# POTASSIUM BICARBONATE FROM POTASSIUM CHLORIDE

# AND

# SODIUM BICARBONATE FROM SODIUM CHLORIDE

## (BY ION-EXCHANGE AND WATER-TRANSFER WITH ALCOHOLS)

PROEFSCHRIFT
TER VERKRIJGING VAN DE GRAAD VAN
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DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOR
PROF. DR. IR. J. C. VLUGTER

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To my parents

To Hannie

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# 1. GENERAL

## 1.1. Introduction

Among the minerals which Nature has bestowed on mankind, chlorides take a prominent place. The element chlorine comprises some 480 parts per million in the lithosphere (1), and some 19000 parts per million in the oceans (2). Of the different chlorides encountered, those of sodium and potassium form a considerable part, both on land (e.g. rock salt $NaCl$, Sylvite $KCl$, Carnallite $KCl.MgCl_2.6H_2O$) and in sea.

It is only in some cases, however, that the chlorides of sodium and potassium are used ultimately as such (as $NaCl$ for consumption, and $KCl$ as fertilizer). Often conversion, involving exchange of the chloride, precedes industrial utilization. Conversion to the hydroxides and carbonates is attractive, yielding reactive intermediates for further industrially important compounds.

Salt has since times immemorial formed one of the major mineral resources of the Land of Israel. There exist indications of salt-gathering around the Dead Sea (in Hebrew : Yam HaMelah, the Salt Sea), in very early times. An explicit record of this was given by the Prophet Zephania, some 2600 years ago (3) : "... as Sodom ... as Gomorrah ... (a) salt-pit ". In our times, one of the earliest industrial enterprises undertaken during the reconstruction of the Jewish homeland was the exploitation of the $KCl$ from the Dead Sea by M. Novomeysky, planned in 1911 and put into operation in 1930.

An important expedient in the endeavour to increase the economic value of the Dead Sea sodium and potassium chlorides lies in their upgrading by conversion. The present thesis describes a new process for conversion of the Dead Sea $KCl$ into $KHCO_3$ and $K_2CO_3$. This conversion may be summarized as follows:

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(1) V.M. Goldschmidt, Geochemistry (Oxford 1954) pp. 74-75

(2) Idem, idem, p. 49

(3) Zephania, chapter 2, verse 9

1) KCl in aqueous solution is caustified with $Ca(OH)_2$, using a cation-exchanging resin as auxiliary agent. The solubility of the caustifying agent is increased by the addition of phenol ($C_6H_5OH$).

2) The phenolic potassium hydroxide solution so obtained is carbonated with gaseous $CO_2$, which gives $KHCO_3$ and phenol. The latter is recovered and recycled.

3) Both the $Ca(OH)_2$ and the $CO_2$ stem from limestone.

4) The $KHCO_3$-solution is dehydrated by extraction of the water with an aliphatic alcohol (such as n-butyl alcohol), which in its turn is dried with a saturated NaCl-solution, for reasons which will be explained later, and recycled to the process ("Water-Transfer Method").

5) The obtained solid $KHCO_3$ is eventually converted into $K_2CO_3$.

6) The obtained solutions of $CaCl_2$ (from step 1) and of NaCl (from step 4) are discarded.

By analogous process, sodium chloride is converted into sodium bicarbonate and carbonate.

The concentration of the raw materials, to wit KCl and NaCl, in the Dead Sea, is respectively 13 g/l and 85 g/l (4).

The present process should be regarded as a possible new way for conversion of the chloride of potassium (or sodium) into the bicarbonate or the carbonate, and also as a possible valuable addition to the economy of Israel. This country does not, as far as is known at present, abound in rich natural resources. The process described uses locally available raw materials - potassium chloride, limestone and salt (NaCl) - to produce the more valuable bicarbonate and carbonate of potassium and sodium. Its technically and commercially successful operation might thus be beneficial to an economy which has to support a growing population.

It is the author's belief that the present thesis contains the basic information necessary for the further development of this process.

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(4) The Dead Sea Commission 1955/56, Prof. Ir. A. de Leeuw, Chairman; 2nd report(Jerusalem 1956), Appendix 1, page 14 (in Hebrew).

## 1.2. Methods of Caustification and Carbonation

### 1.2.1. Introduction

The present thesis deals with the caustification and carbonation of the chlorides of potassium and sodium. It is therefore instructive to review the known methods of attaining this aim, those of technical importance as well as those which have not (yet) outgrown the laboratory or pilot plant stage. The method developed can then be appraised in the light of this review.

Caustification and carbonation of the chlorides of potassium and sodium have been proposed in a multitude of ways. Reviewing might be facilitated by their division according to the following scheme :

1) Caustification by electrolysis;

2) Caustification and carbonation by the action of suitable agents, such as calcium hydroxide on sodium silicate (made from sodium chloride);

3) Caustification with the intermediate of ion-exchanging resins, where the caustification agent serves as regenerant.

### 1.2.2. Caustification by Electrolysis

The conversion of sodium or potassium chloride into the corresponding hydroxide by electrical current is by no means a new reaction. In the year 1807 Sir Humphrey Davy published (5) his account of this conversion. It served him in the identification of chlorine as an element, contrary to the current belief at that time (6).

This caustification of sodium and potassium chloride is nowadays by far the most important method of preparing their hydroxides (7). The process yields products at a high purity and - in the case of the aqueous alkali hydroxides - at considerable concentration, up to 50 wt.% NaOH or KOH.

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(5) H. Davy, Phil. Trans. Roy. Soc. (London) 1807 23

(6) Imperial Chemical Industries, Ancestors of an Industry (Great Britain 1950) p.55

(7) C.L. Mantell - Electrochemical Engineering (4th Ed., New-York 1960) chapter 11, pp. 249-307

In the U.S.A., chlorine is the primary product of the electrolysis, while the caustic soda (or, on a smaller scale, caustic potash) is the secondary. This is one of the reasons, that in spite of the advantages of the process, part of the caustic soda is still made by other means of caustification. In less developed countries, the accent is frequently on the caustic soda (7). This last statement holds also for Israel.

One of the most important factors limiting the application of this process on a wider scale in the so-called under-developed countries is the high amount of energy required. The following facts illustrate the point (data from ref. 7) : For the production of 1.0 t NaOH (25 kmol), 3610 kWh + 3.14 t steam are required (all tons are metric). Together with this amount of alkali hydroxide, 0.89 t chlorine are obtained. In view of the accent in the production as noted above, the discussion is limited to alkali hydroxide. Chlorine, as well as the refrigeration required for its liquefaction, is left out.

Generation of the electrical energy proceeds with loss of a part of the chemical energy of the fuel used. The magnitude of this loss may be calculated in the following manner :-

The thermal efficiency of a modern, oil-fired power station, selling power but no heat and employing units of at least 50 MW, is 37%. Losses incurred in the distribution amount on the average to 12% of the power on the bus-bars (9). The total energy - efficiency of generation and distribution is then 0.37 x 0.88 = 0.326.

For the production of 1 ton of NaOH, the chemical energy in the fuel equals 3610/0.326 = 11100 kWh.

The generation of steam required for the NaOH-production may take place at an energy efficiency of 90% (8). Assuming that the energy contents of the steam are, at first approximation, equal to the heat of evaporation of the water, about

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(7) C. L. Mantell - Electrochemical Engineering (4th Ed., New-York 1960) chapter 11, pp. 248-307

(8) F.S. Aschner - The Combined Generation of Power and Heat, Handasa weAdrikhalut (Engineering & Architecture) 17 (1959) 79 (in Hebrew)

(9) O. Lyle - The Efficient Use of Steam (London 1947) p. 68

$2.25 \times 10^6$ J/kg, the chemical energy in the fuel, generating such steam for 1 ton of NaOH, equals $3.14 \times (2.25 \times 10^9/0.90 \times \times 3.6 \times 10^6) \sim$ 2200 kWh/t NaOH.

The total energy requirement of this process (excluding refrigeration for chlorine liquefaction) is then about 11100 + 2200 = 13300 kWh/t NaOH. This energy comes in the form of fuel for the generation of steam and electricity.

If we assume that on a kWh/mol-basis the efficiency of the production of KOH equals that of NaOH, then the energy in the fuel needed for the production of the electricity for 1 ton KOH is 11100 x 40/56.1 = 8000 kWh.

As the steam is used mainly for evaporation of water, and as the weight concentrations of NaOH and KOH are of the same order (50%), we may assume that the steam consumption per ton KOH equals that per ton NaOH, to wit 2200 kWh/t. The total energy requirement of the caustification of KCl to KOH is then (excluding the chlorine) 8000 + 2200 = 10200 kWh/t of KOH.

For a small-sized plant of, say, 5 t caustic/day, the energy requirements of the fuel would then be 66500 respectively 51000 kWh/day, or, in terms of a quantity of fuel, of , say, $10^4$ kcal/kg, respectively 5700 and 4400 kg/day.

It follows that the weight of fuel required (exclusive of the chlorine) is of the same order as the weight of the pure caustic produced. In the development of a new process for the caustification of alkali metal chlorides, we should strive for a smaller energy consumption. The process which is the subject of the present thesis, answers this claim. This will be set out in detail below.

### 1.2.3. Caustification and Carbonation by the Action of Suitable Agents

This paragraph includes the earlier process of Leblanc, now redundant, and the later one of Solvay, now of considerable technical importance. Other processes proposed the use of the hydroxides or carbonates of the alkaline earth metals; the oxides or hydroxides of iron, lead and zinc; the carbonates of magnesium, nickel and cobalt; steam; carbon dioxide and ammonia; and watergas.

### 1.2.3.1. Calcium Hydroxide and Carbonate

The use of calcium hydroxide for caustification has been proposed for many processes. This is not astonishing, since lime is "the lowest-cost alkali available" (10) (note 1a).

One of the oldest technical processes for making sodium carbonate was that invented by Nicholas Leblanc at the end of the eighteenth century (11). Sodium chloride was reacted with sulfuric acid to yield sodium sulfate ("salt cake"), which was heated in a furnace with carbon and limestone. Reduction of the sulfate to the sulfide was followed by conversion to sodium carbonate. Low temperature extraction with water yielded a $Na_2CO_3$-solution. This process is equally applicable to the conversion of potassium chloride to potassium carbonate.

The caustification of sodium carbonate to sodium hydroxide with calcium hydroxide was a further step in the same process. It was, however, complicated by the appearance of the double salts $CaCO_3 \cdot Na_2CO_3 \cdot 5H_2O$ and $CaCO_3 \cdot Na_2CO_3 \cdot 2H_2O$ (12) which had obviously to be prevented. A compromise between the increased yield at dilution, and the costs of subsequent concentration, had therefore to be found.

Leblanc's process for sodium carbonate has wholly been replaced (13) by the ammonia-soda process, named after Solvay (14). This method dates from the beginning of the 19th century. Its product is purer than that of Leblanc's. Also, Leblanc's process yielded two by-products, which were difficult to dispose - HCl and CaS. Solvay's process yields only $CaCl_2$ as by-product and this can easily be discarded, for example into the sea. According to this process, a con-

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(10) Chemical Lime Facts, Bull. 214, National Lime Association (Washington 1951) p. 7

(11) J.R. Partington, Textbook of Inorganic Chemistry (London 1944, 5th ed.) p. 756

Note 1a $Ca(OH)_2$ costs currently about 0.4 \$/keq;
NaOH costs 4.4. \$/keq (prices from (11a)).

(11a) Chem.Eng.News, Quarterly Report on Current Prices, June 27, 1960.

(12) N.Leblanc & K.Novotny, Z.anorg.Chem. 51 (1906) 181-201

(13) Z.G.Deutsch, in R.E.Kirk & D.F.Othmer, Encyclopedia of Chemical Technology (New-York 1947) vol.I, 385

(14) J.R.Partington, Textbook of Inorganic Chemistry (London 1944 5th Ed.) p. 761.

centrated sodium chloride solution is treated with ammonia and carbon-dioxide, when sodium bicarbonate is precipitated. This is calcined to the carbonate. The ammonium-chloride solution from the first step is treated with burnt lime to recover the ammonia. Non-attainment of efficient ammonia-recovery was one of the main initial difficulties of this process. The burnt lime and part of the carbon dioxide stem from limestone. The balance of the $CO_2$ stems from the calcination. Due to the higher solubility of potassium bicarbonate as compared with sodium bicarbonate, $K_2CO_3$ cannot be made by this method. The Solvay process, started in 1875, made some 280.000 t in 1880, when Leblanc's process was at its climax (550.000 t). In 1913, when Leblanc's process had stopped operating, Solvay's process made over 2.2 million t, while in 1944 the industry in the whole world had a capacity of nearly 10 million t (13).

Other processes for caustification or carbonation of sodium or potassium chlorides, which were of lesser technical importance or did not outgrow the stage of proposals, include the following :-

Calcium hydroxide has been proposed to caustify potassium chloride via intermediates. One way involved converting KCl with boric acid into $K_2O.5B_2O_3$, which on reacting with $Ca(OH)_2$ yielded KOH and $Ca(BO_2)_2$, from which latter compound hydrochloric acid or ammonia recovered the boric acid (15). The HCl obtained in the first step amounts theoretically to 20% of that required in the last step. The analogous conversion of sodium chloride into sodium hydroxide was also put forward, after the decomposition of sodium borate with lime had been shown possible (16).

According to another proposal potassium chloride was converted with calcium fluoride and silica, in the presence of hydrochloric acid, into potassium silicofluoride. Its treatment with ammonia was said to free potassium fluoride, which, with calcium hydroxide, formed potassium hydroxide (and calcium fluoride for the first step) (17).

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(13) Z.G.Deutsch, in R.E.Kirk & D.F.Othmer, Encyclopedia of Chemical Technology(New-York 1947)vol.I p.385

(15) L.Hackspill & A.R.Rollet, Germ.Pat.562005 (13.2.1930)

(16) L.J.F. Margueritte, Brit.Pat. 159 (1885) - W. Garroway, Brit.Pat. 17395 (1889)

(17) M.Buechner, U.S.Patent 1776064 (16.9.1926),and others

The analogous conversion of sodium chloride into sodium hydroxide via the silicofluoride has also been brought forward (18). Likewise the conversion of sodium chloride with hydrofluoric acid into sodium fluoride, and the subsequent processing with calcium oxide or hydroxide into sodium hydroxide , has been proposed (19). The last step yielded calcium fluoride, from which the hydrofluoric acid and the calcium oxide were claimed to be recovered on heating with steam.

An indirect conversion of sodium chloride into sodium hydroxide was suggested, as follows:- (20) Sodium chloride was treated with ammonia and sulfur dioxide, to yield sodium ammonium sulfite. This compound was said to decompose on heating into sodium sulfite, which was amenable to caustification with calcium hydroxide.

Another indirect conversion entailed treating sodium chloride vapours with steam and silica. This reaction, known by itself, was proposed as a technical possibility in 1862, after development of the necessary oven (21). Caustification of the formed sodium silicate with aqueous calcium hydroxide was said to yield sodium hydroxide.

For the conversion of potassium chloride into its hydroxide or carbonate, calcium hydroxide has been suggested in the following manner (22):

A KCl-solution was treated with nickel hydroxide respectively nickel carbonate (or the cobalt compound) and ammonia, when potassium hydroxide respectively carbonate was formed and hexammino-nickelchloride was precipitated. The latter's treatment with calcium hydroxide freed ammonia and nickel hydroxide, which eventually on carbonation yielded the initially required nickel carbonate.

The analogous conversion of sodium chloride into sodium hydroxide or carbonate has also been proposed (22).

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(18) W.Siegel, Chem.-Ztg 53 (1929) 145-7
(19) E.L.M.Brochon, French Pat. 208754 (10.10.1890);
W.Weldon, Brit.Pat.628 (1.3.1866)
(20) G.Tauber, Germ.Pat. 43921 (11.9.1887)
(21) W.Gossage, Brit.Pat. 2050 (1862)
(22) H.A.Frasch, Germ.Pat. 164725 (24.9.1901)

The overall reaction was thus a combined caustification and (eventually) carbonation with calcium hydroxide and carbon dioxide.

Sodium sulfate (e.g., as made in the first step of Leblanc's process) was said (23) to be caustifiable with calcium hydroxide at a 2% $Na_2SO_4$-concentration, this dilution possibly serving to prevent formation of one of the double salts of the two sulfates. Replacing calcium hydroxide by calcium aluminate for this process was mentioned (24), claiming a decreased solubility of calcium sulfate in presence of the aluminate.

The conversion of potassium sulfate (from potassium chloride and sulfuric acid) with calcium hydroxide gives low yields (25), due to the relatively high $CaSO_4$-solubility and the low $Ca(OH)_2$-solubility, which is further decreased by the KOH formed.

The combination of secondary calcium orthofosfate ($CaHPO_4.2H_2O$) and steam was said (26) to convert potassium chloride (or sodium chloride) into monopotassium (or monosodium) calcium orthofosfate ($KCaPO_4$), which, on suspension in water and under pressure of carbon dioxide, would yield potassium bicarbonate (respectively sodium bicarbonate).

The caustification of disodium orthofosfate ($Na_2HPO_4$) with calcium hydroxide was proposed (27) as a way of producing sodium hydroxide.

Based on a British patent (28) of some eleven years earlier but enlarging the scope considerably in a subsequent patent of nearly a century ago (29), the following conversion of sodium chloride was suggested. Conversion with oxalic acid gave $Na_2C_2O_4$, which on treatment with the oxide, hydroxide or carbonate of calcium or such other metal as forms an insoluble oxalate, gave a solution of NaOH or $Na_2CO_3$ and a precipitate of

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(23) O. Rebuffat, Giorn.Chim.Ind.Applic. 11 (1929) 529-31

(24) A. Travers, Bull.Soc.Chim. (5) 2 (1935) 2124-8

(25) G. Gallo, Ann.Chim.applicata 25 (1935) 623

(26) M. Sourdet & J. Martin, French Pat. 1001853(28.2.1952); U.S.Pat. 2601066 (17.6.1952); Brit.Pat. 672655(21.5.1952)

(27) S.S. Sadtler, U.S. Pat. 1351693 (31.8.1919)

(28) A. Vogel, Dinglers Polyt. J. 136 (1855) 237

(29) W. Weldon, Brit. Pat. 629 (1.3.1866)

the metal's oxalate. Recovery of the oxalic acid with sulfuric acid was claimed to result in minute losses only, and the process was claimed to surpass that of Leblanc in economy of operation (Note 1).

