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A Mathematical Model of a Chemical Reaction Mechanism for Self-healing Cement

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Abstract

Cement structures play an integral role in modern day society but can suffer from many ailments. These ailments usually start as cracks in the cement. Research has been done to create a type of cement that will heal itself with the aid of Aspergillusnidulans fungi. The goal of this project is to use the data gathered from this research and create a mathematical model. Using concepts from physical chemistry and different equations this model will serve as a standard for this research.

1. Introduction

This is a project that utilizes chemistry and mathematics. The motivation of this project stems from a self healing cement experiment. We will first give a brief synopsis about the self healing cement experiment. Self-Healing Cement is a type of cement that heals without the aid of a maintenance team. In this experiment, the cement uses aspergillusnidulans fungi as a healing factor. The relative humidity of cement specimens was then plotted with respect to time. The mathematical part picks up from this point. Using the data points collected from a self healing cement experiment, we will create a mathematical model that will serve as a standard for a self healing cement project.

2. Definitions

There are a few definitions that need to be known before this project can be fully under-stood. The first is an elementary reaction. An **elementary reaction** shows how each molecule reacts to form the overall chemical reaction. This leads us to our next definition. A **chemical reaction mechanism** is the step by step sequence of elementary reactions by which overall chemical occurs. This is an important part of this project because we will convert these mechanisms into differential equations. The next definition is the rate law. The **rate law** is an equation that links the reaction rate with concentrations or pressures of reactants and constant parameters. The rate law is important because without it, we would not be able to create our model. For a generic chemical reaction aA + b$B \rightarrow C$, the rate law is r = k[A][B] where k is the rate constant and [A] , [B] are the concentrations of A and B in mol/L.

3. Creating a Reaction Mechanism that Yields a Differential Equation

In this section, we will see how a chemical reaction mechanism yields a differential equation. Consider the following set of elementary equations:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

This equation is equivalent to the following two equations: $A \overset{k_1}{\rightarrow} B$ and $B \overset{k_2}{\rightarrow} A$. We will use these two equations to get a set of differential equations. We would like to get a differential equation for each chemical in this equation. Let's begin with A. The chemical A is seen in each elementary equation so will have to use both.

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Chemical A is being consumed at a rate of k_1 and B is being created at a rate of k_2. This means A will have a negative rate while B will have a positive rate. So we now can create our first differential equation:

$$\frac{d[A]}{dt} = -k_1 [A] + k_2[B]$$

We must now construct our differential equation for B. Looking at our elementary equations once again, we see that B is being consumed at a rate of k_2 and A is being created at a rate of k_1 . This means B will have a negative rate while A will have a positive rate. We can now create our second differential equation.

$$\frac{d[B]}{dt} = k_1 [A] - k_2[B]$$

So, from our elementary equations we get the following system of equations:

$$\frac{d[A]}{dt} = -k_1 [A] + k_2[B]$$
$$\frac{d[B]}{dt} = k_1 [A] - k_2[B]$$

This will be the format for finding the differential equations for our chemical reaction mechanism.

4. Examples

In this section, we will give an example of how to find the differential equations from an actual chemical reaction. Consider the following chemical reaction mechanism:

Complex Reaction: $2N_2O_5 \rightarrow 4NO_2 + O_2$

Elementary Step 1: $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

Elementary Step 2: $NO_2 + NO_3 \overset{k_2}{\rightarrow} NO + NO_2 + O_2$

Elementary Step 3: $NO + NO_3 \overset{k_3}{\rightarrow} 2NO_2$

Using the same method discussed earlier, we get the following differential equations:

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3]$$
$$\frac{d[NO_2]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] + 2k_3[NO][NO_3]$$
$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - (k_{-1} + k_2)[NO_2][NO_3] + 2k_3[NO][NO_3]$$
$$\frac{d[O_2]}{dt} = k_2[NO_2][NO_3]$$

We will now find an expression for $\frac{d[NO_2]}{dt}$ with the help of the steady state approximation and some algebra. The chemical NO_3 is not present in the final product of our complex reaction. This means it reacts so fast that we can set its derivative equal to zero. In other words, we have applied the steady state approximation to NO_3.

Apply the Steady State Approximation to NO_3:

$$\frac{d[NO_3]}{dt} \overset{SSA}{\approx} 0$$
$$[NO_3] \overset{SSA}{\approx} \frac{k_1[N_2O_5]}{(k_{-1} + k_2)[NO_2] + k_3[NO]}$$

Substituting $\frac{d[NO_2]}{dt}$ into the equation we now have:

$$\frac{d[NO_2]}{dt} \overset{SSA}{\approx} k_1[N_2O_5]\{1 - \frac{k_1[NO_2] - 2k_3[NO]}{(k_{-1} + k_2)[NO_2] + k_3[NO]}\}$$
$$\frac{d[NO_2]}{dt} \overset{SSA}{\approx} k_1[N_2O_5]\{\frac{k_2[NO_2] - 3k_3[NO]}{(k_{-1} + k_2)[NO_2] + k_3[NO]}\}$$

If we look at our complex reaction again, we will see that the chemical NO is not present in the final solution. This means that we can apply the steady state approximation just as we did with NO_3.

