Saving the Homosassa

Robert Garrison

As today's underground infrastructure ages, more force mains are at risk of rupture. Unfortunately, most municipalities and private utilities wait until a crisis to take action. That's just what happened at the Homosassa River in Citrus County this past April. A six-inch force main that lay 26 feet beneath the river ruptured. Potentially thousands of gallons of raw sewage per day could have begun leaking into the pristine river with drastic consequences.

The Homosassa River is a showcase of bird and animal life. A vast spring of fresh, clear water is the centerpiece of a 179-acre state park and the headwater of the river. The sparkling water flows for about 12 miles to eventually merge into the Gulf of Mexico. Resorts, hotels, marinas, and retailers make their living from the natural attraction.

So when the pipe began to leak, the call to action was immediate. The pipeline was shut down and a trucking company hired at $5,000 per day to transport the untreated waste water 12 miles around the headwater of the spring to a lift station on the opposite side of the river. RHV Utilities, which manages the lift stations on both sides of the river, called its consulting engineers, Berryman & Henigar of Crystal River, to resolve the situation as quickly as possible.

In years past when the 12-year old ductile pipe leaked, divers had placed steel repair clamps over the leaks. These two-foot repair sections worked well enough, but there were now 36 clamps in place. The leaks had become more frequent, and adding more clamps was no longer an option because clamps cannot overlap. Furthermore, the river water had turned from fresh water to brackish over the years, creating conditions which accelerated the corrosion process.

The consulting engineers determined the leaks had to be stopped immediately with no chance of failure. They specified a polyvinyl chloride (PVC) liner as the necessary repair material because of its low coefficient of linear thermal expansion, durability, and long-life expectancy.

Berryman & Henigar contracted Griner's Pipeline Services of Mount Dora to install AM-LINER, an EPA-approved, strong, seamless, PVC pipe. It would need to cover a distance of 525 linear feet across the river. AM-LINER was especially appealing because it is not susceptible to tracking or shrinkage. Most important, as a fold and form material, it could be put into operation quickly and cost effectively.

If the liner did not work, there would be no way to lay a replacement force main. EPA will not issue new permits for pipeline river crossings. Estimates were in the millions to lay pipe for the 12 miles around the river, not to mention the disturbance it would cause to the trees, businesses and homes along the river's edge. Permitting alone for the project could take more than six months.

Installation of the liner would cost less than $100,000, would be treated as maintenance to the existing pipe and not require any permits, and could begin immediately.

We inspected the site and noted with concern that the force main was in abysmal condition and at risk of further rupture at any moment. The liner would have to act as a stand-alone pipe in places where the force main was completely deteriorated. We devised a plan that would rehabilitate the pipe with no disturbance to the river's infrastructure and with minimal downtime.

Work began on March 4, 1996, with a six-man crew. Overseeing the project were the engineering consultants and representatives from EPA and DEP.

During the first day pit excavations were made on both sides of the river, and the old pipe was cut away to allow entry of cleaning equipment. Using high pressure jet equipment, our crew cleaned the pipe of debris. Years of raw sewage build-up made even this initial task a challenge and further revealed the poor condition of the ductile pipe.

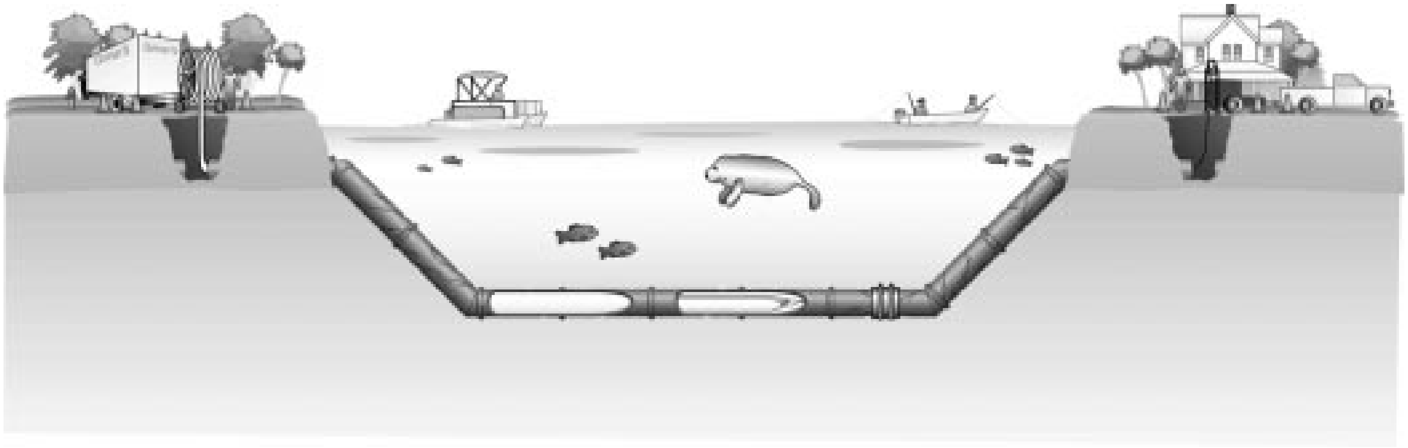
Next, we sent a state-of-the-art robotic camera through the pipe. The camera, purchased in Germany and the only one of its kind in the United States, was able to propel itself forward, backward, and even sideways through the pipe to provide an accurate picture of the interior condition of the fractured pipeline. Our crew studied the video to further assess the seriousness of the situation.

