REINHOLD ENVIRONMENTAL Ltd.

2012 APC Round Table
& Expo Presentation

July 16-17, 2012, in Baltimore, MD / Hosted by Duke Energy, Entergy,
FirstEnergy, Southern Company & TVA

Scrubber Material ORP Update

July 17, 2012

All information presented in this PowerPoint is <u>Proprietary & Confidential</u> *to B&W.*

Shannon Brown
B&W Power Generation Group

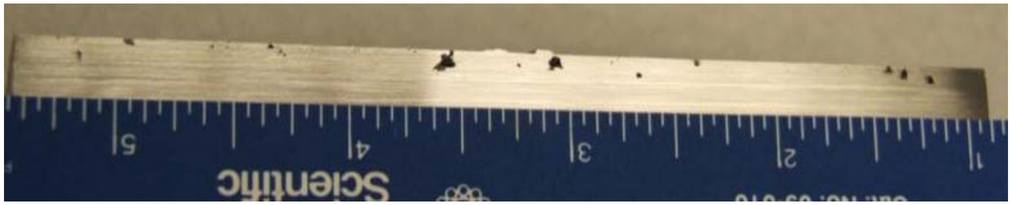
Overview

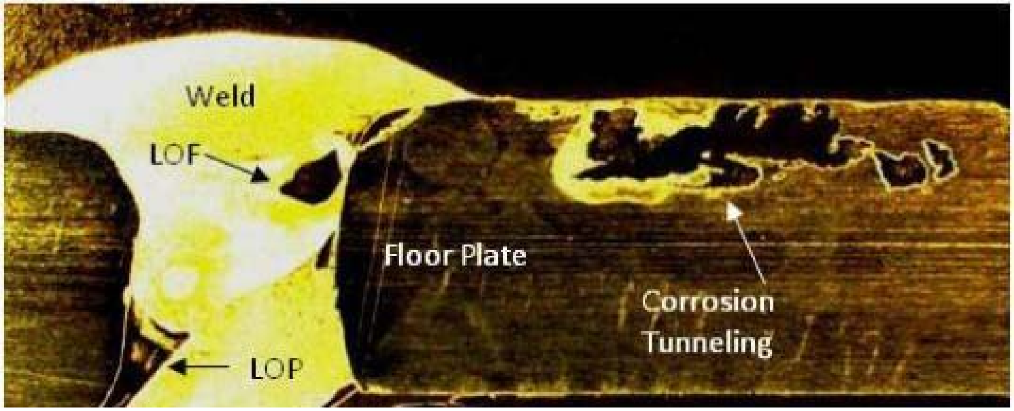
- Less Aggressive Fluoride-Induced Under-Deposit Corrosion (FIUDC)
  - Surface pitting
  - Sub-surface attack
- High Oxidation Reduction Potential (ORP) Aggressive Corrosion Mechanism
- Process Chemistry Effects
  - Open Circuit Potential (OCP) versus ORP
  - Phase partitioning in absorber slurries
  - Effects of strong oxidizers and kinetics
  - Process control of ORP

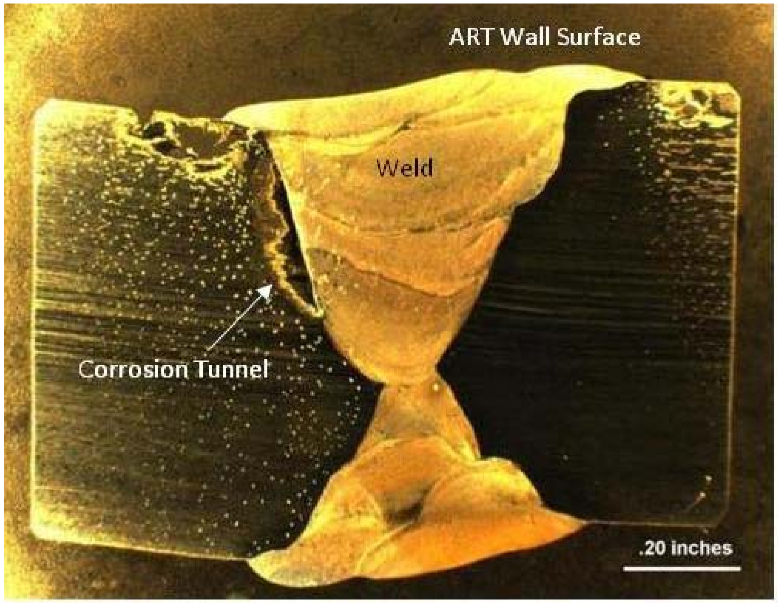
Less Aggressive Fluoride-Induced Under-Deposit Corrosion (FIUDC)

Less Aggressive Corrosion

Less Aggressive Corrosion







Less Aggressive Corrosion

Scale-Slurry Interface

- Crystalline scale is predominantly gypsum
- Much higher fluoride concentration at scale-alloy interface than elsewhere in the scale
- Variable attack severity, morphology and locations

