

Improving Chloramine Residuals and Minimizing Nitrification

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The Florida Keys Aqueduct Authority provides potable water to the residents of Monroe County through a 130-mile long transmission pipe and 650 miles of distribution system piping. The FCAA's water treatment plant in south Dade County treats an average of 14.0 MGD of groundwater. The treatment process consists primarily of lime softening, disinfection, filtration, and fluoridation. Disinfection is by chloramination.

For systems using a chloramine disinfectant residual, the threat of nitrification is of great concern and can present significant distribution system operating problems. A nitrification episode can lead to loss of combined chlorine residual, increased heterotrophic plate counts, increased positive total coliform, and loss of consumer confidence if public notification is required.

Past Experience and Strategies

The FCAA changed disinfection treatment from free chlorine to chloramines in 1991 to meet the requirements of the Trihalomethane Rule. The following year, as a result of complaints of rusty water, lime addition was reduced to maintain an alkalinity greater than 30 mg/L, and that reduced the average pH in the finished water from 9.5 to 7.8. The modification resulted in fewer complaints about rusty water, but it appeared to affect the stability and chloramine residuals throughout the transmission and distribution system.

Prior to lowering the treated water's pH in 1992, its chloramine level leaving the plant was 3.5 mg/l. When it reached Key West after two to three days in the 130-mile pipeline, the chloramine level was 3.0 mg/l. After 1992, the chloramine residual leaving the treatment plant was 5.0 mg/l, and the level reaching Key West was 2.5 mg/l.

From 1993 to 1996 nitrification episodes occurred at the lower pH, especially during the summer in water storage tanks with long detention times. Several strategies to improve chloramine residuals and minimize the occurrence of nitrification were implemented, but none was effective. These strategies included optimizing operation of the water storage tanks in the distribution system, practicing breakpoint chlorination, and minimizing the available free ammonia by optimizing the feed ratio of chlorine to ammonia (4.5:1) at the treatment plant.

The FCAA needed a plan of action to provide long-term improvements to system-wide treatment and operation and control measures to minimize the occurrence of nitrification.

