# REINHOLD ENVIRONMENTAL Ltd.


# 2011 APC Round Table
# & Expo Presentation

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# ORP in WFGD Systems:
## Impacts on Corrosion and Trace Metals

*July 12, 2011*



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# *Overview*

- **What is ORP?**
- **ORP & Phase Partitioning of Chemical Species**
- **WFGD Alloy Corrosion**
- **Process Chemistry & Wastewater Treatment**
- **Process Control Parameters**
- **Conclusions**

# What is ORP?

# *What is ORP?*

- **Oxidation Reduction Potential (ORP)**
  - **A single voltage measurement against a reference electrode**
  - **The strength of oxidizers and reducers in a solution in relation to their respective concentration**
  - **The more positive the voltage, the more strongly a solution would oxidize (attract electrons from) other sources**
    - **Oxidizers accept electrons, reducers lose electrons.**
  - **Oxidizing slurry may oxidize its constituents**

# *What is ORP?*

- **A wide range of ORP is observed in filtrate samples from operating units**
- **ORP can be negative**
- **Measurement technique similar to pH**
- **Can be monitored on-line**

# ORP & Phase Partitioning of Chemical Species

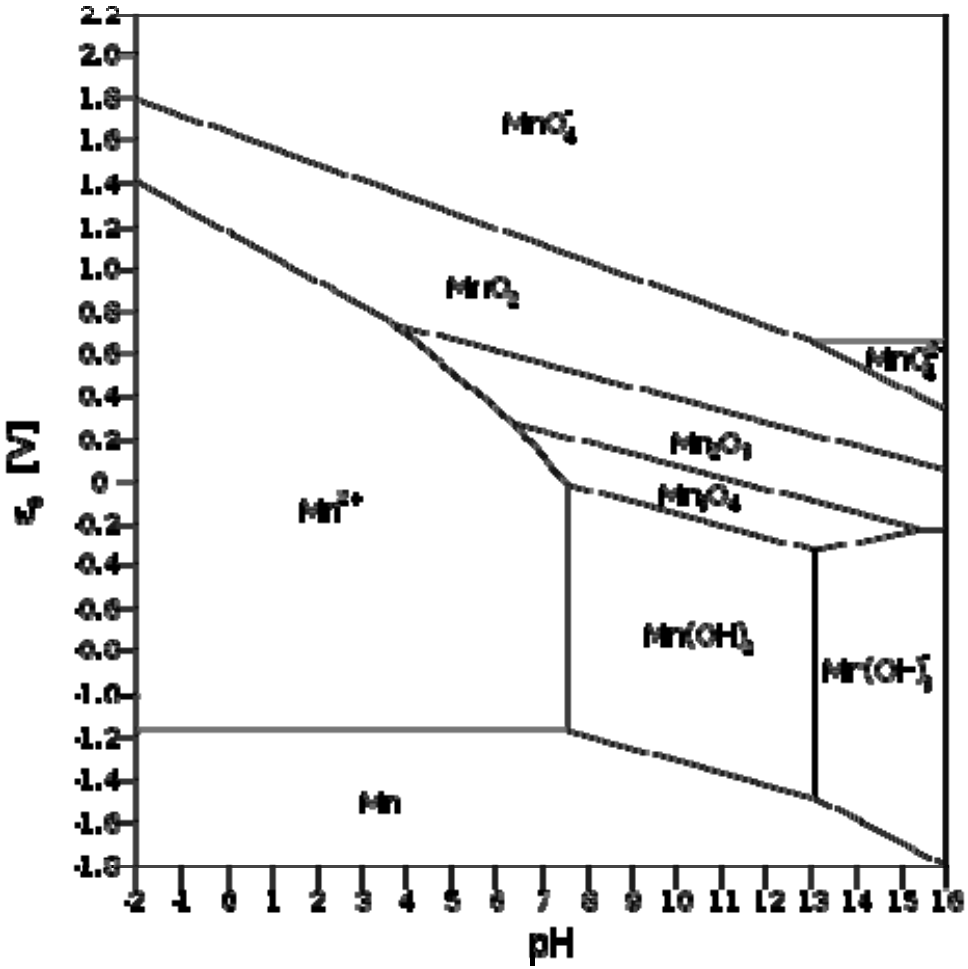
# *ORP & Phase Partitioning of Chemical Species*

## ORP will affect the oxidation state of the slurry constituents

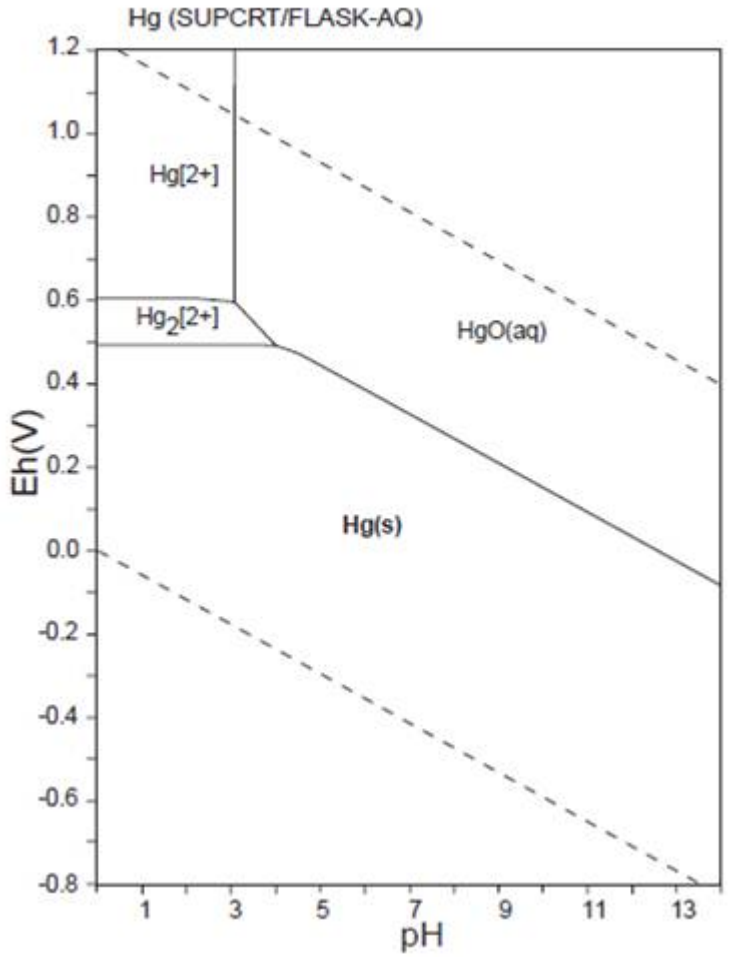
- Oxidation state often controls solubility
- ORP will impact phase partitioning of many species

| *ORP* | *Mercury* | *Selenium* | *Manganese* |
|---|---|---|---|
| High | $Hg^{+2}$ Soluble | $Se^{+6}$ Soluble | $Mn^{+4}\downarrow$ Precipitate |
| Low | $Hg^{+2}$ Soluble | $Se^{+4}\downarrow$ Precipitate | $Mn^{+2}$ Soluble |
| Very Low | $Hg^{0}\uparrow$ Vaporous | $Se^{+4}\downarrow$ Precipitate | $Mn^{+2}$ Soluble |

# ORP & Phase Partitioning of Chemical Species



# ORP & Phase Partitioning of Chemical Species



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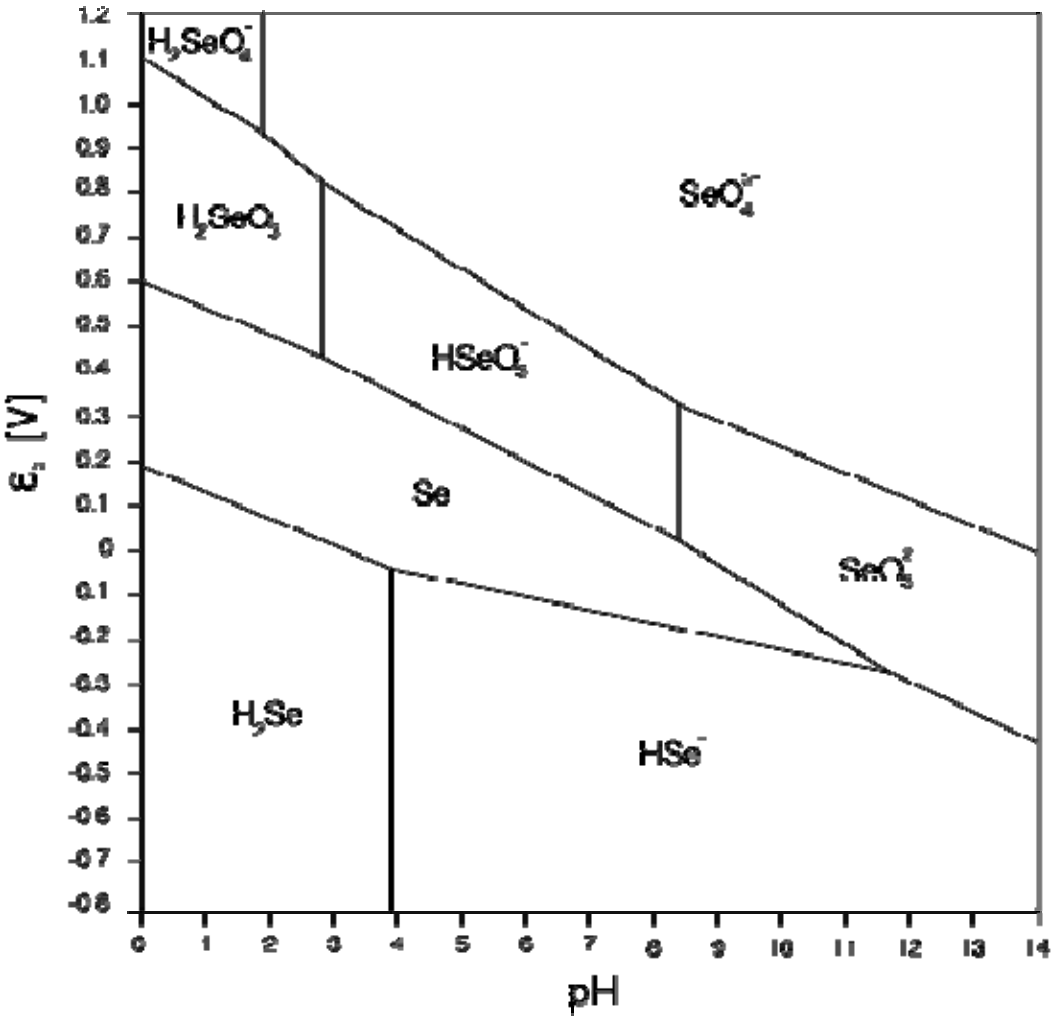


