

# Chapter 1

## The Fundamentals of Bubble Formation in Water Treatment

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**Abstract:** Water utilities can experience problems from bubble formation during conventional treatment, including impaired particle settling, filter air binding, and measurement as false turbidity in filter effluent. Coagulation processes can cause supersaturation and bubble formation by converting bicarbonate alkalinity to carbon dioxide by acidification. A model was developed to predict the extent of bubble formation during coagulation which proved accurate, using an apparatus designed to physically measure the actual volume of bubble formation. Alum acted similar to hydrochloric acid for initializing bubble formation, and higher initial alkalinity, lower final solution pH, and increased mixing rate tended to increase bubble formation. Lastly, the protocol outlined in Standard Methods for predicting the degree of supersaturation was examined, and when compared to this work, the Standard Methods approach produces an error up to 16% for conditions found in water treatment.

### Introduction:

Gas bubble formation is of established importance to divers and fish (i.e., the bends), carbonated beverages, solid liquid separation in mining, cavitation in pumps, gas transfer, stripping, and dissolved air flotation processes. Moreover, it is common knowledge that formation of gas bubbles in conventional sedimentation and filtration facilities is a significant nuisance at many utilities, because bubbles are believed to hinder sedimentation, cause headloss in filters through a phenomenon referred to as “air binding,” and measure as turbidity in effluents without posing a microbial hazard. Utilities have come to accept these problems, and to the knowledge of these authors there is currently no rigorous basis for predicting when such problems will occur or correcting them when they do.

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In the past, many utilities having problems with bubble formation from waters supersaturated with dissolved gas have traced the source of the problem to air entrainment at water intakes. However, with the increasing popularity of “enhanced coagulation” at lower pHs, utilities may increasingly see problems arising from carbon dioxide driven bubble formation upon acidification of waters under some circumstances. Even if a source water is initially at equilibrium with the atmosphere and has no potential to form bubbles, the water can become supersaturated with carbon dioxide upon coagulant addition by conversion of bicarbonate to carbon dioxide:



Since treatment plants operate as closed systems with respect to gas transfer (Letterman et al. 1996), supersaturation from the newly formed carbon dioxide can lead to bubble formation through various mechanisms.

The goal of this paper is to describe the fundamental chemistry of bubble formation, with a particular emphasis on carbonate supersaturation in water treatment plants. Equations are developed to predict the volume of bubbles that potentially form during treatment processes, and a new device to physically measure the gas formation potential of a water is introduced. The merits and drawbacks of other approaches to predict bubble formation are also discussed.

## **Fundamentals of Bubble Formation:**

### *Bubble Nucleation*

Following supersaturation of a dissolved gas, a nucleation step is necessary before bubbles can form in solution. Homogenous or *de novo* nucleation describes spontaneous bubble formation within the bulk water. This typically occurs only if the difference between the ambient and dissolved gas pressure is greater than 100 atm. (Harvey 1975); consequently, homogenous nucleation is not expected to be observed in water treatment.

Bubbles can also form within pre-existing gas pockets located in surface cracks and imperfections of solids in a process known as heterogeneous nucleation (Figure 1). Supersaturated gas diffuses into the gas pockets, causing bubble growth and eventual detachment from the solid support. Unlike homogeneous nucleation, significantly less

dissolved gas supersaturation is required for heterogeneous bubble formation. Heterogeneous bubble nucleation can occur whenever a water is supersaturated (Hey et al. 1994) and is expected to prevail in most environmental systems.

### *Factors Impacting Nucleation*

The size and number of bubbles nucleated depends on the history of the water body and type of suspended particles (Keller 1972). The number of nucleation sites generally increases in the presence of surface active agents (Jackson 1994). Rough hydrophobic surfaces nucleate bubbles easily even at low supersaturations, while hydrophilic or even smooth hydrophobic surfaces nucleate bubbles only at exceptionally large supersaturations (Ryan and Hemmingsen 1998; Ryan and Hemmingsen 1993). The gaseous nucleation site can persist indefinitely on surfaces (Liebermann 1957; Tikuisis 1984). Surfactants such as soap reduce bubble nucleation at low micelle concentrations; whereas, above the critical micelle concentration they can increase nucleation (Hilton et al. 1993).

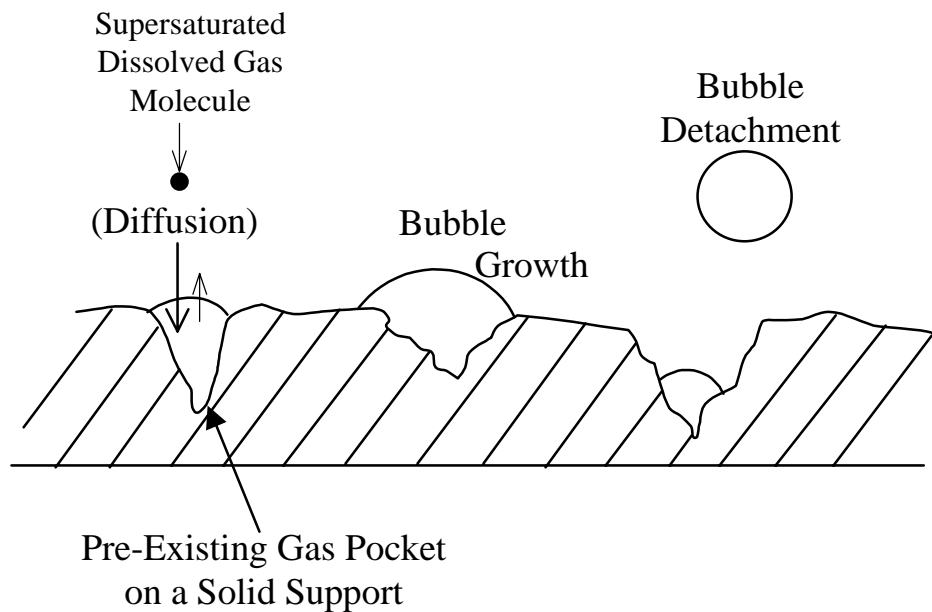


Figure 1 – Heterogeneous Nucleation

The crevice surface geometry dictates the curvature and internal pressure of the pre-existing gas pockets. This can be estimated using various approaches for use in modeling and predicting bubble formation. Unfortunately, no reliable analytical techniques can currently validate the predictions experimentally for the ideal geometries (Hey et al. 1994), although successful data can be obtained with arbitrary, irregular surfaces (Ryan and Hemmingsen 1998).

Other system factors affect bubble formation. Increasing gas supersaturation activates previously dormant nucleation sites and generates more bubbles from these sites (Hilton et al. 1993; Hikita and Konishi 1984), as will increased mixing intensity (Jackson 1994; Hikita and Konishi 1984). Finally, the tendency for bubble formation increases with temperature due to reduced Henry's equilibrium constants and more rapid diffusion kinetics (Hikita and Konishi 1984).

### *Model Conceptualization*

The preceding section described how supersaturated waters could form bubbles. Although models exist for other gas stripping processes, no model has been proposed for bubble formation in water treatment (Boulder, 1994; Hess et al. 1996). A simple conceptualization was developed to predict the volume of bubbles formed from this phenomenon (Figure 2). Consider an alkaline water initially at equilibrium with the atmosphere with no bubble forming potential. Upon acid addition, the bicarbonate is converted to carbon dioxide and the system will become supersaturated. If nucleation occurs, a new equilibrium can be approached by forming a volume of gas ( $\Delta V_{\text{gas}}$ ). In this conceptualization, the supersaturated carbon dioxide drives the bubble formation, but the volume of gases includes nitrogen, oxygen, and carbon dioxide.