Scale-Alloy Interface

Detailed SEM/EDS Examination Results for Alloy 2205 Base Metal ; Alloy 625 Weld Metal Specimens

Solution 1

- **10,000 ppm Cl (as NaCl)**
- **500 ppm F (as NaF)**
- **Initial pH 5.5 (H_2SO_4)**
- **Specimens fully immersed in deposit**
  - **CaF_2 (≈ 150 grams)**

Solution 2

- **10,000 ppm Cl (as NaCl)**
- **500 ppm F (as NaF)**
- **Initial pH 5.5 (H_2SO_4)**
- **Specimens fully immersed in deposit**
  - **CaF_2 (≈ 100 grams)**
  - **MnO_2 (≈ 300 grams)**

- Base Metal Specimens Immersed & Polarized
- Weld/HAZ/Base Metal Specimens Immersed (No Polarization)
- Localized HF Generation Suspected in Solution C Test
- pH Elevation/ORP Reduction during Polarization
- 34 Days Total Exposure
- Chemistry under deposit apparently is different from bulk chemistry

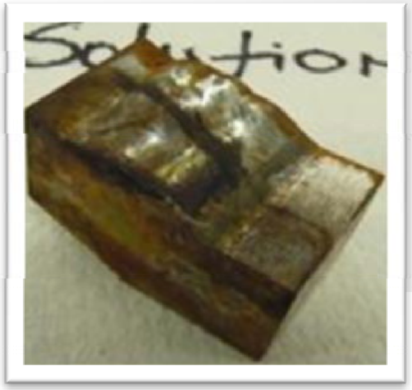
Overall Post Test Specimen Appearance - Solutions C and D

Base Solution C

Weld/HAZ Solution C

Weld/HAZ Solution C

Base Solution D



Weld/HAZ Solution D

- Polarization results in severe corrosion
- Noticeable pitting of weld/HAZ/base metal specimen (non-polarized) in Solution D
- Different coloration on weld/HAZ/base metal specimen (non-polarized) in Solution C indicates that different sides of the specimen experienced different micro-environments

Observations from EDS Analyses Weld/HAZ/Base - Solutions C & D

- 34 Days exposure in Solution C immersed in CaF_2 resulted in localized breakdown of the protective oxide on the base metal.
- 34 Days exposure in Solution D immersed in CaF_2 + MnO_2 resulted in pitting of the base metal.
- No Mn found in the pits. It appears that the Mn acts as an accelerant to the pitting mechanism but not a reactant in the pit itself.
- All pits contained some level of F inside of the pit, but not necessarily associated with Ca.
- No Mn in the pits, along with F in the pits not associated with Ca, indicates that the F in the pits is a result of chemical reactions and not the original CaF_2 added.
- F played a significant role in the breakdown of the oxide and pitting on these specimens.

Less Aggressive FIUDC Mechanism

Evaluations

Electrochemical Immersion

Base Solution

- 10,000 ppm Cl (as NaCl)
- 500 ppm F (as NaF)
- Initial pH 5.5 (H_2SO_4)
- Sparging
    - Air
    - Nitrogen

Incremental Additions

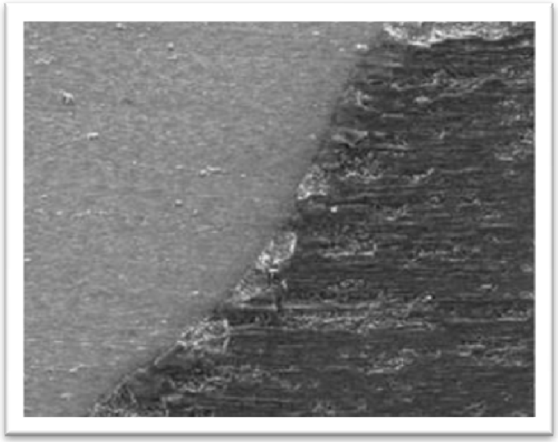
- Tests 1 & 2 (Mn^{+2} as $MnSO_4$)
- Tests 3 & 4 (Fe^{+3} as $Fe_2(SO_4)_3$)
- Tests 5 & 6 (Fe^{+2} as $FeSO_4$)
- Tests 7 & 8 (Ca^{+2} as $CaCl_2$)
- Tests 9 & 10 (Mg^{+2} as $MgSO_4$)
    - Odd Number - Air
    - Even Number - Nitrogen

- Better understanding of ionic additions on OCP and ORP
- Input into solutions for the corrosion tests
- Monitor ORP and pH
- Monitor OCP of alloy 2205

