

Supplementary Materials

Alkalinity Release from Particle-Containing Oil-in-Water Emulsions and Particle Suspensions

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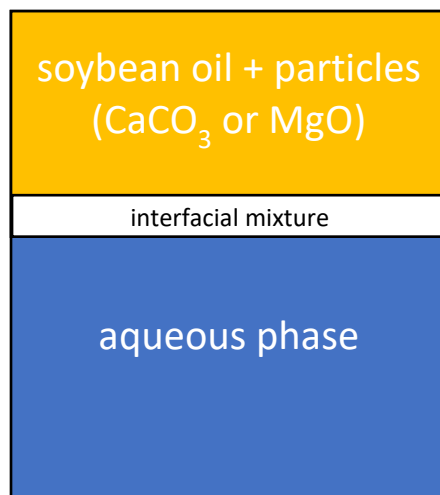


Figure S1. Phases present in the experiments described in Section 3.1.

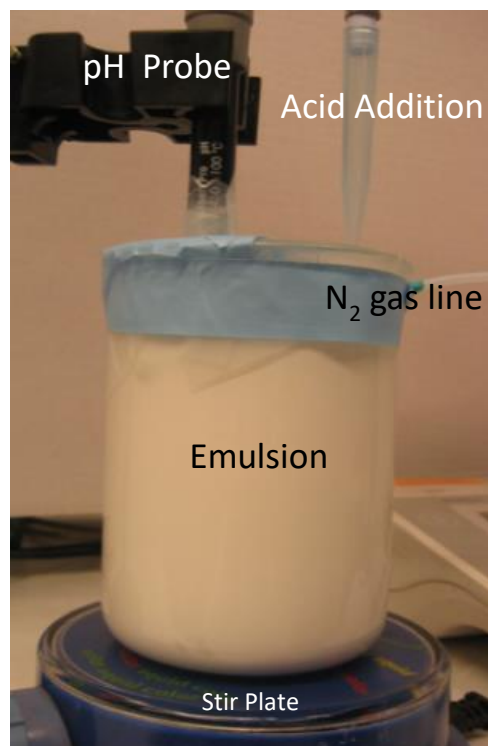


Figure S2. Experimental setup for non-destructive sampling of emulsions and particle suspensions described in Sections 3.3 and 3.4.

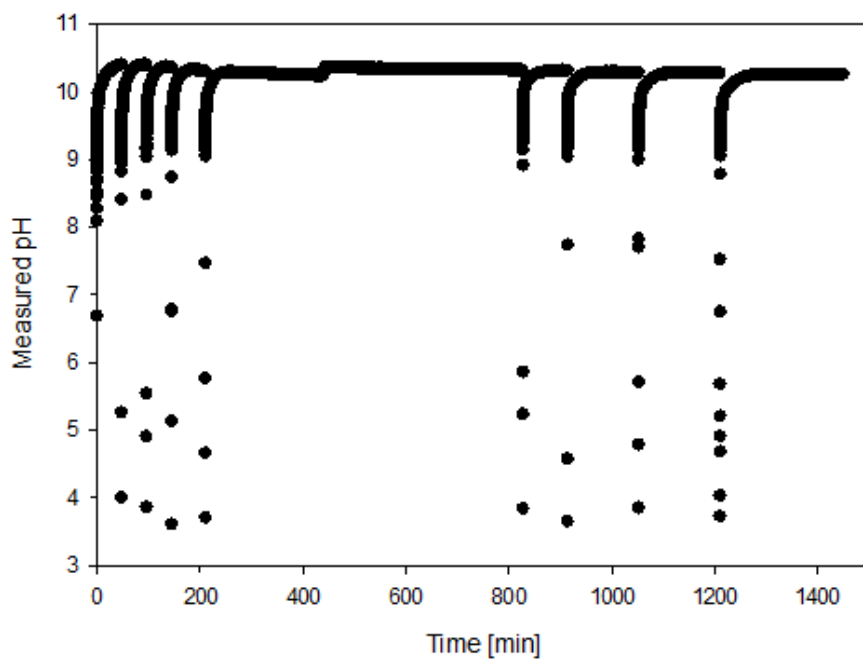


Figure S3. pH data related to the release of alkalinity in response to repeated additions of HCl to an aqueous suspension of 0.04% wt. MgO particles.

