REINHOLD ENVIRONMENTAL Ltd.

# 2014 Wastewater-Ash Round Table & Expo Presentation

September 22, 2014, in Birmingham, AL / Hosted by Southern Company

# FGD Chemistry Optimization

**September 22, 2014**

**Shannon R. Brown,**
*AQCS Engineer*

# *Overview*

- Wet FGD Waste Water
- Waste Water Characterization
- Oxidation Reduction Potential
- Trace Metal Impacts
- Alkalinity & Oxidizer Concentration
- System Impacts, Control, & Optimization

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# Nominal Flowrates and Bulk Properties of Wastewater Streams in a Power Plant*

| Water Source | Normalized Flow Rate (gpd/MW) | TSS (mg/L) | TDS (mg/L) |
|---|---|---|---|
| WFGD Blowdown | 300 | 10,000 | 30,000 |
| Boiler Blowdown | 200 | 5 | 50 |
| Cooling Tower Blowdown | 3,600 | 20 | 2,000 |
| Ash Pond Effluent | 5,000 | 10 | 1,000 |

*As reported by the EPA in 2009 report, DOE/NETL in 2010 report

# WFGD Effluent Composition

| *Nominal WFGD Effluent Stream Composition* | |
|---|---|
| **Species** | **mg/L** |
| **Boron** | **300** |
| **Calcium** | **5,000** |
| **Magnesium** | **2,000** |
| **Sodium** | **1,000** |
| **Chloride** | **11,000** |
| **Sulfate** | **5,000** |
| **TDS** | **25,000** |

**Typical WFGD Blowdown Streams Pose Challenges:**

- **High in Halogens**
- **High TDS**
- **Selenite (IV)/Selenate (VI)**
- **Mercury**
- **Boron**

**Significant variation exists with WFGD absorber slurry samples**

- **TDS std. dev. of 15,000 mg/L**

*As reported by the EPA in October 2009 report

# *Gypsum Supersaturation – ART Slurry Filtrate*

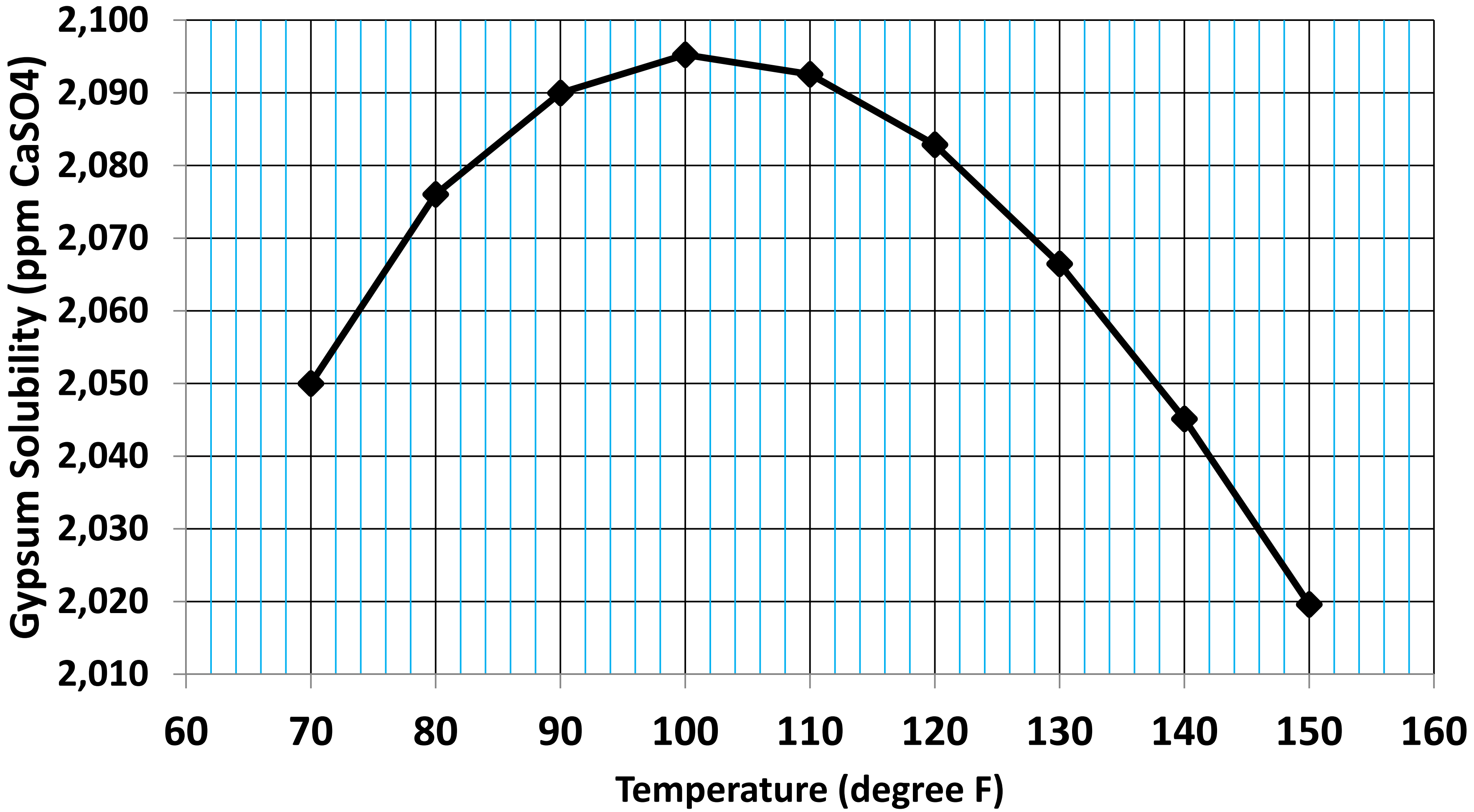
- **Saturation (S) – Amount of gypsum that can dissolve in a given volume of water at a specified temperature (~ 2.1 g/L)**

- **Supersaturation (SS) – Amount of gypsum that can dissolve in a given volume of ART slurry filtrate at a specified temperature (~ $55^{o}$ C), greater than saturation due to the operating conditions of the WFGD system**

- **Relative Saturation (RS) – Relative measure of super-saturation (RS > 1) existing in the ART slurry filtrate**

$$RS = SS/S \quad \text{and also, } RS = [Ca^{+2}] \bullet [SO_4^{2-}] \bullet [H_2O]^2 / K_{sp\ gypsum}$$

