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Extraction of Carbon Dioxide from Seawater by Ion Exchange Resin Part I: Using a Strong Acid Cation Exchange Resin

DENNIS R. HARDY
MEAGAN ZAGROBELNY
HEATHER D. WILLAUER
FREDERICK W. WILLIAMS

*Navy Technology Center for Safety and Survivability
Chemistry Division*

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EXTRACTION OF CARBON DIOXIDE FROM SEAWATER BY ION EXCHANGE RESIN PART I: USING A STRONG ACID CATION EXCHANGE RESIN

1.0 BACKGROUND

Extracting carbon dioxide from seawater is part of a larger project to create liquid hydrocarbon fuel from seawater using the CO₂ as a source of carbon. As a source of electricity, excess nuclear power on ships can initially be used. This electricity can be used to electrolyze the seawater, allowing hydrogen to be collected. This hydrogen, if reacted catalytically with carbon dioxide, could then form oil. This would provide an alternative energy source to fossil fuels. This process is intended to especially benefit the U.S. Navy, which uses a large amount of fuel to power its ships and aircraft. The fuel cost for the Navy was in excess of \$1.6 billion in 2004. Because this fuel is intended for use by the U. S. Navy and because the Navy nuclear ship-bound electricity is involved in its creation, it is necessary that this process is able to be performed aboard ships at sea.

2.0 INTRODUCTION

When carbon dioxide gas is dissolved in water, it undergoes several reactions. In the first, gaseous carbon dioxide becomes dissolved as in equation 1.



The dissolved carbon dioxide (CO₂ (l)) then reacts to form carbonic acid as shown in equation 2.



The carbonic acid then ionizes to form bicarbonate ions, which ionize further to form carbonate ions in equations 3 and 4.



The equilibrium for these reactions coexists with the equilibrium for the ionization of water.

The second source of carbonate alkalinity is the dissolution of rocks in contact with the sea over geological time frames. This can be represented most directly by the following equilibrium reaction shown in equations 5 and 6 where X is typically (Ca, Mg, Na, etc.) to generically represent any mineral matter.





This is also the equilibrium from biological sources for carbonate and bicarbonate in the sea. Under the basic pH conditions that exist in seawater most of the carbonate from these sources, rock and biological, is converted to bicarbonate. From our previous observations with seawater and gaseous carbon dioxide under STP equilibrium conditions, we observed that most of the ocean's carbonate and bicarbonate arise from dissolved species of rock and biological origin and not atmospheric origin. Regardless of the source, however, the problem can be viewed primarily as maximization of the CO₂ recovery from seawater which means maximum recovery of the bicarbonate species.

Carbonate alkalinity is complicated by four factors. The first is the ionization of boric acid. The second is the ion pairs formed between major cations and carbonate or bicarbonate ions. The third factor is the presence of weak acids, such as hydrogen sulfide, in organic-rich waters. The final factor is the existence of carbamino-carboxylic acids, which form through the reaction of carbon dioxide and amino acids. Changes in salinity influence the concentration of reactants in all reactions, both because of complexing of reactants and because activity coefficients are functions of ionic strength. The concentrations of the various forms of carbon dioxide can theoretically be calculated by pH and alkalinity [1].

Through ion exchange, waters with a high degree of salinity can be effectively deionized. Because in principle equivalent amounts of acid and base are required per equivalent of salt removed, the economic advantages of ion exchange decrease as the salinity of the water increases. There are four main requirements for ion exchange to be used economically. First, the exchangers used must be capable of being regenerated with cheap acids and bases at nearly theoretical levels. Secondly, the exchangers must operate at high capacity. Thirdly, the resins must be freed of waste regenerants without exhausting the resin and with only small amounts of water. Finally, waste regenerants must only cause a minimal disposal problem. Originally, weak electrolyte resins were only used along with strong electrolyte resins, but a technique has been developed to use weak electrolyte ion exchange resins in a reverse deionization system. This system allows salts in brackish water and seawater to be changed to alkalinity with little leakage from one resin bed to the next. This resulting alkalinity may then be removed with typical weak acid cation exchange resin beds. All resins used can be easily regenerated with cheap acids and bases [2].