On the second day the folded liner was installed by sending a tow line through the pipe that pulled the deformed PVC material in place. Two-way radios were used to coordinate work on opposite sides of the river. Next, steam was introduced through the liner to make it pliable and to form it to the existing host pipe. The steam pressure was then used to propel a squeegee through the pipe, removing trapped air and water. The squeegee especially helped to mold the material at the pipe's two 45 degree angles, ensuring that no large rib or bubble formed which would diminish flow capacity.

Finally, the liner was cooled under pressure with compressed air to complete the molding process and lock the pipe in place. The repaired pipeline was fully functional and ready to return to service in only a few hours.

We estimate the AM-LINER will last approximately 50 years, two or three times as long as metal or ductile pipes. No excavation had been required making installation fast and economical. The liner created a jointless interior, impervious to exfiltration and highly resistant to corrosion and abrasion.

To ensure the new pipe structure's strength, EPA required that it endure a 25-psi pressure test for two hours with zero loss



of pressure. A nearby fire hydrant was turned wide open, flushing 600 gallons of water per minute through the new pipeline. The system passed easily. In fact, it was found that flow had actually increased with the new pipeline because of the low friction coefficient of PVC.

No restrictions were imposed on the pump station. The portable treatment plant was able to be removed, and the force main put back in operation.

Today, life is as it should be back on the Homosassa River. Oblivious to the life-threatening contamination that had once put the river in peril, manatees, fish, birds, and visitors all take pleasure in its beauty and natural resources.

But while an emergency at the Homosassa River was averted, it should serve as a lesson to municipalities and private utilities, which often wait until a catastrophe to react. The force main network that winds beneath our roads, rivers, and buildings is subject to deterioration that makes the threat of an eventual contamination accident a likelihood. A routine maintenance program, including inspecting, cleaning and relining force mains, is badly needed. The Homosassa River was a close call. Next time, we may not be so lucky.

Robert Garrison is vice president of engineering/technical services, Griner's Pipline Services, Inc., Mount Dora.

The Impact of Water Management Initiatives and Everglades Restoration on Public Water Supplies in South Florida

Fred Rapach and Patrick J. Gleason

Times are a changin' in South Florida. A plethora of water management initiatives are changing forever the way water is managed. Water management and water availability for public water supplies in southeast Florida are at a major turning point as a consequence of efforts to restore the Everglades and meet the needs of future growth. The federal government has decided to make restoration of the Everglades a campaign issue in the 1996 presidential race. Although the 1996 Florida Legislature elected not to perform major surgery on Florida water law after considering about 40 water bills, water allocation and policy issues will return in the 1997 session. Within the next two to three years, planning and legislative efforts will change the way public water suppliers go about the development of water needed for future growth, not just for South Florida, but for the entire state. However, four major water resource planning initiatives are currently underway in South Florida that will significantly alter the way water is managed for urban, environmental and agricultural uses.

The need for an improved water management system is recognized at state and federal levels. However, these efforts are largely oriented towards Everglades ecosystem restoration and to a lesser extent, meeting the needs of future urban growth. Local governments are concerned about their current level of representation in the four major water resources initiatives retooling the Everglades ecosystem because these initiatives will determine future water cost and availability to the urban areas.

Four major water resource initiatives currently underway in Southeast Florida are: The Everglades Forever Act, the Governor's Commission for Sustainable South Florida, the U.S. Army Corps of Engineers Central and Southern Florida Project Restudy (COE Restudy), and the South Florida Water Management District's (SFWMD) Lower East Coast Regional Water Supply Plan (LEC Plan).

Everglades Forever Act

The 1994 Florida Everglades Forever Act (EFA) is a $1.1 billion plus effort and a multi-faceted program that will develop over 40,000 acres of Stormwater Treatment Areas to remove phosphorus from water discharged to the Everglades. The Legislature has indicated that "The Everglades Program is an appropriate foundation on which to build a long term program to ultimately achieve restoration and protection of the Everglades Protection Area." Design and land acquisition of the Stormwater Treatment Areas is currently underway. Some of the original conceptual planning is changing due to a realization that additional "superior treatment technology" may be necessary to remove phosphorus to a level around 10 ug/L. Chemical treatment, filtration, limerock and submerged aquatic vegetation are being looked at as technologies to bring about the removal of phosphorus.

The federal "Farm Bill" providing $200 million for Everglades projects may allow purchase of the Talisman property (55,000 acres) and perhaps 100,000 additional acres if the price is right. These additional areas will remove lands that are contributors to the phosphorus problem, provide storage of stormwater generated by the Everglades Agricultural Area, and potentially eliminate all backpumping into Lake Okeechobee. The efficacy of storing water in the Everglades Agricultural Area is being challenged by the sugar industry. SFWMD is planning an investigation of storage reservoirs in the Everglades Agricultural Area after October, 1996.