Using conventional equations for all equilibria, partial pressures, and mass balance equations for nitrogen, oxygen, and carbon dioxide,  $\Delta V_{\text{gas}}$  can be computed (Appendix D). The model also considers the presence of water vapor, and for simplicity the percentage of remaining trace gases, like argon, are included with nitrogen through the convention known as "atmospheric nitrogen" (Harvey 1975). The carbon dioxide mass balance includes terms that considers the conversion of bicarbonate to carbon dioxide depending on the final pH. For simplicity in calculation of bubble volumes, the

ideal gas law was used since use of the real gas law only alters predictions by less than 0.4% under conditions typical of water treatment.

### *Illustrative Calculations*

With the initial alkalinity, final pH (or moles of acid addition), and the ambient temperature and pressure as starting inputs, a computer program was used to solve the system of equations for various circumstances. For example, consider a closed system containing 1 L water with 300 mg/L as CaCO<sub>3</sub> alkalinity initially at pH of 8.7 and at equilibrium with the atmosphere (Figure 3). Following acidification to pH 6.3, the system will shift to a new equilibrium with 1.62 mL of gas predicted to form. Although nitrogen and oxygen were not supersaturated with respect to the atmosphere before acidification, they constitute approximately 90% of the nucleated bubble volume with the remainder attributed to carbon dioxide (7.7%) and water vapor (2.3%). At equilibrium in this closed system, the final carbon dioxide concentration remains supersaturated 100 times relative to the external atmosphere.

Intuitively, higher initial alkalinity or lower pH after acidification would be expected to lead to more bubble formation. The model confirms this expectation with a direct relationship between the initial alkalinity and bubble volume for a given final pH (Figure 4). For a water at a given initial alkalinity, predicted bubble volume increases roughly linearly as pH decreases from about pH 7.5 down to 5.5.

