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**COMMON COMPUTERIZED METHODS
FOR CALCULATING AQUEOUS SPECIATION**

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ABSTRACT

In the realm of ion-pairing theory, ions exist in solution as free and complexed species and the calculated concentrations of these species is often called "speciation". Although there are numerous computer programs for calculating speciation at chemical equilibrium most of these programs employ only a few common methods. This paper classifies these methods into groups based on programming approaches and mathematics. Discussions and algorithms for several methods are presented using the simple system of Ca^{2+} , SO_4^{2-} , and CaSO_4^0 . Comparison of the methods indicates that the efficiencies of the methods are unique to each method and vary with the size of the aqueous system. Furthermore, convergence characteristics are method-specific and depend in part on the chosen master species from which all other species are calculated.

1. INTRODUCTION

Water-quality specialists have the option of either treating dissolved solids as bulk parameters (for example, dissolved calcium = 111 ug/L) or determining the aqueous species of the dissolved solids (for example, free Ca^{2+} = 6 ug/L, CaSO_4^0 = 188 ug/L). When the latter alternative is chosen, the determination of major aqueous species, often called "speciation", usually cannot be made by standard water-quality analysis. Instead, bulk parameters are measured and concentrations of species are obtained by mathematical calculation. In the realm of ion-pairing theory, the calculation of equilibrium-based aqueous speciation draws on experimentally determined equilibrium constants or thermodynamic data to provide chemical concentrations of ion pairs, aqueous complexes, and free ions. Further calculations can then be made for mineral saturation indices and toxicity.

There are apparently dozens of computer programs in existence to calculate aqueous speciation as well as additional complications such as chemical activity and solid-liquid interactions. Many of these programs are reviewed in Nordstrom et al. (1979) and Nordstrom and Ball (1984). The purpose of this paper however is to look behind the programs and examine the few mathematical methods employed by the programs to calculate speciation. In order to avoid the abundance of superscripts, subscripts, and mathematics in the original references which can lead to confusion, the methods are examined here through the simple system of Ca^{2+} , SO_4^{2-} , and CaSO_4^0 . This approach was first used by Morin (1985) and is refined and expanded in this paper.

2. CLASSIFICATION OF COMMON METHODS

Methods of speciation can be gathered into various groups based on arbitrary criteria. Morin (1985) identified three groups based on techniques of programming: (1) repetitive sequences of equations, (2) solution of matrix equations, and (3) minimization of Gibbs Free Energy. The first two groups employ equilibrium constants rather than thermodynamic data.

These groups are generally consistent with the pure-iteration (or "successive approximation"), Newton-Raphson, and Free-Energy-Minimization groups of Nordstrom et al. (1979) and Nordstrom and Ball (1984). Alternatively, Smith and Missen (1982) show

that the matrix-solver and minimization groups are closely related mathematically and can thus be considered as one group. Because the methods are presented in this paper as short algorithms, the programming classification will be retained.

3. METHODS INVOLVING REPETITIVE SEQUENCES OF EQUATIONS

This group contains all methods which calculate trial concentrations of species during execution of a stack of equations. This group differs from the following group (Section 4) in that no matrix is evaluated and this difference has a major implication on the relative efficiencies of the methods (Section 6). This repetitive-sequences group includes such methods as brute force, Continuous Fraction, and Monotone Sequences. The Continuous Fraction Method (for example, Wigley 1977) is the most efficient and thus is the only member of the group examined here. A description of the brute-force method is presented in Wigley (1977). A detailed presentation of Monotone Sequences can be found in Wolery and Walters (1975) with a simplified example presented in Morin (1985).

Algorithm 1 presents the Continuous-Fraction Method for the system of Ca^{2+} , SO_4^{2-} , and CaSO_4^0 . In the algorithm, activities ($[X]$) are assumed to be equal to concentrations, that is, ionic strength is close to zero and activity coefficients (g) are close to one. If activity coefficients deviate from one, activities are replaced by $[X] = g_x (X)$.

```

** INPUT VALUES AND INITIAL GUESSES (1)
   Total Ca (input)
   Total SO4 (input)
   ERROR (acceptable error, input)
    $(\text{Ca}^{2+}) = \text{Total Ca}$ 
    $(\text{SO}_4^{2-}) = \text{Total SO4}$ 
   K = equilibrium constant for  $\text{CaSO}_4^0$  (input)

** COMPUTATION
100  $[\text{CaSO}_4^0] = K * [\text{Ca}^{2+}] * [\text{SO}_4^{2-}]$ 
     $(\text{Ca}^{2+}) = (\text{Ca}^{2+}) * \{\text{Total Ca} / ((\text{Ca}^{2+}) + (\text{CaSO}_4^0))\}$ 
     $(\text{SO}_4^{2-}) = (\text{SO}_4^{2-}) * \{\text{Total SO4} / ((\text{SO}_4^{2-}) + (\text{CaSO}_4^0))\}$ 
    If CHANGE in species > ERROR go to 100
    PRINT RESULTS
    Stop

