pH

An acceptable range for drinking water pH is from *6.5 to 8.5*. Corrosion effects may become significant below pH 6.5, and the frequency of incrustation and scaling problems may be increased above pH 8.5. With increasing pH levels, there is also a progressive decrease in the efficiency of chlorine disinfection processes.

Definition and Measurement

The p value of any entity is defined as the negative common logarithm of that entity. Thus,

$$pM = -\log_{10} M$$

where M is an activity, concentration or equilibrium constant, for example. The pH of a solution is the negative common logarithm of the hydrogen ion activity, a_{H^+}:

$$pH = -\log_{10}(a_{H^+})$$

In a dilute solution, the hydrogen ion activity is approximately equal to the concentration of hydrogen ion.

The pH of an aqueous sample is usually measured electrometrically with a glass electrode.[1,2] The pH may therefore be operationally defined in terms of E, the electromotive force in volts between a glass electrode and a reference electrode when the electrodes are immersed in the sample, and E_B, the electromotive force obtained when the electrodes are immersed in a reference buffer solution, the assigned pH of which is designated pH_B.[2] Thus,

$$pH = pH_B + [(E - E_B)F/2.3026RT]$$

where F is the faraday, R is the gas constant and T is the absolute temperature. The reference buffer solution is thus an integral part of the standard method used.
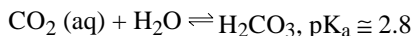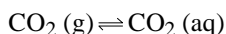
Temperature exerts two significant effects on pH measurement.[1,2] The change in potential per pH unit varies (according to the term in the defining equation) from about 55 mV/pH unit at 5°C to about 66 mV/pH unit at 60°C[2]; this can be overcome electronically by a temperature compensation adjustment provided on the better commercial instruments. The constants of chemical equilibria existing in a buffer solution vary and therefore affect pH_B; pH_B values must accordingly be corrected for temperature. The pH values at various temperatures of standard buffer solutions are known. Changes of temperature also affect the ionization equilibria of any weak acids and bases that are present in a water sample. The magnitude of this effect depends, to a large extent, on the alkalinity of the sample. The temperature of the sample should therefore be recorded together with the pH measurement.

At high pH levels, glass electrodes suffer from interference by alkali metal and alkaline earth metal cations. This is commonly referred to as the "sodium ion effect." For normal general-purpose glass electrodes, this effect becomes noticeable at pH levels above about 10.5, when a positive error is observed.[3] To reduce the possibility of such errors, measurements above pH 10 should be made with a high-alkalinity type of electrode.[1,2]

Factors Influencing pH Ranges

The pH of an aqueous system is a measure of the acid–base equilibrium achieved by various dissolved compounds and, in most natural waters, is controlled by the carbon dioxide – bicarbonate – carbonate equilibrium system. The following equilibria are involved[4]:

$$H_2O \rightleftharpoons H^+ + OH^-, pK_w = 14.0$$

$$CO_2 (g) \rightleftharpoons CO_2 (aq)$$

$$CO_2 (aq) + H_2O \rightleftharpoons H_2CO_3, pK_a \cong 2.8$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-, pK_1 = 6.35$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}, pK_2 = 10.3$$

where the pK values are those at 25°C.

All these component equilibria are affected by temperature; K_w exhibits the largest variation. In pure water, a decrease in pH of about 0.45 occurs as the temperature is raised by 25°C.[5] In waters with a buffering capacity that is imparted by bicarbonate, carbonate and hydroxide ions, this temperature effect is modified.[5]

The pH of most raw water sources lies within the range 6.5 to 8.5.[6] In some soft water areas, however,

the pH can be considerably lower as a result of the leaching of organic acids from decaying vegetation[7] and the presence of dissolved carbon dioxide.[8] In some groundwater sources, carbon dioxide, generated by bacteriological oxidation, is unable to escape to the atmosphere, and even lower pH levels will result.[9]

Hydrogen ion concentration may be significantly altered during water treatment. Chlorination tends to lower the pH, whereas water softening using the excess lime/soda ash process raises pH levels. In a survey of the water supplies of the 100 largest U.S. cities,[10] it was found that although all the cities used a raw water supply with a pH less than 9, 17 cities provided drinking water with pH levels greater than 9. The range of pH in finished water encountered in this survey was from 5.0 to 10.5, with a median level of 7.5.

Relationship of pH to Corrosion and Incrustation

The economic loss caused by corrosion in water mains and water treatment facilities has been estimated at $375 million annually in the United States.[11] In contrast to the corrosion problem is the loss of distribution capacity and the concomitant increase in pumping costs that result from calcium carbonate deposition.[12]

Metals used in distribution systems, such as cast iron, steel and copper, tend to corrode in contact with water because of their thermodynamic instability. The deterioration of concrete, asbestos-cement and cement-lined cast iron pipe, all of which are commonly used in distribution systems, may also occur. Natural waters contain gases, colloidal matter and a variety of electrolytes and non-electrolytes that, together with pH, determine the extent to which corrosion is possible in a given situation.[7] In general, the presence of anions that form soluble compounds with a metal increases the corrosiveness of the water with respect to that metal, whereas the presence of anions that form insoluble compounds may increase its passivity.