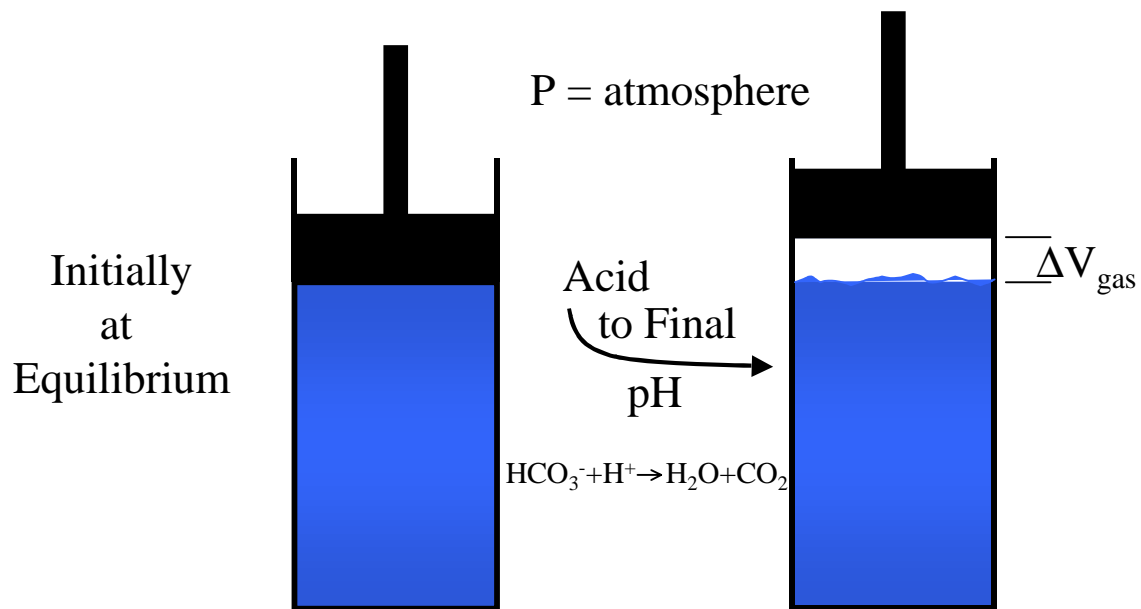


Figure 2 – Model Conceptualization

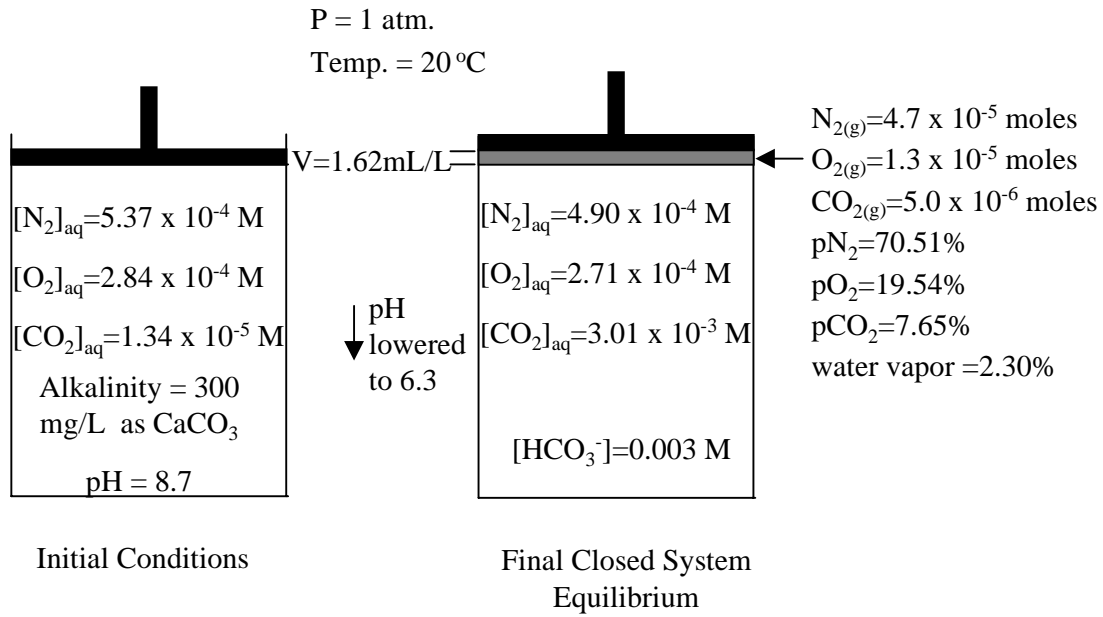


Figure 3 – Model Illustrative Example

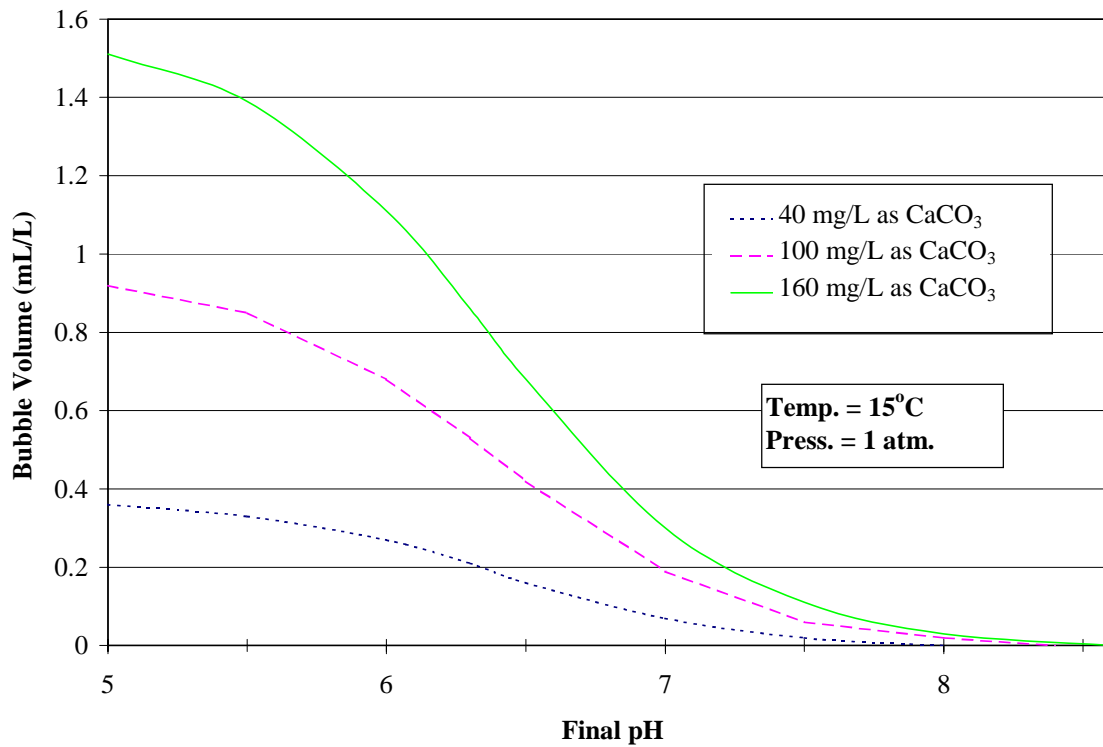


Figure 4 – Bubble Formation Potential as a Function of Initial Alkalinity and pH

The model also predicts increased gas volume production at higher temperatures (Figure 5). For example, a water with 250 mg/l as CaCO<sub>3</sub> alkalinity initially at equilibrium with the atmosphere would form about 50% more bubbles at 25 °C than for the corresponding conditions at 5 °C. The enhanced bubble formation at higher temperatures is due to the changing Henry's constant with temperature. The carbon dioxide from acidification in the water at 25 °C exerts a partial pressure of 0.15 atm. when pH is depressed to below 5 (1.15 atm. initial total pressure) compared to 0.08 atm. (1.08 atm. total pressure) at 5 °C. This effect overwhelms the decreased volume of initial dissolved gas in solution at the higher temperature. Of course, all equilibrium constants should be corrected to the actual system temperature or significant errors will result.

Like temperature, the ambient pressure or the depth of the solution can impact bubble formation. The model assumes atmospheric pressure for the pre-existing gas pockets and the final internal pressure of nucleated bubbles. Hydrostatic forces increase pressures, and the net result is that at a depth of 1.5 meters the bubble formation potential is greatly reduced (Figure 6).

## **Model Confirmation:**

### *Development of Bubble Apparatus*

In order to validate the model predictions and provide a tool for use in practical situations, an apparatus was developed to physically measure the total volume of gas released from solution. The apparatus (Figure 7) follows the idealized conceptualization (Figure 2), with gas release occupying some volume within the closed system as indicated by a water level drop within the measuring pipette. Volume measurements are taken after the pressure within the pipette is normalized with respect to the atmosphere by moving the pipette upwards until the water levels (and pressure) in the pipette and holding container are equal.

Gases formed in the apparatus can either be located as bubbles in the original liquid volume (a), producing a rise in the flask's water level  $\Delta WL$ , or transferred to the headspace of the container (b). In either case, the total volume of gas formed appears as  $\Delta V_g$  (Figure 7), and  $\Delta WL$  directly measures bubbles remaining in solution.