```

In Algorithm 1, the concentrations of free Ca^{2+} and free SO_4^{2-} (the "master species" from which other species are calculated) are initially assumed to equal the total dissolved concentrations of calcium and

sulfate, respectively. After the first iteration through the computation portion, new trial concentrations of free Ca^{2+} and SO_4^{2-} are obtained which are likely to be significantly different from the original assumptions. Consequently, further iterations are made through the computation portion until changes in species concentrations from one iteration to the next iteration decrease to a specified acceptable error.

The computation portion can be simplified in this case by removing Ca^{2+} or SO_4^{2-} from the right-hand side of the species equations:

** COMPUTATION (2)

```

100 (Ca2+ = Total Ca/(1 + K*[SO42-])
    (SO42-) = Total SO4/(1 + K*[Ca2+])
    If CHANGE > ERROR go to 100
    [CaSO40] = K*[Ca2+]*[SO42-]
    PRINT RESULTS
    Stop

```

This simplification is most useful when a master species such as Ca^{2+} can be totally eliminated from the right-hand side. For example, if Ca_2SO_4 replaced CaSO_4 , then statement #100 in Algorithm 2 would be: $(\text{Ca}^{2+}) = \text{TOTAL Ca}/(1 + K*[\text{Ca}^{2+}]*[\text{SO}_4^{2-}])$, which is less useful.

4. METHODS INVOLVING SOLUTION OF MATRIX EQUATIONS

This group of methods solve matrix equations in order to calculate the change in species activities at each iteration. Calculations continue until the change is less than a preselected error. The matrix equations are derived from the Taylor's Series with $d(x)$ representing the change in activities at one iteration:

$$f(x + d(x)) = f(x) + d(x)*f'(x) + (d(x)/2^2)*f''(x)+... \quad (3)$$

where $f'(x)$ and $f''(x)$ are the first and second derivatives of $f(x)$, respectively. Upon assuming only the first two terms on the right-hand side of Equation 3 are significant, the series can be truncated to:

$$f(x + d(x)) = f(x) + d(x)*f'(x) \quad (4)$$

When f is formulated so that it has the value of zero at equilibrium and if $d(x)$ is specified to attain equilibrium, then

$$f(x + d(x)) = 0 = f(x) + d(x)*f'(x) \quad (5)$$

Manipulation of Equation 7 leads to:

$$f'(x) * d(x) = -f(x) \quad (6)$$

Because f is often large and non-linear and because the series in Equation 4 is truncated, $d(x)$ cannot be calculated simply. Instead, an iterative approach to the calculation is employed.

The methods in this group differ in their definition of $f'(x)$. For example, the Secant method employs a finite-difference approximation of $f'(x)$ (that is, Morin, 1985). Certainly one of the most popular and one of the more stable methods in this group is the Newton-Raphson Method which employs the true $f'(x)$. Only this method will be addressed in this section and a detailed discussion of it can be found in Parkhurst *et al.* (1980).

Because there are n number of master species and complexes present in a water, $f'(x)$ a matrix of size $n \times n$ and $f(x)$ and $d(x)$ are vectors of length n . $f'(x)$ and $f(x)$ are chosen so that they contain only known values at an iteration and $d(x)$ can then be solved for by matrix-solver techniques such as Gaussian Elimination. This $d(x)$ is then added to the trial concentration for the next iteration:

$$x(k + 1) = x(k) + d(x)(k) \quad (7)$$

where k = iteration number. $f'(x)$ and $f(x)$ are then recalculated and a new $d(x)$ is then solved for. These iterations continue until the change is less than the preselected error. The basic form of $f(x)$ is indicated by Equation 5 which indicates that every equation in $f(x)$ must equal zero because $d(x) = 0$ at equilibrium. The unknowns are the activities of the master species and of the complexes/ion pairs. $f(x)$ contains an equal number of equations as unknowns of two types: (1) mass-action equations to create each species from the master species and (2) mass-balance equations. For the Ca^{2+} , SO_4^{2-} , and $CaSO_4^0$ system, the vectors for $d(x)$ and $f(x)$ are:

$$d(x_1) = d[CaSO_4^0] \quad d(x_2) = d[Ca^{2+}] \quad d(x_3) = d[SO_4^{2-}] \quad (8)$$

$$f(x_1) = [CaSO_4^0] - K * [Ca^{2+}] * [SO_4^{2-}] \quad (9)$$

$$f(x_2) = (CaSO_4^0) + (Ca^{2+}) - (Total Ca)$$

$$f(x_3) = (CaSO_4^0 + (SO_4^{2-}) - (Total SO_4))$$

The $f'(x)$ matrix is:

$$\begin{array}{ccc}
 \frac{\partial f(x_1)}{\partial [\text{CaSO}_4^0]} & \frac{\partial f(x_1)}{\partial [\text{Ca}^{2+}]} & \frac{\partial f(x_1)}{\partial [\text{SO}_4^{2-}]} \\
 \\
 \frac{\partial f(x_2)}{\partial [\text{CaSO}_4^0]} & \frac{\partial f(x_2)}{\partial [\text{Ca}^{2+}]} & \frac{\partial f(x_2)}{\partial [\text{SO}_4^{2-}]} \quad (10) \\
 \\
 \frac{\partial f(x_3)}{\partial [\text{CaSO}_4^0]} & \frac{\partial f(x_3)}{\partial [\text{Ca}^{2+}]} & \frac{\partial f(x_3)}{\partial [\text{SO}_4^{2-}]}
 \end{array}$$

Evaluating Matrix 10 through Equation 9 yields :

$$\begin{bmatrix}
 1 & -K \times [\text{SO}_4^{2-}] & -K \times [\text{Ca}^{2+}] \\
 \frac{1}{g_1} & \frac{1}{g_2} & \emptyset \\
 \frac{1}{g_1} & \emptyset & \frac{1}{g_3}
 \end{bmatrix}
 \begin{bmatrix}
 d [\text{CaSO}_4^0] \\
 d [\text{Ca}^{2+}] \\
 d [\text{SO}_4^{2-}]
 \end{bmatrix}
 =
 \begin{bmatrix}
 -f(x_1) \\
 -f(x_2) \\
 -f(x_3)
 \end{bmatrix} \quad (11)$$

Where g_1 = activity coefficient of CaSO_4^0
 g_2 = activity coefficient of Ca^{2+}
 g_3 = activity coefficient of SO_4^{2-}

The basic algorithm is (variations exist):

```
** INPUT VALUES AND INITIAL GUESSES (12)
Total Ca (input)
Total SO4 (input)
ERROR (acceptable error, input)
Initial guess for [Ca2+]
Initial guess for [SO42-]
Initial guess for [CaSO40]
K = equilibrium constant for CaSO40 (input)
** COMPUTATION
100 F(1) = [CaSO40] - K*[Ca2+]*[SO42-]
F(2) = (CaSO40) + (Ca2+) - (Total Ca)
F(3) = (CaSO40) + (SO42-) - (Total SO4)
FPRIME(1,1) = 1.0
FPRIME(1,2) = [SO42-]*(-K)
FPRIME(1,3) = [Ca2+]*(-K)
FPRIME(2,1) = 1/g1
FPRIME(2,2) = 1/g2
FPRIME(2,3) = 0.0
FPRIME(3,1) = 1/g1
FPRIME(3,2) = 0.0
FPRIME(3,3) = 1/g2
[CaSO40] = K*[Ca2+]*[SO42-]
* SUB-PROGRAM to calculate dx
[Ca2+] = [Ca2+] + d[Ca2+]
[SO42-] = [SO42-] + d[SO42-]
If CHANGE in concentrations > ERROR go to 100
PRINT RESULTS
Stop
```

5. METHODS INVOLVING MINIMIZATION OF GIBBS FREE ENERGY

The Free-Energy methods solve for chemical equilibrium by finding the minimum value for the sum of: each species' Gibbs Free-Energy of formation (adjusted for temperature, pressure, and activity) multiplied by its molal concentration. In their excellent text on equilibrium analysis, Smith and Missen (1982) have succeeded in gathering published algorithms employing free energies and a few algorithms employing equilibrium constants into two sub-groups: "Stoichiometric algorithms" and "Non-stoichiometric algorithms". Stoichiometric algorithms involve the iterative calculation of an "extent-of-reaction" value for each reaction explicitly entered in the algorithm and mass balance is implicitly maintained. Non-stoichiometric algorithms do not explicitly contain chemical reactions, but iteratively reach equilibrium by changing mole fractions of components while minimizing the free energy of the system. Both sub-groups require good initial guesses of the final results in order to obtain convergence.

