

REINHOLD ENVIRONMENTAL Ltd.



2016 APC-Wastewater Round Table & Expo Presentation

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APC – Wastewater
Round Table
2016

Effects of MATS Control and Variable Unit Load on ORP and Trace Metals in FGD Wastewater



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Presentation Outline

- What is ORP?
- Why is ORP an important measurement?
- How to measure ORP
- How does ORP relate to FGD chemistry?
- What affects ORP?
- How to control ORP
- Discussion

What is ORP and Why is it important?

Oxidation/Reduction Potential (ORP)

- “measures an aqueous system’s capacity to either release or accept electrons from chemical reactions” [Hach]

Why is it important?

- Measure of sulfite oxidation rate
- Provides insight to trace metal behavior in scrubber slurry

Useful tool to help troubleshoot:

- Compliance issues (MATS & ELG)
- Process chemistry issues (corrosion, sulfite oxidation)

How is ORP measured?

- Easy measurement, made using a probe
- Handheld or in-line probes available
- Units = mV



Tips for Obtaining Accurate Measurements

Important to have a probe cleaning and QC Plan

Inspect and clean inline probes regularly

- Frequency = monthly? quarterly? Similar frequency as for pH probes

Perform QC checks to check probe accuracy

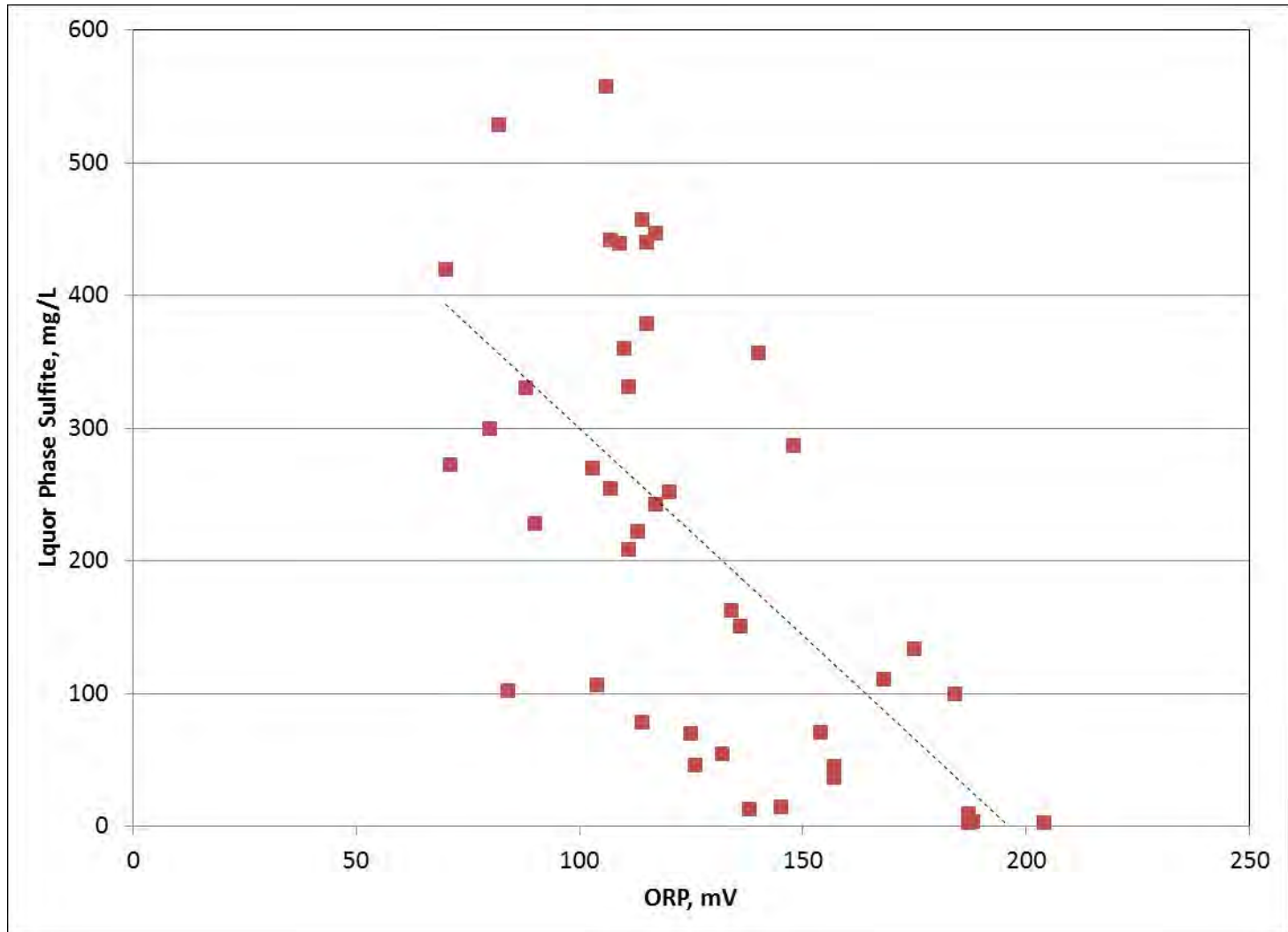
- Take measurement in QC standard
 - Use standard with a value in the same range as slurry measurement
- Frequency of checks included in plan
 - Handheld – before each measurement
 - Inline probe – weekly, monthly? Again, base on pH experience