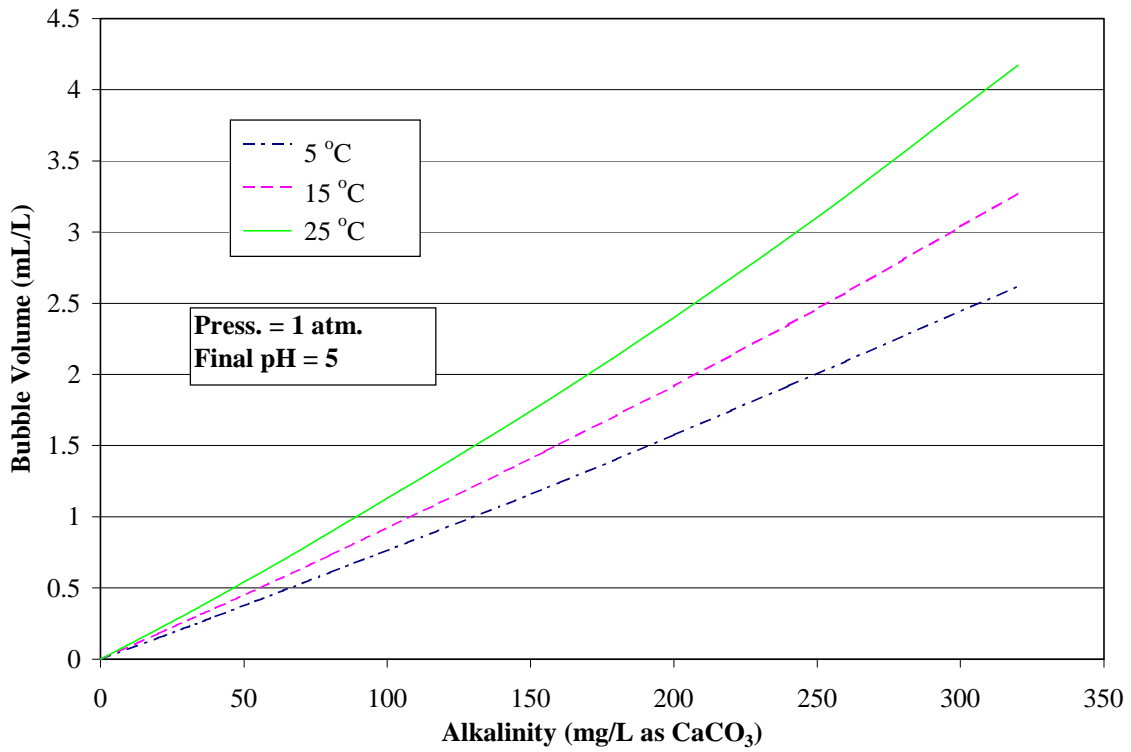


Figure 5 – Bubble Formation Potential as a Function of Temperature

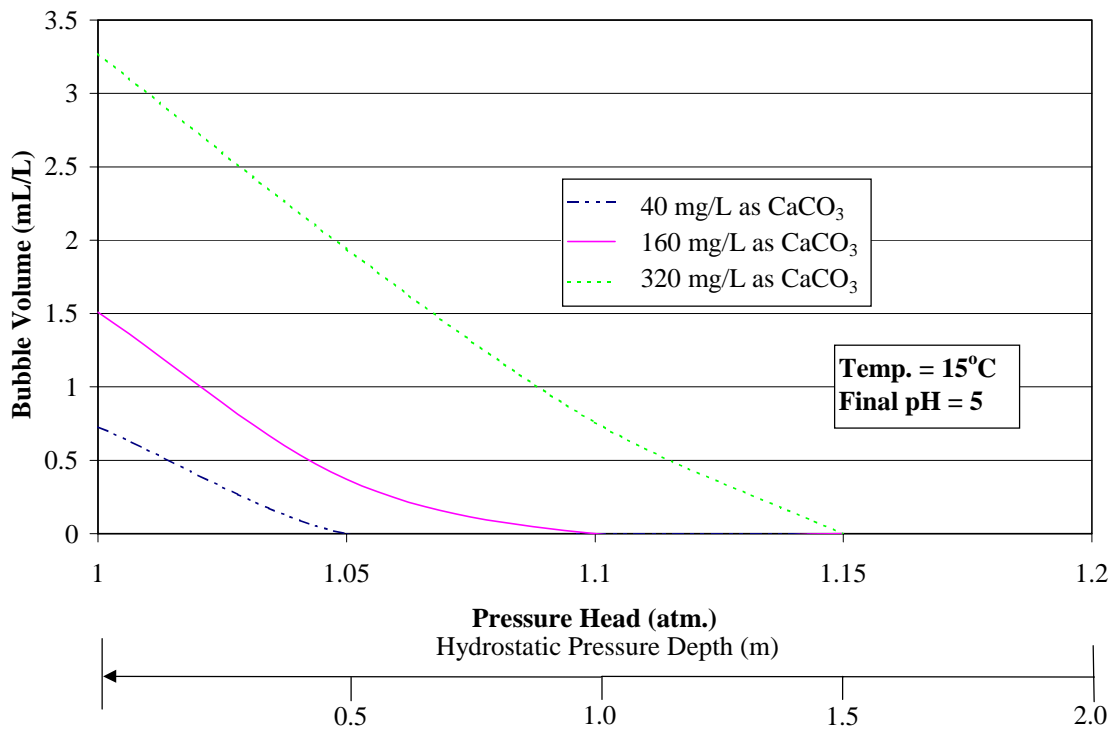


Figure 6 – Bubble Formation Potential as a Function of Pressure



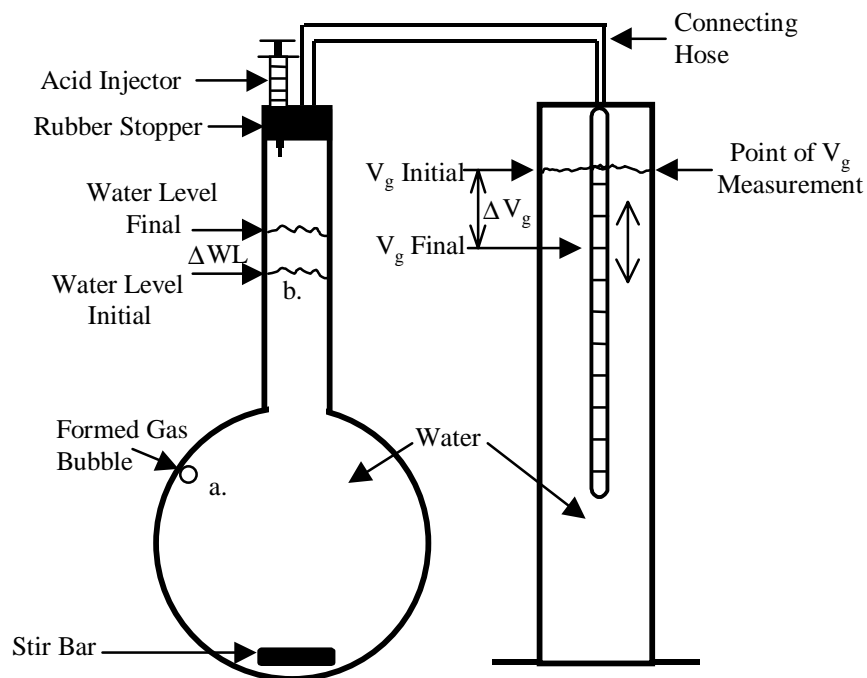


Figure 7 – Schematic of Bubble Volume Measuring Apparatus

### *Materials and Methods*

Construction materials included either a 1 or 2 L volumetric flask with a rubber stopper and teflon stirbar. Rubber stoppers were fitted with a 10 mL syringe for acid addition and nonexpandable teflon tubing—both secured with silicon glue. A 10 mL with 0.1 mL graduations pipette, submerged in a 1 L graduated cylinder containing water equilibrated with temperature and dissolved gases, actually measured the bubble volume produced. In a modified experiment to measure the bubble volume contained in solution, the neck of the 1 and 2 L flasks were reduced from their original 2 and 2.5 cm diameter, respectively, to a consistent 0.6 cm diameter, creating greater sensitivity for measuring the change in water level ( $\Delta WL$ ). With a 10 mL pipette, standard deviations in measurement were typically  $\pm 0.03$  mL. The practical quantitation limit ( $\pm 20\%$  RSD) for the instrument is approximately 0.28 mL.

Sample waters were prepared with 0.01 M sodium nitrate (electrolyte) and aerated overnight in constant temperature rooms, and alkalinity was added as sodium bicarbonate immediately before experiments began. After checking the system for leaks, the sample was acidified by either 8.8 M hydrochloric acid or 0.2 M  $Al_2(SO_4)_3 \cdot 18H_2O$  (alum), rapid

mixed for 10 seconds at 300 rpm, and then stirred slowly at the desired rate for the remainder of the test. Experiments were conducted in constant temperature rooms of either 20 or 5 °C ± 0.1.

At least two apparatuses were simultaneously operated during initial experimental runs: one with analyte water for the actual gas measurement and the other with plain distilled water (containing no alkalinity or supersaturated dissolved gases) as a control. Any movement in the control pipette, due to barometric pressure changes or temperature warming, was subtracted from the measurements of the actual sample trial. In later experiments, alternative methods of dealing with these errors were developed as discussed in the text.

### *Experimental Kinetics*

As an example of a typical experimental run three testing flasks were filled with water containing 160 mg/L as CaCO<sub>3</sub> and acidified to a pH of 5 (Figure 8). Although the trial lasted for a longer duration, gas bubble production ceased around four hours. This appeared consistent with other tests; consequently, all subsequent experiments were stopped after four hours. When gas supersaturation was rather low (80 mg/L as CaCO<sub>3</sub> lowered to pH 6.3), gas exolution ended as quickly as two hours. Figure 8 also illustrates the reproducibility of the bubble apparatus.

### *Mixing Effects*

More available energy or increased mixing intensity promotes and enhances bubble nucleation and growth (Jackson 1994). Consistent with expectations, a water, initially at 160 mg/L as CaCO<sub>3</sub> alkalinity lowered to pH 5, stirred at 500 rpm significantly reached equilibrium quicker than the same water mixed at 120 rpm (Figure 9). An arbitrary mixing rate of 200 rpm was chosen for all remaining tests, but it is noted that a higher mixing rate would evolve gas faster. Modeling the treatment process with mixing rates that correlate to the rapid mix and flocculation cycles is expected to provide valuable information on kinetics in an actual treatment plant.

