Case Study:
CO_2 for pH Control Following Lime Softening in Drinking Water Treatment

Background

Hardness is a property of water defined as the concentration of calcium and magnesium ions. Within the United States, the central part of the country has water sources with hardness above 180 mg/L as $CaCO_3$. While there is no health concern nor regulatory standard, hard water is more difficult to use and most water utilities reduce hardness to levels between 50 – 150 mg/l as $CaCO_3$.

Lime softening is employed to reduce hardness by raising the water pH, in order 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 reduce water reduce pH for product quality and to prevent deposition of a hard carbonate scale on the piping and filters.

The City of Bloomington (IL) water purification plant has been operating since 1929. The facility supplies drinking water to 70,000 residents and a major manufacturing customer in the city and the townships of Hudson and Towanda. The current average daily demand is 14 million gallons per day (MGD) with daily max at 18 MGD. The treatment plant uses Lake Bloomington and Lake Evergreen as surface water sources. These water sources are very hard with an average hardness value of 195 mg/l as $CaCO_3$. 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. For hardness reduction, the treatment plant uses a single stage lime softening process to reduce calcium- and magnesium associated hardness in water to below 120 mg/l as $CaCO_3$. The lime-treated water has high pH which can cause scaling and can eventually clog the piping and filters in the plant. Following lime softening, the treatment process adds carbon dioxide to meet product water pH requirements and prevent scaling due to subsequent $CaCO_3$ precipitation.

Linde's Approval

Re-carbonation with CO_2 is commonly used to lower the pH below 9.5 and dissolve the $CaCO_3$ into bicarbonate form. The main reactions for the process are as follows:

Lime Softening

$$Ca(HCO_3)_2 + Ca(OH)_2 \leftrightharpoons 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3)2 + 2Ca(OH)_2 \leftrightharpoons Mg(OH)_2 + CaCO_3 \downarrow + 2H_2O$$

Recarbonation

$$CaCO_3 + CO_2 + H_2O \leftrightharpoons Ca(HCO_3)2$$
$$Mg(OH)_2 + CO_2 \leftrightharpoons MgCO_3 + H_2O$$

The CO_2 system for this process consists of different subsystems: 1) CO_2 supply, 2) flow control, 3) the injection system (1-3) and 4) pH measurement and control. Bulk CO_2 is stored on-site in liquid form (99.5% purity) in an insulated storage tank at the customer's site.

The gaseous CO_2 is vaporized from liquid using an electrically-heated vaporizer and piped to the point of use via a CO_2 flow control panel. On the flow control panel, the process flow-control valve is controlled with feedback from a pH probe controller. From the CO_2 flow-control panel, the CO_2 gas line extends to the dissolution system. Based on the plant configuration, Linde can design a dissolution system, with CO_2 dissolved into water using spargers, diffusers or venturi injectors either in contact basins or in the pipe directly (in-line or sidestream). Linde is a leader in CO_2 supply and has a number of merchant CO_2 source plants in the US and Canada with a fleet of delivery vehicles and can provide assistance in designing complete system for CO_2 use.

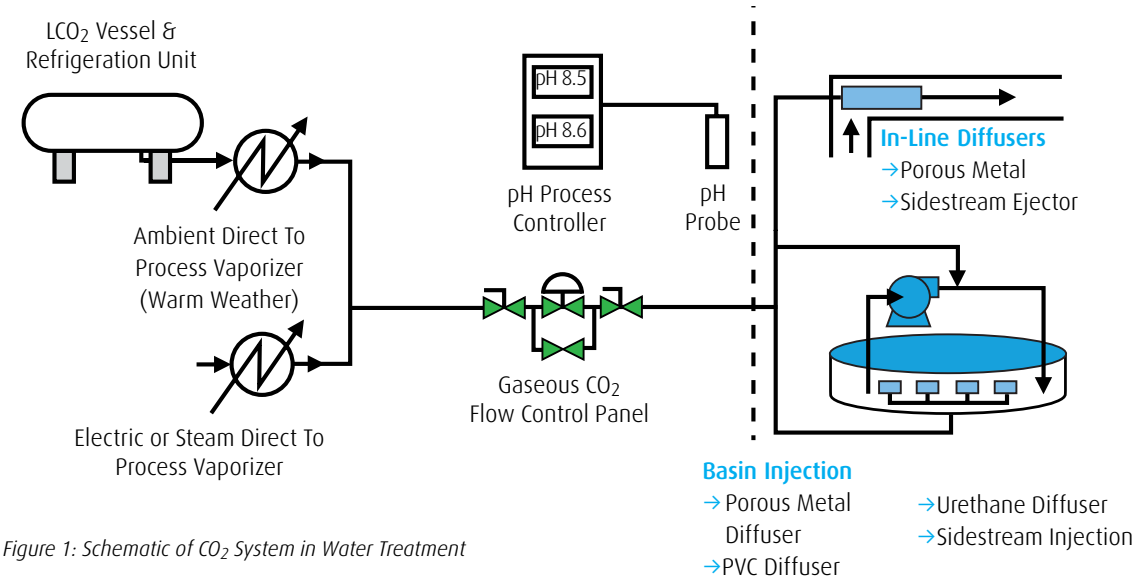

Figure 1: Schematic of CO_2 System in Water Treatment

Competitive Options

Mineral acids like sulfuric or hydrochloric have traditionally been used for pH reduction. The mineral acids are easily mixed into water. They are often gravity fed, non-refrigerated and contained in a non-pressurized system. However, acids pose many safety hazards, maintenance issues and high price volatility. They destroy the alkalinity and can easily overshoot the pH target, so they, are not suitable for use when tight pH control is required or low pH excursion cannot be tolerated. On the whole, CO_2 offers safety and process advantages shown in Table 1:

Figure 2: CO_2 Storage Vessel and Vaporizer.

