Smart News from Aqua Smart, Inc.

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Inside this Newsletter

1

Chlorine is chlorine is chlorine

All forms of chlorine used for drinking water disinfection (whether gas, on site generation, sodium hypochlorite, calcium hypochlorite, etc.) result in two main chemical fractions--the more active hypochlorous acid ion (HOCl-) and the less active hypochlorite ion (ClO-). It is important to note that hypochlorous acid ion is the most effective disinfectant of all the chlorine residual fractions. This simply is due to the relative ease by which the hypochlorous acid ion can penetrate bacteria cell walls. In other words, of all chlorine fractions, nothing kills bacteria better and quicker than the hypochlorous acid ion.

In order to produce the greatest proportion of hypochlorous acid ion in drinking water supplies, it is necessary to take a very close look at pH effects on each main fraction.

solution concentration 5000 mg/l			
pH	%Cl2	%HOCl-	%OCl-
6.5	.0063	92.28	7.71
7.0	.0017	79.10	20.89
7.5	.0004	54.84	45.21
8.0	.0001	27.46	72.54
8.5	.0000	10.69	89.31
9.0	.0000	3.65	96.35

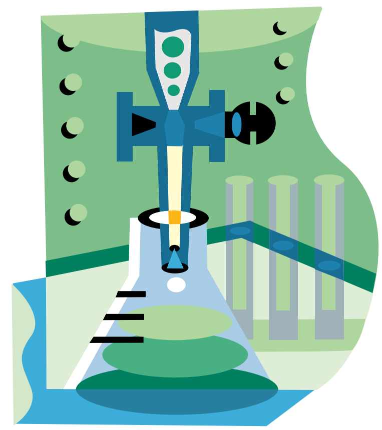
solution concentration 7000 mg/l			
pH	%Cl2	%HOCl-	%OCl-
6.5	.0088	92.28	7.71
7.0	.0024	79.10	20.89
7.5	.0004	54.49	45.21
8.0	.0001	27.46	72.54
8.5	.0000	10.69	89.30
9.0	.0000	3.65	96.35

solution concentration 10,000 mg/l			
pH	%Cl2	%HOCl-	%OCl-
6.5	.0126	92.28	7.71
7.0	.0034	79.10	20.89
7.5	.0007	54.49	45.51
8.0	.0001	27.46	72.54
8.5	.0000	10.69	89.30
9.0	.0000	3.65	96.35

Clearly seen, lowering finished pH raises active hypochlorous acid ion levels. Is it no wonder that systems running at higher pH's vie for chlorine disinfection alternatives (ozone, chlorine dioxide, chloramines, UV, etc.). Would it not be better, much cheaper, and far less labor intensive to simply lower finished water pH to 6.5-7.0 maximizing hypochlorous acid ion concentration...given appropriate corrosion control can be maintained? Of course it would.

continued

2 Sodium hypochlorite stability



As many systems switch from gas chlorine to liquid sodium hypochlorite for ease of handing, safety, and lowering insurance risk rates, there are decomposition problems which need reviewing. The following are the likely causes:

Sunlight (UV light)	Temperature
Presence of transition cations	pH
Chlorate presence	

Sunlight (UV light)

It is clear that the shelf-life of a 10-15% available chlorine solution decreases three to four times by sunlight. Interestingly, stronger solutions decrease even faster. Therefore, it is best to store sodium hypochlorite solutions away from direct (or even indirect) sunlight.

Presence of transition cations

The presence of either iron, copper, nickel, or cobalt catalyze deterioration of sodium hypochlorite solutions. Iron is the worst offender and can usually be tagged to the sodium hydroxide used in sodium hypochlorite manufacture. Iron, even in quantities as low as 0.5 ppm will rapidly deteriorate sodium hypochlorite solutions. Copper levels should not exceed 0.5 ppm. Copper is generally found in flexible connections and brass body valves.

