FGD Additives: Organic Acids

WPCA – Virtual
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Agenda

1. Acid Basics
2. What are Organic Acids
3. How did Organic Acids get into FGD
4. How do they impact stack Hg
5. How do they impact WWT
6. Questions

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Acid Basics

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Types of Solutions

Component	Component	Solution	Example
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda Water
Gas	Solid	Solid	Hydrogen in Pallidum
Liquid	Liquid	Liquid	Vodka (Ethanol & Water)
Liquid	Solid	Liquid	Sweet Tea (Sugar & Water)
Solid	Solid	Solid	Brass (Tin & Copper)

Types of Solutions in FGD

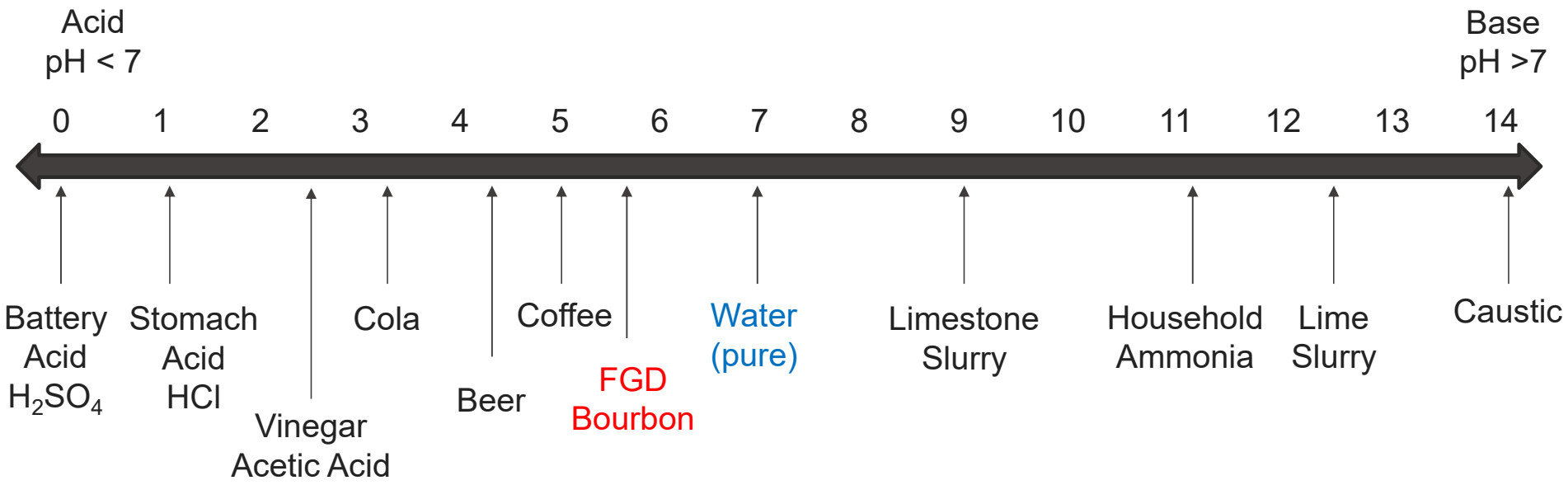
Component	Component	Solution	Example
~~Gas~~	~~Gas~~	~~Gas~~	~~Air~~
Gas	Liquid	Liquid	Soda Water
~~Gas~~	~~Solid~~	~~Solid~~	~~Hydrogen in Pallidum~~
Liquid	Liquid	Liquid	Vodka (Ethanol & Water)
Liquid	Solid	Liquid	Sweet Tea (Sugar & Water)
~~Solid~~	~~Solid~~	~~Solid~~	~~Brass (Tin & Copper)~~

Liquid phase chemistry for acids

Acid Basics

pH

$$pH = -\log [H^+]$$



pK_a – Acid Disassociation Constant

$$pK_a = -\log \frac{[A^-][H^+]}{[AH]}$$

The smaller the pK_a the more completely the compound disassociates in solution.

Acid	pK_a
Sulfuric	-2.8
Hydrochloric	-5.9
Perchloric	-15

What are Organic Acids?

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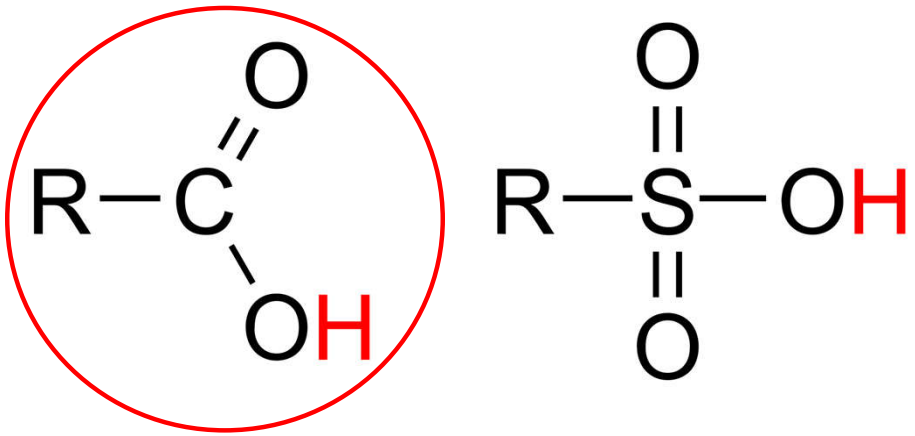
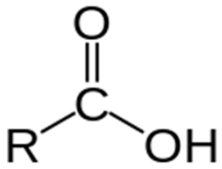
Organic Acid

