

Carbonate Reactions

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Chapter 1

Carbonate Equilibria with Bionapl

For the inclusion of carbonate equilibria a few assumptions had to be made:

- The variable to be determined is the pH
- The input variable is the concentration of CO_2 (can also be $[Ca^{2+}]$, $[Na^+]$, $[SO_4^{2-}]$)
- All species are in solution
- There is no precipitation or dissolution
- All activities are equal to 1

These assumptions simplify the problem greatly, but maybe are too simplified for the simulation of all data from Borden,

1.1 Mass action equations

All units are defined as moles per litre, except the equilibrium constants, that are adimensional, The mass action equations used are:

CO_2 to H_2CO_3 :



H_2CO_3 to HCO_3^- :



HCO_3^- to CO_3^{2-} :



$CaCO_3$ to Ca^{2+} :



$CaSO_4$ to Ca^{2+} and SO_4^{2-} :



Water dissociation:



1.2 Charge balance equation

The charge balance equation for a system in equilibrium with CO_2 is equal to

$$2[Ca^{2+}] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [SO_4^{2-}] + [OH^-] \tag{1.7}$$

1.2.1 Na^+ Inclusion

Equation (1.7) can be modified to include the concentration of Na^+ from the dissociation of persulfate:

$$2[Ca^{2+}] + [H^+] + 2[Na^+] = 2[CO_3^{2-}] + [HCO_3^-] + 2[SO_4^{2-}] + [OH^-] \tag{1.8}$$

1.3 Species to be Transported by Bionapl

The species that need to be transported by Bionapl are the ones that are *inputs* to the geochemistry package, The species concentrations that are generated *from* the geochemistry packge don't need to be transported, as they're going to be overwritten by the next iteration step,

For example, in a system where $[CO_2]$ and $[Ca^{2+}]$ are input parameters, only these two should be transported, All other species (HCO_3^- , CO_3^{2-}) are calculated from the equilibrium reactions and have no relation to the concentrations from the previous step or adjacent elements,

Chapter 2

Concentrations of Species in Solution

2.1 Species Concentrations in function of CO_2

The approach used is to find the pH in function of the input concentration of CO_2 , The equations from (1.1) to (1.6) are substituted in each other, so they can be functions of the known CO_2 concentration and $[H^+]$:

$$[HCO_3^-] = \frac{k_1[H_2CO_3]}{[H^+]} \quad (2.1)$$

and substituting (1.1) into (2.1) the expression for $[HCO_3^-]$ in function of $[CO_2]$ is:

$$[HCO_3^-] = \frac{k_h k_1 [CO_2]}{[H^+]} \quad (2.2)$$

All other equations can be substituted in the same fashion, The equation for $[CO_3^{2-}]$ concentration in function of $[CO_2]$ concentration is

$$[CO_3^{2-}] = \frac{k_2[HCO_3^-]}{[H^+]} = \frac{k_2 k_1 k_h [CO_2]}{[H^+]^2} \quad (2.3)$$

where $[HCO_3^-]$ was replaced by (2.2), The same approach is used for the calcite equation:

$$[Ca^{2+}] = \frac{k_a}{[CO_3^{2-}]} = \frac{k_a [H^+]^2}{k_2 k_1 k_h [CO_2]} \quad (2.4)$$

The water dissociation can be written as

$$[OH^-] = \frac{k_w}{[H^+]} \quad (2.5)$$

The sulfate and sodium cases are more complicated as they're generated outside the geochemistry package, and is considered only as a input parameter,

2.2 Substitution in the Charge Balance Equation

Considering that the Ca^{2+} concentration will be found from the input CO_2 concentration too, the equations from section (2.1) can be substituted in the charge balance equation (1.7):

$$\frac{k_a [H^+]^2}{k_2 k_1 k_h [CO_2]} + [H^+] = 2 \frac{k_2 k_1 k_h [CO_2]}{[H^+]^2} + \frac{k_h k_1 [CO_2]}{H^+} + 2[SO_4^{2-}] + \frac{k_w}{[H^+]} \quad (2.6)$$