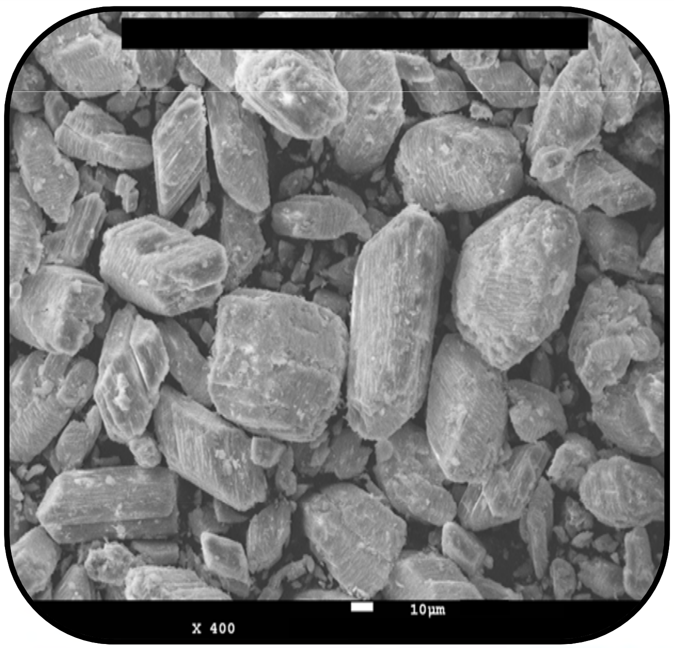
# *Gypsum Solubility as a Function of Temperature*

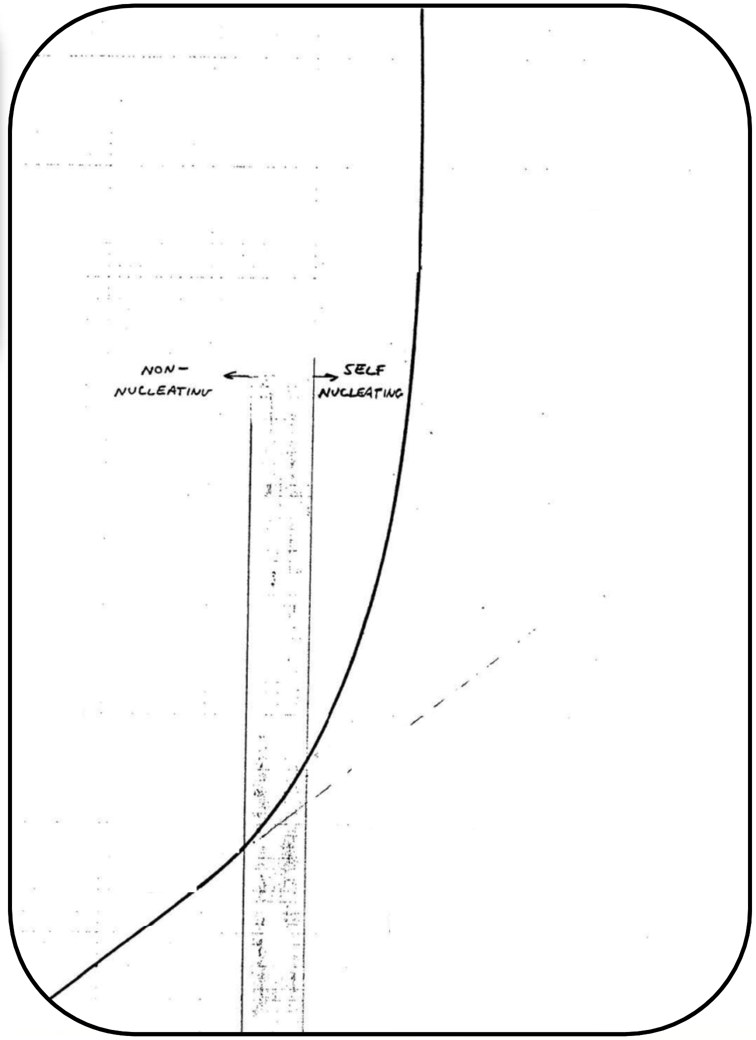


# *Relative Saturation of Gypsum Crystals*

**Super-saturation**

- **Secondary nucleation (Non)**
  - **Min TSS value**
- **Primary nucleation (Self)**
  - **Max TSS value**
- **Ratio of Calcium to Sulfate concentrations**



# *Gypsum Relative Saturation (RS) and ART Scaling*

- RS Affects the Rate of Gypsum Crystallization
- Higher RS Increases the Rate of Crystallization
- Faster Rate of Crystallization Increases Potential for Nucleation and Smaller Gypsum Crystals
- Nucleation Increases Potential for Scaling and/or Deposition

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# *WFGD Chemistry: Characterization*

## Online Measurement

- Can be fed into process controls
- Real time

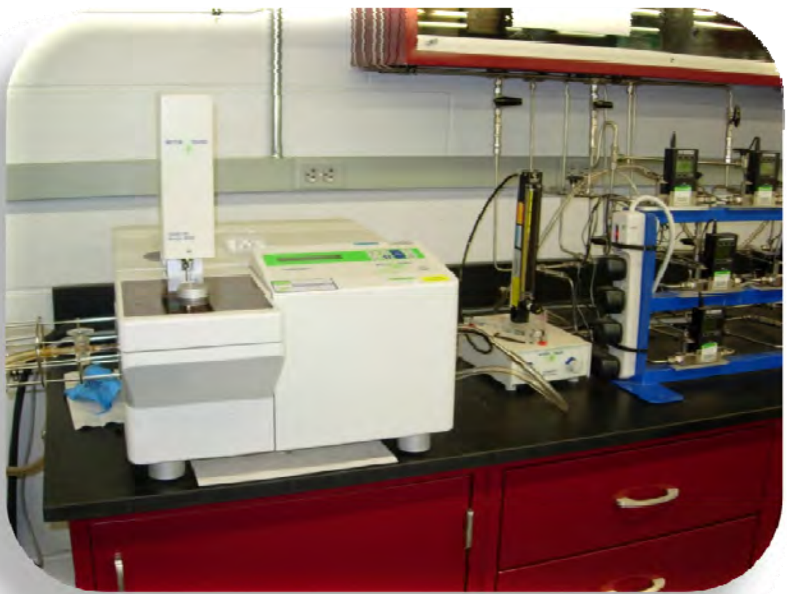
## Grab Samples

- Measure more species
- Significant time lag from time of sampling

# *Characterization*

- Online process measurement affords the means to trend, predict and control process chemistry
  - Flowrate
  - Density
  - pH
  - ORP
- Ideally, measure pH and ORP at process effluent and waste water technology influent points
- As many WFGD systems are kinetically controlled, reactions may continue downstream of the effluent point

# *Notes about WFGD Characterization*



- **Perform routine calibration and verification of online monitoring instrumentation**
- **Use proper sampling techniques for grab samples**
  - **Glass sample containers needed for mercury analysis**
  - **Some analyses are time sensitive**
- **Validate laboratories**
  - **Due diligence in making sure results reported are accurate and repeatable**
  - **Certification**

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# *What is ORP?*

## Oxidation Reduction Potential (ORP)

- **A single voltage measurement against a reference electrode**
  - **Measurement technique similar to pH**
  - **Can be monitored on-line**
- **Measures tendency for a solution to donate or accept electrons**
- **The more positive the voltage, the more strongly a solution would oxidize (attract electrons from) other sources**
  - **Oxidizers accept electrons, reducers lose electrons.**
- **ORP can be negative**
  - **Indicator of Problem with Oxidation – Check Ox Air Compressors**

# Oxidation Reduction Potential

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln(Q)$$

where:

$E_{cell} = electrochemical\ potential\ of\ the\ cell$

$E^0_{cell} = standard\ electrode\ potential$

$n = number\ of\ moles\ of\ electrons\ transferred$

$F = Faraday\ constant$

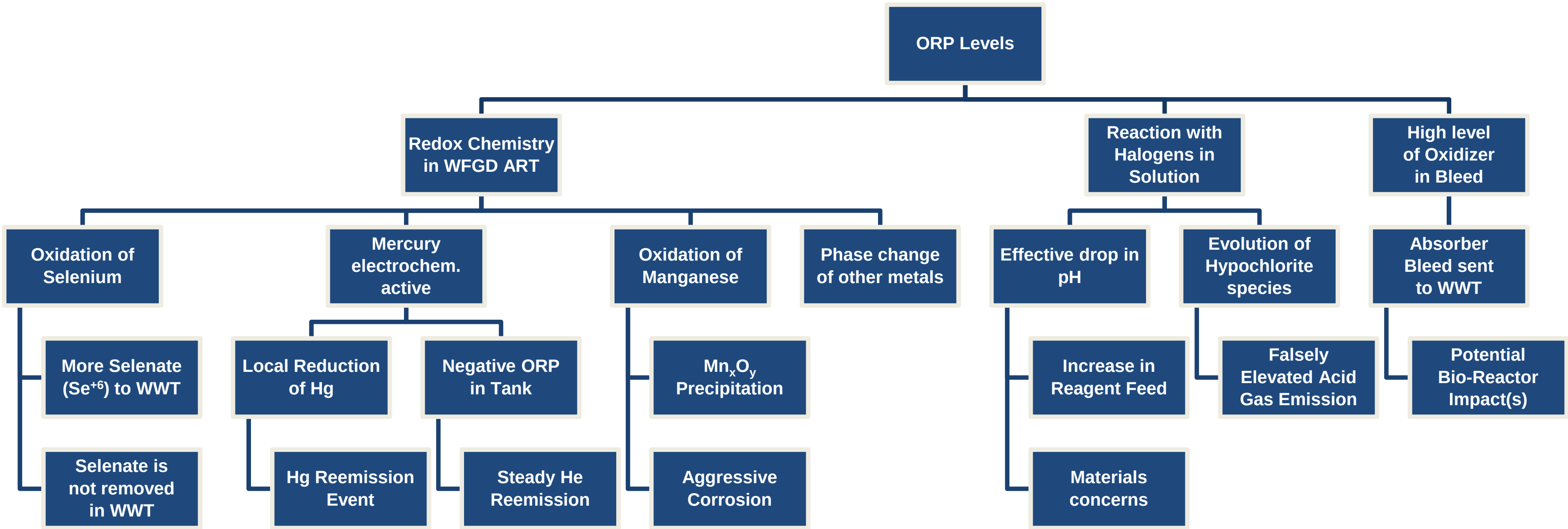
$Q = reaction\ quotient$

$$E_{cell} \propto ln\left[\frac{oxidized\ material}{reduced\ material}\right]$$

where:

$E_{cell} = electrochemical\ potential\ of\ the\ cell$

# *Impacts of ORP on WFGD Blowdown*



# *Contributors to ORP*

## Flue Gas Composition

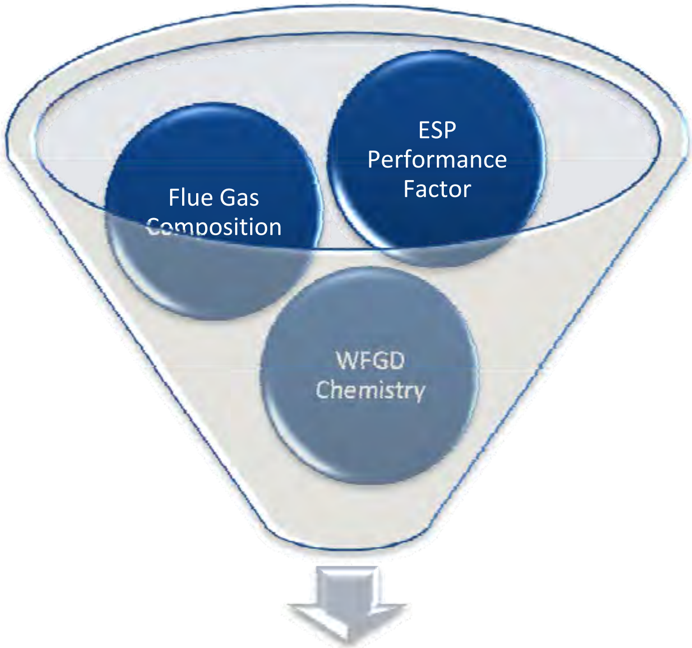
- Boiler Load/Gas Flow
- Coal Blends

## ESP Performance Factor

- Variability of ESP responses to swinging load

## Wet FGD Chemistry

- Ratio of dissolved species
- Purge Rate




**ORP Risk Factor**

# LSFO WFGD ORP Ranges

**<0 mV**
- Reducing environment
- Not found in LSFO systems under normal conditions

**100-350 mV**
- Normal operating range
- Somewhat oxidative slurry

**350-450 mV**
- Transitional Range
- Oxidative slurry
- Few sites measured in this range

**>450 mV**
- High ORP Conditions
- Strongly oxidative slurry

For operating WFGD Units, ±50 mV is common.

# *Why is ORP important?*

- **High ORP Excursions can Disable Bioreactors**
- **High ORP can Promote Corrosion via manganese oxide deposition**
- **Oxidation state often controls solubility and phase partitioning of many species, particularly dissolved metals – ORP can affect ease of treatment in Waste Treatment System**
- **ORP may affect Reagent Use in Wastewater Treatment**

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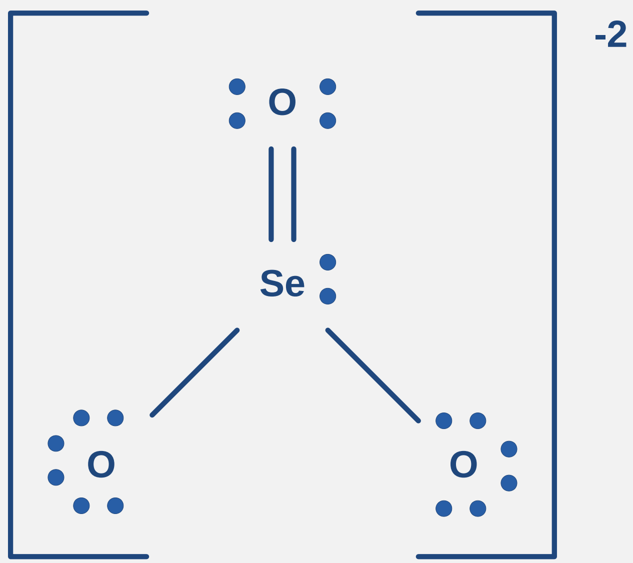
# Metals Speciation and ORP in WFGD Absorber Slurry and Effluent

