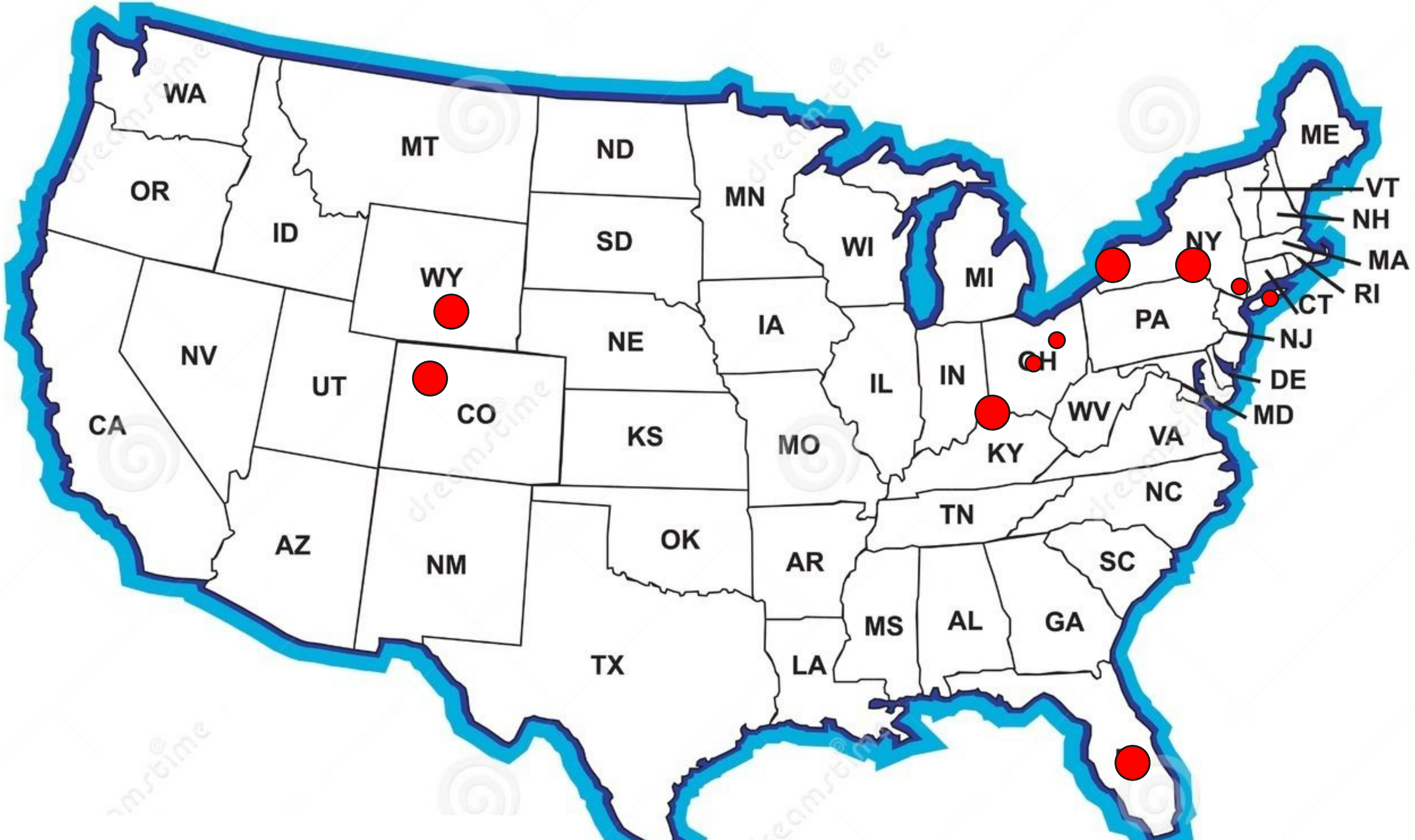
2018 APC & Wastewater Roundtable

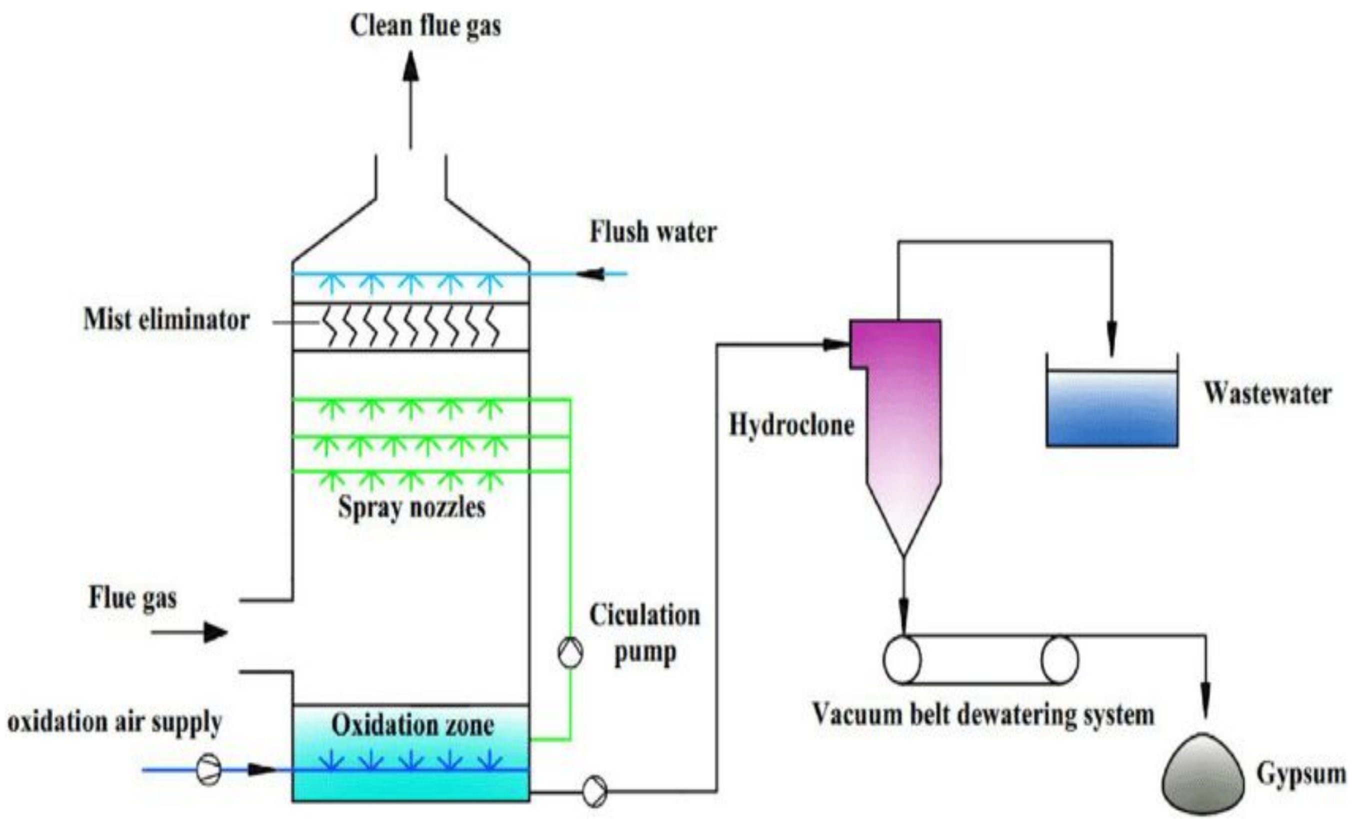
Cycling Load Impacts On WFGD Mass Transfer

Steve Feeney Consulting
July 24, 2018
Workshop 21



Map Courtesy Dreamstime.com