Governor's Commission for a Sustainable South Florida

The Governor's Commission for Sustainable South Florida (Governor's Commission), created by Executive Order 94-54 of Governor Lawton Chiles, is a blue-ribbon panel of 35 gubernatorial appointees. The goal of the Governor's Commission has been to develop recommendations to the Governor for developing a sustainable South Florida—a community that does not achieve growth today at tomorrow's expense. On October 1, 1995 the Governor's Commission transmitted to the Governor a report entailing 110 recommendations and hundreds of action steps for restoring the Everglades ecosystem, achieving a clean healthy environment, combating the spread of exotic species, limiting urban sprawl, protecting wildlife and natural areas, creating quality communities and jobs, improving the quality of life, improving intergovernmental partnerships, and improving scientific information coordination.

On December 1, 1995, the Governor's Commission developed a list of options for transmittal to the COE as a preferred alternative for use by the COE in the restudy of the Central and South Florida Project. This list is being refined and a conceptual plan developed that would enable restoration of the Everglades and provide for future water supply. The commission would like to have the conceptual plan ready by the end of summer 1996 for transmittal to the COE as the guiding document and basis for congressional appropriations for their restudy.

U.S. Army Corps of Engineers Restudy of the Central and Southern Florida Project

The COE Restudy is a congressionally-authorized project to restore the Everglades ecosystem (Kissimmee River to Florida Bay) and improve future water supplies through 2050. The emphasis of the COE Restudy has been primarily environmental. Only extensive lobbying by the urban area has resulted in a commitment to examine future urban water supply demands.

The existing system of nearly 1000 miles of canals and levees and 240 water control and pumping stations does not meet today's environmental, water supply and flood control needs. The COE is currently in the first year of the Feasibility portion of the four-year Restudy. The COE will evaluate the Governor's Commission Conceptual Plan for southeast Florida beginning this summer and will come out with its own draft plan by

August 1997. At that time, the COE will produce an environmental impact statement on the plan. After completion of the EIS, the COE will go to congress with a final plan and request funding to fix the existing water management system.

Six draft conceptual plans have been developed, the most extensive of which will cost $2 billion to implement. Continuous lobbying by the urban area will be necessary to keep the COE on track to develop a plan that will assist the needs of urban communities along the southeast coast. Decision-making by the COE Restudy will greatly influence the LEC Plan.

Lower East Coast Water Supply Plan

SFWMD is developing the LEC Plan, a water supply plan for Monroe, Dade, Broward, and Palm Beach counties to meet water demands through 2010. Population in the plan area will increase from 5 million to 8 million by 2010. While this is a water supply plan for meeting agricultural and urban demands, it is inherently tied to Everglades restoration. Meeting ecosystem restoration demands will be a priority. Less water from existing facilities will be available for urban water supply. The plan is still in review and a selection of options known as Alternative 5 is currently being modeled. The plan options include reducing seepage out of the Everglades towards the coastal areas, a revised schedule for Lake Okeechobee, and operational changes to the existing water management system, including a plan to route L08 water to northern Palm Beach County. The plan examines an option to place a portion of future population water demands in new wellfield locations farther inland. The plan examines the impact of using regional scale aquifer storage and recovery around Lake Okeechobee and the development of local utility aquifer storage and recovery to boost available water supplies.

The expectation is that the cost of water for urban water supplies will increase in the future. SFWMD has decided to develop an "Interim LEC Plan" to cover the next five years until the COE's Feasibility Study is completed. A Final LEC Plan will probably follow the COE's Restudy plan. The Interim Plan will be out in draft form by September 1996. SFWMD will be taking cues from the Governor's Commission Conceptual Plan. SFWMD intends to convert the Interim Plan's recommendations into policy, and where applicable, rules for permitting.

SFWMD is working with the Southeast Florida Utility Council to develop a plan for implementation of regional aquifer storage and recovery to provide more water to public water supplies. In addition, the district is awaiting a reply from EPA on development of an untreated surface water aquifer storage and recovery project using raw Okeechobee water as its source.

The state found that when the population growth detailed in every municipality's comprehensive plan is tallied up, a population of nearly 90 million people is projected for the state, which currently has a population of about 14 million. As a consequence of this, the 1996 Florida legislature worked long and hard to attempt changes to Florida's water management legislation, but it was not to be. The legislature dealt primarily with bills originating from Representative John Rayson's House Select Committee on Water Policy, Senator Phil Lewis' Water Management District Review Commission, and the Governor's office acting through DEP and the water management districts.

After yeoman effort by utility representatives, only one minor bill was passed. It affects the development of minimum flows and levels in Hillsborough, Pasco, and Pinellas counties; requires a reevaluation of the West Coast Regional Water Supply Authority; and authorizes the Governor's office to approve water management district budgets. The bill will not affect South Florida but may set the stage for legislative changes in the 1997 session.

