Soil Buffering Mechanisms

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Introduction

The effect of acid rain on soil is dependent on the mineral content. This effect varies based on the mineral systems which can buffer the pH of the soil once exposed to the acid rain. Calcareous minerals (reaction 1), silicate clays (reaction 2), and aluminosilicate clays (reaction 3) are the three mineral systems that provide soil the capacity to withstand acid attack before a major pH drop occurs. One way to differentiate between these systems could be to observe the reaction orders of the underlying mechanisms.

\[
\begin{align*}
\text{CaCO}_3(s) + 2 H^+(aq) &\rightleftharpoons \text{Ca}^{2+}(aq) + H_2O(l) + CO_2(g) & (1) \\
M\text{-soil}(s) + n H^+(aq) &\rightleftharpoons H_n\text{-soil}(s) + M^{+n}(aq) & (2) \\
\text{Al-soil}(s) + 3H^+(aq) &\rightleftharpoons H_3\text{-soil}(s) + Al^{3+}(aq) & (3)
\end{align*}
\]

One hypothesis that this project sought to test was that each of these reactions would have a different kinetic mechanism and/or different rate constants.

If the mechanisms are different and they can be detected, then it might be possible to extract the mineral % composition in an environmental sample which is likely to be a mixture. Therefore, the purpose of this project was to determine the reaction orders of the kinetic mechanisms of these mineral systems. Specifically, fayalite (Fe$_2$SiO$_4$) and forsterite (Mg$_2$SiO$_4$) were used as representatives of reaction (2). Previous experiments showed that the addition of strong acid to these samples results in an initial, rapid decrease in the pH followed by a partial recovery of in the pH as a result of the buffering mechanism. These recovery curves (see Figure 2) decrease in amplitude until the buffering system is exhausted. The recovery curve provides the opportunity to observe the reaction kinetics.

Experimental

To determine the reaction orders of these systems, quantitative chemical analysis was conducted using an autotitration technique. Hydrochloric acid (1 M) was added to a finely ground mineral sample in controlled increments using a modified Metrohm Titrino 360 autotitrator which monitored pH as a function of time. In order to verify the ability of the method to track reaction kinetics a standard $S_{\text{n1}}$ reaction was tested. Next, different samples (CaCO$_3$, Na$_2$CO$_3$, MgCO$_3$, CaSiO$_3$, and MgSiO$_3$) were analyzed in order to simulate natural minerals. Finally, the minerals fayalite and forsterite were analyzed.

Kinetic data was analyzed using nonlinear regression analysis with SPSS once model equations were developed using Mathematica.

Results and Discussion

To verify the system, data was collected for a known first order reaction of tert-butyl chloride and ethanol as shown in Figure 1. The forward and reverse rates and uncertainties of three trials can be seen in Table 1. I was able to show that for the first few seconds the reaction was indeed first order this method of calculating forward and reverse reaction rates.

Data was collected for the titration of forsterite producing the graph shown in Figure 2. Using the model reaction equations, data only from the first recovery curve (9.3s – 60.1s) was fit in SPSS with the shown three combinations of x and y. The fits were then shown graphically using Excel (Figure 3). The forward and reverse rates and the uncertainties are shown in Table 2.

Future Work

Work includes the continuation of data fitting of forsterite using all possible combinations of x and y as well as the different recovery curves as the reaction progresses over time. This data fitting technique can also be used on previously collected data from titrations of CaCO$_3$, Na$_2$CO$_3$, MgCO$_3$, CaSiO$_3$, MgSiO$_3$, and Fe$_2$SiO$_4$. Once these kinetic mechanisms are understood, we could potentially develop a model that could determine the mineral content in an unknown sample and predict the percentage of each mineral in the soil sample.

Acknowledgements & References

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