ION EXCHANGE

USING MEMBRANE CONTACTORS FOR CO_2 REMOVAL TO EXTEND RESIN BED LIFE

In today's economic environment when profits are reduced due to rising costs, it is necessary to find ways to save time and money. City Public Service, San Antonio, Texas, had a need to be more cost effective with their water system. The utility had an older system that could not be completely upgraded. Budget constraints prevented a complete system replacement; therefore, efforts were focused on improving operating efficiency of the existing system.

After a water analysis was performed (see Table A), it was determined that a high amount of bicarbonate alkalinity present in the water was having a negative effect on the anion bed life. They investigated ways to remove this high amount of alkalinity from the system. After evaluating all of the options, City Public Service made the decision to put in a membrane degassing system between the cation and anion beds to remove the free carbon dioxide (CO_2).

Ion Exchange Fundamentals

The process of ion exchange (IX) removes positive and negative ions from water and replaces them with a selected positively or negatively charged ion. As water moves through a cation bed, the cation-exchange resin will attract positively charged ions (e.g., calcium [Ca^{++}] or magnesium [Mg^{++}]) to negatively charged sites on the resin. The positive ion then bonds to the resin, and the hydrogen (H^+) ion that was there is released to the water. The cation-exchange process lowers water pH with the release of the H^+ ions into the water stream.

Water entering an anion bed passes over positively charged anion-exchange resin, attracting negative ions (e.g., nitrate [NO_3^-] or bicarbonates [HCO_3^-]). At this stage, the anion-exchange resin releases hydroxyl radicals (OH^-). The addition of OH^- groups increases the water pH level to approximately neutral (pH = 7).

Ion-exchange resins have limited capacity for ion storage known as resin capacity. When resin capacity has been reached, the resin is exhausted. Carbon dioxide is weakly charged and will not be attracted to the resin bead. The CO_2 molecule, however, can combine with a hydroxide ion to form bicarbonate. A regenerated bead is loaded with hydroxide ions and with the presence of CO_2, the resin bead will be quickly exhausted (Figure 1). The exhausted resin must be removed from service, washed, and regenerated.

Regeneration of a cation bed requires acid (hydrochloric or sulfuric) to be pumped through the resin bed. The acid supplies the necessary H^+ ions that attach to the negative site of the resin. The resin will release bonded ions from the water due to the high concentration of H^+ ions available. For anion bed regeneration, caustic (sodium hydroxide) is used to supply OH^- ions. The high concentration of OH^- ions will cause the resin to release negatively charge ions and bond the OH^- ions.

Once the wash and regeneration steps are completed, the IX bed can be put back into service. A high amount of ions in the water will put unnecessary load on the exchange resin and cause washing and regeneration to be performed more often.

Bicarbonate alkalinity exists naturally in most water sources with a pH range of 6.5 to 8.0. Carbonate alkalinity can exist if the pH is in the range from 8.3 or above. In water, HCO_3^- ions and carbonate ions (CO_3^{-2}) are in equilibrium with dissolved CO_2 and carbonic acid (H_2CO_3), as represented in Equation 1. *Editor's note: The article equations appear together in an Equations Table placed within the article.*

As carbon dioxide dissolves into water, H_2CO_3 is produced. This is a weak acid that dissociates to produce hydrogen ions and bicarbonate ions. In waters with low pH (high [H^+]), the reaction would not produce more hydrogen ions, which therefore allows the CO_2 to dissolve in the water and be free CO_2.

At pH levels below 4.5, the equilibrium is shifted such that virtually all of the CO_2 dissolved in the water is present as free CO_2 gas. It is at this point where mechanical deaeration is highly effective at removing a large percentage of the total free CO_2 dissolved in the water. If free CO_2 is not removed at this point, it will convert back into bicarbonate ions as the pH increases.

City Public Service Process

It was calculated that City Public Service had about 180 parts per million (ppm) of free CO_2 in the water after the
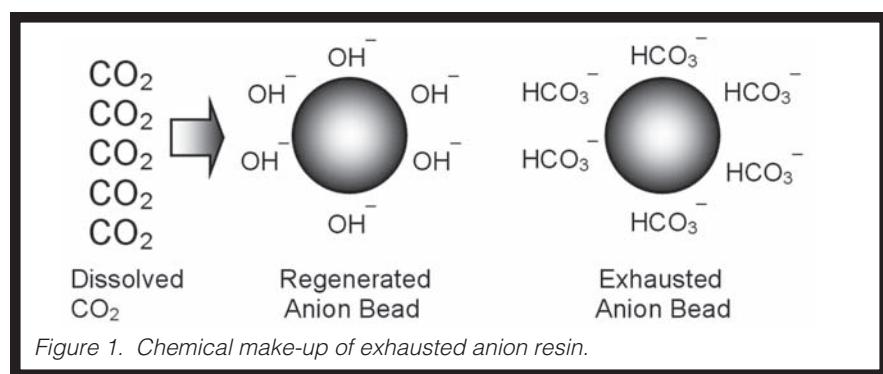
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Figure 1. Chemical make-up of exhausted anion resin.