| 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 |

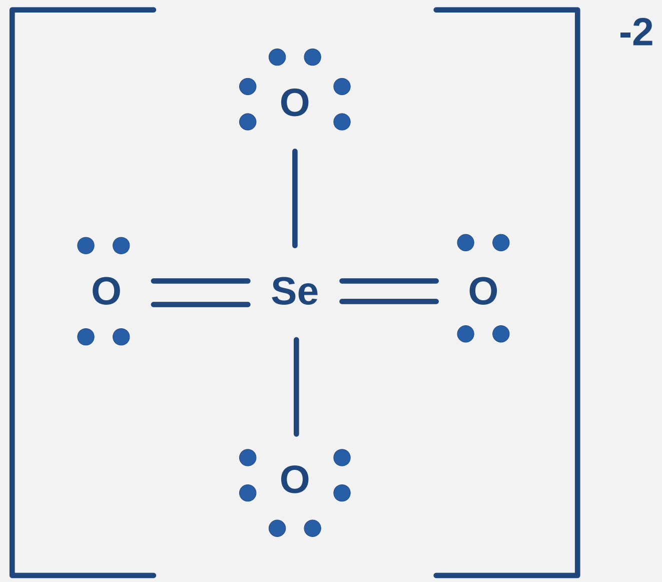
# Selenium Chemistry

## Selenite




- Selenium in +4 oxidation state
- $Se^0 \rightarrow Se^{+4} + 4e^-$

## Selenate




- Selenium in +6 oxidation state
- $Se^0 \rightarrow Se^{+6} + 6e^-$

# *Selenium*

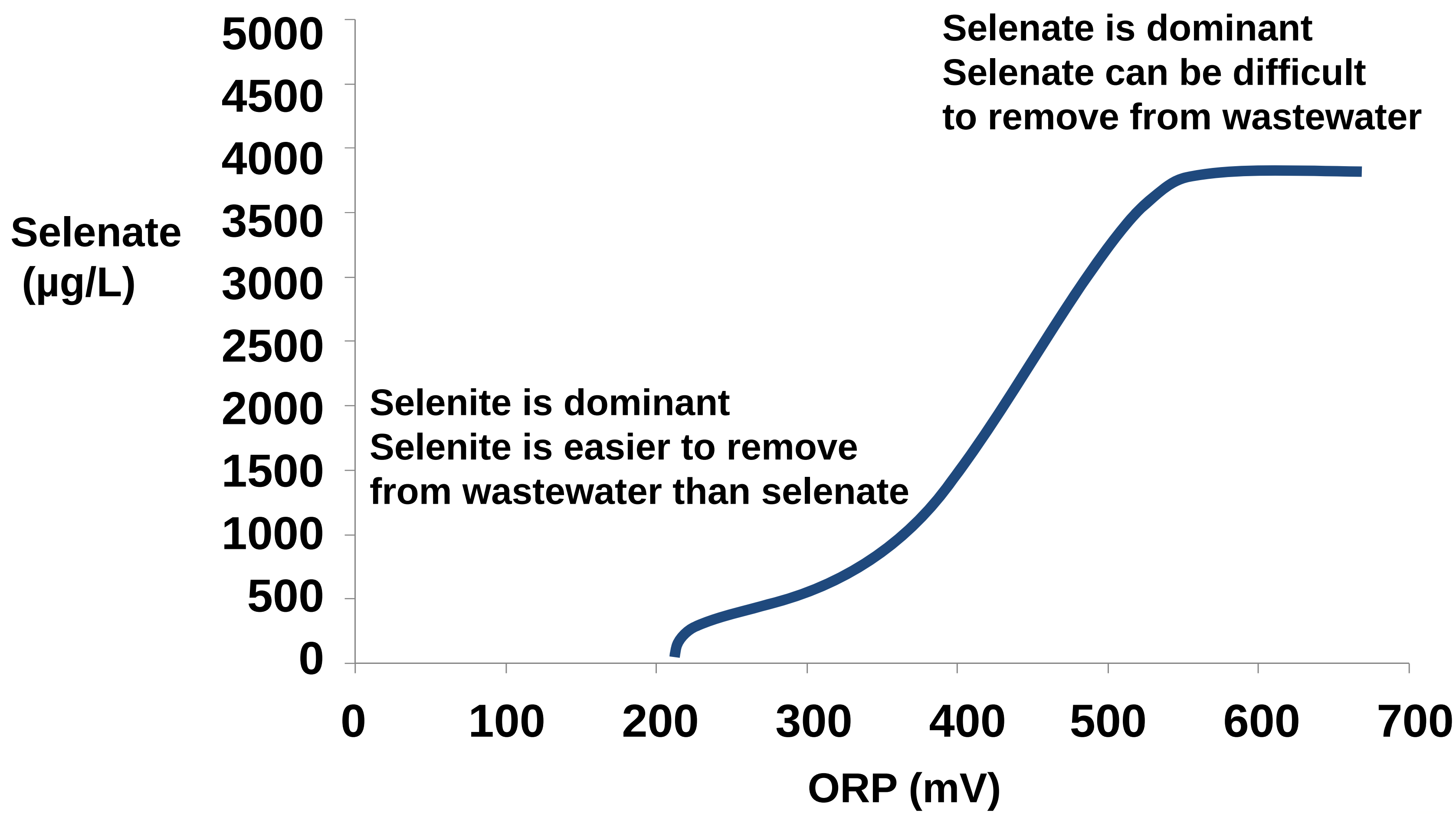
## In a ORP environment < 300 mV

- Selenite, $Se^{+4}$ will be the dominate form
- Selenium removal is optimal for waste water treatment
- Solid phase

