REINHOLD ENVIRONMENTAL Ltd.

2015 APC Round Table & Expo Presentation

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Collision of MATS and ELG Compliance at the FGD System

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Reinhold APC

Overview

- **Introduction**
- MATS Overview
- ELG Overview
- WFGD Chemistry
- System View
- Mitigation Strategies

MATS & ELG

- Two regulations by EPA that aim at reducing emissions of select species from coal-fired power generation:

  1. **MATS:** reduce mercury leaving the system with stack gases

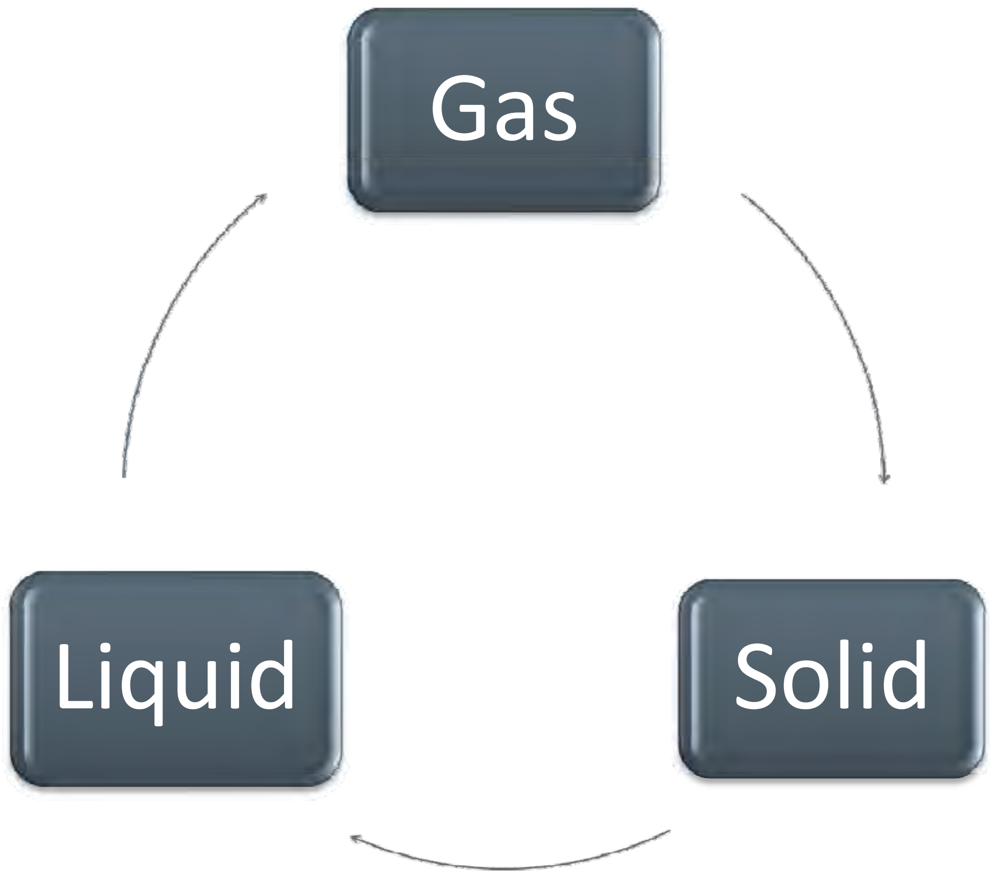
  2. **ELG:** limit mercury, selenium, arsenic, and nitrate-nitrite compounds, leaving the system with the waste water

MATS & ELG

- Written for best-case scenarios, with little impacts on overall system chemistry taken into account

- Important to understand impact that control strategies to meet one regulation has upon the compliance and costs to also meet the other

MATS & ELG



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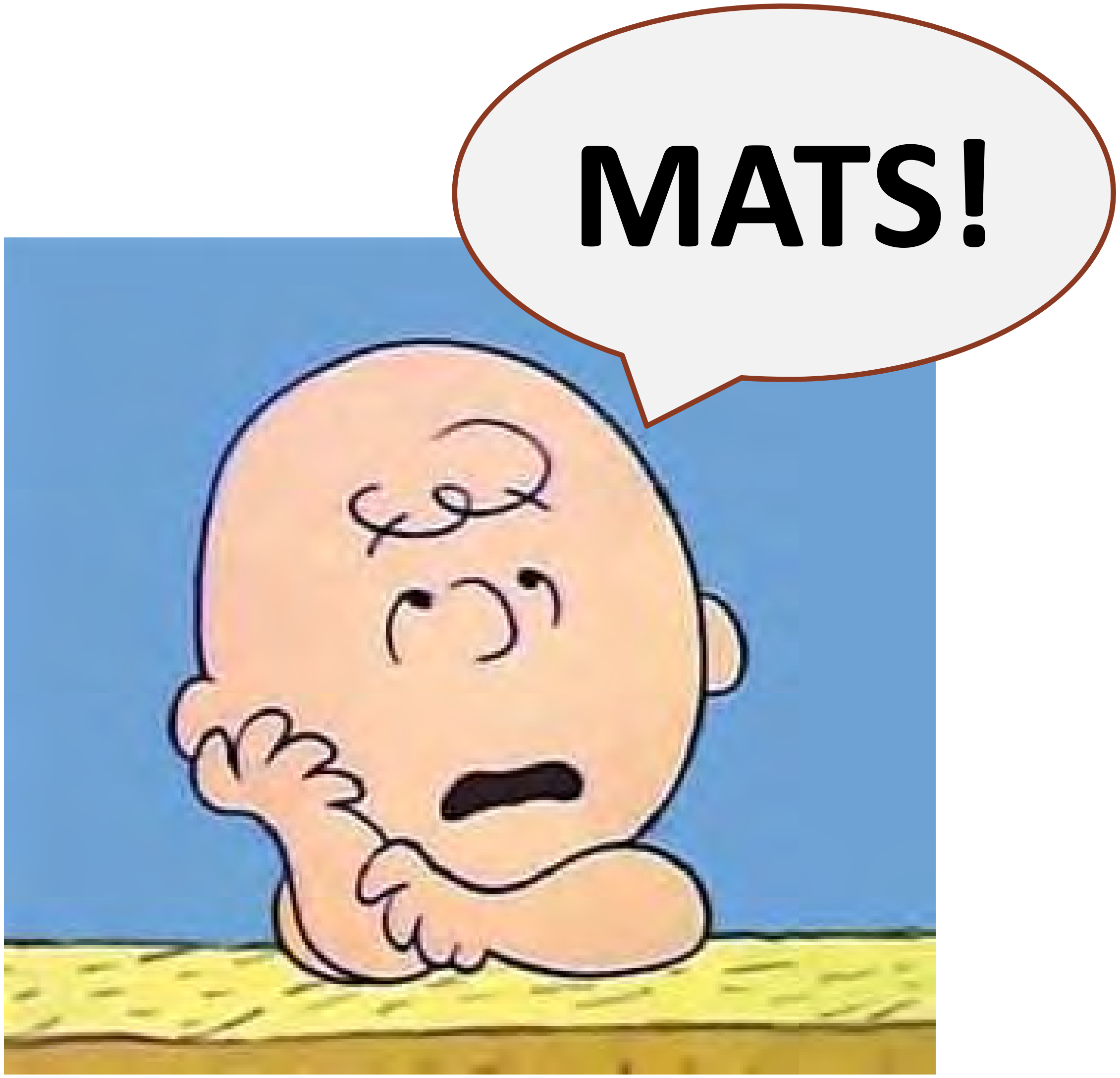
Mercury and Air Toxics Standards (MATS) for Existing Utility Steam Generating Units

Subcategory	*Filterable Particulate Matter*	*Hydrogen Chloride (acid gases)*	*Mercury*
Existing Unit, "not" low rank virgin coal (most coals)	*0.030 lb/MMBtu (0.30 lb/MWh)*	*0.0020 lb/MMBtu (0.020 lb/MWh)*	*1.2 lb/TBtu (0.013 lb/GWh)*
*Existing Unit, low rank virgin coal (mine-mouth lignite**)*	*0.030 lb/MMBtu (0.30 lb/MWh)*	*0.0020 lb/MMBtu (0.020 lb/MWh)*	*4.0 lb/Tbtu* (0.040 lb/GWh*)*

December 21, 2011 - The U.S. Environmental Protection Agency announced standards to limit mercury, acid gases and other toxic pollution from power plants.

