Graphical Calculation of Ion Concentrations in Calcium Carbonate and/or Gypsum Soil Solutions[1]

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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 ($CaCO_3$) and/or gypsum dissolution or precipitation is presented. The procedure requires the assumption that the water is in an open system with CO_2, i.e., CO_2 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.**

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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 CO_2 partial pressure than is present at the soil surface.

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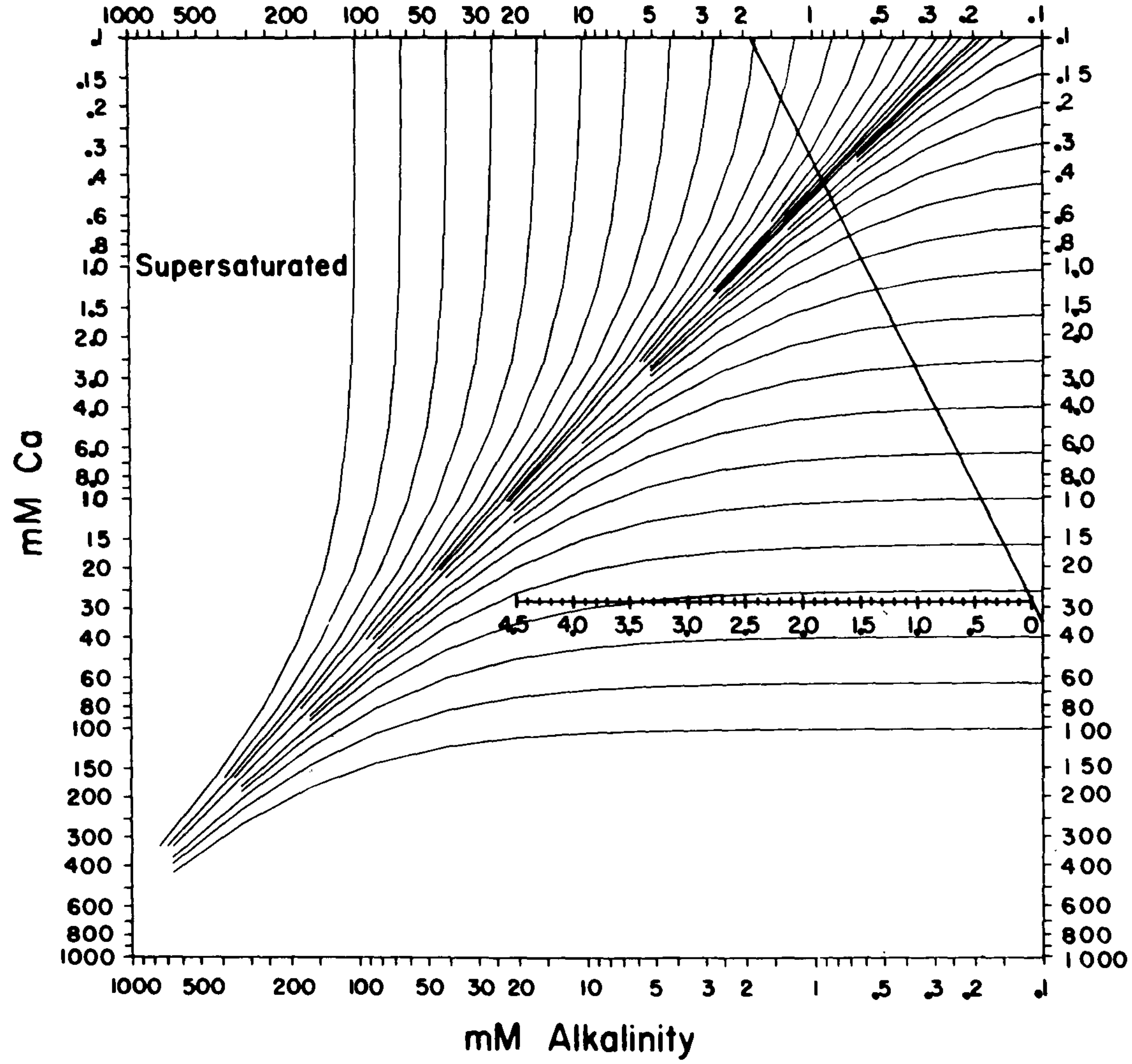

Fig. 1—Graphical solution for $CaCO_3$ solubility plotted for Ca and inorganic C alkalinity. Curved lines represent precipitation-dissolution path, straight line represents equilibria.[3]

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 alkalinities are very high in a calcareous soil).