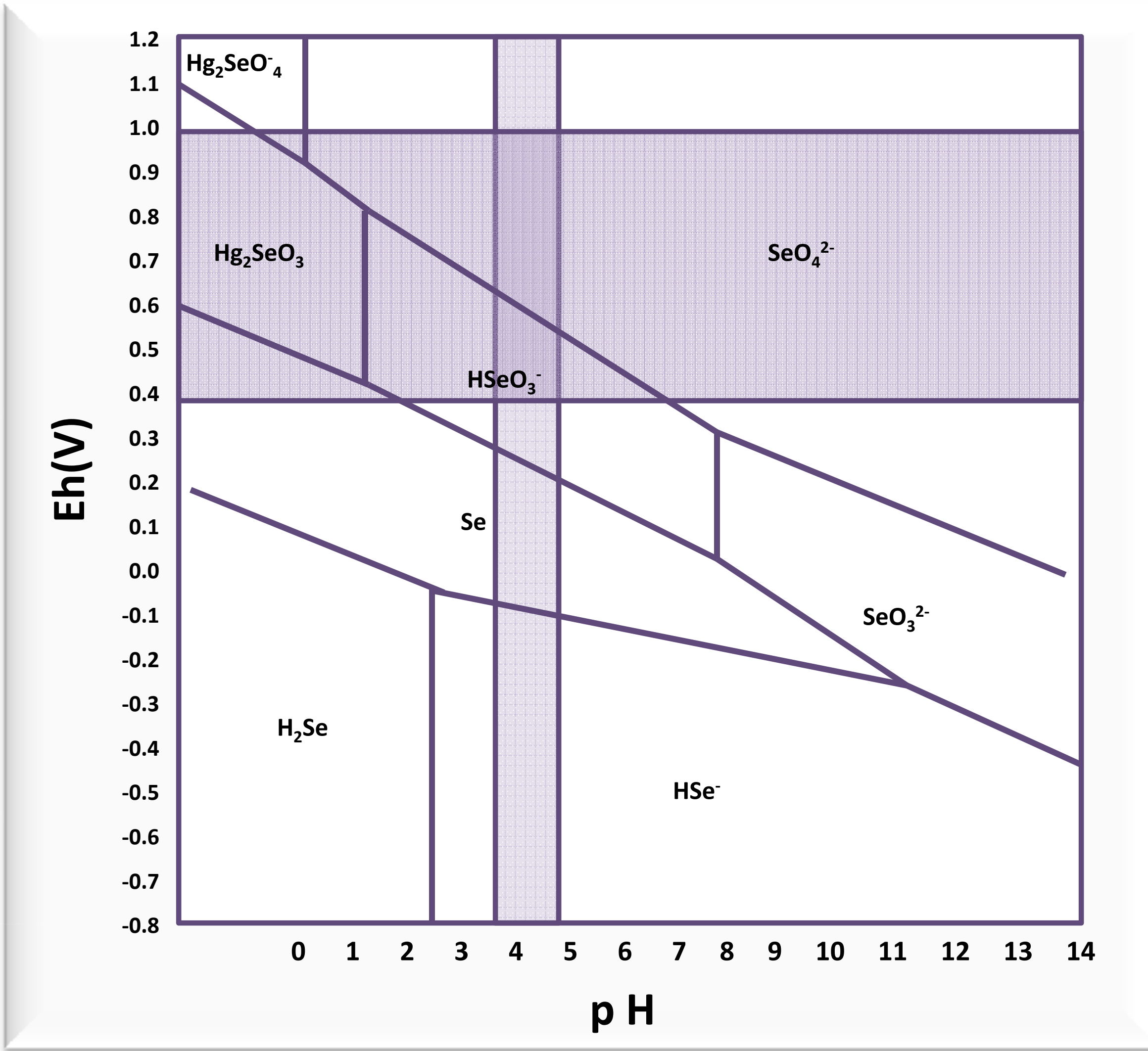
## In a ORP environment > 300 mV

- Selenate, $Se^{+6}$ will be dominate form
- Selenium will pass through wet-lands
- Dissolved phase
- Difficult to remove by chemical precipitation

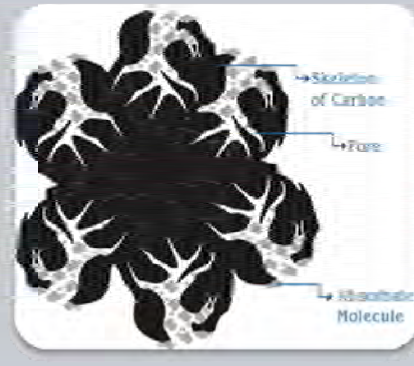
# Selenate vs. ORP in Wet FGD Absorber Recirculation Tank (ART) Slurry



# Phase Partitioning– Selenium



# *Forms of Mercury*




## $Hg^0$

- Elemental Mercury
- Vapor
- Sparingly Soluble

## $Hg^{+2}$

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

## $Hg^P$

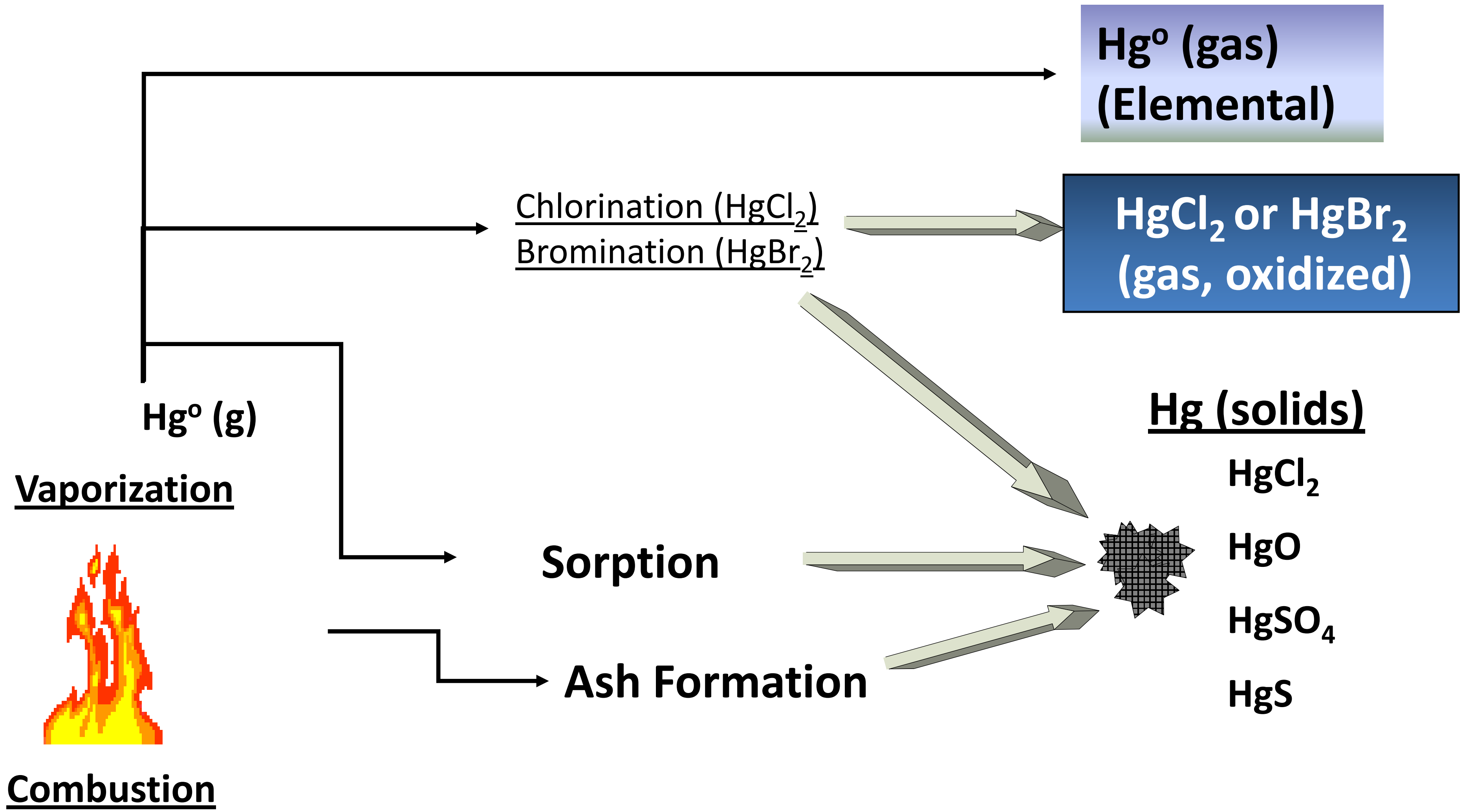
- Particle Bound Mercury
- Mercury is Adsorbed to the Particle