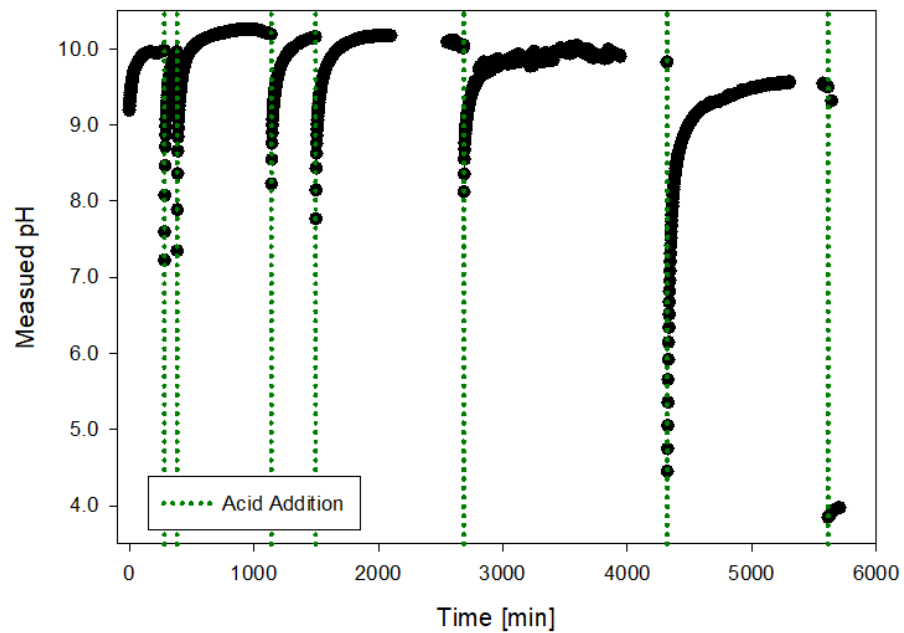


Figure S4. pH data related to the alkalinity release from an oil-in-water emulsion containing 0.04% wt. MgO particles.

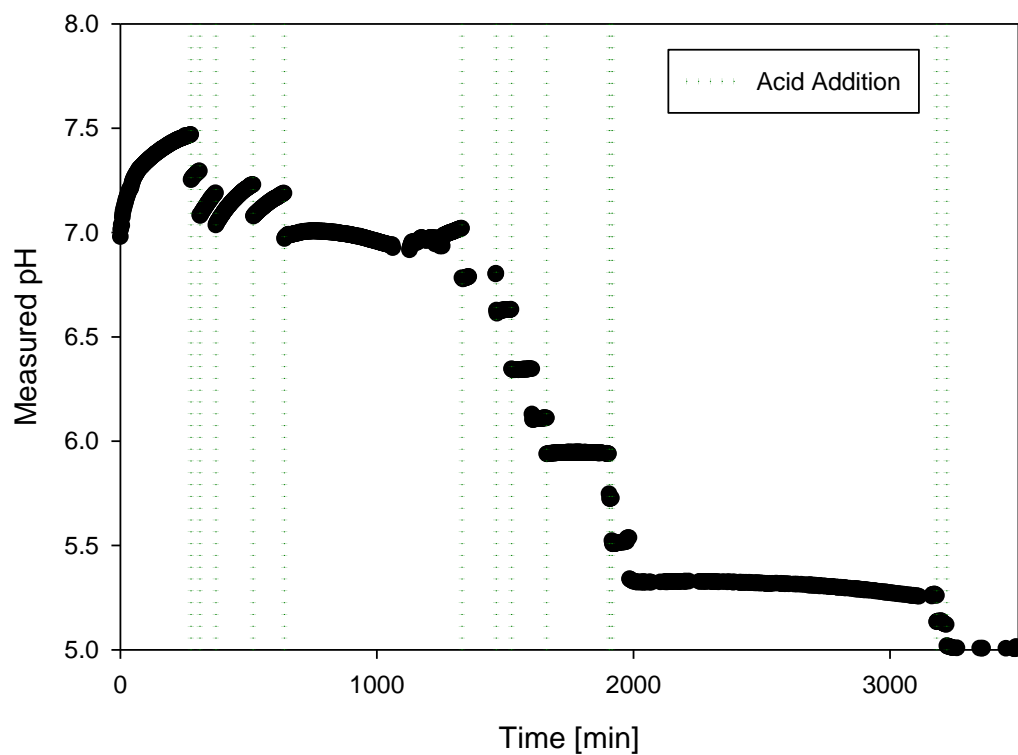


Figure S5. pH data related to the alkalinity release from an oil-in-water emulsion containing 0.02% wt. CaCO_3 particles.

