

REINHOLD ENVIRONMENTAL Ltd.



**2018 APC & Wastewater Round Table
& Expo Presentation**

July 23 & 24, 2018 in Lexington, KY / Hosted by East Kentucky Power Coop

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2018 APC & Wastewater Roundtable

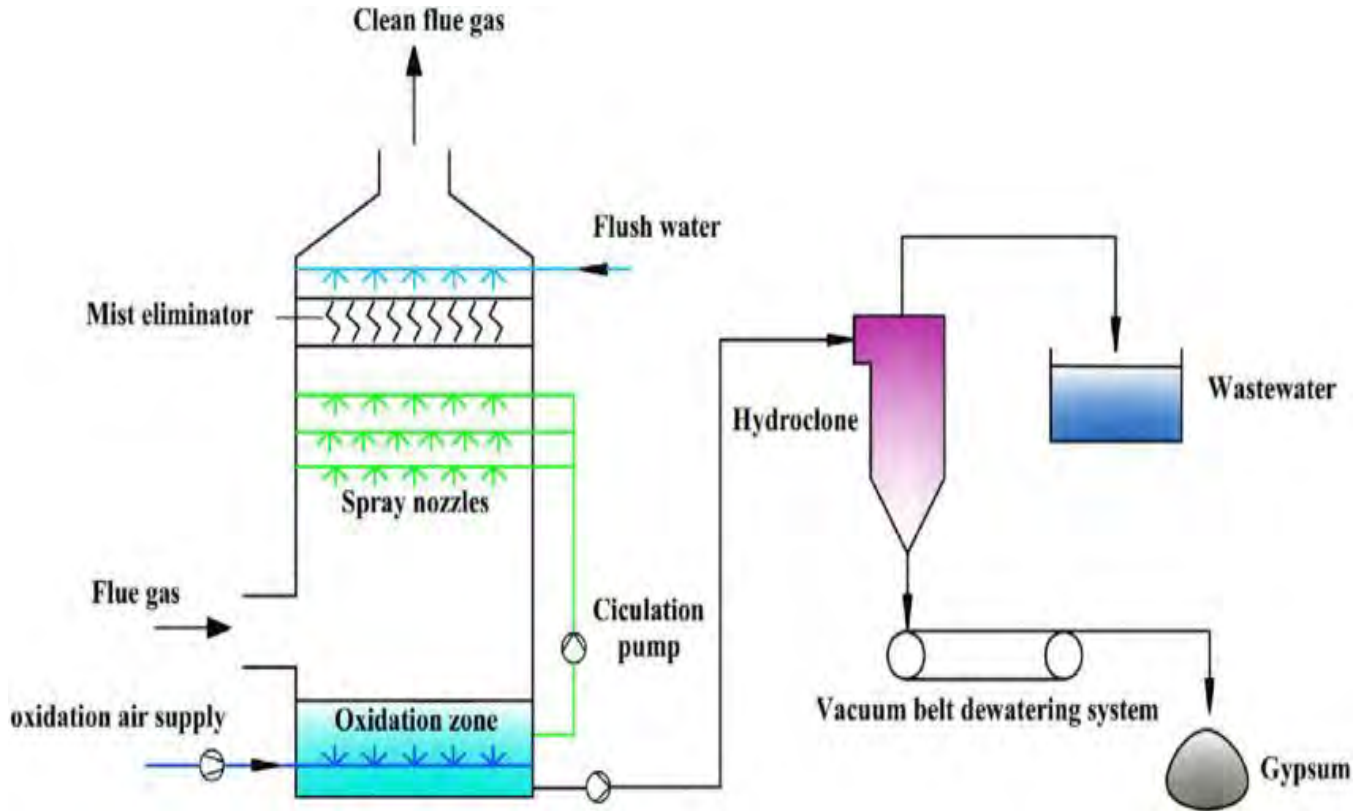
Cycling Load Impacts On WFGD Mass Transfer