Chlorate presence

Formation of chlorates are a direct result of sodium hypochlorite decomposition. In fact, the monitoring of chlorate can, and is, used as a mechanism for monitoring stability and activity of fresh solutions. The lower the chlorate levels, the more stable the sodium hypochlorite. The higher the chlorate levels, the less stable the sodium hypochlorite.

Temperature

The chart below gives the half life of various sodium hypochlorite concentrations versus temperature:

Half-life, Days				
% Cl_2	212°F	140°F	77°F	59°F
10.0	0.079	3.5	220	800
5.0	0.25	13.0	790	5000
2.5	0.63	28	1800	
0.5	2.5	100	6000	

Obviously, it is best to store sodium hypochlorite in the coolest areas of the water plant or well house.

pH

Under no circumstances should any solution of sodium hypochlorite go below a pH of 11.0 and preferably should be at least 11.2. Raising pH much above 11.2 does not seem to add stability.

NOTE: In the realm of black art in the sodium hypochlorite manufacturing process, it also has been found over the years that a small amount of sodium carbonate present in sodium hypochlorite improves stability significantly. (It could be because sodium carbonate buffers very well between a pH of 11-11.2). When purchasing supplies, check with your manufacturer if they are adding sodium carbonate to their solutions.

3 Improving water quality and piping

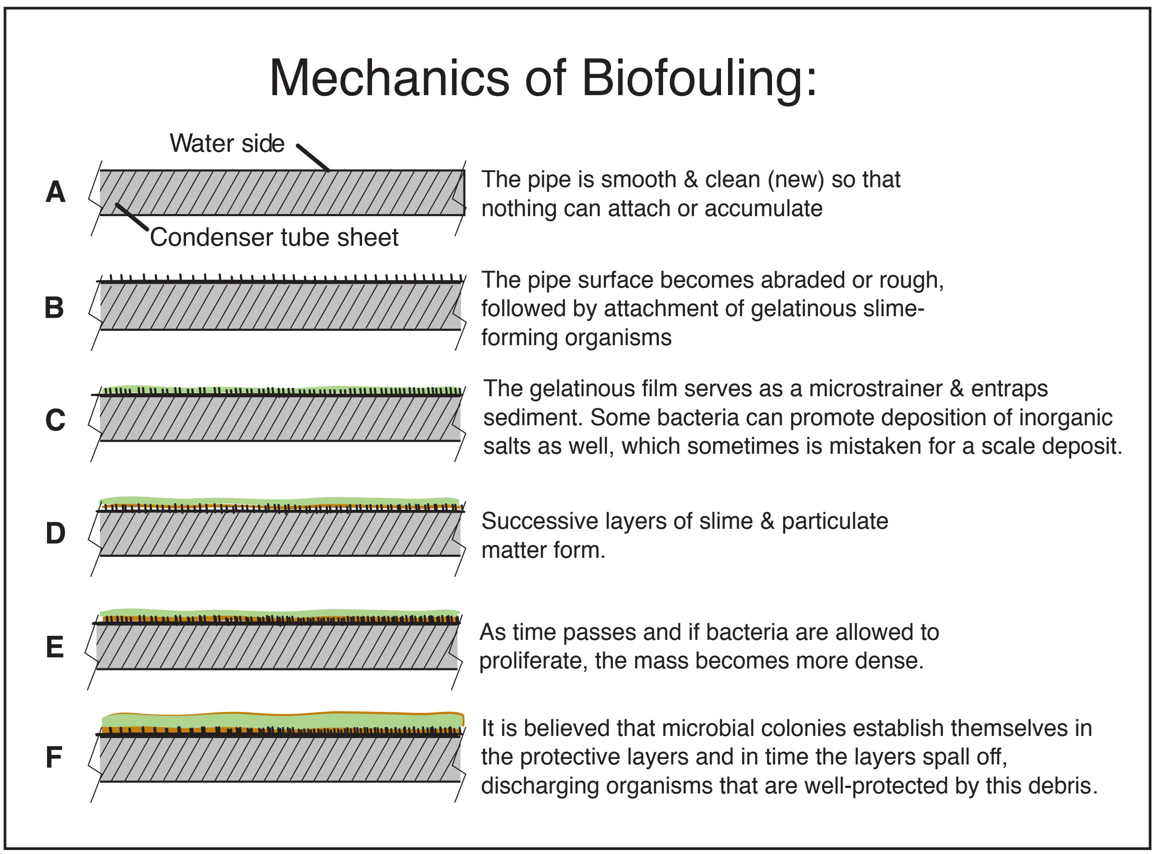
Adverse water quality from distribution piping usually depends on three interrelated chemical and biological processes taking place at pipe water interfaces.