The role of pH in the corrosion of metals used in water distribution has been summarized by Drane[7] as follows:

1. Steel corrodes at approximately the same rate at all pH levels commonly found in natural waters. The form that the corrosion takes is, however, affected by pH. At values between 7.5 and 9.0, there is a tendency for the corrosion products to adhere in a hard, crusty deposit. At lower pH values, adherent corrosion products are not so evident, although a very hard form of deposit is sometimes seen in pipes that have been in service for some years. Loss of head, owing to scaling of a pipe, is more commonly found in the higher pH range; at lower pH values, "red water" complaints arising from corrosion products in suspension are more common. Cast iron behaves in a manner similar to steel

at alkaline pH values, but at lower pH values it is subject to graphitization.

2. Copper is markedly affected by pH. In aggressive waters, slight corrosion occurs, and the small amount of copper in solution may cause staining of fabrics and plumbing fixtures. In addition, redeposition of copper on aluminum or galvanized surfaces sets up electrochemical cells resulting in pitting of these metals. In most waters, the critical pH value is about 7.0, but in soft waters containing organic acids it may be higher.

3. Lead corrosion is affected by carbonate content, pH and mineral constituents. The simplest method of control is usually to increase the pH by adding alkali. Few waters are plumbo-solvent if the pH is above 7.0.

Zinc coatings on iron and galvanized steel are attacked in the same way as iron, but usually more slowly. Very alkaline waters, above about pH 10.5, can be aggressive to zinc[13] and will often remove galvanized coatings.

Corrosion control may result from calcium carbonate deposition. The factors affecting this process are temperature, pH, total dissolved solids, hardness, carbon dioxide and alkalinity. A rigorous treatment of the calcium carbonate – bicarbonate equilibrium is invariably impossible under practical conditions. Accordingly, a number of semi-empirical and empirical relationships using easily measured parameters have been developed.

One of the earliest relationships was developed by Langelier,[5,14] who studied the mathematical relationship between calcium carbonate, calcium bicarbonate and carbon dioxide in water. The simpler form of his equation, which is applicable when pH_s lies between 6.5 and 9.5, is[15]:

$$pH_s = pCa^{2+} + pAlk + (pK_2 - pK_s)$$

where pH_s (the saturation pH) is the pH at which, with no change of alkalinity, calcium content or dissolved solids, the water would neither deposit nor dissolve calcium carbonate; the other terms are as follows:

pCa^{2+} is the negative logarithm of the calcium concentration, expressed as mg $CaCO_3$/L,

$pAlk$ is the negative logarithm of the alkalinity to methyl orange, expressed as mg $CaCO_3$/L,

pK_2 is the negative logarithm of the ionization constant of HCO_3^-, and

pK_s is the negative logarithm of the solubility product of $CaCO_3$.

The term $(pK_2 - pK_s)$ is a function of ionic strength and temperature. Nomograms relating this quantity to readily measured water parameters — for example, pH, total dissolved solids, alkalinity and temperature — have been published.[5,6,14]

The Langelier saturation index (SI) is defined as the difference between the actual pH of the water and the saturation pH:

$$SI = pH - pH_s$$

A positive value for SI indicates scale-forming tendencies, and a negative value indicates scale-dissolving or aggressive qualities.

Although the solubility product of calcium carbonate decreases with increasing temperature, leading to increased deposition at higher temperatures under most conditions, this is not true for waters of low alkalinity (<50 mg/L as calcium carbonate). In such waters, the decrease in pH with temperature outweighs the decrease in solubility of calcium carbonate. This decrease in pH at temperatures above about 55°C actually increases the solubility of calcium carbonate. The effect on saturation index is particularly acute below 25 mg/L alkalinity in hot water systems, because there is insufficient alkalinity to buffer the effect of temperature on pH.[16]

Ryznar introduced an empirical relationship, based on the Langelier saturation pH, named the stability index[17]:

$$\text{stability index} = 2\,pH_s - pH$$

Values of the index greater than about 7.0 indicate corrosive water, and values less than 7.0 indicate scale-forming tendencies. This index is of interest in evaluating waters of widely different compositions.

An aggressivity index (AI) has been established by the American Water Works Association for use with asbestos-cement pipe[18]:

$$AI = pH + \log (Alk)\,(Ca^{2+})$$

A value of less than 10 indicates that the water is unsuitable for use in such pipes.