Cycling WFGD Mass Transfer Affect - LSFO



WFGD Schematic courtesy Researchgate

Wet/Dry Interface

Residence Time

Purge/Water

Gypsum Chemistry

Cl

Buffering Agents

pH/ORP

Hg

Se

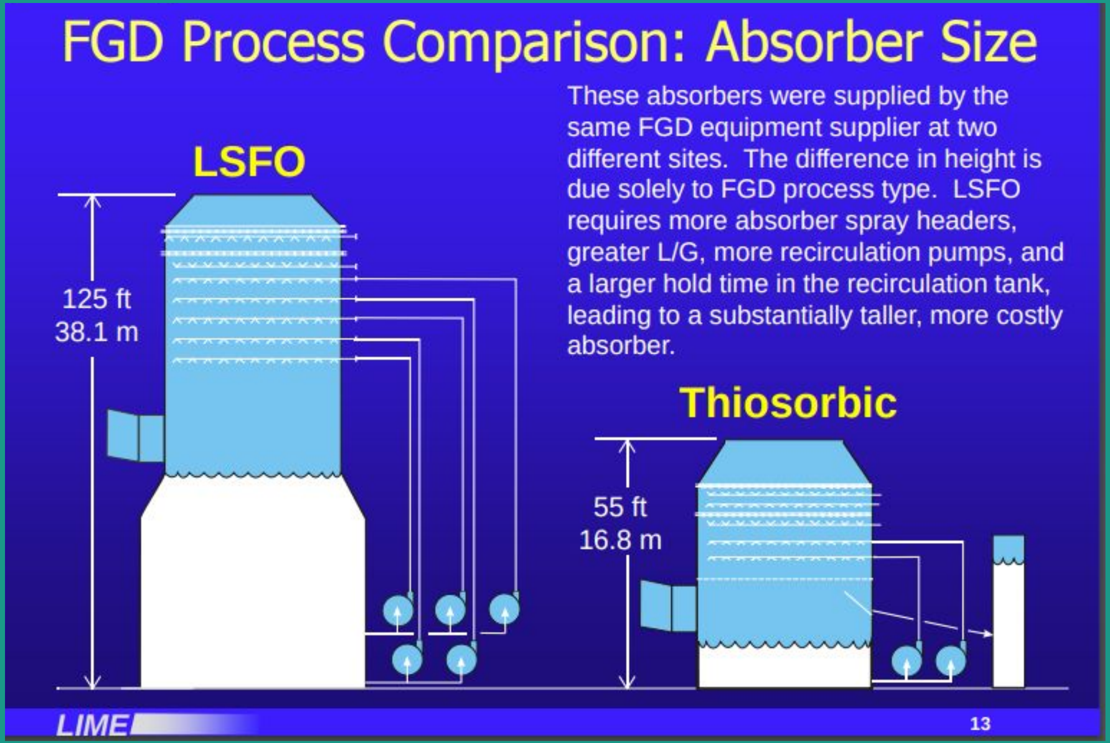
Lower Loads Tend To Improve SO2 Eff.

