Worldwide Pollution Control Association

WPCA/LG&E and KU
Coal-fired APC Environmental Seminar
May 23-24, 2017

WPCA

Visit our website at www.wpca.info

What’s the Best Approach for Controlling Forced Oxidation Air Rates?

Presented at the WPCA/LG&E and KU Coal-fired APC Environmental Seminar

Gary Blythe, AECOM

May 24, 2017

Why Control Forced Oxidation Air Rates?

- Historically not required on LSFO FGD systems
  - Large coal units typically base loaded
  - High air rates at low load ensure low liquid-phase sulfite, high gypsum purity
  - Minor auxiliary power savings not important
- More drivers to control ox air rates today:
  - Coal units cycling and operating at low load
  - Wet FGD used as a mercury control device
  - ELGs likely to require control of Hg, As, Se, NO_3^- in FGD wastewater discharges
  - Better net heat rate makes plant more competitive

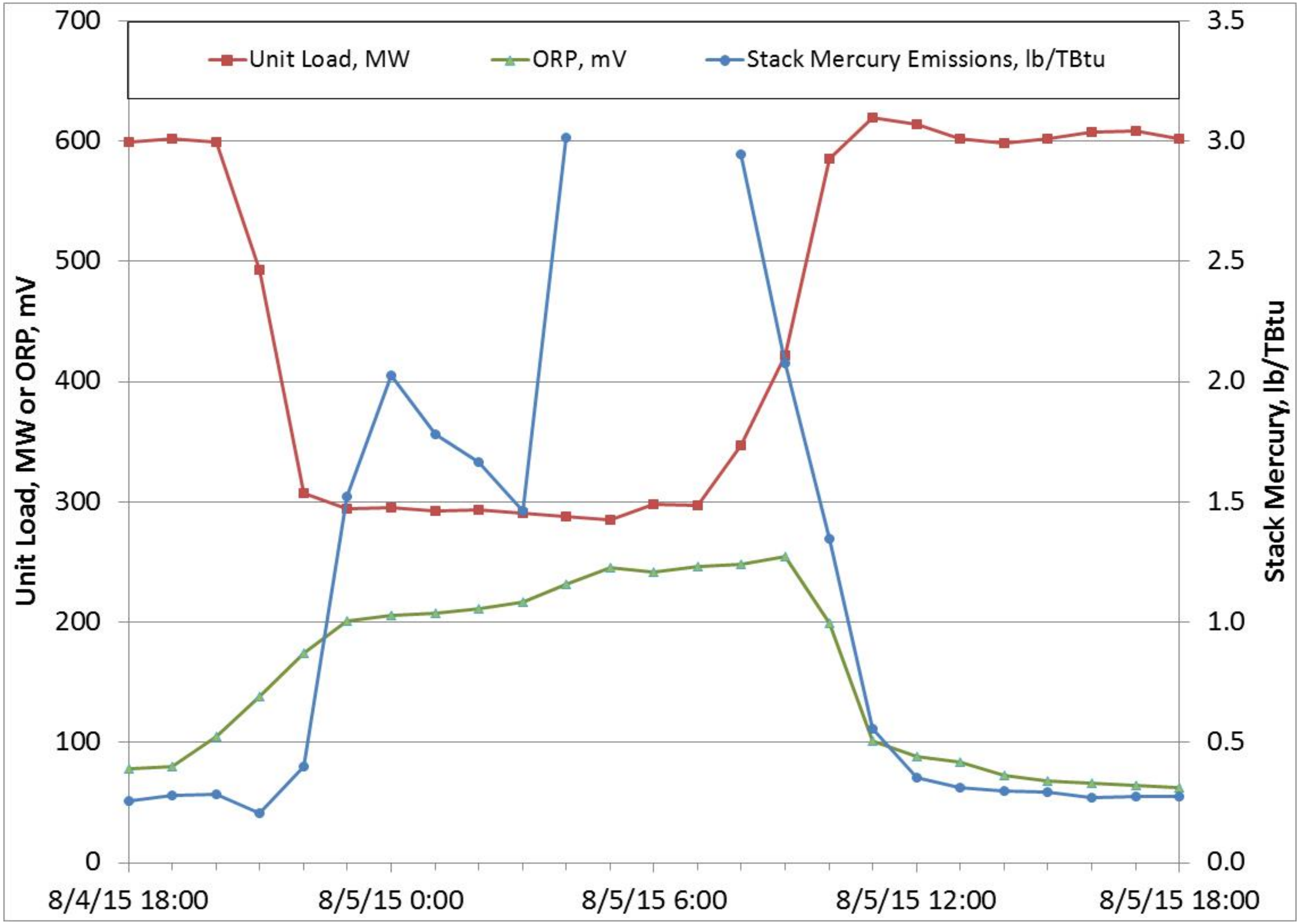
How to Best Control Forced Oxidation Air Rates?