EQUATIONS

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow H^+ + CO_3^{-2}$$ Eq. 1
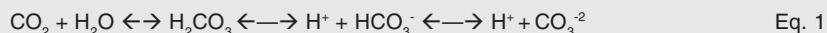
$$[CO_2\ free_{ppm}]_{pH7.8} = \frac{[Bicarbonate\ Alkalinity]\ (mg/L\ as\ CaCO_3)}{X\ value\ from\ Graph}$$ Eq. 2

$$[Alkalinity]_{as\ ppm} = \frac{([Alkalinity]\ as\ CaCO_3 * M.W.\ HCO_3)\ X\ 2}{M.W.\ CaCO_3}$$ Eq. 3

$$[Alkalinity]_{as\ mol/L} = [Alkalinity]_{as\ ppm} \frac{X\ mol}{MW_{HCO3}} \frac{X\ grams}{1{,}000\ mg}$$ Eq. 4

$$[CO_2]_{as\ mol/L} = [CO_2\ free]_{pH\ 7.8}\ (as\ mg/L) \frac{X\ mol}{M.W._{HCO2}} \frac{X\ grams}{1{,}000\ mg}$$ Eq. 5

$$[CO_2]_{combined} = [Alkalinity]_{as\ mol/L} + [CO_2]_{as\ mol/L}$$ Eq. 6

$$[CO_2]_{combined\ ppm} = [CO_2]_{combined} \frac{X\ 44\ gr}{mol} \frac{X\ 1{,}000\ mg}{gr}$$ Eq. 7

cation bed. This concentration of CO_2 was the majority of the load on the anion exchange resin. As shown in Table B, by removing only 70% of free CO_2, the anion-exchange resin load could be reduced by more than half. By removing the CO_2, the system was able to operate for longer periods of time before regeneration was needed (Table C).

Calculating Free CO_2
Given a water analysis, the amount of free CO_2 can be calculated very simply. There are only two variables necessary to calculate free CO_2: pH and bicarbonate alkalinity. Bicarbonate is generally expressed as milligrams per liter (mg/L) as calcium carbonate ($CaCO_3$). To estimate the amount of free CO_2 in the water, the graph shown in Figure 2 is commonly used in the water industry.

The inlet water pH is shown on the y-axis of the graph. Follow this value horizontally to the right until it intersects the bold diagonal line. At the intersection point, move down the chart to the x-axis and record this number. To determine the free CO_2 value, use Equation 2.

All numbers need to be converted into like units. Conversion to mole volume is simple. The following steps shown in Equations 3 through 5 outline this conversion.

1. In Equation 3, convert from $CaCO_3$ equivalent to ppm of bicarbonates.

2. In Equation 4, convert bicarbonate ppm to moles per liter (L). This is the amount of bicarbonate moles found in a liter of water.

3. To determine the mole volume of CO_2, convert the weight of CO_2 to mole/L as seen in Equation 5.

Carbon dioxide removal will occur between the cation and anion beds at City Public Service where the pH = 2.8. As discussed earlier, since the pH is less than 4.5, we can assume that all of the CO_2 will be in the free gas form. Equations 6 and 7 can be used to combine the bicarbonate CO_2 and the free

CO_2 to calculate the total free CO_2.
At the pH of 2.8, it was calculated that the free CO_2 level was around 180 ppm.

Carbon Dioxide Removal Technology
Currently there are three methods commercially used to remove free CO_2 from the process water. Those include membrane degasifiers, forced draft degasifiers, and vacuum degasifiers.

Forced draft degasifiers consist of a tower filled with packing material, a clearwell water reservoir, a blower and a pump to circulate water from the clearwell to downstream equipment. Water enters the top of the tower and is sprayed over the packing material. As the water runs over the packing material, air is forced up counter currently through the packing and water. Air has a low CO_2 partial pressure and CO_2 will leave the water and be swept away in the air stream. Forced draft towers are generally low in capital costs, but have large footprints, height requirements, require a second pump for repressurization and usually demand greater attention during times of system start-up and flow adjustment.