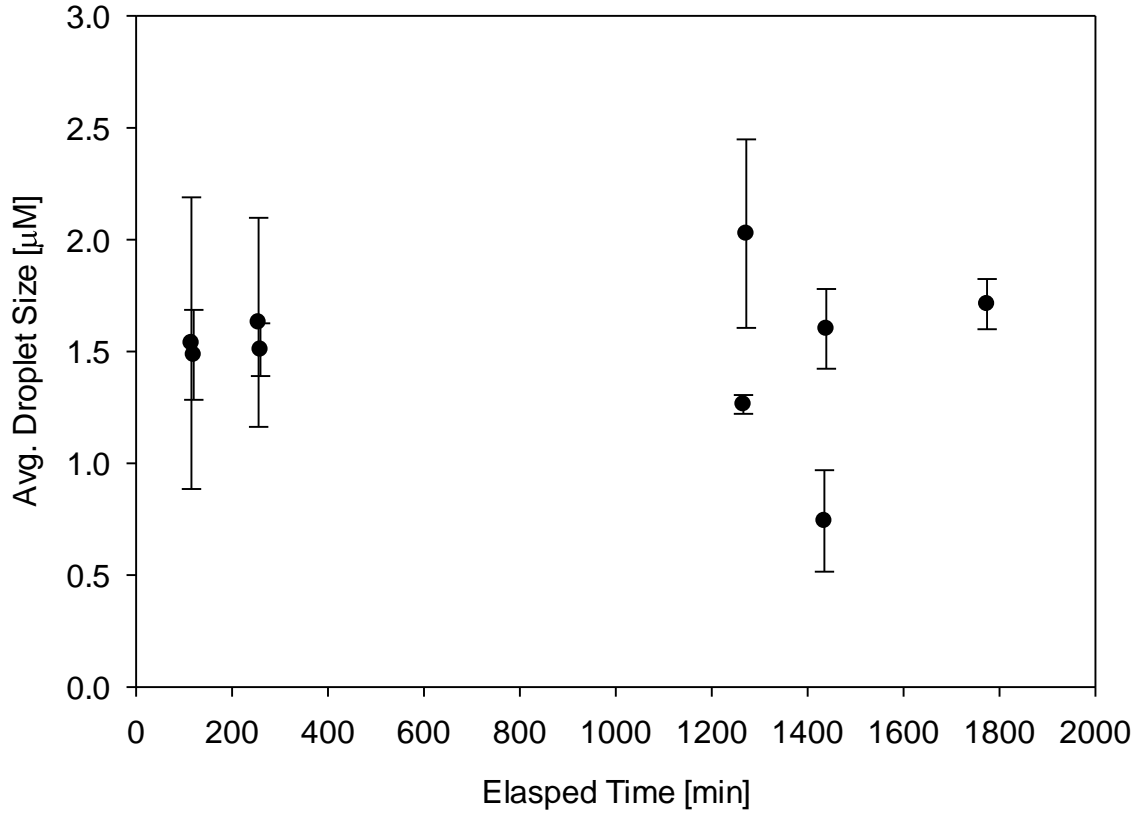


Figure S6. Illustrative data showing emulsion droplet sizes through the alkalinity release process.

Fractionation Calculation

The fraction of mass located in the oil phase (ω_{oil}), aqueous phase (ω_{aq}), and interfacial mixture (ω_{im}) were determined using Equations S-1 through S-3.

$$\omega_{oil} = \frac{C_{oil}V_{oil}}{C_{oil}V_{oil} + C_{aq}V_{aq} + C_{im}V_{im}} \quad (S1)$$

$$\omega_{aq} = \frac{C_{aq}V_{aq}}{C_{oil}V_{oil} + C_{aq}V_{aq} + C_{im}V_{im}} \quad (S2)$$

$$\omega_{im} = \frac{C_{im}V_{im}}{C_{oil}V_{oil} + C_{aq}V_{aq} + C_{im}V_{im}} \quad (S3)$$

Where, C_{oil} , C_{aq} and C_{im} are the mass concentrations of magnesium in the oil phase, aqueous phase, and interfacial mixture, respectively. Concentrations were determined via ICP-OES as described in Section 2.5 in the manuscript. Volumes of the oil phase (V_{oil}), aqueous phase (V_{aq}), and interfacial mixture (V_{im}) were determined using 10 mL graduated, conical bottom centrifuge tubes having 0.1 mL gradations.

