

PROGRAM FOR COMPUTING EQUILIBRIUM SOLUTION
COMPOSITION IN CaCO_3 and CaSO_4 SYSTEMS FROM
IRRIGATION WATER COMPOSITIONS

Water Management Technical Report No. 29

by

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Supported by

United States Agency for International Development
Contract No. AID/csd-2162
Water Management Research in Arid and Subhumid
Lands of the Less Developed Countries

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October, 1973

Rai, Dhanpat and W. T. Franklin. Program for Computing Equilibrium Composition of CaCO₃ and CaSO₄ Systems from Irrigation Water Compositions.
Council of U. S. Universities for Soil and Water Development in Arid and Sub-Humid Areas, Water Management Technical Report No. .
(Fort Collins: Colorado State University), October, 1973.

ABSTRACT

A computer program was developed to calculate equilibrium solution compositions in calcareous and gypsiferous systems. The calculations in the program are based upon published solubility products of calcite and gypsum and take into account ion-pair formation and the solubility enhancement of calcite resulting from the presence of Mg⁺⁺ and SO₄⁼ in the solution. For a given pre-equilibrium solution, the program predicts equilibrium ionic strength, ionic activity coefficients, dissociated (free) ions, ion-pairs, and total concentration of solution species, amount of CaCO₃ precipitated or dissolved at a specified partial CO₂ pressure, and the amount of gypsum precipitated. Lime and gypsum solubility results predicted with the computer closely agree with published experimental results. The program is suitable for assessing the sodium and salinity hazards of marginal quality waters using other independently developed parameters, such as the concentrating effects taking place in the soil solution due to evapotranspiration during the cropping cycle and partial CO₂ pressures developed under particular soil and cropping conditions.

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INTRODUCTION

The precipitation or dissolution of lime (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) during irrigation operations can significantly affect the soil solution concentration and sodium-adsorption-ratio (SAR). Lime and gypsum dissolution and precipitation phenomena have been studied extensively under laboratory conditions. Precise quantitative calculation of lime dissolution or precipitation is made complex by a number of variables, such as partial CO_2 (gas) pressure, pH, ionic strength of the solution, presence of salts more soluble than lime ("salt effects" and "common ion" effects). Temperature, through its effect on the solubility of CO_2 , affects lime solubility considerably (Frear and Johnson, 1929). A decrease in temperature increases the amount of weakly dissociated H_2CO_3 formed from increased CO_2 dissolved in solution and thus increases lime solubility. Ion-pair formation in equilibria calculations has only recently been recognized as an important consideration (Nakayama, 1968, 1969). Several forms of CaCO_3 , each varying in solubility, can exist in solution (Brooks, et al., 1950). Calcite is the least soluble form of CaCO_3 . Magnesium, sulfate, strontium, and the presence of other foreign material, such as clay, protein, organic matter cause CaCO_3 to precipitate in metastable forms (Akin and Lagerwerff, 1965; Brooks, et al., 1950; Doner and Pratt, 1969).

The "residual sodium carbonate (RSC)" concept ($\text{RSC} = [\text{CO}_3 + \text{HCO}_3] - [\text{Ca} + \text{Mg}]$) was one of the first approaches for assessing potential lime precipitation in irrigation water (Eaton, 1950). This approach has been proven to be too simple to be of much quantitative value because some waters with relatively high RSC values are undersaturated with respect to lime. Bower, et al. (1965) used a "closed system" (fixed CO_2 and pH) approach based upon the solubility of calcite. The use of the solubility product of

calcite to calculate CaCO_3 dissolution or precipitation in soil solutions usually results in an underestimation of dissolution and an over-estimation of precipitation because of the presence of metastable CaCO_3 forms in soils. The pHc values (tendency of a water to precipitate or dissolve lime) used in the closed system approach is of limited value for use in dynamic systems. "Open system" approaches (varying CO_2 and pH) have been used by Olsen and Watanabe (1959) and Akin and Lagerwerff (1965). The presence of metastable forms of CaCO_3 which caused the solubility of soil lime to increase with decreasing soil:solution ratios was reported by Olsen and Watanabe (1959). Akin and Lagerwerff (1965) reported that the solubility of metastable CaCO_3 was related to Mg/Ca and SO_4/CO_3 ion ratios in the solutions.

Computerization makes it possible to avoid the almost impossible task of solving the many simultaneous equations used in calculating equilibrium solution compositions. Computerized open system models for computing solution compositions in equilibrium with CaCO_3 were reported by Tanji and Doneen (1966) and Dutt, et al. (1972). These models did not include the effects of ion-pair formation. The computerized model of Oster and McNeal (1971) included provisions for ion-pair calculations and the buffering capacity of the soil.

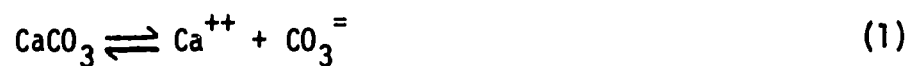
Thermodynamic principles have been applied to gypsiferous systems, also (Adams, 1971; Nakayama, 1961; Nakayama and Rasnick, 1967; Tanji, 1969). The difficulties in applying the thermodynamic approach were discussed by Nakayama (1971). However, the solubility product concept has been applied to soils systems at relatively low salt concentrations with reasonable success (Bennett and Adams, 1971; Dutt and Doneen, 1963; Dutt, 1964; Tanji, et al., 1967).

The present work was undertaken to develop a computer program for predicting equilibrium solutions in calcareous and gypsiferous systems. An open system model was adopted which includes the effects of ion-pair formation and the "solubility enhancement" feature of Akin and Lagerwerff (1965). The CaCO_3 equilibrium data published by Akin and Lagerwerff (1965) were used for comparison with values obtained with the computer program. The gypsum equilibrium data published by Tanji (1969) were compared with equilibrium values obtained with the computer program. The main purpose was to develop a program suitable for assessing the sodium and salinity hazards of marginal quality waters using other independently developed parameters, such as the concentrating effects taking place in irrigation waters due to evaporation during the cropping cycle and CO_2 partial pressures developed under particular soil and cropping conditions.

THEORY

General Reactions and Equations

The equilibrium reactions of CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in water can be written as:



The activities (a) in moles/liter of the ion species can be related to their thermodynamic solubility products (K_{sp}) with the usual assumption that the activity of the solid phase is equal to 1 as follows:

$$K_{sp} = a_{\text{Ca}} a_{\text{CO}_3} \quad (3)$$

$$K_{sp} = a_{\text{Ca}} a_{\text{SO}_4} \quad (4)$$

The activity of an ion species is defined as:

$$a = M\gamma \quad (5)$$

where: M = total concentration (moles/liter)

γ = activity coefficient

Ion activity is designated by () and concentration by [] throughout this paper. Single-ion activity coefficients are approximated by the extended Debye-Huckel equation:

$$\log \gamma = -AZ^2 \frac{\mu^{1/2}}{1 + Ba_1\mu^{1/2}} \quad (6)$$

where: A and B are temperature dependent constants; at 25 °C

A = 0.5085 and B = 0.3281 (Butler, 1964)

Z = valence of the ion

a_i = hydrated ion-size parameter of the ion (Table 1)

μ = ionic strength of the solution

Ionic strength is defined as:

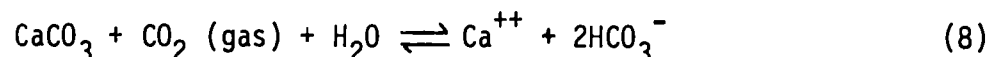
$$\mu = 1/2 \sum C_i Z_i^2 \quad (7)$$

where: C = total concentration (moles/liter) of each ion species

The reactions and equilibrium constants used in the development of the program are given in Table 2.

Equilibrium Reactions of CaCO₃

The HCO₃⁻ activity exceeds the CO₃⁼ activity by many times at pH values usually found in natural waters and soil solutions. Since HCO₃⁻ concentrations can usually be determined more accurately than CO₃⁼, it is convenient to determine equilibrium relations in terms of Ca⁺⁺ and HCO₃⁻. By combining reactions 1, 3, 5, and 6 (Table 2), the reaction of CaCO₃ (calcite) in terms of Ca⁺⁺ and HCO₃⁻ can be written as:



The equilibrium constant (K) for equation 8 can be shown as:

$$K = \frac{K_{\text{CaCO}_3}^0 K_{\text{CO}_2}^0 K_{\text{H}_2\text{CO}_3}^0}{K_{\text{HCO}_3^-}^0} \quad (9)$$

Log K for the above equilibrium expression can be found by adding log K⁰ of reactions 1, 3, 5, and 6 (Table 2) as follows:

$$\text{Log } K = -8.35 - 1.46 - 6.35 + 10.33 = -5.83$$

Equilibrium ion activities can now be expressed as:

$$(\text{Ca})(\text{HCO}_3)^2 = 10^{-5.83} (\text{CO}_2) \quad (10)$$

where: CO₂ = partial CO₂ pressure in atmospheres (atm)

Table 1. Individual ion-size parameters, a_i , used in the extended Debye-Huckel Equation (From Kielland, 1937).

Ion	a_i value (angstrom)
Mg^{++}	8
Ca^{++}	6
$CO_3^{=}$	4.5
Na^+, HCO_3^-	4.3
$MgHCO_3^+, CaHCO_3^+, NaCO_3^-, NaSO_4^-, KSO_4^-$	4.3 ^a
$SO_4^{=}$	4
K^+, Cl^-	3

^a assumed, as suggested by Garrels and Christ (1965)

Table 2. Equilibrium constants, reactions, and log of constants at 25 °C.