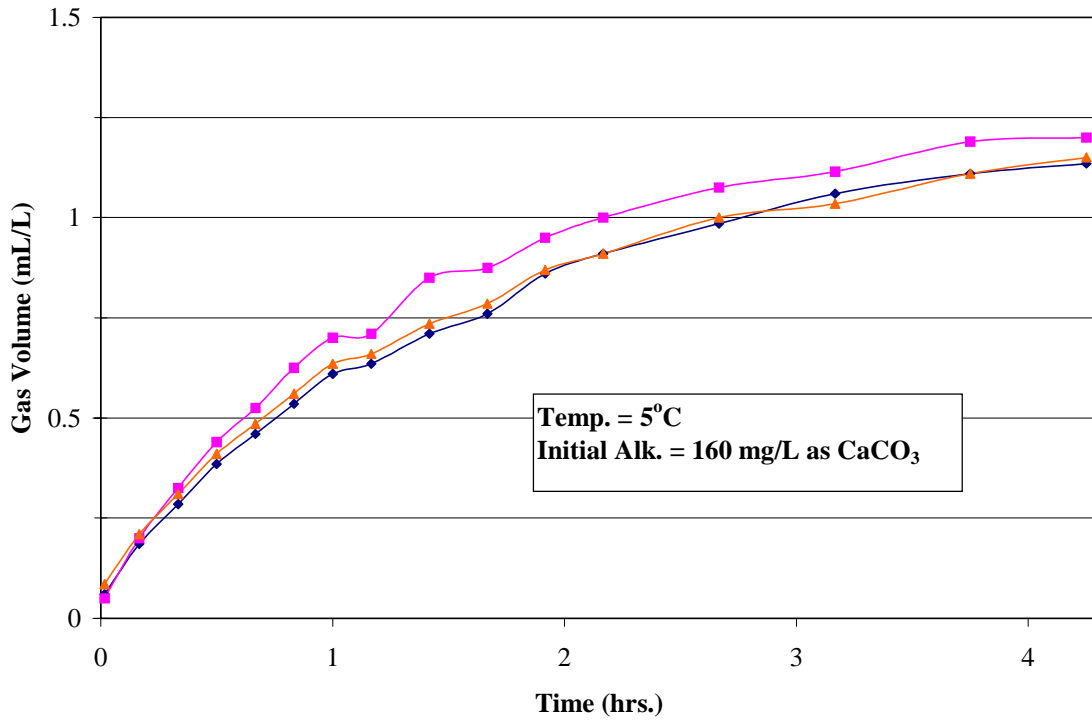


Figure 8 – Bubble Volume Kinetics

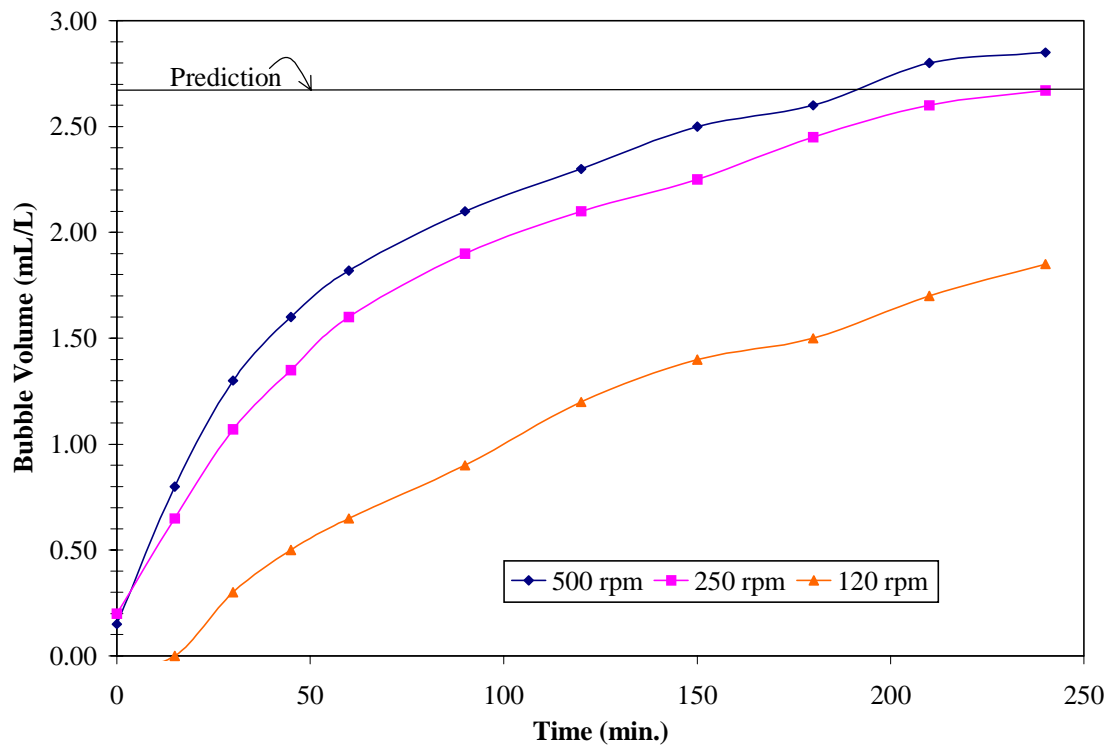


Figure 9 – Mixing Intensity Effects on Bubble Kinetics

### *Realistic Water Condition Testing*

The model predictions were compared to experimental data at a variety of conditions. A simple ratio (R) was developed to compare the experimental data to the mathematical prediction, with a ratio of 1 indicating a perfect prediction for the experiment.

$$R = \frac{\text{Actual Bubble Volume Produced Experimentally}}{\text{Bubble Volume Predicted by the Model}}$$

Initial alkalinities ranging between 40 and 320 mg/L as CaCO<sub>3</sub> and pH's lowered to 5 provided practical and extreme testing parameters (Figure 10). Although a few data points deviate in excess of 20% from the model, the majority lie well within this region of accuracy. There was no distinguishable difference between the effects of hydrochloric acid (HCl) and alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•18(H<sub>2</sub>O)), and the mathematical model functioned equally well at temperatures of 20 and 5°C. The model was also accurate when more realistic coagulation pHs were examined (Figure 11).

With higher gas supersaturations (320 mg/l as CaCO<sub>3</sub> lowered to pH 5), bubbles became visible on the glass surface and teflon stirbar minutes after acidification, characteristic of heterogeneous nucleation. Bubbles grew progressively and detached from the stirbar, eventually becoming visible on the glass flask.

### *Modified Analysis*

The modified flasks with the reduced neck diameter were used to quantify bubble formation the solution. Almost instantly noticeable differences in the water level occurred in solutions of 320 mg/L as CaCO<sub>3</sub> initial alkalinity at 5 and 20 °C. The quantity of *in situ* bubbles seemed to level to a relatively constant value of 0.15 mL/L average for both temperatures; whereas, the ultimate gas production steadily increased implying a certain number of nucleation sites growing, emitting, and re-forming bubbles.