The surplus or deficit of water available that will be determined in the LEC Plan is unknown at this time. However, Everglades restoration and long-term growth will likely show a shortfall of water available over a long-term planning horizon when compared with water quantities that are currently available over a long-term planning horizon when compared with water quantities that are currently available from existing water management facilities. Based on existing water resource initiatives and proposed legislation, it is our opinion that public water supplies would benefit by positioning themselves or promoting the following prior to March 1997:

- *Supporting maintenance of a fluctuating Lake Okeechobee Operational Schedule that achieves ecosystem "sustainability."* Lake Okeechobee is a historical source of groundwater recharge to coastal wellfields during dry periods and is the most efficient water storage area in southeast Florida. A schedule that provides for storage of water rather than discharge to estuaries, and that is able to provide water for Everglades restoration and coastal communities as well as benefit in-lake environment, is essential.
- *Development of regional or sub-regional water supply plans.* The Governor's Commission is strongly emphasizing this approach. Central and Northern Palm Beach County water utilities and drainage districts are currently discussing such a relationship to increase storage, restore wetlands, and reuse 30 MGD of reclaimed water. All these uses would have the effect of increasing water availability for public supply.
- *Development of inland wellfields or sources for coastal public water supplies.* Modeling studies by SFWMD suggest that more water will be available if future demands of the coastal utilities are placed at new locations farther inland. Existing demands would continue to be met from existing facilities.
- *Increasing surface water storage in order to retain storm water.* More than 2 million acre feet of water is wasted by discharge to tidewater along the southeast coast based on a report by the Governor's Commission. The SFWMD is currently evaluating storage of water in a Lake Belt/Water Preserve Area in Dade County. Development of a Lake Belt/Water Preserve Area is a key element to restoration of flows to Everglades National Park and the provision of water to Miami Dade Water and Sewer Department's Northwest Wellfield. SFWMD has acquired land for a reservoir in southwestern Palm Beach County. Other land may potentially be available in Palm Beach County in the Agricultural Reserve Area or east of the Florida Turnpike. In some cases, storage of excess surface water may be possible in Aquifer Storage and Recovery (ASR) wells.
- *Implementation of Alternative Water Supplies, where available.* ASR, indirect potable reuse, reuse for aquifer recharge purposes, and reverse osmosis are some of the choices available. These need to be technically, economically, and environmentally feasible prior to implementation by utilities.

Fred Rapach is with the Palm Beach County Utilities Department, West Palm Beach. Patrick J. Gleason, P.E., is with Camp Dresser and McKee, West Palm Beach.

Review of Carbonate and Sulfide Equilibrium in Drinking Water Systems

Steven J. Duranceau and Erik L. Melear

Chemical equilibrium reactions involve solid, liquid, and gas phases, or any combination thereof, and can be established in systems involving more than one phase. Many of the reactions important to drinking water treatment and distribution systems do not proceed to completion, but instead tend to result in two opposing reactions that occur at the same rate. Chemical reactions in water are used to shift the chemical equilibrium to improve or enhance the removal of substances from solution.

The two most common methods for shifting chemical equilibrium include precipitate formation and pH adjustment. Both methods are used extensively in water treatment, as in applications that remove excess calcium and magnesium ions, strip hydrogen sulfide, or reduce corrosivity of groundwater supplies. As an example, hydrogen sulfide removal can be enhanced significantly by decreasing the pH of the groundwater from 7.6 to 6.3. In a similar manner, the copper corrosivity of groundwater can be eliminated by raising the pH to approximately 8.0.

Operation of a water treatment plant is dynamic and can be challenging. One treatment method can produce conflicting or opposite chemical reactions and alter the optimal operating conditions for the facility. Many water treatment processes, such as pH adjustment and air stripping or aeration, are based on the chemical reactions of the carbonate and sulfide systems. A working knowledge of these chemical reactions and equilibrium would improve unit process design and promote economical, efficient facility operation, particularly for those facilities relying on such chemistry. The purpose of this paper is to present an overview of chemical equilibrium reactions and several examples to illustrate how to apply and use equilibrium constants for the carbonate and sulfide systems.

The Equilibrium Constant

Most chemical reactions are reversible to some degree. The final state of equilibrium determines the concentration of the reactants and products. Chemical equilibrium occurs whenever two exactly opposite chemical reactions take place at the same time and rate. A chemical reaction in equilibrium can be expressed as a constant by the law of mass-action, which was discovered by Guldber and Peter Waage in 1864. For the general chemical reaction expressed by equation (1) below, an increase in either chemical A or B shifts the equilibrium to the right, while an increase in concentration of chemical C or D drives the reaction to the left.

The equilibrium constant, K, can be expressed as the ratio of the products to the reactants. For the chemical reaction, aA + bB = cC + dD, the equilibrium constant can be expressed as shown in equation (1):

$$K = \text{products/reactants} = [C]^c[D]^d / [A]^a[B]^b \qquad (1)$$

The law of mass action has many applications in water treatment and is widely applicable (Zumdahl 1986). It correctly describes the equilibrium behavior of many chemical systems in drinking water. One such application is calcium removal with quick lime as shown in Example 1.

Example 1. Write the equilibrium expression for the addition of one mole of lime [CaO] to water having an appreciable calcium hardness.

