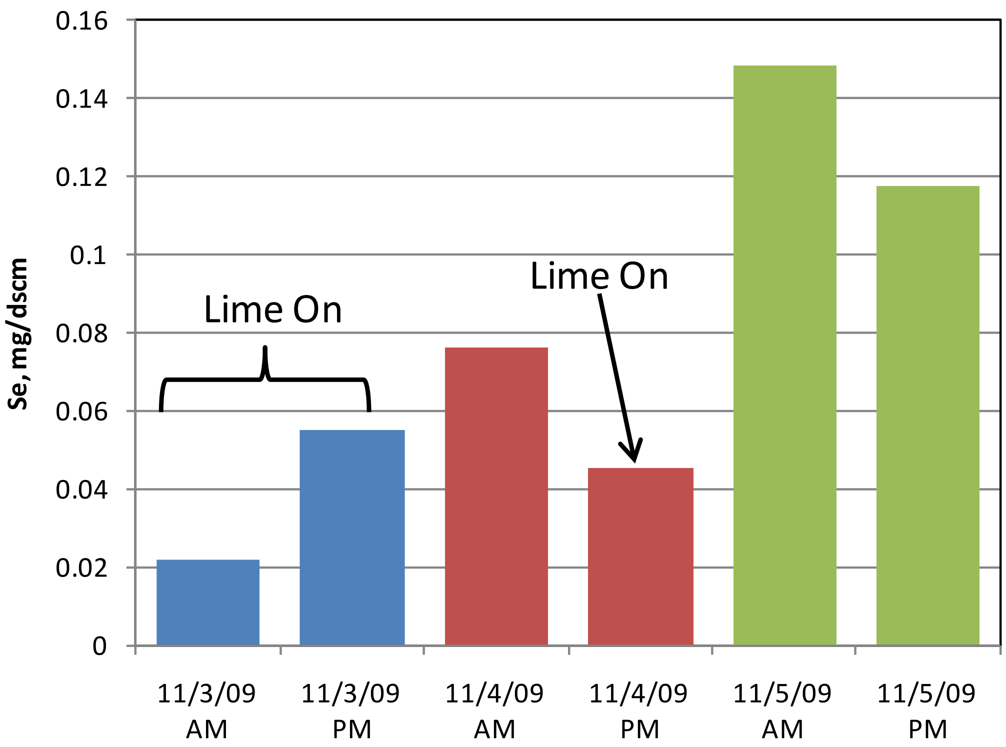
Selenium Reaction at Post-APH Temperatures

