Graphical Calculation of Ion Concentrations in Calcium Carbonate and/or Gypsum Soil Solutions

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ABSTRACT

Water quality specialists and agricultural extension personnel, among others, need estimates of soil solution Ca concentrations when evaluating the soil chemistry of irrigated arid lands. Existing prediction methods require computer models or extensive numerical calculations, which are often not convenient to use by field personnel. A new graphical method for calculating the equilibrium chemical concentration of waters undergoing calcium carbonate (CaCO₃) and/or gypsum dissolution or precipitation is presented. The procedure requires the assumption that the water is in an open system with CO₂, i.e., CO₂ is not affected by carbonate dissolution/precipitation reactions but rather is controlled by respiration and diffusion. The procedure can be utilized to calculate steady-state ion concentrations of soil and drainage waters.

The method of calculation permits corrections to be made for ionic strength (activity coefficient). Simplified numerical methods for correcting for ion complexation are also presented. The graphical procedures allow quick prediction of equilibrium concentration of major species in solutions in the absence of ion exchange. An evaluation of the procedure, based on various western U.S. irrigation waters and different leaching fractions, shows that the graphical method is comparable to computer simulations.

Additional Index Words: soil-water composition, calcium, bicarbonate, sulfate.


Existing methods of satisfactorily predicting the chemical composition of waters undergoing precipitation or dissolution of calcite and/or gypsum require computer models or extensive numerical calculations (4, 13, 16). Although computer simulation models yield thermodynamically correct predictions, field personnel require both a satisfactory program and access to computing facilities each time a water is to be evaluated. Such programs are primarily research tools and are often not convenient for use by water quality specialists, engineers, or agricultural extension personnel. Yet there is an acute need for calculations of Ca concentrations in evaluating the soil chemistry of arid regions. Waters percolating through the soil may undergo large concentration changes through evapotranspiration and are in contact with a much higher CO₂ partial pressure than is present at the soil surface.
Estimates of soil solution concentrations are frequently needed in evaluating the suitability of waters for irrigation. Low Ca concentrations result in high exchangeable Na percentages (ESP) on soil cation exchange sites. High ESP causes decreased hydraulic conductivity of soils because of swelling and dispersion of clay, and results in deterioration of soil structure. Low Ca concentrations can also cause Ca deficiency in the crop (typically when alkalinites are very high in a calcareous soil).

The procedure developed by Langelier (10) to predict the CaCO₃ concentration at saturation was designed for closed systems such as municipal water supplies. His model assumes that the partial pressure of CO₂ (Pₐ) controlled by carbonate dissolution-precipitation reactions, with no other sources or sinks of CO₂. This procedure is not suitable for soil scientists because the root zone is usually regarded as an "open system," as described by Garrels and Christ (4), in that the Pₐ is externally fixed. The Pₐ in the soil can be considered to be the result of a dynamic equilibrium between the production of CO₂ by plant roots and microbial respiration and the loss of CO₂ by diffusion to the overlying atmosphere. In a cropped soil, mineral reactions that consume or produce CO₂ are regarded as negligible sources or sinks of CO₂.

This paper describes a graphical method for calculating soil-water Ca concentrations and discusses simplifying procedures to correct for ionic strength and complexation effects. This procedure enables prediction of the major species in solution at steady state, assuming CaCO₃ and/or gypsum are the only solid-phase controls on solution composition. The graphical procedure is compared with computer model predictions.

DEVELOPMENT OF THE GRAPHICAL PROCEDURE

The requirements of a satisfactory graphical procedure are that (i) the evaluation of the equilibrium status of a given water be made in terms of the activities of the dissolved species, and (ii) the precipitation or dissolution of a mineral proceeds by changes in concentration such that for each mole of cation charge, removed a corresponding mole of anion...
charge is also removed (law of electroneutrality). Although plots of Ca vs. alkalinity and Ca vs. SO₄, have been used in many studies, these have been either activity plots that do not show the precipitation path in concentration units, or concentration plots that show equilibrium at fixed ionic strengths and do not indicate the path that a precipitating or dissolving water must follow as it moves towards equilibrium.