Solution. Only one equation needs to be written for addition of pure solid lime [CaO] to hard water:

$$CaO + Ca(HCO_3^{1-})_2 - 2\ CaCO_3(s) + H_2O$$

Consequently, $K = [CaCO_3]^2\ [H_2O] / [CaO][Ca(HCO_3^{1-})_2]$

Dissociation of Water and pH

When clusters of water molecules collide with sufficient energy and orientation, the relatively weak hydrogen-oxygen bonds break, and the resulting protons can bond to unshared electron pairs of oxygen atoms. Since water is considered to be a weak electrolyte, it will become dissociated according to the equation

$$H_2O + H_2O = H_3O^+ + OH^- \qquad (2)$$

In all aqueous solutions, the dissociation equilibrium of water exists and must satisfy the mathematical condition presented in equation (1). Using the law of mass action, the equilibrium constant for water can be defined as:

$$K = [H_3O^+][OH^-]/[H_2O]^2 \qquad (3)$$

In all dilute solutions, such as drinking water systems, the concentration of water can be considered a constant and combined with the constant. Using the equilibrium constant K from equation (3), K_w can be expressed as follows:

$$K_w = K[H_2O]^2 = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \qquad (4)$$

K_w is usually called the dissociation constant or ion product of water, and has a value of 1.0×10^{-14} at 25 degrees Centigrade. In pure water, all the H_3O^+ and OH^- must come from the dissociation of water molecules, and hence, both are equal to 1.0×10^{-7} moles/liter (*M*) at equilibrium.

Since a liter of water at 25°C weighs 997 grams, and a mole of water weighs 18.0 grams, one liter of water contains 997/18, or 55.4 moles. This means that on average, there is one hydronium ion [H_3O^+] and one hydroxide ion [OH^-] for every 554 million water molecules. As a convenience for working with such small aqueous concentrations, the pH scale was developed to express the concentration of H_3O^+, often referred to as a H^+.

The pH scale is defined as:

$$pH = -\log [H_3O^+] \text{ or } [H_3O^+] = 10^{-pH} \qquad (5)$$

Because pH is based on a log-10 scale, a pH change of 1 unit is equal to a 10 fold change in the hydrogen ion [H^+] concentration. Consequently, the pH decreases as the [H^+] increases.

Example 2. Calculate [OH^-] and the pH in (a) 0.02 *M* H_3O^+, (b) a solution containing 0.002 mole of H_2SO_4 per liter, and (c) 1.0×10^{-10} *M* H_3O^+.

Solution. (a) Since $H_3O^+ = 0.02$, [OH^-] can be found using equation (3) and pH using equation (4):

$$[OH^-] = (1.0 \times 10^{-14}) \div [H_3O^+] = (1.0 \times 10^{-14}) \div (0.02) = 5.0 \times 10^{-13} M$$

$$pH = -\log [H_3O^+] = -\log [0.02] = 1.7.$$

(b) H_2SO_4 is a strong acid, hence $[H_3O^+] = 0.002\ M$ and the $[OH^-]$ is:

$[OH^-] = 1.0 \times 10^{-14} \div [H_3O^+] = (1.0 \times 10^{-14}) \div (0.002) = 5.0 \times 10^{-12}\ M$

$pH = -\log [H_3O^+] = -\log [0.002] = 2.7.$

(c) $[OH^-] = 1.0 \times 10^{-14} \div [H_3O^+] = (1.0 \times 10^{-14}) \div (1.0 \times 10^{-10}) = 1.0 \times 10^{-4}\ M$

$pH = -\log [H_3O^+] = -\log [1.0 \times 10^{-10}] = 10.$

The Carbonate System

Carbon dioxide gas dissolves in water to an extent determined by its partial pressure, and by the interaction of dissolved carbon dioxide with other solutes in the water. When carbon dioxide dissolves in water, it reacts with water (hydrates) to yield carbonic acid as follows:

$$CO_2 + H_2O = H_2CO_3 \qquad (6)$$

If the pH of the water is greater than 4.5, carbonic acid quickly dissociates (or ionizes) into a hydrogen ion and bicarbonate ion according to the reaction:

$$H_2CO_3 = H^+ + HCO_3^{1-} \quad pK_1 = 6.3 \qquad (7)$$

Equation (7) states that at a pH of 6.3, half of the dissolved species for any given concentration is bicarbonate, and the other half remains as carbonic acid in the form of a dissolved gas. At pH values above approximately 8.3, bicarbonate ion is transformed to carbonate in solution, as follows:

$$HCO_3^{1-} = H^+ + CO_3^{2-} \quad pK_2 = 10.3 \qquad (8)$$

Equation (8) states that at a pH of 10.3, half of the dissolved species of the carbonate system is in the form of bicarbonate, and half will exist as the carbonate ion. A distribution diagram for the carbonate system is shown in Figure 1. The pK values occur at the intersection of each chemical species lines.

At pH values above 10.3, solid calcium carbonate seeks to attain an equilibrium with calcium and carbonate ions in solution. The precipitation potential for calcium carbonate depends upon the pH, hardness, and alkalinity of the potable water. The precipitation potential increases as these three parameters increase. Since the equilibrium reaction favors the carbonate ion as pH rises, this in turn provides a driving force for the calcium ion equilibrium to form calcium carbonate solid.

