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Investigating The Effect of Sulphuric Acid on Various Metals to Mimic Acid Rain Exposure

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Background Information

Acid rain is known to cause many environmental and ecological imbalances which can have negative effects on the sustainability of the environment as well as the organisms living there. Some such impacts of acid rain exposure are loss of fish in lakes, ponds, and streams, as well as the several direct and indirect affects it has on trees and other vegetation. Further, acid rain aggravates – and in some cases, causes – respiratory diseases like asthma. In addition to these effects however, acid rain, due to its acidity, increases the rate of erosion of many metals and minerals that are exposed to it. This not only washes an excess of minerals into the ecosystem, it also causes irreparable damage to historical buildings made of materials such as limestone.

Since acid rain is caused by air pollution like sulphur dioxide and nitrogen oxides, acid rain is more predominant in areas of the world that are more highly industrialized. Some such examples of this are Tokyo, Japan and the United States of America, where rain has been known to reach pHs of 4.7ⁱ and 4.3ⁱⁱ, respectively.

Introduction

This experiment will expose ten different metals and minerals to four varying concentrations of sulphuric acid for a period of four days to mimic acid rain exposure in nature. This data will then be used to draw conclusions regarding the short and long-term effects of acid rain in the environment. For the experiment, two of the four concentrations of sulphuric acid are designed to recreate the 4.300 and 4.700 pHs from Japan and the USA. The third concentration of acid will have a pH of 6.100 which was determined experimentally to be the pH of rain locally in St. John's, NL, Canada. Finally, the fourth pH will be of 2.000 to allow for further extrapolation on the data to gain an understanding of more long-term effects.

Some aspects of the results that will be studied are whether the acidity of local rain has a pronounced effect on the samples, at what point does the acidity of rain reach a critical point where its effects are much more drastic below this point, and which metals are affected most and least by acid rain exposure.

Note that in this experiment, both marble and limestone are being tested. Though both of these minerals are chemically the same since they're made primarily of calcium carbonate, the marble is pure calcium carbonate while the limestone is mined. For this reason, the limestone sample gives a more accurate perspective on the effect of acid rain on structures that are made of limestone whereas the marble shows the effect of acid rain on pure CaCO_{3 (s)}.

This topic was chosen based on a discussion with a teacher who told me that rain in Newfoundland and Labrador is acidic compared to other places in the world. Based on the experimental data on the following pages, I now know this statement to be false but nevertheless it inspired me to investigate the topic.

Research Question

What effect does sulphuric acid found in acid rain have on various metals and minerals in the environment?

Materials

- 20.0 cm³ 0.500 mol dm⁻³ H₂SO_{4 (aq)}
- 80 clean plastic disposable cups
- Scale (four or more decimal places)
- Deionized water
- 1.0 dm³ beaker
- Paraffin film

Method

- 1. Using deionized water, dilute the stock 0.500 mol dm $^{-3}$ H_2SO_4 (aq) solution to 0.0100 mol dm $^{-3}$, 0.0000501 mol dm $^{-3}$, 0.0000199 mol dm $^{-3}$, and 0.000000794 mol dm $^{-3}$. This will create solutions with pH of 2.000, 4.300, 4.700 and 6.100, respectively. You will need at least 550.00 cm 3 of each solution.
- 2. Using a 25.00 cm³ pipette, transfer 25.00 cm³ of each solution into clean plastic cups. This should produce 80 cups, 20 of each concentration.
- 3. Using a weighing boat and a scale which reads to four or more decimal places, weigh eight samples of each of the 10 metals or minerals being tested for acid rain exposure. The initial mass of each sample should not be more than ten grams. Record the measurements in a lab book.
- 4. Place a sample of each metal or mineral in a cup so that there are two trials of each for each concentration of acid. Seal the cups.
- 5. Allow the samples to remain submerged in the acid for four days. Remove them after this time and rinse away any pieces of mineral or precipitate which would be washed away in the environment due to rainfall and erosion.
- 6. Hand dry each sample with paper towel to remove most of the liquid that has stuck to the metal and then air dry in a warm area for another three days to ensure all liquid has evaporated.
- 7. Reweigh each sample using the same scale as before and record the new masses.