Constant (K)	Reaction	Log K
1. $K_{sp} = 4.47 \times 10^{-9}$	CaCO_3 (calcite) $\rightleftharpoons \text{Ca}^{++} + \text{CO}_3^{=}$	- 8.35 ^e
2. $K_{sp} = 2.50 \times 10^{-5}$	CaSO_4 (gypsum) $\rightleftharpoons \text{Ca}^{++} + \text{SO}_4^{=}$	- 4.60 ^d
3. $K_f = 3.44 \times 10^{-2}$	$\text{CO}_2(\text{gas}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$	- 1.46 ^c
4. $K_D = 1.00 \times 10^{-14}$	H_2O (liquid) $\rightleftharpoons \text{H}^+ + \text{OH}^-$	- 14.00 ^c
5. $K_D = 4.47 \times 10^{-7}$	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	- 6.35 ^b
6. $K_D = 4.65 \times 10^{-11}$	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{=}$	- 10.33 ^b
7. $K_D = 6.30 \times 10^{-4}$	$\text{Ca}^{++} + \text{CO}_3^{=} \rightleftharpoons \text{CaCO}_3^0$	3.20 ^c
8. $K_D = 4.90 \times 10^{-3}$	$\text{Ca}^{++} + \text{SO}_4^{=} \rightleftharpoons \text{CaSO}_4^0$	2.31 ^c
9. $K_D = 3.98 \times 10^{-4}$	$\text{Mg}^{++} + \text{CO}_3^{=} \rightleftharpoons \text{MgCO}_3^0$	3.40 ^e
10. $K_D = 6.30 \times 10^{-3}$	$\text{Mg}^{++} + \text{SO}_4^{=} \rightleftharpoons \text{MgSO}_4^0$	2.20 ^f
11. $K_D = 1.78$	$\text{Na}^+ + \text{HCO}_3^- \rightleftharpoons \text{NaHCO}_3^0$	0.25 ^e
12. $K_D = 5.53 \times 10^{-2}$	$\text{Ca}^{++} + \text{HCO}_3^- \rightleftharpoons \text{CaHCO}_3^+$	1.26 ^e
13. $K_D = 6.91 \times 10^{-2}$	$\text{Mg}^{++} + \text{HCO}_3^- \rightleftharpoons \text{MgHCO}_3^+$	1.16 ^e
14. $K_D = 1.12 \times 10^{-1}$	$\text{Na}^+ + \text{SO}_4^{=} \rightleftharpoons \text{NaSO}_4^-$	0.95 ^a
15. $K_D = 5.39 \times 10^{-2}$	$\text{Na}^+ + \text{CO}_3^{=} \rightleftharpoons \text{NaCO}_3^-$	1.27 ^e
16. $K_D = 1.45 \times 10^{-1}$	$\text{K}^+ + \text{SO}_4^{=} \rightleftharpoons \text{KSO}_4^-$	0.84 ^c

^a Breeman (1973); ^b Garrels and Christ (1965); ^c Helgeson (1969);

^d Nakayama and Rasnick (1967); ^e Sillen and Martelli (1964); ^f Tanji (1969)

Solubility Enhancement

The "solubility enhancement" (E) of calcite with increasing Mg/Ca and SO₄/CO₃ ratios can be calculated with the following equation given by Akin and Lagerwerff (1965):

$$E = \frac{1 + 1.96 \frac{[\text{Mg}][\text{CO}_3]}{K'_{\text{sp}}} + 0.0025 \frac{[\text{Ca}][\text{SO}_4]}{K'_{\text{sp}}}}{1 + 0.76 \frac{[\text{Mg}][\text{CO}_3]}{K'_{\text{sp}}} + 0.00074 \frac{[\text{Ca}][\text{SO}_4]}{K'_{\text{sp}}}} \quad (11)$$

where: K'_{sp} = ion concentration product for calcite

$$\left(K'_{\text{sp}} = \frac{10^{-8.35}}{\gamma_{\text{Ca}^{++}} \gamma_{\text{CO}_3^-}} \right)$$

To change ion activities to ion concentration and include the enhancement factor (E), equation 10 becomes:

$$[\text{Ca}^{++}][\text{HCO}_3^-]^2 = \frac{10^{-5.83} (\text{CO}_2)}{\gamma_{\text{Ca}^{++}} \gamma_{\text{HCO}_3^-}^2} \times E \quad (12)$$

Equation 12 would hold for calcite equilibrium conditions. A given electrolyte solution can be tested for equilibrium with CaCO₃ by comparing initial (i) $[\text{Ca}^{++}][\text{HCO}_3^-]^2$ with the right hand side of equation 12 in the following way:

$$D = \frac{10^{-5.83} (\text{CO}_2)}{\gamma_{\text{Ca}^{++}} \gamma_{\text{HCO}_3^-}^2} - E - [\text{Ca}^{++}][\text{HCO}_3^-]^2 \quad (13)$$

If D in the above equation is <0 then the solution is supersaturated with respect to CaCO₃ and lime would precipitate. On the other hand, if D is >0 the solution is undersaturated with respect to CaCO₃ and lime would dissolve. The amount of CaCO₃ (Z moles) that would dissolve or precipitate can be calculated by utilizing equation 12. The equilibrium (e) Ca⁺⁺ and HCO₃⁻

concentrations can be related to the initial concentrations as follows:

$$[\text{Ca}^{++}]_e = [\text{Ca}^{++}]_i + Z \quad (14)$$

$$[\text{HCO}_3^-]_e = [\text{HCO}_3^-]_i + 2Z \quad (15)$$

where: Z = moles of Ca^{++} and HCO_3^- required to bring the solution to equilibrium with CaCO_3

For a given set of $[\text{Ca}^{++}]_i$ and $[\text{HCO}_3^-]_i$ values, the unknown, Z , can be calculated from the following polynomial equation derived by substituting the right hand side of equations 14 and 15 into equation 12 and rearranging:

$$4Z^3 + 4Z^2([\text{Ca}^{++}]_i + [\text{HCO}_3^-]_i) + Z(4[\text{Ca}^{++}][\text{HCO}_3^-]_i + [\text{HCO}_3^-]_i^2) + ([\text{Ca}^{++}][\text{HCO}_3^-]_i^2 - \frac{10^{-5.83} (\text{CO}_2)}{\gamma_{\text{Ca}^{++}} \gamma_{\text{HCO}_3^-}} E) = 0 \quad (16)$$

Equilibrium Reaction of Gypsum

The equilibrium ion activity product of gypsum can be expressed as:

$$(\text{Ca}^{++})(\text{SO}_4^-) = 10^{-4.60} \quad (\text{Table 2}) \quad (17)$$

and the equilibrium concentration product expressed by:

$$[\text{Ca}^{++}][\text{SO}_4^-] = \frac{10^{-4.60}}{\gamma_{\text{Ca}^{++}} \gamma_{\text{SO}_4^-}} \quad (18)$$

A given solution can be tested as to whether or not it is in equilibrium with gypsum by comparing the solution ion product, $[\text{Ca}^{++}][\text{SO}_4^-]_i$ with the right hand side of equation 18:

$$DG = \frac{10^{-4.61}}{\gamma_{\text{Ca}^{++}} \gamma_{\text{SO}_4^-}} - [\text{Ca}^{++}][\text{SO}_4^-]_i \quad (19)$$

If DG is <0 , then the solution is supersaturated with respect to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

and gypsum would precipitate. If DG is >0 , the gypsum will dissolve. The amount of CaSO_4 (G moles) that would dissolve in the presence of solid phase gypsum or precipitate with an initially supersaturated solution of Ca^{++} and $\text{SO}_4^{=}$ can be calculated as follows:

$$[\text{Ca}^{++}] = [\text{Ca}^{++}]_i + G \quad (20)$$

$$[\text{SO}_4^{=}] = [\text{SO}_4^{=}]_i + G \quad (21)$$

For a given set of $[\text{Ca}^{++}]_i$ and $[\text{SO}_4^{=}]_i$ values, the unknown, G, can be calculated from the following quadratic equation derived by substituting the right hand side of equations 20 and 21 into equation 18 and rearranging:

$$G^2 + G([\text{Ca}^{++}]_i + [\text{SO}_4^{=}]_i) + ([\text{Ca}^{++}][\text{SO}_4^{=}]_i - \frac{10^{-4.61}}{\gamma_{\text{Ca}^{++}}\gamma_{\text{SO}_4^{=}}}) = 0 \quad (22)$$

Equilibrium Equations for Ion-Pairs, Free Cations, and Anions

Cations and anions in most irrigation waters are Ca^{++} , Mg^{++} , Na^+ , K^+ , H^+ , $\text{CO}_3^{=}$, HCO_3^- , Cl^- , $\text{SO}_4^{=}$, NO_3^- and OH^- . Some of these cations and anions form "neutral ion-pairs" which behave as if un-ionized while others form "charged ion-pairs". According to the data presented by Garrels and Christ (1965) the ion-pairs that could be present in significant amounts are CaSO_4^0 , MgSO_4^0 , NaSO_4^- , KSO_4^- , CaHCO_3^+ , MgHCO_3^+ , NaHCO_3^0 , CaCO_3^0 , MgCO_3^0 , NaCO_3^- and H_2CO_3 . For accurate determination of activity coefficients, accurate values of ionic strength are needed. The ionic strength depends upon charged chemical species (free cations and anions and charged ion-pairs) only.

