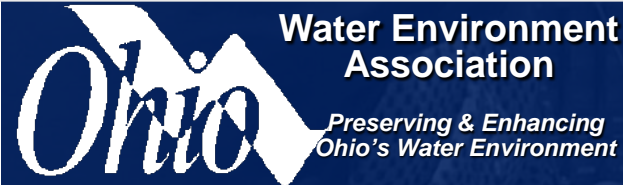


Plant Operations and Laboratory Analysis Specialty Workshop

Water Chemistry and Plant Performance

September 1, 2010

Dan Miklos



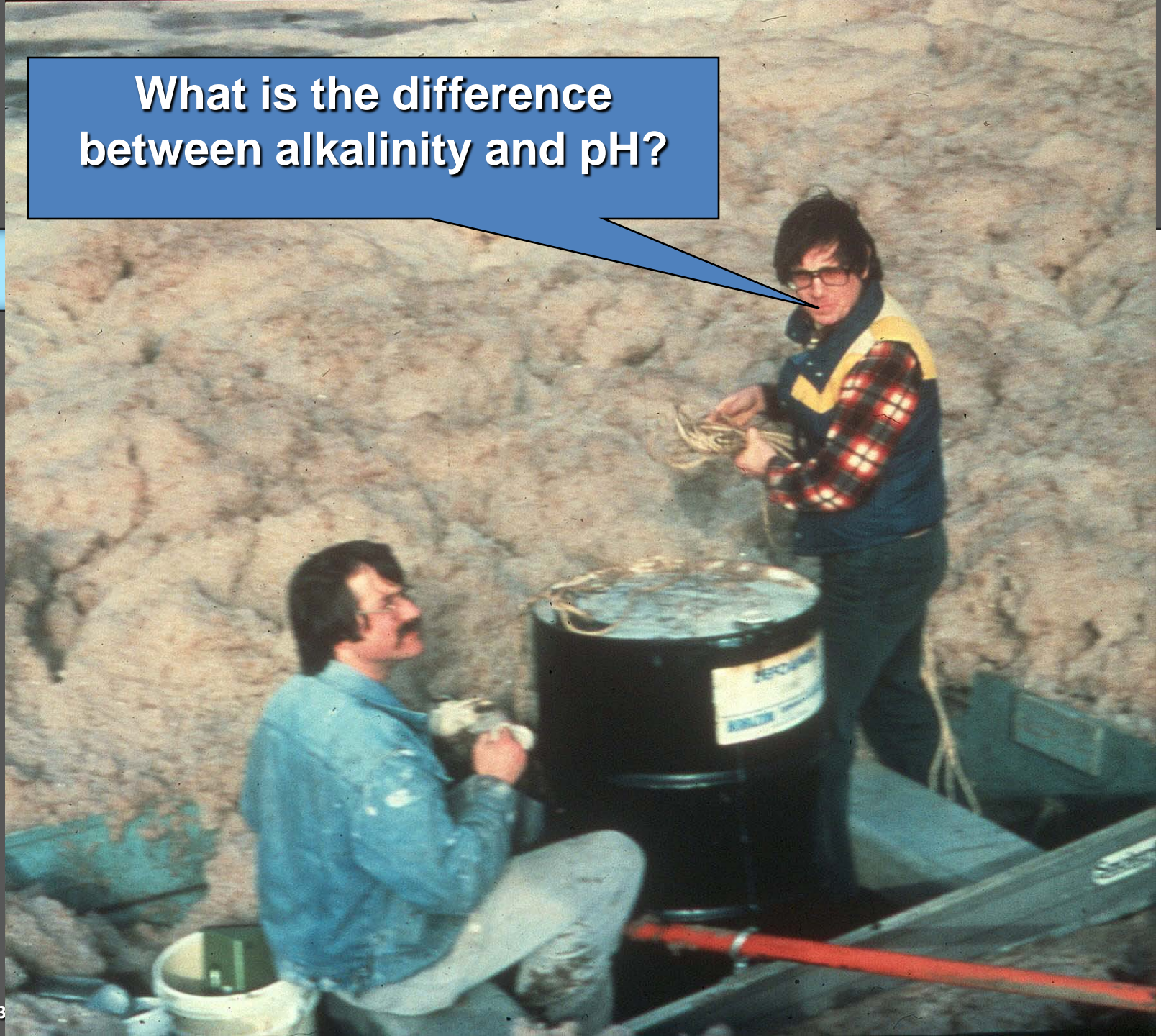
HAZEN AND SAWYER
Environmental Engineers & Scientists

