

An Index of the Tendency of CaCO₃ to Precipitate from Irrigation Waters¹

C. A. BOWER, L. V. WILCOX, G. W. AKIN, AND MARY G. KEYES

WHEN WATERS HAVING appreciable concentrations of bicarbonates are employed for irrigation, a variable fraction of this constituent precipitates in the soil as CaCO₃ according to the equation:



The precipitation causes a decrease in soil salinity but an increase in the proportion of Na in the soil solution, and, therefore, on the exchange complex. While the extent of bicarbonate precipitation from irrigation waters is governed in a complex manner by water management practices and soil conditions, as well as by water composition, an index of the tendency of CaCO₃ to precipitate from waters should prove useful in appraising water quality.

Langelier (4) has devised an index, termed the saturation index, for indicating the extent to which waters flowing in a closed system (no loss of CO₂) will precipitate or dissolve CaCO₃. The saturation index is defined as the actual pH of a water (pH_a) minus the theoretical pH (pH_c) that the water would have if it were in equilibrium with CaCO₃, viz.:

$$\text{Saturation index} = \text{pH}_a - \text{pH}_c \quad [2]$$

Positive values of the index indicate that CaCO₃ will precipitate from the water whereas negative values indicate that the water will dissolve CaCO₃. Langelier's equation for calculating pH_c from a water analysis is:

$$\text{pH}_c = (\text{pK}_2' - \text{pK}_c') + \text{pCa} + \text{pAlk} \quad [3]$$

The last two terms of the equation are the negative logarithms of the molal concentration of Ca and of the equivalent concentration of titratable base (CO₃ + HCO₃), respectively, while pK₂' and pK_c' are the negative logarithms of the second dissociation constant for H₂CO₃ and the solubility constant of CaCO₃, respectively, both corrected for ionic strength.

In greenhouse and lysimeter experiments, Bower (1) and Pratt et al. (4) found the fraction of applied HCO₃ that precipitated in the soil to be highly related to a modified Langelier saturation index. The modification of the index consisted simply of substituting the pH of the highly-buffered soil for the actual pH (pH_a) of the poorly-buffered irrigation water. Thus, although Langelier's equations were derived for a closed system, the above findings suggest that, for application of irrigation water to soil of a given pH reading, the pH_c value is a measure of the tendency of CaCO₃ to precipitate from the water. The purpose of this note is to present data that (1) facilitate the calculation of pH_c values from water analyses, (2) verify Langelier's equation for calculating pH_c, and (3) relate the amount of HCO₃ that precipitates from waters upon saturation with CaCO₃ to the initial pH_c value.

Calculation of pH_c Values

Table 1 gives values for constructing graphs that facilitate the calculation of pH_c values from water analyses. It is convenient to plot the variables on semilog paper with the Ca, titratable base, and total cation concentrations on the log axis. The values for (pK₂' - pK_c') are based on

the following equation, the last term of which gives the Debye-Huckel correction for ionic strength, μ:

$$(\text{pK}_2' - \text{pK}_c') = \left(2.0269 + 0.5092 \frac{4(\mu)^{1/2}}{1 + 2(\mu)^{1/2}} + \frac{(\mu)^{1/2}}{1 + 1.45(\mu)^{1/2}} \right) \quad [4]$$

The number 2.0269 is the difference between pK₂ and pK_c, using K₂ = 4.7 × 10⁻¹¹ and K_c = 5.0 × 10⁻⁹ as the numerical values of the constants. The ionic strength and total cation concentration of natural waters are highly correlated. A statistical study² of these variables developed the regression equation,

$$1000\mu = 1.3477C + 0.5355 \quad [5]$$

where C is total cation concentration in meq per liter. Values for ionic strength derived from equation [5] were substituted in equation [4] to give the values for (pK₂' - pK_c') shown in Table 1. These values are slightly lower than those of Langelier (3) owing to use of a more refined Debye-Huckel correction and improved constants.

Verification of Langelier's Equation for Calculating pH_c

Twenty-three synthetic waters containing various proportions of Ca and HCO₃ were prepared from NaHCO₃, NaCl, and CaCl₂. The composition and pH_c values of the waters are given in columns 1 to 5 of Table 2. To test the validity of equation [3], a sample of each water was placed in a 500-ml Erlenmeyer flask containing 2 g of pure precipitated CaCO₃ and a magnetic stirring bar. The flasks were filled completely, stoppered, and then placed in a water bath supported on two magnetic stirrers. After equilibrating the waters with the CaCO₃ at 23 ± .1C by vigorous stirring over a period of 90 min, the pH of the suspensions, and the Ca and HCO₃ concentrations of the filtered waters were measured using methods given by the U. S. Salinity Laboratory Staff (5).

The results of the Ca, HCO₃, and pH measurements are given in columns 6, 7, and 8 of Table 2, respectively. Column 9 of Table 2 gives the theoretical pH values of

² The data used in this study were obtained from the analyses of 200 natural waters, 100 of which were surface waters and 100 ground waters. In each group, the concentration ranged uniformly from about 1 to 50 meq/liter of total cations. The statistical constants are: correlation coefficient, r, 0.9946; coefficient of determination, r², .9892%; and standard error of estimate, \bar{S} , ± 1.96.

