The Role of CO_2 in Corrosion Control

Treatment Methods and Equipment

Mike Dirth
Municipal Water Manager

TOMCO2 SYSTEMS

April 17, 2019

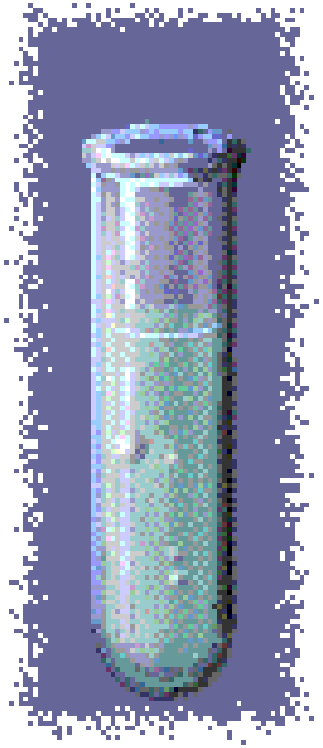
The Role of CO_2 in Corrosion Control
Treatment Methods and Equipment

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_2CO_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

Exhibit 3.1: Typical Chemical Processes for pH/Alkalinity Adjustment

Chemical	Use	Composition	Alkalinity Change	DIC Change	Notes
Baking Soda, $NaHCO_3$, (sodium bicarbonate)	Increases alkalinity with moderate increase in pH.	95% purity. Dry storage with solution feed.	0.60 mg/L as $CaCO_3$ alkalinity per mg/L as $NaHCO_3$	0.14 mg/L as C per mg/L as $NaHCO_3$	Good alkalinity adjustment chemical but expensive.
Carbon Dioxide, CO_2	Lowers pH. Converts hydroxide to bicarbonate and carbonate species.	Pressurized gas storage. Fed either through eduction or directly.	None	0.27 mg/L as C per mg/L as CO_2	Can be used to enhance NaOH or lime feed systems.
Caustic Soda, NaOH (sodium hydroxide) Or KOH (potassium hydroxide)[1]	Raises pH. Converts excess carbon dioxide to carbonate alkalinity species.	93% purity liquid bulk, but generally shipped and stored, at < 50% purity to prevent freezing. KOH has a higher freezing point and may be stored at higher concentrations.	1.55 mg/L as $CaCO_3$ alkalinity per mg/L as NaOH	None	pH control is difficult when applied to poorly buffered water. Is a hazardous chemical, requires safe handling and containment areas
Hydrated Lime, $Ca(OH)_2$ (calcium hydroxide)[2]	Raises pH. Increases alkalinity and calcium content (i.e., hardness).	95 to 98% purity as $Ca(OH)_2$. 74% active ingredient as CaO. Dry storage with slurry feed.	1.21 mg/L as $CaCO_3$ alkalinity per mg/L as $Ca(OH)_2$	None	pH control is difficult when applied to poorly buffered water. Slurry feed can cause excess turbidity. O&M is intensive.
Soda Ash, Na_2CO_3 (sodium carbonate) Or Potash, KCO_3 (potassium carbonate)	Increases alkalinity with moderate increase in pH.	95% purity. Dry storage with solution feed.	0.90 mg/L as $CaCO_3$ alkalinity per mg/L as Na_2HCO_3	0.11 mg/L as C per mg/L as Na_2CO_3	More pH increase caused compared with $NaHCO_3$, but less costly. Has increased buffer capacity over hydroxides.
Sodium Silicates Na_2SiO_3	Moderate increases in alkalinity and pH	Available in liquid form mainly in 1:3.2 or 1:2 ratios of $Na_2O:SiO_2$	Depends on formulation	None	More expensive than other options but easier to handle than lime and other solid feed options. Has additional benefits in sequestering or passivating metals.

Source: Adapted from USEPA, 1992a. Additional detail on characteristics from AwwaRF, 1990, pages 133–143; USEPA, 2003; AWWA, 1999. Schock, 1996.

ONE WATER: Together We Make a Difference

pH, Alkalinity and DIC
-EPA Optimal Corrosion Control Treatment 816-B-16-003

- **pH**
  - Measurement of the Hydrogen Ion Concentration (H^+ or H_3O^+)
  - 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 = $2CO_3^{2-} + HCO_3^- + OH^- - H^+$
- **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= $CO_2 + H_2CO_3 + CO_3^{2-} + HCO_3^-$

ONE WATER: Together We Make a Difference

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 CO_2 increases DIC and lowers pH

ONE WATER: Together We Make a Difference

Control for Lead only or Lead & Copper
-EPA Optimal Corrosion Control Treatment 816-B-16-003

