THE REGENERATION OF MIXED ION
EXCHANGE RESINS BY
ELECTRODIALYSIS

by

DONALD OWEN CHESSMORE

B.S., Stanford University
(1950)

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

(1952)

Signature of Author ....
Department of Chemical Engineering

Certified by ....
Thesis Supervisor

....
Chairman, Departmental Committee on Graduate Students

May 16, 1952

ABSTRACT

THE REGENERATION OF MIXED ION EXCHANGE RESINS BY ELECTRODIALYSIS

by

DONALD OWEN CHESSMORE

Submitted to the Department of Chemical
Engineering on May 16, 1952 in partial
fulfillment of the requirements for the
Degree of Master of Science

Mixed bed deionization has become an important industrial operation. The use of a mixed bed introduces a regeneration problem. The techniques which are currently being used to regenerate a mixed resin all involve physical separation of the mixture into its component resins and then regenerating them separately by treating them with a solution containing the ions originally present in the fresh resin.

It was the purpose of this thesis to investigate the possibility of using electrodialysis to regenerate a mixed resin without separation. The membranes used in the cell were cellophane, filter paper, and ion exchange membranes. The runs were made on a mixed resin in either the sodium chloride or magnesium sulfate form. Several combinations of membranes were used.

ampton (Chem Eng) Nov 7, 1952

The two best methods of regeneration both involved the ion exchange membranes. The first of these methods used one anion and one cation membrane in the cell. This method had a good current efficiency but a very low rate of cation removal. The second method used two anion membranes. The resin was given an acid wash before being electrodialyzed. This method successfully removed both ions from the resin but has the disadvantage of increased cost due to the cost of acid.

The results indicate that it is possible to regenerate a mixed ion exchange resin by electrodialysis and that with some improvement it would be an economical method to accomplish this regeneration.

Thesis Supervisor: Prof. E. R. Gilliland
Title: Professor of Chemical Engineering

Chemical Engineering Department
Massachusetts Institute of Technology
Cambridge, Massachusetts
May 16, 1952

Professor Joseph S. Newell
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir;

In accordance with the regulations of the Faculty, this thesis entitled, "The Regeneration of Mixed Ion Exchange Resins by Electrodialysis" is hereby submitted in partial fulfillment of the degree of Master of Science in Chemical Engineering.

Respectfully submitted,

Donald O. Chessmore

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Professor E. R. Gilliland for his helpful advice and suggestions in supervising the work on this thesis.

The resins and ion exchange materials were kindly donated by Ionics Incorporated.

CONTENTS

SUMMARY

The development of organic ion exchange resins of the anion as well as the cation variety have made possible a new ion exchange operation which is becoming industrially important. This operation is mixed bed deionization and is accomplished by passing the solution to be treated through a bed containing a mixture of an anion and a cation resin. The deionized product from a single mixed bed unit has a conductivity equivalent to that of distilled water.

The present techniques used to regenerate a mixed ion exchange resin involve the separation of the mixed resin into its two component resins and then regenerating each of the resins separately by treating it with the proper wash solution. Because special equipment is necessary to regenerate the resins by this separation technique, it would be desirable to be able to regenerate a mixed resin without first having to separate it. The purpose of this thesis was to investigate the possibility of regenerating a mixed resin by electrodialysis. Electrodialysis is a process very similar to electrolysis except that in electrodialysis two membranes are placed between the electrodes of the cell. These membranes allow the flow of ions to the electrodes but keep the solution being treated from mixing with the solutions at the electrodes. The cell for electrodialysis has three parts, the center section for the solution being treated and the two end sections for the electrode solutions.

Electrodialysis has been used on a laboratory scale to purify clays. Since most clays are naturally occuring ion exchange materials, these experiments were indications that electrodialysis could be used as a method for regenerating a mixed ion exchange resin without having first to separate the mixture into its two component resins.

Four different types of experimental runs were made in this investigation. The runs differed in the membranes used in the cell. The four different membrane pairs used were the following; both cellophane, both filter paper, both anion exchange membranes, and one anion and one cation membrane. These ion exchange membranes are made by imbedding an ion exchange resin in a plastic matrix to form a thin sheet. The sample of mixed resin to be treated was placed in the center section of the cell between the membranes. The resin was in the salt form in each case. The salt used was sodium chloride except for two runs which were made with the resin in the magnesium sulfate form. The electrodes used in the cell were platinum foil. The electrical power was obtained from the laboratory direct current system. During the runs which were five or six hours in length, a record of the cell current was kept. The electrode solutions were removed from the cell after each hour of operation and analyzed for the ions being removed from the resin. The solutions used in the electrode sections at the start of each hour were dilute acid and base. The runs were made at constant voltage but the voltage was changed between runs to determine the effect of current on current efficiency.