In the normal sense of ion exchange, cations are exchanged for hydrogen ions, and anions are exchanged for hydroxide ions or bicarbonate ions. Ion exchange as a method of desalinating water has three major advantages. The first is its ability to be operated at high flow rates. Second is the fact that it can be operated intermittently without losses in efficiency. The third major advantage is that it can be used for a wide variety of water compositions due to the many types of ion exchange resins, which are commercially available. When considering the cost and practicality of using ion exchange, the regeneration and rinse time, which can sometimes be the limiting factor of whether or not a process can be effectively used, must be considered. It is important that ion exchange processes take full advantage of the resin's capacity, in order that the rinse time can be minimized [3].

An application of ion exchange resins is the removal of electrolyte resins from water by the combined use of cation and anion exchange resins. Cation exchange resins exchange the cations in water for hydrogen ions, and anion exchange resins exchange the anions in water for hydroxide ions. By combining these two processes, all ions can be removed from water. Various combinations of cation and anion exchange resins are used for different purposes. Ion exchange is a simple and flexible technique [4].

At the National Energy Technology Laboratory (NETL, Morgantown, WV) the capability of anion exchange resins to regenerate ammonia from ammonium bicarbonate was demonstrated. Ammonia was saturated with carbon dioxide as shown in equation 7.



Then the resulting bicarbonate was passed through a column containing resin, causing the pH of the solution to increase from 9.1 to 11.2. The basicity of the amine group in the resin (R) caused the ammonium bicarbonate to decompose (equation 8).



Some of the ammonia then reacted with the remaining ammonium bicarbonate to form ammonium carbonate. When the solution was recycled to absorb CO₂, it only absorbed 38% of the CO₂ originally absorbed (equation 9) [5].



Using the National Energy Technology Laboratory (NETL) work as a starting point, this report describes the attempt to use a single strong acid cation exchange resin to directly acidify seawater to the minimum pH which would allow the dissolved bicarbonate to re-equilibrate to CO₂. This CO₂ would be removed by vacuum or by air sparging. Both of these techniques can easily remove gaseous CO₂ from the water.

Johnson, et al [6] have shown that when the pH of seawater is decreased to 6 or less that the entire carbonate/bicarbonate equilibrium is shifted to the left so that total CO₂ exists only in the dissolved gas form. They demonstrate that in this dissolved gas form the total removal is easily accomplished by a simply nitrogen sparge for a brief period through the acidified seawater. This has been the basis of all standard quantitative ocean CO₂ measurements for the last 25 years. This finding has been confirmed in our laboratory in a separate set of experiments, that lowering the pH of seawater to 6 or less (by any means) allows one to easily sparge or degas the entire carbonate/bicarbonate concentration in seawater.

3.0 EXPERIMENTAL

Ion exchange resin was obtained from Aldrich Chemical Co. The resin was an Amberlite IR-130 (plus) ion-exchange resin, sodium form (gel-type resin, sulfonic acid functionality, useful in catalytic applications). Before any experiments could be performed using the strong acid cation exchange resin, it was changed from the sodium form to the acid form by adding 5-10%

hydrochloric acid to approximately 50 grams of the resin. The resin was mixed for several hours using a magnetic stirrer. The resin beads then were rinsed with deionized water (Millipore Q grade) to remove excess acid.

Synthetic seawater was used in all experiments. The synthetic seawater was made by deionized water and Instant Ocean sea salt combined in a large jug with a concentration of 41.1 g of Instant Ocean per liter of deionized water. The synthetic sea salt (Instant Ocean) was obtained from a local aquarium supply company. When the seawater was initially made it was mixed for several hours using a magnetic stirrer. Before each experiment, the seawater was shaken vigorously for approximately one minute to dissolve any salts which may have precipitated out. The measured pH of the synthetic seawater was about 7.8. All pH measurements were conducted with a Fisher combination glass electrode.