Water Chemistry and Plant Performance

Agenda

1. Introduction
2. What is the difference between pH and Alkalinity
3. Case Study – Turkey Processor
 - Loss of nitrification due to loss of viable biology
 - Mass Balance problems with inerts
 - Sludge Quality as a function of inerts
4. Questions

What is the difference between alkalinity and pH?



pH and Alkalinity

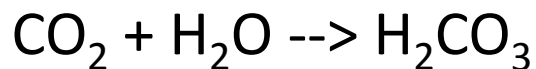
- pH is the measure of hydrogen ions or the concentration of the acid. It is expressed as the negative logarithm of the hydrogen ion concentration. 0.0000001 is a pH of 7 (neutral). 0.000001 is the pH of 6 (10 times the concentration of hydrogen ions).
- Unlike our other measurements, a change of 1 S.U. represents a logarithmic change (10 times). So a slight shift in the background water chemistry of pH is a big difference.
- In relation to biochemistry, pH is how the food industry controls shelf life

pH and Alkalinity

- Homemade mayonnaise would go bad in an afternoon at a picnic. Today the mayonnaise would help preserve the other items in the potato salad. It sits for months on the shelf. The pH is lowered (3.8 to 4.2 S.U.) to essentially stop any biological activity.
- As the concentration of hydrogen ions increases (low pH), the biological activity is reduced.
- The pH of Pepsi is 2.5 S.U. The shelf life of that sugar water is measured in months. The pH is reduced by adding carbon dioxide under pressure and creating carbonic acid. There are other acids (citrus and phosphoric), but CO_2 is the primary agent.

pH and Alkalinity

- The carbon dioxide is under pressure and forms a very unstable solution. As you release the pressure and allow the pressure to reach atmosphere, the CO₂ comes out of solution and the pH shifts.
- As the CO₂ changes to a gas due to the drop in pressure (fizzes), the pH increases.
- As we add more pressure, more of the CO₂ dissolves into solution and the pH is lowered as more carbonic acid (H₂CO₃) is formed.



- Henry's Law governs these reactions.

Henry's Law

- The solubility of a gas in a liquid depends on
 - temperature,
 - the partial pressure of the gas over the liquid,
 - the nature of the solvent (water in our case), and
 - the nature of the gas (carbon dioxide in the Pepsi example)
- Another example is temperature and oxygen solubility in water. Lower temperature – more dissolved oxygen. Higher temperature – lower dissolved oxygen. Colder water makes for better trout streams.

Henry's Law

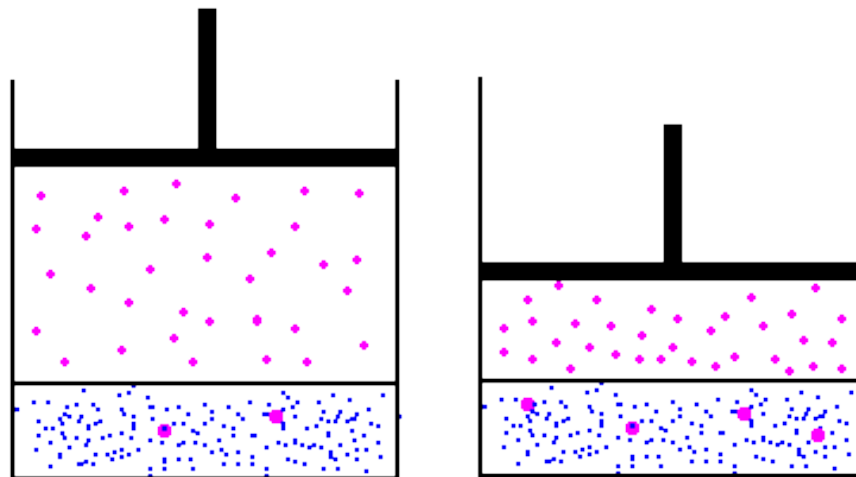
- Temperature (if you see bubbles in the BOD₅ bottle and there were none at the beginning of the test):
- BOD₅ Test – cold effluent sample in a BOD Incubator shows Henry's Law.
 - Oxygen gas bubbles form as the solubility of oxygen in the sample decreases due to the temperature increase.
 - In winter, an effluent sample could start at 10°C and warms to 20°C in the incubator.
 - Solubility of oxygen decreases from 11.37 mg/L to 9.07 mg/L. Oxygen comes out of solution as the sample warms. The bubbles were not there at the start of the test.