2.2.1 Na^+ Input Concentration

A similar expression can be obtained for equation (1.8):

$$\frac{k_a [H^+]^2}{k_2 k_1 k_h [CO_2]} + [H^+] + 2[Na^+] = 2 \frac{k_2 k_1 k_h [CO_2]}{[H^+]^2} + \frac{k_h k_1 [CO_2]}{H^+} + 2[SO_4^{2-}] + \frac{k_w}{[H^+]} \quad (2.7)$$

2.3 Definition of the Polynomial Equation for $[H^+]$

In (2.7) the concentrations of $[Na^+]$ is considered to be fixed and given as input, The same is valid for $[SO_4^{2-}]$ in both (2.6) and (2.7), Multiplying equation (2.6) by $[H^+]^2$ and rearranging the terms so the polynomial equation is monic¹, the following systems are found,

2.3.1 System with only Carbonates

For the system with only carbonates there is no concentrations of $[Ca^{2+}]$, $[SO_4^{2-}]$ or $[Na^+]$, The equation to be solved for H^+ in function of $[CO_2]$ is equal to

$$[H^3] - (k_1 k_h [CO_2] + k_w) [H^+] - 2k_2 k_1 k_h [CO_2] = 0 \quad (2.8)$$

2.3.2 System with $[Ca^{2+}]$

The charge equation (2.6) for $[H^+]$ in function of $[CO_2]$ is equal to

$$\begin{aligned} [H^+]^4 + \frac{k_1 k_2 k_h [CO_2]}{2k_a} [H^+]^3 - \frac{k_1 k_2 k_h [CO_2]}{k_a} [SO_4^{2-}] [H^+]^2 - \\ - \left(\frac{k_1 k_2 k_h [CO_2]}{2k_a} \right) (k_h k_1 [CO_2] + k_w) [H^+] - \frac{(k_1 k_2 k_h [CO_2])^2}{k_a} = 0 \end{aligned} \quad (2.9)$$

2.3.3 System with $[Ca^{2+}]$ and $[Na^+]$

For the system with $[Na^+]$ the equation for $[H^+]$ is slightly changed:

$$\begin{aligned} [H^+]^4 + \frac{k_1 k_2 k_h [CO_2]}{2k_a} [H^+]^3 + \left(\frac{k_1 k_2 k_h [CO_2]}{2k_a} ([Na^+] - 2[SO_4^{2-}]) \right) [H^+]^2 - \\ - \left(\frac{k_1 k_2 k_h [CO_2]}{2k_a} \right) (k_h k_1 [CO_2] + k_w) [H^+] - \frac{(k_1 k_2 k_h [CO_2])^2}{k_a} = 0 \end{aligned} \quad (2.10)$$

2.4 Solving the Polynomial equations for $[H^+]$

The equations (2.8), (2.9) and (2.10) are polynomial equations in function of $[H^+]$ and can be solved by graphical or numerical methods, *Finding the solution* for a polynomial equation is also called finding the *roots*, The roots found can be less than zero, so a physical constraint is needed to check if the root is correct for the problem, The physical constraint in this case is that the value of pH cannot be lower than zero or higher than 14, so if a root is found for the concentration of $[H^+]$ that gives the pH outside this interval, it must be discarded, Remembering that the pH is found in function of $[H^+]$ as

$$pH = -\log_{10}([H^+]) \quad (2.11)$$

Two methods are implemented in bionapl-fpc: the Newton method (sometimes called Newton-Raphson method) and the companion matrix method, There are plenty of references for the Newton method, so the companion matrix method will be described,

2.4.1 Companion Matrix Method

Every monic polynomial

$$p(x) = c_0 + c_1 x + c_2 x^2 + c_3 x^3 + \dots + c_{n-1} x^{n-1} + c_n x^n \quad (2.12)$$