The procedure developed by Langelier (10) to predict the $CaCO_3$ concentration at saturation was designed for closed systems such as municipal water supplies. His model assumes that the partial pressure of CO_2 (P_{CO_2}) is controlled by carbonate dissolution-precipitation reactions, with no other sources or sinks of CO_2. 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 P_{CO_2} is externally fixed. The P_{CO_2} in the soil can be considered to be the result of a dynamic equilibrium between the production of CO_2 by plant roots and microbial respiration and the loss of CO_2 by diffusion to the overlying atmosphere. In a cropped soil, mineral reactions that consume or produce CO_2 are regarded as negligible sources or sinks of CO_2.

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 $CaCO_3$ 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

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[3] Enlarged copies of this figure are available from the author.

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

μ	P_{CO_2} $10^{-3.5}$	$10^{-3.0}$	$10^{-2.5}$	$10^{-2.2}$	$10^{-2.0}$	$10^{-1.5}$	$10^{-1.2}$	$10^{-1.0}$	$10^{-0.5}$	10^{0}	$-\log(\gamma_{Ca^{2+}} \cdot \gamma_{SO_4^{2-}})$
0.001	0.09	0.59	1.09	1.39	1.59	2.09	2.39	2.59	3.09	3.59	0.12
0.002	0.14	0.64	1.14	1.44	1.64	2.14	2.44	2.64	3.14	3.64	0.17
0.005	0.20	0.70	1.20	1.50	1.70	2.20	2.50	2.70	3.20	3.70	0.26
0.007	0.23	0.73	1.23	1.53	1.73	2.23	2.53	2.73	3.23	3.73	0.30
0.01	0.27	0.77	1.27	1.57	1.77	2.27	2.57	2.77	3.27	3.77	0.35
0.02	0.35	0.85	1.35	1.65	1.85	2.35	2.65	2.85	3.35	3.85	0.47
0.03	0.42	0.92	1.42	1.72	1.92	2.42	2.72	2.92	3.42	3.92	0.55
0.04	0.46	0.96	1.46	1.76	1.96	2.46	2.76	2.96	3.46	3.96	0.61
0.05	0.50	1.00	1.50	1.80	2.00	2.50	2.80	3.00	3.50	4.00	0.66
0.07	0.57	1.07	1.57	1.87	2.07	2.57	2.87	3.07	3.57	4.07	0.75
0.10	0.64	1.14	1.64	1.94	2.14	2.64	2.94	3.14	3.64	4.14	0.84
0.15	0.72	1.22	1.72	2.02	2.22	2.72	3.02	3.22	3.72	4.22	0.95
0.20	0.78	1.28	1.78	2.08	2.28	2.78	3.08	3.28	3.78	4.28	1.03
0.25	0.83	1.33	1.83	2.13	2.33	2.83	3.13	3.33	3.83	4.33	1.09
0.30	0.87	1.37	1.87	2.17	2.37	2.87	3.17	3.37	3.87	4.37	1.14
0.40	0.92	1.42	1.92	2.22	2.42	2.92	3.22	3.42	3.92	4.42	1.22
0.50	0.96	1.46	1.96	2.26	2.46	2.96	3.26	3.46	3.96	4.46	1.27

† Use the IAP value of $10^{-8.0}$ for $[Ca^{2+}][CO_3^{2-}]$ by adding 0.47 to the values determined above.

charge is also removed (law of electroneutrality). Although plots of Ca vs. alkalinity and Ca vs. SO_4 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 $[Ca^{2+}]$, (Ca^{2+}), and Ca (comprised of $Ca^{2+} + CaSO_4^0 + CaCO_3^0$, etc.), respectively.