- **biofouling--due to microorganism growth causing taste, odors, and discolored water**
- **chemical and electrolytic corrosion--resulting in metallic tastes as well as causing premature hot water and piping failure**
- **appearance of organisms in piping indicating recontamination.**

All three cause deterioration of water quality leading to customer complaints.

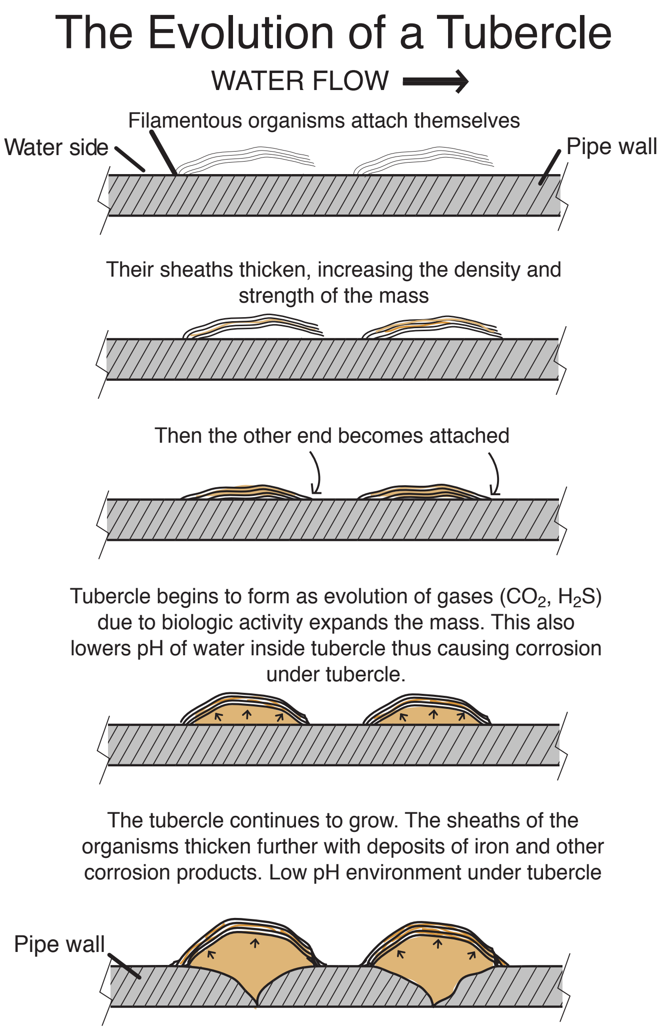
Bacterial colonies form and adhere to pipe walls and surfaces of suspended particulate matter. This can take place in summer months particularly in the presence of low level chlorine residuals (0.1 - 0.2 ppm) evident in low flow and dead end areas.

These bacterial colonies eventually lead to biofouling and harboring of various microorganisms. The presence of calcium scales actually enhance this mechanism. This can be seen more clearly in the following diagram.



Bacteria are always present in water...even in the most efficient and modern operating plants. Many bacteria which are not able to flourish under particular environments become dormant within piping and wait for the environment to improve for their favorable growth.