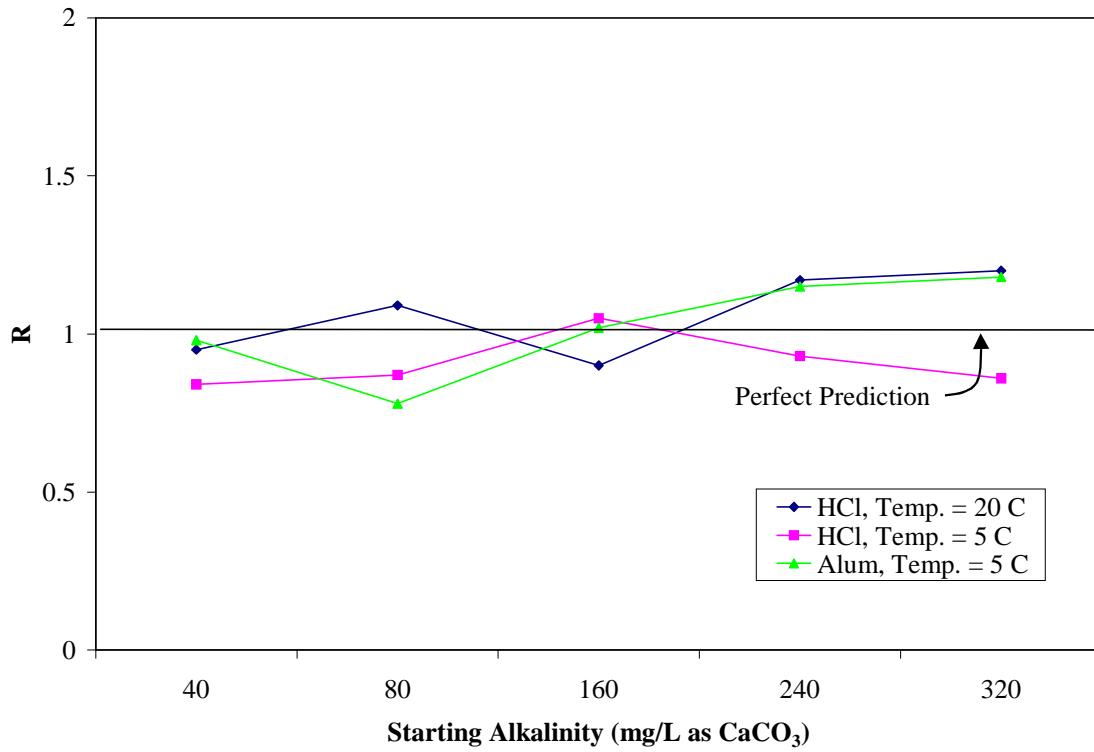


Figure 10 – Model Verification with Extreme Conditions

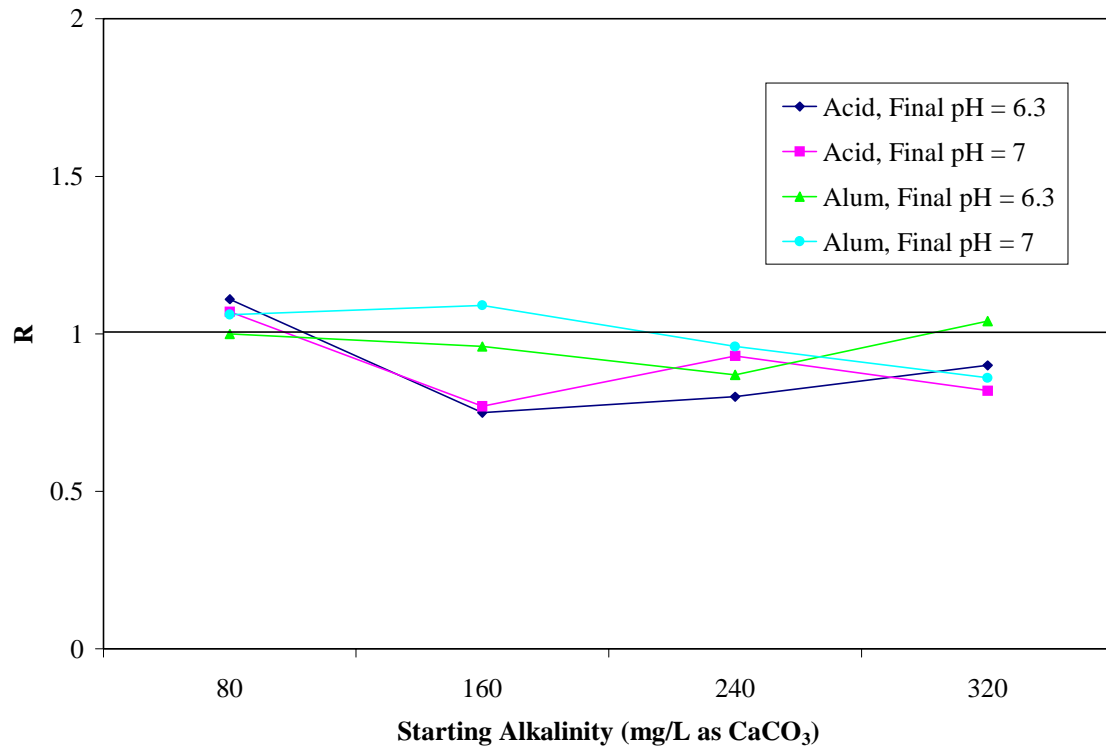


Figure 11 – Model Verification for 2 Different Acids and pH's

The overall gas production was significantly lower than that produced during the normal tests, even with an extended test time length of 12 hours. For example, at 20 °C with the normal volumetric flask 6.7 mL/L of gas evolved compared to 3 mL/L for the same water within the modified flask. Surface gas transfer probably constituted a considerable amount to the measured bubble volume for the experiments in Figures 10 and 11, and modified flasks might be more appropriate.

### *Modeling and Experimental Errors*

The system pressure where the supersaturated dissolved gas transfers (pre-existing gas pockets, pre-existing bubbles, or surface interfacial transfer) was assumed equal to atmospheric pressure. The assumption holds for interfacial surface gas transfer, but a bubble at depth would have a higher internal pressure limiting gas transfer, which may indicate the overall reduced measured volume in the modified experiment. Since the Laplace equation can predict internal pressures for the pre-existing nuclei either greater or less than solution pressure, atmospheric pressure was the safest assumption.

For most of the experiments, aeration incurred via compressed air jets located on the lab benches. Coupled with the air entering the solution at depth and probably being at a pressure greater than barometric, part or all of the solution water could have been supersaturated with dissolved gases prior to usage.

Ultimately, ambient pressure proved to be the largest factor. On a typical day, the barometric pressure varied up to 2% during experiments and changes the amount of bubbles produced. For instance, a water with 160 mg/L as CaCO<sub>3</sub> initial alkalinity at 5 °C acidified to pH 5 produces 1.23 mL/L of bubbles when the pressure was 1 atm. at the beginning and end of the test. If pressure drops 2% during the test, the model predicts 1.78 mL/L of bubble produced (45% increase), and a 2% increase in pressure during the test would decrease bubbles products by 41%. Use of a digital barometer during tests allowed for compensation of these effects.

## **Practical Extensions:**

### *Other Analytical Techniques*

Most analytical procedures only measure the aqueous gas supersaturation rather than a physical bubble volume produced. Although volumetric extraction and gas

chromatography can measure dissolved gas concentration, these tests are labor intensive and expensive. The current edition of Standard Methods outlines a test for measuring gas supersaturation in a liquid by use of a sampling probe. Gases diffuse through the membrane until the pressure within the hose is at equilibrium and total pressure in solution is measured.

These devices report the data in terms of partial pressures, which indicates a potential for bubble formation but does not translate directly to a volume of gas formed. Standard Methods and other sources state that the main constituents of gas supersaturation are oxygen and nitrogen with carbon dioxide and argon considered negligible. The equations defined in this work and the measured supersaturation can be used to predict bubble formation potential, assuming that only nitrogen and oxygen contribute and the internal bubble pressure is atmospheric pressure (Appendix II). Using this approach, the volume of bubbles that can be formed in a water increases almost linearly with the degree of supersaturation at two different temperatures (Figure 12).

The error introduced by ignoring carbon dioxide is dependent on the initial alkalinity, system temperature, and final pH. For example, ignoring carbon dioxide in a water at 25 °C with 320 mg/L as CaCO<sub>3</sub> initial alkalinity and acidified to pH 3, 3.69 mL/L of bubbles are predicted. This produced an error of 16% compared to the model calculation of 4.4 mL/L. The error increases substantially when very large alkalinities become acidified and results from incorrect assumptions stated in Standard Methods (Figure 13). As shown with the hypothesis and model, carbon dioxide cannot be ignored in all circumstances. This is especially true in anaerobic digesters, where the alkalinity is typically greater than 2,000 mg/L as CaCO<sub>3</sub> (Droste 1997).

Other problems can arise with these sampling probes. Accurate pressure readings typically arrive after long sampling time frames, up to two hours. Operators skilled in instrument usage are required for measurement precision because considerable errors results when bubbles form on the sampling hose. Although a 1.5 – 2% precision is documented for skilled operators, some researchers noticed up to 20% error from bubble growth on the sampling hose (Bouck 1982). Even though modifications of the original device helped eliminate this problem, usage of these dissolved gas probes mandates consciences operators and considerable care.