- No control – deal with Hg emissions using PAC injection upstream or re-emission additives; use WWT downstream
- Control ox air rates based on slurry ORP measurements
- Use empirical, feed-forward control strategy
- Measure slurry liquid-phase sulfite concentration with on-line monitor, vary ox air rates to control sulfite at set point

Impacts of Not Turning Down Ox Air Rate at Low Load and/or Low Inlet SO_2

- Dissolved sulfite concentration below detection limits
- High ORP (>300 mV)
- Hg in slurry transfers back to liquor phase & re-emits, or:
  - High PAC injection rates required upstream of FGD to control Hg in flue gas below MATS limit, and/or
  - High addition rates of re-emission additive to lower ORP, control re-emission
- Selenite in liquid phase oxidizes to selenate
- Dissolved manganese oxidizes, precipitates on reaction tank walls, other wetted surfaces

Example Data with Forced Ox Air at Maximum Rate and Cycling Load



Remaining Three Options Involve Adjusting Forced Ox Air Rates

– ORP control, feed-forward approach, dissolved sulfite control all need a wide range of turndown of air flow to be most effective
  - Turndown is limited on many FGD systems
  - Range of turndown depends on blower/compressor type, air system design details, type of air sparger in reaction tank

Modifying Forced Ox Air Systems to Increase Turndown

- Replace manual valves with remotely operated valves
- Modify piping to allow one blower to supply air to two FGD systems
- Possibly use VFD on blower motor
- Add blow-off valves and silencers to provide additional turndown
- Take some fixed sparger headers out of service

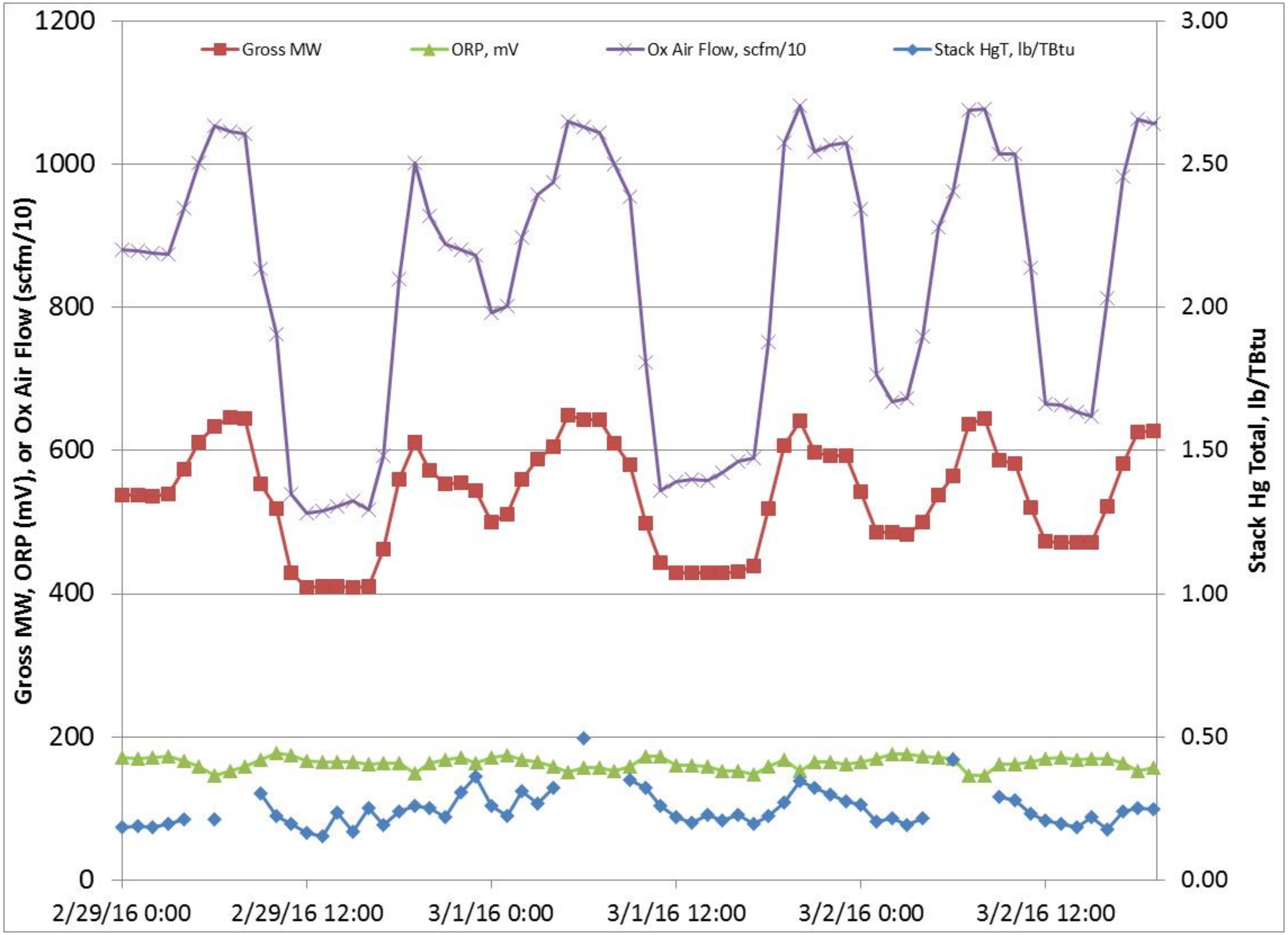
Option 1: Adjusting Forced Ox Air Rates to Control ORP