5.1 Stoichiometric Algorithm

The general stoichiometric algorithm for the species, Ca^{2+} , SO_4^{2-} , and CaSO_4^0 , is:

```

** INPUT VALUES AND INITIAL GUESSES (13)
TEMPERATURE (input)
ERROR (acceptable error, input)
Gibbs Free Energy of Formation of  $\text{Ca}^{2+}$  (GCA),
 $\text{SO}_4^{2-}$  (GSO4), and  $\text{CaSO}_4^0$  (GCASO)
Stoichiometric coefficients for the reaction:
 $\text{Ca}^{2+} + \text{SO}_4^{2-} - \text{CaSO}_4^0 = 0$  (V(1)=1, V(2)=1,
V(3)=-1)
Initial guesses for ( $\text{Ca}^{2+}$ ), ( $\text{SO}_4^{2-}$ ), ( $\text{CaSO}_4^0$ ),
where ( $\text{Ca}^{2+}$ ) + ( $\text{CaSO}_4^0$ ) = Total Ca
and ( $\text{SO}_4^{2-}$ ) + ( $\text{CaSO}_4^0$ ) = Total  $\text{SO}_4$ 

** COMPUTATION
RT = R * TEMP
VBAR = V(1)+V(2)+V(3)
100 CTOTAL = ( $\text{Ca}^{2+}$ ) + ( $\text{SO}_4^{2-}$ ) + ( $\text{CaSO}_4^0$ )
X = -V(1)*[GCA/RT+ln(( $\text{Ca}^{2+}$ ))]
      -V(2)*[GSO4/RT+ln(( $\text{SO}_4^{2-}$ ))]
      -V(3)*[GCASO/RT+ln(( $\text{CaSO}_4^0$ ))]
A = V(1)*V(1)/( $\text{Ca}^{2+}$ ) + V(2)*V(2)/( $\text{SO}_4^{2-}$ ) +
V(3)*V(3)/( $\text{CaSO}_4^0$ ) - 3*(VBAR*VBAR/CTOTAL)
D = X/A
( $\text{Ca}^{2+}$ ) = ( $\text{Ca}^{2+}$ ) + V(1)*D
( $\text{SO}_4^{2-}$ ) = ( $\text{SO}_4^{2-}$ ) + V(2)*D
( $\text{CaSO}_4^0$ ) = ( $\text{CaSO}_4^0$ ) + V(3)*D
If D > ERROR go to 100
PRINT RESULTS
STOP

```

5.2 Non-stoichiometric Algorithm

The general non-stoichiometric algorithm for the species, Ca^{2+} , SO_4^{2-} , and CaSO_4^0 , is:

```

** INPUT VALUES AND INITIAL GUESSES (14)
TOTAL Ca (input)
TOTAL  $\text{SO}_4$  (input)
TEMPERATURE (input)
RT = R * TEMP
ERROR (acceptable error, input)
Number of  $\text{Ca}^{2+}$  in  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and
 $\text{CaSO}_4^0$ : (A(1,1)=1, A(1,2)=0, A(1,3)=1)
Number of  $\text{SO}_4^{2-}$  in  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and
 $\text{CaSO}_4^0$ : (A(2,1)=0, A(2,2)=1, A(2,3)=1)
Free energies of  $\text{Ca}^{2+}$  (GCA),  $\text{SO}_4^{2-}$  (GSO4),
 $\text{CaSO}_4^0$  (GCASO)
Initial guesses for ( $\text{Ca}^{2+}$ ), ( $\text{SO}_4^{2-}$ ), ( $\text{CaSO}_4^0$ )