Henry's Law

- The solubility of a gas solubility is also limited by the equilibrium between the gas and a saturated solution of the gas. The dissolved gas will always follow Henry's law.
- The concentration of dissolved gas depends on the partial pressure of the gas. The partial pressure controls the number of gas molecule collisions with the surface of the solution. If the partial pressure is doubled the number of collisions with the surface will double. The increased number of collisions produces more dissolved gas (Pepsi under pressure).
- Partial pressure is a function of gas pressure and gas concentration.

Henry's Law

- Carbon dioxide is at approximately 380 mg/L in the atmosphere (increasing about 1 mg/L each year). Oxygen in comparison is 209,500 ppm (21%).
- In a pure oxygen plant, for example, you add close to 100% oxygen or 5 times the oxygen in the atmosphere. As a result, pure oxygen plants can have dissolved oxygen levels of 20 mg/L in the MLSS or 40 mg/L in the effluent. Pure oxygen plants have “decks” and actually create a pressurized gas space.



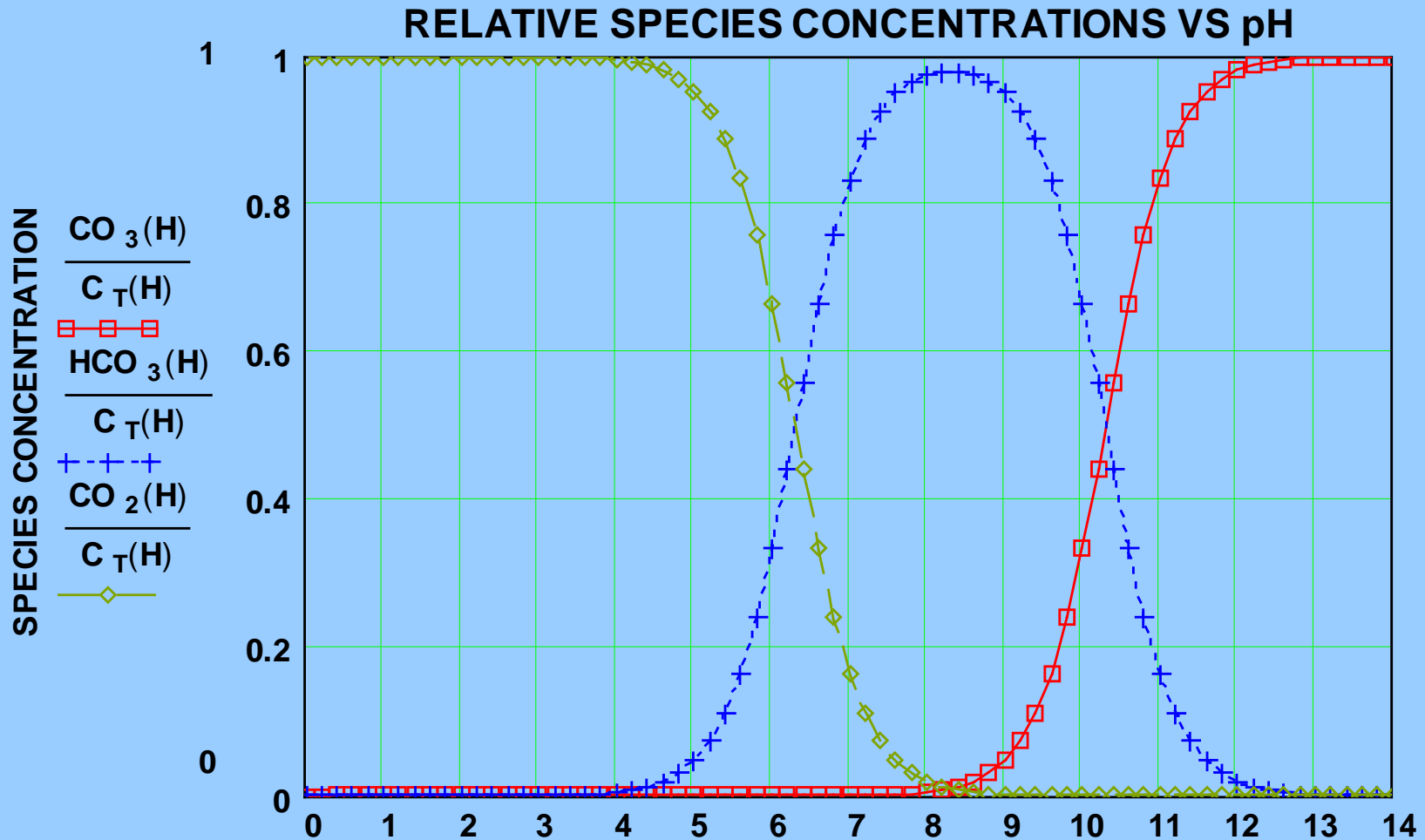
pH and Alkalinity

- Alkalinity is a measure of the water's capacity to neutralize an acid, or H⁺ ions, thereby keeping the pH at a fairly constant level.
- Do not confuse this with our term alkaline substance (meaning basic or higher than neutral pH). A basic substance would have a high concentration of OH⁻ ions.
- Alkalinity is reported in units of mg/L CaCO₃, because the carbonate ion, CO₃²⁻, is its primary constituent.

pH and Alkalinity

- Alkalinity is measured by titrating a water sample with sulfuric acid. The Vernier pH System is used to monitor pH during the titration. The equivalence point will be at a pH of approximately 4.5. The volume of sulfuric acid added at the equivalence point of the titration is then used to calculate the alkalinity of the water.
- One problem is total alkalinity is misleading.
