"Impact of increased water acidity on coral reefs based on a study of the kinetics of $CaCO_3$ and HCl"

1. *The Context*

Coral reefs are a touristic attraction in many countries including Australia, the Red Sea and the Caribbean Islands. At times this seems to reduce their true importance. Their preservation is crucial for many forms of marine life which will become endangered or extinguished if coral reefs are destroyed (1). It is estimated that reef fish and mollusks feed between 30 to 40 million people yearly (2) while an overall of 500 million somehow depend on them (3). Food availability has increasingly turned into a global issue (4) and reducing resources will only worsen the current situation.

Coral reefs result from the secretion of corals and are underwater structures whose main component is $CaCO_3$ (5). One of the major problems these structures are facing is the decreasing pH of oceanic water as more CO_2 resulting from anthropogenic activities dissolves in it (7). Since the Industrial Revolution the pH of seawater has decreased in 0.1units (8) but recent studies provide solid evidence that this problem is becoming increasingly worrying: *"To the best of our knowledge, the ocean has never experienced such a rapid acidification. By the end of this century, if concentrations of CO_2 continue to rise exponentially, we may expect to see changes in pH that are three times greater and 100 times faster than those experienced during the transitions from glacial to interglacial periods. Such large changes in ocean pH have probably not been experienced on the planet for the past 21 million years"* (7). The production rate of $CaCO_3$ must exceed that of removal but this situation has been severely affected by current Ocean acidification and it is reported that a doubling of atmospheric CO2 results in 3-60% decline in the calcification rate (16).

2. *The research question*

The purposed of this investigation is to determine the order of the reaction between $CaCO_3$ and HCl.

The system under study is:

$CaCO_{3(s)} + HCl_{(aq)} -> CaCl_{2(aq)} + H_2O (l) + CO_{2(g)}$

The use of carbon dioxide dissolved in water would have made a better model as the resulting acid is of weak character while HCl is strong. This does impose important limitations as the dissociation of carbonic acid depends on an equilibrium which is affected by several variables. The situation is entirely different for hydrochloric acid which goes to full dissociation. Nonetheless, I opted for this acid because I tried in a pilot experience to work with dry ice as a source of carbon dioxide and it was too difficult to control amounts.

3. *Hypothesis*

Considering that the rate expression depends on concentration and $CaCO_3$ has an extremely low solubility I hypothesize that the order is going to be one for the concentration of added acid. This will be valid in as far as I work with initial rates.

In terms of this increment the destruction of coral reefs will be boosted as oceanic water becomes more acidic as a consequence of anthropogenic activities.

Carbonates are basic in nature therefore their solubility should be modified with varying acidic conditions. This was confirmed by literature (8):

pH	$p\alpha_2$	molar solubility
2	12.68	170
4	8.68	1.70
6	4.84	0.020
8	2.34	0.0011
10	0.49	1.4×10^{-4}

In pure water the solubility is very low: 0.15 g/100 mL at 25°C (9) but when acidity increases so does the solubility as hydrogen ions react with the base.

4. *The method*

I have used the method described in several texts (9) introducing some modifications:

1. Place a conical flask with a known mass of $CaCO_3$ on top of a balance.

2. Using a $25.0cm^3$ burette add $10cm^3$ of HCl of concentration 1.0M and loosely cover the flask with cotton to prevent mass losses.

3. Add 10g of CaCO3 which should have been previously sieved in order to work with the same surface area.

4. As soon as the acid is added start timing and replace the cotton.

5. Repeat the trial

6. Use another flask and repeat the procedure with remaining concentrations (1.5M, 2.0M, 2.5M and 3.0M)

I tried to use a water bath for controlling the temperature but it was very cumbersome and affected errors in mass.

As CO_2 is released, the balance shows decreasing masses because that of the acid remains constant. The modifications I have introduced include monitoring the temperature, pressure and controlling the surface area using a sieve. For the latter I used a kitchen sieve that allowed pebbles of intermediate size to be selected. I have also used a burette instead of a measuring cylinder for greater precision. I initially worked with pilot concentrations of HCl ranging 0.0001-0.0001M which are more representative of ranges presented by acid depositions. Unfortunately reactions were too slow at such low concentrations and I was unable to collect necessary data. Therefore I

gradually increased concentrations until reaching those shown in the method. These concentrations far exceed usual levels of acid depositions but allowed me to complete the investigation within time allocations.