The electrodialysis operation was successful in regenerating the mixed resin. The rate of regeneration and the current efficiency varied greatly with the type of membranes used in the cell. The runs made using filter paper and cellophane in the cell were the least satisfactory due to the low current efficiency. In contrast to this low efficiency with filter paper and cellophane, the runs made with ion exchange membranes had a very satisfactory current efficiency. The runs made with one anion and cation membrane, and the runs made with filter paper and cellophane membranes had a very low rate of cation removal as compared to the rate at which anions were removed. To try to solve this problem one run was made with a resin which had been given an acid wash before being electrodialyzed. This wash replaced the cation of the resin with hydrogen ion. The membranes used for this run were both anion exchange membranes. This method does solve the problem of low cation removal and promises to be a good method of completely regenerating the mixed resin. The runs made with one anion and one cation membrane also are promising even with the low rate of cation removal. This is a disadvantage because as the regeneration nears completion the anions will be exhausted and with only the cations to be removed the current efficiency will be very low and the power consumption high. The acid wash run has one disadvantage since there is an acid cost to be added to the cost of regeneration which makes this method less attractive as a technique of regenerating a mixed resin.

From a cost point of view, the cost of regenerating a mixed resin by electrodialysis will be about the same as the cost of regeneration by separation techniques. There is another factor to be considered and that is the ease of regeneration and the cost of the necessary equipment. Both of these factors would seem to make the regeneration by electrodialysis more attractive than regeneration by separation. No matter what this last effect actually does to the cost figure, the regeneration of mixed resins by electrodialysis is promising enough to merit further study and consideration.

INTRODUCTION

The phenomenom which is called ion exchange is not a recent discovery. For centuries it has been known that water was purified by running through soils. The ability of certain clays and soils to absorb ions from a solution of one salt and to replace those ions with ions from a different salt has been recognized and understood since the middle of the nineteenth century. Ion exchange however, remained a laboratory curiosity until the beginning of this century. The growth of ion exchange in the last few years has been very fast and today it is a widely used and important industrial operation.

An ion exchange material is a substance which has a molecule of sufficient size to make it insoluble in water but which has ionizable groups present as a part of the large molecule. Any such substance can undergo ion exchange. When this ion exchange material is placed in a strongly polar medium such as water, the net attractive forces binding the ion to the large molecule are diminished to such an extent that an exchange of this ion for another ion from the solution becomes quite possible. It is this process that is called ion exchange.

One recent development in the technology of ion exchange has greatly increased the number of practical applications of the process of ion exchange. This development was the discovery of organic polymers which could undergo an ion exchange reaction.

These organic polymers or resins owe their ability to exchange ions to the presence of certain substituted groups on the repeating unit of the long chain molecule. Through the proper choice of this substituted group, the resin can be made to exchange either anions or cations. The substituted groups which are responsible for cation exchange are primarily sulfonic acid, phenolic, or carboxyl groups, while the anion exchanging groups are either amines or polyamines. With this choice of substituted groups it is possible to make a resin which will fill the requirements of a specific job. The factors which can be controlled by changing the substituted group are the exchange strength and the ions which can be exchanged.

One important industrial use of ion exchange is the operation called deionization. Deionization is the simultaneous removal of both anions and cations from a solution. This operation can be done by one of two different techniques. The solution can be passed through successive beds which are alternately anion and cation resins until the desired degree of deionization has been accomplished. The large number of beds is necessary because the exchange is an equilibrium reaction and only part of the exchange is possible in one unit. In the second method of deionization the solution to be treated is passed through a single bed which contains a mixture of an anion and a cation resin. The two resins forming the mixed resin must both be strong resins if the deionization is to be a complete one. Because the rates of exchange with two resins are fast and about equal the deionization proceeds rapidly and at neutral pH.

A comparison of the two methods of deionization shows that the mixed bed system is superior to the successive beds system in so far as the actual deionization is concerned. A single mixed bed can accomplish a more complete deionization than is possible with several pairs of alternate anion and cation beds. This means that a single bed will provide a considerable saving in space and equipment cost over the group of successive beds which would be required to do the same job of deionization. The mixed bed system also has the advantage of having a neutral pH throughout the exchange process. In the successive beds the resins used are in the hydrogen and hydroxyl forms. If the solution is to be treated first by the cation resin a strong-acid cation resin and a weak-base anion resin are used. The solution is strongly acidic when it leaves the cation bed but the acid is neutralized after passing through the anion bed. This is called conventional deionization. The opposite of the above is also used and is called reverse deionization. In this case the solution first passes through a strong-base anion resin and then through a weak-acid cation resin. The solution is strongly basic after leaving the anion bed. The neutral pH at which the deionization takes place in a mixed bed can be a big advantage in cases where the solution to be treated is affected by a pH which is not neutral. One example of this is the deionization of sucrose solutions which would be inverted in an acid solution. It is usually possible however to use either normal or reverse deionization since only rarely would there be a case in which the solution to be treated would be affected in both acidic and basic solutions.

A mixed bed deionization system presents a serious regeneration problem. It is not possible to regenerate a mixed resin by the usual technique of washing the resin with a solution of the ions originally present on the fresh resin since these two ions are hydrogen and hydroxyl ions. This problem is solved by separating the two resins and treating each one separately. The cation resin is given an acidic wash and the anion resin is given a basic wash. The regenerated resins are then remixed and are ready to be used again. This method of regeneration introduces the problem of separating the two resins. Two techniques are used. If the two resins particles have a difference in diameter they may be separated by screening. A difference in density can also be utilized to accomplish a separation. A backwash will hydraulically separate two such resins. The hydraulic separation is usually used because it is possible to build a bed in which the resins can be hydraulically separated and treated and yet not remove the resin from the bed. This difficulty of separation is not a a problem in the alternate bed system since the beds are always separated and so can be treated in the normal way to regenerate them.