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] \overset{SSA}{\approx} 0$$
$$[NO] \overset{SSA}{\approx} \frac{k_2}{k_3}[NO_2]$$

so

$\frac{d[NO_2]}{dt} \overset{SSA}{\approx} k_1[N_2O_5]\{\frac{k_2[NO_2]+3k_2[NO_2]}{(k_{-1}+k_2)[NO_2]}\}+$

this implies that our solution is:

$$\frac{d[NO_2]}{dt} \overset{SSA}{\approx} \frac{4k_1k_2}{k_{-1} + 2k_2}[N_2O_5]$$

5. My Chemical Reaction

This brings us to the chemical reaction that is at the focus of this project. This mechanism has many chemicals, so keep in mind the methods discussed on how to find differential equations from chemical reaction mechanisms.

$$Ca_3SiO_5 + Ca_2SiO_4 + Ca_3Al_2O_6 + 2(Ca_2AlFeO_5) + nH_2O \rightarrow$$
$$Ca_6Al_2(SO_4)_3(OH)_{12..}26H2O).H_2O + H_2CaO_4Si + 3Ca(OH)_2$$

Elementary Step 1: $Ca_3Al_2O_6 + SO_4 \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12..}26H_2O$
Elementary Step 2: $(Ca_3SiO_5)_2 + (H_2O)_7 \rightarrow H_2CaO_4Si + Ca_3(OH)_6$
Elementary Step 3: $Ca_4Al_2Fe_2O_{10} + (H_2O)_4 \rightarrow Fe(OH)_3 + Ca(FeO_2)_2$

Now that we have our elementary steps, we can create a differential equation for each element. We will take each elementary step individually and create the differential equations.

Elementary Reaction 1:

$Ca_3Al_2O_6 + SO_4 \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12..}26H_2O$

Using the same method discussed earlier we get the following differential equations:

$$\frac{d[Ca_3Al_2O_6]}{dt} = -k_1[Ca_6Al_2(SO_4)_3(OH)_{12..}26H_2O]$$
$$\frac{d[SO_4]}{dt} = -k_1[Ca_6Al_2(SO_4)_3(OH)_{12..}26H_2O]$$
$$\frac{d[Ca_6Al_2(SO_4)_3(OH)_{12..}26H2O)]}{dt} = k_1[Ca_3Al_2O_6][SO_4]$$

Elementary Reaction 2:

$(Ca_3SiO_5)_2 + (H_2O)_7 \rightarrow H_2CaO_4Si + Ca_3(OH)_6$

Using the same method discussed earlier we get the following differential equations:

$$\frac{d[(Ca_3SiO_5)_2]}{dt} = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$$

$$\frac{d[(H_2O)_7]}{dt} = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$$
$$\frac{d[H_2CaO_4Si]}{dt} = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$$
$$\frac{d[Ca_3(OH)_6]}{dt} = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$$

Elementary Reaction 3:

$Ca_4Al_2Fe_2O_{10} + (H_2O)_4 \rightarrow Fe(OH)_3 + Ca(FeO_2)_2$

Using the same method discussed earlier we get the following differential equations:

$$\frac{d[Ca_4Al_2Fe_2O_{10}]}{dt} = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$$
$$\frac{d[(H_2O)_4]}{dt} = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$$
$$\frac{d[Fe(OH)_3]}{dt} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$$
$$\frac{d[Ca(FeO_2)_2]}{dt} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$$

So now, our system of differential equations is as follows:

$$\frac{d[Ca_3Al_2O_6]}{dt} = -k_1[Ca_6Al_2(SO_4)_3(OH)_{12}.\,.26H_2O)]$$
$$\frac{d[SO_4]}{dt} = -k_1[Ca_6Al_2(SO_4)_3(OH)_{12}.\,.26H_2O)]$$
$$\frac{d[Ca_6Al_2(SO_4)_3(OH)_{12}.\,.26H_2O]}{dt} = k_1[Ca_3Al_2O_6][SO_4]$$

$$\frac{d[(Ca_3SiO_5)_2]}{dt} = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$$
$$\frac{d[(H_2O)_7]}{dt} = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$$
$$\frac{d[H_2CaO_4Si]}{dt} = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$$
$$\frac{d[Ca_3(OH)_6]}{dt} = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$$
$$\frac{d[Ca_4Al_2Fe_2O_{10}]}{dt} = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$$
$$\frac{d[(H_2O)_4]}{dt} = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$$
$$\frac{d[Fe(OH)_3]}{dt} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$$
$$\frac{d[Ca(FeO_2)_2]}{dt} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$$

Now that we have our system of differential equations, we would like to solve it. Before we can solve this, we must prove that there exist a unique solution for a system of equations.