5. *The raw data*

$10cm^3$ of 1.0M, 1.5M, 2.0M, 2.5M and 3 M HCl (for each trial)
The technician provided the solutions as the initial pilot experiences were too time consuming and I ran out of time. Therefore the solutions were provided by the technician and their concentrations are therefore considered as exact values.
10 g of marble chips of intermediate size as determined by 1.50 (±0.05cm) sieve
Mass of conical flask with HCl: 160.80 (±0.01g)
Mass of $CaCO_3$: 10.00 (±0.01g)
Volume of 2 M HCl: 40.00 (±0.05 cm^3)
Temperatures (averages as measured for each concentration) :
Initial: 24.5 (±0.1°C)
Final: 24.9°C (±0.1°C)
In spite of using the sieve I could observe though that not all particles had exactly the same size.
Pressure: 101.2 (±0.1kP) This value remained constant throughout the investigation

Qualitative observations: when acid made contact with pebbles bubbles and fizzing were observed. In the last two concentrations I also detected some fumes. The colour of the pebbles was not absolutely white and the 3.0M concentration was slightly yellowish.

Table 1. Overall mass in terms of time for 1M HCl

Mass (±0.01g)*	Time (± 1s)**
170.80	0
170.74	10
170.61	20
170.41	30
170.32	40
170.07	50
170.02	60
170.02	70
169.75	80
169.69	90
169.48	120
169.29	150
169.08	180
169.07	210
169.06	240
169.01	300

* The first value has an uncertainty of ±0.02g because the masses of container, cotton and acid were added to that of the carbonate.

** The recorded error corresponds to my measured time of reaction. The uncertainty of the instrument is negligible in comparison

Table 2. Overall mass in terms of time for 1.5M HCl

Mass (±0.01g)*	Time (± 1s)
170.80	0
170.69	10
170.47	20
170.41	30
170.24	40
170.14	50
169.96	60
169.83	70
169.69	80
169.63	90
169.43	120
169.24	150
169.03	180
169.01	210
169.01	240
168.99	300

Table 3. Overall mass in terms of time for 2.0M HCl

Mass (±0.01g)*	Time (± 1s)
170.80	0
170.63	10
170.26	20
170.21	30
170.18	40
169.99	50
169.86	60
169.76	70
169.65	80
169.58	90
169.38	120
169.17	150
169.08	180
168.99	210
168.98	240
168.97	300

Table 4. Overall mass in terms of time for 2.5M HCl

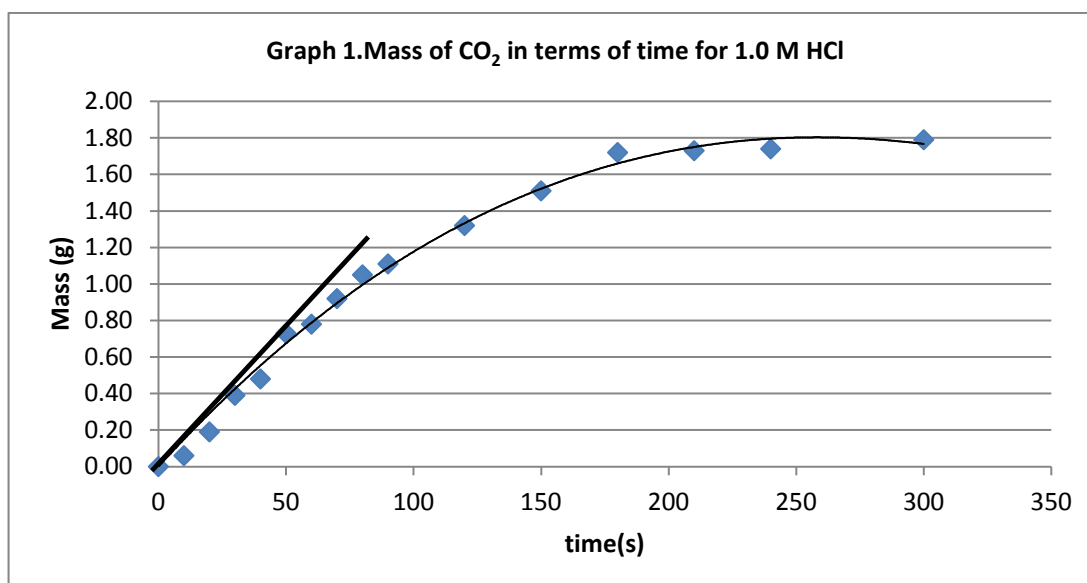| Mass (±0.01g)*	Time (± 1s)
170.80	0
170.49	10
170.18	20
170.12	30
169.99	40
169.86	50
169.67	60
169.59	70
169.61	80
169.51	90
169.35	120
169.22	150
169.01	180
168.98	210
168.98	240
168.97	300

