

Comparative Efficacy of Montmorillonite, Calcium Hydroxide, Calcium Carbonate in pH Restoration of Acidified Freshwater Bodies



Figure 1. Freshwater Marsh (Fotoscott, 2016)

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Acknowledgements

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Abstract

Freshwater acidification is the result of acid rain precipitating over a freshwater body. There are significant ecological consequences that result from such precipitation, as ecosystems surrounding freshwater bodies are destroyed because many of the organisms in these ecosystems cannot tolerate the pH change caused by acid rain. Current solutions involve a technique known as liming, where powdered calcium carbonate is added to freshwater bodies creating a buffer that helps neutralize the acidity caused by acid rain. However, scientists have been searching for alternative methods to combat the decrease in pH caused by freshwater acidification, by using substitute compounds. In this experiment, we test the efficacy of alternate solutions involving montmorillonite and calcium hydroxide when compared to the currently employed method of using calcium carbonate to combat acidification.

Review of Literature

While many global efforts are made to stop continuing man-made emissions, new regulations fail to repair pre-existing damage to natural bodies of water. Though deacidification processes already exist, most notably liming (introducing calcium carbonate (CaCO_3)), these processes are not cost efficient, permanent, and most importantly, fail to restore the preexisting environmental equilibrium established prior to the impacts of acid rain. Standard liming procedure involves the mass surface dispersion of CaCO_3 compounds to water, so experimentation with different minerals would allow for the integration of more environmentally-friendly compounds for long-term deacidification. Achieving an environmentally alternative sought a definite replacement, prioritizing restoration of pre existing pH and ion concentration, long term efficacy, and cost efficiency, in descending order of value. Our investigation would mimic the liming procedure through a scaled down model, utilizing different compounds as independent variables while analysing for our criteria dependent variables.

“As a countermeasure (to acidification), liming is used to increase the pH and reduce the concentration of Ali-species; in particular low molecular mass (LMM) Ali-species by hydrolyses. However, very toxic high molecular mass (HMM) Al polymers can form in the unstable mixing zone immediately after liming,” (Teien, Kroglund, Salbu, Rosseland, 2006). Traditional liming consists of fine particle dispersion on the surface of water bodies; however, these methods fail to consider the ion concentration in water following treatment, as the capability to sustain life is built on more than pH change. Common foreign anions (SO_4^{2-} , NO_3^- , HCO_3^-) continue to exist in water bodies following dissociation from their respective acids, and the introduction of Al^{3+} cations pose environmental threats beyond the scope of pH changes, (Wang, Zang, Gong, Liu, Li, 2017). These ions will accumulate in respiratory systems of marine life, and further degrade structural support of aquatic invertebrates in interactions with exoskeletons and shells. A holistic approach to environmental maintenance necessary to provide conditions for life to rebuild, and reverse the damage of human pollution.

The process of ion exchange occurs when larger mineral compounds are composed of matrix of framing atoms surrounding charged ions. Upon introduction to water, the polarity of water removes central non-framework atoms while water molecules temporarily fill the void. The liquid form of water combined with inherent hydrogen bonds between water and preexisting intramolecular bonds between the mineral compounds prevent collapse allowing for a “empty casing” particle. Upon interaction with cations or anions, dependent on the polarity of the framework atoms, aqueous ions will fill in the compound void and recreate a stable molecule, (Chotpantarat, Kiatvarangkul, 2018). This phenomenon occurs through the crystallization process when certain molecules in compounds are not bonded to the framework molecules, instead covered in the shell as the molecules are created through geological movement. This process is notably found in certain clays due to molecular disturbance of moisture in clay, creating a low density molecule when water is evaporated out due to fissures between clay molecules in their semi-solid state, (Pusch, Kasbohm, Thao, 2010).

“Neutralisation by progressive addition of acid combined with XRD analyses of dissolution residues allows investigation of the acid buffering contribution of individual alkaline components, in particular, DSP, calcite, tricalcium aluminate and free Fe oxides. Neutralising with copperas, gypsum and seawater has also been investigated as ameliorative methods to facilitate the environmental use and rehabilitation of the red mud,” (Snars, Gilkes, 2009). The presence of natural clays exhibiting ion exchange in lake beds has allowed water bodies resistance to pH changes in comparison to nearby lakes without ion exchange substrates, (Vandermoere, Ralaizafisolovonony, Ranst, Neve, 2018). The avoidance of excess ion pollution points towards montmorillonite $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$, a compound with a small aluminum central atom to molecule ratio.