**Beyond-the-floor limit. The MACT floor for this subcategory is 11.0 lb/TBtu (0.12 lb/GWh).*

**<8,300 Btu/lb


MATS!

Summary - Regulations and % Removal

Existing Units

Federal Requirements

- Bituminous and Sub-bituminous = 1.2 lbs/TBtu
- Lignite = 4 lbs/TBtu

Recent Specifications for Bit and Sub = 0.8 or 1.0

State or Local

- 90-95%
- Other?

Required % Removal

- Average Hg = 85 – 92%
- Maximum = 94-97%

Typical Hg Concentrations in Coal

Coal	PRB	Lignite	Eastern Bituminous
Typical, ppmd	0.08	0.1	0.1
Typical maximum, ppmd	0.15 to 0.2	0.15 to 0.2	0.15 to 0.2
Typical HHV, BTU/lb	8,400	6,400	12,300
Average Hg, lbs/TBtu	7.2	8.7	7.7
Maximum Hg, lbs/TBtu	18	22	15

Mercury & Air Toxics Standards (MATS)

- On June 29, 2015, the Supreme Court of the United States issued an opinion on MATS.
- The opinion stated that EPA must consider the costs for meeting the standard in making the rule.
- The D.C. Circuit court will decide how to implement the ruling.

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Effluent Limitation Guidelines (ELG)

- Federal Effluent Limitation Guidelines (ELG) will require control of Hg, As, Se, and nitrate-nitrite in FGD wastewater discharge

FEDERAL REGISTER

Environmental Protection Agency

40 CFR Part 423
Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category; Proposed Rule

- Other local regulations may exist with different limits or additional constituents

Technology Basis for WFGD Wastewater

<table>
<tr><th>Option</th><th>1</th><th>3a</th><th>3b</th><th>2</th><th>3</th><th>4</th><th>4a</th><th>5</th></tr>
<tr><td>< 2000 MW Scrubbed Capacity</td><td rowspan="2">Chemical Precipitation</td><td rowspan="2">BPJ</td><td>BPJ</td><td colspan="3" rowspan="2">Chemical Precipitation + Biological Treatment</td><td rowspan="2">Chemical Precipitation + Biological Treatment</td><td rowspan="2">Chemical Precipitation + Vapor Compression Evaporation</td></tr>
<tr><td>> 2000 MW Scrubbed Capacity</td><td>Chemical Precipitation + Biological Treatment</td></tr>
</table>

BPJ = Best Professional Judgment

*For FGD Wastewater Options 1, 2, 3, 3b (2000 MW or more), 4, and 4a there would also be “flow minimization for plants with high FGD discharge flowrates (>1000 gpm)”

Expected ELG Limits for WFGD Wastewater

	Daily Maximum	Monthly Average
Total Arsenic [µg/L]	8	6
Total Mercury [ng/L]	242	119
Total Selenium [µg/L]	16	10
Nitrate/Nitrite as N [mg/L]	0.17	0.13

Limits near instrumentation detection limits
Levels are for total concentration in the sample

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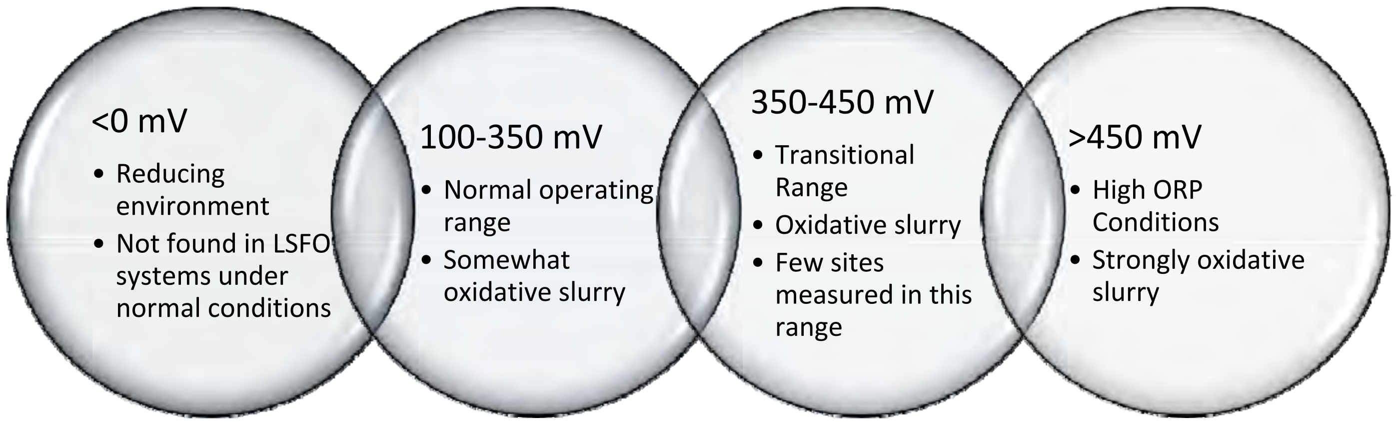
Chemistry of WFGD and WWT

- While at steady state, the WFGD absorber reaction tank does not operate at thermodynamic equilibrium when metals of concern are considered.
- Complex chemical interactions dominate speciation and phase partitioning of Hg and Se within WFGD and absorber effluent, complicating treatment options.
- Some reactions appear to be dominated by upstream chemistry rather than traditionally considered reactions of absorber reaction tank.
- Foremost amongst these, Redox chemical reactions are crucial for exploring scrubber chemistry.

