Production of sodium hydroxide solution by ion exchange

Harry Stern
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UMI
PRODUCTION OF SODIUM HYDROXIDE SOLUTION BY ION EXCHANGE

by

Harry Stern

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1950
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I. INTRODUCTION

A. Objectives and Significance of the Investigation

This research is primarily an investigation of the possibility of producing sodium hydroxide solutions of commercial value by the ion exchange method. Closely related to this objective is an understanding of the mechanism and limitations of the ion exchange process.

Four materials find wide industrial use as alkalizing reagents: sodium carbonate, sodium hydroxide, lime, and ammonia. Sodium hydroxide has several important advantages over the other three. Its high solubility and dissociation makes it possible to secure strongly alkaline solutions, and it is nonvolatile. Sodium hydroxide finds application in so many fields of human activity that any improvement in its production would have a considerable effect on our culture. For this reason, new methods of production and improvements in the old methods are continually being advanced. This research is one such attempt in which it is sought to utilize the principle of exchange of ions on a solid surface to convert sodium chloride to sodium hydroxide in the form of a solution ready for use.

The ion exchange phenomenon, although known for one
hundred years, has only recently begun to be applied in fields other than water softening. Its application to the manufacture of chemicals is an activity that is relatively unexplored.

B. Methods of Sodium Hydroxide Manufacture

Sodium hydroxide is made commercially either by double decomposition of sodium carbonate and lime or by the electrolysis of salt brine.

Sodium carbonate was found by the ancients in natural deposits and a small portion of our output is still obtained in this way. Artificial production of soda ash was first accomplished in 1793 by the Le Blanc process which utilized common salt, sulfuric acid, and limestone as raw materials. However, due to its large fuel consumption, the impurity of the product, and the large amount of solids handling, the Le Blanc process was gradually superseded, around 1888, by the Solvay process which obtains sodium carbonate by treating salt brine with ammonia and carbon dioxide with subsequent recovery of the ammonia (67).

At present, less than one third of the sodium hydroxide produced is obtained from sodium carbonate, the larger portion being produced by the electrolysis of salt brine. Electrolytic caustic became commercially important around 1900 and surpassed chemical caustic in production in 1937 (100).
Various other methods for the production of sodium hydroxide have been proposed from time to time but none of these have gained commercial prominence. A partial list is given below:

1. \[2 \text{NaCl} + 4 \text{PbO} + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + 3 \text{PbO. PbCl}_2\] (96)
2. \[2 \text{NaCl} + 4 \text{ZnO} + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + 3 \text{ZnO. ZnCl}_2\] (96)
3. \[\text{Na}_2\text{S} + 2 \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{Na}_2\text{S}_2\text{O}_3\] (108)
4. \[\text{NaCl} + \text{KF} \rightarrow \text{NaF} + \text{KCl}\]
   \[2 \text{NaF} + \text{Ca(OH)}_2 \rightarrow 2 \text{NaOH} + \text{CaF}_2\] (37)
5. \[\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3 \xrightarrow{850^\circ\text{C}} \text{Na}_2\text{O. Fe}_2\text{O}_3 + \text{CO}_2\] (158)
   \[\text{Na}_2\text{O. Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{Fe}_2\text{O}_3\]
6. \[\text{NaNO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{Na}_2\text{O. Fe}_2\text{O}_3 + \text{NO}_2\] (78)
   \[\text{Na}_2\text{O. Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{Fe}_2\text{O}_3\]

The ion exchange method of producing sodium hydroxide, which is described on page 6, was first proposed by Dr. O. R. Sweeney (135) in 1916 and a patent (66) based on this suggestion was obtained. In 1933 it was suggested (43) that sodium hydroxide of a strength suitable for cooking vegetable materials could be obtained by this method. However, except for a few tests performed by Moses and Benson (20) in 1940, no experimental work on this process has been reported.
C. Description and History of Ion Exchange

Ion exchange may be defined as a reversible interchange of ions between a liquid phase and a solid body which does not involve any radical change in the body structure. Although the mechanism of the process is still in doubt, the final result is that of a double decomposition reaction in which one of the ions is in the form of a solid, but is nevertheless active in the reaction.

Cation exchange is exemplified by a reaction such as the following, in which R represents the solid anion:

$$\text{MgCl}_2 + 2 \text{NaR} \rightarrow \text{MgR} + 2 \text{NaCl}$$

The solid is known as the exchanger and the reaction is brought about by passing a solution of magnesium chloride through a bed of the sodium loaded exchanger, the effluent being a solution of sodium chloride. During the flow the solution has replaced the sodium on the exchanger by magnesium.

Anion exchange can take place in an analogous manner, but in this case the solid is a cation and the process may actually be acid adsorption rather than anion exchange.

The phenomenon of ion exchange, as it is understood at the present time, is fully discussed in Part II. Its history will be traced briefly in the following paragraphs.
The discovery that soils have the power of exchanging cations with solutions was the outgrowth of observations dating back to the remote past. The first quantitative measurements were made by Thompson and reported by Way (153) who, in 1850, clearly showed that cations in the solution were exchanged for cations in the soil when solution and soil were brought into contact. In the period between 1850 and 1900 almost all of the investigations on ion exchange were conducted by soil chemists who were interested in its effect upon soil fertility. The chief exchange material in soils was found to be the hydrated alumino-silicate clay. Artificial alumino-silicates were also shown to have ion exchange properties and found industrial application in water softening. Later work showed that a rather wide variety of materials could exhibit cation exchange properties. These included greensand, casein, the so-called humic acids in soils, and sulfonated peat, lignite and coal.

In 1935, Adams and Holmes (1) showed that cation exchange could take place on synthetically produced organic resins of the phenolic type. They also produced amine-formaldehyde resins which are capable of adsorbing acids from solution. The effectiveness of these resinous cation exchangers was later improved by sulfonation, and recently both carboxylated and sulfonated polystyrene types of resin, showing high exchange capacity and high chemical resistance, were produced. These improved resinous exchangers have found use in such applications
as removal of undesirable impurities from solution, separation of metals, catalysis, and recovery of valuable substances from very dilute solutions. The application of these new resins to the production of sodium hydroxide solutions is the purpose of this research.

D. Description of Proposed Process for Sodium Hydroxide Production by Ion Exchange

In this process sodium chloride is converted to sodium hydroxide and hydrochloric acid, in the course of which strontium hydroxide is used as an intermediate substance, much as ammonia is used in the Solvay process for soda ash. The process may be delineated briefly in three essential steps. Let the symbol, R, represent the solid resin to which replaceable cations may be attached. The resin will first be assumed to be saturated with sodium ions as designated by the symbol NaR.

Step 1. Pass strontium hydroxide solution through a bed of the sodium loaded resin. The reaction is:

\[
\text{Sr(OH)}_2 + 2 \text{NaR} \rightarrow 2 \text{NaOH} + \text{SrR}_2
\]

The strontium ions remain on the resin while the effluent contains the sodium hydroxide product.

Step 2. Pass sodium chloride solution through the resin bed. The reaction is:

\[
2 \text{NaCl} + \text{SrR}_2 \rightarrow \text{SrCl}_2 + 2 \text{NaR}
\]
The resin is thus regenerated with sodium ions and the effluent contains strontium chloride in the presence of excess sodium chloride.

Step 3. Separate the strontium chloride from the solution and calcine it in the presence of steam. The reaction is:

$$\text{SrCl}_2 + 2\text{H}_2\text{O} \xrightarrow{1650^\circ\text{F}} \text{Sr(OH)}_2 + \text{HCl}$$

The strontium hydroxide is recycled for use in Step 1 while the hydrogen chloride is condensed with the excess steam to give a solution of hydrochloric acid.

A simplified flow sheet illustrating the three essential steps is given in Figure 1. Compare this with the final detailed flow sheet (p. 169) which was derived from information based on the experimental data.

It will be observed that the overall reaction for the process is:

$$\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{HCl}$$

that is, the process is an indirect means of bringing about the hydrolysis of sodium chloride into sodium hydroxide and hydrochloric acid at a temperature that is industrially available and considerably lower than that required by the direct hydrolysis of sodium chloride. This direct reaction has intrigued chemists for over a century and has been the basis of considerable experimental work and much discouragement (68).
Figure 1. Simplified schematic flow sheet for production of sodium hydroxide by ion exchange.
E. Advantages of the Proposed Process and Field of Use

Sodium hydroxide, as made commercially by either the chemical process from soda ash or by the electrolytic process from salt brine, is produced in about a ten per cent solution on a large scale. The solution is concentrated to fifty per cent or to the solid state and shipped to users who generally redilute the solution to the required concentration. It can be seen that there is a field of use for a small scale plant that can produce pure dilute sodium hydroxide solution where needed and thus save the cost of concentration and shipping and the inconvenience of redilution.

Uses of sodium hydroxide solutions with concentrations of only a few per cent can be found in a number of industries. These include the kiering of cotton textiles, bottle washing in breweries, dairies, distilleries, and the beverage industry, production of sodium hypochlorite bleach, regeneration of anion exchangers, cooking of vegetable materials, neutralization operations in oil refineries, purification of vegetable oils, water softening, and adjustments of pH in solution (109) (40) (28) (122) (128).
II. LITERATURE REVIEW ON ION EXCHANGE

Numerous papers on ion exchange have appeared in the past ten years and the number is multiplying rapidly. Various reviews have been presented from time to time (73) (80) (81) (82) (157) (104) (116) (150) (6) (107) (119) in which both the theory and applications are discussed. However, these reviews are for the most part rather general in nature and are not particularly suited for the purpose of this thesis. For this reason, a rather complete survey was made in which all original papers pertaining to this problem were carefully scrutinized for data which could throw light on the observations reported in Part III. This material, therefore, serves as background information on the nature and mechanism of ion exchange with special emphasis on exchange in concentrated basic solutions.

In addition, information on exchanger properties is discussed to enable selection of suitable exchangers for test.

A. Structure and Properties of Exchange Materials

Ion exchange materials may be classified as organic and inorganic (150). The organic exchangers include:

1. Humic acids in soils.
2. Proteins, especially casein. Wool adsorbs acid dyes.
3. Lignite, peat, and brown coal. The exchange capacities of these materials can be increased by mild oxidation, dehydration or sulfonation.

4. Bituminous coal, which can be sulfonated to give a good cation exchanger. It is resistant to acids but shows a tendency to peptize in alkaline solutions.

5. Synthetic resins.
   a. Catechol-formaldehyde resins.
   b. Tannins, lignin sulfonic acid, and casein, which can be condensed with formaldehyde to give insoluble resins with cation exchange power.
   c. Sulfonated phenol-formaldehyde resins.
   d. Polystyrene resins, which can be sulfonated to give cation exchangers.
   e. Polyalkyl acrylate resins, which can be partially saponified to give a carboxylic resin cation exchanger.
   f. Aromatic amine-formaldehyde resins, which behave as adsorbers of strong acids.
   g. Resins containing quaternary amino groups or guanidino groups which are capable of adsorbing very weak acids or of exchanging anions (30).

The inorganic exchangers include:

1. Zeolites. These are alumino-silicate crystals consisting of tetrahedra arranged so as to allow channels through which water and exchange ions can easily pass.
2. Scapolites. These minerals can exchange both cations and anions. Their formula is Na\text{Al}_3\text{Si}_3\text{O}_9\text{Cl}_2.

3. Greensand. The main constituent is the mineral glauconite, a hydrated iron and potassium silicate. This material is highly permeable to ions which diffuse between the crystal units rather than within them as in the case of zeolites.

4. Montmorillonite. This is a clay mineral of the alumino-silicate type. It is made up of flat plates between which the spaces are large enough to admit small cations such as sodium or calcium but not the larger cations like quaternary ammonium ions.

5. Apophyllite. This mineral is similar to montmorillonite but contains no aluminum. This shows that aluminum is not necessary for cation exchange.

6. Phosphate rock. This consists of micro-crystals of apatite CaF_2.3Ca_3PO_4 which exhibit anion exchange. Halogen ions can be exchanged for other halogen ions and for hydroxyl ions.

7. Synthetic gel type alumino-silicates. These are amorphous, porous solids with pore diameter of 4 or 5 Å as compared with 50 to 60 Å for silica gel or coconut charcoal. The pores are smaller than in crystalline zeolites, yet they exchange their ions much faster. This may be due to weaker binding of the ions to the synthetic gels. This agrees with the fact that the synthetic gels show a higher electrical
conductivity. When heated to redness, they sinter and lose practically all their exchange capacity.

Cation exchange bodies are commonly considered to be gel-like structures bearing fixed negative charges, with mobile positive ions distributed through the gel cavities (151). The exchangeable cations are held on or near the surface of the solid. In most ion exchange reactions the amount and overall chemical composition of the solid phase are not greatly altered. Thus the process is roughly distinguished from ordinary chemical reactions involving solids and solutions. The principles governing the process seem to be similar for all kinds of materials. The exchangeable cations are held mainly by electrostatic forces (73).

In order to be an ion exchanger a material must not only be studded with active points on which ions are held but must also be so constructed molecularly that channels permeate the entire structure, permitting ions accessibility to practically every active point in the mass (150). In the case of the inorganic silicate exchangers such as montmorillonite clays, the source of the negative charge which attracts exchangeable cations is believed to be "isomorphous replacement" (65). By this is meant the substitution of a divalent atom, such as magnesium, for a trivalent atom, such as aluminum within the crystal lattice. Such a substitution is possible because of the similarity of the space requirements of the two atoms but
it results in a deficiency of one positive charge per atom in the lattice. This gives the crystal lattice a negative charge near each substitution and it is this charge which attracts positive ions from solution. The framework of atoms in the crystal is such that large spaces exist among them and these spaces are connected by channels in such a manner that water can easily pass through them. In this way the cations in the water solution have access to every negative charge in the crystal.

In the case of the organic resinous type of cation exchanger, such as the sulfonated phenol-formaldehyde type, the source of the negative charge which attracts cations from solutions is a definite anionic radical. This is bound to the resin structure by covalent chemical bonds and is therefore firmly fixed to it. The anionic radicals are generally the carboxyl, sulfonic and phenolic groups, all of which have acidic properties when hydrogen ion is the cation. The exchanging groups responsible for the adsorptive capacity of the resin are known from X-ray diffraction data to be dispersed randomly throughout the interior of the solid (25). The resin structure must be regarded as an organic gel in which water of gelation is a vital structural element (12). Removal of this water as by excessive drying results in a greatly lowered adsorptive capacity. The loss, however, is not irreversible for upon prolonged soaking in water the adsorbent slowly regains its
exchange capacity. The gel structure must be fairly open since the exchanging groups in the interior seem freely accessible. The resinous structure is cross linked in three dimensions, but in spite of this there is appreciable elasticity so that a sizable swelling or shrinking occurs when the concentration of the electrolyte outside the resin varies widely.

The resinous exchangers offer the advantages over the inorganic silicate exchangers of a higher exchange capacity, higher exchange velocity, better stability to acids, alkali, heat and mechanical pressure, and uniformity of product (101). The silicate lattice suffers a strain during the exchange of a heavily hydrated ion for one less hydrated, and disruption often occurs after a period of use. But the flexible structure of synthetic resins readily permit exchange of a large ion for a small ion without disruption of the resin lattice. In the following paragraphs, some of the synthetic ion exchange resins that are produced commercially are described briefly.

Dewex - 30 (also known as Dow MX) is produced by the Dow Chemical Company (16). It is a condensation product of O- and p- phenolsulfonic acid with formaldehyde whose structure may be represented by the formula

$$\text{[OH}$$

$$\text{SO}_3\text{H}$$

$$\text{CH}_2^-$$

$$x$$
The resin is produced in the form of hard block granules of irregular shape with screen size of about 20 mesh. In its wet form it weighs 50 pounds per cubic foot and contains approximately 55 per cent moisture. The density of the wetted granules is 1.30 and of the dried granules, 1.67. An operating bed of the resin contains about 38 per cent free space. The resin contains phenolic groups and nuclear sulfonic acid groups, both of which possess ion exchange activity. However, the phenolic groups become active only at pH values above 9.5, the conversion to the phenolate salt being very slow below pH 11.5. The nuclear sulfonic acid groups are stable to hydrolysis at elevated temperatures in the presence of either acid or alkali. Some softening of the particles and loss in capacity are obtained in sodium cycle operation at combined high pH and high temperature. The resin, because of its highly cross linked structure is insoluble in all organic or inorganic liquids and is infusible. Decomposition of the dry acid form starts at about 200°C.

Amberlite IRC-50, produced by the Resinous Products Division of Rohm and Haas Company (118) is a synthetic cation exchange resin produced in the form of white, opaque beads of about 30 or 40 mesh screen size. In its wet form its density is 40 to 48 pounds per cubic foot but it swells by 55 per cent in transferring from the hydrogen form to the sodium form. The free space in a resin bed is 35 to 40 per cent. The resin
possesses only one kind of functional group, the carboxyl group, which has a strong affinity for hydrogen ions, that is, it is a weak acid. The rate of exchange and the resins affinity for hydrogen ion are increased as the temperature is elevated. The resin is stable in the presence of strong alkalies and acids, organic solvents, and oxidizing and reducing agents. The hydrogen form can be converted to the sodium form by leaching with 4 per cent sodium hydroxide. In the sodium form, the resin undergoes reactions typical of the salt of a weak acid and strong base.

Dowex 50 (Dow HCR), produced by the Dow Chemical Company (17) (63) is a polystyrene resin containing nuclear sulfonic acid groups as the sole active group, and is stable to strong acid, strong alkali, and oxidizing agents even at elevated temperatures. It is produced in the form of amber-colored spherical particles of about 20 mesh screen size. In the wet form its density is about 54 pounds per cubic foot. The resin probably has the structural formula

\[
\begin{array}{c}
\text{SO}_3^- \\
\text{Na}^+ \\
\end{array} \\
\text{CH}_2-\text{CH}_2-
\]

In the sodium form the resin undergoes reactions typical of the salt of a strong acid and strong base.

The foregoing three resins were described in some detail
because they are the ones selected for experimental test in the production of sodium hydroxide as described on page 128. They are representative of the most recently developed resins and show higher exchange capacity, greater resistance to caustic solutions, and longer life than previously used organic or inorganic exchangers. Other commercially produced resins of the same types as those described are made by competing firms. Thus amberlite IRC-120 (118) is similar to Dow HCR; and amberlite IR100 (118) and Wofatit K (157) are similar to Dow MX. A complete list of commercially available ion exchangers is given by Nachod (107).

B. Exchange Capacity

Generally, exchange capacity is taken to mean the number of gram-milliequivalents (m.e.) of a certain cation which 1 gram of air dried exchanger is able to adsorb at a pH of 7.00 in the final external solution (157). Some investigators (95), however, consider exchange capacity to be the m.e. of base added to the hydrogen form of the exchanger when the midpoint of the titration curve is reached. Still others, in recognition of the fact that the exchange capacity varies somewhat with the concentration and the type of cation as well as with pH, prefer to give the capacity at any conditions and then specify the conditions. This latter procedure is probably to be preferred.

The exchange capacity of the sulfonated phenol-formaldehyde
type resin is independent of the particle size but is strongly
dependent on the pH of the solution. The capacity increases
with the pH presumably due to the fact that the phenolic OH
groups are not active until the pH is raised above a certain
value (124). Thus the removal of sodium ion from solution by
a hydrogen saturated resin was found to be much more effective
when sodium carbonate or sodium hydroxide was employed than when
sodium chloride was treated (103). The exchange capacity at
pH=5 agrees with the number of -SO_3H groups as found by sulfur
analysis (157). At higher pH the capacity is as much as 75
per cent greater, indicating that other functional groups,
such as phenolic OH, are being used (106). Thus, for example,
the exchange capacity of a hydrogen saturated exchanger was
1.47 m.e. per gram with sodium chloride solution, 2.22 m.e.
per gram with sodium carbonate solution and 3.18 m.e. per gram
with sodium hydroxide solution (103).

The increase in the capacity of an exchanger, which is
originally saturated with hydrogen ions, as the pH is raised,
is readily explained by the fact that the anions of weak acids,
such as carbonate or hydroxyl ions, remove active hydrogen ions
from solution. This causes more hydrogen ions to leave the
exchanger and be replaced by sodium ions or other cations, thus
exhibiting a higher exchange capacity. However, there is
evidence that factors other than pH come into play. Thus in
experiments on alumino-silicate exchangers (150) the nature of
the anion was found to affect the cation exchange of calcium for potassium although the hydrogen ion was not involved. The calcium-saturated alumino-silicate exchanger, when treated with solutions of potassium salts of different anions, showed increasing exchange capacity as the anion of the potassium salt was varied in the order 
\[ \text{CNS}^- < \text{I}^- < \text{ClO}_3^- < \text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-} < \text{CrO}_4^{2-} < \text{Fe(CN)}_6^{3-}. \]
The exchange was the greater, the more hydrated the anion, and the effect of the anion was the greater, the more hydrated the cation. The effect is ascribed to the dehydration of the dissolved cations by the anions. The relative exchange powers of different cations are believed to be largely governed by their affinities for the solvent.

The anion may also affect the cation exchange capacity through its influence on solubility. Thus, ultramarine (an alumino-silicate exchanger containing sulfur) after being saturated with silver ions, was treated with solutions of the chlorides of the alkali metals in one series of tests and with the iodides of these same metals in another series of tests (70). The substitution of silver ions by the alkali metal ions proceeded, in all cases, appreciably farther when using iodides than when using chlorides. This increase in cation exchange capacity was attributed to the fact that silver iodide, being less soluble than silver chloride, reduces the silver ion concentration in solution. This in turn causes more silver
ions to leave the resin to be replaced by alkali ions, thus showing a higher exchange capacity.

A comparison of the exchange capacities of the various known cation exchangers is difficult because of the wide variations even with the same exchanger, depending on conditions as described above. Furthermore, the exchange capacity of a resin bed in actual operation is considerably less than that determined by equilibrium studies, since in operation no attempt is made to reach equilibrium. Nevertheless, for the sake of at least a rough comparison, an attempt was made to adjust reported values of exchange capacities to a common basis. These values, presented in Table I, are equilibrium values in neutral solution. Operating values are generally about one third of the equilibrium values, although this depends on the exchange rate and flow rate.