Steve Feeney Consulting
July 24, 2018
Workshop 21



Map Courtesy Dreamstime.com

Cycling WFGD Mass Transfer Affect - LSFO



Wet/Dry Interface

Residence Time

Purge/Water

Gypsum Chemistry

Cl

Buffering Agents

pH/ORP

Hg

Se

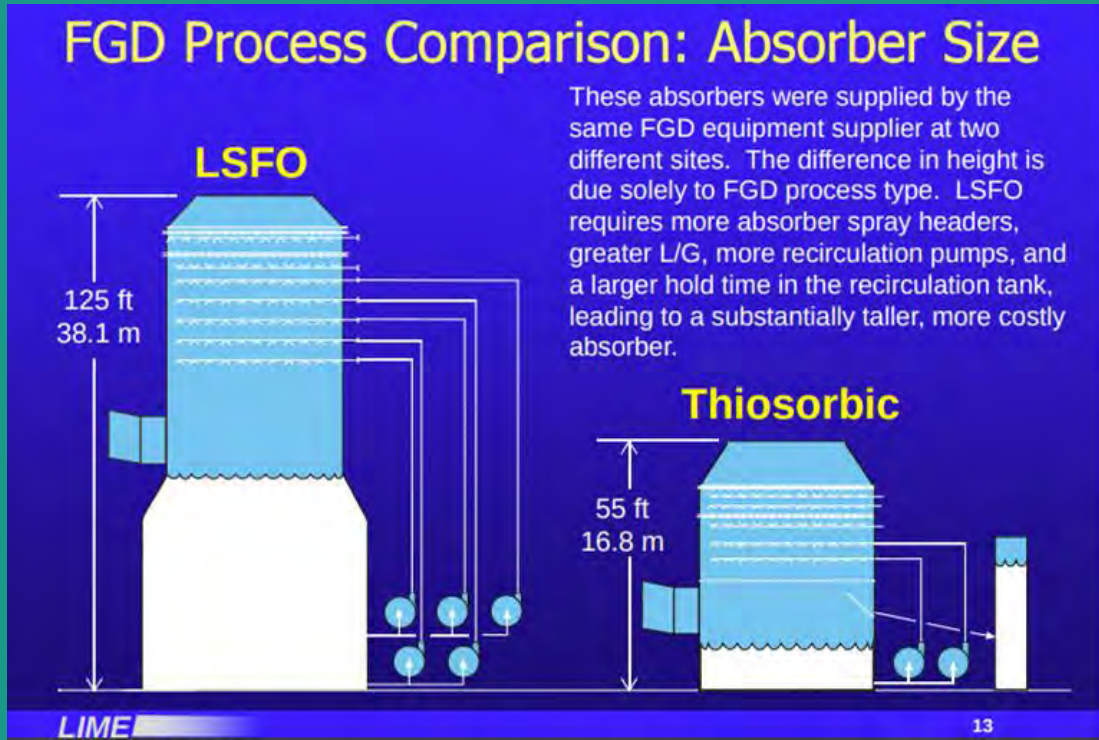
Lower Loads Tend To Improve SO₂ Eff.

Table 1. Comparison of Different Conditions and WFGD Parameters

Unit	Inlet SO ₂ (ppm)	Boiler Load (MW)	Swinging Load (yes/no)	SO ₂ 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