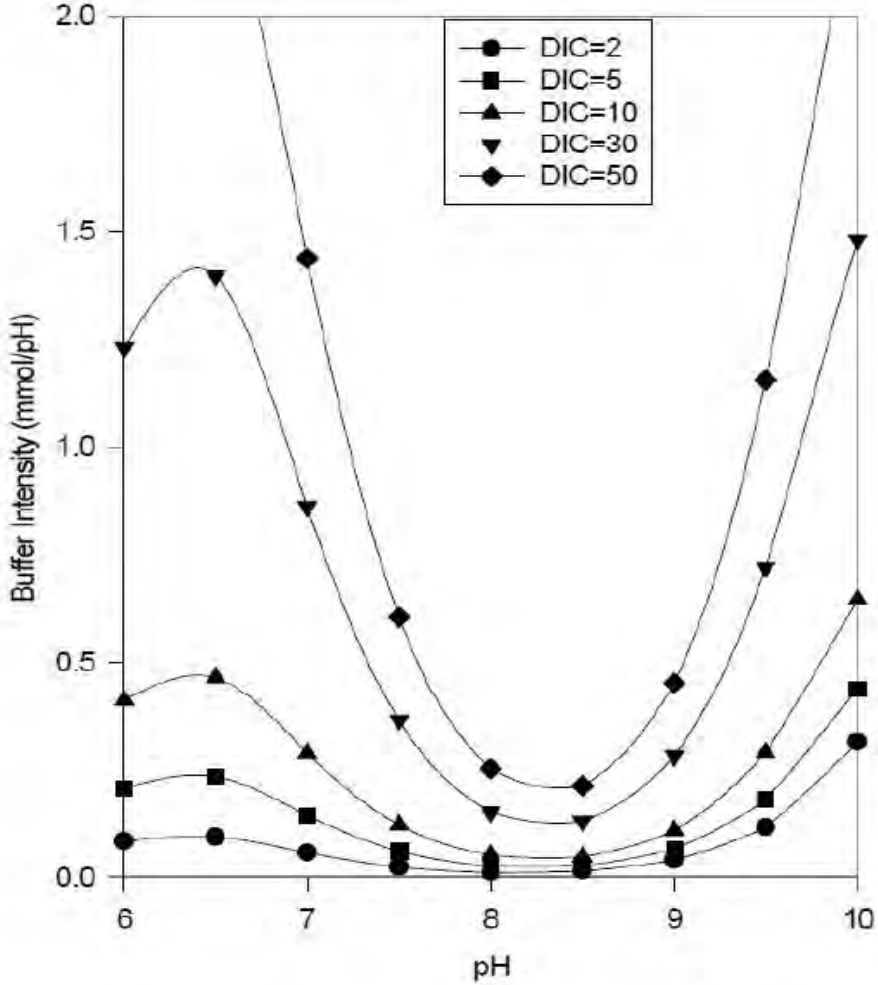
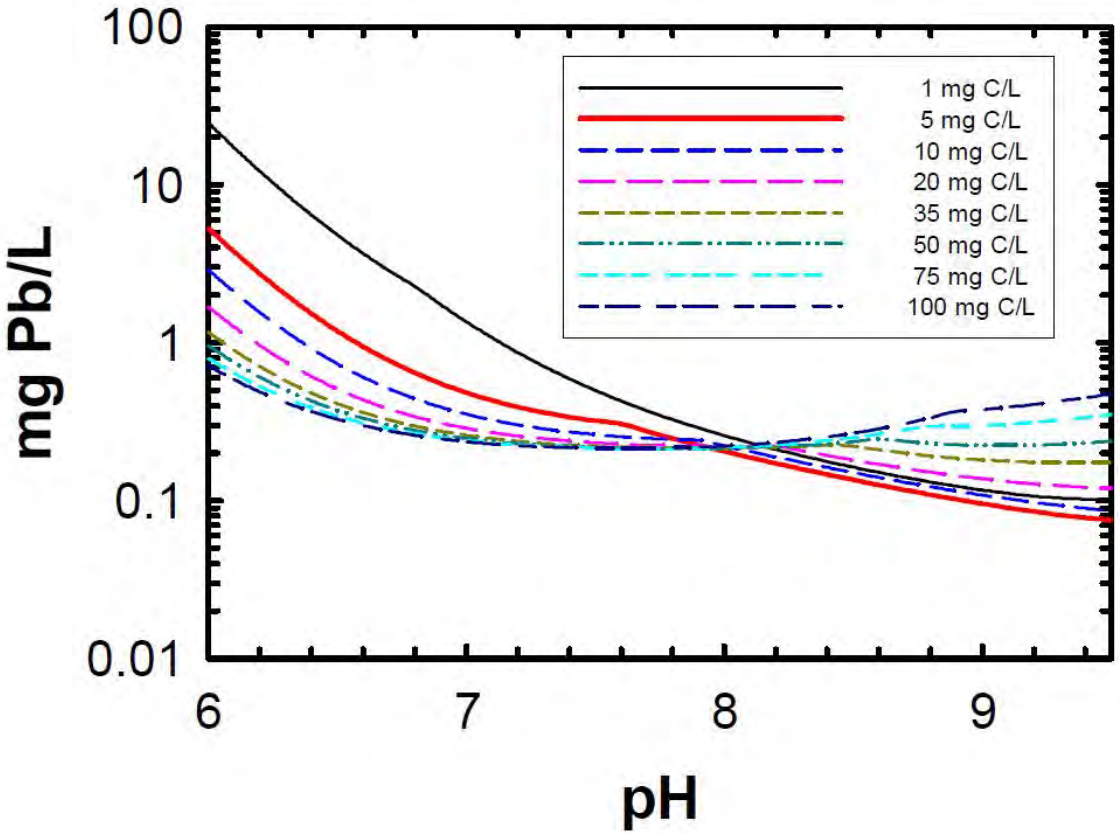


Exhibit 2.3: Buffer Intensity as a Function of pH at Different DIC Values (Clement and Schock, 1998b, Figure 1)

ONE WATER: Together We Make a Difference

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

ONE WATER: Together We Make a Difference

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]