C. Adsorption of Hydroxides by Cation Exchangers

During cation exchange, the anions are considered to remain in the external solution and to play no significant role in the mechanism of exchange. However, if the anion is the hydroxyl ion, it is found that a substantial fraction of the anions is adsorbed on the exchanger along with the cations. This phenomenon has not been extensively investigated although a number of workers have reported it and have offered some explanations.
### Table I

Relative Exchange Capacities of Cation Exchangers

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<tr>
<td>Synthetic alumino-silicate</td>
<td>0.5</td>
<td>(16) (150)</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>0.5</td>
<td>(150)</td>
</tr>
<tr>
<td>Greensand</td>
<td>0.2</td>
<td>(16)</td>
</tr>
<tr>
<td>Casein</td>
<td>0.7</td>
<td>(150)</td>
</tr>
<tr>
<td>Sulfonated coal</td>
<td>0.8</td>
<td>(150) (16)</td>
</tr>
<tr>
<td>Sulfonated phenol-formaldehyde resin</td>
<td>operating 2.0</td>
<td>(103) (16)</td>
</tr>
<tr>
<td>Sulfonated polystyrene resin</td>
<td>operating 3.4</td>
<td>(157) (58)</td>
</tr>
<tr>
<td>Carboxylated resin</td>
<td>8.0</td>
<td>(118)</td>
</tr>
<tr>
<td>Catechol-formaldehyde resin</td>
<td>11.0</td>
<td>(150)</td>
</tr>
</tbody>
</table>
Way (153) discussed the question as to whether there was a total absorption of hydroxides on clays. It was his opinion that the whole molecule was absorbed.

Wiegner (156), working with clays, was of the opinion that total absorption plays a smaller part than had usually been assumed. Very often the disappearance of caustic soda, ammonia, and other bases from solution may be explained by saying that hydrogen ions in the gel are neutralized by hydroxyl ions and that the cation of the hydroxide takes the place of the hydrogen.

Tuorila (144) has shown that adsorption of hydroxyl ions can take place on clays without neutralization by hydrogen ions, but Wiegner believes that such adsorption plays a negligible role. To show this Wiegner (156) performed the following experiment: Sodium permutite was treated with potassium chloride solution and with potassium hydroxide solution. Also, potassium permutite was treated with sodium chloride solution and with sodium hydroxide solution. In both cases, potassium and sodium were exchanged in equivalent amounts and neither potassium hydroxide nor sodium hydroxide disappeared by total adsorption.

Akeroyd and Broughton (3), working with synthetic resins of the catechol-formaldehyde type (not sulfonated) studied the adsorption of calcium hydroxide, barium hydroxide, sodium hydroxide and trimethylbenzyl ammonium hydroxide. They brought 0.27 gram of resin in contact with 500 c.c. of .02 N base and found that rate of adsorption obeyed the equation
\[
\frac{x}{m} = kt^n
\]

where \(\frac{x}{m}\) is the adsorption in milliequivalents of base per gram resin, \(t\) is the time of contact in hours, and \(k\) and \(n\) are constants. Their data are given in Table II.

Table II

<table>
<thead>
<tr>
<th>Base</th>
<th>(k)</th>
<th>(n)</th>
<th>Equilibrium adsorption (3 months) millimols per gram resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>5.09</td>
<td>.17</td>
<td>14.0</td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>11.9</td>
<td>.12</td>
<td>13.6</td>
</tr>
<tr>
<td>Ba(OH)(_2)</td>
<td>9.17</td>
<td>.16</td>
<td>13.4</td>
</tr>
<tr>
<td>((CH_3)_3(C_6H_5CH_2))HNOH</td>
<td>2.92</td>
<td>.21</td>
<td>8.6</td>
</tr>
</tbody>
</table>

It will be noted that both the rate of adsorption (\(k\) values) and the equilibrium values are lower for the large organic molecule than for the inorganic molecules. This may be ascribed to lower mobility of the organic molecule and to steric hindrance; i.e. the large organic molecule has more difficulty moving about in the interstices of the resin than do the smaller inorganic molecules.

It is significant that in terms of millimols per gram, the equilibrium capacity is roughly the same for calcium hy-
droxide, barium hydroxide and sodium hydroxide, whereas in terms of milliequivalents per gram, the capacity of the resin for adsorbing calcium hydroxide and barium hydroxide is about double that for sodium hydroxide. This is a strong indication that the adsorption is molecular rather than ionic in nature. It is believed that the base is adsorbed by virtue of direct chemical reaction with the phenolic groups of the resin, thus:

$$\text{Ca(OH)}_2 + R-O-H \rightarrow R-O-Ca-OH + \text{H}_2\text{O}$$

where $R-O-H$ is the resin structure presenting phenolic groups to the solution. This reaction is rather slow, following the exponential function given and requires about 3 months to reach equilibrium.

Evidence for this chemical reaction hypothesis is as follows:

1. Calculation of the theoretical amount of adsorption based on the molecular weight of the resin unit checks the actual amount of adsorption of base.
3. Non-phenolic resins, such as glyptal or vinylite, do not adsorb bases.
4. Calcium sulfate is not adsorbed by the phenolic resins, indicating that the hydrogen on the weakly acidic phenolic group is active only at high pH.
5. Increased polymerization decreases the amount of base adsorbed.
Beaton and Furnas (19) in a study of the Cu—H exchange on a sulfonated phenol-formaldehyde resin noted that at low pH, the exchange capacity of the resin was equivalent to the sulfur content, i.e. exchange took place entirely on the sulfonic acid groups on the resin, which amounted to 2 m.e. per gram resin. But at high pH, the exchange capacity rose to as high as 6 m.e. per gram resin. In explanation of this, the following suggestions were made:

1. Hydration of the resin units takes place in such a manner that hydrogen ions from the attached water molecules are made available for exchange at high pH. Such behavior is possible in colloidal dispersions, and the resinous exchangers in many respects behave as colloidal systems.

2. At high pH, (CuOH)⁺ ion may be the exchanging ion rather than Cu⁺⁺. Since each equivalent of (CuOH)⁺ ion contains two equivalents of Cu, the exchange capacity based on the copper analysis would be double the true exchange capacity. However, this explanation is not sufficient since the observed increase in capacity was as much as threefold.

3. Other active groups such as phenolic OH contribute to a higher exchange capacity at higher pH. Walton (151), in a study of the Ca—H equilibrium on Zeo-Karb, a sulfonated coal type resin, found that the intake of calcium ion by the resin increased with pH of the solution up to surprisingly large values, without showing any sign of reaching saturation,
a quite unexpected result. As far as could be judged by comparing the final pH with the composition of the original solution, hydrogen was being released in quantity equivalent to the calcium taken in. The conclusion was drawn that a good proportion of the exchangeable hydrogen must be bound to an acid of very low dissociation constant to account for the great increase in hydrogen replacement and uptake of calcium at high pH. If the dissociation constant of this acid could somehow be increased, this would greatly increase the capacity of the resin.

Bower and Truog (24) found that the exchange capacity of a clay in terms of m.e. per gram clay, was a function of the valence of the cation used. In general, the higher the valence of the cation, the higher was the apparent exchange capacity of the clay. Results obtained with monovalent cations were in good agreement, while those obtained with polyvalent cations gave increasingly higher values with decrease in strength of base which the respective cations form.

These results were explained by the formation of basic exchange salts by hydrolysis. Thus, magnesium acetate solution, at a pH of 7, will partially hydrolyze as follows:

\[ \text{Mg}(\text{Ac})_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{HAc} \]

Part of this magnesium hydroxide will then react with the clay:

\[ \text{Mg(OH)}_2 + \text{H-clay} \rightarrow \text{clay-MgOH} + \text{HOH} \]
In this latter reaction, only one equivalent of (MgOH)$^+$ is adsorbed on the clay, but in calculating the exchange capacity, each atom of magnesium is assigned two equivalents so that the apparent capacity is higher than the true capacity. The same phenomenon occurs with calcium, but since calcium hydroxide is a stronger base than magnesium hydroxide, there is less hydrolysis of calcium salts in solution and consequently less adsorption of (CaOH)$^+$ ion by the clay to form the basic exchange salt. Consequently the apparent exchange capacity for calcium will be less than for magnesium. Table III gives the exchange capacity of a clay determined for cations of varying valence.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Exchange capacity m.e. per gram</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4^+$</td>
<td>1.167</td>
</tr>
<tr>
<td>Ca$^{++}$</td>
<td>1.268</td>
</tr>
<tr>
<td>Mg$^{++}$</td>
<td>1.314</td>
</tr>
<tr>
<td>Be$^{++}$</td>
<td>2.280</td>
</tr>
<tr>
<td>Fe$^{+++}$</td>
<td>3.060</td>
</tr>
<tr>
<td>Th$^{++++}$</td>
<td>3.550</td>
</tr>
</tbody>
</table>
The basic exchange salt hypothesis is supported by the fact that when exchange capacities are measured using 99 per cent methanol in place of water as solvent, the values for mono-, di-, and trivalent cations are all the same. This is because in alcoholic solution, hydrolysis of the salt cannot occur and the basic exchange salt cannot form.

Elgabaly and Jenny (43) found that when 100 grams of a bentonite clay saturated with calcium ions was treated with zinc chloride solution, the final equilibrium distribution of ions on the clay surface was as follows:

\[ \text{Ca}^{++} 10.5 \text{ m.e.}, \text{Zn}^{++} 52.5 \text{ m.e.}, (\text{ZnOH})^+ 11.5 \text{ m.e.}, (\text{ZnCl})^+ 17.5 \text{ m.e.} \]

Thus these authors postulate not only the adsorption of (ZnOH)$^+$ ion but also that of (ZnCl)$^+$ ion.

The release of zinc from zinc clay by sodium chloride and calcium chloride is restricted mainly to divalent zinc. The clay shows a strong selective adsorption of the monovalent complex ion (ZnOH)$^+$, over the divalent zinc ion, Zn$^{++}$.

Zinc clays possess pronounced anion exchange properties. The anions Cl$^-$, OH$^-$, and NO$_3^-$ are mutually replaceable. The hydroxyl ion is held more tightly on the clay than either the nitrate or the chloride ion.

To explain these facts, Elgabaly and Jenny visualized the ions on the clay surface as follows:
The right hand picture satisfies the requirement of simultaneous cation and anion exchange which is found to take place at pH less than 7. The left hand picture seems to be favored in alkaline systems. For example, from zinc clays, prepared by leaching the clay with zinc chloride solution, sodium hydroxide will replace all the zinc in the adsorption layer, whereas sodium chloride will displace only divalent zinc. This indicates that zinc in the inner layer is not readily replaceable near and below the neutral point.

According to Walton (150), if a synthetic alumino-silicate containing barium ions is shaken with small amounts of sodium hydroxide solution, barium is exchanged for sodium but at the same time hydroxyl ions are adsorbed from solution, the adsorption being the greater, the greater the valence of the cation in the exchanger.

D. Equilibrium Relations

Many attempts have been made to find a quantitative relation connecting the relative amounts of the ions in solution
and on the exchanger after equilibrium has been reached. A
general equation of this kind would be useful in predicting ion
exchange behavior in practical applications and would also
indicate the mechanism involved. However, no such general
relation, applicable to all cases, has been developed. The
problem has been approached from both the theoretical and the
empirical point of view and a controversy as to whether the
mechanism is adsorption or mass action has been raging since
the days of Liebig. The various investigators have presented
their individual equations with highly diversified nomenclature
and concepts, often with inadequate description of the units
used. In order to compare these equations, the writer has
transformed all of them to a single consistent nomenclature and
to a uniform arrangement.

The case in which the most disagreement occurs and which
is of greatest interest in this investigation is that in which
a divalent cation exchanges with a monovalent cation. Let a
solution of volume $v$ c.c. containing $B'_0$ m.e. (milli-equivalents)
of the divalent cation be brought in contact with $m$ grams of
exchanger containing $A'_1$ m.e. of the monovalent cation. After
equilibrium is reached the outside solution contains $B_0$ m.e.
of the divalent cation and $A_0$ m.e. of the monovalent cation
while inside the exchanger there are $B_1$ m.e. of the divalent
cation and $A_1$ m.e. of the monovalent cation. The reaction is:

$$B_0 + 2A_1 \rightarrow B_1 + 2A_0$$
Let $k$ and $n$ be arbitrary constants. Using this nomenclature, the equilibrium equations are as given in Table IV.

Table IV

**Equilibrium Equations for Exchange between Divalent and Monovalent Cations**

<table>
<thead>
<tr>
<th>No.</th>
<th>Equation</th>
<th>Mechanism</th>
<th>Author</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$k = \frac{B_1}{A_1B_0 + B_1B_0}$</td>
<td>adsorption</td>
<td>Freundlich</td>
<td>(48)</td>
</tr>
<tr>
<td>2</td>
<td>$k = \frac{B_1}{A_1B_0}$</td>
<td>adsorption</td>
<td>Langmuir</td>
<td>(87)</td>
</tr>
<tr>
<td>3</td>
<td>$k = \frac{B_1}{A_1B_0 + B_1A_1}$</td>
<td>adsorption</td>
<td>Vageler</td>
<td>(148)</td>
</tr>
<tr>
<td>4</td>
<td>$k = \frac{B_1A_0^2}{A_1^2B_0} \cdot \frac{A_1 + B_1}{V}$</td>
<td>mass action</td>
<td>Kerr</td>
<td>(74)</td>
</tr>
<tr>
<td>5</td>
<td>$k = \frac{B_1A_0^2}{A_1^2B_0} \cdot \frac{2A_1 + B_1}{2V}$</td>
<td>mass action</td>
<td>Vanselow</td>
<td>(149)</td>
</tr>
<tr>
<td>6</td>
<td>$k = \frac{B_1A_0^2}{A_1B_0} \cdot \frac{B_1}{V}$</td>
<td>displacement probabilities</td>
<td>Davis</td>
<td>(34)</td>
</tr>
<tr>
<td>7</td>
<td>$k = \frac{B_1A_0^2}{A_1B_0} \cdot \frac{2A_1 + B_1}{2V}$</td>
<td>empirical</td>
<td>Rothmund</td>
<td>(121)</td>
</tr>
<tr>
<td>8</td>
<td>$k = \frac{B_1A_0^2}{A_1B_0} (A_1 + B_1)$</td>
<td>mass action</td>
<td>Beaton</td>
<td>(19)</td>
</tr>
</tbody>
</table>

It will be noted that no two of the eight equations given can be considered as equivalent. The various mass action equations differ among themselves as much as they differ from the
adsorption equations, which also differ among themselves, so that there is no reason to favor one mechanism over the other. Each author has presented data covering limited ranges of concentrations and solution volumes in support of his equation. However, when the equation is applied to wider ranges the constant \( k \) is no longer constant, indicating that the equation is not valid. The apparent validity of such a wide variety of equations, in limited ranges, to the same phenomenon may perhaps be traced to the following factors:

1. The equilibrium relation may vary with the nature of the exchanger.

2. The introduction of a second empirical constant such as \( n \) in Equations 1 and 7 is an artificial means of fitting the equation more closely to the data. The less empirical constants an equation contains, the more useful and significant it becomes.

3. Errors in the chemical analyses may be of such a magnitude that the variations in \( k \) are about the same for each equation so that the superiority of one equation over another cannot be decided.

It is very probable that ion exchange is neither an adsorption nor a mass action phenomenon. In the case of pure adsorption, the solid phase contains active unsaturated points to which ions from solution can attach themselves and satisfy the unsaturation. But in the case of ion exchange, the active spots are not unsaturated points. Instead of satisfying an
unsaturated position, an ion in solution must displace a second ion already on the solid, and the tendency of the latter ion to leave the solid will depend on its concentration in solution. These facts are not considered in the adsorption equations.

On the other hand, the mass action equation assumes a chemical reaction to take place between the solution and the exchanger. If the concentration of each constituent in the outer solution is expressed as m.e. per c.c. of solution and that inside the exchanger as m.e. per gram exchanger, Equation 4 is obtained. This equation is among those that show the poorest agreement with experiment (35). In Equation 5, the concentrations in the outer solution are expressed as m.e. per c.c. of solution, but the concentrations of the ions in the exchanger are expressed as mol fractions of the total number of mols of both ions in the exchanger. Equation 6 is not the ordinary mass action equation of Guldberg and Waage but is derived from an analysis of displacement probabilities (34). It will be noted that the exchange capacity, \((A_1 + B_1)\) in Equation 4 is replaced by \((A_1 + B_1/2)\) in Equation 5 and by \(B_1\) in Equation 6, the other terms being identical. Equations 5 and 6 generally are more applicable than Equation 4 but both show some deviation in \(k\) when applied over wide ranges of concentration (35). Equation 7 expresses the observed data more closely than any other equation (151), but the presence of the extra empirical constant \(n\) invalidates its theoretical
significance. Equation 8 was derived from data obtained on
the Cu — H exchange (19). It is based on molecular rather
than ionic reaction and is included here to illustrate the
variety of form the equilibrium equations for ion exchange may
take. The eight equations given were derived from data ob­tained with both organic and inorganic exchangers.

The proponents of the mass action mechanism are certain
that their equation would hold exactly if the "activities" of
the various ions could be substituted for their concentrations.
It should be pointed out that if the correct activity for each
ion were substituted into the mass action equation, the
equilibrium constant would indeed be constant, but it would
not prove that the mechanism was mass action. For the mass
action equation in terms of activities is derived as a math­
ematical necessity from the definition of activity and there­fore does not express a physical law. Furthermore the activities
are not directly measurable, as are concentrations. However,
if the activity of each ion could be found as a function of
its corresponding concentration, the mass action equation would
provide a simple means of relating the concentrations of the
various ions. The relation between activity and concentration
is expressed in the form

\[ a = fc \]

where \( a \) = activity, \( c \) = concentration and \( f \) is the activity
coefficient. The determination of the activity coefficients
of the ions involved in an ion exchange reaction has proved to involve great difficulty.

The activity coefficients of the ions in dilute solutions may be estimated from the Debye-Hückel theory (157):

\[ -\log f = 0.5 Z^2 \sqrt{u} \quad u < 0.01 \]

\[ -\log f = \frac{0.5 Z^2 \sqrt{u}}{1 + A\varepsilon \sqrt{u}} \quad u < 0.10 \]

In these formulas \( f \) is the activity coefficient of a cation in the solution, \( Z \) is its valence, \( u \) is the ionic strength of the solution, \( A \) is a constant depending on the temperature and the dielectric constant of the solvent, and \( \varepsilon \) is the sum of the radii of the hydrated cations and anions. These simple formulas are limited in their application. For solutions so dilute that \( u < 0.01 \), \( f \) may generally be taken as unity anyhow, while for values of \( u \) between 0.01 and 0.10 it is necessary to find the constants \( A \) and \( \varepsilon \), which are generally unknown. For \( u > 0.10 \) no formula is valid. It is for this reason that most investigators have conducted their equilibrium studies in very dilute solutions.

It is possible to construct tables of activity coefficients of salts as a function of their concentrations as determined by cryoscopic or electromotive force measurements. The use of these tables is limited by the fact that the activity coefficient of a pure salt changes when another salt is added to the solution. Furthermore although the relation

\[ a \pm = \sqrt{a} \]
is used to determine the activity of an ion from the activity of its salt, the procedure is questioned by some authorities. Thus Davis (35) rejects the use of ion activity because it cannot be thermodynamically defined and exactly determined by experiment. In this connection, it is interesting to note that Marshall and Gupta (92) carried out direct potentiometric measurements of the activities of the cations Tl\(^+\), H\(^+\), and Ag\(^+\). Using these values in place of concentrations they found that the constancy of the equilibrium constant \(k\) was improved in some cases but not in others.

The quantitative estimation of the activity coefficients of ions in solution is thus seen to be very difficult, if not impossible. However, some qualitative statements may be made (157). Due to the decrease of interionic forces by hydration of ions, the activity coefficient for monovalent and chemically closely related ions is the greater, the more hydrated the ion. Thus for the alkali ions \(f\) increases in the order

\[
C_3 Rb K Na Li.\]

Ions of high valence and small radius are largely associated at higher concentrations. The alkaline earth chlorides show a tendency toward association even at rather low concentrations. The activity coefficient is reduced by association according to the formula

\[
f = f_0 (1-x)
\]

where \(x\) is the degree of association and \(f_0\) is the Debye-Hückel activity coefficient. The decrease of \(f\) through association is particularly noticeable with polyvalent ions.
Thus far the discussion has dealt with the ions in solution. To determine the activities of the ions in the exchanger, even greater difficulties are encountered. It is not possible to measure these activities by independent methods as by potentiometric or cryoscopic determinations. Consequently it is meaningless to speak of the activities of the ions in the exchanger except in terms of values that will satisfy the mass action equation.

The significance of the above discussion on activities may be clarified by tracing through the development of the activity concept in the light of our purposes. Our purposes are twofold: (1) to prove or disprove that mass action is the mechanism of ion exchange and (2) to select an equation that will relate the concentrations of the ions in the solution and on the exchanger at equilibrium.

The original mass action equation, as proposed by Guldberg and Waage to relate the equilibrium concentrations of a chemical reaction, was derived on the basis of collision probabilities for the forward and reverse reaction (132). When we speak of the mass action mechanism, therefore, we mean that based on the collision probabilities of the constituents in a chemical reaction. The equation was found to hold only for perfect gases or ideal solutions (infinite dilution). Later, as reported in Glasstone (53), Gibbs showed that the same equation could be derived by thermodynamic methods, but again, only if the assumption is
made that the gases or liquids involved are ideal. In this derivation, Gibbs made use of the fact that at equilibrium the free energy change for a reaction is zero and that the free energy of each constituent is given by the relation

\[ F = RT \ln c + F^0 \]

where \( F \) is the free energy, \( c \) is the concentration and \( F^0 \) is a constant. Although the mass action relation is not true for actual reactions, it is approximately true, the approximation depending on the deviation from ideality. Lewis (88) suggested that instead of searching for an equilibrium relation among the concentrations that is more nearly true, it might be simpler to define a quantity in terms of which the mass law must hold, and then try to find the relation between this quantity and the corresponding concentration. This quantity is known as the activity, \( a \), and is defined by the relation

\[ F = RT \ln a + F^0 \]

This definition is identical with the relation between free energy and ideal concentration and therefore must, of necessity, lead to the mass action equation as derived by Gibbs. It is clear, therefore, that if the activity differs appreciably from the concentration, the mass action mechanism cannot be proved by showing that the equilibrium constant is constant when activities are used, for the activity is not a physical entity but is, in essence, any quantity that will satisfy the mass action equation.
However, the relation involving activities might be useful if it were possible to find independent methods for relating activity with concentration. As already pointed out, in the case of ions in solution as well as on the ion exchanger, this is very difficult if not impossible. It would appear, therefore, to be desirable to abandon the use of activities in ion exchange and to fall back on an equation expressed entirely in terms of concentrations. Of the equations listed in Table IV, Equation 7 is the most reliable to use in correlating or predicting equilibrium concentrations, but it has no theoretical significance. Equation 6, however, also correlates the experimental data fairly well and moreover is indicative of the mechanism of ion exchange. As derived by Jenny and Reitemeier (72) for monomonovalent ion exchange and extended by Davis (34) to monodivalent ion exchange, the cations on the exchanger are visualized to be oscillating about fixed positions within a volume which is characteristic of the cation. The cations in the solution outside this volume are uniformly distributed. The displacing ability of one cation for another will depend on the relative oscillation volumes, migration mobilities and concentrations. Oscillation volumes may be calculated from measured zeta potentials. One cation can displace another whenever it comes within the oscillation volume of the latter. A statistical analysis on this picture made by Davis for monodivalent cation exchange yielded an equation in the form of an infinite series.
Equation 6 is the result of using only the first term of this series, which term is a good approximation for the total series. The mechanism thus presented is neither adsorption nor mass action but may be considered specific for the ion exchange phenomenon.