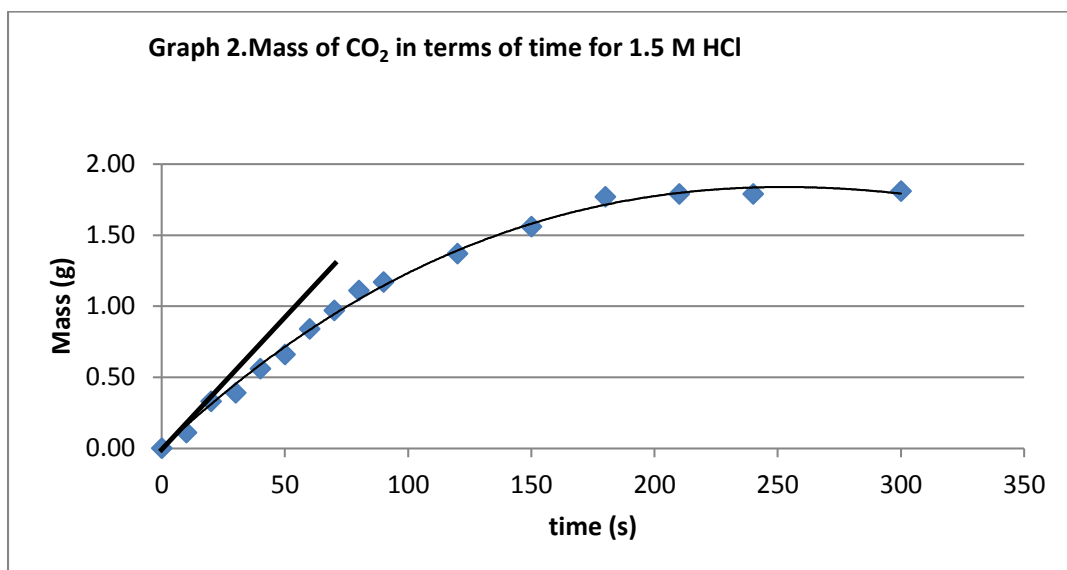Table 5. Overall mass in terms of time for 3.0M HCl

Mass (±0.01g)*	Time (± 1s)
170.80	0
170.39	10
169.91	20
170.07	30
170.01	40
169.79	50
169.69	60
169.62	70
169.59	80
169.53	90
169.43	120
169.32	150
169.21	180
169.09	210
169.05	240
168.96	300

6. _**Processed data**_

Table1. Mass of CO_2 in terms of time for concentrations of HCl under consideration

Time(± 1s)	1.0 M	1.5 M	2.0M	2.5M	3.0M
	Mass (±0.02g	Mass (±0.02g	Mass (±0.02g	Mass (±0.02g	Mass (±0.02g
0	0.00	0.00	0.00	0.00	0.0
10	0.06	0.11	0.17	0.31	0.41
20	0.19	0.33	0.54	0.62	0.89
30	0.39	0.39	0.59	0.68	0.73
40	0.48	0.56	0.62	0.81	0.79
50	0.73	0.66	0.81	0.94	1.01
60	0.78	0.84	0.94	1.13	1.11
70	0.92	0.97	1.04	1.21	1.18
80	1.05	1.11	1.15	1.19	1.21
90	1.11	1.17	1.22	1.29	1.27
120	1.32	1.37	1.42	1.45	1.37
150	1.51	1.56	1.63	1.58	1.48
180	1.72	1.77	1.72	1.79	1.59
210	1.73	1.79	1.81	1.82	1.71
240	1.74	1.79	1.82	1.82	1.75
300	1.79	1.81	1.83	1.83	1.84