Table 1. Comparison of Different Conditions and WFGD Parameters

Unit	Inlet SO_2 (ppm)	Boiler Load (MW)	Swinging Load (yes/no)	SO2 Removal (%)	Purge Flow (gpm)	pH	ORP (mV)	Ox Air to Reaction Tank	Residence Time (hr)	Reagent Flow (gpm)
Unit A Design	1276	825	no	97	248	5.6	-	Design	17.5	232
Unit A	568	590	no	97.7	75	5.6	227	Design	52.4	78
Unit A	598	590	no	97.5	75	5.5	503	Design	50.1	81
Unit A	517	688	yes	97.4	98	5.4	532	Design	50.0	77
Unit A	311	456	yes	98.3	60	5.4	556	Design	107.0	35
Unit A	455	642	yes	98.6	82	5.6	486	Design	60.2	60
Unit C	1502	352	yes	98.0	100	5.9	560	Design	36.3	108
Unit C	1705	599	yes	96.1	100	5.9	543	Design	21.5	183
Unit C	1682	600	yes	98.0	100	5.9	414	Design	21.5	198
Unit C	1683	598	no	97.8	100	5.9	228	Design	20.9	189
Unit C	1711	600	no	98.2	125	5.9	177	Design	20.6	206
Unit C	1678	600	no	98.2	150	5.9	164	Design	20.7	193
Unit C	1639	599	no	98.1	127	5.9	168	High	21.2	192
Unit C	1594	601	no	97.5	150	5.6	87	Off	20.9	236
Unit C	1649	601	no	97.4	140	5.9	192	Design	21.3	181

Courtesy B&W
MEGA 2014

Chemistry Comparison - LSFO vs. Mag-lime
Cycling Load at LSFO vs. Mag-lime



Courtesy Carmeuse Website

Alkalinity
- Mag-lime: high
- Limestone: low

Dewatering
- Mag-lime: Thickeners, Vacuum filters, pug mills
- Limestone: hydroclones, belt filter

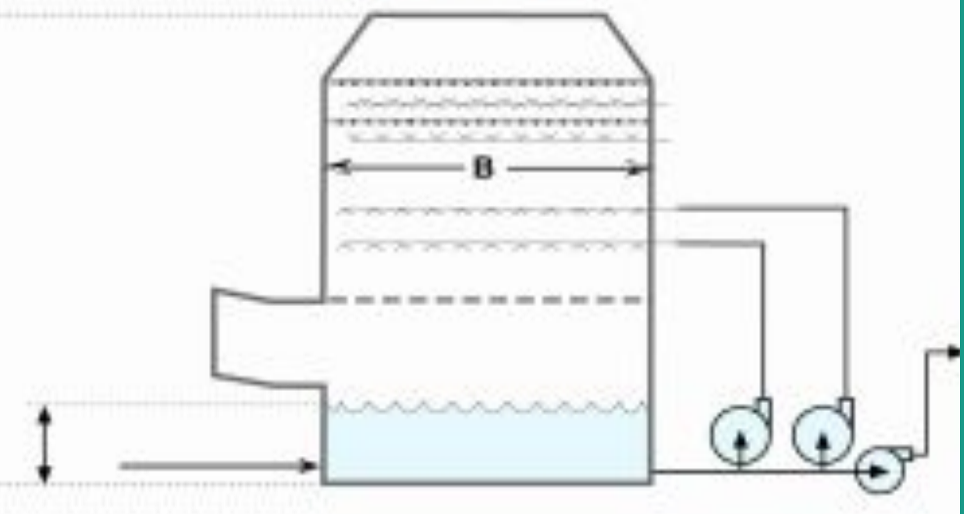
Oxidation
- Mag-lime: Emulsified sulfur
- LSFO: Air