Because of ion-pair formation, a solution ion may be present as several different species. For example, solution SO_4 may be present as $\text{SO}_4^{=}$ free, CaSO_4^0 , MgSO_4^0 , NaSO_4^- , and KSO_4^- . However, routine analytical procedures for determining solution SO_4 do not differentiate between the ion and

ion-pair species. Hence, the measured $[SO_4]_{total}$ can be equated as follows:

$$[SO_4]_{total} = [SO_4]_{free} + [CaSO_4^0] + [MgSO_4^0] + [NaSO_4^-] + [KSO_4^-] \quad (23)$$

From the dissociation or formation constants given in Table 2, the concentrations of all the species except $[SO_4]_{free}$ can be written in terms of ion products and activity coefficients as follows:

$$[CaSO_4^0] = \frac{10^{2.31} [Ca^{++}][SO_4^{=}] \gamma_{Ca^{++}} \gamma_{SO_4^{=}}}{\gamma_{CaSO_4^0}} \quad (24)$$

$$[MgSO_4^0] = \frac{10^{2.20} [Mg^{++}][SO_4^{=}] \gamma_{Mg^{++}} \gamma_{SO_4^{=}}}{\gamma_{MgSO_4^0}} \quad (25)$$

$$[NaSO_4^-] = \frac{10^{0.95} [Na^+][SO_4^{=}] \gamma_{Na^+} \gamma_{SO_4^{=}}}{\gamma_{NaSO_4^-}} \quad (26)$$

$$[KSO_4^-] = \frac{10^{0.84} [K^+][SO_4^{=}] \gamma_{K^+} \gamma_{SO_4^{=}}}{\gamma_{KSO_4^-}} \quad (27)$$

Following the suggestion of Garrels and Christ (1965), the activity coefficients of neutral species are assumed to be unity. It can be noted from Table 1 that Na^+ , HCO_3^- , $MgHCO_3^+$, $CaHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$ and KSO_4^- under the assumed conditions would have the same activity coefficient value at a given temperature and ionic strength. Substituting the values of $[CaSO_4^0]$, $[MgSO_4^0]$, $[NaSO_4^-]$, and $[KSO_4^-]$ (equations 24-27) into equation 23, knowing $\gamma_{CaSO_4^0} = \gamma_{MgSO_4^0} = 1$ and $\gamma_{Na^+} = \gamma_{NaSO_4^-}$, and rearranging, the equation

becomes:

$$[SO_4^{=}]_{free} = \frac{[SO_4]_{total}}{1 + 10^{2.31} [Ca^{++}] \gamma_{Ca^{++}} \gamma_{SO_4^{=}} + 10^{2.20} [Mg^{++}] \gamma_{Mg^{++}} \gamma_{SO_4^{=}} + \dots + \frac{10^{0.95} [Na^+] \gamma_{SO_4^{=}} + 10^{0.84} [K^+] \gamma_{K^+} \gamma_{SO_4^{=}}}{\gamma_{KSO_4^-}}} \quad (28)$$

Hence, the $[SO_4^{=}]_{free}$ which is needed in describing equilibrium constants can be calculated from activity coefficients and concentrations of appropriate free cations. Similarly, the concentrations of other free anions and cations can be calculated also. The final equations for these ions are given below.

$$[HCO_3^-]_{free} = \frac{[HCO_3^-]_{total}}{1 + 10^{1.26} [Ca^{++}] \gamma_{Ca^{++}} + 10^{1.16} [Mg^{++}] \gamma_{Mg^{++}} + 10^{-0.25} [Na^+] \gamma_{Na^+} \gamma_{HCO_3^-}} \quad (29)$$

$$[Ca^{++}]_{free} = \frac{[Ca]_{total}}{1 + 10^{2.31} [SO_4^{=}] \gamma_{Ca^{++}} \gamma_{SO_4^{=}} + 10^{1.26} [HCO_3^-] \gamma_{Ca^{++}} + 10^{3.20} [CO_3^{=}] \dots} \dots \frac{1}{\gamma_{Ca^{++}} \gamma_{CO_3^{=}}} \quad (30)$$

$$[Mg^{++}]_{free} = \frac{[Mg]_{total}}{1 + 10^{2.20} [SO_4^{=}] \gamma_{Mg^{++}} \gamma_{SO_4^{=}} + 10^{1.16} [HCO_3^-] \gamma_{Mg^{++}} + 10^{3.40} [CO_3^{=}] \dots} \dots \frac{1}{\gamma_{Mg^{++}} \gamma_{CO_3^{=}}} \quad (31)$$

$$[Na^+]_{free} = \frac{[Na]_{total}}{1 + 10^{0.95} [SO_4^{=}] \gamma_{SO_4^{=}} + 10^{-0.25} [HCO_3^-] \gamma_{Na^+} \gamma_{HCO_3^-} + 10^{1.27} [CO_3^{=}] \gamma_{CO_3^{=}}} \quad (32)$$

$$[K^+]_{free} = \frac{[K]_{total}}{1 + \frac{10^{0.84} [SO_4^{=}] \gamma_{K^+} \gamma_{SO_4^{=}}}{\gamma_{KSO_4^-}}} \quad (33)$$

The equations to calculate concentrations of free cations and anions are given above. The concentrations of charged ion-pairs can be similarly calculated following the form of equations 26 and 27. The following equations were derived from equilibrium reactions and constants given in Table 2.

$$[CaHCO_3^+] = 10^{1.26} [Ca^{++}] [HCO_3^-] \gamma_{Ca^{++}} \quad (34)$$

$$[\text{MgHCO}_3^+] = 10^{1.16} [\text{Mg}^{++}] [\text{HCO}_3^-] \gamma_{\text{Mg}^{++}} \quad (35)$$

$$[\text{NaCO}_3^-] = 10^{1.27} [\text{Na}^+] [\text{CO}_3^{=}] \gamma_{\text{CO}_3^{=}} \quad (36)$$

The (H^+) can be calculated from given $[\text{HCO}_3^-]$, $\gamma_{\text{HCO}_3^-}$, and $\text{CO}_2(\text{gas})$ partial pressure (atm). The equilibrium (H^+) can be obtained by combining reaction 3 and 5 (Table 2) and adding the $\text{Log } K$ values for these reactions to form the following equation:

$$\frac{(\text{H}^+) (\text{HCO}_3^-)}{(\text{CO}_2) (\text{H}_2\text{O})} = 10^{-7.81} \quad (37)$$

Considering activity of H_2O as unity, and rearranging, equation 37 becomes:

$$(\text{H}^+) = \frac{10^{-7.81} (\text{CO}_2)}{[\text{HCO}_3^-] \gamma_{\text{HCO}_3^-}} \quad (38)$$

Since there exists an equilibrium between $[\text{HCO}_3^-]_{\text{free}}$, (H^+) , and $[\text{CO}_3^{=}]_{\text{free}}$ and if $[\text{HCO}_3^-]_{\text{free}}$ and (H^+) are known, the concentration of $[\text{CO}_3^{=}]_{\text{free}}$ can be calculated from the reaction in Table 2.

$$[\text{CO}_3^{=}]_{\text{free}} = \frac{10^{-10.33} [\text{HCO}_3^-] \gamma_{\text{HCO}_3^-}}{\gamma_{\text{CO}_3^{=}} (\text{H}^+)} \quad (39)$$

Total $[\text{CO}_3]$ is equal to the sum of $[\text{CaCO}_3^0]$, $[\text{MgCO}_3^0]$, $[\text{NaCO}_3^-]$, and $[\text{CO}_3^{=}]_{\text{free}}$. Since concentration of free cations and $\text{CO}_3^{=}$ are known, the concentration of $[\text{CO}_3]_{\text{total}}$ can be calculated as follows:

$$[\text{CO}_3]_{\text{total}} = 10^{3.20} [\text{Ca}^{++}] [\text{CO}_3^{=}] \gamma_{\text{Ca}^{++}} \gamma_{\text{CO}_3^{=}} + 10^{3.40} [\text{Mg}^{++}] [\text{CO}_3^{=}] \gamma_{\text{Mg}^{++}} \gamma_{\text{CO}_3^{=}} + 10^{1.27} [\text{Na}^+] [\text{CO}_3^{=}] \gamma_{\text{CO}_3^{=}} + [\text{CO}_3^{=}] \quad (40)$$

Since Cl^- and NO_3^- do not form any significant complexes with cations (Garrels and Christ, 1965), the following equation would hold:

$$[\text{Cl}^-]_{\text{free}} = [\text{Cl}^-]_{\text{total}} \quad \text{and} \quad [\text{NO}_3^-]_{\text{free}} = [\text{NO}_3^-]_{\text{total}} \quad (41)$$

PROCEDURE

Assumptions

It was assumed that:

1. $[Cl^-]_{total} = [Cl^-] + [NO_3^-]$ because neither form ion-pairs and $[NO_3^-]$ is usually minor in water and soil solutions compared to $[Cl^-]$.
2. Loss of $[Mg^{++}]$ and $[SO_4^{=}]$ from solution by coprecipitation with $CaCO_3$ is sometimes measurable (Akin and Lagerwerff, 1965) but the loss would be offset by dissolution of Mg from soil minerals and oxidation of S from soil organic matter or soil minerals.
3. Solid phase $MgCO_3$ is absent in soils and the solubility products of forms of $MgCO_3$, possibly formed in soils, is not exceeded.
4. Solid phase $CaCO_3$ is present in all soils.

Computations

Based upon the theory presented in the previous section and the above assumptions, a Fortran computer program was developed. The computation scheme is presented in Figure 1 in the form of a flow chart. Most of the Fortran IV Statements in the flow chart have been reduced to conventional language. The actual program with Fortran IV statements is given in Appendix I.

