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Source: *Journal (American Water Works Association)*, OCTOBER, 1936, Vol. 28, No. 10 (OCTOBER, 1936), pp. 1500-1521

Published by: Wiley

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THE ANALYTICAL CONTROL OF ANTI-CORROSION WATER TREATMENT

By W. F. Langelier

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It is the purpose of this paper to discuss certain chemical relationships involved in the action of natural oxygen containing waters on the interior of iron or galvanized pipe and to attempt to place upon a more rational basis the analytical control of preventive treatment. It is hoped that the data presented will be subjected to critical examination by water technologists in various parts of the country, in order that they may ascertain the degree of correlation which exists between theory and laboratory experiment as presented herein and their observations in practice.

It is a well established fact that the composition of water is only indirectly a factor in corrosion. Any water, regardless of its composition, after a certain period of contact with a clean iron surface will cause corrosion of the metal. If, however, certain of the products of the corrosive action are held at the boundary surface, the corrosion rate is reduced and, if the conditions are favorable, further corrosion will be practically eliminated. The problem therefore resolves itself into one of obtaining a suitable protective coating. Users of pipe recognize this and usually specify pipe which has been coated by the manufacturer. Although these coatings are generally useful and necessary, they frequently lack permanence under conditions of use, and often the need of a self-forming or self-healing coating or film, the formation and permanence of which is assured by the composition of the water, is indicated.

In natural oxygen containing water, calcium carbonate is the salt which is most useful in forming or, together with rust,[1] assisting in the formation of a self-healing or natural protective coating. In

[1] A rust coating not containing $CaCO_3$ is too porous and is not sufficiently dense and continuous to offer protection, and on the contrary may even accelerate corrosion in the form of pitting.

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order that this salt may deposit on the pipe interior, it is necessary that the product of the concentration of the calcium ions and the carbonate ions present in the water *at a given point in the system* shall exceed a certain value known as the "solubility product constant," or in more modern chemical terminology, the "activity product," of the salt in question. If the water is deficient in either of these ions so that the activity product is not equaled, not only will a carbonate film not form, but also, any existing film will be dissolved. Many surface waters are of this type, and these in general are the ones known to be most corrosive. In such waters, a sufficient increase in either or both of these constituents is all that is needed to attain saturation. Any base added to water will convert existing bicarbonate ions into carbonate ions; but the addition of lime has the advantage of increasing both the calcium and the carbonate ions simultaneously. Because lime is relatively cheap and readily available, it is the chemical which is most often used for this purpose.

It is important to note that as the film is laid down in the pipe, the separate calcium and carbonate ions in the water may decrease to the point where the activity product is no longer exceeded, in which case the water is incapable of furnishing any further protection. Applied to a given distribution system, this would mean that the pipes nearest the source would receive the greatest protection. This tendency, however, is offset by the fact that the deposition from a supersaturated solution is not instantaneous but requires a certain induction period, which for low degrees of supersaturation and at low temperatures may be as great as several hours. Also, there is reason to believe that under conditions of operation there is a leveling process whereby material deposited at one point may be picked up by solution and deposited at a point farther out in the system. This could be brought about by irregularities in treatment and by temperature changes.

Where corrosion of water pipes is not a problem, difficulties due to excessive incrustation with a carbonate scale are often encountered. In these cases, the calcium ion and carbonate ion concentrations exceed too greatly the activity product. This is likely to occur where the water has been softened by the lime-soda process. Here the calcium ion concentration has been decreased by the treatment, but this has been more than offset by an increase in the carbonate ion concentration. A remedy for this condition is recarbonation

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with CO_2 gas. This is merely a chemical device to convert some of the carbonate ions into bicarbonate ions, in which form they do not participate in the activity product equation.

A survey of the water-supply literature has failed to reveal an adequate and practical formulation of the chemical mechanism of the carbonate film theory. We owe a great deal, however, to the German chemist Tillmans (1) for his work in this field. It was he who in 1912 proposed the carbonate saturation theory of pipe protection. In several papers on this subject he has elaborated his earlier views, but his formulation of carbonate saturation is in terms of free carbon dioxide, a constituent which in the small quantity present near the saturation point for soft waters is not directly determinable in the laboratory. Moreover, his equation does not take into consideration the total ion concentration of the water, an item which may be of major importance.

In the United States, Baylis (2) has been the leader in the application of this theory to practice, and he has written several excellent papers on the subject. He has published a graph, based upon his experiences at Baltimore and elsewhere, of carbonate saturation in terms of pH and total alkalinity. He states, however, that his equilibrium curve must be modified for different waters. Since it fails to take into consideration the calcium content of the water, it of course could not have a general application. Oceanographers have formulated the mechanism of buffer action in sea waters, and bio-chemists have considered the precipitation of calcium salts in tissues. Physical chemists, notably Johnson (3), have studied the chemistry of carbonate solutions and have supplied the several constants needed in the solution of problems in applied chemistry.

In the Sanitary Engineering Laboratory of the University of California this problem has been considered and an attempt has been made to formulate calcium carbonate saturation in natural waters in terms of pH, calcium, alkalinity, total salinity, and temperature. By the use of certain limiting assumptions of conditions not encountered in practice, a final equation has been obtained which is extremely simple to use and which is believed to be entirely rational in its development.