Numerous other indices are also in use — for example, momentary excess, driving force index, marble test, Enslow's stability indicator — all of which are based on the calcium carbonate – bicarbonate equilibrium system. These have been discussed[15] with respect to water softening.

The effectiveness of corrosion protection by altering pH and calcium content (normally by using lime and/or carbon dioxide) depends on judicious balance of the carbonate–bicarbonate equilibrium system. A water that is exactly in equilibrium — i.e., just stabilized — with respect to calcium carbonate is normally corrosive to iron and steel because it has no power to form a calcium carbonate deposit. Supersaturated water, on the other hand, will form substantial scale unless suitably treated. This scale may or may not inhibit corrosion, depending on how well it adheres to the metal and on its porosity. The relationship between pH and the quality of deposited carbonate films has been studied by McClanahan and Mancy.[12]

Ideal conditioning of water with respect to inhibition of corrosion and incrustation is given by the following characteristics[19]:

- the water should be oversaturated by 4 to 10 mg/L with calcium carbonate;
- calcium and alkalinity values should each be greater than 40 mg/L, expressed as calcium carbonate;
- the alkalinity:(chloride plus sulphate) ratio should be at least 5:1, with all concentrations being expressed equivalent to calcium carbonate; and
- pH should be in the range 6.8 to 7.3.

Waters that are excessively hard do not usually lead to severe corrosion problems, but they are prone to excessive incrustation and also reduce the effectiveness of soaps. Hardness is usually removed in water treatment by precipitation of the hardness-producing cations — calcium as the carbonate and magnesium as the hydroxide. Lime is added, usually in a calculated excess, precipitating most of the calcium carbonate and magnesium hydroxide; this is followed by soda ash addition to remove the excess lime and any non-carbonate hardness. Water treated in this manner will have a pH of the order of 10.9 and will have scale-forming tendencies.[15] Stabilization can be achieved by recarbonation (addition of carbon dioxide) to a pH of 9.7 to 10 and by the addition of 0.25 to 0.5 mg sodium polyphosphate per litre.[15] However, other authorities[20] have recommended recarbonation to pH 8.6, to stabilize the water against subsequent excessive calcium carbonate deposition in the distribution system.

There is one final area that should be mentioned with respect to corrosion and incrustation, and that is the buildup of either beneficial or harmful biological slime on distribution pipe surfaces. The slime may serve to prevent the removal of oxidation products from and the penetration of oxygen to the pipe walls, thus inhibiting corrosion. Alternatively, excessive growths could create regions of locally low pH at the pipe surface by generating carbon dioxide. This could lead to localized corrosion, even though the bulk water might possess favourable stability and aggressivity indices.[21] Red water complaints are often the result of sudden growth of iron bacteria, which produce ferric hydroxide as the metabolic end product. The development of iron bacteria may be such that severe blocking of water pipes can occur in a matter of weeks. The growth of iron bacteria is very pH dependent, occurring over the range 5.5 to 8.2, with an optimum pH of about 6.5.[22]

Relationship with Other Water Quality Parameters

Insofar as aqueous chemical equilibria invariably involve hydrogen (and hydroxyl) ions, pH will be related, in one or more of several different ways, to almost every other water quality parameter.

Physical Characteristics

Taste and odour in drinking water arise from a wide variety of sources, and no generalizations as to the effect of pH on these parameters can be made. In waters prone to sulphur contamination, the formation of gaseous hydrogen sulphide, which leads to "bad egg" odours, is thermodynamically favoured at pH values less than about 7.0.[13] Nitrogen trichloride, which has an objectionable pungent odour,[23] tends to be formed in greater concentrations at low pH values (<pH 7) during the chlorination process.[24] It has also been reported that at high pH levels drinking water acquires a bitter taste.[25]

The colour intensity in a given water sample is increased by raising the pH.[26] This effect, known as the "indicator effect," has led to the suggestion that all colour measurements for water quality control be carried out at a standard pH of 8.3.[27]

Turbidity, taste- and odour-producing compounds, micro-organisms and colour can be removed by a combination of coagulation, flocculation and filtration. The efficiencies of coagulation and flocculation processes are markedly dependent on pH, and it is standard practice in water treatment to adjust pH so that optimum floc formation is achieved.[28,29] In certain instances, filtration efficiency is also sensitive to pH.[30]

Microbiological Characteristics

Although most micro-organisms tolerate the pH range commonly found in water sources, rapid growth is usually confined to one pH unit or less.[22,31,32]