### 1.2.3.2. The Hydroxides of Strontium and Barium

The caustification of potassium sulfate (from KCl and $H_2SO_4$) with strontium or barium hydroxide proceeds more satisfactorily than with calcium hydroxide, due to the smaller solubility of $SrSO_4$ and $BaSO_4$. The regeneration of $BaSO_4$ to BaO was said (25) not to be workable economically. The recovery of SrO from $SrSO_4$ was claimed, however, to proceed very favourably. The strontium sulfate was boiled with a solution of sodium carbonate; strontium carbonate was said to be formed. Calcination of the $SrCO_3$ at 1200° yielded the SrO (25).

### 1.2.3.3. Magnesium Carbonate

The conversion of potassium chloride into potassium carbonate with the aid of magnesium carbonate (the Engel-Precht process) dates from the end of the last century (31) (32). The process has been the subject of considerable research, although it is not in actual operation (33) (Note 1b). The process entails the precipitation of Engel's salt $MgCO_3.KHCO_3.4H_2O$ from a suitable grade of magnesium carbonate trihydrate and potassium chloride under introduction of carbon dioxide, preferably at a low temperature :

$$3(MgCO_3.3H_2O) + 2\ KCl + CO_2 \longrightarrow 2(MgCO_3.KHCO_3.4H_2O) + MgCl_2.$$

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Note 1. The description of this patent, as given in ref. 30, has hardly anything in common with the patent itself.

(30) Gmelin's Handbuch der Anorganischen Chemie (8e Auflage, Berlin 1931) volume 21 (Natrium) page 712

(31) Ch.R.Engel, Germ. Pat. 15218 (29.1.1881);

(32) G. von Knorre, Z. anorg.Chem. <u>34</u> (1903) 260-85

(33) H.Epler & P.Lumbeck in Ullmanns Encyklopaedie der Technischen Chemie, Herausgegeben von W. Foerst, 3.Auflage (Muenchen-Berlin 1957) 9. Band, S. 235

(34) N.S. Bayliss & D.F.A. Koch, Austr. J.Appl.Sci. <u>3</u> (1952) 237-51

Note 1b: The process was apparently operated in the Salzbergwerk Neu-Stassfurt until 1938 (34)

The separated double salt may be heated with a recycled $K_2CO_3$-solution (35). $MgCO_3.3H_2O$, suitable for recycle, and an enriched solution containing $KHCO_3$ and $K_2CO_3$ are then obtained. The solution is partially evaporated to precipitate $KHCO_3$, which is converted to $K_2CO_3$ by calcination.

One third of the magnesium introduced is converted into magnesium chloride. This can be regenerated either by caustification with calcium hydroxide or by high-temperature decomposition to magnesium oxide and hydrochloric acid vapour.

Aiming at circumvention of the regeneration of magnesium chloride a suggestion has been made whereby the carbon dioxide and one third of the magnesium carbonate trihydrate are replaced by the equivalent amount of sodium carbonate or bicarbonate (35). Instead of $MgCl_2$, NaCl is formed:

$$MgCO_3.3H_2O + KCl + NaHCO_3 + H_2O \longrightarrow MgCO_3.KHCO_3.4H_2O + NaCl.$$

After precipitation of Engel's salt, the mother liquor containing the NaCl, can be used once more. Thus, an overall conversion of potassium chloride with sodium (bi)carbonate to potassium carbonate and sodium chloride is obtained.

A conversion of sodium chloride into sodium carbonate with the aid of magnesium carbonate and carbon dioxide was suggested nearly a century ago. Regeneration of the magnesium chloride with steam, to give hydrochloric acid and magnesium oxide, was also proposed. (36)

A later proposal (37) entailed a similar conversion of sodium chloride; the solution of magnesium bicarbonate had preferably to be saturated to magnesium chloride, in order to decrease the solubility of the sodium bicarbonate obtained. Separation of the sodium bicarbonate precipitate was followed by readdition of magnesium oxide or hydroxide or carbonate. Regeneration of the magnesium chloride was executed essentially as described above (36).

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(35) I. Schnerb, Bull.Res.Council Israel 5C (1955) 115-20

(36) P. Pichard, Comptes Rendus 83 (1876) 1104

(37) C. White, Brit. Pat. 21546 (24.9.1913)

The proposal to precipitate the double salt $MgCO_3.Na_2CO_3$ from a solution containing both NaCl and $MgCO_3$, with the aid of ammonia and $CO_2$, was made in 1930 (38). Subsequent treatment with boiling water was said to decompose this salt and to dissolve the $Na_2CO_3$.

A more recent proposal (39) mentioned the precipitation of $NaHCO_3$ in a method similar to that of (36), as part of a more general process to utilise $MgCO_3$ in a cyclic process.

A quite recent claim (40) for a similar process considered a $CO_2$-pressure of 4 atmospheres necessary, and proposed cooling to 0°. to precipitate the $NaHCO_3$. After calcination, a purity of 96-97% (as $Na_2CO_3$) was claimed, along with 1% as chlorides. A yield of 70% (on the Na) was claimed.

Another conversion of sodium chloride into sodium carbonate was proposed as follows (41). Sodium chloride was treated with equimolar quantities of hydrochloric acid and magnesium oxalate, to yield sodium dioxalate and magnesium chloride. By double conversion with magnesium carbonate, the $NaHC_2O_4$ was turned into $NaHCO_3$. Magnesium oxalate for the first step was then obtained. Decomposition of the magnesium chloride was effected with steam. Half the amount of hydrochloric acid formed here served for the first step. Finally, flue gases converted the MgO into $MgCO_3$. The overall reaction thus represents the conversion of sodium chloride with steam and carbon dioxide into sodium bicarbonate and hydrochloric acid.

### 1.2.3.4. Zinc Oxide + Carbon Dioxide

In analogy to the Engel-Precht process, $K_2CO_3$ was said to be precipitated as a "potassium-zinc carbonate" (perhaps identical with the reported $6ZnCO_3.4K_2CO_3.H_2CO_3.7H_2O$ (42)) from a KCl-solution to which ZnO or $Zn(OH)_2$ and $CO_2$ were added (43). Insoluble in cold water, the precipitate

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(38) E. Urbain, French Pat. 724539 (23.12.1930)

(39) J.C. Séailles, French Pat. 972735 (2.2.1951)

(40) A.M. Ponizovskii & B.A.Shoikhet, USSR Pat.117965 (20.2.1959)

(41) E. Bohlig, Dingl. J. 224 (1877) 621

(42) H. Sainte-Claire Deville, Ann.Chim.Phys.(3)33(1851)75-82

(43) B. Wittjen & E. Cuno, Germ.Pat. 19197 (21.1.1882)

was isolated, and subsequently treated with hot water, when a $K_2CO_3$-solution was obtained.

### 1.2.3.5. Plumbous Hydroxide

The reaction of sodium chloride with plumbous hydroxide yielding lead oxychloride and caustic soda, and the analogous reactions with potassium chloride, were discovered in 1773 and published some twelve years later (44). The reaction was patented to yield the subsequently called "Turner's Yellow" about one century later (45). The combined caustification with $Pb(OH)_2+Ca(OH)_2$ was proposed at about the same time (46). Regeneration of the lead oxychloride with lime was published in the same period (47). Regeneration of the oxychloride with ammonium carbonate, and treatment of the ammonium chloride so formed with lime for the regeneration of the $NH_3$, was suggested some years later (48). Composition of the oxychloride was determined (49) and found to be either $3PbO.PbCl_2$ (in concentrated solutions) or $4PbO.PbCl_2$. A different recovery of the lead was proposed more recently (50). $3PbO.PbCl_2$ was dissolved in nitric acid, and the hydrochloric vapours were distilled off. Ammonia then precipitated plumbous hydroxide required for the first step. The overall reaction

$$NaCl + 4HNO_3 + 4NH_4OH \longrightarrow NaOH + HCl + 3H_2O + 4NH_4NO_3$$

thus represented the hydrolysis of sodium chloride to sodium hydroxide and hydrochloric acid, with the accompanying neutralisation of nitric acid by ammonia. No recovery of the nitric acid was envisaged.

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(44) C.W.Scheele, Crell's Ann. II 1785 220
(45) J.Turner, Brit. Pat. 1281 (1871)
(46) W.R.Lake, Brit. Pat. 939 (29.3.1869)
(47) M.Bachet, Fr. Pat. 93983 (1872)
(48) D.C.Knab, Brit. Pat. 3082 (13.8.1877)
(49) E.Berl & G.Austerweil, Z. Elektrochem. 13 (1907) 165
(50) J.Kersten, Germ.Pat. 255688 (31.10.1911)

### 1.2.3.6. Potassium Carbonate

The double conversion

$$2NaCl + K_2CO_3 \longrightarrow Na_2CO_3 + 2KCl$$

was advocated at the end of last century because potassium carbonate was then "more easily obtained" than the sodium compound. The reactants were mixed and carbon dioxide was led in. The least soluble component, sodium bicarbonate, was said to precipitate (51).

### 1.2.3.7. Ammonia and Carbon Dioxide

A proposal to convert sodium chloride into sodium bicarbonate was as follows (52). Solid sodium chloride was treated with a solution of urea containing free ammonia. Carbon dioxide was led in, when sodium bicarbonate was precipitated. The filtrate was claimed to serve - after concentration - as fertilizer, while calcination of the precipitate converted it into sodium carbonate.

### 1.2.3.8. Gases containing Carbon Monoxide

The conversion of sodium chloride with water-gas was suggested at the end of last century (53). Reacting NaCl with $CO + H_2$ was said to yield sodium oxide $Na_2O$, along with carbon and hydrochloric acid. A somewhat similar proposal entailed (54) (55) reacting sodium chloride with carbon monoxide and dioxide, when the mixture was said to yield sodium carbonate and phosgene. Other sodium compounds, such as the sulfate, the sulfide and the nitrate, were claimed to serve equally well as raw materials. The thermodynamic feasibility of these two reactions has not been checked.

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(51) W.Weldon, Brit. Pat. 980 (8.3.1881)

(52) T.Okada and E.Ohtsuka, Jap. Pat. 8 ('51) (9.1.1951)

(53) Mills, Brit. Pat. 4661 (1891) & French Pat. 221314 (18.8.1892)

(54) F.von Hardtmuth & L.Benze, Germ.Pat. 74937 (3.1.1893); 74976 (14.4.1893)

(55) M.Benze, Germ.Pat. 73935 (21.7.1893)

### 1.2.3.9. Steam

Many proposals have been made for caustification with the simplest, cheapest and most abundant "hydroxide" - water. No such caustification has, however, reached the stage of technical execution.

The claimed processes include the following.

Molten or gaseous sodium chloride was said to hydrolyse on contact with steam, and to form hydrochloric acid and sodium hydroxide (56). Platinum and pumice were named as catalysts for this process. A more recent method (57) involved the conversion of sodium chloride by electrolysis into sodium-lead alloy, which, on being treated with ammonia, gave sodium amide. Contacting this with superheated steam was said to yield sodium hydroxide.

The earlier (par 1.2.3.3.) mentioned regeneration of magnesium chloride, obtained from carbonation of sodium or potassium chloride with magnesium carbonate, with the aid of steam (36), might be regarded as an additional proposal for an overall caustification with steam.

### 1.2.4. Caustification and Carbonation with the Intermediate of Ion-Exchangers

With ion-exchangers double conversions of the type

$$AB + CD \longrightarrow AC + BD$$

which, because of unfavourable equilibria could not be executed directly, are attainable. Thus, many proposals were in this manner made to produce the hydroxides (and their derivatives) of potassium and sodium, starting with the respective chlorides and one of the hydroxides of calcium, strontium, barium or even (in dilute state) of sodium and potassium.

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(56) S.Cabot, Chem. News 31 (1875) 243

(57) E.A.Ashcroft, Germ. Pat. 268826 (27.2.1912)

Because of their preponderance, proposals including anion-exchangers will be dealt with first; then, those involving cation-exchange will be reviewed, to be followed by the suggestion involving liquid ion-exchangers. *

### 1.2.4.1. Anion Exchanging Resins

Anion-exchangers have been used for industrial purposes since 1935 only. The first resins, of the polyamine type, were made and investigated by B.A.Adams and E.L.Holmes (57a). In their first publication (57b) they mentioned the possibility of exchanging anions.

The oldest reference to the mode of operation represented by the equation

$$R\text{-}Cl + \tfrac{1}{2}Ca(OH)_2 \longrightarrow R\text{-}OH + \tfrac{1}{2}CaCl_2$$

is from 1939 (58). The production of chemicals by anion exchange was then probably not yet considered. The authors therefore proposed this reaction for the regeneration of resins exhausted during the treatment of water. The resin utilised was not specified. This proposal, however, might equally be applicable to a caustification, of which the subsequent step would then be

$$R\text{-}OH + NaCl \longrightarrow R\text{-}Cl + NaOH.$$

This sequence was specifically named in a patent of 1951 (59).

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* Note on nomenclature:- The resin-skeleton (or rather, radical) is noted R-. For the sake of brevity, it is proposed to call anion-exchanging resins to which e.g. the hydroxide ion is attached, "resin-hydroxide". For cation-exchanging resins with e.g. sodium ions, the name "sodium-resin" is proposed. These names are unambiguous, and shorter than the sometimes used "resinate" or "anion-resin hydroxide form", etc.

(57a) R.Kunin, Ion Exchange Resins (New York 1958) p. 4

(57b) B.A.Adams & E.L.Holmes, French Pat. 796797 (15.4.1936) and Brit.Pat. 450309 (13.7.1936)

(58) L'Auxiliaire des Chemins de Fer & G.V.Austerweil, French Pat. 850556 (20.12.1939)

(59) Dow Chemical Co., Brit. Pat. 662314 (5.12.1951), U.S. Pat. 2606098 (5.8.1952)

The use of cation-exchangers was considered unsatisfactory, as sodium hydroxide would then be formed in the step in which the calcium hydroxide solution would be introduced, yielding a very dilute (0.2% or less) NaOH-solution. Anion-exchangers, of the quarternary ammonium type, were preferred. Solutions of 5% or more of sodium hydroxide were claimed to be produceable in this way in single pass operation. Contamination by chloride was high. Recycling of a rather significant part of the effluent solutions (up to about 60%), especially those fractions of lower hydroxide concentrations, was claimed to raise the NaOH-contents in one fraction, comprising about 7% of the effluent, to about 13%, with approximately 2% NaCl accompanying it. The use of the hydroxides of strontium and barium instead of $Ca(OH)_2$ was mentioned, without entering into any details of the regeneration.

A proposal somewhat like (58) but naming the resin specifically, dates from 1950 (60). A slurry of calcium hydroxide in water (3-4% by weight) was claimed to regenerate Amberlite IR-4B, a resin of the polyamine aldehyde type, which had "absorbed" acids in a previous loading step. Some clogging, noticed on passing the slurry downwards, was claimed not to appear when operating upwards. The possibility of using the hydroxides of strontium, barium and magnesium was named as well (note 2).

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(58) L'Auxiliaire des Chemins de Fer & G.V.Austerweil, French Pat. 850556 (20.12.1939)

(60) J.H.Payne & H.P.Kortschak, U.S.Pat. 2507992 (16.5.1950)

(61) T.R.E.Kressman, Ion Exchangers (Commercial Materials) in C.Calmon and T.R.E.Kressman, Ion Exchangers in Organic and Biochemistry (New York 1957), p.120

Note 2: The capacity of the resin was 3.0 meq/ml in the wet state (61). The authors used 100 ml, containing 0.3 eq, on which 0.19 - 0.21 eq of acids were "absorbed". The regenerant was claimed to remove 90-95% of these acids.

The conversion of sodium hydroxide with potassium chloride and carbon dioxide into potassium bicarbonate was suggested in 1951 (62). Resin-hydroxide, when treated with a weak acid and a salt of a strong acid, would yield the salt of the weak acid. The following example was given:

$$R\text{-}OH + CO_2 + KCl \longrightarrow R\text{-}Cl + KHCO_3$$

A pressure of about 35 atmospheres was required for this example. Regeneration was proposed with sodium hydroxide, thus yielding the overall conversion

$$NaOH + KCl + CO_2 \longrightarrow KHCO_3 + NaCl$$

The conversion of sodium chloride into sodium bicarbonate was suggested in 1949 (63). Resin-hydroxide was mixed with its weight of water and one tenth its weight of NaCl, and $CO_2$ was introduced. A solution containing $NaHCO_3$ and NaCl was obtained. By precipitation of sodium sesquicarbonate ($NaHCO_3.Na_2CO_3$) separation from the chloride was ascertained. Heating converted the sesquicarbonate to $Na_2CO_3$. The resin-chloride was regenerated with calcium-hydroxide.

The conversion of sodium chloride into sodium bicarbonate was claimed in another Japanese patent (64). A solution containing sodium chloride and sodium bicarbonate was passed over resin hydroxide, and carbon dioxide was led in simultaneously, when sodium bicarbonate was precipitated. After filtration, the mother-liquor was made up with NaCl. The resin was regenerated with an aqueous solution of $Ca(OH)_2$. Resin utilisation per pass was rather low, of the order of 10%.

The same patentee (65) suggested a process with the same loading as above, but utilizing gaseous ammonia (in the presence of water or water vapour, presumably) for the regeneration. Whether the $NH_4Cl$ formed would be reconverted to $NH_3$ was not stated.