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



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

Source: Tyree, et al., EUEC 2011

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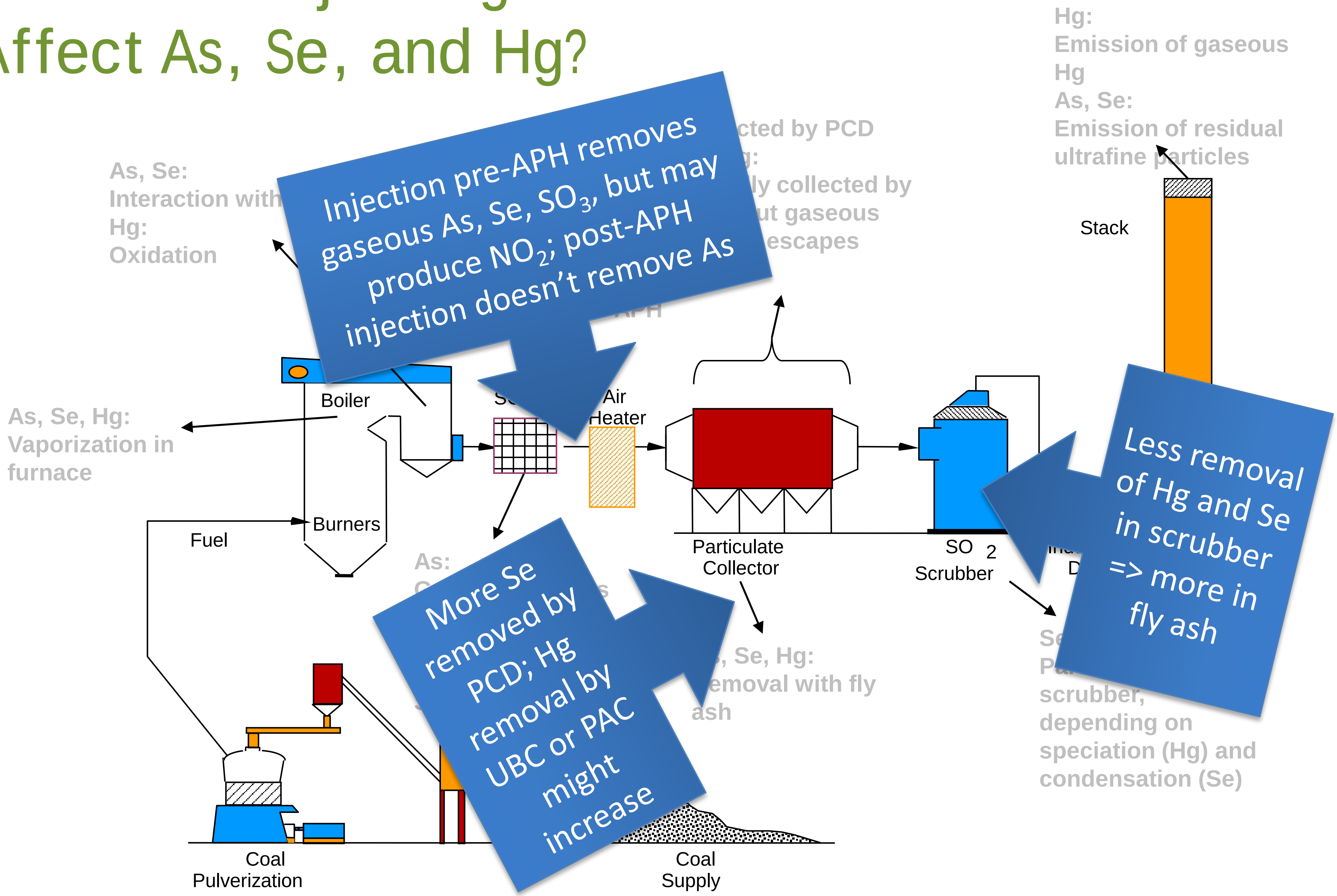
How Does Injecting DSI Sorbents Affect As, Se, and Hg?



Leaching of Metals from DSI-Fly Ash Mixtures

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

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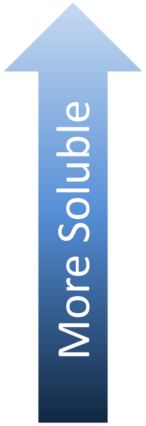
Solubility of Selenium Compounds

- 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



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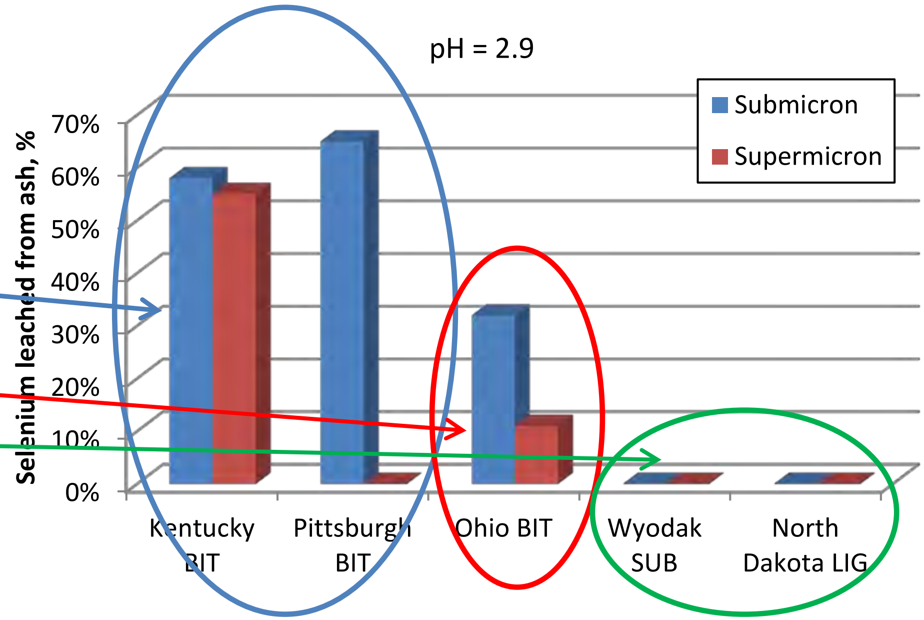
Solubility of Selenium in Fly Ash

- Pilot-scale data from Seames:
  - Fly ash from different coals collected at ~1000ºF
  - Size-segregated with cascade impactor
  - Leaching of submicron ash vs. supermicron ash
- According to Seames, Se speciation in ash varied from predominantly
  - $FeSeO_4$
  - SeO_2
  - $CaSeO_3$
- 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]

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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

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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.

