Reducing Facilities Chemical Costs By Proper Management of Total Alkalinity (TA) and pH

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Fallacies

- ~~Carbon Dioxide (CO_2) Injection Raises TA~~
- Truth: **Adding CO_2 Lowers pH With No Change in TA**
- ~~Total Alkalinity (TA) Stabilizes pH~~
- Truth: **TA* is a SOURCE of rising pH**

*Only the carbonate alkalinity has the pH rise; cyanuric acid or borates do not cause rising pH

Acid vs. CO_2 Injection

- Adding acid and bicarbonate is the same as injecting carbon dioxide (CO_2), but is a LOT more expensive!

- $HCl + NaHCO_3 = CO_2 + H_2O + NaCl$
  -TA +TA
  Acid + Bicarb = Carbon Dioxide + Water + Salt

Acid +	Bicarb =	CO_2
1 gallon 31.45% Hydrochloric (HCl)	7.015 lbs.	3.676 lbs.
1 gallon 38.5% Sulfuric (H_2SO_4)	6.880 lbs.	3.605 lbs.
1 pound 93.2% Bisulfate ($NaHSO_4$)	0.6521 lbs.	0.3417 lbs.

Use CO_2 Instead of Acid+Bicarb

- Only **use acid** to counter base (excess lye in chlorinating liquid) **to maintain TA** (i.e. to lower it); no need for bicarbonate
- **Use CO_2** injection to counter CO_2 outgassing **to maintain pH** (i.e. to lower it)
  - Important to use a booster pump with a properly sized efficient gas transfer Venturi injector into a slip-stream joining the main return stream

Net pH of Chlorine Sources

- Hypochlorite chlorine sources are *net* pH neutral except for
  - excess lye added for stability
  - chlorine outgassing (minimal when CYA is used and water temps not hot)
  - filtered/removed combined chlorine (minimal)
- *Net* pH neutral because chlorine usage/consumption is acidic

% Lye	pH*	31.45% HCl Acid per Gallon Chlorine	Comments
0.00%	10.6	no acid needed	not stable so not sold
0.25%	12.5	0.75 fluid ounces	high quality
0.79%	13.0	2.4 fluid ounces	low quality

*pH for 12.5% Chlorinating Liquid

What is Total Alkalinity (TA)?

- Mostly bicarbonate ion (HCO_3^-)
  - In equilibrium with aqueous carbon dioxide
  - TA is not the same as total carbonates (incl. CO_2)
- Pools and spas are open systems
  - Carbon dioxide (CO_2) slowly exchanges between water and air
- **TA* is a SOURCE of rising pH**

*Only the carbonate alkalinity has the pH rise; cyanuric acid or borates do not cause rising pH

Pools/Spas are Over-Carbonated

- TA 80 ppm, pH 7.5 has <u>over 7 times</u> the CO_2 in water compared to balance with air
- Why are pools and spas over-carbonated?
  - To provide a pH buffer to reduce swings in pH from *external* sources
  - To saturate the water with calcium carbonate to protect plaster surfaces

Carbon Dioxide Outgassing

- Carbon dioxide outgassing raises pH with no change in TA

$$CO_{2(aqueous)} \rightarrow CO_{2(gas)}\uparrow$$

- By removing both bicarbonate and acid

+TA -TA

$$HCO_3^- + H^+ \rightarrow CO_{2(aqueous)} + H_2O$$

Bicarbonate + Acid → Carbon Dioxide + Water

Factors Affecting Rise in pH

- Outgassing is faster with:
  - Higher TA
    - More bicarbonate and $CO_{2(aq)}$
  - Lower pH
    - More $CO_{2(aq)}$

      CO_3^{2-} **+ H^+** → HCO_3^- **+ H^+** → H_2CO_3 → H_2O + **$CO_{2(aq)}$** → $CO_{2(g)}\uparrow$

      Carbonate Ion → Bicarbonate Ion → Carbonic Acid → Carbon Dioxide
  - Greater aeration (waterfalls, spillovers, fountains, splashing, longer pump runtime)
    - Greater surface area for water/gas transfer and faster mixing (less slow diffusion)

Degree of Over-Carbonation

1.0 = CO_2 balance; 2.0 = twice as much CO_2 in water than in balance with air

<---------------- **pH** ---------------->

TA*	**7.0**	**7.2**	**7.4**	**7.5**	**7.6**	**7.8**	**8.0**	**pH_{EQ}**
20	5.8	3.6	2.3	1.8	1.4	0.9	0.6	7.75
40	11.5	7.3	4.6	3.6	2.9	1.8	1.1	8.04
60	17.3	10.9	6.9	5.4	4.3	2.7	1.7	8.21
80	23.1	14.6	9.1	7.2	5.7	3.6	2.2	8.33
100	28.9	18.2	11.4	9.1	7.2	4.5	2.8	8.42
120	34.6	21.8	13.7	10.9	8.6	5.4	3.3	8.49

*Adjusted TA (carbonate alkalinity) excluding cyanuric acid or borates

Lowering TA and Raising pH

- Reduce CO_2 outgassing and therefore lower pH/TA chemical usage
  - By at least* 35% lowering TA** from 120 to 80 or at least 25% lowering TA from 80 to 60
  - By over 50% raising pH from 7.3 to 7.6

*Outgassing rates vary as the square of the TA level and are not reflected in the over-carbonation table

**Adjusted TA (carbonate alkalinity) excluding cyanuric acid and borates

Putting It All Together

- Annual usage and costs for sum of multiple pools total over 400,000 gallons (Eastern U.S. waterpark with **high** bather-load and **high** aeration including wave pool)
- Using 12.5% Sodium Hypochlorite and 38.5% Sulfuric Acid
- TA 80-120 ppm, pH 7.4 (except last example)

Bleach	**Acid**	**Bicarb**	**CO_2**	**Total Cost**	
$1.79/gal	*$3.79/gal*	*$0.34/lb*	*$0.25/lb*		
18,000 gal	32,700 gal	225,700 lb	0 lb	$232,900	
18,000 gal	11,300 gal	78,400 lb	77,600 lb	$121,100	Actual
18,000 gal	800 gal*	0 lb	118,700 lb	$62,300	
18,000 gal	800 gal*	0 lb	40,000 lb	$42,200	TA↓ pH↑

(annual $32,220 for 15 ppm FC usage per day)

*would only be 108 gal assuming use of high-quality chlorinating liquid (345 gal from low-quality chlorinating liquid) and no outgassing of chlorine, no filtration/removal of combined chlorine, no plaster curing or degradation, no water dilution/exchange

Saturation Index to Protect Plaster

- Increase CH if lower TA results in negative saturation index
- Higher pH target loses more chlorine from UV in sunlight
  - More than 50% higher rate of loss at pH 7.6 vs. 7.3 (with CYA present; about 30% with no CYA)
  - But most chlorine usage in high bather-load pools is oxidizing bather waste, not loss from sunlight

Takeaways

- Adding CO_2 lowers pH with no change in TA
- Reduce chemical costs: **Use carbon dioxide instead of acid and bicarbonate to control pH**
- **Use acid only to control TA** rise from hypochlorite

- TA is a source of rising pH
- Reduce chemical costs: **Lower TA and raise pH target**

Questions/Comments?
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