It is interesting to note that the equation derived by the above analysis for mono-monovalent cation exchange is identical with the mass action equation.

Equation 6 was also derived by Gapon (52) from kinetic considerations, but his concepts were less definite than those of Jenny.

E. The Dilution Effect and Hysteresis

Many investigators have observed that divalent cations are more strongly attracted to the exchanger than monovalent cations when the solutions are dilute; but in concentrated solutions the attraction for the two ions is more nearly the same. In other words dilution favors the retention of the divalent ion. This is known as the dilution effect (73) (150) (157) (34) (17). With cation pairs of the same valence, such as K⁺ vs NH₄⁺ and Ca²⁺ vs Ba²⁺, dilution has relatively little effect on exchange.

Several explanations have been offered for this phenomenon. Examination of Equation 6, Table IV, reveals that with increased dilution (increase in v) there must be a greater displacement
of divalent cations ($B_1$) for monovalent cations ($A_1$) on the exchanger. Thus, the dilution effect is a further confirmation of the validity of the hypothesis upon which Equation 6 is based. This hypothesis includes the assumption that cations are held to the exchanger in a diffuse ion swarm rather than in a single monomolecular layer. Such a picture facilitates an understanding not only of the dilution effect but also of the phenomenon known as hysteresis. To explain these effects the assumption must be made that in the concentrated portion of the swarm immediately adjacent to the exchanger, the monovalent and divalent ions are held with about equal strength, whereas in the diffuse outer portion of the swarm the divalent ions are held more tenaciously than the monovalent ions. Thus in dilute solution only the outer ions enter the exchange and the adsorption of divalent ions is favored, whereas in concentrated solution the entire swarm enters the exchange and the average effect is to show less favor toward adsorption of the divalent ions.

Hysteresis is the name given to the observation that in certain cases of ion exchange, the point of equilibrium depends on the direction from which it is approached. Thus if a calcium saturated exchanger is treated with a solution of sodium chloride, at equilibrium the exchanger will retain more calcium than if the sodium saturated exchanger were treated with calcium chloride. This phenomenon is observed, for the
most part, with mono-divalent cation exchange (151) (124) (73). It can be explained on the basis of the diffuse ion swarm if the further assumption is made that an ion in the swarm close to the exchanger surface is held more firmly than an ion farther out in the swarm. Then whichever ion is placed on the exchanger first will take up positions next to the surface of the exchanger and consequently will be removed with greater difficulty. Hysteresis may thus be looked upon as a kind of friction which prevents the system from coming to true equilibrium.

F. Ion Hydration, Order of Cation Replacement, and Zeta Potential

Ions in solution are assumed to be hydrated. The water molecules are attracted to the ion by induced polarization in a diffuse mass, but only the most inwardly situated water molecules are strongly bound. Degree of hydration is high when the charge on the ion is high and the crystallographic radius is small. Therefore the hydration order for the alkali ions should be Li > Na > K > Rb > Cs and for the alkaline earth ions Mg > Ca > Sr > Ba. This is confirmed by ionic velocity measurements. Hydration tends to diminish with concentration and temperature. The size of the hydrated ions is in the order Mg > Ca > Sr > Ba > Li > Na > K (157).
The higher the valence of an ion and the less hydrated it is in solution, the more the ion is attracted to an exchanger (152). Ions may be dehydrated by addition of alcohol. When dehydrated the ions are alike with respect to ion exchange. Thus in pure water cesium shows 54 per cent more exchange than sodium while in 80 per cent alcohol it shows only 2 per cent more exchange (156). Ions may also be dehydrated at high temperatures. Thus in exchange with a silver saturated silicate exchanger (ultramarine), the order of replacing power for the alkali ions at room temperature was Cs > Rb > K > Na > Li as expected, but at 130 - 160°C (in sealed tubes) this order was completely reversed, presumably due to dehydration (70).

The replacing power of cations varies considerably according to the nature of the ion exchanger, the solution concentration and the degree of replacement of the exchanger. With sulfonated organic resins, the hydrogen ion has a rather low replacing power, but with clays and organic exchangers containing weak acid groups, such as the carboxyl or phenolic radicals, the hydrogen ion has a much greater replacing power (64) (157) (124). With Dow HCR (sulfonated polystyrene type resin) saturated with hydrogen ion, the order of replacement for monovalent ions in tenth normal solution is Ag > Tl > Rb > Cs > K > NH₄ > Na > Li (17).

The higher the hydration of an adsorbed cation, the greater is the water content of the exchanger (156) (124). A remarkable
correlation between hydrated ionic radius and exchange capacity was observed by Nachod and Wood (106).

Ion exchange has been connected with the Zeta potential in colloidal clay suspensions (71). This is further confirmation of the existence of a diffuse ionic swarm at the surface of an ion exchanger. The active points on the solid surface of the exchanger are charged negatively and as a consequence attract positive ions from the solution. These positive ions arrange themselves in a diffuse swarm near the solid surface, the density of the swarm decreasing with distance from the surface. The electromotive force that exists between the center of gravity of the positively charged swarm and the main body of the solution outside it, is known as the Zeta potential. The value of the Zeta potential may be calculated either from measurements of the migration velocity of colloidal particles in an electric field, or from measurements of the streaming potential produced when a solution is passed through a bed of the solid particles (155).

The Zeta potential is proportional to the thickness of the cation swarm. This thickness increases with hydration of the cation but decreases with increasing valence. High Zeta potential, therefore, should correspond to easily exchangeable cations. This was found to be the case (71). The degree of exchange varied with the sixth power of the Zeta potential and when the Zeta potential was zero, no exchange took place. The
electrical conductivity of clay suspensions containing various cations was found to be in the order Na > Ca > Ba. This is in the order of diminishing zeta potential and exchangeability as expected (27).

G. Rate of Ion Exchange

The rate of the cation exchange reaction was observed to be rapid by the earliest investigators. Way (153) recognized this in 1850. Subsequent rate measurements have been made with difficulty owing to the great rapidity of the reaction. The general conclusion to be drawn from these early investigations, mainly on soils, is that equilibrium is substantially reached within a few minutes but complete equilibrium may require several hours, days, or even months depending on the type of exchanger (151) (73).

Domaine, Swaine, and Hougen (39) established differential rate equations for a water softening ion exchange process using a thin cation exchanger bed 5.5 inches in diameter and 0.5 inch thick. Distilled water was first passed up through the bed to displace air which would cause channeling, then the test run was made by passing hard water down through the bed, presumably displacing the distilled water ahead of it. One of the results obtained was that the reaction velocity was greater with smaller particle size indicating that diffusion was a controlling factor.
Using various exchange materials and various cations, Nachod and Wood (105) showed that in solutions of about .005 N the rate data fit the bimolecular second order reaction equation

$$\frac{dx}{dt} = k_1 (a-x)(b-x)$$

rather closely. The rate constant $k_1$ for various exchange materials and reactions at 27° C. is given in Table V.

**Table V**
Comparison of Ion Exchange Rate Constants

<table>
<thead>
<tr>
<th>Exchanger</th>
<th>Reaction</th>
<th>$k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeo-Karb 20-30 mesh</td>
<td>$H_1 + Ca_0$</td>
<td>.66</td>
</tr>
<tr>
<td>Amberlite 1R-100</td>
<td></td>
<td>.66</td>
</tr>
<tr>
<td>Zeo-Karb 1R-100</td>
<td>$Ca_1 + H_0$</td>
<td>.84</td>
</tr>
<tr>
<td>Zeo-Karb 1R-100</td>
<td>$Na_1 + Ca_0$</td>
<td>.60</td>
</tr>
<tr>
<td>Amberlite 1R-100</td>
<td></td>
<td>.29</td>
</tr>
<tr>
<td>Greensand</td>
<td></td>
<td>1.60</td>
</tr>
<tr>
<td>Synthetic silica gel</td>
<td></td>
<td>.26</td>
</tr>
</tbody>
</table>

Note that greensand gave the fastest exchange rate although it has the lowest exchange capacity (see Table I). This is probably due to the fact that the exchange positions in greensand are all on the surface of the particles, whereas in the other exchangers a good portion of the exchange positions is in the
interstices of the resin or silicate structure within the particles.

Monovalent ions approach equilibrium faster than divalent ions, the order being Cs = Rb = K > Na > Li for the monovalent ions, and Ba > Sr = Ca > Mg for the divalent ions. The variation of rate constants among the cations is approximately what one would expect from their respective diffusion rates. But diffusion is not the only rate determining factor, others being hydrated ionic size, charge, and steric availability (106).

The sulfonated resinous organic cation exchangers exhibit a high rate of diffusion and usually are much more rapid in exchange than are the inorganic natural or synthetic aluminosilicates (152) (16). An exception is the catechol-formaldehyde type of resin in which the phenolic radical is the sole exchanging group. The exchange rate for this resin is extremely slow, requiring as much as three months to reach equilibrium (150) (3) although the exchange capacity is very high (see Table I).

Bauman and Eichhorn (17) found that the rate of diffusion of sodium chloride and hydrochloric acid in spherical particles of Dowex-50 resin is about one fifth as rapid as diffusion in dilute aqueous solutions. Ninety per cent of the capacity of Dowex-50 may be exhausted in 33 seconds in the sodium-hydrogen exchange.

Schubert, Boyd, and Adamson (124) believe that the rate
of diffusion is controlling when concentrations exceed 0.1M. They also found that the exchange rate constant was lower for larger particles and deeper beds. When a solution was passed through a shallow bed of the exchanger particles the exchange rate constant was from five to ten times greater than when passed through a deep bed.

H. Effect of Temperature on Ion Exchange

Generally speaking, temperature has little effect on ion exchange especially with ions of equal valence. With ions of unequal valence, increase in temperature favors the adsorption of the ion with higher valence, the effect being greater in concentrated solutions (150) (45).

Nachod and Wood (105) reported that ion exchange rate was about 10% slower at 0°C than at 27°C but at 60°C it was the same as at 27°C. This temperature effect is probably due to changes in diffusion rate rather than in exchange rate. Jaeger (70), working with the mineral ultramarine, treated Ag-ultramarine with sodium iodide solution at 100°C and 160°C in sealed tubes. At 160°C, equilibrium was reached in about one hour, but at 100°C the exchange was much slower and equilibrium was not completely reached even after fifty hours. This effect may be attributed to the dehydration of the sodium ions at the higher temperature.
I. Swelling

When an organic ion exchanger or a clay of the montmorillonite type is placed in water after being dried, it swells considerably in volume. Thus Zeo-Karb swells from a bulk volume of 1.42 c.c. per gram in air to 2.04 c.c. per gram in water (151). The amount of swelling depends on the cation that is adsorbed on the exchanger. The bulk volume of a sulfonic acid type resin in c.c. per gram for various adsorbed cations is as follows (57): H 1.283, Na 1.655, K 1.434, Cs 1.388, Mg 1.655, Ca 1.585, Ba 1.453, Ag 1.283. The swelling of Mg, Ca, and Ba sulfonic acid type resins is directly proportional to the solubility of the corresponding benzene sulfonates. The silver form of Dow HCR resin occupies only 87% of the volume of the equivalent lithium resin (16).

Dry exchange materials swell in water chiefly because of hydration of the adsorbed cations. This is evident from the fact that the amount of swelling for the various cations is in the same order as their hydration. An interesting theory relating to swelling, hydration, and osmotic pressure is suggested by Flory and Rehner (46). Exchange materials expand less in concentrated salt solutions than in pure water because the ions in the solution compete with the cations on the exchanger for the water of hydration.
J. Anion Exchange

The exchange of anions on an anion exchange material is, in theory, analogous to the exchange of cations on a cation exchanger. Actually, however, anion exchange behavior is significantly different.

Inorganic materials exhibiting anion exchange properties include dolomite, heavy metal silicates (103) and phosphate rock (150). The exchange capacity of these materials is very low and they have no commercial significance. However, gels of ferric and aluminum oxides have been used to remove fluoride ions from water by anion exchange with chloride ions (56).

The commercially important anion exchangers are all organic resins in which an amine or ammonium group is the seat of exchange. Those resins which contain primary, secondary, or tertiary amine groups behave as weak bases and serve to adsorb relatively strong acids from solution. Letting R represent the resin structure, the reaction may be written

\[
\text{RNH}_2 + \text{H}^+ + \text{A}^- \rightarrow \text{RNH}_3^+ \text{A}^-
\]

where \( \text{A}^- \) is the anion of the acid. Thus the mechanism appears to be adsorption of the entire acid rather than exchange of anions (103). The reaction cannot be written

\[
\text{RNH}_2 + \text{HA} \rightarrow \text{RNH}_3^+ \text{A}^-
\]

for there is evidence to show that adsorption of the undissociated acid does not occur. Very weak (undissociated) acids,
such as silicic acid, phenol, and hydrocyanic acid, are not adsorbed by the amine type resins. Also, adsorption of even strong acids does not take place in non-aqueous solvents in which the acid is undissociated (104). Data on the adsorption of acids from dilute solutions by these resins fit the Freundlich adsorption equation better than any other, thus confirming the adsorption mechanism (101) (23). The heat of adsorption of acids by anion exchangers of the amine type is not large but it is a good deal more than the heat of reaction of cation exchange (84). This suggests that the mechanism is first the adsorption of hydrogen ion by a somewhat covalent link with the evolution of heat,

$$\text{RNH}_2 + H^+ \rightarrow \text{RNH}_3^+ + \Delta$$

followed by adsorption of the anion by the ionic link with no evolution of heat,

$$\text{RNH}_3^+ + A^- \rightarrow \text{RNH}_3^+ A^-$$

Since the salt formed by the amine group and the acid is the salt of a weak base, it is to be expected that some of the salt will hydrolyze to give

$$\text{RNH}_3^+ A^- + \text{HOH} \rightleftharpoons \text{RNH}_3^+ \text{OH}^- \rightleftharpoons \text{RNH}_2 + \text{H}_2\text{O}$$

so that the resin will contain both $A^-$ ions and $\text{OH}^-$ ions, the relative amounts depending on the strength of the base: the stronger the base, the less $\text{OH}^-$ ions on the resin at the equivalent point.
Up to this point the discussion has dealt with acid adsorption rather than anion exchange. True anion exchange is possible between a salt in solution and the salt formed on the resin after adsorption of a strong acid,

$$\text{RNH}_3^+ \text{Cl}^- + \text{Na}_2\text{SO}_4 \rightleftharpoons (\text{RNH}_3)_2\text{SO}_4 + 2\text{NaCl}$$

In this reaction, sulfate ion is exchanged for chloride ion in neutral solution.

The acid adsorption capacity of Amberlite IR4B, an amine type resin containing 14% nitrogen, is 10 m.e. per gram to HCl which corresponds to one Cl for each N (84). But to H$_2$SO$_4$ the capacity is 11.6 m.e. per gram and to H$_3$PO$_4$, 27.7 m.e. per gram. This indicates that the ions HSO$_4^-$, H$_2$PO$_4^-$ and HPO$_4^{2-}$ are also active. High concentrations of acids (above 0.2N) are needed to saturate the resins.

In the NaOH regeneration of a resin which has adsorbed HCl, the reaction is probably

$$\text{RNH}_3^+ \text{Cl}^- + \text{NaOH} \rightarrow \text{RNH}_2 + \text{NaCl} + \text{H}_2\text{O}$$

with a slight formation of RNH$_3$OH.

The rate of acid adsorption by an amine type resin is much slower than the exchange of cations on a cation exchanger (125) (105) (101). The rate determining step is diffusion. The rate of acid adsorption for various acids is in the order H$_3$PO$_4$ > H$_2$SO$_4$ > HAc > HCl. True anion exchange, as for example the chloride-sulfate exchange indicated above is much more
rapid than acid adsorption and is comparable in speed with cation exchange (85).

New anion exchange resins have recently been developed which are strongly basic in character and are capable of exchanging hydroxyl ion for other anions by true anion exchange at any pH (83). They are also capable of adsorbing very weak acids such as silicic acid from solutions. These feats were not possible with the weak base amine type resins. The new resins derive their strong basicity from quaternary ammonium groups or from guanidino groups incorporated in the resin structure. The basicity of these groups is comparable with that of sodium hydroxide.

The behavior of these resins is in every way comparable to the sulfonic acid type cation exchangers (85). The anion exchange capacity of one of these resins, Amberlite IRA-400, is 2.0 m.e. per gram which is comparable to the capacities of the cation exchangers listed in Table I. The rate of exchange for the strong base anion exchangers is as high as for the strong acid cation exchangers. Equilibrium concentrations for mono-monovalent anion exchange is very well correlated by the Rothmund-Kornfeld equation (121) as in cation exchange. For the OH-Cl exchange this equation is

\[
\frac{\text{OH}_0}{\text{OH}_1} = 2.95 \quad \frac{\text{Cl}_0}{\text{Cl}_1}^{-0.75}
\]

where subscript 0 signifies concentration in m.e. per gram in the outside solution and subscript 1 inside the resin. As
with cation exchange, the divalent anions showed stronger
affinity for the resin than the monovalent anions. The order
of replacing power is citrate sulfate oxalate iodide nitrate
chromate bromide thiocyanate chloride formate hydroxyl
fluoride acetate. Amberlite IRA-400 is operable at pH values
as high as 10.

A complete list of commercially available anion exchangers
is given by Nachod (107).

K. Ion Exchange Operation

The technique of carrying out an ion exchange process on
an industrial scale rests largely on the experience gained in
the water treatment field in the past 40 years. The primary
function of the equipment is to provide a convenient means of
contacting solutions with the particles of ion exchange mater­
ial in a series of steps composing the operating cycle. The
most frequently used method is to pass the liquid downward
through a granular bed of ion exchange material placed in a
rubber lined steel tank with means for supporting the material
and distributing the solution over it uniformly. For minimum
loss of valuable constituents the cycle of operations is car­
ried out in six steps (119) (107):

(1) Pass solution to be treated down the bed to displace
rinse water from previous cycle.
(2) When effluent concentration is constant start drawing off main product.

(3) When ion exchange material is exhausted, introduce water to displace the solution.

(4) Backwash by running water up through the bed to loosen it and remove dirt and foreign matter.

(5) Pass regenerating solution down through the ion exchanger to replace the original ions.

(6) Rinse the ion exchanger free of regenerant with water.

The volume of the bed is determined by the capacity of the exchanger, the quantity of ions to be exchanged and the length of the operating cycle desired. The latter is determined by a proper balance between initial equipment costs and operating labor costs. The bed depth is seldom under 30 inches and is usually considerably more than this. From 50 to 100\% "free-board" or rising space is left above the exchanger bed to provide for expansion of the bed during backwashing so that dirt can be carried away without loss of exchanger particles.

Multiple units are often employed to permit continuous flow of product by switching units after each step in the cycle. The external piping and valve system is rather complicated and highly specialized. Automatic control is used in complicated systems using short cycles.

In a few cases, such as in the pectin industry (21), ion exchange is carried out by agitating as a slurry the exchanger
granules and the liquid to be treated. The granules are then separated by centrifuging and regenerated in the conventional columnar bed.

In columnar operation attempts have been made to remove the exhausted portion of the ion exchange bed continuously and to regenerate it externally to the column. This would permit keeping the ion exchange column in continuous operation and avoid shutdowns. However, all such schemes have thus far proven unsuccessful and have not been adopted for commercial use.

L. Applications of Ion Exchange Materials

A number of recent reviews (107) (4) (41) describe the many and varied applications, both old and new, to which ion exchange has been put. New applications are being proposed almost daily. In general it might be said that these ion exchangers may have possible value wherever the removal, exchange, or separation of ions in solution are involved. Only a few representative examples from the various fields will be mentioned here.

The oldest and still the most important use is in the water softening and purification field. Sodium and potassium cations are removed from sugar juices to obtain higher yields of sucrose. Metals such as copper, silver, and chromium can be recovered from very dilute solutions. Sea water can be desalted on a small scale for emergency use. Many of the ion
exchangers are excellent catalysts for a large number of chemical reactions. Amino acids can be separated by chromatography on ion exchangers. Cow's milk may be modified for infant feeding. Copper and sodium may be removed from hydrocarbons. Blood may be modified for transfusions. Ulcers may be treated with anion exchangers. Vitamin B₁ may be recovered and purified.

M. Preparation of Chemicals by Ion Exchange

The preparation of chemicals is singled out here because it is the application of ion exchange with which this thesis is concerned. It is not listed among the important uses of ion exchange because of the serious limitations encountered in most cases. These limitations will be discussed after a few examples have been given.

Ammonium sulfate has been prepared from urine (159). The urine was first treated with urease and then passed through an acid regenerated cation exchanger which adsorbed the ammonia. Regeneration with sulfuric acid yielded ammonium sulfate in the effluent, the overall yield being 80% based on the original nitrogen content of the urine.

Free acids have been prepared by passing alkali salts over an acid regenerated cation exchanger (93). Conversion could not be made complete. The acid used in regeneration contaminated the effluent and the solutions were more dilute than desirable.
A special case of the preparation of acids is the preparation of silicic acid sols (123). Sodium silicate solution was passed through an acid regenerated cation exchanger, the sodium ion in solution being replaced by the hydrogen ion from the exchanger. This application was rather successful because of the favorable equilibrium for the formation of silicic acid. Because the acid is extremely weak the sodium in the solution can be almost completely replaced by the hydrogen from the exchanger even from rather concentrated solutions.

Lead acetate and calcium nitrate were obtained in separate solutions using lead nitrate and calcium acetate in conjunction with an interesting ion exchange technique (10). A solution of lead nitrate was first passed down a column of calcium zeolite and lead zeolite mixed in such a way that the concentration of calcium zeolite decreased and the concentration of lead zeolite increased in the direction of flow. The effluent was a solution of calcium nitrate. The column was then washed and inverted and a solution of calcium acetate passed down the tube, the effluent being lead acetate. It is likely, however, that the solutions of lead acetate and calcium nitrate thus obtained were either impure or very dilute or both. The principles involved in this process were discussed by Austerweil (11) (12).

An ion exchange process for making sodium nitrate from calcium nitrate and sodium chloride has actually been employed in Norway (110). The sodium saturated cation exchanger is
treated with calcium nitrate solution, the effluent being sodium nitrate with some excess calcium nitrate which is not objectionable. The exchanger is then regenerated by passing sea water through it, the effluent being calcium chloride in a large excess of sodium chloride all of which is discarded.