- An organic compound with acidic properties
- Usually a weak acid
- Common examples are carboxylic and sulfonic compounds

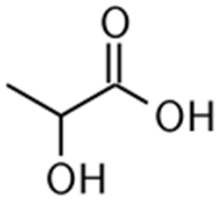


Carboxylic Acids

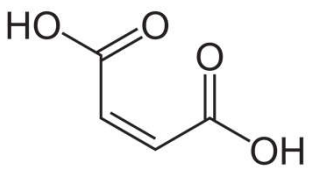


Carbon atoms	Common name	Chemical formula	Common location or use	pK_a
1	Formic acid	$HCOOH$	Insect Stings	3.75
2	Acetic acid	CH_3COOH	Vinegar	4.76
3	Propanoic acid	CH_3CH_2COOH	Body odor, milk, butter, cheese	4.88
4	Butyric acid	$CH_3(CH_2)_2COOH$	Butter	4.82
5	Valeric acid	$CH_3(CH_2)_3COOH$	Valerian	4.82
6	Caproic acid	$CH_3(CH_2)_4COOH$	Goat fat	4.88

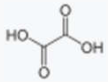
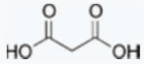
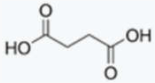
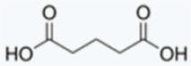
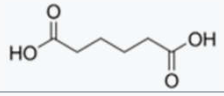
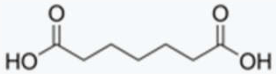
Other Organic Acids



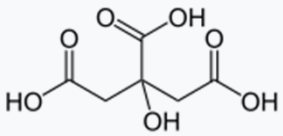
Carbon atoms	Common name	Chemical formula	Common location	pK_a
3	Lactic acid	$CH_3CH(OH)COOH$	Blood & Tooth Decay	3.86
4	Maleic acid	$HO_2CCH=CHCO_2H$	Pharmaceuticals	1.9



Dicarboxylic Acids

n	Common name	Structure	pK_a1	pK_a2
0	Oxalic acid		1.27	4.27
1	Malonic acid		2.85	5.05
2	Succinic acid		4.21	5.41
3	Glutaric acid		4.34	5.41
4	Adipic acid		4.41	5.41
5	Pimelic acid		4.50	5.43
6	Suberic acid		4.53	5.50

Tricarboxylic Acids

Common name	Molecular formula	Structural formula	pK_a
Citric acid	$C_6H_8O_7$		$pK_{a1} = 3.13$ $pK_{a2} = 4.76$ $pK_{a3} = 6.39$

DBA – Dibasic or Polybasic Acids

Polybasic acids are able to donate more than one proton per acid molecule, in contrast to monobasic acids that only donate one proton per molecule. Specific types of polybasic acids have more specific names, such as dibasic acid (two potential protons to donate), and tribasic acid (three potential protons to donate).

Sulfuric acid (H_2SO_4) is a dibasic acid.
Phosphoric acid (H_3PO_4) is a tribasic acid.

DBA (Dry Bottom Ash?!?) is not a good technical term as used around a coal plant.

DBA as a FGD Misnomer

DBA is a waste product of adipic acid production for Nylon 6,6 manufacture

Glutaric and Succinic acid formation is sought to be minimized and only the “pure” adipic acid is used for polymerization.

So why do we use it?

- ✓ It has a reasonable pK_a ~4.5
- ✓ It is usually readily available
- ✓ It is relatively inexpensive!

How did Organic Acids get into FGD?

