

# Calcium Carbonate Scaling Spring 2013 Report

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## Introduction

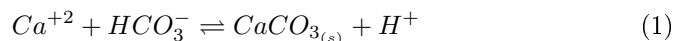
The municipality of Las Vegas, Honduras is currently experiencing a decrease in the capacity of their water distribution network due to the accumulation of scale in pipes. Our hypothesis is that this is caused by the karst topography of the region. The water source for Las Vegas is a groundwater spring. Groundwater, initially at a low temperature, flows across sediments containing calcium carbonate,  $CaCO_{3(s)}$ . The water heats up when it reaches the surface and as it flows through shallow pipes to the end of the distribution system. As the water warms and reaches equilibrium at a new temperature, calcium carbonate precipitates, coating the pipes in a hard scale. An AguaClara plant could solve this problem by dosing acid, which would drop the pH and prevent the formation of scale by keeping calcium in aqueous form. The purpose of the present analysis is to determine how much acid in the form of aluminum sulfate,  $Al_2(SO_4)_3$ , should be added and provide further analysis giving evidence for the present solution.

## Analysis

### Background

The scale is largely calcium based in origin. According to a composition analysis conducted by a laboratory in Honduras of the solid scale in four pipes in Las Vegas, concentrations of calcium oxide (CaO) ranged from 26.03% to 38.19%, silicon dioxide  $SiO_2$  ranged from 3.82% to 5.14%, and the remaining constituents ( $K_2O$ ,  $Na_2O$ , Alkalis, MgO,  $Al_2O_3$ ,  $SO_3$ , and  $Fe_2O_3$ ) were less than 1% in all samples (Fundación Hondureña de Investigación Agrícola, 2008).

The reaction of calcium carbonate,  $CaCO_{3(s)}$ , precipitating in a water system in the presence of bicarbonate,  $HCO_3^-$ , is represented by Equation 1, where  $Ca^{+2}$  is calcium ion and  $H^+$  is hydrogen ion.



The equilibrium constant  $K_{eq}$  is given by Equation 2, where the brackets indicate concentrations of each species in moles per liter (mol/L).

$$K_{eq} = \frac{[H^+]}{[Ca^{+2}][HCO_3^-]} \quad (2)$$

The equilibrium constant varies with changes in temperature, and can be calculated by rearrangement of the Van't Hoff equation as shown by Equation 3, where  $K_{25}$  is the equilibrium constant at a standard reference temperature of  $25^\circ C$  with a value of  $10^{-2}$ ,  $T_{25}$  is  $25^\circ C$ ,  $R$  is the ideal gas constant ( $1.987 \text{ kcal/mol} \cdot K$ ), and  $\Delta H^\circ$  (kcal/mol) is the enthalpy of a chemical reaction, or the amount of heat that is released or taken up during the course of the reaction.

$$K_{Final} = \frac{K_{25}}{\exp\left[\frac{\Delta H^\circ}{R}\left(\frac{1}{T_{Final}} - \frac{1}{T_{25}}\right)\right]} \quad (3)$$

$\Delta H^\circ$  can be calculated by Equation 4, where  $\nu_i$  is the stoichiometric coefficient of species  $i$  and  $\bar{H}_i^\circ$  are tabulated values representing the enthalpy of species  $i$  in kcal/mole at standard conditions of  $25^\circ C$  and 1 atm pressure.

$$\begin{aligned} \Delta H^\circ &= \left(\sum v_i \Delta \bar{H}_i^\circ\right)_{products} - \left(\sum v_i \Delta \bar{H}_i^\circ\right)_{reactants} \quad (4) \\ &= \left(\Delta \bar{H}_{CaCO_3(s)}^\circ + \Delta \bar{H}_{H^+}^\circ\right) - \left(\Delta \bar{H}_{Ca^{+2}}^\circ + \Delta \bar{H}_{HCO_3^-}^\circ\right) = 6.78 \text{ kcal/mol} \end{aligned}$$

Figure 1 shows the variation of  $Ca^{+2}$  with temperature. As the temperature increases, the concentration of aqueous  $Ca^{+2}$  decreases, resulting in increased formation of the precipitate  $CaCO_3(s)$ .