Many bacteria found in water supplies, including filamentous and stalked, have the ability to tuberculate themselves easily onto the pipe surface as shown in the following diagram.



Once this occurs, severe corrosion results from the formation of very strong acids within the hollow of the tubercle. The growth of the tubercle into bubblelike form continues (from the production of CO_2 or O_2 gases) eventually reducing the pipe C factor resulting in lower flows and pressures.

In order to counter such growth, it is best to avoid such problems from the beginning.

This means maintaining;

a) adequate disinfection,

b) adequate corrosion control,

c) complete removal of all pre-existing deposits,

d) and prevention of new deposit (tubercle) formation.

Adequate Disinfection

In order to maintain adequate disinfection, it is absolutely necessary to accomplish two things:

1. One is to lower the disinfection demand within distribution and

2. Two is to increase distribution disinfection residuals.

The best (and least costly) way to do both is to run the distribution system finished water pH as low as possible negating the use of most or all pH control. By doing this, the levels of more stable hypochlorous acid ion predominates over the less stable hypochlorite ion.

The only proven successful corrosion control technology at lower pH levels is SeaQuest.

Operating at lower pH ranges (6.5-7.0) also produces another benefit. That is chlorine demand needed to keep appropriate residuals in distribution lowers. For example, at a pH of 8.5, it takes 10 ppm of chlorine to keep 1 ppm of hypochlorous acid in the system. At a pH of 7.0, it only takes 1.5 ppm. This also results in lower potential THM and HAA formation.

Adequate Corrosion Control

From comparative studies, the product which provides the best corrosion control results is SeaQuest.

Completely Removing All Pre-existing Deposits

The ability to completely remove all pre-existing corrosion/scale deposits lowers chlorine demand. Upon SeaQuest use, a municipal system will show a 20-30% (and often higher) increase in distribution chlorine levels. This has been documented and reported in a presentation made at the WQA conference in Tampa, Florida in 1999 (report available upon request).

Prevention of New Deposit (tubercle) Formation

Once an integral metal phosphate coating is formed and total sequestration is maintained, more chlorine is available for better disinfection, deposit reformation stops, and pipes stay clean.

All the above add up to improved water quality at the tap for your customers, and fewer complaints for you.

4 On line

There are some very interesting problems which drinking water operators face daily from customer complaints having nothing to do with water quality being produced. Operators need to respond to their customers providing help avoiding potentially embarrassing news media publication of the these problems.

One interesting problem recently posed to us involved opaque glassware stains which were impossible to remove by any known simple methods without destroying the glassware. Of all glassware stains known, only one responds in this manner--silicates. The question becomes what was the source of the silicates? We know that water departments use hydrofluosilicic acid regularly as a source of fluoride in the water, but if the silicate portion of this compound was the culprit, the problem would be everywhere.

After thorough testing and more thought, we suggested our customer contact his customer and find out if they had changed machine dishwashing powder brands recently. Well, what do you know! The complaining customer had just switched to a cheaper product. Why was this the source of the problem? Because such products contain a large proportion of sodium silicate in the formula. If it is not balanced properly with other ingredients in the formula, or is a cheaper source of sodium silicate containing high percentages of contaminant insolubles, opaque stains can deposit on glassware. The reason the stain is so difficult to remove is that glass itself is silica (made from sand) and silicate loves to bond very tightly with silica being in the same chemical family.

Listen to another story. A plant operator approached us with a pair of blue sweat pants which were stained and his customer put the blame on the water department after buying a new washing machine and still having the problem. We cut out samples of the stain, analyzed it by mass miscroscopy, and determined that the stain was not a lubricant grease, oil, or fuel oil stain. We already knew the water quality had been reviewed and found to be within specification. After further conversations with the microscopy specialists, it was determined the stain was a food grease or oil stain (such as from salad dressing, gravy, food toppings, etc.). How can this happen while the pants had been through even the new washing machine? The customer switched to a liquid laundry detergent. How could this be the cause of the problem? Liquid laundry detergents simply do not have the ability to stop redeposition during the quiet settling cycle of a washing machine. This quiet cycle is exactly the time that such soils, greases, and oils can resettle on clothing. Dry laundry detergent formulations sold in the stores contain antideposition agents which are not included in liquid formulations. Too, dry formulations generally are phosphate based and there is no ingredient better at removing stains and preventing restaining.