During calcite precipitation, every mole of Ca precipitated reduces the alkalinity (as HCO_3^-) by 2 mol. The curvilinear lines in Fig. 1 represent the chemical evolution of a water as $CaCO_3$ precipitates or dissolves. The curves are drawn such that $Ca_i = Ca_e + 1/2\,X$ and $\text{alkalinity}_i = \text{alkalinity}_e + X$ 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 $CaCO_3$-H_2O-CO_2 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 HCO_3 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^{2+}) and (HCO_3^-) assuming calcite equilibrium (8), ionic strength = 0, and $P_{CO_2} = 10^{-3.5}$ atm. This represents the minimum solubility line for $CaCO_3$, since calcite is the least soluble $CaCO_3$ phase at 25°C and 1 atm total pressure, and P_{CO_2} cannot be below $10^{-3.5}$ in an open system. Shown below is the theoretical equation of the line. If we combine the equations for the first and second dissociation constants of carbonic acid (H_2CO_3), the solubility expression for H_2CO_3, and the solubility equation for calcite, then:

$$[Ca^{2+}] = \frac{K_{CO_2} K_1 K_{sp} P_{CO_2}}{K_2\,[HCO_3^-]^2} = \frac{K_T P_{CO_2}}{[HCO_3^-]^2}, \qquad [1]$$

where K_{CO_2} is the solubility constant of H_2CO_3; K_1 and K_2 the first and second dissociation constants of H_2CO_3, respectively; K_{sp} the solubility product; and K_T the combined constant. At any fixed K_{sp} and P_{CO_2}, this solubility equation can be represented graphically by the straight line, $\log [Ca^{2+}] = \log K_T + \log P_{CO_2} - 2 \log [HCO_3^-]$. The straight line shown in Fig. 1 is for $K_{sp} = 10^{-8.47}$ (8), $K_{CO_2} = 10^{-1.46}$ (6), $K_1 = 10^{-6.36}$ (6), and $K_2 = 10^{-10.33}$ (7) at 25°C. If we assume that the ionic strength equals zero and there is no complexation then the line also represents (Ca^{2+}) and (HCO_3^-) concentrations at equilibrium. Since $(Ca^{2+}) = [Ca^{2+}]/\gamma_{Ca^{2+}}$ and $(HCO_3^-) = [HCO_3^-]/\gamma_{HCO_3^-}$, Eq. [1] can also be written as follows:

$$(Ca^{2+}) = \frac{K_T \cdot P_{CO_2}}{(HCO_3^-)^2 \cdot \gamma_{Ca^{2+}} \cdot \gamma^2_{HCO_3^-}} = \frac{K'_T \cdot P_{CO_2}}{(HCO_3^-)^2}, \qquad [2]$$

where γ's are the activity coefficients. Plotted in Fig. 1 is a scale for different values of $K'_T P_{CO_2}$. Table 1 gives the scale values calculated from $K'_T P_{CO_2}$ for different values of ionic strength and P_{CO_2}. Activity coefficients were calculated using an extended Debye-Huckel equation fit to experimental mean salt data at high ionic strength (17).

Soil waters from arid and semi-arid regions are generally supersaturated with respect to calcite. For waters undergoing $CaCO_3$ precipitation, an ion activity product (IAP) value of $10^{-8.0}$ is more appropriate for predictive purposes (14). Use of this value changes the value of K'_T, and 0.47 must be added to the values given in Table 1 for waters at 25°C. Combining the 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

$$\gamma_{Ca^{2+}} \cdot \gamma^2_{HCO_3^-} \cdot (Ca^{2+} - X) \cdot (HCO_3^- - 2X)^2 = K_T \cdot P_{CO_2}, \qquad [3]$$

with X being 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_{CO_2}. We assume no ion exchange and no dissolution/precipitation reactions other than $CaCO_3$ 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., Cl = $Cl_a \cdot F$, where Cl_a is the initial applied Cl concentration and F is the concentration factor. In terms of the leaching fraction, L, often used in irrigation studies, Cl = Cl_a/L; L is the fraction of water applied (irrigation + rainfall) that passes through the root zone, and Cl_a is the average Cl concentration of the water applied. Next estimate ionic strength (μ) from the empirical equation

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

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

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

where EC is electrical conductivity, in mmhos/cm at 25°C (5). Using an estimate of P_{CO_2} and μ, 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 estimate of Ca and HCO_3, i.e., Ca = Ca_a/L, HCO_3 = HCO_{3a}/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 values, 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^{2+}) = 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^{2+}) than in Ca and the error in (Ca^{2+}) 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^{2+}) = Ca. In a study with ground waters undergoing precipitation, the standard deviation of the water's IAP from the apparent value was $10^{-8.00\pm0.15}$ (14). The K_{sp} for calcite is $10^{-8.47}$ at 25°C, and this K_{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 $10^{-8.47}$ and $10^{-8.0}$.
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_{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_{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 semiarid irrigated soils if P_{CO_2} data are not available.