Table 1—Data for the construction of graphs for use in the calculation of pH_c. Relate (pK₂' - pK_c') to total cation concentration, and pCa and pAlk to calcium and titratable base concentrations, respectively

Concentration meq/liter	(pK ₂ ' - pK _c ')	pCa	pAlk
0.1	----	4.30	4.00
0.5	2.11	3.80	3.30
1	2.13	3.30	3.00
2	2.16	3.00	2.70
4	2.20	2.70	2.40
6	2.23	2.52	2.22
8	2.25	2.40	2.10
10	2.27	2.30	2.00
15	2.32	2.12	1.82
20	2.35	2.00	1.70
25	2.38	1.90	1.60
30	2.40	1.82	1.52
35	2.42	1.78	1.46
40	2.44	1.70	1.40
50	2.47	1.60	1.30

¹ Contribution from U. S. Salinity Laboratory, Soil and Water Conservation Research Division, ARS, USDA, Riverside, California in cooperation with the 17 Western States and Hawaii. Received Jan. 19, 1964. Approved Aug. 25, 1964.

Table 2—Ca²⁺ and HCO₃⁻ concentrations of synthetic waters saturated with CaCO₃ in a closed system and at P_{CO₂} = 0.00033 atm

No.	Synthetic water					Synthetic water saturated with CaCO ₃ in a closed system					Synthetic water saturated with CaCO ₃ at P _{CO₂} = 0.00033 atm			
	Ca	Na	HCO ₃	Cl	pH _c	Ca	HCO ₃	pH		ΔHCO ₃	P _{CO₂} †	Ca †	HCO ₃ †	ΔHCO ₃
	meq/liter					meq/liter		Measured	Calculated*	meq/liter	atm	meq/liter		
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
1	5.00	15.00	10.00	10.00	6.95	2.68	7.65	7.30	7.33	2.35	0.02300	0.10	5.10	4.90
2	2.50	7.50	5.00	5.00	7.47	1.89	4.37	7.70	7.65	0.63	0.00626	0.26	2.76	2.24
3	1.25	3.75	2.50	2.50	8.01	1.24	2.40	8.20	8.04	0.10	0.00141	0.54	1.79	0.71
4	0.25	0.75	0.50	0.50	9.33	0.44	0.68	9.10	8.97	-0.18	0.00004	1.00	1.25	-0.75
5	10.00	10.00	10.00	10.00	6.65	6.38	6.40	7.00	7.00	3.60	0.03800	1.27	1.27	8.73
6	5.00	5.00	5.00	5.00	7.17	4.03	3.90	7.40	7.37	1.10	0.01050	1.23	1.23	3.77
7	2.50	2.50	2.50	2.50	7.71	2.35	2.23	7.90	7.79	0.27	0.00229	1.20	1.20	1.30
8	0.50	0.50	0.50	0.50	9.03	0.83	0.78	8.80	8.63	-0.28	0.00011	1.15	1.15	-0.65
9	4.00	13.00	5.00	12.00	7.33	3.29	4.10	7.60	7.49	0.90	0.00825	0.73	1.73	3.27
10	3.00	11.00	8.00	6.00	7.23	1.52	6.50	7.60	7.61	1.50	0.01040	0.09	5.09	2.91
11	3.00	18.00	11.00	10.00	7.13	1.08	8.95	7.80	7.66	2.05	0.01250	0.05	8.05	2.95
12	6.00	5.00	5.00	6.00	7.10	4.83	3.78	7.30	7.31	1.22	0.01150	1.97	0.97	4.03
13	3.00	6.00	6.00	3.00	7.30	2.01	6.04	7.60	7.55	0.86	0.00916	0.19	3.19	2.81
14	8.00	11.00	11.00	8.00	6.70	4.44	7.43	7.20	7.10	3.57	0.03680	0.21	3.21	7.79
15	4.00	14.00	14.00	4.00	6.89	1.18	11.21	7.50	7.50	2.79	0.02290	0.03	10.03	3.97
16	3.00	6.00	6.00	3.00	7.30	2.04	5.01	7.60	7.54	0.99	0.00919	0.19	3.19	2.81
17	5.00	3.00	3.00	5.00	7.37	4.71	2.58	7.60	7.47	0.42	0.00551	2.80	0.80	2.20
18	4.00	2.00	2.00	4.00	7.63	3.98	1.90	7.85	7.65	0.10	0.00285	2.80	0.80	1.20
19	5.00	4.00	4.00	5.00	7.26	4.32	3.25	7.45	7.42	0.75	0.00793	1.98	0.96	3.04
20	4.00	6.00	6.00	4.00	7.19	2.86	4.86	7.45	7.41	1.15	0.01170	0.34	2.34	3.66
21	6.00	5.00	5.00	6.00	7.10	4.91	3.86	7.35	7.29	1.14	0.01220	1.97	0.97	4.03
22	6.00	69.00	3.00	72.00	7.57	5.60	2.61	7.75	7.66	0.39	0.00327	3.99	0.99	2.01
23	16.00	55.00	5.00	66.00	6.93	14.44	3.46	7.15	7.12	1.54	0.01500	11.57	0.57	4.43

* Calculated by the equation $\text{pH} = (\text{pK}_a' - \text{pK}_c') + \text{pCa} + \text{pHCO}_3$ using the values for Ca and HCO₃ given in columns 6 and 7.
 † Calculated essentially by methods of Frear and Johnston (2).

the CaCO₃-saturated waters calculated from their Ca, HCO₃, and total cation concentrations by equation [3]. The substantial agreement of the measured and calculated pH values verifies the validity of equation [3] for calculating pH_c, i.e., the pH value of a water in equilibrium with CaCO₃.