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(62) W.W.Durant & C.B.Clark, U.S.Pat. 2543658 (27.2.1951)
(63) Sh.Akabori & M.Yamada, Jap. Pat. 179487 (26.9.1949)
(64) Sh.Akabori, Jap. Pat. 27 ('50) (11.1.1950)
(65) Sh.Akabori, Jap. Pat. 276('51) (30.1.1951)

This patentee (66) also gave a rather complicated method of obtaining the sodium chloride solution, necessary for the above-mentioned conversion, starting with sea water. Essentially, the method consists of conversion of the magnesium chloride in the sea-water into magnesium hydroxide with the aid of $Ca(OH)_2$, which then gives $CaCl_2$. The $CaCl_2$ is removed by precipitation as $CaCO_3$ with the aid of R-OH and $CO_2$. Supply of the hydroxyl ions for the resin is effected with an additional amount of $Ca(OH)_2$; the formed $CaCl_2$ is discarded with the impurities in the sea-water, after isolation of the NaCl with the aid of an additional cation exchange cycle.

In view of the considerable number of intermediate reactions required by this method, its feasibility is open to question.

The same patentee also claimed the possibility (67) of a fractional bicarbonation of sodium chloride and potassium chloride by treating a diluted solution of both chlorides (containing about 1 equivalent of each) with about 10 equivalents of resin-hydroxide, and with carbon dioxide. The filtrate from the resin, after evaporation, was said to yield pure, solid $NaHCO_3$ (72% of the Na), while a further treatment with about 5 equivalents resin-hydroxide and $CO_2$ yielded a precipitate of pure $KHCO_3$ (40% of the K). Regeneration of the resin was proposed with aqueous $Ca(OH)_2$.

A conversion of sodium chloride into sodium hydroxide with the aid of Amberlite IRA-400 (a strongly basic anion exchanger of the quarternary trimethyl-ammonium type) in the hydroxide-form was proposed in 1951 (68). Regeneration of the resin-chloride to resin-hydroxide was proposed with aqueous calcium hydroxide. The same author claimed (69) to attain similar results with Amerlite IRA-410 (with triethanol-ammonium groups). For nearly complete regeneration with the aid of lime-water an excess of 1.34

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(66) Sh. Akabori, Jap. Pat. 1336 ('51) (12.3.1951)
(67) Sh. Akabori, Jap. Pat. 7 ('51) (9.1.1951)
(68) M. Sekino, Jap. Pat. 6712 ('51) (29.10.1951)
(69) M. Sekino, Jap. Pat. 6617 ('53) (23.12.1953)

times only (in terms of meq) over the total resin capacity was required (note 3). A process utilising the same resin, and regenerating with concentrated ammonia, has been claimed (71). Loading with 2 N NaCl yielded 0.37 N NaOH only.

An American patent (72), stressing the usefulness of a regeneration with lime-water for resins used for removing acids from industrial effluents prior to discard, could equally well be applied to caustification. Regeneration of the weakly basic ion-exchanger took place preferably in a direction opposite to that used in the loading step. To prevent clogging, the regenerant was filtered before use.

An American publication (73), considering the use of ion-exchangers for the demineralization of brackish waters, held that regeneration of the weakly basic anion-exchanger Amberlite IR-4B with aqueous $Ca(OH)_2$ was cheaper than that with sodium hydroxide or carbonate in chemicals but more expensive in handling and equipment, and hence recommendable in large-scale installations only, where the advantage might be up to $ 0.10/1000 gallons treated.

Finally, a recent patent (74) proposed to improve the execution of the caustification of sodium chloride to sodium hydroxide with calcium hydroxide and an anion-exchanger. The resin was premixed with solid calcium hydroxide, which was said to improve the degree of regeneration. Secondly, the interstitial liquid was blown out prior to the loading step,

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Note 3: 420 ml resin, of 1.2 meq/ml (61), were used, i.e. in all some 500 meq. 15 l regenerant were passed; at a $Ca(OH)_2$-solubility of 44.5 meq/l (70), the regenerant contained some 670 meq, and its excess was thus 670/500=1.34. The completeness of regeneration was tested by loading with 5.4 N NaCl, when 5 N NaOH was obtained.

(70) C.D.Hodgman, Handbook of Chemistry and Physics (Cleveland 1957) p. 1596
(71) T.Yamabe & S.Suzuki, J.Chem.Soc. Japan, Ind.Chem. Sect. 59 (1956) 20-22
(72) W.Juda & M.Carson, U.S. Pat. 2599558 (10.6.1958)
(73) K.S.Spiegler, W.Juda & M.Carson, J.Amer.Water Works Assoc. 44 (1952) 80-88
(74) N.W.Rosenberg and W.E.Katz, U.S. Pat. 2884310 (28.4.1959)

whereby higher sodium hydroxide concentrations were said to be obtained (note 4).

The considerable number of patents on such a limited subject, nearly all of which were issued within the last twelve years, would indicate the amount of work performed, and might cause one to suppose that many instances of technical application had materialized. Actually, only two such applications have been reported (75): the production of KOH from KCl and NaOH, and the production of NaOH from NaCl and $Ca(OH)_2$, with the aid of anion-exchangers, utilising a slurry of $Ca(OH)_2$ and countercurrent movement of resin and solution. Hardly any details are given.

### 1.2.4.2. Cation-Exchanging Resins

The first attempts at using cation exchange for industrial purposes date from the beginning of the twentieth century (75a), when R. Gans employed natural aluminium silicates for softening water. Synthetic resins, first made by B.A.Adams and E. L. Holmes (75b), overcame the limitations of natural materials and widened the scope of utilisation of cation exchange considerably.

The oldest reference to the caustification of sodium chloride with calcium hydroxide and a cation-exchanger dates from the year 1917 (76). The patentee proposed to utilise the ion-exchanging properties of the naturally occurring zeolites. By loading "exhaustively" with sodium chloride solution and regenerating with aqueous $Ca(OH)_2$, dilute NaOH would be obtained. Local use was probably assumed, or else thermal concentration envisaged.

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Note 4:- It is the present author's opinion that the numerical results given in this patent show little if any improvement over "prior art", and that part of them are obviously impossible.

(75) Anonymous, Chem.Engng 66 (1953) No. 12, 76

(75a) R. Kunin, Ion Exchange Resins (New York 1958) p. 3

(75b) B.A. Adams & E.L. Holmes, French Patent 796796 (15.4.1936); Brit. Pat. 450308 (13.7.1936)

(76) C.P. Hoover, U.S. Pat. 1238916 (4.9.1917)

The other proposals for the use of cation exchangers for the conversion of NaCl and KCl into their bicarbonates or hydroxides are of a much later period (1941 and later). These proposals have been classed in the following paragraphs according to the product they lead to.

The use of mixtures of $NH_3 + CO_2$ (or of preformed $(NH_4)_2CO_3$) for conversion of NaCl or KCl into their respective (bi)carbonates was proposed by several authors.

As part of a general patent of executing cation-exchange reactions with excess of volatile reactants, recovering the excess at a later stage, it was proposed (77) to convert ammonium-zeolite with NaCl into sodium-zeolite, which, on treating with excess $(NH_4)_2CO_3$, yielded $Na_2CO_3$, from which the $(NH_4)_2CO_3$ was recovered by volatilisation.

Instead of the direct treatment of ammonium-resin with NaCl, another proposal (78) embodied a two-step reloading, first with $CaCl_2$ and subsequently with NaCl. $NH_3$ was liberated from the $NH_4Cl$-solution with $Ca(OH)_2$, and combined with $CO_2$ and $H_2O$ to give the ammonium carbonate required. The analogous conversion of KCl into $K_2CO_3$ was suggested recently (79). Loading of the Ammonium-resin was effected with KCl. After washing, $NH_3+CO_2$ (1:1) in a twofold excess (in equivalents) over the KCl were introduced, when ammonium-resin and a solution of $KHCO_3$ and $NH_4HCO_3$ were obtained. Thermal decomposition yielded $K_2CO_3$, $\frac{3}{4}$ of the $CO_2$ needed and half of the $NH_3$. The overall reaction would then be:-

$$2KCl + CO_2 + 2NH_3 + H_2O \longrightarrow 2NH_4Cl + K_2CO_3$$

The alternatively possible conversion of $KHCO_3$ to $K_2CO_3$ with lime would introduce impurities, and hence be undesirable.

Improvements to the analogous process of conversion of sodium chloride with a mixture of $NH_3+CO_2$ (1:2) were suggested in a recent patent (80).

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(77) H.L. Tiger & P.C. Goets, Can.Pat. 396040 (22.4.1941)
(78) F.C. Godfrey & G.Miller, U.S.Pat. 2755169(17.7.1956)
(79) A.G. Follows, E.B. Hoyt & E.W. Smith, U.S.Pat. 2767051 (16.10.1956)
(80) S. Vajna, West German Pat. 1049839 (5.2.1959)

(a) The number of equivalents NaCl respectively $NH_4$ had to be equal to the total capacity of the resin;

(b) The temperature had to be increased to 80°;

(c) Countercurrent of resin and solutions had to be employed.

Several authors proposed to use $Mg(HCO_3)_2$ for conversion of NaCl into $NaHCO_3$. Five proposals to convert the sodium of sea-water into $NaHCO_3$ in this way were made in 1948-1951 (81-85). Sodium-resin was treated with a magnesium-bicarbonate solution, to yield $NaHCO_3$. The magnesium-resin was regenerated with calcium- and magnesium-free sea-water, or brine. It might be added that usually the $Mg(HCO_3)_2$ would be made from $Mg(OH)_2$ precipitated from sea-water by $Ca(OH)_2$, and that it would be bicarbonated with $CO_2$ obtained (along with the $Ca(OH)_2$) from lime-stone.

The conversion of sodium chloride into sodium bicarbonate with carbon dioxide was proposed in the following manner (86). Sodium-resin was converted to hydrogen-resin by treating with liquid carbon dioxide under a pressure of 50-60 atmospheres, in the presence of water. $NaHCO_3$ was formed. Although the patentee mentioned the possibility of direct regeneration of the hydrogen-resin with a sodium chloride solution, he considered it difficult to execute, and preferred a two-stage regeneration, first with a calcium hydroxide solution, and then with the sodium chloride. The use of a potassium-selective resin, based on poly-(pentanitro-diphenylamine), was claimed to enable $K_2CO_3$ to be obtained from a solution containing both sodium and potassium salts.

Some years later it was proposed (87) to execute the same conversion with a carboxylic type resin.

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(81) Sh. Nakahara, B. Kuwabara & Y. Fujita, Jap.Pat. 177239 (20.12.1948)
(82) M. Funaoka & Y. Fujita, Jap.Pat. 180564(10.10.1949)
(83) T. Yamamura & Y.Nomiyama, Jap.Pat. 181089 (7.12.1949)
(84) "Private Communication" in reference 88,undated & unnamed
(85) Sh. Akabori, Jap.Pat. 881 ('51) (23.1.1951)
Sh. Akabori, Repts.Res.Lab.Asahi Glass Co. 2 (1952) 148-72
(86) A. Skogseid, Norw.Pat. 74138 (25.10.1948)
(87) M. Sekino, Jap.Pat. 7717 ('51) (18.12.1951)
M. Sekino, A. Nishihara & Y. Sagane, Repts. Res.Lab. Asahi Glass Co. 2 (1952) 134-47

As the conversion of sodium-chloride (as sodium-resin) into its hydroxide with the aid of aqueous $Ca(OH)_2$ would yield a very diluted solution, several authors tried to circumvent the difficulty by substituting a different hydroxide for the regeneration.

The use of strontium hydroxide was proposed in 1950 (88). A $Sr(OH)_2$-solution was passed over sodium-resin (in a "main" cation-exchanger) to yield a 3.5% NaOH-solution. By heating, excess $Sr(OH)_2$ precipitated from this solution and was recycled. The regenerant was NaCl. A recycled Sr(OH)Cl-solution was saturated with solid NaCl, and then led over an "auxiliary" cation-exchanger from which any $Sr^{\cdot\cdot}$ present was thus recovered, after which regeneration of the "main" exchanger took place (Sr-resin $\longrightarrow$ Na-resin). Addition of solid $Sr(OH)_2.H_2O$ to the effluent was claimed to precipitate $Sr(OH)Cl.4\,H_2O$, and the solution was recycled for resaturation with NaCl (note 5). The wash-water after the regeneration of the "main" exchanger was freed of its $Sr^{\cdot\cdot}$ in the "auxiliary" exchanger; the remaining NaCl-solution was discarded. The $Sr(OH)Cl.4H_2O$ crystals were calcined in the presence of silica and steam, when HCl-vapour was obtained. The remaining SrO served to prepare anew $Sr(OH)_2$.

The overall reaction would thus consist of a hydrolysis of NaCl to NaOH and HCl.

Another proposal utilizing $Sr(OH)_2$ for the caustification of NaCl dates from 1956 (89). A sodium chloride solution reloaded the cation-exchanger. To obtain pure $SrCl_2$ from this effluent (for reconversion to $Sr(OH)_2$), it was passed over resin-hydroxide, when resin-chloride and a precipitate of $Sr(OH)_2$ were obtained. A hot-water wash regenerated the resin and dissolved the precipitate to yield a pure $SrCl_2$-solution.

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(88) H.Stern, Production of Sodium Hydroxide by Ion Exchange. Ph.D.Thesis, Iowa State College (1950)

<u>Note 5</u>:- A study of the complete text of (88) shows clearly that the author did not claim to have solved the problem of precipitation of basic strontium chloride completely and satisfactorily. The impression gained from the abstracts, both in Iowa State College J.Sci. <u>25</u> (1951) 358-60 and in Chem.Abstr. <u>45</u> (1951) 6896e, that this precipitation had proceeded as well as expected from the data of phase equilibria, is quite misleading.

(89) G.Miller & F.C.Godfrey, U.S.Pat. 2743165 (24.4.1956)

This was mixed with ammoniacal cupric hydroxide, $[Cu(NH_3)_2](OH)_2$ when $Sr(OH)_2$ precipitated. The $Cu(NH_3)_2Cl_2$ obtained was then treated with $Ca(OH)_2$ to give $Cu(OH)_2$ and free $NH_3$.

The possibility of replacing Sr by Ba was mentioned.

The overall reaction would thus be a caustification with $Ca(OH)_2$, although a considerable number of steps was involved.

Another way of circumventing the low solubility of $Ca(OH)_2$ was to replace it by $Ca(HS)_2$ (90). The sodium - hydrosulfide formed was caustified with a mixture of ferric and aluminium hydroxides. The calcium-resin was regenerated with sea-water, and the ferric sulfide by boiling with water after acidification.

Another possibility of circumventing the low $Ca(OH)_2$-solubility was the use of a $Ca(OH)_2$-slurry (91). The slurry was passed downward, while subsequent backwashing upwards removed the excess solid. Production of 0.226 N NaOH was claimed in this way.

As far as is known, no application of cation-exchangers to the process under consideration has been reported, and this, in spite of the advantages inherent in cation-exchange over anion-exchange. These advantages include : Cheaper, and more stable resins (chemically as well as thermally), and freedom from chloride in the alkali metal hydroxide solutions. This fact suggests that the answers offered to the problem of dilute solutions are not satisfactory from the technical or economic point of view.

### 1.2.4.3. Liquid Ion-Exchangers

The impossibility of caustifying KCl by Solvay's method has resulted in investigations attempting to shift the equilibrium

$$KCl + NH_3 + CO_2 + H_2O \rightleftharpoons KHCO_3 + NH_4Cl$$

with the aid of amines instead of ammonia.

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(90) Y. Okayama, Jap. Pat. 172643 (9.5.1946)
(91) W. Juda & K.S. Spiegler, Israeli Pat. 4942 (25.8.1949)

Amines of higher dissociation constant ($K_b$) than ammonia were found (91a) to attain the desired shift. Two patents have recently been based on this fact, both utilizing liquid amines. As the amine-salts formed require regeneration, the amines can be regarded as liquid ion-exchangers.

In a claim of 1954(92) a mixture of primary or secondary amines was proposed for the conversion of KCl into $KHCO_3$; a $CO_2$-pressure of 3 atmospheres was used. $KHCO_3$ 94% pure, containing 90% of the initial K, was said to be precipitated. Regeneration of the carbonate and hydrochloride salts of the amines was effected with calcium hydroxide followed by distillation, to recover the pure amines.

A higher purity of $KHCO_3$ (up to 99.7%) was claimed in a later patent (93). The proposed amines include mono-isopropyl amine, n-butyl amine, ethylene diamine and others. For the precipitation of $KHCO_3$, cooling to -20° was said to be required. Regeneration of the amine-salt was proposed with calcium hydroxide, or even sodium or potassium hydroxide (the last two, in a dilute solution probably).

The conversion of NaCl into $NaHCO_3$ with the aid of $CO_2$ and liquid ion-exchangers (amines) was suggested in 1956 (94). A temperature of 80° and a $CO_2$-pressure of 3 atmospheres were said to be required. No details of the amine-regeneration were given.

The separation of Na° from K° by fractional carbonation with the aid of liquid ion-exchangers was claimed in 1958 (95). From a KCl-NaCl mixture, 90% of the Na° were claimed to precipitate as $NaHCO_3$ practically free from K°, on the addition of isopropylamine-bicarbonate. Regeneration of the amine-chloride was proposed by calcium hydroxide.

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(91a) Aktien-Gesellschaft Croix, Dinglers Polyt. J. <u>234</u> (1880) 304-6; and various other publications by same

(92) A.Birman, Brit.Pat. 702279 (13.1.1954), French Pat. 1073302 (23.9.1954) and others

(93) A.G. Follows, U.S.Pat. 2768060 (23.10.1956)

(94) W.J. Burkholder, U.S.Pat. 2773739 (11.12.1956)

(95) J. Lafont, Brit.Pat. 791410 (5.3.1958), referring to Brit.Pats. 702279 (13.1.1954), 703526 (3.2.1954); U.S. Pat. 2900232 (18.8.1959)

The principle of executing metatheses with the aid of liquid ion-exchangers, including the examples

$$2KCl + Na_2CO_3 \longrightarrow K_2CO_3 + 2NaCl$$

and

$$KCl + NaOH \longrightarrow KOH + NaCl$$

was patented in 1957 (96).