Metals Speciation and ORP in WFGD Absorber Slurry and Effluent

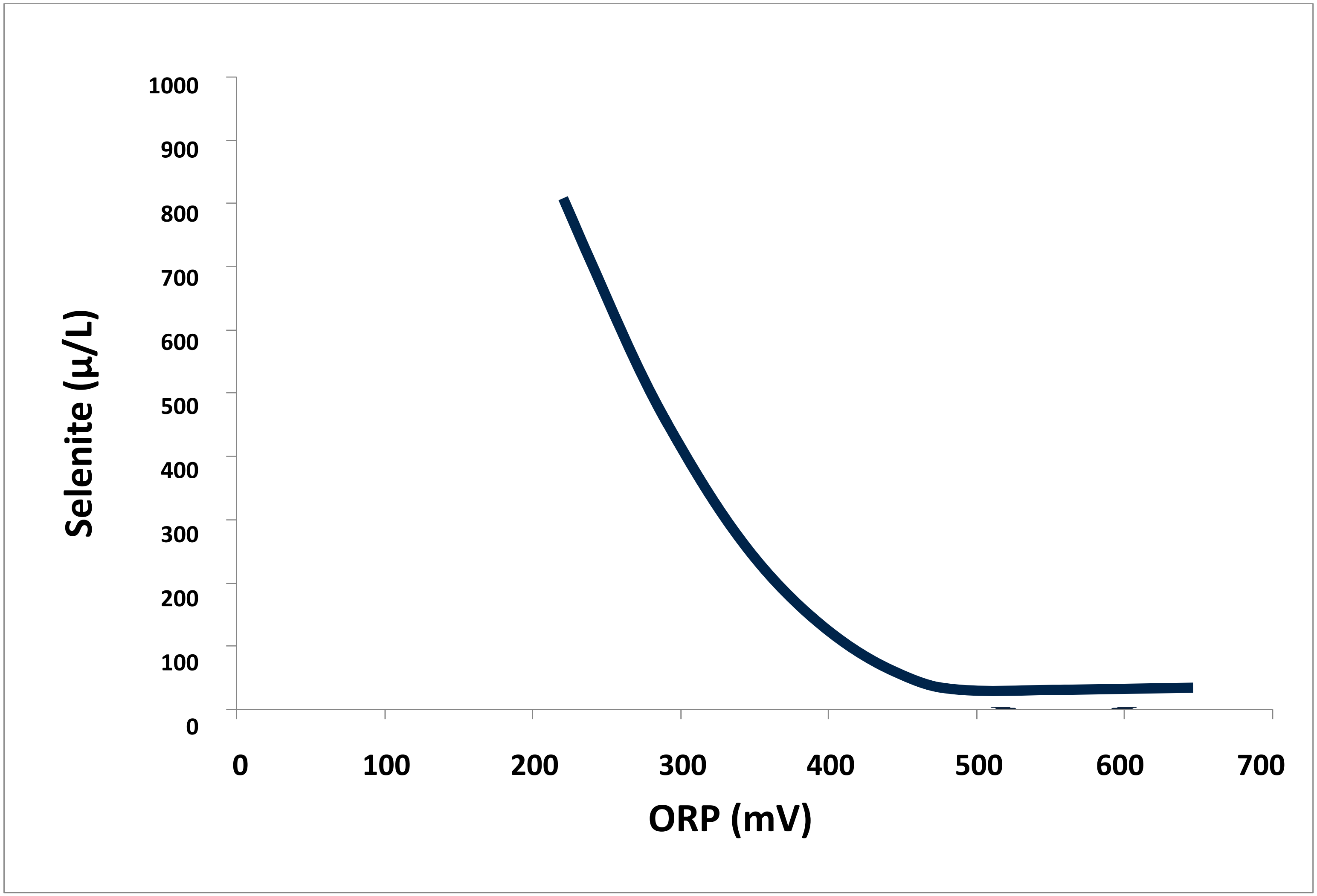


For operating WFGD Units, ±50 mV is common.

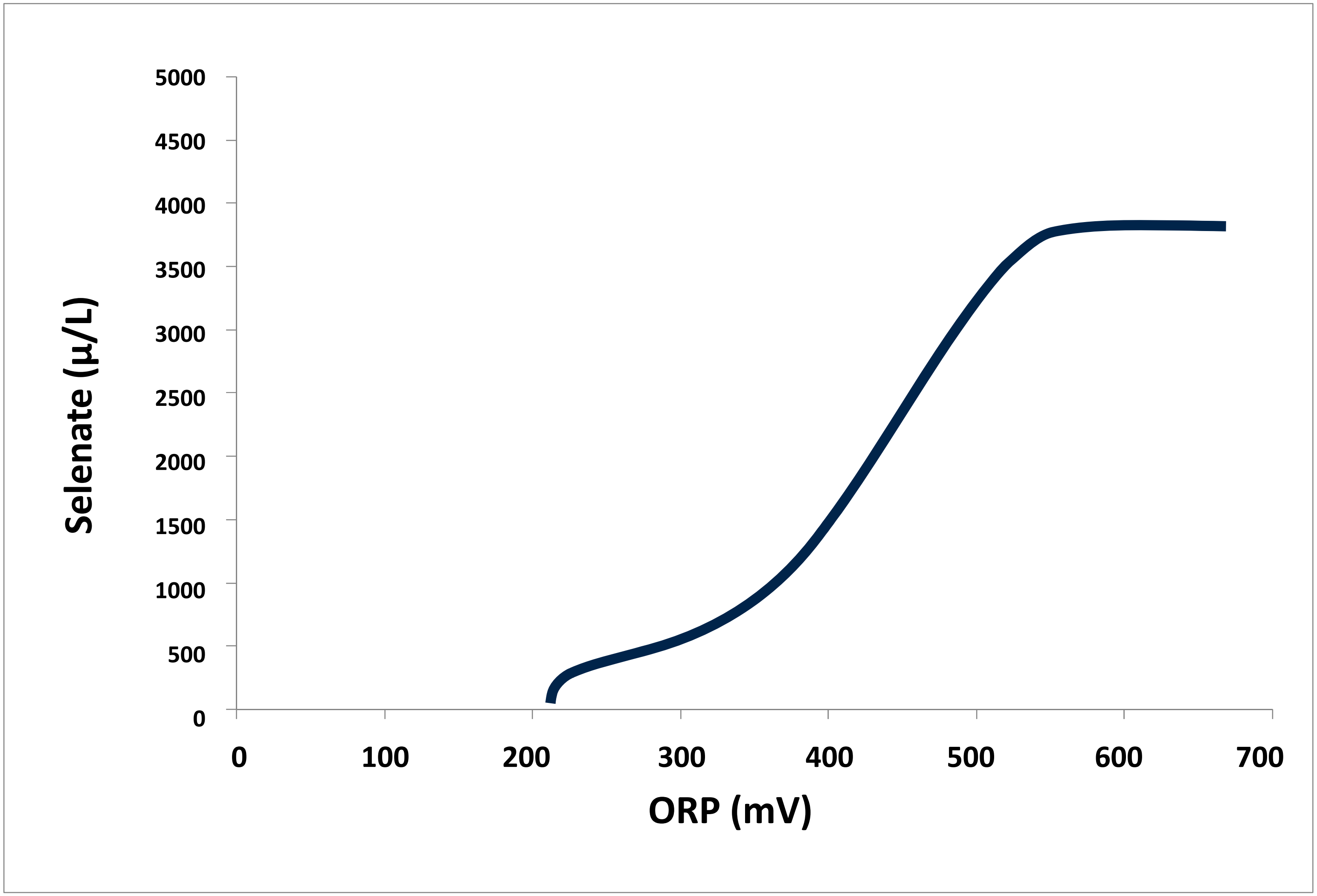
ORP Range	Selenium	Mercury	Manganese
≤300 mV	Selenite dominant	Associated with solids dominant	Dissolved ion
300-500 mV	Transitional	Transitional	Transitional
≥500 mV	Selenate dominant	Dissolved ion dominant	Oxide precipitate