DERIVATION OF THE GENERAL EQUATION

The derivation of the equation for pH_s, which is the pH at which a water of given calcium content and alkalinity is in equilibrium

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(neither over nor under-saturated with calcium carbonate) is based upon three well known mass law equations and one stoichiometric equation, as follows:

$$(Ca^{++}) \times (CO_3^{--}) = K_s' \tag{1}$$

$$\frac{(H^+) \times (CO_3^{--})}{(HCO_3^-)} = K_2' \tag{2}$$

$$(H^+) \times (OH^-) = K_w \tag{3}$$

$$(Alk) + (H^+) = 2(CO_3^{--}) + (HCO_3^-) + (OH^-)^* \tag{4}$$

In these and all subsequent equations, the chemical symbols imply concentrations of the respective ions. Also, all concentrations are molal, with the exception of (Alk) which is an equivalent concentration, i.e. titratable equivalents of base per liter. The two constants K_s' and K_2' are apparent constants, applicable only in solutions of the same total mineral content and at a given temperature, but which for any given condition can be computed from the corresponding known thermodynamic constants, commonly written without the primes. Equation 4 defines what is meant by the term "Total Alkalinity to Methyl Orange," as used in Standard Methods of Water Analysis. It represents the equivalent concentration of titratable base, and not the hydroxyl ion concentration which is sometimes called the "true alkalinity." The other terms in this equation have the same significance as in the mass law equations. The validity of this equation as applied to natural waters assumes only that the salts of weak acids other than carbonic acid are absent.

Proceeding with the derivation,

from (2):

$$(CO_3^{--}) = \frac{(K_2') \times (HCO_3^-)}{(H^+)} \tag{2a}$$

and from (4):

$$(CO_3^{--}) = \frac{(Alk) - (HCO_3^-)}{2}$$

* Within the range of natural waters (pH 4.5 to 10.3) the values of (H^+) and (OH^-) are relatively so small that they may be neglected in this equation without error.

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therefore

$$(HCO_3^-)\left(\frac{K_2'}{(H^+)} + \frac{1}{2}\right) = \frac{(Alk)}{2}$$

and

$$(HCO_3^-) = \frac{(Alk)}{1 + \frac{2K_2'}{(H^+)}} \tag{5}$$

By substituting this value of (HCO_3^-) in (2a), we obtain

$$(CO_3^{--})^* = \frac{K_2'}{(H^+)} \times \frac{(Alk)}{1 + \frac{2K_2'}{(H^+)}} \tag{6}$$

Now, by substituting this value of (CO_3^{--}), we obtain from (1)

$$(Ca^{++}) \times \frac{K_2'}{(H_s^+)} \times \frac{(Alk)}{1 + \frac{2K_2'}{(H_s^+)}} = K_s' \tag{7}$$

Since it is the practice to represent (H^+) in terms of pH, which is a symbol for $\log \frac{1}{(H^+)}$, it is convenient to rearrange (7) in terms of logarithms using this same convention, whence we obtain for pH_s, the pH at saturation:

$$pH_s = (pK_2' - pK_s') + pCa + pAlk + \log\left[1 + \frac{2K_2'}{(H_s^+)}\right] \tag{8}$$

A more general equation, not limited to waters in the range specified above, is obtained by correcting the alkalinity term for hydrogen and hydroxyl ions, as follows:

$$pH_s = (pK_2' - pK_s') + pCa + p\left[Alk + (H^+) - \frac{K_w}{(H^+)}\right] + \log\left[1 + \frac{2K_2'}{(H_s^+)}\right] \tag{9}$$

* It should be stated here that the method of determining the concentration of carbonate, as given in Standard Methods by means of a two indicator titration is (within a certain range of pH) too inaccurate for our present purpose. Equations 5, 6, and similarly derived equations for H_2CO_3 and OH could well be included in Standard Methods to supplement the present discussion of Alkalinity.

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The correction to (Alk) as well as the term, $\log\left[1 + \frac{2K_2'}{(H_s^+)}\right]$, is ordinarily small, and in all cases where pH_s falls between approximately 6.5 and 9.5, both can be omitted, and we have for this range:

$$pH_s = (pK_2' - pK_s') + pCa + pAlk \qquad (10)$$

In the event that pH_s as obtained by (10) is greater than 9.5, the corresponding value of (H_s^+) may be substituted in the last term of (8) and a closer approximation to the correct pH_s will be obtained by that equation. In order to facilitate the use of equations 8 or 9, applicable when pH_s is greater than approximately 9.5, table 1 has

TABLE 1

Values of $\log\left[1 + \frac{2K'_2}{(H^+_s)}\right]$ *as a Function of* $(pK'_2 - pH_s)$

$(pK_2' - pH_s)$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.3
$\log\left[1 + \frac{2K'_2}{(H^+_s)}\right]$	0.48	0.41	0.35	0.30	0.25	0.21	0.18	0.15	0.12	0.10	0.08	0.06	0.05

been included. This table gives values of $\log\left(1 + \frac{2K_2'}{(H_s^+)}\right)$ for different values of $(pK_2' - pH_s)$. The correction of the (Alk) for caustic ions need not be made unless pH_s exceeds 10.5. This condition is encountered so rarely that a table to simplify its computation has not been included.

The algebraic difference between the actual pH of a sample of water and its computed pH_s is the logarithm of its degree of carbonate saturation. We have called this the "Calcium Carbonate Saturation Index." Actually this index is the logarithm of the ratio of the hydrogen ion concentration which the sample must have if saturated (without change in composition) to its actual hydrogen ion concentration. If the index is zero, the sample is in equilibrium. A plus sign before the index indicates over-saturation and a tendency to crystalize, or to lay down a protective coating of $CaCO_3$ in the pipe, and a minus sign indicates under-saturation, or a tendency to dissolve an existing carbonate coating. Expressed mathematically:

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Saturation Index = $pH_{actual} - pH_{saturation} = \log \frac{1}{(H^+)} - \log \frac{1}{(H_s^+)}$ $= \log \frac{(H_s^+)}{(H^+)}$. The significance of this Index and its applications to pipe corrosion problems will be discussed later.