Operation of a process making $KHCO_3$, based on the KCl of the Alsace, France, and on the use of liquid ion-exchangers, seems to be a fact (97). The product is said to be "fertilizer grade" potassium bicarbonate.

## 1.3. Concentration of Aqueous Solutions

The aqueous solutions obtained from installations of caustification and carbonation often require concentration, either because of the further uses contemplated, or because of economy of transport of the products. Some electrolysis installations, in particular those employing mercury cathodes and a separate amalgam decomposition chamber yield highly concentrated solutions and are an exception to this statement. Ion-exchange operations, on the other hand, are usually conducted profitably in diluted solutions (97a), and subsequent concentration is then required.

The classical method of concentration is evaporation of the water. This method suffers from high energy requirements, because as a rule only part of the latent heat of evaporation can be recovered. If contamination is of small consequence, direct contact of the flue gases with the solution (as in the Poriot evaporator) improves the heat transfer, and decreases the fuel requirements. This is seldom the case, and the then needed separation of heating medium and solution increases the overall resistance to heat transfer. Fuel economy can be improved in multiple-effect evaporators. The advantage is then partially offset by increased investment in apparatus, and an economic optimum usually limits the number of effects used.

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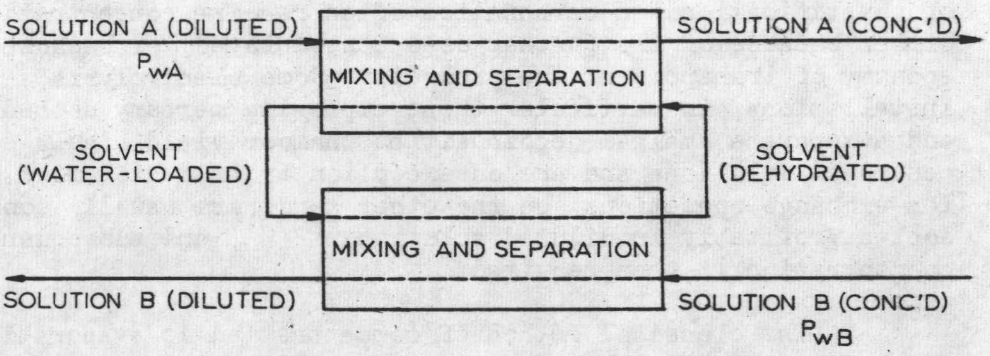
(96) G.L. Cunningham, Germ. Pat. 1012591 (25.7.1957)
(97) Private communication from Ir. Y. Araten, Haifa
(97a) E. Schmidt, Chem. Techn. (Berlin) 10 (1958) 527

For substances which are temperature-sensitive, evaporation under partial vacuum is usually employed. The energy needed is then as a rule even higher, for although less free heat is required, the latent heat of vaporization increases with decreased temperature. Also, operation of the vacuum pump adds to the energy requirements.

A new method for the concentration of aqueous solutions has recently been proposed (97b). It is based on the difference of partial water vapour pressures ($P_W$) of two aqueous solutions, the one to be concentrated (A) and an auxiliary one (B). The method is executed as follows (see fig. 1.1.).

FIGURE 1.1.

THE WATER-TRANSFER PROCESS (97b)



Solution A is mixed with a solvent partially miscible with it (for example, a $C_4$- or $C_5$- aliphatic alcohol). On separating the phases, the solvent is found to have taken up some water, the amount of which is determined by the solubility of water in that solvent in presence of the particular electrolyte.

The water-loaded solvent is then mixed with the aqueous solution B. B is chosen thus, that its partial water vapour pressure ($P_{wB}$) is smaller than that of A, $P_{wA}$. Therefore part of the water from the solvent is deposed in B, and the partially dehydrated solvent is ready for recycle to fresh A.

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(97b) A. Baniel, J. Appl. Chem. 8 (1958) 611-6; 9 (1959) 521-5

Through this process of "water transfer" A becomes more concentrated (and hence $P_{wA}$ decreases), while B is diluted (and $P_{wB}$ increases). As long as the difference $P_{wA}-P_{wB}$ represents a sufficiently high driving force, the process just described can be repeated. A KCl-solution, for example, can be completely dehydrated by using a saturated NaCl-solution as water-acceptor. Brine, when available, then represents a "water-sink".

This method has the following advantages over evaporation : It requires (for pumping) but a fraction of the energy used formerly for evaporation; and it can be executed at room temperature, being therefore eminently suitable for temperature-sensitive substances, or for substances causing corrosion (e.g., by decomposition) at elevated temperatures. The method is limited by the availability of a cheap "water-sink" : a solution subsequently rejectable or easily regenerable (e.g., by solar energy), and of initial sufficiently low $P_w$.

Also, economic operation requires recovery of the solvent from the water-acceptor (such as the aforementioned brine) prior to discard. Another limitation of this method is that it requires a considerable investment in both water-transfer solvent (such as the aforementioned alcohols) and in mixing-settling equipment, in which the transfer operation takes place.

The applicability of this method to the present process of $KHCO_3$-preparation from KCl (and $NaHCO_3$-preparation from NaCl) will be discussed in chapter 2.

# 2. DISCUSSION OF THE OPERATING METHODS AND THEIR APPLICABILITY

## PRELIMINARY DESCRIPTION OF THE PROCESS

### 2.1 Applicability of the Methods of Caustification and Carbonation.

The methods of caustification and carbonation reviewed in Chapter 1 show a preponderance of the use of calcium hydroxide as primary caustification agent, even in those cases where another agent is used in the first instance. Those methods involving the lesser number of stages will then be preferable, unless any longer method is proved to operate more economically. Several methods involving intermediate substances have, as far as is known, not been tested in this respect. They include those involving the intermediates $K_2O.5B_2O_3$; $K_2SiF_6$ and $KF$; $Na_2SiO_3$ ; $NaNH_4SO_3$; $KCaPO_4$; $NiCO_3$ and $Ni(NH_3)_6Cl_2$; $Na_2C_2O_4$.

It might prove interesting to retrace these methods and find the circumstances under which they might have technical and economic application. For the aim of the present thesis, they will not be considered further.

The ammonia-soda process ("Solvay") has been proved sound technically as well as economically. Its economic exploitation requires however a considerable minimal size of production, as well as a low total cost of the raw materials (salt, limestone), fuel and transportation to the markets. Per plant, the average of production in the U.S.A. is 1500 t/day, and that in Europe and India 250 t/day or about 80,000 t/year. As the Israeli domestic consumption is about 10,000 t/year, export would have to be assured, either of soda-ash or of its upgraded forms, such as glass and phosphate fertilizer. A comprehensive market analysis in potential customer-countries would be required. We might assume, that such a market would be found. Even then higher manufacturing costs than in the U.S. would be inevitable, as is illustrated by the following partial analysis. The final product, 58% $Na_2CO_3$ requires (on the basis of 1 ton 100% $Na_2CO_3$) fuel, 1.45 t (inclusive coke for the lime-kilns), at an average cost of 12.00 $/t; electricity, 106 kWh, at

0.005 \$/kWh. At a soda-ash price of 34 \$/t, these items therefore form about 53% of the f.o.b. value. As the domestic fuel price is about 60 IL/t (24 \$/t)[x] and that of electricity approximately 0.04 IL/kWh, these two items would already total at more than the current sales price of 34 \$/t(98-103).

In view of these facts, promises of the application of the "Solvay"-process in this country seem small at present. Moreover, in its "classical" form, the process is, as pointed out earlier, unapplicable to the carbonation of potassium chloride. A variant of the Solvay process which does permit the conversion of KCl to $KHCO_3$ will be discussed later in this thesis.

The caustification of the sulfates of potassium and sodium, not found locally as such, would require the expenditure of sulfuric acid, and hence probably not be attractive.

The use of $Sr(OH)_2$ and $Ba(OH)_2$ instead of $Ca(OH)_2$ being limited to carbonates, they will not be considered here. Moreover, as they are more expensive than the alkali hydroxides formed, regeneration would be required, and the economic feasibility of this operation is doubtful. The Engel-Precht process, using $MgCO_3$ as carbonating agent, depends both on an economic conversion of the $MgCl_2$ to a suitable grade of $MgCO_3$ (as the trihydrate), as well as on solution of the problems of the precipitation and subsequent isolation of the potassium

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[x] IL = Israel Pounds

(98) Z.G.Deutsch, in R.E.Kirk and D.F.Othmer, Encyclopedia of Chemical Technology, (New York 1947), vol.I, p.385-408

(99) R.S.Aries and R.D.Newton, Chemical Engineering Cost-Estimation, (New York 1955), p.169, 172

(100) Chem.Eng.News, Quarterly Report on Current Prices, 27.6.60

(101) W.L.Faith, D.B.Keyes and R.L.Clark, Industrial Chemicals (New York 1950) p.659

(102) Z.G.Deutsch, Outline of the Technical and Economic Factors which have to do with the Building of a Soda-Ash Factory in Israel. Memorandum to Dr.Dov Joseph, Minister of Development. Jerusalem, September 1, 1955.

(103) Private communication from Prof. O. Schaechter, Haifa

compound. The scope of these problems is underlined if it is recalled that in spite of a vast amount of research, this process has not, as far as is known, outgrown the stage of the pilot plant (note 6).

The economic feasibility of the other processes utilizing $MgCO_3$ (in conjunction with $CO_2$) as carbonation agent is also dependent on the conversion of the $MgCl_2$ obtained to $MgCO_3$. This does not apply to the proposal to utilise $Na_2CO_3$ along with $MgCO_3.3H_2O$(35) but then this method would require local preparation or else importation of $Na_2CO_3$ to make $K_2CO_3$.

The process employing $ZnO + CO_2$ resembles the Engel-Precht process. Further research is required to establish its suitability for this country, as an economic way of carbonation of potassium chloride.

The variants of the process to caustify with plumbous hydroxide require regeneration of the (basic) lead chloride. The regeneration involving the neutralisation of ammonia with nitric acid would probably be unprofitable, unless the $NH_4NO_3$ in the purity and amount obtained were disposable. The other regeneration, with $Ca(OH)_2$, poses the problem of numerous intermediate steps, where the final agent might obtain the same caustification effect.

At the current relative prices of potassium carbonate and sodium carbonate (where the former is about 8 times as expensive as the latter, on an equivalent basis), the conversion of NaCl to $Na_2CO_3$ with $K_2CO_3$ would not be considered now.

The combined use of $NH_3$ and $CO_2$ requires a special combination of fertilizer needs, and is certainly not of general application. The suggestion involving water-gas is not applicable to this country, because of the high cost of coal. The proposals to convert chlorides into hydroxides with the aid of steam would probably be too expensive from the point of view of energy-consumption.

As regards the use of ion-exchangers for caustification and carbonation, the following remarks may be made.

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Note 6: The Engel-Precht process is reported to have been operated on a technical scale in one location, during a limited period(34)

Solid anion exchangers convert, as explained above, potassium (or sodium) chloride to the hydroxide in the following manner:

$$R\text{-}OH + KCl \longrightarrow R\text{-}Cl + KOH$$

$$R\text{-}Cl + \tfrac{1}{2}Ca(OH)_2 \longrightarrow R\text{-}OH + \tfrac{1}{2}CaCl_2$$

The concentration of the KOH-solution obtained could therefore be considerable, due to the relatively high solubility of the KCl.

The use of anion-exchangers entails, however, two problems: that of chloride in the product and that of the considerable amount of water required in view of the low solubility of calcium hydroxide.

The first problem might be solved partially by a considerable internal recycle (as in (59)). This method, however, considerably lowers the production per unit volume of apparatus, and increases the pumping requirements. Another solution would be the precipitation od sodium bicarbonate or sesquicarbonate. While this method requires operation in saturated solutions, which entails higher viscosities and thus increased pressure drops over the columns, and $CO_2$ pressures over the atmospheric, i.e. more complicated apparatus, its applicability to potassium compounds, noted for their higher solubilities, is open to doubt.

The second problem, that of the low solubility of $Ca(OH)_2$, is of course common to both cation - and anion exchanges utilising this caustification agent. The problem may be overcome by using a slurry of $Ca(OH)_2$, although the handling of a slurry requires additional precautions against clogging of tubes or resin. Another proposal to solve this problem is perhaps the premixing of resin with solid calcium-hydroxide (74), although the numerical results given there do not justify the claim for "improvement over prior art" (note 4). A third way is to replace the calcium hydroxide entirely by a more soluble hydroxide, such as that of ammonia or sodium. For economic operation this way probably requires the presence of diluteor impure solutions of these hydroxides, say as a by-product of some other operation; this method will therefore not be considered further here (note 7).

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Note 7: An economic recovery might make the application of this method possible (Prof.O. Schächter, Haifa).

The use of liquid ion-exchangers (such as the above mentioned amines, which exchanges anions), enabling the conversion of KCl to $KHCO_3$, also results in the presence of chlorides in the final product. For some purposes, such as fertilizers, this might be tolerated. Their use is certainly not of general applicability, although the solubility of $Ca(OH)_2$ does not play any role, as it can be added as a solid, or concentrated slurry, prior to distillation of the free amines.

Thus, the use of anion-exchangers seems justified under two conditions. One, that the presence of chloride in the product can be tolerated. Two, that the costs of concentration of solutions are such, that the use of cation-exchangers is uneconomical. It is recalled here that cation-exchangers convert potassium (or sodium) chloride to the hydroxide in the following way:

$$Ca_{\frac{1}{2}}\text{-}R + KCl \longrightarrow K\text{-}R + \tfrac{1}{2}CaCl_2$$

$$K\text{-}R + \tfrac{1}{2}Ca(OH)_2 \longrightarrow Ca_{\frac{1}{2}}\text{-}R + KOH$$

KOH is thus obtained in the regeneration step, and in a concentration dependent on that of the $Ca(OH)_2$. Now, several suggestions for overcoming the low solubility of $Ca(OH)_2$ have been made. The use of $Ca(OH)_2$ - slurry and the drawbacks imposed thereby were noted above. Another method is to increase the solubility of $Ca(OH)_2$ by converting it to $Ca(HS)_2$ (at a $H_2S$ - partial vapour pressure of 100 mm mercury only, the solubility of $Ca(HS)_2$ at 20° is about 250 g/l (104)). This method then requires the NaHS to be caustificated with ferric or aluminium hydroxide, and thus complicates the process considerably.

The use of $Mg(HCO_3)_2$ for carbonation was proposed in several patents. It adds to the operations of the process:

(a) the isolation of $Mg(OH)_2$, mostly through precipitation by $Ca(OH)_2$ from some brine or sea-water;

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(104) A. Seidell, Solubilities of Inorganic and Metal-Organic Compounds (New York, 1940) Volume I p. 326

(b) the carbonation to magnesium bicarbonate. The solubility of $Mg(HCO_3)_2$ is about 0.4 N, unless a high $CO_2$-pressure is used (105). Whether the complications would be economically justified by the greater concentration of the carbonates produced, is questionable.

The direct use of carbonic acid (86) circumvents the low solubility of $Ca(OH)_2$, or might even eliminate the use of that chemical altogether, if the regeneration of hydrogen-resin to sodium-resin with a NaCl-solution were possible in one step. Otherwise, due to the split regeneration with $Ca(OH)_2$ and NaCl, respectively, one extra operation is introduced. Moreover, the method suffers from the low solubility of $CO_2$, unless the considerable pressure of 50-60 atmospheres (recommended by reference 86) is applied. Hence, equipment to withstand that pressure is needed. The attractiveness of that method might lie in the possibility of extracting potassium from its mixture with sodium, using a potassium-selective resin. The stability of the resin, and its initial cost, would then have to be ascertained. The consideration of selectivity does not apply to the circumstances of the present work, where pure KCl is available.

The method proposed in (88) is based on the use of $Sr(OH)_2$ instead of $Ca(OH)_2$, and on the final regeneration by thermal decomposition of Sr(OH)Cl. As has been remarked, the feasibility of the precipitation of basic strontium chloride is open to question, as (as reported) the author experienced difficulties with this operation.

The other proposal to utilise $Sr(OH)_2$, which would then be regenerated in a number of steps using ultimately $Ca(OH)_2$, complicates the process considerably. The same holds for the carbonation with $(NH_4)_2CO_3$. There, the process requires the liberation and complete recovery of ammonia, as an additional step.

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(105) A. Seidell, Solubilities of Inorganic and Metal-Organic Compounds (New-York, 1940) Volume I p.326.

A process with a chance of technical and economic success in this country will have to possess the following characteristics. It will have to use preferably local raw materials; its energy requirements, and its need for fresh water, will have to be low. Decrease of the scale, due to the relatively small domestic market, must not increase the costs per unit to any great extent.

The review of the methods of caustification and carbonation then points out, that ion-exchange and the use of $Ca(OH)_2$ as regenerant answer these demands. The use of anion-exchange promises a more concentrated KOH-solution, although contamination with KCl will very probably occur. Experimentation is required to ascertain these points. The use of cation-exchange prevents this contamination. The problem of the dilute KOH-solution might be overcome by increasing the solubility of $Ca(OH)_2$ through the addition of chemicals. Here as well, experimentation is required.

The experimental part of the present thesis (chapter 3) is therefore concerned with both anion- and cation-exchangers.

## 2.2. The Dehydration of the $KHCO_3$-Solution.

The principles of the conventional concentration methods for aqueous solutions, as well as the nature of the water-transfer method and its advantages and limitations, were discussed in par. 1.3.