Hypothesis

Since the area of Japan in which the literature value of 4.7 pH comes from is so developed, I expect the effects of acid rain to be obvious from the trials using pH of 4.700, 4.300 and 2.000. The first pH of 6.1 which represents local precipitation I expect to have very little effect on the mass of the metals because although a pH of 6.1 is technically acidic, it's actually more basic than the $5.6^{\text{iii,iv}}$ pH that rain is expected to be due to carbonic acid in the rain which is present due to dissolved CO_2 content. For this reason I predict the most significant change in mass to occur between exposure to a solution with a pH of 6.100 and that of 4.700.

I also expect the calcium, magnesium, marble and limestone to exhibit the largest mass change due to their grouping on the periodic table as well as what I know about acid rain's effect on limestone. This is because calcium and magnesium are the only two metals that were used from the alkaline earth metal group. Elements in this group have only two valence electrons and thus are very prone to reacting with acid. Since marble and limestone are chemically the same substance, CaCO₃, I expect them to have a significant mass change due to the calcium atom in each molecule which will react with the acid in a similar manner as the pure calcium metal.

Data Collection

Raw Numerical Data

Table 1: Raw data from experiment (mass changes of sample at pH of 2.000)

Mass of Sample (g)				
Metal	Trial 1 (±0.0003 g)		Trial 2 (±0.0003 g)	
	Before	After	Before	After
Charcoal	2.9848	2.9407	2.5341	2.2958
Copper (Cu)	2.5778	2.5755	3.6395	3.6349
Steel	4.9581	4.9312	4.7618	4.7333
Lead (Pb)	6.8156	6.8139	6.4694	6.4666
Magnesium (Mg)	0.3652	0.3605	0.4555	0.4297
Marble (CaCO₃)	2.5109	2.4529	2.0051	1.9487
Tin (Sn)	3.7263	3.7211	4.0167	4.0095
Zinc (Zn)	5.6383	5.6382	5.6480	5.5311
Calcium Carbonate (CaCO ₃)	4.2113	4.1548	3.6882	3.6358
Calcium (Ca)	3.0212	1.1420	2.4123	0.2415

Table 2: Raw data from experiment (mass change of sample at pH of 4.300)

	Mass of Sample (g)			
Metal	Trial 1 (±0.0003 g)		Trial 2 (±0.0003 g)	
	Before	After	Before	After
Charcoal	3.2605	3.2306	6.9339	6.8745
Copper (Cu)	3.0334	3.0309	3.1011	3.0984
Steel	7.0959	7.0849	4.3873	4.3842
Lead (Pb)	7.5663	7.5586	5.5084	5.5038
Magnesium (Mg)	0.3823	0.3828	0.3463	0.3472
Marble (CaCO ₃)	4.5757	4.5607	5.4297	5.4179
Tin (Sn)	4.6606	4.6585	4.5578	4.5557
Zinc (Zn)	5.9006	5.8992	5.3740	5.3719
Calcium Carbonate (CaCO₃)	4.9545	4.9210	5.6093	5.5955
Calcium (Ca)	2.5255	0.6714	2.1325	0.5000

Table 3: Raw data from experiment (mass change of sample at pH of 4.700)

	Mass of Sample (g)			
Metal	Trial 1 (±0.0003 g)		Trial 2 (±0.0003 g)	
	Before	After	Before	After
Charcoal	4.8352	4.8212	3.6721	3.6612
Copper (Cu)	2.8493	2.849	3.169	3.1689
Steel	5.2297	5.2279	6.8015	6.7991
Lead (Pb)	6.2338	6.2248	7.4266	7.4236
Magnesium (Mg)	0.3906	0.3935	0.4332	0.4369
Marble (CaCO ₃)	5.6399	5.6267	4.1413	4.1188
Tin (Sn)	4.1189	4.1146	4.4903	4.4806
Zinc (Zn)	6.3549	6.3579	5.9108	5.911
Calcium Carbonate (CaCO ₃)	4.4779	4.4719	5.6765	5.657
Calcium (Ca)	2.4845	1.4119	1.4135	0.1202