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

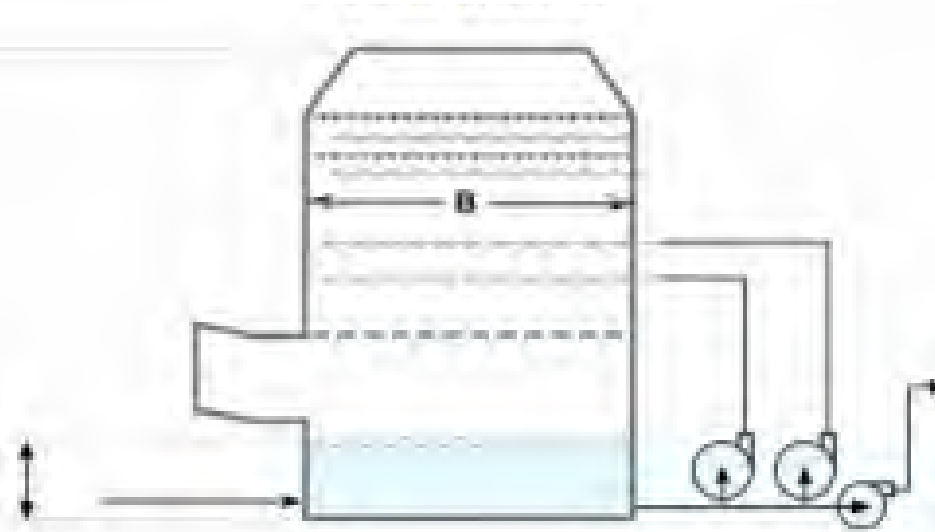
L/G

Mag-lime: Low
Limestone: High

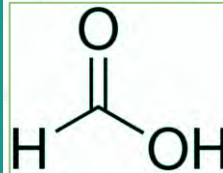
ORP

Mag-lime: Low
LSFO: Med - High

Mag-enhanced Lime

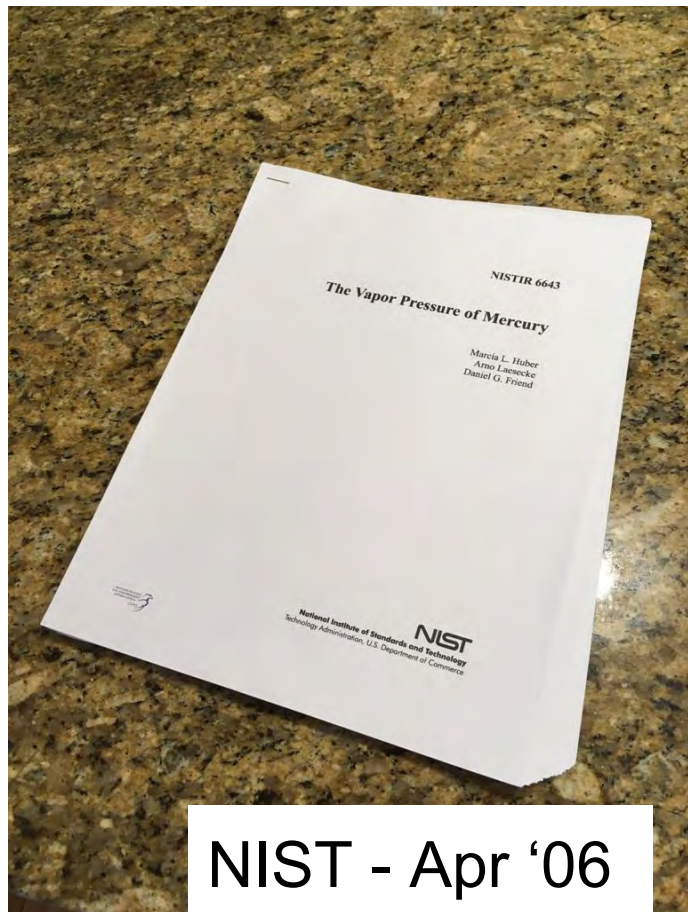


Limestone Inhibited Oxidation



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)