As far as is known at present, this country (Israel) does not possess large reserves of natural energy sources, such as oil or gas. The process under consideration should thus have low thermal energy requirements. This consideration points to the use of "water transfer". Moreover, if Sdom (Sodom), the seat of the potassium chloride plant, is envisaged for the present process as well, NaCl, which is a by-product from the KCl-manufacture, is available in considerable amounts. Its diluted solution, obtained in course of the water-transfer process, is rejectable (after solvent recovery).

Not all the streams of chemicals in the process requiring complete or partial dehydration can be treated by the water-transfer method exclusively, due to the limit imposed by the $P_w$ of a saturated NaCl-solution. The use of thermal energy (for evaporation) has therefore been introduced as well, but on a scale as limited as possible. The product $KHCO_3$ is completely dehydratable by water transfer with a saturated NaCl-solution.

## 2.3. Preliminary Description of the Process.

From the considerations in the two preceding paragraphs, a relatively simple flowsheet emerges, as follows: Solid KCl - obtainable as such - is dissolved in water. The solution is passed through an ion-exchanger. The resin is then washed with water and subsequently treated with a solution of $Ca(OH)_2$. In the case of anion-exchangers, the first step yields a solution of KOH containing KCl, and the second step, a solution of $CaCl_2$ containing $Ca(OH)_2$. The first solution is then processed further, and the latter is discarded. In the case of cation-exchangers, the situation is reversed, inasmuch as the first step yields a $CaCl_2$- solution containing KCl (which solution is, after KCl-recovery, discarded), while the second step yields a KOH-solution containing $Ca(OH)_2$, used for further processing. If an extra material is added to the $Ca(OH)_2$ - solution to increase its solubility, this addition is then found in the process-solution.

Let us assume at the present stage that in both cases the process-solution contains nearly pure KOH, and that the impurities (KCl respectively $Ca(OH)_2$ + eventual addition) are of little consequence, requiring no additional steps for either their removal or recovery.

It might now seem to be interesting, economically, to produce KOH by the present method, as this chemical would form a raw material not only for the production of $KHCO_3$ and $K_2CO_3$, but for numerous other potassium compounds as well. The use of ion-exchangers results, however, in diluted KOH-solution only. For anion-exchange utilizing the the reaction $R\text{-}OH + KCl \longrightarrow R\text{-}Cl + KOH$ theoretically solutions 2 to 3 normal (about 100-150 g/l) are obtainable;

for cation-exchange, where the reaction is

$$K\text{-}R + \tfrac{1}{2}Ca(OH)_2 \longrightarrow Ca_{\frac{1}{2}}\text{-}R + KOH$$

this concentration would be 1 normal (50 g/l) or less, depending on the nature of the addition used (or dispensed with). In both cases, a considerable amount of water would have to be removed. As stated in the discussion in paragraph 2.2., water-transfer would be a suitable method of water removal. It can then be shown, that the limit imposed by that water removal method, namely, the presence of a sufficiently high difference in the partial water vapour pressures between the solution to be dehydrated, and that of the dehydrant, limits the concentration of the KOH-solutions (even when NaCl, which is superior to KCl, is used as dehydrant ) to about 100 g/l. As the KOH is produced as a chemical intermediary, further concentration prior to transportation would be mandatory. This would then require thermal evaporation. The drawback of this method, a considerable dependence on expensive, imported fuel, might partially or wholly offset any other advantage of the process. The limitation imposed by the in itself desirable use of water-transfer requires then, that the KOH be transformed into $KHCO_3$, for which substance complete dehydration in this way is possible, as will be shown below.

A similar argument holds for the dehydration of NaOH and $NaHCO_3$ made in the described manner from NaCl as raw material. Here as well, water-transfer requires that carbonation precede dehydration.

Thus, both when using anion- as well as when using cation-exchange, the ion-exchange is followed by carbonation with $CO_2$. The resulting $KHCO_3$-solution (respectively, $NaHCO_3$-solution) is dehydrated with the aid of normal butyl-alcohol, for example, which in its turn is dried with a saturated NaCl-solution.

It might seem logical to execute the dehydration of $KHCO_3$ with KCl (as ultimate dehydrant), and that of $NaHCO_3$ with NaCl. The dehydrant solution would then serve as influent for the first ion-exchange step, thereby limiting the water requirements of the process. This arrangement is, however, not possible. It will be discussed in the set-up of the complete flowsheet. At this stage it suffices to state that the volume of wash water following the loading step is such, that the dissolution of KCl (respectively NaCl) in it yields all the ion-exchange influent required. No KCl (respectively, NaCl as raw material) is available for the purpose of water transfer.

The final step of this simple flowsheet is then the washing of the solid $KHCO_3$ (respectively $NaHCO_3$), and the drying in a furnace at a low temperature. This last operation is eventually combined with low-temperature calcination to the carbonates.

At this stage, one extra operation over those, strictly required for the production, suggests itself. The NaCl-solution from the water transfer is saturated with the water-transfer agent, such as the normal butyl-alcohol mentioned. Economic operation requires that this agent be recovered. Recovery is in principle possible by several ways, one of which would be the separation by distillation, or by extraction followed by distillation from the extractant.

The experiments described in the next chapters will cause unavoidable additions to this simple flowsheet. Comparison with the complete flowsheet discloses this.

# 3. ION EXCHANGE EXPERIMENTS.

## 3.1. Introduction.

As stated earlier review of the literature showed that the feasibility of anion-exchangers was considered much higher than that of cation-exchangers for the caustification of alkali-metal chlorides.

It was therefore decided to start with anion exchanging resins, mainly, in view of the higher concentration of alkali metal hydroxides theoretically expectable. The main disadvantage of these resins, namely the presence of chloride in the hydroxide, was evident from the beginning. Hopes were cherished that this could be limited to industrially acceptable proportions by proper choice of the conditions, such as flow-rates, the ratio of column height to diameter, and others, or else by subsequent treatment.

## 3.2. Anion Exchange.

### 3.2.1. Choice of the Resin.

There are commercially available two kinds of anion-exchanging resins, both based on the polystyrene-divinylbenzene skeleton, the weakly basic and the strongly basic exchangers. The former possess amine groups attached to the skeleton. Their activity is dependent on the pH of the solution; in alkaline media the equilibrium

$$R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH_3^{\cdot} + OH'$$

is shifted towards the left, with a resulting decrease in exchange capacity. As the process under consideration entails operation on the alkaline side of the pH scale, the weakly basic exchangers show little promise of application.

The strongly basic exchangers have a quarternary ammonium group, as a result of the increased dissociation of which, their activity is not impaired even at high pH-values. These resins were therefore chosen for the present aim. They are mainly of two types, depending on the nature of the groups attached to the nitrogen. "Type 1" has 4 alkyl groups, usually methyl, one of which serves for attachment to a benzene ring of the skeleton (this group is therefore rather a methylene group). In "type 2" one alkyl group is replaced by a hydroxyl-alkyl group, such as $CH_2CH_2OH$, attached to the nitrogen atom. The choice between the two types was made on the basis of their equilibrium exchange constants for the particular reaction considered.

This equilibrium constant k is defined as follows: For an ion-exchange reaction of the general type $R\text{-}A + B \rightleftharpoons R\text{-}B + A$ (where R is the resin skeleton, and A and B the exchangeable ions), k is defined according to

$$k = (A)_S(B)_R/(B)_S(A)_R,$$

where the subscripts S and R refer to the solution and the resin-phase, respectively, and the brackets denote activities. As a rule, the activity-coefficients, especially in the resin-phase, are unknown, and concentrations are used instead. The value of k after this replacement is then still constant "within engineering accuracy" (108), that is, within some percent. For the particular reaction under consideration, we have

$$k = (OH')_R(Cl')_S/(OH')_S(Cl')_R.$$

For type 1, $k = 0.09 \left[\text{at } (Cl')_S = 0.77\right]$.

For type 2, $k = 0.65 \left[\text{at } (Cl')_S = 0.56\right]$(109).

Assume that $(Cl')_S/(OH')_S = a$, a constant value.

Then for type 1, $k = a\,(OH')_R/(Cl')_R = 0.09$,

and for type 2, k = 0.65. It follows then, that a type-2 resin will be more selective towards hydroxide ions (in the presence of chloride ions) than a type-1 resin. As the process under consideration requires that the reaction represented by both arrows of $R\text{-}Cl + OH' \rightleftharpoons R\text{-}OH + Cl'$ be

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(108) G.E. Boyd, J.Schubert & A.W. Adamson, J.Am.Chem.Soc. 69 (1947) 2818-29; N.K. Hiester & R.C. Phillips, Chem. Engng 61 (1954) No. 10, 162

(109) S. Peterson, Ann.N.Y. Acad. Sci. 57 (1953) 144-58.

executable with similar ease, the exchange should possess as little selectivity of one ion over the other as possible. Thus, a resin with an equilibrium constant near to 1.0 should be preferred over one with a constant further removed (lower or higher). Limited by commercial availability, a resin of type 2 ($k = 0.65$) was therefore preferred here.

There is little fundamental difference between resins of different producers claimed to possess the same reactive group (110) (this reference, for example, gives "equivalence tables"). Due to its availability on short notice, a resin of the Dow Chemical Company, Midland, Michigan, U.S.A., to wit "Dowex 2", was taken for the experiments.

Among resins of the same type, differences in the so-called "degree of cross-linking" have been introduced. This "degree" is represented by the percentage of divinyl-benzene in the original mixture. This percentage is a measure of the degree of cross-linking between the monodimensional chains of polystyrene, interlocked subsequently into a three-dimensional skeleton with the aid of the divinylbenzene. Commercially, degrees of cross-linking from 2 to 16%, increasing in 2% at a time, are available. The higher this degree, the smaller the solubility of the resin and its swelling in water, and the lower the diffusion of ions into it. As "8% cross-linking" is an average, usual value, which has been used in industrial applications, a resin of this "degree" was therefore chosen for the experiments.

To summarize : The experiments on anion-exchange were executed with Dowex-2, 8% cross-linking.

### 3.2.2. The Mode of Operation.

There are two modes of operation with ion exchangers, both of which have found industrial application. The simplest is the batch method. A certain quantity of resin and solution are mixed for some time, and then separated. This method is

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(110) J.Calmon, in J.Calmon and T.R.E.Kressman, Ion Exchangers in Organic and Biochemistry (New York, 1957), p. 126-7

useful for the determination of equilibirium data. In the second method, resin is confined in a column, through which solutions are percolated. This permits, at well-chosen contact times, to obtain higher conversion than in the first case due to the constantly fresh solution contacting the resin. It is the method usually employed in the laboratory and on an industrial scale, except in those cases where the solution would clog the resin because of suspended solids. In such a case, the first method is used, but the resin is then contacted successively with fresh batches of solution, to increase the conversion ("resin in pulp method"), by which the column method is approached. Both methods were used in the present work, the first for equilibrium measurements and for contacting resin with slurries of $Ca(OH)_2$, the second (more frequently) for all other experiments.

### 3.2.3. Preparation of the Resin for the Experiments.

Preparation of the resin for the experiments includes two operations, the so-called swelling and conditioning. The first saturates the commercial product with water. This is carried out not in the ultimate column in which it is intended to execute the ion-exchange, as the pressure formed by this swelling would shatter this column. Soaking, during about one hour, took place in a beaker, after which the resin was transferred to the water-filled column. The "conditioning" - operation includes cycling the resin between two states. For anion-exchangers, these are the chloride and hydroxide state. This treatment removes foreign bodies, such as traces of metals and unpolymerized materials left over from the resin production (111). The cycling was carried out with approximately $\frac{1}{2}$ N HCl- and KOH- solutions. An approximate tenfold excess (in terms of meq) was taken of each chemical. Between these conversions of the exchanger, it was washed with distilled water until the effluent was free of chloride or hydroxide.

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(111) J. Calmon and T.R.E.Kressman, Ion Exchangers in Organic and Biochemistry (New York, 1957) p. 112

### 3.2.4. Capacity of the Resin.

The capacity of the resin was given by the producer as 1.9 meq/g of the "commercial product" (112). The exact water-contents of the resin (determined, say, according to some standard procedure) corresponding to the given capacity, were not given. Since the moisture might vary as the result of conditions of storage, a new determination was required. The method of Fisher and Kunin (113) for determination of the total capacity was followed. Of the resin in the chloride form, a part was dried at 110° to determine the water-contents (see, however, paragraph 3.2.5.), while another part was treated with a considerable excess of sodium sulphate, and chloride determined volumetrically in the effluent (see fig. 3.1.). Exactly 10.000 g of the commercial resin as received (i.e., in the chloride form) (referred to further on as "A") were treated with 1 liter of 1 molar hydrochloric acid, to complete the conversion, and then washed until neutral to methyl orange with ethyl alcohol; this, to prevent hydrolysis. Of this resin ("B"), 5.5754 g were dried at 110° until constant weight. The weight decreased by 1.5410 g. Hence, "B" contained (1 - 1.5410/5.5754) 100% = 72.35% of oven-dry material ("C"). The remaining 2.6815 g of "B" were treated with 1 liter 4% $Na_2SO_4$. 100.00 ml effluent required 6.83 ml 0.1044 N $AgNO_3$. Hence, the resin contained 6.83 x 0.1044 x (1000/100) / (2.6815 x 0.7235)= 3.68 meq/g of oven-dry resin. From 10.000 g "A", 5.5754 + 2.6815 = = 8.2569 g "B" were obtained, which equals 8.2569 x 0.7235 = = 5.9739 g oven-dry material; the capacity of the resin was

3.68 x 5.9739 / 10.000 = 2.2 meq/g

of the commercial product. This is about 15% higher than the value given by the producer.

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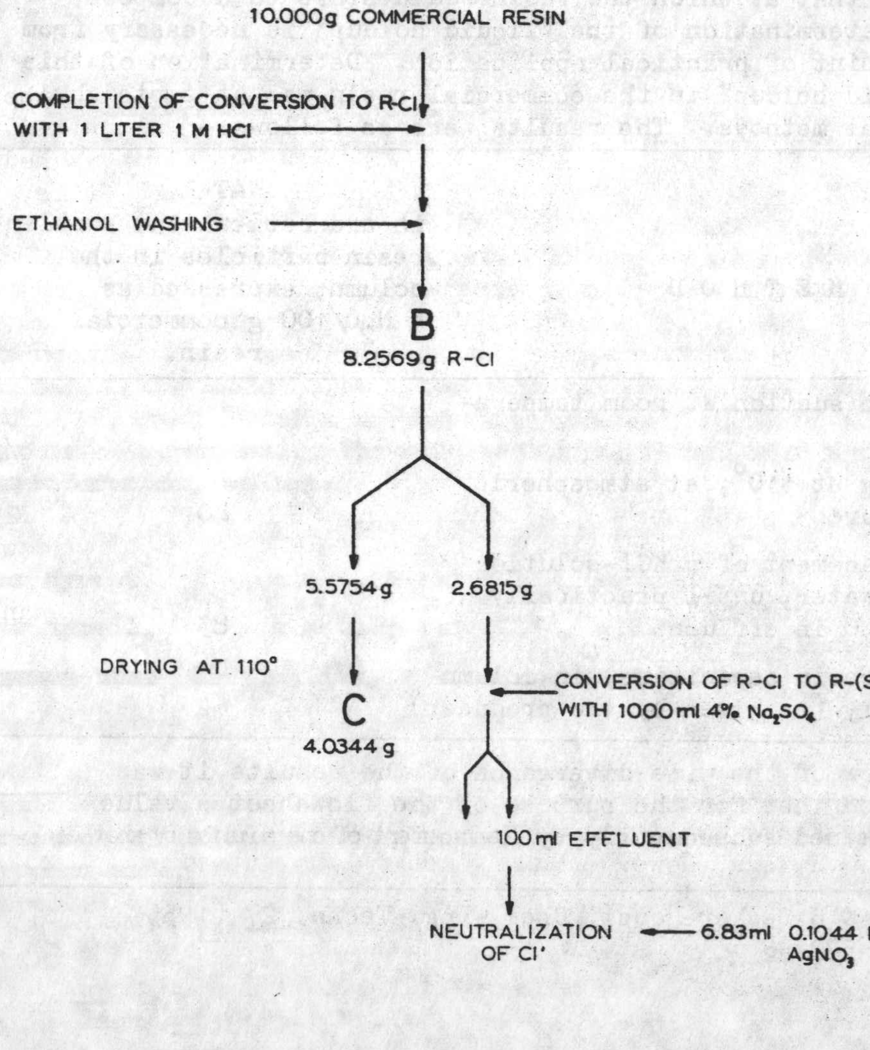
(112) Fluka Société Anonyme - Produits Chimiques, Buchs, Suisse: Dowex - Echangeurs d'Ions, p. 11 (undated).

(113) S. Fischer and R. Kunin, Anal. Chem. 27 (1955) 1191-4.

FIGURE 3.1.
DETERMINATION OF THE RESIN CAPACITY (113)



### 3.2.5. Water Contents of the Resin.

The water contents of the resin determine partly the holdup of the column, i.e. that part of the solution immobilized in and around the resin particles. The limits of these water-contents are not definable exactly. There exists a gradual transition between external (i.e., interstitial) water and that in the pores of the resin, and between that in the pores and the water of hydration of the ions, both of those attached to the skeleton as well as of those which are exchangeable. Although this state prevents an exact determination of "water contents" (114), because the last traces of $H_2O$ would leave the resin at a temperature above that at which the resin would start to decompose, the determination of the "liquid holdup" is necessary from the point of practical application. Determination of this "liquid holdup" in the commercial resin was attempted by several methods. The results were as follows:-

| METHOD | WATER in and between the swollen resin particles in the column, expressed as g $H_2O$/100 g commercial resin. |
|---|---|
| Vacuum suction at room temperature | 50 |
| Drying at 110°, at atmospheric pressure | 40 |
| Displacement of a KCl-solution with water, until practically Cl' = 0 in effluent | 83 |
| From resin capacities, in column and dry (as given by the producer) | 62 |

In view of the wide divergence of the results it was decided that for the purpose of the flowsheet a value determined subsequently by displacement of one solution by another

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(114) E.H.Becker-Boost, Chem.-Ing.-Techn. 27 (1955) 579-96

would be used. This value represents that "practical holdup" with which the flowsheet is concerned.