# WFGD Alloy Corrosion

# *High ORP Aggressive Corrosion Mechanism*

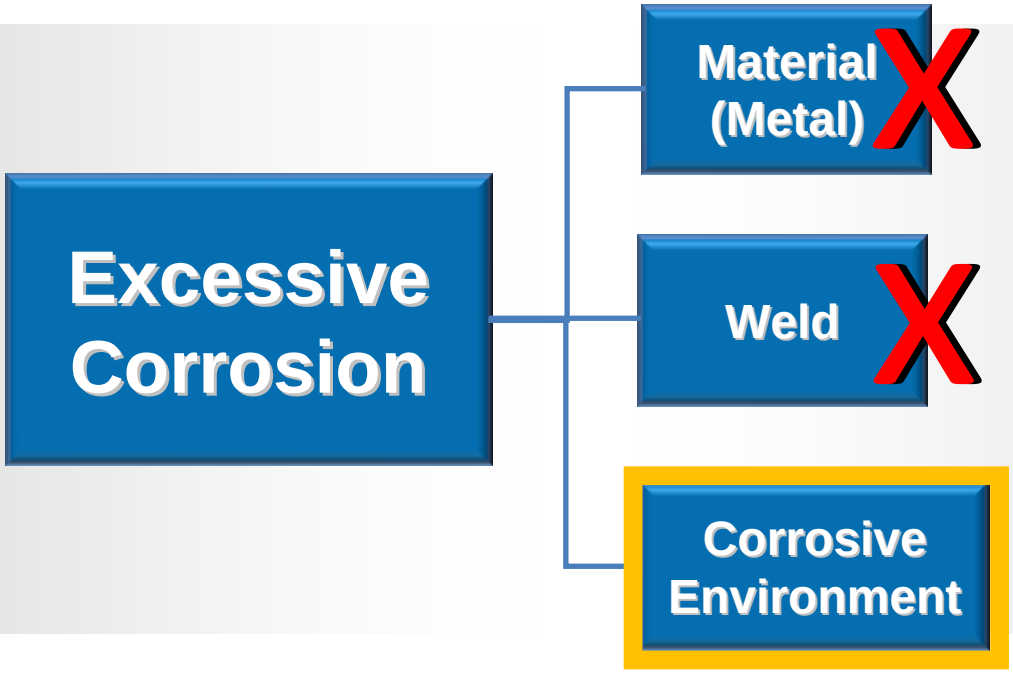
## *Observations*

- **Widespread deep corrosion observed on floor and walls**
- **Attack was only slightly worse along HAZ than at locations distant from the welds**
- **Alloy 625 weld metal was not attacked**
- **Attack was not observed in areas where there was no deposit**
- **Attack severity decreased with elevation along the walls**

# Aggressive ART Shell Corrosion

# *Aggressive Corrosion of ART Vertical Weld Seam*

# *Aggressive Corrosion - Top Level Cause Map*



# *High ORP Aggressive Corrosion Mechanism*

## *Initial Evaluations*

- **Slurry & process stream samples taken**
  - **Limestone slurry**
  - **Service water**
  - **Reclaim water**
  - **Absorber slurry**
- **Standard analyses did not yield obvious differences between the scrubber solutions**
- **Initial sampling from 8 units**

  **More plants sampled over the course of the project**

# High ORP Aggressive Corrosion Mechanism

## Initial Evaluations

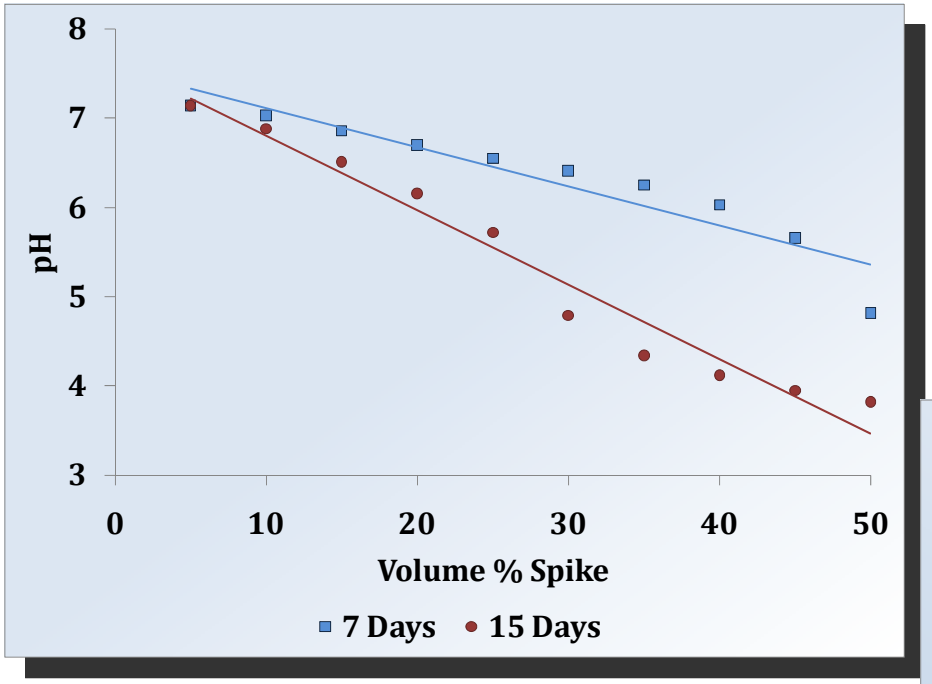
- However, slurry filtrate from units with aggressive corrosion behaved differently
  - Mn rich precipitate formation
  - pH drop
  - ORP increase
  - Gas evolution
- Spiking study

# Composition of Filtered Solids

*(due to Spontaneous Precipitation in the Filtrates)*

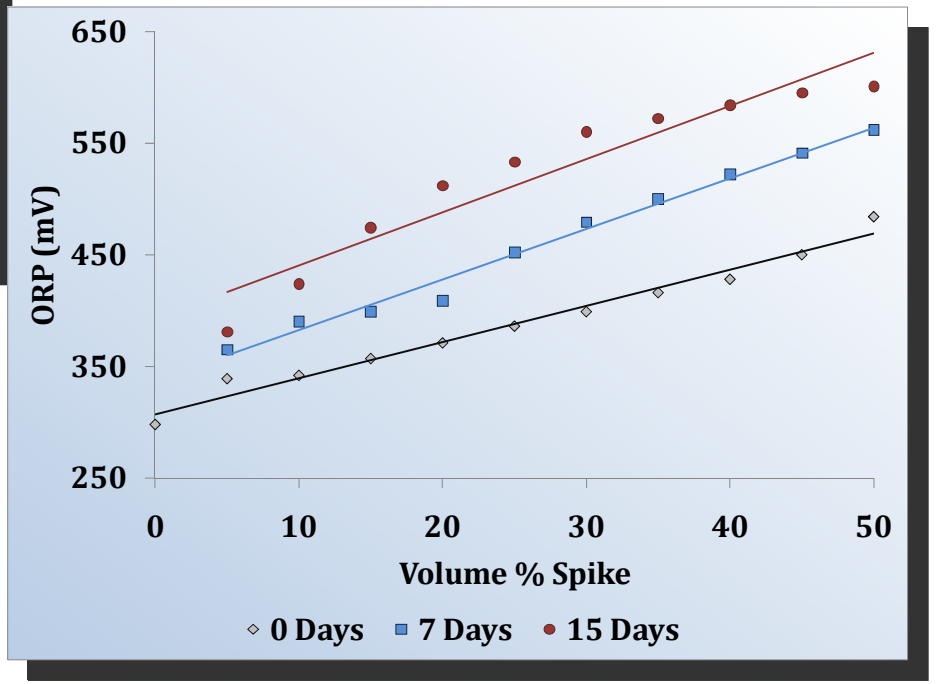
| EDS Analysis | | | | | | |
|---|---|---|---|---|---|---|
| Wt% | Corrosion | | No Corrosion | | | |
| O | 47.83 | 47.72 | 55.14 | 54.63 | 52.80 | 67.47 |
| F | 1.89 | 1.17 | 0.59 | 1.62 | 2.72 | 2.41 |
| Na | <0.01 | <0.01 | 0.35 | 2.04 | <0.01 | 0.34 |
| Mg | 6.02 | 6.05 | 18.86 | 10.37 | 0.67 | 6.80 |
| Al | 3.75 | 3.72 | 0.20 | 1.45 | 13.60 | 1.81 |
| Si | 1.31 | 1.20 | 0.93 | 2.87 | 21.77 | 3.19 |
| S | 5.45 | 6.03 | 21.68 | 7.45 | 0.52 | 3.68 |
| Cl | 3.10 | 3.19 | 0.24 | 12.61 | 1.54 | 8.66 |
| K | 0.26 | 0.17 | 0.07 | 0.78 | 0.20 | 0.55 |
| Ca | 2.31 | 2.71 | 1.23 | 3.00 | 5.09 | 1.82 |
| Mn | 23.34 | 23.78 | 0.06 | 0.31 | 0.09 | 0.27 |
| Fe | 0.83 | 0.73 | 0.10 | 1.30 | 0.23 | 0.87 |
| Ni | 0.53 | 0.50 | 0.10 | 0.36 | 0.25 | 0.46 |
| Cu | 0.61 | 0.59 | 0.24 | 0.69 | 0.32 | 1.06 |
| Zn | 2.13 | 2.45 | 0.21 | 0.52 | 0.19 | 0.60 |