If greater precision is desired, corrections can be made for complexation, primarily for $CaSO_4^0$, $MgSO_4^0$, and to a lesser extent, $CaCO_3^0$, $MgCO_3^0$, and $NaSO_4^-$. The complexes $CaHCO_3^+$, $CaCl^+$, $NaCO_3^-$, and KSO_4^- are usually small percentages of the major species and thus can usually be neglected. If $HCO_3^- \gg CO_3^{2-} + CaCO_3^0$, then we can usually assume that alkalinity = HCO_3^-, which greatly simplifies the calculation. If this assumption is not reasonable, CO_3^{2-} must be calculated. Since these waters are not gypsum-saturated, the solutions rarely contain large quantities of SO_4. For many purposes complexing can be neglected for these waters. Whenever $HCO_3^-/Ca > 5$, correction should be made for CO_3^{2-}, and the first approximation that HCO_3^- equals carbonate alkalinity is not acceptable. Appendix A describes simplified procedures to correct for complexation.

Figure 2 showing gypsum equilibrium is constructed in a manner similar to Fig. 1. Since Ca and SO_4 react on an equal molar basis, the curved lines in Fig. 2 are constructed by using the relationships $Ca_i = Ca_e + X$ and $SO_{4_i} = SO_{4_e} + X$. The straight line in the figure is the solubility line for gypsum equilibrium, given by

$$\log\,[Ca^{2+}] + \log\,[SO_4^{2-}] = \log K_{sp} = -4.62 \qquad [5]$$

(15). This equation can also be written as

$$\log Ca^{2+} + \log SO_4^{2-} = \log\,(K_{sp}/\gamma_{Ca^{2+}}\cdot\gamma_{SO_4^{2-}}). \qquad [6]$$

Plotted in Fig. 2 is a scale for different values of $\gamma_{Ca^{2+}}\cdot\gamma_{SO_4^{2-}}$. Table 1 gives the scale values to be used with Fig. 2 for different values of ionic strength. The graph is used in the same manner as that for Fig. 1. Once the ionic strength is estimated and the scale value from Table 1 is determined, a line is drawn through that scale value parallel to the straight line in Fig. 2. The point Ca_a/L, SO_{4_a}/L is plotted and moved along the curved lines until the drawn straight line is intersected. This point represents (Ca^{2+}), (SO_4^{2-}) at saturation with gypsum, uncorrected for complexation. Complexation is significant for gypsum-saturated waters, thus it must be considered. The appendix describes the procedures for correcting for complexes and the calculations for simultaneous equilibria for $CaCO_3$ and gypsum.

EVALUATION OF PROCEDURE

The accuracy in predicting field data depends on the accuracy of the input data and equilibrium assumptions, as does the accuracy of the computer model. The major use of the graphical procedure is expected to be for waters where $CaCO_3$ (and not gypsum) precipitation occurs. For these conditions the complex corrections are not generally needed and the graphical method is easy to use. While detailed thermodynamic studies should consider all known species for calculations of accurate activity values, these complex corrections are not a major factor in improving $CaCO_3$ solubility *predictions* for the reasons discussed earlier.

Ca determined with the graphical procedure and total Ca calculated with a computer program considering all relevant ion pairs are compared in Fig. 3. The computed values for Ca were based on irrigation water compositions of major western rivers used in the lysimeter experiment of Rhoades et al. (13). The data shown are for waters that did not precipitate gypsum at the leaching fractions examined. For the purpose of a simple comparison between the computer program and graphical estimates of Ca, P_{CO_2} was taken as 0.10 atm. Oster and Rhoades (11) equilibrated the hypothetical drainage water with an IAP of $10^{-8.19}$ (uncorrected K_{sp}) for aragonite; the graphical procedure utilizes the apparent IAP of $10^{-8.0}$ 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 IAP = $10^{-8.0}$ is offset by neglect of complexation; the resulting Ca values are very close to the computer-generated values. The straight line shown in