Very recently, a process has been proposed for preparing soda ash from sea water by ion exchange (76). The sea water is first treated with calcium hydroxide to precipitate magnesium hydroxide and leave a purified sea water. The magnesium hydroxide precipitate is then converted to magnesium bicarbonate by contacting it with carbon dioxide gas. The soluble magnesium bicarbonate is dissolved and the solution passed through a sodium saturated cation exchanger to give an effluent to dilute sodium bicarbonate. The exchanger is then regenerated by passing the purified sea water through it, the effluent being a solution of magnesium chloride in a large excess of sodium chloride, all of which is discarded. It is believed that by suitable recycling procedures, more concentrated solutions of sodium bicarbonate may be obtained. Upon heating, sodium bicarbonate is converted to sodium carbonate. The process is only in the research stages of development and no claims are made for it as yet.

The foregoing examples suggest the limitations that are inherent in the general preparation of chemicals by a double decomposition reaction carried out on ion exchangers. It can be seen that in the general case the desired product must be
obtained in the form of a dilute solution, and the higher the purity of the product desired, the more dilute must be the solution. This is because of the equilibrium relation existing among the ions and the limited exchange capacity of a given volume of exchanger. To elucidate this, consider an exchanger bed having a total exchange capacity c m.e. and saturated with ion A. If a volume v c.c. of solution containing B m.e. of ion B is passed through the exchanger bed, the maximum concentration of A that could possibly be obtained in the effluent in one pass would be c/v. This concentration of A could be obtained free of B only if the original solution contained exactly c m.e. of B ions and during exchange all of the B ions replaced all of the A ions on the exchanger. However, due to the equilibrium relation only a part of the A ions are replaced so that the effluent solution is more dilute than c/v and moreover is contaminated with unexchanged B ions. It is possible to raise the concentration of A in the effluent to a value close to c/v by starting with a concentration of B in the feed solution far in excess of c/v. However, in that case, the effluent will be highly contaminated with unexchanged B ions. It is also possible to obtain an effluent almost free of B by starting with a concentration of B in the feed solution very much less than c/v. In that case almost all of the B ions will be exchanged but the effluent solution will be very dilute in A since it will contain no more A ions than the original solution contained B ions.
These difficulties may be obviated in cases where the equilibrium is very favorable as in the case of the production of silicic acid sols cited above, or where contamination of the product with one of the reactants is not objectionable as in the production of sodium nitrate. In the problem with which this thesis is concerned, the limitations described above were circumvented by taking advantage of the solubility characteristics of strontium hydroxide. Strontium hydroxide is soluble in hot solution but insoluble in cold sodium hydroxide solution. Thus, by passing a hot concentrated strontium hydroxide solution over a sodium saturated exchanger, the maximum concentration of sodium hydroxide in the effluent was obtained together with a large excess of strontium hydroxide. But this strontium hydroxide in the effluent was easily removed from solution by precipitation on cooling, leaving a pure sodium hydroxide solution as product.
III. EXPERIMENTAL

The following experiments were designed to explore all possible means by which sodium hydroxide can be produced by the ion exchange process. Specifically, it was desired to secure data indicating the concentration of sodium hydroxide obtainable, the efficiency of the exchange, the capacity of the exchange material, the conditions for regeneration of the exchangeable cation, and the optimum conditions for exchange. The effect, on the above quantities, of the type of exchangeable hydroxide used, the type of exchange material used, temperature, concentration, contact time, and solution to resin ratio comprised the major portion of the investigation. Attention was given to the theoretical significance of the results obtained. Some study was made of the possibility of recovery of the exchangeable cation from the regenerant effluent and its reconversion of the hydroxide. A quantitative flowsheet based on the experimental data was developed and the economic possibilities discussed.

A. Investigation of Suitable Exchangeable Hydroxides

It is clear that to produce sodium hydroxide by ion exchange in aqueous solution, the hydroxide of the cation with which sodium ion is to exchange must be soluble in water. The list of common soluble hydroxides is not large and consists of
the following: ammonium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, lithium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide and thallous hydroxide.

Selection of the most suitable exchangeable hydroxide is based on solubility behavior, cost, exchange characteristics of the cation and concentration of sodium hydroxide obtainable.

1. **Solubility behavior and costs of the various hydroxides.**

A major difficulty encountered when attempts are made to produce salts by ion exchange is the incompleteness of exchange, resulting in a product which is contaminated with the unexchanged portion of the salt fed to the ion exchanger. In the case at hand, if a solution of a hydroxide, $MOH$, is fed to a sodium loaded exchanger, $M^+$ will replace $Na^+$ on the exchanger to form sodium hydroxide in the solution but the portion of the $MOH$ which does not exchange will be discharged along with $NaOH$ in the exit solution. The unexchanged portion of the $MOH$ is the result of an equilibrium existing among the ions in solution and on the exchanger. It is true that in ordinary water softening operations by ion exchange, the calcium and magnesium ions in solution are almost completely removed from solution by the exchanger; but this is possible only so long as there is a large excess of sodium ions on the exchanger over calcium and magnesium ions in solution. This is the situation in water softening because even in hard waters the solu-
tions are very dilute. However, in the case of salt manufacture by ion exchange, it is necessary to feed a concentrated solution in order to obtain a product of reasonable concentration.

It is proposed to obviate this difficulty by selecting a hydroxide which is soluble when hot but relatively insoluble when cold. Thus the concentrated hydroxide solution could contact the exchanger when hot and after leaving the exchanger it could be cooled, whereupon the unexchanged portion would precipitate leaving the pure sodium hydroxide in solution.

The solubilities of the various soluble hydroxides in hot and cold water are compared in Table VI.

The solubility-temperature curves for calcium hydroxide, strontium hydroxide and barium hydroxide are shown in Figure 2.

It appears that calcium, strontium, barium, and thallous hydroxides have low enough solubilities when cold to conceivably be precipitated from the sodium hydroxide effluent. Ammonium hydroxide could be removed from the effluent by boiling the solution. The other hydroxides, those of lithium, potassium, rubidium and cesium are highly soluble and therefore would not precipitate from sodium hydroxide solution. Calcium hydroxide has the disadvantage of having an inverted solubility curve and therefore cannot be expected to give a high degree of exchange when hot; but in view of its advantage of very low cost it was decided to investigate its exchange characteristics in
Table VI

Solubilities of Hydroxides in Gram-equivalents per 1000 Grams Water

<table>
<thead>
<tr>
<th>Hydroxide</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>NH₄</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0° C.</td>
<td>0.050</td>
<td>0.067</td>
<td>0.5615</td>
<td>52.8</td>
<td>5.31</td>
<td>10.51</td>
<td>24.22</td>
<td>17.578</td>
<td>26.4015</td>
<td>1.17</td>
</tr>
<tr>
<td>100° C.</td>
<td>0.021</td>
<td>3.59</td>
<td>6.007</td>
<td>84.38</td>
<td>7.31</td>
<td>86.7</td>
<td>44.5</td>
<td>v.s.</td>
<td>---</td>
<td>6.69</td>
</tr>
</tbody>
</table>
Fig. 2. Solubility curves for alkaline earth hydroxides

Solubility - equivalents per 1000 g. water

Temperature °C.

\((\text{Ba(OH)}_2)\)

\((\text{Sr(OH)}_2)\)

\((\text{Ca(OH)}_2)\)
the hope of overcoming the effect of its low solubility during exchange.

The costs (III) of the various soluble hydroxides are compared in Table VII.

Table VII
Comparison of Costs of Hydroxides

<table>
<thead>
<tr>
<th>Hydroxide</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>NH₄</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost $/lb. equiv.</td>
<td>.22</td>
<td>26.6</td>
<td>15.2</td>
<td>11.7</td>
<td>26.3</td>
<td>2.62</td>
<td>6.2</td>
<td>--</td>
<td>--</td>
<td>44.30.0</td>
</tr>
</tbody>
</table>

This table shows that the cost of thallous hydroxide is so extremely high as compared with the other hydroxides as to eliminate it from consideration.

This leaves calcium hydroxide, strontium hydroxide, barium hydroxide and ammonium hydroxide as feasible agents for exchange. In the case of the latter three hydroxides, recovery of the cation is necessary since each of these is more costly than the sodium hydroxide product.

In view of the foregoing analysis, experimental examination of exchange characteristics was limited to the four hydroxides just mentioned.
2. Exchange characteristics

The ion exchange material used in these tests was a highly cross-linked sulfonated phenol-formaldehyde resin produced by the Dow Chemical Company and known as Dow MX. This resin which is more fully described on page 15 was selected because of its relatively high exchange capacity and fair stability to strong caustic solutions as compared with other organic and inorganic exchangers available at the time.

a. Exchange characteristics of calcium hydroxide.

(1) Single contact with calcium hydroxide solution. Three cycles of exchange and regeneration were carried out on one gram of resin using fresh calcium hydroxide solution during each exchange and fresh sodium chloride solution for each regeneration. The resin was thoroughly washed after treatment with each solution. The solutions were analyzed for hydroxyl ion by titrating with HCl, for calcium ion by the oxalate-permanganate method and for chloride ions by the Mohr method. The conditions for the test and the results are given in Table VIII.

The results of Table VIII show that the maximum sodium hydroxide concentration obtainable by cation exchange with calcium hydroxide solution in one pass is about 0.1% solution. The experiment also shows that exchange on new resin is not as great as in subsequent cycles and that hydroxyl ions are adsorbed during exchange but chloride ions are not adsorbed during
Table VIII

Exchange of Calcium for Sodium from Calcium Hydroxide Solution

(Units are milliequivalents unless otherwise noted)

Exchange at 25°C.

<table>
<thead>
<tr>
<th></th>
<th>1st cycle</th>
<th>2nd cycle</th>
<th>3rd cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. e. Ca and OH in feed solution</td>
<td>3.30</td>
<td>3.30</td>
<td>3.30</td>
</tr>
<tr>
<td>M. e. OH adsorbed by resin</td>
<td>1.16</td>
<td>0.70</td>
<td>0.71</td>
</tr>
<tr>
<td>M. e. Ca adsorbed by resin</td>
<td>2.30</td>
<td>2.98</td>
<td>2.82</td>
</tr>
<tr>
<td>M. e. Ca exchanged for Na</td>
<td>1.14</td>
<td>2.28</td>
<td>2.11</td>
</tr>
<tr>
<td>Weight % NaOH made</td>
<td>.045</td>
<td>.09</td>
<td>.08</td>
</tr>
<tr>
<td>% of original Ca adsorbed</td>
<td>69.7</td>
<td>90.3</td>
<td>77.2</td>
</tr>
<tr>
<td>% of original Ca exchanged</td>
<td>34.6</td>
<td>69.2</td>
<td>64.0</td>
</tr>
</tbody>
</table>

Regeneration at 25°C.

<table>
<thead>
<tr>
<th></th>
<th>1st cycle</th>
<th>2nd cycle</th>
<th>3rd cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. e. Cl adsorbed by resin</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>M. e. Ca released from resin</td>
<td>2.52</td>
<td>2.52</td>
<td>2.66</td>
</tr>
<tr>
<td>Ca released/Ca adsorbed</td>
<td>1.10</td>
<td>.846</td>
<td>.943</td>
</tr>
<tr>
<td>M. e. OH released from resin</td>
<td>.20</td>
<td>.31</td>
<td>.34</td>
</tr>
</tbody>
</table>
regeneration. The explanation for these phenomena is not clear from this experiment alone but later experiments will show that the adsorption of hydroxyl ion is due partly to the neutralization of acidic hydrogen present in the phenolic type resin and partly to the fact that a portion of the calcium exchanges in the form of the cation \((\text{CaOH})^+\). This latter hypothesis explains the reappearance of some of the adsorbed hydroxyl ions in the regenerant solution.

(2) Single contact with calcium hydroxide suspension. In view of the fact that only a 0.1% solution of sodium hydroxide resulted from the exchange with a solution initially 80% saturated with calcium hydroxide (.033N) from which most of the calcium was removed by exchange, it was felt that higher concentration of sodium hydroxide would result if the solution was at all times saturated with calcium hydroxide during exchange. This could be done by using a calcium hydroxide suspension.

In the following tests, Dow MX resin, calcium hydroxide power, and water in various proportions were stirred for periods of time deemed sufficient to reach equilibrium conditions. The solution in each case was then filtered off and a sample of filtrate was analyzed for hydroxyl and calcium ions. The conditions for the tests and the results are given in Table IX.
Table IX

Exchange of Calcium for Sodium from Calcium Hydroxide Suspension

<table>
<thead>
<tr>
<th>Test</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams resin (air dry)</td>
<td>1</td>
<td>10.2</td>
<td>10.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Condition of resin</td>
<td>regen.</td>
<td>fresh</td>
<td>regen.</td>
<td>regen.</td>
<td>regen.</td>
</tr>
<tr>
<td>Grams Ca(OH)(_2)</td>
<td>0.122</td>
<td>1.1</td>
<td>1.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Grams H(_2)O</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>% Ca(OH)(_2) in feed</td>
<td>0.12</td>
<td>1.09</td>
<td>0.99</td>
<td>4.75</td>
<td>14.29</td>
</tr>
<tr>
<td>Contact time, hrs.</td>
<td>1</td>
<td>8</td>
<td>18</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>Grams NaOH made</td>
<td>0.0913</td>
<td>0.0862</td>
<td>0.368</td>
<td>0.512</td>
<td>0.186</td>
</tr>
<tr>
<td>Wt. % NaOH in solution</td>
<td>0.09</td>
<td>0.086</td>
<td>0.366</td>
<td>0.510</td>
<td>0.62</td>
</tr>
<tr>
<td>Exchange efficiency, m.e. NaOH made</td>
<td>69.1</td>
<td>7.3</td>
<td>34.0</td>
<td>9.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Examination of Table IX reveals that the maximum sodium hydroxide concentration obtained with a calcium hydroxide suspension was 0.62% NaOH by weight. This was obtained in the case where the ratio of resin to solution was the greatest and where the concentration of calcium hydroxide was the greatest as might be expected. The variation of sodium hydroxide concentration and exchange efficiency with calcium hydroxide concentration in suspension is shown graphically in Figure 3. It will be noted that while the sodium hydroxide concentration increases to a
Fig. 3. Ion exchange with calcium hydroxide suspension.
maximum as the concentration of calcium hydroxide suspension and resin is increased, the exchange efficiency drops sharply. This is significant because the ratio of calcium hydroxide to resin was the same in all cases. This behavior is indicative of a mass action type effect in which accumulation of sodium hydroxide in solution suppresses the tendency toward further exchange. This effect is enhanced by the diminution of the solubility of calcium hydroxide as the sodium hydroxide concentration is increased. This diminution (127) is rather sharp as shown in Figure 4 and the approximate parallelism of the exchange efficiency curve and the solubility curve of calcium hydroxide suggests that the exchange efficiency is influenced by the diminished solubility of calcium hydroxide as well as by the increase in sodium hydroxide concentration.

(3) multiple contact with calcium hydroxide suspension. Attempts were made to increase the sodium hydroxide concentration obtainable by contacting the calcium hydroxide suspension with small portions of sodium saturated resin successively rather than by using the total amount of resin in one contact. It was expected that by such a procedure the reverse reaction, i.e. the exchange of sodium for calcium on the resin, would be lessened, since no large amount of calcium loaded resin could be present at any one time. However, the results showed that in no case in which this multiple contact procedure was used was the resultant sodium hydroxide solution of a higher con-
Fig. 4. Comparison of CaO solubility exchange efficiency.
centration than when using a single contact with the same total amount of resin, and in most cases it was the same. This rather surprising result suggests that the reverse reaction mentioned above may not be of great importance in the exchange and that the factor that limits exchange as the sodium hydroxide concentration builds up is largely the lowered solubility of calcium hydroxide.

(4) Multiple contact by flow through resin bed. It is believed by some investigators (136) that exchange efficiency is greater when the solution is allowed to flow over a stationary bed of the resin than when the solution and resin particles are stirred together in a batch exchange. To test this idea, a column of resin was set up in a glass tube 2.3 cm. in diameter and 27.6 cm. long. After saturating the resin with sodium by passing concentrated sodium chloride down through the bed and washing, saturated calcium hydroxide solution was repeatedly recycled through the bed, keeping the solution saturated with calcium hydroxide by passing it through a column of calcium hydroxide powder before it came in contact with the resin bed. After the resin was exhausted of sodium it was regenerated with sodium chloride and the procedure repeated with the same calcium hydroxide solution. This procedure was repeated until the sodium hydroxide content of the solution showed no further increase. The maximum sodium hydroxide concentration obtained in this manner was 0.47% by weight. This is somewhat less than the
0.62% produced by stirring calcium hydroxide powder with the resin in water suspension, and shows that the flow procedure is not advantageous in this case as far as degree of exchange is concerned.

(5) Effect of temperature. To determine the effect of temperature on the exchange, three samples were prepared, each containing 100 c.c. of 5% calcium hydroxide suspension. To two of the samples 50 grains of sodium-saturated resin were added but not to the third. All three samples were stirred for 45 minutes during which time one of the samples containing the resin was kept at 75° C. while the others were at 23° C. The suspensions were filtered and the solutions analyzed. The results are shown in Table X.

Table X
Effect of Temperature on Exchange of Calcium Hydroxide

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>5 g. Ca(OH)_2</td>
<td>5 g. Ca(OH)_2</td>
<td>5 g. Ca(OH)_2</td>
</tr>
<tr>
<td>100 g. H_2O</td>
<td>100 g. H_2O</td>
<td>100 g. H_2O</td>
<td></td>
</tr>
<tr>
<td>50 g. resin</td>
<td>50 g. resin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>75° C.</td>
<td>23° C.</td>
<td>23° C.</td>
</tr>
<tr>
<td>Solution analysis</td>
<td>After exchange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.e. OH</td>
<td>6.92</td>
<td>11.84</td>
<td>3.92</td>
</tr>
<tr>
<td>M.e. Ca</td>
<td>.46</td>
<td>.68</td>
<td>3.93</td>
</tr>
<tr>
<td>M.e. NaOH</td>
<td>6.46</td>
<td>11.16</td>
<td>0</td>
</tr>
</tbody>
</table>
The diminished sodium hydroxide content of the solution which underwent exchange at the higher temperature is the result of the lowered solubility of calcium hydroxide at the higher temperature (see Figure 2). This is another bit of evidence to support the contention that the degree of exchange is limited by the low solubility of calcium hydroxide.

(6) Effect of contact time. The effect of time of contact of the solution with resin on the degree of exchange and adsorption is shown in Figure 5. In these experiments 20 g. of sodium-saturated resin were shaken with 150 c.c. of .0342 N calcium hydroxide solution for a definite time after which a sample was immediately taken and analyzed. A number of such experiments were performed using various contact times. The curves in Figure 5 show that all of the calcium in solution was adsorbed by the resin in 5 minutes, but the maximum sodium hydroxide concentration was obtained in 1 minute, after which it dropped steadily until a constant value was reached in about 2 hours. This clearly shows that after the sodium hydroxide is formed in solution by exchange it is slowly readSORBED by the resin, most likely on the phenolic OH groups which, because of their weakly acidic properties tend to adsorb bases slowly (see page 25).

(7) Effect of non-aqueous solvents. The effect of non-aqueous solvents on the degree of exchange and adsorption of calcium hydroxide is shown in Figure 6. In these experiments
150 c.c. feed solution, 0.0342 N Ca(OH)$_2$
20 g. Dow MX resin

Fig. 5. Effect of contact time on calcium hydroxide exchange.
150 c.c. methanol-water solution saturated with Ca(OH)$_2$.
20 g. Dow MX resin
Contact time: 20 min.

Fig. 6. Effect of non-aqueous solvents on calcium hydroxide exchange.
20 g. of sodium saturated resin were shaken for 20 minutes with 150 c.c. of saturated solutions of calcium hydroxide in various methanol-water mixtures. The curves of Figure 6 show that methanol has the effect of lowering the amount of calcium adsorbed and also the amount of sodium hydroxide formed by exchange. Similar experiments with ether-water and acetone-water solvents showed similar results.

(8) Use of calcium hydroxide in anion exchange. Inasmuch as cation exchange of Ca for Na produced a maximum sodium hydroxide concentration of only 0.6%, an attempt was made to improve on this by using anion exchange. By the anion exchange scheme, the reactions would be as follows:

Exchange:

\[ \text{NaCl} + \text{R-OH} \rightleftharpoons \text{NaOH} + \text{R-Cl} \]

Regeneration:

\[ 2 \text{R-Cl} + \text{Ca(OH)}_2 \rightleftharpoons 2 \text{R-OH} + \text{CaCl}_2 \]

where \( \text{R-} \) represents the anion exchange resin (see pages 51-55).

Since sodium chloride is highly soluble, in contrast to calcium hydroxide, such a process would be capable of producing sodium hydroxide solutions of correspondingly high concentrations if the chloride ions could be induced to exchange more or less completely with the hydroxyl ions on the anion exchanger. The exchanger could then be regenerated by repeated leaching with calcium hydroxide solution.

At the time this investigation was started the only anion
exchangers commercially available were the amine type acid adsorbers described on page 51. In order to exchange hydroxyl ions the resin must contain a functional group that has strongly basic properties. An investigation was therefore undertaken to explore means by which resins containing strongly basic functional groups could be synthesized.

Tertiary sulfonium compounds are known to be capable of forming soluble hydroxides which are strong bases (32). If these could be produced in resin form, the hydroxyl ions should be highly ionized and exchangeable. Triphenol-sulfonium chloride was prepared by the method of Smiles (131) and polymerized under various conditions with furfural and with formaldehyde in the presence of both acid and basic catalysts. The resins thus formed were hard solid materials of various colors and had other interesting properties but they did not exhibit the ability to exchange anions.

Quaternary ammonium hydroxides are also known to be strong bases soluble in water. Attempts were made to form anion exchangers by adsorbing these hydroxides on activated carbon and activated alumina, but the adsorbents so treated did not differ in exchange capacity from the untreated adsorbents.

