Water Stability

Presenter: Michael Urrutia, Division Manager, GBRA

Outline

- Corrosion
- pH theory – How does a pH meter work?
- Baylis Curve
- Langlier Saturation Index
- Alkalinity
- Calcium Hardness
- TDS

Corrosion

- Green hair in blonde haired children
- Due to low alkalinity water and copper pipes
- Added corrosion inhibitor
- Problem went away and lowered first draw lead levels
Corrosion – Taste, smell and see

- Iron causes stains in bathroom and laundry
- Taste iron – metallic taste
- Smell – sometimes a musty smell

Classify Your Water

- Scaling – hard waters over saturated with calcium carbonate
- Neutral – in equilibrium, may need to adjust water to slightly scaling
- Corrosive – tends to dissolve piping

pH Theory

- pH is a measurement of the relative acidity of an aqueous solution
- pH is a measurement of hydrogen ion concentration
**pH Theory**

- **Acid** - increases the hydrogen ion (H+) concentration in a solution
- **Base** - increases the hydroxide ion (OH-) concentration in a solution

**pH Scale**

- pH is a negative logarithmic function
- Each decrease in pH unit = 10X increase in acidity
  - Solution at pH 4 is 10X more acidic than solution at pH 5
  - Solution at pH 4 is 100X more acidic than pH 6 solution
How Does a pH Probe Work?

- Probe measures hydrogen ion concentration
  - Two electrodes in probe - sensing half-cell, reference half-cell

Half-Cells

- Ion sensing pH half cell
  - Glass bulb that is sensitive to H⁺.
- Reference half-cell
  - Glass tube filled with salt solution to complete circuit.
Reference Half-Cell

- Dispenses reference solution which completes circuit for meter

Sensing Half-Cell

*H* conc the same both inside and outside glass bulb

*No potential develops*
Sensing Half-Cell

**pH 7 Solution**
- H⁺ conc the same both inside & outside glass bulb
- *No Potential develops*

Sensing Half-Cell

**pH 4 Solution**
- H⁺ conc 1000x greater outside glass bulb
- *Potential develops*

Hydrogen ion concentration fixed at pH 7

- 1000H⁺
- 1000H⁺
- 1000H⁺

Sensing Half-Cell

**pH 4 Solution**
- H⁺ conc 1000x greater outside glass bulb
- *Potential develops*
Sensing Half-Cell

**pH 10 Solution**
- H⁺ conc 1000x greater inside glass bulb
- Potential develops

Hydrogen ion concentration fixed at pH 7

1000 H⁺
1000 H⁺
1000 H⁺
1000 H⁺

H⁺
H⁺
H⁺
H⁺

- Potential develops

Calibration

- A calibration curve allows the meter to convert a measured millivolt potential into a pH reading.
Calibration

- The optimal slope for pH is \(-59.16 \text{ mV/decade}\) *
- Acceptance criteria = \(\pm 5\% \text{ or } 3 \text{ mV}\)
  * at 25 degrees Celsius

What does this mean?

Calibration

- \(-180\text{ mV}\) difference measured between pH4 and pH7
- pH4 to pH7 (3 pH units) is 1000x concentration change
- Decade = 10-fold concentration change = 1pH unit
- \(-180/3 = -60 \approx -59.16 \text{ mV/decade}\)
Calibrate

• Calibrate pH meters daily using two or three fresh buffer solutions

Measurement

• Place probe into sample, stir, and wait for readings to stabilize
• Rinse and dry between measurements
• Storage between measurements
  – Sample or solution of similar ionic strength to sample
  – pH4 buffer
  – Electrode storage solution (i.e. 3M KCl)

Troubleshooting

• mV reading in pH 7 buffer
  – Should read $0 \pm 30$ mV in pH 7 buffer
• Response time
  – May require cleaning if slow in buffered solution
• Slope
  – Optimal slope is $-59.16 \pm 3$ mV/decade (5%)
Measurement - Special Considerations

- Low ionic strength solutions
  - Absorption of atmospheric carbon dioxide is a major source of drift
  - Low ionic strength sample chamber
  - Condition electrode in a solution of comparable ionic strength before use

Cleaning

- Slow response may indicate need for cleaning
  - Immerse and agitate in a warm dilute mild detergent solution for a few minutes. Rinse with DI and blot dry before use.
  - Alternate soaking in dilute hydrochloric acid and dilute sodium hydroxide. Rinse with DI water and condition in pH 7 buffer before use.

Estimating Corrosion

- Baylis Curve
- Langlier Saturation Index
Baylis Curve

- Relationship between the pH values and the alkalinity
- Quick tests only pH and alkalinity – Takes 10 minutes

Langlier Saturation Index (LSI)

- Determines the tendency of water to either scale or corrode piping and tanks.
- Calcium hardness, alkalinity, TDS, pH and temperature
### Langlier Saturation Index (LSI)

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<th>Date</th>
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<th>TW pH</th>
<th>TW Alkalinity</th>
<th>TW Alkalinity (as CaCO₃)</th>
<th>TW Calcium Hardness</th>
<th>TW Calcium Hardness (Ca+² as CaCO₃)</th>
<th>TW Temp</th>
<th>TW TDS</th>
<th>TW LSI</th>
<th>Target TW LSI</th>
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### Common Titrations

- **Alkalinity**
- **Hardness**
- **Calcium Hardness**

### Alkalinity

- The acid neutralizing (buffer) capacity of a water
- The ability of water to resist a pH change
- Primarily due to the presence of:
  - Hydroxides (OH⁻)
  - Carbonates (CO₃²⁻)
  - Bicarbonates (HCO₃⁻)
Expressions of Alkalinity

- Total (MO) Alkalinity
  - Determined by a titration to a pH of 5.1, 4.8, 4.5, or 3.7 (depending on the amount of carbon dioxide present)
  - Color change = green → gray/violet/pink
  - Measures all carbonate, bicarbonate and hydroxide alkalinity

Hardness

- Traditional measure of the capacity of a water sample to precipitate soap
- Primarily due to the presence of divalent cations
  - Calcium (Ca$^{2+}$)
  - Magnesium (Mg$^{2+}$)

Importance of Hardness

- Tests available for total hardness and calcium hardness (magnesium by difference)
- Significant in the treatment processes for potable water and wastewater
Expressions of Hardness

• Total Hardness
  – Determined by titration with a standard EDTA and Calmagite indicator to an endpoint of a pure blue color at a pH of 10.1.
  – This registers the hardness in solution (calcium and magnesium)

Expressions of Hardness

• Calcium Hardness
  – Determined by titration with a standard EDTA and Calmagite indicator to an endpoint of a pure blue color at a pH of > 12.
  – Calcium hardness measures only calcium ions in solution
Total Dissolved Solids

- Same as Total Dissolved Salts
- Easy to perform with TDS meter
- Place sample in beaker and insert TDS probe
- Takes 30 seconds to get reading
- Another method is to evaporate all water in 180°C oven and measure/weigh salt or solids residue

Water Stability Take Home Messages

- Explain corrosive versus plating water—Why is it important to know this?
- Spend quality time to explain pH in depth
- Take time to explain Alkalinity, Calcium Hardness and TDS—How do they work?
- Show Baylis Curve and go over results of different Alkalinity or pH water
- Show LSI spreadsheet and change parameters to show change in LSI
- Explain what to do if water is corrosive—Add caustic/sequestering agent?

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Thank You!