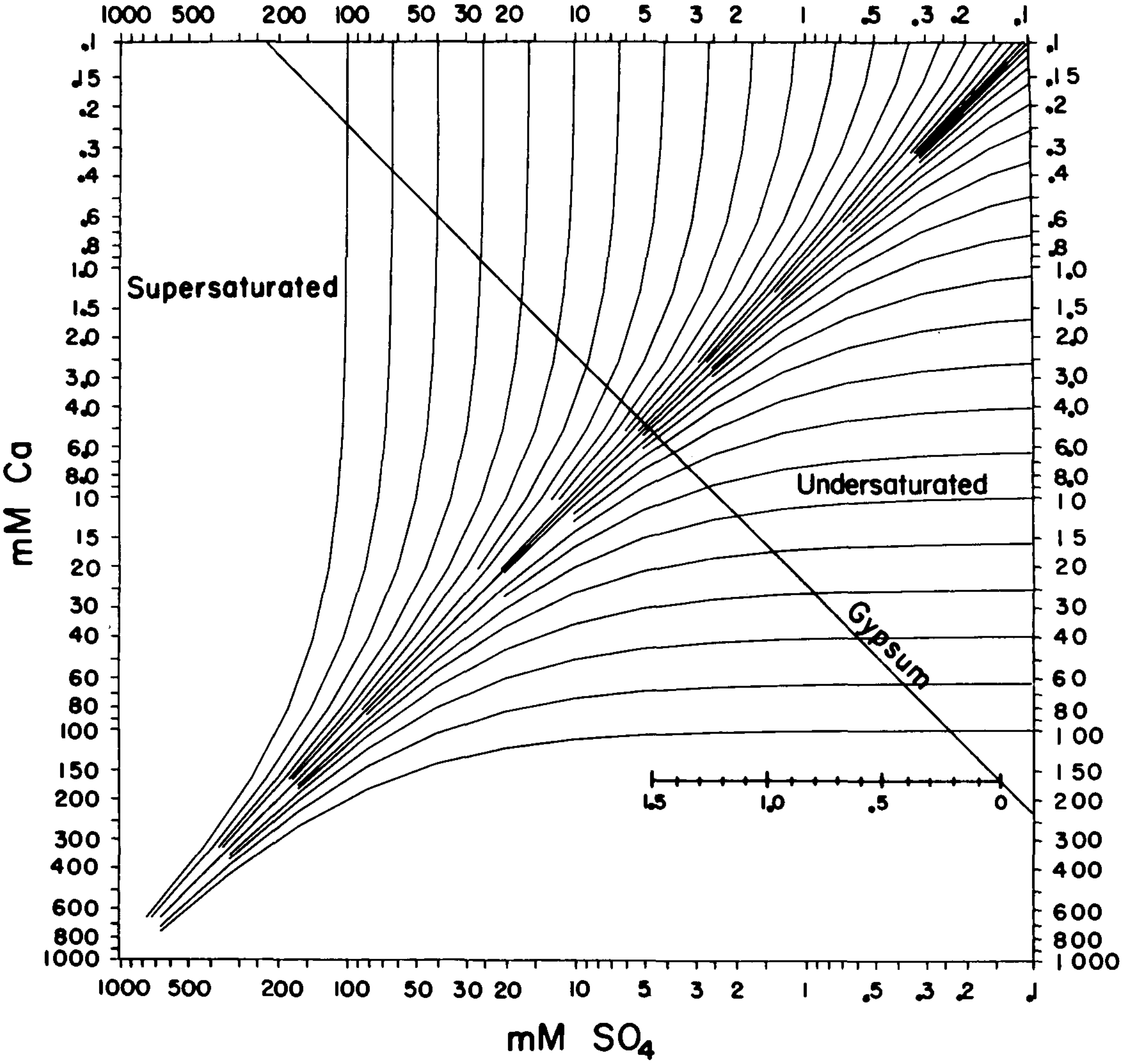

Fig. 2—Graphical solution for gypsum solubility, plotted for Ca and SO_4. Curved lines represent precipitation-dissolution path, straight line equilibria.[3]

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 CO_2, errors in estimating the concentration factor (*F*), and differences in $CaCO_3$ 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 $CaCO_3^0$, $MgCO_3^0$, $MgSO_4^0$, and $CaSO_4^0$ (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 $CaCO_3$ system.