Impacts of ORP on WFGD Blowdown

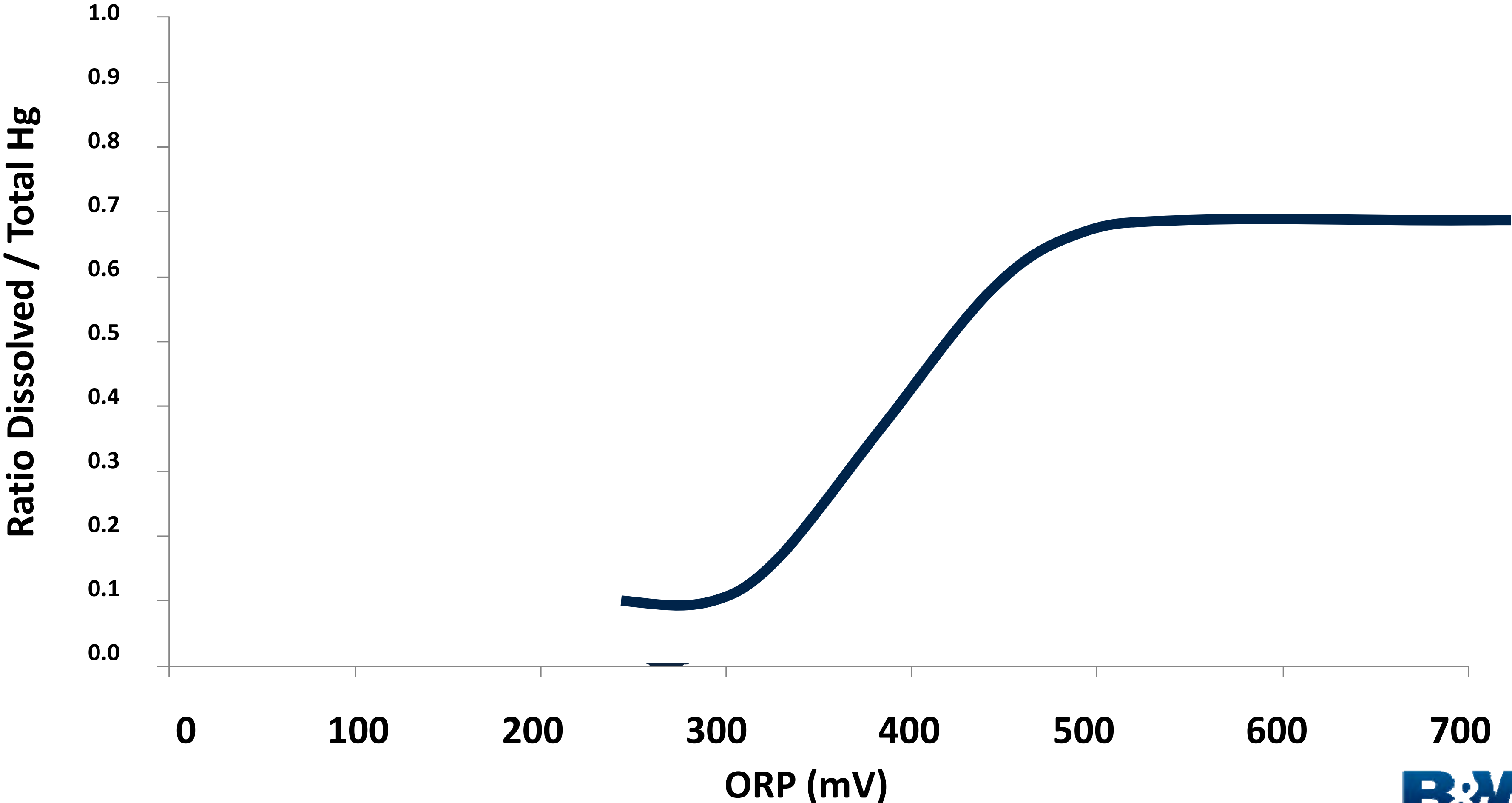
Selenite vs. ORP in WFGD ART Slurry



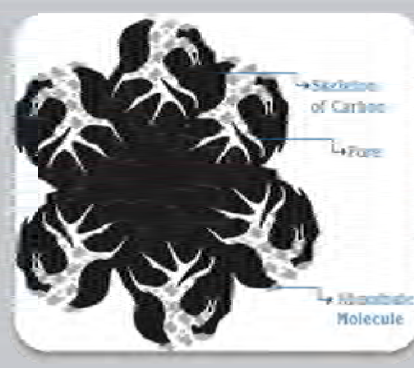
Selenate vs. ORP in WFGD ART Slurry



Dissolved Mercury vs. ORP in WFGD ART Slurry



Forms of Mercury



Hg^0

- Elemental Mercury
- Vapor
- Sparingly Soluble

Hg^{+2}

- Oxidized Mercury
- Readily Soluble Ion
- $HgCl_2$, $HgBr_2$

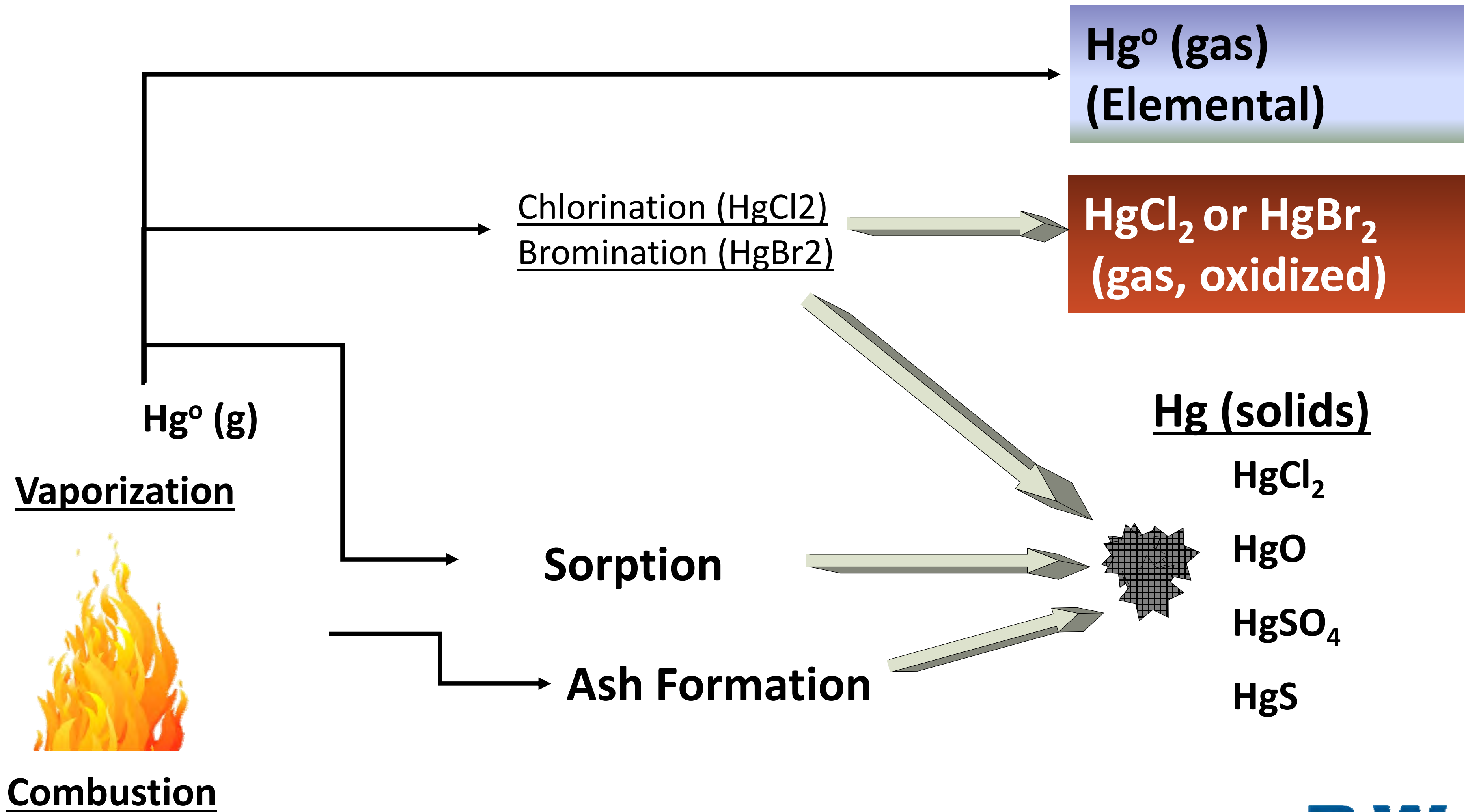
Hg^P