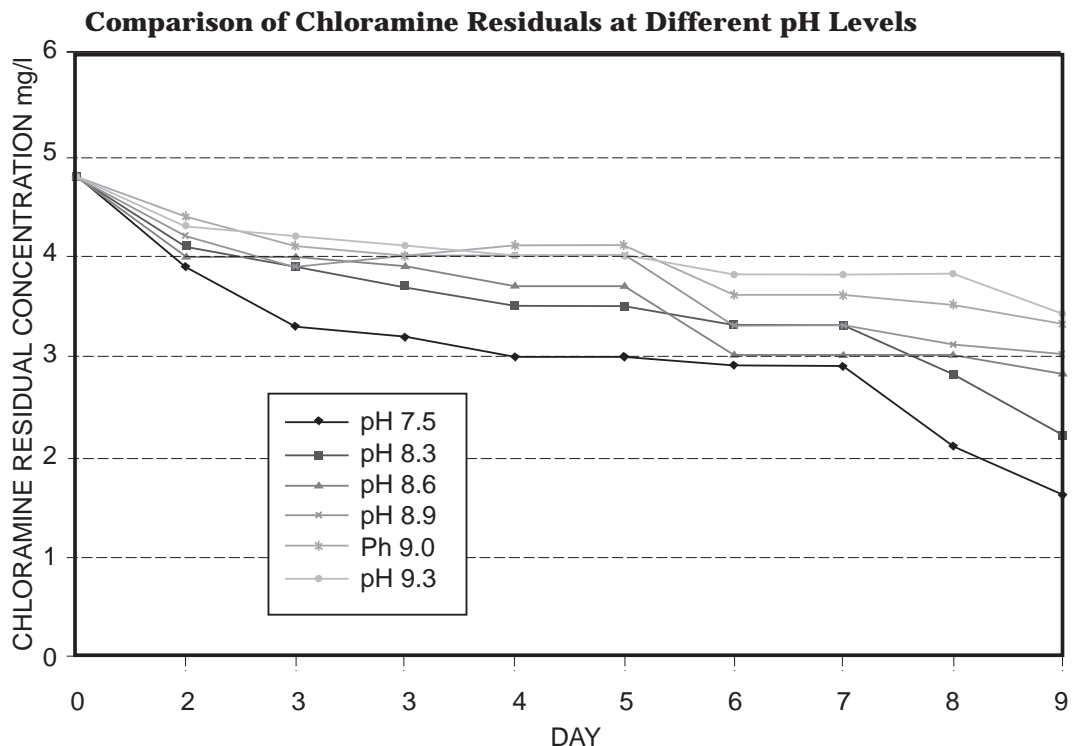
Since 1993, the FCAA has

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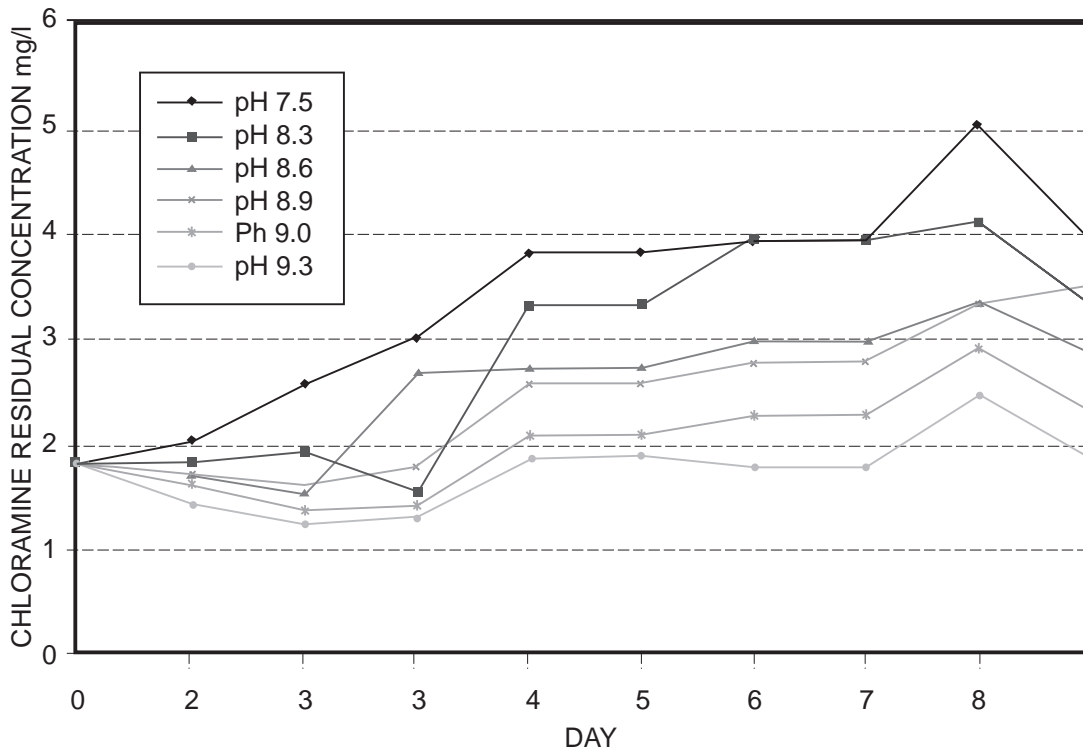
expanded the water quality parameters and monitoring. Sample locations representing low flow and dead end areas with long detention times were identified to define the magnitude of the problem in the distribution system. Action level concentrations have been established as indicators of nitrification based on water quality monitoring data. Action levels that indicate nitrification may be occurring are decreases in pH, alkalinity, chloramine residual, dissolved oxygen, and ammonia, and increases in nitrate, nitrite, and HPC.

It has been reported^{1,2,3,4} that nitrification consumes alkalinity at a rate of 8.6 mg/l of ammonia-nitrogen oxidized, and a potential exists for a drop in pH in poorly buffered waters. Loss of chloramine residual has been the most common indicator of nitrification occurring in the distribution system. Drops in dissolved oxygen and ammonia are also good indications of nitrification occurring. The oxidation of 1 mg/l of ammonia to nitrite requires 3.22 mg/l of oxygen. An additional 1.11 mg/l of oxygen is needed to oxidize nitrite to nitrate. The increase in nitrite has been reported^{4,5} to exert a chlorine demand of 5 mg/l for every 1 mg/l of nitrite. From past practices, this seems to be evident when chlorine boosting of the water leaving the tanks did not successfully increase the chloramine residuals. Also, increase in HPC populations have been observed with nitrification occurrences in larger water storage tanks.

