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Ion-Exchange Removal of Sodium Chloride from Water with Calcium Hydroxide as Recoverable Regenerant

Abstract. *A mixture of cation- and anion-exchange resins, in proportions corresponding to their particular exchange properties and charged with calcium hydroxide, removes seawater salts from solution exchanging calcium hydroxide for the sodium chloride. The regenerant is recoverable. A portion of it may be used again without handling.*

Ion-exchange resins have been seriously considered for desalting seawater (1). The prevalent opinion is that large-scale use of such resins depends on finding a suitable regenerating agent.

Such a regenerant should be safe and easy to handle; its deleterious effects on the resin should be nearly negligible; its affinity for the resin should allow the desalting to proceed at a reasonable rate; it should be readily available; and its cost should be low. It must be taken up by the resin from solutions of sodium in preference to that ion, and yet be held lightly enough to permit exchange for sodium from solutions in which it is present at concentrations lower than those of equilibrium, in terms of relative affinities. It must also be recoverable at low cost.

Of the recoverable regenerants investigated, thermolabile salts, as represented by ammonium carbonates, were unsuitable owing to the high cost of reclaiming them (2). For economical recovery, low solubility in water would allow the regenerant of the ion-exchange system to precipitate and to be used over and over again for column regeneration. The solubility of calcium hydroxide at prevalent temperatures is low enough for a reasonably direct recovery of the regenerant during the desalting run [92 percent of regenerant at $\text{Ca}(\text{OH})_2$ solubility of 1.65×10^{-2}], as well as for recovery of the excess regenerant used during the regeneration cycle. The precipitate is removed by simple mechanical means.

Lime slurries have been used for regeneration of anion-exchange resins (3), of cation-exchange resins (4), and for the simultaneous regeneration of both the cation- and anion-exchange resins in mixed systems (5). The direct taking up of solids by ion-exchange resins is described by Deuel and Krishnamoorthy (6).

The percentage of removal of an electrolyte from its solution by exchange for another pair of ions can be calculated with reasonable accuracy; the exchange is stoichiometric (7). Thus, when the electrolyte content of seawater is exchanged for Ca^{++} and OH^- ions, the resulting medium contains 2.215-percent $\text{Ca}(\text{OH})_2$.

We have used calcium hydroxide as a recoverable regenerant for the removal by ion-exchange of sodium chloride from its solutions at concentrations slightly higher than those encountered in seawater.

In a simplified fashion we have demonstrated the basic principle of removal of sodium chloride from its solutions by replacement with calcium hydroxide, and the feasibility of regenerating a mixed bed in the sodium and chloride form by a slurry of calcium hydroxide in a 3.5-percent solution of sodium chloride. Also, we have shown that the deposited regenerant may be used directly to regenerate the ion-exchange system.

We have examined only the exchange of sodium chloride for calcium hydroxide. In the demineralization of sea-

water, other cations present (calcium, magnesium, and so forth) would be taken up by the resin before or together with the sodium ion, and hence would affect the process only insofar as available active resin sites are concerned. Because of the higher affinity of the resin for these ions, the useful volume of the column, if seawater were used, would be somewhat bigger.

Water suitable for drinking, irrigation, or industrial uses may be attained by one of several techniques. For example, spraying through the air will precipitate some calcium carbonate; ion exchange of remaining $\text{Ca}(\text{OH})_2$ for sodium chloride will yield utility water containing 0.25-percent NaCl; ion exchange for the Cl ion will give water with a 0.25-percent CaCl_2 content; or, ion exchange of the calcium ion for another cation will precipitate an insoluble hydroxide.

For demineralization of water, we used a 150-cm Lucite column, with a 2.5-cm inside diameter, both ends of which were fitted with stainless-steel housings having dacron filters, needle valves as outlets, and capped vents without valves. The useful volume was 740 ml.

The ion-exchange resins in the column were a mixture of 471 ml of 12-percent divinylbenzene cross-linked polystyrene sulfonic cation-exchange resin with 269 ml of trialkylalkanolammonium polystyrene anion-exchange resin.

The cation-exchange resin was converted to the calcium form and the anion-exchange resin to the hydroxyl form, by downward passage of water of lime. The column was then rinsed with distilled water and left full.

A 3.62-percent solution of technical sodium chloride was fed into the column under gravity at a flow rate of 10

Table 1. Salt removal from 3.62-percent NaCl solution on column of mixed ion-exchange resin in Ca^{++} and OH^- form.

Effluent (ml)	NaCl	
	Concentration (%)	Total removal (meq)
100 to		
500	0.00	312.05
600	0.00	374.46
700	0.05	435.99
800	0.6	488.05
900	1.1	530.64
1000	1.3	570.64
1100	1.6	605.53
1500	2.45	699.8
2000	2.85	779.3
2250	3.1	805.2

Table 2. NaCl desorption from a mixed bed of ion-exchange resins by 0.15-percent calcium hydroxide (4.05 meq per 100 ml). The column originally was exhausted with a 3.62-percent NaCl solution in water.