Because water operators do not necessarily have a background in formulating household cleaning products, it would be most difficult for them to think of asking their customers the appropriate questions in order to resolve the matter. We hope that these stories will encourage operators to ask such questions with the hope of resolving the matter for their customers and at the same time, make a friend.

5

Thought of the month

Next time there is a suggestion to go to bid on any product, consulting services, or equipment, remember you get what you pay for. Sometimes you even get more than you bargained for... see section 10-- The Bidding Process.

6

Anyone know the answers?

1) What sources of water supplies have suffered the largest number of disease outbreaks?

2) At a water pH of 8.5, how much titratable chlorine is required to produce 0.3 mg/l of undisassociated HOCL (hypochlorous acid)... enough to inactivate Coxsackie A2 virus in 20 minutes at 5^{O}C?

3) How many different types of corrosion can you name?

7

Fe & Mn reality check

There have been major efforts across the United States, as well as around the world, for years to remove iron and manganese from water supplies. The main thrust for removal, of course, is esthetics. Higher levels of iron and manganese (above 0.3 ppm) simply cause staining problems and are not tolerated in finished drinking water supplies, whether these supplies are surface or ground water. Methods of removal include oxidation, aeration, permanganate treatment, flocculation, filtration, green sand filtration, etc. Many millions of dollars are spent annually to effect and maintain this removal. So what if it is left in the water... as long as it does not oxidize nor cause stains? Let's see.

The World Health Organization produces some very interesting iron and manganese facts:

• Several animal studies suggest manganese may have an anticarcinogenic effect.

• Adverse health effects can be caused by inadequate intake of manganese.

• Laboratory animal studies support a provisional health guideline of 0.5 ppm for manganese to adequately protect public health.

• Drinking mineral water regularly can add significantly to manganese uptake.

• Daily human intakes of iron from food is 10-14 mg and drinking water containing 0.3 ppm would contribute 0.6 mg to the total intake.

• With the exception of the genetic iron overload disease called haemochromatosis, human intake of 0.4-1 mg iron per kg of body weight over long periods of time are unlikely to cause adverse effects.

• Both iron and manganese are essential trace elements necessary for all living organisms

So, as long as the iron and manganese are kept from oxidizing and causing stains, they really are a benefit for human consumption. Why not simply keep them sequestered and leave it at that? The key is to keep them completely sequestered all the way to the tap...even through the higher temperatures of hot water heaters. Only SeaQuest can do that and only SeaQuest can continue to keep higher levels of iron and manganese sequestered when all other sequestering products can't or lose this ability over time and temperature.

Understand that this is not an advocation against removing these minerals from water supplies, simply an acceptable alternative approach should the cost and maintenance of removal become so high that it simply is no longer worth it.

While we're at it, let's look at some other minerals (which every living cell on this great planet of ours depends on for proper function and structure) often found at very low levels in drinking water supplies . They are:

• Boron--needed for healthy bones and metabolism of calcium, phosphorus, and magnesium

• Calcium--needed for strong bones, teeth, and healthy gums and blocks absorption of lead into bones and teeth

• Chromium--directly involved in the metabolism of glucose, (i.e. glucose tolerance factor)

• Magnesium--vital catalyst in enzyme activity, especially those enzymes involved in energy production

• Molybdenum--promote normal cell function

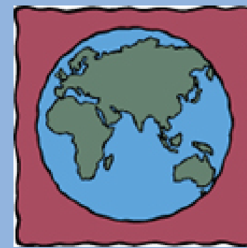
• Selenium--vital antioxidant protecting the immune system