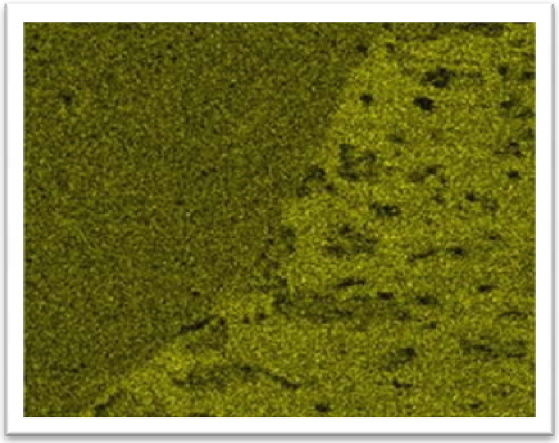
Observations from Bench Scale Immersion Solution Tests

- Tests indicate that Mn while it is maintained in solution plays a small role in the corrosion process. Same can be said for the Ca and Mg ions in solution.
- Fe^{+3} plays a role in crevice corrosion of the 2205 in a Cl + F environment.
- The Fe^{+3}/Fe^{+2} ratio plays a role in the crevice corrosion of the 2205 in a Cl + F environment.

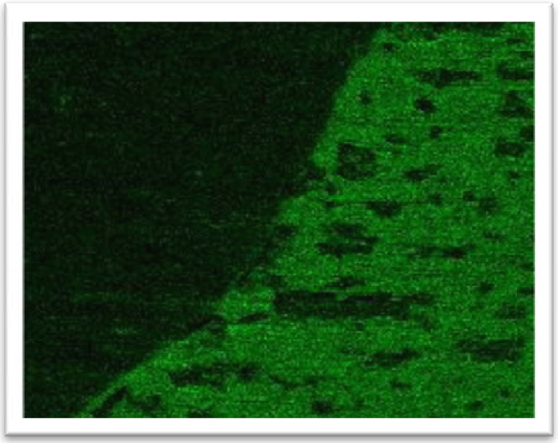
EDS Maps ***Solution C*** *Weld/Base Interface (Darker Base Metal Oxide)*



Weld/Base Interface @ 100X

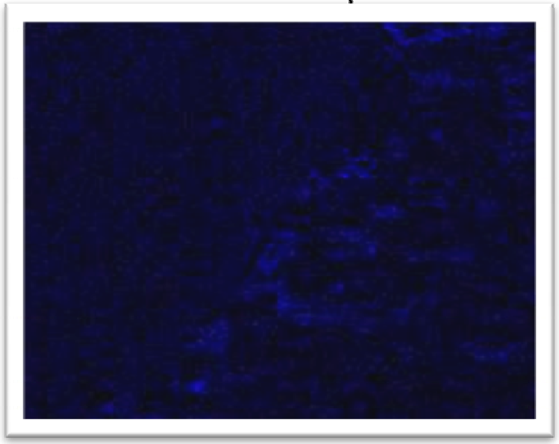


EDS Cr Map

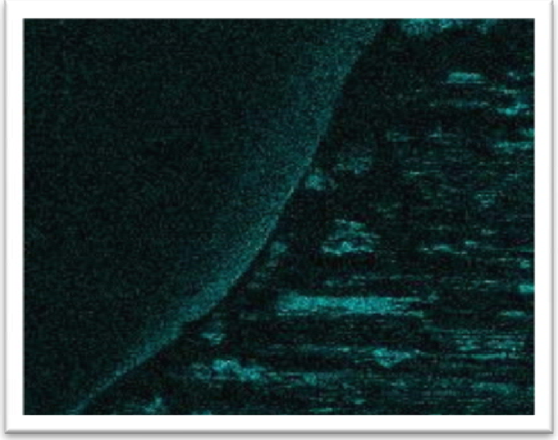


EDS O Map

EDS Ca Map



EDS F Map

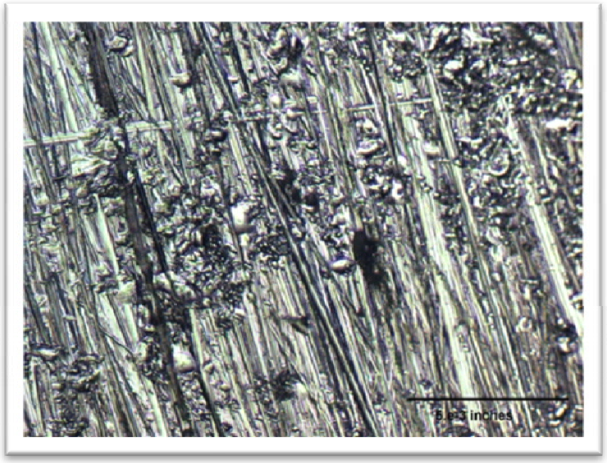


EDS Fe Map

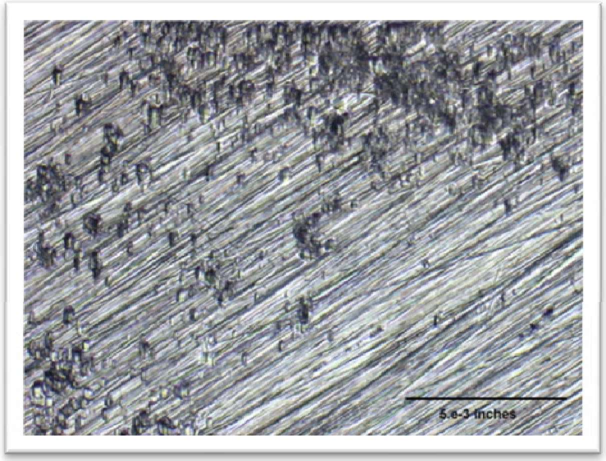
- EDS maps confirm breaks in base metal oxide
- CaF_2 appears to be associated with the oxide breaks
- Areas of oxide breaks show enrichment in Fe