The difficulties encountered in regenerating a mixed ion exchange bed by separational techniques make it desirable to develop a method where by a mixed resin could be regenerated without separation. It was the purpose of this thesis to investigate the possibilities of regenerating a mixed ion exchange bed by electrodialysis. In this case regeneration means replacing the anions and cations of a spent resin with hydrogen and hydroxyl ions and so return the resin to its original form.

Dialysis is a separational technique which accomplishes a separation of two materials from a solution by allowing one material to move through a membrane and out of the solution under the influence of a concentration gradient while the other material remains behind because its size is too great to permit it to pass through the membrane. Dialysis is a slow process and so electrodes are often added to increase the rate of diffusion. The process when electrodes are used iscalled electrodialysis. This is usually done in a three part cell with membranes making the divisions. The electrodes are placed in the outer sections of the cell while the solution to be treated is placed in the center section between the two membranes.

The technique of electrodialysis has been applied to ion exchange materials and the results can be found in the literature. In each case however the ion exchange material was a clay and was not being used in an ion exchange capacity. These clays are natural ion exchange materials but exchange only cations. The results obtained with clays indicated that it should be possible to Regenerate a mixed resin by electrodialysis.

Holton (2) used electrodialysis on a laboratory scale to purify clays for use in the catalytic cracking of petroleum. The membranes used in the cell were parchment. The impurities removed were sodium, calcium, and magnesium. The purification achieved in the operation was only partially complete and the power consumption of the cell was high. The large resistance of the cell and consequently high power consumption were in a large part due to the large separation of the electrodes in the cell.

Mattson (5) also investigated the affect of electrodialysis on clays. In this case, as in the case of Holton, the cell resistance and power consumption were high. After the clay had been electrodialyzed it was treated with a neutral calcium solution. The calcium chloride solution was titrated with sodium hydroxide to determine the amount of acid present. The clay was then electrodialyzed a second time to determine the amount of calcium absorbed during the calcium chloride wash. These tests indicated that during electrodialysis the metal ions in the clay were replaced by hydrogen ion. The calcium chloride wash produced an exchange of calcium ions for hydrogen ions. The second electrodialysis reversed this and released the calcium ion. The exchange reactions were very nearly quantitative. This work on the electrodialysis of clays has shown that it can be used to regenerate an ion exchange material. The difficulties encountered are the high resistance and power consumption as well as the degree of regeneration. In this investigation a mixed ion exchange resin was used in place of clay. In order to lower the power consumption the cell was made thin in comparison to the cross sectional area and different membranes were used. The membranes of primary importance were ion exchange membranes. These membranes are made by imbedding an ion exchange resin in a plastic matrix. Both anion and cation membranes were used. These ion exchange membranes were Permionic ARX-102 anion membranes and Permionic CR-51 cation membranes. The membranes are manufactured by Ionics Incorporated, Cambridge, Massachusetts. The conductivity of these ion exchange membranes is very high. The combination of ion exchange membranes which have a high conductivity and a mixed ion exchange resin which is a much stronger exchange material than clays made it possible to reduce the resistance of this cell as compared to the cells of Holton and Mattson.

DESCRIPTION OF APPARATUS

The experimental equipment is shown in Figure 1. The three part cell was machined from Lucite. The end sections are square blocks with a circular well cut into one face. The center section is a short piece of heavy wall tubing. A hole was drilled in the top of each section to permit materials to be added and removed from the sections while the cell was in operation. A glass tube for cooling water was put in each section to remove the heat that was generated during the cell operation. The membranes are clamped between the center section and end blocks of the cell when it is bolted together. The three parts are held together by a bolt in each of the four corners of the blocks. A variable resistance was used to control the voltage across the cell. The resistance was connected with the leads from the D-C system across the coil and the leads to the cell coming from the slide and one side of the coil. This was done so that the voltage to the cell would not be affected much by the amount of current flowing through the cell. The ammeter and voltmeter were connected to the cell to measure the current and voltage at the cell. The electrodes were platinum foil.