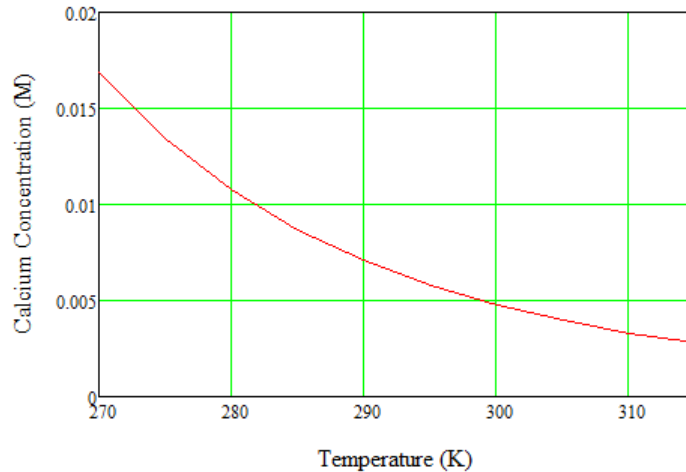


Figure 1: Aqueous Calcium Ion Concentration ( $Ca^{+2}$ ) vs. Temperature

## pH Determination

Given the pH, total alkalinity, and  $Ca^{+2}$  concentrations of the source water, we can determine the pH required to satisfy the equilibrium constant at the new temperature assuming that the  $Ca^{+2}$  concentration in the source water is the same as the  $Ca^{+2}$  concentration at the end of the distribution line to indicate that no  $CaCO_{3(s)}$  will form. The bicarbonate concentration varies with pH and is equal to the total carbonate species,  $C_T$ , multiplied by  $\alpha_{1F}$ , as shown by Equation 5.  $\alpha_{1F}$ , the fraction of total carbonate species as  $HCO_3^-$  at the final temperature, is a function of proton ion concentration, and can be calculated by Equation 6.  $C_T$  is assumed to be constant and can be calculated by Equation 7.  $\alpha_{1S}$  is the fraction of total carbonate species as  $HCO_3^-$  at the source water and is a function of proton ion concentration, and can be calculated by Equation 8.  $K_1$  and  $K_2$  are constants with the values of  $10^{-6.3}$  and  $10^{-10.3}$ , respectively. The  $Ca^{+2}$  concentration, pH, and total alkalinity of the source water were entered from given water quality data (Polanco, 2011). Since total alkalinity is equal to the bicarbonate concentration in the water quality data, in order to convert from a mass concentration (milligrams per liter) to a molar concentration (moles per liter), the molecular weight of total alkalinity was assumed to be equal to the molecular weight of bicarbonate (Polanco, 2011).  $K_{Final}$  was calculated at an assumed final temperature of  $35^\circ C$ . Equations 5, 6, 7, and 8 were then combined to form equation 9, and the result was solved implicitly to determine  $[H^+]$ .

$$[HCO_3^-]_F = \alpha_{1F} C_T \quad (5)$$

$$\alpha_{1F} = \left( \frac{[H^+]_F}{K_1} + 1 + \frac{K_2}{[H^+]_F} \right)^{-1} \quad (6)$$

$$C_T = \frac{\text{Total Alkalinity}}{\alpha_{1S}} \quad (7)$$

$$\alpha_{1S} = \left( \frac{[H^+]_S}{K_1} + 1 + \frac{K_2}{[H^+]_S} \right)^{-1} \quad (8)$$

$$K_{Final} = \frac{[H^+]_F}{[Ca^{+2}] \left( \frac{[H^+]_F}{K_1} + 1 + \frac{K_2}{[H^+]_F} \right)^{-1} \frac{\text{Total Alkalinity}_S}{\left( \frac{[H^+]_S}{K_1} + 1 + \frac{K_2}{[H^+]_S} \right)^{-1}}} \quad (9)$$

The pH was determined from Equation 10.

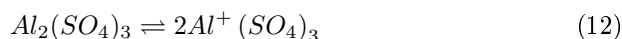
$$pH = -\log[H^+] \quad (10)$$

## Volume, Flow Rate, and Concentration of Acid Needed

Alkalinity is a measure of the capacity of a water to neutralize strong acid. Using Equation 11 we can determine the total equivalents of alkalinity that must be neutralized in order to adjust the pH. In Equation 11  $Alk_{req}$  is the alkalinity that must be neutralized, in equivalents per liter.

$$Alk_{req} = [Total\ Alkalinity] (\alpha_{1S} - \alpha_{1F}) \quad (11)$$

Per Equation 12, the normality (N) of alum is 6, indicating that there are 6 equivalents per liter of alum.



The total volume required to neutralize the alkalinity is shown by Equation 13, where  $V_{Acid}$  is the volume in units of liters of acid per liter of water.

$$V_{Acid} = \frac{Alk_{req}}{N} \quad (13)$$

The total flow rate of acid required to neutralize the alkalinity,  $Q_{Acid}$ , can then be obtained with Equation 14, where  $Q_{Plant}$  is the flow rate of the plant (44 L/s).

$$Q_{Acid} = V_{Acid} \times Q_{Plant} \quad (14)$$

Finally, the coagulant dose in mg/L,  $C_{Plant}$ , can be determined, assuming a stock concentration or  $C_{Acid}$  of 166.7 g/L, as shown in Equation 15.

$$C_{Plant} = \frac{Q_{Acid}C_{Acid}}{Q_{Plant}} \quad (15)$$

## Results

The pH of the water that is necessary to prevent formation of  $CaCO_{3(s)}$  and corresponding acid flow rate and dosage, for a plant flow rate of 44 L/s, are shown below. Results from the Piedras Amarillas storage source are shown in Table 1, and results from the Montevideo source are shown in Table 2. Asterisks (\*) indicate situations where the final pH (at the end of the distribution line) was higher than the source pH from the water quality data. For these cases, no acid dosage is required.