Since these tests were made, anion exchange resins of the strong base type have been developed and made available by the Resinous Products Company and by Liquid Conditioning Corp. These resins, Liquonex AD and Amberlite IRA400, were tested
in the OH — Cl exchange. It was found that the equilibrium involving the chloride ions and the hydroxyl ions was such that only a very small fraction of the chloride ions from a sodium chloride solution exchange for hydroxyl ions from the resin. The solution thus produced in one contact had a concentration of about 0.1% sodium hydroxide in a solution almost saturated with sodium chloride. In short, the affinity of the resin for hydroxyl ion is so much greater than its affinity for chloride ion that the exchange is not practicable.

b. Exchange characteristics of ammonium hydroxide. Sodium-saturated Dow MX resin was stirred with ammonium hydroxide solutions of concentrations 15N, 5N, 1N, 0.1N, 0.01N, 0.001N. After 30 minutes stirring at 23°C the solution was filtered and evaporated to dryness to drive off all ammonia. If there was any exchange of ammonium ion for sodium ion, the residue should consist of sodium hydroxide. This could be dissolved and titrated with standard acid. In the case where 15N ammonium hydroxide was used it was found that a trace of sodium hydroxide was formed by ion exchange. In all other cases, not even a trace of sodium hydroxide was formed. The tests were repeated through several cycles of exchange and regeneration with sodium chloride with the same results. The same tests were carried out in methanol-water and acetone-water solutions. With these solvents no trace of sodium hydroxide was formed even with 15N ammonium hydroxide.
These results may be explained by the fact that in the equilibrium

\[ \text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

the reaction from right to left predominates to such a great extent that the concentration of ammonium and hydroxyl ions is extremely small even in concentrated ammonia solutions (132). Since the ion exchange equilibrium depends on the ammonium ion concentration and not on the total ammonia concentration it is clear that very little exchange of ammonium ion for sodium ion can take place on the resin.

c. **Exchange characteristics of strontium hydroxide.**

(1) Effect of contact time on the exchange adsorption of strontium hydroxide on fresh Dow MX resin. Twenty grams of dry fresh resin were shaken with 150 c.c. of strontium hydroxide solution (saturated at 20°C) for exactly 1 minute. The solution was immediately decanted and analyzed for strontium ion by precipitation as sulfate (126) and for hydroxyl ion by titration with standard HCl. This test was repeated for various contact times. The results are given in Figure 7.

It appears that the adsorption of strontium is more rapid than the adsorption of hydroxyl ion, and the exchange efficiency and the sodium hydroxide concentration exhibit a maximum at about 4 minutes contact time in this case. It will be noticed that prior to the maximum point at 4 minutes, the m.e. Sr adsorbed is exactly twice the m.e. OH adsorbed. This suggests
Reactants:
150 c.c. of 0.0791N Sr(OH)$_2$ solution
20 g. fresh Dow MX resin
20° C.

Fig. 7. Rate of adsorption of Sr and OH.
that up to 4 minutes, \((\text{SrOH})^+\) ion, which contains 2 m.e. Sr to 1 m.e. OH, is exchanging with \(\text{Na}^+\) ion on the resin until all the Sr is adsorbed. After this point, the sodium present in the solution as NaOH is readorsorbed slowly on the phenolic OH groups on the resin. This is shown by the lowest curve of Figure 7.

(2) Effect of regeneration with NaCl solution. The 20 g. resin samples of the previous test, on which contact times of 10 seconds, 1 minute, and 1 hour were used, were regenerated by tumbling each with 50% saturated NaCl solution for 1 hour then washing thoroughly with distilled water. After removing loose water by suction the three resin samples were again tested with 0.0791N \(\text{Sr(OH)}_2\) as in the previous test for 10 seconds, 1 minute and 1 hour respectively. The results are given in Table XI together with the corresponding results on the fresh resin.

Examination of Table XI reveals that after regeneration the resin adsorbs Sr more rapidly and OH more slowly than does fresh unregenerated resin. This results in a higher maximum exchange efficiency and also a higher maximum NaOH concentration.

The improved exchange properties of the regenerated resin might be ascribed to a certain orientation of the active spots on the resin for the cation being exchanged. Thus the first contact with \(\text{Sr(OH)}_2\) solution would orient the exchange spots for Sr thus facilitating the Sr exchange in subsequent contacts.
<table>
<thead>
<tr>
<th>Contact time, sec.</th>
<th>Regenerated resin</th>
<th>Fresh resin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>Total Sr adsorbed</td>
<td>5.53</td>
<td>11.38</td>
</tr>
<tr>
<td>OH adsorbed</td>
<td>2.48</td>
<td>3.76</td>
</tr>
<tr>
<td>Initial Sr in solution</td>
<td>11.78</td>
<td>11.78</td>
</tr>
<tr>
<td>Sr exchanged for Na</td>
<td>3.05</td>
<td>7.62</td>
</tr>
<tr>
<td>Sr exchanged/total Sr adsorbed, %</td>
<td>55.1</td>
<td>67.0</td>
</tr>
<tr>
<td>Sr adsorbed/initial Sr, %</td>
<td>47.0</td>
<td>96.6</td>
</tr>
<tr>
<td>OH adsorbed/initial OH, %</td>
<td>21.1</td>
<td>31.9</td>
</tr>
<tr>
<td>G. NaOH made per g. resin</td>
<td>.0061</td>
<td>.0152</td>
</tr>
<tr>
<td>Conc. of NaOH sol'n, wt. %</td>
<td>.0813</td>
<td>.2035</td>
</tr>
</tbody>
</table>
after regeneration. Experimenters with exchange resins have known for some time that a resin that has been "run in" by several exchange and regeneration cycles shows better exchange properties than fresh resin. The reason usually given is removal of metallic impurities of the resin, but the removal of the usual small amount of such impurities would not account for the rather large improvement shown in this experiment.

Some of the improved performance may be due to the fact that the resin was wet before making contact with the solution. As discussed on pages 14 and 50, a wet resin is swollen, its interstices are more open and accessible to ions for exchange. Of course the dry resin will swell up on contact with the solution but the wetting process takes time.

(3) Comparison of the effect of dry fresh resin, wet fresh resin and regenerated wet resin on the exchange adsorption of \( \text{Sr(OH)}_2 \). Three samples of Dow MX resin were prepared as follows: Sample 1; 20 g. of fresh dry resin. Sample 2; 20 g. of fresh dry resin tumbled for 10 minutes with 150 c.c. of water then sucked free of excess water. Sample 3; sample 1, after treatment with \( 0.0791 \text{NSr(OH)}_2 \) was regenerated as in Experiment (2).

The samples were tumbled with \( 0.0791 \text{NSr(OH)}_2 \) for 4 minutes and the solutions analyzed. The results are given in Table XII.
Table XII

Effect of Resin Condition on Exchange

(Values are in milliequivalents unless otherwise indicated)

<table>
<thead>
<tr>
<th>Condition of resin</th>
<th>fresh, dry</th>
<th>fresh, wet</th>
<th>regenerated, wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sr adsorbed</td>
<td>11.40</td>
<td>11.38</td>
<td>11.75</td>
</tr>
<tr>
<td>OH adsorbed</td>
<td>5.77</td>
<td>6.67</td>
<td>4.90</td>
</tr>
<tr>
<td>Initial Sr in solution</td>
<td>11.78</td>
<td>11.78</td>
<td>11.78</td>
</tr>
<tr>
<td>Sr exchanged for Na</td>
<td>5.63</td>
<td>4.71</td>
<td>6.85</td>
</tr>
<tr>
<td>Sr exchanged/total Sr adsorbed, %</td>
<td>53.0</td>
<td>41.4</td>
<td>58.3</td>
</tr>
<tr>
<td>Sr adsorbed/initial Sr, %</td>
<td>97.0</td>
<td>96.7</td>
<td>99.9</td>
</tr>
<tr>
<td>OH adsorbed/initial OH, %</td>
<td>49.0</td>
<td>56.6</td>
<td>41.6</td>
</tr>
<tr>
<td>NaOH made per g. resin</td>
<td>.282</td>
<td>.236</td>
<td>.343</td>
</tr>
<tr>
<td>Conc. of NaOH sol'n, wt. %</td>
<td>.150</td>
<td>.126</td>
<td>.183</td>
</tr>
<tr>
<td>Colorimeter reading on solution</td>
<td>96</td>
<td>91</td>
<td>86</td>
</tr>
</tbody>
</table>

(100 = colorless, 0 = black)
Table XII shows that the regenerated wet resin gives a greater degree of exchange than the fresh resin either dry or wet. Moreover the dry fresh resin gives a slightly better degree of exchange than the wet fresh resin. These results clearly indicate that the improved performance shown in Experiment (2) is actually due to regeneration and not to merely wetting the resin. The slight advantage of the dry over the wet fresh resin may be explained by the slight dilution caused by the water initially present in the wet resin.

It is interesting to note that the color throw from the regenerated resin is somewhat greater than that from the fresh resin.

(4) Effect of solution: resin ratio. Three samples of fresh resin weighing 1 g., 10 g. and 20 g. respectively were shaken with 150 c.c. of 0.0791N\text{Sr(OH)}_2 solution for 2 minutes and the solutions analyzed. Each sample of resin was then washed and regenerated with NaCl as described in Experiment (2). The test with \text{Sr(OH)}_2 solution was then repeated on these regenerated samples. The results are given in Table XIII.

Table XIII shows that the amount of exchange increases with the amount of resin present as is to be expected since the more resin present the more sodium is available for exchange. However, the "NaOH made per gram resin," that is, the exchange per gram resin, falls off with the solution: resin ratio. This can be explained by the assumption that the higher NaOH
Table XIII

Effect of Solution: Resin Ratio on Exchange

(Values are in milliequivalents unless otherwise noted)

<table>
<thead>
<tr>
<th>Condition of resin</th>
<th>Fresh</th>
<th>Regenerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams resin</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>G.c. solution</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Solution: resin ratio</td>
<td>150</td>
<td>15</td>
</tr>
<tr>
<td>Total Sr adsorbed</td>
<td>1.53</td>
<td>7.88</td>
</tr>
<tr>
<td>OH adsorbed</td>
<td>.84</td>
<td>3.74</td>
</tr>
<tr>
<td>Initial Sr in solution</td>
<td>11.78</td>
<td>11.78</td>
</tr>
<tr>
<td>Sr exchanged for Na</td>
<td>.69</td>
<td>4.14</td>
</tr>
<tr>
<td>Sr exchanged/Sr adsorbed, %</td>
<td>45.1</td>
<td>52.5</td>
</tr>
<tr>
<td>Sr adsorbed/initial Sr, %</td>
<td>13.0</td>
<td>66.9</td>
</tr>
<tr>
<td>OH adsorbed/initial OH, %</td>
<td>7.1</td>
<td>31.8</td>
</tr>
<tr>
<td>NaOH made per g. resin</td>
<td>.690</td>
<td>.414</td>
</tr>
<tr>
<td>Conc. of NaOH sol'n, wt. %</td>
<td>.0184</td>
<td>.1104</td>
</tr>
<tr>
<td>Colorimeter reading on sol'n</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

(100 = colorless, 0 = black)
concentration, which resulted from the presence of the larger amount of resin per c.c. of solution, serves to diminish the tendency for further exchange. Thus the last part of the resin to enter exchange will do so to a much smaller degree than the first part and the average exchange per gram resin for a large amount of resin will be less than for a small amount. Another contributing factor could be the varying degrees of affinity exhibited by different exchange spots on the resin, as discussed on page 43. The more resin present, the less is the tendency to utilize the less active exchange spots so that the exchange per gram resin is diminished.

The data of Table XIII again verify the fact that regeneration improves the exchange properties of the resin but increases the color throw.

(5) Effect of presaturation of the resin with Sr(OH)$_2$.
Ten g. of fresh Dow MX resin was tumbled with a suspension of 5 g. Sr(OH)$_2$·8H$_2$O in 150 c.c. water for 1 hour to completely saturate the resin. The resin was then washed thoroughly and regenerated with NaCl in the usual manner and washed. This regenerated resin was then tested with 150 c.c. of 0.0791N Sr(OH)$_2$ for 2 minutes. The results of this test together with that of the 10 g. dry and regenerated sample of Experiment (4) are given in Table XIV.

It is apparent from Table XIV that presaturation of the resin with Sr(OH)$_2$ depresses the adsorption of OH and enhances
Table XIV

Effect of Presaturation of Resin

(Values are in milliequivalents unless otherwise indicated)

<table>
<thead>
<tr>
<th>Condition of resin</th>
<th>Fresh</th>
<th>Partially saturated, regenerated</th>
<th>Totally saturated, regenerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sr adsorbed</td>
<td>7.88</td>
<td>11.44</td>
<td>10.87</td>
</tr>
<tr>
<td>OH adsorbed</td>
<td>3.74</td>
<td>3.51</td>
<td>2.21</td>
</tr>
<tr>
<td>Initial Sr in solution</td>
<td>11.78</td>
<td>11.78</td>
<td>11.78</td>
</tr>
<tr>
<td>Sr exchanged for Na</td>
<td>4.14</td>
<td>7.93</td>
<td>8.66</td>
</tr>
<tr>
<td>Sr exchanged/total Sr adsorbed, %</td>
<td>52.5</td>
<td>69.3</td>
<td>79.8</td>
</tr>
<tr>
<td>Sr adsorbed/initial Sr, %</td>
<td>66.9</td>
<td>97.2</td>
<td>92.4</td>
</tr>
<tr>
<td>OH adsorbed/initial OH, %</td>
<td>31.8</td>
<td>29.8</td>
<td>18.8</td>
</tr>
<tr>
<td>NaOH made per g. resin</td>
<td>.414</td>
<td>.793</td>
<td>.866</td>
</tr>
<tr>
<td>Conc. of NaOH sol'n, wt. %</td>
<td>.1104</td>
<td>.2115</td>
<td>.231</td>
</tr>
<tr>
<td>Colorimeter reading on sol'n</td>
<td>98</td>
<td>82</td>
<td>86</td>
</tr>
</tbody>
</table>

(100 = colorless, 0 = black)
the degree of cation exchange after regeneration with NaCl. Moreover, the more complete the presaturation, the greater is the effect. This supports the contention that pretreatment of the resin with a cation orients the exchange position for that cation in such a way that subsequent exchange with the same cation is facilitated.

(6) Effect of initial concentration of Sr(OH)$_2$ solution. Several 10 g. samples of fresh Dow MX resin were saturated with Sr(OH)$_2$ as described in Experiment (5), regenerated, washed the sucked free of loose water. The samples were then shaken with 150 c.c. of Sr(OH)$_2$ solution of varying concentration for 2 minutes at room temperature. The results are shown in Figure 8.

It appears from Figure 8 that while the absolute adsorption and exchange of strontium increases with increasing initial concentration the per cent of the original strontium adsorbed and exchanged decreases. On the other hand, both the absolute amount of OH adsorbed and the per cent of the original OH adsorbed increase with increasing initial concentration.

These phenomena may be explained by the hypothesis already described, namely (1) the unequal affinity for the cation of the various exchange points on the resin and (2) the partial ionization of Sr(OH)$_2$ to (SrOH)$^+$ and OH$^-$. Thus at the higher initial concentrations of solution, more of the weakly
Fig. 8. Effect of initial concentration of Sr(OH)$_2$ in solution.
adsorbing exchange points on the resin must be utilized with the result that the per cent of the original Sr adsorbed will be lower. The fact that the Sr exchanged/Sr adsorbed ratio also decreases with increasing concentration suggests that the points on the resin that adsorb cations most readily are also the ones that exchange them most readily. This further suggests that the difference in adsorption and exchange ability of the various active points on the resin is very likely due to differences in spatial accessibility and that exchange requires greater accessibility than adsorption. If it is assumed that in very dilute solution Sr(OH)\(_2\) dissociates to Sr\(^{++}\) and 2 OH\(^-\) while in more concentrated solution a portion of the Sr(OH)\(_2\) dissociates to (SrOH)\(^+\) and OH\(^-\) and if it is further assumed that most of the OH adsorbed on the resin is in the form of (SrOH)\(^+\) then the behavior of OH adsorption shown in Figure 8 becomes intelligible. For the greater the initial concentration the greater will be the proportion of (SrOH)\(^+\) in solution and consequently the greater the per cent of original OH adsorbed.

It is interesting to inquire as to the simultaneous effect of initial concentration and quantity of resin for a given volume of solution. Such information can be derived from the data already gathered and is presented in Table XV and Figure 9. The data are taken from the tests on the exchange adsorption of 150 c.c. Sr(OH)\(_2\) solution on regenerated Dow MX resin for contact time of 2 minutes at room temperature.
Table XV

Effect of Initial Concentration and Solution: Resin Ratio

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Initial m.e. Sr g. resin</th>
<th>Initial m.e. Sr g. resin</th>
<th>Sr adsorbed g. resin</th>
<th>OH adsorbed g. resin</th>
<th>Sr exchanged g. resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.78</td>
<td>1</td>
<td>11.78</td>
<td>2.04</td>
<td>.97</td>
</tr>
<tr>
<td>2</td>
<td>11.78</td>
<td>10</td>
<td>1.178</td>
<td>1.144</td>
<td>.351</td>
</tr>
<tr>
<td>3</td>
<td>11.78</td>
<td>20</td>
<td>.589</td>
<td>.586</td>
<td>.233</td>
</tr>
<tr>
<td>4</td>
<td>27.75</td>
<td>10</td>
<td>2.775</td>
<td>1.478</td>
<td>.570</td>
</tr>
<tr>
<td>5</td>
<td>20.60</td>
<td>10</td>
<td>2.060</td>
<td>1.350</td>
<td>.489</td>
</tr>
<tr>
<td>6</td>
<td>2.05</td>
<td>10</td>
<td>.205</td>
<td>.205</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>8.40</td>
<td>1</td>
<td>8.40</td>
<td>1.990</td>
<td>.954</td>
</tr>
</tbody>
</table>
Fig. 9. Effect of initial m.e. Sr in solution per g. resin.
It is to be noted that although there is a variation of the quantity of resin in these tests as well as a variation in the concentrations used, the points in Figure 9 all fall on smooth curves. This shows that the correlation on the per gram resin basis is valid.

The curves of Figure 9 may be interpreted as follows: at low concentrations the Sr(OH)$_2$ in solution is completely dissociated into Sr$^{++}$ and 2 OH$^-$. This permits complete exchange of Sr$^{++}$ for 2 Na$^+$ with no adsorption of OH$^-$ as shown by Test No. 6, Table XV. As the concentration is increased some of the Sr(OH)$_2$ dissociates into (SrOH)$^+$ and OH$^-$. Thus OH is adsorbed on the resin in the form of (SrOH)$^+$ ion which exchanges with Na$^+$. Two reactions take place simultaneously, viz,

(1) $\text{Sr(OH)}_2 + \text{Na}_2\text{R} \rightleftharpoons \text{R-Sr} + 2 \text{NaOH}$

(2) $\text{Sr(OH)} + \text{Na}_2\text{R} \rightleftharpoons \text{Na-R-SrOH} + \text{NaOH}$

The dotted line in Figure 9 represents the adsorption of Sr as (SrOH)$^+$ and is obtained by doubling the ordinates of the curve representing OH adsorbed per gram resin. This is because there are two milliequivalents of Sr for each milliequivalent of OH adsorbed, assuming all the OH is adsorbed as (SrOH)$^+$. The difference in ordinates between the curves for total Sr adsorbed and (SrOH)$^+$ adsorbed is the me. Sr adsorbed and exchanged as Sr$^{++}$ ion. Thus Figure 9 shows that for all but very dilute solutions (less than .002 N) much of the
strontium is adsorbed and exchanged as \((\text{SrOH})^+\) ion by reaction (2) given above and the predominance of reaction (2) over reaction (1) increases as the concentration increases.

The curve representing Sr exchanged per gram resin is obtained by subtracting the ordinates of the curve for OH adsorbed from those of the curve for total Sr adsorbed per gram resin. This curve shows that the exchange capacity of Dow MX resin for this reaction is about 1 me./g. as compared with 2 me./g. reported for the Ca-Na exchange in neutral solution (16).

(7) Production of more concentrated NaOH solution.
(a) Multiple contact at room temperature. From the previous experiments it appears that the optimum conditions for exchange at room temperature are as follows: Contact time should be 1 to 6 minutes; the resin should be thoroughly saturated with \(\text{Sr(OH)}_2\) and regenerated with NaCl before test; a value of 7.5 for the ratio of c.c. solution of g. resin is satisfactory; and the \(\text{Sr(OH)}_2\) concentration should be no higher than necessary for exchange to take place.

At room temperature saturated \(\text{Sr(OH)}_2\) is about .18 N. Since the final solution after one contact with the resin can never be any more concentrated in OH than the initial solution it is clear that in order to produce a more concentrated NaOH solution at room temperature, the initial solution must repeatedly be brought into contact with regenerated resin with additions of solid \(\text{Sr(OH)}_2\) to the solution before each contact.
It is necessary to use solid $\text{Sr(OH)}_2$ rather than $\text{Sr(OH)}_2$ solution to avoid dilution with water.

Fresh Dow MX resin was saturated with $\text{Sr(OH)}_2$ and regenerated with $\text{NaCl}$ as previously described. The wet regenerated resin was divided into 10 portions each of which was placed in a wide mouthed bottle. To the first bottle was added 150 c.c. of saturated $\text{Sr(OH)}_2$ solution, shaken 3 minutes, then decanted into a beaker. Four g. of $\text{Sr(OH)}_2.8\text{H}_2\text{O}$ crystals were added to the solution with stirring. The suspension was then poured into the second bottle containing the second portion of resin and again shaken for 3 minutes. This procedure was repeated 5 times, a small sample of solution being withdrawn after each contact for titration with HCl. The results are shown in Table XVI and Figure 10.

The results of this experiment may be interpreted as follows: the drop in OH content on the first contact is due to normal adsorption of $(\text{SrOH})^+$ ion. The rise of OH content on the second contact is, of course, due to the addition of solid $\text{Sr(OH)}_2$ to the solution. However, it was expected that the OH content would continue to rise above that of the original solution since $(\text{SrOH})^+$ was being exchanged for Na$^+$ and the NaOH thus formed in solution would be more soluble than the original $\text{Sr(OH)}_2$. As shown in Figure 10, this was not the case. The OH content of the solution never exceeded the original concentration and as a matter of fact continued to
Table XVI

Multiple Contact Exchange at Room Temperature

<table>
<thead>
<tr>
<th>Contact</th>
<th>Original solution</th>
<th>1st contact</th>
<th>2nd contact</th>
<th>3rd contact</th>
<th>4th contact</th>
<th>5th contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH content, m.e.</td>
<td>25.2</td>
<td>15.8</td>
<td>23.8</td>
<td>23.0</td>
<td>21.6</td>
<td>18.2</td>
</tr>
<tr>
<td>Contact time</td>
<td>3 minutes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>23° C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 g. Sr(OH)$_2$.8H$_2$O added to the solution before each contact</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26 g. resin in each contact</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 10. Effect of multiple contact with Sr(OH)$_2$ at 23$^\circ$ C.
drop in subsequent contacts despite the addition of solid Sr(OH)$_2$ before each contact. This behavior could be due to the adsorption of part of the NaOH formed onto the resin as discussed on page 86.

(b) Multiple contact at elevated temperatures. Since the solubility of Sr(OH)$_2$ is greatly increased by raising the temperature (see Figure 2, page 67), more NaOH will be formed per contact with hot saturated Sr(OH)$_2$ solution than with cold saturated solution, and the NaOH content of the solution will thus have a better chance to be built up by multiple contact.

Dow MX resin was pretreated with Sr(OH)$_2$ as before, regenerated, washed and divided into 10 equal parts. Each part was then shaken successively with 150 c.c. of Sr(OH)$_2$ solution preheated to 95° C. and containing enough Sr(OH)$_2$ to be saturated at 80° C. The hot solution was poured onto the resin in a bottle, shaken for 1 minute then decanted from the resin and cooled to room temperature, whereupon most of the Sr(OH)$_2$ precipitated. After taking a 1 c.c. sample from the supernatant liquid for analysis the solution was reheated to 95° C. to redissolve the precipitated Sr(OH)$_2$.8H$_2$O and poured into the bottle containing a second portion of resin and the process repeated. In all 10 contacts were made with the same solution. The results are recorded in Table XVII and Figure 11.