How ORP Relates to FGD Slurry Chemistry

- Sulfite oxidation
- Oxidant formation
- Mercury partitioning
- Selenium speciation
- Arsenic speciation
- Manganese partitioning

How ORP Relates to Sulfite Oxidation

Example Data

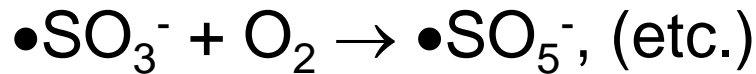


How ORP (sulfite oxidation) Relates to Gypsum Purity

ORP, mV	Composition of Scrubber Solids, wt%		
	Gypsum	Calcium Sulfite Solids	Excess Limestone
190	97.3	0	2.7
187	98.1	0	1.9
132	98.3	0.3	1.4
126	97.6	0.3	2.1
115	63.1	31.8	5.1
71	54.3	32.3	13.4

Formation of Oxidants in High ORP Slurry

Initiation of Sulfite Oxidation Reactions:

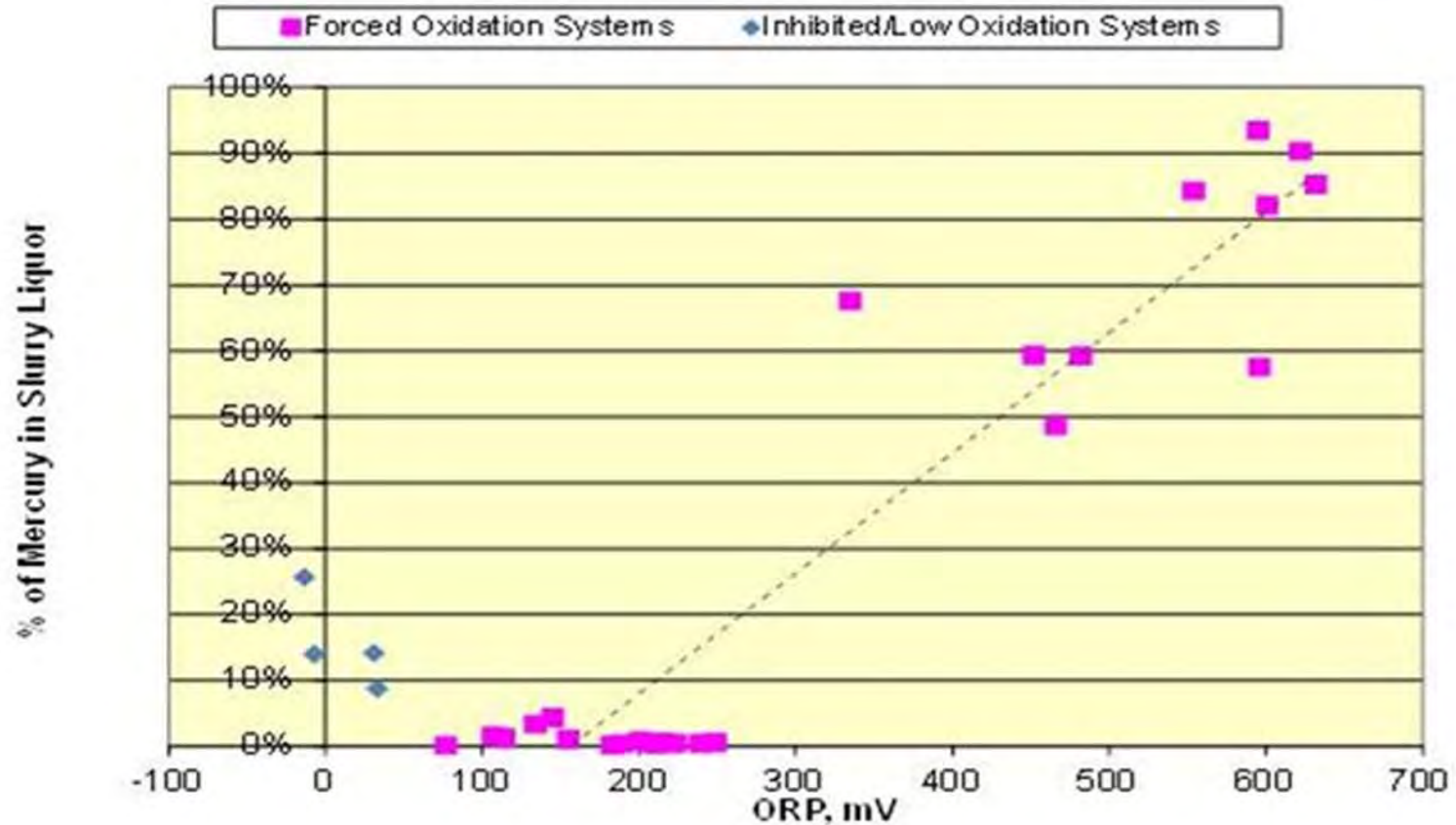


Formation of Sulfite Oxidation Byproducts:



- **In high ORP FGD systems, peroxodisulfate can be present at levels of 100s to 1000s of ppm**

How ORP Relates to Dissolved Hg



- The percentage of mercury in the liquor phase increases with ORP

Liquor Phase Mercury Concentrations at High ORP (>400 mV)

Plant ID	ORP (mV)	Liquor Phase Hg ($\mu\text{g/L}$)
A	650	26
	590	49
	608	44
	594	61
B	527	450
	610	452
	625	355
	599	325
	619	400
	606	471
	620	328
	588	400
C	524	91
	510	82
D	605	196

- High ORPs (>400 mV)
Hg conc. reaches high ppb range
- Low ORP (<250 mV)
typical Hg Conc. single digit ppb or less

How will this change impact Hg removal in wastewater downstream of the WWT plant?