- Automating control may be covered by a MHI patent
- Manual adjustment approach requires considerable operator attention
  - Operators unsure how big an adjustment to make on air rates
  - Air flow rate instruments often inaccurate or inoperable, makes it difficult for operators to gauge “where they are”
- How reliable is ORP measurement?
  - Probes require as much diligence to maintain as pH
  - ORP measurements impacted by other redox reactions in wet FGD slurry

Option 2: Empirical Correlation to Control Forced Ox Air Rates

- Automates forced ox air rates to adjust for unit load, FGD inlet SO_2 concentration
- Empirical control algorithm programmed into DCS
  - Upgraded air flow instrumentation may be needed
  - Works best with a reliable inlet SO_2 monitor
  - Adjustments needed to account for higher O_2 in flue gas at low load, how many recycle pumps are running, etc.
- Low capital cost
  - No slurry probes or monitors needed
- Tuning may be needed to maintain control of sulfite oxidation rates as plant operations change

Example Data with Feed Forward Forced Ox Air Control



Option 3: Sulfite Probe for Feedback Control of Forced Oxidation Air Rates

– Proprietary instrument developed by Alstom AQCS Service Solutions (now part of GE)
  - Continuous dissolved sulfite concentration measurements in a flowing, ambient pressure slipstream sample
  - Voltammetry method
  - Calibrated by comparing to manual measurements

– Patented approach of using analyzer output as set point for controlling ox air flow rate