6. Theorem and Proof of the Existence of a Unique solution

We will now state and prove the existence theorem. Consider the system of differential equations with unknown functions$y_1, y_2, \ldots, y_m$

$$y'_1(x) = F_1(x, y_1(x), y_2(x), \dots, y_m(x))$$
$$y'_2(x) = F_2(x, y_1(x), y_2(x), \dots, y_m(x))$$
$$\vdots$$
$$y'_m(x) = F_m(x, y_1(x), y_2(x), \dots, y_m(x))$$

Theorem

Suppose that *F* is continuous and has continuous bounded partial derivatives. Then there is a unique set of functions $(y_1(x), y_2(x), \dots, y_m(x))$ defined in $[x_0 - a, x_0 + a]$ for all

$$x \in [x_0 - a, x_0 + a]$$

Proof

Suppose that *F* is continuous and has continuous bounded partial derivatives.

Define Region

$$R = \{(x, y_{1,} y_{2,} \dots, y_m): x_0 - a \le x \le x_0 + a, -\infty < y_1 < \infty, -\infty < y_2 < \infty \dots -\infty < y_m < \infty\}$$

Let $\Phi_{0,1}(x) = y_{1,0}$; $\Phi_{0,2}(x) = y_{2,0} \dots \Phi_{0,m}(x) = y_{n,m}$

Then $\Phi_{n,1} = y_{1,0} + \int_{x_0}^{x} F_1\left(t, \Phi_{n-1,1}(t), \Phi_{n-1,2}(t)\right) dt$

$$\Phi_{n,2} = y_{2,0} + \int_{x_0}^{x} F_2\left(t, \Phi_{n-1,1}(t), \Phi_{n-1,2}(t)\right) dt$$

$$\vdots$$

$$\Phi_{n,m} = y_{n,m} + \int_{x_0}^{x} F_m\left(t, \Phi_{n-1,1}(t), \Phi_{n-1,2}(t)\right) dt$$

Because we can integrate, we can find a unique solution to this set of differential equations within this region. This is a general proof of the existence of a unique solution. We will now model our system based off of the proof. Beginning with our first differential equation, we will continue until all the equations are done:

Equation 1

$$\frac{d[Ca_3Al_2O_6]}{dt} = -k_1[Ca_6Al_2SO_4)_3(OH)_{12..}26H_2O]$$

$$y'_1(x) = \frac{d[Ca_3Al_2O_6]}{dt}$$

$$F_1 = -k_1[Ca_6Al_2SO_4)_3(OH)_{12..}26H_2O]$$

$$y_3 = Ca_6Al_2SO_4)_3(OH)_{12..}26H_2O$$

Equation 2

$$\frac{d[SO_4]}{dt} = -k_1[Ca_6Al_2(SO_4)_3(OH)_{12..}26H_2O)]$$

$$y'_2(x) = \frac{d[SO_4]}{dt}$$

$$F_2 = -k_1[Ca_6Al_2SO_4)_3(OH)_{12..}26H_2O]$$

$$y_3 = Ca_6Al_2SO_4)_3(OH)_{12..}26H_2O$$

Equation 3

$$\frac{d[Ca_6Al_2(SO_4)_3(OH)_{12..}26H_2O]}{dt} = k_1[Ca_3Al_2O_6][SO_4]$$

$$y'_3(x) = \frac{d[Ca_6Al_2(SO_4)_3(OH)_{12..}26H_2O]}{dt}$$

$$F_3 = k_1[Ca_3Al_2O_6][SO_4]$$

$y_1 = [Ca_3Al_2O_6]$
$y_2 = [SO_4]$

Equation 4

$$\frac{d[(Ca_3SiO_5)_2]}{dt} = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$$
$$y'_4(x) = \frac{d[(Ca_3SiO_5)_2]}{dt}$$
$F_4 = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$
$y_6 = [H_2CaO_4Si]$
$y_7 = [Ca_3(OH)_6]$

Equation 5

$$\frac{d[(H_2O)_7]}{dt} = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$$
$$y'_5(x) = \frac{d[(H_2O)_7]}{dt}$$
$F_5 = -k_2[H_2CaO_4Si][Ca_3(OH)_6]$
$y_6 = [H_2CaO_4Si]$
$y_7 = [Ca_3(OH)_6]$