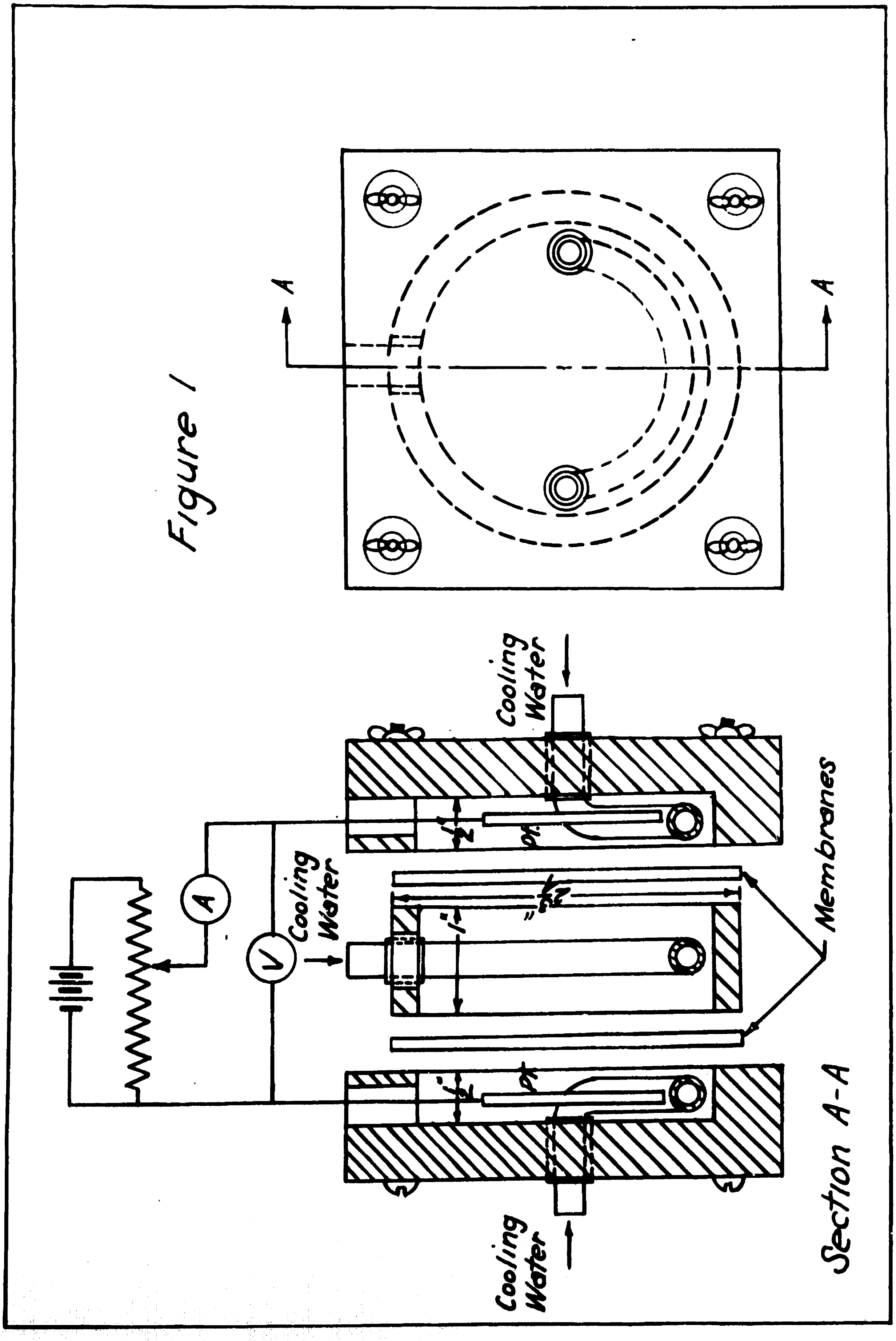
A
A
Cooling Water
Cooling Water
Cooling Water
Cooling Water
A
V
1"
1/2"
1/2"
Membranes
Section A-A

Figure 1

PROCEDURE

The experimental work can be divided into four groups depending upon the type of membranes used in the cell. These four groups are; runs with one anion and one cation membrane, one run with two cellophane membranes, one run with two filter paper membranes, and one run with two anion membranes. The runs of group one were made with one anion and one cation membrane in the cell. The membranes were put in the sodium and chloride form by soaking them in a solution of sodium chloride. The mixed resin used was composed of stoichiometric proportions of Dowex-50, a cation resin in the sodium form, and IRA-400, an anion resin in the chloride form. A weighed amount of the mixed resin was placed in the center section of the cell between the membranes and the section was filled with distilled water. The anode section was filled initially with N/4 sodium hydroxide. The cathode section was filled initially with N/4 hydrochloric acid. The cell was then connected to the laboratory D-C system with a variable resistance in the system to adjust the cell voltage. The cell current was recorded at five or ten minute intervals throughout the run. At the end of each hour of operation the solutions in the electrode sections were removed from the cell and the sections were refilled with the acid and base solutions used initially. The length of the runs was five or six hours. The electrode solutions removed from the cell during operation were analyzed to determine the amount of sodium chloride ions which were removed from the resin. The cathode solution was evaporated to dryness and weighed to determine the sodium removed. The anode solution was titrated for chloride ion. One run in this group was made with the resin in the magnesium sulfate form. The initial electrode solutions were dilute sulfuric acid at the anode and dilute sodium hydroxide at the cathode. Both solutions were analyzed by titration.

One of the runs using one anion and one cation membrane was made at two voltages. The cell was operated at one voltage until the current became nearly constant and then the voltage was reduced to half the initial value and the run continued. The purpose of this voltage change was to determine the affect of the concentration gradients in the resin section on the current and current efficiency.

There was one run made with cellophane membranes. The resin was in the magnesium sulfate form. The solution initially in the cathode section was dilute sodium hydroxide and the solution initially in the anode section was dilute sulfuric acid. The run was conducted in the same manner as those of group one except that the magnesium and sulfate analyses were both done by titration.