- We titrate to 4.5 S.U. Alkalinity that is available at that low of a pH is not available to our biology. So we can have “left over” alkalinity, but alkalinity is still limiting the process.
- Looking at the graph, bicarbonate alkalinity, is available in our biology’s pH range.

pH effect on Distribution of CO₂ Ions in Solution

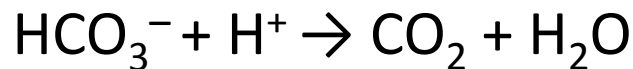
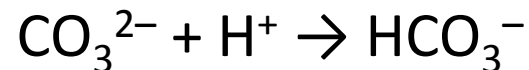
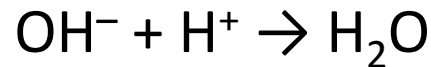


**Process
Control is
Hard Work!!**



Restoring Alkalinity for Nitrification

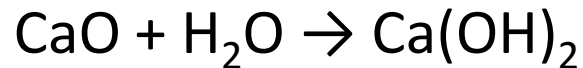
- The alkalinity of in our water is primarily due to the presence of hydroxide, OH^- , carbonate, CO_3^{2-} , and bicarbonate, HCO_3^- , ions. These ions react with H^+ ions by means of the following chemical reactions:



- As we treat wastewater and bacteria generate carbon dioxide and the nitrifiers generate a nitrous acid, natural or native alkalinity is necessary to complete the reactions and neutralize the acid. If enough alkalinity is not present, we must add it or the process stops as pH decreases.

Restoring Alkalinity for Nitrification

- In our Case Study, lime is being used for pH adjustment.
- Calcium Hydroxide Ca(OH)_2 . Also commonly referred to as slaked lime or hydrated lime; calcium hydroxide is formed as a result of hydrating lime (calcium oxide, CaO).



- Lime is by far the most economically favorable alkaline reagent to use for acid neutralizations. Lime is significantly cheaper than caustic (NaOH).

Restoring Alkalinity for Nitrification

- Lime is very basic and the hydroxide ion removes the hydrogen ion (acid) in solution in the plant and raises the pH.
- The free calcium ions also react with the excess carbon dioxide and form an insoluble milky product, calcium carbonate.
- Enough lime has to be added to restore the alkalinity for 200 mg/L of ammonia oxidation. Remember, 7.14 mg/L of alkalinity is required for every mg/L of ammonia oxidized.
- In addition, we have carbon dioxide (carbonic acid) from respiration that also must be neutralized.