By-product
- Mag-lime: Calcium sulfite
- Limestone: gypsum

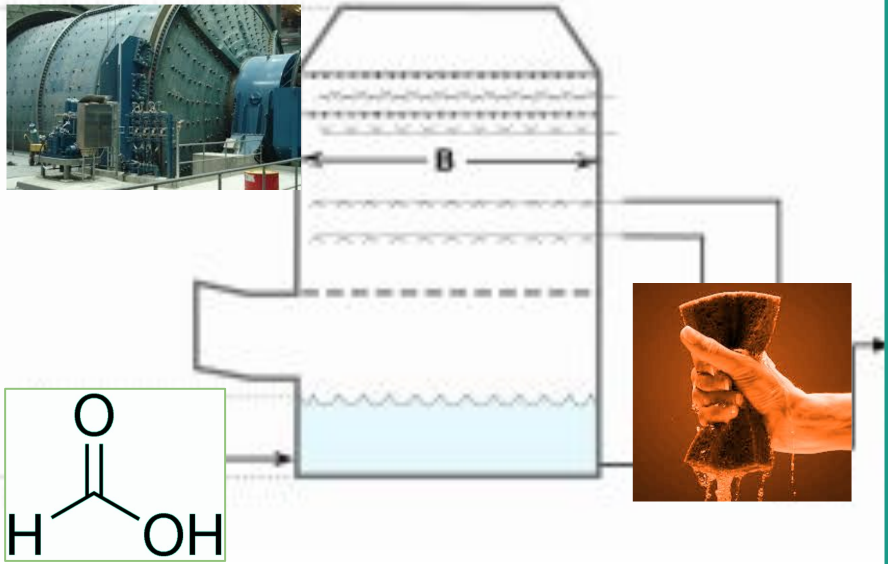
L/G
- Mag-lime: Low
- Limestone: High

ORP
- Mag-lime: Low
- LSFO: Med - High

Mag-enhanced Lime

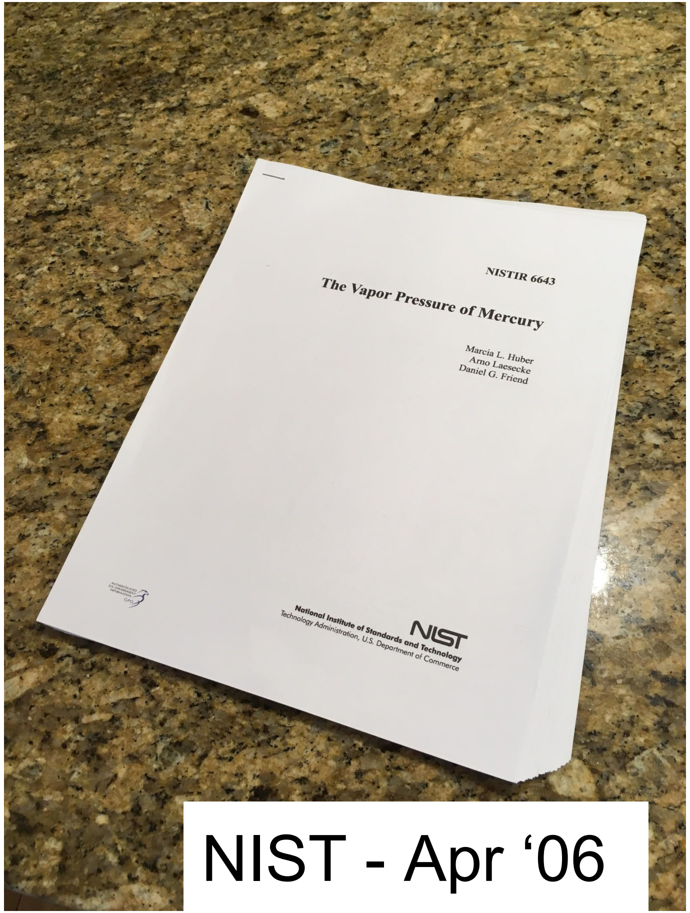


Limestone Inhibited Oxidation



1000MW Unit: Reagent - $6M vs. $17M per yr.

MERCURY



NIST - Apr ‘06

Hg^0 vapor pressure: 0.00036 psi (55C)

Hg^0 ideal gas density: 184 ng/mL (55C)

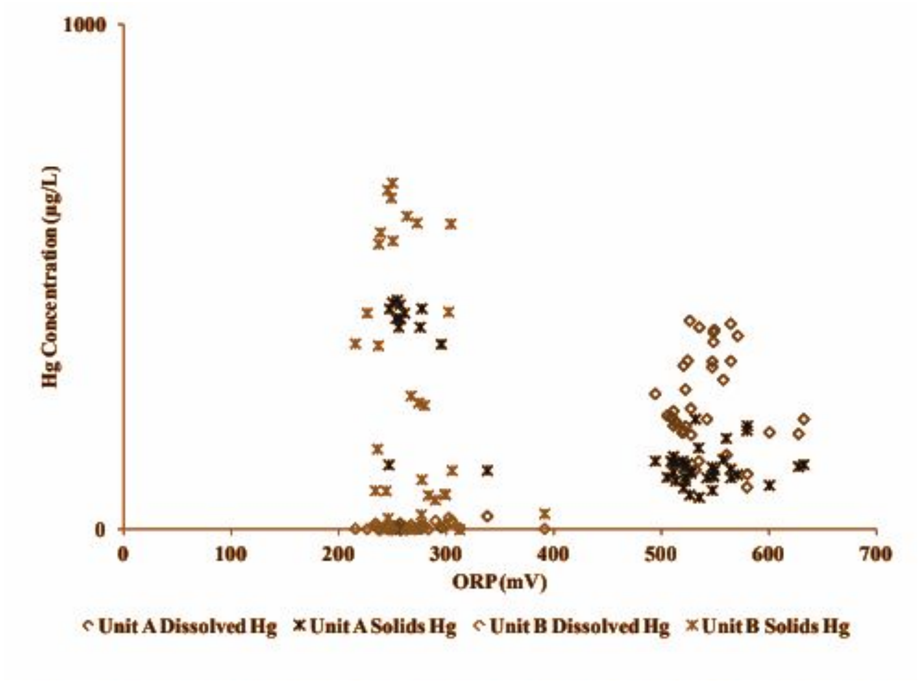
~150 - 200 ppmw for flue gas

Hg^0 solubility: 2 - 63 ppb (25C)

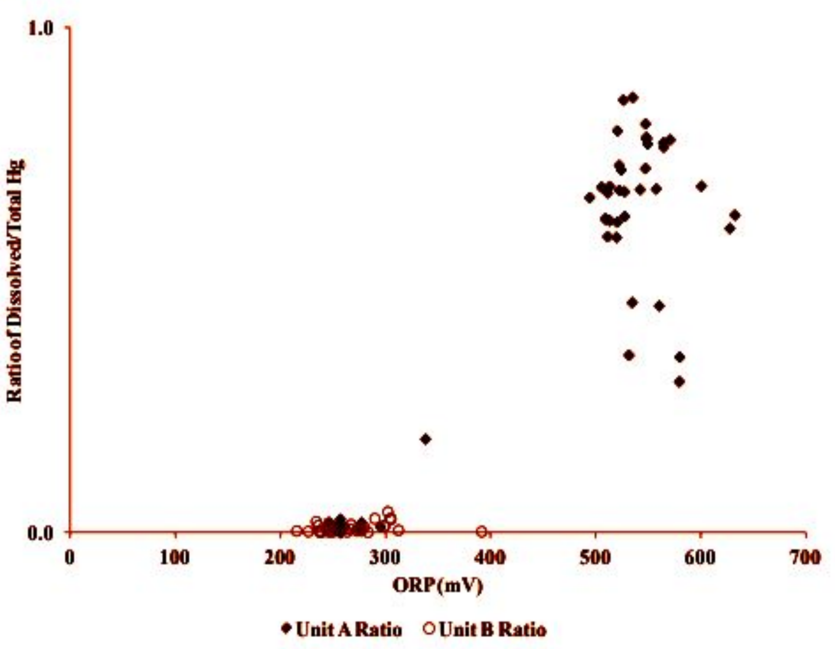
HgS: $K_{sp} = 10^{-53}$

ORP IMPACT ON Hg PHASE PARTITIONING - LSFO

Concentrations of Dissolved Mercury and Mercury Associated with the Solids Measured in Absorber Slurry Samples as a Function of ORP