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Background

Organic Acid for Increased SO_2 Removal

Early 80's brought increased focus on SO_2 reduction

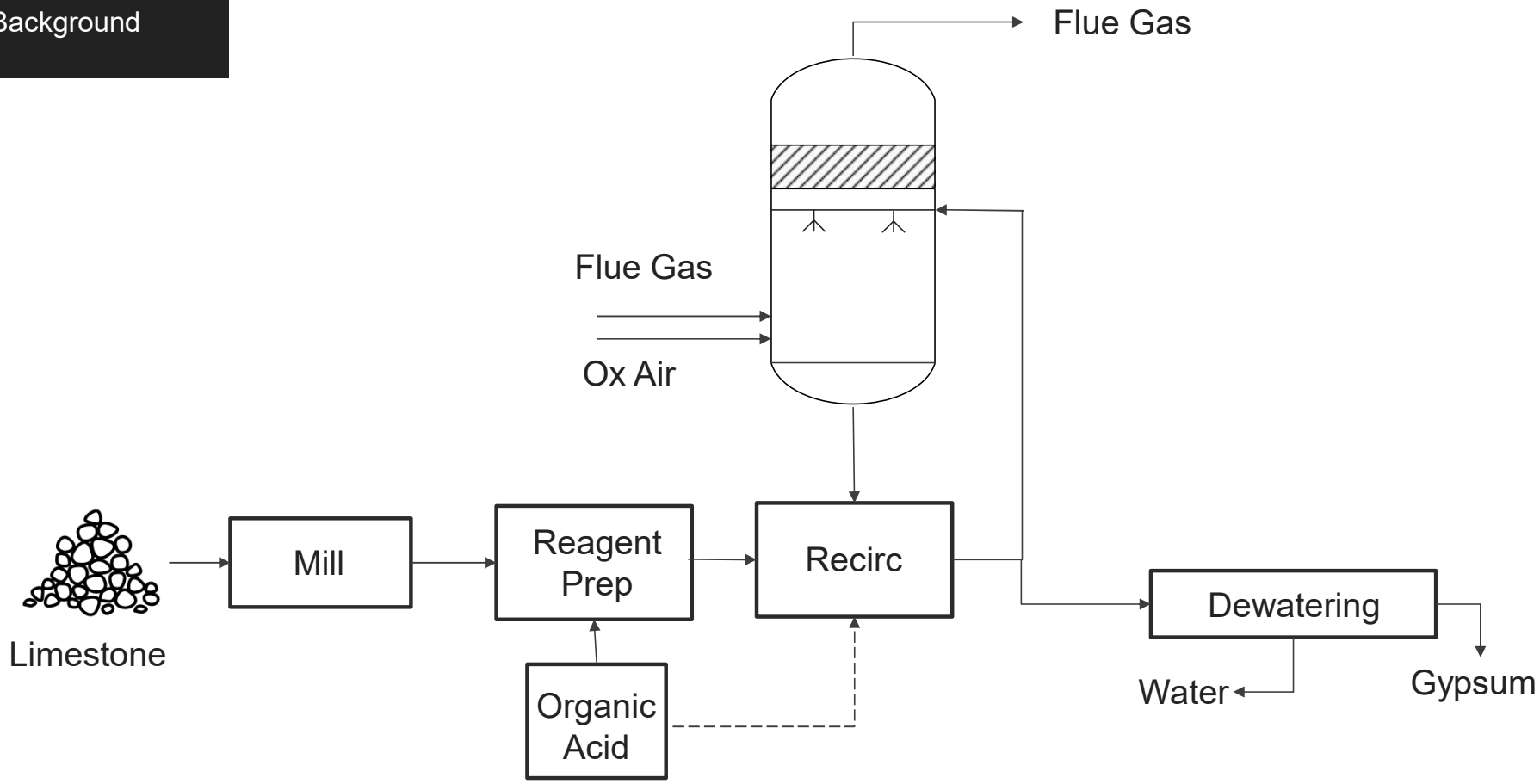
Save $$$ by:

- ✓ Switching to low sulfur bituminous coal
- ✓ Switching to low sulfur sub-bituminous coal
- ✓ Build smaller scrubbers
- ✓ Get more out of the undersized scrubbers
- ✓ Sell sulfur credits

Holistic View ???