- Particle Bound Mercury
- Mercury is Adsorbed to the Particle

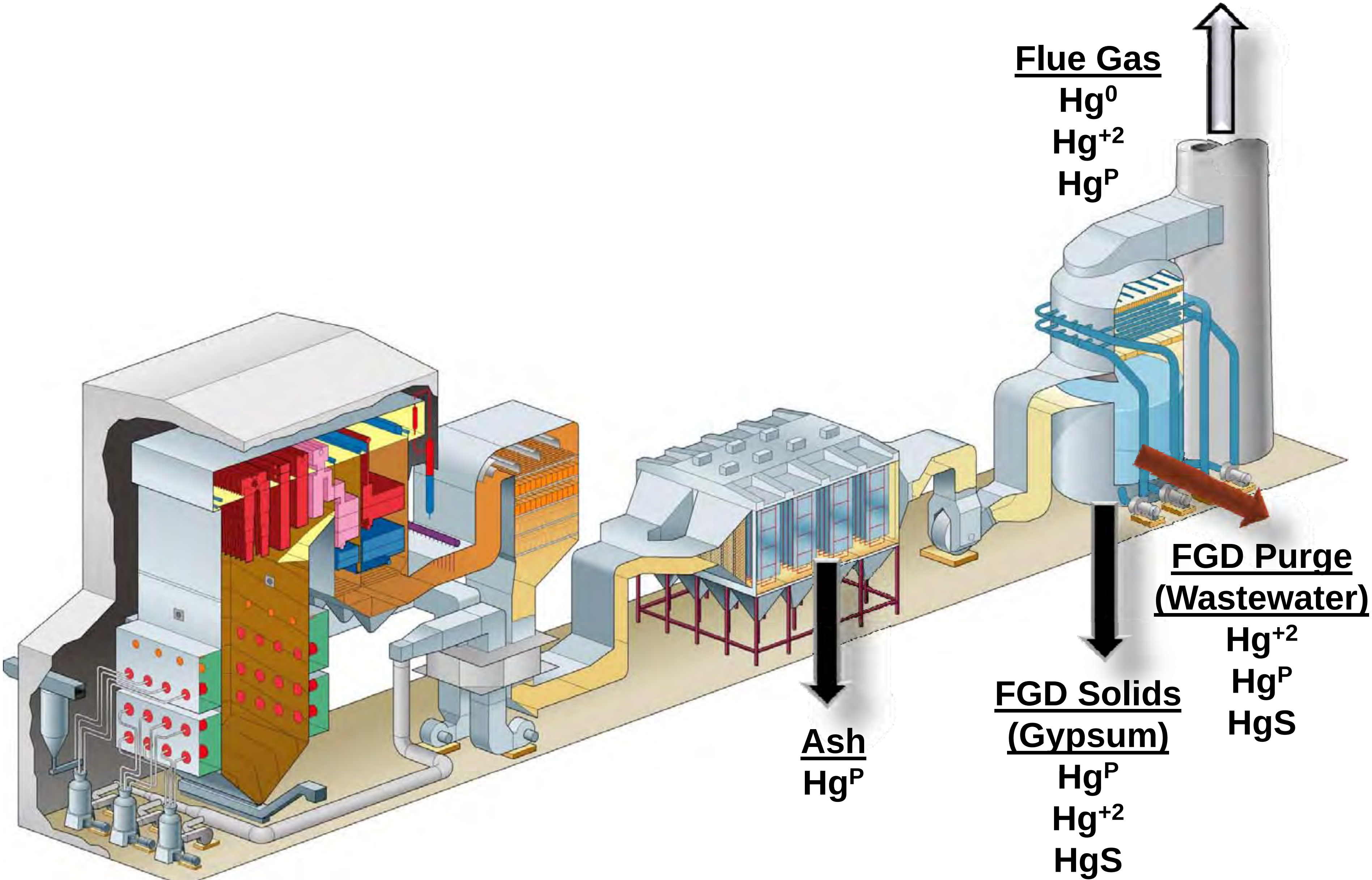
HgS

- Mercury Sulfide
- ***Subset of Hg^{+2}***
- Insoluble Compound
- Stable compound

Fate of Hg in Coal Combustion



Mercury Mass Balance

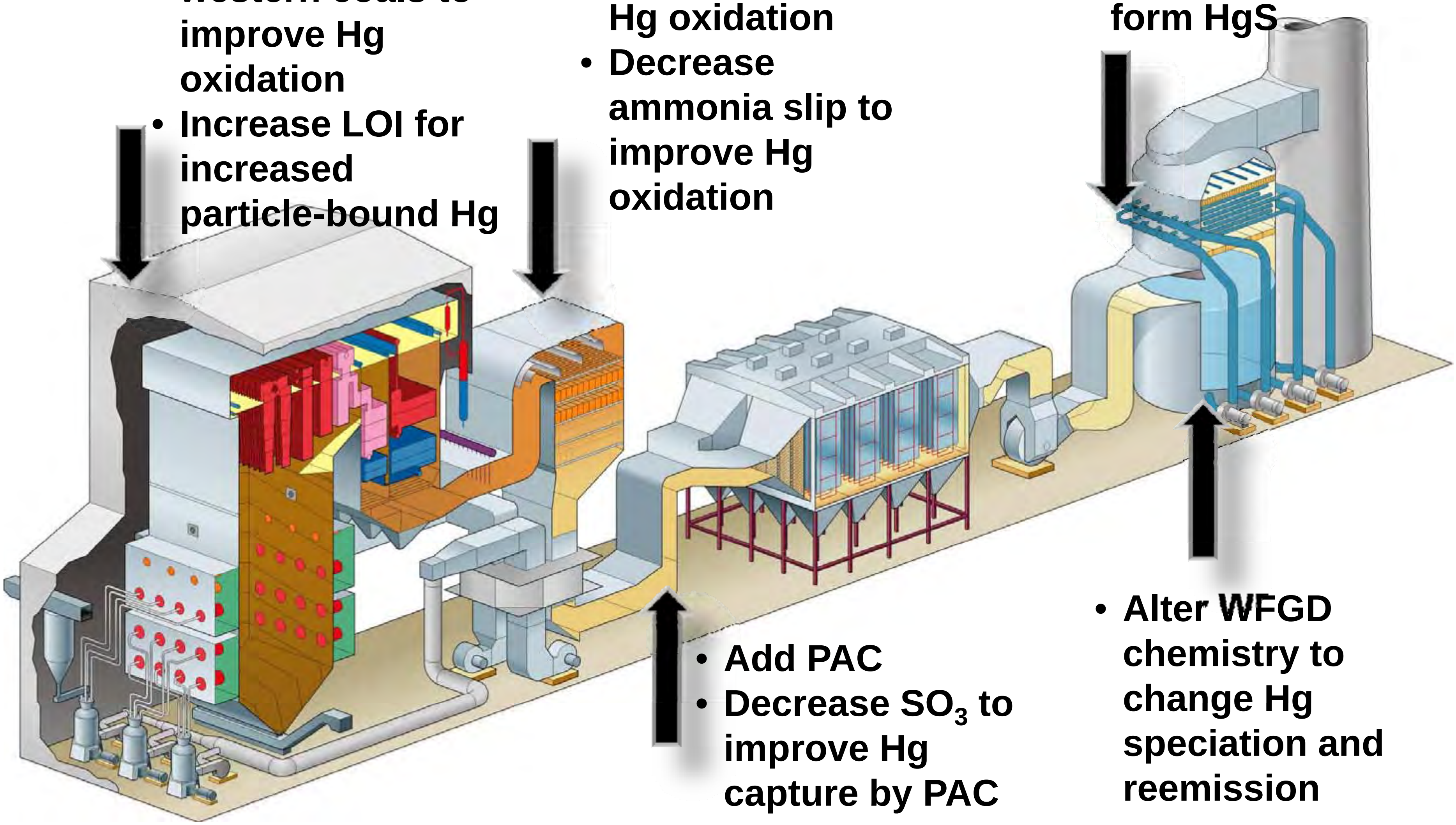


Shifting the Mercury Removal Balance

- Add halides to western coals to improve Hg oxidation
- Increase LOI for increased particle-bound Hg