– Requires an analyzer on each absorber reaction tank

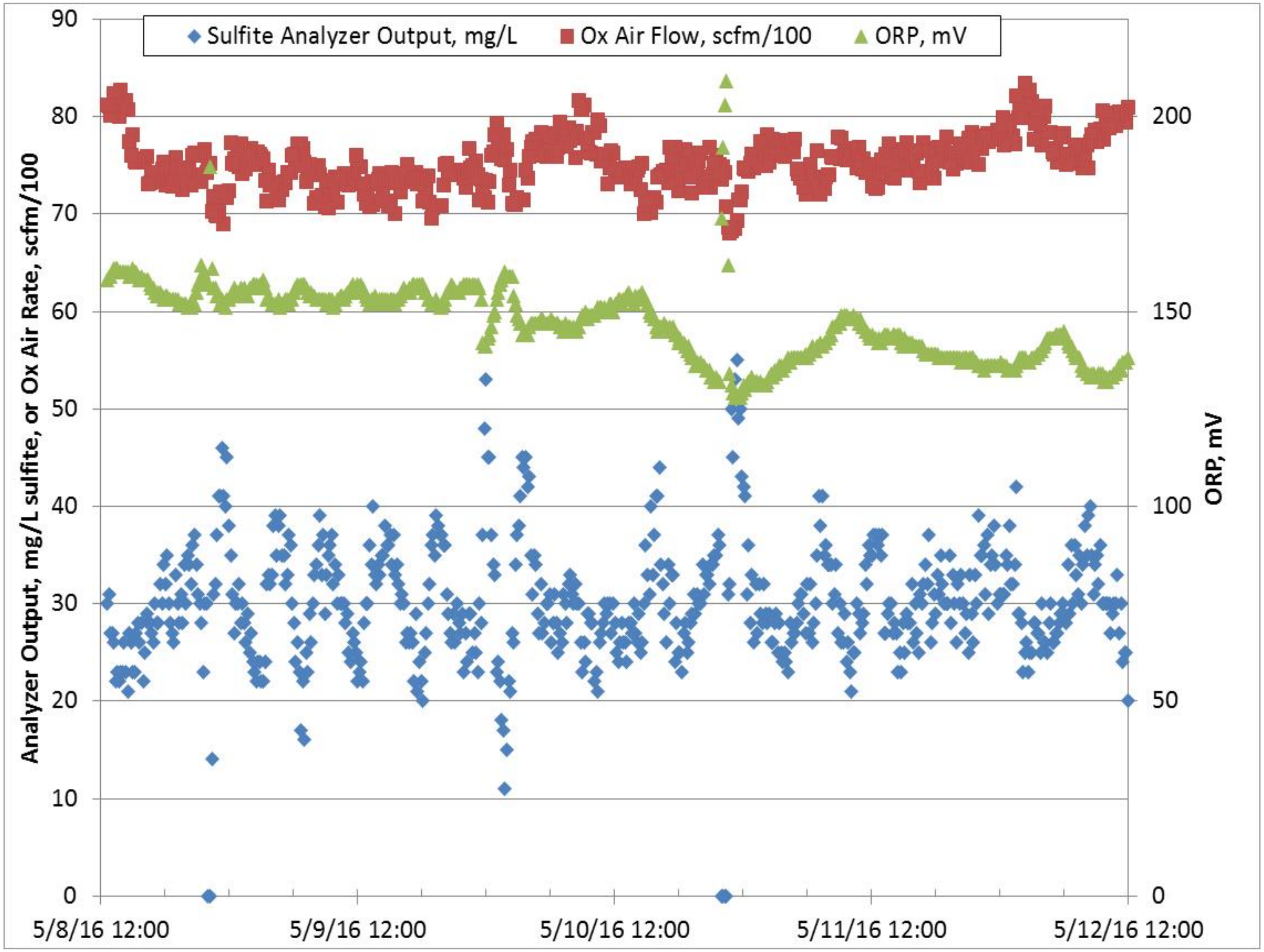
GE Commercial Sulfite Analyzer

- Designed to operate in slurry service
  - “Wiper” rotates to keep probe tip clean
  - Weekly cleanup with soft brush to avoid solids buildup

Results for Sulfite Control of Forced Oxidation Air Rates

- Test conducted on 1 of 3 absorber modules on a 1300-MW unit firing medium-sulfur bituminous coal
  - Spray towers with fixed sparger grids in reaction tanks
  - Tests conducted at 60% load and greater to avoid minimum air flow limits imposed by fixed sparger design
- Note that similar results could be achieved with the other technologies if adequate control of sulfite oxidation rate is achieved