# *Spiking Study – pH & ORP Change*




**pH ↓as spike↑**
**pH ↓as time ↑**
**∴ the reaction decreases pH**

**ORP ↑ as spike ↑**
**ORP ↑ as time ↑**
**∴ the Rxn increases ORP**



# *Spiking Studies - Conclusions*

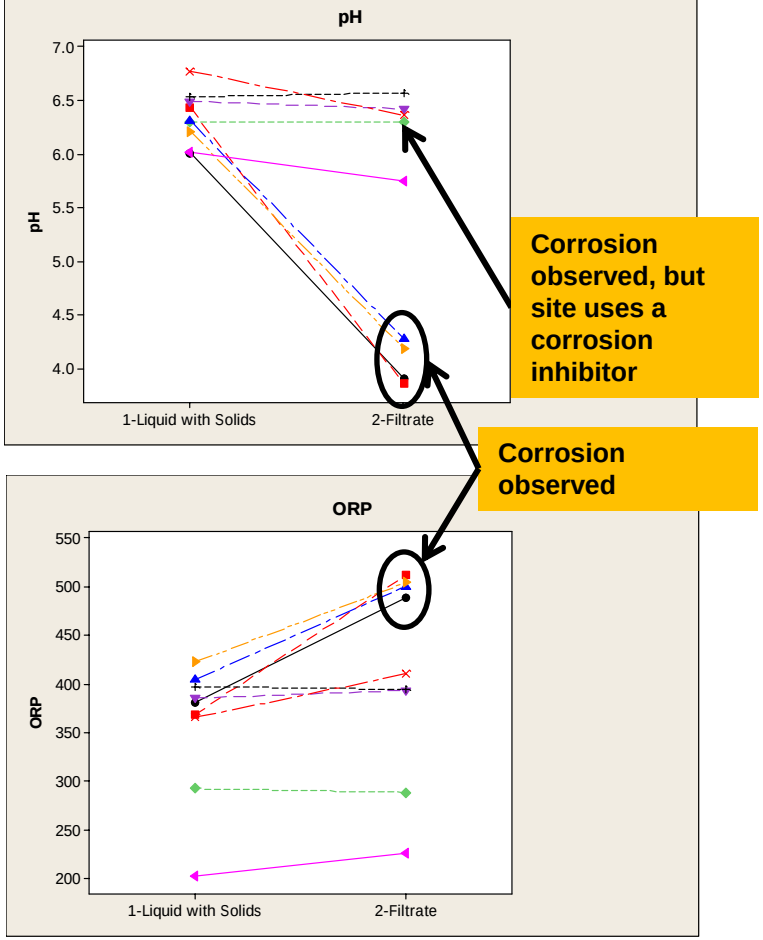
- **The reaction which causes $MnO_X$ to precipitate is accompanied by a reduction in pH and an increase in ORP**
- **The reaction produces a volatile species when $MnO_X$ is formed**
- **The active agent in the filtrate from the corroded unit is stable (i.e. still present after sitting >1 yr in the lab)**
- **Very little of the active ingredient in filtrate from the corroded unit is required to cause precipitation**
- **The reaction is accelerated when the sample is heated to 80$^oC$**

# High ORP Aggressive Corrosion Mechanism

## Evaluations – Removing Solids & Heating

***Slurry Testing: pH and ORP Data***

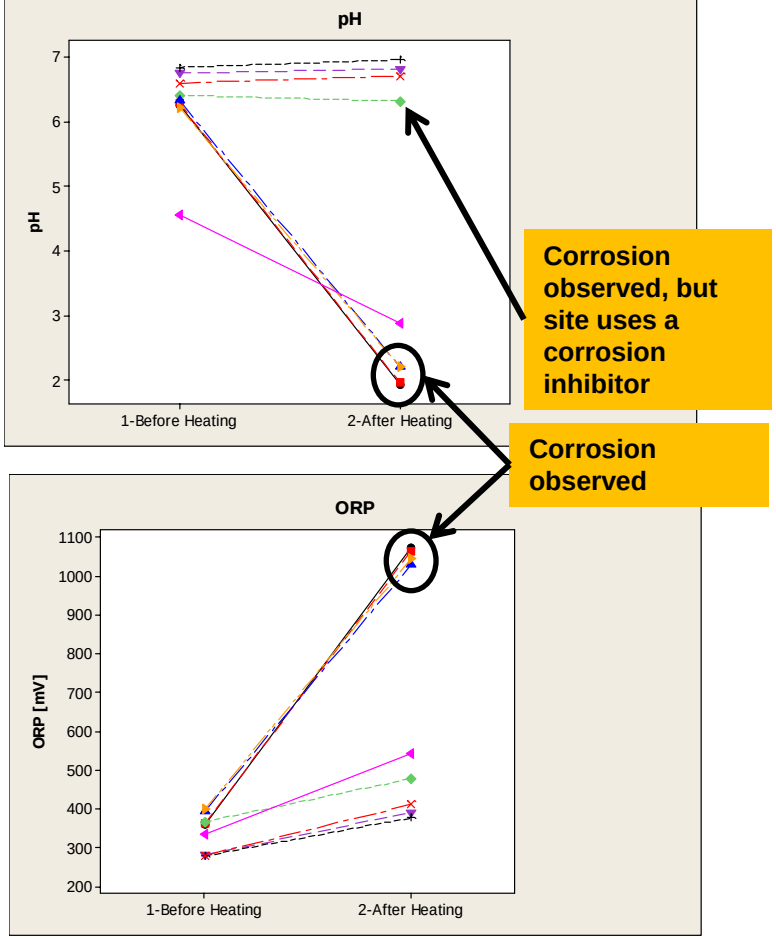
### Effect of Removing Solids




**Corrosion observed, but site uses a corrosion inhibitor**

**Corrosion observed**

### Effect of Heating




**Corrosion observed, but site uses a corrosion inhibitor**

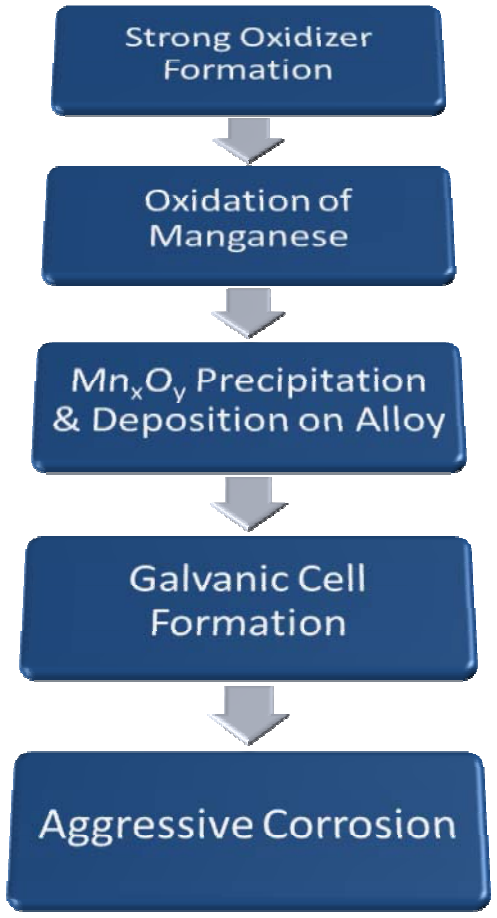
**Corrosion observed**

# *WFGD Alloy Corrosion*

| Titration Results | |
|---|---|
| Unit | Oxidizer (ppm) |
| Corrosion | 1680 |
| Corrosion | 1592 |
| Corrosion | 1574 |
| Corrosion | 1571 |
| No $Mn_xO_y$ Scale | 227 |
| No $Mn_xO_y$ Scale | 169 |
| No $Mn_xO_y$ Scale | 50 |
| No $Mn_xO_y$ Scale | 29 |
| No $Mn_xO_y$ Scale | 27 |
| Uses Additive | 19 |
| No $Mn_xO_y$ Scale | 10 |
| No $Mn_xO_y$ Scale | <2 |

- **A strong oxidizer is present it absorbers exhibiting Mn-catalyzed rapid corrosion**
- **This oxidizer raises the slurry ORP**
- **The oxidizer reacts to precipitate out soluble manganese**

# *Mechanism – Current Working Hypothesis for Units Exhibiting "Severe" Corrosion*

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***$MnO_2$ deposits that physically contact metal surfaces, no matter how it occurs, serve as a galvanic cathode to promote corrosion of the metal.***

**-Lutey**

# *WFGD Alloy Corrosion*

- **Eliminate $MnO_2$ precipitation by maintaining ORP at a suitable level**
- **Perform regular ORP monitoring of slurries**
- **If high ORP conditions exist, evaluate system for source of strong oxidizer**