Total solution concentrations of Ca, Mg, Na, K, SO_4 , Cl, and $(CO_3 + HCO_3)$ in moles/liter and CO_2 (gas) as pressure in atmospheres are read into the computer and values of above parameters are subsequently printed. First, assuming all cations and anions exist as free ions (no ion-pairs), the ionic strength is estimated by equation 7. The activity coefficients of cations, anions and charged ion-pairs are calculated using equation 6. The concentration of $CaCO_3$ and $CaSO_4$ is set equal to zero. Knowing activity

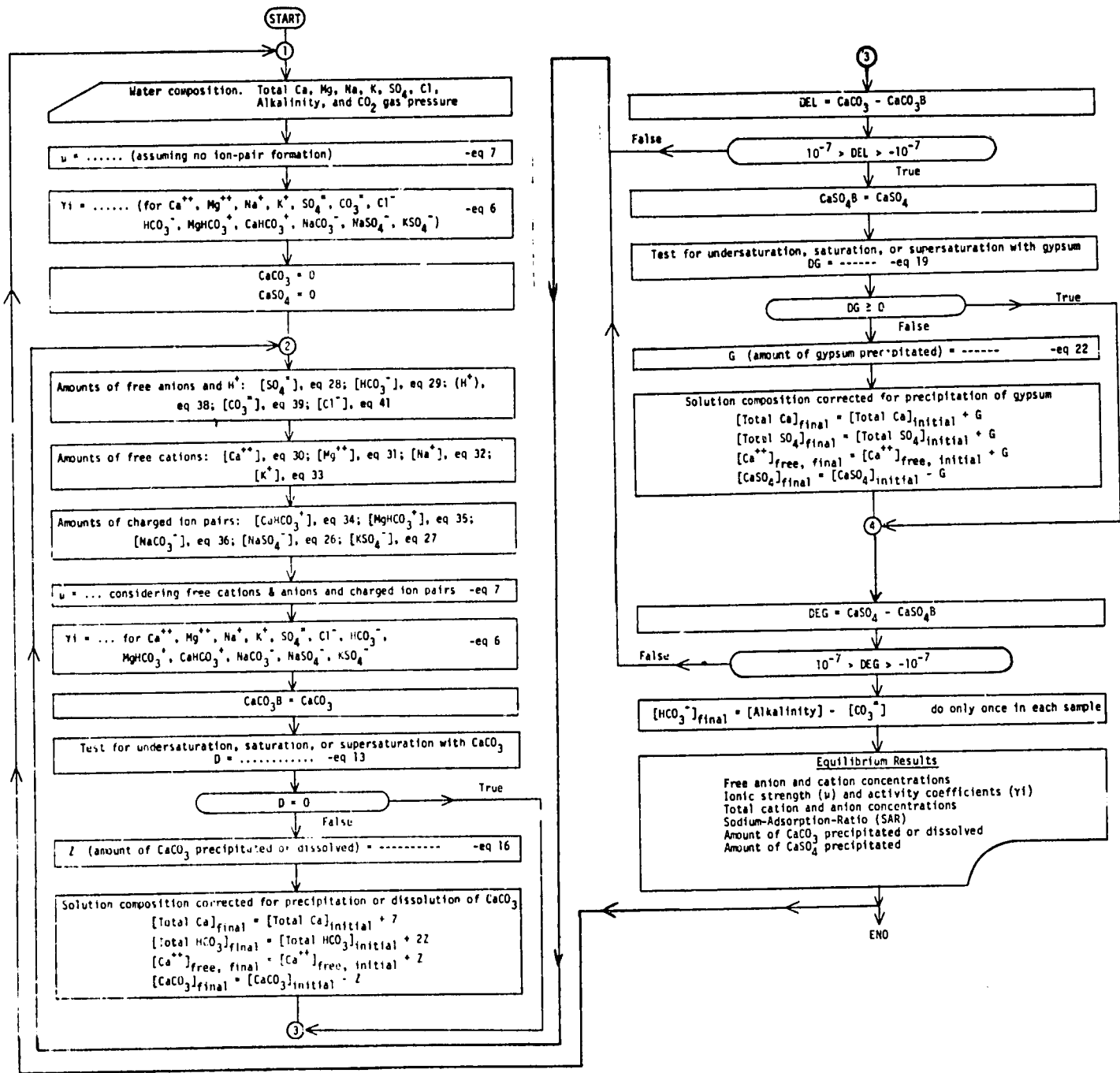




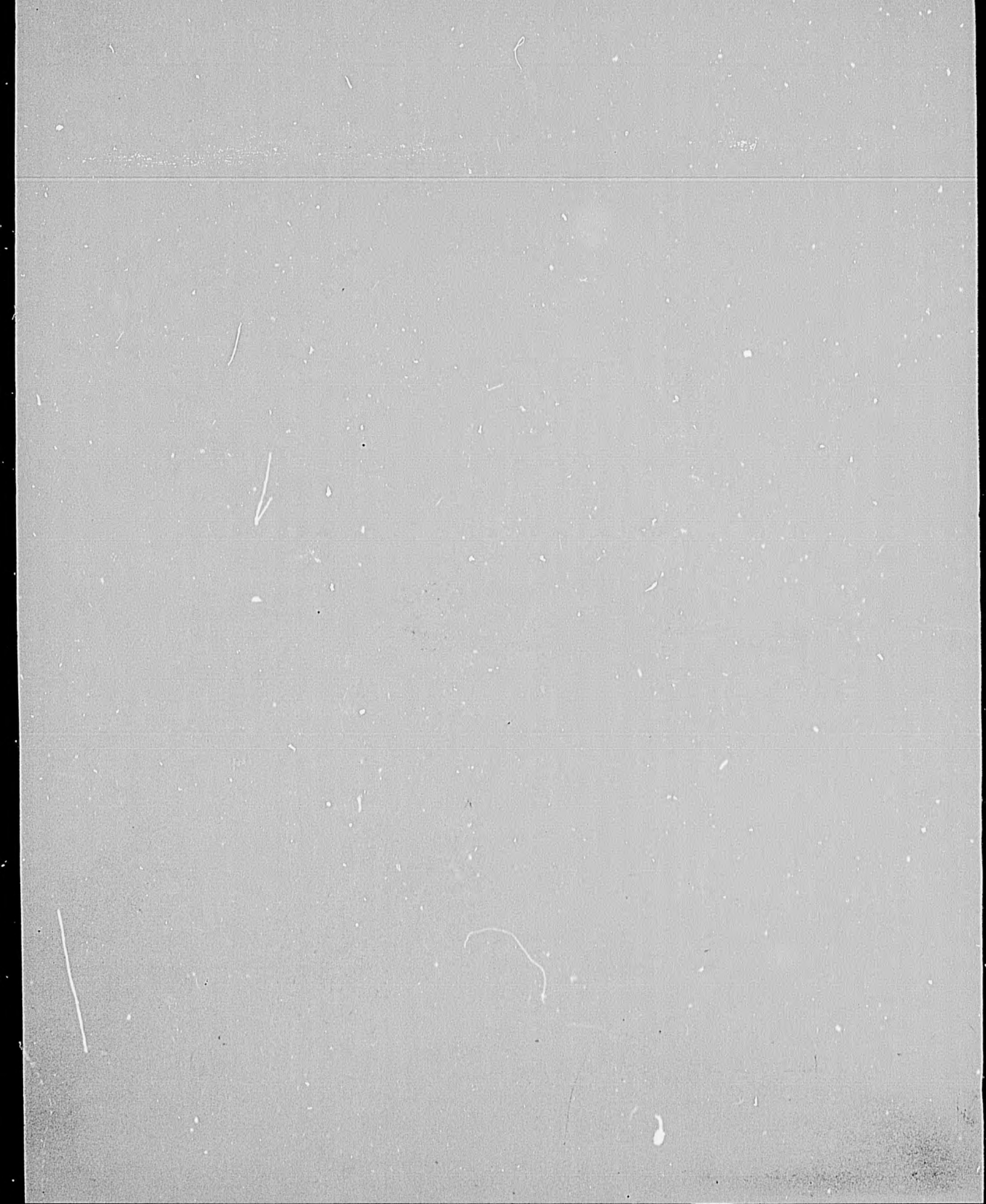


Figure 1. Scheme of computation for determination of water composition at 25 °C and one atmosphere pressure in equilibrium with CaCO_3 . If $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precipitates, then equilibrium with CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

[In the figure, Box  = Read,  = execute the statements,  = conditional statement, and  = Print.]



coefficients, total anion concentrations, and assuming concentrations of free cations the same as their total concentration, the estimates of free anions and H^+ can be made using equations 28, 29, 36, 37, and 39. The amounts of free cations can now be calculated from equations 30 to 33 using appropriate equilibrium constants, activity coefficients, and concentrations of free cations and anions.

A better estimate of ionic strength based upon free cations, anions, and charged ion-pairs can now be made using equation 7. This ionic strength value is then used to calculate activity coefficients. The value of $CaCO_3(\text{initial})$ is stored in $CaCO_3B$ for later reference.

A test, using equation 13, is made to check the degree of saturation of the solution with respect to $CaCO_3$. The amount of $CaCO_3$ dissociated or precipitated (Z moles) is calculated by equation 16. The solution Ca and HCO_3 concentrations are changed to correct for precipitated or dissolved $CaCO_3$. The concentration of initial $CaCO_3$ is compared with final $CaCO_3$ [$CaCO_3 \text{ initial} - Z$]. Of the difference (DEL) between the initial and the final concentration is $>10^{-7}$ or $<10^{-7}$, then the equilibrium cycle is started again at statement number 2 (i.e., calculation of free anion concentrations). This iterative process is continued until DEL is between $\pm 10^{-7}$.

The $CaSO_4$ computation is started at the end of $CaCO_3$ cycle. The initial value of $CaSO_4$ is stored in $CaSO_4B$ for later reference. A test, using equation 19, is made to check the degree of saturation of the solution with respect to $CaSO_4$. If the solution is not supersaturated (undersaturated or right at saturation) then a few statements are skipped and computation started at statement 4. On the other hand, if the solution is supersaturated, the amount (G moles) of gypsum that would precipitate is calculated by

equation 22. The solution Ca and SO_4 concentrations are reduced by G moles to correct for precipitated CaSO_4 . This brings us to statement 4. The concentration of initial CaSO_4 is compared with final CaSO_4 [CaSO_4 initial - Z]. If the difference (DEG) between the initial and the final concentration is $>10^{-7}$ or $<-10^{-7}$, then the equilibrium cycle is started again at statement number 2 and followed through the CaCO_3 and CaSO_4 cycles until the difference between the initial and the final concentrations of CaCO_3 and CaSO_4 are between $\pm 10^{-7}$.