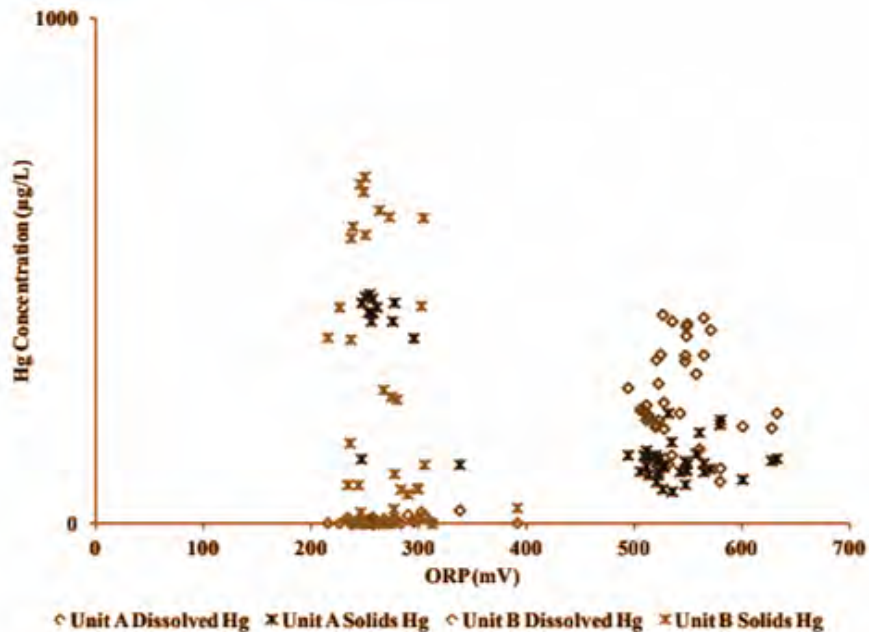
~150 - 200 ppmw for flue gas

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

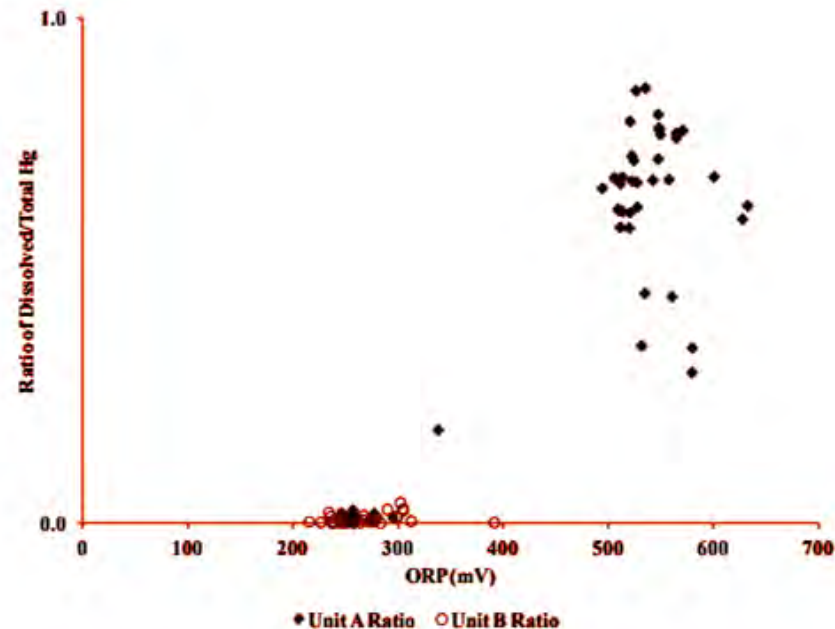
HgS : $K_{sp} = 10^{-53}$

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



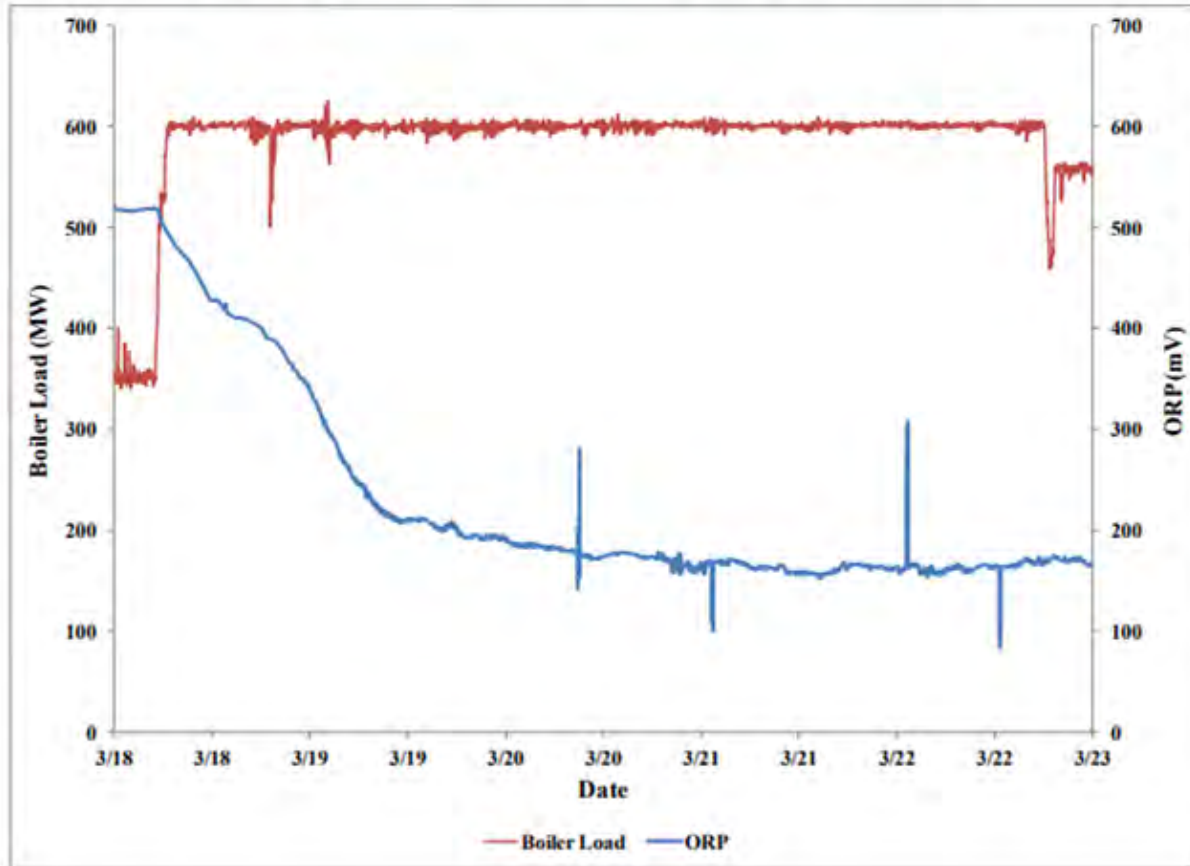
Ratio of Dissolved to Total Mercury Measured in WFGD Absorber Slurry Samples as a Function of ORP