A stainless steel column (9 mm ID by 30 cm long) with stainless steel pressure fittings was packed with approximately 15 g of the acidified resin. The resin beads are spherical (about 0.7 mm diameter) and were retained in the column by a stainless steel screen with an opening of about 0.5 mm. This column was attached to a pump and a glass flow cell using Teflon tubing, so that water could be pumped through the column containing resin, into the flow cell where the pH was measured, and finally out into a waste water container. The liquid pump was a stainless steel single piston from ISCO, Inc. The glass electrode flow cell was made of Teflon from Fisher Scientific. The pH of the water in the flow cell was constantly being measured with a recording combination glass electrode pH meter. The recorder was a Kipp and Zohen set to 200 mV full span.

As seawater flowed through the column of resin, in its initial acid form, the pH of the effluent seawater decreased significantly, and as the resin became spent the pH increased. The minimum pH was noted and recorded by hand during each experimental run. For the **first** set of experiments, the influent water was switched from the seawater to the regenerant, deionized water, once the resin was exhausted. This is the point where data begins to be collected and is shown as Run #1 (12-Dec) in Table 1. The pH of the influent deionized water was between pH 6.0 and 7.0. When the switch was made from Instant Ocean Seawater (IO) to deionized water (DI), the effluent pH began to decrease until it equilibrated to the pH of the influent DI pH.

In later experiments (Run #7 in Table 1), the influent was switched from seawater to deionized water once the effluent seawater pH reached 6.0, since water above this pH is not acidic enough for CO₂ to be converted from bicarbonate ion and physically removed from the seawater. Deionized water was pumped through the column to regenerate the resin at 10 mL/min. The deionized water was pumped for different lengths of time, varying from 17 hours to 30 minutes, to see if that affected how completely the resin was regenerated. The resin was challenged again with seawater. The same column of resin was used for all experiments; the influent water alternated between seawater and deionized water. The charts produced during the experiments were used to collect and interpret data and all the major useful raw data are given in Table 1 as explained below.

4.0 RESULTS

The volume of deionized water was calculated based on the most recent experimentally measured flow rate and actual measured times. In general, the minimum pH values were read from the pH meter and recorded during the experiment, rather than being collected from the chart produced by the recorder. The chart was used as a convenient constant timer during the experimental runs.

In order to calculate the volume of seawater with a pH below 6, the chart scale was calculated using the minimum pH and the distance between the middle of the chart (calibrated to pH 7) and the minimum pH: $\text{scale} = (7.00 - \text{minimum pH})/\text{distance}$. This scale was used to mark a horizontal line on the chart where the pH is equal to six. The line drawn by the chart recorder intersected this horizontal line twice, once when the pH fell and once when the pH rose; the distance between these two intersections was measured. The volume was calculated using this distance, the chart speed, and the flow rate: $\text{volume} = \text{distance} * \text{flow rate} / \text{chart speed}$. The volume of seawater below pH 6 per gram of resin was found by dividing the volume of seawater explained above by 15 grams, the approximate mass of the resin in the column. The volume of deionized water per volume of seawater below pH 6 was found by dividing the two volumes described previously.

Table 1. Summary of all raw experimental data recorded. DI refers to the Deionized Water. IO refers to the Instant Ocean Seawater. The initial pH of the IO was about 7.8.