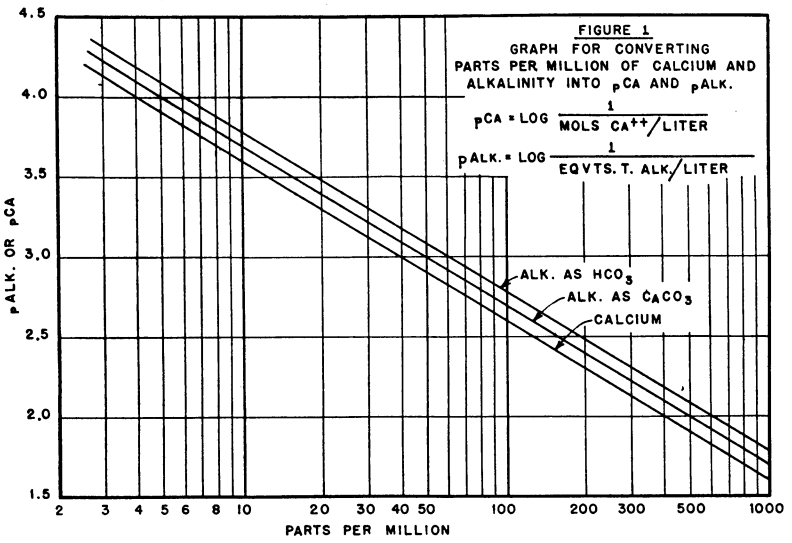

FIG. 1

PROVISION FOR TOTAL SALINITY OR IONIC STRENGTH

In the proposed equation for pH_s, the effects of variable salinity upon saturation are provided for in the term, $(pK_2' - pK_s)$. For any given water the exact values of these constants can be computed from the true thermodynamic constants K_2 and K_s (the values of which are known) by multiplying each with a certain activity coefficient, in accordance with the principles of the "activity" concept of the theory of electrolytic dissociation. This concept, which has only recently come into general acceptance, assumes complete dissociation of all the salts in a dilute solution, but requires that all concentration terms appearing in a mass law equation shall be converted into activity terms by combining each with an activity coefficient. These coefficients are related to the total salt content of the solution and to the valences of the ions present. A conven-

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ient method of expressing the combined effect of salinity and valence of the ions present is in terms of "ionic strength" represented by the symbol, μ. The ionic strength of a solution is defined as one half the sum of the molality of each ion in solution multiplied by the square of its valence, or if c is the molal concentration of the ion and v is the valence of that ion, the ionic strength of the solution μ equals $1/2[c_1v_1^2 + c_2v_2^2 + \cdots]$. An example in the computation of the ionic strength of the water of the Mississippi River at New Orleans, from a mineral analysis of same, follows:

MONOVALENT IONS, P.P.M.	MOLAL CONCENTRATION	DIVALENT IONS, P.P.M.	MOLAL CONCENTRATION
$Na^+ = 18$	0.00078	$Mg^{++} = 10$	0.0004
$Cl^+ = 28$	0.00079	$Ca^{++} = 39$	0.0010
$HCO_3^- = 116$	0.00190	$SO_4^{--} = 42$	0.0004
$\Sigma(c_1)$	0.00347	$\Sigma(c_2)$	0.0018
$\Sigma(c_1v_1^2)$	0.00347	$\Sigma(c_2v_2^2)$	0.0072

Ionic strength $\mu = 1/2(0.00347 + 0.0072) = 0.0054$

It will be noted that for this water, which has a total dissolved solids content of 220 p.p.m., the sum of the equivalent concentrations of the monovalent ions is about equal to the sum of the equivalent concentrations of the divalent ions, and it is believed that his is reasonably typical of other natural waters with respect to the relative proportions of monovalent and divalent ions. In this example, 40 parts per million of total solids is equal to 0.001 unit of ionic strength. Computation of the ionic strength of several typical waters indicates that for the purpose under consideration this value may be used as a general relationship applicable to most waters.

With this means of computing the ionic strength of a sample of water from its total dissolved solids, we are now able to compute the activity coefficient f for any given ion by the equation, $-\log f = 0.5v^2\sqrt{\mu}$. This is the Brönsted-La Mer modification of the Debye-Hückel equation. In this equation, which has been found to hold for ionic strengths up to 0.02, v is the valence of any ion having the activity coefficient f.

Consider now the application of the individual ion activity coefficients obtained in this way to the computation of the value pK_s' from pK_s, the true thermodynamic constant which varies only with

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TABLE 2

Values of pK_2' and pK_s' at 25°C. for various ionic strengths and of the difference ($pK_2' - pK_s'$) for various temperatures