Effect of F Concentration and Alloy Composition on Crevice Corrosion Behavior

- Minor crevice attack observed on all specimens
- Additional specimens were removed after 2 months of exposure
- Fluoride attack under inert ceramic crevice washers was not as severe as that observed under gypsum WFGD deposits



2205 in 5 ppm F



2205 in 50 ppm F

2205 in 500 ppm F

Less Aggressive FIUDC Mechanism
Observations

- Variable morphology – widespread shallow pitting, localized “coral pattern” attack, sub-surface attack
- Attack is associated with deposits, but not all under-deposit areas exhibit attack
- Variable attack location – some associated with HAZ, some not associated with HAZ
- Alloy 625 weld metal was not attacked
- X-ray indications were not observed above the tank liquid level

Less Aggressive FIUDC Mechanism

Conclusions

- The observed attack is consistent with an under-deposit corrosion mechanism, and fluoride ions appear to be playing a role in the attack
- It appears that only the soluble fluoride ions are causative (not precipitated forms of fluoride such as CaF_2)
- It appears that soluble fluoride ions penetrate the gypsum scale and concentrate at the scale-metal interface

High Oxidation Reduction Potential (ORP) Aggressive Corrosion Mechanism

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

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
- Deposits on units displaying this attack contained significant concentrations of Mn

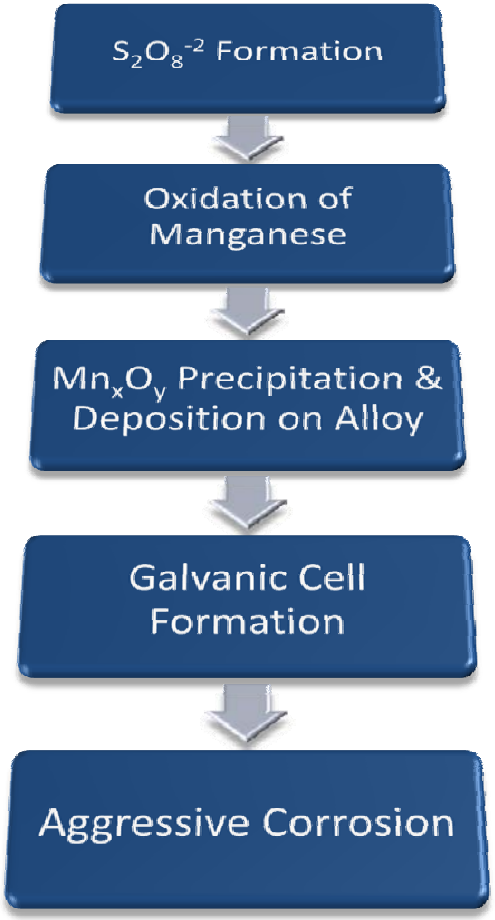
Aggressive ART Shell Corrosion

Aggressive Corrosion of ART Vertical Weld Seam

Spiking Study Results

- 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^{o}C.

Mechanism – Current Working Hypothesis for Units Exhibiting “Severe” Corrosion



$S_2O_8^{-2}$ Formation

Oxidation of Manganese

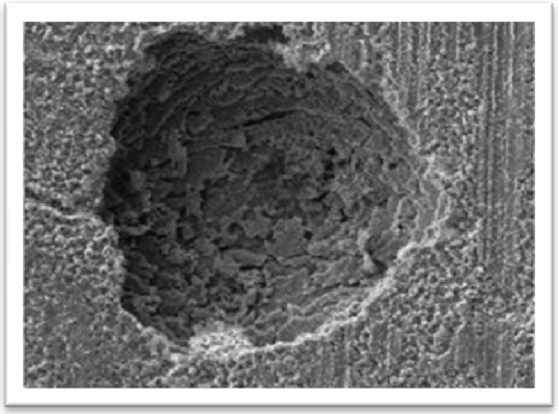
Mn_xO_y Precipitation & Deposition on Alloy