Similarly, vacuum degasifiers use a packing-filled tower design, have a clearwell and a large vacuum pump (29 to 29.5 inches [in] high). Water is sprayed from the top over the packing material. A deep vacuum is drawn inside the tower lowering the partial pressure. As the water runs over the packing material, the CO_2 in the water escapes solution and is drawn to the vacuum. Vacuum degasifiers are custom designed for each application and typically range from 20 to 60 feet (ft) in height. They will remove a large percentage of all dissolved gases in the water, but have higher capital costs, are quite large and also require an additional pump for re-pressurization.

Membrane degasifiers are constructed very differently than the other two options. The membrane contactors contain thousands of microporous polypropylene hollow fibers, which are knitted into an array that is wound around a distribution tube with a central baffle. Because the hollow fiber membrane is hydrophobic, the liquid stream will not penetrate the pores. The gas/liquid interface is immobilized at the pore by applying a higher pressure to the liquid stream relative to the gas stream.

In operation, liquid flows on the outside of the hollow fibers. The patented baffled design of the contactor forces

TABLE B
Total Load and Projected Load after CO_2 Removal

Ion Exchange Load:	Actual					Predicted	
Cations	As Ion (ppm)	As $CaCO_3$ (ppm)	Anions	As Ion (ppm)	As $CaCO_3$ (ppm)	As Ion (ppm)	As $CaCO_3$ (ppm)
Calcium	77.28	193.2	Chloride	15.6	22.0	15.6	22.0
Magnesium	15.32	63.1	Sulfate	26.5	27.6	26.5	27.6
Sodium	8.8	19.2	Silica	13.0	10.8	13.0	10.8
			Carbon dioxide	184.0	209.8	55.2	62.9
Total cations		275.5	Total anions		270.1		123.2
gr/gal		16.1	gr/gal		15.8		7.2

gr/gal = grains per gallon

TABLE C
Effect of CO_2 removal on Ion Exchange Bed Life before Regeneration

Cation		Anion	
Before CO_2 Removal	After CO_2 Removal	Before CO_2 Removal	After CO_2 Removal
	No change in run time	114,000 gal	230,000 gal

TABLE D
Estimated Costs without CO_2 Removal in Place

Cation			Anion		
Average Run (gal)	210,000	$225.89	Average Run (gal)	114,000	-
H_2SO_4 regen. level (lb/ft³)	10.00		NaOH regen. level (lb/ft³)	4.00	
Capacity (Kgr/ft³)	7.90		Capacity (Kgr/ft³)	7.90	
Regen. water (gal)	16,500	$17.75	Regen. water (gal)	20,000	$29.74
Volume of IR 120 (ft³)	168.00		Volume of ASB-1P (ft³)	228.00	
H_2SO_4 needed (lb)	1,806	$68.65	NaOH needed (lb)	1,824	$178.39
Total		$312.29	Total		$208.13
Cost/thousand cation		$1.4871	Cost/thousand anion		$1.8257
		Combined cost/1,000 gal $3.3128			

Kgr/ft³ = kilograins per cubic feet   lb/ft³ = pounds per cubic feet   regen. = regeneration

TABLE E
Predictions of Cost Summary with CO_2 Removal

Cation			Anion		
Average run (gal)	210,000	$225.89	Average run (gal)	229,822	-
H_2SO_4 regen. level (lb/ft³)	10.00		NaOH regen. level (lb/ft³)	4.00	
Capacity (Kgr/ft³)	7.90		Capacity (Kgr/ft³)	7.90	
Regen. water (gal)	16,500	$17.75	Regen. water (gal)	20,000	$29.74
Volume of IR 120 (ft³)	168.00		Volume of ASB-1P (ft³)	228.00	
H_2SO_4 needed (lb)	1,806	$68.65	NaOH needed (lb)	1,824	$178.39
Total		$312.29	Total		$208.13
Cost/thousand cation		$1.4871	Cost/thousand anion		$0.9056
		Combined cost/1,000 gal $2.3927			

Notes: 93% H_2SO_4 : $0.0380/lb   50% NaOH: $0.0978/lb   City water: $1.0757/1,000 gal
Notes: The supplier predicts an average removal of 83.86% City Public Service chose to use 70% removal for cost analysis

the liquid radially across the hollow fiber array. A strip gas, vacuum or combination of the two flows counter currently inside of the hollow fiber and creates a driving force for the gasses to pass from the liquid phase to the gas phase. The absence of CO_2 in the gas phase creates a partial pressure differential and allows gasses to transfer from the liquid side of the membrane to the gas side.