One run was made with filter paper membranes and the resin in the sodium chloride form. The anode solution was hydrochloric acid and the cathode solution sodium hydroxide. In this run the cell was operated for four hours and the electrode solutions were not changed during this time. The resin was removed from the cell at the end of the run and titrated to determine how much sodium and chloride had been removed during the run. The amount of chloride removed was obtained by titrating the resin for chloride before and after the electrodialysis and taking the difference. The amount of sodium removed was obtained by titrating the resin for hydrogen ion with sodium hydroxide.

The last run was made with two anion exchange membranes. Both electrode compartments were initially filled with N/4 sodium hydroxide. The resin was given a hydrochloric acid wash before being placed in the cell for electrodialysis. The run was five hours in length and the electrode solutions were removed for analysis. Only the catholite was analyzed, the analysis being for chloride ion.

The data were evaluated by calculating the number of equivalents of anion and cation which were removed from the resin during the electrodialysis process. These calculations were made from the results of the analyses of the electrode solutions removed from the cell during the runs. The voltage and current readings were used to calculate the power consumed during the runs. The current and the equivalents of ion removed were used to calculate the current efficiency of regeneration.

RESULTS

The calculated results are given in Table 1. The values were calculated from the experimental data. The values given for each run include the average cell current, the cell voltage, the integrated power, the current efficiency, and the milliequivalents of the ion removed during the run. The actual experimental values are given in the appendix.

TABLE I

Run 1 - Cellophane Membranes - Magnesium Sulfate
Weight of Resin = 39.1 grams
Magnesium ion on resin = 3.6 meq
Sulfate ion on resin = 27.3 meq.
Volts = 75

Period	Length	Average Current (Amps)	Average Power (watts)	Anion Removed meq.	Cation Removed meq.	Current Eff.
1.	1 hr	.513	38.5	1.04	.422	15.2%
2.	"	.418	31.4	1.26	.450	21.8%
3.	"	.364	27.3	1.36	.330	24.8%
4.	"	.315	23.6	.995	.330	22.5%
5.	"	.297	22.3	.901	.283	21.4%
6.	"	.287	21.5	.725	.245	18.0%
				6.275	2.060	

Run 2 - Anion-Cation Membranes - Magnesium Sulfate
Weight of Resin = 41.1 grams
Magnesium ion on resin = 43.5 meq.
Sulfate ion on resin = 19.2 meq.
Volts = 50

1.	1 hr	.537	26.8	5.85	2.02	78.6%
2.	"	.352	17.6	3.47	.907	66.8%
3.	"	.257	12.8	2.42	.938	70.0%
4.	"	.235	11.7	1.79	.413	50.2%
5.	"	.207	10.3	1.25	.400	42.8%
6.	"	.196	9.8	1.04	.357	38.3%
				15.82	5.055	

Run 3 - Anion-Cation Membranes - Sodium Chloride
Weight IRA-400 = 25.99 grams (Capacity 2.3 meq./gram)
Weight Dowex-50 = 14.05 grams (Capacity 4.25 meq./gram)
Volts = 30

1.	1 hr.	.353	10.60	9.03	6.293	116%
2.	50 min.	.307	9.21	5.11	1.920	73.7%
3.	1 hr.	.224	6.72	3.54	.772	51.7%
4.	50 min.	.214	6.42	1.97	.645	37.8%
5.	1 hr.	.210	6.30	1.96	.657	33.5%
				21.61	9.287	

Run 4 - Anion-Cation Membranes - Sodium Chloride
Weight of IRA-400 = 26.02 grams
Weight of Dowex-50 = 14.03 grams
Volts = 20

1.	1 hr.	.123	2.46	3.98	2.585	143%
2.	"	.113	2.26	2.69	.910	85.4%
3.	"	.0852	1.70	1.93	.575	79.2%
4.	"	.0888	1.78	1.60	.304	57.3%
5.	"	.0831	1.66	1.59	.500	67.5%
				11.79	4.874	

Run 5 - Anion-Cation Membranes - Sodium Chloride
Weight IRA-400 = 25.99 grams
Weight Dowex 50 = 14.03 grams
Volt = 25-13 (Changed half way through period 3)

Period	Length	Average Current(Amps)	Average Power(watts)	Anion Removed meq.	Cation Removed meq.	Curr Ef
1.	50 min.	.1125	2.81	2.59	.939	101
2.	"	.1285	3.21	3.30	.977	107
3.	"	.0777	1.70	1.93	.612	10
4.	"	.0361	.468	.805	.407	108
5.	"	.034	.442	.625	.221	80
				9.26	3.155	

Run 6 - Anion Membranes - Acid Washed Resin
Weight of IRA-400 = 25.99 grams
Weight of Dowex-50 = 14.98 grams
Volts = 25

1.	50 min.	.323	8.08	3.055	0	30.
2.	"	.219	5.47	2.546	"	37.
3.	"	.144	3.60	1.915	"	42.
4.	"	.138	3.45	1.739	"	40.
5.	"	.119	2.98	1.501	"	40.
				10.756		

Run 7 - Filter Paper Membranes - Sodium Chloride
Weight of IRA-400 = 25.5 grams
Weight of Dowex-50 = 13.6 grams
Volts = 15

1.	4.08 hrs.	0.79	11.8	40.6	0	33.