Galvanic Cell Formation

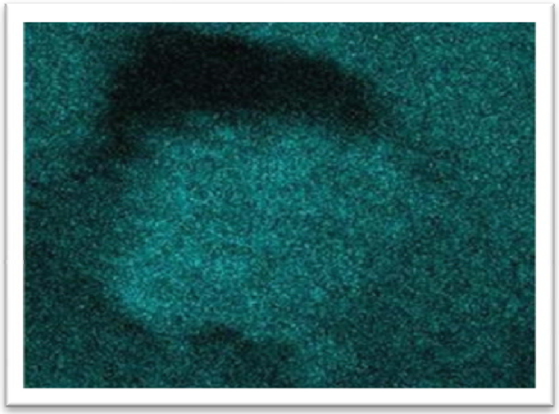
Aggressive Corrosion

> ***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**

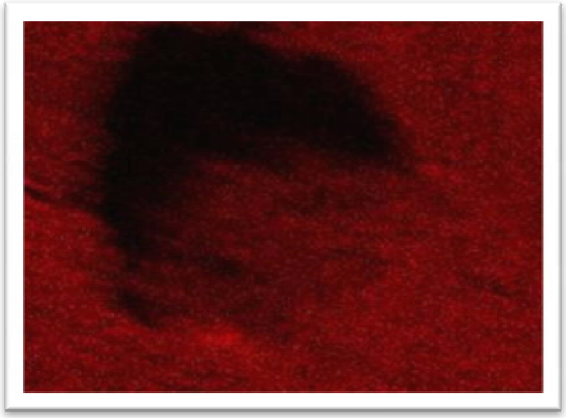
EDS Maps – Bench Scale Specimen - Pit in Weld Seam on Specimen Top



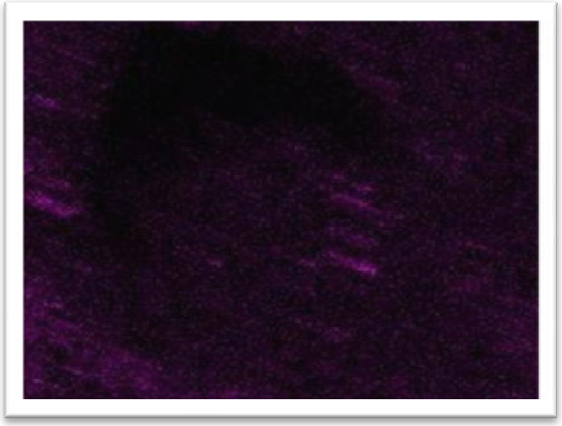
Pit @ 350X



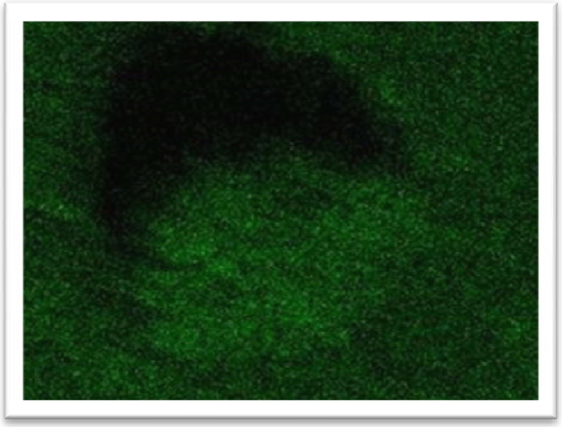
EDS Cr Map



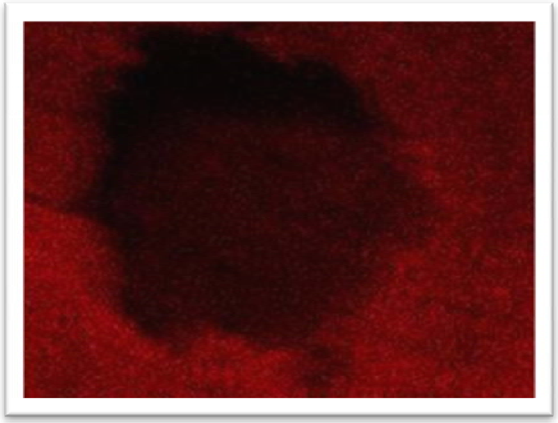
EDS O Map



EDS Ca Map



EDS F Map



EDS Mn Map

- Most of the F not associated with Ca
- No Mn inside of the pit
- Mn that is present surrounds the pit

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 in 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

High ORP Aggressive Corrosion Mechanism
Recommendations

- 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 Effects

Process Chemistry Effects

Observations

- Large variations in ORP were observed between different units
- ORP can be controlled in a WFGD process
- OCP is more important to corrosion rate than ORP
- CaF_2 precipitation was favored at some units while MgF_2 precipitation was favored at other units

Process Chemistry Effects
Oxidation Reduction Potential (ORP)

- A wide range of ORP is observed in filtrate samples from operating units (approximately 150 to 700 mV)
- ORP can be negative
- Measurement technique similar to pH
- Can be monitored on-line