The amount of available ammonia is routinely monitored on finished water, distribution sites, and larger water storage tanks utilizing an ammonia ion selective electrode. The water treatment operators are taking free ammonia readings at least once per shift and after every flow change to check that minimal



Free Ammonia Concentration at Different pH Levels



To test this hypothesis, the FKAA conducted a jar test to observe the stability of chloramines and free ammonia concentrations at different pH values. For the jar test, samples of finished water were adjusted to a pH of approximately 7.5 (original pH value) and ranging up to 9.3 and stored in opaque plastic containers. The chloramine residual concentration and free ammonia concentration of each sample at the different pH values were measured daily. The chloramine residual concentration appears to experience a sudden decrease in concentration and then level off. However, at higher pH levels, the chloramine residual concentration decreases less and levels off sooner, maintaining a higher concentration. The

free ammonia level is available. Free ammonia levels on the finished water have been observed in the range of 0.1 to 0.3 mg/l.

Free ammonia levels are also measured at sample locations in the transmission/distribution system. The results appear to indicate that the free ammonia increases over time, probably from the degradation of the chloramine residual. The average free ammonia level measured in Key West, which represents 3 to 4 days detention time, is 0.46 mg/l. It may be hypothesized that at the lower pH levels the combined chlorine and ammonia dissociate allowing the free ammonia to become available as a food source for the nitrifying bacteria. The high temperatures during the summer may contribute to this rate of dissociation. It is possible that as pH increases to 9.0, the chloramine residual does not react or dissociate at the same rate as at lower pH levels, and that is why the chloramine residuals last longer at the higher pH levels.

free ammonia concentrations at the lower pH appeared to increase over time while the free ammonia concentrations at the higher pH appeared to remain consistent over time.

Other utilities, such as Ann Arbor, Michigan, which have experienced nitrification episodes during summer months, have found that operating at elevated pH levels has been an effective method for controlling nitrification. For the past four years Ann Arbor has had one nitrification occurrence at the elevated pH levels⁴.

Based on Ann Arbor's and FKAA's experiences with nitrification and findings of increasing pH, the FKAA investigated alternative treatment modifications to increase finished water pH as an effective long-term nitrification control measure.

Alternative Treatment Modifications

Three alternative treatment modifications were considered

to reduce the potential for nitrification and minimize iron corrosion with the distribution system. The alternatives were developed to achieve water quality goals that would increase the finished water pH to 9.0 and maintain a minimum alkalinity of 40 mg/l as calcium carbonate. The three alternatives were:

Alternative 1 - Increase lime softening pH and add soda ash to the softening process to provide more available alkalinity in the softened water;

Alternative 2 - Increase lime softening pH and add carbon dioxide after softening to produce a level of alkalinity desired; and

Alternative 3 - Operate one lime softening unit at high pH

Summary of Treatment Alternatives To Increase pH

Alternative Process	Advantages	Disadvantages
1. Soda Ash	<ul style="list-style-type: none"> Provide additional alkalinity in source water to allow high pH softening without loss of alkalinity 	<ul style="list-style-type: none"> Additional process at WTP Messy dry chemical feed equipment Additional O&M requirements Difficult process to control More complex to operate Higher operating costs
2. Carbon dioxide	<ul style="list-style-type: none"> Converts hydroxide alkalinity to carbonate alkalinity which provides better buffering in finished water Easy process to control Clean operation 	<ul style="list-style-type: none"> Additional process to maintain Higher operating costs Can cause calcium post precipitation if overdosed
3. Split Treatment	<ul style="list-style-type: none"> No capital cost Can be implemented immediately 	<ul style="list-style-type: none"> Difficult process to control Cannot achieve desire optimum water quality condition (but is close) Potential post precipitation on filter media or in clearwell

Summary of Capital and Operating Costs for Various Alternatives To Increase pH

Alternative Process	Capital Cost (\$)	Operating Cost ^a (\$/1000 gal)
1. Soda ash addition	60,000 ^b	0.080
2. Carbon dioxide addition	80,000	0.030
3. Split treatment	0	0.015

^aOperating cost based on annual average flow of 14 million gallons per day

^bCost includes assumption that a new building is not required for dry chemical feed equipment

and the other unit at current softening pH and blend waters from two softening basins.

Alternative 2 appeared to provide the best solution from a process control standpoint. Its costs could be reduced because FKAA already has a 13-ton carbon dioxide storage facility onsite. Only injection feed equipment is required to implement this alternative.