DISCUSSION

A qualitative look at the experimental runs shows the electrodialysis performed as was expected. The resistance of the cell was much less than the cells used by the previous workers to electrodialyze clays. The resistance of the cell increased as the run progressed. The major increase in resistance came during the early part of the run and then became almost constant for the remainder of the time.

The runs were consistent and the values reproducible. The only consistent irregularity was the high initial current efficiency of over 100% but this can be satisfactorily explained. The run which was made at two different voltages (Run 5) started with the usual high current efficiency but remained above 100% until the last hour of the run. The current seems to be a little low in comparison with the other runs made at about the same voltage. An error in the current value due to the zero reading of the meter would explain both the high current efficiency and the low current reading.

The results of the experimental runs indicate that it is possible to regenerate a mixed ion exchange resin by electrodialysis. The cost, on a laboratory scale, of this regeneration process is of the same order of magnitude as the cost of the chemicals necessary to regenerate the component resins after separation. The degree and rate of regeneration accomplished by the electrodialysis process depended to a large extent on the membranes and electrode solutions used in the cell.

Electrodialysis with one anion and one cation membrane was investigated more thoroughly than the three other methods. The electrode solutions were N/2 sodium hydroxide at the anode and N/2 hydrochloride acid at the cathode. During the run water was dissociated in the resin compartment and the hydrogen and hydroxyl ions formed exchanged with the sodium and chloride ions on the resin. The released chloride ion together with some hydroxyl ion migrated toward the anode, through the anion membrane, and into the anode solution. The released sodium ions together with some of the hydrogen ions migrated in the opposite direction and into the cathode solution.

This group of runs, made with one anion and one cation membrane, were the most satisfactory from the point of view of current efficiency. The current efficiency for this group was above 100% for the first hour and became lower during each successive hour. The rate at which the current efficiency decreasedwas a function of the cell voltage. The initial value of current efficiency greater than 100% was due to ion exchange between the electrode solutions and the membranes. The membranes had been treated with a normal sodium chloride solution before they were placed in the cell. With the strong electrode solutions in contact with the membranes there was an initial exchange reaction between the membranes and the electrode solutions. This exchange was not a result of a flow of current. When these ions due to normal exchange are added to the ions which actually carried the current, an apparent current efficiency of over 100% resulted.

The effect of a change in cell voltage, and hence current, on the current efficiency is not appreciable. The current efficiency is high at the start of the run and then decreases. The rate of decrease is greater at the higher voltages. The run in which the voltage was cut in half while the run was in progress showed that the rate of regeneration was primarily a function of the cell current and not of the concentration gradient in the cell.

The primary disadvantage of the electrodialysis with one anion and one cation membrane was the small amount of sodium which was removed. The number of milliequivalents of sodium ion which were removed was less than half the value for chloride ion.

There was no noticeable change in the ratio of sodium to chloride during the runs at least for the length of runs made in this investigation. It is probable that a very long regeneration time would be necessary if the mixed resin were to be completely regenerated. The current efficiency during the last portion of such a long run would be very low especially for the period after most of the chloride had been removed and only sodium ions were left on the resin.

From the mobilities of the ions involved in the exchange reaction and the experimental values it should be possible to calculate the ion concentration in the resin section of the cell. The amount of material removed during an hour is equal to the product of the mobility, the concentration, and the potential gradient. Using this relationship the average concentration of the sodium and chloride ions in the resin section can be calculated. To determine the concentration of hydrogen ion in cell from the sodium and chloride ion concentrations, some assumption must be made as to the concentration of hydroxyl ions. If it is assumed to be zero the minimum hydrogen ion concentration could be obtained. The experimental values obtained for the third hour of Run 3 gave the following concentrations; hydrogen ion concentration .00184 equivalents per liter, chloride ion concentration .00275 equivalents per liter, and sodium ion concentration .000912 equivalents per liter. Since this resin at this point in the run is still principally in the sodium form, equilibrium would require a solution stronger in sodium ion than in hydrogen ion. The calculated concentrations have the ratio reversed with the hydrogen ion concentration twice that of the sodium ion. Assuming that these calculations are approximately correct it would appear that the rate of exchange is the controlling factor in such dilute solutions. This theory would explain the low rate of sodium removal.

The magnesium sulfate run which belongs in this first group shows that the type of salt has little affect on the current efficiency. The amount of material removed at the same current will change with the salt as can be seen from this magnesium sulfate run. This difference is due to the divalence of magnesium sulfate.

The run with the cellophane membranes and the magnesium sulfate form of the resin was not very satisfactory. The magnesium and sulfate removed was much lower than the values for the runs with ion exchange membranes. The current efficiency was also very low. The anode section contained a dilute solution of sulfuric acid and at this electrode sulfate and hydroxyl ions entered the compartment while the ions leaving were hydrogen ions. The cathode section contained dilute sodium hydroxide and at this electrode magnesium and hydrogen ions entered the compartment while hydroxyl ions left it. Of the four types of runs investigated, the cellophane run was the least satisfactory.