Montmorillonite is a naturally occurring phyllosilicate capable of buffering and neutralizing acidic conditions due to anion exchange which lowers H_3O^+ concentration while simultaneously removing foreign ions due to the similarity in charge and atomic size of the aforementioned common cations create from acid rain dissociation in solution. When present in the floors of aquatic bodies, the compound can continue to buffer without degradation of shell atoms in increased alkaline presence, (Kisiel, Skiba, Skoneczna, Maj-Szeliga, Błachowski, 2018). This allows for long term opportunities to continue buffering when manually introduced and allowed to rest. In the presence of high heat and gamma radiation, montmorillonite remained structurally sound in small scales measured at temperatures of 100°C , well above what any large

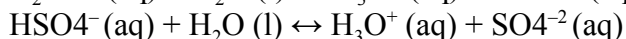
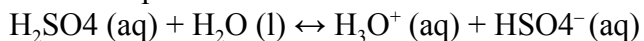
natural body of water could be, (Pusch, Kasbohm, Thao, 2010). Structural integrity allows for greater pH buffering capability without the introduction of high concentrations of foreign ions in completely dissociated pH regulation strategies such as traditional liming.

The compound further creates a viable opportunity for potential environmental regulation due to its increasing density upon interaction with polar water molecules, (Pusch, Kasbohm, Thao, 2010). As density increases, the clay will settle in the water bed over time, and be able to provide buffering capabilities while not directly contacting marine life. Unlike the aqueous toxic aluminum ions inherent to traditional liming, the loss of contact prevent interaction with aquatic respiratory systems and leaching of invertebrate structure. Although more expensive due to the inability to artificially synthesize the ion exchange cage, dependent upon natural clay discoveries, the expansion factor allows for greater H_3O^+ absorption per molecule compared to the impact of a lower H_3O^+ buffer per molecule in traditional weak base usage.

The ability to reduce pH and foreign ion concentration suggest montmorillonite as a viable alternative and solution to natural water body acidification due to acid rain. The synergistic effect between the clay and water to benefit aquatic life in comparison to traditional liming techniques will be beneficial to the preservation of environment and sustainment of aquatic life upon reemerge or reintroduction from acidified water. When in the context of a potentially cheaper alternative when a single montmorillonite molecule would have greater buffering capability than traditional liming techniques, along with the removal of foreign ion, pH reduction, and avoiding introduction of new particle inherent to the conjugate byproducts created by weak base usage for neutralization, the ion exchange phenomenon present an opportunity for experimentation concerning the viability the compound for usage in the commercial and global sphere.

Background

Freshwater acidification is the process by which the pH of freshwater lakes decreases substantially due to the introduction of acidic compounds. Freshwater acidification is the result of a variety of different environmental processes, including dry deposition and wet deposition. The most prevalent of these environmental processes is wet deposition, a process in which acid rain is precipitated over a freshwater body. Acid rain is the byproduct of gases produced primarily by power generators, factories, and vehicle emissions. The most common of these gases are SO_2 (g) (sulfur dioxide) and NO_x (g) (nitrogen oxides). When these gases are released into the atmosphere, they react with the water content in the atmosphere (H_2O) to form H_2SO_4 (sulfuric acid), HNO_3 (nitric acid), and carbonic acid H_2CO_3 (carbonic acid). Sulfuric acid comprises approximately 60-70% of acid rain and nitric acid comprises approximately 30-40% of acid rain with the rest being composed of carbonic acid. This acid rain in the atmosphere then precipitates over freshwater bodies, increasing the concentration of H_3O^+ . This is how H_2SO_4 (as well as other acids) decrease the pH when dissolved in water:



In some cases, the acidity of the acid rain is enough to drop pH levels all the way to 4.00. Such a dramatic change in pH has profound ecological consequences on the organisms living in these freshwater bodies. The increase in H^+ ions inhibits many metabolic functions of these organisms, causing them to die. Organisms in these freshwater bodies survive at different pH

levels, with different tolerances for a decrease in pH level. They also have different critical pH levels, which is the pH level at which the organisms start to die off in large quantities.