# Process Chemistry & Wastewater Treatment

# *Wastewater Treatment*

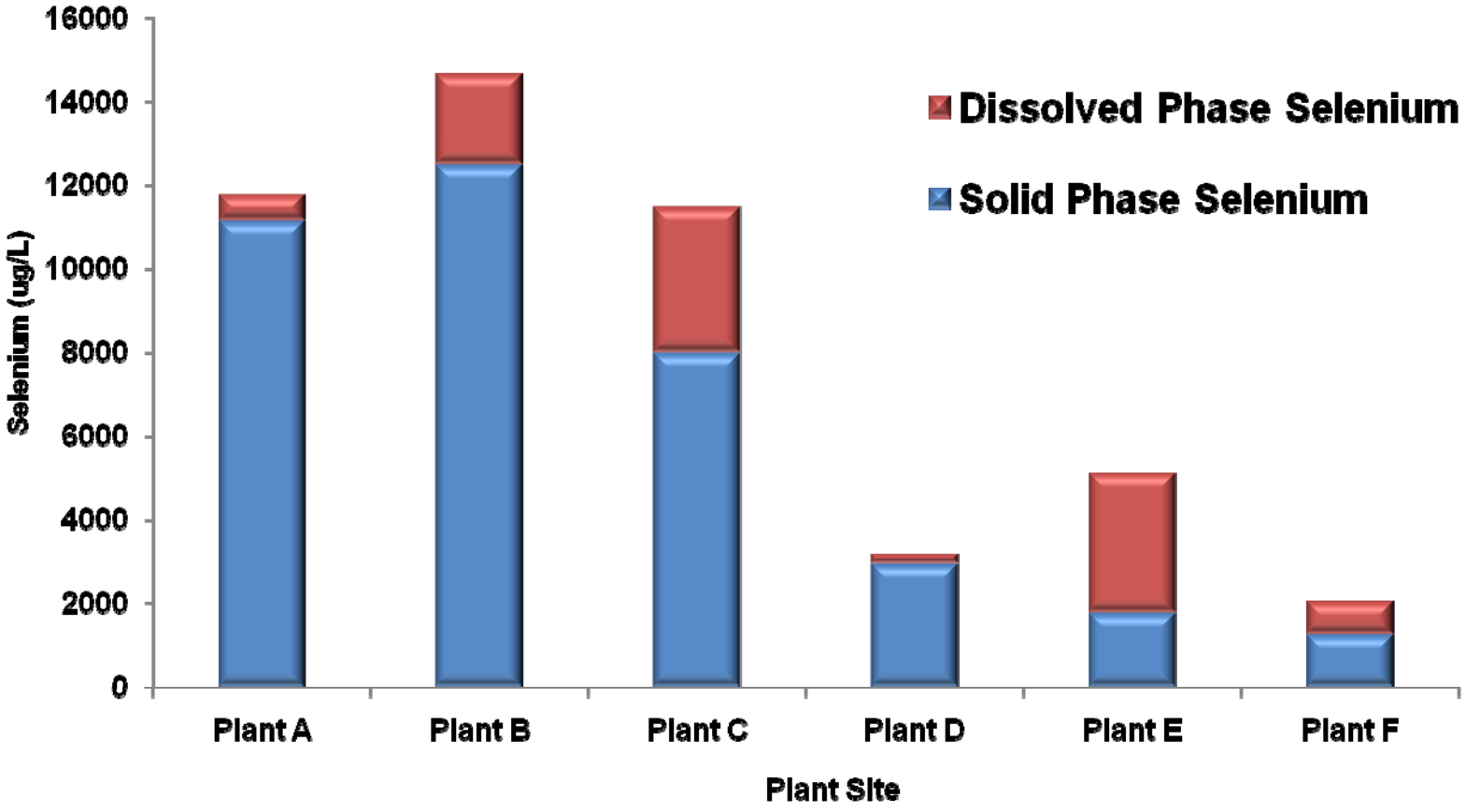
**Selenite (IV) and Selenate (VI) are dominant forms in FGD waters**

- **Exception: Scrubber with DBA additions**

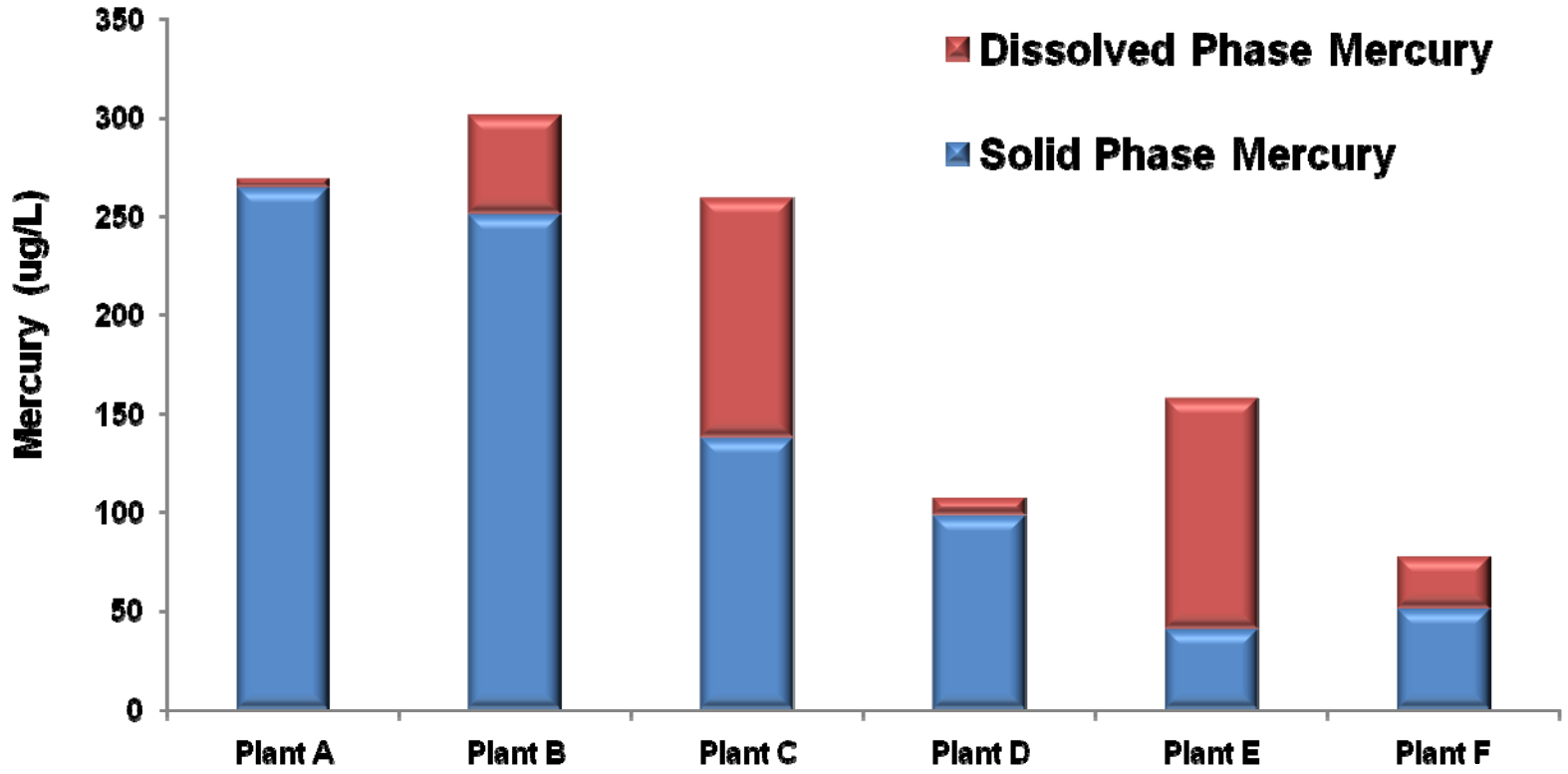
**Selenate formation is problematic**

- **Inability to be removed via chemicals**
  - **(e.g. $Fe^{3+}$ and $Fe_2O_3$)**
  - **Exception: $Fe^0$ (difficult to apply)**
- **Removal via biological remediation**