Total Alkalinity	pH																				
	6.4	6.6	6.8	7.0	7.2	7.4	7.6	7.8	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6	9.8	10.0	10.2	10.4
0	0																				
2	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0					
4	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0			
6	3	2	2	2	2	2	2	1	1	1	1	1	1	1	1	1	1	0	0		
8	4	3	3	2	2	2	2	2	2	2	2	2	2	2	2	1	1	1	0		
10	4	4	3	3	3	3	3	2	2	2	2	2	2	2	2	2	2	1	1	0	
12	5	4	4	3	3	3	3	3	3	3	3	3	3	3	2	2	2	2	1	1	
14	6	5	4	4	4	4	4	3	3	3	3	3	3	3	3	3	2	2	1	1	0
16	7	6	5	5	4	4	4	4	4	4	4	4	4	4	3	3	3	2	2	1	0
18	8	7	6	5	5	5	5	4	4	4	4	4	4	4	4	4	3	3	2	2	1
20	9	7	6	6	5	5	5	5	5	5	5	5	5	4	4	4	4	3	3	2	1
22	10	8	7	6	6	6	6	5	5	5	5	5	5	5	5	4	4	4	3	2	1
24	11	9	8	7	7	6	6	6	6	6	6	6	5	5	5	5	4	4	3	2	2
26	11	10	8	8	7	7	7	6	6	6	6	6	6	6	6	5	5	4	4	3	2
28	12	10	9	8	8	7	7	7	7	7	7	7	6	6	6	6	5	5	4	3	2
30	13	11	10	9	8	8	8	7	7	7	7	7	7	7	6	6	6	5	4	3	2
35	15	13	11	10	9	9	9	9	9	8	8	8	8	8	8	7	7	6	5	4	3
40	18	15	13	12	11	10	10	10	10	10	10	9	9	9	9	8	8	7	6	5	4
45	20	16	14	13	12	12	11	11	11	11	11	11	10	10	10	9	9	8	7	6	5
50	22	18	16	14	14	13	13	12	12	12	12	12	12	11	11	10	10	9	8	7	5
55	24	20	18	16	15	14	14	14	13	13	13	13	13	12	12	11	11	10	9	8	6
60	26	22	19	17	16	16	15	15	15	14	14	14	14	14	13	12	12	11	10	8	7
65	29	24	21	19	18	17	15	16	16	16	15	15	15	15	14	14	13	12	10	9	8

OCCT Evaluation Technical Recommendations for Primacy Agencies and Public Water Systems

ONE WATER: Together We Make a Difference

Carbon Dioxide pH Control Equipment

- CO_2 Storage
- Vaporizer
- Vapor Heater
- Pressure Regulator
- CO_2 / H_2CO_3 Feed Panel
- Diffuser

CO_2 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

CO_2 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

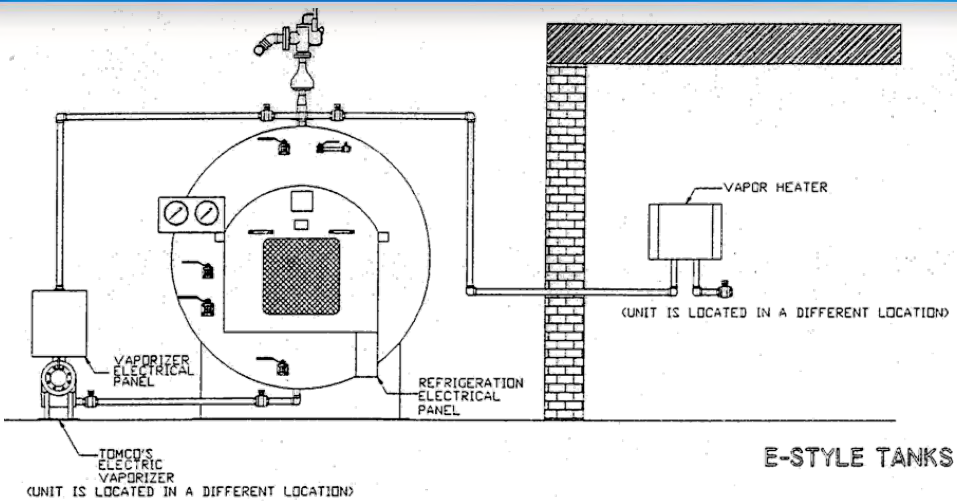
ONE WATER:
Together We Make a Difference