Analyzer Output, Ox Air Rate, and ORP during Sulfite Control Operation

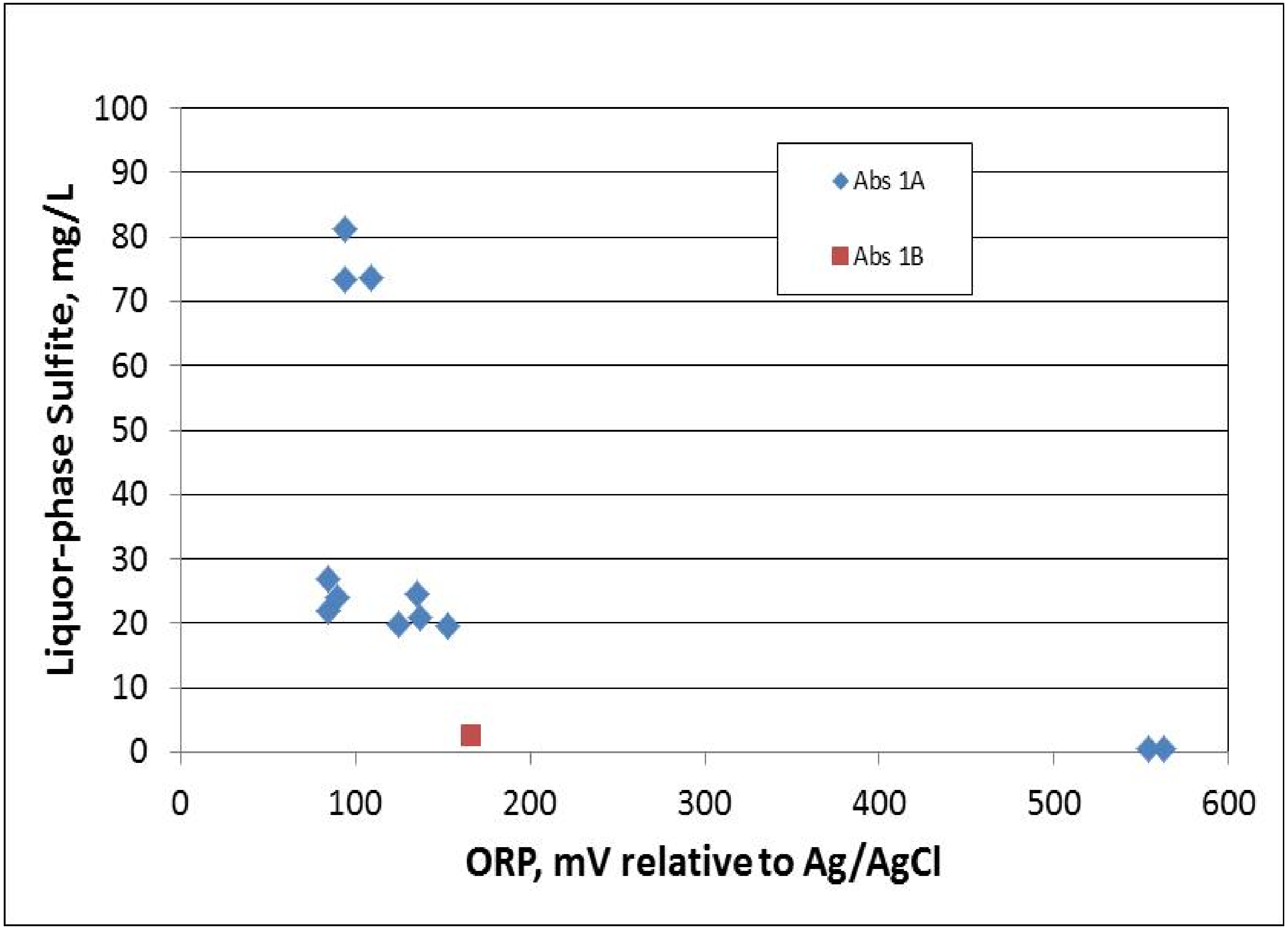


Analyzer Output versus Lab Measurements during Sulfite Control Operation

Date	SO_3^{2-} by IC, mg/L	SO_3^{2-} by Analyzer Output, mg/L	Relative % Difference
10/19/15	<1.1	Not in service	-
10/20/15	<1.1		-
5/11/16	20	27	30
5/11/16	21	29	32
5/11/16	20	33	49
5/12/16	25	35	33
6/15/16	81	79	3
6/15/16	73	79	6
6/15/16	74	78	5
2/16/17	22	24	8
2/16/17	24	23	6
2/16/17	27	27	4