Co (1) Run #	Col (2) Date	Col (3) Time DI (hrs)	Col (4) Volume DI (mL)	Col (5) Minimum pH	Col (6) Volume IO below pH 6 (mL)	Col (7) Volume IO below pH 6 per gram of resin (mL/g)	Col (8) Volume DI per volume IO below pH 6
1	12-Dec	6	3200	3.89	45	3	71.1
2	14-Dec	17.3	9600	3.31	46	3.07	209
3	16-Dec	12.3	6800	3.97	34	2.27	200
4	19-Dec	9.8	5000	4.35	25	1.67	200
5	19-Dec	2	1000	5.75	8.4	0.56	119
6	19-Dec	1	500	7.03	0	0	n/a**
7	21-Dec	1	500	6.16	0	0	n/a
8	21-Dec	0.5	250	7.42	0	0	n/a
9	21-Dec	1	500	7.08	0	0	n/a
10	6-Jan*	3.4	1850	4.34	21.6	1.44	85.6
11	6-Jan	2	1080	4.85	18	1.2	60
12	6-Jan	1	540	5.67	10.8	0.72	50
13	6-Jan	0.5	270	6.46	0	0	n/a
14	11-Jan	7.5	4374	3.36	48	3.2	91.1
15	11-Jan	2	1152	5.18	21	1.4	54.9

*On January 6 and all experiments afterwards, the influent was switched to deionized water as soon as the pH reached 6.0.

**n/a Signifies that the value cannot be calculated since that would involve dividing by zero.

Table 1 begins after the initial IO challenge to the initially acidified resin which was soaked in 5-10% HCL followed by DI water wash before it was packed into the column. Run #1 (12-Dec) signifies the start of the first DI water regeneration and the volume and time regeneration is in columns 3 and 4. Column 5 refers to the minimum pH achievable on the next switch to IO, and column 6 is the volume of IO effluent below pH 6.0. The final two columns are calculated based on the weight of the resin (constant at 15 grams) and the volume of regenerant DI per volume of effluent IO below pH 6.0 for that particular run. Run #2 (14-Dec) gives the data beginning with the next subsequent switch to regenerant with DI.

Figure 1 shows the effect of the volume of regenerant DI on subsequent IO challenges. It is apparent that the minimum volume of DI regenerant needed to achieve subsequent maximum IO acidification is about 2000 mL of DI. Greater regenerant volumes did not increase the maximum IO acidification possible on subsequent runs.