Alternative 3, however, provides the lowest cost in terms of new capital expenditures and lowest operating costs. At the time, there was concern that Alternative 3 might not meet optimum water quality conditions and would most likely produce finished water with a pH of 8.5 and minimum alkalinity of 25 to 30 mg/l as calcium carbonate. These goals are marginally acceptable for increasing pH and minimizing iron corrosion.

Although Alternative 3 may not meet optimum water quality

lime softening unit between pH 9.0 and 9.5. Blending of the water from the two softening units results in the present FKAA finished water quality summarized in the accompanying table.

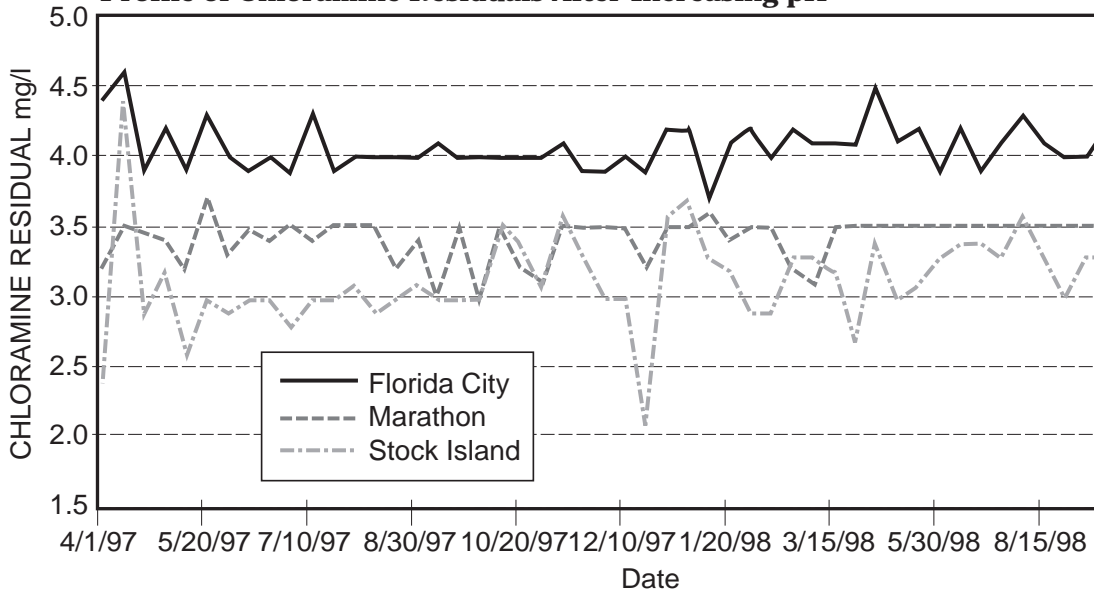
Chloramine residuals are more stable and longer-lasting in the water storage tanks and distribution system since the implementation of Alternative 3. Currently, the chloramine residual leaving the plant is 4.0 mg/l. It reduces to an average of 3.5 mg/l at Marathon and 3.0 mg/l at Stock Island. Water storage tanks have maintained a chloramine residual equal to or greater than 2.4 mg/l since the finished water pH was increased. In addition, free ammonia concentrations appear to be consistent with free ammonia concentrations of the finished water. Free ammonia concentrations have decreased from 0.46 mg/l at pH 7.8 to 0.20 mg/l at pH 8.7. Nitrification has not been observed in the FKAA water supply system for the two years.

The FKAA is optimistic that this approach will provide a long term solution and will continue to be effective in improving chloramine residual stability and preventing nitrification episodes.

References

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Profile of Chloramine Residuals After Increasing pH



conditions, the FKAA recognized Alternative 3 as an acceptable interim, if not a long-term solution, to the nitrification problem. However, FKAA was prepared, if necessary, to implement the CO₂ system (Alternative 2) if Alternative 3 could not meet the water quality goals.

Implementation of Alternative 3

In April 1997, the FKAA treatment plant implemented Alternative 3. It split treatment in an effort to achieve optimum water quality goals by increasing the pH to 9.0 and maintaining total alkalinity at greater than 40 mg/l. The FKAA plant operates the larger lime softening unit between pH 8.5 and 8.8 and the smaller

Finished Water Quality After Alt. 3 Implemented

pH	NH ₃ -N	NO ₃ -N	p	Total	Total	Total
	(mg/l)	(mg/l)	Alkalinity	Alkalinity	Hardness	Chlorine Residual
8.7	1.2	0.2	3	50	127	4