Final ion-pair concentrations are calculated at this point. $[\text{CO}_3]_{\text{total}}$ is calculated by equation 40. In order to obtain electro-neutrality and true $[\text{HCO}_3]_{\text{total}}$, the amount of total CO_3 is subtracted (only once in each sample) from the existing $[\text{HCO}_3]_{\text{total}}$ and the calculations are started at statement number 2. At the conclusion of the whole cycle, the SAR is calculated, the equilibrium results are printed and calculations are started for a new sample at statement 1.

The original compositions of water samples given by Akin and Lagerwerff (1965) were used as the input data (Table 3) to test the CaCO_3 cycle of the computer program. Also, the compositions were multiplied by 10 to simulate a 10-fold concentration effect. In addition to the original CO_2 pressures, the water compositions were run at CO_2 pressures 10-fold higher (about 3 matm), 30, 100, and 150 matm. The CaSO_4 cycle of the program was tested with the electrolyte solutions (Table 4) given by Tanji (1969).

Table 3. Original composition of water samples (after Akin and Lagerwerff, 1965).

Sample No.	Original Concentrations (me/l)						CO ₂ gas (matm)
	Ca	Mg	Na	SO ₄	Cl	Alk ^c	
<u>Synthetic Solutions</u>							
AL 1	4.23	0.25	0.0	0.0	0.25	4.23	0.298
AL 2	5.83	0.75	0.0	0.0	0.76	5.91	0.298
AL 3	5.54	2.52	0.0	0.0	2.49	5.55	0.294
AL 4	4.74	10.01	0.0	0.0	10.07	4.76	0.323
AL 5	4.63	0.0	2.50	2.54	0.0	4.64	0.283
AL 6	4.76	0.0	10.07	10.26	0.0	4.76	0.290
AL 7	33.76	0.0	0.0	30.62	0.0	3.95	0.322
<u>Natural Solutions</u>							
AL 8	4.198	1.127	4.645 ^a	5.27	1.728 ^b	2.972	0.334
AL 9	1.918	0.578	3.474 ^a	0.57	0.718 ^b	4.682	0.328
AL10	16.70	12.59	40.40 ^a	22.14	37.941 ^b	9.609	0.337
AL11	11.05	6.16	16.66 ^a	13.06	13.261 ^b	7.549	0.315
AL12	0.943	0.179	8.708 ^a	5.83	2.037 ^b	1.963	0.326
AL13	1.243	0.257	2.28 ^a	0.51	0.731 ^b	2.539	0.333

^a estimated from Akin and Lagerwerff's data [(total cations) - (Ca + Mg)]

^b estimated from Akin and Lagerwerff's data [(total cations) - (SO₄ + Alk)]

^c Alk = Alkalinity (CO₃⁼ + HCO₃⁻)

Table 4. Composition of mixed aqueous salt solutions used for gypsum equilibration studies (after Tanji, 1969).

	mmole/l				
	Ca	Mg	Na	SO ₄	Cl
T- 1	25.0	--	25.0	25.0	25.0
T- 2	25.0	25.0	--	25.0	15.0
T- 3	--	--	12.4	2.5	9.9
T- 4	--	--	101.5	2.5	99.0
T- 5	--	--	22.5	7.5	15.0
T- 6	--	--	37.7	7.5	30.2
T- 7	--	3.8	26.3	7.5	22.6
T- 8	--	5.2	15.0	10.2	10.0
T- 9	--	5.0	50.1	--	55.1
T-10	--	5.0	100.0	--	105.0
T-11	--	5.2	266.0	--	271.2
T-12	--	25.1	50.1	--	75.2
T-13	--	25.1	100.0	--	125.1
T-14	--	50.0	50.1	--	100.1

RESULTS AND DISCUSSION

The program predicts equilibrium ionic strength, activity coefficients, ions (free), ion-pairs, and total concentration of solute species, amount of CaCO_3 precipitated or dissolved at a given partial CO_2 pressure, and the amount of gypsum precipitated from a given pre-equilibrium solution composition.

Equilibrium Calcium-Alkalinity Predictions

The predicted and experimental equilibrium Ca, total alkalinity, Mg, and SO_4 concentrations for the pre-equilibrium solution compositions (Table 3) are shown in Table 5. The results predicted with the computer program agree closely with Akin and Lagerwerff's experimental results. The predicted Ca values are consistently below the experimental Ca values if the "solubility enhancement" factor (E) is not incorporated into the CaCO_3 solubility calculations in the program. Thus, even when ion-pair formation is taken into account, the E factor appears to be necessary to account for increased CaCO_3 solubility in the presence of Mg and SO_4 ions.

Samples AL 1-AL 6 should contain equal amounts of Ca and alkalinity in the pre-equilibrium and equilibrium solutions. Small Ca-alkalinity imbalances in pre-equilibrium solution samples AL 2, 3, 4, and 5 (Table 3) produced small imbalances in the predicted equilibrium Ca and alkalinity values. The predicted Ca and alkalinity values of samples AL 3 and 4 closely equal the averages of the experimental Ca and alkalinity values reported. The predicted Ca and alkalinity values tend to be slightly higher than the experimental values in most cases. The maximum difference in predicted and experimental Ca values was 0.20 me/l for sample AL 7. In

Table 5. Predicted (Pred) and experimental (Exp) equilibrium solution compositions.

Sample No.	Ca		Alkalinity		Mg		SO ₄	
	Pred ^a	Exp ^b	Pred ^a	Exp ^b	Pred ^a	Exp ^b	Pred ^a	Exp ^b
	----- me/l -----							
AL 1	1.20	1.18	1.20	1.15	0.25	0.25	0.00	0.00
AL 2	1.29	1.31	1.37	1.29	0.77	0.71	0.00	0.00
AL 3	1.53	1.58	1.54	1.49	2.52	2.43	0.00	0.00
AL 4	1.84	1.96	1.85	1.72	10.10	10.10	0.00	0.00
AL 5	1.23	1.19	1.24	1.19	0.00	0.00	2.54	2.54
AL 6	1.55	1.41	1.55	1.40	0.00	0.00	10.26	10.21
AL 7	30.54	30.34	0.73	0.49	0.00	0.00	30.62	30.62
AL 8	2.56	2.52	1.33	1.25	1.13	1.08	5.27	NR
AL 9	0.42	0.39	3.15	3.03	0.58	0.47	0.57	NR
AL10	8.39	8.49	1.30	1.14	12.59	12.32	22.14	NR
AL11	4.85	4.89	1.35	1.23	6.16	6.00	13.06	NR
AL12	0.95	0.91	1.97	1.91	0.18	0.17	5.83	NR
AL13	0.65	0.65	1.97	1.87	0.26	0.24	0.51	NR

^a present work; ^b Akin and Lagerwerff (1965); NR - not reported

general, it was concluded that the CaCO_3 cycle developed in the program predicts equilibrium solution concentrations quite satisfactorily.

Equilibrium Gypsum Solubility and Ionic Strength Predictions

Predicted and experimental equilibrium gypsum concentrations for the pre-equilibrium salt solution compositions (Table 4) and predicted ionic strength values are shown in Table 6. The equilibrium gypsum concentrations predicted by the gypsum cycle of the program agree very closely with the experimental values of Denman (1961) and with most experimental values of Ostroff and Metler (1966). The predicted gypsum solubility is very close to the experimental value at an ionic strength of 0.36 moles/liter in a predominately NaCl solution (T-11). However, when the pre-equilibrium solution contains greater amounts of MgCl_2 (T-12, 13, 14), the predicted values are lower than the experimental values. For a $\text{CaCl}_2 - \text{Na}_2\text{SO}_4$ salt solution (T-1) the predicted gypsum solubility was lower than the experimental value. The predicted gypsum solubility was higher than the experimental value for a $\text{CaCl}_2 - \text{MgSO}_4$ salt solution (T-2).

The predicted gypsum solubility values of Tanji (1969) were generally higher at lower ionic strengths but were lower at higher ionic strengths than in the present study. The ionic strength values predicted by Tanji's program were higher in all cases except one (T-11). The main differences between the two programs are in the gypsum solubility products used and the equations used to estimate ion activity coefficients. Tanji (1969) used a solubility product of 2.4×10^{-5} as compared to 2.5×10^{-5} in this study. The Davies (1962) equation was used to estimate ion activity coefficients by Tanji whereas, single-ion activity coefficients were estimated by the Debye-Huckel equation in this study. The gypsum solubility values obtained

Table 6. Predicted (Pred) and experimental (Exp) equilibrium gypsum concentrations and ionic strength values in mixed aqueous salt solutions.

	Gypsum Concentration			Ionic Strength	
	Pred ^a	Pred ^b	Exp	μ^a	μ^b
	----- mmole/l -----				
T- 1	17.71	18.94	19.0 ^b	73.4	--
T- 2	21.66	20.15	20.1 ^b	107.6	--
T- 3	15.3	15.5	15.4 ^c	55.9	58.9
T- 4	21.5	21.1	21.3 ^c	163.2	166.8
T- 5	14.2	14.5	14.2 ^c	67.6	74.0
T- 6	15.3	15.6	15.3 ^c	85.9	92.7
T- 7	15.3	15.5	15.2 ^c	80.5	85.1
T- 8	13.8	14.1	13.8 ^c	69.3	74.5
T- 9	20.7	20.5	21.5 ^d	116.8	122.3
T-10	23.6	23.0	23.9 ^d	175.6	180.5
T-11	31.0	28.1	30.9 ^d	362.9	361.8
T-12	24.5	24.1	28.4 ^d	168.0	186.5
T-13	26.9	25.9	29.8 ^d	226.0	242.7
T-14	28.5	27.2	33.7 ^d	232.3	264.9

^a Present work; ^b Tanji (1969); ^c Denman (1961); ^d Ostroff and Metler (1966)

with the program in this study appear to be an improvement over those of Tanji (1969).

