

**REINHOLD ENVIRONMENTAL Ltd.**



**2013 APC Round Table  
& Expo Presentation**

**July 8-9, 2013, in St. Louis, MO / Hosted by Ameren**

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# The water Hierarchy. Making sense of water balance in the new millenium.

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Bruce Salisbury, Arizona Public  
Service Company



# New Regulations? What a surprise....

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- By adhering to best business practices, you will make the regulations irrelevant.



“Whiskey’s for Drinkin, water’s  
for fighting over.”

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- An unsubstantiated quote of Mark Twain, after a trip to the southwestern United States.



# Water in the present and in the Future

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- Strategists and think tankers have expressed concern for years that wars will be fought over the ownership of water.
- As population and industrial pressures increase, this concern will not wane.



# New Mexico Water Facts

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- Only 0.02% of the state of new Mexico is covered with water.
- Any lake in New Mexico larger than ½ acre is man made.
- The Four Corners area receives 6" of precipitation a year, half of that as snow.
- The Four Corners area has gotten 1.7 " of rainfall, in 12 minutes.



# New Mexico Water Facts

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- The water in the Rio Grande is owned by Three States, and two countries.
- The San Jun and Rio Grande Rivers contain at least three endangered species of fish: The Colorado Pikeminnow, the Razor back sucker, and the Rio Grande, silvery-back minnow. So we have to share.



# A comparison between the San Juan and Ohio River.

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- There are three major(?) rivers that leave New Mexico, the Mighty Rio Grande, the San Juan and the Pecos.
- The San Juan has 24,600 square miles of drainage and 2,192 cu ft/s average flow
- The Mighty Rio Grande drains 182,200 sq mi and has 2,403 cu ft/s average flow.



# The Ohio River

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- The Ohio's drainage basin covers 189,422 square miles, and 281,000 cu ft/s, 128 times the flow of the San Juan. It drains an almost identical area as the Rio Grande, but has 116 times the flow.
- So this commodity can seem like it is abundant, and almost free.
- Nothing can be further from the truth.

# The cash value of water.



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- Adjudicated water, the acre-foot.
  - Water is a cash asset.
  - In typical Colorado River Water Auctions, Adjudicated water sells for 18,000 to 20,000\$/acre-foot.
  - A plant that consumes 50,000 acre-feet of water per year, must buy the water, or own a 900,000,000\$ asset.



# The cash value of water.

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- Palo Verde Nuclear Generating station is a 4000 megawatt station in Western Phoenix.
- It's entire water supply is sewage effluent from the 91<sup>st</sup> avenue sewage treatment facility.
- This water is typically purchased at 500\$ per acre-foot.
- Because sometimes, you can't be picky about your water supply.

# Purchased water.



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- The value of water that is purchased, one acre-foot, one time, is higher than you think.
- Recent purchases in Prescott Arizona were made at over 600 \$/ acre-foot.
- So if this is a major expense, then why aren't you controlling it?



# So how did we get here?

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- While New Mexico continues in a drought, drought conditions bottomed out in 2003.
- The Four Corners facility consumed 33,000 acre-feet, but was told we could only take 29,450 acre-feet from the San Juan River.
- We needed to get smarter, very quickly.

# So what's the water hierarchy?



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- “Water that comes out of a well, lake or river is not clean enough to put in a boiler, but is too clean to put into a cooling tower”.
- Make clean water dirty, get dirty water dirtier.
- Allow yourself to be surprised.
- Let mother nature help you.



# So what's the water hierarchy?

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- Boilers need very clean water.
  - Processes like Reverse Osmosis, Brine Concentrators, and demineralization make very clean water.
  - While making clean water, you make dirty water.
  - Dirty water can have interesting benefits.

# Closed Loop Cooling Towers deserve dirty water.



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- You may be in an area that limits TDS in the cooling tower to no more than 35,000 ppm tds to limit particulate emissions from cooling towers.
- While anti-scaling chemical control is important, things such as chloride help keep solids in solution.
- When you are finished with water in a cooling tower, either recycle what little you can through a brine concentrator, or throw it away.



# Cooling Lakes

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- Cooling lakes are more common than you think in the southwest.
- Cooling lakes or ponds can assist with the operation of cooling towers.
- Cooling lakes may have NPDES restraints
  - Oil and Grease Limits.
  - TDS
  - Temperature.