Case Study – Turkey Processor

- If too much lime is added, a significant amount of insoluble calcium carbonate is formed. Those inert solids become incorporated in the MLSS and begin to crowd out the biology.
- In our Case Study, lime is used to support nitrification.
- The direct discharger believed raising the pH to 8.0 S.U. would improve nitrification (anaerobic reactor COD reduction resulted in a reduced carbon load but a relatively high ammonia loading).
- Nitrification was a noncompliance issue as a single aerobic reactor was used for full nitrification. Influent ammonia was reduced from a concentration of 200 mg/L to less than 1 mg/L in the effluent (when in compliance).

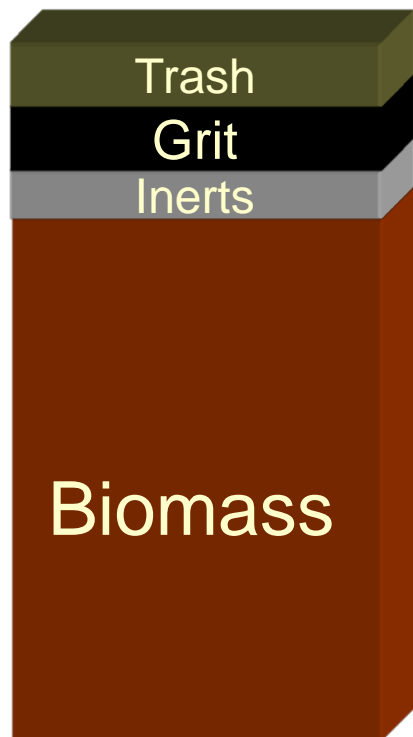
Mixed Liquor Suspended Solids as Biomass

- Based on a consultant's recommendation, the pH was increased based on the "literature" stating the nitrification rate increases with an increase in pH just north of 8.0 S.U.
- Mixed liquor suspended solids were maintained within target MCRT values as was typical for the facility (why not? the nitrification rate was going to increase as the pH increased).
- The end result, nitrification was lost as the nitrifying population was crowded out by inert solids (calcium carbonate moving out of solution as pH increased).
- An example of the solids balance is shown on the next slides.

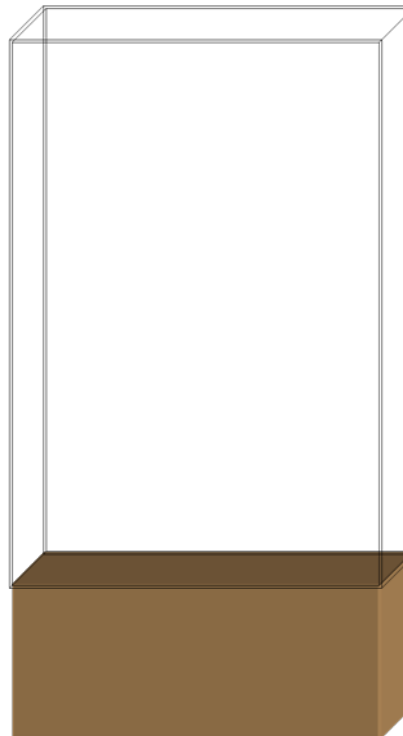
I Wonder How Much of that
MLSS is Biomass?



Traditional Solids Balance



Solids
Production



Solids
Destruction

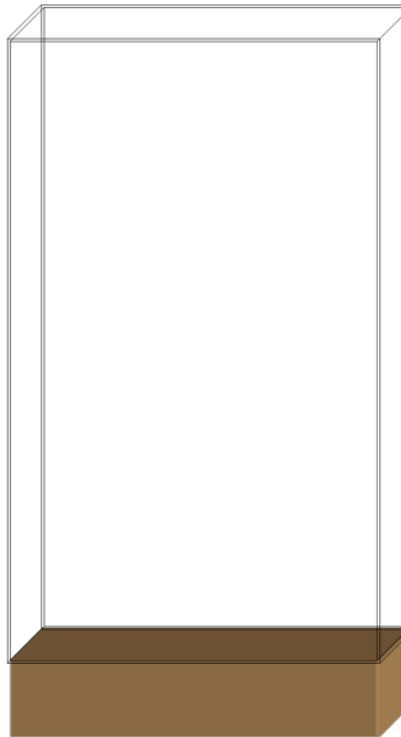


Excess
Solids to
Disposal

Solids Balance with Lime Addition to a pH of 8.0 S.U.