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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.*

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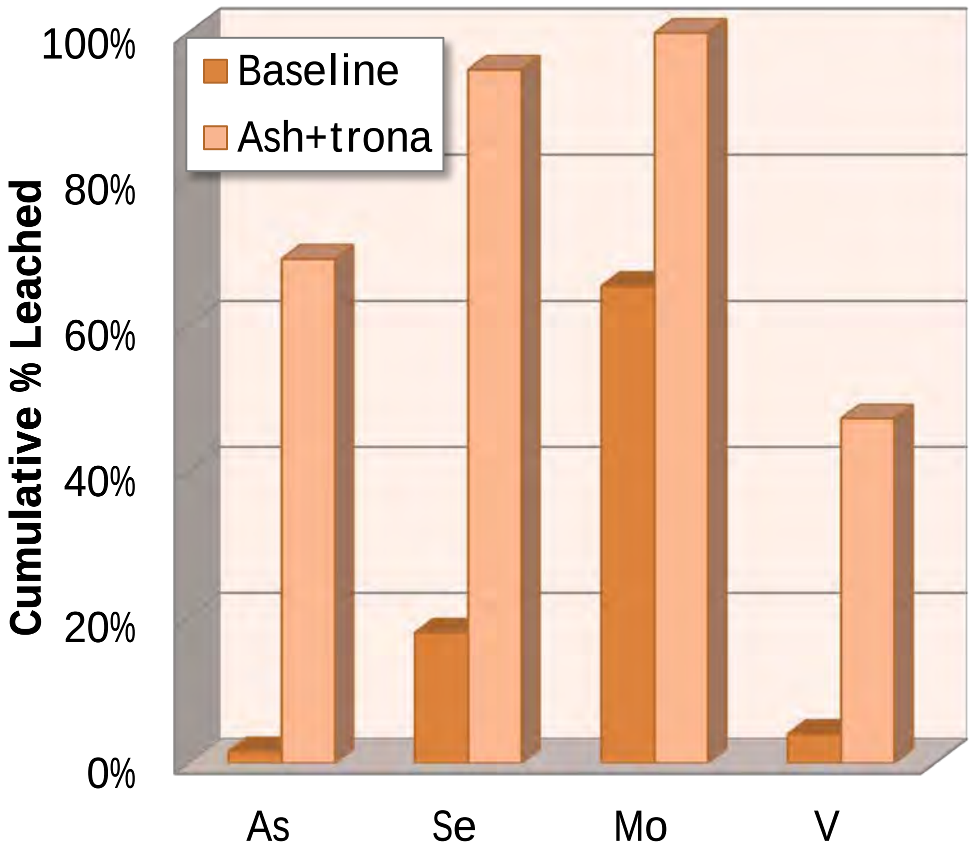
Leaching from Ash-Trona Mixtures: Subbituminous Ash

- 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*.