The run with filter paper membranes was quite similar to the cellophane run. The resin was in the sodium chloride form for this run. The anode solution was N/2 hydrochloric acid and at this electrode chloride and hydroxyl ions entered the compartment and hydrogen ions left it. The cathode solution was N/2 sodium hydroxide. The ions entering this

this compartment were sodium and hydrogen ions while the ions leaving were hydroxyl ions. It was impossible to analyze the anode solution for chloride since chlorine was given off at the cathode. The resin was electrodialyzed for four hours and no analysis was made until the end of the run. To determine the amount of regeneration, the resin was analyzed for chloride before and after treatment, and also for hydrogen ion after treatment of the resin. The chloride removed was taken as the difference between the two titrations. No hydrogen ion was found on the resin after the electrodialysis. The chloride value determined in this way might be considerably in error because of the difficulty in obtaining a representative sample of the mixed resin which had about a two to one ratio of anion resin to cation resin. Since no sodium ion was removed during the electrodialysis this method was not satisfactory.

In order to overcome the difficulty of sodium removal that was encountered no matter which membranes were used, one run was made on the mixed resin after it had been washed with hydrochloric acid to exchange the sodium ion for hydrogen ion before the treatment in the cell. The membranes used in the cell were both anion membranes and thus no cations could enter or leave the resin compartment. Both electrode solutions were N/4 sodium hydroxide. This produced a flow of hydroxyl ions from the cathode section into the resin section. The current efficiency of this run was not very high being about 40% but in spite of this low efficiency it is possible that this technique may offer the best method of regenerating the mixed resin. It does at least offer a method for nearly complete regeneration without encountering the very low current efficiency that would occur if sodium were to be completely removed by the cell. From the point of view of cost, this method of regeneration has the disadvantage of an acid cost as well as a power cost. For this reason it is unlikely that the cost of regeneration by a combination of an acid wash and electrodialysis could compete with the cost for chemicals needed to regenerate the mixed resin after separation unless the convenience of regeneration without separation could overcome this cost difference.

CONCLUSIONS AND RECOMMENDATIONS

The experimental results indicate that a mixed resin can be regenerated by electrodialysis. The cost of this regeneration is about the same as the cost of regenerating the mixed resin by treatment of the separate resins.

The rates at which the cation and anion resins are regenerated are not at all equal. The relative rates depend on the mobilities of the ions involved in the exchange reaction. The high mobility of the hydrogen ion reduces the rate at which the cations are removed from the resin. The rate of cation removal was less than half the rate of anion removal with both sodium chloride and magnesium sulfate. This rate difference is a distinct difficulty and must be overcome if the regeneration by electrodialysis is to be successful.

The most promising method of complete removal of both anions and cations from the resin is the combination of an acid wash with electrodialysis. This acid wash makes possible a complete exchange of hydrogen for the cation of the resin, while the electrodialysis will remove the anions from the resin. This method has one disadvantage over the other methods and that is the added cost due to the cost of the acid necessary for the wash. This method of regeneration offers many possibilities for further investigations.

The runs made with one anion and one cation membrane were the most satisfactory with respect to the current efficiency. The primary disadvantage with this method is the slow rate of removal of cations from the resin. If this difficulty could be corrected this method of regeneration would be the most efficient of those investigated.

One possible solution to this problem of slow cation removal is to change the ratio of anion to cation resin in the mixture. Instead of using a stoichiometric ratio, the amount of cation resin in the mixture could be increased until the rate of removal of the cations and anions during regeneration is the same. Except for this first time this new mixture was used, it would behave as if the component resins were present in stoichiometric amounts. The only trouble this would make on the initial use of this resin would be to have sections in the bed which had a pH other than neutral.

A change in the ratio of cation resin to anion resin would be a solution to the problem of cation removal only if the rate of exchange of hydrogen ion for sodium ion is slow enough to be controlling. The previous calculations seem to indicate that this is actually the case. If equilibrium is reached in the cell, changing the amount of cation resin relative to the anion resin would not change the rate at which cations are removed from the cell. In the absence of conclusive evidence of which factor is controlling, this method is worth considering.

Another possible solution to the problem of cation removal is a change of the cation resin used. A change from a strong acid resin to a weaker one is indicated. The weaker acid resin would hold the sodium less firmly to the resin and so make possible a better exchange of hydrogen for sodium ion.

The cost of using electrodialysis to regenerate a mixed resin is the primary factor to be considered when comparing this technique with the technique of separate regeneration. This cost of electrodialysis is about the same or slightly higher than the cost of separate regeneration depending on whether an acid was used before the regeneration. The factors which counterbalance the difference in operating cost are the difference in equipment cost, space saving, and the convenience of not having to separate the resins before regeneration. The feasibility of using electrodialysis as a commercial process will depend on the balance of these costs but it certainly appears to be worth additional study and consideration.