Membranes are inherently modular and can be placed in parallel to meet flow requirements and/or series to meet outlet removal specifications. They are installed inline and do not need an additional recirculation pump.
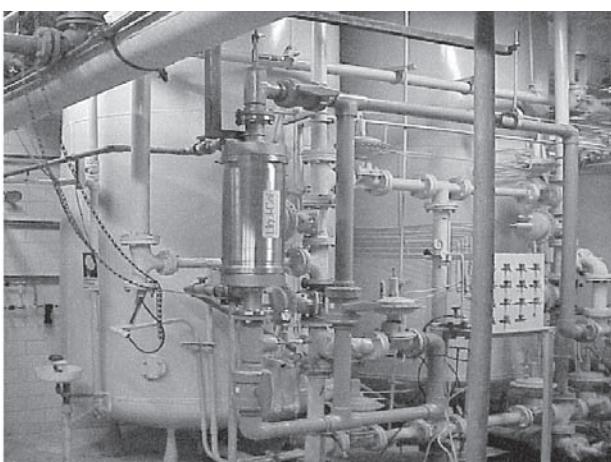
Figure 3. A membrane contactor system and the cation and anion beds.

Figure 2. Approximate relationship between bicarbonate alkalinity, pH and CO_2.

Why Membrane Contactors?

A complete cost analysis was generated (see Tables D and E) to estimate the projected savings and support implementation of this improvement. City Public Service determined that the membrane degassing technology was a good option to quickly and cost effectively meet their needs and fit in the small space available in the plant. One 10 x 28-in membrane contactor was installed to do the job.

The water plant was constructed many years ago and there was not much extra room to install new equipment. The modular design of the membrane contactors made it very simple to add to the existing plant system with minimal space requirements. A small frame was constructed to support the module, a slight piping change was completed and the degas system was ready within a matter of 3 months to go online and improve the performance of the water system.

It is also now safer for the employees of City Public works because they are handling less chemicals than would be required for IX regeneration.

The System Design

The City Public Service planned to use the people already employed at the facility to design and install this simple system. They received training from the supplier[a].

The overall system includes a cation bed that feeds one 10 x 28-in membrane contactor. Instrument air, already available in the plant, provides the air sweep to the contactors. This air sweep, as described earlier, lowers the partial pressure of the CO_2 gas on the inside of the membrane. Because there is less CO_2 in the air sweep than in the liquid stream, a partial pressure gradient is created. The gas phase wants to reach equilibrium with the liquid phase; this promotes the CO_2 gas to move freely from the liquid phase to the gas phase. The degassed effluent liquid from the contactor then feeds the anion bed. Figure 3 shows a the installed degassing membrane.

Results

The system has been in operation since November of 2001. It was cost justified based on a 70% CO_2 removal rate. The system is actually performing with an 84% removal rate and has exceeded expectations.
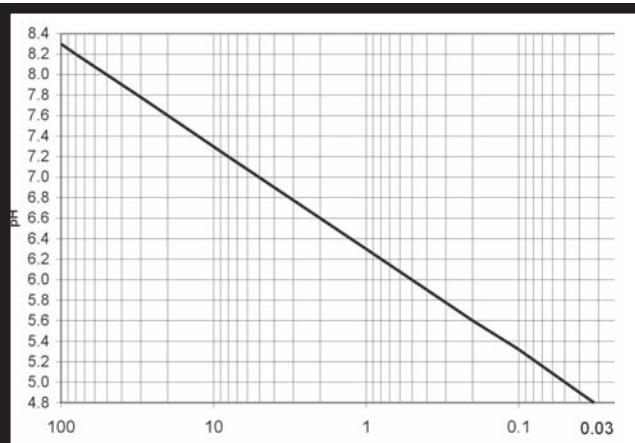
The average run on the anion bed has been increased to 280,000 gallons (gal) from 140,000 gal. The savings in operating costs came in higher than the estimated cost saving projections of $10,822. This can be contributed to the use of the conservative removal percentage of 70%. The actual savings is currently $14,000/year and the payback on capital used for putting the system in place is less than 3 years. That savings is based on yearly water use of 12 million gal. The water cost before decarbonation was $39,750 and the water cost after installation of membrane decarbonation was $25,750.■

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Endnote

[a]The Liqui-Cel®Membrane Contactor came from Membrana, which also provided technical support.

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