This test of the effect of hot concentrated Sr(OH)$_2$ solution in exchange with Dow MX resin revealed the following facts:
Table XVII

Multiple Contact Exchange from Hot Concentrated Sr(OH)$_2$ Solution

<table>
<thead>
<tr>
<th>Contact</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.e. OH in supernatant solution</td>
<td>40.7</td>
<td>56.2</td>
<td>66.9</td>
<td>70.9</td>
<td>78.6</td>
<td>93.4</td>
<td>103.0</td>
<td>98.6</td>
<td>101.2</td>
<td>96.1</td>
<td></td>
</tr>
<tr>
<td>M.e. Sr in supernatant solution</td>
<td>17.5</td>
<td>15.3</td>
<td>11.5</td>
<td>10.6</td>
<td>9.2</td>
<td>4.2</td>
<td>1.4</td>
<td>1.1</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>M.e. NaOH in supernatant solution</td>
<td>23.2</td>
<td>40.9</td>
<td>55.4</td>
<td>60.3</td>
<td>69.4</td>
<td>89.2</td>
<td>101.6</td>
<td>97.5</td>
<td>100.5</td>
<td>95.8</td>
<td></td>
</tr>
<tr>
<td>Wt. % NaOH in supernatant solution</td>
<td>0.62</td>
<td>1.09</td>
<td>1.48</td>
<td>1.61</td>
<td>1.85</td>
<td>2.38</td>
<td>2.71</td>
<td>2.60</td>
<td>2.68</td>
<td>2.56</td>
<td></td>
</tr>
<tr>
<td>M.e. NaOH made per g. resin</td>
<td>23.2</td>
<td>17.7</td>
<td>14.5</td>
<td>4.9</td>
<td>9.1</td>
<td>19.8</td>
<td>12.4</td>
<td>-4.1</td>
<td>3.0</td>
<td>-4.7</td>
<td>101.6</td>
</tr>
<tr>
<td>M.e. NaOH made per g. resin</td>
<td>0.89</td>
<td>0.68</td>
<td>0.55</td>
<td>0.19</td>
<td>0.35</td>
<td>0.76</td>
<td>0.48</td>
<td>-0.16</td>
<td>0.12</td>
<td>-0.18</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Contact time 1 minute

Temperature 95 to 70° C.

26 g. resin in each contact
Fig. 11. Multiple contact exchange from hot conc. Sr(OH)$_2$ solution.
A maximum concentration of about 2.7% NaOH was obtained. Such a concentration is applicable to the uses given on page 9. The final NaOH solution is almost free of strontium due to the very low solubility of Sr(OH)$_2$ in 2.7% NaOH at room temperature. The Sr(OH)$_2$ in this solution is 0.012%. As shown in Figure 11, the Sr content drops as the OH content rises. The maximum exchange capacity, which occurred in the first contact, was 0.89 m.e./g. resin. The NaOH content of the solution continued to rise for the first seven contacts but subsequent contacts could not produce any more NaOH.

This last point is of special significance. It discloses that the NaOH content of the solution cannot be increased indefinitely simply by increasing the initial Sr(OH)$_2$ concentration and the number of contacts with fresh Na-loaded resin. Instead, an equilibrium is reached among the Sr(OH)$_2$ and NaOH in solution and the cations on the resin. As the concentration of NaOH in the solution is increased the ionization of Sr(OH)$_2$ is inhibited until the point is reached where the effective Sr$^{++}$ or (SrOH)$^-$ ion concentration is too low to exchange with Na$^+$ on the resin. The presence of a large excess of Sr(OH)$_2$ would also inhibit its own ionization. This suggests that there is an optimum concentration of Sr(OH)$_2$ below which the concentration is too low to provide enough ions for maximum exchange and above which the concentration is too high to permit adequate ionization.
The high solubility of \( \text{Sr(OH)}_2 \) in hot solutions coupled with its very low solubility in NaOH solutions at room temperature is a clear advantage. These properties permit relatively great exchange of Sr for Na when hot and easy separation by precipitation of \( \text{Sr(OH)}_2 \) from the NaOH product solution when cold.

d. **Exchange characteristics of barium hydroxide.**

(1) Experiments in which the resin particles are agitated with the solution. The experiments with strontium hydroxide involving exchange on Dow MX resin at room temperature from dilute solutions were repeated with barium hydroxide. The behavior of barium hydroxide under these conditions was entirely similar to the behavior of strontium hydroxide. Thus the effect of contact time shown in Figure 12 is very similar to that for strontium hydroxide as shown in Figure 7. Likewise the effect of regeneration with sodium chloride on the exchange behavior of the resin shown in Table XVIII is similar to that for strontium hydroxide shown in Table XI; and the effect of the solution: resin ratio shown in Table XIX is similar to that shown in Table XIII.

In order to produce a more concentrated sodium hydroxide solution, multiple contact exchange with concentrated barium hydroxide solution at elevated temperatures was performed using the procedure described on page 104. In this case the results for barium hydroxide shown in Figure 13 were not at
Reactions:
150 c.c. of .0879 Na(OH)$_2$ solution
20% Dow MX resin
20°C.

Fig. 12. Rate of adsorption of Ba and OH.
Table XVIII

Effect of Regeneration of Resin on Exchange Adsorption of Barium Hydroxide

(Values are in m.e. unless otherwise indicated)

<table>
<thead>
<tr>
<th></th>
<th>Fresh resin</th>
<th></th>
<th></th>
<th>Regenerated resin</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>60</td>
<td>3600</td>
<td>10</td>
<td>60</td>
<td>3600</td>
</tr>
<tr>
<td>Contact time, sec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Ba adsorbed</td>
<td>5.03</td>
<td>9.95</td>
<td>12.03</td>
<td>8.10</td>
<td>12.00</td>
<td>12.04</td>
</tr>
<tr>
<td>OH adsorbed</td>
<td>2.56</td>
<td>3.98</td>
<td>10.32</td>
<td>2.83</td>
<td>3.71</td>
<td>8.12</td>
</tr>
<tr>
<td>Ba exchanged for Na</td>
<td>2.47</td>
<td>5.97</td>
<td>1.71</td>
<td>5.27</td>
<td>8.29</td>
<td>3.92</td>
</tr>
<tr>
<td>Ba exchanged/Ba adsorbed, %</td>
<td>49.1</td>
<td>60.0</td>
<td>14.2</td>
<td>65.1</td>
<td>69.1</td>
<td>32.5</td>
</tr>
<tr>
<td>Ba adsorbed/initial Ba, %</td>
<td>41.8</td>
<td>82.6</td>
<td>99.9</td>
<td>67.3</td>
<td>99.7</td>
<td>100.0</td>
</tr>
<tr>
<td>OH adsorbed/initial OH, %</td>
<td>21.3</td>
<td>33.0</td>
<td>85.7</td>
<td>23.5</td>
<td>30.9</td>
<td>67.4</td>
</tr>
<tr>
<td>G. NaOH made per g. resin</td>
<td>.0049</td>
<td>.0119</td>
<td>.0024</td>
<td>.0105</td>
<td>.0166</td>
<td>.0078</td>
</tr>
<tr>
<td>Conc. of NaOH sol'n, wt. %</td>
<td>.0659</td>
<td>.1591</td>
<td>.0456</td>
<td>.1405</td>
<td>.2210</td>
<td>.1045</td>
</tr>
</tbody>
</table>
Table XIX

Effect of Solution: Resin Ratio on Exchange

(Values are in m.e. unless otherwise indicated)

<table>
<thead>
<tr>
<th>Condition of resin</th>
<th>Fresh</th>
<th>Regenerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams resin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>C.c. solution</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Solution: resin ratio</td>
<td>150</td>
<td>15</td>
</tr>
<tr>
<td>150</td>
<td>15</td>
<td>7.5</td>
</tr>
<tr>
<td>150</td>
<td>15</td>
<td>7.5</td>
</tr>
<tr>
<td>Total Ba adsorbed</td>
<td>2.02</td>
<td>7.65</td>
</tr>
<tr>
<td>3.26</td>
<td>11.20</td>
<td>12.04</td>
</tr>
<tr>
<td>OH adsorbed</td>
<td>.80</td>
<td>3.32</td>
</tr>
<tr>
<td>1.20</td>
<td>3.13</td>
<td>4.44</td>
</tr>
<tr>
<td>Initial Ba in solution</td>
<td>12.04</td>
<td>12.04</td>
</tr>
<tr>
<td>12.04</td>
<td>12.04</td>
<td>12.04</td>
</tr>
<tr>
<td>Ba exchanged for Na</td>
<td>1.22</td>
<td>4.33</td>
</tr>
<tr>
<td>2.06</td>
<td>8.07</td>
<td>7.60</td>
</tr>
<tr>
<td>Ba exchanged/Ba adsorbed %</td>
<td>60.4</td>
<td>56.6</td>
</tr>
<tr>
<td>63.2</td>
<td>72.0</td>
<td>63.1</td>
</tr>
<tr>
<td>Ba adsorbed/initial Ba %</td>
<td>16.8</td>
<td>63.5</td>
</tr>
<tr>
<td>97.0</td>
<td>27.1</td>
<td>93.0</td>
</tr>
<tr>
<td>100.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 13. Multiple contact exchange with hot conc. barium hydroxide.
all similar to those for strontium hydroxide shown in Figure 11. In comparing the behavior of barium hydroxide with that of strontium hydroxide the following facts stand out:

The maximum sodium hydroxide concentration produced from barium hydroxide was 1.82% as compared with 2.71% from strontium hydroxide the following facts stand out:

The maximum sodium hydroxide concentration produced from barium hydroxide was 1.82% as compared with 2.71% from strontium hydroxide.

The final NaOH solution is highly contaminated with barium hydroxide to the extent of 2.76% Ba(OH)₂ as compared with only 0.012% Sr (OH)₂ in the final NaOH solution.

The Ba content tends to parallel the OH content. This is in contrast to the drop in Sr content with the rise in OH content. This suggests that much of the barium hydroxide is adsorbed by the resin in molecular form while strontium is adsorbed in the ionic form.

(2) Experiments in which the solution flows through a stationary bed of the resin particles. (a) Apparatus and general procedure. Up to this point the experiments with strontium hydroxide and barium hydroxide were conducted by stirring, tumbling, or shaking a suspension of the resin particles in the solution to be contacted and then decanting or filtering the solution. In order to investigate more fully the peculiar behavior of hot concentrated barium hydroxide
solution reported in the previous experiment and to make a more thorough study of the hot strontium hydroxide exchange in later experiments it was deemed advisable to devise an apparatus that would permit close and convenient control of temperature, contact time, and other process variables. In order to simulate industrial ion exchange practice the resin particles were to be held in a stationary bed with the solutions flowing up or down through this bed. A description of the apparatus follows and illustrations are shown in Figures 14 and 15.

The main body of this apparatus was composed of four plates and three frames from 7" x 7" cast iron plate and frame filter press. The resin was packed into the lower part of the central 1 inch frame F, Figure 14, while a mixture of water and steam was passed through the two outer one half inch frames G to keep the resin, and the solution in contact with it, at any desired temperature. The temperature was controlled by adjusting the ratio of water to steam. Feed solution, wash water, and regenerant solutions were placed in the 3-necked flasks K and I. The solutions were passed up and down through the resin at any desired rate by means of suction from an aspirator. Upflow was induced by opening valve E, turning the 3-way cock C and closing valve D. Downflow was accomplished by opening valve D, turning cock C and closing valve E. The 3-way cock A, allowed solution to flow from either flask
Fig. 14. Diagram of apparatus for obtaining ion exchange rate and equilibrium data.
Fig. 15. Photograph of apparatus for obtaining ion exchange rate and equilibrium data.
K or I. Flask J provided surface for air cooling and condensing any vapors arising from the hot solution in the center frame. The glass tee L was filled with resin and submerged in the resin bed to afford better distribution of the solution. The mercury manometer M gave the pressure drop across the resin bed. The 3-necked flask I was immersed in a water bath so that the solution could be brought to the desired temperature before contact with the resin. The path IAL was insulated with asbestos string to prevent precipitation from the hot concentrated solution caused by cooling.

The plate and frame assembly was bolted together through the lead holes with hollow bolts through which the steam-hot water mixture could pass into and out of the outer frame G. Rubber gaskets were inserted between the plates and frames. The unnecessary holes in the plates and frames were plugged with iron cement.

The ion exchange unit constructed in this manner provided the following desirable features:

- Temperature of the solution and resin was easily and conveniently maintained and controlled.
- The cast iron chamber provided good heat transfer and heat distribution and was resistant to corrosion by the hot alkaline solutions.
- The resin was easily and conveniently contacted, washed and regenerated.
The contact of the solution with the resin was of a batch character, which is best for equilibrium and rate studies; yet flow characteristics such as pressure drop and flow rate could be observed simultaneously.

The resin was conveniently loaded and unloaded from the unit.

This apparatus was employed not only for the tests with barium hydroxide about to be described, but also with strontium hydroxide and with the different kinds of resin to be described in the next section. A general procedure for one of these tests was as follows:

A known weight of sodium loaded resin was placed in the ion exchange unit and the hot concentrated hydroxide solution to be tested was placed in the 3-necked flask I. The resin and solution were brought to the same temperature and then the solution was repeatedly passed up and down through the resin bed until practical equilibrium was reached. By analyzing the solution after each timed pass, the exchange rate could be easily determined. The resin was then washed by passing water up and down through the resin bed and then regenerated with sodium chloride solution and washed again. The regeneration and wash solutions started from and were returned to flask K. In the case of multiple contact exchange, solid barium or strontium hydroxide was added to the solution in flask I after each contact to replace that which was exchanged.
during contact. After these crystals were dissolved the cycle of operations was repeated until the sodium hydroxide concentration in the solution showed no further increase. The solution was then cooled to precipitate the barium or strontium hydroxide. All solutions including the hydroxide and regenerant solutions as well as the two wash solutions were analyzed for each cycle.

(b) Exchange with hot concentrated barium hydroxide in flow apparatus, single contact. Using the above procedure, 450 g. of Dow MX resin was contacted with 400 c.c. of 2 N barium hydroxide solution at 70° C., washed with water, regenerated with sodium chloride solution and washed free of chlorides. This test was repeated several times on the same resin bed. The contact time with the barium hydroxide solution was one minute. The results are shown in Table XX.

From Table XX the following facts may be gleaned:

More than 60% of the Ba(OH)$_2$ in hot concentrated solution is adsorbed as the whole molecule by the resin while only about 10% of the Ba ions in solution is exchanged for Na ions on the resin. The Ba that is exchanged for Na is subsequently recovered in the NaCl regeneration step but the Ba that is adsorbed molecularly as Ba(OH)$_2$ seems to be fixed on the resin and is not recoverable.

Despite the high concentration of Ba(OH)$_2$ present in the hot solution, the concentration of NaOH produced, 0.7%, was
Table XX

Exchange Adsorption with Hot Concentrated Barium Hydroxide

(Values are in per cent of original m.e. of Ba(OH)$_2$ in solution unless otherwise indicated)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba OH</td>
<td>Ba OH</td>
<td>Ba OH</td>
<td>Ba OH</td>
</tr>
<tr>
<td>% adsorbed</td>
<td>93</td>
<td>82</td>
<td>82.1</td>
<td>63.0</td>
</tr>
<tr>
<td>% exchanged</td>
<td>5.2</td>
<td>9.4</td>
<td>14.8</td>
<td>19.6</td>
</tr>
<tr>
<td>% recovered by regeneration</td>
<td>8.3</td>
<td>.01</td>
<td>12.3</td>
<td>0.4</td>
</tr>
<tr>
<td>% recovered by washes</td>
<td>3.3</td>
<td>7.5</td>
<td>4.8</td>
<td>10.7</td>
</tr>
<tr>
<td>% retained by resin</td>
<td>82.1</td>
<td>81</td>
<td>65.9</td>
<td>60.8</td>
</tr>
<tr>
<td>Weight % NaOH in hot product solution</td>
<td>0.69</td>
<td>0.76</td>
<td>0.69</td>
<td>1.65</td>
</tr>
<tr>
<td>Weight % Ba(OH)$_2$ in hot product solution</td>
<td>1.83</td>
<td>2.96</td>
<td>1.0</td>
<td>5.18</td>
</tr>
<tr>
<td>Exchange capacity m.e./g.</td>
<td>0.113</td>
<td>0.30</td>
<td>0.52</td>
<td>0.56</td>
</tr>
<tr>
<td>Regeneration capacity m.e./g.</td>
<td>0.137</td>
<td>0.29</td>
<td>0.41</td>
<td>0.30</td>
</tr>
</tbody>
</table>

*Carried out on resin presaturated with NaOH as described in part (d) page 123.
not appreciably greater than the 0.6% produced by cold Ca(OH)$_2$
suspension (page 72). Moreover the supernatant solution,
after precipitation of the excess Ba(OH)$_2$ on cooling, was
still contaminated with much Ba(OH)$_2$ (1-3%).

After contact with hot concentrated Ba(OH)$_2$ solution,
the resin was washed with a volume of water equal to the
original Ba(OH)$_2$ solution. The ratio of NaOH to Ba(OH)$_2$ in
this wash water was always much higher than in the product
solution. This is evidence that the "dilution effect" dis-
cussed on page 41, pertains to this case. This effect is the
tendency of a divalent cation to displace a monovalent cation
more easily in dilute solution than in concentrated solution.

(c) Saturation of the resin with sodium hydroxide solu-
tion. If the adsorption of hydroxyl ions from highly basic
in the resin, then presaturation of the resin with sodium
hydroxide solution should prevent this adsorption.

Five hundred c.c. of 36% NaOH solution at 80°C was
slowly passed up and down through the resin bed after the tests
of part (b). The solution was allowed to stand in contact
with the resin overnight after which it was drained from the
resin bed and the resin was washed with water. This NaOH
treatment was repeated twice more to insure thorough satura-
tion of the resin with NaOH. Analysis of the various solu-
tions are given in Table XXI.

The results of this experiment indicate that NaOH is much
Table XXI

Saturation of the NaCl-regenerated Resin with NaOH

(Values are in m.e.)

<table>
<thead>
<tr>
<th>Treatment No.</th>
<th>Na</th>
<th>OH</th>
<th>Ba</th>
<th>Na</th>
<th>OH</th>
<th>Ba</th>
<th>Na</th>
<th>OH</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed solution</td>
<td>1790</td>
<td>1790</td>
<td>0</td>
<td>1790</td>
<td>1790</td>
<td>1790</td>
<td>1790</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Product solution</td>
<td>1338</td>
<td>1485</td>
<td>154</td>
<td>1533</td>
<td>1627</td>
<td>94</td>
<td>1658</td>
<td>1700</td>
<td>42</td>
</tr>
<tr>
<td>Wash solution</td>
<td>790</td>
<td>837</td>
<td>47</td>
<td>920</td>
<td>947</td>
<td>27</td>
<td>490</td>
<td>494</td>
<td>4</td>
</tr>
</tbody>
</table>
more effective in regenerating the resin (i.e. replacing Ba by Na) than is NaCl. The adsorption of NaOH may be visualized as due to very weakly acidic hydrogen atoms on the resin, such as alpha hydrogens which are too strongly held to the resin to be detached but which can hold NaOH loosely to the resin. This attachment, though loose, nevertheless concentrates the NaOH at the surface and thus leads to a higher degree of exchange than with NaCl which is not attracted as such to the resin.

After each treatment of the resin with NaOH solution the combined product and wash solutions contained considerably more NaOH than the original NaOH solution. This surprising result may be explained by assuming that after the last regeneration with NaCl in part (b) the resin had attached to it the following ions: Na, (BaOH)^+. In the presence of hot concentrated NaOH the following reaction takes place on the surface of the resin:

\[
(BaOH)^+ + Na^+ \rightarrow Ba^{++} + NaOH
\]

where the divalent Ba^{++} remains attached to the resin while the NaOH goes into solution.

(d) Exchange with hot concentrated barium hydroxide after presaturation of the resin with sodium hydroxide. The procedure of Part (b) was repeated on the resin, now presaturated with NaOH and thoroughly washed. The results are given in Table XX as test No. 4.
The results show that presaturation with NaOH does indeed decrease the adsorption of the OH by the resin and increase the exchange of Ba for Na but the amount of OH adsorbed is still substantial. This may be interpreted to mean that a considerable portion of the OH is adsorbed by virtue of acidic hydrogen in the resin which can be preneutralized with NaOH; but the larger part of the OH is adsorbed in the form of the (BaOH)^+ ion. Adsorption of OH by the latter mechanism cannot be prevented by pretreatment of the resin with NaOH.

In this experiment the hot product solution containing NaOH and Ba(OH)_2 was cooled to precipitate the Ba(OH)_2. The solution was analyzed before and after the precipitation with the following results:

<table>
<thead>
<tr>
<th></th>
<th>Before precipitation m.e.</th>
<th>Supernatant liquid after precipitation m.e.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>422</td>
<td>180</td>
</tr>
<tr>
<td>Ba</td>
<td>251</td>
<td>89</td>
</tr>
<tr>
<td>Na</td>
<td>171</td>
<td>91</td>
</tr>
</tbody>
</table>

Thus it appears that when 251-89 = 162 m.e. Ba(OH)_2 precipitated, 171-91 = 80 m.e. NaOH were precipitated with it. Since this precipitate was in the ratio of 2 m.e. Ba(OH)_2 to 1 m.e. NaOH, it is reasonable to suppose that the precipitation was in the form of the double base Ba(OH)_2·NaOH. The ability of Ba(OH)_2 to form this double base with sodium hydroxide and thus remove it from solution explains the failure
to build up the NaOH concentration of the solution by multiple contact exchange as was done with strontium hydroxide, which does not form this double base. (See Figures 11 and 13 and the discussion on page 113.)

It would appear that formation of the double base would preclude the possibility of using barium hydroxide in multiple contact exchange since most of the sodium hydroxide formed by exchange would finally be precipitated from solution as Ba(OH)_2·NaOH. To test this the following multiple contact exchange experiment was performed in the flow apparatus:

After regenerating and washing the resin, 400 c.c. of concentrated barium hydroxide solution containing 850 m.e. of barium hydroxide were passed up and down through the resin bed at 70° C. The resin was then regenerated and washed. Twenty grams of solid Ba(OH)_2·8H_2O crystals were added to the product solution from the first contact and the procedure repeated. Four such contacts were made with the same solution, adding 20 g. of Ba(OH)_2·8H_2O between contacts. The solution was analyzed before and after each contact with the following results:

<table>
<thead>
<tr>
<th>Contact No.</th>
<th>Weight % NaOH in cold solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.95</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>0.52</td>
</tr>
<tr>
<td>4</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Thus, as predicted, multiple contact did not succeed in raising the sodium hydroxide concentration of the product above that produced in a single contact, and in fact lowered it.