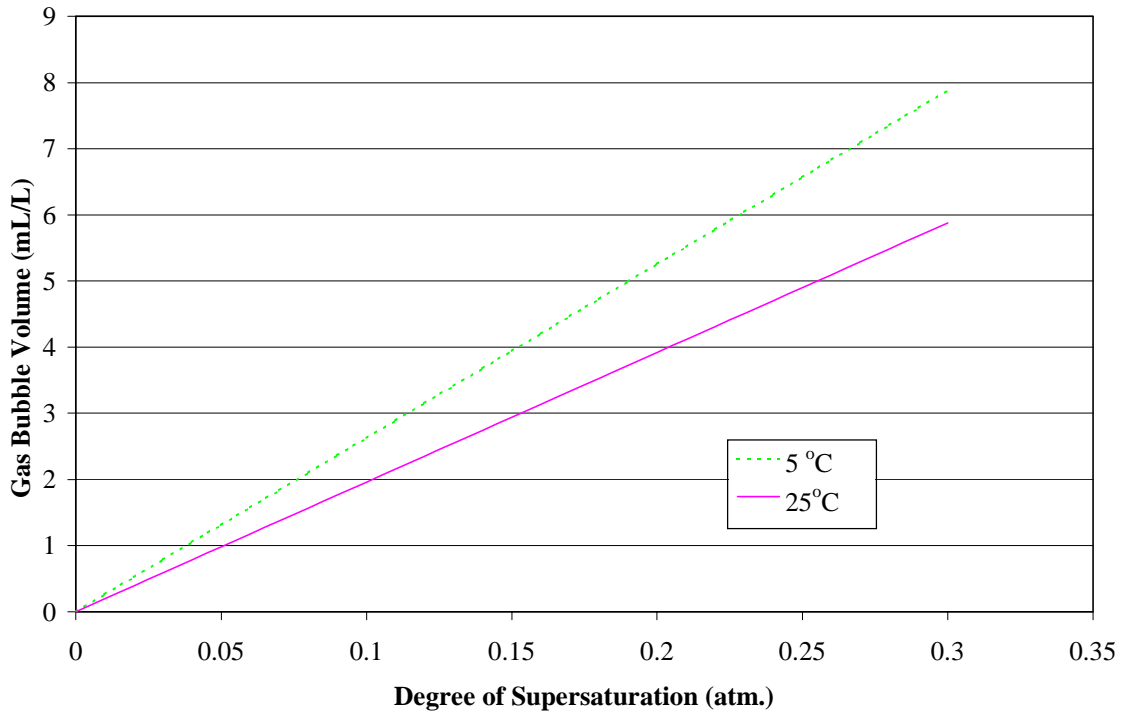


Figure 12 – Bubble Volume Estimation with Standard Methods Approach

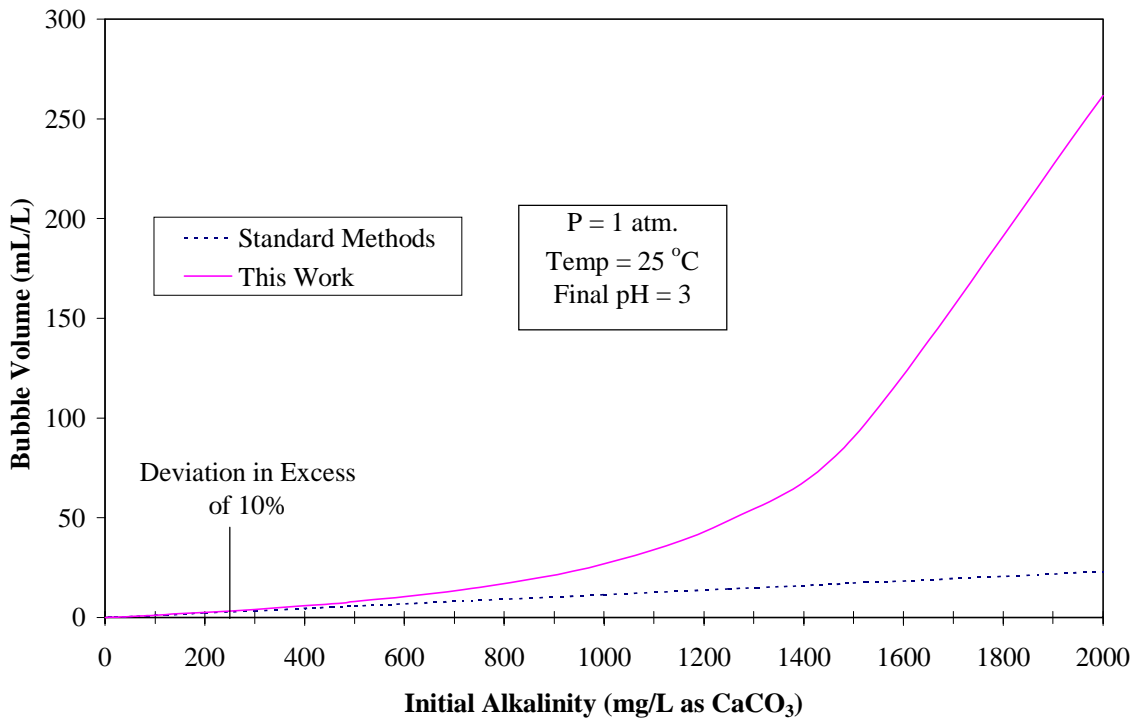


Figure 13 – Predictions of this Work Considering CO<sub>2</sub> Compared to Standard Methods Assumptions



To summarize, two possible techniques can be used to predict and measure gas bubble formation potentials of liquid solutions. Each inherently contains advantages and limitations (Table 1), and in some cases, use of both techniques may be desirable.

### *Future Work*

The enhanced coagulation rule with possible reductions in coagulation pH will increase the likelihood of air binding problems. Thus, future work will apply these principles to a practical study of settling problems and filter binding which result from bubble formation.

Table 1 – Comparison of Standard Methods and the Bubble Apparatus

	<b>Standard Methods Approach</b>	<b>Bubble Apparatus</b>
Indicates Supersaturation	Yes	Yes
Physical Measurement	Total Dissolved Gas Partial Pressure	Generated Bubble Volume & Rate
Experiment Duration	15 min. - 2 hrs	2 hrs. - 4 hrs
Experiment Setup	Little	Moderate
Skill Required	Moderate	Moderate
Operator Assistance	Continual Attention Required, Unless Probe Contains External Mixer	Zero Following Setup
Measurement Errors/Problems	Bubble Forming on Probe	Solution Must Remain at Same Temperature as Bulk, Second Apparatus Needed for Correction Measurements
Capable of Physically Modeling Plant Treatment Cycle	No	Yes
Instrument Cost	\$1000+	\$150

### **Conclusions:**

- A model was developed to apply the science of bubble formation to the water treatment field. Bubble forming potential (mL gas/L solution) can be readily predicted or measured in waters, and this is likely to be an important operational parameter under some circumstances.
- Acidifying normal alkalinity waters, even if the water is not initially supersaturated with gas, can drive bubble formation.
- The model accurately predicted the volume of bubbles using a new apparatus.
- It is possible to measure bubble formation potential using a variety of approaches.

