

Re:	Evaluation of CO <sub>2</sub> use for pH adjustment prior to WBA treatment
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То:	City of Glendale Water and Power
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Pilot study results indicated that Cr(VI) removal through the WBA exchange resins is optimal, in terms of capacity and minimizing Cr(VI) concentrations in the effluent, at a pH of 6. Currently, the planned method of pH adjustment is the addition of a strong acid (hydrochloric, or HCl). However, the feasibility of using pressurized CO<sub>2</sub> was considered in this analysis to determine if CO<sub>2</sub> is another possible option. In particular, factors evaluated included the amount of CO<sub>2</sub> required to achieve the target pH adjustment, operational issues associated with the use of pressurized CO<sub>2</sub>, and the cost-effectiveness of CO<sub>2</sub> compared to HCl.

Based on the alkalinity and pH of the water from the GS-3 Well (Table 1), 300 mg/L  $CO_2$  would be required to reduce the pH from 6.8 to 6.0. Discussions with the vendor TOMCO2 revealed that they have successfully applied  $CO_2$  injection systems to plants with equivalent or higher starting alkalinity than Glendale and achieved pH values below 5.0. Therefore, the use of  $CO_2$  to achieve the pH adjustment at the Glendale demonstration plant would not be expected to present any unforeseen difficulties in terms of achieving the target pH.<sup>1</sup>

addition					
	pН	Alkalinity (mg/L as CaCO <sub>3</sub> )	$C_{T}(M)$	pCO <sub>2</sub> (atm) <sup>*</sup>	Pressure required to keep CO <sub>2</sub> in solution (psi)
GS-3 Well	6.8	194	2.55e-3	10-1.75	NA
WBA influent after pH adjustment with a strong acid	6.0	$85^\dagger$	2.55e-3	10 <sup>-1.31</sup>	NA
WBA influent after pH adjustment via carbonation	6.0	194	9.37e-3 <sup>‡</sup>	10 <sup>-0.74</sup>	NA
City of Fontana, ARA WBA	4.0	NA	1.51e-3	10 <sup>-236</sup>	10 - 20

 Table 1. Water Quality before and after pH adjustment with a strong acid or CO2

 addition

NA - Not available

Process

<sup>\*</sup> Based on the Henry's Law constant,  $K_{\rm H} = 10^{-1.46} (\text{M-atm}^{-1})$ 

<sup>†</sup> Alkalinity will decrease due to the addition of a strong acid

<sup>‡</sup> Based on the total carbonate ( $C_T$ ) concentration in the water prior to  $CO_2$  addition and the amount of  $CO_2$  required to reduce the pH from 6.8 to 6.0 calculated via RTW modeling

<sup>&</sup>lt;sup>1</sup> Communication with Mike Dirth of TOMCO2.

Other issues associated with  $CO_2$  addition include the potential for calcium carbonate scaling in the air stripper downstream of the ion exchange process due to increased total carbonate and the potential for formation of gas pockets of excess  $CO_2$  within the ion exchange resin bed. The increase in total carbonate concentrations from the use of  $CO_2$ for pH adjustment will increase the likelihood of calcite scaling in downstream treatment processes (e.g., the aeration tower). However, if the pH in the air stripper influent remains low and/or a phosphate sequestrant continues to be used, calcium carbonate scaling is not expected to be a concern even with the higher total carbonate concentration from  $CO_2$  addition.

Depending on the pressure maintained in the ion exchange column, dissolved  $CO_2$  could come out of solution, forming gas bubbles within the ion exchange media. Gas formation in the ion exchange column would decrease process efficiency due to reduced effective surface area for ion exchange and the potential for short circuiting. The typical partial pressure of  $CO_2$  in the atmosphere is  $10^{-3.5}$  atm. The greater partial pressure of  $CO_2$  under all conditions listed in Table 1 indicates that  $CO_2$  would be released to the atmosphere if the water was not under pressure. However, based on communication with Applied Research Associates (ARA) and Siemens,  $CO_2$  dissolution into the gas phase within the resin bed will not be a concern if the pressure at the influent to the ion exchange column is between 15 and 20 psi. However, any loss of pressure during a power outage or other process upset could release dissolved  $CO_2$  as bubbles, which might complicate any resumption of operation.

## Cost Assessment: HCl vs. CO<sub>2</sub>

Capital costs for  $CO_2$  injection are high at \$165,000.<sup>2</sup> This  $CO_2$  injection system estimate is more than three times the cost estimate for the HCl feed system (\$48,280).<sup>3</sup>

An initial cost estimate indicates that the total annual O&M cost for HCl is slightly higher than for CO<sub>2</sub>. Although the annual material cost is lower for CO<sub>2</sub>, the power costs associated with the CO<sub>2</sub> injection system are an order of magnitude higher than the power costs associated with HCl addition. Additionally, since the pH needs to be adjusted to below the carbonic acid-bicarbonate pKa (where buffering is high<sup>4</sup>), a significant amount of dissolved CO<sub>2</sub> is required to achieve the target pH.

<sup>&</sup>lt;sup>2</sup> Cost estimate provided by TOMCO2 for a 425 gpm system and pH adjustment from 6.8 to 6.0. The cost includes a 14-ton storage tank. TOMCO2 recommends a larger storage tank (26 tons) for a more permanent system, with an associated cost increase of \$30,000.

<sup>&</sup>lt;sup>3</sup> McGuire Malcolm Pirnie Opinion of Probable Cost, September 2007.

<sup>&</sup>lt;sup>4</sup> The addition of CO<sub>2</sub> also increases the buffering capacity.

Table 2. Annual O&M Cost for Addition of HCl or CO2 to Reduce the pH from 6.8to 6.0

Type of Acid	Acid Required <sup>‡</sup>	Acid Feed Rate <sup>§</sup>	Cost of Acid	Annual Material Cost	Power Cost^	Energy Cost <sup>†</sup>	Total Annual O&M Cost
Carbonic acid (pressurized CO <sub>2</sub> )	300 mg/L	1,529 lb/day	\$0.08/lb	\$44,647	\$3,960	\$4,840	\$53,447
Hydrochloric acid	69 mg/L	100 gal/day	\$1.47/gal*	\$53,655	\$396	\$920	\$54,971

<sup>‡</sup> Based on RTW modeling and assuming 100% acid solution

<sup>§</sup> Assumes plant flow of 425 gallons per minute

<sup>\*</sup> Price based on 36% HCl solution provided by Brenntag, September 2007. The density of 36% HCl is 9.83 lb/gal

<sup>^</sup> Assuming installation of a 20 kW CO<sub>2</sub> system and a 2 kW HCl system. Monthly power demand charge =  $\frac{16.49}{kW}$  listed on the City of Glendale's power bill for the month of August 2007.

<sup> $\dagger$ </sup> Energy cost = 0.055/kWh listed on the City of Glendale's power bill for the month of August 2007. The calculated energy requirement for the carbonic acid system is based on information provided by TOMCO2.

## Recommendations

The use of  $CO_2$  for pH adjustment is not recommended, since it will be more expensive than addition of HCl. While the use of HCl poses some safety concerns, HCl addition is commonly applied at water treatment plants and with proper storage, handling, and safety training, those concerns can be minimized. In addition, storage of pressurized  $CO_2$  would also present a safety concern and must be properly handled.