I will proceed to find the initial rate of the reaction by finding the tangent to a point as close to the onset of the reaction as possible and always using the point corresponding to 30s.
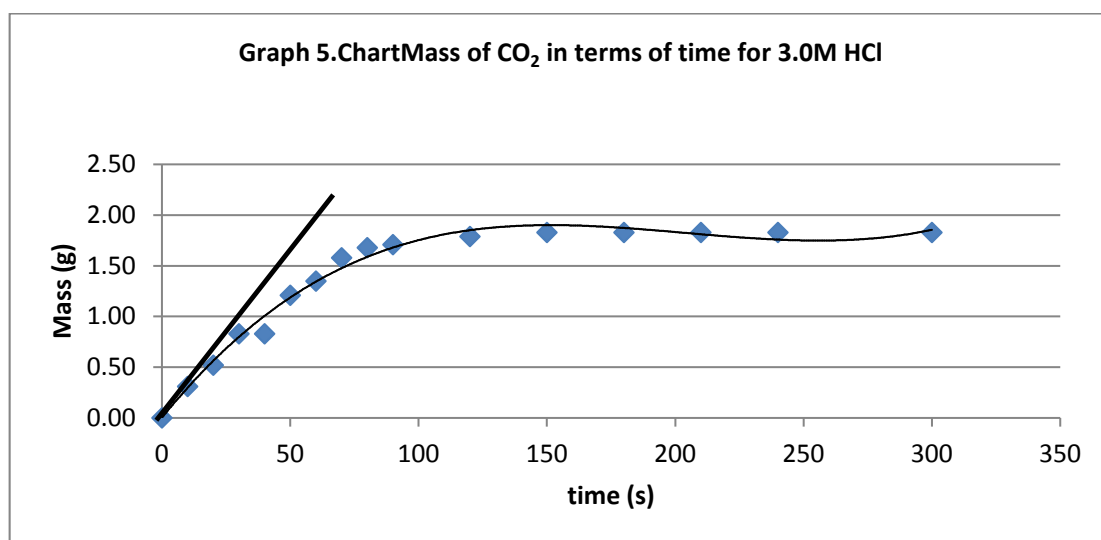