Table 4: Raw data from experiment (mass change of sample at pH of 6.100)

	Mass of Sample (g)			
Metal	Trial 1 (±0		Trial 2 (±0.0003 g)	
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	Before	After	Before	After
Charcoal	3.6941	3.6913	3.6667	3.6543
Copper (Cu)	2.5157	2.5175	2.2444	2.245
Steel	5.8151	5.8111	8.6229	8.6191
Lead (Pb)	5.9433	5.9416	6.204	6.2027
Magnesium (Mg)	0.3233	0.3261	0.3469	0.3516
Marble (CaCO ₃)	4.8535	4.8439	4.7454	4.7351
Tin (Sn)	4.8388	4.0022	7.3086	7.3078
Zinc (Zn)	5.7881	5.7874	8.54	8.5374
Calcium Carbonate (CaCO ₃)	4.8861	4.8754	6.5008	6.4888
Calcium (Ca)	1.8699	0.9355	-	-

Qualitative Observations

When each of the samples of metal were placed into their respective acid solutions, some of them were visually unreactive while others slowly emitted small bubbles of hydrogen gas. The three samples which, in general, produced the most hydrogen gas were calcium metal, magnesium metal and marble. Calcium was so reactive that for the 2.000, 4.300 and 4.700 pH levels, it needed to be reacted in glass beakers since plastic cups melted too easily.

Another observation was that after being submerged in acid and then dried with a paper towel (prior to air-drying), the charcoal was very brittle and prone to crumble when pressure was applied.

Data Processing

Next, using the formula in Figure 1, the above changes in mass were converted to percentages to allow easier comparison between samples of differing initial mass. The average values shown in the last column of Tables 5 through 8 are calculated using the formula in Figure 2. Sample calculations for each of these are included below in Figure 3 through 6.

Figure 1: Percent Difference

$$\% difference = \frac{\left(m_{\textit{final}} - m_{\textit{initial}}\right)}{\left(\frac{m_{\textit{final}} + m_{\textit{initial}}}{2}\right)} \times 100\%$$

Figure 2: Average

$$\overline{x} = \frac{x_{\scriptscriptstyle n} + x_{\scriptscriptstyle n-1} + \cdots + x_{\scriptscriptstyle 1}}{n}$$

Figure 3: Percent Difference Sample Calculation Using Data from Charcoal for pH of 2.000

$$\% difference = \frac{\left(m_{\tiny final} - m_{\tiny initial}\right)}{\left(\frac{m_{\tiny final} + m_{\tiny initial}}{2}\right)} \times 100\%$$

$$\% difference = \frac{\left(2.9407g - 2.9848g\right)}{\left(\frac{2.9407 + 2.9848}{2}\right)} \times 100\%$$

$$\% difference = -1.4885\%$$

Figure 4: Uncertainty of Percent Difference Sample Calculation Using Data from Charcoal for pH of 2.000

$$uncertainty = \frac{\left(\pm 0.0003g \div 2.9407g + \pm 0.0003g \div 2.9848g\right)}{\left(\frac{\pm 0.0003g \div 2.9407g + \pm 0.0003g \div 2.9848g}{2}\right)}$$

$$uncertainty = \frac{\left(\pm 0.0102\% + \pm 0.0101\%\right)}{\left(\frac{0.0102\% + \pm 0.0101\%}{2}\right)}$$

$$uncertainty = \pm 2.000\%$$

Figure 5: Average Percent Difference Calculation Using Trials 1 and 2 of Charcoal in a pH of 2.000

$$\overline{x} = \frac{-1.4885\% + -9.8677\%}{2}$$

$$\overline{x} = -5.6781\%$$

Figure 6: Uncertainty of Average Percent Difference Calculation Using Trials 1 and 2 of Charcoal in a pH of 2.000

$$\begin{aligned} uncertainty_{\bar{x}} &= \frac{\pm 2.000\% + \pm 2.000\%}{2} \\ uncertainty_{\bar{x}} &= \pm 2.000\% \end{aligned}$$