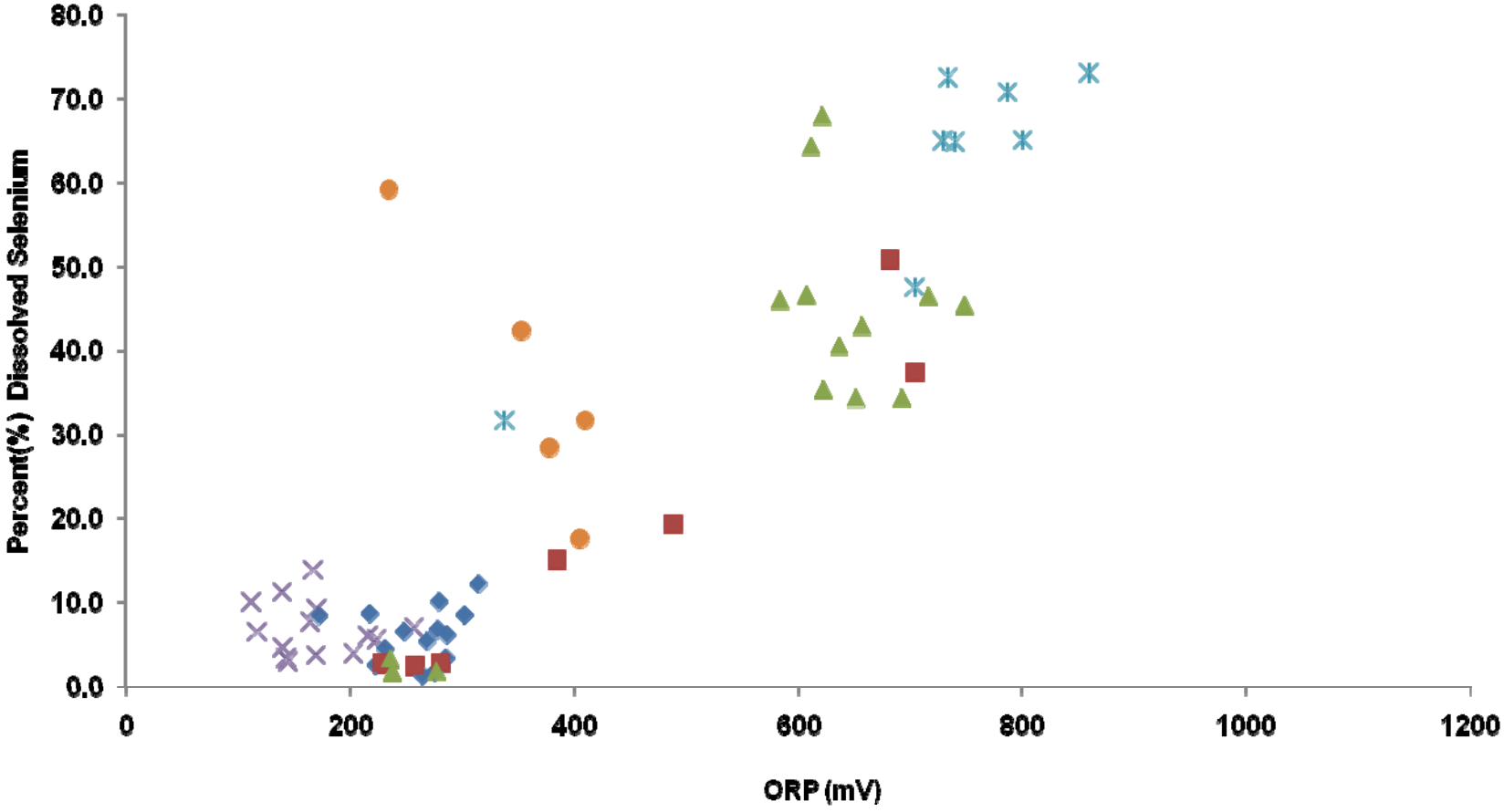
# Selenium Distribution



# Mercury Distribution



# Dissolved Selenium vs. ORP



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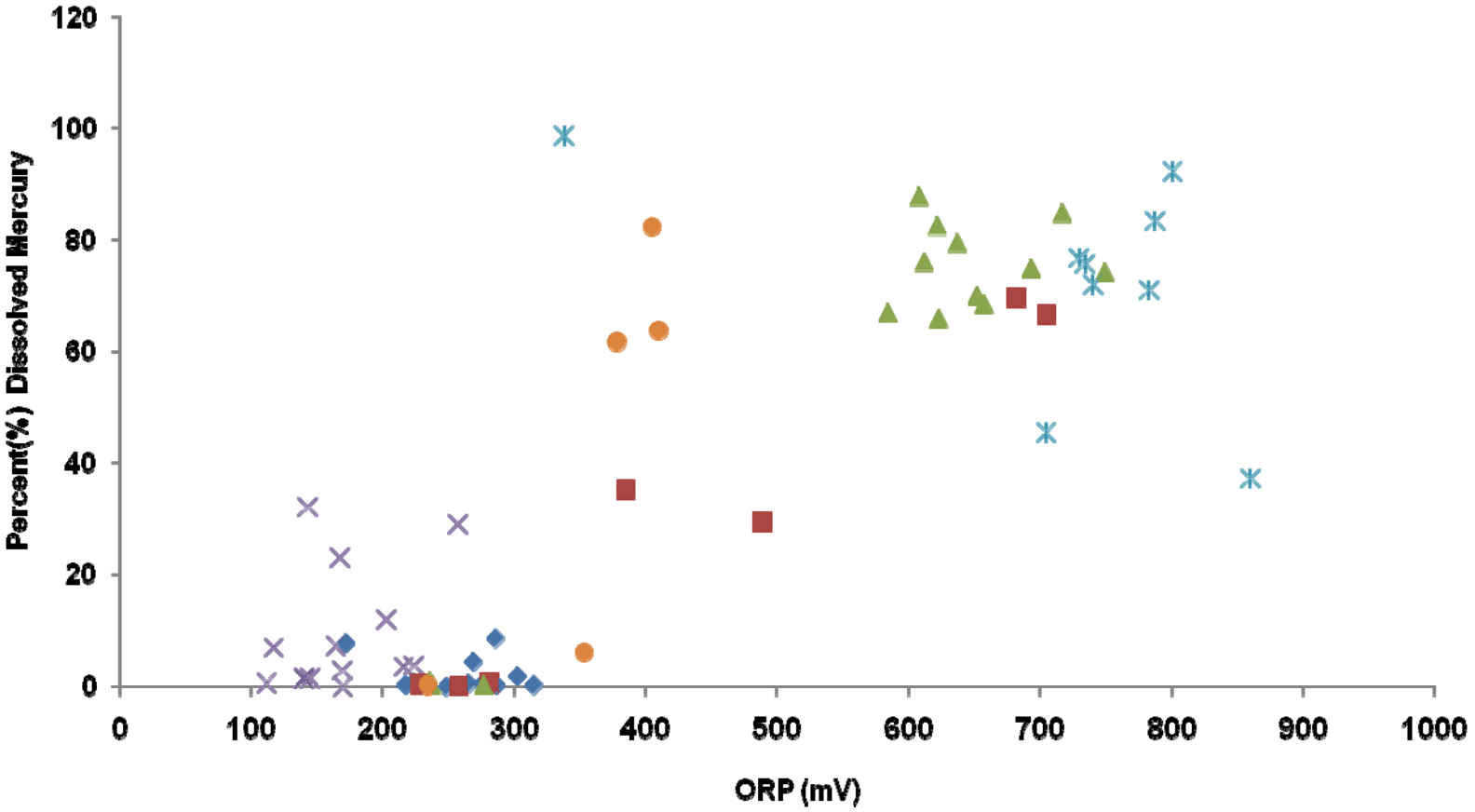
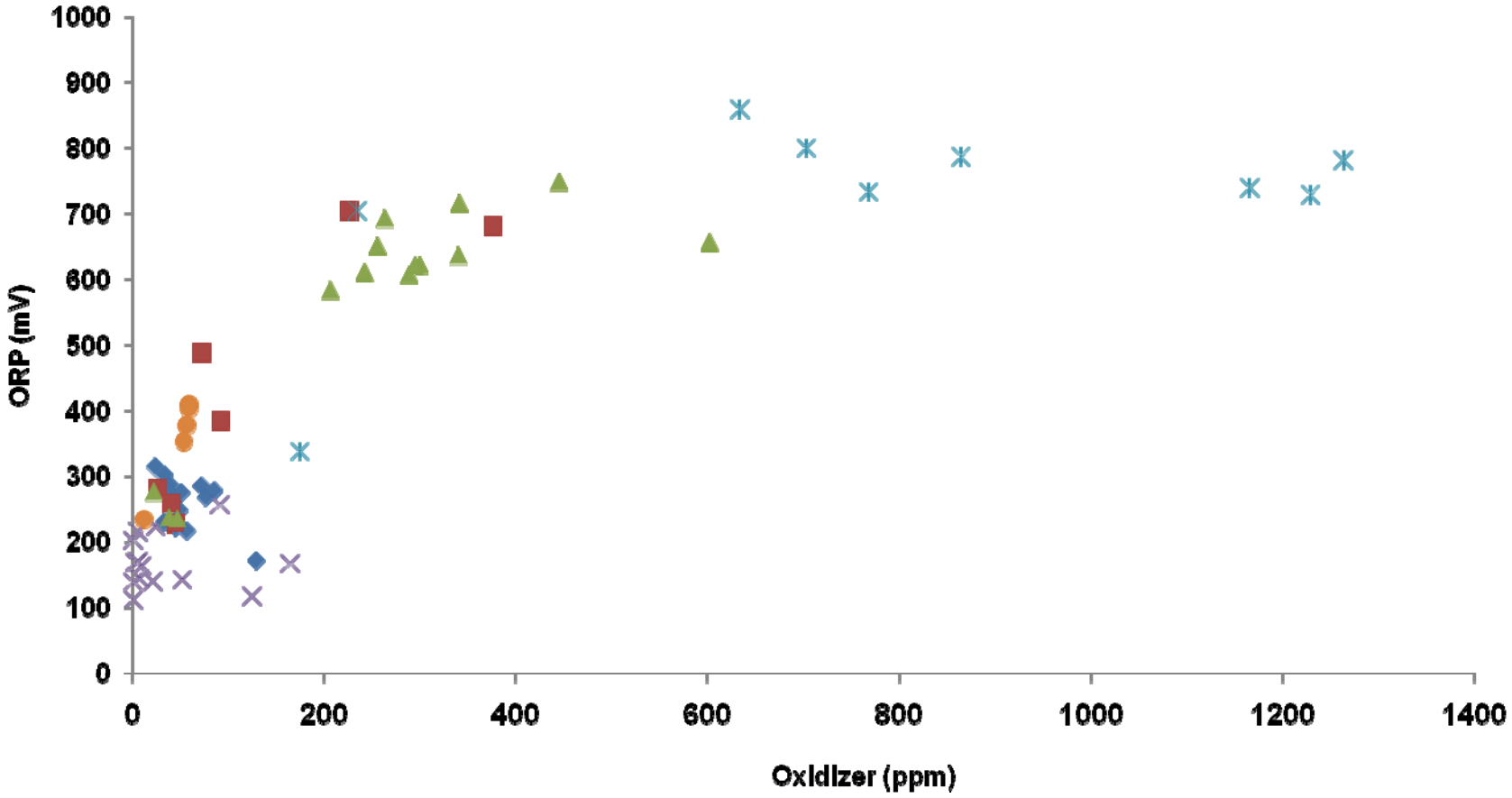
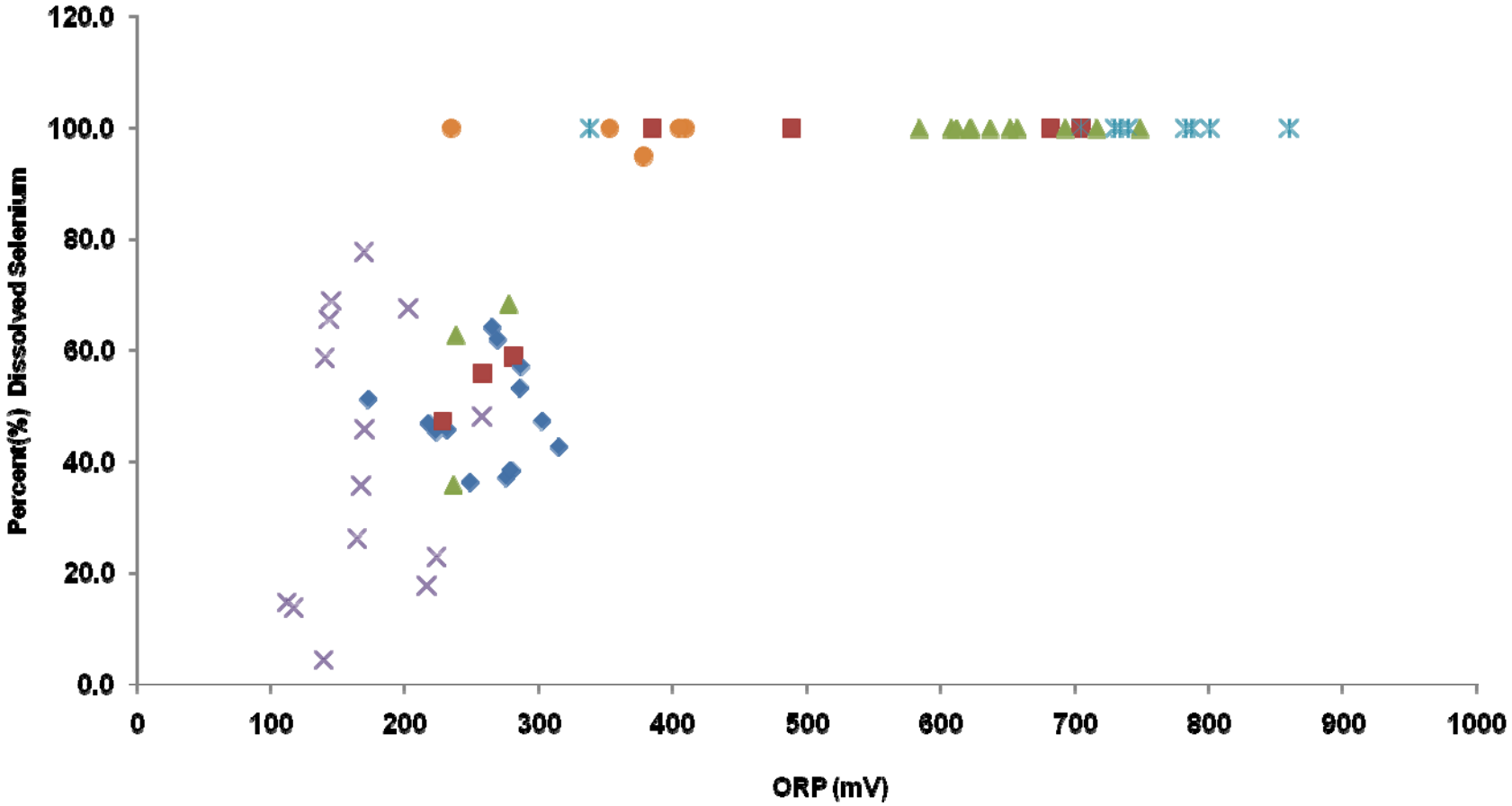