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



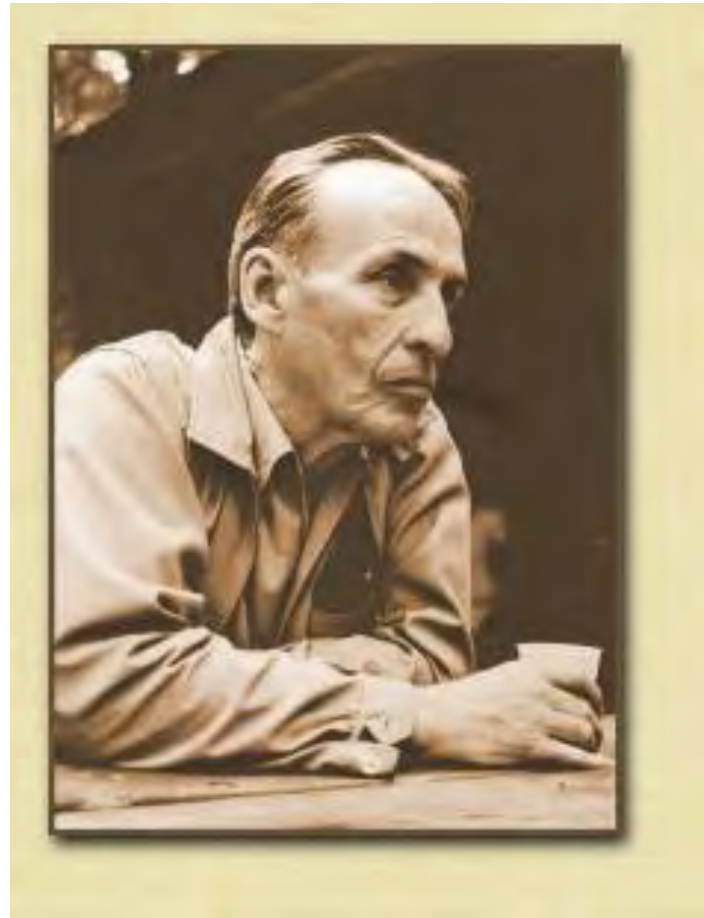
Is this an ORP decrease with steady-state conditions, or is it more accurate to say the ORP does what we would expect - a steady decline in ORP as load moves from ~50% to 100%. Once ORP reaches new “steady state”, ORP remains fairly constant at 170 mV.

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



Hg⁰(llq)–Hg⁰(solution) Equilibrium and Solubility of Elementary Mercury in Water

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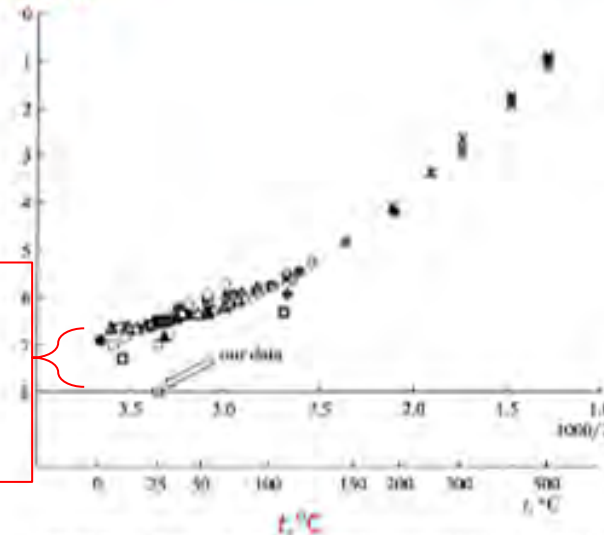
e-mail: alekhin@geol.msu.ru

Received May 25, 2011

Спасибо.