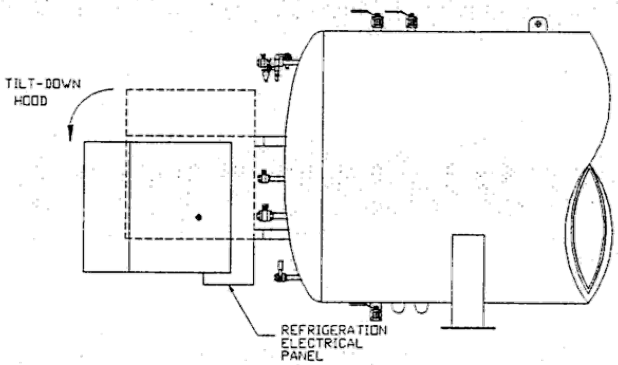
CO_2 Vapor Heaters

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

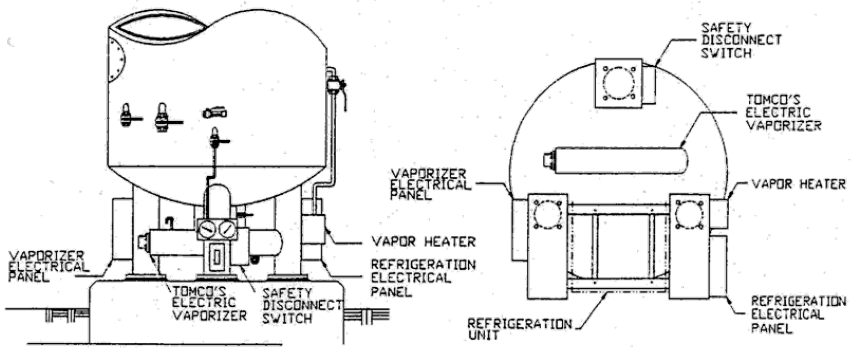
- Steam
  - 500 lb/hr to 6,000 lb/hr

General Tank Layout

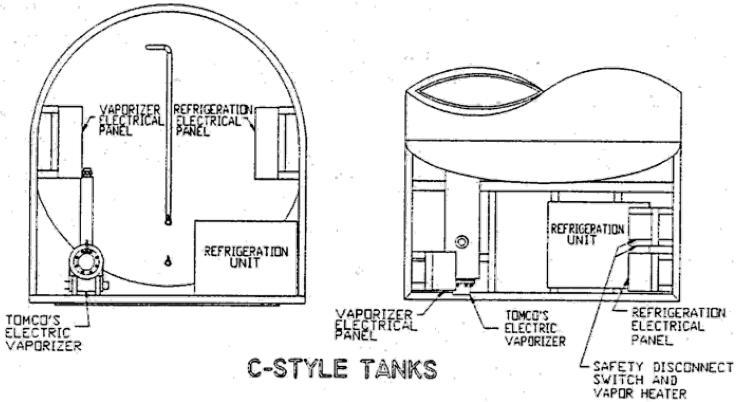




E-STYLE TANKS



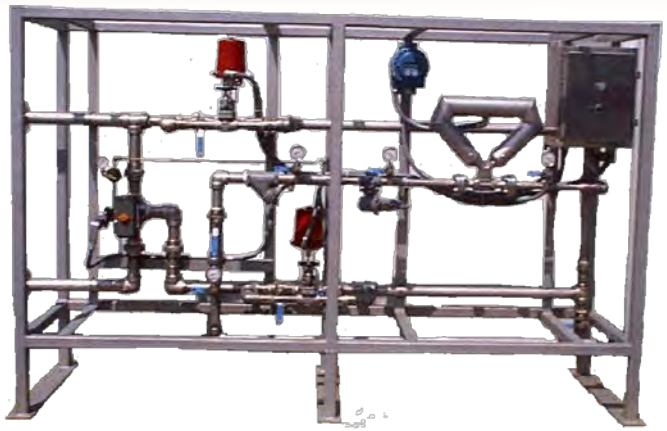
VERTICAL-STYLE TANKS



C-STYLE TANKS

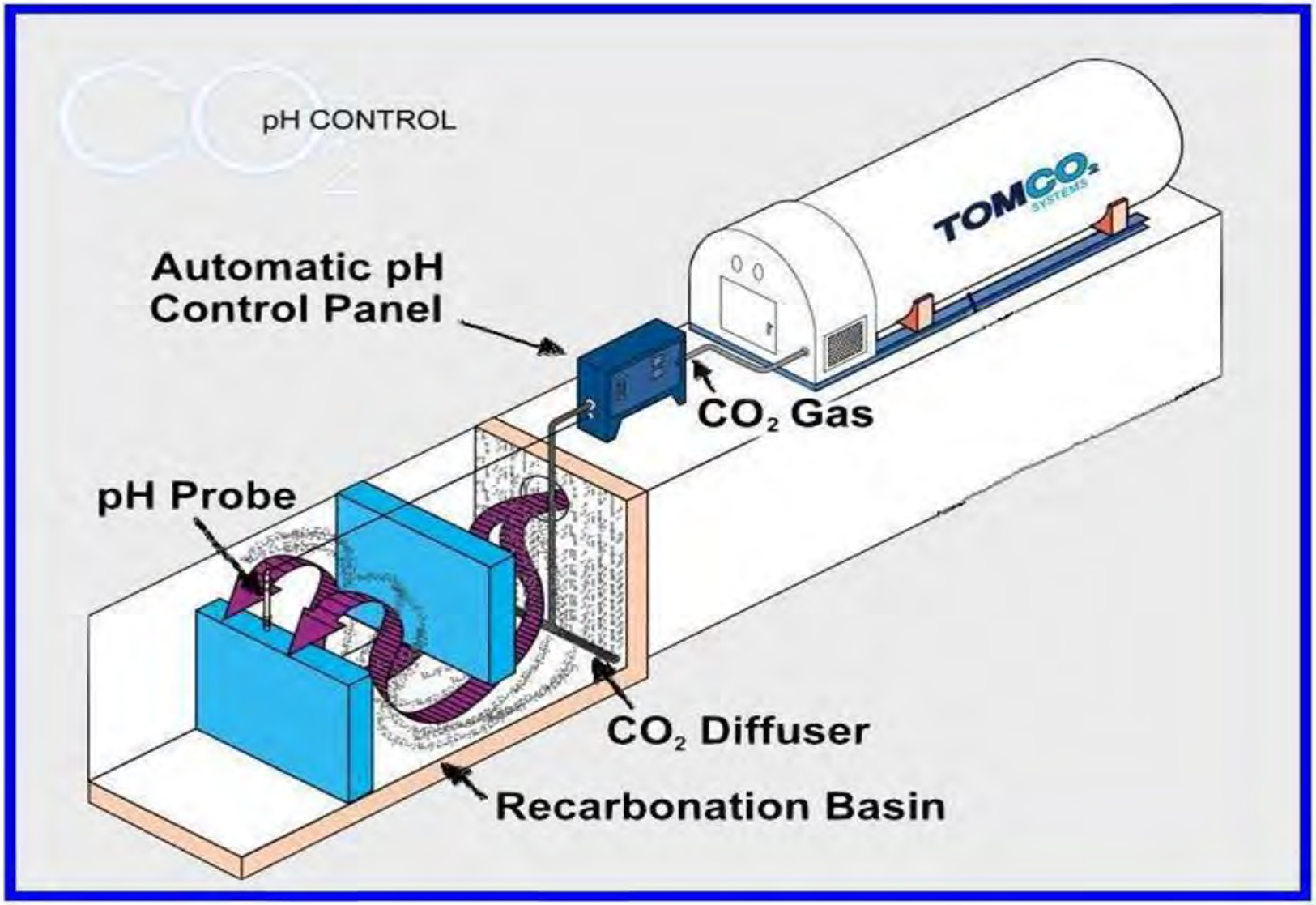
ONE WATER: Together We Make a Difference