Precipitation or Dissolution of CaCO_3 as Affected by CO_2 Level

Predicted Ca concentrations and CaCO_3 precipitated or dissolved at different partial CO_2 pressure for the pre-equilibrium solutions (Table 3) are given in Table 7. A 10-fold increase in CO_2 from approximately 0.3 to 3 matm approximately doubles the Ca concentration in most of the samples, except AL 7, which was saturated with gypsum.

The natural water samples (AL 8-AL13) are of interest because they show a rather wide range in degree of saturation with respect to CaCO_3 . Two samples are surface waters (AL 8 and 13) while the rest are well waters. Sample AL12 is approximately at equilibrium at atmospheric pressure (about 0.3 matm). An increase in CO_2 to 150 matm (about 15% CO_2) dissolves 12.7 me/l of CaCO_3 . Samples AL10 and 11 are drainage and irrigation wells, respectively, and indicate a high degree of supersaturation. Saturation with respect to CaCO_3 appears to be at approximately 30 matm (about 3% CO_2) for the latter samples. The other surface and well waters appear to be saturated with CaCO_3 mainly within the range of 0.3 - 3 matm. However, this does not take into account possible differences in CaCO_3 solubility related to water temperature differences under natural conditions.

Increase in SAR as Affected by Concentration of Solution

In evaluating potential SAR changes of irrigation waters containing Ca^{++} , HCO_3^- , and $\text{SO}_4^{=}$, an important consideration is the loss of Ca by precipitation as CaCO_3 or gypsum as the soil solution becomes more concentrated during the evapotranspiration process. Pre-equilibrium and predicted equilibrium SAR values of unconcentrated solutions (Table 3) and of solutions

Table 7. Predicted calcium concentration and CaCO₃ dissolution or precipitation at various partial CO₂ pressures.

Sample No.	0.3 matm		3 matm		30 matm		100 matm		150 matm	
	Ca	CaCO ₃	Ca	CaCO ₃	Ca	CaCO ₃	Ca	CaCO ₃	Ca	CaCO ₃
	----- me/l -----									
AL 1	1.20	+ 3.03	2.54	+ 1.79	--	--	--	--	--	--
AL 2	1.29	+ 4.54	2.70	+ 3.13	--	--	--	--	--	--
AL 3	1.53	+ 4.01	3.16	+ 2.38	--	--	--	--	--	--
AL 4	1.84	+ 2.90	3.89	+ 0.85	--	--	--	--	--	--
AL 5	1.23	+ 3.40	2.77	+ 1.86	--	--	--	--	--	--
AL 6	1.55	+ 3.20	3.52	+ 1.24	--	--	--	--	--	--
AL 7	30.54	+ 3.21	31.78	+ 1.76	--	--	--	--	--	--
AL 8	2.56	+ 1.63	4.41	- 0.21	8.68	- 4.41	13.08	- 8.89	15.18	- 10.98
AL 9	0.42	+ 1.50	1.52	+ 0.40	4.53	- 2.61	7.90	- 5.98	9.52	- 7.57
AL10	8.33	+ 8.31	10.66	+ 6.04	16.07	+ 0.63	21.82	- 5.12	24.48	- 7.79
AL11	4.85	+ 6.20	6.97	+ 4.08	12.01	- 0.96	17.23	6.18	19.65	- 8.60
AL12	0.95	- 0.01	2.69	- 1.75	6.95	- 6.01	11.50	-10.55	13.62	- 12.68
AL13	0.67	+ 0.56	1.99	-0.75	5.18	- 3.94	8.60	- 7.36	10.21	- 8.96

precipitation: - dissolution

concentrated by 10-fold are given in Table 8. The equilibrium SAR values shown in Table 8 are those predicted with the computer program at atmospheric CO_2 partial pressure and 25 °C and those calculated with a formula proposed by Bower, et al. (1968):

$$\text{SAR}_{\text{eq}} = \left(\frac{1}{\text{LF}}\right)^{1/2} \text{SAR}_{\text{iw}} [1 + 8.4 - \text{pHc}]$$

The unconcentrated solution would correspond with a leaching fraction (LF) of 1.0 (100%) and the concentrated solution corresponds to a 0.1 (10%) leaching fraction. The pHc value as used in the formula above is defined as the theoretical pH value that a water would have if it was in equilibrium with calcite at 25 °C and atmospheric CO_2 partial pressure. Bower, et al. (1968) used a modified pHc value with the above formula in which Mg was added with Ca in the calculation of pHc.

Precipitation of CaCO_3 from the pre-equilibrium solution increased the SAR of the equilibrium solutions calculated in the computer program, except sample AL12. The SAR values of the unconcentrated solutions calculated by Bower; et al. (1968) formula are higher than the values predicted by the computer program in all cases except sample AL 9. When the solutions are concentrated by 10-fold, the Bower, et al. (1968) formula predicted substantially lower SAR values for 4 samples (AL 5, 6, 12, and 13). The computer program predicted lower SAR values than those calculated by the Bower, et al. (1968) formula in solutions which contained more than 0.5 me/l of Mg (see Table 3). Precipitation of gypsum was predicted in samples AL10 and 11, moreover.

There appears to be no good theoretical basis in the Bower, et al. (1968) formula for multiplying SAR_{iw} by $1 + 8.4 - \text{pHc}$ as a quantitative measure of the change in SAR as CaCO_3 is precipitated or dissolved. The Bower, et al.

Table 8. Initial SAR and predicted equilibrium SAR values of unconcentrated and concentrated solutions.

Sample	SAR of unconcentrated solution			SAR of solution concentrated 10-fold	
	Pre-Equil.	Equil. ^a	Equil. ^b	Equil. ^a	Equil. ^b
AL 5	1.6	2.5	3.6	26.2	11.3
AL 6	7.0	11.3	14.8	85.6	46.7
AL 8	2.8	3.0	5.7	13.2	18.1
AL 9	3.1	6.5	6.0	18.7	19.1
AL10	10.6	12.5	32.1	44.6	101.5
AL11	5.7	6.9	16.4	24.5	52.0
AL12	11.6	11.6	13.5	80.8	42.8
AL13	2.6	3.4	3.9	19.5	12.3

^a predicted equilibrium SAR from present study; ^b predicted value calculated from: $SAR_{eq} = \left(\frac{1}{LF}\right)^{1/2} SAR_{iw} [1 + 8.4 - pHc]$, Bower, et. al. (1968)

(1968) formula does not differentiate between the greater solubility of MgCO_3 compared with CaCO_3 . Thus, the formula over-estimates the potential Na hazard of waters containing substantial amounts of Mg. Also, the formula underestimates the Na hazard of waters in which gypsum precipitation may take place. Therefore, it is concluded that the computer program which was developed is more theoretically sound and provides better quantitative values for assessing the Na hazard of marginal quality waters.

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APPENDIX I

PROGRAM LISTING

C PROGRAM FOR CALCULATION OF TOTAL CALCIUM IN SOLUTION AT
 C EQUILIBRIUM W CALCITE AND GYPSUM(ONLY IF LATTER PPT) AT 25C 1 ATM

C T AND I AT END OF VARIABLE REFER TO TOTAL AND FREE ION CONC.
 C M= IONIC STRENGTH, Y= ACTIVITY COEFFICIENT
 C ONLY H IN ACTIVITY. ALL OTHERS CONC.

COMPLEX Z

DIMENSION A(100),Z(100)

REAL MGT,MGI,NAT,NAI,KT,KI,M,NASO4,NACO3,KS04,MGHCO3

1 READ (5,90) SAMPLE,CAT,MGT,NAT,KT

IF (EOF(5))500.5

5 IFLAG = 0

WRITE (6,50)

READ (5,91) S04T,CO2,HCO3T,CLT

50 FORMAT (1H1)

90 FORMAT (A4,2X,(4(F10.4,4X)))

91 FORMAT (6X,(4(E10.4,4X)))

WRITE (6,92)

92 FORMAT(* WATER COMPOSITION (MOLES/LITER), EXCEPT CO2 (ATM) *,//)

WRITE (6,93)

93 FORMAT (1X,*SAMPLE NO.*,2X,*TOTAL CA*,4X,*TOTAL MG*,4X,*TOTAL NA*

1,4X,*TOTAL K*,5X,*SULFATE*,5X,*CARBON DIOX*,1X,*TOTAL HCO3*,2X,

2*CHLORIDE*)

WRITE (6,94) SAMPLE,CAT,MGT,NAT,KT,S04T,CO2,HCO3T,CLT

94 FORMAT (1X,A9,(8(E10.4,2X)),//)

IP = 0

CACO3 = 0.

CASO4 = 0.