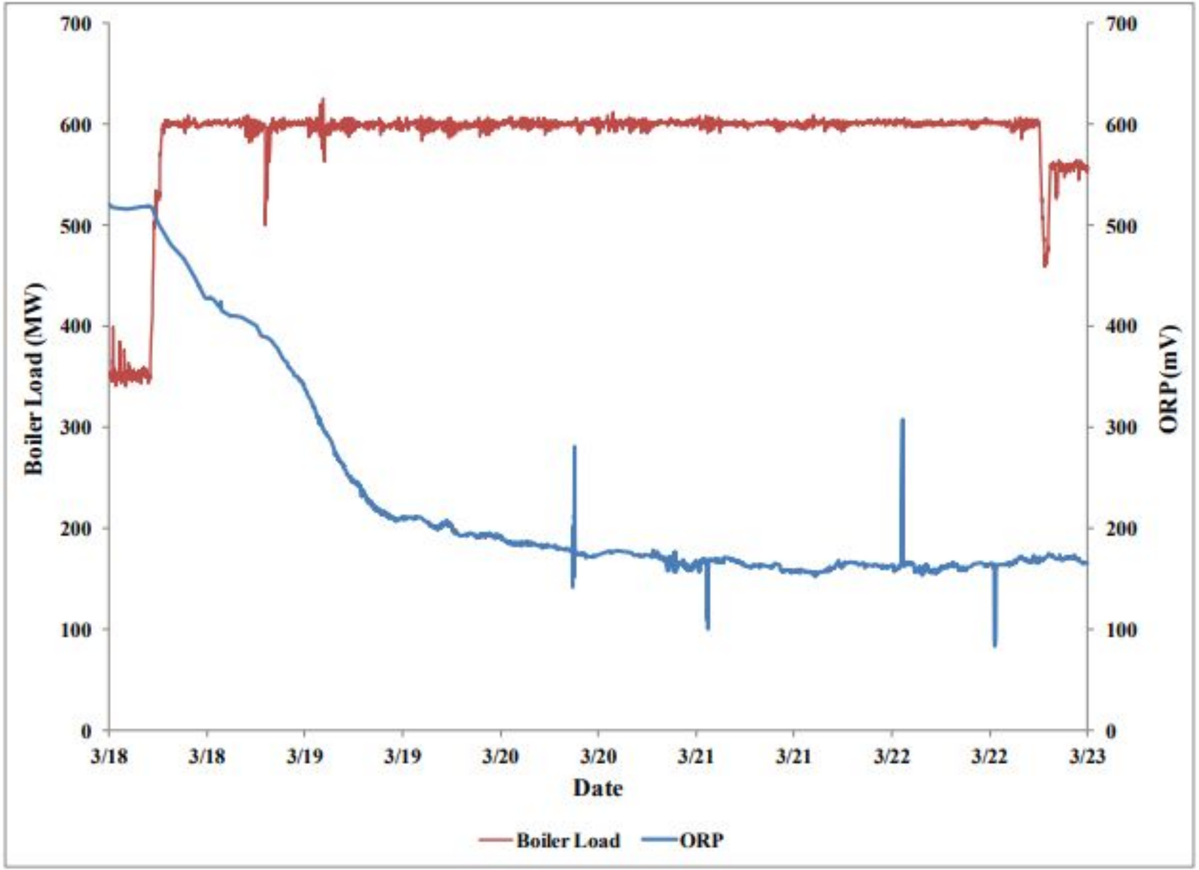
Ratio of Dissolved to Total Mercury Measured in WFGD Absorber Slurry Samples as a Function of ORP



From: “Optimization and Process Control of Air Quality Control Systems for Improved WFGD Oxidation Chemistry and Effluent Composition for Wastewater Treatment”: Power-Gen 2013, B&W, DTE and SRI.

Swinging Load impacts - 2014

Figure 1. Unit C ORP Decrease with Steady-State Conditions



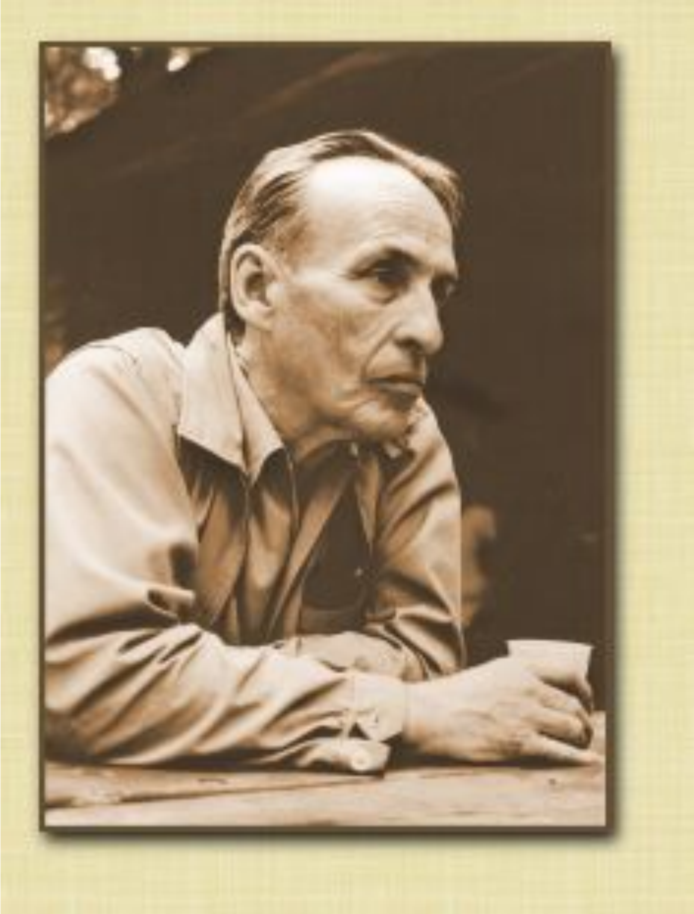
Is this an ORP decrease with steady-state conditions, or is it more accurate to say the ORP does what could be expected - a steady decline in ORP as load moves from ~50% to 100%. Making claims that turn out to be incorrect, while we are on the right path. Once ORP reaches new "steady state", ORP remains fairly constant at 170 mV.