In the following discussions, activities are represented by square brackets, concentrations by parenthesis, and total quantities by the element without designation of charge. For Ca these terms are represented as [Ca⁺], (Ca²⁺), and Ca (comprised of Ca⁺² + CaSO₄° + CaCO₃°, etc.), respectively.

During calcite precipitation, every mole of Ca precipitated reduces the alkalinity (as HCO₃⁻) by 2 mol. The curvilinear lines in Fig. 1 represent the chemical evolution of a water as CaCO₃ precipitates or dissolves. The curves are drawn such that Ca = Ca₀ + 1/2 X and alkalinity = alkalinity₀ + X for any value of X, where i represents initial concentrations; e, equilibrium concentrations; and X, the change in concentration (mol/liter). The central line, Ca = 1/2 alkalinity, drawn between the curves represents a solution containing equivalent amounts of Ca and alkalinity. This may or may not be a simple CaCO₃·H₂O·CO₂ system. All other lines represent solutions in which either Ca > 1/2 alkalinity or Ca < 1/2 alkalinity, i.e., in which other ions besides Ca and HCO₃⁻ are present.

Estimates of equilibria require corrections for activity coefficients. The straight line in Fig. 1 (crossing the curved lines) represents the equilibrium values of (Ca⁺) and (HCO₃⁻) by 2 mol. The curvilinear lines drawn for precipitation or dissolution in concentration units (curvilinear lines) with the general solution to Eq. [1] (straight lines) gives a relatively simple graphical procedure for calculating equilibrium.

The advantage of using a graphical solution can be clearly seen if we consider the numerical solution to Eq. [1] for a specific water. The solution for equilibrium would be derived from the relationship

$$\gamma_{Ca^{++}} \cdot \gamma_{HCO_3^-} \cdot (Ca^{++} - X) \cdot (HCO_3^- - 2X)^2 = K_r \cdot P_{CO_2}$$  \[3\]

where X is the quantity precipitated or dissolved (in mol/liter) to achieve equilibrium. The solution to the cubic equation such as Eq. [3] requires extensive computation (1), or iteration, in addition to calculation of activity coefficients.

### Use of the Graphical Procedure

Use of the procedure requires that we know the initial solution composition, the concentration factor, or reduction in volume and the P_{CO₂}. We assume no ion exchange and no dissolution/precipitation reactions other than CaCO₃ and/or gypsum. The graph is used as follows. First assume that no precipitation or dissolution occurs upon concentration or dilution and that the final concentration is related to the initial

### Table 1—Scale values to be used for determining solubility lines for Fig. 1 and 2

<table>
<thead>
<tr>
<th>(P_{CO_2})</th>
<th>(10^{-3.5})</th>
<th>(10^{-4})</th>
<th>(10^{-4.5})</th>
<th>(10^{-5})</th>
<th>(10^{-5.5})</th>
<th>(10^{-6})</th>
<th>(\log (C_{Ca^{++}} \cdot \gamma_{HCO_3^-}))</th>
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<td>0.001</td>
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<td>3.22</td>
</tr>
<tr>
<td>0.500</td>
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<td>1.46</td>
<td>1.96</td>
<td>2.26</td>
<td>2.46</td>
<td>2.96</td>
<td>3.26</td>
</tr>
</tbody>
</table>

† Use the IAP value of 10⁻⁴ for [Ca⁺][CO₃²⁻] by adding 0.47 to the values determined above.