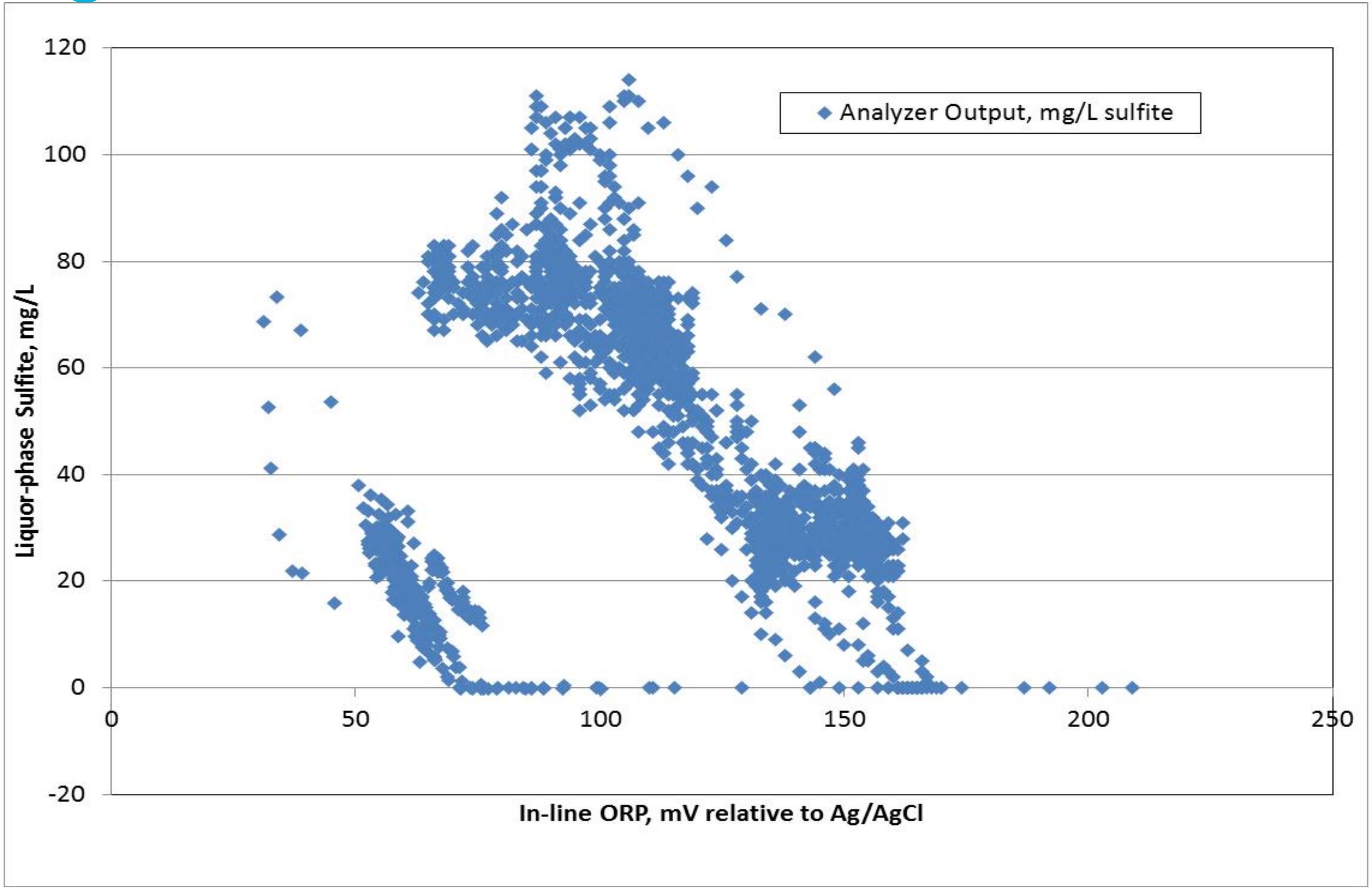
All sulfite values by analyzer reflect calibration from 10/21/15

Liquor-phase Sulfite (lab result) vs. ORP (hand-held instrument)



Note range of sulfite values at ORP ~90 mV

Sulfite Analyzer Results vs. ORP Probe during Three Test Periods



Note discontinuity of sulfite vs. ORP for different time periods

Test Absorber Average Hg Control Results

Condition	**Inlet Hg Oxidation, %**	**Hg Removal across FGD Absorber, %**	**Hg Re-emission across FGD, % of inlet Hg^{2+}**	**Outlet Hg, lb/TBtu**
Baseline, no sulfite control	98	60	38	1.0
Sulfite control, 20-30 mg/L	97	98	0	0.2
	99	99	0	0.1
Sulfite control, 70-80 mg/L	95	96	0	0.1