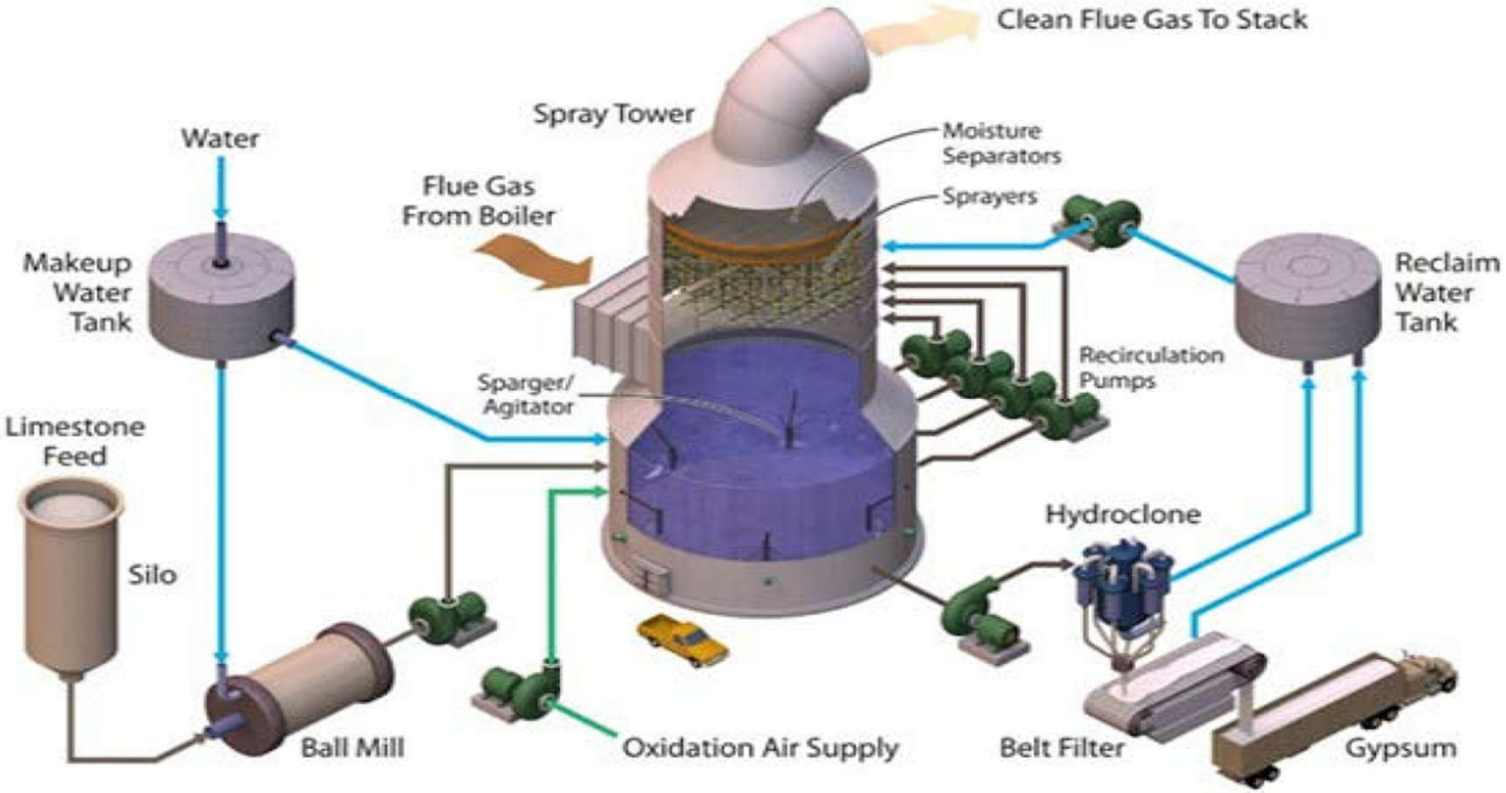
Background

Organic Acid for Increased SO_2 Removal



Background

Organic Acid for Increased SO_2 Removal



EPRI

Scrubber Chemistry...sort of

$$SO_2 + CaCO_3 + O_2 \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

Background

Surface Chemistry

SO2 Absorption

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

Limestone Dissolution

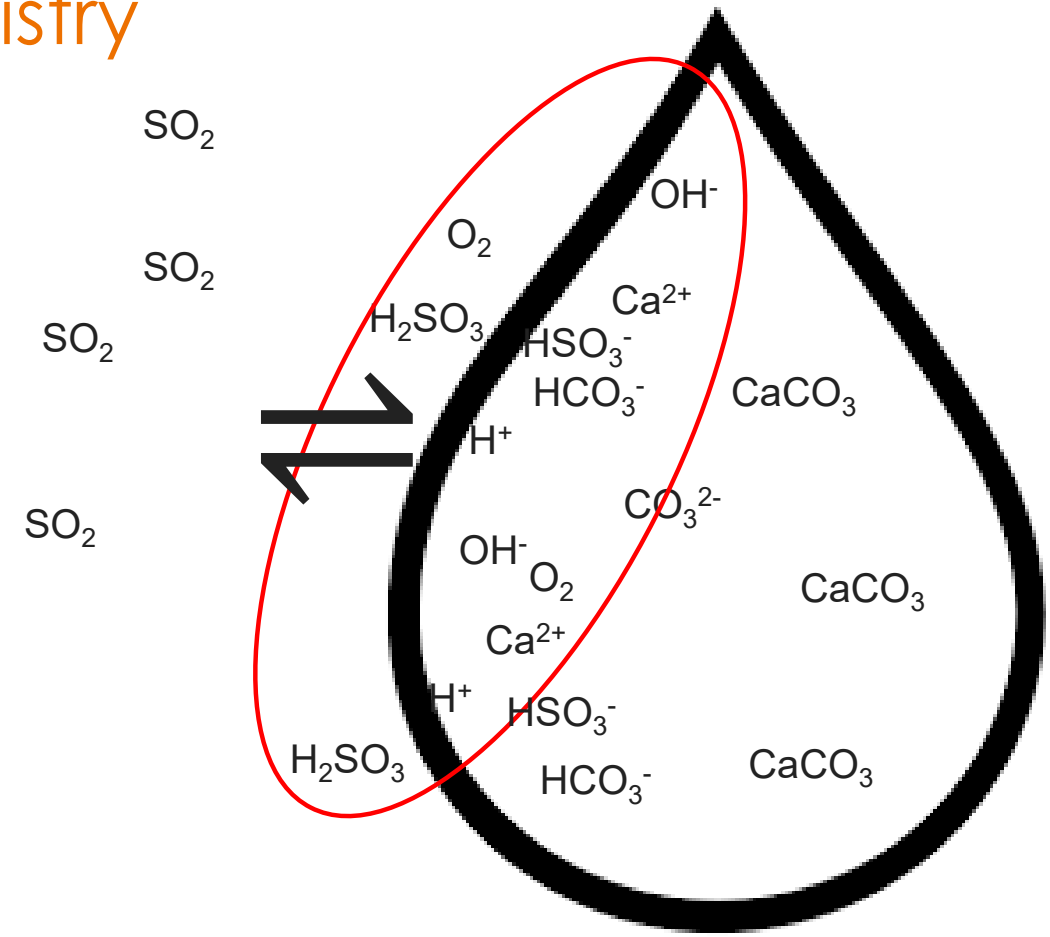
$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^-$$

Oxidation

$$HSO_3^- + \tfrac{1}{2} O_2 \rightleftharpoons H^+ + SO_4^{2-}$$

Precipitation

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightleftharpoons CaSO_4 \cdot 2H_2O$$