Graph 1.Mass of CO_2 in terms of time for 1.0 M HCl

Graph 2.Mass of CO_2 in terms of time for 1.5 M HCl

Graph 3.Mass of CO_2 in terms of time for 2.0 M HCl

Graph 4.ChartMass of CO_2 in terms of time for 2.5M HCl

Graph 5.ChartMass of CO_2 in terms of time for 3.0M HCl
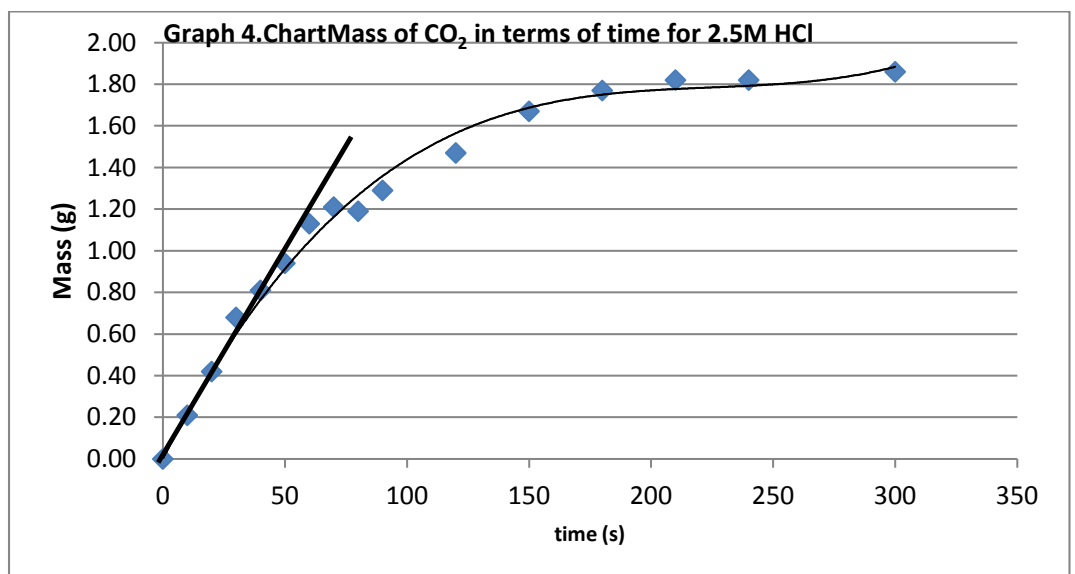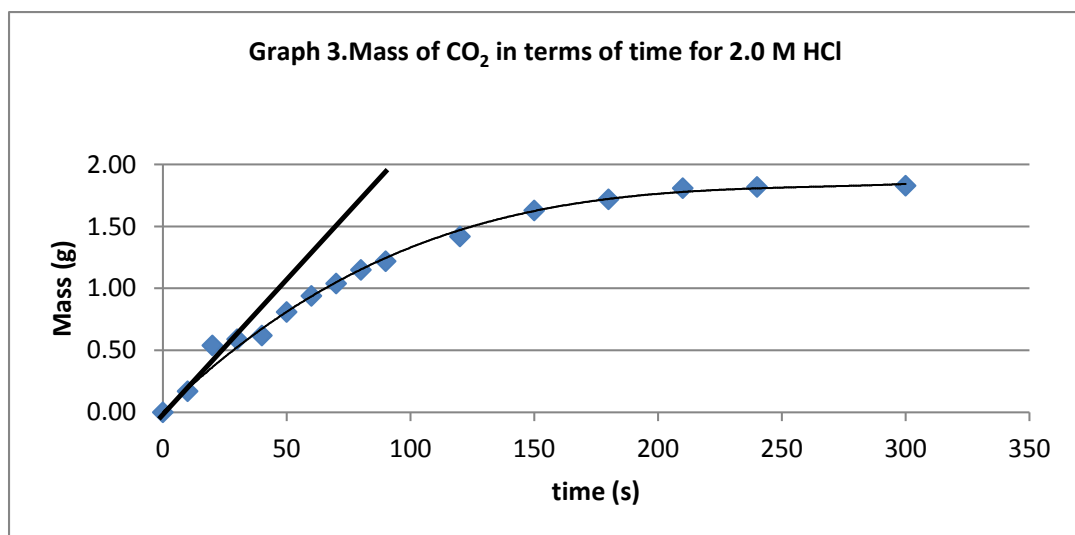
Table 6. Rates of reaction in terms of concentration of HCl

Concentration of HCl (M)	Rate of reaction (gs^{-1})*
1.0	0.0115
1.5	0.0139
2.0	0.0216
2.5	0.0221
3.0	0.0274

*Calculations were performed using Excel

Graph 6. Rates of reaction in terms of concentration of HCl

$R^2 = 0.9124$
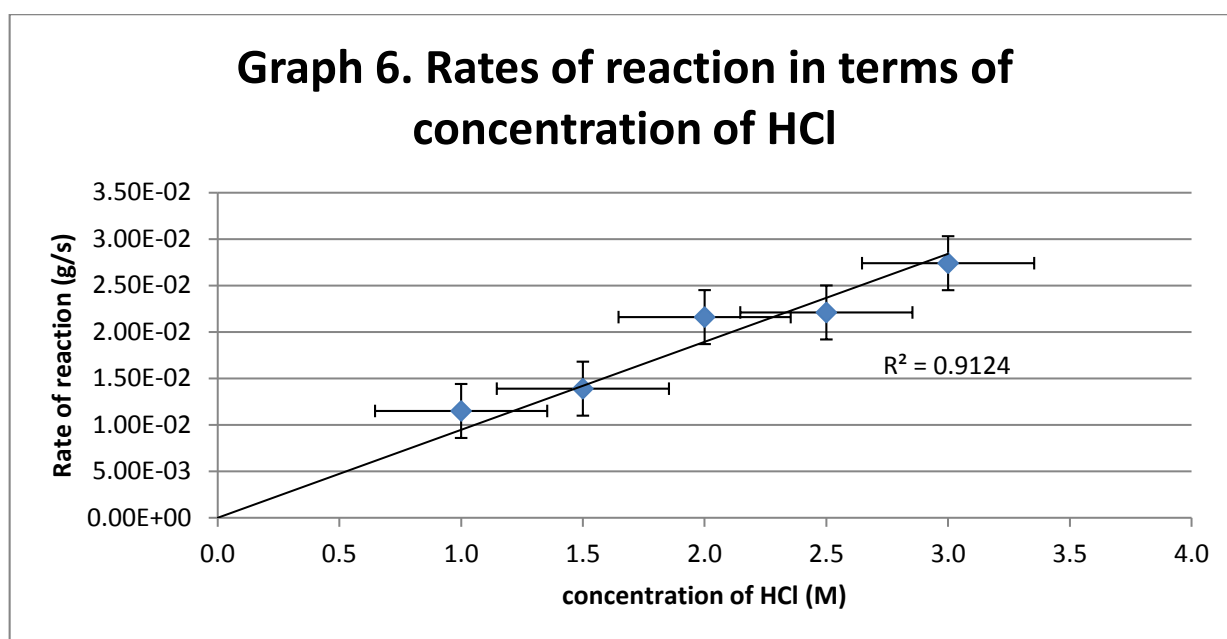
As it may be observed the trend is directly proportional which indicates order 1 (10). Considering R^2 is barely acceptable if we consider the optimum value is 1. The large errors are clearly shown by the error bars. It is quite evident that the investigation would be more reliable with a larger number of trials and this should be taken into account for future investigations. Graph 5 also shows a rather unsatisfactory shape but no other polynomial function offered a better alternative.