The alkalinity of most natural water supplies is caused by dissolved bicarbonate $[HCO_3^-]$ species. In the pH range of 4.4 to 8.2, equilibrium is defined as the balance between excess carbonic acid and bicarbonate ions. Alkalinity is responsible for buffering pH changes in water. Alkalinity of a water is a measure of its capacity to neutralize acids (or absorb hydrogen ions without significant pH changes). It is important to maintain a balanced alkalinity in the water distribution system to avoid pH decline, fluctuations in equilibrium, and potential increases in lead and copper concentrations at consumer taps.

In most potable waters, alkalinity is described as follows:

$$\text{Total alkalinity (Alk)} = [HCO_3^{1-}] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (9)$$

When other bases besides carbonates and hydroxides are present, such as orthophosphate (inhibitor), hypochlorite (disinfectant), ammonia, and silica, then the alkalinity definition can be expanded to include these ions:

$$\text{Alk} = [HCO_3^{1-}] + 2[CO_3^{2-}] + 2[HPO_4^{2-}] + [OCl^-] + [NH_3] + [H_3SiO_4^-] + [OH^-] - [H^+] \qquad (10)$$

Abbreviations & Symbols

Alk	alkalinity
pH	negative logarithm of the hydrogen ion molar concentration
pK	negative logarithm of the equilibrium constant
~	approximately
[ ]	molar concentration, moles per liter
K	equilibrium constant
K_w	equilibrium constant for water
M	molar concentration, moles per liter
mg/L	milligrams per liter
H_2O	water
H_3O^+	hydronium ion
SO_4^{2-}	sulfate
Na^+	sodium
H_2S	hydrogen sulfide
HS^{1-}	bisulfide
S^{2-}	sulfide
OH^-	hydroxide ion
CO_2	carbon dioxide
H_2CO_3	dissolved carbon dioxide
HCO_3^{1-}	bicarbonate ion
CO_3^{2-}	carbonate ion
$CaCO_3$	calcium carbonate
OCl^-	hypochlorite

Waters that are buffered and slightly oversaturated with calcium carbonate (as is the case with many Florida groundwater supplies) tend to be less corrosive than poorly buffered or undersaturated calcium carbonate waters, primarily because a coherent film of calcium carbonate helps protect internal pipe metal surfaces in buffered systems. Water systems that are poorly buffered will fluctuate between oversaturation and undersaturation, and the calcium carbonate film will be tubercular and loosely adherent, offering limited corrosion protection (Stumm 1960, Butler 1991).

Groundwater from the Floridan Aquifer has moderate hardness (100 mg/L to 175 mg/L as $CaCO_3$). pH adjustment is ideal for copper corrosion control for these potable water systems. The pH can be adjusted in 0.15 pH unit increments until the desired operating setpoint is achieved. The benefits of pH adjustment for copper corrosion control with this type of groundwater include: (1) the low solubility of copper at pH values above 7.7; (2) cost-effectiveness of this treatment method; and (3) simplicity of operation.

However, an increased operating pH may prove troublesome for those water supplies containing elevated levels of iron. At higher pH values, iron will precipitate out of solution, and cause aesthetic problems for consumers (yellow-brown and red water). In addition, if the groundwater contains appreciable noncarbonate hardness (sulfates), or is a hard groundwater (hardness greater than 175 mg/L as $CaCO_3$), pH adjustment may be limited due to excessive scale in water mains, on pump impellers, and on the heating elements of hot water heaters. The use of pH adjustment for corrosion control is further complicated because (1) chlorine residuals are not as effective at elevated pH values and (2) total trihalomethane concentrations can be significantly increased.

Inhibitors, such as phosphoric acid or blended phosphate products, have also been shown to be effective for corrosion control treatment. Use of phosphoric acid in a moderate hardness Floridan Aquifer groundwater increases the phosphate alkalinity of the water, resulting in reduced copper concentrations at the consumer tap without significant pH changes being required by the system. Care should be taken, however, on selection of the type of inhibitor, and independent corrosion control engineering studies are encouraged prior to selection and implementation of a phosphate-based inhibitor for corrosion control in potable water systems.

Example 3. How many pounds of pure sodium hydroxide are required to neutralize a sulfuric acid treated drinking water with an acidity equivalent to 45 pounds of sulfuric acid per million gallons of treated water ?

Solution. First write the equation of sodium hydroxide and sulfuric acid in water, which can be represented as: $4H^+ + SO_4^{2-} + 2Na^+ + 2OH^- = 2H_2O + 2Na^+ + SO_4^{2-}$. It can hence be seen that 2 moles of NaOH (molecular weight of 40 lb/lb-mole) react to neutralize 1 mole of H_2SO_4 (molecular weight of 98.1 lb/lb-mole). This means (2 x 40.0) pounds of sodium hydroxide react with (1 x 98.1) pound of sulfuric acid. So the number of pounds of sodium hydroxide required to neutralize the acid treatment would be {80 lb NaOH ÷ 98.1 lb H_2SO_4}x{45 lb H_2SO_4}= 36.7 lb NaOH per million gallons acid treated water.