C CALCULATE IONIC STRENGTH AND ACTIVITY COEFFICIENTS

M= 2.0*CAT+2.0*MGT+2.0*S04T+0.5*NAT+0.5*KT+0.5*HCO3T+0.5*CLT

SQ = SQRT (M)

YCA = 10.0**(-((2.034*SQ)/(1.0+1.9886*SQ)))

YMG = 10.0**(-((2.034*SQ)/(1.0+2.6248*SQ)))

YNA = 10.0**(-((0.5085*SQ)/(1.0+1.4108*SQ)))

YK = 10.0**(-((0.5085*SQ)/(1.0+0.9843*SQ)))

YSO4 = 10.0**(-((2.034*SQ)/(1.0+1.3124*SQ)))

YCO3 = 10.0**(-((2.034*SQ)/(1.0+1.4765*SQ)))

YHCO3 = YNA

YCL = YK

YKS04 = YHCO3

YNASO4 = YHCO3

YNACO3 = YHCO3

YMGHCO = YHCO3

YCAHCO = YHCO3

CAT = CAT

MGI = MGT

NAI = NAT

KI = KT

CLI = CLT

C CALCULATE FREE ANION CONCENTRATIONS

$$\begin{aligned}
 2 \text{ SO4I} &= (\text{SO4T}) / (((10.0^{**}0.95) * \text{NAI} * \text{YNA} * \text{YSO4}) / (\text{YNASO4}) + ((10.0^{**} \\
 &10.84) * \text{KI} * \text{YK} * \text{YSO4}) / (\text{YKSO4}) + ((10.0^{**}2.31) * \text{CAI} * \text{YCA} * \text{YSO4}) + ((10.0^{**} \\
 &22.20) * \text{MGI} * \text{YMG} * \text{YSO4}) + 1.0) \\
 \text{HCO3I} &= (\text{HCO3T}) / (((10.0^{**}1.26) * \text{CAI} * \text{YCA}) + ((10.0^{**}1.16) * \text{MGI} * \text{YMG}) \\
 &3 + ((10.0^{**}(-0.25)) * \text{NAI} * \text{YNA} * \text{YHCO3}) + 1.0) \\
 \text{H} &= ((10.0^{**}(-7.81)) * \text{CO2}) / (\text{HCO3I} * \text{YHCO3}) \\
 \text{CO3I} &= ((10.0^{**}(-10.33)) * \text{HCO3I} * \text{YHCO3}) / (\text{YCO3} * \text{H})
 \end{aligned}$$

C CALCULATE FREE CATION CONCENTRATIONS

$$\begin{aligned}
 \text{CAI} &= (\text{CAT}) / (((10.0^{**}2.31) * \text{SO4I} * \text{YCA} * \text{YSO4}) + ((10.0^{**}1.26) \\
 &6 * \text{HCO3I} * \text{YCA}) + ((10.0^{**}3.20) * \text{CO3I} * \text{YCA} * \text{YCO3}) + 1.0) \\
 \text{MGI} &= (\text{MGT}) / (((10.0^{**}2.20) * \text{SO4I} * \text{YMG} * \text{YSO4}) + ((10.0^{**}1.16) * \text{HCO} \\
 &7 * \text{YMG}) + ((10.0^{**}3.40) * \text{CO3I} * \text{YMG} * \text{YCO3}) + 1.0) \\
 \text{NAI} &= (\text{NAT}) / (((10.0^{**}0.95) * \text{SO4I} * \text{YNA} * \text{YSO4}) / (\text{YNASO4}) + ((10.0^{**}(-0.25) \\
 &8 * \text{HCO3I} * \text{YNA} * \text{YHCO3}) + ((10.0^{**}1.27) * \text{CO3I} * \text{YNA} * \text{YCO3}) / (\text{YNACO3}) + 1.0) \\
 \text{KI} &= (\text{KT}) / (((10.0^{**}0.84) * \text{SO4I} * \text{YK} * \text{YSO4}) / (\text{YKSO4}) + 1.0)
 \end{aligned}$$

C CALCULATE CHARGED ION-PAIR CONCENTRATIONS

$$\begin{aligned}
 \text{CAHCO3} &= ((10.0^{**}1.26) * \text{CAI} * \text{HCO3I} * \text{YCA}) \\
 \text{MGHCO3} &= ((10.0^{**}1.16) * \text{MGI} * \text{HCO3I} * \text{YMG}) \\
 \text{NASO4} &= (((10.0^{**}0.95) * \text{NAI} * \text{SO4I} * \text{YNA} * \text{YSO4}) / (\text{YNASO4}) \\
 \text{NACO3} &= (((10.0^{**}1.27) * \text{NAI} * \text{CO3I} * \text{YNA} * \text{YCO3}) / (\text{YNACO3}) \\
 \text{KSO4} &= (((10.0^{**}0.84) * \text{KI} * \text{SO4I} * \text{YK} * \text{YSO4}) / (\text{YKSO4})
 \end{aligned}$$

C CALCULATE IONIC STRENGTH AND ACTIVITY COEFFICIENTS

$$\begin{aligned}
 \text{M} &= 2.0 * (\text{CAI} + \text{MGI} + \text{SO4I} + \text{CO3I}) + 0.5 * (\text{NAI} + \text{KI} + \text{CLI} + \text{HCO3I} + \text{NASO4} + \text{NACO3} \\
 &9 + \text{KSO4} + \text{CAHCO3} + \text{MGHCO3}) \\
 \text{SQ} &= \text{SQRT}(\text{M}) \\
 \text{YCA} &= 10.0^{**}(-((2.034 * \text{SQ}) / (1.0 + 1.9886 * \text{SQ}))) \\
 \text{YMG} &= 10.0^{**}(-((2.034 * \text{SQ}) / (1.0 + 2.6248 * \text{SQ}))) \\
 \text{YNA} &= 10.0^{**}(-((0.5085 * \text{SQ}) / (1.0 + 1.4108 * \text{SQ}))) \\
 \text{YK} &= 10.0^{**}(-((0.5085 * \text{SQ}) / (1.0 + 0.9843 * \text{SQ}))) \\
 \text{YSO4} &= 10.0^{**}(-((2.034 * \text{SQ}) / (1.0 + 1.3124 * \text{SQ}))) \\
 \text{YCO3} &= 10.0^{**}(-((2.034 * \text{SQ}) / (1.0 + 1.4765 * \text{SQ}))) \\
 \text{YHCO3} &= \text{YNA} \\
 \text{YCL} &= \text{YK} \\
 \text{YKSO4} &= \text{YHCO3} \\
 \text{YNASO4} &= \text{YHCO3} \\
 \text{YNACO3} &= \text{YHCO3} \\
 \text{YMGHCO} &= \text{YHCO3} \\
 \text{YCAHCO} &= \text{YHCO3}
 \end{aligned}$$

C CALCITE CYCLE (EVALUATION OF PRECIPITATION AND DISSOCIATION EFFECT)

```

CACO3H = CACO3
ENP = (MGI*CO3I*YCA*YCO3)/(10.0**(-8.35))
ENG = (CAI*SO4I*YCA*YCO3)/(10.0**(-8.35))
ENF=(1.0+1.96*ENP+0.0025*ENG)/(1.0+0.76*ENP+0.00074*ENG)
D=((10.0**(-5.83))*CO2)/(YCA*YHCO3*YHCO3)*ENF-(CAI*HCO3I*HCO3I)
+IVE VALUE OF D WILL HAVE +IVE Z AND CACO3 WILL DISSOCIATE
IF (D.EQ.0.) GO TO 4
3 H2CO3T = (10.0**(-1.46))*CO2
A(1) = 4.0
A(2) = 4.0*(HCO3I+CAI)
A(3) = (4.0*CAI*HCO3I+HCO3I*HCO3I)
A(4)=CAI*HCO3I*HCO3I-(((10.0**(-4.37))*H2CO3T)/(YCA*YHCO3*YHCO3))
1*ENF
N = 3
Z(1) = 0.0
Z(2) = 0.0
Z(3) = 0.0
CALL ZPOLYR (A,N,7,7,IFR)
IF (IER.EQ.1.OR.IER.EQ.2.OR.IER.EQ.3)PRINT 61,IER
81 FORMAT (1X, * ZPOLYR ERROR MESSAGE NO. *,13)
DO 200 I = 1,3
IT = I
FI = AIMAG (Z(IT))
FR = REAL (Z(IT))
IF (FI.NE.0.) GO TO 200
IF (D.LT.0.) GO TO 4
7 IF (D.GT.0.) GO TO 6
9 IF (FR.LT.0.) GO TO 10
GO TO 200
6 IF (FR.GT.0.) GO TO 10
GO TO 200
10 IF ((HCO3T + (2*FR)).LT.0.) GO TO 200
IF ((CAT + FR).LT.0.) GO TO 200
CAT = CAT + FR
HCO3T = HCO3T + 2*FR
CACO3 = CACO3 - FR
CAI = CAI + FR
HCO3I = HCO3I + 2*FR
GO TO 4
200 CONTINUE
WRITE (6,110)
110 FORMAT(//,1X,*CALCULATIONS STOPPED(ERROR DETECTED AT DO-LOOP 200*)
GO TO 1
4 DEL = CACO3-CACO3H
IF (DEL.GE.(10.0**(-7))) GO TO 2
IF (DEL.LE.(-10.0**(-7))) GO TO 2
IF (IP.NE.0) GO TO 250
HCO3T = HCO3T-CO3I
IP = 1
GO TO 2

```

C GYPSUM CYCLE (EVALUATION OF PRECIPITATION AND ITS EFFECTS)

```

250 CAS04H = CAS04
    DG = CAI*S04I
    IF (DG.LT.((10.0**(-4.60)) / (YCA*YS04))) GO TO 240
    IF (DG.EQ.((10.0**(-4.60)) / (YCA*YS04))) GO TO 240
    W = CAI + S04I
    Y = (CAI*S04I) - (10.0**(-4.60)/(YCA*YS04))
    IF (SQRT(W*W-4*Y).LT.0) PRINT 108
108 FORMAT (1X,*BOTH G ROOTS IMAGINARY*)
    G = (-W+SQRT(W*W-4*Y))/2
    IF (G.GT.0.) GO TO 205
    IF (ABS(G).GT.CAI) GO TO 205
    IF (ABS(G).GT.S04I) GO TO 205
    GO TO 210
205 G = (-W-SQRT(W*W-4*Y))/2
    IF (G.GT.0.) PRINT 109,G
109 FORMAT (1X,*ERROR -ALL G ROOTS +IVE AND ONE VALUE OF G=#.E10.4.
210 CAT = CAT + G
    CAI = CAI + G
    S04I = S04I + G
    S04T = S04T + G
    CAS04 = CAS04 - G
    DEG = CAS04 - CAS04H
    IF (DEG.GE.(10.0**(-7))) GO TO 2
    IF (DEG.LE.(-10.0**(-7))) GO TO 2