¹A *monic* polynomial equation has the coefficient for the highest order term equal to 1, The monic form is required to find the roots of the polynomial equation by the method of the companion matrix, See section (2.4.1),

has a *companion matrix*, defined as

$$C(p) = \begin{bmatrix} 0 & 0 & \dots & 0 & -c_0 \\ 1 & 0 & \dots & 0 & -c_1 \\ 0 & 1 & \dots & 0 & -c_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & 1 & -c_{n-1} \end{bmatrix} \quad (2.13)$$

As this matrix has the characteristic polynomials properties, the eigenvalues are the roots of the equation, so finding the eigenvalues of the matrix C is equivalent to finding the roots of the polynomial equation p ,

We apply this principle to the equation in function of $[H^+]$ to find the roots, using the eigenvalue solver from the package LAPACK, The use of the companion matrix is also the reason why the charge balance equation must be rearranged to a monic form,

2.5 Calculating the Concentrations of all Species

After the $[H^+]$ is found, with the initial $[CO_2]$ all the concentrations for all the species can be found recalculating from the mass action equations (1.4) to (1.1), It should be noted that if the concentration of a species was used as input ($[Ca^{2+}]$ or $[Na^+]$, for example) they *cannot* be recalculated using the mass action equations,

Chapter 3

Examples

3.1 Carbonate System

Varying the initial concentration of $[CO_2]$ the concentration of the other species and the pH can be calculated, The carbonate code was validated against table (3.1):

pCO_2 atm	pH	$[CO_2]$ mol/l	$[H_2CO_3]$ mol/l	$[HCO_3^-]$ mol/l	$[CO_3^{2-}]$ mol/l
1,00E-08	7	3,36E-10	5,71E-13	1,42E-9	7,90E-13
1,00E-07	6,94	3,36E-9	5,71E-12	5,90E-9	1,90E-12
1,00E-06	6,81	3,36E-8	5,71E-11	9,16E-8	3,30E-11
1,00E-05	6,42	3,36E-7	5,71E-10	3,78E-7	4,53E-11
1,00E-04	5,92	3,36E-6	5,71E-9	1,19E-6	5,57E-11
3,50E-04	5,65	1,18E-5	2,00E-8	2,23E-6	5,60E-11
1,00E-03	5,42	3,36E-5	5,71E-8	3,78E-6	5,61E-11
1,00E-02	4,92	3,36E-4	5,71E-7	1,19E-5	5,61E-11
1,00E-01	4,42	3,36E-3	5,71E-6	3,78E-5	5,61E-11
1,00E+02	3,92	3,36E-2	5,71E-5	1,20E-4	5,61E-11
2,50E+00	3,72	8,40E-2	1,43E-4	1,89E-4	5,61E-11

Table 3.1: Parameters for carbonate system, From http://en.wikipedia.org/wiki/Carbonic_acid

The program carbonate.f was able to reproduce this table with both the companion matrix method and the Newton method.

3.2 Carbonate Equilibrium with Calcium

Including $[Ca^{2+}]$, the pH and the $[CO_2]$ concentrations are described in table (3.2):

pCO_2 atm at 25C	pH	$[Ca^{2+}]$ mol/l
1,00E-12	12	5,19E-3
1,00E-10	11,3	1,12E-3
1,00E-08	10,7	2,55E-4
1,00E-06	9,83	1,20E-4
1,00E-04	8,62	3,16E-4
3,50E-04	8,27	4,70E-4
1,00E-03	7,96	6,62E-4
1,00E-02	7,3	1,42E-3
1,00E-01	6,63	3,05E-3
1,00E+00	5,96	6,58E-3
1,00E+01	5,3	1,42E-2

Table 3.2: Parameters for carbonate system, From http://en.wikipedia.org/wiki/Calcium_carbonate