Use of the Graphical Procedure

Use of the procedure requires that we know the initial solution composition, the concentration factor, or reduction in volume and the P_{CO₂}. We assume no ion exchange and no dissolution/precipitation reactions other than CaCO₃ and/or gypsum. The graph is used as follows. First assume that no precipitation or dissolution occurs upon concentration or dilution and that the final concentration is related to the initial
concentration of the water, e.g., $\text{Cl} = \text{Cl}_o \cdot F$, where $\text{Cl}_o$ is the initial applied Cl concentration and $F$ is the concentration factor. In terms of the leaching fraction, $L$, often used in irrigation studies, $\text{Cl} = \text{Cl}_o / L$; $L$ is the fraction of water applied (irrigation + rainfall) that passes through the root zone, and $\text{Cl}_o$ is the average Cl concentration of the water applied. Next estimate ionic strength ($\mu$) from the empirical equation

$$1,000\mu = 1.348C + 0.536,$$  \[4a\]

where $C$ is total cation concentration in meq liter$^{-1}$ (3), or the relationship

$$\mu = 0.0127 \text{EC},$$  \[4b\]

where EC is electrical conductivity, in mmhos/cm at 25°C (5). Using an estimate of $P_{\text{CO}_2}$ and $\mu$, choose the appropriate scale value from Table 1. Find this scale value in Fig. 1 and draw a line through this point parallel to the straight line shown. Plot the point that represents the initial estimates of Ca and HCO$_3^-$, i.e., $\text{Ca} = \text{Ca}_o / L$, $\text{HCO}_3^- = \text{HCO}_3^-_o / L$. Move from this point, along the curved lines (interpolate between the two nearest curves), until the drawn straight line is intersected. This point represents the equilibrium Ca and HCO$_3^-$ concentrations, uncorrected for carbonate ion or complexing.

The omission of ion exchange reactions is justified if soils have been irrigated with the same water for a number of years, since ion exchange equilibria is likely to have been attained. Ion exchange can also be neglected if drainage waters are collected into a closed basin and concentrated by evaporation.

The approximation that (Ca$^{++}$) = Ca will be sufficient for many applications. The error in the predicted Ca concentration resulting from neglecting complexation is relatively minor when compared with errors generated by equilibria assumptions and input data accuracy for the following reasons:

1) In many cases we are more interested in (Ca$^{++}$) than in Ca and the error in (Ca$^{++}$) is smaller than the error in total Ca.

2) The uncertainty in ion activity products (IAP) or the equilibrium assumption produces a far greater error in predicted Ca than the assumption (Ca$^{++}$) = Ca. In a study with ground waters undergoing precipitation, the standard deviation of the water’s IAP from the apparent value was $10^{-0.04 \pm 0.15}$ (14). The $K_{\text{sp}}$ for calcite is $10^{-10.67}$ at 25°C, and this $K_{\text{sp}}$ is applicable for ground waters that have approached equilibrium from the dissolution side. Waters undergoing concentration but not yet precipitating CaCO$_3$ could be expected to be between $10^{-9.6}$ and $10^{-8.8}$.

3) Concentration predictions for soil waters require estimation of the concentration factor, i.e., the degree to which the water has been reduced in volume. This factor is rarely well-known.

4) The $P_{\text{CO}_2}$ in the soil varies considerably and is a function of temperature, soil moisture content, soil texture, porosity, irrigation frequency, soil fertility, and crop, among other factors. The assumption that $P_{\text{CO}_2} = 0.03$ atm at the bottom of the root zone for clay soil and 0.01 atm for sandy soil is a possible approximation in semi-arid irrigated soils if $P_{\text{CO}_2}$ data are not available.

If greater precision is desired, corrections can be made for complexation, primarily for CaSO$_4^-$, MgSO$_4^-$, and to a lesser extent, CaCO$_3^-$, CaCl$^-$, NaCO$_3^-$, and KSO$_4^-$ for aragonite; the graphical procedure utilizes the apparent IAP of $10^{-8.6}$ found to be applicable to waters that have undergone precipitation in the root zone (14). In the graphical procedure, the slightly higher Ca estimate obtained by using $\text{IAP} = 10^{-8.9}$ is offset by neglect of complexation; the resulting Ca values are very close to the computer-generated values. The straight line shown in
Fig. 2—Graphical solution for gypsum solubility, plotted for Ca and SO₄. Curved lines represent precipitation-dissolution path, straight line equilibria.