### 3.2.6. Preliminary Experiments with a Short Column (13 cm)

Preliminary experiments were executed in a short glass column of 27 mm inner diameter. The resin (50 g of the commercial product) rested on a sintered glass disc, below which a stopcock regulated the flow rates. The height of the resin column was 13 cm only (note 8). Loading and regeneration were carried out in downflow.

With this column, the resin was loaded with KCl solutions of different concentration (from 0.6 to 3 molar, approximately) at a constant feed rate (in terms of meq/min) and with a KCl solution of constant concentration (1.3 M), at varying feed rates (from 1 to 14 ml/min). With a second, equal, resin column, regeneration with $Ca(OH)_2$ was effected. A saturated $Ca(OH)_2$ solution was used, at varying feed rates (from 10 to 83 ml/min). In an effort to decrease the amount of water required, a slurry of $Ca(OH)_2$ (about 100 g/l) was passed through the resin, as well as a clear mixture of $CaCl_2$ and $Ca(OH)_2$ in ratio's of up to 1:1.

Analysis of the outcome of these experiments indicated that the small column height very probably influenced the results. Formation of channels in the resin could account for the irregularities observed. Moreover, the feed rates were much lower than those practised industrially. At a cross-section area of about 5.7 $cm^2$, the highest feed rate, 83 ml/min would yield a linear velocity (calculated on the empty column) of about $14\frac{1}{2}$ cm/min. Industrial practice utilises values up to ten times as high. The low feed rates might also have contributed to irregularities of the results, due to the resultant lower transversal movement in the interstitial liquid, and the possibility of lesser chances of contact.

All these considerations invalidate considerably the results of these preliminary experiments. They would not have

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Note 8: This height results in a bulk density of
$50 \,/\, (\pi \times 2.7^2 \times 13)\frac{1}{4} = 0.67$ g/ml.

been mentioned here at all, were it not for three important results, of which at least the first two could not have been influenced adversely by eventual channeling and reduced transversal mixing :-

1) That regeneration with an amount of $Ca(OH)_2$ equimolar with the amount of KOH produced in the loading step, removes a number of meq Cl' from the resin at least equal to that, loaded on the resin during the first step. The importance of this will be detailed below, when considering a cyclic balance.

2) That although regeneration with a lime-slurry is perhaps possible, clogging of the resin would require another mode of operation than the downflow practised. Possibilities are either "resin-in-pulp", or upflow of the slurry through a fluidized resin bed. Both methods require considerable complication of equipment over simple percolation of clear solution.

3) That mixtures of $CaCl_2$ and $Ca(OH)_2$, even in the equivalents' ratio of 1:1.9, do not remove the required number of meq Cl' from the resin. Apparently the driving force for the regeneration, which is represented by the difference in the concentration of (Cl') between the regenerant solution and the resin, is lowered too much by the $CaCl_2$ present, even in the low concentration taken. Any decrease in the water requirements when using a clear $Ca(OH)_2$ solution (as in contradistinction to slurries) would have to be found by other methods, such as the increase of the solubility of $Ca(OH)_2$ by the addition of chemicals.

### 3.2.7. Experiments with a Column 80 cm High.

#### 3.2.7.1. Introduction.

A glass column of 1.20 m height and 27 mm inner diameter was filled with 275 g Dowex-2 anion-exchanger. The resin occupied 80 cm of the height, this varying some 10% with the state of the resin (chloride or hydroxide) and the position in the cycle with relation to backwash and downflow (Note 9). The resin rested on 2 cm of glass wool, supported by a perforated glass disc.

The required flow rates were obtained with the aid of a hydrostatic head of 2-2½ m for the process solutions; the rates were regulated by clamps on the tubing, and measured with the aid of measuring cylinderes and a stop-watch. The feed-rates were expressed as volumetric throughput, ml/min, divided by the cross-section of the empty column, $cm^2$. The obtained $ml/min/cm^2$ equalled cm/min, an average linear velocity in the empty column. Experiments with coloured solutions percolating through the column indicated that roughly 62% of the column cross-section were occupied by the resin. The true average linear velocities were therefore approximately three times as high as the feed-rates, as defined above.

Process solutions were prepared by dissolving KCl ("analytical reagent" quality, further on denoted "A.R.") in distilled water. Cl' was determined according to the method of Mohr (115) after assuring a pH of 6-7 required for this determination. The pH-adjustment was obtained by adding to the sample one drop of methyl-red indicator, a small excess of nitric acid and (chemically pure) calcium carbonate until gas-evolution had stopped. The calcium hydroxide solution was prepared by mixing distilled water with an excess of $Ca(OH)_2$ A.R. Saturation (or nearly so) was arrived at only after protracted mixing, which was effected mechanically in a rubber-lined vessel of 25 l capacity for at least one hour. After settling, the clear solution was siphoned off and filtered through sintered glass. Air was admitted through tubes with soda-asbest, to prevent entry of carbon dioxide. Determination of the OH'-contents was carried out volumetrically with standardized hydrochloric acid, with methyl-red as indicator. At a later

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Note 9: The resulting bulk density is 0.60 ± 0.06 g/ml.

(115) A.I.Vogel, A Textbook of Quantitative Analysis (London, 1955) p.250

stage, the determinations of OH' and Cl' were combined by replacing the HCl by standarized 1/10 N sulphuric acid, and determining in the same - now neutral - sample Cl', as set out above.

### 3.2.7.2. Preliminary Loading Experiments.

The loading experiments were executed in a column regenerated with KOH until no Cl' was discernible in the effluent, after which the column was washed with water until free of OH'. With a solution of 100.8 g KCl/l, the influence of the feed rate was tested at two different values. Effluent solutions were divided into fractions and analysed. Results were as follows (Table 3.1., fig. 3.2.):-

Table 3.1.

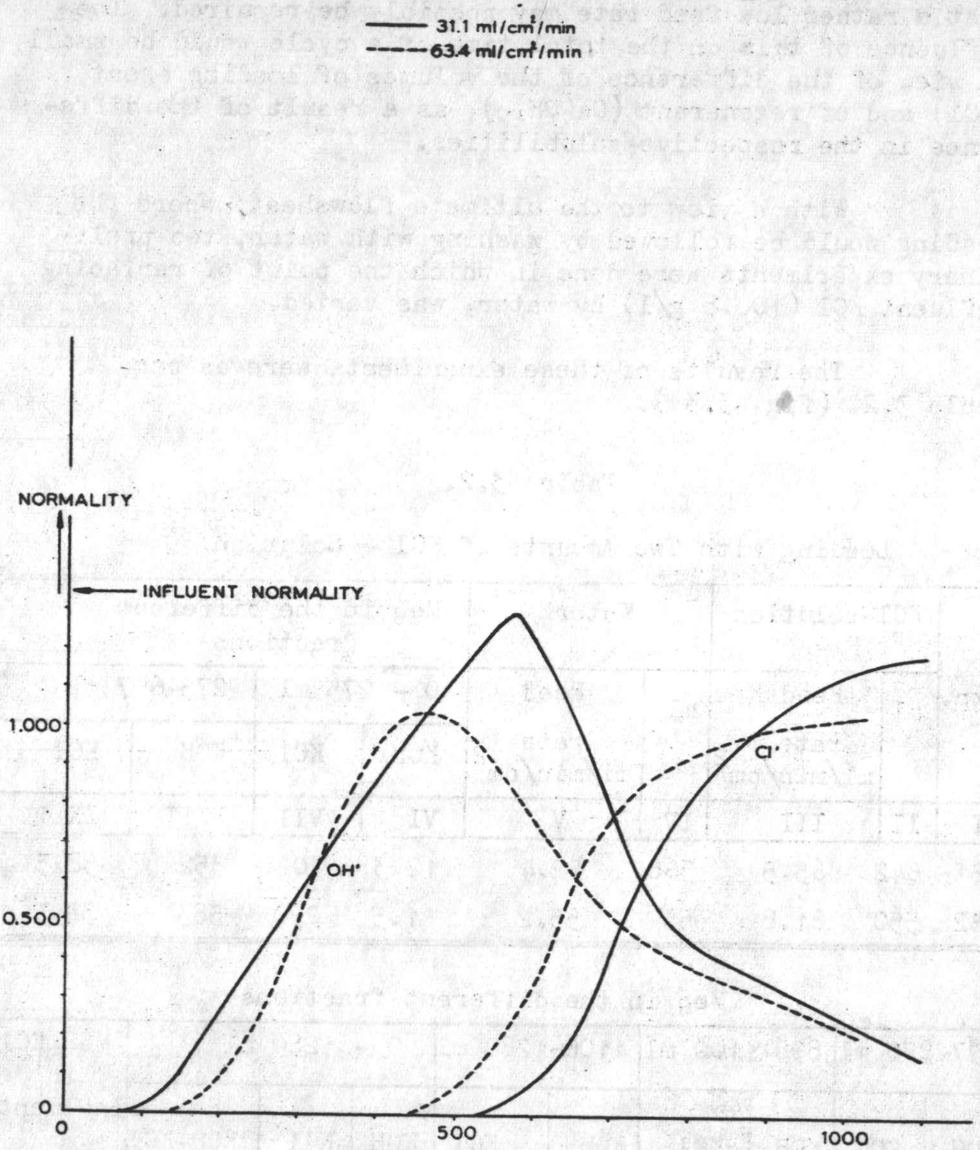
Loading at Two Feed - Rates.

| Exp. No. | Feed rate ml/min/cm$^2$ | Meq in the different fractions | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 - 200 ml | | 200-475 ml | | 475-700 ml | | 700-950 ml | | 0 - 950 ml | | |
| | | KOH | KCl | KOH | KCl | KOH | KCl | KOH | KCl | KOH | KCl | KOH+KCl |
| I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII | XIII |
| 2A2 | 31.1 | 10.8 | 0 | 183 | 0.3 | 243 | 24.2 | 107 | 208 | 544 | 233 | 777 |
| 2A5 | 63.4 | 4.3 | 0 | 210 | 1.5 | 187 | 76.5 | 93 | 221 | 494 | 299 | 793 |

The difference between the two totals of meq obtained from the column amounts to some 2%. The results show the following tendencies:- At the higher feed rate, the production of KOH is smaller than at the lower; 2A2 yielded (column XI) 544 meq, and 2A5 only 494 meq. The more diluted KOH-solution is, as a result, contaminated to a greater degree by KCl.

The second tendency noted is for the KCl contents to start rising earlier. In column VIII 2A2 yielded 24.2 meq KCl, while 2A5 yielded 76.5 meq.

FIGURE 3.2.
LOADING AT TWO FEED RATES



Contamination of the KOH-solution by KCl should be as low as possible. The tendencies noted above then indicate that a rather low feed rate may possibly be required. The influence of this on the total time of a cycle would be small, in view of the difference of the volumes of loading agent (KCl) and of regenerant ($Ca(OH)_2$), as a result of the difference in the respective solubilities.

With a view to the ultimate flowsheet, where the loading would be followed by washing with water, two preliminary experiments were done in which the point of replacing influent KCl (100.8 g/l) by water, was varied.

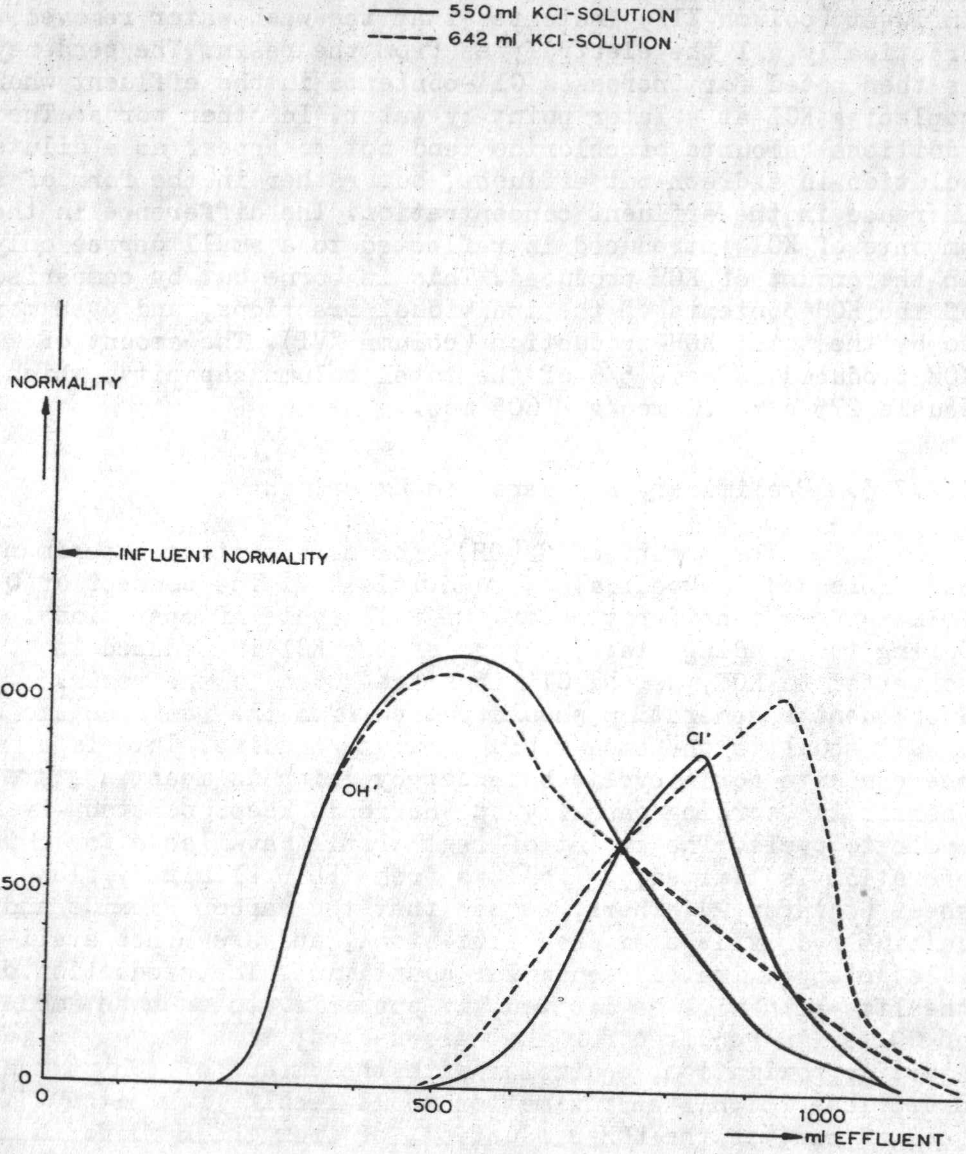
The results of these experiments were as per table 3.2. (fig. 3.3.).

Table 3.2.

Loading with Two Amounts of KCl - Solution.

| Exp. No. | KCl-solution |  | Water |  | Meq in the different fractions |  |  |  |  |  |  |  |  |  |  |  |  | Meq KCl in influent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | ml | Feed rate ml/min/cm$^2$ | ml | Feed rate ml/min/cm$^2$ | 0 - 275 ml |  | 275-697 ml |  | 697-890 ml |  | 890-1100 ml |  | 1100-1280 ml |  | 0 - 1280 ml |  |  |  |
|  |  |  |  |  | KOH | KCl | KOH | KCl | KOH | KCl | KOH | KCl | KOH | KCl | KOH | KCl | KOH+KCl |  |
| I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII | XIII | XIV | XV | XVI | XVII | XVIII | XIX |
| 2B1 | 642 | 65.5 | 568 | 52.4 | 12.3 | 0 | 352 | 58.5 | 98.5 | 144 | 43.0 | 135 | 7.8 | 10 | 514 | 348 | 862 | 868 |
| 2B2 | 550 | 61.8 | 550 | 55.2 | 1.5 | 2.0 | 383 | 34.2 | 92.6 | 142 | 18.5 | 54 | - | - | 496 | 232 | 728 | 743 |

FIGURE 3.3.
LOADING WITH TWO AMOUNTS OF KCl



The small difference between the total meq KOH + KCl in the effluent (column XVIII) and that, in the influent (column XIX) indicates that the wash water removed practically all the electrolytes from the resin. The tendency is then noted for increased Cl'-contents in the effluent when replacing KCl at a later point by water. In other words: The additional amounts of chloride tend not to appear as a diluted solution in a drawn-out effluent, but rather in the form of an increase in the effluent concentration. The difference in the amounts of KCl introduced is reflected to a small degree only in the amount of KOH produced. This is borne out by comparison of the KOH-contents of the individual fractions, and even more so by the total KOH-production (column XVI). The amount of KOH produced is some 5/6 of the total column capacity, which equals 275 g x 2.2 meq/g = 605 meq.

### 3.2.7.3. Preliminary Regeneration Experiments.

The amount of $Ca(OH)_2$ for regeneration experiments was expressed in "equivalent quantities" **Q**. The concept of **Q** follows from consideration of the full cycle of operations. During the loading stage, a part of the KCl introduced is converted to KOH, as the Cl'-ions are bound to the resin. Subsequent regeneration should remove from the resin an amount of Cl' equal to the amount bound during loading. This is a prerequisite for a cyclic balance, by which is meant a state wherein the working capacity of the resin keeps constant from cycle to cycle. The amount of regenerant available for this operation is limited, as follows from the preliminary flow-sheet (chapter 2). There, we saw that the carbon dioxide and calcium hydroxide stem from lime-stone, and are hence available in approximately equimolar quantities. The production of the lime-kiln will be limited, if possible, to such an amount of $CO_2$ as is required for the carbonation; this amount is ,at first approximation, equimolar with the amount of KOH formed. Exceptions to this approximation would result from either discard of part of the KOH-production, or from the need for a considerable excess of $CO_2$ during carbonation, which excess would not be recoverable. In general, however, the amount of $Ca(OH)_2$ would be roughly equimolar with that of KOH in the ion-exchange effluent, or doubly that amount in terms of equivalents. This double amount of $Ca(OH)_2$ has been termed "two equivalent quantities", or 2 **Q**.