Table 5: Raw data from experiment (percent mass change of sample at pH of 2.000)

	· · ·			
	Percent Difference (%)			
Metal	Trial 1	Trial 2	Average	
	(±2.000%)	(±2.000%)	(±2.000%)	
Charcoal	-1.4885	-9.8677	-5.6781	
Copper (Cu)	-0.0893	-0.1265	-0.1079	
Steel	-0.5440	-0.6003	-0.5722	
Lead (Pb)	-0.0249	-0.0433	-0.0341	
Magnesium (Mg)	-1.2953	-5.8292	-3.5622	
Marble (CaCO₃)	-2.3369	-2.8530	-2.5949	
Tin (Sn)	-0.1396	-0.1794	-0.1595	
Zinc (Zn)	-0.0018	-2.0914	-1.0466	
Calcium Carbonate (CaCO ₃)	-1.3507	-1.4309	-1.3908	
Calcium (Ca)	-90.2767	-163.5994	-126.9380	

Table 6: Raw data from experiment (percent mass change of sample at pH of 4.300)

	Percent Difference (%)			
Metal	Trial 1	Trial 2	Average	
	(±2.000%)	(±2.000%)	(±2.000%)	
Charcoal	-0.9213	-0.8603	-0.8908	
Copper (Cu)	-0.0824	-0.0871	-0.0848	
Steel	-0.1551	-0.0707	-0.1129	
Lead (Pb)	-0.1018	-0.0835	-0.0927	
Magnesium (Mg)	0.1307	0.2596	0.1951	
Marble (CaCO₃)	-0.3284	-0.2176	-0.2730	
Tin (Sn)	-0.0451	-0.0461	-0.0456	
Zinc (Zn)	-0.0237	-0.0391	-0.0314	
Calcium Carbonate (CaCO₃)	-0.6784	-0.2463	-0.4624	
Calcium (Ca)	-115.9936	-124.0266	-120.0101	

Table 7: Raw data from experiment (percent mass change of sample at pH of 4.700)

	Percent Difference (%)			
Metal	Trial 1	Trial 2	Average	
	(±2.000%)	(±2.000%)	(±2.000%)	
Charcoal	-0.2900	-0.2973	-0.2936	
Copper (Cu)	-0.0105	-0.0032	-0.0068	
Steel	-0.0344	-0.0353	-0.0349	
Lead (Pb)	-0.1445	-0.0404	-0.0924	
Magnesium (Mg)	0.7397	0.8505	0.7951	
Marble (CaCO ₃)	-0.2343	-0.5448	-0.3896	
Tin (Sn)	-0.1045	-0.2163	-0.1604	
Zinc (Zn)	0.0472	0.0034	0.0253	
Calcium Carbonate (CaCO ₃)	-0.1341	-0.3441	-0.2391	
Calcium (Ca)	-55.0559	-168.6510	-111.8535	

Table 8: Raw data from experiment (percent mass change of sample at pH of 6.100)

	Percent Difference (%)			
Metal	Trial 1	Trial 2	Average	
	(±2.000%)	(±2.000%)	(±2.000%)	
Charcoal	-0.0758	-0.3388	-0.2073	
Copper (Cu)	0.0715	0.0267	0.0491	
Steel	-0.0688	-0.0441	-0.0564	
Lead (Pb)	-0.0286	-0.0210	-0.0248	
Magnesium (Mg)	0.8623	1.3457	1.1040	
Marble (CaCO ₃)	-0.1980	-0.2173	-0.2076	
Tin (Sn)	-18.9255	-0.0109	-9.4682	
Zinc (Zn)	-0.0121	-0.0304	-0.0213	
Calcium Carbonate (CaCO ₃)	-0.2192	-0.1848	-0.2020	
Calcium (Ca)	-66.6144	-	-66.6144	

Using the data in Tables 5 through 8, the graph on the following page (Figure 7) was made. This graph illustrates the relationship between each type of metal in each level of acidic solution. Note that as the data came from Tables 5-8, it is the average percent differences being graphed, not each trial individually.