Fig. 3 is the idealized 1:1 correspondence of the Ca values. A linear regression of computed total Ca concentration vs. Ca determined graphically (not shown) gives a slope of 1.04, with an intercept of -0.53 and a correlation coefficient of 0.996. Also shown in Fig. 3 is a comparison of the graphical procedure and the computer-calculated total Ca values when an IAP of 10⁻⁸.0 is used in the computer model. As can be seen, the graphical values are about 1 mmol/liter lower than the computer-generated values. This difference is due to the fact that we did not correct for complexing when using the graphical method. For these waters a shift in the IAP value compensates for failure to correct for complexing. Corrections for complexing, as described in the appendix, allows for greater precision (resulting in 1:1 correspondence between graphical and computer-generated values).

A high degree of precision in the predicted Ca value is not required when the discrepancy between estimated and analyzed drainage water compositions is considered. These discrepancies are due to fluctuations in CO₂, errors in estimating the concentration factor (F), and differences in CaCO₃ saturation status. As previously mentioned, most arid-land soil waters are calcite-supersaturated, and the calcite $K_{sp}$ will thus underestimate ($Ca^{2+}$) and ($HCO_{3}^{-}$). A computer program utilizing the $K_{sp}$ for calcite and correcting for all known complexes will predict thermodynamically correct results, but will poorly predict Ca levels in soil waters. Although an average ion activity product value such as 10⁻⁸.0 can be used, this does not imply that each soil water will be at that level of supersaturation. The uncertainty in concentrations implicit in this choice in IAP produces more uncertainty in the predictions than do the relatively minor effects of $CaCO_{3}^{s}$, $MgCO_{3}^{s}$, $MgSO_{4}^{s}$, and $CaSO_{4}^{s}$ (unless $SO_{4}^{2-}$ concentration is very high) on Ca, as shown in Fig. 3. If additional precision is desired, corrections must be made for complexing. The gypsum-saturated solutions are usually at a higher total concentration and may contain larger amounts of ($SO_{4}^{2-}$), which forms more stable complexes. These factors make complexing more important for gypsum-saturated waters, and complexing must be taken into account for good accuracy. Kinetic problems may also exist in the gypsum system but are not as serious as those for the CaCO₃ system.
CONCLUSION

The procedure developed incorporates graphical representations of the solubility equations and curves representing the changes in concentration during precipitation or dissolution. The combination of the curves (drawn in concentrations) and solubility lines, allow the calculation of equilibrium concentrations for any solution saturated with a CaCO₃ and/or gypsum phase. The procedure incorporates correction for activity coefficients. Water quality changes can be predicted for evaporating waters in the absence of ion exchange. If high accuracy is desired the graphical procedure can be coupled with simplified calculations of important complexes. The methods are not designed to replace computer techniques, but rather to be used when such programs are not available.

APPENDIX

Before proceeding it is convenient to distinguish: (i) equilibration of waters with a CaCO₃ solid phase, (ii) equilibration of waters with gypsum, and (iii) equilibration of waters with both CaCO₃ and gypsum.

Correction for Complexation: CaCO₃ Equilibration Only

Corrections for concentrations of complexed species are especially important when large concentrations of SO₄ or Mg are present. The complexes of importance for solving the CaCO₃ solubility case are CaCO₃°, CaSO₄°, and MgCO₃°. To correct for CaCO₃°, 1.6 × 10⁻⁴ mol/liter is added to the (Ca++) value calculated from Fig. 1 to obtain Ca, and 3.2 × 10⁻⁴ mol/liter is added to the (HCO₃⁻) value to obtain HCO₃⁻. The concentration of CaCO₃° is fixed independent of pH or PCO₂ at this value, since

\[
\frac{[\text{Ca}^{++}][\text{CO}_3^{2-}]}{[\text{CaCO}_3^{+}]} = 10^{-2.1}
\]  