## Appendix I. Model Equations

### *Known Parameters*

Assume a 1 L Solution

Alk. = Initial Solution Alkalinity

[H<sup>+</sup>] or pH = Final pH (or acid addition)

T = System Temperature

P<sub>b</sub> = Pressure of Gases within Bubble (Assumed Atmospheric Pressure)

P<sub>wv</sub> = Water Vapor Pressure

P<sub>atm</sub> = Atmospheric Pressure

% O<sub>2</sub>, % N<sub>2</sub>, % CO<sub>2</sub> = Normal Atmospheric Percentages for Air

k = Henry's Law Constant for Oxygen, Nitrogen, and Carbon Dioxide

K<sub>HCO<sub>3</sub><sup>-</sup></sub> = First Acid Dissociation Constant for Bicarbonate

R = Ideal Gas Constant

### *Known Parameters Used in the following System of Equations*

#### *Bubble Atmosphere and Solution Equilibrium*

$$O_{2(w)} = k_{O_2} pO_2$$

$$N_{2(w)} = k_{N_2} pN_2$$

$$CO_{2(w)} = k_{CO_2} pCO_2$$

#### *Sum of Bubble Partial Pressures*

$$pO_2 = (P_b - P_{wv}) \times \frac{O_{2(g)}}{O_{2(g)} + N_{2(g)} + CO_{2(g)}}$$

$$pN_2 = (P_b - P_{wv}) \times \frac{N_{2(g)}}{O_{2(g)} + N_{2(g)} + CO_{2(g)}}$$

$$pCO_2 = (P_b - P_{wv}) \times \frac{CO_{2(g)}}{O_{2(g)} + N_{2(g)} + CO_{2(g)}}$$

#### *Gaseous Mass Balances*

$$P_{atm} (\% O_2) k_{O_2} = O_{2(w)} + O_{2(g)}$$

$$P_{atm} (\% N_2) k_{N_2} = N_{2(w)} + N_{2(g)}$$

$$P_{atm} (\% CO_2) k_{CO_2} + Alk. - \frac{K_{HCO_3^-} \times CO_{2(w)}}{[H^+]} = CO_{2(w)} + CO_{2(g)}$$

*Solving the System of Equations Gives Solutions to the following Variables*

$O_{2(w)}$ ,  $N_{2(w)}$ ,  $CO_{2(w)}$  = Final Amount of Dissolved Gas in Solution (moles)

$pO_2$ ,  $pN_2$ ,  $pCO_2$  = Final Bubble Gas Partial Pressures (atm.)

$O_{2(g)}$ ,  $N_{2(g)}$ ,  $CO_{2(g)}$  = Final Bubble Gas Quantity (moles)

*The Bubble Volume can then be Calculated with Ideal Gas Law*

$$PV_g = nRT$$

$$P = P_b - P_{wv}$$

$$n = O_{2(g)} + N_{2(g)} + CO_{2(g)}$$

$$\frac{P_{wv}}{P_b} = \frac{V_{wv}}{V_b}$$

$$V_b = V_{wv} + V_g$$

*Ideal Equations Compute Bubble Volume*

$V_g$  = Bubble Volume from Aqueous Dissolved Gases

$V_{wv}$  = Bubble Volume from Water Vapor

$V_b$  = Total Bubble Volume

## Appendix II. Equations for Standard Methods Approach

### *Known Parameters*

Assume a 1 L Solution

$P_s$  = Supersaturated Dissolved Gas Pressure in Solution (measured)

$P_{atm}$  = Atmospheric Pressure

$P_b$  = Pressure of Gases within Bubble (Assumed Atmospheric Pressure)

$P_{wv}$  = Water Vapor Pressure

$T$  = System Temperature

%O<sub>2</sub>, %N<sub>2</sub> = Normal Atmospheric Percentages for Air

$R$  = Ideal Gas Constant

$k$  = Henry's Law Constant for Oxygen and Nitrogen

### *Bubble Volume Calculated with Ideal Gas Law and Thermodynamic Ratio*

$$PV'_g = nRT$$

$$P = P_{atm} - P_{wv}$$

$$n = (P_s - P_{atm})[k_{O_2} (\%O_2) + k_{N_2} (\%N_2)]$$

$$\frac{P_{wv}}{P_b} = \frac{V_{wv}}{V_b}$$

$$V_b = V_{wv} + V'_g$$

### *Ideal Equations Compute Bubble Volume*

$V'_g$  = Bubble Volume from Aqueous Dissolved Gases

$V_{wv}$  = Bubble Volume from Water Vapor

$V_b$  = Total Bubble Volume

### Appendix III. References

- Bouck, G. R. (1982). "Gasometer: An Inexpensive Device for Continuous Monitoring of Dissolved Gases and Supersaturation." *Trans. American Fisheries Society*, 111, 505-516.
- Boulder, CO. (1994). Conceptual Design Memorandum. Report prepared by Richard P. Arber Associates for Boulder, CO.
- "Dissolved Gas Supersaturation." (1998). *Standard Methods for the Examination of Water and Wastewater*. L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, eds., United Book Press, Inc., Baltimore, 2-90-2-94.
- Droste, R. L. (1997). *Theory and Practice of Water and Wastewater Treatment*. John Wiley and Sons, Inc., New York, 626.
- Harvey, E. N., Barnes, D. K., McElroy, W. D., Whiteley, A. H., Pease, D.C., and Cooper, K. W. (1944). "Bubble Formation in Animals." *J. of Cellular and Comparative Physiology*, 24 (1), 1-22.
- Harvey, H. H. (1975). "Gas Disease in Fishes—A Review." *Proc., Chemistry and Physics of Aqueous Gas Solutions., Electrothermics and Metallurgy and Industrial Electrolytic Divisions, Electrochemical Society*, Princeton, N.J., 450-485.
- Hess, T.F., Chwirka, J.D., and Noble, A.M. (1996). "Use of Response Surface Modeling in Pilot Testing for Design." *Environmental Technology*, 17, 1205-1214.
- Hey, M. J., Hilton, A. M., Bee, R. D. (1994). "The Formation and Growth of Carbon Dioxide Gas Bubbles from Supersaturated Aqueous Solutions." *Food Chemistry*, 51, 349-357.
- Hikita, H. Konishi, Y. (1984). "Desorption of Carbon Dioxide from Supersaturated Water in an Agitated Vessel." *AIChE J.*, 30 (6), 945-950.
- Hilton, A. M., Hey, M. J., Bee, R. D. (1993). "Nucleation and Growth of Carbon Dioxide Gas Bubbles." *Food Colloids and Polymers: Stability and Mechanical Properties, Special Publication 113*, Royal Society of Chemistry, Cambridge, U.K., 365-375.
- Jackson, M. L. (1994). "Energy Effects in Bubble Nucleation." *Ind. Eng. Chem. Res.*, 33, 929-933.

- Keller, A. (1972). "The Influence of the Cavitation Nucleus Spectrum on Cavitation Inception, Investigated with a Scattered Light Counting Method." *J. Basic Eng., Trans. ASME*, 94 (4), 917-925.
- Letterman, R., Shankar, S. (1996). "Modeling pH in Water Treatment Plants: The Effect of Carbon Dioxide Transport on pH Profiles." Poster at the 1996 AWWA National Conference in Toronto, Canada.
- Liebermann, L. (1957). "Air Bubbles in Water." *J. of Applied Physics*, 28 (2), 205-211.
- Ryan, W. L., Hemmingsen, E. A. (1993). "Bubble Formation in Water at Smooth Hydrophobic Surfaces." *J. of Colloid and Interface Science*, 157, 312-317.
- Ryan, W. L., Hemmingsen, E. A. (1998). "Bubble Formation at Porous Hydrophobic Surfaces." *J. of Colloid and Interface Science*, 197, 101-107.
- Tikuisis, P., Johnson, R. (1984). "Conditions for Heterogeneous Nucleation in the Physiological Environment." *Underwater Physiology VIII, Proceedings of the Eighth Symposium on Underwater Physiology*. A. J. Bachrach and M. M. Matzen, eds., Undersea Medical Society, Bethesda, MD, 107-118.