The Role of CO$_2$

in Corrosion Control

Treatment Methods and Equipment

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Municipal Water Manager
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Treatment Methods and Equipment

Mr. Michael Dirth

Mr. Dirth earned his Bachelor’s of Science degree in Chemical and Petroleum Refining Engineering from the Colorado School of Mines – Golden, Colorado in 1983. He immediately began a career in the Industrial Gas Industry as a Sales Engineer for Liquid Air Corporation in Willowbrook, Illinois. Several years later he became a CO$_2$ Applications Engineer and Technical Services Manager for Carbonic Industries Corporation and Airgas Carbonic in Duluth, Georgia. (1986-1989; 1993-2002). In the early ‘90’s Mr. Dirth worked as a Process Engineer for the Clorox Company where he developed the process for the National production of Clorox 2 in the Company’s state of the art manufacturing facility in Dyersburg, TN. In 2002 he joined TOMCO$_2$ Systems in his current role as Product Manager for the Water Technologies Division. Mr. Dirth has over 25 years of Applications Engineering experience in the CO$_2$ Industry and utilizes this experience assisting Consulting Engineering firms with the design of CO$_2$ pH control systems for Municipal Water Treatment Plants throughout the United States and Canada. Mr. Dirth has designed over 500 CO$_2$ pH control systems in his career.
What is CO$_2$? How is it Made?

- Carbon Dioxide is a gas at normal atmospheric temperature and pressure. It is a colorless, odorless gas that is about 1.5 times more dense than air. It dissolves in water to form carbonic acid; H$_2$CO$_3$. Carbon dioxide gas is formed from the combination of two elements: carbon and oxygen.
- CO$_2$ is produced from the combustion of coal or hydrocarbons, the fermentation of alcohols, the production of anhydrous ammonia, by-product of other chemical processes, occur naturally in deep CO$_2$ wells and the breathing of humans and animals. Found in small proportions in the atmosphere, it is assimilated by plants which in turn produce oxygen.
Why Do We Adjust pH?

• Stabilize Water Chemistry
• Corrosion Control
• Discharge Water (Permit)
• Reduce or prevent Carbonate Scaling
• Enhance a chemical reaction or process
  • Polymers, Chlorine, Lime, Filtration, Contaminant removal
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Use</th>
<th>Composition</th>
<th>Alkalinity Change</th>
<th>DIC Change</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baking Soda, NaHCO₃ (sodium bicarbonate)</td>
<td>Increases alkalinity with moderate increase in pH.</td>
<td>95% purity. Dry storage with solution feed.</td>
<td>0.60 mg/L as CaCO₃ alkalinity per mg/L as NaHCO₃</td>
<td>0.14 mg/L as C per mg/L as NaHCO₃</td>
<td>Good alkalinity adjustment chemical but expensive.</td>
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<td>Carbon Dioxide, CO₂</td>
<td>Lowers pH. Converts hydroxide to bicarbonate and carbonate species.</td>
<td>Pressurized gas storage. Fed either through eduction or directly.</td>
<td>None</td>
<td>0.27 mg/L as C per mg/L as CO₂</td>
<td>Can be used to enhance NaOH or lime feed systems.</td>
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<tr>
<td>Caustic Soda, NaOH (sodium hydroxide) Or KOH (potassium hydroxide)¹</td>
<td>Raises pH. Converts excess carbon dioxide to carbonate alkalinity species.</td>
<td>93% purity liquid bulk, but generally shipped and stored, at &lt; 50% purity to prevent freezing. KOH has a higher freezing point and may be stored at higher concentrations.</td>
<td>1.55 mg/L as CaCO₃ alkalinity per mg/L as NaOH</td>
<td>None</td>
<td>pH control is difficult when applied to poorly buffered water. Is a hazardous chemical, requires safe handling and containment areas.</td>
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<td>Hydrated Lime, Ca(OH)₂ (calcium hydroxide)²</td>
<td>Raises pH. Increases alkalinity and calcium content (i.e., hardness)</td>
<td>95 to 98% purity as Ca(OH)₂. 74% active ingredient as CaO. Dry storage with slurry feed.</td>
<td>1.21 mg/L as CaCO₃ alkalinity per mg/L as Ca(OH)₂</td>
<td>None</td>
<td>pH control is difficult when applied to poorly buffered water. Slurry feed can cause excess turbidity. O&amp;M is intensive.</td>
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<td>Soda Ash, Na₂CO₃ (sodium carbonate) Or Potash, K₂CO₃ (potassium carbonate)</td>
<td>Increases alkalinity with moderate increase in pH.</td>
<td>95% purity. Dry storage with solution feed.</td>
<td>0.90 mg/L as CaCO₃ alkalinity per mg/L as Na₂HCO₃</td>
<td>0.11 mg/L as C per mg/L as Na₂CO₃</td>
<td>More pH increase caused compared with NaHCO₃, but less costly. Has increased buffer capacity over hydroxides.</td>
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<td>Sodium Silicates Na₂SiO₃</td>
<td>Moderate increases in alkalinity and pH.</td>
<td>Available in liquid form mainly in 1:3.2 or 1:2 ratios of Na₂O:SiO₂</td>
<td>Depends on formulation</td>
<td>None</td>
<td>More expensive than other options but easier to handle than lime and other solid feed options. Has additional benefits in sequestering or passivating metals.</td>
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pH, Alkalinity and DIC
-EPA Optimal Corrosion Control Treatment 816-B-16-003