Gas Feed Equipment



- CO_2 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.

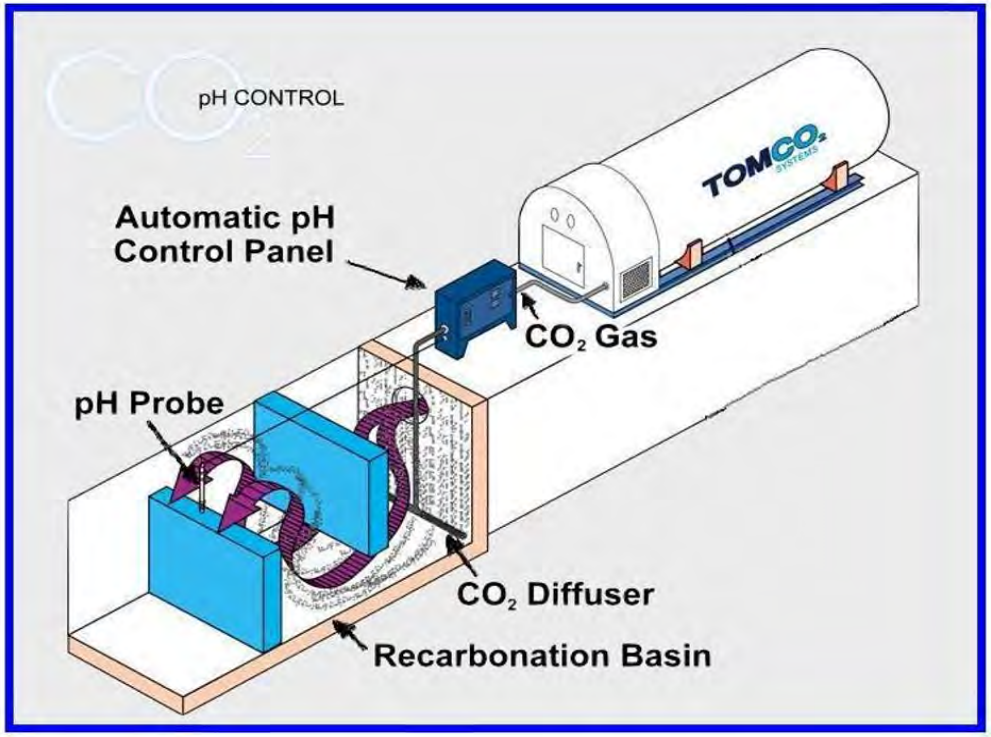
CO_2 Gas Injection



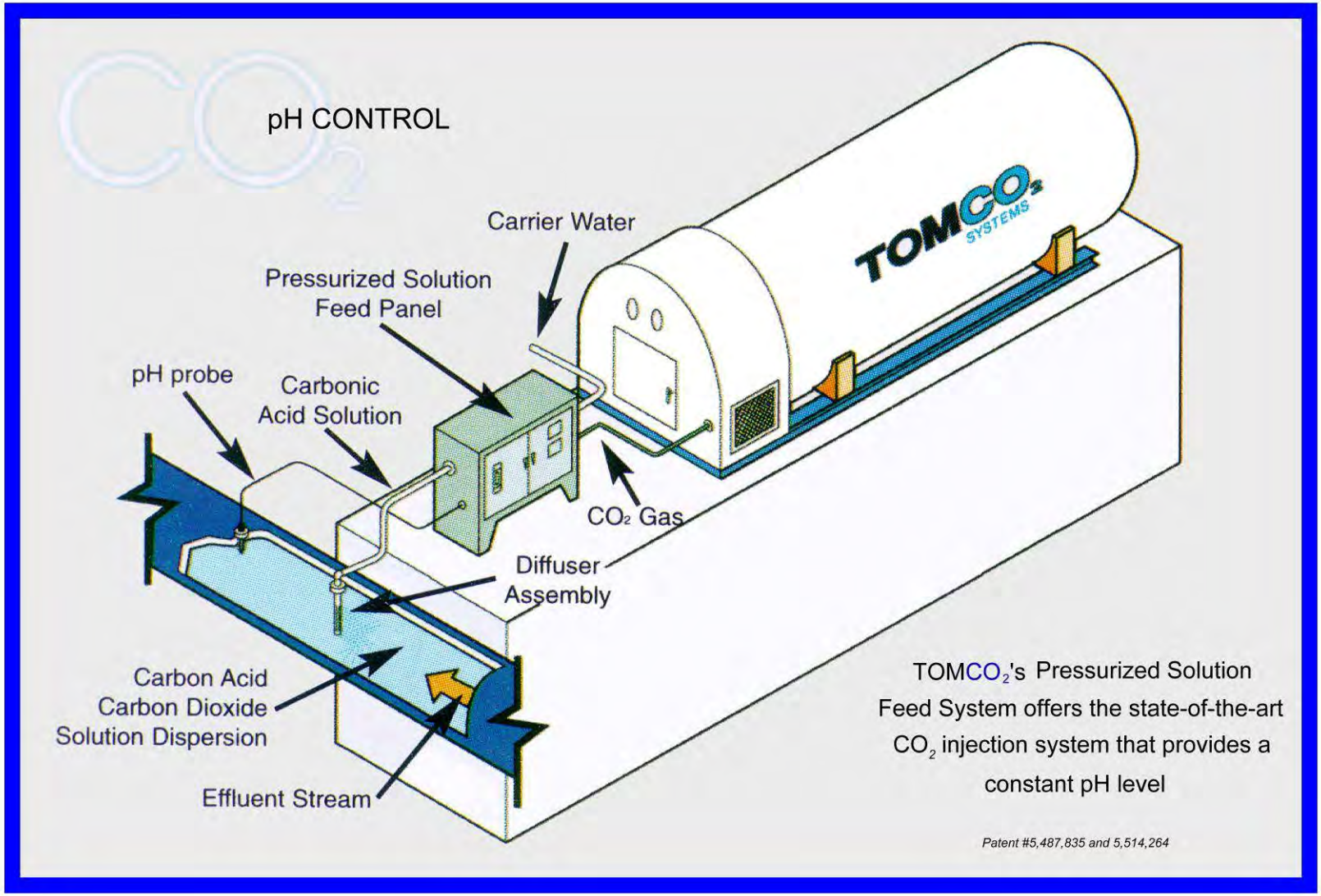
ONE WATER: Together We Make a Difference

CO_2 Gas Injection

- Gas (CO_2) + 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



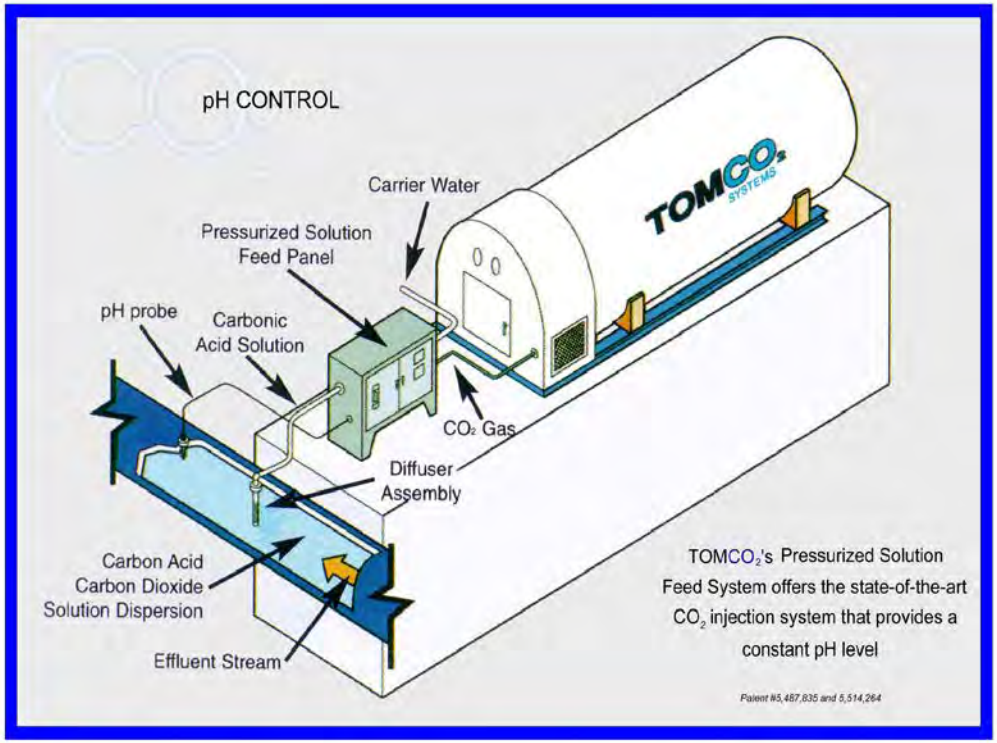
Carbonic Acid Injection (PSF)



ONE WATER: Together We Make a Difference

Carbonic Acid Injection (PSF)

- CO_2 pre-reacted to form Carbonic Acid
- Liquid / Liquid (Carbonic Acid / Water) Reaction
- Immediate reaction (Requires less time)
- Close to 100% efficiency
- Higher pressure improves CO_2 solubility
- More effective pH control
- Faster reaction time reduces scale potential.