Effluent (ml)	NaCl	
	Concentration (%)	Total removal (meq)
100	3.64	64.3
200	3.75	128.9
300	3.75	193.5
350	2.85	217.9
400	2.15	236.4
500	1.75	266.4

ml every 40 seconds. The effluent was collected on a fraction collector in 10-ml portions. Sodium was analyzed in the flame on a Beckman model B; and pH readings were taken to determine the presence of the OH⁻ ion, and hence the replacement of the chloride. The results of this experiment (Table 1) show an observed capacity of 805 milliequivalents (meq).

According to an often accepted generalization (8), 30 to 40 percent of the total column volume of 740 ml is void volume; this means that there is 296 ml of water in the system. At an input concentration of 3.62-percent NaCl, this volume is to be interpreted as a dilution by 185 meq. Hence the true capacity was 620 meq.

At the rated capacity of the column (1036 meq referred to calcium), the efficiency shown for the sodium-calcium exchange was 60 percent.

A mixed bed of cation- and anion-exchange resin was converted independently to the sodium and chloride forms by passage of a solution of 3.5-percent sodium chloride. A part of this solution was set aside for use in subsequent regeneration. Part of the exhausted resin (50 ml tamped volume) was transferred to a beaker by washing with a portion of the solution which was used to convert the resin into the sodium and chloride forms. Free-flowing water was drawn off by gentle tipping and rotating of the beaker. Thirty milliliters of a 5-percent slurry of calcium hydroxide, suspended in the 3.5-percent solution of sodium chloride that had been set aside, was then added to the decanted resin. The mixture was stirred for 5 minutes with a magnetic stirrer at low speed, with a Teflon-coated, football-shaped, stirring bar. Subsequently, the resin was allowed to settle and the supernatant liquid was analyzed by taking sodium readings in the flame.

The salt content of the supernatant liquid was 4.5 percent; this is equivalent to a concentration increase of 12.8 percent when the volume of the regenerant is 60 percent.

The anion-cation exchange column, exhausted by passage of the NaCl solution as in the initial experiment, was inverted and a solution of 0.15-percent calcium hydroxide, that is, 4.05 meq per 100 ml, was percolated downward. Samples were collected as already described.

The analytical results are given in Table 2. The total salt in the effluent from this regeneration amounted to 266.4 meq. The interstitial volume (at the most, 296 ml) was full of remaining liquid at the beginning of the regeneration; an interpolation of the preceding run's end phase indicates that the maximum concentration of salt in the interstitial liquid was 3.25 percent—the column thus contained 165 meq of electrolytes that were not taken up. The input of 104 ml of water of lime (to make up the 500 ml of the effluent) resulted in a further addition to 173.26 meq.

The difference between the effluent ionic load of 266.4 meq and the input of 173.26 meq shows the intervention of another desorbent—the deposit of the insolubilized portion of the counterionically evolved lime which, owing to the action of the solubilizing water, goes from the insoluble to the soluble form, and then proceeds to dissociate. The ion-exchange resin takes up the available ions, causing a shift in equilibrium; and more hydroxide then dissolves and dissociates. These experiments point to the availability of the interstitially deposited lime for regeneration without physical handling.

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Chlorine Pentafluoride

Abstract. *The bonding in the halogen polyfluorides is similar to that in the xenon fluorides. Since XeF₄ exists, the previously unreported ClF₅ should exist. This compound has been prepared by heating ClF₃ in the presence of fluorine at high pressure. Chlorine pentafluoride is a square pyramidal molecule. It has a lower melting point than ClF₃ and a higher vapor pressure. It is also less reactive than ClF₃.*

Descriptions of the bonding in the xenon compounds have been of two different kinds. One involves a covalent-ionic resonance, the other primarily covalent bonding, but with *d* electrons involved. One of the minor difficulties with both descriptions is that they apply as well to the unreported compound ClF₅ as they do the xenon compounds (1).

The compound ClF₅ has now been successfully prepared by the combination of chlorine trifluoride and fluorine at high temperatures and with high fluorine pressures. Typically, a 14:1 mixture of F₂ and ClF₃ has been heated to 350°C for 1 hour at a pressure of about 250 atm (2).

The infrared spectrum of ClF₅ is similar to the spectra of BrF₅ and XeOF₄, indicating that ClF₅ has the same square pyramidal configuration with the chlorine atom nearly in the plane of the four fluorine atoms forming the pyramid base. The asymmetric stretching vibration, ν_7 , involving the four fluorine atoms, corresponds to a very strong band at 732 cm⁻¹. The stretching vibration, ν_1 , involving the apex fluorine atom, corresponds to a weaker but still strong band at 786 cm⁻¹. The symmetric stretching vibration involving the four fluorine atoms, ν_2 , at 544 cm⁻¹ is very weak compared with ν_7 , indicating the bond angles are close to 90°.

The identification of ClF₅ has been verified in the mass spectrometer. Samples free of ClF₃ have not yet been prepared. A sample thought to contain a few percent ClF₃ is a white solid