Abstract.— The solubility metallic mercury in water and its dominating forms were studied. The predominance of the Hg_{aq}²⁺ form in the high-temperature range was confirmed and the reaction constant $\text{Hg}_{\text{llq}}^0 \rightleftharpoons \text{Hg}_{\text{aq}}^0$ ($\log K = \log m = -8.01$) at 25 °C with the predominance of oxidized forms of mercury for the 20–30 °C area of low temperatures was found.

$-\log m$



- (Raichardt and Boshoffler, 1931)
- (Sasaki, et al., 1934)
- ▲ (Pirland and Arimondi, 1942)
- (Moser and Vogt, 1957)
- ◄ (Choi and Fock, 1962)
- (Spencer and Vogt, 1965)
- △ (Glow and James, 1971)
- × (Simkin, 1973)
- ◊ (Simkin, Alekhin and Dudze, 1978)
- ◄ (Onat, 1974)
- (Sanozawa, 1975)
- ▲ (Sorokin, Pokrovskii and Dudze, 1981)
- ◊ (Clover, 1987)
- × (Pushkova, 1988)

Hg⁰ solubility in an oxidizing, versus non-oxidizing environment

The solubility of mercury in water as an inverse temperature function. The used experimental data obtained methods are given from (Alekhin, Pokrovskii, and Dudze, 1988).

Expectations for Hg as ORP changes

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

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

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

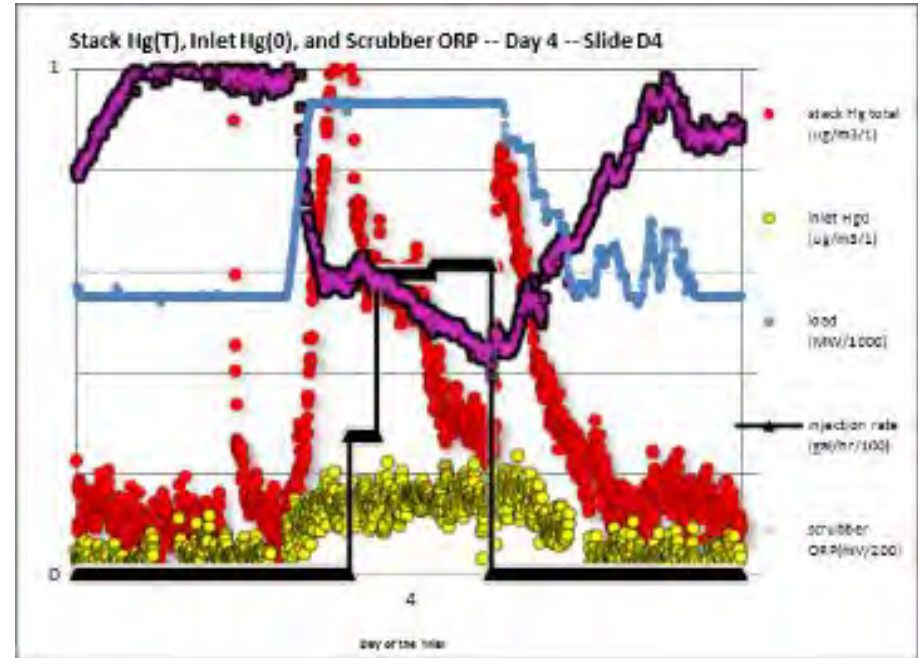
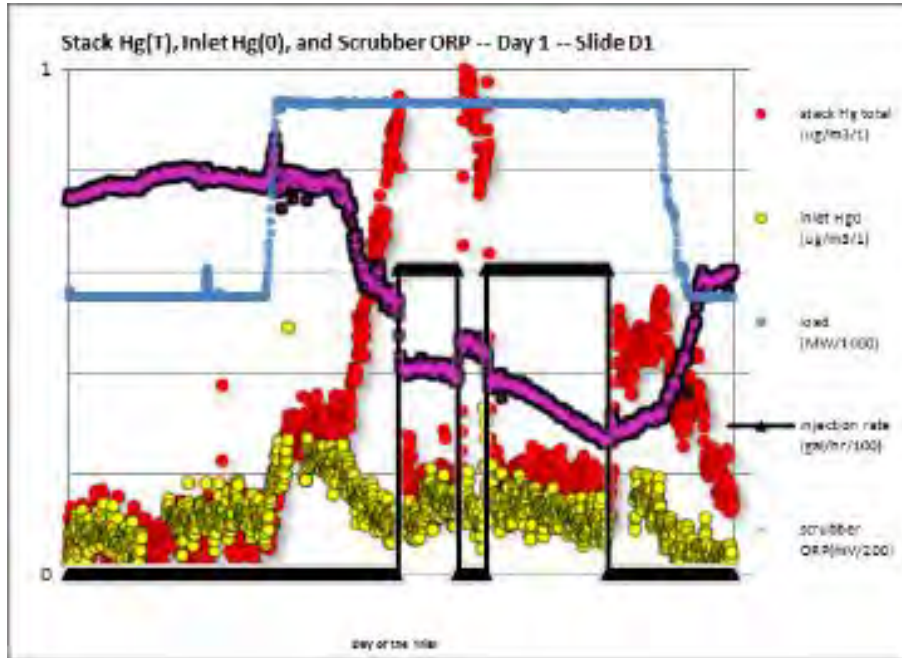
Alternatively, when ORP decreases, expect less Hg in aqueous phase.