Hydrogen Sulfide Equilibria

Hydrogen sulfide is frequently found in Florida groundwater. As little as 0.5 mg/L of hydrogen sulfide in potable water is noticeable to most consumers. In fact, the odor imparted by 1.0 mg/L of hydrogen sulfide can be considered offensive (White 1972). The minimum detectable taste of hydrogen sulfide in water is approximately 0.05 mg/L. Of the thirty or more ionic and molecular sulfur species that exist, only five are thermodynamically stable under conditions found in potable water. These include H_2S, HS^{1-}, elemental sulfur [S^o], sulfate, and HSO_4^{1-} (Garrels and Naeser 1958).

In aqueous solutions, hydrogen sulfide reacts with water, and can be described by the following equilibrium equations:

$$H_2S + H_2O = H_3O^+ + HS^{1-} \quad pK_1 = 7.0 \qquad (11)$$

$$HS^{1-} + H_2O = H_3O^+ + S^{2-} \quad pK_2 = \sim 13.8 \qquad (12)$$

Equation (11) states that at a pH of 7.0, half of the dissolved sulfide species for any given concentration is bisulfide [HS^{1-}], and half remains as hydrogen sulfide (gas), as is shown in Figure 2. Since most groundwaters occur near a neutral pH of 7.0, only a portion of the total sulfide can be removed unless a change in pH occurs and the equilibrium of the system is artificially shifted. At pH values above 12, sulfur chemistry becomes very complex and is not discussed further in this article.

The total sulfide species in water is dependent upon the pH, such that only that portion of the total sulfide that is present as hydrogen sulfide gas can be removed from water by aeration (tray, packed-tower, diffused air, or spray-nozzle methods). Beneficial effects of hydrogen sulfide treatment using aeration include: (1) the elimination of taste and odors; (2) a decrease in the corrosive effects of hydrogen sulfide on metals and concrete; and (3), a reduction in the demand of chlorination disinfection.

Carbon dioxide is a smaller molecule than hydrogen sulfide and will be released at a faster rate than hydrogen sulfide (Rubin 1974). Thus, as the carbon dioxide and hydrogen sulfide are removed as gases, the pH rises as water passes through the tower, causing the ionization of hydrogen sulfide and carbonic acid, and decreases the removal efficiency of the tower. However, if carbon dioxide is present in concentrations of about 10 percent (whether present initially or is added as a packed tower pretreatment method), the hydrogen ion concentration is raised to favor the release of hydrogen sulfide gas (Li 1975).

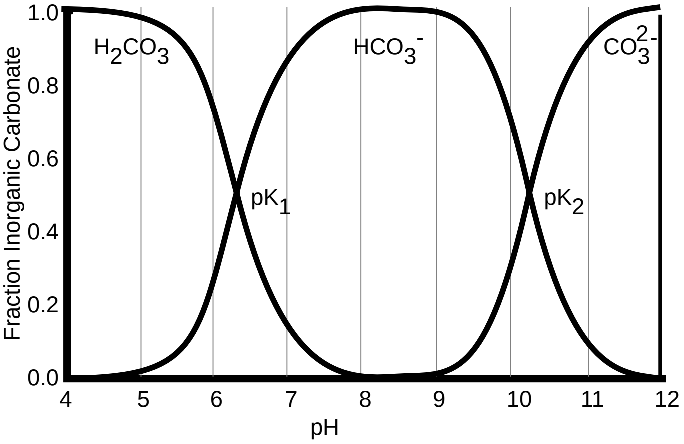


Figure 1. Inorganic Carbonate Species Distribution Diagram

Chlorination or oxygenation of groundwater containing hydrogen sulfide can result in the formation of elemental sulfur and colloidal polysulfides (which can impart a milky-white turbidity to the water), the removal of which can reduce copper corrosion rates in metallic distribution systems (Rubin 1974, Hausler 1979, Duranceau 1993).

Example 5. (a) Calculate the [H_2S], [HS^{1-}], and [S^{2-}] in a solution prepared by dissolving 6.0 x 10^{-5} moles of H_2S in a liter of solution. (b) What is the pH of this solution? (c) How much sulfide could be removed from this solution if the pH was 7.0 entering an aeration tower ?

Solution: (a) Using equations (11) and (12), it can be shown that [H^+] = [HS^{1-}] + 2[S^{2-}], and assuming that the solution is acidic, then [H^+] >>[OH^-]. Consequently, [H_2S] + [HS^{1-}] + [S^{2-}] = 6.0 x 10^{-5}. Since K_2 in equation (12) is very small, only a small amount of bisulfide [HS^{1-}] is ionized to produce sulfide [S^{2-}], so the approximation [HS^{1-}] >> [S^{2-}] is valid, and [H^+] ~ [HS^{1-}]. Also, since K_1 is also relatively small, it can be assumed that [H_2S] >> [HS^{1-}] is valid, and [H_2S] ~ 6.0 x 10^{-5} *M*. Using these approximations, one can obtain the expression from equation (11):

$$[H^+]^2 \div [6.0 \times 10^{-5}] = 1.0 \times 10^{-7}$$

$$[H^+] = [HS^{1-}] = 2.45 \times 10^{-6}$$

and from equation (12):

$$\{[H^+] \times [S^{2-}]\} \div [HS^{1-}] = K_2$$

$$\{(2.45 \times 10^{-6})[S^{2-}]\} \div (2.45 \times 10^{-6}) = 1 \times 10^{-13.8}$$

such that,

$$[S^{2-}] = 1 \times 10^{-13.8} \text{ (an insignificant amount).}$$

(b) Since [H^+] = 2.45 x 10^{-6}, the solution pH = 5.6.