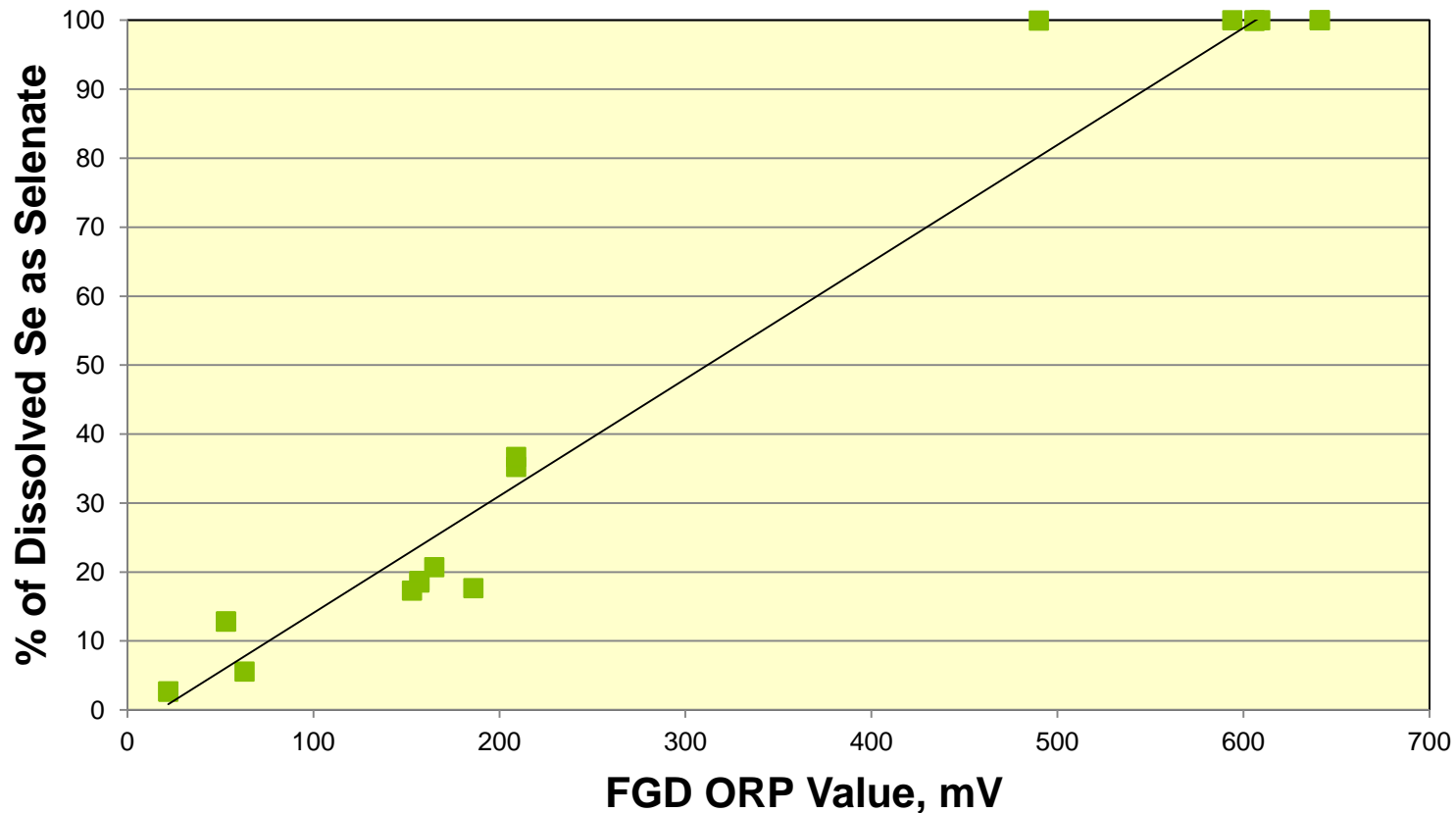
Example Effect of ORP Change on Mercury

Parameter	With Forced Oxidation Air	No Forced Oxidation Air
ORP, mV	>250	160
Net Hg Removal across FGD, %	33	73
Dissolved Hg, µg/L	50-80	<10

Lowering the ORP of the scrubber:

- (1) Reduced the dissolved mercury in the FGD liquor
- (2) Increased the net mercury removal across the scrubber

How ORP Relates to Dissolved Se Oxidation



- Scrubbers operating at high ORP have higher percentages of selenate
- Total dissolved Se in FGD liquor generally increases with ORP