IONIC STRENGTH	TOTAL DISSOLVED SOLIDS	25°C.			($pK'_2 - pK'_s$)							
		pK'_2	pK'_s	$pK'_2 - pK'_s$	0°C.	10°C.	20°C.	50°C.	60°C.	70°C.	80°C.	90°C.
.0000	0	10.26	8.32	1.94	2.20	2.09	1.99	1.73	1.65	1.58	1.51	1.44
.0005	20	10.26	8.23	2.03	2.29	2.18	2.08	1.82	1.74	1.67	1.60	1.53
.001	40	10.26	8.19	2.07	2.33	2.22	2.12	1.86	1.78	1.71	1.64	1.57
.002	80	10.25	8.14	2.11	2.37	2.26	2.16	1.90	1.82	1.75	1.68	1.61
.003	120	10.25	8.10	2.15	2.41	2.30	2.20	1.94	1.86	1.79	1.72	1.65
.004	160	10.24	8.07	2.17	2.43	2.32	2.22	1.96	1.88	1.81	1.74	1.67
.005	200	10.24	8.04	2.20	2.46	2.35	2.25	1.99	1.91	1.84	1.77	1.70
.006	240	10.24	8.01	2.23	2.49	2.38	2.28	2.03	1.94	1.87	1.80	1.73
.007	280	10.23	7.98	2.25	2.51	2.40	2.30	2.05	1.96	1.89	1.82	1.75
.008	320	10.23	7.96	2.27	2.53	2.42	2.32	2.07	1.98	1.91	1.84	1.77
.009	360	10.22	7.94	2.28	2.54	2.43	2.33	2.08	1.99	1.92	1.85	1.78
.010	400	10.22	7.92	2.30	2.56	2.45	2.35	2.10	2.01	1.94	1.87	1.80
.011	440	10.22	7.90	2.32	2.58	2.47	2.37	2.12	2.03	1.96	1.89	1.82
.012	480	10.21	7.88	2.33	2.59	2.49	2.39	2.13	2.04	1.97	1.90	1.83
.013	520	10.21	7.86	2.35	2.61	2.50	2.40	2.15	2.06	1.99	1.92	1.85
.014	560	10.20	7.85	2.36	2.62	2.51	2.41	2.16	2.07	2.00	1.93	1.86
.015	600	10.20	7.83	2.37	2.63	2.52	2.42	2.17	2.08	2.01	1.94	1.87
.016	640	10.20	7.81	2.39	2.65	2.54	2.44	2.19	2.10	2.03	1.96	1.89
.017	680	10.19	7.80	2.40	2.66	2.55	2.45	2.20	2.11	2.04	1.97	1.90
.018	720	10.19	7.78	2.41	2.67	2.56	2.46	2.21	2.12	2.05	1.98	1.91
.019	760	10.18	7.77	2.41	2.67	2.57	2.47	2.21	2.12	2.05	1.98	1.91
.020	800	10.18	7.76	2.42	2.68	2.58	2.48	2.22	2.13	2.06	1.99	1.92

temperature. In accordance with the activity concept, we may write for the activity product of calcium carbonate

$$f_{Ca} \cdot (Ca^{++}) \times f_{CO_3} \cdot (CO_3^{--}) = K_s$$

Also, equation (1)

$$(Ca^{++}) \times (CO_3^{--}) = K_s'$$

therefore

$$K_s' = \frac{K_s}{f_{Ca} \times f_{CO_3}}$$

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Since the calcium and carbonate ions have the same valence f_{Ca} will be equal to f_{CO_3}, and therefore

$$pK_s' = pK_s - 2 \log f_{Ca} = pK_s - 4\sqrt{\mu} \quad (11)$$

The values of pK_s' for the various ionic strengths (or salinities) given in table 2 were computed by this method from Frear and Johnston's (4) value of K_s which is 4.8×10^{-9} at 25°C.

The values of pK_2' given in this table are from MacInnes and Belcher (5).

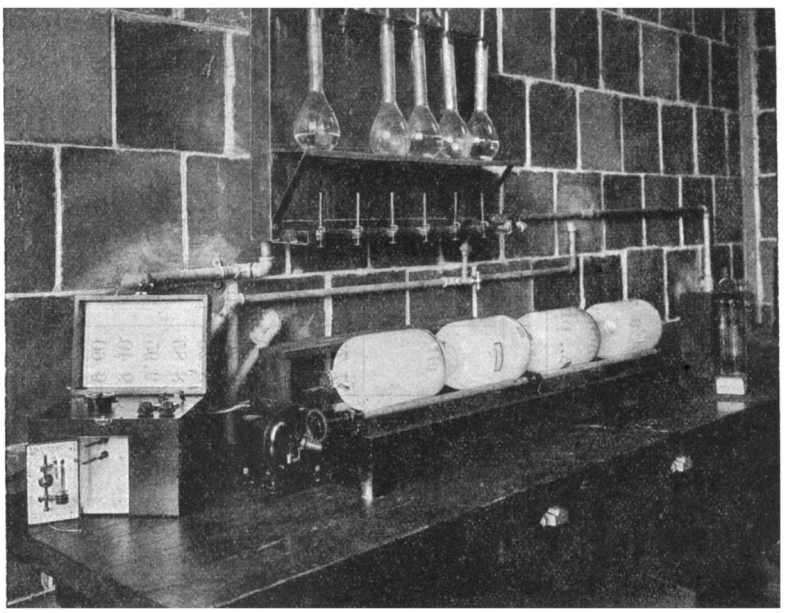

FIG. 2. (READING FROM LEFT TO RIGHT), *1*, BECKMAN GLASS ELECTRODE; *2*, "BALL" MILL FOR SATURATING WATER SAMPLES WITH $CaCO_3$; *3*, BIOCOLORIMETER

VALIDITY OF EQUATION

In order to check the validity of the theoretical equation (9) for use in connection with natural waters, a series of laboratory tests was undertaken. For this purpose, each of ten samples of water from widely different sources was treated with an excess of pure calcium carbonate powder. The bottles were filled to the top and tightly stoppered, so as to exclude all air, and at frequent intervals, the bottles were rotated in a specially made "ball" mill, illustrated in figure 2. No attempt was made to hold the temperature abso-

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TABLE 3

Experimental confirmation of the theoretically derived equation for the saturation pH of natural waters:

$$pH_s = (pK'_2 - pK'_s) + pCa + pAlk + \log\left(1 + \frac{2K'_2}{(H_s^+)}\right)$$

Results of experiments in which several raw and conditioned waters were brought into equilibrium with solid calcium carbonate; i.e., pH_s equals pH