```

```

** COMPUTATION
TOT = (Ca2+) + (SO42-) + (CaSO40)
OMEGA(1) = EXP(GCA/RT)
OMEGA(2) = EXP(GSO4/RT)
OMEGA(3) = EXP(GCASO/RT)
R(1) = 0.0
R(2) = TOTAL SO4/TOTAL Ca
BETA(1,1) = 1.0 + R(1)*A(1,1)
BETA(1,2) = 1.0 + R(1)*A(1,2)
BETA(1,3) = 1.0 + R(1)*A(1,3)
BETA(2,1) = A(2,1) - R(2)*A(1,1)
BETA(2,2) = A(2,2) - R(2)*A(1,2)
BETA(2,3) = A(2,3) - R(2)*A(1,3)
ALPHA(1,1) = A(1,1)
ALPHA(1,2) = A(1,2)
ALPHA(1,3) = A(1,3)
ALPHA(2,1) = BETA(2,1)
ALPHA(2,2) = BETA(2,2)
ALPHA(2,3) = BETA(2,3)
(The following calculates the Lagrangian Multipliers,
ALAMB, through AA*ALAMB = RIGHT to obtain initial
estimates of mole fractions, X)
AA(1,1) = AA(2,2) = 1.0
AA(1,2) = AA(2,1) = 0.0
RIGHT(1) = -GCA - RT*ln((Ca2+)/TOT)
RIGHT(2) = -GSO4 - RT*ln((SO42-)/TOT)
(*Sub-program to solve for ALAMB(1) and ALAMB(2)
goes here)
Z(1) = EXP(ALAMB(1)/RT)
Z(2) = EXP(ALAMB(2)/RT)
THETA(1) = Z(1) * Z(2)**R(2)
THETA(2) = Z(2)
X(1) = OMEGA(1) * Z(1)**ALPHA(1,1) *
      Z(2)**ALPHA(2,1)
X(2) = OMEGA(2) * Z(1)**ALPHA(1,2) *
      Z(2)**ALPHA(2,2)
X(3) = OMEGA(3) * Z(1)**ALPHA(1,3) *
      Z(2)**ALPHA(2,3)
(The following iterative routine solves for changes in
THETA's by solving for ln(DTHETA) in PF*ln(DTHETA)=F)
100 F(1) = (OMEGA(1) * THETA(1)**ALPHA(1,1) *
          THETA(2)**ALPHA(2,1) * BETA(1,1))
          +(OMEGA(2) * THETA(1)**ALPHA(1,2)
          * THETA(2)**ALPHA(2,2) * BETA(1,2))
          +(OMEGA(3) * THETA(1)**ALPHA(1,3)
          * THETA(2)**ALPHA(2,3) * BETA(1,3))
F(1) = 1.0 - F(1)
F(2) = -(OMEGA(1) * THETA(1)**ALPHA(1,1)
          * THETA(2)**ALPHA(2,1) * BETA(2,1))
          -(OMEGA(2) * THETA(1)**ALPHA(1,2)
          * THETA(2)**ALPHA(2,2) * BETA(2,2))
          -(OMEGA(3) * THETA(1)**ALPHA(1,3)
          * THETA(2)**ALPHA(2,3) * BETA(2,3))

```

```

PF(1,1) = ALPHA(1,1)*X(1)*BETA(1,1)
          + ALPHA(1,2)*X(2)*BETA(1,2)
          + ALPHA(1,3)*X(3)*BETA(1,3)
PF(1,2) = ALPHA(2,1)*X(1)*BETA(1,1)
          + ALPHA(2,2)*X(2)*BETA(1,2)
          + ALPHA(2,3)*X(3)*BETA(1,3)
PF(2,1) = ALPHA(1,1)*X(1)*BETA(2,1)
          + ALPHA(1,2)*X(2)*BETA(2,2)
          + ALPHA(1,3)*X(3)*BETA(2,3)
PF(2,2) = ALPHA(2,1)*X(1)*BETA(2,1)
          + ALPHA(2,2)*X(2)*BETA(2,2)
          + ALPHA(2,3)*X(3)*BETA(2,3)
(*Sub-program to solve for ln(DTHETA) goes here)
THETA(1) = EXP(ln(THETA(1) + LNDTHETA(1)))
THETA(2) = EXP(ln(THETA(2) + LNDTHETA(2)))
Z(2) = THETA(2)
Z(1) = THETA(1)/Z(2)**R(2)
X(1)  = OMEGA(1) * Z(1)**ALPHA(1,1) *
          Z(2)**ALPHA(2,1)
X(2)  = OMEGA(2) * Z(1)**ALPHA(1,2) *
          Z(2)**ALPHA(2,2)
X(3)  = OMEGA(3) * Z(1)**ALPHA(1,3) *
          Z(2)**ALPHA(2,3)
IF LNDTHETA > ERROR go to 100
TN = TOTAL Ca/(A(1,1)*X(1) + A(1,2)*X(2) +
          A(1,3)*X(3))
(Ca2+) = X(1) * TN
(CaSO40) = X(3) * TN
(SO42-) = TOTAL SO4 - (CaSO40)
PRINT RESULTS
STOP