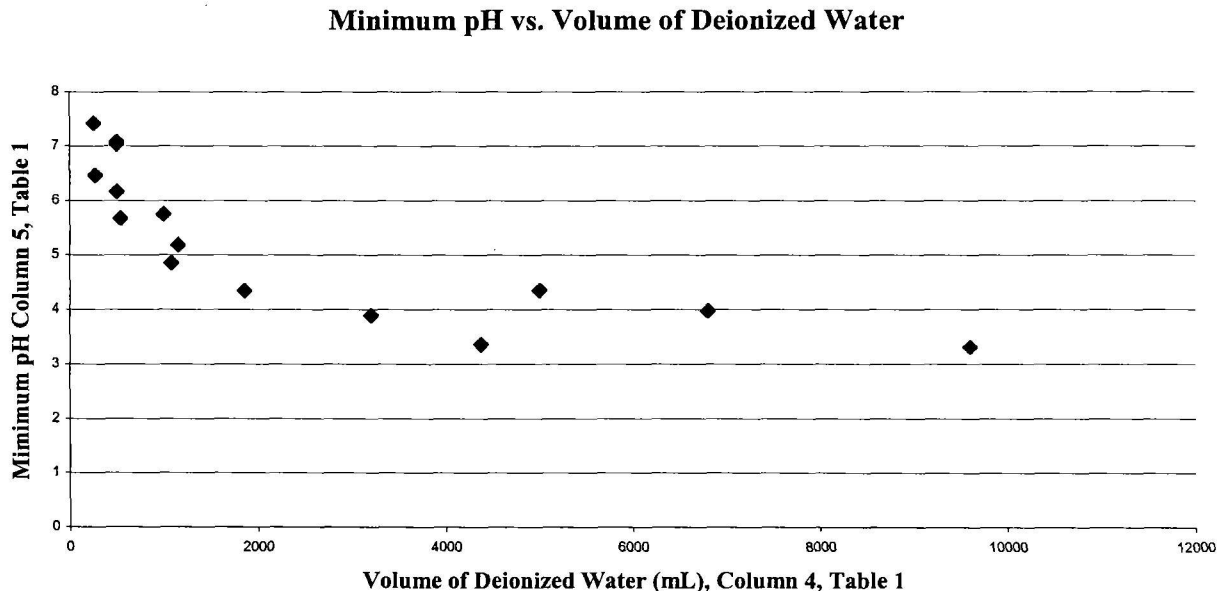


Figure 1. Typical graph showing the effect of the regenerant (deionized water) volume on the completeness of the regeneration, based on minimum pH that was achievable when synthetic seawater was flowing through the “regenerated” resin.

Volume of Deionized Water (mL) vs. Volume of Seawater Below pH 6 (mL)

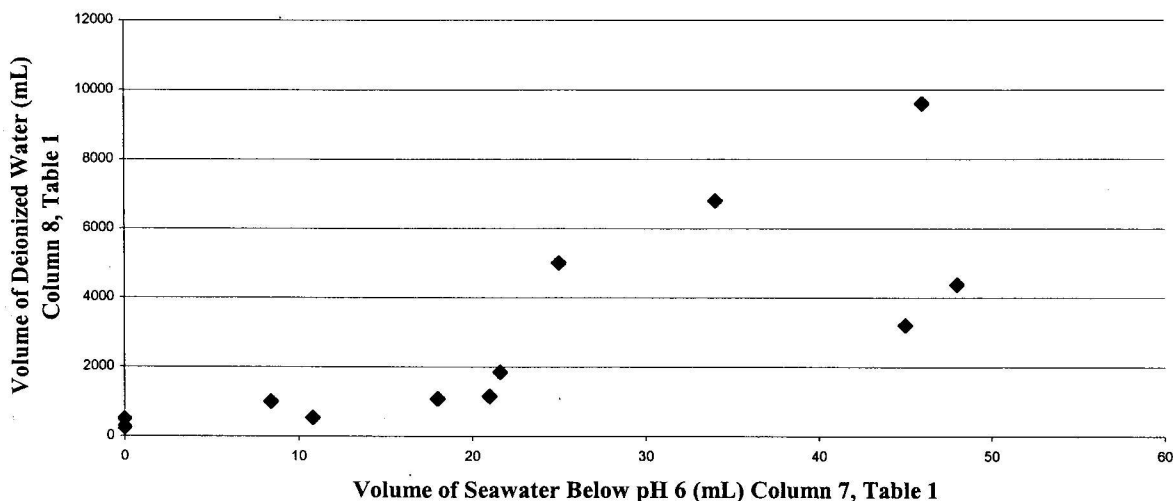
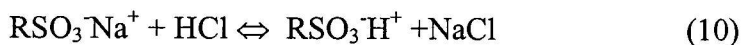


Figure 2. Typical graph showing the amount of deionized water needed to regenerate resin in order to acidify a certain amount of seawater.

Figure 2 shows the phenomenon that with greater amounts of deionized water regenerant, greater volumes of seawater in subsequent runs could be acidified below the needed pH of 6.0. The trade off is time and fresh water volume verses amount of acidified seawater (and CO₂ recovery) in each subsequent run. For this work (and for actual real world scale up) it is easier to simply add additional ion exchange resin to increase CO₂ recovery rather than add additional deionized regenerant.

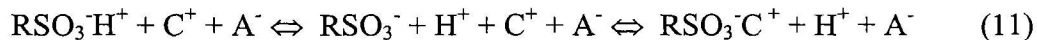
The data from Table 1 were used to conclude that this simple method was capable of acidifying seawater below pH 6.0 using a relatively small amount of resin (see volume IO per gram of resin), as long as significant amounts of regenerant deionized water had been used just prior to the seawater acidification step. Furthermore, the raw data in Table 1 serve to demonstrate clearly that the process is repeatable over long time periods with no loss in ion exchange ability to cycle through the simple process.