SOURCE OF SAMPLES	RESULTS OF ANALYSES				$(pK'_2 - pK'_s)_{25°}$	pCa	pAlk	$\log\left(1 + \frac{2K'_2}{(H_s^+)}\right)$	pH_s	SATURATION INDEX $(pH - pH_s)$
	pH	Parts per million								
		Ca^{++}	Total Alk as $CaCO_3$	Total diss. solids						
1. Hard surface water (Calaveras Res.)	7.75	55	178	410	2.30	2.85	2.45		7.60	+0.15
2. Hard ground water (San Mateo Well)	7.55	64	204	868	2.43	2.80	2.40		7.63	−0.12
3. Hard ground water (Milpitas)	7.82	41	198	372	2.29	3.00	2.40		7.69	+0.13
4. Hard ground water (Hayward)	7.80	40	202	400	2.30	3.00	2.40		7.70	+0.10
5. Surface water (Crystal Springs Res.)	8.20	20	78	166	2.17	3.30	2.80		8.27	−0.07
6. Zeolite softened (San Mateo)	8.20	11	224	786	2.42	3.57	2.35		8.34	−0.14
7. Soft surface water (Irvington)	8.85	8.75	34	60	2.09	3.65	3.18	0.04	8.96	−0.11
8. Soft surface water (Berkeley)	9.95	7.5	30	50	2.08	3.72	3.22	0.05	9.07	−0.12
9. Distilled water	9.40	6.0	18	28	2.05	3.82	3.45	0.09	9.41	+0.01
10. Lime-soda softened (San Mateo)	9.60	4.0	44	650	2.39	4.00	3.06	0.13	9.58	+0.02

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lutely constant and it varied between 20° and 25°C. throughout most of the period. The clear saturated waters were then syphoned off and tests for pH, Total Alk, Calcium, and Total Dissolved Solids were immediately made. The pH tests were made electrometrically with a Beckman glass electrode and were checked with a specially built bicolorimeter of the Gillespie type. Both of these instruments are illustrated in figure 2. The biocolorimeter and the ball mill previously mentioned were found to be especially useful pieces of equipment and will be described in a separate paper.

The results from this series of tests are given in table 3. A maximum deviation of ± 0.15 pH unit was obtained. The data confirm the validity of the equation reasonably well. The failure to control temperature and the employment of ordinary routine methods of analysis are sufficient to account for the deviations shown. Attention is called to the fact that in pH measurement of slightly buffered solutions the relative errors may be small, but the absolute error under routine working conditions may appreciably exceed one tenth of a pH unit.

SALINITY AND TEMPERATURE EFFECTS IN PIPE PROTECTION

It has been shown that in natural fresh waters an increase in salinity causes an increase in the solubility of calcium carbonate such that a water of 800 p.p.m. total solids requires about threefold more of the salt at saturation than does distilled water. This increase in solubility is very appreciable in brackish waters and brines and is undoubtedly one of the principle reasons why such waters, unable to form a protective carbonate film on pipe interiors and exteriors, are so very corrosive. It is known that calcium carbonate is approximately 500-fold more soluble in sea than in fresh water. Attention is called to the fact that equation (11), with the salinity correction as given, holds only for waters containing not more than 800 parts per million total solids. Other correction factors are available for more saline waters.

In practice it is commonly observed that the tendency of water to corrode or incrust pipe is greatest at elevated temperatures. Actually, an increase in temperature exerts two effects: (1) a shift of the Index in the direction of higher saturation, and (2) an increase in the speed of the reaction in either direction, as a result of decreasing viscosity. Each of these effects is important and will be discussed further.

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(*1*) *The effect of temperature on the 25°C. saturation index.* The values of pH, pK_2' and pK_s', each of which is used in computing the Saturation Index, vary with temperature, and although ordinarily for any given water it is sufficient to know the value of the Index at 25°C., it is desirable to have a conversion factor for estimating the Index for any other temperature encountered in practice. Considering first the temperature coefficients of pH and pK_2, it is unfortunate that these are not known throughout the complete temperature range of 0°C. to 100°C. However, it is known that for at least the lower part of this range, pH and pK_2' decrease at approximately the same rate, i.e. about 0.01 units per degree C. Assuming this to be correct for the entire range, and since it is with their difference that we are concerned, the 25°C. values may be used in the equation for any temperature. This is an advantage because pH measurements are most conveniently made at room temperature. Thus it is neces-

TABLE 4

Effect of temperature on solubility of calcium carbonate

	t, °C.								
	0	10	20	25	50	60	70	80	90
r	1.8	1.4	1.1	1.0	0.62	0.51	0.44	0.37	0.32
pK_s'	8.06	8.17	8.27	8.37	8.53	8.61	8.60	8.75	8.82

sary to consider only the temperature correction for pK_s'. This correction is given by Frear and Johnston as $\log r = (830/T) - 2.78$. In this equation r is the ratio of solubility of $CaCO_3$ at t°C. to that at 25°C., the values of which, together with the values of the corresponding pK_s', are given in table 4.

It should be noted here that the effect of increasing temperature from 25°C. to 90°C. is to decrease the solubility of calcium carbonate[2] threefold. The significance, of course, is that heating of water will

[2] In the literature of water supply, there seems to be much confusion as to the correct solubility of $CaCO_3$ and also the effect of temperature upon its solubility. The lower values (13 p.p.m.) refer to pure water in which there is no free CO_2, and the higher values (35 to 50 p.p.m.) are for waters in equilibrium with the CO_2 of the air. As to the direction of change with temperature, several water technologists state that the solubility of $CaCO_3$ increases with temperature rise. The work of Johnston and of other authorities indicates that this is incorrect.

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cause a change in the Index toward saturation. For example, a water which has an Index of -0.3 at 25°C. will have an Index of $+0.2$ at 90°C.

(*2*) *Effect of temperature on reaction velocity.* Temperature is the most important factor in controlling reaction velocity. In general, for reactions of this kind, involving a solid and a liquid, a rise in temperature of 10°C. increases the speed of the reaction about two-fold. The importance of this is noted when it is realized that a temperature rise from 25°C. to 75°C. increases the speed of the reaction about 32-fold. The higher the temperature, the more vigorous the activity in either direction.