Two regeneration experiments were carried out, with the aim of ascertaining whether 2 Q of Ca(OH)$_2$ would suffice for the required regeneration. In experiment 2C1, the resin prior to the regeneration had been converted wholly to resin-chloride with the aid of a tenfold excess of dilute hydrochloric acid, and contained 605 meq Cl'. Of the Ca(OH)$_2$-solution, containing 34.0 meq/l, 1 Q thus equalled 605/34.0 = 17.8 liter. In experiment 2C2, the resin prior to regeneration had served for loading (exp. 2B1), during which it had produced (table 3.2., column XVI) 514 meq KOH. Since before 2B1 the resin had been wholly in R-OH state, its Cl'-contents after 2B1 were 514 meq. 1 Q, where the regenerant contained 42.1 meq/l, was thus 514/42.1∼12.2 liter. The experimental results of the regeneration were as per table 3.3. (fig. 3.4.)

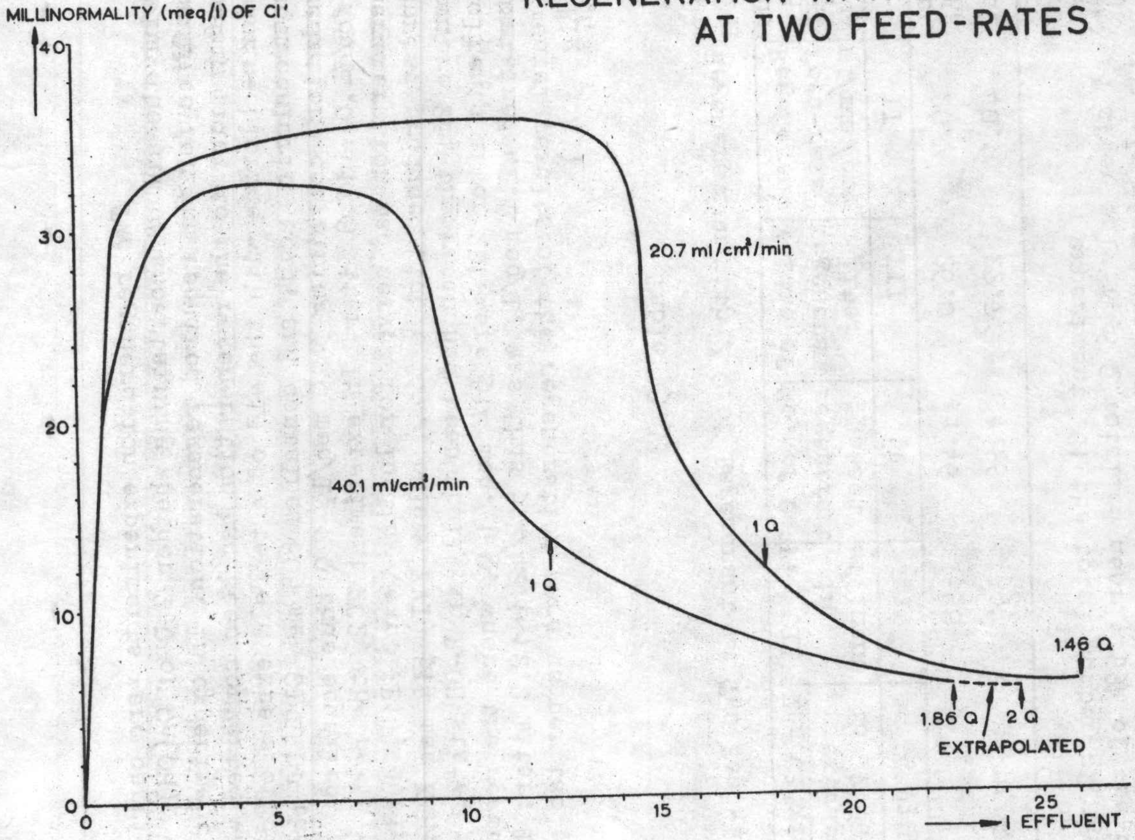
Table 3.3.

Regeneration with 2 Q of Regenerant at Two Feed-Rates.

| Exp. No. | Regenerant feed-rate ml/min/cm$^2$ | Volume of regenerant liter | No. of Q regenerant passed | Meq Cl' in effluent | Meq Cl' in effluent extrapolated to 2.00 Q |
|---|---|---|---|---|---|
| I | II | III | IV | V | VI |
| 2C1 | 20.7 | 26.0 | 1.46 | 598 | |
| 2C2 | 40.1 | 22.7 | 1.86 | 397 | 406 |

In experiment 2C1 the total number of meq Cl' removed after only 1.46 Q totalled nearly 99% of the resin capacity. In view of the considerations about cyclic balance, this may be considered satisfactory. Experiment 2C2 was executed at a considerably increased feed-rate. Also, the driving force in this experiment, as given by the difference in OH'-concentration between the resin phase and the regenerant phase, was smaller than in 2C1, due to the initially present OH' in the resin. It seems, however, that the influence of the feed-rate increase is much greater than that of the relative small decrease of the driving-force. Then the decrease in meq Cl' liberated from the resin (table 3.3., column V and VI) from nearly 99% to less than 79% of those initially present

FIGURE 3.4.
REGENERATION WITH 2Q OF REGENERANT
AT TWO FEED-RATES



would have considerable influence on the final results. In view of the low solubility of the regenerant, a major part of the time of the cycle would be taken up by the regeneration. Any need for a low feed-rate during that period would imply a lower production per unit time or an increased investment in resin and vessels for attainment of a given production. If a way were found to increase the concentration of the $Ca(OH)_2$ in the regenerant solution, the resulting increased driving force, as represented by the difference in the OH'-concentration between the resin and the regenerant solution, might partially or wholly counteract the effect of increased feed-rates (equal to shorter residence times).

### 3.2.7.4. Loading on a Column of Increased Diameter (46 mm).

The influence of the column diameter was investigated preliminarily by conducting a loading and washing experiment in a column of 46 mm inner diameter. To obtain a column of equal height as in former experiments, 800 g resin (weighed as shipped) were taken, and after swelling and conditioning converted to resin-hydroxide and washed.

With the final flowsheet in mind, the loading effluent was divided into four fractions. The first, containing the initially present interstitial water, and a small part of the KOH (as a dilute solution), was considered as primary discard. The second fraction, containing the major part of the KOH produced, contaminated with some KCl, formed the process solution. The third fraction, containing the major part of the unconverted KCl along with a part of KOH, formed the recycle solution, while the last fraction, a dilute KOH-KCl-solution, was considered as ultimate discard. This experiment on the broader column (2D1) was compared with exp. 2B1, carried out in the narrower column. The results were as per table 3.4.

Table 3.4.

Loading on Two Columns of Different Diameter

| Exp. No. | Resin g | KCl- solution | | | Water | | Primary Discard | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Vol. ml | Conc. g/l | Feed-rate ml/min/cm$^2$ | vol. ml | Feed-rate ml/min/cm$^2$ | vol. ml | KOH meq | KCl meq |
| I | II | III | IV | V | VI | VII | VIII | IX | X |
| 2B1 | 275 | 642 | 100.8 | 65.5 | 568 | 52.4 | 200 | 2.3 | 0 |
| 2D1 | 800 | 2700 | 100.8 | 81.3 | 1700 | 32.5 | 700 | 12.8 | 0 |
| Ratio | 2.9 | | | | | | 3.5 | | |

| Process solution | | | | Recycle solution | | | | Ultimate discard | | |
|---|---|---|---|---|---|---|---|---|---|---|
| vol. | K O H | | KCl | vol. | K O H | | KCl | vol. | KOH | KCl |
| | meq | % of resin capacity | meq | ml | meq | % of resin capacity | meq | ml | meq | meq |
| XI | XII | XIII | XIV | XV | XVI | XVII | XVIII | XIX | XX | XXI |
| 420 | 304 | 50.2 | 22.5 | 480 | 200 | 33 | 315 | 180 | 7.8 | 10 |
| 1315 | 919 | 52.2 | 67.5 | 1485 | 584 | 33.2 | 1170 | 900 | 36 | 148 |
| 3.1 | 3 | 1 | 3 | 3.1 | 2.9 | 1 | 3.7 | | | |

The results obtained indicate, that in spite of the difference in feed-rates, the yields show a considerable degree of similarity. This holds especially for the two process-solutions (columns XI-XIV), where the percentages of resin capacities utilised (i.e., meq KOH in process solution/total resin capacity, in meq) were very nearly the same (column XIII), and where the amounts of both KOH (column XII) and KCl (column XIV) appeared in the same proportion (3.0), which was, furthermore, very near to the ratio of resin weight in the two columns (column II).

If the method of operation, as described here, were adopted for the final flowsheet, "process development" would probably require the influence of the diameter to be investigated on a more comprehensive scale. The results of table 3.4. indicated, on the other hand, that little would be gained at that stage of experimentation from the use of the broader column while the expense of chemicals incurred (and to some degree of time as well) would be considerably greater than in the case of the narrower column. The work was therefore continued with the narrower column exclusively.

### 3.2.7.5. Successive Cycles - Cyclic Balance.

Experiments were carried out in the form of several successive cycles, to approach the operation of a continuously working installation.

The first point requiring investigation was whether cyclic balance could be established, while limiting the quantity of regenerant to 2 **Q**. The amount of KOH determining **Q** can be calculated in two ways, depending on the division of the loading effluent into fractions. This effluent contains namely both formed KOH as well as unconverted KCl. The breakthrough of KCl occurs after the appearance of KOH. The greater the volume of effluent which is relegated to further processing, the greater its KCl-contents will be. This KCl will appear unchanged in the subsequent $KHCO_3$-solution. Now it is shown (116) that if water is withdrawn from an aqueous mixture of KCl and $KHCO_3$, no KCl will precipitate (in a solution saturated to $KHCO_3$) unless its mol-% exceeds 75.1. On the other hand, mother liquor will adhere to the $KHCO_3$-precipitate, and the higher its KCl-contents, the more washing of crystals will be required.

Two possible ways of division of the effluent can now be considered: According to the first, only that fraction containing little KCl (the limit being set arbitrarily at about

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(116) Appendix: The system $KCl-KHCO_3-H_2O$

15 mol-%) would be considered for the process solution, the remainder of the KOH, heavily contaminated by KCl, being recycled through the ion-exchanger. The process solution would then be relatively pure, but contain only a part of the KOH, whereby Q would be limited. According to the second way, the whole effluent (except for some minor discards at its beginning and end) containing all the KOH produced would be further processed, thereby increasing the available Q. On the other hand, this solution would be contaminated with all the unconverted KCl. As long as the KCl mol-% did not exceed 75.1, precipitation of pure $KHCO_3$ would be possible. The nearer this percentage approached that limit, the smaller the amount of $KHCO_3$ precipitable-per-pass.

A set of three experiments was carried out to ascertain whether the limit of KCl-contamination of 15 mol-% was tenable. As the first cycle was done on resin hydroxide completely in the R-OH state, its loading results should be viewed with reserve. The two other loading experiments were carried out on a resin regenerated with the proper amount of $Ca(OH)_2$. The eperimental results were as per table 3.5.(fig. 3.5.)

The results show a steady deterioration. At a KCl-mol% approximately constant and not over 15.4 (column XIV), the meq KOH formed (column XI) decrease from 455 (in 3B1) to 302 (in 3B2) to 195 (3B3), while that part of the KOH, in the recycle solution (column XV), increases. As a result, Q decreases steadily, with it the amount of regenerant (column XXI), and thus the degree of regeneration, as represented by the amount of Cl' removed from the resin (column XXIII), from 374 to 291 meq. Such a course of events would terminate at a negligible, if not actually zero, production of KOH in the process solution.

It was therefore decided to consign all the effluent, including those fractions heavily contaminated by KCl, to the process solution. A set of six experiments was carried out, with results as per table 3.6. Experiment 3C1 was done on a resin completely in the hydroxide state.

Table 3.5.

Cyclic experiments (with recycle of the KCl-rich loading effluent)

| Experiment Number | KCl-solution | | | Water | |
|---|---|---|---|---|---|
| | KCl-conc. g/l | No. of meq Cl' introd. | Feed-rate ml/min/cm$^2$ | vol. ml | Feed-rate ml/min/cm$^2$ |
| I | II | III | IV | V | VI |
| 3B1 | 99.9 | | | | |
| 3B2 | 99.9 | 617 | 20.9 | 586 | 22.6 |
| 3B3 | 99.9 | 606 | 19.0 | 598 | 37.0 |

| Primary Discard | | | Process solution | | | | Recycle solution | | |
|---|---|---|---|---|---|---|---|---|---|
| Vol. ml | KOH meq | KCl meq | Vol. ml | KOH meq | K C l | | Vol. ml | KOH meq | KCl meq |
| | | | | | meq | % total mols | | | |
| VII | VIII | IX | X | XI | XII | XIII | XIV | XV | XVI |
| 150 | 5.0 | 0 | 500 | 455 | 63.4 | 12.3 | 150 | 39.5 | 64.2 |
| 150 | 3.0 | 0.3 | 375 | 302 | 53.4 | 15.1 | 275 | 107 | 187 |
| 125 | 4.5 | 0.2 | 275 | 195 | 35.5 | 15.4 | 500 | 198 | 321 |

| Ultimate Discard | | | $Ca(OH)_2$ - solution | | | Regeneration Effluent; No. of meq Cl' removed from resin |
|---|---|---|---|---|---|---|
| Vol. ml | KOH meq | KCl meq | vol. ml | No.of meq introduced | Feed-rate ml/min/cm$^2$ | |
| XVII | XVIII | XIX | XX | XXI | XXII | XXIII |
| 240 | 6.1 | 5.6 | 21500 | 910 | 14.2 | 374 |
| 245 | 2.3 | 9.5 | 14300* | 603 | 21.7 | 361 |
| 115 | 6.3 | 10.3 | 10740 | 391 | 27.4 | 291 |

* As a result of an experimental error, the volume of $Ca(OH)_2$ utilized in experiment 3B2 was 17800 ml instead of 14300 available from the loading stage. The calculations were based on the correct amount of $Ca(OH)_2$, but the picutre of the next cycle, 3B3, is too optimistic.

FIGURE 3.5.

CONSECUTIVE CYCLES (WITH RECYCLE OF KCl-RICH LOADING EFFLUENT) - RESULTS OF THE LOADING

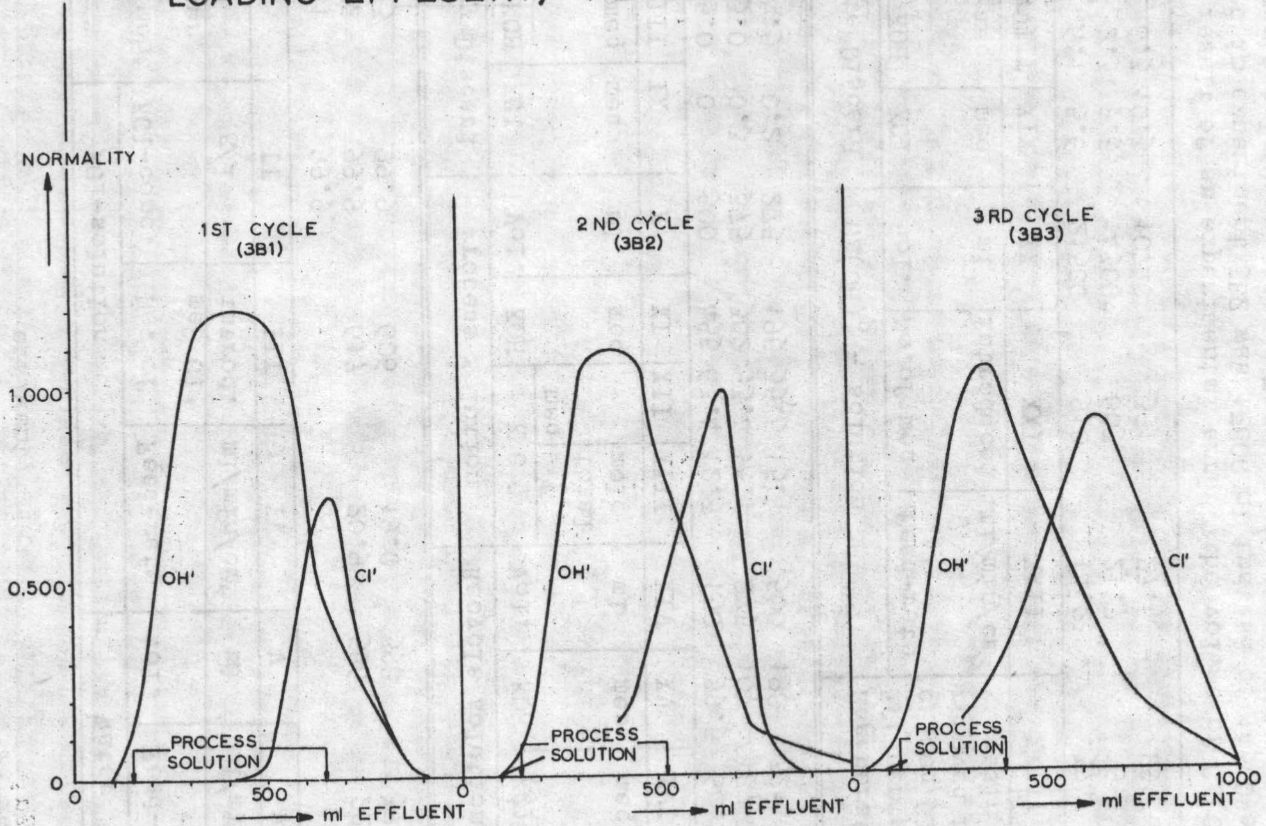

Table 3.6

Successive cycles (without recycle of the KCl-rich solution)