Courtesy MEGA Symposium 2014: "Swinging and Low Load Operation: Impacts on WFGD Chemistry, Waste Water Effluent Management and Air Emissions." B&W/Duke

“For a scientist, this is a good way to live and die, maybe the ideal way for any of us, excitedly finding we were wrong and excitedly waiting for tomorrow to come so we can start over…and basically being on the right track when we were wrong.”

Norman Maclean

Young Men and Fire



Hg^0(liq)–Hg^0(solution) Equilibrium and Solubility of Elementary Mercury in Water

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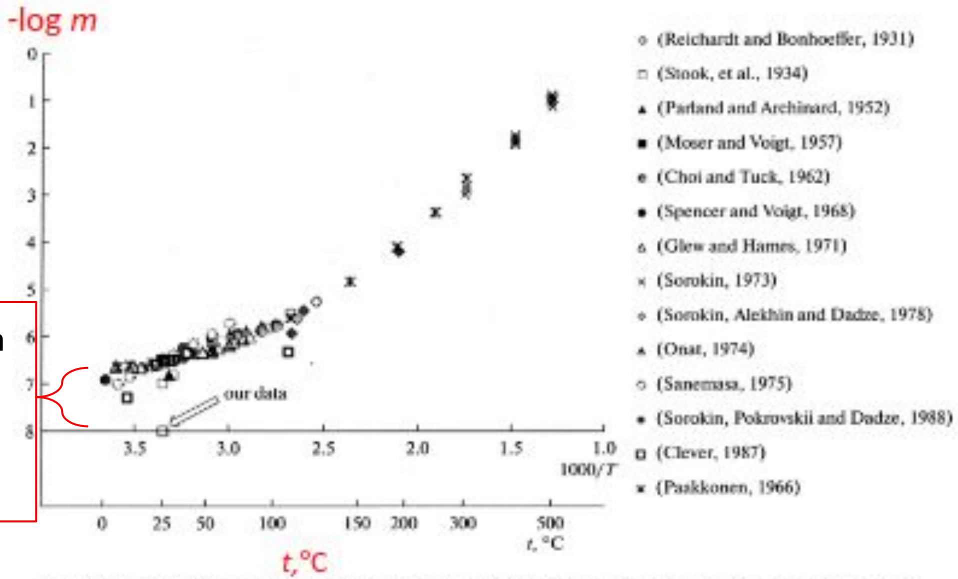
Спасибо.

Abstract—The solubility metallic mercury in water and its dominating forms were studied. The prevalence of the Hg^0_{aq} form in the high-temperature range was confirmed and the reaction constant $Hg^0_{liq} \rightleftharpoons Hg^0_{aq}$ ($\log K = \log m = -8.01$) at 25°C with the predominance of oxidized forms of mercury for the 20–80°C area of low temperatures was found.

Hg^0 solubility in an oxidizing, versus non-oxidizing environment.



The solubility of mercury in water as an inverse temperature function. The initial experimental data of various authors are given from (Sorokin, Pokrovskii, and Dadze, 1988).

Expectations for Hg as ORP changes

In an oxidizing environment, at 25C, ideal conditions, 63 ppb $Hg^0_{(aq)}$.

In a reducing environment, at 25C, ideal conditions, 2 ppb $Hg^0_{(aq)}$.

$Hg^0_{liq} \rightleftarrows Hg^0_{aq}$ when ORP increases, expect more Hg in aqueous phase.

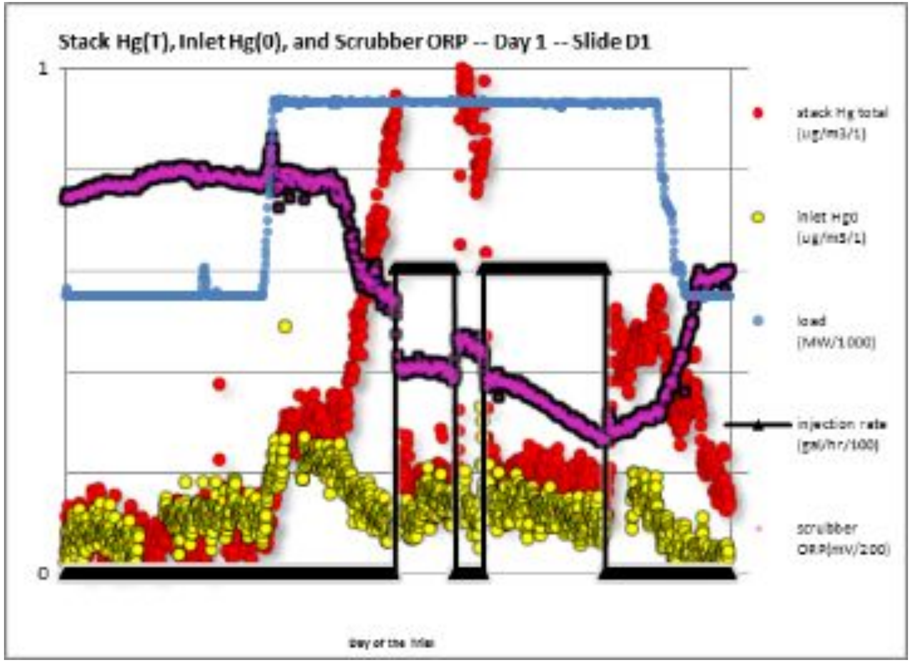
Alternatively, when ORP decreases, expect less Hg in aqueous phase.