- **pH**
  - Measurement of the Hydrogen Ion Concentration (H⁺ or H₃O⁺)
  - Lower Buffer Intensity can create wide swings in distribution system pH

- **Alkalinity**
  - The capacity of water to neutralize acid
  - The sum of carbonate, bicarbonate and hydroxide anions
  - Alkalinity = 2CO₃²⁻ + HCO₃⁻ + OH⁻ - H⁺

- **DIC (Dissolved Inorganic Carbon)**
  - Closely related to corrosion
  - Available carbonate species in the water that can react with lead and copper to form passivating scales
  - DIC = CO₂ + H₂CO₃ + CO₃²⁻ + HCO₃⁻
Control for Lead only or Lead & Copper
-EPA Optimal Corrosion Control Treatment 816-B-16-003

- Target pH should be 8.8 to 10
  - Lower pH (8.2 – 8.5) can result in poor buffer intensity
  - Lower Buffer Intensity can create wide swings in distribution system pH
  - See graph 2.3 Buffer Intensity as a function of pH at different DIC levels

- Sufficient Alkalinity and DIC are Needed
  - Provides better buffer intensity
  - Results in protective scale
  - Too much DIC can solubilize lead (>20 mg/l as C)

- DIC for Minimum Lead Solubility
  - Optimum DIC of 5-10 mg/l as C
  - See figure 1.4

- pH, Alkalinity and DIC are Interrelated
  - If you know two of them you can estimate the third.
  - See Appendix B

- Calcium Carbonate Precipitation
  - Maintain pH below the Saturation pH
  - Adding CO₂ increases DIC and lowers pH
Control for Lead only or Lead & Copper
-EPA Optimal Corrosion Control Treatment 816-B-16-003

Exhibit 2.3: Buffer Intensity as a Function of pH at Different DIC Values (Clement and Schock, 1998b, Figure 1)
Control for Lead only
-EPA Optimal Corrosion Control Treatment 816-B-16-003

Source: Adapted from Schock and Lytle 2011

Figure 1.4 Theoretical impact of pH and DIC on lead solubility in drinking water under ideal equilibrium conditions - assumes Pb(II) and no orthophosphate
Control for Lead only or Lead & Copper
-EPA Optimal Corrosion Control Treatment 816-B-16-003

Appendix B – Estimated Dissolved Inorganic Carbon (mg/L as C) based on Alkalinity and pH (with water temperature of 25 degrees C and TDS of 200)¹,²

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OCCT Evaluation Technical Recommendations for Primacy Agencies and Public Water Systems
Carbon Dioxide pH Control Equipment

- CO₂ Storage
- Vaporizer
- Vapor Heater
- Pressure Regulator
- CO₂ / H₂CO₃ Feed Panel
- Diffuser
CO₂ Bulk Storage