SIGNIFICANCE OF THE SATURATION INDEX

From the foregoing discussion it might be assumed that in practice a zero Saturation Index would be ideal. This is correct, provided that the Index is zero at those points in the system where the water is most active. If such activity occurs principally in hot water systems, obviously the high-temperature Index should be zero; on the other hand, if cold-water mains or services require protection, the low-temperature Index should be zero. Since most corrosion troubles occur in hot-water systems, it would seem that an Index of, say, -0.4 at 20°C. (which is equivalent to 0.0 at 70°C.) might prove best for most supplies.

It should be emphasized that the Saturation Index is an indication of directional tendency and of driving force but that it is in no way a measure of capacity. The capacity to coat or corrode the pipe will depend upon the property of the water to resist change in the value of its Index following attack. Obviously, a high concentration of both calcium and carbonate ions will permit of a more extensive deposit of calcium carbonate than will a low concentration, yet both waters might well have the same Index. This buffer property, or ability to resist change, will be least in soft waters; more accurately, those with the higher values of pH_s. The upper limit for this value in practice is not known, but it would seem to be somewhere in the neighborhood of 9.6. In waters of this type, the total alkalinity may need building up and for this purpose limestone contact, possibly followed with lime dosage, would seem to be the best treatment.

Moreover, the Saturation Index does not indicate the quantity of chemical required to establish equilibrium. In general the lower

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the value of pH_s the greater will be the dosage. It can be computed, but is best determined by treating several portions of the water with the chemical which is to be used and computing the Index of each from its analysis. This method would seem to possess considerable merit over the time-consuming and not two dependable marble test. It makes use of standard analytical procedures and yields more complete information.

WATER CONDITIONING AND THE SATURATION INDEX

It is interesting to note that most processes of water treatment result in a change of one or more of the several factors which determine the Saturation Index. Tables 5 and 6 furnish examples from practice, illustrating the actual effects of various treatments upon the shifting of the Saturation Index.

In table 5-A it will be noticed that raising the temperature of water from 10°C. to 90°C. changes the Index from −0.7 (one-fifth saturated) to −0.1 (practically saturated). This is due to the fact that calcium carbonate solubility decreases with temperature rise.

In table 5-B, the effect of zeolite softening (6) is indicated. Here the decrease in calcium tends greatly to increase the corrosive nature of the water, but, in the case of this particular zeolite, this tendency is partly neutralized by the removal of hydrogen ions. Incidentally, it has been found that in proportion to concentration, hydrogen ions are more readily adsorbed by zeolites than are calcium and magnesium ions. By the same token, however, hydrogen ions are not so easily removed from the zeolite during regeneration. Not all zeolites increase the pH of the softened water to the same degree, and it is believed that this property of certain zeolites in reducing the corrosiveness of the softened water has not been featured commercially.

Table 5-C was prepared from operating data of the Frankfurt (7) City Water Works plant in Germany. This plant has been in operation since 1908 and is perhaps the oldest plant of its kind in the world. The treatment of this very soft acid ground water increases both the calcium and carbonate ions by direct addition through contact with crushed limestone. The hardness is increased from 31 to 95 p.p.m., and the free carbon dioxide is reduced from 30 to 3 p.p.m. by the treatment. The index indicates that the water is not rendered completely nonaggressive.

Table 5-D is included to show how the index varies at successive stages of the complete treatment of the soft Sacramento River water.

To the student of anti-corrosion water treatment, the data of the

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TABLE 5

Examples of computed effects of various treatments upon the Saturation Index

SOURCE OF SAMPLES	RESULTS OF ANALYSIS				$(pK'_2 - pK'_s)$	pCa	pAlk	pH_s	SATURATION INDEX $(pH - pH_s)$
	pH*	Parts per million							
		Ca^{++}	Total Alk as HCO^-_3	Total diss. solids					
A. Effect of temperature change									
City of Detroit Supply, temperature 10°C	7.7	26	89	153	2.3	3.2	2.9	8.4	−0.7
City of Detroit Supply, temperature 20°C	7.7	26	89	153	2.2	3.2	2.9	8.3	−0.6
City of Detroit Supply, temperature 50°C	7.7	26	89	153	2.0	3.2	2.9	8.1	−0.4
City of Detroit Supply, temperature 90°C	7.7	26	89	153	1.7	3.2	2.9	7.8	−0.1
B. Effect of zeolite softening									
Raw water (England), temperature 15°C	7.0	113	150	370	2.4	2.5	2.5	7.4	−0.4
Zeolite softened, ½ hour after start	7.8	1	160	455	2.4	4.6	2.5	9.5	−1.7
Zeolite softened, 3 hours after start	7.5	1	153	430	2.4	4.6	2.5	9.5	−2.0
Zeolite softened, 6 hours after start	7.5	2	150	420	2.4	4.3	2.5	9.2	−1.7
Mixed raw and softened as supplied	7.3	56	151	415	2.4	2.8	2.5	7.7	−0.4
C. Effect of contact in limestone filter									
Raw water (Frankfurt, Germany) temperature 15°C.	5.8	8	32		2.3	3.7	3.3	9.3	−3.5
Filtered water	7.0	33	108		2.4	3.1	2.7	8.2	−1.2
D. Effect at various stages of complete treatment									
Raw water (Sacramento, California), temperature 15°C	7.1	8	31	50	2.2	3.7	3.3	9.2	−2.1
After aeration	7.3	8	31	50	2.2	3.7	3.3	9.2	−1.9
After coagulation (16 p.p.m. alum)	6.7	8	18	50	2.2	3.7	3.5	9.4	−2.7
After filtration + 8 p.p.m. hydrated lime	9.2	12	33	60	2.2	3.5	3.3	9.0	+0.2
Outer end of distribution system	9.0	12	33	60	2.2	3.5	3.3	9.0	+0.0

* All pH determinations made at room temperature.