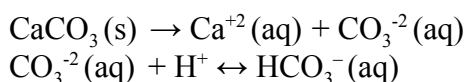
Animal		Critical pH Level
Snails		6
Clams		6
Bass		5.5
Crayfish		5.5
Mayfly		5.5
Trout		5
Salamanders		5
Perch		4.5
Frogs		4

Figure 1. Critical pH Levels for Aquatic Organisms (EPA, 2016)

When acid rain lowers the pH of freshwater bodies below these critical pH levels, it is devastating to these ecosystems not only because it kills the organisms in these freshwater bodies, but also because it disrupts the food webs of these ecosystems. When these aquatic organisms perish, predators which rely on a diet composed of these organisms struggle to find a reliable food source, and thus also perish. The only way to completely solve this problem of freshwater acidification is to completely eliminate sulfur dioxide, nitrogen oxide, and carbon dioxide emissions. However, in today's increasingly industrial and modernizing world, it is impossible to expect such change to happen. Therefore, the only way to prevent these ecological consequences is to reduce the dramatic change in pH caused by acid rain precipitation. Although much research on this topic has already been done, environmental biologists still work to find more cost effective and long term solutions to this ongoing problem. One such method that current environmental biologists are using to gain insight into this problem and add onto ongoing methodology is predictive modeling. With predictive modeling, environmental biologists are able to use past data on freshwater acidification—such as the pH changes that different treatments induce—to predict the outcomes of using the same/similar treatments in different areas. Research gathered through this system has led environmental biologists to employ a technique known as liming, although this could change as more data becomes available for predictive models to make more accurate predictions. Liming is the process by which large quantities of powdered CaCO_3 (calcium carbonate) are added to freshwater bodies to counteract the change in pH caused by acid rain. This is because CaCO_3 creates an acid neutralizing buffer when it is added to water, as shown in the two step reaction below:



First, CaCO_3 dissociates into its calcium cations and its carbonate anions. Then, the carbonate ions react with the H^+ ions (equivalent to H_3O^+) created by acids HNO_3 and H_2SO_4 . When the carbonate ions react with the H^+ ions, they completely neutralize them and produce HCO_3^{-} , a weak acid that will cause a negligible change in pH. Thus, the dissociation of CaCO_3 is able to create a buffer that neutralizes the acidity created by HNO_3 and H_2SO_4 in freshwater bodies. The purpose of this research is to explore other options besides CaCO_3 and see if they are more effective per gram in stabilizing the pH of acidified freshwater bodies. The two compounds

we've selected to compare to CaCO_3 are $\text{Ca}(\text{OH})_2$ (calcium hydroxide) and montmorillonite. Calcium hydroxide was selected because of the fact that it is a strong base, indicating that it ionizes completely into $(\text{OH})^-$ ions in water due to the ionic bond between the calcium atom and the hydroxide. The $(\text{OH})^-$ ions are then able to immediately react with the H^+ ions in the acidified solution, neutralizing them and subsequently increasing the pH.

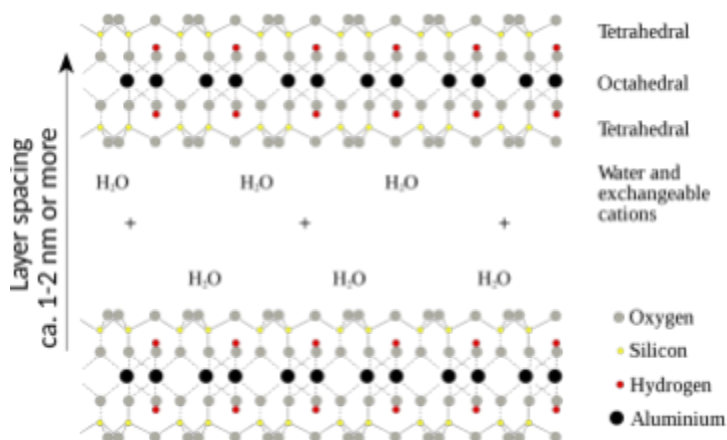


Figure 2. Montmorillonite Structure (Trepte, 2007)