Table 1: Piedras Amarillas Water Quality Data and Results

#	Sample Date	$Ca^{+2}$ (mg/L)	Total Alkalinity (mg/L)	Source pH	Final pH	Alum Flow Rate (mL/s)	Alum Concentration (mg/L)
1	10/19/2011	21.12	112.46	7.85	7.86*	-	-
2	5/12/2011	35.90	139.39	7.64	7.54	0.17	0.66
3	5/13/2008	59.40	176.65	7.10	7.2*	-	-
4	5/15/2008	59.20	180.00	8.06	7.24	1.74	6.59
5	9/18/2007	53.28	172.50	7.05	7.25*	-	-
6	8/16/2007	52.20	169.63	7.85	7.31	1.19	4.52
7	5/9/2006	59.14	159.89	7.39	7.27	0.42	1.58

Table 2: Montevideo Water Quality Data and Results

#	Sample Date	$Ca^{+2}$ (mg/L)	Total Alkalinity (mg/L)	Source pH	Final pH	Alum Flow Rate (mL/s)	Alum Concentration (mg/L)
1	10/19/2011	51.84	113.22	6.41	7.26*	-	-
2	5/12/2011	16.74	118.12	6.74	7.82*	-	-
3	5/13/2008	64.00	149.79	7.00	7.22*	-	-
4	5/15/2008	49.60	150.00	8.30	7.39	1.03	3.89
5	8/16/2007	47.52	165.60	7.77	7.36	0.91	3.45
6	5/22/2007	52.00	145.48	7.40	7.36	0.12	0.45
7	5/9/2006	37.63	132.72	7.87	7.55	0.41	1.54

## Assumptions and Suggestions for Further Sampling

The model discussed in the present analysis assumes that the system has reached equilibrium at the final temperature of the water at the end of the distribution line, and that the total carbonate species,  $C_T$ , is constant throughout the system. A final temperature was assumed to be  $35^\circ C$  in this model. However, the temperature at the end of the distribution line should be measured to reflect actual conditions. If possible, the temperature should be measured under the “worst case scenario”, such as during midday in the summer. Further water quality data that can be collected and input into this model, both at the source and at the end of the distribution line, include:

- Temperature
- pH
- Calcium ion concentration

- Bicarbonate concentration
- Total alkalinity.

This model only considered the contribution of carbonate species in the water. In reality, the required acid dose may need to be higher to counteract the neutralizing capacity of ions (other than carbonate species, such as  $SiO_2$ ) present.

## Conclusions

The problem of calcium carbonate scaling in the source water in Las Vegas Honduras can be solved using an AguaClara plant to dose the water with acid, which will drop the pH and prevent calcium carbonate from precipitating. Depending on the necessary doses of coagulant, which acts as an acid, an additional dosing system may not be required. If the calculated dose suggests the need for additional acid beyond the coagulant an additional doser could be added. Assuming a 6 N acid solution of aluminum sulfate  $Al_2(SO_4)_3$  and a stock concentration of 166.7 g/L, the resulting acid flow rates required ranged from 0.12 mL/s to 1.74 mL/s, corresponding to plant doses ranging between 0.45 mg/L and 6.59 mg/L. There were also cases where no acid dosage was required due to a low source pH. These flow and dosage rates are within the design range of an AguaClara chemical dosing system.

## References

Water quality data was reviewed from:

- *Fundación Hondureña de Investigación Agrícola, Muestra de Incrustación Sumetido por Municipalidad de Las Vegas* (Honduran Agricultural Investigation, Scaling Sample Submitted by the Municipality of Las Vegas), June 19, 2008.
- *Polanco, Ing. Lizeira. Informe de Resultados Estudio de Tratabilidad Para el Sistema de Agua de Las Vegas, Santa Barbara* (Report of Treatability Sampling Results for the Water System of Las Vegas, Santa Barbara), September 2007.

Water quality data used in calculations was obtained from:

- *Polanco, Ing. Lizeira. Informe de Resultados Estudio de la Fuente de Abastecimiento Piedras Amarillas, Las Vegas, Santa Barbara* (Report of Sampling Results for the Storage Source Piedras Amarillas, Las Vegas, Santa Barbara), November 2011.