Example Effect of ORP Change on Dissolved Se Oxidation

In-line Absorber ORP, mV	472	139	142
Dissolved Total Se, $\mu\text{g/L}$	617	219	205
% Selenate	100	52	44
% Selenite	0	47	53
% SeCN	0	1	3

Benefits of lowering the ORP:

- Reduces the percentage of selenate formed
- Increases the percentage of selenite remaining in the liquor (readily removed in WWT, more likely to adsorb/co-precipitate to solids)

Effect of Organic-based Reduced-Sulfur Additive on Dissolved As in Low ORP FGD System

Test Condition	Additive Rate (gph)	ORP (mV)	% As in Liquor	Dissolved As (µg/L)
Baseline	0	157	0.1%	3.48
350 ppm Br	0	138	0.3%	4.01
600 ppm Br	2	90	6.8%	48.5
500 ppm Br	2	109	13%	58.8

- Apparent adverse effect: percentage of As in liquor increases with additive rate and/or lower ORP
- Likely an effect from the lower ORP/less oxidizing conditions than a direct effect of the re

How ORP Relates to Manganese Partitioning

Test Condition	ORP (mV)	% Mn in Solids	Dissolved Mn (mg/L)
Site 1	193	4.7%	631
	194	4.1%	668
Site 2	524	72.5%	12.5
	510	73.9%	11.6

- Data shown are for identical FGD systems on similar units at different stations
- At highly oxidizing conditions, Mn^{2+} oxidizes to insoluble Mn^{3+} or Mn^{4+}
- Mn scaling on alloy vessel walls can lead to under-deposit corrosion, through-wall penetration

Parameters that Impact ORP (high level)

- Mass rate of SO_2 scrubbed
- Amount of O_2 scrubbed from flue gas in the absorber
- O_2 transfer from forced ox air in the reaction tank
- pH (direct effect and indirect effect through solubility of transition metal catalysts)
- Transition metal catalysts in the slurry (Cu, Mn, Fe)
 - From limestone or fly ash scrubbed
- Reducing or oxidizing species added to scrubber (organic acid buffers, sulfur/thiosulfate, re-emission additives)
- Others?