The rate expression would then be: Rate= k [HCl]

References report though that changing conditions could result in fractional orders as well (14)

I did not calculate k because this depends on several variables including the type of mineral (11)(14). This investigation could continue by using different minerals, increasing the number of trials and identifyng the k for each type.

Propagation of errors

The overall uncertainty in the order will result from adding the errors in rates and in time at 10 and 20s.

Error in rate= Error in mass + error in time

1.0M

%uncertainty in mass at 10s=$\frac{0.002}{0.06}$ x 100= 3.33%= 3%

%uncertainty in mass at 20s=$\frac{0.002}{0.19}$ x 100= 1.05%= 1%

%uncertainty in time at 10s=$\frac{1}{10}$ x 100= 10%

%uncertainty in time at 20s=$\frac{1}{20}$ x 100= 5%

The uncertainties in time are the same for the remaining trials.

Overall uncertainty for 1M= 19%

1.5M

%uncertainty in mass at 10s=$\frac{0.002}{0.11}$ x 100= 1.82%= 2%

%uncertainty in mass at 20s=$\frac{0.002}{0.19}$ x 100= 0.61%

Overall uncertainty for 1.5M= 17.61%= 18%

2.0M

%uncertainty in mass at 10s=$\frac{0.002}{0.17}$ x 100= 1.18%= 2%

%uncertainty in mass at 20s=$\frac{0.002}{0.54}$ x 100= 0.37%

Overall uncertainty for 2M= 17.61%= 17.37%= 17&

2.5M

%uncertainty in mass at 10s=$\frac{0.002}{0.31}$ x 100= 0.65%= 0.65%

%uncertainty in mass at 20s=$\frac{0.002}{0.62}$ x 100= 0.32%

Overall uncertainty for 2.5M= 17.61%= 15.97%= 16%

3.0M

%uncertainty in mass at 10s=$\frac{0.002}{0.41}$ x 100= 0.49%

%uncertainty in mass at 20s=$\frac{0.002}{0.89}$ x 100= 0.22%

Overall uncertainty for 3.0M= 17.61%= 15.71%= 16%

7. *Limitations of the investigation*

My method evidenced several limitations:

- The control of temperature for establishing the order of the reaction was limited. While I tried to produce a water bath using beakers the temperature did not remain constant during the experiment and was very difficult to work on top of the balance. This is a challenging situation as this is an exothermic reaction. As the impact of temperature on rate is exponential as shown by Arrhenius equation slight changes have serious impact. The school has one bath with automatic regulation but because we had to share it I opted for the older system. In the future it is clear it is worth waiting for the automatic device. This error is mostly systematic and therefore will not be eliminated by increasing the number of repetitions. Nonetheless, considering the rates were initial the impact of this error should not be substantial
- The largest error was in measuring time and actually was my reaction time the most significant, even when the time for adding the reactant also contributed. I measured this value using a virtual experiment (12). I believe though, that when repeating so many times and in a crowded lab this time is not likely to remain constant. This could improve if I had another student measuring my reaction time throughout the experiment.
- The surface area of the carbonate used was not constant. I used a sieve to homogenize it but you could see that surfaces of chips had different indentations so that even if size was