Buffer Capacity Calculation

The total buffering capacity was calculated based on amount of acid added required to reach the operationally defined pH endpoint of 4.2 during the titration experiment. The total amount of acid added

was recorded and provides the total mols of H^+ needed to neutralize the solution. That is, the buffering capacity = $\sum V_{HCl} * C_{HCl} = \text{mols } H^+ \text{ or equivalents}$. Equivalents can be converted to alkalinity in terms of $\text{mg-CaCO}_3 \cdot L^{-1}$ by dividing the equivalents by the volume of the reactor and multiplying by the equivalent weight of CaCO_3 ($50 \text{ mg-CaCO}_3 \cdot \text{meq}^{-1}$). For more information on buffer capacity, titrations, and the associated calculations the interested reader is referred to textbooks on water chemistry. The alkalinity utilization percentage was then computed by dividing the experimentally determined buffering capacity by the theoretical amount of alkalinity each emulsion should be able to supply. Here, we assume that the alkalinity-releasing particles are the sole source of the buffering capacity and thus percentage of particle mass utilized may serve as a marker for the extent of alkalinity release.

Modeling Approach

Kinetic descriptions of alkalinity release are provided by the mineral dissolution and linear driving force models as described in the manuscript. Simulations were conducted in Matlab R2014a (MathWorks, Natick, MA USA) with equilibrium solution chemistry provided from PHREEQC via the approach described in Figure S7. The mineral dissolution model had no fitting parameters. The linear driving force model was fit to the pH data by adjusting the lumped mass transfer coefficient, k_L , and solubility product, $K_{sp, MgO}$. Fits were obtained by minimizing the sum squared errors via the `fmincon` function in Matlab. The overall modeling approach is described in Figure S8. Notes related to both Figures S7 and S8 are provided in Table S1.