```

Because of the tendency for exponent underflow or overflow on some systems during the calculation of OMEGA, the free-energy data may have to be adjusted in order to calculate equilibrium (Smith and Missen, 1982).

6.0 COMPARISON OF METHODS

The fact that there are several common methods for calculating speciation is a result of the specific advantages and disadvantages offered by each method. These include such characteristics as ease of programing, rate of convergence to a solution efficiency of the method, and frequency of convergence.

The rate of convergence is qualitatively defined by the "order of convergence":

$$\lim_{k \rightarrow \infty} \frac{|e_{(k+1)}|}{|e_{(k)}|^p} = \text{CONSTANT} > 0 \quad (15)$$

where k = iteration number
 $|e|$ = absolute value of (calculated concentration of a species) - (actual concentration at equilibrium)
 p = order of convergence

The methods discussed in this paper have p of approximately 1, except $p = 2$ for the Newton-Raphson Method. An example will clarify this importance. If the constant in Equation 15 is assumed to be 0.1 and $|e_{(k)}| = 0.01$, then the error at the next iteration has the approximate value of 0.001 and 0.00001 for $p = 1$ and $p = 2$, respectively. Although the order of convergence suggests the Newton-Raphson Method is preferable, the more important characteristic of "efficiency" indicates preferences are condition on the number of species. Efficiency is a evaluation of the number of iterations required to reach equilibrium relative to the number of calculations performed during each iteration. Inspection of Algorithms 12 and 1 or 2 indicates the Continuous-Fraction Method is more efficient than the Newton-Raphson Method for the system of Ca^{2+} , SO_4^{2-} , and CaSO_4^0 . For larger systems, the Newton-Raphson Method becomes more efficient. The Free-Energy Methods are apparently less efficient in most cases.

The point at which two methods have equal efficiencies depends on such factors as the ratio of total species to master species, the total number of species, the number and ratios of polymolecular complexes (more than one cation and anion). In general, the Newton-Raphson Method probably becomes most efficient when total species surpass 40 - 150 in number.

Under certain input conditions, the methods fail to converge to solution. The predominant cause of non-convergence may often be related to the choice of masters species to represent each element. Often a satisfactory master species is the free ion such as Ca^{2+} for calcium as long as it is one of the dominant species of an element in concentration. However, for pH dependent species the best master species depends on solution pH. In very low pH water, H_2CO_3^0 for carbonate and HSO_4^- for sulfate are best master species. Unfortunately, master species are currently chosen before programming and

cannot be changed during execution (this option is not formidable, but has apparently not yet been implemented). Programmers thus commonly choose master species based on common near-neutral pH's. Consequently, attempts at speciation of water such as acid drainage with low pH and high dissolved solids are not always successful. Techniques to minimize non-convergence with pre-determined master species exist (for example, Parkhurst *et al.*, 1980; Peterson *et al.*, 1986). Morin (1985) further addresses this topic. In general, the Continuous-Fraction appears to be more stable than the Newton-Raphson Method which requires "good guesses" to the final solution to ensure convergence.

7. CONCLUSION

This paper has examined the common methods for calculating aqueous speciation at chemical equilibrium. Specifically, simplified algorithms were used to demonstrate the Continuous-Fraction, Newton-Raphson, and Free-Energy-Minimization Methods, which belong to different groups of methods based on programming approaches.

The methods were compared on the basis of their efficiencies, which is an evaluation of the number of calculations performed during each iteration relative to the number of iterations required to reach equilibrium. From this perspective, the Continuous-Fraction Method is the most efficient method for programs containing fewer species (<40 - 150) and the Newton-Raphson Method is the most efficient for larger programs.

The methods occasionally display non-convergence which is related, at least in part, to the choice of master species and the input of less common types of analytical data.

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