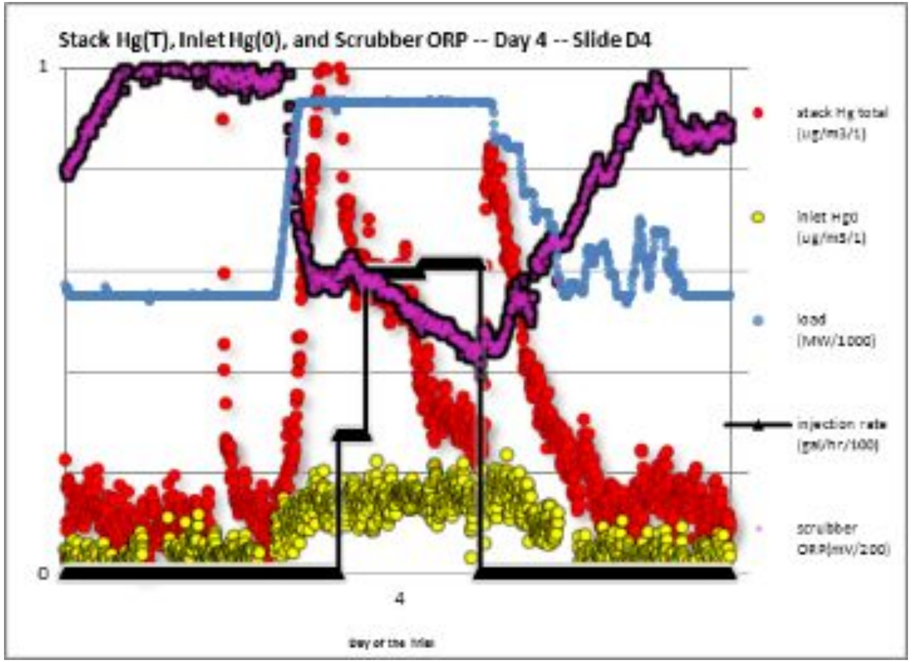
How can we assure that Hg^0 does not desorb from slurry aqueous phase?

Is it necessary to control ORP to control mercury?

Precipitate HgS at low ORP? Yep.

500MW+, SCR, ESP, Chiyoda, Sulfide Testing





WFGD Mass Transfer of SO2 and Hg
Similarities and Differences

Absorb SO2
SO2 absorption stops when slurry liquid is saturated.

Provide Ca^{2+}

CaSO3 and/or CaSO4 precipitation

Deplete the liquid of bisulfite ion so more SO2 can be absorbed.

Slurry aqueous phase is cleared out via precipitation of bisulfite so more SO2 can be absorbed.

Absorb Hg^{2+} and Hg^{0}.
Hg absorption stops when saturated.

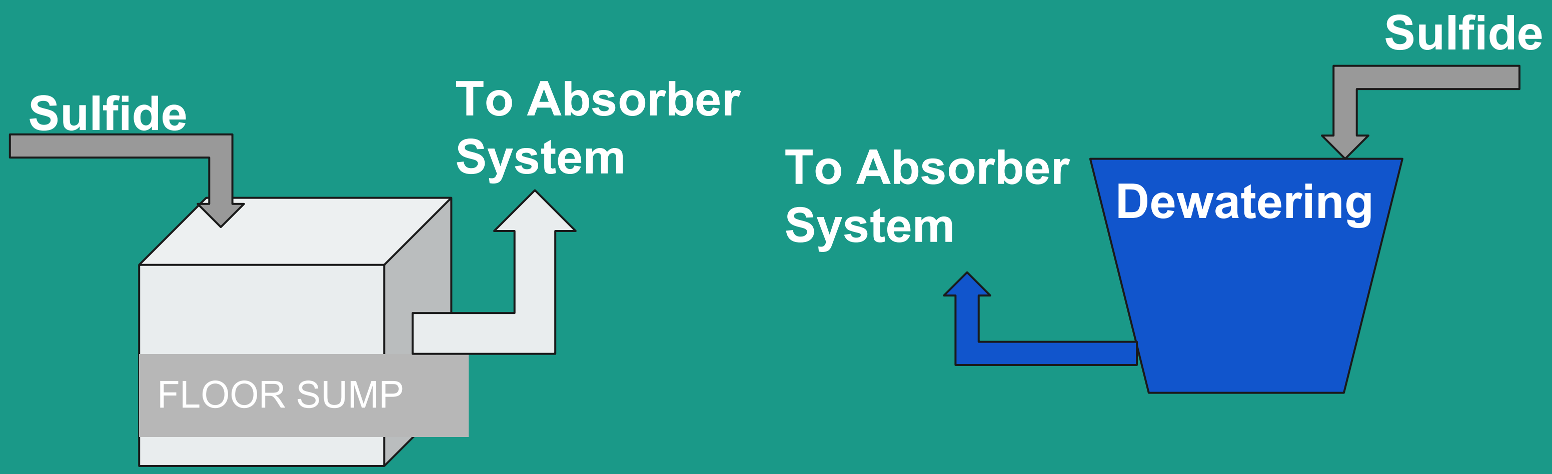
Provide sulfide.

HgS
Deplete the liquid of Hg so more can be absorbed.