Parameters that Contribute to ORP Variation

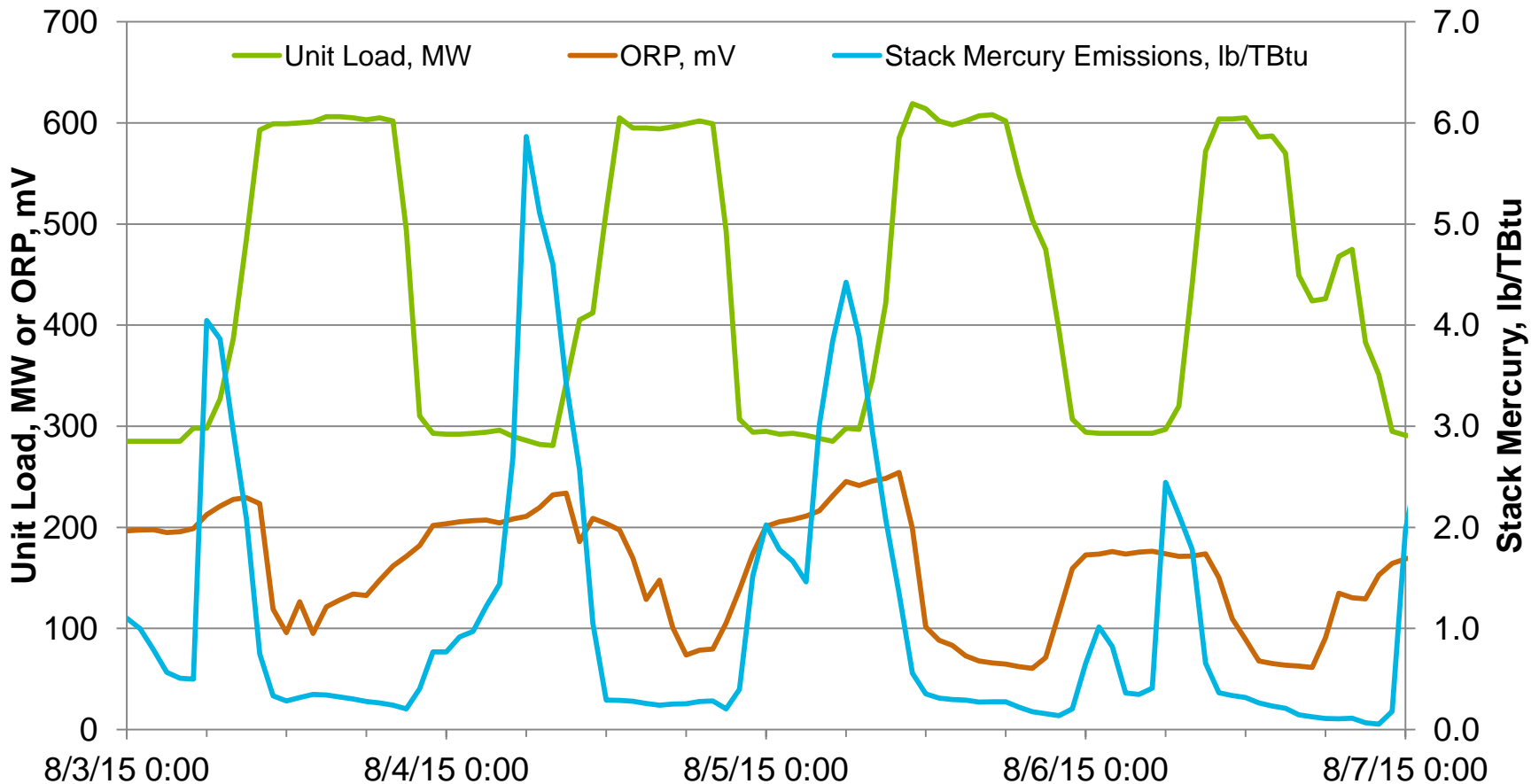
Key Ratios

- Flue Gas O:SO₂ ratio
- Reaction Tank O:SO₂ ratio
- L/G ratio

Individual Variables

- pH
- Unit load
- Excess O₂ in flue gas
- Fuel sulfur
- SO₂ removal level
- Fly ash capture in scrubber
- Impurities in limestone
- Number of recycle pumps running
- Forced oxidation air rate
- Air sparger depth in reaction tank
- TDS in slurry liquor

Example Impact of Variable Load Operation



- Variable load operation impacts ORP and Hg emissions
- Load affects L/G, O:SO₂ ratio in flue gas and rxn tank

How to Control ORP

Methods for Lowering ORP in Wet FGD:

- Lower forced ox air rate or turn off air, if possible
- Raise pH set point
- Lower L/G ratio (fewer pumps running) when extra pumps not needed to achieve SO₂ compliance
- Higher SO₂:O₂ ratio in inlet flue gas
 - Lower excess air in flue gas
 - Fire higher sulfur coal
- Tighten water balance to increase TDS
- Lower slurry level in reaction tank, if possible
- Improve ESP performance
- Possible limestone change?
- Use reducing additives (e.g., organosulfides)

Presentation Summary

- ORP is an indicator of the status of many chemical reactions going on in the FGD slurry
- There are variables that can be adjusted to keep the slurry ORP within desired ranges (e.g., 150-250 mV)
- Most FGD systems are not currently operated such that ORP is a controlled parameter, but this may change in future operations to achieve MATS and ELG compliance

Discussion Points

- Experience with monitoring ORP
- Impact of changes in mercury concentrations on WWT system
- Impact of oxidants on biological systems
- Experience with changes in ORP
- Experience with controlling ORP

Thank You!

Name
Title
Email