• Vanadium--necessary for cellular metabolism and formation of bones and teeth

• Zinc--essential for prostrate gland function and growth of reproductive organs

So what do you think of your water supply now? Feeling better? You should. With all the time, effort, money, and worry spent trying to eliminate these minerals, it pays to take a mineral reality check once in a while. We really do need to ask ourselves, "Is it really worth it? What are we gaining? **...but even more so... what are we losing?**

8 News from over there



In North America, one of our distributors (who services private water supply systems) came across two private water well supplies both containing over 10 ppm iron, 5 ppm manganese, 1700 ppm hardness, and 2500 ppm TDS for one and 9000 TDS for the other. Even though these wells were not used for drinking purposes, our distributor decided the easiest and least costly approach would be to use SeaQuest. He installed liquid feed systems to treat the well waters and all color complaints completely disappeared... even toilet stains.

How's that for sequestration!

9 "All phosphates are the same!"

About two years ago, one of our customers (Mario Gonzales) came up with an excellent on line test to differentiate sequestering ability between phosphate drinking water additives as each supplier told him their product was the same. Being a reasonable customer, he said, "Okay, let's see how your product does in our sequestering test."

Let's see what he did... and of course how the products did. The test protocol he developed is as follows:

Working Solutions

500 mg/ T-Cl_2 Bleach Solution

1. Dilute 5 ml concentrate 5.25% bleach to 500 ml
2. Store in dark until use.

1000 mg/L Total Product (TP) Solution

Liquid Products make up:

1. mg/l TP = (TP) x (1000 mg/g) x (1000 ml/l)
2. Pipette [X ml TP] = {(1000 ml x 1000 mg/l)/mg/l TP} into 1000 ml volumetric flask and dilute to 1000 ml

Dry Products make up:

1. Store in desiccator until use
2. Weigh out exactly 1.0000 g TP and dilute to 1000 ml in a volumetric flask

Sample Collection

1. Take 2 x 5 gal Carboys to each well to be used as a test matrix
2. Collect sample before treatment (NO Chlorine or Phosphate products). Care should be taken not to aerate sample (to prevent Fe & Mn from being oxidized).
3. Perform routine field tests (pH, Conductivity, Temp, etc.)
4. Deliver sample to lab promptly after collection

Lab tests

1. Test T(total)-Cl_2 residual Chlorine electrode Method. If Chlorine is detectable reject and re-sample.
2. Add 1 ml 500 mg/l bleach solution to 500 ml of well water. After 5 minutes test spiked solution for F(free)-Cl_2 residual and record. (Should = 1.0 mg/l F-Cl_2)
3. From each well sample (for routine external analysis) collect 500 ml for dissolved iron and manganese, total Calcium and Magnesium, 500 ml for Total Phosphate, and 500 ml for Alkalinity analysis.
4. Pour exactly 500 ml sample into each of prelabeled 500 ml beakers (Well 29 = 42 beakers, Well 30 = 42 beakers).
5. Spike the designated sample with the product volume that corresponds to agreed upon dosage (mg/l Total product: expected mg/l Fe + Mn).
6. Stir the samples with stirring rods.
7. Spike each of the well samples with 1 ml bleach solution (Stir while slowly adding bleach solution).
8. Split total number of samples.
   a) To one set make initial observations and let stand in cool dark place for 4 days (detention times can be adjusted based on expected field conditions or company claims of product effectiveness).
   b) At the end of each 24 hour period note color variations, particulate formation, and other physical differences for each test sample. Stir sample thoroughly and slowly filter half through 0.45 micron filter paper. Repeat filter procedure with other half at end of day 4.
9. From the second set, stir thoroughly after 1st hour and slowly filter through a white 0.45 micron filter paper. Repeat filter procedure after 3rd hour and then again after 5th hour. After filters dry, line up and compare. See following results chart.

