Wastewater Treatment Case Study

Case Study: CO₂ for pH Control in and Re-Carbonatiton in Drinking Water Treatment
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**Background:**
Hardness in natural waters is caused by dissolved minerals, mainly calcium and magnesium compounds. General guidelines for classification of waters are: 0 to 60 mg/l as CaCO₃ as soft; 61 to 120 mg/l as moderately hard; 121 to 180 mg/l as hard; and more than 180 mg/l as very hard. Within the United States, the central part of the country has hard and very hard water sources. Most water utilities treat to hardness levels between 50 – 150 mg/l as CaCO₃ based on the public acceptance, cost of chemicals and sludge production. It is important to note that the US EPA has not set a standard for hardness in water as the constituents that contribute to hardness are not a concern for human health. Lime softening process is often employed to raise the water pH to precipitate the calcium and magnesium salts out of water. The effluent from lime softening process is supersaturated with carbonates at high pHs (10 or greater) and it is necessary to stabilize the water to prevent deposition of a hard carbonate scale on the piping and filters.

**Situation:**
The City of Bloomington’s water purification plant on Lake Bloomington has been operating since 1929, supplies drinking water to 70,000 residents and a major manufacturing customer in the city of Bloomington, Hudson, Towanda townships. The current average daily demand is 14 million gallons with daily max at 18 MGD. The treatment plant uses Lake Bloomington and Lake Evergreen as surface water sources. The City of Bloomington’s raw water is very hard with an average hardness value of 195 mg/l as CaCO₃. Such high levels of hardness can result in increased use of soap and detergents for the consumers and can cause objectionable scaly deposits on plumbing fixtures and water heaters at homes. So, the treatment plant uses a single stage excess lime softening process to reduce calcium- and magnesium-associated hardness in water to below 120 mg/l as CaCO₃. The lime-treated water has high pH which can cause scaling and can eventually clog the piping and filters in the plant. So, the plant needs to re-carbonate the water thereby lowering and stabilizing the pH.

**Praxair’s Proposal**
Re-carbonation with CO₂ is commonly used to lower the pH below 9.5 and dissolve the CaCO₃ into bicarbonate form. The main reactions for the process are as follows:

**Lime Softening**
\[
\text{Ca(HCO}_3\text{)}_2 + \text{Ca(OH)}_2 \rightleftharpoons 2\text{CaCO}_3 + 2\text{H}_2\text{O} \\
\text{Mg(HCO}_3\text{)}_2 + 2\text{Ca(OH)}_2 \rightleftharpoons \text{Mg(OH)}_2 + \text{CaCO}_3 + 2\text{H}_2\text{O}
\]

**Re-carbonation**
\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca(HCO}_3\text{)}_2 \\
\text{Mg(OH)}_2 + \text{CO}_2 \rightleftharpoons \text{MgCO}_3 + \text{H}_2\text{O}
\]

The suggested CO₂ system for pH control in this process consists of different subsystems: 1) CO₂ supply, 2) flow control, 3) pH measurement and process control and 4) the injection system (Figures 1-3). Bulk CO₂ is stored on-site in liquid form (99.5% purity) in an insulated storage tank at the customer’s site.

The gaseous CO₂ is vaporized from liquid using ambient or electrically heated vaporizer and piped to the point of use via a CO₂ flow control panel with process feedback from a pH probe. CO₂ is dissolved into water using spargers, diffusers or venturi injectors either in contact basins or in the pipe directly (in-line or sidestream). The contact basins require a detention time 30 minutes and depths greater than 15 feet to achieve 60 – 85% transfer efficiency. Alternately, pipeline injection requires significantly less reaction time (on the order of few minutes) and can give greater than 95% transfer efficiency. Praxair is a leader in CO₂ supply and has a number of merchant and production plants in the US and Canada with a fleet of delivery vehicles and can provide assistance in designing complete system for CO₂ use.
Competitive Considerations

Mineral acids like sulfuric acid or hydrochloric acid have traditionally been used for pH reduction. The mineral acids are easier to mix into water. They are often gravity fed, non-refrigerated and contained in a non-pressurized system. However, acids pose many potential safety hazards, maintenance issues and high price volatility. They destroy the alkalinity and offer poor quality control of pH compared to CO2 and hence, are not suitable for use when tight pH control is required or low pH excursion cannot be tolerated. Acids should be used when the pH must be lowered below 6. On the whole, CO2 offers safer and more robust system over acids and can replace them due to following advantages:

<table>
<thead>
<tr>
<th>Safety</th>
<th>CO2</th>
<th>H2SO4</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permit for use</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
<tr>
<td>Availability</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
<tr>
<td>Price Variability</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
<tr>
<td>Ease of Storage</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
<tr>
<td>System Maintenance</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
<tr>
<td>Environment-friendliness</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
<tr>
<td>Process Control</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
<tr>
<td>Effect of Overdosing</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
<tr>
<td>Cost of Implementation</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
<tr>
<td>Limitations for Use</td>
<td>●</td>
<td>○</td>
<td>●</td>
</tr>
</tbody>
</table>
Results:

Re-carbonation at City of Bloomington Water Treatment Plant:
The full schematic of the plant and water quality parameters are given in Figure 4 and Table 2 respectively. The calcium hydroxide slurry for softening process is produced from quick lime (CaO) in a batch slaking system. The lime feed rate for the plant is about 1,100 lb per million gallons of water. The lime is dosed to the water in the clarifiers where it raises the pH of the water and precipitates calcium and magnesium salts out of the water. The coagulated particles, slurry and precipitates flocculate together and settle down in the clarifier. The clarified water has pH between 10.5 to 11.5 and flows into recarbonation basins. The plant has two circular recarbonation basins with 1/2 million gallon capacity each and the CO₂ is added at the head of the basins with bubble diffusers installed at 18' depth (Figure 5). The basins are designed to provide sufficient contact time of 30 min for the stabilizing reactions to occur and also serve as secondary settling basins. The average CO₂ usage for the plant is 330 lb/MG which is close to the theoretical CO₂ requirement. This can be attributed to the high solubility of CO₂ in water that almost all of the gas is dissolved in water resulting in very high gas transfer efficiencies.

Recently, the plant has found incrustation in the piping between the clarifiers and recarbonation basins which has become a major bottleneck for the plant during peak flows. This is due to high pH of clarified water supersaturated with carbonates that precipitate out and deposit in the pipes.

Table 2: Summary of treatment outcomes. Note the reduction in secondary clarifier effluent following Ozonation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Raw Water</th>
<th>Finished Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Hardness</td>
<td>mg/L as CaCO₃</td>
<td>195</td>
<td>120</td>
</tr>
<tr>
<td>Ca Hardness</td>
<td>mg/L as CaCO₃</td>
<td>110</td>
<td>80</td>
</tr>
<tr>
<td>Mg Hardness</td>
<td>mg/L as CaCO₃</td>
<td>85</td>
<td>40</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg/L as CaCO₃</td>
<td>130</td>
<td>55</td>
</tr>
<tr>
<td>Non-carbonate Hardness</td>
<td>mg/L as CaCO₃</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>pH</td>
<td>mg/L as CaCO₃</td>
<td>8</td>
<td>8.8-9.2</td>
</tr>
</tbody>
</table>

Figure 4: Schematic of Water Treatment Plant at City of Bloomington
Summary

CO₂ is an effective and safe chemical that offers treatment flexibility for a utility doing pH control. Praxair, one of the world’s largest suppliers of CO₂, provides everything you need for superior CO₂ water treatment systems including custom design of gas injection and control system, installation services and product supply through its production plants and reliable delivery vehicles. In addition, Praxair’s Water Treatment Sample Program provides complete analysis and technical support to determine how much CO₂ is required to adequately treat water to a desired pH.

leading to reduction in the effective radial area of the piping. So, the plant is upgrading to a presurized sidestream injection system in which CO₂ will be added at the outlet of the clarifier. By reducing the pH, the carbonates will stay suspended in water and also dissolve the scaly deposits from the piping. The alternative of replacing the piping at the plant would have been cost-prohibitive.
A Global Leader

Praxair is one of the largest industrial gas companies in the world, and the largest in North and South America. We operate in more than 30 countries and serve one million customers in a wide variety of industries including: energy, manufacturing, chemicals, metal production, and healthcare. To learn more about Praxair’s gas supply expertise, call us at 1-800-PRAAXAIR or visit our website at www.praxair.com.

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