- SCRs improve Hg oxidation
- Decrease ammonia slip to improve Hg oxidation

- Additives to form HgS

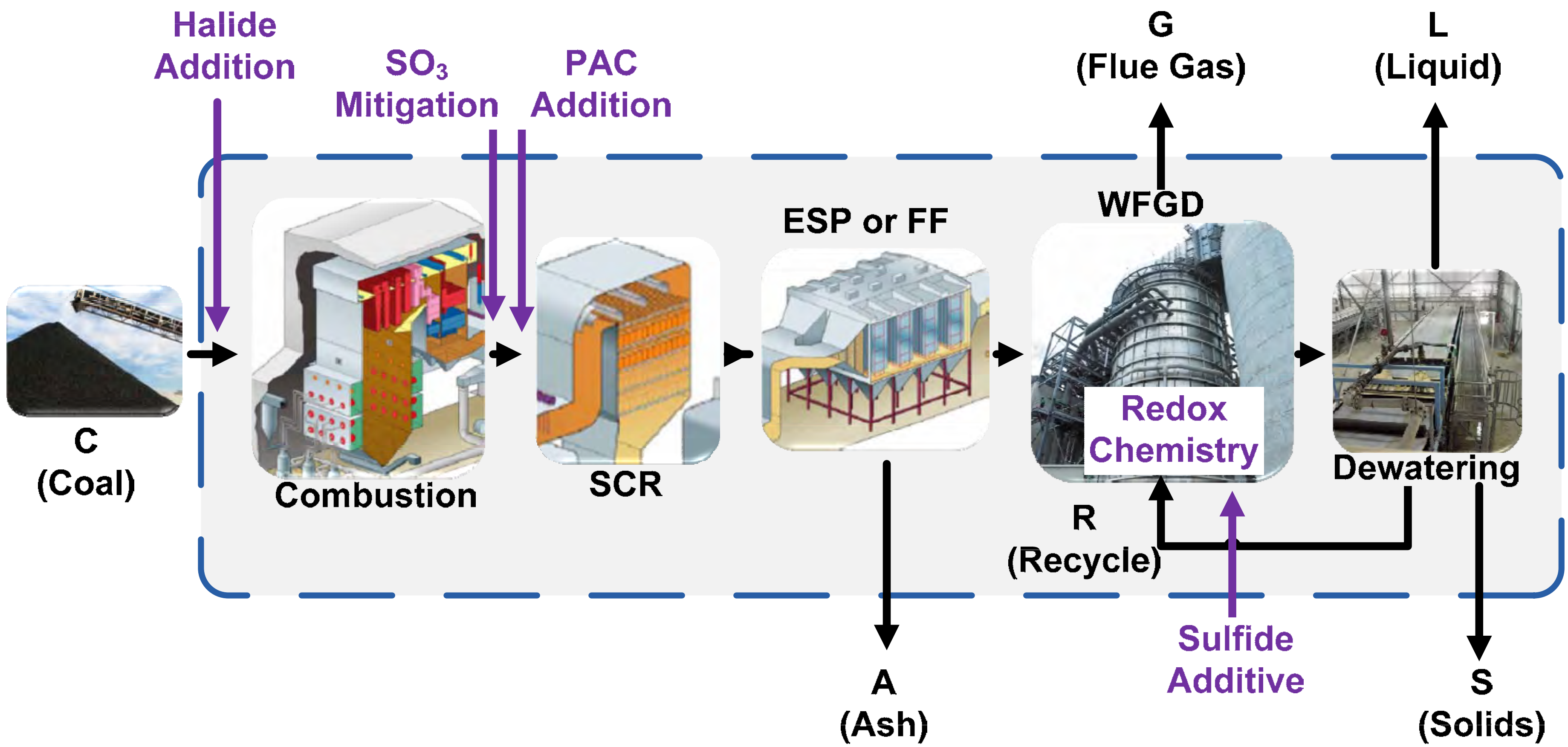


- Add PAC
- Decrease SO_3 to improve Hg capture by PAC

- Alter WFGD chemistry to change Hg speciation and reemission

Mercury Mass Balance

- System Boundary



Accumulation

- Where in the system can mercury accumulate?

Positive

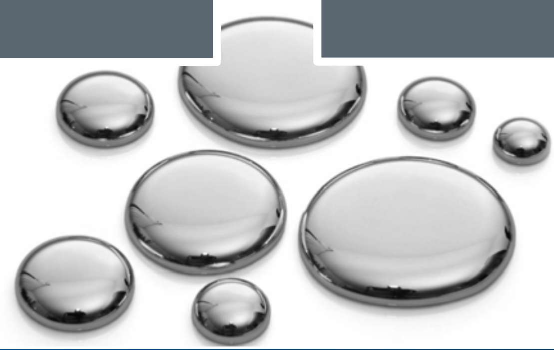
Accumulation:

- Mercury builds up on FF with PAC ($FF_{Accum.}$)
- Increase in stored mercury within WFGD (*unsteady-state or below saturation*) ($WFGD_{Accum.}$)

Negative

Accumulation

- Stored mercury is emitted from WFGD ART slurry -($WFGD_{Accum.}$)
- More mercury is purged than added to the system *(unsteady-state*)



Input - Output

- Input:
  - Mercury enters with the coal (Stream C)
  - Addition of mercury from other sources (*limestone, additives, etc.*) is neglected

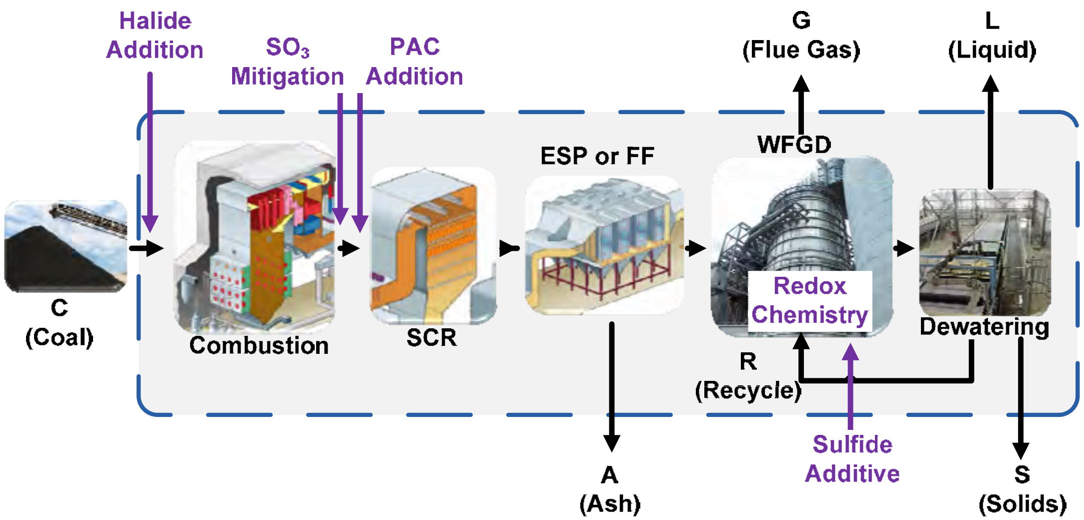
- Output:
  - Mercury leaves the system with the:
    - Ash (Stream A)
    - Gas (Stream G)
    - Liquid (Stream L)
    - Solids (Stream S)

Generation - Consumption

$$Hg^{T} = Hg^{P} + Hg^{0} + Hg^{+2}$$

- Total Mercury
  - Total mercury is neither generated nor consumed
- Fraction of Particulate Mercury:
  - Combustion (LOI), SO_3 mitigation, PAC injection
- Fraction of Oxidized/Elemental Mercury
  - Coal composition, Halide injection
  - WFGD Redox Reactions
  - Sulfide Addition (NaHS)

Mercury Species Mass Balances



Let:

U = Conversion of $Hg^{+2} \longrightarrow Hg^{P}$

V = Conversion of $Hg^{0} \longrightarrow Hg^{P}$

W = Conversion of $Hg^{0} \longrightarrow Hg^{+2}$

X = Conversion of $Hg^{P} \longrightarrow Hg^{+2}$

Y = Conversion of $Hg^{+2} \longrightarrow Hg^{0}$

Z = Conversion of $Hg^{P} \longrightarrow Hg^{0}$

- Species: $\omega_{Hg,P} + \omega_{Hg,+2} + \omega_{Hg,0} = 1$
- Hg^T: $\omega_{Hg,T}FF_{Accum} + \omega_{Hg,T}WFGD_{Accum} = \omega_{Hg,T}C - \omega_{Hg,T}A - \omega_{Hg,T}G - \omega_{Hg,T}L + \omega_{Hg,T}S$
- Hg^P: $\omega_{Hg,P}FF_{Accum} = \omega_{Hg,P}C - \omega_{Hg,P}A - \omega_{Hg,P}G - \omega_{Hg,P}L - \omega_{Hg,P}S + U\omega_{Hg,+2}C + V\omega_{Hg,0}C$
- Hg^{+2}: $\omega_{Hg,+2}WFGD_{Accum} = \omega_{Hg,+2}C - \omega_{Hg,+2}A - \omega_{Hg,+2}G - \omega_{Hg,+2}L - \omega_{Hg,+2}S + W\omega_{Hg,0}C + X\omega_{Hg,P}C$
- Hg^0: $\omega_{Hg0}WFGD_{Accum} = \omega_{Hg,0}C - \omega_{Hg,0}A - \omega_{Hg,0}G - \omega_{Hg,0}L - \omega_{Hg,0}S + Y\omega_{Hg,+2}C + Z\omega_{Hg,P}C$