(1), and \(\gamma_{\text{CaCO}_3} = 1\) and \([\text{Ca}^{++}] / [\text{CO}_3^{2-}] = 10^{-0.8}\) when the apparent activity product is used. If the concentration of Mg is large, the effect of MgCO₃° is considered as follows. The amount 6.5 × 10⁻³ × (Mg²⁺/Ca²⁺) is subtracted from the (HCO₃⁻) concentration to obtain the new (HCO₃⁻) estimate. This calculation is justified since the stability constant for MgCO₃° is about twice that for CaCO₃° (12) and \(\gamma_{\text{MgCO}_3} \approx \gamma_{\text{CaCO}_3}\). The value of Mg²⁺ is obtained from Mg/L. The solution needs to be re-equilibrated with the CaCO₃ solid phase, since the calculated solution is now undersaturated (as complexes enhance solubility). To correct for CaSO₄°, the following equation is solved:

\[
\text{CaSO}_4^° = 205 [\text{Ca}^{++}][\text{SO}_4^{2-}]
\]  

(2), using the estimate of [Ca⁺⁺] and estimating [SO₄²⁻] by \(\gamma_{\text{SO}_4} \cdot \text{SO}_4 / L\). The \(\gamma\) values are plotted in Fig. 4. The value of (CaSO₄°) is subtracted from (Ca⁺⁺) to obtain a new estimate of (Ca⁺⁺). Using the complex-corrected values of (Ca⁺⁺) and (HCO₃⁻), the saturation values of (Ca⁺⁺) and (HCO₃⁻) are recalculated. The total Ca is obtained by adding (Ca⁺⁺) and (CaSO₄°). The concentration of CaCO₃° is usually an insignificant portion of Ca.

The pH can be calculated from the following equation:

\[
[H^+] = 10^{0.63-P_{\text{CO}}}/[\text{HCO}_3^-],
\]  

where \(K_1\), the first dissociation constant for H₂CO₃, = \(10^{-6.36}\), and \(K_{\text{CO}_2}\), the solubility constant of CO₂ in water at 25°C, = \(10^{-1.46}\) (6), pH = −log [H⁺], and PCO₂ is expressed in atmospheres. At pH values above 8.0–8.5 significant quantities of CO₃²⁻ are usually present. The correction for CO₃²⁻ can be made by first calculating pH using Eq. [A3]. The pH and [HCO₃⁻] values are then inserted into Eq. [A4] using a value of \(10^{-1.46}\) for the second dissociation constant of H₂CO₃ (7):

\[
[\text{CO}_3^{2-}] = 10^{0.63}[\text{HCO}_3^-]/[H^+].
\]  

The (CO₃²⁻) concentration is obtained from

\[
[\text{CO}_3^{2-}] = [\text{CO}_2^{3-}]/[\gamma_{\text{CO}_3}^{2-}],
\]  

assuming \(\gamma_{\text{CO}_3^{2-}} \approx \gamma_{\text{SO}_4} \cdot \text{SO}_4 / L\). The concentration of HCO₃⁻ is then corrected by subtracting twice the (CO₃²⁻) value from (HCO₃⁻). The corrected values of (HCO₃⁻) and (Ca⁺⁺) are then
replotted on Fig. 1 to resolve for the equilibrated (Ca\(^{2+}\)) and (HCO\(_3\)) concentrations.

**Correction for Complexation for Gypsum-Saturated Waters**

The SO\(_4^{2-}\) complexes must be considered for accurate (Ca\(^{2+}\)) and (SO\(_4^{2-}\)) predictions of gypsum-saturated solutions, since the SO\(_4^{2-}\) concentrations are often large and SO\(_4^{2-}\) ions complex to a significant degree. For a gypsum-saturated solution the concentration of CaSO\(_4\) is 4.9 x 10\(^{-3}\) mol liter\(^{-1}\) (obtained by combining Eq. [5] and Eq. [A2]). This value is added directly to the (Ca\(^{2+}\)) and (SO\(_4^{2-}\)) values determined with Fig. 2, to obtain Ca and SO\(_4\). If Mg and Na values are much greater than SO\(_4^{2-}\), correction should also be made for MgSO\(_4\) and NaSO\(_4\) complexation. MgSO\(_4\) is determined from the relationship