# Strong Oxidizer vs ORP



# Selenate vs. ORP

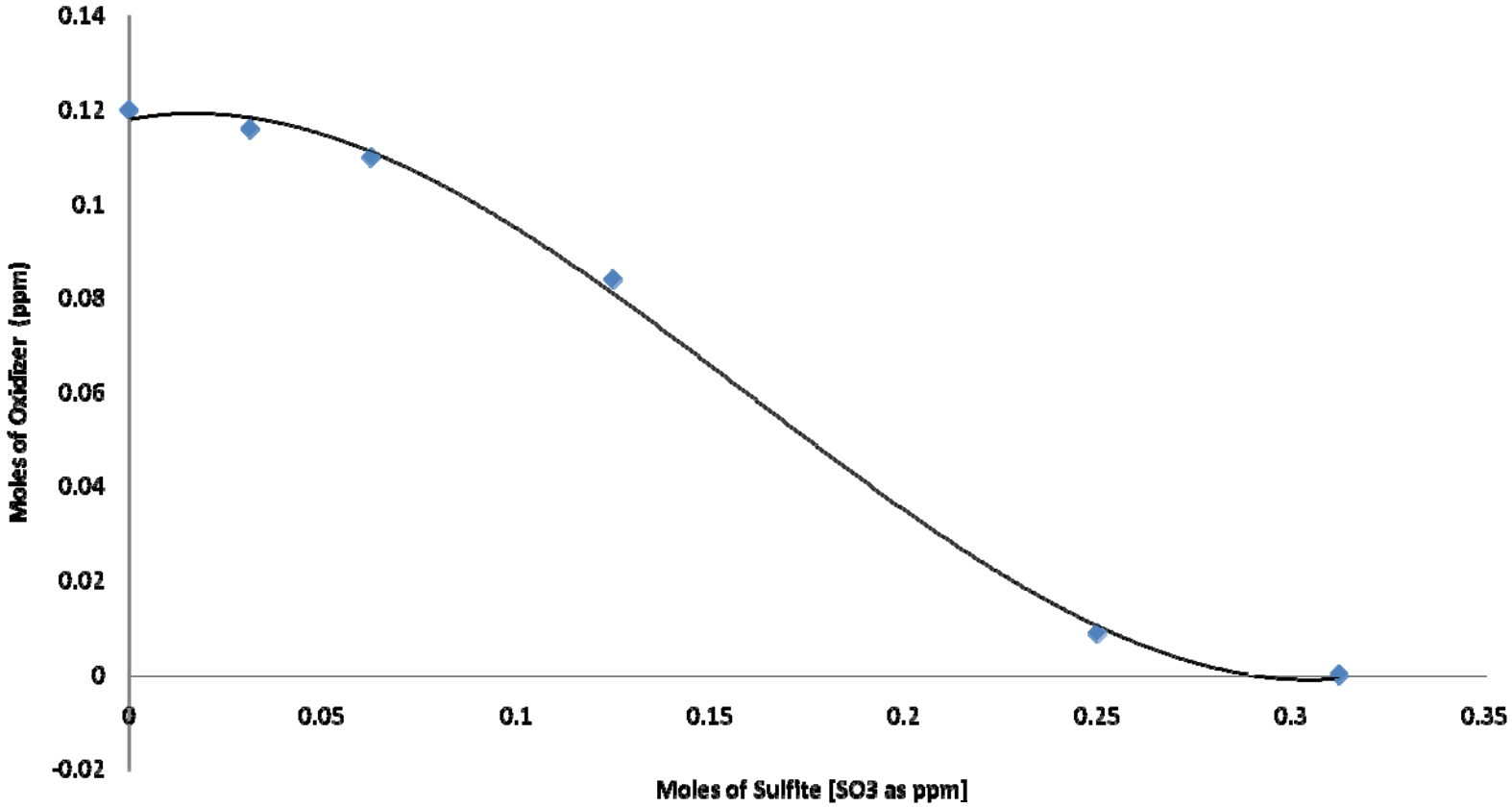


# Process Control Parameters

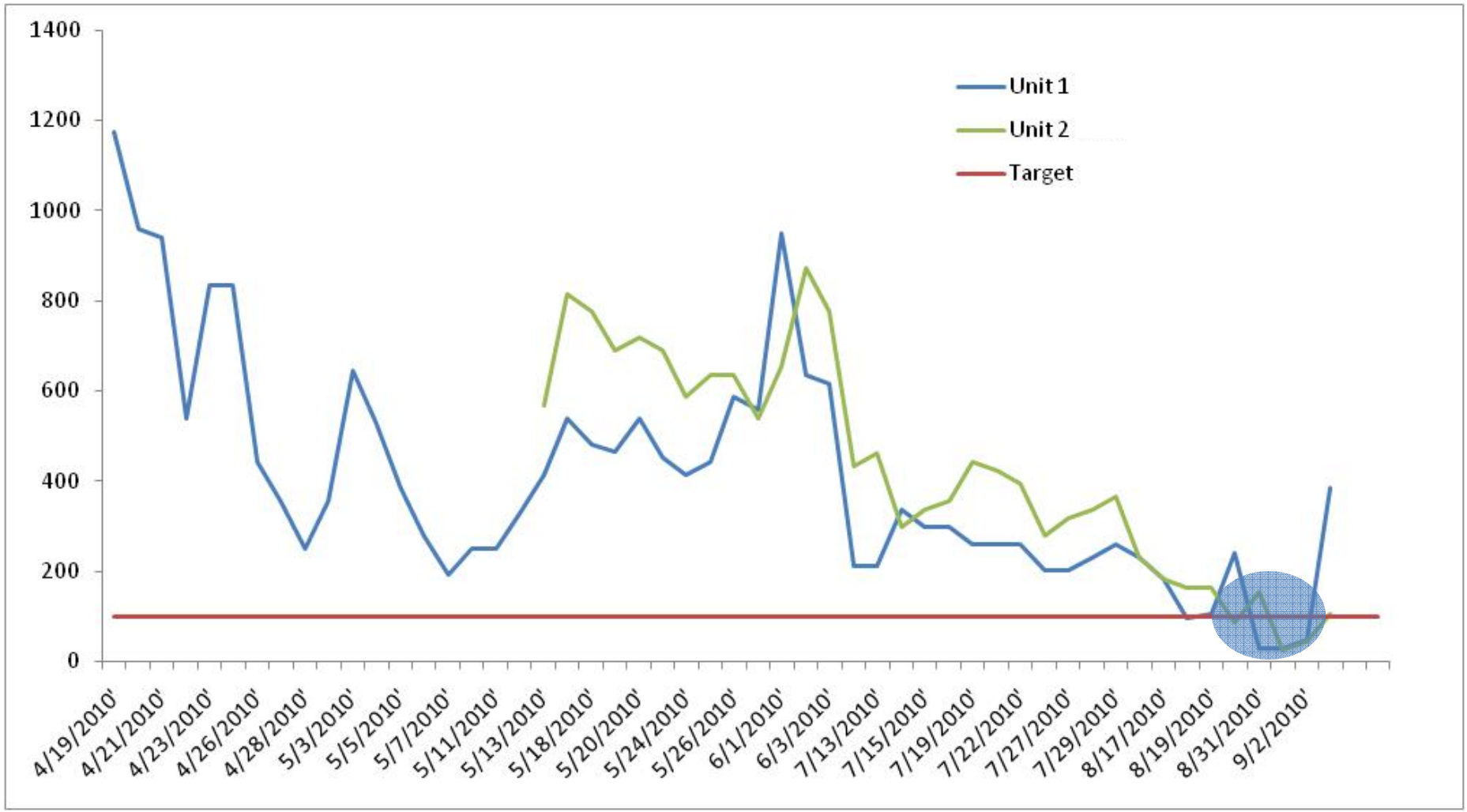
# *Process Control Parameters*

- **Oxidation Air Reduction has been used to reduce slurry ORP in the field**
- **Other Parameters are being explored**