Mercury Species Conversions

$Hg^{+2}, Hg^{0} \rightarrow Hg^{P}$

- ↑ PAC addition
- ↑ Combustion (LOI)
- ↑ SO_3 mitigation

$Hg^{0} \rightarrow Hg^{+2}$

- Coal Composition
- Halide Addition
- WFGD Redox Chemistry

$Hg^{P} \rightarrow Hg^{+2}, Hg^{0}$

- WFGD Chemistry
- *Needs further testing*

$Hg^{+2} \rightarrow Hg^{0}$

- WFGD Redox Chemistry

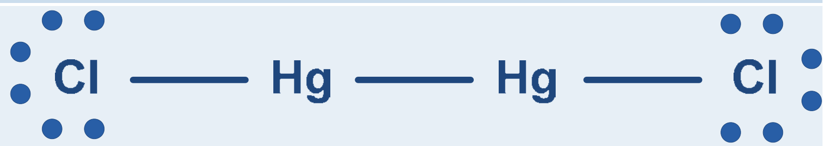
$Hg^{+2} \rightarrow HgS$

- Sulfide Additive
- Reaction for Sequestration of Hg
- *Technically a form of* Hg^{+2}

WFGD Mercury Chemistry

First Ionization

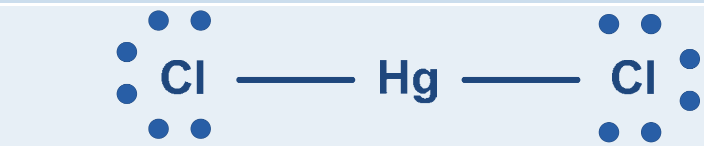
$Hg^0 \rightarrow Hg^{+1} + e^-$



- $HgCl$, Hg_2Cl_2
- Mercury in +1 oxidation state
- Less Stable

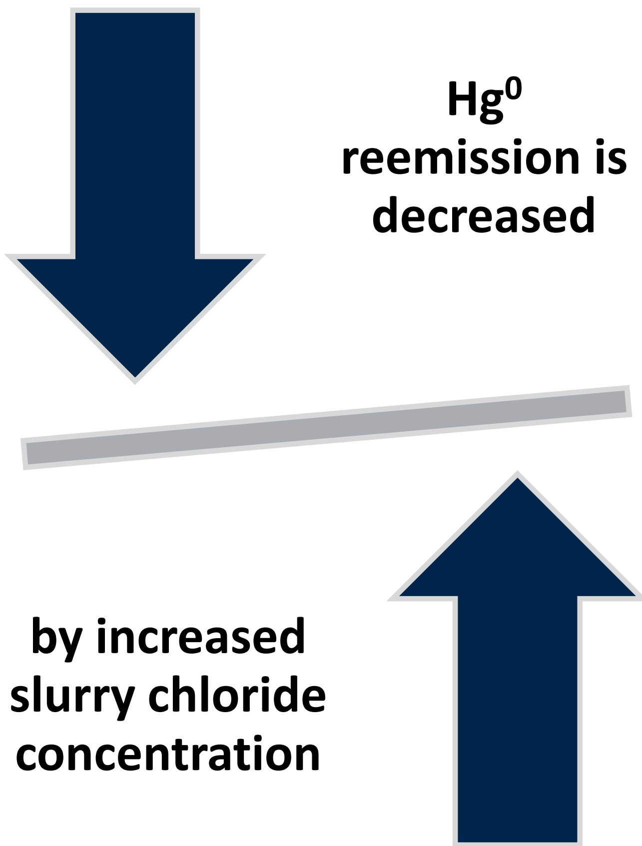
Second Ionization

$Hg^0 \rightarrow Hg^{+2} + 2e^-$



- $HgCl_2$
- Mercury in +2 oxidation state
- More Stable

WFGD Chemistry: Halide Concentration



- **Mercury is more stable in solutions with higher Cl^- concentration**
  - Reported in literature
  - Supported by field trials
  - Mercury is more stable in +2 oxidation state
- **Impact of increased bromide concentration is uncertain**

Halide Addition

- Halide can be introduced through specific injection for Hg oxidation or can be from brominated PAC
  - Any injected halogen will make its way to the FGD wastewater
  - In water, these can form THMs
- Oxidizes Hg for capture in WFGD, which goes to wastewater
- Increases overall Se concentration in flue gas and WFGD, speciation impact not known
- No known impact on As

WFGD Redox Reactions

Oxidized Mercury Absorption:

$$Hg^{+2}(g) \rightarrow Hg^{+2}(aq)$$

Mercury Reduction:

$$Hg^{+2} + HSO_3^- + H_2O \rightarrow Hg^0(aq) + SO_4^{-2} + 3H^+$$

$$Hg^{+2} + 2Me^{+2} \leftrightharpoons Hg^0(aq) + 2Me^{+3}$$

Emission of Elemental Mercury:

$$Hg^0(aq) \leftrightharpoons Hg^0(g) \uparrow$$

WFGD Redox Reactions

Elemental Mercury Absorption:

$$Hg^0(g) \leftrightharpoons Hg^0(aq)$$

Possible Reactions for Mercury Oxidation:

$$Hg^0(aq) + 2Me^{+3} \leftrightharpoons Hg^{+2} + 2Me^{+2}$$

$$S_2O_8^{-2} + 2Ca^{+2} + Hg^0(aq) \rightarrow 2CaSO_4 + Hg^{+2}(aq)$$

Sulfide Additives

- Sulfide additive for mercury control
- Such additives bind mercury so that the following reactions will not occur:

$$\mathbf{Hg^{+2} + HSO_3^- + H_2O \rightarrow Hg^0(aq) + SO_4^{-2} + 3H^+}$$

$$\mathbf{Hg^{+2} + 2Me^{+2} \leftrightharpoons Hg^0(aq) + 2Me^{+3}}$$

$$\mathbf{Hg^0(aq) \leftrightharpoons Hg^0(g)\uparrow}$$

Cinnabar

Sorbent Injection

- PAC and Amended Silicates
  - Adsorbs Hg^{2+} from flue gas
  - Br from BPAC ends up in wastewater
  - No impact on Se
- DSI
  - Reduces As and Se through reactions
  - No impact on Hg
  - Can increase Br required for Hg oxidation

Mercury Removal Requirements

- Mercury entering the system must be removed.
- Mercury rules include both Stack (MACT) and Effluent (EPA Guidelines) emissions
- Transferring Hg from the gas to the WFGD purge effluent won't be acceptable
- For true mercury control, mercury will need to be bound in a form from which it does not dissolve, does not desorb and does not leach.

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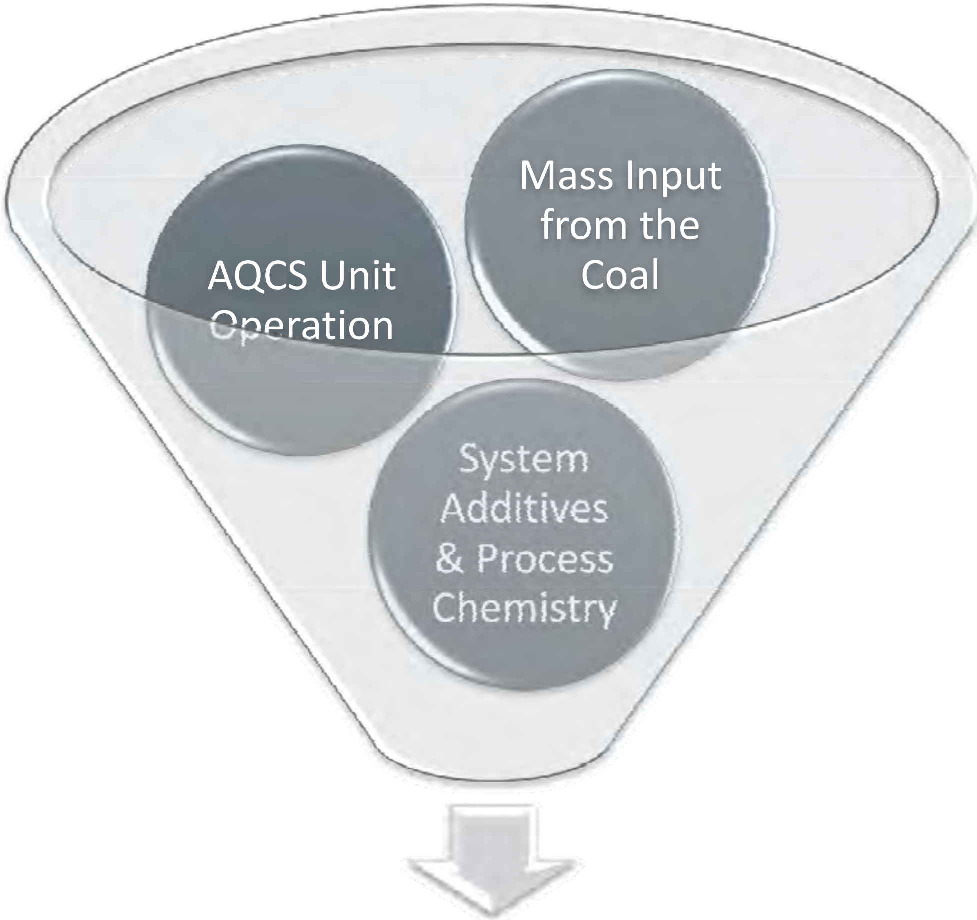
System View