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

Is it necessary to control ORP to control mercury?

Are we able to precipitate HgS at low ORP?

900MW, 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 Ca²⁺

CaSO₃ and/or CaSO₄ precipitation

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

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

Absorb Hg²⁺ and Hg⁰.

Hg absorption stops
when saturated.

Provide sulfide.

HgS

Deplete the liquid of Hg so
more can be absorbed.

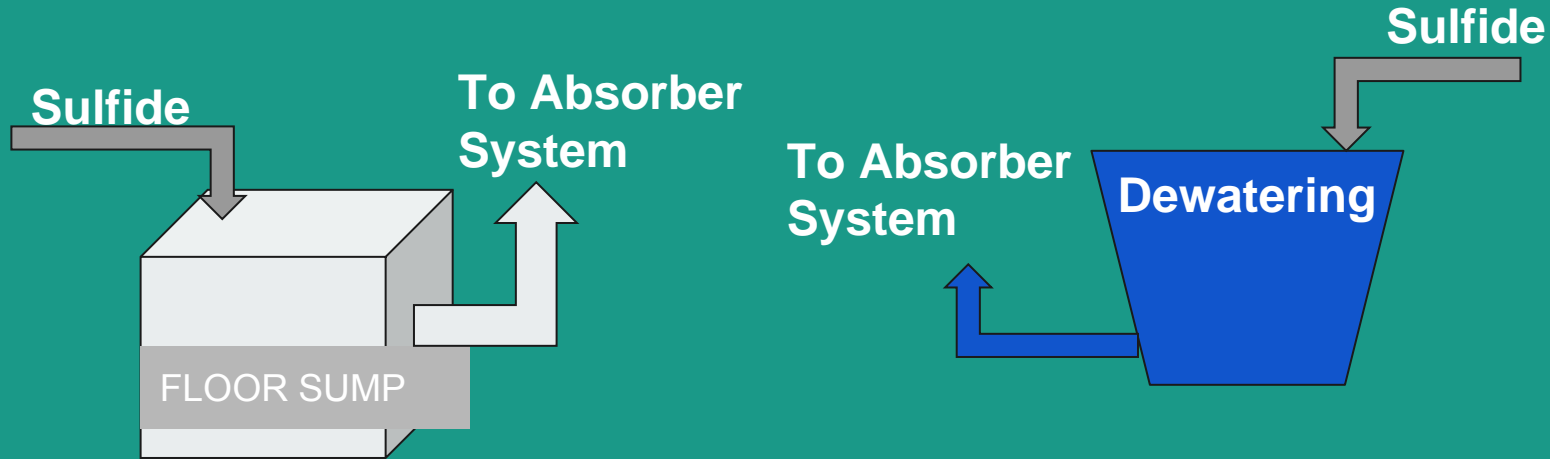
Differences

Reclaim water Hg
saturated

High molar Ratio S/Hg
1,000,000 times less Hg⁰

Seller	\$	Chemical	Phases	Comments
#1	\$	Sodium Bisulfide	One	The only “simpler” sulfide would be 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 requirements

Mass Transfer Implications of injection location?