The ion exchange resin comes in sodium form, which means that a sodium ion is attached to the end of the resin chain (R--SO₃⁻--Na⁺). When the resin (R) is pretreated by adding hydrochloric acid, the sodium on the resin is replaced by the hydrogen in the acid as shown in equation 10.



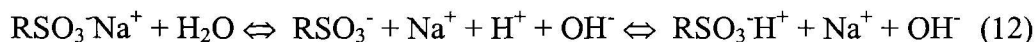
No chemical reactions should occur when the resin is rinsed with deionized water; this only serves to rinse any excess acid off the remaining beads, to allow the most accurate pH measurement to be recorded.

When seawater flows through the resin, this process is essentially reversed. The major monovalent cations in seawater, sodium and potassium, are replaced by the hydrogen ions in the resin, thus acidifying the seawater (equation 11).



C^+ and A^- represent all monovalent ions found in seawater. When all the hydrogen ions in the resin have been replaced by cations from the seawater, the resin is expended and can no longer acidify seawater. The purpose of regenerating the resin is to again replace these cations with hydrogen ions.

The resin is usually regenerated with a strong acid, which is what occurred when the resin was pretreated. In these experiments, deionized water, acting as a weak acid, was used as a regenerant (equation 12).



Deionized water acts as a weak acid, and so re-acidified cations occur very slowly and larger amounts of deionized water are needed to regenerate the resin.

Many dynamic regeneration attempts were successful. When the volume of deionized water was greater, the volume of seawater below pH 6.0 was also greater, making the regeneration more complete. When the influent water was switched to deionized water immediately after the pH reached 6.0, a larger volume of seawater acidified, again making the regeneration more successful. The amount of deionized water needed to regenerate the resin was significantly greater than the amount of seawater acidified by the resin.

5.0 CONCLUSIONS

This experiment dealt with the simplest ion exchange and regenerate system possible: only one column of resin was used, and water served as the regenerant. This simple system was able to acidify seawater, and this work provides quantitative evidence of this system's success, as shown by the volume of Instant Ocean acidified per gram of resin.

For this, the simplest ion exchange resin system possible, the volume of regenerant deionized water per unit weight of the resin appears to be much greater than the volume of acidified seawater per unit weight of resin. Using the amount of CO_2 recoverable per unit volume of seawater and unit weight of resin, the unit volume of hydrocarbon that can theoretically be generated from this process can be determined. Further calculations of the amount of regenerant deionized water required, show the volume ratio is approximately 5000:1, where the second value is the relative volume of hydrocarbon.

Further work using more complex systems could show that other systems are more efficient and practical. As an example of this, experiments were performed using pH 7.0 seawater. The neutral seawater proved to be an unsuccessful regenerant, but many possibilities remain for

further experimentation. In addition to experimenting only with different regenerants, experiments using more than one type of resin bed could be particularly useful.

6.0 REFERENCES

1. Riley, J. P., and Chester, R. "The Dissolved Gases in Sea Water: Carbon Dioxide." Introduction to Marine Chemistry. London: Academic Press, 1971. 121-151.
2. Kunin, Robert. "Deionization of Water IV Desalination of Brackish Waters." Amber-Hi-Lites 89 (Sept. 1965).
3. Kunin, Robert. "Deionization of Water V Desalination of Brackish Waters." Amber-Hi-Lites 90 (Nov. 1965).
4. Kunin, Robert. "Applications of Ion Exchange VII Deionization of Water." Amber-Hi-Lites 98 (Mar. 1967).
5. Huang, Houping, and Shih-Ger Chang. "Method to Regenerate Ammonia for the Capture of Carbon Dioxide." Energy and Fuels 16 (2002): 904-910.
6. Johnson, K. M., King, A. E., Sieburth, J. "Coulometric Total CO₂ Analyses for Marine Studies: An Introduction" Marine Chemistry 16 (1985): 61-82.