Solids
Production



Solids
Destruction

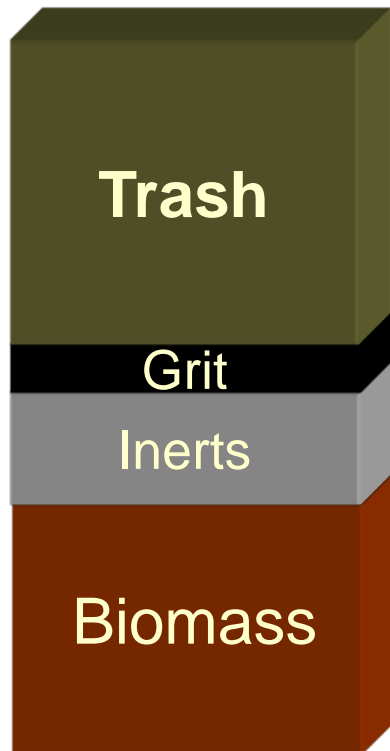


Excess
Solids to
Disposal

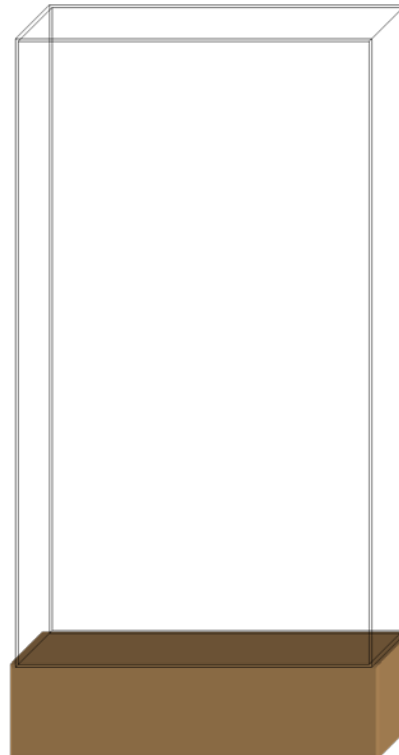
Inert Suspended Solids versus Biomass

- Other industrial plants have similar problems. In the paper industry, rather than inerts (trash or paper fiber) is a non biological solid that crowds out the biology.
- Significant levels of trash will be oxidized at 550 degrees. Paper mill wastewater operations actually uses increasing volatile solids concentrations as an indication of “lowering of viability”.
- Most mills in our region are recycle mills where spent fiber and starch is discharged to the wastewater treatment facility. Primary settling with chemical addition is the first line of defense for excess paper fiber loading.
- In the cases of the paper mill, if volatile solids show an increase, it means less biology is available in the MLSS

Solids Balance with Spent Fiber Loading



Solids
Production



Solids
Destruction



Excess
Solids to
Disposal

Volatile Suspended Solids as Biomass for the Case Study?

- Structural Water (water of hydration) examples:
 - Calcium Carbonate ($\text{CaCO}_3 \cdot 6 \text{H}_2\text{O}$) – 52% water. Water starts leaving at 101°C and is gone by 220°C . Much of the solids in our Case Study example would have tested as volatile solids even though they could be inert solids. It does not have to be trash to burn.
 - Concrete – based on curing (water loss), will show approximately 38% water loss (volatile solids) when raised from 103°C to 550°C .



Volatile Suspended Solids as Biomass?

- Options for analysis if it is necessary to compensate for volatile suspended solids test inaccuracy
 - Nitrogen content of solids can be used to back calculate the maximum amount of biological solids possible (divide result by 12.5% - the nitrogen content of cells) .
 - If nitrogen containing compounds such as polymer are used, nitrogen can be a little misleading.
 - Carbon can be used to back calculate the maximum biological population potential (divide result by 50% - the carbon content of cells).