  - **SCR Performance**
  - **Ammonia Slip**
  - **Load**
  - **Coal Type**
  - **Particulate Control**

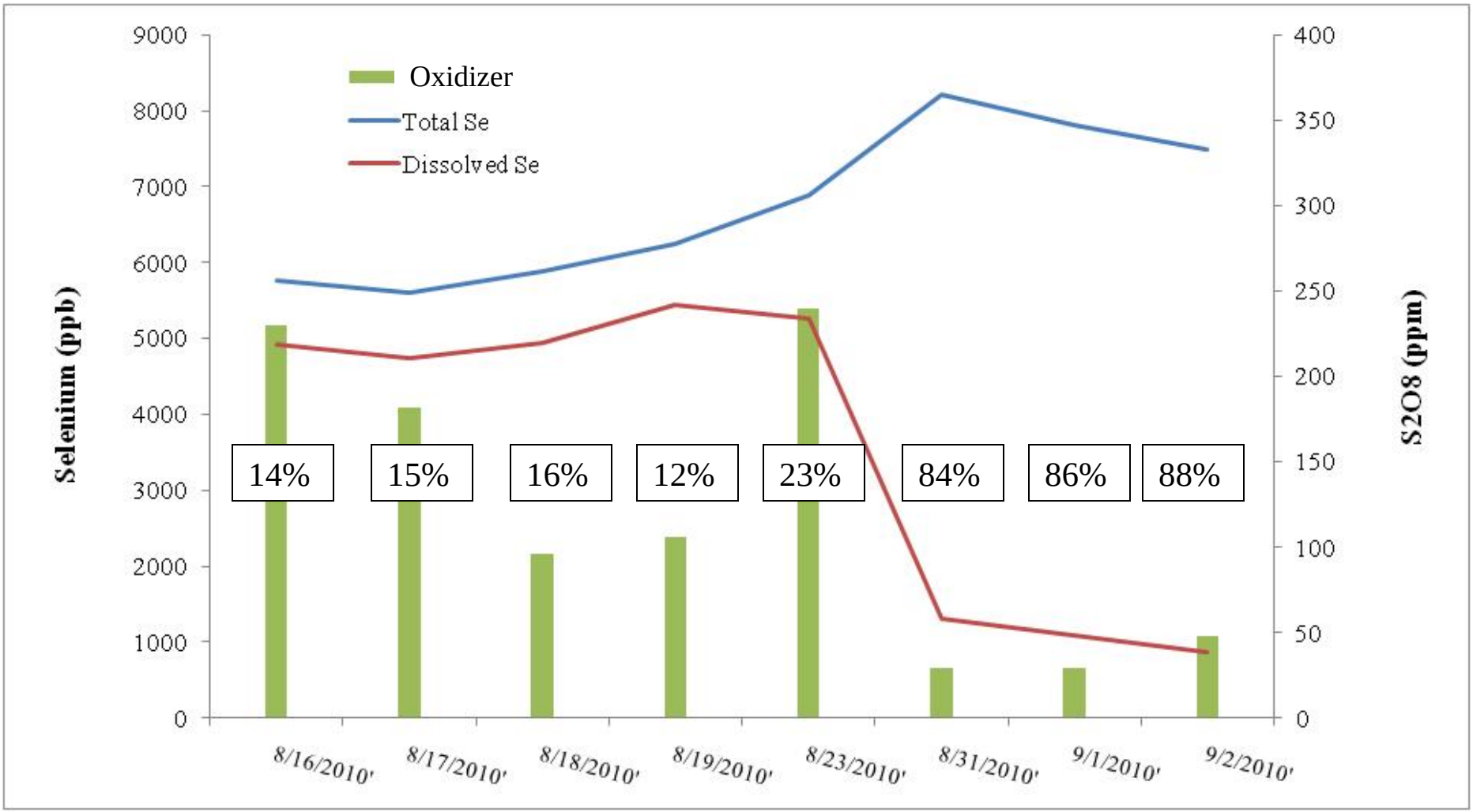
# Oxidizer vs. Sulfite



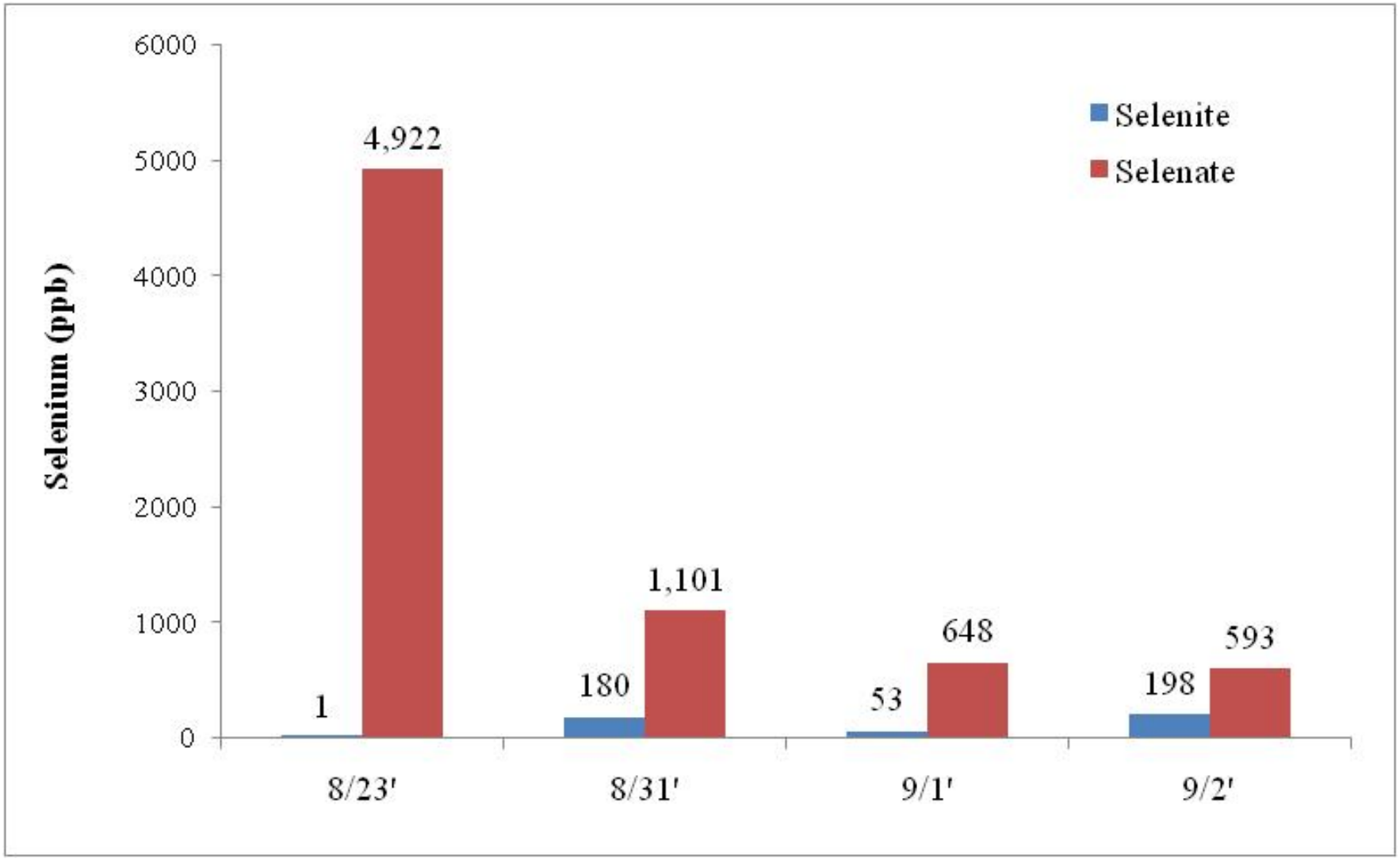
# Process Control Parameters: Oxidizer Reduction vs. Time