Montmorillonite, a phyllosilicate mineral, is another promising compound because its chemical structure facilitates the neutralization of H^+ ions in aqueous solution. Montmorillonite has a two-layered structure through which water is able to flow through and interact with the montmorillonite structure. When water flows through the montmorillonite, it facilitates the substitution of lower valence cations within the montmorillonite double layer structure. This substitution imparts a negative charge on the exposed oxygen atoms within each layer, giving them the ability to attract cations. In an acidified freshwater solution, these oxygen anions would be able to pull H^+ ions out of solution, thus decreasing the concentration of H^+ ions and increasing the pH. Furthermore, montmorillonite is already being used in freshwater bodies as a source of food for fish such as koi and carp, demonstrating that it is an environmentally friendly compound to use in a freshwater environment. In order to simulate an acidified freshwater sample, we've calculated that 60 microliters of H_2SO_4 and 40 microliters of HNO_3 will change the pH of a DI water sample to roughly 4.00. Furthermore, the 60:40 ratio reflects the real life 60-70% H_2SO_4 and 30-40% HNO_3 percent composition of acid rain. The methodology we determined was to use 0.50 grams of each substance and test acid neutralization capabilities when compared to 0.50 grams of CaCO_3 . Even if a compound causes the pH to reach levels above the safe levels for freshwater organisms, it should not be discounted because the goal here is to test the comparative efficacy of compounds by using uniform amounts of solute across the board. Whichever 0.50 gram sample is able to cause the greatest increase in pH will be considered the most effective short term solution for neutralizing acidic solution.

Materials

- 1X 1.00L Beaker
- 1X 200mL Beaker

- 9X 50mL Beaker
- 1X 100mL graduated cylinder
- Deionized water
- Micropipette & Micropipette tips
- 1.0M H_2SO_4
- 1.0M HNO_3
- Stirring rod
- Vernier® pH Probe
- Vernier® LabQuest
- Vernier® Graphical Analysis 4
- Vernier® pH Buffer Capsules Kit
 - 4.00 pH capsules
 - 10.00 pH capsules
 - Hydron Color Key Buffer Preservative
- Laptop (windows or mac)
- 10.0 gram sample of powdered calcium carbonate ($CaCO_3$)
- 10.0 gram sample of Powdered calcium hydroxide ($Ca(OH)_2$)
- 10.0 gram sample of powdered montmorillonite
- Balance
- Weigh boat

Procedure

PART I - Artificial Water Contamination

1. Put on a pair of lab goggles, and rinse hands with soapy water
2. Obtain 1.00L beaker labeled *Beaker X*
3. Obtain 1.00L *deionized water sample*
 - a. Use 100.0mL *graduated cylinder* to measure 100.0mL of DI water, add to Beaker X. Repeat until Beaker X contains 1.00L of DI water
4. Using *micropipette* and attached *micropipette tip*, pipette out 60.00 μL 1.0M H_2SO_4 , add to Beaker X. Stir mixture with *stirring rod* for 20 seconds

Figure 1. H_2SO_4 addition utilizing micropipette



5. Using micropipette and replaced micropipette tip, pipette 40.00 μL of 1.0M HNO_3 , add to beaker X. Stir mixture with stirring rod for 20 seconds
6. Calibrate pH probe
 - a. Connect Vernier® Labquest apparatus to computer via USB
 - b. Connect Vernier® pH probe to Labquest apparatus
 - c. Install and open Vernier® Graphical Analysis 4

- d. Using *Vernier® pH Buffer Capsules Kit*, create two buffer solutions
 - i. Obtain 100mL beaker, fill with 100mL of DI water
 - ii. Pour contents of *4.00 pH capsule* into DI water, and stir the solution for ten seconds
 - iii. Add 3 drops of *Hydriion Color Key Buffer Preservative* to sample, creating orange solution
 - iv. Repeat steps i. through iii., using *10.00 pH capsule* in lieu of *4.00 pH capsule*, creating blue solution
- e. Conduct two-point calibration
 - i. Rinse tip and sensor of pH probe, submerge tip into orange buffer solution, manually setting pH on *Graphical Analysis 4* to value of 4.00
 - ii. Thoroughly rinse tip and sensor of pH probe, submerge tip into blue buffer solution, manually setting pH on *Graphical Analysis 4* to value of 10.00
7. Submerge pH probe into Beaker X, wait until displayed pH stabilizes
8. Record initial pH value of Beaker X solution into data table