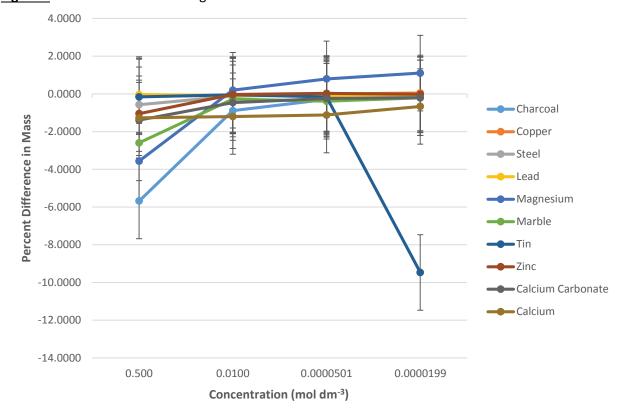


Figure 7: Concentration vs. Average Percent Mass Difference

In Figure 7, the line which shows the trend for tin takes a very steep drop between a concentration of 5.01×10^{-5} mol dm⁻³ and 1.99×10^{-5} mol dm⁻³ when compared to all the other samples. This would lead a viewer to think that tin is somehow affected very much by the higher pH conditions when in fact this average value is being thrown off by one piece of non-representative data. The cause for this could be something as simple as a small piece of metal which somehow was misplaced and thus is creating the appearance that the mass decreased a false amount.

In an effort to remediate this, all non-representative data was removed from the sample population. Since there would only be two values for each metal-concentration combination, using the conventional formula to determine outliers would not be practical since the standard deviation and mean would be very inaccurate. As an alternative to this, numbers which were too low or high for the particular concentration (relative to the other three) or the level of reactivity of the metal were removed from the calculations and graphics.

Shown below in Figure 8 is the average percent difference for each metal-concentration combination with all of the misrepresenting data removed. As demonstrated by the error bars, the uncertainty is still $\pm 2.000\%$. Also, in the graph, note that rather than labelling the x-axis with the varying pH levels, it is labelled using the concentration of the solutions on a logarithmic scale. This is to allow for a more accurate analysis since it provides a more visual approach to viewing the real difference in H_2SO_4 concentration – the pH scale is a man-made scale that is used for the purpose of avoiding very small or large numbers.

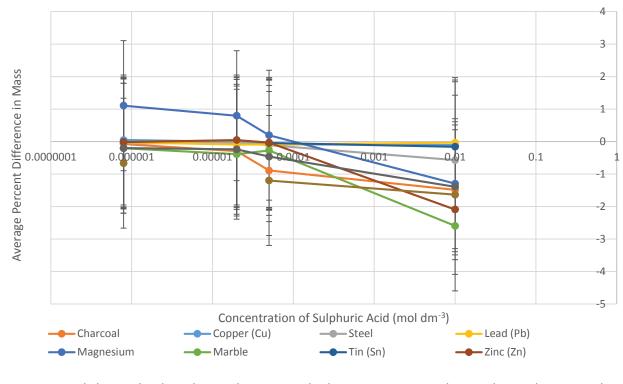


Figure 8: Concentration vs. Average Percent Difference in Mass (sans non-representative data)

For increased clarity, the data shown above is graphed again in Figure 9. This graph is without error bars since, although a best practice, they add very little value to the data due to the way they overlap one another so much. This instead makes the graph more difficult to read.