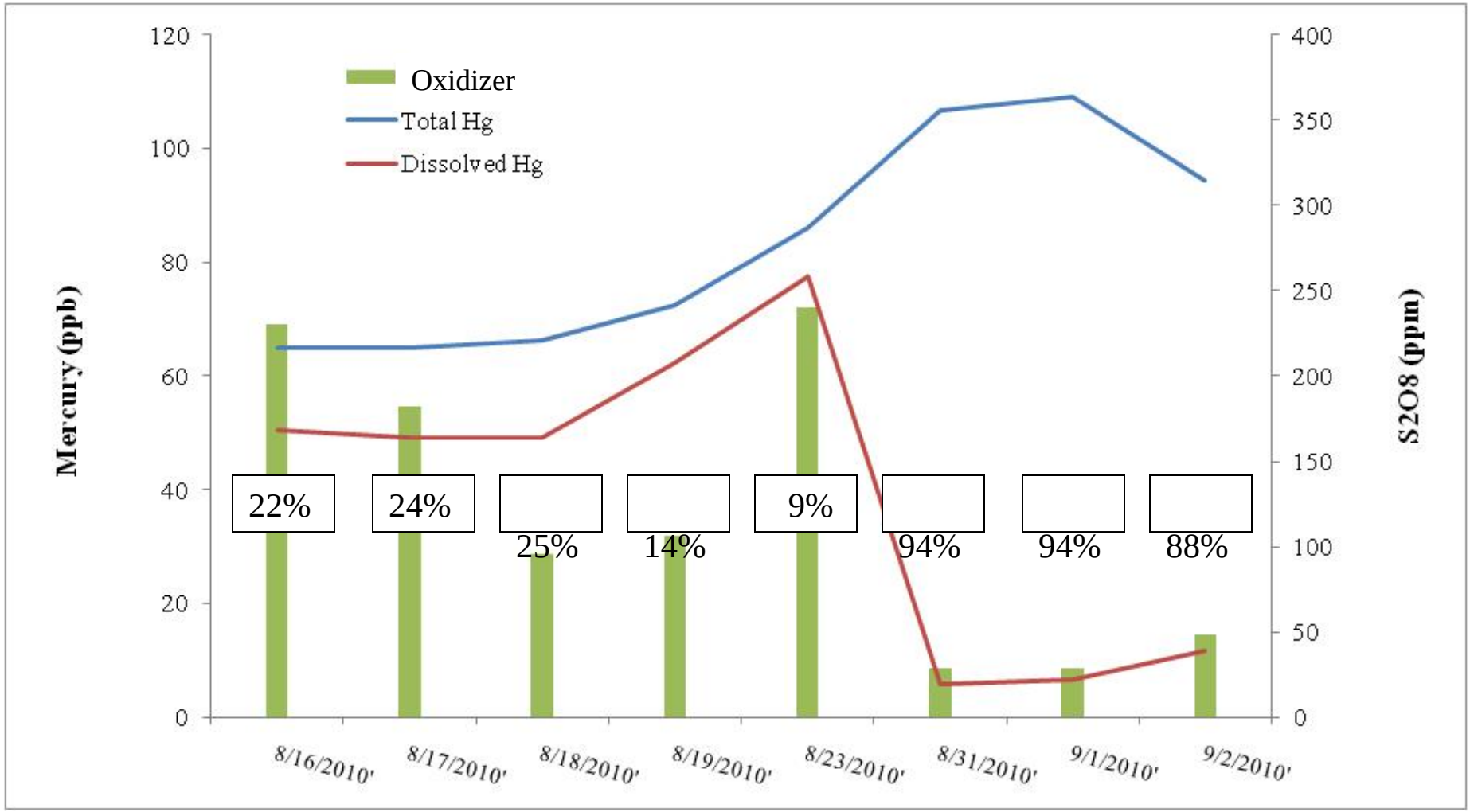
# Process Control Parameters: Selenium vs. Time



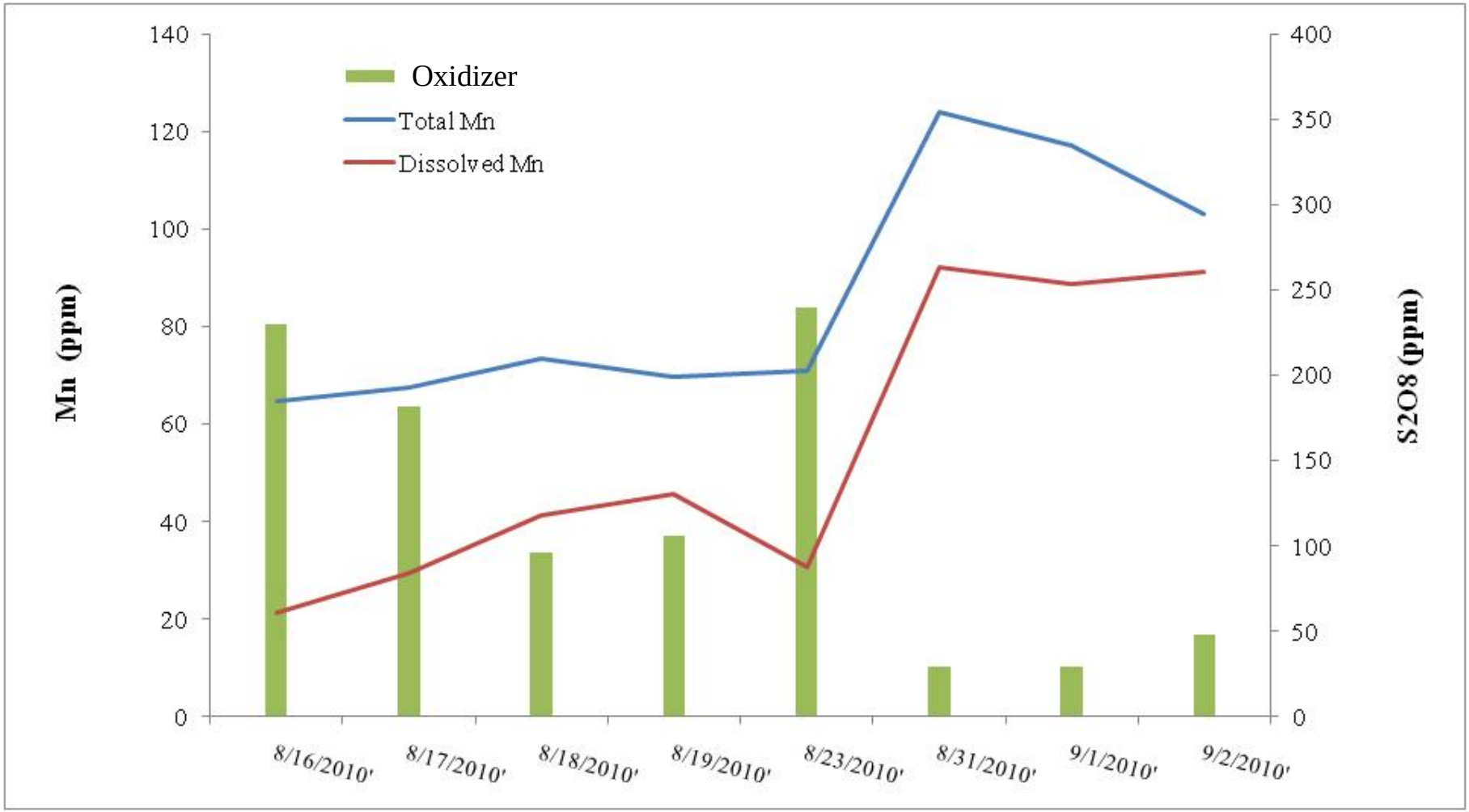
# Selenium Speciation



# Mercury in Absorber Slurry vs. Time



# Manganese in Absorber Slurry vs. Time



# Conclusions

# *High ORP Aggressive Corrosion Mechanism Conclusions*

- **Precipitated $MnO_2$ exacerbates an under-deposit corrosion mechanism**
- **$MnO_2$ precipitation is due to high ORP conditions that exist is some units**
- **High ORP conditions are due to the presence of a strong oxidizer**
- **Without high ORP conditions, Mn ions within the slurry are innocuous**

# *Process Control Parameters Conclusions*

- **Reduction in forced air causes lower Se and Hg concentrations in the dissolved phase**
- **With clarification, treatment of Se and Hg with occur before the wetland treatment system**
- **Need for additional data to develop a logic system (automated forced air)**

# *Process Chemistry Effects Conclusions*

- **ORP can be lowered from a high to a low regime by lowering oxidation air, in some cases**
  - **ORP controls phase partitioning of many elements**
  - **ORP may change with coal type**
  - **ORP is predominantly controlled by a strong oxidizer, the formation of which is being studied**
- **Other causes of corrosion exist**

# *Questions*


# *Thank You*