- fairly similar the surface area would still be different. Using powder would eliminate this error but concentrations would have to be adapted for the much faster reaction rate.
- During my calculations I did not take into account that part of the carbon dioxide could actually dissolve in the solution. This is less likely at higher temperatures given the inverse relationship between gases and temperature. This limitation is difficult to overcome at school level.
- My investigation does not consider transport processes such as diffusion of the acid to and away from the surface of the calcium carbonate. It is possible that the solution surrounding the surface has been neutralized.
- Due to time constraints I used concentrations of acid that exceed those usually reported for acid depositions. This does not invalidate the investigation as during the course we have learnt that the order of the reaction is reported as independent of the concentration. Some references seem to question this though (13).
- The acid was not standardized and hence any uncertainty in the concentration ignored. In future investigations the acid should be standardized.
- The colour of the carbonate was not white and it remains unclear whether the impurities interfered. As my school does not have carbonates of better quality I should purify the reagent before using it. This may prove time consuming but would eliminate errors resulting from possible interferences.

6   *Further considerations*

I have established the purpose of this investigation was determining the order for the reaction between $CaCO_3$ and HCl. I have validated my hypotheses as the order of the reaction is 1 for the acid and this means that as the concentration of acid increases the rate of the reaction will also increase. HCl is a strong acid and this implies that as the concentration of H^+ increases the rate of the reaction will change in a proportional way.

HCl is probably not the most suitable choice of acid as the problem I am researching is related to carbonic acid. Nonetheless is the one that presented less environmental risk and lab hazards. Because it is a strong acid my stance is that it provides an acceptable model for making some predictions involving increasing amounts of H^+ in oceanic water.

Considering my results it is evident that the problems with coral reefs will continue to increase unless carbon dioxide emissions are reduced. To have a more detailed understanding, this investigation should also research the changes that temperature introduces on rate of reaction. The increased carbon dioxide in the atmosphere also causes global warming and this will further contribute to the destruction of coral reefs as the reactions will be faster.

7 *Bibliography*

(1) http://library.thinkquest.org/CR0215471/coral_reef.htm (Accessed March 2012)

(2) http://oceanworld.tamu.edu/students/coral/coral4.htm (Accessed March 2012)

(3) http://www.lrrd.org/lrrd20/1/leng20008.htm (Accessed March 2012)

(4) http://www.wri.org/publication/content/8384 (Accessed March 2012)

(5) http://en.wikipedia.org/wiki/Coral_reef (Accessed March 2012)

(6) http://www.livescience.com/2135-increasing-acid-kill-coral-2050.html (Accessed March 2012)

(7) What is Ocean acidification?
http://www.pmel.noaa.gov/co2/story/What+is+Ocean+Acidification%3F (Accessed April 2012)

(8) Priorities for Research on the Ocean in a High-CO2 World (2004) from the international science symposium The Ocean in a High-CO2 World (Accessed March 2012)

(9) Lal, R. (2002): Soil carbon dynamics in cropland and rangeland. Environ. Pollution 116: 353–362.

(10) http://coralreef.noaa.gov/education/educators/resourcecd/ (Accessed March 2012)

(11) http://en.wikipedia.org/wiki/Calcium_carbonate#cite_note-0 (Accessed March 2012)

(12) Emerson and Hedges, Chemical Oceanography, Chapter IV, Carbonate Chemistry, http://courses.washington.edu/pcc588/readings/EH_IV_CarbSys.pdf (Accessed April 2012)

(13) Factors Influencing the Reaction Rate of Hydrochloric Acid and Carbonate Rock, Mumallah NA, SPE International Symposium on Oilfield Chemistry, 20-22 February 1991, Anaheim, California

(14) Kleypas J.A. and C. M. Eakin (2006), Scientists' perceptions of threats to coral reefs: Results of a survey of coral reef researchers, Bulletin of Marine Science, 80: 419-436.