```

C CALCULATE ION-PAIR CONCENTRATIONS AND TOTAL CARBONATE

```

240 CAHCO3 = ((10.0**1.26)*CAI*HCO3I*YCA)
    MGHCO3 = ((10.0**1.16)*MGI*HCO3I*YMG)
    NAS04 = ((10.0**0.95)*NAI*SU4I*YNA*YS04)/(YNAS04)
    NACO3 = ((10.0**1.27)*NAI*CO3I*YNA*YCO3)/(YNACO3)
    KS04 = ((10.0**0.84)*KI*S04I*YK*YS04)/(YKS04)
    CACO30 = ((10.0**3.20)*CAI*CO3I*YCA*YCO3)
    MGC030 = ((10.0**3.40)*MGI*CO3I*YMG*YCO3)
    H2CO3T = (10.0**(-1.46))*CO2
    CAS040 = ((10.0**2.31)*CAI*S04I*YCA*YS04)
    MGS040 = ((10.0**2.20)*MGI*S04I*YMG*YS04)
    CO3T = CACO30 + MGC030 + NACO3 + CO3I

```


C EQUILIBRIUM RESULTS

```

250 WRITE (6,112)
112 FORMAT (////,* EQUILIBRIUM RESULTS-AMOUNTS OF ALL SPECIES IS AS
      1CONC(MOLES/LITER), EXCEPT H IN ACTIVITY(MOLES/LITER) *)
      IF (CASO4.EQ.0.) WRITE (6,270)
270 FORMAT (////,1X,*EQUILIBRIUM SOLUTION IS UNDERSATURATED WITH GYPSUM
      1*,//)
      IF (CASO4.GT.0.) WRITE (6,280)
280 FORMAT (////,1X,*EQUILIBRIUM SOLUTION IS SATURATED WITH GYPSUM*,//)
      WRITE (6,103)
103 FORMAT (1X,*IONIC STREN*,1X,*Y CA*,8X,*Y MG*,8X,*Y NA*,8X,*Y K*,9X
      7,*Y SO4*,7X,*Y CO3*)
      WRITE (6,101) M,YCA,YMG,YNA,YK,YSO4,YCO3
101 FORMAT (1X,(11(E10.4,2X)),/)
      WRITE (6,107)
107 FORMAT (/)
      WRITE (6,100)
100 FORMAT (1X,*SULFATE ION*,1X,*BICARB ION*,2X,*CARB ION*,4X,*CA ION*
      5,6X,*MG ION*,6X,*NA ION*,6X,*K ION*,7X,*HYDROGEN ION*,3X,
      6*CHLORIDE (ION OR TOTAL)*)
      WRITE (6,101) SO4I,HCO3I,CO3I,CAI,MGI,NAI,KI,H,CLI
      WRITE (6,107)
      WRITE (6,255)
255 FORMAT (1X,*CA HCO3*,5X,*MG HCO3*,5X,*NA SO4*,6X,*NA CO3*,6X,*K SO
      24*,7X,*CA CO3 0*,4X,*MG CO3 0*,4X,*TOTAL H2CO3*,1X,*TOTAL CO3*)
      WRITE (6,101) CAHCO3,MGHCO3,NASO4,NACO3,KSO4,CACO30,MGCO30,
      3H2CO3T,CO3T
      WRITE (6,107)
      CAME = (CAT)*(10.0**3.0)**2.0
      MGME = (MGT)*(10.0**3.0)**2.0
      NAME = (NAT)*(10.0**3.0)
      SAR = (NAME)/(SQRT((CAME+MGME)/(2.0)))
      WRITE (6,113)
113 FORMAT (1X,*TOTAL CA*,4X,*TOTAL MG*,4X,*TOTAL NA*,4X,*TOTAL K*,5X,
      1*SAR*,9X,*CA CO3 (+IVE VALUE=PPT)*,4X,*TOTAL HCO3*,
      26X,*GYPSUM*,6X,*TOTAL SO4*)
      WRITE (6,114) CAT,MGT,NAT,KT,SAR,CACO3,HCO3T,CASO4,SO4T
114 FORMAT (1X,(6(E10.4,2X)),17X,E10.4,4X,E10.4,4X,E10.4)
      GO TO 1
500 STOP
      END

```

CALL ZPOLYR(A,N,Z,Z,IER) is a subroutine that calculates the roots of a polynomial equation (IMSL,1972). This subroutine is on a computer file in Colorado State University. If CALL ZPOLYR(A,N,Z,Z,IER) is not available, then

a comparable subroutine that calculates the roots of a 3rd degree polynomial can be used in lieu of CALL ZPOLYR(A,N,Z,Z,IER).

A brief description of CALL ZPOLYR(A,N,Z,Z,IER) as given by International Mathematical and Statistical Libraries (IMSL)¹, Inc., 1972, in their "Library 3 Manual" is given below.

FUNCTION		- COMPUTES THE NDEG ZEROS OF A GIVEN POLYNOMIAL OF DEGREE NDEG
USAGE		- CALL ZPOLYR (A,NDEG,Z,Z,IER)
PARAMETERS	A	- INPUT VECTOR OF LENGTH NDEG+1, CONTAINS THE COEFFICIENTS OF THE POLYNOMIAL $A(1)*X^{NDEG}+A(2)*X^{(NDEG-1)}+\dots+A(NDEG+1)$
	NDEG	- DEGREE OF THE POLYNOMIAL
	Z	- OUTPUT, COMPLEX VECTOR OF LENGTH N CONTAINING THE COMPUTED ROOTS OF THE POLYNOMIAL. Z MUST APPEAR TWICE IN THE CALLING SEQUENCE.
	IER	- ERROR PARAMETER TERMINAL ERROR = 128 + N N = 1 INDICATES THE DEGREE OF POLYNOMIAL IS GREATER THAN 79 N = 2 INDICATES LAGUERRE'S METHOD HAS FAILED TO CONVERGE. N = 3 INDICATES AN ERROR OCCURS IN SUBROUTINE ZQUADR
PRECISION		- SINGLE
REQD. IMSL ROUTINES		- UERTST,ZQUADR,VABMXF
AUTHOR/IMPLEMENTER		- O.G. JOHNSON/E.W. CHOU
LANGUAGE		- FORTRAN

ZPOLYR computes the NDEG zeros of the polynomial $P(Z) = A_1 Z^{NDEG} + A_2 Z^{NDEG-1} + \dots + A_{NDEG} Z + A_{NDEG+1}$ where the coefficients, A_1 , are real. The

¹ IMSL. 1972. Library 3 Manual. IMSL, 6200 Hillcroft, Suite 510, Houston, Texas 77036.

zeros are stored in the complex array Z with complex conjugate pairs stored contiguously. (See Example).

ZPOLYR uses Laguerre's method. The routine is a modification of Smith's (1967) routine ZERPOL². ZPOLYR iterates toward a zero using Laguerre's method, which is cubically convergent for isolated zeros and linearly convergent for multiple zeros. The maximum length of the step between successive iterates is restricted so that the iterate x_{j+2} lies inside a certain region about the iterate x_j proved to contain a zero of the polynomial. An iterate is accepted as a zero when the polynomial value at that iterate is smaller than a computed bound for the rounding error in the polynomial value at that iterate. The original polynomial is deflated after each real zero or pair of complex zeros is found, and subsequent zeros are found using the deflated polynomial.

IMSL has tested ZPOLYR on approximately 70 different polynomials. Sample accuracies were very good.

Programming Notes

1. In the main program Z must appear in the calling sequence twice.
2. If the user desires to solve a polynomial of degree (NDEG) greater than 79, then the dimension statement in ZPOLYR for DU(79) should be changed to the desired degree and LIBWSP should be given dimension 2*NDEG+2. Also, the number 79 in the statement:

IF (N.LE.79) GO TO 10 (the next statement after statement number 5)

should be changed to show the desired maximum degree.

² Smith, B. T. 1967. ZERPOL, a zero finding algorithm for polynomials using Laguerre's method. Department of Computer Science, University of Toronto, Canada.

Example

Input:

NDEG = 4

A = (1.0, -4.0, 14.0, -4.0, 13.0)

CALL ZPOLYR(A,NDEG,Z,Z,IER)

Output:

Z = (2.0 3.0, 2.0 -3.0, -0.0 -1.0, -0.0 1.0)

Note: The zeros given by Z should be interpreted as follows:

Z = (2.0+3i, 2.0-3i, -i, i)

APPENDIX II

DATA INPUT

The input data are fed into the program with cards. Two data cards are required for each sample. The concentration of the ionic species is expressed in terms of moles/liter and the data are punched on cards in E format.

Card No. 1 (cationic concentrations)

Col. 1- 4	Sample No.
Col. 7-16	Total Ca (e.g., if total Ca = 2.53×10^{-2} moles/l, then punch 2.5300E-03)
Col. 21-30	Total Mg
Col. 35-44	Total Na
Col. 49-58	Total K

Card No. 2 (anionic concentrations)

Col. 1- 4	Sample No.
Col. 7-16	Total SO_4
Col. 21-30	CO_2 gas pressure (in atmospheres)
Col. 35-44	Alkalinity (Total $\text{HCO}_3 + 2 \times \text{Total CO}_3$)
Col. 49-58	Total $\text{Cl} + \text{NO}_3$