Concentration & Partitioning
of Species of Concern

Collision of MATS and ELG Controls

- For MATS compliance, mercury must be removed from the air. The mercury is shifted to the fluid phase or to the solids. Fine solids may report within the total measured for a waste water sample.
- For ELG compliance, metals must be removed from the aqueous phase and from any solids exiting with the waste water.
- Control strategies for one regulation may shift the species to a phase that would negatively impact reported values with regard to the other regulation.
- Species of concern should, ideally, be removed from both the flue gas and waste water, sequestered in a stable solid that is removed from the system, for compliance of both regulations.

Coal Changes

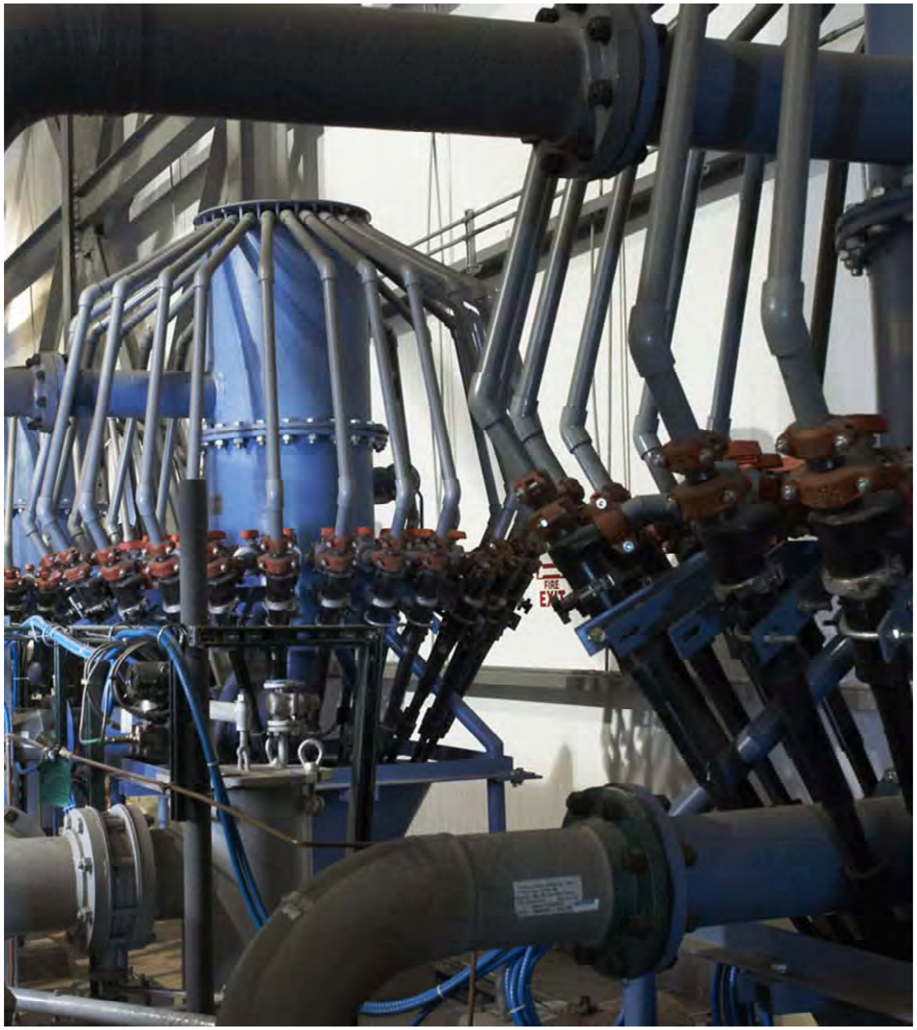
- Load swings and changes in coal are prevalent

- May change loading of species of concern to unit operations
- Can alter performance of AQCS unit operations
- May impact wet FGD purge rate and chemistry

- Prediction and design for control of all scenarios becomes complicated

Sorbents and Additives for MATS vs. ELG

- Particle size distribution is important
- Fine solids may report to waste water, counting towards total limits
- When exiting with the solids, leachability may be important



Additives for MATS vs. ELG

Halide Additives to Oxidize Mercury and Reduce Reemission

May impact wet FGD system chemistry forcing more metals to the aqueous phase

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Upstream Wastewater Treatment

- Case Study: B&W customer experienced rapid SCR catalyst deactivation
- Gas-phase P might be poisoning catalyst (PRB Fuel ~1% P in ash)
- Evaluation of additive (Mitagent™) impact on boiler performance
- Technical feasibility of injection
- Short-term testing /long-term testing
- Multiple foreign and domestic patents pending
- This is a recent B&W development

Combustion and Combustion Additives

- Combustion Effects
  - LOI/UBC – excess carbon can adsorb Hg, resulting in less Hg in the FGD wastewater

- Refined coal
  - Hg
    - Hg emissions are reduced through oxidation and capture in WFGD, but results in greater concentration in wastewater
  - As
    - Calcium in the product binds As in solid form, so it doesn't get to the wastewater
  - Se
    - No effect

Combustion Additive

- Combustion additives with catalytic impact in flue gas such as Mitagent™
  - Hg
    - Positive effect on Hg capture due to increased oxidation
    - Reduces halogen required, so halogen is reduced in wastewater
  - As
    - No effect
  - Se
    - Reduces Se in gas, likely results in less in wastewater

Effect of Combustion Additive on Hg Oxidation

PRB unit with ESP

Br Addition Rate (ppm dry)	% Oxidized Hg w/out Mitagent	% Oxidized Hg w/ Mitagent
0	37	38
35	Not Tested	56
60	47	75
100	63	84

***Leads to greater Hg capture**

Effect of Combustion Additive on Emissions

PRB unit with SCR, ESP, CDS, FF

Additive Injection Rate	Gas phase selenium lb/Mbtu	Gas phase arsenic lb/MBtu
Baseline	3.95* 10 E -6	2.32 *10 E -6
100 ppm of $CaBr_2$ solution	4.91 * 10 E -6	2.20 * 10 E -6
30 lb/hr Mitagent + 70 lb/hr S-SORB III+ 100 ppm of $CaBr_2$ solution	3.69 * 10 E -6	1.76 *10 E -6

- * Reduces gas phase Se

Options for ORP Control

System Impact	• Integrated Control & System Optimization
Fine Adjustment	• Local WFGD Tuning
Additives	• Chemical Additive Addition
?	• Other

Environmental Optimizer Program

Bias control program to optimize and integrate the air quality control system (AQCS) chain

- Help systems respond to unsteady state and/or non design operation
- Ability to provide a feed forward and feedback controls for the AQCS train
- Integration of individual AQCS equipment responses
- Preparing for full-scale field trial in 2015

1. **Reduce power**

   Lower parasitic power for improved plant efficiency

2. **Reduce chemical costs**

   Mercury control additive, DSI/PAC, waste water treatment costs

3. **ORP Control**

   Stable chemistry for treatment, lowered risk for ELG, mitigation of bio-reactor size

Stable chemistry for ELG and MATS

Questions

Thank you