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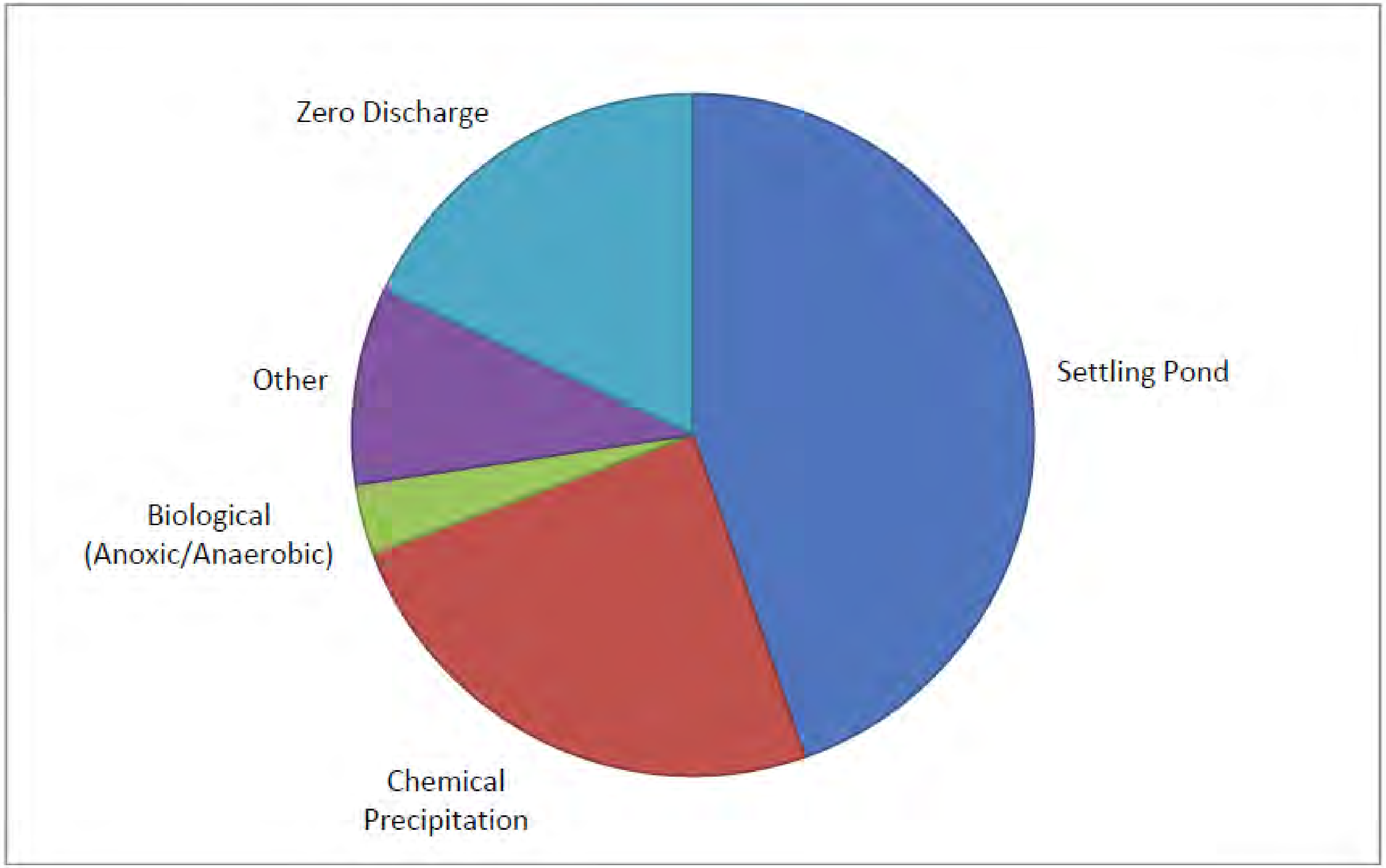
Let's Make It More Complicated and Talk About Wastewater Treatment