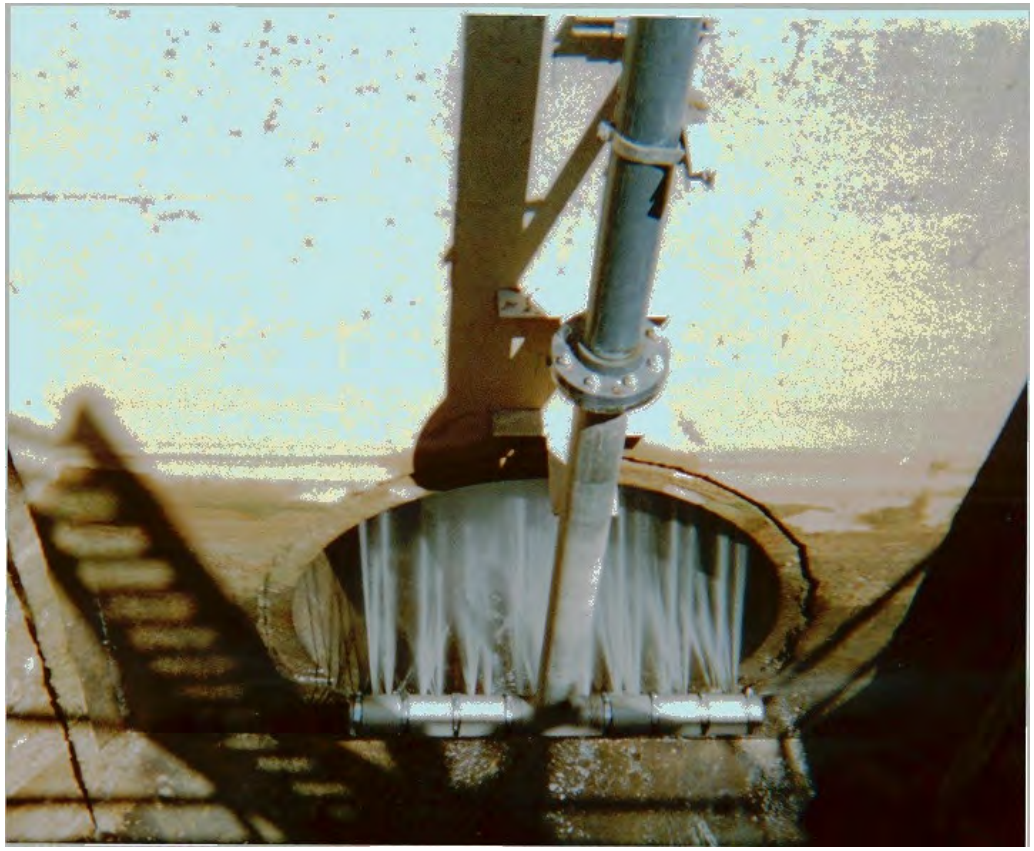
CO_2 Diffusers

- Gas Feed
  - Uses fine porous diffuser to disperse the CO_2 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

ONE WATER: Together We Make a Difference

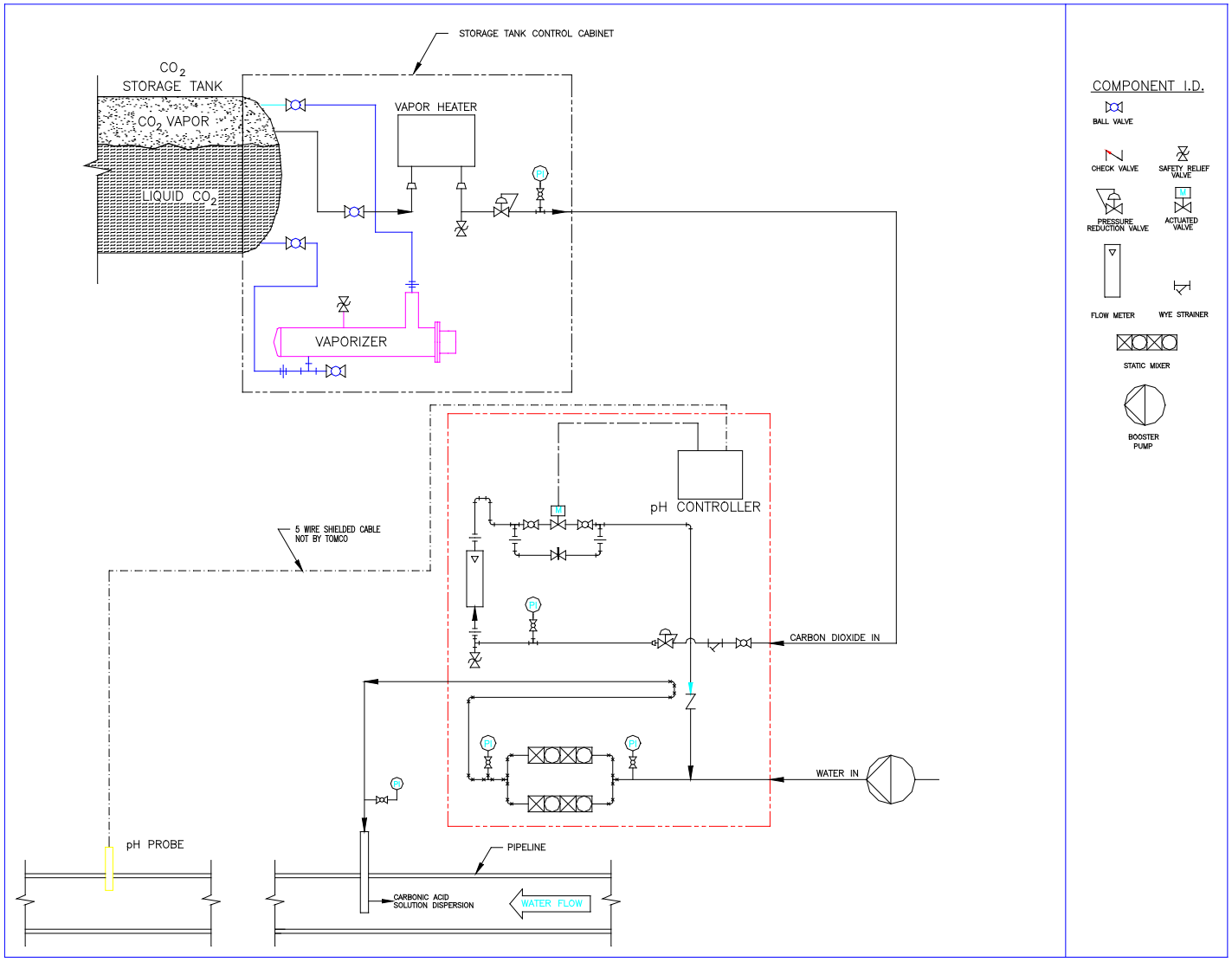
Carbonic Acid Diffuser Patent # 6637731 & 6767008