Relation of pH_c to the Amount of HCO₃ that Precipitates upon Saturation with CaCO₃

Column 10 of Table 2 gives the decrease or increase in HCO₃ concentration (ΔHCO₃) of the 23 synthetic waters discussed in the previous section upon saturation with CaCO₃ in a closed system. Also given in Table 2 (column 11) are the partial pressures of CO₂ (P_{CO₂}) in the closed systems containing the CaCO₃-saturated waters calculated essentially by the methods of Frear and Johnston (2). For the 21 waters where precipitation of CaCO₃ occurred (HCO₃ concentration decreased), the coefficients of correlation (r) between the indicated variables are as follows:

$$\begin{aligned} P_{\text{CO}_2} \text{ vs } \Delta\text{HCO}_3 \text{ (col. 10)} & \quad r = .96 \\ \log P_{\text{CO}_2} \text{ vs } \text{pH}_c \text{ (col. 5)} & \quad r = -.98 \\ \log \Delta\text{HCO}_3 \text{ vs } \text{pH}_c \text{ (col. 5)} & \quad r = -.94 \end{aligned}$$

The high values of the three correlation coefficients show that the ΔHCO₃, pH_c, and P_{CO₂} values for the closed systems are highly interrelated. Moreover, in view of the well-known effect of P_{CO₂} on CaCO₃ solubility, the close relations between ΔHCO₃ and P_{CO₂}, and between pH_c and log P_{CO₂} probably account for the close relation found between log ΔHCO₃ and pH_c. Because the latter relation should have practical applications, the regression equation was calculated and found to be $\log \Delta\text{HCO}_3 = 8.93 - 1.24 (\text{pH}_c)$.

Having found a good relation between pH_c and the decrease in HCO₃ concentration for closed systems with variable P_{CO₂}, the question arises as to whether there are similar relations for systems in which the P_{CO₂} is constant and in the range commonly found in soil, i.e., .00033 to

.01 atm. Theoretical values for the Ca and HCO₃ concentrations of the 23 synthetic waters in equilibrium with CaCO₃ at P_{CO₂} = .00033 atm are given in columns 12 and 13 of Table 2 along with the resulting ΔHCO₃ values (column 14). For the 21 synthetic waters where ΔHCO₃ is positive, the coefficient of correlation between pH_c and log ΔHCO₃ is -.97, and the regression equation is $\log \Delta\text{HCO}_3 = 5.88 - .746 (\text{pH}_c)$. Theoretical concentrations of Ca and HCO₃ were also calculated for water nos. 2, 3, 4, 5, 8, and 23 at P_{CO₂} = .01 atm. The equilibrium Ca and HCO₃ concentrations at P_{CO₂} = .01 atm were from 2.15 to 2.73 meq/liter higher than at P_{CO₂} = .00033 atm, and the average difference in concentration (2.45 meq/liter) is nearly equal to the increase in the solubility of Ca(HCO₃)₂ at P_{CO₂} = .01 atm as compared to the solubility at P_{CO₂} = .00033 atm. Thus, for both closed systems and those having constant P_{CO₂}, the pH_c value of a water is an index of the tendency of CaCO₃ to precipitate from the water.—C. A. BOWER, *Director*, L. V. WILCOX, *Soil Scientist*, and G. W. AKIN and MARY G. KEYES, *Physical Science Technicians*, U. S. Salinity Laboratory, Riverside, Calif.

LITERATURE CITED

1. Bower, C. A. 1961. Prediction of the effects of irrigation waters on soils. Proc. UNESCO Arid Zone Symposium, "Salinity Problems in the Arid Zones" (Tehran, Iran): 215-222.
2. Frear, G. L. and Johnston, J. 1929. The solubility of calcium carbonate (calcite) in certain aqueous solutions at 25°. J. Amer. Chem. Soc. 51:2082-2093.
3. Langelier, W. F. 1936. The analytical control of anti-corrosion water treatment. J. Amer. Water Works Assn. 28:1500-1521.
4. Pratt, P. F., Branson, R. L., and Chapman, H. D. 1960. Effect of crop, fertilizer, and leaching on carbonate precipitation and sodium accumulation in soil irrigated with water containing bicarbonate. Trans. Intern. Soil Sci. Soc. Cong. 7th, Madison. 2:185-192.
5. United States Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. USDA Handbk. 60, 160 pages.