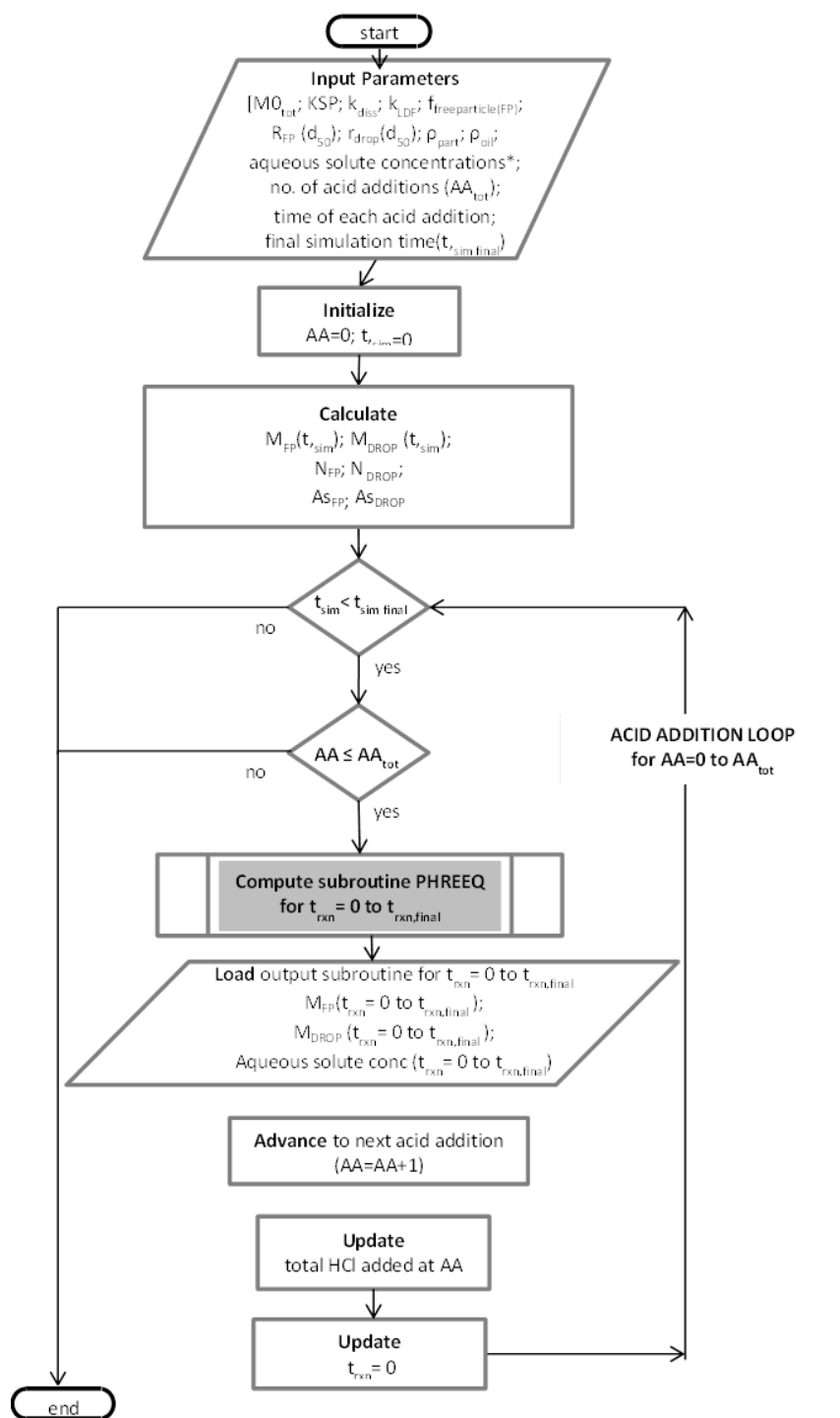


Figure S7. Equilibrium chemistry via PHREEQC. See Table S1 for notes and definitions.