Differences
- Reclaim water Hg saturated
- High molar Ratio S/Hg
- 1,000,000 times less Hg^{0}

Seller	$	Chemical	Phases	Comments
#1	$	Sodium Bisulfide	One	The only “simpler” sulfide would by hydrogen sulfide. Well-known in Mining Industry.
#2	$$	Polythiocarbonate	One	Well-known water treatment chemical.
#3	$$	Sodium diethyldithiocarbamate	One	Not used much anymore due to certain safety concerns.
#4	$$	Mercaptan	One	Well-known, used frequently. Added to Natural Gas.
#5	$	Metal sulfide	Two	Particle Size. Dissolution

Mass Transfer Implications of injection location?



Hg Phase Partitioning - Gypsum vs. Calcium Sulfite

LSFO - low alkalinity, lower ionic strength, gypsum (sulfate) versus sulfite.

Mag-lime - high alkalinity, salting out effect, sulfur. Likely need lower dissolved Hg.

LSIO - buffering acid, sulfur, larger calcium sulfite particles, good dewatered solids.

I don't think there is any set ratio, but you need to partition enough Hg to the solids such that liquid needs to be sub-saturated w/r to Hg^0. This depends on the type of system you have.

Remember,

Hg^0 relative vapor pressure is high.
Hg^0 solubility is low.
Ksp is extremely low.
Precipitate HgS, regardless of ORP.

Selenium - Background

NIKSA

SENIOR

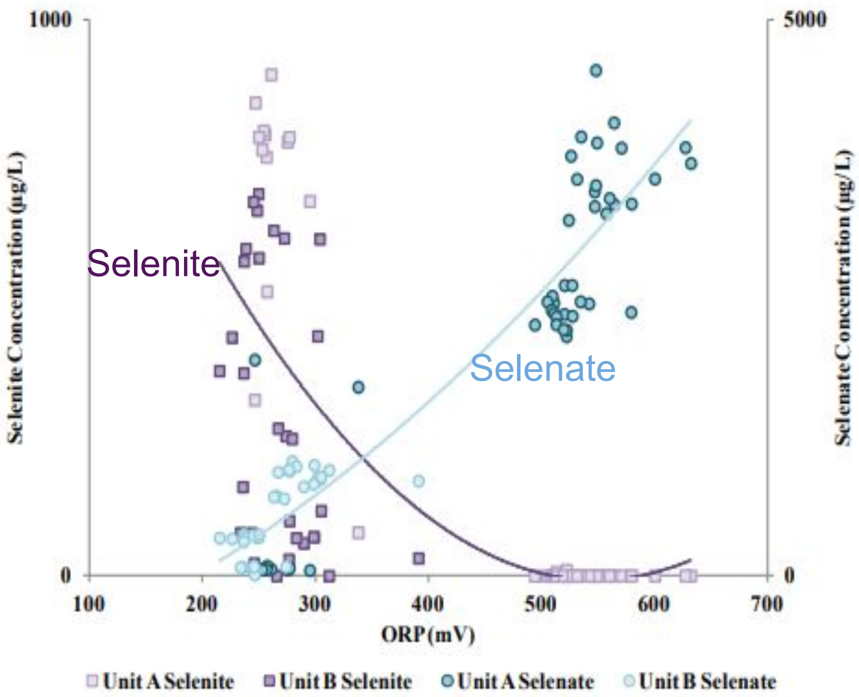
WFGD SO_2 removal exceeds WFGD SeO_2 removal in most cases.

SeO2 WFGD removal generally 50% - 90%. ORP related?

Lower ORP leads to less dissolved selenium in LSFO systems.

Preference for Selenite versus Selenate: LSFO, Mag-lime, LSIO

Selenium vs. ORP

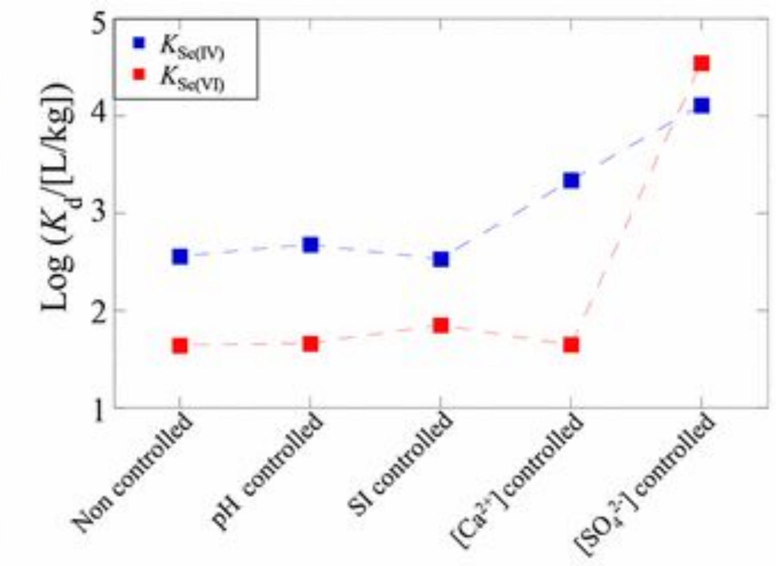


Data from LSFO system, DESP upstream

Lower ORP leads to higher selenite

Taken from Power-Gen 2013: B&W/DTE/SRI "Optimization and Process Control of Air Quality Control Systems for Improved WFGD Oxidation Chemistry and Effluent Composition for Wastewater Treatment"

Several recent Tech Papers on Se Precipitation

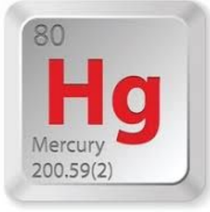


Se is known to react with Fe, Ca and Ba.

Sulfate has been shown to improve precipitation under certain conditions (see graph).

Selenite can be treated with “typical” phys-chem systems at coal plants.

Certain LSFO systems could potentially receive a co-benefit by using sulfide reducing agents.



Your WFGD can easily maintain high SO2 efficiency, Hg capture, while minimizing liquid phase Se, even with cycling operation.