## HgS

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

$Hg^0$ Image : http://www.newmoa.org/prevention/mercury/projects/legacy/religious.cfm, Accessed: 17 Sept 2013
$Hg^{+2}$ image : http://www.enn.com/pollution/article/43796 Accessed 17 September 2013
PAC Image: Jankura, Bryan. “Wygen 1 2006 Mercury Control Project: Background, Equipment and Test Results.” 5 April 2007.
HgS image: http://www.dartmouth.edu/~rpsmith/Heavy_Metals.html Accessed 18 September 2013

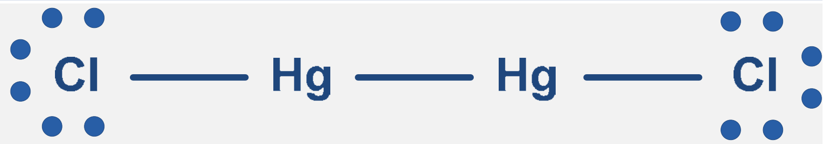
# *Fate of Hg in Coal Combustion*



# *Mercury Chemistry*

## First Ionization

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



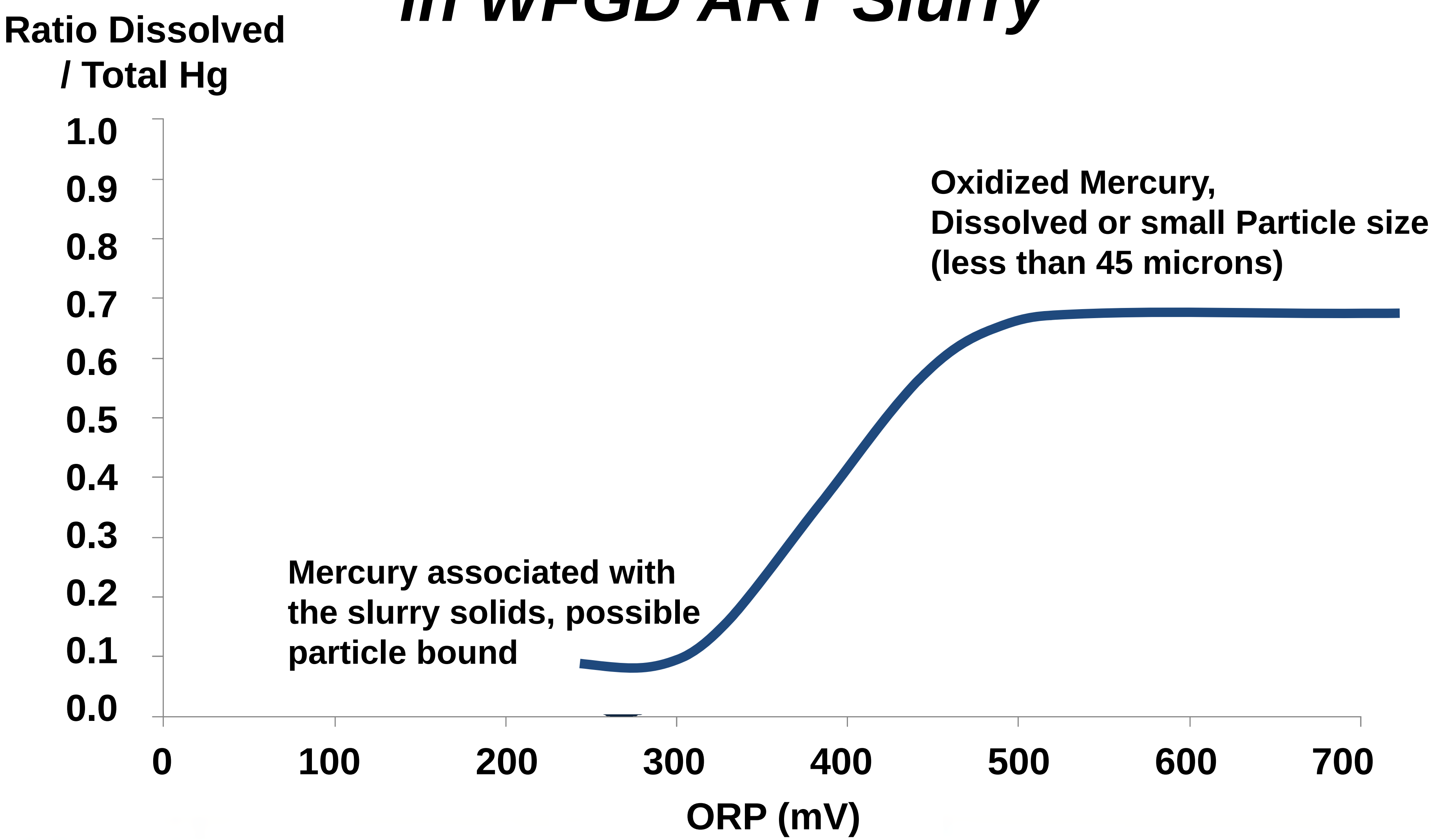

- $HgCl$, $Hg_2Cl_2$
- Mercury in +1 oxidation state
- Less Stable

## Second Ionization

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


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

# *Dissolved Mercury vs. ORP in WFGD ART Slurry*



# *Mercury Re-emission in WFGD*

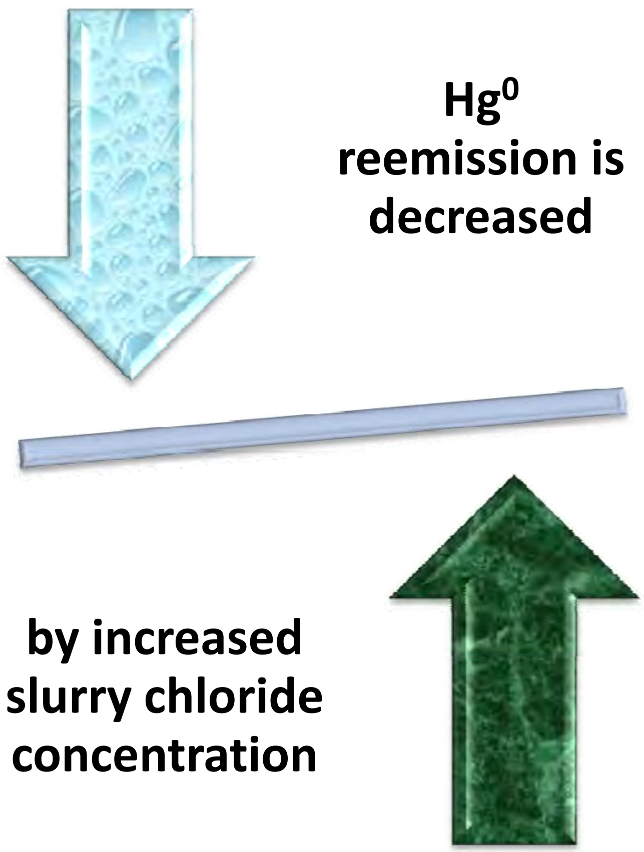
***Overall Reactions:***

1. $HgCl_2 + HSO_3^- + H_2O \rightarrow Hg^o\uparrow + SO_4^{2-} + 3H^+ + 2Cl^-$
2. $2Me^{2+} + Hg^{2+} \rightarrow Hg^o\uparrow + 2Me^{3+}$