Of greater importance to the microbiological quality of water is the influence of pH on the effectiveness of chlorine disinfection. The germicidal efficiency of chlorine in water is lower at higher pH values; this has been attributed to the reduction in hypochlorous acid concentration with increasing pH.[33–36] Hypochlorous acid has a germicidal effectiveness about 100 times greater than that of the hypochlorite ion.[37] Most natural waters, however, contain ammonia-nitrogen, which reacts with chlorine and hypochlorous acid to form mono-, di- and trichloramines (combined available chlorine), the relative amounts of which depend on pH. In many, if not most, treatment plants using chlorine disinfection, sufficient chlorine is added to oxidize all the ammonia and to provide excess free chlorine (break-point chlorination). Under these conditions, the hypochlorous acid concentration reaches a maximum at a pH of about 7.5, with lower concentrations at lower and higher pH values.[24]

Chlorination in water treatment serves two purposes. The first is to inactivate pathogenic organisms in the water before entry into the distribution system. The second is to ensure that a free chlorine residual persists to the user's tap. It may be argued that high pH, with the attendant reduction in the rate of germicidal action, is detrimental to the effectiveness of free chlorine in the distribution system. However, it must be remembered that the hypochlorous acid – hypochlorite ion system is a chemical equilibrium, and removal of hypochlorous acid by reaction with micro-organisms wil lead to further formation of the acid, provided that there is a free chlorine residual. The reaction rate of hypochlorous acid disinfection is slower at lower pH levels, but this may be compensated for by longer contact times. The important parameter is the total available chlorine (as both $HOCl$ and OCl^-).

Ozone, which is used in more than 20 water treatment facilities in Quebec,[38] and chlorine dioxide, which is primarily employed in Canada for taste and odour control, are alternative disinfection agents. The effectiveness of both is unchanged by pH within the range of pH values encountered in drinking water. Chlorine dioxide has a germicidal effectiveness similar to that of hypochlorous acid, whereas that of ozone is considerably greater.[24]

Chemical Characteristics

A major source of metal contamination in drinking water is corrosion in the water supply system.[39] Two of the potentially most troublesome metals are lead and cadmium. Lead is immune to corrosion at all pH levels above 6 in pure water; in the presence of carbonates and bicarbonates, lead is passive between about pH 4 and 12, but it becomes subject to corrosion above pH 12.[13] In a study of drinking water with a low alkalinity and a fairly low pH, high levels of lead were found in the drinking water of households that had lead plumbing.[40] Cadmium, in pure water, is passive between about pH 9 and 13.5, but experimental data show that corrosion is significant only below pH 6.[13]

Water with an aggressivity index below 10 has been shown, in laboratory studies, to promote the release of asbestos fibres from asbestos-cement pipes.[40] It was also pointed out that pipes coated with coal tar enamel might be a source of polynuclear aromatic hydrocarbons (PAHs) owing to the leaching action of water.[40]

Trihalomethanes are formed during the chlorination of waters with an organic carbon content. Postulated mechanisms for the formation of trihalomethanes involve initial reaction of hypochlorous acid with the organic precursors: electrophilic aromatic substitution of positive chlorine species and electrophilic addition of

positive chlorine to appropriately activated double bonds,[41] and, more specifically, the reaction of chlorine with m-dihydroxybenzene structures within a fulvic acid lattice.[42] Such reactions, like the simpler haloform reaction, are base catalysed. It has been shown, both in the laboratory[43] and under practical conditions in a water treatment plant,[44] that, for a given organic carbon content and chlorine dose, higher concentrations of trihalomethanes are formed at higher pH values.

Health Effects

Because pH is related to a variety of other parameters, it is not possible to determine whether pH has a direct relationship with human health. Insofar as pH affects the unit processes in water treatment that contribute to the removal of viruses, bacteria and other harmful organisms, it could be argued that pH has an indirect effect on health. The destruction of viruses by the high pH levels encountered in water softening by the lime/soda ash process could also be considered beneficial. On the other hand, the increased yield of trihalomethanes at high pH values may be detrimental.

In one of the few epidemiological studies carried out on drinking water supplies in which pH was one of the parameters considered, Taylor and co-workers[45] were unable to obtain any significant correlation between the incidence of infectious hepatitis and finished water pH. Sixteen U.S. cities that used surface water as a source of drinking water were considered in the study.

Rationale

1. There are no specific health effects on which to base limits for the pH of drinking water. The main purpose in controlling pH is to produce water in which corrosion and incrustation are minimized. These processes, which can cause considerable damage to the water supply system, result from complex interactions between pH and other parameters such as dissolved solids, dissolved gases, hardness, alkalinity and temperature.

2. As a generalization, metal corrosion may become significant below a pH of about 6.5; incrustation and scaling problems are most commonly encountered above about pH 8.5.

3. The acceptable range for drinking water pH is therefore from 6.5 to 8.5. In general, waters with a pH within this range can be stabilized with respect to corrosion and incrustation by simple pH adjustment. By keeping the pH below 8.5, the rate of chlorine disinfection is increased and the production of trihalomethanes is reduced.

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