Figure 2. pH recording setup

9. Label nine 50mL beakers CO1, CO2, CO3, CA1, CA2, CA3, M1, M2, M3 respectively
10. Obtain 200mL beaker labeled Beaker Y
11. Transfer 175mL solution from Beaker X to Beaker Y

PART II - pH monitoring through experimental compound addition

1. Obtain 10 gram sample of powdered *calcium carbonate* (CaCO_3)
2. Using graduated cylinder, measure 50mL of solution in Beaker Y, pour into Beaker CO1
3. Using *weighboat* and *balance*, separate 0.50 grams of CaCO_3 sample, add to Beaker CO1
4. Stir Beaker CO1 for 60 seconds
5. Rinse pH probe with DI water, submerge tip into Beaker CO1, and begin data collection for 120 seconds. Save data locally after collection completion
6. Rinse pH probe with DI water
7. Conduct a second and third trial repeating steps 2-6 using Beaker CO2 and Beaker CO3 instead of Beaker CO1, respectively
8. Refill Beaker Y with 150mL of Beaker X solution
9. Obtain 10 gram sample of powdered *calcium hydroxide* (Ca(OH)_2)
10. Using graduated cylinder, measure 50mL Beaker Y solution, pour into Beaker CA1.
11. Using weighboat and a balance, separate 0.50 grams of Ca(OH)_2 sample, add to Beaker CA1
12. Stir contents of Beaker CA1 for 60 seconds

13. Rinse pH probe with DI water, submerge tip into Beaker CA1 and begin data collection for 120 seconds. Save data locally after collection completion
14. Rinse pH probe with DI water
15. Conduct a second and third trial repeating steps 10-14 using Beaker CA2 and CA3 instead of Beaker CA1, respectively
16. Refill Beaker Y with 150mL of Beaker X solution
17. Obtain a 10 gram sample of powdered *montmorillonite*
18. Using graduated cylinder, measure out 50mL of solution in Beaker Y, pour into Beaker M1.
19. Using a weighboat and a balance, separate 0.50 grams of original montmorillonite sample, add to Beaker M1
20. Stir contents of Beaker M1 thoroughly for 60 seconds
21. Rinse pH probe with DI water, submerge tip into Beaker M1, begin data collection for 120 seconds. Save data locally collection completion
22. Use DI water to thoroughly rinse off pH probe
23. Conduct a second and third trial repeating steps 18-22 using Beaker M2 and Beaker M3 instead of Beaker M1, respectively

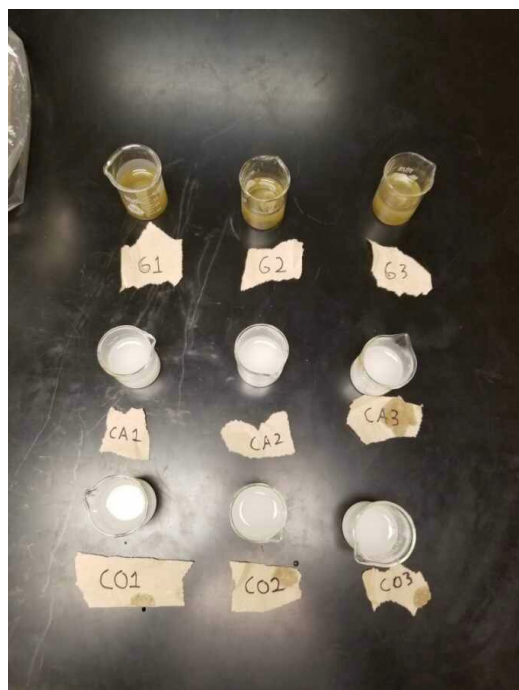


Figure 3. Sample display following compound introduction

Variables

Independent Variable - The compounds added to simulated acidified freshwater sample (calcium carbonate, calcium hydroxide, montmorillonite)

- Negative control - The acid and DI water mixture of Beaker X
- Positive control - The CaCO_3 added to beakers CO1, CO2, and CO3