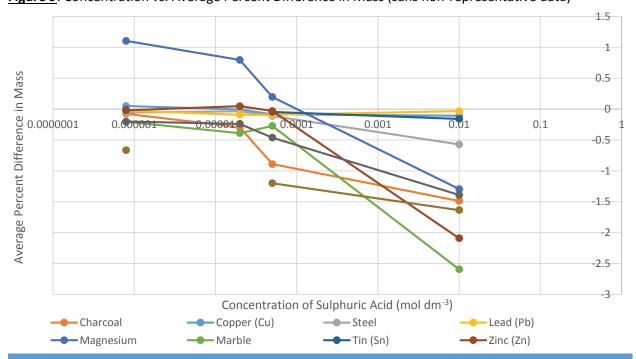


Figure 9: Concentration vs. Average Percent Difference in Mass (sans non-representative data)

By displaying the x-axis as a concentration rather than a pH, visually it becomes clear where each of the four concentrations are placed relative to the other three. From this, one can observe that the most significant drop in percentage relative to the spacing between points is between 5.01×10^{-5} mol dm⁻³ and 1.99×10^{-5} mol dm⁻³, or in other words, the slope of the line is much steeper between a pH of 4.300 and 4.700 which are represented by the two middle clusters of points on the graphs.

This finding forces the rejection of the hypothesis because it shows the critical value is somewhere between a pH of 4.700 and 4.300 – not 6.100 and 4.700 as predicted.

Another point that Figures 8 and 9 demonstrate is that the effect of the local 6.100 pH is negligible in mass decrease. This fits the expectation since acid rain has never been a concern in a city as small as St. John's. A question that may arise when analysing the values at a pH of 6.100 is "why is the rain in St. John's actually more alkaline than pure rain water?" Though outside the scope of the investigation, a correct explanation for this is required to rule out several other explanations which would just be conjecture. Due to the fact that the Holyrood Thermal Generating Station – a power generation plant which is responsible for up to 25% of the province's energy production – is about a half hour via road away from the location the sample of rain was collected, this sample likely contained pollutants from the power station which influenced its pH.

A final observation from Figure 8 is that the type of metal also has a significant effect on its vulnerability to acid rain damage. Copper, lead and tin all have near negligible mass decreases even at the highest concentration of acid. This is to be expected and is due to the elements' physical location on the periodic table – which in turn shows that they have similar unreactive properties. Copper is a transition metal and lead and tin are both basic metals, all of which are fairly unreactive. On the other hand calcium exhibited an extreme mass drop over both short and long (represented by the 2.000 pH trial) periods of time. Magnesium seemed to exhibit a similar trend when exposed to lower pHs and both samples of calcium carbonate (pure and mined) also showed a significant decrease in mass. Once again, this is due to the presence of Group II elements in each of these samples.

Conclusion

Overall, this experiment was a success and many of the data points agreed with one another when indicating that the critical point in pH is somewhere between 4.700 and 4.300. Although part of the hypothesis about the location of this point had to be rejected, another part of the hypothesis regarding the reactivity of differing metals was correct.

The two metals from the second group of the periodic table proved to have the most discernible reaction as these elements are fairly reactive with acid. Since the calcium is of an atomic number that is eight more than magnesium, the sample of magnesium created lots of bubbles while the calcium violently bubbled and boiled – slightly melting the plastic cup. This explains why so little calcium was left but doesn't explain the *increased* mass of the magnesium in the three trials with higher pHs. One explanation for this is that because magnesium is less reactive than calcium, the solution must be more acidic for there to be a noticeable decrease in mass. Above this concentration – which evidentially is somewhere between a pH of 2.000 and a pH of 4.300 – the mass decrease is negligible. Further, what small amount of mass decrease that did occur, would not be able to be observed because of the mass gain caused by oxidation. Shown

by the formula below in Figure 10, magnesium metal will react with water to form magnesium oxide and hydrogen gas – the bubbles that were observed. This oxide will adhere to the magnesium metal, thus increasing the mass.