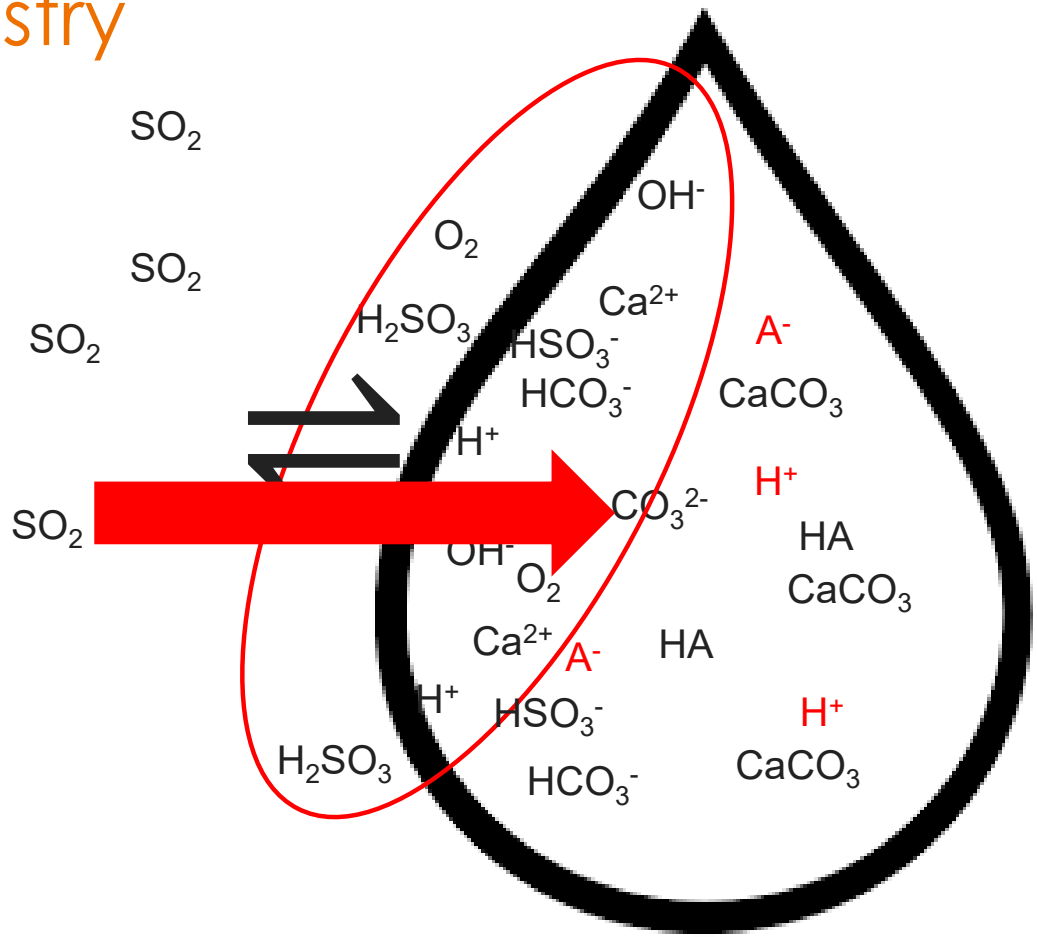


Background

Surface Chemistry

Le Chatelier's Principle:

The addition of organic acid (HA) will increase the solubility of limestone, ultimately increase the absorption rate of SO_2 and the precipitation of gypsum.

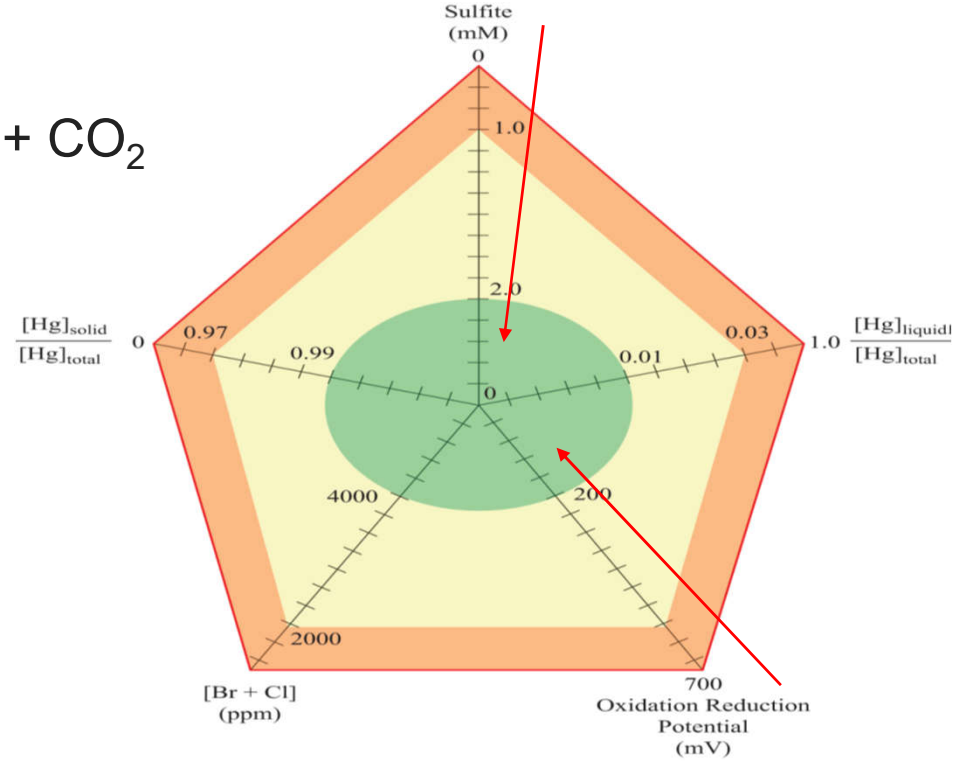


What Happens to Hg?