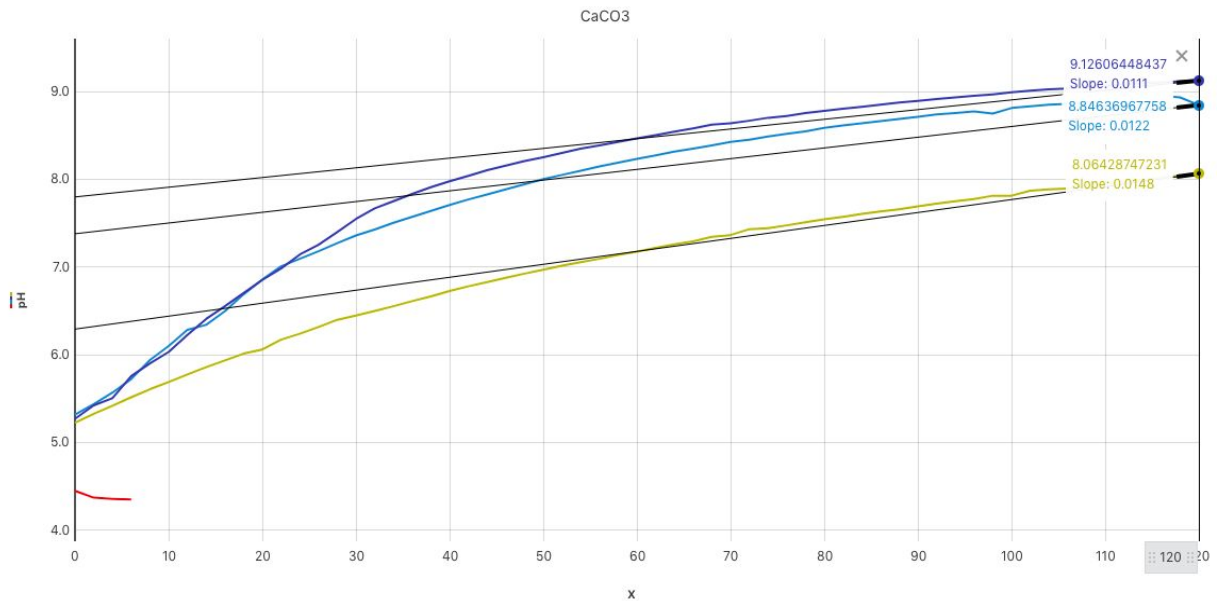
Dependent Variable - The pH of respective mixtures

Constants:

1. Temperature of environment - 22.0°C
2. Volume of experimental beakers - 50.0mL
3. Duration of mixture - 60.0 seconds
4. Duration of pH graphing - 120.0 seconds
5. Balance used for weighing
6. pH probe used to measure pH

Data

Figure 1. pH over time of artificially acidified freshwater sample following CaCO_3 addition. Blue: CO1 | Purple: CO2 | Yellow: CO3 | Red: Contaminated sample reference | (Experimental trials include linear slope at 120 second mark)