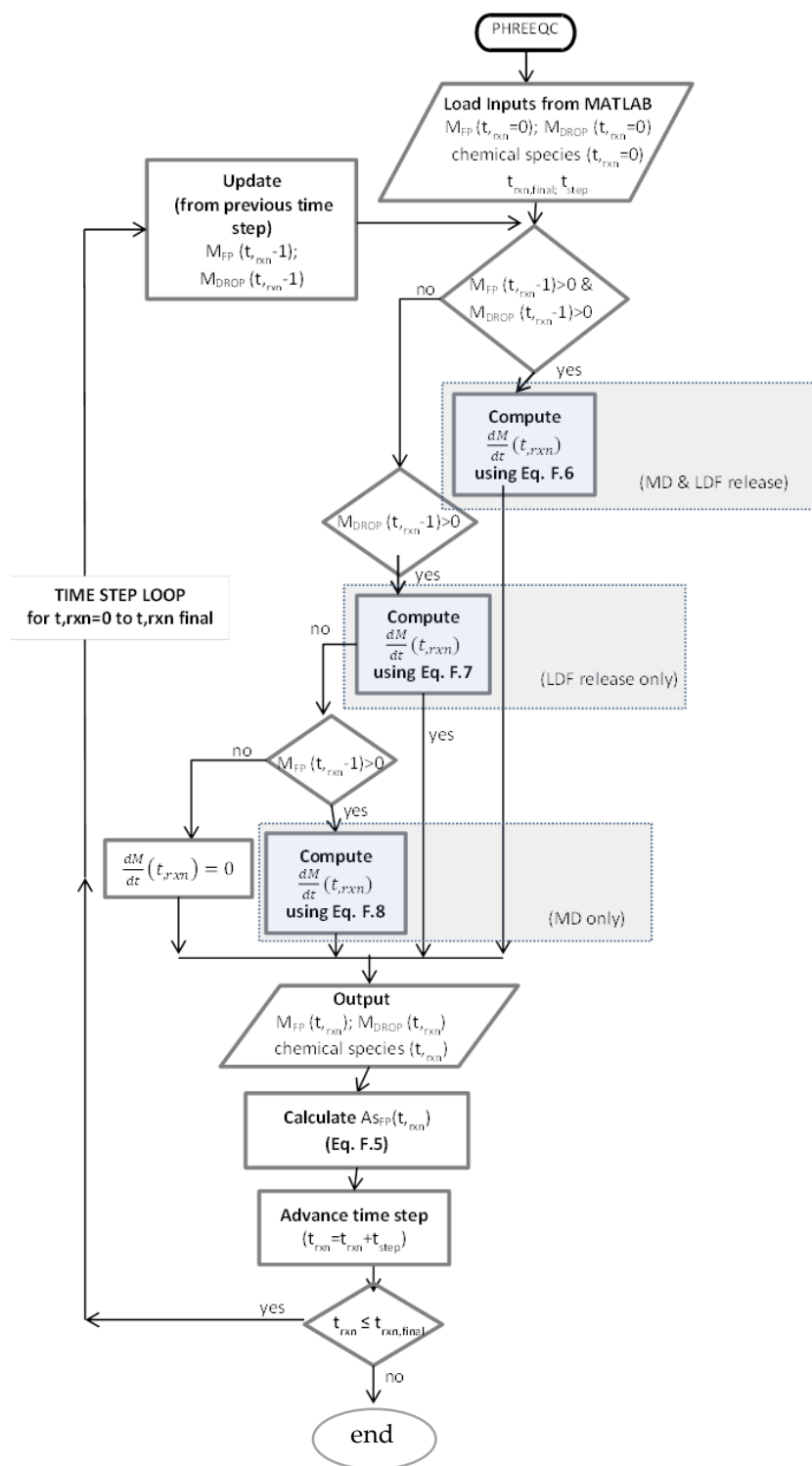


Figure S8. Overall modeling approach. Model types shown in grey boxes: Mineral Dissolution (MD); Linear Driving Force (LDF). See Table S1 for notes and definitions.

Table S1. Notes for Figures S7 and S8.

Symbols Referenced in Flow Chart	
M_{FP} =mass of free particles f_{FP} = fraction of total input particle mass present as free particles $M_{0,tot}$ =input particle mass M_{drop} =mass of particles encapsulated within droplets f_{drop} = fraction of total input particle mass encapsulated within droplets r_{FP} = radius of free particles (d_{50}) r_{drop} = radius of droplets (d_{50}) N_{FP} =total number of free particles N_{drop} =total number of droplets k_{diss} = mineral dissolution rate constant $A_{s,FP}$ =total surface area of free particles $A_{s,drop}$ =total surface area of droplets k_{LDF} =interphase mass transfer coefficient C^* =equilibrium ion concentration (e.g., $[Mg^{2+}]$ equilibrium magnesium ion concentration) $\{C\}$ = ion activity	
Equations Referenced in Flow Chart	
Note: chemical equations F.7-F.9 have been shown release from magnesium particles to provide a more complete illustration of the interconnectedness of the release expressions through chemical species when both LDF and MD models are considered. Equations F.7-F.9 can be written to describe release from calcium carbonate particles.	
$M_{FP} = f_{FP} M_{0,tot}$	(F.1)
$M_{drop} = (1 - f_{FP}) M_{0,tot}$	(F.2)
$N_{FP} = \frac{\frac{M_{FP}}{\rho_{FP}}}{\frac{4}{3}\pi(r_{FP})^3}$	(F.3)
$N_{drop} = \frac{V_{DP,tot}}{\frac{4}{3}\pi(r_{drop})^3}$	(F.4)
$A_{s,FP}(t) = N_{FP} 6^{4/3} \pi^{1/3} \left(\frac{M_{FP}(t)}{\rho_{FP}} \right)^{2/3} = N_{FP} \cdot 4\pi(r_{FP}(t))^2$	(F.5)
$A_{s,drop} = N_{drop} \cdot 4\pi(r_{drop})^2$	(F.6)
$\frac{dC_{Mg^{2+}}}{dt} = -k_{diss} A_{s,FP}(t) \{H^+\}^{0.397} \left(1 - \left(\frac{\{Mg^{2+}\} \{OH^-\}^2}{K_{sp}} \right)^2 \right) + \dots$	(F.7)
$\dots k_{LDF} A_{s,drop} ([Mg^{2+}] - [Mg^{2+}])$	(F.8)
$\frac{dC_{Mg^{2+}}}{dt} = [-k_{diss} A_{s,FP}(t) \{H^+\}^{0.397} \left(1 - \left(\frac{\{Mg^{2+}\} \{OH^-\}^2}{K_{sp}} \right)^2 \right) + k_{LDF} A_{s,drop} ([Mg^{2+}] - [Mg^{2+}])]$	(F.9)