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TABLE 6

*Application of index to New York City pipe corrosion experimental data**

DESCRIPTION OF TEST	RESULTS OF ANALYSIS				$(pK'_2 - pK'_s)15°$	pCa	pAlk	pH_s	SATURATION INDEX (pH − pH_s)
	pH	Parts per million							
		Ca^{++}	Total Alk as HCO^-_3	Total diss. solids					
Raw water, Catskill Supply, Test 111	6.9	4	8.5	20	2.1	4.0	3.8	10.3†	−3.5
Treated soda ash, 5.0 p.p.m., Test 411	7.4	4	12.5	25	2.1	4.0	3.6	9.9†	−2.5
Treated soda ash, 10.0 p.p.m., Test 511	8.3	4	16	35	2.2	4.0	3.5	9.9†	−1.6
Treated caustic soda, 4.0 p.p.m., Test 711	8.3	4	12.5	25	2.1	4.0	3.6	9.9†	−1.6
Treated hyd. lime, 4.5 p.p.m., Test 611	8.4	6	12.5	25	2.1	3.8	3.6	9.6†	−1.3
Treated hyd. lime, 13.0 p.p.m., Test 471-A	9.7	10	22	35	2.2	3.6	3.4	9.3†	+0.4
Treated hyd. lime, 23.0 p.p.m., Test 571	10.1	16	32	45	2.2	3.4	3.3	8.9	+1.2
Treated hyd. lime, 63.0 p.p.m., Test 671-A	10.3	35	72	80	2.2	3.1	2.9	8.2	+2.1
Treated hyd. lime, 100.0 p.p.m., Test 771-A	10.7	54	120	120	2.3	2.9	2.7	7.9	+2.7

* See J. A. W. W. A. *26*, 1315–1347 (1934); *27*, 1199–1224 (1935).

† Corrected for $\log\left(1 + \frac{2K'_2}{(H_s^+)}\right)$

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New York City pipe corrosion experiments (8) are of greatest value. These experiments were broad in scope and conducted with thoroughness, and most of the tests were continued over a sufficiently long period of time as to give conclusive results. It is particularly fortunate that these experimental results are available to check the predictions of the Saturation Index theory. Table 6 has been prepared from these data. The failure of each treatment of the first series (Tests 411 to 611) to render the water noncorrosive checks with the moderately high negative values for the computed Index. Also, the success of some of the lower lime treatments in the second series of tests (471-A to 771-A) is indicated by the change in the sign of the Index. It would seem that this water might best be treated by a combination of limestone contact and dosage with lime. This treatment, as compared with the use of lime alone, would reduce the causticity at the equilibrium point. In any event, a -0.5 index at 15°C. should give adequate protection to the consumer-owned hot-water systems, since at the higher temperatures the Index would change to about $+0.1$. It is believed that such treatment need not increase the hardness more than about 15 parts per million.

Tables 7-A to 7-D inclusive were prepared from analytical data from various sources but mostly from U. S. G. S. Water Supply Paper 659, The Industrial Utility of Public Water Supplies (1932). These tables contain the computed Index for several typical municipal water supplies throughout the United States and are grouped in accordance with the kind of pH adjustment practised. In examining these tables it should be borne in mind that the data were computed from analyses made five or six years ago, and they may or may not represent conditions as they are today. Also, in most instances the analyses represent the average of conditions which may fluctuate between rather wide limits. It is believed, however, that from them certain general conclusions may be safely drawn. First, it is apparent that most untreated natural waters, both from ground and surface sources, lie on the acid side of equilibrium, the surface waters to a greater extent than the ground waters, and second, in most cities where either upward or downward pH adjustment is practised, the tendency is slightly to undertreat. The average Index numbers (15°C.) for the four classifications are as follows:

Unadjusted ground waters (California only)	−0.48
Unadjusted surface waters (raw and filtered)	−1.54
pH adjusted upward	−0.76
pH adjusted downward	−0.04

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TABLE 7

Saturation Index of various existing municipal water supplies

SOURCE OF SAMPLES	RESULTS OF ANALYSIS				$(pK'_2 - pK'_s)15°$	pCa	pAlk	pH_s	SATURATION INDEX (pH − pH_s
	pH	Parts per million							
		Ca^{++}	Total Alk as HCO^-_3	Total diss. solids					
A. Anti-corrosion treatment practised; pH adjusted upward									
Atlanta, Ga.; C. River filtered	7.5	4	12	26	2.1	4.0	3.7	10.0*	−2.3
Baltimore, Md.; Res. filtered	7.8	15	52	70	2.2	3.4	3.1	8.7	−0.9
Cambridge, Mass.; Res. filtered	8.3	15	22	91	2.2	3.4	3.5	9.1	−0.8
Charleston, S. C.; Res. filtered	7.5	7	25	42	2.2	3.8	3.4	9.5*	−2.0
Charleston, W. Va.; River filtered	8.9	10	38	40	2.2	3.6	3.2	9.0	−0.1
Cincinnati, Ohio; Ohio River filtered	8.4	34	45	207	2.3	3.1	3.1	8.5	−0.1
Oakland, Calif.; Mokelumne Res.	8.7	6	22	44	2.2	3.8	3.5	9.6*	−0.9
Philadelphia, Pa.; S. River filtered	7.2	37	63	230	2.3	3.0	3.0	8.3	−1.1
Providence, R. I.; Res. filtered	8.7	12	17	54	2.2	3.5	3.6	9.4*	−0.7
W. Palm Beach, Fla.; Lake filtered	9.5	15	14	91	2.2	3.4	3.6	9.3*	+0.2
Wheeling, W. Va.; Ohio River, filtered	9.4	35	16	350	2.4	3.1	3.6	9.1	+0.3
B. Stabilization treatment practised; pH adjusted downward following lime-soda softening									
Bloomington, Ill.; Reservoir	9.1	11	54	108	2.2	3.6	3.1	8.9	+0.2
Cedar Rapids, Iowa; Cedar River	8.6	28	36	154	2.3	3.2	3.2	8.7	−0.1
Grand Rapids, Mich., G. River	8.6	70	94	156	2.3	2.8	2.8	7.9	+0.7
Sandusky, Ohio; Lake Erie	8.8	26	52	187	2.3	3.2	3.1	8.6	+0.2
S. Pittsburg, Pa.; Mon. River	8.0	28	24	371	2.4	3.2	3.4	9.0	−1.0
Springfield, Ill.; Mixed River and Wells	9.0	17	50	176	2.3	3.4	3.1	8.8	+0.2
St. Louis Mo.; Missouri R. Supply	8.9	21	51	222	2.3	3.3	3.1	8.7	+0.2
Thomasville, Ga.	9.1	16	30	180	2.3	3.4	3.3	9.0	+0.1