Example

Day 1 Filtration

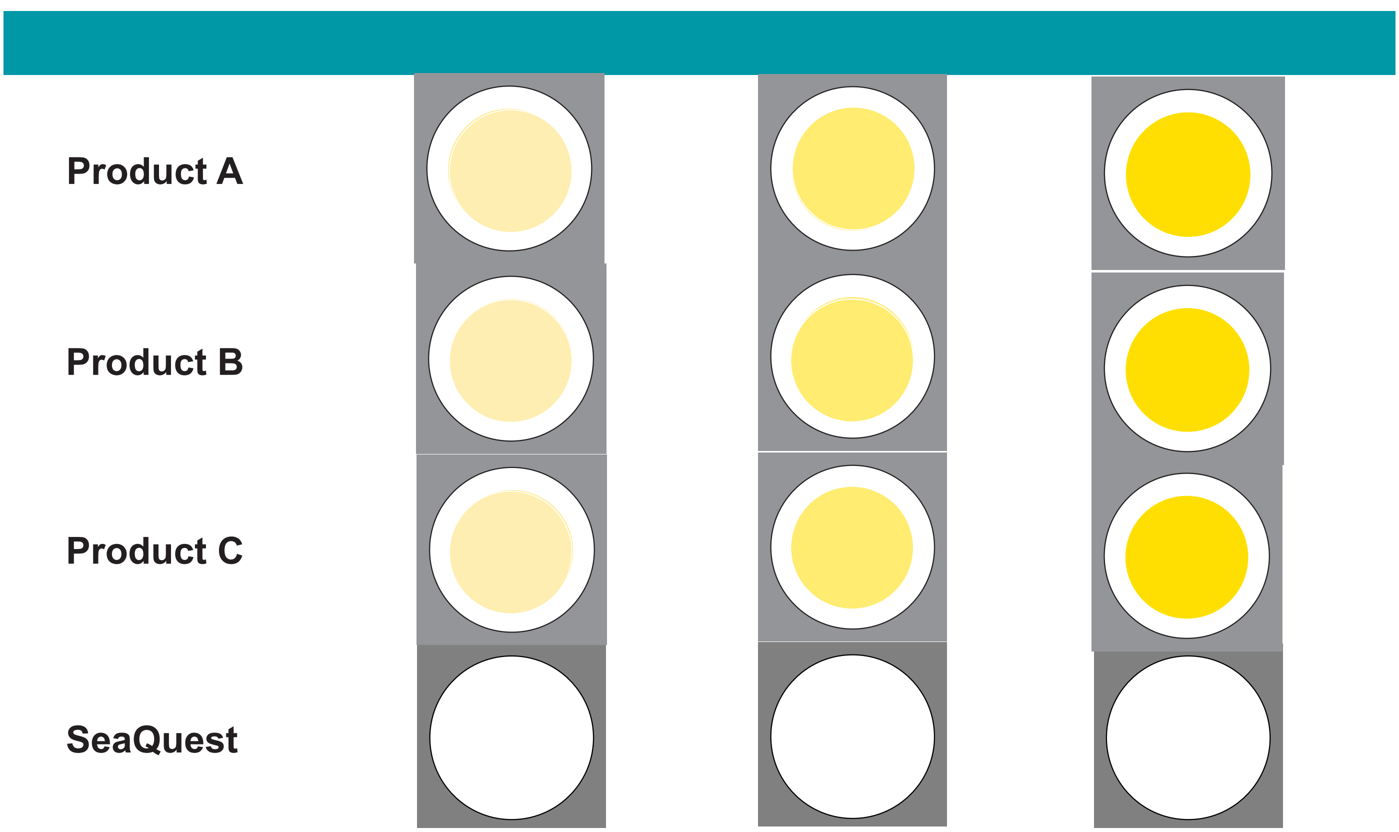
Location	Test Ratio
Well 29	2 mg/l TP:1mg/l Exp Fe+Mn
Well 29	4 mg/l TP:1mg/l Exp Fe+Mn
Well 29	8 mg/l TP:1mg/l Exp Fe+Mn
Well 29	10 mg/l TP:1mg/l Exp Fe+Mn
Well 30	2 mg/l TP:1mg/l Exp Fe+Mn
Well 30	4 mg/l TP:1mg/l Exp Fe+Mn
Well 30	8 mg/l TP:1mg/l Exp Fe+Mn
Well 30	10 mg/l TP:1mg/l Exp Fe+Mn