I wish he wouldn't do that

I smell nitrification problems



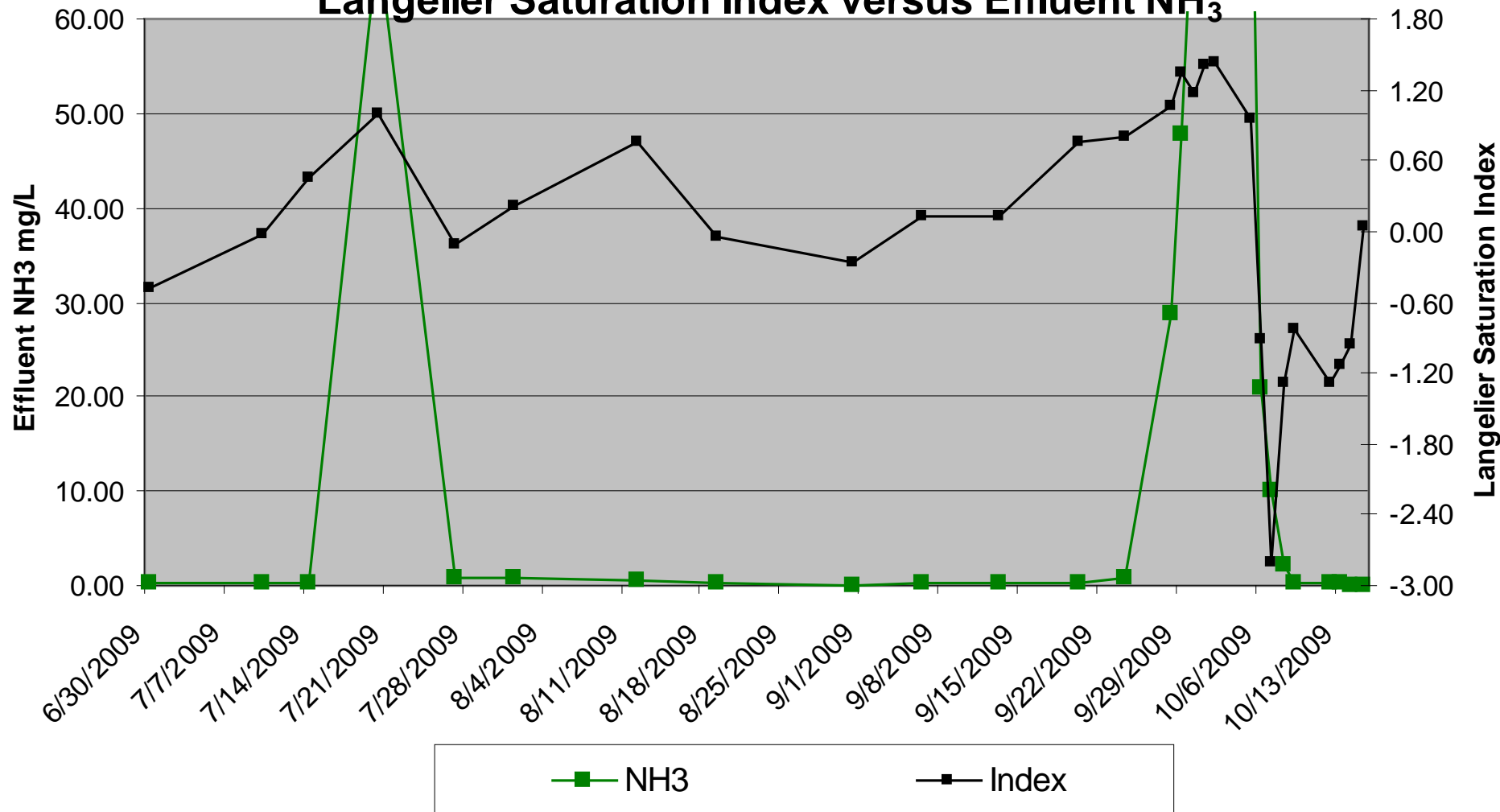
Reuters / Jim Young

Using Calcium Carbonate Solubility to Control Nitrification

- Since calcium carbonate solubility is primarily a function of calcium hardness, pH, alkalinity and water temperature; those four (4) variables were analyzed and compared to effluent quality.
- A solubility or precipitation index was applied that is typically used in drinking water treatment operations. The Langelier Saturation Index (LSI) is typically used as a method of determining corrosive or scaling water chemistry.
- In the Case Study application , the LSI was applied assuming there was some slight interference from total dissolved solids and other ionic particles, but the LSI tracked losses in nitrification.