\[
\text{MgSO}_4 = \left[\frac{\text{Mg}^{2+}}{\text{Ca}^{2+}}\right] \times 4.9 \times 10^{-3},
\]

combining Eq. [5] and Eq. [A2] and assuming \(K_{\text{CaSO}_4} = K_{\text{MgSO}_4}, \gamma_{\text{Mg}^{2+}} = \gamma_{\text{Ca}^{2+}}, \gamma_{\text{Na}^{+}} = \gamma_{\text{HCO}_3}, \) and NaSO\(_4\) is determined from

\[
[\text{NaSO}_4] = \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3}} \times \frac{\gamma_{\text{Na}^{+}}}{\gamma_{\text{HCO}_3}} = 1.26 \times 10^{-4},
\]

obtained using \(K_{\text{sp}} \text{ gypsum} = 2.4 \times 10^{-5}\) (15) and \(K_{\text{NaSO}_4} = 1.91 \times 10^{-9}\). The values for these complexes should then be subtracted from (SO\(_4^{2-}\)). Then (Ca\(^{2+}\)) and (SO\(_4^{2-}\)) are reetermined using Fig. 2. The total amounts of Ca and SO\(_4\) are given by Ca = (Ca\(^{2+}\)) + (CaSO\(_4\)) and SO\(_4\) = (SO\(_4^{2-}\)) + (CaSO\(_4\)) + (MgSO\(_4\)) + (NaSO\(_4\)).

**Simultaneous Gypsum—CaCO\(_3\) Equilibria**

Determination of concentrations of waters in simultaneous equilibrium with gypsum and CaCO\(_3\) usually requires use of both Fig. 1 and 2. If the expression for gypsum solubility (Eq. [5]) is combined with that for CaCO\(_3\) solubility (Eq. [1]) the following relationship for simultaneous equilibria is obtained:

\[
\frac{[\text{SO}_4^{2-}]}{[\text{HCO}_3^-]^2} = \frac{7.4}{P_{\text{CO}_2}},
\]

where \(P_{\text{CO}_2}\) is expressed in atmospheres. If essentially all the precipitation of Ca occurs as gypsum (SO\(_4^{2-}\) >> HCO\(_3^-\)), then the Ca\(^{2+}\) and SO\(_4^{2-}\) concentrations are calculated from Fig. 2 and Eq. [A8] is solved for [HCO\(_3^-\)]. The HCO\(_3^-\) concentration is equal to [HCO\(_3^-\)]/\(K_{\text{HCO}_3^-}\). The difference in HCO\(_3^-\) between the value calculated and the initial value HCO\(_3^-\)/\(L\) equals the quantity precipitated. If this quantity of precipitation or dissolution is small relative to the Ca concentration in solution, then its effect on Ca can be neglected. In a similar manner, if essentially all the precipitation is expected to be from CaCO\(_3\), values of (Ca\(^ {2+}\)) and (HCO\(_3^-\)) can be calculated from Fig. 1; Eq. [A8] can then be solved for [SO\(_4^{2-}\)].

In most instances substantial amounts of both CaCO\(_3\) and gypsum may precipitate; under these conditions some iteration is required. The initial values of (Ca\(^ {2+}\)) and (HCO\(_3^-\)) are obtained from Fig. 1. The (Ca\(^ {2+}\)) and (SO\(_4^{2-}\)) concentrations, corrected for gypsum saturation, are calculated from Fig. 2 using (Ca\(^ {2+}\)) determined from Fig. 1 and (SO\(_4^{2-}\)) determined from SO\(_4^-\)/\(L\). After subtracting the (MgSO\(_4\)) and (NaSO\(_4\)) values from (SO\(_4^{2-}\)), the determination of (Ca\(^{2+}\)), (HCO\(_3^-\)), and (SO\(_4^{2-}\)) concentrations from Fig. 1 and 2 is repeated. The total concentration values are obtained by adding the concentrations of (CaSO\(_4\)) (which are fixed), (MgSO\(_4\)) (which are calculated), and (NaSO\(_4\)).

**LITERATURE CITED**