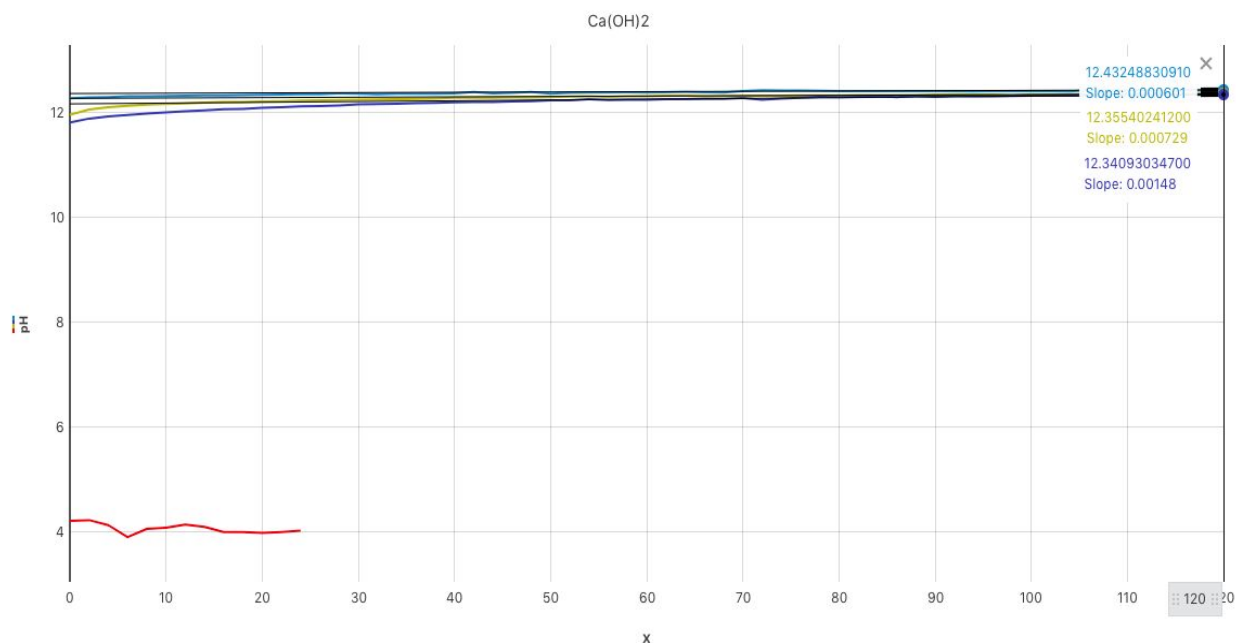


Figure 2. pH over time of artificially acidified freshwater sample following $\text{Ca}(\text{OH})_2$ addition. Blue: CA1 | Purple: CA2 | Yellow: CA3 | Red: Contaminated sample reference | (Experimental trials include linear slope at 120 second mark)
 Figure 3. pH over time of artificially acidified freshwater sample following *Montmorillonite* addition. Blue: M1 | Purple: M2 | Yellow: M3 | Red: Contaminated sample reference | (Experimental trials include linear slope at 120 second mark)

Discussion

The data suggests a viability of montmorillonite as a buffer based upon pH change from the .5 grams of compound for each sample, with roughly a .45 higher pH in comparison to the positive control of CaCO_3 . Although $\text{Ca}(\text{OH})_2$ demonstrates the greatest pH change, this must be understood in the context of the compound being a strong base, with the other two compounds capping at certain pH growth due to the creation of conjugate buffers. All three compounds were deemed to be completed in reaction after 120 seconds due to the near 0 tangent value of pH change, suggesting little further growth. All three quickly change pH upon dissolution, as the disparity between starting pH and the 0 second mark of each of the 9 trials suggest rapid pH change.

Sources of Error:

The most prominent source of error was the effect of time constraints dividing our experimentation periods, effectively forcing our experimentation of montmorillonite trials to be the day preceding the trials of CaCO_3 and Ca(OH)_2 . This difference could create disparity between the accuracy of our pH measurements. We utilized a Vernier pH sensor to record pH, and due to the sensor's requirement of calibration between day to day use, new calibrations would have prevented a truly accurate representation of pH differences from solution to solution.

Another source of error related to the difference in days of experimentation was the temperature. Although the recorded temperature was the same between the days, at least to the tenth degree, this temperature is hardly representative of natural bodies of water. Industrial pollution affects natural bodies of water worldwide, and different temperatures impact the reaction rate of buffering for all three of our compounds, as the potential energy of particles, notably between shell molecules to the central atoms is heavily dependent upon polarity, where speed of molecules affects the opportunity for free floating atoms to create necessary collisions for ion exchange to occur.

A final source of error is the lack of biological material within our solutions. The presence of marine life, dead or alive, impacts the pH bases on their independent interactions with pH. To create an experimental scenario, a scenario is created that would be common to all practical applications, and our experimentation, although unavoidable, is unable to factor in the effects of biological life that exist in all natural bodies of water seeking preservation. Further small-scale experimentation is necessary to determine efficacy of compound buffers for specific bodies of water, allowing for factors only present in that body of water.