Scrubber Hg Chemistry with Organic Acids

$$SO_2 + CaCO_3 + O_2 \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

- ❑ Increased SO2 absorption leads to
- ❑ Increased gypsum precipitation leads to
- ❑ Increased O2 utilization leads to
- ❑ Decreased ORP leads to
- ❑ Decreased Hg emissions…sometimes



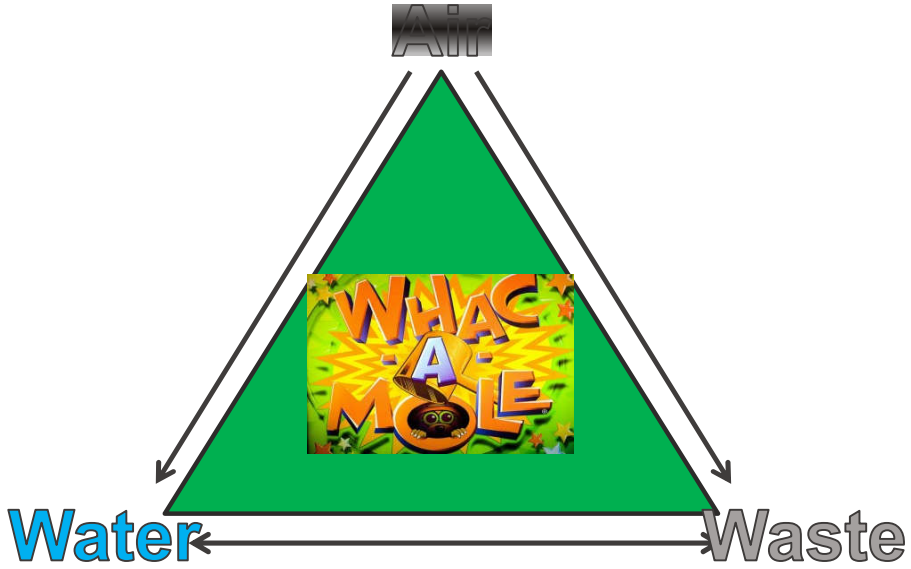
Berry, M.S., "Full Scale Calcium Bromide Injection with Subsequent Mercury Oxidation and Removal within Wet Flue Gas Desulfurization System: Experience at a 700 MW Coal Fired Power Facility," PhD Thesis, University of Alabaman at Birmingham, 2012.

Scrubber Hg Chemistry

$$SO_2 + CaCO_3 + O_2 \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

NO_3 Zn B Cl Cd Y SO_4 Se Hg As Cr

Scrubber Hg Chemistry



What About Se?

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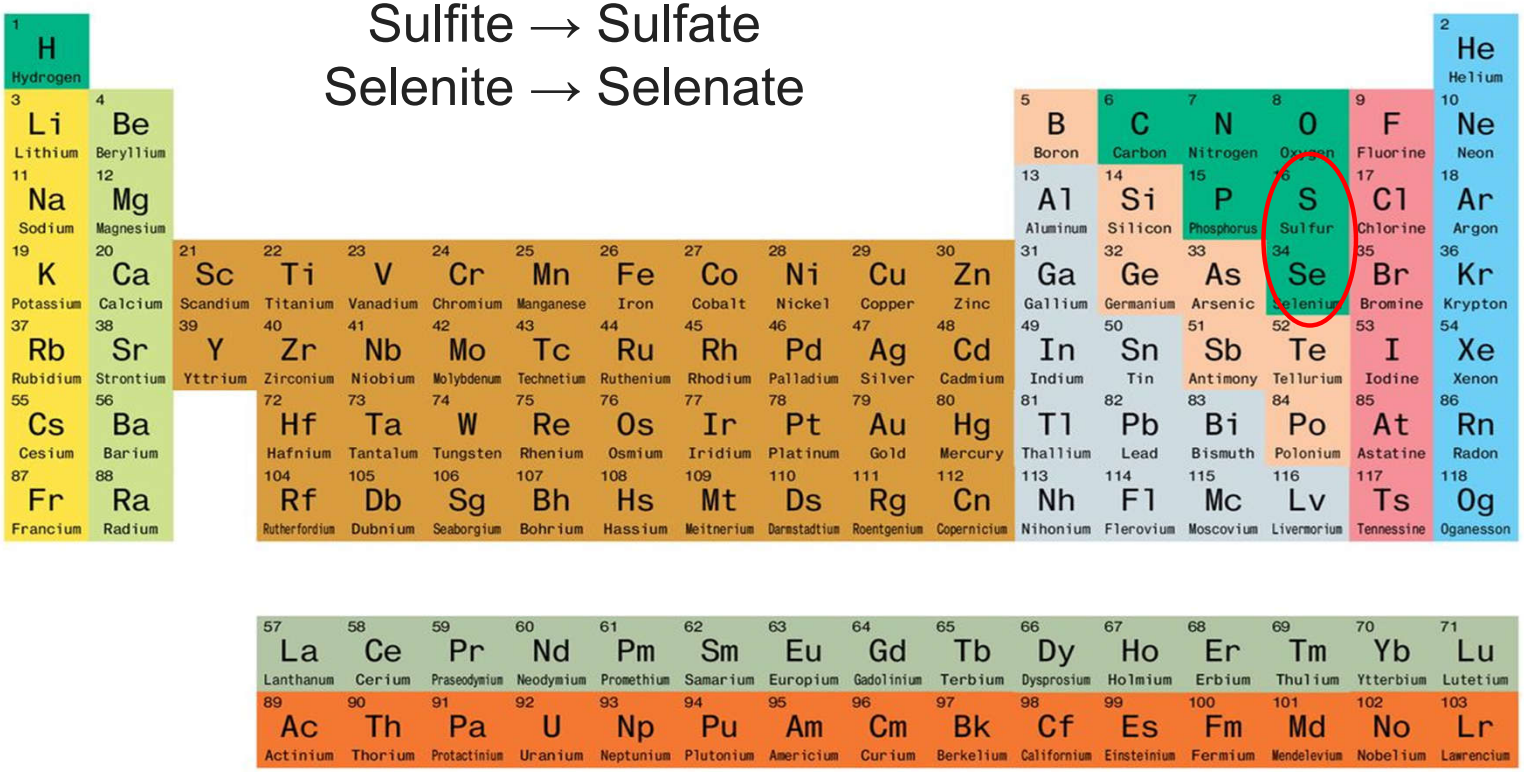
Selenium