Equation 6

$$\frac{d[H_2CaO_4Si]}{dt} = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$$
$$y'_6(x) = \frac{d[H_2CaO_4Si]}{dt}$$
$F_6 = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$
$y_4 = (Ca_3SiO_5)_2$
$y_5 = (H_2O)_7$

Equation 7

$$\frac{d[Ca_3(OH)_6]}{dt} = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$$
$$y'_7(x) = \frac{d[Ca_3(OH)_6]}{dt}$$
$F_7 = k_2[(Ca_3SiO_5)_2][(H_2O)_7]$
$y_4 = (Ca_3SiO_5)_2$
$y_5 = (H_2O)_7$

Equation 8

$$\frac{d[Ca_4Al_2Fe_2O_{10}]}{dt} = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$$
$$y'_8(x) = \frac{d[Ca_4Al_2Fe_2O_{10}]}{dt}$$
$F_8 = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$
$y_{10} = Fe(OH)_3$
$y_{11} = Ca(FeO_2)_2$

Equation 9

$$\frac{d[(H_2O)_4]}{dt} = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$$

$y'_9(x) = \frac{d[(H_2O)_4]}{dt}$
$F_9 = -k_3[Fe(OH)_3][Ca(FeO_2)_2]$
$y_{10} = Fe(OH)_3$
$y_{11} = Ca(FeO_2)_2$
Equation 10
$\frac{d[Fe(OH)_3]}{dt} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$
$y'_{10}(x) = \frac{d[Fe(OH)_3]}{dt}$
$F_{10} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$
$y_8 = Ca_4Al_2Fe_2O_{10}$
$y_9 = (H_2O)_4$
Equation 11
$\frac{d[Ca(FeO_2)_2]}{dt} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$
$y'_{11}(x) = \frac{d[Ca(FeO_2)_2]}{dt}$
$F_{11} = k_3[Ca_4Al_2Fe_2O_{10}][(H_2O)_4]$
$y_8 = Ca_4Al_2Fe_2O_{10}$
$y_9 = (H_2O)_4$

So, our system of differential equations is as such:

$y'_1(x) = F_1(y_3)$
$y'_2(x) = F_2(y_3)$
$y'_3(x) = F_3(y_1, y_2)$
$y'_4(x) = F_4(y_6, y_7)$
$y'_5(x) = F_5(y_6, y_7)$
$y'_6(x) = F_6(y_4, y_5)$
$y'_7(x) = F_7(y_4, y_5)$
$y'_8(x) = F_8(y_{10}, y_{11})$
$y'_9(x) = F_9(y_{10}, y_{11})$
$y'_{10}(x) = F_{10}(y_8, y_9)$
$y'_{11}(x) = F_{11}(y_8, y_9)$

As shown in the above equations, we can fit our system of differential equations into the format of the proof. So how does this proof let us know that our system of differential equations has a unique solution? Let's look at the two criteria for the theorem. Firstly, our equations must be continuous. All of our equations are polynomials. Polynomials are continuous so all our equations are continuous. The second states that all the partial derivatives must be continuous and bounded. We will now take the partial derivatives of our system and check whether this is true.

7. Partial Derivatives

As stated in the previous section, we must take the partial derivatives of each equation. They are as follows:

$$\frac{\partial F}{\partial[Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O]} = -k_1$$

$$\frac{\partial F}{\partial [Ca_3Al_2O_6]} = k_1[SO_4]$$
$$\frac{\partial F}{\partial [SO_4]} = k_1[Ca_3Al_2O_6]$$
$$\frac{\partial F}{\partial [H_2CaO_4Si]} = -k_2[Ca_3(OH)_6]$$
$$\frac{\partial F}{\partial [Ca_3(OH)_6]} = -k_2[H_2CaO_4Si]$$
$$\frac{\partial F}{\partial [(Ca_3SiO_5)_2]} = k_2[H_2O]$$
$$\frac{\partial F}{\partial [H_2O]} = k_2[(Ca_3SiO_5)_2]$$
$$\frac{\partial F}{\partial [Fe(OH)_3]} = -k_3[Ca(FeO_2)_2]$$
$$\frac{\partial F}{\partial [Ca_4Al_2Fe_2O_{10}]} = k_3[(H_2O)_4]$$
$$\frac{\partial F}{\partial [(H_2O)_4]} = k_3[Ca_4Al_2Fe_2O_{10}]$$

So now we have our partial derivatives. Each partial derivative is a polynomial so we know it is continuous. We define these partial derivatives on a finite region which means they are bounded by that region. With the criteria of the theorem met, we now know that there exists a unique solution for our system of equations.

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