Figure 3: CO_2 Flow Panel for pH Control.

Table 1: Comparison of chemicals for pH control at water treatment plant

	CO_2	H_2SO_4	HCl
Safety	●	◔	◔
Permit for use	●	◑	◑
Availability	●	●	●
Price Variability	●	◑	◑
Ease of Storage	●	◔	◔
System Maintenance	●	◔	◔
Environment-friendliness	●	◔	◔
Process Control	●	●	●
Effect of Overdosing	●	◔	◔
Cost of Implementation	◕	●	●
Limitations for Use	◑	◕	◕

Table 1: Comparison of chemicals for pH control at water treatment plant

	Units	Raw Water	Finished Water
Total Hardness	mg/L as $CaCO_3$	195	120
Ca Hardness	mg/L as $CaCO_3$	110	80
Mg Hardness	mg/L as $CaCO_3$	85	40
Alkalinity	mg/L as $CaCO_3$	130	55
Non-carbonate Hardness	mg/L as $CaCO_3$	65	65
pH	mg/L as $CaCO_3$	8	8.8-9.2

Plant Design

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) mixed with water. The lime slurry 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 which has pH between 10.5 to 11.5 then flows into recarbonation basins. The plant has two circular recarbonation basins with 1/2 million gallon capacity each. CO_2 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 CO_2 usage for the plant is 330 lb/MG which is close to the theoretical dissolved CO_2 requirement. Based on this observation, it 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 the high The alternative of replacing the piping at the plant would have been cost-prohibitive.

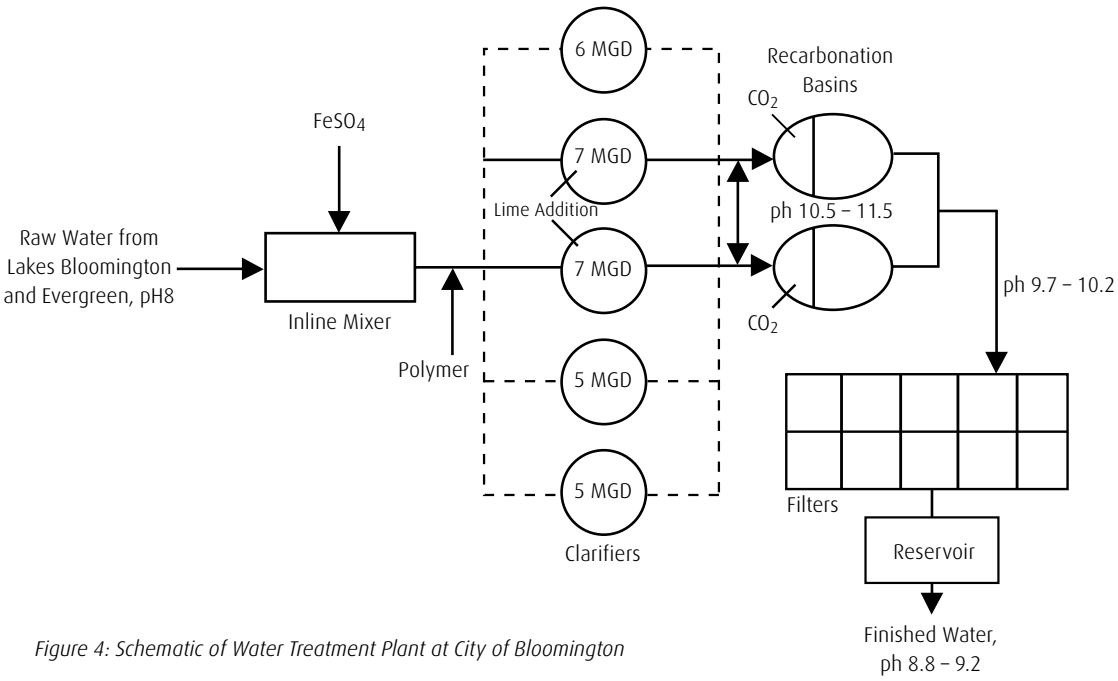

Figure 4: Schematic of Water Treatment Plant at City of Bloomington

Figure 5: Re-carbonation Basins: (a) Influent to Recarbonation Basin and CO_2 Injection, (b) Main Reaction Basin.

Summary

CO_2 is an effective and safe chemical that offers treatment flexibility for a utility doing pH control. Recognized as one of the world's largest suppliers of CO_2, we provide everything you need for superior CO_2 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, Linde's Water Treatment Sample Program provides complete analysis and technical support to determine how much CO_2 is required to adequately treat water to a desired pH.

Linde
10 Riverview Drive
Danbury, CT 06810
Phone 1.844.44LINDE (1.844.445.4633), Fax 1.800.772.9985; 716.879.2040
www.linde.com