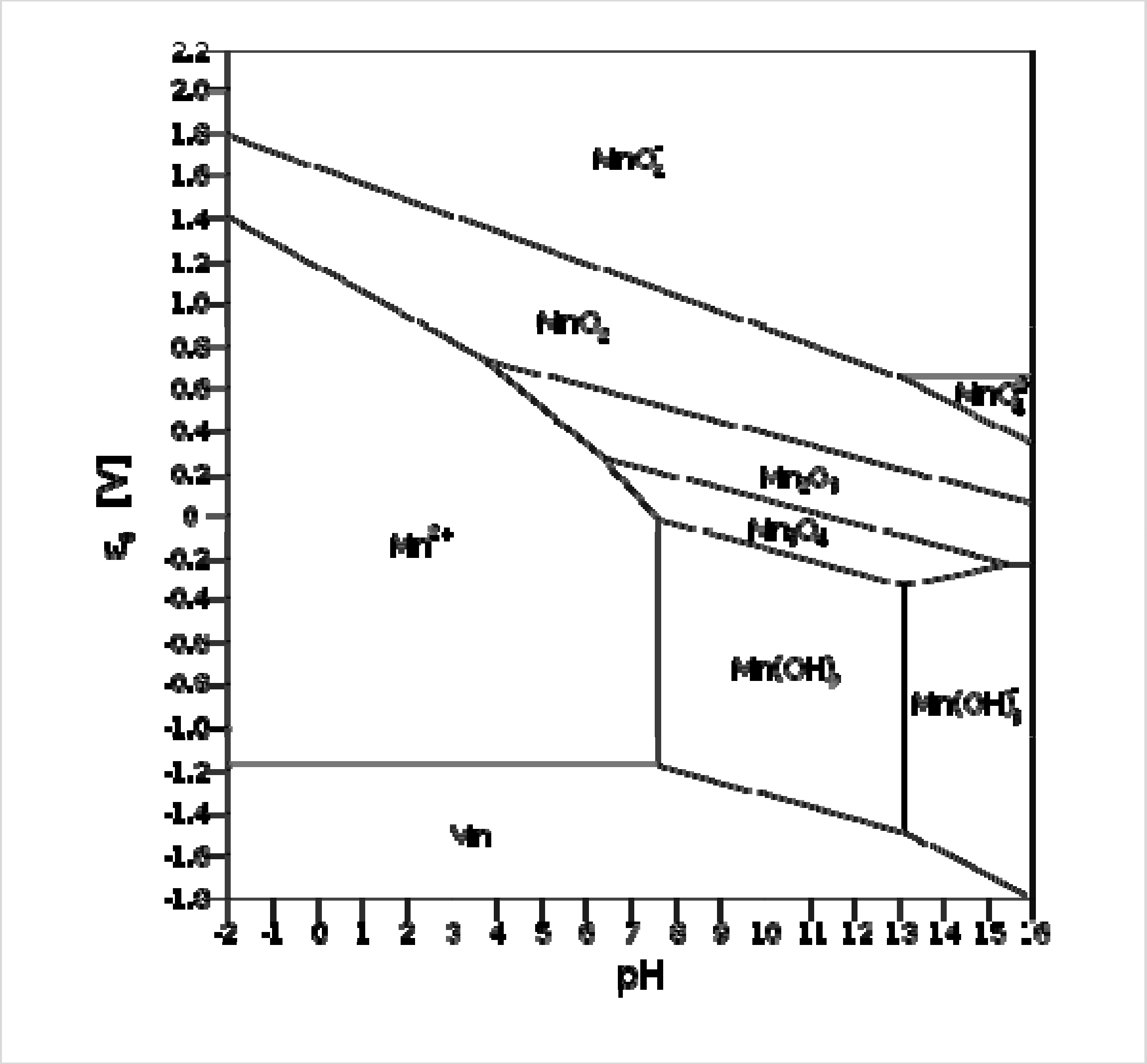
ORP & Phase Partitioning of Chemical Species

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} ↓ Precipitate
Medium	Hg^{+2} Soluble	Se^{+4} ↓ Precipitate	Mn^{+2} Soluble
Low	Hg^{0} ↑ Vaporous	Se^{+4} ↓ Precipitate	Mn^{+2} Soluble

Why is ORP Important?



What Causes Very High ORP?

$S_2O_8^{-2}$ Titration Results

Unit	***Observations***	***Oxidizer (ppm)***
1	Corrosion	1680
2	Corrosion	1592
3	Corrosion	1574
4	Corrosion	1571
5	No Mn_xO_y Scale	227
6	No Mn_xO_y Scale	169
7	No Mn_xO_y Scale	50
8	No Mn_xO_y Scale	29
9	No Mn_xO_y Scale	27
10	Uses Additive	19
11	No Mn_xO_y Scale	10
12	No Mn_xO_y Scale	<2

- Peroxodisulfate is present in absorbers exhibiting Mn-catalyzed rapid corrosion
- This oxidizer raises the slurry ORP
- The oxidizer reacts to precipitate out soluble manganese