3. Summary and comparison of the properties of the various hydroxides

In order to be suitable for use in the production of sodium hydroxide by ion exchange, a hydroxide must meet certain requirements.

The first requirement is solubility in water. This is met by the hydroxides of calcium, strontium, barium, ammonium, lithium, potassium, rubidium, cesium, and monovalent thallium.

The second requirement is the ability to be precipitated fairly completely from sodium hydroxide solution at room temperature. This eliminates lithium potassium, rubidium and cesium hydroxides.

The third requirement is a cost that is within reason. This eliminates thallous hydroxide. Thallous hydroxide, moreover, has a rather high solubility when cold and therefore much of it would be lost as a contaminant in the NaOH product solution.

The fourth requirement is the ability of the cation of the hydroxide to exchange with the sodium ion on the resin. This eliminates ammonium hydroxide which was shown to exhibit virtually no exchange at all with sodium ions in basic solution.
This leaves calcium hydroxide, strontium hydroxide and barium hydroxide. A comparison of the properties of these hydroxides is given in Table XXII.

Table XXII

Comparison of the Properties of the Suitable Hydroxides

<table>
<thead>
<tr>
<th></th>
<th>Ca(OH)$_2$</th>
<th>Sr(OH)$_2$</th>
<th>Ba(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility at 70$^\circ$ C., m.e./l</td>
<td>36</td>
<td>880</td>
<td>4480</td>
</tr>
<tr>
<td>Solubility in NaOH solution at 20$^\circ$ C., m.e./l</td>
<td>5</td>
<td>2</td>
<td>222</td>
</tr>
<tr>
<td>Cost, $/lb. equivalent</td>
<td>0.22</td>
<td>26.6</td>
<td>15.2</td>
</tr>
<tr>
<td>Maximum NaOH conc. obtained by ion exchange, weight %</td>
<td>0.62</td>
<td>2.71</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Calcium hydroxide has the advantage of having a cost that is lower than that of sodium hydroxide. This makes it unnecessary to recover the calcium chloride in the regenerant effluent. However, the maximum concentration of sodium hydroxide solution that could be obtained by ion exchange with calcium hydroxide solution or suspension under a wide variety of conditions was only 0.6% NaOH. This concentration is too low for many commercial uses.

Strontium hydroxide has by far the best exchange properties. It can produce a pure sodium hydroxide solution with concentration of at least 2.7% NaOH which is suitable for many of the
industrial applications given on page 9. In contrast, barium hydroxide can produce a sodium hydroxide solution of only 1.8% NaOH that is highly contaminated with unprecipitated barium hydroxide as shown by the solubility data in Table XXII. Moreover, barium hydroxide has the undesirable property of forming a double base with sodium hydroxide, Ba(OH)$_2$·NaOH, which removes sodium hydroxide from solution when it precipitates. Strontium hydroxide does not have this property. The only advantage of barium hydroxide over strontium hydroxide is its lower cost, but both are more expensive than sodium hydroxide and would require recovery.

Thus, by a process of elimination, strontium hydroxide must be selected as the most suitable hydroxide for use in the production of sodium hydroxide by ion exchange.

B. Investigation of Suitable Cation Exchange Materials

A general discussion of the various materials known to exhibit cation exchange properties is given in Part II, page 10. The inorganic materials such as aluminosilicates, greensand and clays tend to be unstable both mechanically and chemically. Acids, alkalis and heat disrupt them rather readily. Furthermore their exchange capacities are lower than the better organic exchangers. On the other hand, many of the organic exchangers such as proteins, peat, lignite, coal and their sulfonated derivatives are peptized in alkaline solutions.
Many of the phenolic resins are also adversely affected by alkali but if highly cross-linked they are fairly resistant. The cross-linked sulfonated polystyrene type of resin, is highly resistant to acid, alkali, or heat and moreover has a high exchange capacity.

Of all the available exchange materials, only those that are resistant to hot alkaline solutions could be considered for the application at hand. These are few in number and can be classified into three distinct chemical types. A representative of each of these types was selected for test and comparison: (1) Dow MX, a highly cross-linked and stabilized sulfonated phenolformaldehyde resin. This type has phenolic as well as sulfonic acid groups as active points on which exchange may take place. (2) Amberlite IRC-50, a highly stable resin which contains the carboxyl radical as the sole functional group for exchange. (3) Dow HCR, a sulfonated polystyrene resin in which the sulfonic acid radical is the sole functional group. Further information on these resins, as taken from the literature, is given on page 15. Dow MX will henceforth be designated as MX, Amberlite IRC-50 as IRC and Dow HCR as HCR.

The exchange characteristics and general behavior of each of these resins were tested using strontium hydroxide in multiple contact and sodium chloride in regeneration. Since previous work had shown that it is necessary to use hot con-
centrated strontium hydroxide in multiple contact in order to produce a sodium hydroxide solution of usable concentration, these conditions were employed in testing the resins. To provide these conditions under circumstances which would permit measurement and control of the process variables, the ion exchange unit described on page 114 and illustrated in Figures 14 and 15 was used. The general procedure for operating this unit in multiple contact exchange is given on page 118. The essential conditions under which the tests were performed are given in Table XXIII, page 141 together with the results for comparison of the resins.

Each cycle in this multiple contact exchange procedure was composed of four steps:

Step (1): Contact of the sodium loaded resin with hot strontium hydroxide solution. The product from this contact will be designated "solution-1." Figure 16 shows how the sodium hydroxide concentration in this solution is built up to a maximum by repeated contacts with the regenerated resin. With HCR resin, the solution attained a sodium hydroxide concentration of 3.5% which was considerably higher than the concentrations obtained with the other two resins. Figure 17 shows how sharply the exchange capacities of the resins drop as the NaOH content of the solution builds up. HCR is seen to have the highest exchange capacity. As indicated in Figure 18, the exchange efficiency suffers a very sharp drop as
Fig. 16. Comparison of resins: NaOH in product solution.
Fig. 17. Comparison of resins: exchange capacity.
Fig. 18. Comparison of resins: exchange efficiency.
the maximum NaOH concentration is approached, and HCR exhibits the highest efficiency. HCR has the least tendency to adsorb hydroxyl ion while IRC has the greatest as shown in Figure 19.

Step (2): Water wash after step (1). This will be called "wash-1." As shown in Figures 20 and 21, the fraction of the strontium that is removed from the resin by the wash water seems to increase with increasing initial concentration while the corresponding fraction of hydroxyl ion remains fairly constant. Moreover IRC releases a much larger fraction of Sr and OH to the wash water than do MX and HCR.

Step (3): Regeneration of the resin with saturated sodium chloride solution. This solution will be called "regen. sol'n." Figure 22 indicates that the ratio m.e. OH/m.e. Sr desorbed during regeneration is always less than 50%. This suggests that all of the OH desorbed in this step is in the form of (SrOH)$_2^+$ ion and none in the form of molecular Sr(OH)$_2$. HCR had the greatest regenerative capacity.

Step (4): Water wash after regeneration with sodium chloride. This will be "wash-2." As in the case of wash-1, the IRC resin seemed to hold considerably more SR(OH)$_2$ that could be easily removed with wash water than did MX or HCR. The behavior is shown in Figures 23 and 24.

A summary of the comparison of the three resins is given in Table XXIII, page 141. In this table the data for operating performance were gleaned from Figures 16 to 24 by taking values for the three resins at the same abscissa in each graph.
Fig. 19. Comparison of resins: OH adsorption capacity.
Fig. 20. Comparison of resins: Sr in wash-1.
Fig. 21. Comparison of resins: OH in wash-1.
Fig. 22. Effect of adsorption ratio on desorption ratio.
Fig. 23. Comparison of resins: Sr in wash-2.

m.e. Sr on one gram resin before regeneration.
Fig. 24. Comparison of resin: OH in wash-2.
Table XXIII
Comparison of Ion Exchange Resins
in Multiple Contact Exchange

<table>
<thead>
<tr>
<th>Resin</th>
<th>HCR</th>
<th>MX</th>
<th>IRC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk density, g. dry resin/c.c. wet volume</td>
<td>0.67</td>
<td>0.67</td>
<td>0.71</td>
</tr>
<tr>
<td>Screen size, Tyler mesh No.</td>
<td>20-40</td>
<td>14-20</td>
<td>20-50</td>
</tr>
<tr>
<td>% free space, c.c. free space/c.c. wet volume</td>
<td>30.8</td>
<td>33.2</td>
<td>32.2</td>
</tr>
<tr>
<td>Cost, dollars per cubic foot</td>
<td>19</td>
<td>12</td>
<td>86</td>
</tr>
<tr>
<td><strong>Operating conditions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grams resin, dry</td>
<td>29.6</td>
<td>31.3</td>
<td>30.0</td>
</tr>
<tr>
<td>Temperature °C.</td>
<td>93</td>
<td>87</td>
<td>90</td>
</tr>
<tr>
<td>Vol. of solution-1, c.c.</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Vol. of saturated NaCl regen. sol'n, c.c.</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Vol. of wash-1 or wash-2, c.c.</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td><strong>Operating performance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max. NaOH conc. attained in solution-1, weight %</td>
<td>3.5</td>
<td>2.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Exchange capacity, m.e. NaOH made/g. resin, at x = 1, Fig. 17</td>
<td>1.6</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Exchange efficiency, m.e. NaOH made/m.e. Sr adsorbed at x = 1, Fig. 18</td>
<td>75</td>
<td>39</td>
<td>11</td>
</tr>
<tr>
<td>OH adsorption, m.e. OH adsorbed/g. resin at x = 3, Fig. 19</td>
<td>0.6</td>
<td>1.2</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*x* refers to the abscissa in the figure indicated.
Table XXIII (Continued)

<table>
<thead>
<tr>
<th>Resin</th>
<th>HCR</th>
<th>MX</th>
<th>IRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating performance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regeneration capacity, m.e. Sr desorbed/g. resin</td>
<td>1.6</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>OH in wash-1, m.e. OH in wash-1/m.e. OH in sol'n-1 at x = 4, Fig. 21</td>
<td>8</td>
<td>11</td>
<td>27</td>
</tr>
<tr>
<td>Sr in wash-1, m.e. Sr in wash-1/m.e. Sr in sol'n-1 at x = 4, Fig. 20</td>
<td>3</td>
<td>7</td>
<td>33</td>
</tr>
<tr>
<td>OH in wash-2, m.e. OH in wash-2/m.e. OH in regen. sol'n. at x = 1.5, Fig. 24</td>
<td>15</td>
<td>26</td>
<td>54</td>
</tr>
<tr>
<td>Sr in wash-2, m.e. Sr in wash-2/m.e. Sr in regen. sol'n. at x = 1.5, Fig. 23</td>
<td>4</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>Physical stability</td>
<td>excel. softens excel.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color throw</td>
<td>none</td>
<td>some</td>
<td>none</td>
</tr>
</tbody>
</table>
In this way the resins were compared on a common basis. Examination of the table reveals that HCR is by far the best exchange resin in operating performance. It produces the most concentrated NaOH, has the highest exchange capacity and efficiency, the highest regeneration capacity, the lowest hydroxyl ion adsorption, and loses the least strontium and hydroxyl ion in the washes. In these respects IRC is by far the worst and MX is intermediate between the two. The characteristics of these resins must be ascribed to their functional groups. Thus HCR, with the sulfonic acid radical as the sole functional group, behaves like the salt of a strong acid, readily exchanges ions and has small attraction for OH. IRC, on the other hand, with its carboxyl groups, behaves like the salt of a weak acid, tends toward hydrolysis, exchanges ions with difficulty, and shows strong attraction for OH. MX is intermediate between the two because it contains both the strong acid sulfonate group and the weakly acidic phenolic group.

The cost of IRC is much higher than that of the other two. While the cost of HCR is somewhat higher than that of MX, it will probably be reduced eventually because of the large quantities of styrene being produced for synthetic rubber and plastics.

In chemical and physical stability, HCR is much superior to MX.
The final conclusion therefore is that the sulfonated polystyrene type of resin, such as HCR, is by far the best to use in this application.

The performance data for HCR presented in this section were used in deriving the final quantitative flowsheet shown on page 169.

C. Investigation of the Proposed Process Using Strontium Hydroxide and Dow HCR Resin

The proposed process is described in general terms on page 6 and in detail on page 168. In this section, three of the essential steps of the process are examined with regard to the operating conditions required. These three steps are (1) Ion exchange, (2) Precipitation of the strontium chloride from the regenerant effluent and (3) Reconversion of the strontium chloride to strontium hydroxide.

1. Investigation of ion exchange variables

Having found that strontium hydroxide is the best hydroxide to use and that Dow HCR is the best available exchange material to use, it remains to determine the manner in which these should be contacted to give the best exchange operation. The operating variables examined were exchange rate, temperature, ratio of initial strontium to grams resin, and initial concentration of strontium hydroxide in solution.
The rate and equilibrium data for these tests were obtained in the apparatus described on page 11 and illustrated in Figures 14 and 15. The procedure for each test was as follows: a known weight of sodium loaded resin was placed in the ion exchange unit and brought to the desired temperature. Measured amounts of water and strontium hydroxide crystals were put into flask I, Figure 14, and heated in the water bath until solution was complete and the desired temperature was reached. The solution was then repeatedly passed up and down through the resin bed until practical equilibrium was reached. By analyzing the solution after each timed pass, the exchange rate could be easily and accurately determined. The resin was then washed by passing water up and down through the resin bed and then regenerated with sodium chloride and washed again. This prepared the resin for the next test.

The results of these tests are presented in Figures 25 to 27. For each series of tests the rate data are first presented. By rational extrapolation of these data in both directions in time the complete rate curves and equilibrium values were obtained. This extrapolation was based on the assumption that the rate data fit the empirical equation

$$\log A = b - \frac{m}{t}$$

where \( A = \text{m.e. } \text{Sr}^{++} \) or \((\text{SrOH})^+\) adsorbed in time \( t \) seconds, \( m \) and \( b \) are empirical constants. The rate curves drawn in
70 g. resin
150 c.c. solution
Sr¹ = 47 m.e.

Fig. 25A. Effect of temperature on rate and equilibrium of exchange.
Fig. 25B. Effect of temperature on adsorption of OH.
Fig. 26A. Effect of initial concentration (Sr₁).
Fig. 26B. Effect of initial concentration (Sr₁).
Exchange capacity

92° C.
70 g. resin
150 c.c. solution

Exchange efficiency, %

Wt. % NaOH in solution x 10

m.e. initial Sr per gram resin

Fig. 26C. Effect of initial m.e. Sr on equilibrium values.
82° c.
70 g. resin
Sr$_1$ = 75 m.e.

Fig. 27A. Effect of dilution.
Fig. 27B. Effect of dilution.
Exchange capacity

$82^\circ$ C.
70 g. resin
$Sr_1 = 75$ m.e.

Exchange efficiency, %

Wt., % NaOH in solution
x 10

% as indicated

C. c. solution per gram resin

Fig. 27C. Effect of dilution on equilibrium values.
Figures 25A, 26A and 27A were calculated from this equation and are shown together with the experimental points which were used to determine the constants b and m. The equilibrium values were arbitrarily taken as the values at 2000 seconds since the reaction at this time was virtually complete in all cases. The correlation of these equilibrium values with the exchange variables is shown in Figures 26C and 27C.

a. Rate of exchange. The rate curves are typical of those obtained with surface reactions in which diffusion is the controlling factor and a gradual saturation of the surface is reached. This is evidence that for the conditions of these experiments diffusion is the controlling factor in ion exchange and that exchange itself is practically instantaneous. This is in agreement with the conclusions of other investigators (124) (39) and is reasonable since the reaction is ionic and therefore extremely rapid. With diffusion controlling the rate it should be possible to calculate ion exchange columns on the basis of the H.T.U. concept of Chilton and Colburn (31). The representation of ion exchange as a bimolecular second order reaction (105) appears to apply only to very dilute solutions.

It is interesting to note that the ratio of $(\text{SrOH})^+$ adsorbed to total Sr adsorbed is essentially constant with time of reaction as shown in Figures 25B, 26B, and 27B. This is a good indication that the adsorption of hydroxyl ion by Dow
HCR resin is entirely in the form of $(\text{SrOH})^+$ ion with very little if any neutralization by acidic hydrogen atoms that may be on the resin. This is in contrast to the behavior of Dow MX resin which contains acidic phenolic groups and has been shown to absorb hydroxyl ions both by neutralization and as $(\text{SrOH})^+$ ion.

b. **Effect of temperature.** A glance at Figures 25A and 25B shows that temperature has very little effect on the rate or equilibrium of exchange. This is in accord with reports of previous investigators (page 49) on the exchange of neutral salts in dilute solution. The fact that concentrated basic solutions also show a very low temperature coefficient is in agreement with the fact that exchange is ionic here also and therefore has a very low heat of reaction.

c. **Effect of the degree of resin saturation and initial concentration.** In this series of experiments the volume of solution and the weight of resin were kept constant while the initial amount of strontium hydroxide was varied. In this way exchange was studied for various degrees of saturation of the resin with strontium and various concentrations of the solution.

Figure 26C shows that the exchange capacity increases to a maximum and then drops off as the initial strontium in solution is increased. The lowered exchange at the higher concentrations of strontium hydroxide may be ascribed to the fact that at high concentrations dissociation into $\text{Sr}^{++}$ and $2\text{OH}^-$ is
more difficult and the formation of (SrOH)^+ is favored. This is shown by the fact that the exchange efficiency, m.e. NaOH made/m.e. Sr adsorbed, falls off continuously as the initial strontium hydroxide concentration increases. Figure 26C also shows that the maximum sodium hydroxide concentration as well as the maximum exchange capacity occurs when there are initially 2.8 m.e. Sr per gram resin and the initial concentration is 1.3 m.e. Sr per c.c. of solution. These initial values result in the maximum saturation of the exchange points on the resin with an exchange efficiency of 62%.

d. Effect of dilution. In this series of tests the volume of water in solution was varied while the amount of resin and initial strontium was kept constant. It can be seen from Figure 27C that the effect of dilution is to increase the exchange capacity and the exchange efficiency. This can be ascribed to the greater dissociation of strontium hydroxide in dilute solution and also to the "dilution effect" described on page 41. It may well be that the "dilution effect" itself may simply be the result of partial dissociation of the divalent salt or base undergoing exchange. It will be recalled that this effect occurs in mono-divalent exchange but not in mono-monovalent exchange. However, the improvement of the exchange efficiency and capacity on dilution is not marked enough to overcome the effect of dilution itself on the concentration of the sodium hydroxide solution produced with a
given amount of resin. Consequently the net result is that the weight per cent sodium hydroxide in solution diminishes with dilution as shown in Figure 270. The volume of solution should therefore be kept as small as possible.

2. Precipitation of strontium from the sodium chloride regenerant solution.

The flowsheet in Figure 1, page 8, indicates that the effluent from the regeneration step is a solution of sodium chloride containing strontium desorbed from the resin in the form of strontium chloride. However, the tests in Part III B showed that some hydroxyl ion is also desorbed in the form of (SrOH)$^+$ ion and is therefore present in the regenerant effluent together with the strontium chloride and sodium chloride.

The high cost of strontium hydroxide makes it mandatory either to make economic use of this effluent solution or to recover the strontium from it and reconver it to strontium hydroxide. It has been suggested (136) that the effluent might be used in the manufacture of pyrotechnics in which strontium is used as a source of color. However, it seemed desirable to investigate the possibility of recovering the strontium and reusing it as the hydroxide.

The regenerant solution, as it issues from the exchanger contains sodium chloride and strontium chloride in the mol ratio of about 10:3. Precipitation of the strontium salt proves to be a difficult problem but some progress has been
made in this direction. Work on this phase of the project was performed by Mr. Donald Ryan and Mr. Gordon Specht.

First, experimental data on the mutual solubilities of sodium chloride and strontium chloride had to be obtained, for this particular system has never been reported in the literature. By analyzing a series of solutions in equilibrium with an excess of both strontium chloride and sodium chloride at various temperatures the polytherm CD for mutual saturation of the two salts was established and plotted in Figure 28. The solubilities of the pure salts at various temperatures as given by Seidell (127) were then plotted and the isotherms drawn in. With the aid of this diagram a process for the separation of strontium chloride from sodium chloride can be described. One hundred pounds of feed solution, saturated with sodium chloride but not strontium chloride, of composition A is heated to 105° C. and 13.2 lbs. of water is evaporated along A B until the solution is again saturated with sodium chloride. Evaporation is continued along the 105° isotherm B C precipitating 16.05 lbs. of pure sodium chloride and evaporating 39.75 lbs. water. The solution is cooled rapidly from 105° to 23°, precipitating 16.4 lbs. pure SrCl₂·6H₂O at point D. Sodium chloride is not precipitated on cooling because, as is shown by the curved line C D, it has an inverted solubility curve in a solution saturated with strontium chloride. This analysis shows that to precipitate 70.7% of the pure stron-
FIG. 28. POLYTERM FOR THE MUTUAL SOLUBILITY OF SRLCl₂ AND NACL IN WATER
tium chloride from the feed solution, 78% of the water must be evaporated from the solution and 93.9% of the sodium chloride must be precipitated in a previous step.

Since the separation by the above procedure requires excessive evaporation, another method was investigated. This scheme involved the precipitation of strontium chloride by the addition of strontium hydroxide to the hot solution to form the basic salt Sr(OH)Cl·4H₂O. Triangular phase diagrams for the system SrCl₂-SrO-H₂O have been worked out by Milikan (98) at temperatures ranging from 0° to 40° C. His diagram at 40° shows that the basic salt Sr(OH)Cl·4H₂O can exist as a precipitate in equilibrium with a solution in the concentration range 33 to 39% SrCl₂, 2.10 to 1.36% SrO and 64.9 to 59.6% H₂O. At lower temperatures the range narrows and at 0° C. the basic salt phase disappears altogether. It seems reasonable to suppose that in the presence of saturated sodium chloride solution the basic salt would be less soluble than in pure water. Experimental work appeared to confirm this but the amount of basic salt precipitated was much smaller than expected. Precipitation of hydrated double salts is generally a delicate process requiring close control of concentrations, temperatures, and mixing during both reaction and precipitation. It is believed that with further research leading to the determination of the optimum conditions for reaction and precipitation, much larger yields of the basic salt Sr(OH)Cl·4H₂O could be obtained.
3. **Reconversion of strontium chloride to strontium hydroxide.**

Whether the product from the precipitation step is SrCl₂·6H₂O or Sr(OH)Cl·4H₂O, it is necessary to remove the Cl and replace it with OH so that the strontium hydroxide thus formed may be reused in the process. This replacement is accomplished by calcining the salt in the presence of superheated steam. The overall reaction is

\[
\text{SrCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Sr(OH)}_2 + 2\text{HCl}
\]

A few references to this reaction are made in the literature. Kraus (49) states that strontium chloride is decomposed by superheated steam giving hydrochloric acid. Robinson (120) found that from 1 gram SrCl₂, 0.361 gram was hydrolyzed off at 970°C in 30 minutes using steam at 1 atmosphere. The lowest temperature at which hydrolysis was appreciable was 640°C.