Conclusion

The data strongly suggests that montmorillonite and calcium hydroxide are both viable options for deacidification of freshwater bodies. Montmorillonite was shown to be more effective than CaCO_3 , the current compound in use for freshwater deacidification, as it caused the greatest increase in pH based on the same 0.50 gram amount. Calcium hydroxide also increased the pH by a significantly wider margin with the same initial 0.50 gram amount. It is also important to add that the calcium hydroxide dissolved completely, while the montmorillonite did not. This means that the use of calcium hydroxide would represent a better short term solution, while montmorillonite would represent a better long term solution due to the fact that montmorillonite is not completely soluble. Since montmorillonite is not completely soluble, ion exchange can occur over a long period of time, with the montmorillonite gathered at the bottom of the freshwater body continuously increasing the pH in response to increases in H^+ concentration through acid rain precipitation. In freshwater bodies that have experienced a sudden and drastic change to pH, the use of calcium hydroxide can help bring the pH to safe levels, preventing any short term damage to the organisms present in the freshwater body. In freshwater bodies that have shown a gradual but persistent decrease in pH, montmorillonite would be a more effective option, as it would help stabilize the pH and keep it at a safe level for a longer period of time. In both cases, millions of organisms would be saved, as not only would

the aquatic organisms survive by not reaching their critical pH, but food webs in these ecosystems would be repaired, as the predators of these aquatic organisms would have a source of food as well. For example, when phytoplankton present in acidified lakes die off in large quantities, insects are unable to find a food source causing them to perish. Birds, frogs, and salamanders, animals that rely on insects for food, also begin to perish. Using montmorillonite and calcium hydroxide can help prevent the initial death of these phytoplankton, restoring food webs as insects—and subsequently birds, frogs, and salamanders—have a source of food to survive off of.

References

Wang, Y. Y., Zang, B., Gong, X. Y., Liu, Y., & Li, G. X. (2017). Effects of pH buffering agents on the anaerobic hydrolysis acidification stage of kitchen waste. *Waste Management*, 68, 603–609. doi: 10.1016/j.wasman.2017.06.041

Wendt, G. L., & Clarke, A. H. (1923). An Electrometric Study Of The Neutralization Of Phosphoric Acid By Calcium Hydroxide. *Journal of the American Chemical Society*, 45(4), 881–887. doi: 10.1021/ja01657a003

Tyagi, B., Chudasama, C. D., & Jasra, R. V. (2006, April 24). Determination of structural modification in acid activated montmorillonite clay by FT-IR spectroscopy. Retrieved December 15, 19AD, from <https://www.sciencedirect.com/science/article/abs/pii/S1386142505003677>

Chotpantarat, S., & Kiatvarangkul, N. (2018). Facilitated transport of cadmium with montmorillonite KSF colloids under different pH conditions in water-saturated sand columns: Experiment and transport modeling. *Water Research*, 146, 216–231. doi: 10.1016/j.watres.2018.09.010

Pusch, R., Kasbohm, J., & Thao, H. T. M. (2010). Chemical stability of montmorillonite buffer clay under repository-like conditions—A synthesis of relevant experimental data. *Applied Clay Science*, 47(1-2), 113–119. doi: 10.1016/j.clay.2009.01.002

Snars, K., & Gilkes, R. (2009). Evaluation of bauxite residues (red muds) of different origins for environmental applications. *Applied Clay Science*, 46(1), 13–20. Doi: 10.1016/j.clay.2009.06.014

Teien, H.-C., Kroglund, F., Salbu, B., & Rosseland, B. O. (2006). Gill reactivity of aluminium-species following liming. *Science of The Total Environment*, 358(1-3), 206–220. doi: 10.1016/j.scitotenv.2005.04.023

EPA. (2016, March). Critical pH Levels for Aquatic Organisms [Digital image]. Retrieved August 13, 2020, from <https://www.epa.gov/acidrain/effects-acid-rain>

Trepte, A. (2007). Montmorillonite Structure [Digital image]. Retrieved August 13, 2020, from <https://commons.wikimedia.org/wiki/File:Montmorillonite-en.svg>

Fotoscott. (2016, August 14). [The Kleihügelsee in Altgemeinde Espelkamp (district of the town of Espelkamp) is part of the "Altkreis Lübbecke" protected landscape area; many communities of rare animal and plant species find a common retreat here.]. Retrieved August 14, 2020, from <https://commons.wikimedia.org/wiki/File:Kleihügelsee.jpg>