Hg Phase Partitioning - Gypsum vs. Sulfite



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

Mag-lime - high alkalinity, salting out effect, sulfur

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.

- K_{sp} is extremely low.

- Precipitate HgS , regardless of ORP.

Selenium - Background

NIKSA

SENIOR

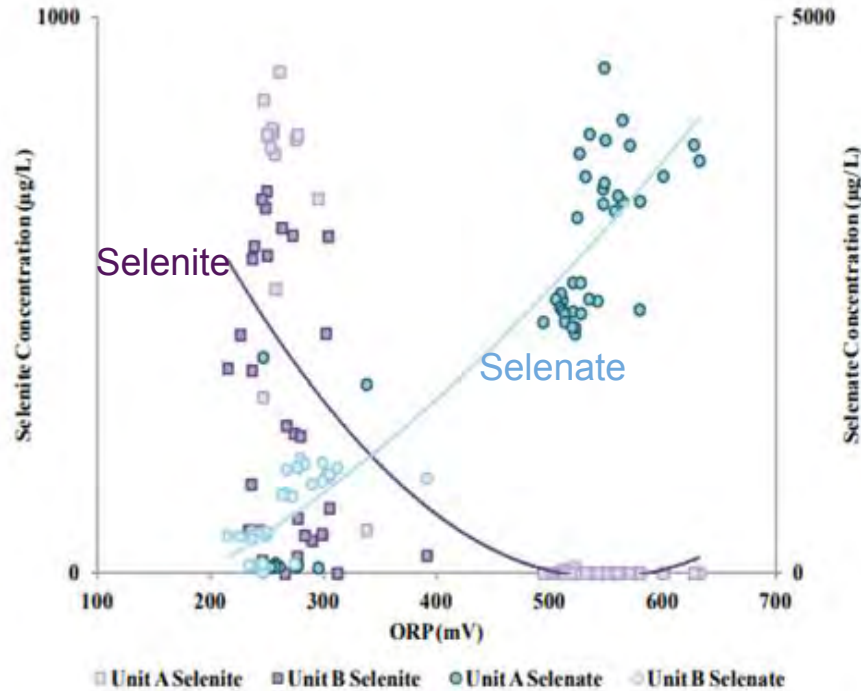
SO₂ removal exceeds SeO₂ removal in most cases.

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

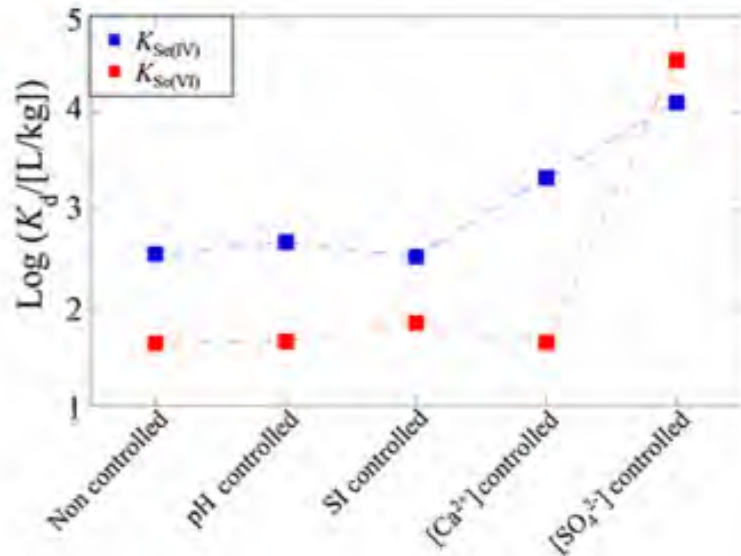


Data from LSFO system, DESP upstream

ORP appears to affect Se solubility

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

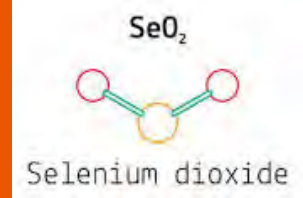


Se is known to react with Fe, Ca and Ba.

Sulfate has been shown to improve precipitation under certain conditions.

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.