APPENDIX

EXPERIMENTAL DATA

Description	Current (amps)	Meq. Anions Removed	Meq. Cations Removed	Anion Analysis		Cation Analysis	
				Sample	Volume (ml)	Sample	Volume (ml)
Run 1	.513	1.038	.422	20 ml of 50	$BaCl_2$ - 6.36 K_2CrO_4 - 0.56	20 ml of 50	NaOH 6.69 H_2SO_4 4.86
Volts = 75	.418	1.256	.450	"	" 8.42 1.09	"	" 9.24 3.60
Resin = 39.1 gms.	.364	1.360	.330	"	" 11.84 2.38	"	" 10.66 9.04
Magnesium = 3.6 mg	.315	.995	.330	"	" 8.74 1.69	"	" 11.86 10.20
Sulfate = 27.3 mq	.297	.901	.283	"	" 7.92 1.50	"	" 10.11 8.68
Cellophane memb.	.287	.725	.245	"	" 7.65 1.70	"	" 10.60 9.30
Run 2	.537	5.85	2.02	20 ml of 50	$BaCl_2$ - 26.90 K_2CrO_4 - .98	20 ml of 50	NaOH 16.21 H_2SO_4 8.06
Volts = 50	.352	3.47	.907	"	" 17.00 90	"	" 15.95 11.96
Resin = 41.1 gms	.257	2.42	.938	"	" 14.00 1.46	"	" 11.46 7.52
Magnesium = 43.5 mq	.235	1.79	.413	"	" 12.75 2.02	"	" 9.98 9.04
Sulfate = 19 meq	.207	1.25	.400	"	" 11.06 2.23	"	" 10.56 8.80
Anion-Cation memb.	.196	1.04	.357	"	" 11.42 2.75	"	" 10.24 8.54

Description	Current (amps)	Meq. Anions Removed	Meq. Cations Removed	Anion Analysis			Cation analysis
				Sample		Volume (ml)	Weight of NaCl (gms)
Run 3	.353	.903	6.29	10 ml of 100	$AgNO_3$	9.91	.3678
Volts = 30	.307	5.11	1.92	"	"	5.65	.1122
IRA-400 = 25.99 g.	.224	3.54	..772	"	"	3.92	.0451
Dowex 50 = 14.05 g.	.214	1.97	.645	20 ml of 100	"	4.35	.0377
Anion-cation memb.	.210	1.96	..657	"	"	4.33	.0384
Run 4	.123	2.46	3.98	10 ml of 100	$AgNO_3$	4.40	.1902
Volts = 20	.113	2.26	2.69	"	"	2.97	.0532
IRA-400 = 26.02 g.	.0852	1.70	1.93	"	"	2.13	.0336
Dowex-50 = 14.03 g.	.0888	1.78	1.60	20 ml of 100	"	3.53	.0148
Anion-Cation memb.	.0831	1.66	1.59	"	"	3.50	.0292
Run 5	.1125	2.59	.939	20 ml of 100	$AgNO_3$	6.72	.0549
Volts = 25-13	.1285	3.30	.977	"	"	7.28	.0571
IRA-400 = 225.99 g	.0777	1.93	.612	"	"	4.25	.0358
Dowex = 14.03 g	.0361	.805	.407	30 ml of 100	"	2.67	.0238
Anion-Cation memb.	.0340	.625	.221	50 ml of 100	"	3.45	.0129
Run 6	.323	3.055	None	10 ml of 100	$AgNO_3$	6.30	None
Volts = 25	.219	2.546	"	"	"	5.25	"
IRA-400-25.99 g	.144	1.915	"	"	"	3.95	"
Dowex 50 - 14.98 g	.138	1.739	"	20 ml of 50	"	7.17	"
2 Anion memb.	.139	1.501	"	"	"	6.19	"
				Anion Analysis Before Run			Anion Analysis after Run
Run 7	0.790	40.6	None	wt = 1.0136 g $AgNO_3$ -22.72			wt = 1.2508 $AgNO_3$ - 15.04
Volts = 15							
IRA-400 = 25.50 g							
Dowex 50 = 14.60 g							
Filter Paper memb.							

ANALYSIS PROCEDURE

Magnesium. Magnesium was determined volumetrically by precipitating it as magnesium hydroxide with excess sodium hydroxide. The excess sodium hydroxide was determined by titration with standard acid.

Sulfate. Sulfate was determined by titration with standard barium chloride. A slight excess of barium chloride was added and then the excess was titrated with potassium chromate.

Chloride. Chloride was determined by the Mohr method. The sample was titrated with silver nitrate to a chromate end point.

Sodium. Sodium was determined by evaporating the solution to dryness and weighing the solid remaining. Solid was sodium chloride.

Solutions used:

Run 1 and 2

Barium chloride - .0986N
Potassium chromate - .2274N
Sulfurid acid - .1073N
Sodium hydroxide - .1033N

Runs 3, 4, 5, 6, 7.

Silver nitrate - .0970N

LITERATURE CITATIONS

1. Furman, N. H., Scott's Standard Method of Chemical Analysis, 5th ed., D. Van Nostrand Co., Inc., New York, 1939.
2. Holton, W. G., Sc.D. Thesis, Dept. of Chem. Eng., M.I.T., 1941.
3. Juda, W., and McRae, W. A., J. Am. Chem. Soc., 72, 1044 (1950).
4. Kunin, R. and Myers, R. J., Ion Exchange Resins, John Wiley and Sons, Inc., New York, 1950.
5. Mattson, S., J. Agr. Res., 33, 553-567 (1926).
6. Perry, J. H., The Chemical Engineers Handbook, 3d. ed., McGraw-Hill Book Company, Inc. New York, 1950.
7. Wyllie, M. R. J., and Patnode, H. W., J. of Phys. and Colloid Chem., 54, 204-227 (1950).