Figure 10: Formation of MgO_(s) and H_{2 (g)}
$$2 \text{ MgO}_{(s)} + 2 \text{ H}_2 \text{O}_{(l)} \rightarrow 2 \text{ MgO}_{(s)} + 2 \text{ H}_2 \text{ }_{(g)}$$

Though there were limitations with the data used to extrapolate to long-term effects, all other conclusions drawn were based upon firm scientific observation and the solution to the other main limitation is very simple and easily implemented in further trials. Other sources of possible error and uncertainty are very small since very accurate lab equipment was used. The scale's uncertainty was ± 0.3 mg and the pipette used for dilutions and pipetting the 25.00 cm³ of acid was 0.03 cm³ or $\pm 0.12\%$.

Perhaps the most respectable aspect of the results obtained is not only that they agree, but that they narrow down the direction in which to head in further investigation. In the scientific community, one of the most important "next steps" is knowing where to go next — what can be done to improve the certainty of an experiment's findings and to verify the results through other studies. The results of this study do just that and they pave the way for many extensions to be done at a later time.

Limitations

Although several measures were taken to avoid error and limitation of this experiment, there were still several main sources of error, the most obvious of which is the use of the $0.0100~\text{mol dm}^{-3}~\text{H}_2\text{SO}_4~\text{(aq)}$ solution to extrapolate and be able to compare extremely short term data to what – in theory – would mimic long-term exposure. In practice, the short-term exposure to a strong acid may not have the same effect on the metals tested as long-term exposure to a concentration which reaches a pH of only 4.700 or 4.300. Another limitation of this is that even if it was to accurately portray long-term effects, how long exactly is "long-term"? From the research conducted and procedure used, it is impossible to know with certainty how much time exposure to a pH of 2.000 for four days would equate to at a pH of 4.300 or 4.700.

One more limitation of the procedure used is that in step number five of the procedure when the precipitate or eroded mineral is rinsed away, the experiment is subject to random human error. Firstly, each sample may not have had the same amount of rinsing to mimic erosion and mineral being washed away. This would cause the final mass for that trial to appear higher than it should have been since there is some solid left over which should have been removed. Secondly, by submerging the metals and minerals and leaving them in one static position for four days, this does not accurately mimic outdoor exposure where it would be subject to the weather and possibly at some point storms that include torrential rain. Conditions such as this would accentuate the effect of the acid by exploiting weaknesses created by the acid, especially in porous solids like charcoal. Under these conditions, charcoal would be likely to crumble if much pressure was applied due to its weakened porous structure. In this scenario, small bits of charcoal would wash away and thus be removed from the system being studied – a feature that this experiment did not account for.

Improvement

Two improvements to the procedure used for this experiment are to conduct more trials in a certain pH range as well as the procedure used for rinsing the samples of solid before weighing a second time.

Based on the four different concentrations of sulphuric acid used in this study, it was concluded that the critical value where damage caused by acid rain becomes most pronounced is somewhere between a pH of 4.700 and 4.300. A good way to extend on these findings is to conduct more trials between these two values – perhaps one at each tenth, 4.600, 4.500, and 4.400, and then using those results maybe go even more precise to narrow down this critical value.

To reduce human error associated with rinsing each sample, a simple but effective improvement would be to place each sample in a strainer and run water through this. That would allow precipitate and small pieces of mineral that became detached to wash away but would do so identically for each sample. One may think that for this application the best practice would be to use a filter paper however this would trap all precipitate and pieces of mineral which is not the desired outcome.

¹ Ministry of the Environment Government of Japan. (n.d.). Countermeasures against Acid Deposition. Retrieved December 19, 2015, from https://www.env.go.jp/en/earth/acid/cm.html

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^v Nalcor Energy. (2015, July 27). Scrubbers and Precipitators - Holyrood Thermal Generating Station. Retrieved January 11, 2015, from

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