Figure 4 - 9

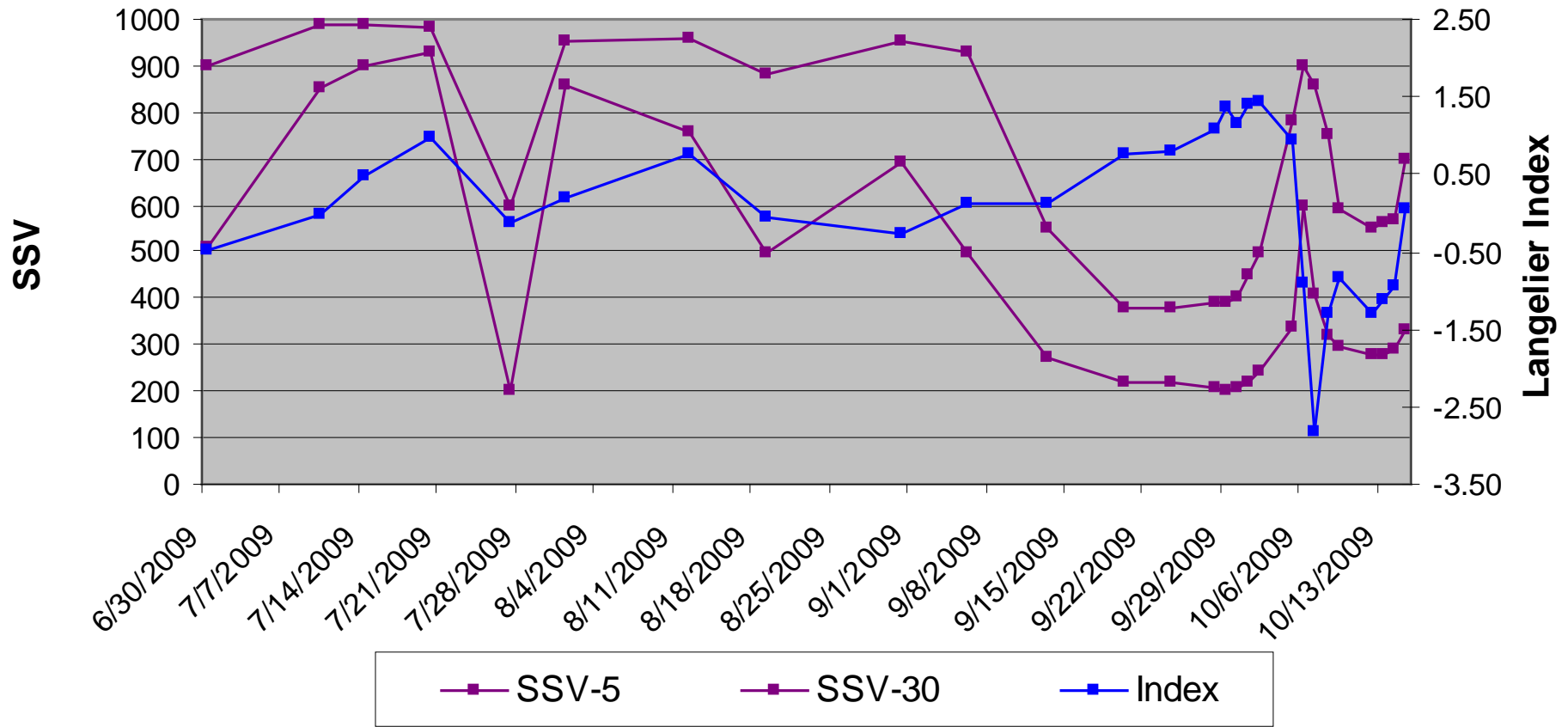
Langelier Saturation Index versus Effluent NH₃



Using Calcium Carbonate Solubility to Control Settling?

- Since calcium carbonate solubility loads the MLSS with fine inerts with a high specific gravity and dense structure, the MLSS settling is affected.
- The result is like adding sand to feathers. As expected, as the insolubility of the calcium carbonate increased, the settling rate increased (the SVI decreased).
- The graph shows settling correlates closely to the MLSS pH (5 minute and 30 minute settling).
- As biological viability increases, the SVI increases and settling slows.

Figure 4 - 8 Langelier Saturation Index versus Settling



Questions????

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