# Cooling Lakes

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- Give your lake a hand.
- If the water comes from a river, don't pump water for TDS control if the TDS in the river is very high.
- If there are periodic issues with Fecal Coliforms or other things from your water supply, measure these things, and don't pump when they are high.
- If suspended solids are high, don't pump to the lake and fill your lake volume up with silt, nitrates, or other things you encounter during high flow times.



# Making the Hierarchy work.

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- Once you have cleaned water up to use in a boiler, every successive reuse of water is to progressively get water dirtier.
- Never move water the other direction, dumping dirty water into a system that is cleaner.



# Typically, in a coal plant

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- Clean up for Boiler water.
- Use as is in service water and makeup water.
- Reuse water for operation of scrubber.
- Send to the cooling towers.
- Throw it away.
- “Clean becomes dirty, dirty becomes dirtier”.



# So what's the net result?

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- While 10 years old, this is still a work in progress.
- The plant has moved from taking 33,000 acre-feet of water, to 27,500 acre-feet.
- Evaporation pond needs have gone from more than 40 acres- to less than 4.



# When do you throw water away?

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- When Chlorides or thiosulfates, or some other chemical parameter becomes so high, you cannot put the water in process vessels.
- Never throw water away because it seems you have too much of it.



# But make sure you are open to being surprised.

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- Look for surprises along the way.
- If you pay attention, the processes, and mother nature will show you some of their processes, that will help you do your job.



# Dry ash disposal isn't dry.

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- While the regulatory environment drives us toward “dry disposal”, there is no such thing.
- A certain amount of water must be mixed with dry fly ash for dust suppression and compaction.
- This material is then stacked in a pile, and compacted.

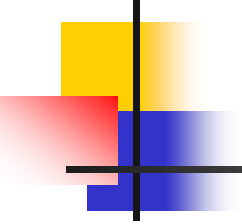


# Dry ash disposal isn't dry.

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- SO anything that is only collected on the surface of an ash particle is rinsed off the surface, and the water accumulated in a sump at the end of the disposal area.
- This allows the accumulation of interesting, and valuable materials like Gallium, and Germanium for recovery

# Ettringite and Selenium.

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- Selenium is a pervasive element in the southwestern United States.
  - Selenium is toxic, and is present in most water sources in the southwest.
  - The cooling lake at Four Corners has little to no Selenium in it, although it pumps from the San Juan River which contains selenium.



# Ettringite and Selenium

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- After investigation, it was found that Morgan lake water, which is used for bottom ash transport and then returned to Morgan Lake, was deficient in selenium.
- Further investigation indicated that the selenium was being tied up by a mineral in Bottom ash called Ettringite.



# Selenium and Copper selenide

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- Analysis of scrubber chemistry indicated profoundly low levels of solution phase selenium.
- A chance discovery indicated that under certain conditions, selenium was bonding with copper as a copper selenide in the scrubber.



# Copper selenide

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- This chemistry ended up being specialized enough that it ended up being licensed to a firm trying to develop thin film Copper Selenide photo-voltaics.



# Chloride

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- Gypsum is 2.5 times more soluble in salty water than in clean water.
- In mist eliminators, there is no alkalinity to neutralize pH, so the scaling index is very high.
- Without the presence of chloride to keep things in solution, mist eliminators will plug.
- In mist eliminators, indeed in all scrubbers, clean water is not your friend. So don't use it.



# Suspended Solids (TSS)

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- Irving Langmuir, Nobel Prize winning chemist said “all chemistry happens on a surface”.
- Scrubbers remove SO<sub>2</sub> at a rate commensurate with the amount of surface area inventory in the box.
- When calcium sulfate cannot plate out on a particle, it will plate out somewhere.



# Suspended Solids (TSS)

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- Reuse TSS along with water and maintain a healthy surface area inventory in your scrubbers.
- Reuse of solids and chemistry are keys to long term SO<sub>2</sub> compliance.

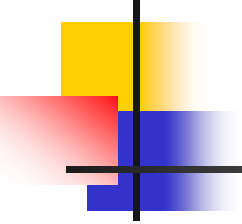
# When Slurries and TDS act Strange



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- Calcium sulfate can become an anhydrite in a low pH.
- We've already established that low pH is caused by the presence of anerobic bacteria.
- This low pH can aid you, in removing water molecules from Calcium sulfate, both reducing the volume needed to store FGD materials, and returning water molecules to the scrubbing process for reuse.
- This can also happen in the mist elimination systems of a scrubber, making hydrophobic particulate, that can leave via the smokestack.

