Worldwide Pollution Control Association

WPCA/TVA

Coal & Gas Seminar

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WFGD Scrubber Chemistry

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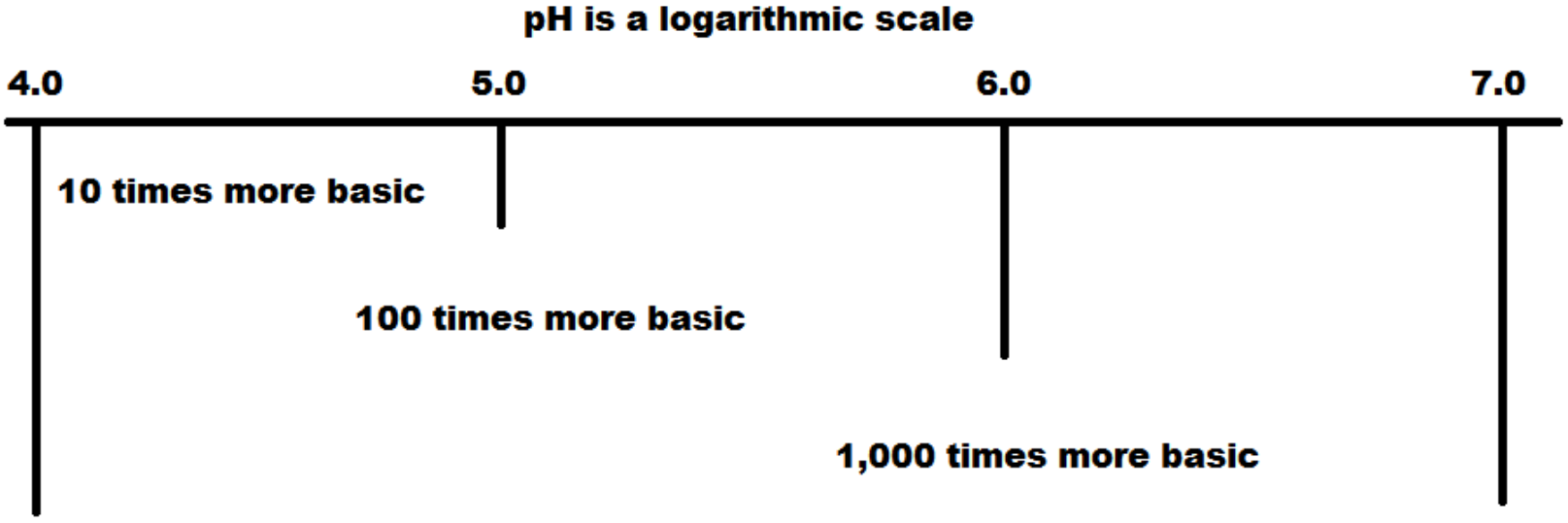
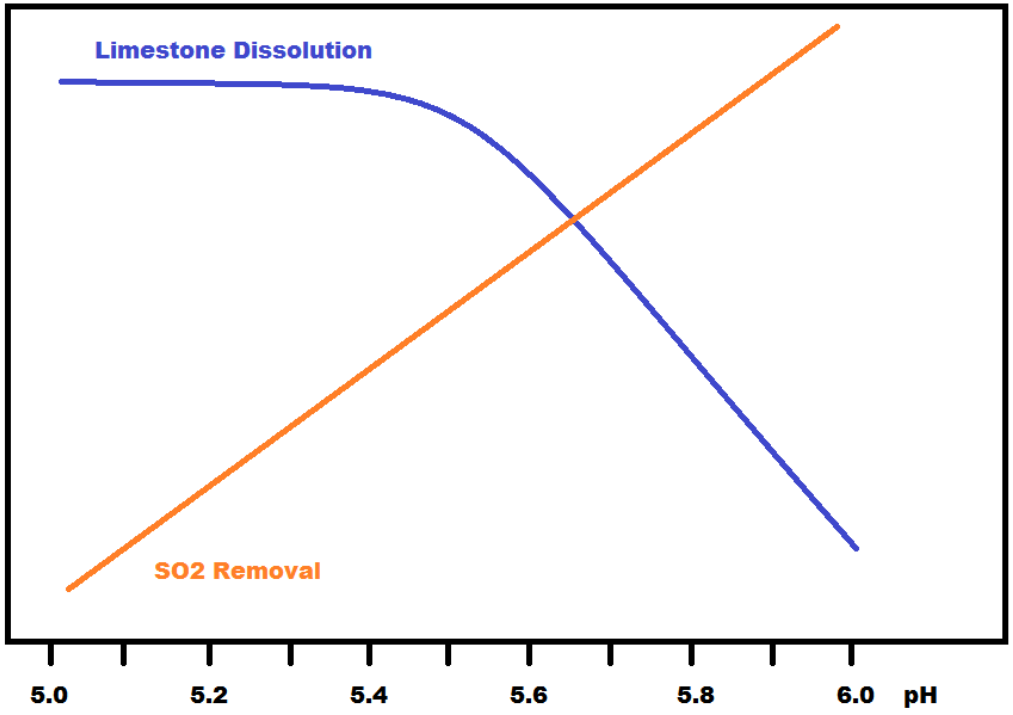
pH