Selenium in the Scrubber

Sulfite → Sulfate

Selenite → Selenate



Selenium in the Scrubber

Sulfite → Sulfate
Selenite → Selenate

Keep scrubber ORP < 250 mV
As low as you can go and still maintain gypsum quality

And don't shift load, fuel, catalyst, ESP performance or have mechanical issues.

Yea, right

FGD Wastewater Treatment

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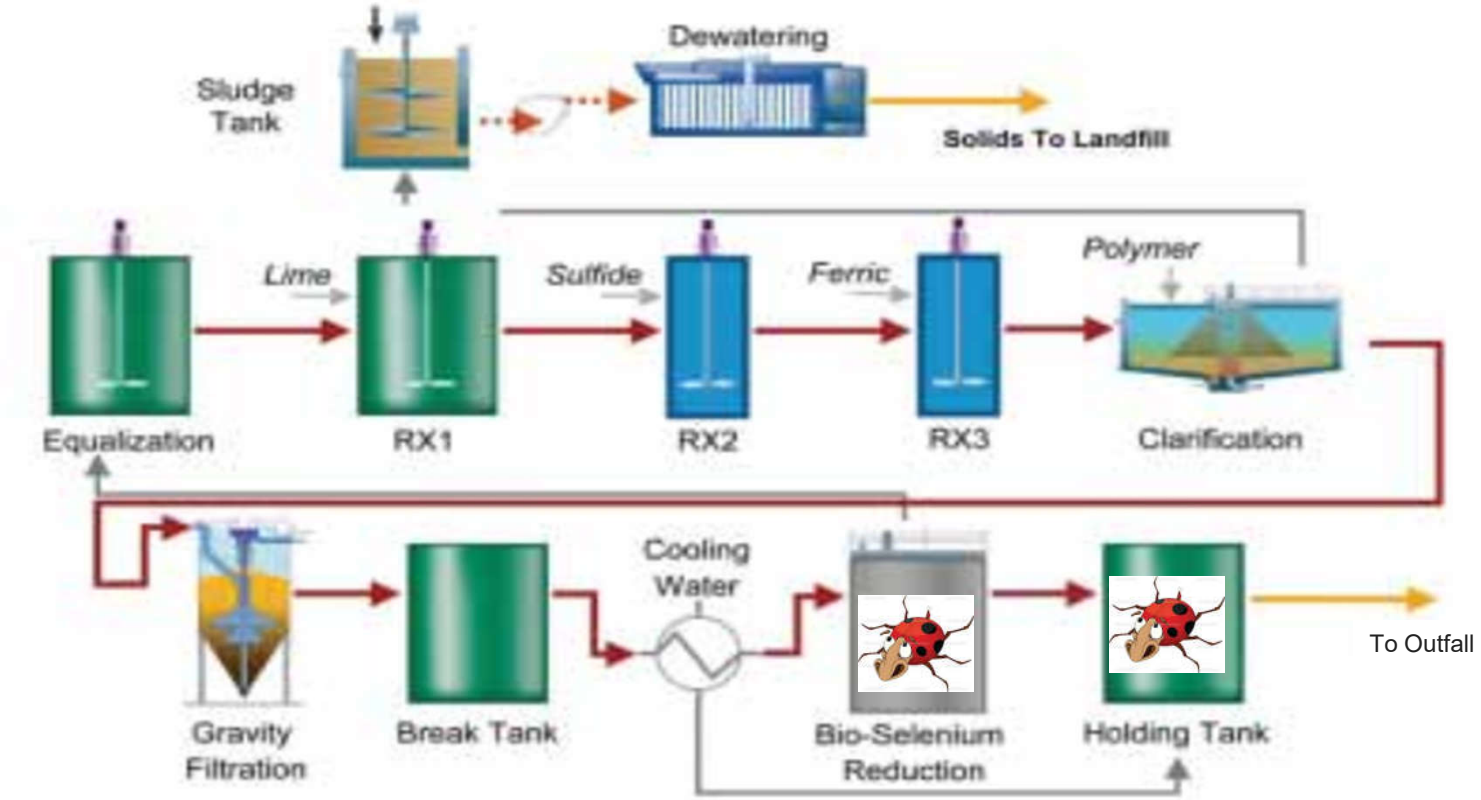
WWT

FGD WWT BAT Vintage 2015



WWT

How do Bioreactors Work?