# *Mercury Re-emission*

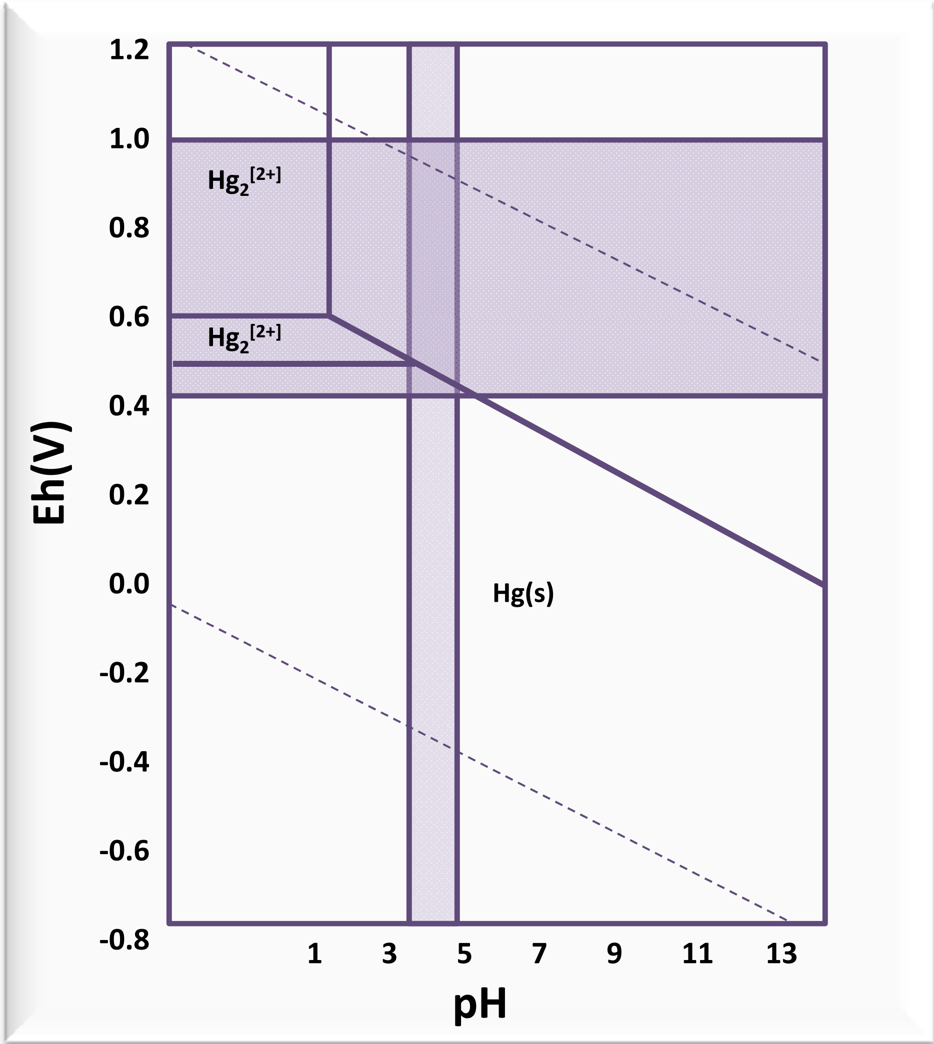
- ORP effects mercury emission in WFGD absorbers
- Strongly reducing conditions within the scrubber will cause $Hg^{+2}$ to be reduced to $Hg^{0}$ and re-emitted
- Mercury is a very electrochemically active species
- Transitions in ORP have been implicated in Hg re-emission events

# *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 the +2 oxidation state**
- **Impact of increased bromide concentration is uncertain**

# Phase Partitioning– Mercury



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# *High ORP & pH Drop*

- High ORP results from a high concentration of strong oxidizers
- Reactions in wastewater stream continue while in transit to treatment
- Buffering capacity of the solids is removed
- Strong oxidizers will react with the halogens in solution
  - Liberating halogen containing gas
  - Releasing hydronium ions in solution
  - After buffering solids are removed, pH could decrease downstream

# *The Relationship Between ORP and Strong Oxidizer Concentration*

| Total Oxidizer Titration Results | | |
|---|---|---|
| Unit | ORP Profile | Oxidizer (ppm) |
| 1 | High ORP | 1680 |
| 2 | High ORP | 1592 |
| 3 | High ORP | 1574 |
| 4 | High ORP | 1571 |
| 5 | Low ORP | 227 |
| 6 | Low ORP | 169 |
| 7 | Low ORP | 50 |
| 8 | Low ORP | 29 |
| 9 | Low ORP | 27 |
| 10 | Low ORP | 19 |
| 11 | Low ORP | 10 |
| 12 | Low ORP | <2 |

# Strength of Oxidizers

- Fluorine
- Atomic Oxygen
- Ozone
- Persulfate
- Hyphochlorous acid
- Chlorine
- Bromine

# $S_2O_8^{-2}$ and pH Drop

$$S_2O_8^{-2} + 2Cl^- + 2Ca^{+2} \rightarrow 2CaSO_4 + Cl_2$$

$$S_2O_8^{-2} + 2Br^- + 2Ca^{+2} \rightarrow 2CaSO_4 + Br_2$$

$$S_2O_8^{-2} + 2I^- + 2Ca^{+2} \rightarrow 2CaSO_4 + I_2$$

**High ORP levels can lead to hypochlorite formation**

$$Cl_2 + H_2O \rightarrow 2H^+ + Cl^- + ClO^-$$

$$Br_2 + H_2O \rightarrow 2H^+ + Br^- + BrO^-$$

$$I_2 + H_2O \rightarrow 2H^+ + I^- + IO^-$$

**pH Drops from Acid Formation**

# Impact Downstream

## Bioreactor and oxidizer

- Strong oxidizer in the effluent stream
- Microbes can be killed

## pH drop with high ORP

- Buffer capability of slurry removed from dewatering
- Low pH may be fed to Wastewater Treatment

$$Cl_2 + H_2O \rightarrow 2H^+ + Cl^- + ClO^-$$

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# *Coal Additives to Alter Chemistry*

- Coal additives, WFGD additives, and other operational parameters affect the mass flow of Hg, As, and Se in the WFGD effluent
- It is possible to reduce the amount of these constituents that require treatment
  - Coal additives lower the gas-phase concentrations of Hg, As, and Se lower concentration in WFGD effluent
  - WFGD additives precipitate Hg and As → lower concentration in WFGD effluent

# *Mercury Emissions Chemistry*

- **In U.S., per MATs rule, Hg emissions will be controlled to 1.2 lb/TBtu (bituminous and subbituminous) and 4.0 lb/TBtu (lignite)**
- **Mercury oxidation and removal is one method**
- **Activated carbon injection (ACI) is most widely used method**
- **Many plants equipped with SCR & FGD rely on these two components for Hg emission control as mercury can be oxidized by SCR and removed by FGD**
- **Ammonia slip negatively affects Hg oxidation by SCR**
- **In absence of SCR, mercury can be oxidized by halogen addition to the coal**