Test Absorber Average Hg Phase Partitioning Results

Condition	ORP, mV	Dissolved Hg, ng/L	Hg in slurry solids, µg/g	% of total Hg in slurry liquor	% of total Hg in slurry solids
Baseline, no sulfite control	560	75,000	0.17	70	30
Sulfite control, 20-30 mg/L	140	90	0.55	0.09	99.91
	90	50	0.55	0.05	99.95
Sulfite control, 70-80 mg/L	100	160	0.58	0.15	99.85
No sulfite control*, Nalco 8034+	170	20	0.55	0.02	99.98

*Sister absorber using Nalco 8034+ re-emission control additive

Test Absorber Average Se Phase Partitioning Results

Condition	ORP, mV	Dissolved Se, µg/L	Se in slurry solids, µg/g	% of total Se in slurry liquor	% of total Se in slurry solids
Baseline, no sulfite control	560	610	1.6**	67	33
Sulfite control, 20-30 mg/L	140	290	3.4**	29	71
	90	140	2.3	25	75
Sulfite control, 70-80 mg/L	100	340	2.8**	39	61
No sulfite control*, Nalco 8034+	170	150	2.7	24	76

*Sister absorber using Nalco 8034+ re-emission control additive

**Result is above MDL but below reporting limit, estimated result

Test Absorber Average Se Speciation Results

Condition	ORP, mV	Dissolved Se, µg/L	% Selenite	% Selenate	% Other Selenium Species
Baseline, no sulfite control	-	-	-	~99*	-
Sulfite control, 20-30 mg/L	90	140	93	6	1
Sulfite control, 70-80 mg/L	100	340	97	3	<1
No sulfite control,** Nalco 8034+	170	150	53	47	1

*Previous data from the same FGD system at baseline operation
** Sister absorber using Nalco 8034+ re-emission control additive

Test Absorber Average Total Nitrate/Nitrite Results

Condition	ORP, mV	Total NO_3^-/NO_2^-, mg/L	Apparent S/N species, mg/L as $SO_4^=$
Baseline, no sulfite control	560	16	80
Sulfite control, 20-30 mg/L	140	5	620
	90	5	NA
Sulfite control, 70-80 mg/L	100	2	260
No sulfite control*, Nalco 8034+	170	8	NA

Nitrate concentrations may be lowered by conversion to sulfur/nitrogen species

Test Absorber Average Mn Phase Partitioning Results

Condition	ORP, mV	Dissolved Mn, µg/L	Mn in slurry solids, µg/g	% of total Mn in slurry liquor	% of total Mn in slurry solids
Baseline, no sulfite control	560	50	22	1	99
Sulfite control, 20-30 mg/L	140	3800	3.5	86	14
	90	5600	4.1	88	12
Sulfite control, 70-80 mg/L	100	3700	4.7	81	19
No sulfite control*, Nalco 8034+	170	5000	7.1	79	21

*Sister absorber using Nalco 8034+ re-emission control additive

Mn becomes insoluble at highly oxidizing conditions; can scale on alloys of construction, exacerbate corrosion

Summary

- Many benefits from controlling forced ox air flow to avoid over-oxidizing conditions
  - Improved Hg capture, less need for PAC injection or re-emission additives
  - Lower concentrations of ELG constituents in wastewater
  - Less tendency for under-deposit corrosion of alloys of construction
- Options for controlling oxidation rates: ORP control, feed forward algorithms, in-line sulfite analyzer with feedback control of air rate
  - ORP control can be imprecise, as other redox reactions impact probe readings
  - Feed forward algorithms are empirical and may have to be tuned as process changes occur
  - Sulfite analyzer approach directly controls the sulfite oxidation rate via the concentration of dissolved sulfite
    - Most significant down side is the cost of the analyzer, particularly for multiple modules
- Any control option may require upgrades to the ox air system to improve turndown

Questions?

Gary Blythe
(512) 419-5321
Gary.Blythe@AECOM.com