A Simulation of the Interaction of Acid Rain with Soil Minerals

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This project incorporates the environmental issue of acid rain into a laboratory experience appropriate for a college freshman chemistry course. More specifically, it focuses on the chemistry involved when acidic rainwater percolates through soils. While normal rainwater has a pH of approximately 5.6, the pH of acid rain is usually 4.5–2.0 and can be lower *(1, 2)*. There are a variety of different mechanisms by which excess acidity is neutralized in soil. These involve the consumption of hydrogen ions by minerals containing aluminum hydroxide such as bauxite, gibbsite, boehmite, and diaspore; by calcium carbonate in limestone and calcite; and by aluminosilicates such as clay minerals, feldspars, and zeolites. These mechanisms vary in their effectiveness at neutralizing acidity and, in the case of calcium carbonate, aluminum hydroxide, and clays, involve the mobilization of cations in solution. Of particular concern is the mobilization of the aluminum ion from $Al(OH)_3$ because of the hazards it creates for aquatic life.

This five-part chemistry project involves passing sulfuric acid (with a molarity to simulate acid rain) through a glass column containing limestone, aluminum hydroxide, montmorillonite clay, or synthetic zeolites. Analysis of the acid solution after its passage through the column provides an excellent means to incorporate two important fundamental quantitative analytical techniques: (i) an acid–base titration to determine the decrease in acidity brought about by the mineral; and (ii) gravimetric analysis of the aqueous cations mobilized by the acid. The final portion of the project involves passing an aluminum sulfate solution through a column containing molecular sieves to simulate the beneficial consumption of aqueous aluminum ions by zeolites. The project can be executed in a number of ways: the instructor can select just one or two parts for the individual student to complete; all five parts can be treated as a multisession lab project to be completed by the individual; or the five parts of the project can be divided up among a class of students, and the results of each part can be shared in a group discussion.

Part 1: Interaction of $Al(OH)_3$ with Simulated Acid Rain

A column containing alternating layers of aluminum hydroxide and sand is constructed using a piece of glass tubing. A standardized sulfuric acid solution with a molarity that simulates acidic rainwater is passed through the column. The resulting solution is quantitatively analyzed in two ways: by titration with NaOH and by precipitating the aqueous aluminum as aluminum oxinate using 8-hydroxyquinoline. The latter process is represented by the following reaction:

$$Al^{3+}(aq) + 3C_9H_6NOH(s) \rightarrow Al(C_9H_6NO)_3(s) + 3H^+(aq)$$

The student determines the effectiveness of soil minerals containing $Al(OH)_3$ at neutralizing excess acidity in rainwater, and gains evidence of the mobilization of aluminum ion according to the following equation:

$$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

Typical student results for the consumption of H^+ and the presence of aqueous aluminum are shown in Table 1. Note on the table that data for sulfuric acid solutions of two different concentrations are included, and that the solution with lower $[H^+]$ seems to experience a decrease in acidity of nearly 100% when it is passed through an $Al(OH)_3$ column. This point is applicable if the instructor chooses to incorporate the enrichment option for this part of the project, which simulates what occurs as rain of varying acidities interacts with minerals having an aluminum hydroxide composition. The instructor may wish to discuss the Lewis adducts the aluminum ion forms when in water. A discussion of the chemistry involved in the gravimetric determination of Al^{3+}

Table 1. Typical Student Results: The Effectiveness of Soil Minerals at Consuming H^+ ions, and the Extent of Al^{3+} and Ca^{2+} Mobilization[a]

Mineral in Column	Initial Concentration of H^+/M	Percent Decrease of $[H^+]$ (%)	Total Moles of H^+ Consumed	Moles Al^{3+} Mobilized	Moles Ca^{2+} Mobilized
$Al(OH)_3$	0.011	27	2.8×10^{-4}	9.7×10^{-5}	–
$Al(OH)_3$	8.6×10^{-5}	~100	8.6×10^{-5}	–	–
Limestone, finely ground powder[b]	0.011	80	8.8×10^{-4}	–	6.3×10^{-4}
Limestone, crushed[c]	0.011	64	7.0×10^{-4}	–	2.2×10^{-4}
Montmorillonite clay	0.011	12	1.4×10^{-4}	n/a	n/a
Molecular sieves	0.011	53	5.9×10^{-4}	–	–

[a]The number of moles of Al^{3+} and Ca^{2+} recorded as mobilized is the number of moles in the 100 mL of solution that passed through the column. Standard deviations for the total moles of hydrogen ion consumed are approximately 10% of the values.

[b]Particle size < < 63 micrometers.

[c]Approximate particle size is between 1 and 2 mm.

(i.e., deprotonation of 8-hydroxyquinoline in basic solution and coordination of the 8-hydroxyquinoline to Al^{3+}) would also be appropriate.