Guberlet Paper

Formation of Peroxodisulfate:

where “M” denotes a transition metal

$$M^{+3} + SO_3^{-2} \rightarrow M^{+2} + SO_3^{\bullet -}$$

$$SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -}$$

$$SO_5^{\bullet -} + HSO_3^{-} \rightarrow HSO_5^{-} + SO_3^{\bullet -} \text{ or } SO_4^{-2} + SO_4^{\bullet -} + H^{+}$$

$$SO_3^{\bullet -} + SO_3^{\bullet -} \rightarrow SO_3^{-2} + SO_3 \text{ or } S_2O_6^{-2}$$

$$SO_3^{\bullet -} + SO_5^{\bullet -} \rightarrow S_2O_8^{-2}$$

$S_2O_8^{-2}$ and pH Drop

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

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

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

Hypochlorite formed

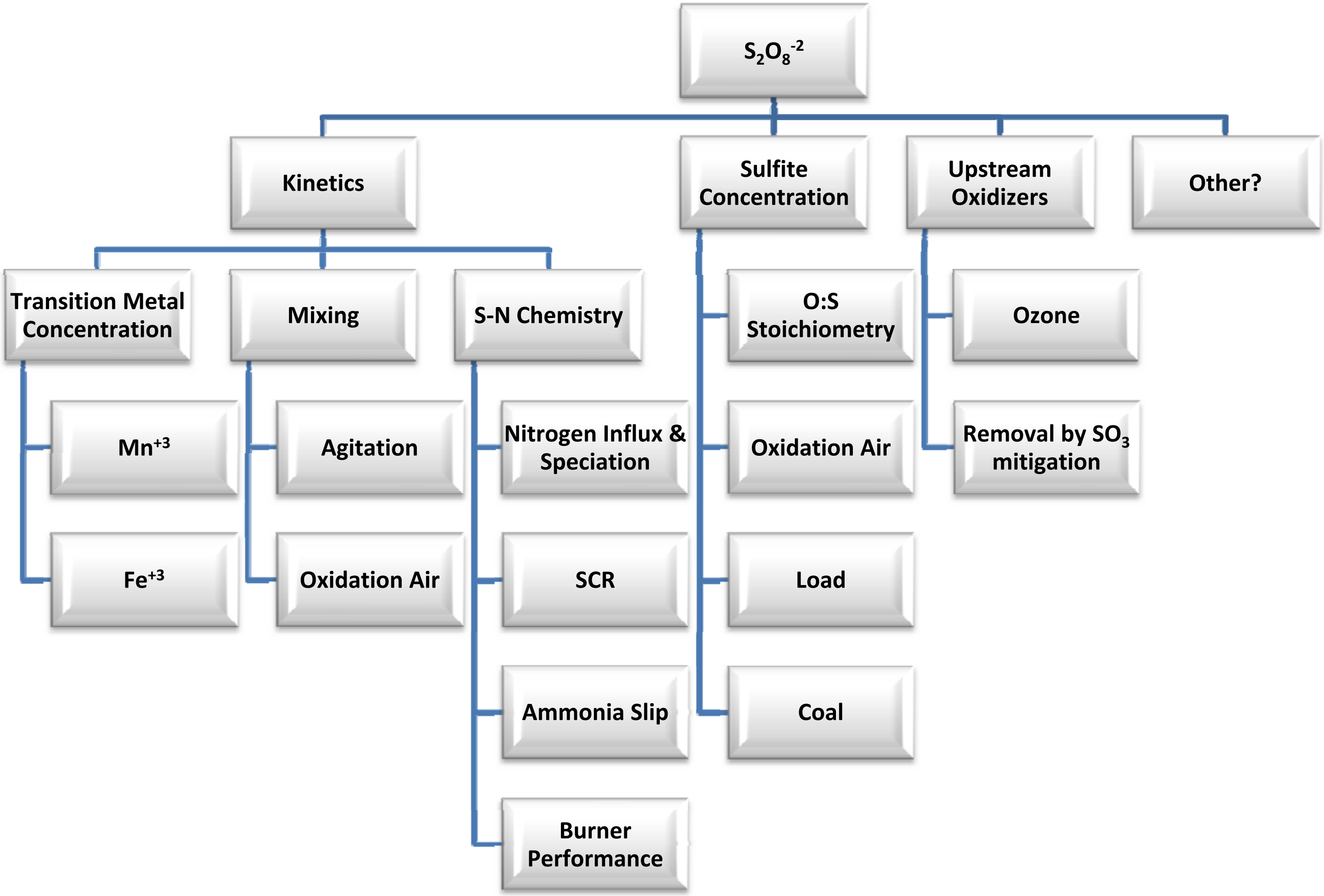
$$Cl_2 + H_2O \rightarrow 2H^+ + Cl^- + ClO^-$$

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

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

pH Drops from Acid Formation

Persulfate Formation



- $S_2O_8^{-2}$
  - Kinetics
    - Transition Metal Concentration
      - Mn^{+3}
      - Fe^{+3}
    - Mixing
      - Agitation
      - Oxidation Air
    - S-N Chemistry
      - Nitrogen Influx & Speciation
      - SCR
      - Ammonia Slip
      - Burner Performance
  - Sulfite Concentration
    - O:S Stoichiometry
    - Oxidation Air
    - Load
    - Coal
  - Upstream Oxidizers
    - Ozone
    - Removal by SO_3 mitigation
  - Other?