• E-Style & WT-C Series
  • 3.75 Tons – 120 Tons Capacity

• C-Style Series
  • 3.75 Tons – 60 Tons Capacity

• V-Style Series
  • 6 Tons – 100 Tons Capacity
CO₂ Vaporizers

- Variety of Vaporizers
  - Electric Pressure Build
    - 245 lb/hr – 2150 lb/hr
  - Direct to Process
    - 375 lb/hr – 2250 lb/hr
  - Steam
    - 500 lb/hr – 18,000 lb/hr
  - Water
    - 500 lb/hr – 20,000 lb/hr
CO₂ Vapor Heaters

- Electric
  - 720 lb/hr to 1440 lb/hr (Wall)
  - 2000 lb/hr to 6000 lb/hr (Floor)

- Steam
  - 500 lb/hr to 6,000 lb/hr
Gas Feed Equipment

- **CO₂ Gas Feed**
  - 60% - 85% efficiency of the carbon dioxide
  - Needs deep contact or holding basins.
  - Able to reduce the pH to 7.0

- **Carbonic Acid (PSF)**
  - Minimum 95% efficiency of the carbon dioxide
  - Able to reduce the pH to 5.5 – 6.0
  - Can be injected in a pipe, basin, tank or shallow channel.
  - Eliminates the need for deep contact or holding basins.
CO₂ Gas Injection
CO₂ Gas Injection

- Gas (CO₂) + Liquid (water) reaction takes time
- Requires tremendous surface area (fine bubbles)
- Interference of other gases; i.e. air
- Requires mixer or baffles to hold the gas down in the water
- Lower efficiencies due to gas bubbles at the surface
Carbonic Acid Injection (PSF)

TOMCO₂'s Pressurized Solution Feed System offers the state-of-the-art CO₂ injection system that provides a constant pH level.
Carbonic Acid Injection (PSF)

- CO₂ pre-reacted to form Carbonic Acid
- Liquid / Liquid (Carbonic Acid / Water) Reaction
- Immediate reaction (Requires less time)
- Close to 100% efficiency
- Higher pressure improves CO₂ solubility
- More effective pH control
- Faster reaction time reduces scale potential.
CO₂ Diffusers

- **Gas Feed**
  - Uses fine porous diffuser to disperse the CO₂ into a deep basin.

- **Carbonic Acid**
  - Disperses Carbonic Acid into a water stream to form the chemical reaction desired. Designed to fit in any situation.
Carbonic Acid Diffuser Patent # 6637731 & 6767008

- Counter Current
- Cross Sectional Coverage
- Pressure
- Efficient Mixing
- Immediate Reaction
Typical Flow Schematic
Other CO$_2$ Storage & Sources

- Dewars (Mini Bulk)
  - 400 # Liquid CO$_2$
- High Pressure Cylinders
  - Multiple Size Gas
- Stack Gas
  - Contains 10 % - 12 % CO$_2$
- Submerged Combustion Burners
  - Uses natural gas, butane, propane or digester gas to produce CO$_2$. 
Areas to Use CO₂

- Municipal Water Plants
  - Lime Softening
  - Enhanced Coagulation
  - Stripping – H₂S
  - Corrosion Control
  - Membranes including RO
  - Disinfection – Sodium Hypochlorite
- Filter Backwash
- Bromate Reduction
- Arsenic Removal
- Chromium-6 Removal
- Well Rehabilitation
- Aquifer Storage & Recovery (ASR)
- Ion Exchange Odor Control
- Wastewater Discharge
Other pH Control Methods

- Liquid CO$_2$ Feed Systems
- Gas Eductor / Vacuum Feeder
- Chlorinater / Solution Feeder
- Carbonated Water Feeder
- Mineral Acids
Manufacturer’s Qualifications

- Experience in CO₂ and Water Treatment Systems
- Over 1,500 systems installed
- Active member of CGA
- Engineering Capability
- Optimized pH control and CO₂ utilization
- Total System Responsibility
- ASME Pressure Vessel shop
- Service Capability
- Made in the USA- Loganville, GA
The Role of CO$_2$ in Corrosion Control

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