(c) Assuming the concentration of hydrogen sulfide in the solution is approximately equal to the difference between [H_2S] and [HS^{1-}], then the hydrogen sulfide concentration would approximate [6.0 x 10^{-5}] - [1.0 x 10^{-7}] = 5.99 x 10^{-5} moles/liter or 2.0 mg/L. Consequently, only approximately half of the hydrogen sulfide, or 1.0 mg/L could be removed during aeration (see Figure 2).

Summary

Understanding the chemical equilibrium reactions for the carbonate and sulfide systems can provide significant benefits

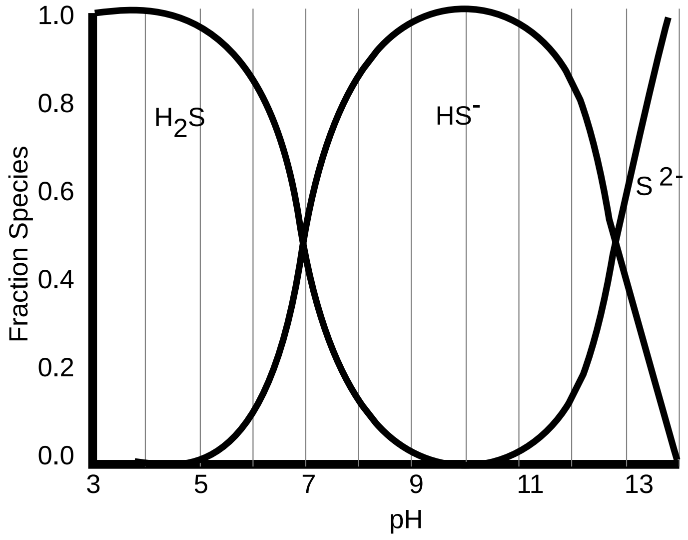


Figure 2. Sulfide Species Distribution Diagram

to the water purveyor or facility owner. These include: (1) increased treatment efficiency; (2) higher quality and better tasting drinking water; (3) delayed capital costs; and (4) lower operating costs.

Alkalinity and/or pH adjustment have been demonstrated to be effective for copper corrosion control. In addition, pH adjustment prior to aeration has also been effective in improving sulfide removal. Many Floridan Aquifer water purveyors treat groundwater using aeration followed by pH stabilization with hydroxide. If a purveyor wanted to increase sulfide removal to lower chlorine demand while maintaining copper and lead corrosion control, the impact of sulfide and carbonate equilibrium chemistry could affect overall metal corrosion rates, taste, and process chemical costs. Consequently, proper chemical process selection is important in order to balance multiple requirements.

Improving the performance of the treatment processes allows the water purveyor to better respond to the needs of the consumer and the requirements of the regulators. Consequently, control of water chemistry is significant and directly impacts operating and maintenance costs, increasing the need for water purveyors to evaluate capital improvements programs that consider '*molecular management*.'

References.

Butler, J.N. 1991. *Carbon Dioxide Equilibria and Their Applications*. Chelsea, MI: Lewis Publishers.

Duranceau, S.J. 1993. *"Membrane Process Post Treatment." Supplement to the Proceedings 1993 Membrane Technology Conference*. Baltimore, MD: American Water Works Association, p. 1-14.

Garrels, R.M. and Naeser, C.R. 1958. *Geochim. Cosmochim. Acta*. 15: 113-117.

Hammer, M.J. 1986. *Water and Wastewater Technology*. New York: John Wiley & Sons.

Hausler, R.H. 1979. "Corrosion Inhibition and Inhibitors." In *Corrosion Chemistry*. Eds. Brubaker, G.R. and Phipps, P.B., ACS Symposium Series 89. Washington D.C.: American Chemical Society, p. 263-320.

Li, E.C.C. 1975. "Significance of Hydrogen Sulfide in Ground Water." *Water & Sewerage Works*. 122 (August): 66-67.

Rubin, A.J. 1974. *Chemistry of Water Supply Treatment and Distribution*. Ann Arbor, MI: Ann Arbor Science Publishers, Inc.

Stumm, W. 1960. Paper No. 2657. *ASCE Journal, Sanitary Engineering Division*. Vol. 86, p. 27-45.

White, G.C. 1972. *Handbook of Chlorination*. New York: Van Nostrand Reinhold Company.

Zumdahl, S.S. 1986. *Chemistry*. Lexington, MA: D.C. Heath and Company.

Steven J. Duranceau, PhD, P.E., is a senior engineer with Boyle Engineering Corporation, Orlando, and Erik L. Melear, P.E., is a senior project manager with Pitman, Hartenstein and Associates, Jacksonville.