Factors that influence the Formation of $S_2O_8^{-2}$

- The **kinetic rate** at which sulfite is oxidized to sulfate is important
- Oxidation air & mixing
- Sulfur-Nitrogen Chemistry - Relationship between S-N chemistry & ORP

Transition Metals

- The currently proposed mechanism for $S_2O_8^{-2}$ formation involves free radicals
  - Oscillation between the +2 and +3 oxidation states of manganese and iron.
  - Mn^{+3} and/or Fe^{+3} begins the proposed initiation step.

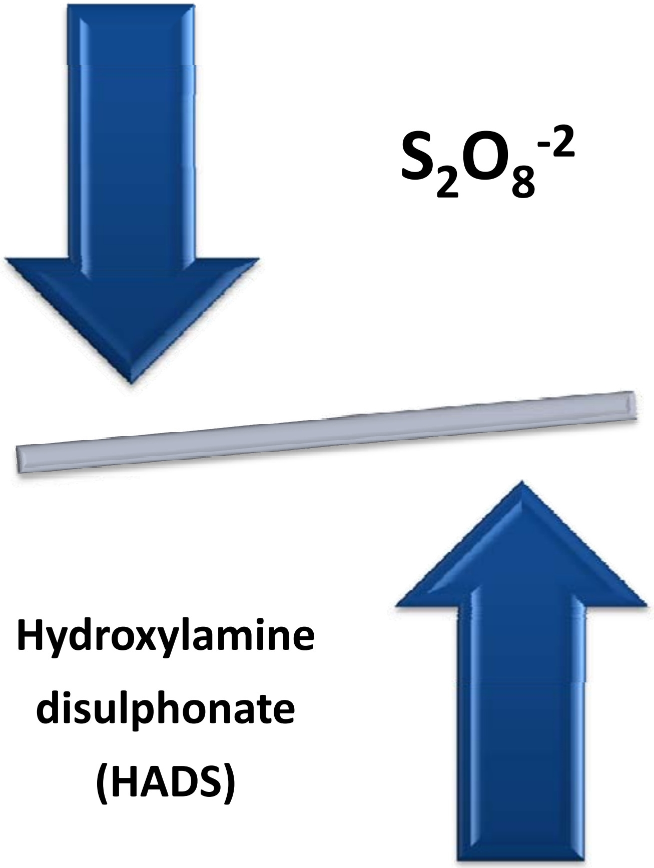
$$M^{+3} + SO_3^{-2} \rightarrow M^{+2} + \cdot SO_3^{-}$$

$S_2O_8^{-2}$ Formation - Sulfite

- Sulfite is important to $S_2O_8^{-2}$ concentration
  - The kinetics of sulfite oxidation are thought to control $S_2O_8^{-2}$ formation
    - $S_2O_8^{-2}$ formation is expected to occur in WFGD absorber slurries
    - The kinetic rate at which sulfite is oxidized to sulfate is important
    - Fast kinetic rates of oxidation are thought to lead to higher levels of $S_2O_8^{-2}$ in the system
    - Less $S_2O_8^{-2}$ should be detectable in absorber slurries when sulfite is allowed to form.
  - It is unknown whether the sulfite reacts directly with $S_2O_8^{-2}$ in solution or if it inhibits $S_2O_8^{-2}$ formation.

$S_2O_8^{-2}$ Formation – Sulfur/Nitrogen Chemistry

- Relationship between S-N chemistry & ORP
  - Nitrogen species react with sulfite in the HADS series
  - Oxidation kinetics
  - May be limiting the chain reaction from happening
  - Chelation or direct reaction w/Mn



$S_2O_8^{-2}$

Hydroxylamine disulphonate (HADS)

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
- FIUDC can occur in low ORP systems
- Other causes of corrosion may exist

Summary

- High ORP Aggressive Corrosion Mechanism
  - MnO_2 precipitation due to strongly oxidizing conditions
  - Maintain ORP at a suitable level
  - Identify/eliminate strong oxidizers
- Fluoride-Induced Under-Deposit Corrosion
  - Variable attack severity, morphology and locations
  - Better understand mechanism and alloy susceptibility
- Process Chemistry Effects
  - ORP can be modified by process control
  - ORP controls phase partitioning of Mn, Hg, Se
  - FIUDC may still occur

In Conclusion

Metals Testing

- B&W has created a new bench-scale screening test for WFGD materials.
- Coupon and/or ER probe testing from field operation will be used to verify the results of the bench test.

Process Chemistry Effects

Path Forward

- Joint Field Test Research with SRI
- Full Scale Test
  - Coal Effects
  - Oxidation Air Effects
  - Upstream Effects

Questions

B&W

power generation group

Thank You