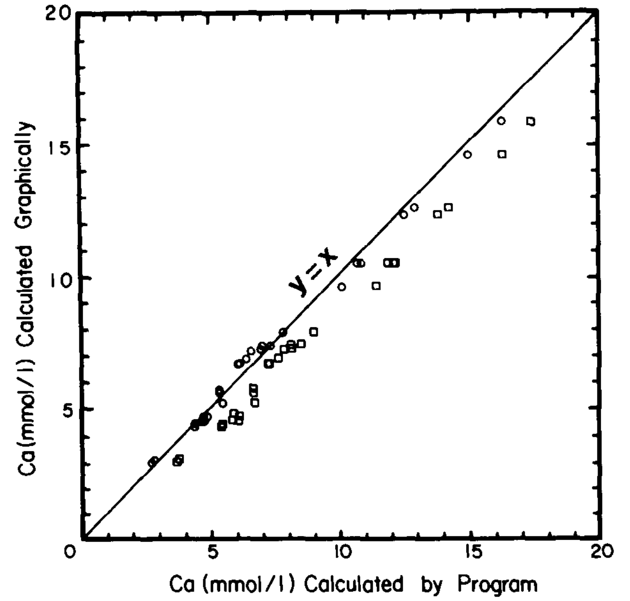

Fig. 3—Comparison of Ca concentrations calculated graphically to those calculated by computer program (correcting for activity coefficients and all complexes). Values indicated by 0 represent computer calculations using IAP of $10^{-8.19}$ values indicated by ☐ indicate computer calculations using IAP of $10^{-8.0}$.

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 $CaCO_3$ 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 $CaCO_3$ solid phase, (ii) equilibration of waters with gypsum, and (iii) equilibration of waters with both $CaCO_3$ and gypsum.

Correction for Complexation: $CaCO_3$ Equilibration Only

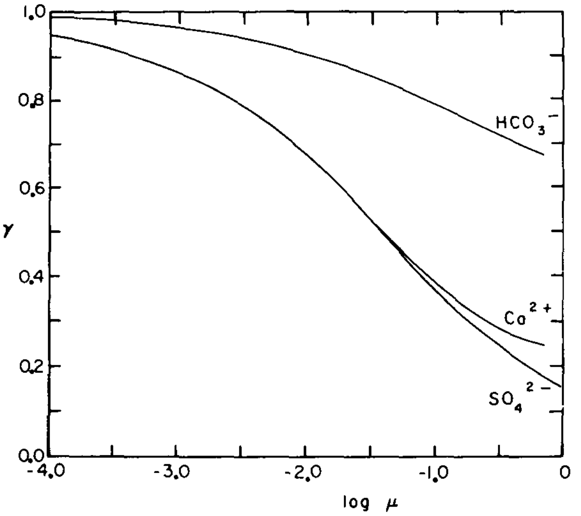

Fig. 4—Activity coefficients (γ's) of Ca^{2+}, HCO_3^- and SO_4^{2-} as a function of ionic strength (μ).

Corrections for concentrations of complexed species are especially important when large concentrations of SO_4 or Mg are present. The complexes of importance for solving the $CaCO_3$ solubility case are $CaCO_3^0$, $CaSO_4^0$, and $MgCO_3^0$. To correct for $CaCO_3^0$, 1.6×10^{-5} mol/liter is added to the (Ca^{2+}) value calculated from Fig. 1 to obtain Ca, and 3.2×10^{-5} mol/liter is added to the (HCO_3^-) value to obtain HCO_3. The concentration of $CaCO_3^0$ is fixed independent of pH or P_{CO_2} at this value, since

$$\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3^0]} = 10^{-3.2} \qquad [A1]$$

(11), and $\gamma_{CaCO_3^0} = 1$ and $[Ca^{2+}][CO_3^{2-}] = 10^{-8.0}$ when the apparent activity product is used. If the concentration of Mg is large, the effect of $MgCO_3^0$ is considered as follows. The amount $6.5 \times 10^{-5} \times (Mg^{2+}/Ca^{2+})$ is subtracted from the (HCO_3^-) concentration to obtain the new (HCO_3^-) estimate. This calculation is justified since the stability constant for $MgCO_3^0$ is about twice that for $CaCO_3^0$ (12) and $\gamma_{Ca^{2+}} \cong \gamma_{Mg^{2+}}$. The value of Mg^{2+} is obtained from Mg_a/L. The solution needs to be re-equilibrated with the $CaCO_3$ solid phase, since the calculated solution is now undersaturated (as complexes enhance solubility). To correct for $CaSO_4^0$, the following equation is solved:

$$CaSO_4^0 = 205\,[Ca^{2+}][SO_4^{2-}] \qquad [A2]$$

(2), using the estimate of $[Ca^{2+}]$ and estimating $[SO_4^{2-}]$ by $\gamma_{SO_4^{2-}} \cdot SO_{4_a}/L$. The γ values are plotted in Fig. 4. The value of ($CaSO_4^0$) is subtracted from (Ca^{2+}) to obtain a new estimate of (Ca^{2+}). Using the complex-corrected values of (Ca^{2+}) and (HCO_3^-) the saturation values of (Ca^{2+}) and (HCO_3^-) are recalculated. The total Ca is obtained by adding (Ca^{2+}) and ($CaSO_4^0$). The concentration of $CaCO_3^0$ is usually an insignificant portion of Ca.

The pH can be calculated from the following equation:

$$[H^+] = 10^{-7.82} P_{CO_2}/[HCO_3^-], \qquad [A3]$$

where K_1, the first dissociation constant for H_2CO_3, = $10^{-6.36}$, and K_{CO_2}, the solubility constant of CO_2 in water at 25°C, = $10^{-1.46}$ (6), pH = −log [H^+], and P_{CO_2} is expressed in atmospheres. At pH values above 8.0–8.5 significant quantities of CO_3^{2-} are usually present. The correction for CO_3^{2-} can be made by first calculating pH using Eq. [A3]. The pH and [HCO_3^-] values are then inserted into Eq. [A4] using a value of $10^{-10.33}$ for the second dissociation constant of H_2CO_3 (7):

$$[CO_3^{2-}] = 10^{-10.33}[HCO_3^-]/[H^+]. \qquad [A4]$$

The (CO_3^{2-}) concentration is obtained from

$$(CO_3^{2-}) = [CO_3^{2-}]/\gamma_{CO_3^{2-}}, \qquad [A5]$$

assuming $\gamma_{CO_3^{2-}} \cong \gamma_{SO_4^{2-}}$. The concentration of HCO_3^- is then corrected by subtracting twice the (CO_3^{2-}) value from (HCO_3^-). The corrected values of (HCO_3^-) and (Ca^{2+}) 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 $CaSO_4^0$ is 4.9×10^{-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 $MgSO_4^0$ and $NaSO_4^-$ complexation. $MgSO_4^0$ is determined from the relationship

$$MgSO_4^0 = \frac{[Mg^{2+}]}{[Ca^{2+}]} \cdot 4.9 \times 10^{-3}, \qquad [A6]$$

combining Eq. [5] and Eq. [A2] and assuming $K_{CaSO_4^0} \cong K_{MgSO_4^0}$, $\gamma_{Mg^{2+}} \cong \gamma_{Ca^{2+}}$, $\gamma_{Na^+} \cong \gamma_{HCO_3^-}$; and $NaSO_4^-$ is determined from

$$[NaSO_4^-] = \frac{\gamma_{HCO_3^-} \cdot Na^+}{\gamma_{Ca^{2+}} \cdot Ca^{2+}} \, 1.26 \times 10^{-4}, \qquad [A7]$$

obtained using K_{sp} gypsum $= 2.4 \times 10^{-5}$ (15) and $K_{NaSO_4^-} = 1.91 \times 10^{-1}$ (9). The values for these complexes should then be subtracted from (SO_4^{2-}). Then (Ca^{2+}) and (SO_4^{2-}) are redetermined using Fig. 2. The total amounts of Ca and SO_4 are given by Ca = (Ca^{2+}) + ($CaSO_4^0$) and SO_4 = (SO_4^{2-}) + ($CaSO_4^0$) + ($MgSO_4^0$) + ($NaSO_4^-$).

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:

$$[SO_4^{2-}]/[HCO_3^-]^2 = 7.4/P_{CO_2}, \qquad [A8]$$

where P_{CO_2} is expressed in atmospheres. If essentially all the precipitation of Ca occurs as gypsum ($SO_4^{2-} \gg HCO_3^-$), 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 $[HCO_3^-]/\gamma_{HCO_3^-}$. The difference in HCO_3^- between the value calculated and the initial value $HCO_3{}^-{}_a/L$ 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_{4a}/L. After subtracting the ($MgSO_4^0$) 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 ($CaSO_4^0$), ($CaCO_3^0$) (which are fixed), ($MgSO_4^0$), and ($NaSO_4^-$).

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