pH Scale

- The pH scale ranges from the strongest acids near pH 0 to the strongest bases near pH 14 with the neutral point in the middle at 7.0. Limestone scrubbers operate in the 5 – 6 range of the scale. Lime scrubbers operate in the 6 – 6.5 range of the scale.


pH is a logarithmic scale
4.0
5.0
6.0
7.0
10 times more basic
100 times more basic
1,000 times more basic

Why Limestone Scrubbers Operate in the 5 -6 pH Range



Density

- The early scrubbers operated with slurry densities in the 10% range. This reduced pump HP required as well as reducing abrasive wear on pumps, mixers and piping.

Density

- As EPRI did research on growing better gypsum crystals, it became apparent that there was a definite advantage to having higher slurry densities if one wanted to improve gypsum quality.

Density

- **With better materials of construction available, most FGD systems operate in the 15% - 20% density range to produce better crystals which dewater more easily.**

Chlorides and Fluorides

- All coals contain varying amounts of chlorine and fluorine.
- When the coal is burned, these become part of the combustion gases and are removed by being condensed onto the fly ash particles or being scrubbed out in the FGD system.

Chlorides and Fluorides

- Chlorides have only a small negative effect on SO_2 removal.
- Chlorides have a major impact on the corrosion of FGD components.
- Most of the fluorides stay condensed on the fly ash particles.

Limestone Blinding

- If fly ash makes it into the absorber towers, the fluorides and aluminum on the fly ash particles will dissolve into the slurry and react with the limestone.
- They will form aluminum fluoride compounds which will prevent the limestone particles from dissolving.

Limestone Blinding

- This will cause the SO_2 removal capacity to drop.
- There is no easy way to recover from this. The most successful remedy is to drain the slurry out of the absorber tower and start over with new slurry.

Temporary Limestone Blinding

- This occurs when the unit is running at significantly reduced load for an extended time (ie: weekend) and then is quickly returned to higher loads.
- The symptoms are:
  - The limestone feed valve is wide open
  - The pH is constant
  - The SO_2 removal is dropping

Temporary Limestone Blinding

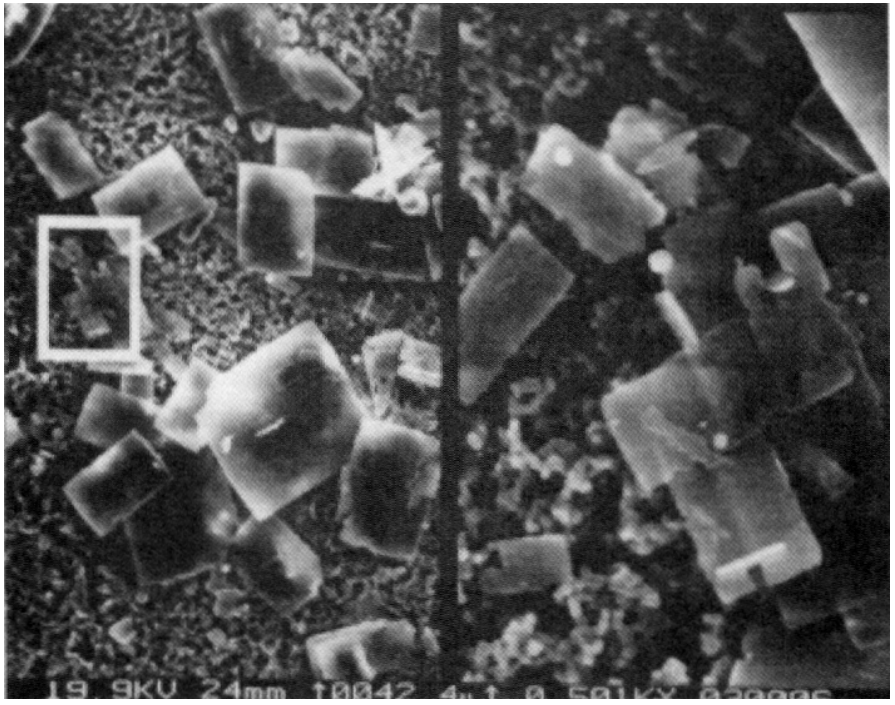
- To recover to normal operation:
  - Close the limestone feed valve
  - As long as the pH remains the same, do nothing but wait
  - When the pH starts to drop, return the limestone feed valve to normal automatic operation

Oxidation

- As the SO2 is removed, it will react with the calcium in the lime or limestone and form calcium sulfite or calcium sulfate depending on how much oxygen is in the absorber slurry.

