WATER CHEMISTRY APP

SCOPE

This App enables the user to examine the outcome of a range of aqueous reactions that are commonly encountered in water treatment practice, including chemical coagulation using iron and/or aluminium salts, pH adjustment using acids or alkalis, alkalinity adjustment and water conditioning to avoid scaling and corrosion problems. The analysis is sub-divided into 5 categories as follows:

Process category	Scope of analysis
Addition of water treatment chemicals	This tab enables the users to evaluate the impact on water pH and alkalinity of chemicals commonly used in water treatment practice. The user can select from a list of eight chemicals, also specifying the dose and water temperature.
Langelier Index and water stabilisation	Chemical coagulation usually results in an unstable water with a negative Langelier Index. This tab calculates the Langelier Index and also the alkali dose required for stabilisation.
Water softening	Hard waters can be softened by raising the pH to precipitate calcium carbonate. This tab enables the user to determine the required alkali dose to reach a residual hardness based on equilibrium considerations.
Carbon dioxide stripping	Many groundwaters are found to have high concentrations of free carbon dioxide. Processes such as chemical coagulation may also lead to high concentrations of free carbon dioxide. This tab calculates the free carbon dioxide concentration, the saturation or equilibrium concentration, thus enabling the user to specify the amount of carbon dioxide to be stripped. The post-stripping pH and Langelier Index are displayed.
Water blending	Based on the input chemical profiles of two water sources and their mixing proportions, this tab determines the blended water chemical profile.

BASIS OF ANALYSIS

The chemical reactions and related equilibrium constants used in the coding of this App are set out in the Appendix to this note.

OUTPUT

The calculated output parameter values are shown on the screen. The user interface includes a Copy command that copies the input data and the calculated parameter values to the clipboard to enable pasting to a written record file.

T J Casey
Aquavarra Research Limited

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Appendix

Water Chemistry Reactions and System Constants

Carbonate system reactions

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad\qquad (A1)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad\qquad (A2)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^= \qquad\qquad (A3)$$

Carbon dioxide solubility

The concentration of free CO_2 in water is proportional to its partial pressure in air in accordance with Henry's law.

$$[CO_2] = K_H P_{CO_2} \ \text{mol}/l \qquad\qquad (A4)$$

where K_H is the Henry's law constant and P_{CO_2} is the partial pressure (atm) of CO_2 in air.

At equilibrium, the ratio of $[CO_2]/[H_2CO_3]$ is about 631:1 (Snoeyink & Jenkins, 1980), hence it is convenient for computational purposes represent the sum of these two species by the hypothetical species H₂CO3*. Thus, equation (A4) becomes:

$$\left[H_2CO_3^*\right] \cong K_H P_{CO_2} \qquad\qquad (A5)$$

Dissociation constants for carbonate species

$$\frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3 *\right]} = K_1 \qquad\qquad (A6)$$

$$\frac{\left[H^+\right]\left[CO_3^=\right]}{\left[HCO_3^-\right]} = K_2 \qquad\qquad (A7)$$

Dissociation constant for water $\qquad\qquad \left[H^+\right]\left[OH^-\right] = K_w \qquad\qquad (A8)$

Calcium carbonate solubility

Calcium carbonate is poorly soluble in water, its solubility being defined by the equilibrium condition:

$$\left[Ca^{2+}\right]\left[CO_3^{2-}\right] = K_{sp} \qquad\qquad (A9)$$

Equations (A5) to (A9), inclusive, are used to calculate the distribution of the carbonate species in water.

Two related composite parameters, namely total alkalinity (Talk) and total inorganic carbon (TIC) are used in these computations. They are defined as follows:

$$T_{alk} = \left[HCO_3^-\right] + 2\left[CO_3^-\right] + \left[OH^-\right] - \left[H^+\right] \ eq/l \qquad (A10)$$

$$TIC = \left[H_2CO_3 \ *\right] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right] \ mol/l \qquad (A11)$$

The changes in T_{alk} and TIC values, due to the addition of 1 mg/l of a range of chemicals used in water treatment, are given in Table 1.

Table 1

Effect of 1 mg/l addition on alkalinity and TIC

Chemical	Alkalinity (meq/l)	TIC(mM)
Al^{3+}	-0.111	0
Fe^{3+}	-0.054	0
H_2SO_4	-0.020	0
HCl	-0.028	0
CO_2	0	+0.023
$NaHCO_3$	+0.011	+0.011
$CaCO_3$	+0.020	+0.010
Na_2CO_3	+0.019	+0.009

Influence of temperature

The magnitudes of the dissociation and other constants are influenced both by the water temperature and ionic strength. Empirical expressions quantifying the temperature dependence of the carbonate system constants are given in Table A1.