Based on 2010 EPA Survey of 150 Plants Operating Wet FGD Systems

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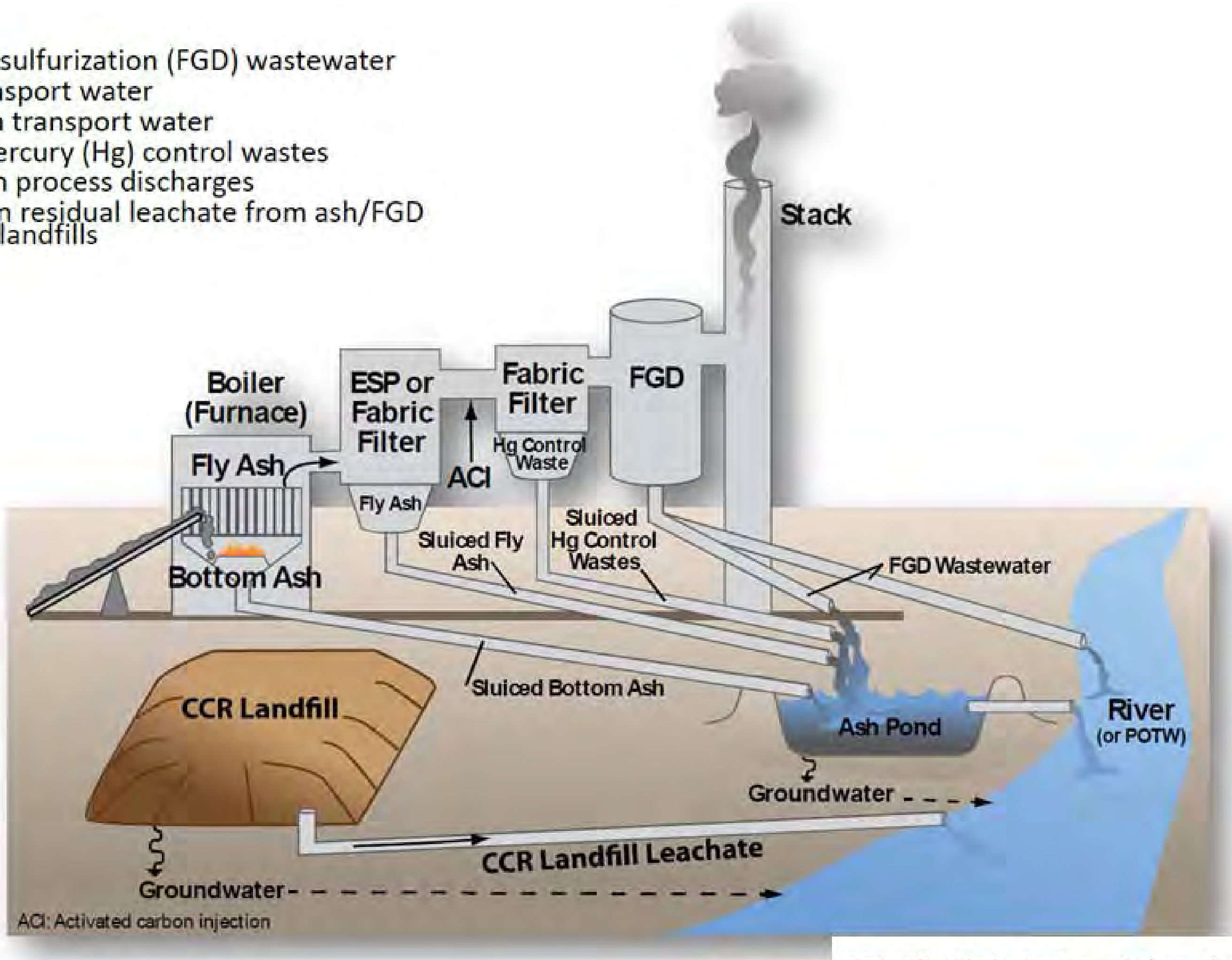
Types of Wastewater Addressed by ELG Revisions

- 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

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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, NO_2+NO_3
    - Technology basis: chemical precipitation plus biological treatment
  - New sources
    - Effluent limits: As, Se, Hg, TDS
    - Technology basis: chemical precipitation plus evaporation

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ELG Voluntary Incentives for FGD Wastewater from Existing Sources

- Provides additional time to comply for those plants that voluntarily adopt more stringent effluent limitations
- Plants that opt in:
  - Agree to comply with the limitation based on the combination of chemical precipitation and evaporation treatment technologies (i.e., same technology as for new sources)
  - May use alternative approaches to comply with the effluent limits (e.g., combination of wet and dry scrubbers to completely eliminate discharge
  - New BAT limits do not apply until December 31, 2023

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Considerations for FGD Wastewater

- Bromine addition to coal or in the FGD absorber has the potential to cause water quality problems and trigger the need for additional water quality based effluent limitations in the NPDES permit
  - Exceedances of water quality criteria in the receiving stream/river
  - Contributes to elevated levels of bromides at downstream drinking water plants, which promote formation of disinfectant byproducts (DBPs) such as trihalomethanes
- Certain compliance approaches can eliminate discharge of FGD wastewater, obviating the need to permit and monitor pollutant concentrations for compliance with effluent limitations
  - Opportunity to use combination of dry and wet FGD systems to completely eliminate FGD wastewater stream
  - Plants opting into voluntary incentive program (if using evaporation or similar treatment technology) can use treatment system effluent as FGD makeup water rather than discharging the wastewater

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What Does It Mean for My Plant?

- Compliance with air rules means choices for air pollution control
- Many APC systems are new and there's still a learning curve
  - Seasonal factors: Will Hg control work as well in the summer as it did in the winter?
  - Interactions: How will ACI and DSI play together? How will an SCR affect Hg emissions?

- And then there's the Whack-a-Mole factor:
  - We're taking Hg and Se out of the flue gas, but are we putting them in the best place?
  - We're adding halogens to the fuel, but will those affect wastewater treatment options?

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QUESTIONS?

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