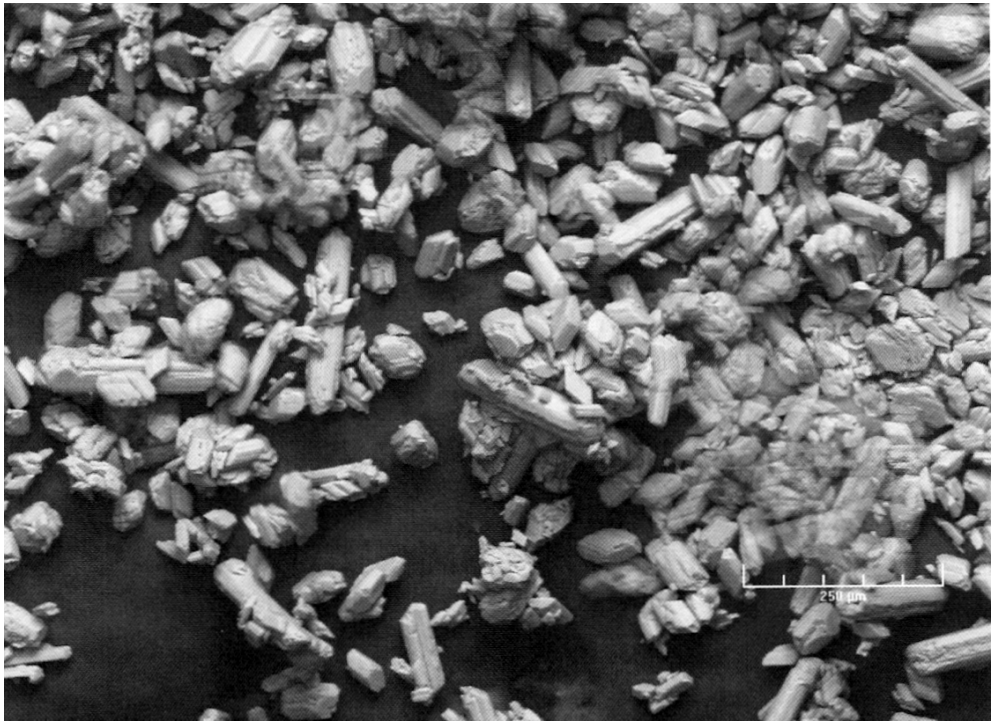
Calcium Sulfite ($CaSO_3$)

- Calcium Sulfite crystals are flat and rectangular like a piece of window glass.



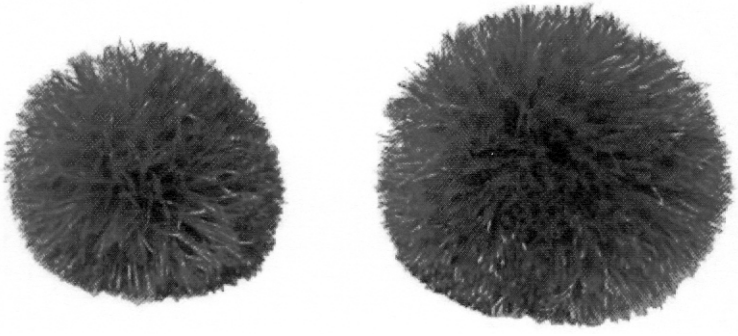
Calcium Sulfate

- **Calcium Sulfate crystals are long thin columns.**



You don't want to grow crystals similar to these

- They are very fragile.
- They have about the same density as the slurry, so they do not settle quickly.



When it comes to oxygen, more is not always better

- The recent severe corrosion of the 2205 duplex absorber towers seems to have been caused by the formation of persulfate which caused a cascade of events which ate holes through the tower walls very quickly.

ORP

- **The Oxidation-Reduction Potential is a measure of the tendency of the solution to either gain or lose electrons when it is subject to change by introduction of a new species. In the case of FGD we are adding oxygen.**

ORP

- It is measured with a probe that is similar to a pH probe.
- It is reported in units of positive or negative millivolts.

What ORP Do You Operate At?

- A negative number means you are in a reducing environment that will drive you towards producing calcium sulfite.
- +100 – +350 mV is considered a normal operating range to operate in.

What ORP Do You Operate At?

- +350 – +450 mV is a transitional zone where changes will begin to take place in the absorber slurry.
- Above +450 mV you will be changing the properties of the selenium, mercury and manganese with possible negative consequences.

Questions