Table A1
Temperature dependence of carbonate system constants
(Loewenthal and Marais, 1976)

Parameters: pK = -log(K); t = ^{o}C; T = absolute temp. (K) = 273 + t

$$pK_1 = \frac{17052}{T} + 215.21 * \log(T) - 0.12675 * T - 545.56$$

$$pK_2 = \frac{2902.39}{T} + 0.02379 * T - 6.498$$

$$pK_W = \frac{4787.3}{T} + 7.1321 * \log(T) + 0.010365 * T - 22.801$$

$$pK_H = 0.0138 * t + 1.12 \qquad for \quad t = 0 \ to \ 35 \ ^oC$$
$$pK_H = 0.0069 * t + 1.36 \qquad for \quad t = 35 \ to \ 80 \ ^o$$

$$pKsp = 0.01183 * t + 8.03$$

Ionic strength correction

The adjustment of the values of the constants to allow for ionic strength is conveniently made on the basis of conductivity, which is a readily measurable parameter. The following empirical relation between ionic strength (μ) and conductivity is taken from Snoeyink & Jenkins (1980):

$$\mu = 1.6 \text{ x } 10^{-5} \text{ x conductivity } (\mu S / cm) \tag{A12}$$

The following ionic strength corrections for the foregoing equilibrium constants are taken from Fair, Geyer & Okun (1968).

$$pK_{1\mu} = pK_1 - (\mu)^{0.5} / \left[1 + 1.4(\mu)^{0.5} \right] \tag{A13}$$

$$pK_{2\mu} = pK_2 - 2(\mu)^{0.5} / \left[1 + 1.4(\mu)^{0.5} \right] \tag{A14}$$

$$pK_{SO\mu} = pK_{SO} - 4(\mu)^{0.5} / \left[1 + 3.9(\mu)^{0.5} \right] \tag{A15}$$

$$pK_{W\mu} = pK_W - (\mu)^{0.5} / \left[1 + 1.4(\mu)^{0.5} \right] \tag{A16}$$

Reaction kinetics

The foregoing relationships define the carbonate system in its equilibrium state. When this state is disturbed by the addition of a strong acid or a strong alkali, the resultant reactions proceed rapidly to completion with the exception of reaction (A1), involving free CO_2 and H_2CO_3 (Snoeyink & Jenkins, 1980), which proceeds at a slower rate than the others. As a consequence there may be an initial overshoot in pH change, while the CO_2:H_2CO_3 equilibrium is being established. This is because the $H_2CO_3 \Leftrightarrow HCO_3^-$ interchange is more rapid than the $CO_2 \Leftrightarrow H_2CO_3$ interchange. For example, in the alum-based chemical coagulation process, used to remove colour and turbidity in the production of drinking water, Al^{3+} reacts with HCO_3^- to form H_2CO_3, thereby reducing the pH. Following the addition of alum, the pH is likely to temporarily drop below the equilibrium value, to which it then gradually returns as the H_2CO_3:CO_2 equilibrium ratio is re-established.

The Langelier Index (LI)

The Langelier Index is a parameter used to define the chemical condition of a water in respect of its tendency to deposit or dissolve calcium carbonate. At CaCO3 saturation, the following correlation exists:

$$\left[Ca^{2+} \right] \left[CO_3^{2-} \right] = K_{sp}$$

The pH at which a water sample would be at $CaCO_3$ saturation, without changing its Ca or T_{alk} values, is generally referred as the saturation pH or pH_s. The Langelier Index (LI), is defined as follows:

$$LI = \log \left[\frac{[Ca][CO_3]}{K_{sp}} \right] = pH - pH_s$$

A positive LI-value for a water sample indicates that it is supersaturated with respect to $CaCO_3$, whereas a negative LI-value indicates under-saturation. Hence, water that has a negative LI is aggressive towards $CaCO_3$ and is considered chemically unstable. The degree of over or under-saturation of a water sample can be calculated from its pH, alkalinity and Ca^{2+} concentrations and is known as the calcium carbonate precipitation potential or CCPP.

References

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Fair, G M, Geyer, J C and Okun, D A (1968) Water Purification and Wastewater Treatment and Disposal, Vol. 2, John Wiley & Sons Inc., New York.