- Nitrates are converted to nitrogen gas

$$NO_3^- + \text{org. C} \rightarrow NO_2^- + \text{org. C} \rightarrow N_2\uparrow + CO_2\uparrow + H_2O$$

- Bacteria reduce oxidized forms of selenium (selenate & selenite) to elemental selenium

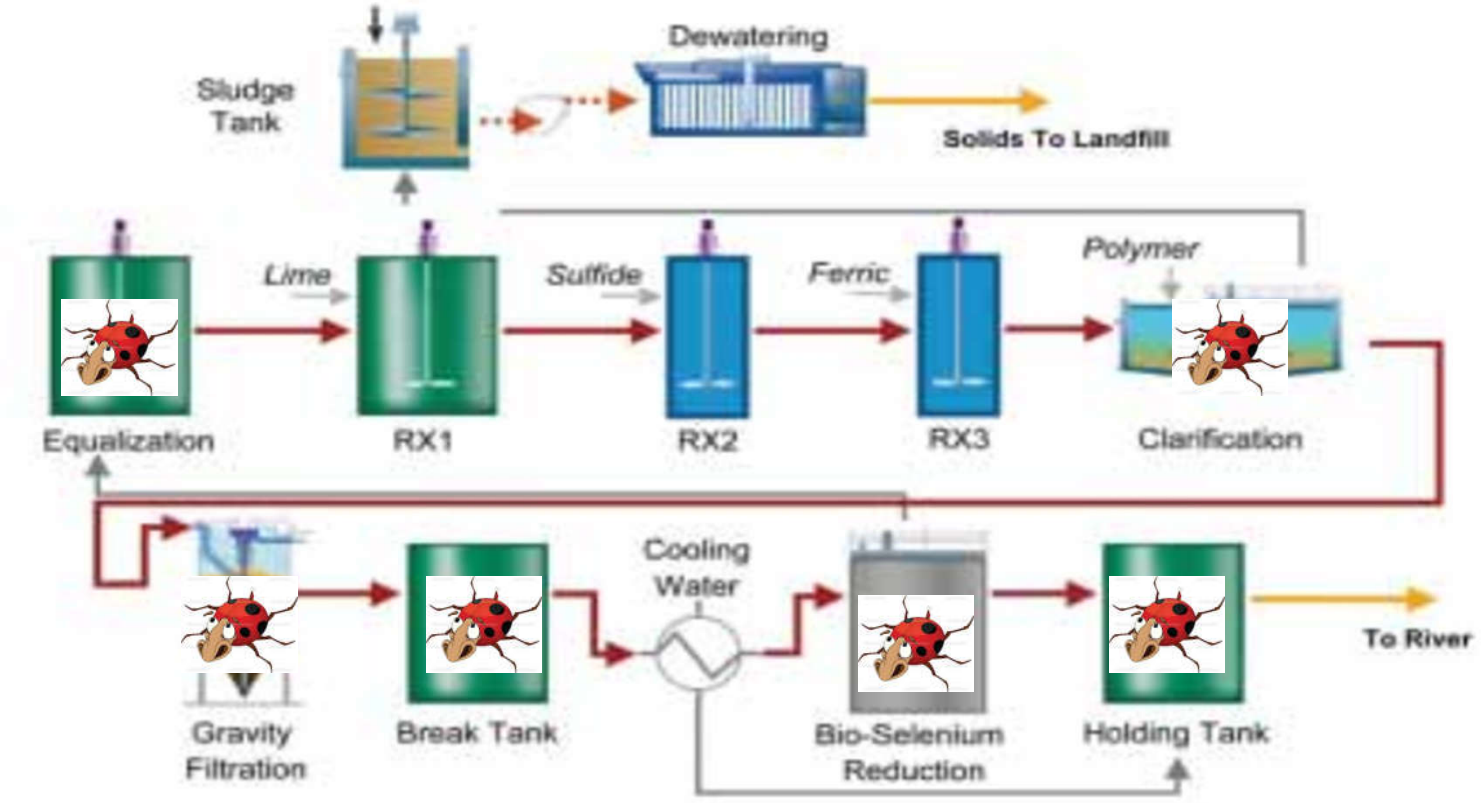
$$SeO_4^{2-} + \text{org. C} \rightarrow SeO_3^{2-} + \text{org. C} \rightarrow Se^0\downarrow + CO_2\uparrow + H_2O$$

- Dissolved metals are converted to metal sulfides and are retained within the system

$$H_2S + M_2 \rightarrow MS\downarrow + 2H^+, \text{ where M= Metal}$$

WWT

FGD WWT BAT with Organic Acid



WWT

Organic Acids are Candy

- Early FGD bio's used molasses based nutrient, i.e., bug food
- Later units use glycerin

Remember…

- Organic acids/compounds are BOD/COD in wastewater systems
- COD is a reducing agent, buffering oxidizers
- Complete denitrification (50+ ppm-N) has occurred in physchem
- Able to turn off nutrient feed and reduce operating costs

WWT

Impact on WWT

- Decreased load on bioreactor
- Slight reduction in clarifier performance due to effervescence
- Potential reduction in equipment size/capital cost
- Possible improved kinetics over glycol/glycerin feeds
- Improved selenium removal
- Monitor effluent chemistry for residual N & P

Questions

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