# Bromide Addition for Mercury

- Br addition (as $CaBr_2$ solution) to the coal is an effective method to achieve mercury oxidation for all types of coal
- At combustion temperature, Br added to the coal forms HBr gas
- HBr does not directly participate in Hg oxidation
- HBr undergoes Deacon reaction to form $Br_2$ as follows:
- $4\ HBr + O_2 \rightarrow 2H_2O + 2Br_2$
- $Br_2$ undergoes an oxidation reaction with $Hg^0$ to yield $HgBr_2$ otherwise known as mercury capture by halogen oxidation
- Br addition rate is substantially lower for units with an SCR as compared to units without an SCR

# *Bromide Addition for Mercury*

- **Mercury oxidation in presence of an SCR catalyst occurs more efficiently**
- **For example, 30 to 40 ppm of Br addition to PRB coal typically produces high Hg oxidation in presence of SCR**
- **Without SCR, the addition rate of Br to the coal may be as high as 100 to 150 ppm to obtain similar performance**
- **Br addition may cause BoP impacts, i.e., back-pass fouling and cold-end air heater corrosion**
- **Br addition may lead to Br discharge from plants with WFGDs, and formation of trihalomethanes (THMs) in lakes and streams**

# *Mitagent Additive Benefits for Br Injection*

- **Pilot- and full-scale test data show that Mitagent additive reduces Br addition rates for Hg oxidation by 50 to 60%**
- **Benefits of Br reduction include**
  - **Decrease in corrosion potential**
  - **Decrease in fouling potential**
  - **Decrease in THMs in water**
  - **Reduction in cost**

# WFGD Redox Reactions

**Oxidized Mercury Absorption:**

Oxidized Mercury is Very Soluble

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

**Mercury Reduction:**

S is Oxidized
Hg is Reduced

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

Metal is Oxidized
Hg is Reduced

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

**Emission of Elemental Mercury:**

Elemental Mercury Above Saturation will Leave the Slurry

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

# Sulfide Reactions

**NaHS Dissociation:**

NaHS forms $H_2S$ upon contact with acid

$$H_2S(g) \leftrightharpoons H_2S(aq)$$
$$H_2S(aq) \leftrightharpoons H^+ + HS^-$$

**Mercury Sulfide Precipitation:**

Mercury Remains in the +2 state
Insoluble precipitate formed

$$HS^- + Hg^{+2} \rightarrow HgS\downarrow + H^+$$

# *Sulfide Addition*

- Added to absorber slurry
  - Evolves $H_2S$ gas on low pH
  - Creates an insoluble product (HgS) with mercury
- HgS (cinnabar) is very stable
  - The reaction is considered irreversible under WFGD conditions
- HgS will exit the system as a solid
  - with the gypsum
  - with the wastewater stream

$$HS^{-} + Hg^{2+} \rightarrow HgS\downarrow + H^{+}$$


HgS image: http://www.dartmouth.edu/~rpsmith/Heavy_Metals.html Accessed 18 September 2013

# Known Sulfide Reactions

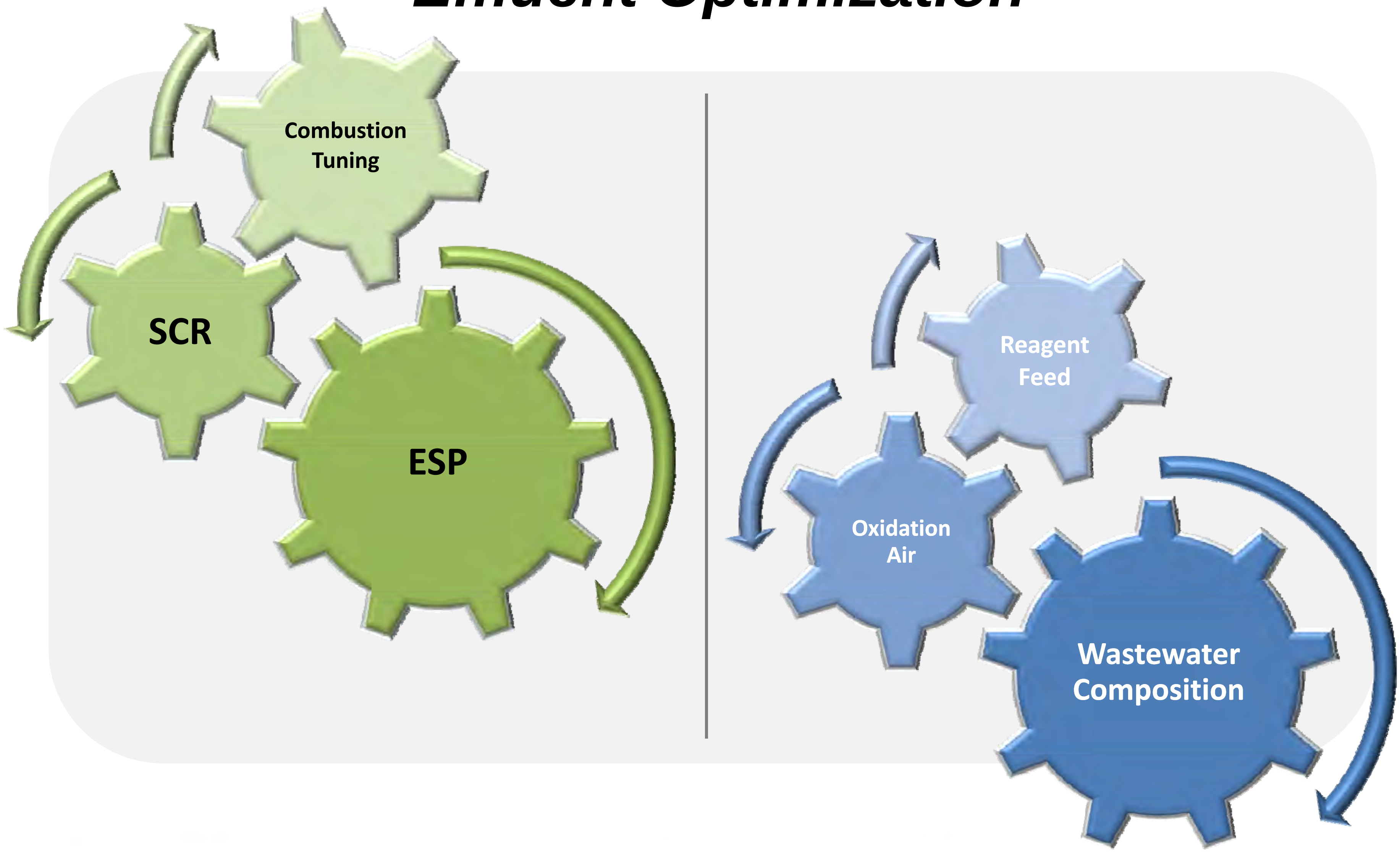
**NaHS Dissociation:**

$$H_2S(g) \leftrightharpoons H_2S(aq)$$
$$H_2S(aq) \leftrightharpoons H^+ + HS^-$$

**Mercury Sulfide Precipitation:**

$$HS^- + Hg^{+2} \rightarrow HgS\downarrow + H^+$$

# Effluent Optimization



# *Questions*

# *Thank you*