# Silica and Diatoms

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- Silica can be pervasive in water and create issues with cleaning water, and with scaling.
  - Diatoms are single cell organisms that fix silica in water to manufacture their skeletons. This effectively removes the silica from the water.



# Silica and Diatoms

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- Allowing diatoms to have access to water first, to remove silica, can be a good way to lower Silica in your cooling towers.
- The Cholla facility is unusual in that two units have a cooling lake, and two units have cooling towers.
- At the Cholla facility, this was done with well water, allowing the cooling lake to fix silica and remove it from solution, before passing water to the cooling towers, sans silica.



# Silica and diatoms.

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- This had the added benefit of increasing the blowdown rate of the cooling lake, lowering its TDS, and summertime temperature.

# Sulfur fixing bacteria



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- This is a more pervasive condition when the scrubber is inhibited oxidation.
- All scrubbers in the APS system are inhibited oxidation, and now, dual sorbent.
- There will be sulfur reducing bacteria in this mix, and oddly enough, they can be beneficial.



# Sulfur Fixing Bacteria.

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- There two species of sulfur reducing bacteria in the Four Corners Scrubbers.
- Thiobacillus Feroxidans and P. Furiosii.
- Both species consume sulfur, and generate Hydrogen Sulfide ( $H_2S$ ) and sulfuric acid ( $H_2SO_4$ )

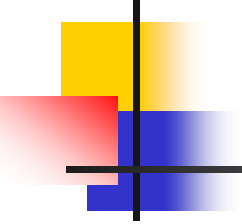


# Sulfur Fixing Bacteria

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- This ends up being very useful, when the liquor is returned to the scrubbers for reuse.
- The Hydrogen Sulfide and sulfuric acid mix with the small amount of sulfurous acid ( $\text{H}_2\text{SO}_3$ ) in the scrubbers and make elemental sulfur.
- Elemental sulfur is used in these scrubbers to inhibit oxidation potential.
- The bugs were saving us money.

# When Bacteria and chemical control become a problem.



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Anerobic/sulfur fixing bacteria create  $\text{H}_2\text{SO}_4$   
 $\text{H}_2\text{SO}_4$  is frequently used for pH control in cooling towers.

These sources of  $\text{H}_2\text{SO}_4$  create two problems, at the cooling towers, and at your evaporation ponds.

$\text{H}_2\text{SO}_4$  is an azeotrope with water. Severely reducing its vapor pressure.



# When bugs go bad...

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Cooling towers run at a higher equilibrium temperature, impacting your condenser back pressure and unit heat rate.

Evaporation ponds don't like to evaporate water.

Neutralization of  $H_2SO_4$ , and or eradication of bacteria are two coping strategies.

Using something like Carbon Dioxide for pH control in a cooling tower is another.



# Deliquescent salts.

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- A large number of salts exist in equilibrium as a liquid. While there is water in these materials, they are a liquid salt, not water.
- When viewed at the bottom of an evaporation pond, they can look like your evaporation pond isn't doing its job.



# Deliquescent salts.

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- Removal of these liquids in a sand filter will leave you with bone dry salts you can throw away, or sell.
- The liquid portion has value too.
- Deliquescents have a tendency to be magnesium or potassium salts, and can be used as a dual sorbent in your scrubber.



# Potassium Nitrate. Yet another surprise.

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- A power plant uses treated sewage effluent for its source water.
- Once the water is used up, the majority of TDS in the water is potassium chloride and potassium nitrate. Both of which are worth a lot of money.
- Traditional evaporation methods can harvest 80% of this material with little to no energy input.



# Magnesium sulfate, a similar story

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- Magnesium accumulates in solution in the waste water of dual sorbent scrubbers.
- As the water evaporates, magnesium salts precipitate long before conventional, low value salts. Like potassium, these materials can be worth a lot of money.



## • Conclusions Part 1.

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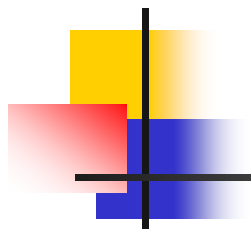
- Look carefully at the process, and have a plan, based on what makes sense.
- Investigate the processes to find places where the process is helping you.
- Figure out how to maximize profits by best management practices.



# Conclusions, part deux.

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- Have a water management plan.
- Have a drought plan.
- Have senior managements buy-in for the plan.
- Stick to the plan.



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Questions?