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C. A few typical ground water supplies in California; pH unadjusted

East Bakersfield	7.6	12	85	119	2.3	3.5	2.8	8.6	−1.0
West Bakersfield	7.1	29	102	206	2.3	3.1	2.8	8.2	−1.1
Chico	7.4	15	115	156	2.3	3.4	2.7	8.4	−1.0
Dixon	7.8	46	415	428	2.4	2.9	2.2	7.5	+0.3
Marysville	7.5	23	156	221	2.3	3.2	2.6	8.1	−0.6
Pleasanton	7.8	67	296	450	2.4	2.8	2.3	7.5	+0.3
Stockton	7.5	14	203	391	2.4	3.4	2.5	8.3	−0.8
Willows	8.0	26	278	299	2.4	3.2	2.3	7.9	+0.1

D. Large municipal water supplies; pH unadjusted

Boston, Mass.; Res.	6.9	5	16	43	2.2	3.9	3.6	9.9*	−3.0
Bridgeport, Conn.; Res.	6.5	5.5	8.3	56	2.2	3.8	3.9	9.9*	−3.4
Chicago, Ill.; Lake Michigan	8.0	34	146	157	2.3	3.1	2.6	8.0	0.0
Cleveland, Ohio; Lake Erie filtered	7.5	34	104	159	2.3	3.1	2.8	8.2	−0.7
Denver, Colo.; mixed supply	7.5	32	103	202	2.3	3.1	2.8	8.2	−0.7
Hartford, Conn.; Res. filtered	6.7	4	15	33	2.1	4.0	3.6	9.9*	−3.2
Los Angeles, Calif.; Owens River	7.9	27	215	302	2.4	3.2	2.4	8.0	−0.1
Minneapolis, Minn.; Wins. R. filtered	6.9	44	167	210	2.3	3.0	2.6	7.9	−1.0
New York, N. Y.; Croton Supply	7.0	13	42	73	2.2	3.5	3.2	8.9	−1.9
San Francisco, Calif.; Hetch Hetchy Supply	7.5	5	24	45	2.2	3.9	3.4	9.6*	−2.1
San Francisco, Calif.; local supply	7.7	45	180	250	2.3	2.9	2.5	7.7	0.0
Seattle, Washington, C. River and Lake	7.1	6	26	41	2.2	3.8	3.4	9.5*	−2.4

* Corrected for the term $\log\left(1 + \frac{2K'_2}{(H_s^+)}\right)$

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ECONOMIES RESULTING FROM pH ADJUSTMENT

It is not the purpose of this paper to discuss at any length the economic merits of the pH adjustment of public water supplies except to point out that great optimism exists among those who are pioneering in this direction. If there is merit in anti-corrosion water treatment, it is apparent from the data of table 7-D that many cities are in a position to take advantage of its adoption. It is believed that water superintendents in cities where the Saturation Index of the water falls well below -1.0 should investigate its possibilities. They will find in general that the annual saving to house owners in cost of repairs and replacements to hot-water systems will greatly exceed the cost of treatment.

SUMMARY AND CONCLUSIONS

An equation is derived for pH_s, the pH at which a given water is in equilibrium with solid calcium carbonate. This equation, in its simplest form and applicable within the pH range 7.0 to 9.5, is: $pH_s = (pK_2' - pK_s') + pCa^{++} + pAlk$. The two latter terms are negative logarithms of the molal and equivalent concentrations of calcium and titratable base, respectively. pK_2' and pK_s' are the negative logarithms of the second dissociation constant for carbonic acid and the activity product of $CaCO_3$, respectively. The difference $(pK_2' - pK_s')$ varies with ionic strength (salinity) and temperature. Its value for a soft water at 20°C. is 2.1 and at 80°C. is 1.6. A table of values for varying salinities and temperatures is given. Experiments with a wide variety of raw and treated waters confirm the validity of the equation at 25°C. The difference $(pH_{actual} - pH_s)$ is called the Saturation Index. If the Index is zero, the water is in equilibrium at that temperature. A positive Index indicates oversaturation and a tendency to crystallize or to lay down a protective coating of $CaCO_3$ in the pipe, and a negative Index indicates undersaturation, or a tendency to dissolve an existing carbonate coating. A rise of temperature increases the algebraic value of the Index, and for a given water very materially increases the degree of activity.

The average Index for the several largest unadjusted municipal water supplies in the United States was found to be -1.58 equivalent to 2.63 percent of saturation. In those cities where pH adjustment is practised, either for corrosion or incrustation control, the tendency is to undertreat.

The effects of various forms of water conditioning, i.e. zeolite soft-

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ening, lime-soda softening, coagulation with alum, contact with limestone, dosing with caustic soda or lime, etc., upon the Saturation Index, are discussed and examples from practice are given.

The Index is shown to correlate with the published results of a six-year study of interior pipe corrosion by the New York City Water Department.

The Index furnishes a new method which can be used in the laboratory control of anti-corrosion water treatment.

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