- Counter Current
- Cross Sectional Coverage
- Pressure
- Efficient Mixing
- Immediate Reaction



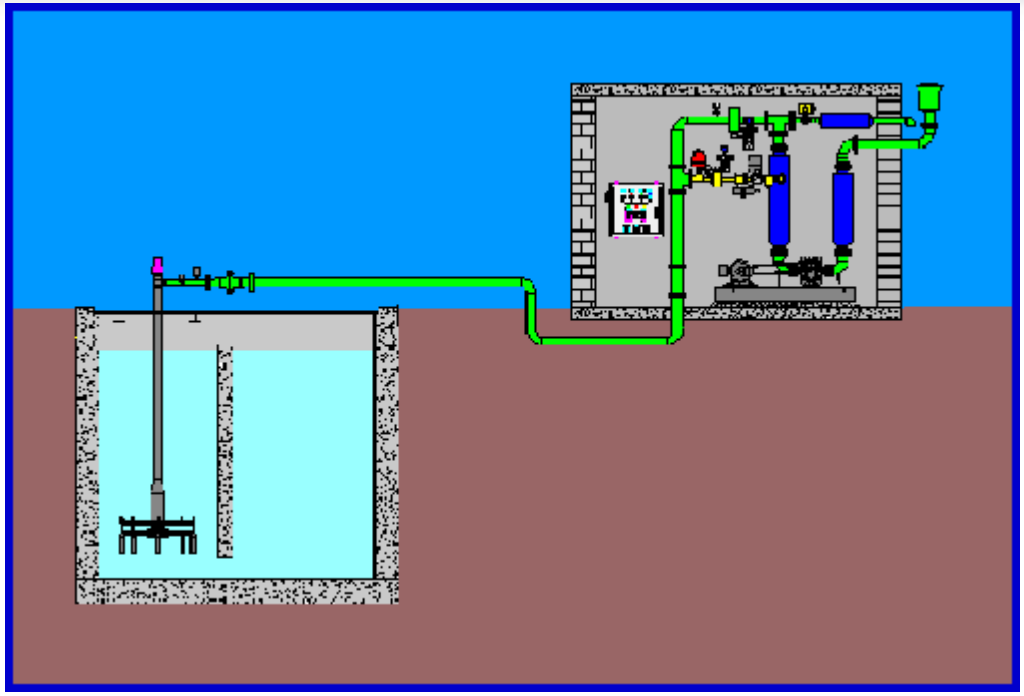
ONE WATER: Together We Make a Difference

Typical Flow Schematic



ONE WATER: Together We Make a Difference

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.

ONE WATER: Together We Make a Difference

Areas to Use CO_2

- Municipal Water Plants
  - Lime Softening
  - Enhanced Coagulation
  - Stripping – H_2S
  - 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

ONE WATER: Together We Make a Difference

Other pH Control Methods

- Liquid CO_2 Feed Systems
- Gas Eductor / Vacuum Feeder
- Chlorinator / Solution Feeder
- Carbonated Water Feeder
- Mineral Acids

Manufacturer's Qualifications

- Experience in CO_2 and Water Treatment Systems
- Over 1,500 systems installed
- Active member of CGA
- Engineering Capability
- Optimized pH control and CO_2 utilization
- Total System Responsibility
- ASME Pressure Vessel shop
- Service Capability
- Made in the USA- Loganville, GA

ONE WATER: Together We Make a Difference

The Role of CO_2 in Corrosion Control

Michael Dirth
Municipal Water Manager
TOMCO$_2$ Systems
Loganville, Georgia
mdirth@tomcosystems.com