The following experiments were intended to explore the effect of such factors as temperature, time, steam rate, catalyst and composition of charge on the conversion of strontium chloride to strontium hydroxide by calcination in the presence of steam. While a thorough study by systematic variation of each of the above factors was not attempted, enough runs were made to draw some general conclusions concerning them.

The apparatus consisted of an electrically heated laboratory combustion furnace fitted with a 30 inch silica com-
bustion tube. After the furnace was brought up to temperature a boat containing the charge was inserted near the discharge end of the tube. Steam was then allowed to flow slowly through the tube utilizing the first portion of the furnace as a steam superheater. The mixture of steam and hydrogen chloride issuing from the tube was condensed in a small pyrex condenser and the condensate collected in a three necked flask fitted with a stirrer and burette containing N/10 sodium hydroxide. The hydrochloric acid condensate was neutralized continuously as it came over, taking readings on the burette at regular time intervals to obtain reaction rate data. Steam rate was obtained by measuring the volume of solution in the receiver flask. After the run the boat was removed from the tube and the residue ground in a mortar and extracted with water by refluxing for 30 minutes. Analyses for Sr, Cl and OH were made on the charge, condensate and residue extract.

The conditions and results for representative experiments are tabulated in Table XXIV. In this table, "% conversion" is m.e. HCl formed/original m.e. Cl in charge; "% recovery" is m.e. Sr(OH)$_2$ leached from residue/original m.e. Cl + OH in charge.

Conclusions that may be drawn from these data are as follows:

The catalyst has considerable effect on the results. Pure strontium chloride in a nickel boat gave a rather low %
Table XXIV
Hydrolysis of Strontium Chloride by Calcining with Steam

<table>
<thead>
<tr>
<th>Charge</th>
<th>Catalyst</th>
<th>Mols Cl₂ in charge/mol catalyst</th>
<th>Temp. °F.</th>
<th>% conversion to HCl</th>
<th>% recovery as Sr(OH)₂</th>
<th>% HCl in condensate solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCl₂</td>
<td>none (Ni boat)</td>
<td>--</td>
<td>1647</td>
<td>32.5</td>
<td>24.3</td>
<td>3.4</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>porcelain boat</td>
<td>--</td>
<td>1663</td>
<td>67.8</td>
<td>14.1</td>
<td>7.0</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>alundum</td>
<td>1.0</td>
<td>1654</td>
<td>79.8</td>
<td>12.4</td>
<td>8.2</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>ferric oxide</td>
<td>1.0</td>
<td>1648</td>
<td>73.5</td>
<td>36.0</td>
<td>7.7</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>silica</td>
<td>1.0</td>
<td>1651</td>
<td>99.6</td>
<td>23.7</td>
<td>10.4</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>silica</td>
<td>0.5</td>
<td>1659</td>
<td>100.0</td>
<td>7.4</td>
<td>10.5</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>silica</td>
<td>1.5</td>
<td>1675</td>
<td>99.4</td>
<td>28.7</td>
<td>10.2</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>silica</td>
<td>2.0</td>
<td>1670</td>
<td>87.3</td>
<td>30.1</td>
<td>9.0</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>silica</td>
<td>6.0</td>
<td>1700</td>
<td>41.6</td>
<td>22.2</td>
<td>4.5</td>
</tr>
<tr>
<td>SrCl₂ + Sr(OH)₂</td>
<td>silica</td>
<td>.75</td>
<td>1695</td>
<td>99.2</td>
<td>20.6</td>
<td>9.7</td>
</tr>
<tr>
<td>SrCl₂ + Sr(OH)₂</td>
<td>SrO·SiO₂</td>
<td>.25</td>
<td>1710</td>
<td>99.7</td>
<td>22.0</td>
<td>10.2</td>
</tr>
</tbody>
</table>
conversion to HCl but a high % recovery of strontium hydroxide. Strontium chloride in a porcelain boat or in a boat lined with alundum gave a higher % conversion but a lower % recovery. This is because the effect of the alumina is to displace the chlorine thus aiding the conversion, but it ties up the strontium as \((\text{SrO})_n\cdot\text{Al}_2\text{O}_3\) from which strontium hydroxide is leached with difficulty thus hindering the recovery. Other acidic solids such as silica and ferric oxide, when ground in a mortar together with strontium chloride and charged into the furnace, had effects similar to alumina but in varying degrees. Silica was capable of effecting complete removal of chlorine and was intermediate in its readiness to release strontium hydroxide by leaching the \((\text{SrO})_n\cdot\text{SiO}_2\) formed. It therefore seems to be the best additive to use since complete removal of chlorine is necessary to prevent contamination of the sodium hydroxide product in the ion exchange step. The mol ratio of \(\text{Cl}_2\) to \(\text{SiO}_2\) in the charge that is most satisfactory for both conversion and leaching appears to be about 1.5.

The calcining and leaching reactions, assuming that the strontium is precipitated as \(\text{Sr(OH)}\cdot\text{Cl}\cdot\text{H}_2\text{O}\), may be set forth as follows:

Initial calcining

\[
1.5 \text{Sr(OH)}\cdot\text{Cl} + \text{H}_2\text{O}(g) + \text{SiO} \rightarrow (\text{SrO})_{1.5}\cdot\text{SiO}_2 + 1.5 \text{HCl} + \text{H}_2\text{O}(g)
\]
Leaching

\[(\text{SrO})_{1.5} \cdot \text{SiO}_2 + \frac{1}{2} \text{H}_2\text{O}(l) \rightarrow \frac{1}{2} \text{Sr(OH)}_2 + \text{SrO} \cdot \text{SiO}_2\]

Calcining

\[\text{SrO} \cdot \text{SiO}_2 + \frac{1}{2} \text{Sr(OH)}_2 + \text{H}_2\text{O}(g) \rightarrow \frac{1}{2} (\text{SrO})_{1.5} \cdot \text{SiO}_2 + \frac{1}{2} \text{HCl} + \text{H}_2\text{O}(g)\]

This series of reactions is similar to that used for the conversion of \(\text{BaCO}_3\) to \(\text{Ba(OH)}_2\) as set forth by Dequide (36).

Charges containing both strontium chloride and sodium chloride exhibited peculiar behavior. Most of the charge vaporized from the boat, probably because of the formation of a low boiling eutectic mixture, \(\text{SrCl}_2 - \text{NaCl}\). The \(\text{SrCl}_2 - \text{NaCl}\) vapors then reacted with the wall of the silica tube to give off HCl and form strontium silicate and sodium silicate. More HCl was formed than that equivalent to the \(\text{SrCl}_2\) in the charge, indicating that some of the \(\text{NaCl}\) was also decomposed. This decomposition of sodium chloride is interesting because it took place at 1650°F, which is considerably below the temperature at which sodium chloride can be induced to decompose even in the presence of a silica catalyst (68). The conclusion must be that the \(\text{SrCl}_2\) acts as a catalyst in the decomposition of \(\text{NaCl}\) and vice versa. Sodium hydroxide, however, cannot be leached from \(\text{Na}_2\text{O} \cdot \text{SiO}_2\).

Charges containing strontium chloride and strontium hydroxide with silica or ferric oxide behaved in a manner similar
to strontium chloride alone with silica or ferric oxide.

The degree of conversion as well as the rate of reaction rises sharply with the temperature. This is shown by the curves of Figure 29. However, the optimum temperature appears to be about 1700° F., for temperatures higher than this caused most of the charges to sinter or melt with a resultant low recovery of strontium hydroxide when the residue was leached. Temperatures below 1200° F. gave negligibly small conversions.

The rate of steam flow over the charge should be kept low. As shown by Figure 29, the reaction is rather slow so that a low steam rate will not result in a deficiency of steam for the reaction. A high steam rate usually led to a lower conversion probably because of the lower steam temperature resulting from too rapid passage through the preheating section of the furnace. A low steam rate has the further advantage of producing a more concentrated solution of hydrochloric acid.
Fig. 29. Effect of temperature on the calcination of strontium chloride with steam.
IV. DESCRIPTION OF THE PROPOSED PROCESS

A. Quantitative Flow Sheet

The final flowsheet, Figure 30, page 169, is an elaboration of the simplified scheme shown in Figure 1, page 8. These elaborations are largely based on the information gleaned from the experimental work reported in Part III. The quantities and conditions for the various steps are indicated on the flowsheet.

Hot concentrated strontium hydroxide solution from the "Sr(OH)₂ dissolver" is passed through the "main ion exchange system" containing sodium-loaded Dow HC8 resin as the exchange material. Sr⁺⁺ ions and (SrOH)⁺ ions exchange with Na⁺ ions forming sodium hydroxide in solution and leaving Sr⁺⁺ and (SrOH)⁺ ions on the resin. The effluent solution is cooled in "crystallizer 1" precipitating the excess strontium hydroxide which is returned to the "Sr(OH)₂ dissolver." The supernatant solution from "crystallizer 1" is the product, containing 3.5% NaOH with 0.01% Sr(OH)₂ as impurity.

"Wash water after Sr(OH)₂ exchange" is passed through the "main ion exchange system" then through the "extraction system" where it leaches Sr(OH)₂ from the (SrO)₁.₅SiO₂ and thence to the "Sr(OH)₂ dissolver" where it serves to make up the concentrated strontium hydroxide solution.

*Items in quotation marks refer to labels on the flowsheet, page 169.
FIG. 30. QUANTITATIVE FLOW SHEET FOR THE PRODUCTION OF NA
"Solid NaCl" is dissolved in the "NaCl dissolver" to form a saturated solution which is passed through the "auxiliary ion exchanger" containing Dow HCR resin where a small amount of (SrOH)\(^+\) ion is released to the solution by exchange with Na\(^+\) ion, and thence through the "main ion exchange system" to regenerate the resin by exchanging Na\(^+\) ions for the Sr\(^{2+}\) and (SrOH)\(^+\) ions previously adsorbed by the resin. The regenerant effluent from the "main ion exchange system" is then sent to the "mixer for Sr(OH)Cl formation" where it is mixed with crystals of Sr(OH)\(_2\).8H\(_2\)O from "crystallizer 3." In this mixer the SrCl\(_2\) reacts with the Sr(OH)\(_2\) under the proper conditions to form the basic salt Sr(OH)Cl. The solution is then sent to "crystallizer 2" where most of the basic salt precipitates as the hydrate Sr(OH)Cl.4H\(_2\)O and the supernatant solution is sent back to the "NaCl dissolver" to make up the regenerant solution.

The precipitated basic salt is mixed with the leached SrO.SiO\(_2\) from the "extraction system" and charged into the "calciner" where it is contacted with a slow stream of steam at 1650\(^\circ\) F. The HCl produced by this reaction is condensed with the steam in the "condenser" and emerges from the process as a 10\% solution of hydrochloric acid. The residue in the "calciner" is (SrO)\(_1.5\).SiO\(_2\). This residue is sent to the "extraction system" where some of the SrO is leached from it by the heated supernatant solution from "crystallizer 3" to produce a concentrated Sr(OH)\(_2\) solution. This solution is sent
back to "crystallizer 3" to precipitate Sr(OH)$_2$.8H$_2$O for use in forming the basic salt with the SrCl$_2$ in the regenerant solution. The remainder of the leachable SrO in the residue is extracted by the wash water from the "main cation exchanger" and sent to the Sr(OH)$_2$ dissolver as already described. The leached residue, SrO.SiO$_2$ is mixed with Sr(OH)Cl.4H$_2$O from "crystallizer 2" and charged into the "calciner" as described above.

To wash the salt water from the "main cation exchanger" after the regeneration step, "wash water after NaCl regeneration" is passed through the resin to remove all the NaCl from it. The first portion of the wash effluent is much more concentrated than the last. The entire wash effluent is mixed together in the "mixer for NaCl wash solution" to make all of the solution uniformly dilute. The dilute solution is then passed through the "auxiliary ion exchanger" where the Sr$^{++}$ and (SrOH)$^+$ ions in the wash water are adsorbed on the resin. This adsorption is possible because of the dilution effect previously discussed. In dilute solution the resin has a much stronger affinity for Sr$^{++}$ and (SrOH)$^+$ ions than for Na$^+$ ions; in concentrated solution the affinities are about the same so that when the saturated NaCl solution from the "NaCl dissolver" is passed through, it can desorb the relatively small amount of strontium from the resin in the "auxiliary ion exchanger." After the strontium is recovered by the "auxiliary
ion exchanger" the wash solution is discharged as a very dilute NaCl solution.

B. Equipment

A brief description of the principal items of equipment required will be given.

The heart of the process is the "main ion exchange system." This could consist of a battery of standard ion exchange units of the type described on page 55, equipped with steam jackets to maintain the desired temperature. The units would be connected in series, with the valves and piping arranged so as to permit operation similar to that of a diffusion battery (15). This arrangement simulates countercurrent flow and produces maximum sodium hydroxide concentration, allows maximum utilization of exchanger capacity, requires minimum amount of resin, and permits continuous operation (119). Solid strontium hydroxide would be dissolved in the solution between units to keep the exchange potential at a maximum and accomplish multiple contact exchange. Regeneration would be carried out in similar fashion. Since the solutions are concentrated, the six step procedure described on page 55 would be applied to each unit. Economic operation calls for a high flow rate and small volume for each exchanger unit (99). Since the exchange reaction has been shown to be rapid, a high flow rate is permissible, but
a small volume of exchanger means frequent regeneration which would entail a high labor cost. This could be obviated by the installation of automatic operation.

The calciner could be a furnace or kiln lined with silica or other heat and acid resistant brick. The charge could be directly fired by combustion or a gaseous hydrocarbon fuel. The steam resulting from this combustion together with the water present in the charge would be sufficient to carry on the reaction. A furnace for the reaction of sand, salt, and steam is described by Iler (68) and may be applicable to this case. Indirectly fired furnaces such as the coke oven type or the type described by Parry (113) might also prove workable.

The extraction system could be a series of Dorr thickeners operated in countercurrent. These units would require heating coils to keep the solutions at the desired temperatures.

The crystallizers could be the Swenson-Walker type. Each crystallizer would be followed by a centrifuge to remove all possible mother liquor from the crystals.

The HCl condenser could be of Karbate construction.

C. Economic Considerations

In order to arrive at a rough evaluation of the process at this stage of development, the comparative method suggested by Tyler (146) will be used. By this method the process is compared with a similar one already in operation. The Solvay
process for the production of soda ash (130) is in many respects similar to this one. Both processes produce cheap heavy chemicals by a method involving much recycling of intermediate substances and much of the equipment, such as calciners, crystallizers, and centrifuges, is similar. The capacity of the proposed process is intended to be much smaller than that of the ordinary Solvay plant, but it is assumed that the ion exchange process lends itself more readily to economical operation on a small scale. Operating and fixed costs were estimated on an equivalent basis, while cost of raw materials and value of products were taken largely from Oil, Paint, and Drug Reporter using works prices for raw materials and stockpoint prices for products. This rough estimation is presented in Tables XXV and XXVI.

This estimation indicates that to be of greatest advantage, the process should fulfill the following conditions: The plant should be near a source of rock salt and fresh water, and distant from a source of sodium hydroxide and hydrochloric acid so that the freight charges can give greatest justification for the manufacture of these two products for direct plant use. The plant in which the process is used should be able to consume all of the sodium hydroxide and hydrochloric acid produced. The value of the sodium hydroxide alone is not enough to justify setting up the process. The strontium compounds circulating in the process must be guarded very carefully against loss, for loss of strontium in this process is even more critical than loss of ammonia in the Solvay process.
<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Unit</th>
<th>Quantity per year</th>
<th>Unit cost ($/works)</th>
<th>Total cost $/per year</th>
</tr>
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<tbody>
<tr>
<td>Rock salt</td>
<td>ton</td>
<td>1,190</td>
<td>12.00</td>
<td>14,300</td>
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<tr>
<td>Water (soft)</td>
<td>1000 gal.</td>
<td>8,333</td>
<td>.25</td>
<td>2,082</td>
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<tr>
<td>Strontium hydroxide loss</td>
<td>ton</td>
<td>16</td>
<td>460.00</td>
<td>7,330</td>
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<tr>
<td>Silica loss</td>
<td>ton</td>
<td>10</td>
<td>12.00</td>
<td>120</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
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<td></td>
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<table>
<thead>
<tr>
<th>Products</th>
<th>Unit</th>
<th>Quantity per year</th>
<th>Unit cost ($/ including freight)</th>
<th>Total value $/per year</th>
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<tr>
<td>Sodium hydroxide</td>
<td>ton</td>
<td>pure NaOH</td>
<td>333</td>
<td>29,000</td>
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<tr>
<td>Hydrochloric acid</td>
<td>ton</td>
<td>pure HCl</td>
<td>304</td>
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<tr>
<td><strong>Total</strong></td>
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<td></td>
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<td><strong>$78,200</strong></td>
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Table XXVI

Economic Evaluation of the Process

<p>| | |</p>
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<tr>
<td>Assumed plant capacity</td>
<td>1 ton pure NaOH per day</td>
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<tr>
<td>Fixed capital</td>
<td>$60,000</td>
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<td>Working capital</td>
<td>10,000</td>
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<td>Total investment</td>
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<td>Years to pay off investment</td>
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</table>
V. CONCLUSIONS

1. The proposed process as outlined in Part IV may be economically feasible in a plant requiring both dilute sodium hydroxide and dilute hydrochloric acid, located near a source of rock salt and fresh water and distant from a producer of sodium hydroxide and hydrochloric acid.

2. Strontium hydroxide is the most suitable hydroxide for use in the ion exchange reaction.

3. The sulfonated polystyrene type resin such as Dow HCR is the best available exchange material for the ion exchange reaction.

4. A pure 3.5% sodium hydroxide solution may be obtained by multiple contact of hot concentrated strontium hydroxide with successive portions of Dow HCR resin, adding solid strontium hydroxide to the solution before each contact.

5. The rate of ion exchange is rapid, practical equilibrium being established in a few minutes.

6. Temperature has little effect on the rate or equilibrium of the ion exchange reaction but it must be kept at about 85° C. to hold enough strontium hydroxide in solution for maximum exchange.

7. The optimum initial concentration of strontium hydroxide in exchange is 1.3 m.e. per c.c. of solution, and the optimum ratio of m.e. initial strontium to grams resin is about 2.8.
8. Dilution of the strontium hydroxide solution increases the exchange efficiency and the exchange capacity but it nevertheless diminishes the concentration of the sodium hydroxide in the product solution.

9. Part of the hydroxyl ions in solution are adsorbed by the resin in the form of (SrOH)$^+$ ions during exchange but they are later desorbed in the same form during regeneration with sodium chloride solution.

10. The apparatus described on page 114 is a convenient means of obtaining accurate rate and equilibrium ion exchange data in hot solutions.

11. Under proper conditions strontium may be precipitated as the basic salt Sr(OH)Cl$\cdot$4H$_2$O from the sodium chloride regenerant solution by the addition of strontium hydroxide. Neutral strontium chloride also may be separated from sodium chloride but this method requires evaporation of water.

12. Neutral or basic strontium chloride may be calcined at 1650$^\circ$ F. in the presence of steam and silica to drive off the chlorine as hydrogen chloride and leave a residue which may be leached to give a strontium hydroxide solution. The hydrogen chloride may be condensed with the steam to give a solution of hydrochloric acid.
VI. SUMMARY

An investigation was carried out to determine the materials and procedures by which the phenomenon of ion exchange could be utilized in a process to produce pure, dilute sodium hydroxide solutions from sodium chloride without evaporation. The process, as developed in this investigation, involves the use of strontium hydroxide as an intermediate. Exchange of strontium ions from hot strontium hydroxide solution for sodium ions on a cation exchange resin, followed by precipitation of the excess strontium hydroxide, produces a pure dilute sodium hydroxide solution of about 3.5%. The resin is then stripped of its strontium ions by passing sodium chloride through it. The effluent solution from this regeneration step contains the strontium ions which may be precipitated as basic strontium chloride. Reconversion of this chloride to the hydroxide is accomplished by calcining at 1700° F. in the presence of steam during which hydrogen chloride is given off. The overall process is thus an indirect means of bringing about the hydrolysis of sodium chloride into sodium hydroxide industrially available and considerably lower than that required by the direct hydrolysis of sodium chloride.

Experimental exploration of this ion exchange process was conducted with the aim of finding the best exchangeable hy-
droxide, the most suitable ion exchange material, and the optimum conditions for exchange and recovery of the exchangeable hydroxide.

Preliminary examination of the properties of all soluble hydroxides indicated that only the hydroxides of calcium, strontium, barium and ammonium would be suitable for use as the exchangeable hydroxide. Experimental determination of the exchange characteristics of these four hydroxides revealed that with calcium hydroxide, due to its low solubility, a sodium hydroxide solution of only 0.6% could be obtained by ion exchange; with ammonium hydroxide almost no cation exchange at all took place; with barium hydroxide, due to the strong molecular adsorption of barium hydroxide by the resin and the formation of the double base NaOH·Ba(OH)₂ when excess barium hydroxide was precipitated from solution, the final sodium hydroxide concentration produced was only 0.7%; strontium hydroxide exhibited none of these undesirable features and produced pure sodium hydroxide solutions with concentrations as high as 3.5%. Strontium hydroxide was therefore selected as the best exchangeable hydroxide.

Of those cation exchangers that are capable of withstanding hot alkaline solutions, three representative resins were selected for test. These were Dow MX, a sulfonated phenol-formaldehyde resin; Amberlite IRC-50, a carboxylated polystyrene resin; and Dow HCR a sulfonated polystyrene resin. The Dow HCR
resin proved to be the most desirable for the purpose at hand. With it, a 3.5% sodium hydroxide solution was produced as compared with 2.1% with Dow MX and 1.0% with Amberlite IRC-50. The Dow HCR resin showed a higher exchange capacity and a lower hydroxyl ion adsorption than the other two resins. It therefore was selected as the best exchange material.

Using strontium hydroxide and Dow HCR resin, rate and equilibrium studies were made on a specially designed ion exchange unit to determine optimum conditions for exchange. These data were correlated and their practical and theoretical significance discussed.

A study was made of the problem of recovery of strontium from the regenerant solution and its reconversion to the hydroxide. This may be accomplished by precipitating the strontium as basic strontium chloride which may be calcined in the presence of steam to give strontium hydroxide and hydrochloric acid.

A quantitative flow sheet for the process based on the experimental data was devised and a rough economic evaluation presented.
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