Day 4 Filtration

Location	Test Ratio
Well 29	2 mg/ITP:1mg/l Exp Fe+Mn
Well 29	4 mg/ITP:1mg/l Exp Fe+Mn
Well 29	8 mg/ITP:1mg/l Exp Fe+Mn
Well 29	10 mg/ITP:1mg/l Exp Fe+Mn
Well 30	2 mg/ITP:1mg/l Exp Fe+Mn
Well 30	4 mg/ITP:1mg/l Exp Fe+Mn
Well 30	8 mg/ITP:1mg/l Exp Fe+Mn
Well 30	10 mg/ITP:1mg/l Exp Fe+Mn

Controls	Quantity
Nanopure water + Bleach Spike	2
Well (29) + Bleach Spike	2
Well (30) + Bleach Spike	2
Well (29) + No Bleach Spike	2
Well (30) + No Bleach Spike	2

Filter Results Chart



SeaQuest surpassed all products tested at 5+ hours.

Anyone know the answers:

1) Water supplies suffering the most outbreaks were the non-community supplies such as cruise ships, resorts, summer camps, boarding schools, and other small private supplies.

2) At a pH of 8.5, it takes 3.0 mg/l of titratable chlorine. At a pH of 7.0 it only takes 1.0 mg/l (66% less).

3) Uniform corrosion, galvanic corrosion, pitting corrosion, concentration cell corrosion, tuberculation, crevice corrosion, erosion corrosion, cavitation corrosion, dealloying or selective corrosion, graphitization, stress corrosion, microbiologically induced corrosion, and stray-current corrosion.

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10 The bidding process

When the least expensive product is bought by bid, what is purchased? Such decisions can and have resulted in a myriad of problems actually costing far more time and money instead of less. Listen to a typical war story:

A SeaQuest customer went to bid for phosphate corrosion control after successfully running on SeaQuest for one year because purchasing wished to save money. The bid was won by a competitor hereafter known as Product D. Their product, which was claimed to be the same and used at the same rate as SeaQuest, started treatment. Six months into treatment, manganese problems got so out of hand it caused the loss of much finished treated water which had to be wasted.

With no other alternative, the customer attempted to solve their manganese problems by increasing pH and pretreatment chlorine dioxide. All this ended up in increasing the THM levels to the point of exceeding limits. So, this bid process choosing the least expensive product actually increased costs to the customer from:

a) increased chlorine usage,
b) increased usage of pH control,
c) and increased water loss sent to waste.

Adding up all these losses versus adding up all the savings from the least expensive winning bid product, who was winner? Certainly not the bidding process.

Another war story:

A SeaQuest customer in New England went to bid after being on successful use of SeaQuest for over two years in order to cut treatment costs. Upon completion of the bidding process, again Product D won. After being on Product D for 9 months, the customer noted that their 90th percentile copper draw numbers were rising rapidly. On top of this, the system began experiencing calcium fallout in their aerators. Needless to say, it did not take too much to get them back on SeaQuest at the same pricing they were paying before going to bid. Will they go to bid again? No, they have been there...done that.

Editor's Note:

We have attempted to provide our readers with topics we believe to be of interest based on numerous questions and responses which have been posted on the AWWA Discussion Forum, Water Technology Forum, and other drinking water forums. We welcome all responses, recommendations, and suggestions on related topics you wish to see discussed.

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