Part 2: Interaction of Limestone ($CaCO_3$) with Simulated Acid Rain

A sulfuric acid solution is passed through a column containing alternating layers of limestone and sand. After the acid solution has passed through the column, it is analyzed by titration and by precipitating the aqueous Ca^{2+} as calcium oxinate, once again by using 8-hydroxyquinoline:

$$Ca^{2+}(aq) + 2C_9H_6NOH(s) \rightarrow Ca(C_9H_6NO)_2(s) + 2H^+(aq)$$

As is evident in Table 1, the particle size of the limestone used in the column plays a role in the quantity of acid consumed. According to the results in the table, limestone's ability to consume H^+ increases as its particle size decreases. The instructor may choose to incorporate this factor into the project by selecting the enrichment option for this part of the project.

Part 3: Interaction of Montmorillonite Clay with Simulated Acid Rain

A sulfuric acid solution is passed through a column containing a mixture of montmorillonite clay, $[(Na, Ca)(Al, Mg)_2(OH)_2Si_4O_{10}]$, and sand. The resulting acid solution is then titrated with NaOH so that the effectiveness of the clays at consuming H^+ is experimentally observed. Table 1 provides typical student results for this portion of the project. Clay minerals are aluminosilicates arranged in stacked sheets, and they constitute a substantial portion of most soils. The presence of cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} between stacked sheets makes possible the consumption of hydrogen ions by a process called ion exchange. It is not particularly useful to precipitate the mobilized cations in this part of the project because Mg^{2+}, Ca^{2+}, and Al^{3+} can all coordinate to 8-hyroxyquinoline to form an insoluble precipitate. The aluminosilicate structure of clay minerals provides a good opportunity for discussion of covalent lattice networks.

Part 4: Interaction of Molecular Sieves with Simulated Acid Rain

A sulfuric acid solution is passed through a column containing molecular sieves, and the resulting solution is titrated with NaOH to determine the quantity of acid consumed. It is not particularly useful in this case for the student to attempt to precipitate any aqueous cations with 8-hyroxyquinoline because, as Table 1 indicates, it is likely that no precipitate will form. (This is most likely due to the fact that 8-hydroxyquinoline does not form an insoluble compound with Na^+ and other alkali metal cations.) Because of the difficulty in obtaining pure samples of naturally occurring zeolites, synthetic zeolites (molecular sieves) provide a good laboratory substitute because they have essentially the same composition and structure as the naturally occurring ones. Molecular sieves (sodium aluminosilicates) closely resemble natrolite, a natural zeolite with the formula $Na_{16}(Al_{16}Si_{24}O_{80})\cdot 16H_2O$. The instructor should briefly discuss the open-holed structure within the zeolite framework and why zeolites can accommodate H^+ ions as well as larger ions and molecules within their structures. Table 1 shows typical student results for the effectiveness of molecular sieves at consuming hydrogen ions.

Part 5: Absorption of Aqueous Aluminum by Molecular Sieves

In this final portion of the project, the student passes an aluminum sulfate solution through a column containing molecular sieves. The main objective is to simulate the consumption of aqueous aluminum (once it has been mobilized by H^+ from $Al(OH)_3$) by zeolites. The quantity of aqueous aluminum in the solution after its passage through the column is determined by precipitating the remaining Al^{3+} as aluminum oxinate. Typical student results indicate that the molecular sieves are between 60–70% effective in consuming aqueous Al^{3+}. For example, one set of results for this procedure indicates that the $Al^{3+}(aq)$ concentration decreased from 2.2×10^{-3} M to 6.4×10^{-4} M after interacting with the sieves in the column. In other words, the molecular sieves consumed 1.5×10^{-4} moles of Al^{3+} ions.

Hazards

The hazards associated with this project stem primarily from the corrosive nature of sulfuric acid and of sodium hydroxide used for the titrations. In addition, dust from the aluminum hydroxide powder and 8-hydroxyquinoline can both potentially cause skin and eye irritation as well as possible irritation of the upper respiratory tract. Contact of molecular sieves with the eyes should be avoided. The use of protective eye goggles is a necessity; lab coats and gloves are recommended. Further, it is strongly advised that all work be done in a fume hood.

Summary

The environmental issue of acid rain is incorporated into a five-part laboratory project that employs quantitative analytical laboratory techniques such as acid–base titrations and gravimetric analysis of aqueous cations. The student observes the effectiveness of soil minerals at consuming excess acidity in rainwater and observes the mobilization of Al^{3+} and Ca^{2+} from these interactions. The first four parts of the project involve passing a sulfuric acid solution through a column containing aluminum hydroxide, limestone, montmorillonite clay, or synthetic zeolites (molecular sieves). In the fifth part of the project, an aluminum sulfate solution is passed through a column containing molecular sieves to observe the absorption of Al^{3+} by zeolites once it has been mobilized from minerals by acid rain.

[W]Supplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

Literature Cited

1. Schwartz, A. T.; Bunce, D. M.; Silberman, R. G.; Stanitski, C. L.; Stratton, W. J.; Zipp, A. P. *Chemistry in Context: Applying Chemistry to Society;* William C. Brown Publishing: Dubuque, IA, 1994.
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