| Experiment | KCl - solution | | | Water | |
|---|---|---|---|---|---|
| | Conc. g/l | No. of meq introduced | Feed-rate ml/min/cm$^2$ | Vol. ml | Feed-rate ml/min/cm$^2$ |
| I | II | III | IV | V | VI |
| 3C1 | 99.9 | - | - | - | - |
| 3C2 | 99.9 | 637 | 21.1 | 604 | 20.0 |
| 3C3 | 99.9 | 598 | 19.8 | 592 | 17.4 |
| 3D1 | 99.9 | 555 | 15.4 | 595 | 11.1 |
| 3D2 | 99.9 | 616 | 20.2 | 601 | 19.7 |
| 3D3 | 99.9 | 627 | 25.0 | 600 | 24.0 |

| Primary Discard | | | Process solution | | | | Ultimate Discard | | |
|---|---|---|---|---|---|---|---|---|---|
| Vol ml | KOH meq | KCl meq | Vol. ml | KOH meq | K C l | | Vol. ml | KOH meq | KCl meq |
| | | | | | meq | % total mols | | | |
| VII | VIII | IX | X | XI | XII | XIII | XIV | XV | XVI |
| 150 | 2.0 | 0 | 750 | 464 | 213 | 31.6 | 140 | 6.8 | 11.1 |
| 150 | 5.6 | 0.3 | 700 | 385 | 277 | 41.8 | 230 | 17.4 | 8.2 |
| 150 | 6.5 | 0.6 | 750 | 443 | 251 | 36.3 | 140 | 6.2 | 2.2 |
| 250 | 5.0 | 1.0 | 550 | 357 | 174 | 32.7 | 235 | 5.1 | 5.9 |
| 150 | 3.0 | 0.5 | 650 | 365 | 258 | 41.4 | 250 | 10.3 | 17.5 |
| 150 | 3.5 | 0.9 | 750 | 410 | 297 | 42.0 | 145 | 12.1 | 4.1 |

| $Ca(OH)_2$ - solution | | | Regeneration Effluent |
|---|---|---|---|
| Vol. ml | No. of meq introduced | Feed-rate ml/min/cm$^2$ | No. of meq Cl' removed from resin |
| XVII | XVIII | XIX | XX |
| 23600 | 928 | 20.1 | 399 |
| 19600 | 770 | 21.4 | 390 |
| 19400 | 884 | 18.0 | 402 |
| 15700 | 715 | 17.9 | 359 |
| 15470 | 730 | 16.4 | 387 |
| 17660 | 820 | 17.0 | 388 |

The results show the following. The maximum mol-% of KCl in the process-solution (column XIII) does not exceed 42.0. This implies that theoretically

$$\left[(100-42.0) - 42.0\,(100-75.1)/75.1\right]/58.0 = 76\%$$ of the $KHCO_3$ subsequently present (assuming a complete conversion of KOH to $KHCO_3$) could be precipitated without contamination by KCl, and that 24% would be recycled. For KCl mol-% of about 33 these values would become approximately 83% (precipitated) and 17% (recycled).

The production of KOH (column XI) - excepting cycle 3C1 - varied between 443 and 357 meq (average 392 meq). The regeneration removed (column XX) from 359 to 402 meq (average 387 meq) of Cl'. A certain variation around average values is thus noted, the probable reason for which will be discussed below. In view of the very small deviation between the averages of meq KOH produced and meq Cl' removed, a cyclic balance seems to have been attained. This then means that regeneration with 2 Q of $Ca(OH)_2$, the excess put at our disposal by the preliminary flowsheet, suffices for the purpose set. At the level of operation as attained in the experiments 3C2-3D3, between 60-70% of the resin capacity is utilised. Of the round 600 meq KCl introduced, roughly 2/3 (400 meq) are converted into KOH. The influent KCl normality in these experiments being 1.34, that of KOH in the process solution is about 0.59. The decrease of concentration is due to two factors. Firstly, dilution takes place by initially present interstitial water, of which part only is removed before KOH appears in the effluent. Secondly, the conversion of KCl to KOH is less than complete. Both factors are evident from table 3.7., (fig. 3.6.) where cycle 3D1 has been taken as example.

The effect of interstitial water is seen from the third column, giving the total normality of the effluent. The maximum value of this total was 1.31 N, that is still somewhat lower than the influent normality. This value was reached after 650 ml of effluent. In all previous fractions, interstitial water caused a lower total normality (the lower total normality in the subsequent fractions was due to the washing water replacing the KCl-solution).

Table 3.7.

Experiment 3D1; influent KCl-normality 1.34
Normality in the several fractions.

| KOH | KCl | KOH + KCl |
|---|---|---|
| 0 | 0 | 0 |
| 0.06 | 0.01 | 0.07 |
| 0.56 | 0.08 | 0.64 |
| 0.86 | 0.10 | 0.96 |
| 0.99 | 0.12 | 1.11 |
| 0.94 | 0.22 | 1.16 |
| 0.81 | 0.38 | 1.19 |
| 0.72 | 0.52 | 1.24 |
| 0.64 | 0.64 | 1.28 |
| 0.61 | 0.69 | 1.30 |
| 0.59 | 0.72 | 1.31 |
| 0.55 | 0.73 | 1.28 |
| 0.36 | 0.59 | 0.95 |
| 0.05 | 0.06 | 0.11 |
| 0 | 0 | 0 |

The effect of the less-than-complete conversion is seen from the appearance of KCl in the very first fractions. After passage of only 200 ml KCl-normality reached the noticeable value of 0.01 N (0.7 g/l). This volume - 200 ml - corresponds closely with the volume of the interstitial voids, as calculated from the formula:

% voids = (1-apparent density/true density) 100

where the apparent density = 275/456 = 0.60 and the true density very near to 1.0(117). The appearance of KCl after passage

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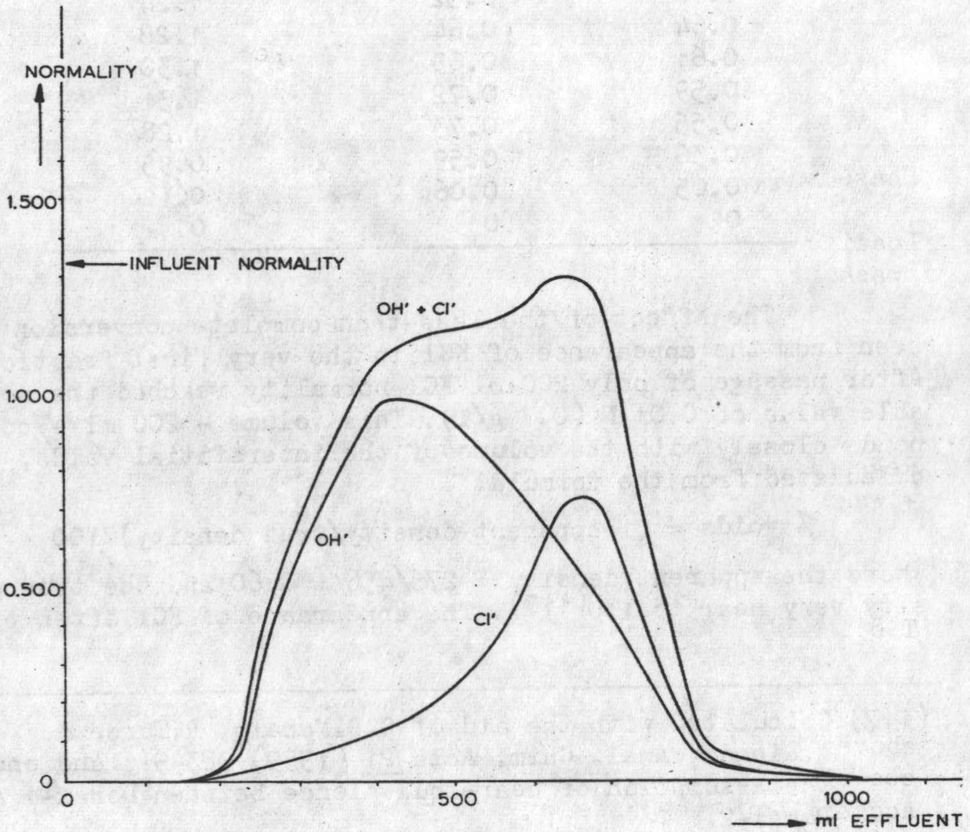
(117) Calculated with the aid of G.D.Manalo, R.Turse & W.Rieman, Anal. Chim. Acta 21 (1959) 383-91, and under the assumption of near-equivalence between Dowex-1 and Dowex-2.

FIGURE 3.6.
EXP. 3D1 - COMPOSITION OF THE LOADING EFFLUENT



of this volume indicates the breakthrough which takes place, due to the less-than-complete conversion. The variation around average values , , as noted in table 3.6., can be ascribed to the following causes: On attempting to draw up a balance of materials over a cycle of operations, a certain lack of balancing will be noted. As in the long run there occurs neither accumulation of material in the resin, nor its depletion therefrom, and as the stoichiometry of ion - exchange has been established beyond doubt, the reasons for lack of balance could be due either to inexactness of analyses or to inequality in the state of the resin or the free electrolytes contained therein at comparable points of successive cycles.

Let us take cycle 3E2 and attempt to draw up a balance of materials (table 3.8.)

Table 3.8.

Experiment 3E2 - A Balance of Materials (in meq).

| Phase | Introduced | | Obtained | | Difference | |
|---|---|---|---|---|---|---|
| | anions | cations | anions | cations | anions | cations |
| Loading + washing | 573 $Cl'$ | 573 $K^{\cdot}$ | 377 $OH'$<br>189 $Cl'$ | | | |
| | | | 566 | 546 $K^{\cdot}$ (+ traces of $Ca^{\cdot\cdot}$) | 1.2% | 4.7% |
| Regeneration + washing | 727 $OH'$ | 727 $Ca^{\cdot\cdot}$ | 271 $OH'$<br>383 $Cl'$ | | | |
| | | | 654 | 657 $Ca^{\cdot\cdot}$ | 10.6% | 10.1% |
| Total | 1300 | 1300 | 1220 | 1203 | 6.4% | 7.8% |

The table shows, that both the latter reasons given above for lack of balance, play a role. The presence of traces of $Ca^{\cdot\cdot}$ was noted in the loading effluent. This would account for the difference in the amount of cations (573 - 546) in that part of the cycle. These $Ca^{\cdot\cdot}$ -ions could have originated only in the previous regeneration, which was followed by a rinsing with water, and terminated at a low, but not zero, electrolyte concentration. A complete rinsing of all free electrolytes from the resin would require very considerable volumes of water, as the driving force for the removal of these electrolytes, formed by the difference in their concentration in the resin and in the wash-water, is directly proportional to the electrolyte-concentration in the resin. On the other hand, a subsequent treatment of the resin by another electrolyte solution (as in the loading of 3E2, which followed the regeneration of 3E1), adds a second driving force to the first, namely the difference in concentration of that second electrolyte between the solution and the resin. Both driving forces work in the same direction. This then accounts for the presence of $Ca^{\circ\circ}$ in the loading effluent.

The "regeneration + washing" - phase of 3E2 shows a very reasonable balance between cations and anions in the effluent. The difference is smaller than 0.5%, and falls within the accuracy of the analyses. The difference between influent and effluent streams is, however, considerable, and is due to an accumulation of part of the electrolyte introduced in the resin. This is supported by the excess of meq $Cl'$ + $OH'$ in the loading effluent of the next experiment, 3E3, immediately following upon the regeneration and rinsing of 3E2. In 3E3, 601 meq of KCl were introduced, while 685 meq $Cl'$ + $OH'$ were obtained in the effluent, giving an excess of 84 meq, very nearly equal to

$$727 - 654 = 73 \text{ meq in 3E2.}$$

From such a transfer of part of the electrolyte from one cycle (or its part) to another, results the deviation around average values noted above. If this method of operation would be recommended for the final flowsheet, then decrease of this "transfer" would be mandatory, as it results in both contamination, and lessening of the yield from the raw materials.

## Table 3.9.

## Loading Experiments at Different KCl - Concentrations

| Experiment number | KCl - solution |  |  | Water |  | Process solution |  |  | Discards |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | meq in | conc. g/l | feed-rate ml/min/cm$^2$ | Vol. ml | feed-rate ml/min/cm$^2$ | Vol. ml | KOH meq | KCl % of total mols | Vol. ml | KOH meq | KCl meq |
| I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
| 3C1 * | 649 | 99.9 | 22.0 | 603 | 23.8 | 750 | 464 | 31.6 | 290 | 8.8 | 11.1 |
| 3C2 | 636 | 99.9 | 21.1 | 604 | 20.0 | 700 | 385 | 44.5 | 380 | 23.0 | 8.5 |
| 3C3 | 599 | 99.9 | 19.8 | 592 | 17.4 | 750 | 443 | 36.3 | 290 | 12.7 | 2.8 |
| 3D1 | 525 | 99.9 | 15.4 | 595 | 11.1 | 550 | 357 | 32.7 | 485 | 10.1 | 6.9 |
| 3D2 | 616 | 99.9 | 20.2 | 601 | 19.7 | 650 | 365 | 41.4 | 400 | 13.3 | 18.0 |
| 3D3 | 627 | 99.9 | 25.0 | 600 | 24.0 | 750 | 410 | 42.0 | 295 | 15.6 | 5.0 |
| 3E1 | 641 | 100.6 | 9.0 | 600 | 6.2 | 600 | 397 | 34.9 | 445 | 21.7 | 29.5 |
| 3E2 | 573 | 100.6 | 6.9 | 600 | 8.8 | 500 | 364 | 31.0 | 525 | 13.1 | 26.2 |
| 3E3 | 601 | 100.6 | 9.3 | 600 | 6.5 | 550 | 386 | 36.8 | 500 | 32.8 | 42.5 |
| 3F1 * | 592 | 185.7 | 13.6 | 600 | 16.6 | 450 | 439 | 26.0 | 395 | 13.7 | 35.0 |
| 3F2 | 647 | 185.7 | 15.4 | 600 | 15.3 | 475 | 262 | 61.8 | 380 | 4.5 | 15.5 |
| 3F3 | 657 | 185.7 | 16.1 | 601 | 15.1 | 450 | 253 | 64.9 | 395 | 3.0 | 85.6 |
| 3G1 * | 547 | 48.5 | 15.3 | 600 | 36.5 | 1050 | 459 | 10.3 | 400 | 8.2 | 6.9 |
| 3G2 | 520 | 48.5 | 25.1 | 600 | 18.6 | 1100 | 379 | 28.0 | 350 | 3.3 | 4.9 |
| 3G3 | 537 | 48.5 | 19.6 | 600 | 19.6 | 1050 | 373 | 30.8 | 550 | 6.1 | 8.8 |
| 3H1 | 573 | 273.0 | 8.5 | 600 | 9.6 | 550 | 478 | 48.0 | 217 | 3.1 | 0.3 |
| 3H2 | 588 | 273.0 | 8.1 | 600 | 11.6 | 475 | 450 | 47.6 | 290 | 5.6 | 3.6 |
| 3H3 | 588 | 273.0 | 9.8 | 650 | 6.3 | 500 | 533 | 31.3 | 315 | 11.0 | 7.5 |

* Preceded by a KOH-regeneration

### 3.2.7.6. Loading with Different KCl-concentrations

The concentration of the KCl in the loading solution is of considerable influence on the process as a whole, as it is one of the important factors which determine the concentration of KOH, and therefore of $KHCO_3$, which determines in its turn the amount of water to be transferred during the dehydration.

Experiments were carried out with KCl-solutions of 48.5 g/l,99.9-100.6 g/l, 185.7 g/l and 273 g/l.

The experimental results were as per table 3.9. (see page 69).

The influence of the KCl-concentration can be visualized by comparing it with that of the KOH in the process solution. In accordance with previous experience the process solution includes the total effluent, except for some minor discards of low electrolyte contents. A factor f is defined, where f = influent KCl-normality/effluent KOH-normality. It is a measure for the conversion-per-pass of KCl; the lower f is, the more favourable the conversion will be.

In view of the variation around average values, noted earlier, each series (3D, 3E etc.) was averaged. The magnitude of f is then as follows: (tables 3.10. and 3.11., and fig. 3.7.):-

---

The Ratio of Influent and Effluent Normalities

Table 3.10.

| Exp. series | $N_1$=average influent KCl-norm. | Average KCl feed-rate ml/min/$cm^2$ | $N_2$=average effluent KOH-norm. | $f=N_1/N_2$ |
|---|---|---|---|---|
| I | II | III | IV | V |
| 3G (excl.3G1) | 0.65 | 22.3 | 0.35 | 1.86 |
| 3C (excl.3C1) | 1.34 | 20.5 | 0.57 ) | 2.29 |
| 3D | 1.34 | 20.2 | 0.60 ) | |
| 3F (excl.3F1) | 2.49 | 15.7 | 0.47 | 5.30 |

Table 3.10. contains the results at about 20 ml/min/$cm^2$, 3.11. those at about 8-9 ml/min/$cm^2$.

Table 3.11.

| Exp. series | $N_1$=average influent KCl-norm. | Average KCl feed-rate ml/min/cm$^2$ | $N_2$=average effluent KOH-norm. | $f=N_1/N_2$ |
|---|---|---|---|---|
| I | II | III | IV | V |
| 3E | 1.35 | 8.4 | 0.70 | 1.93 |
| 3H | 3.68 | 8.8 | 0.96 | 3.84 |

Fig. 3.7. represents graphically the results of tables 3.10. and 3.11.

At very low influent KCl-normalities, the conversion will be considerable, and f will approach 1. At very low feed-rates, f will approach 1 irrespective of the influent KCl-normality.

The figure illustrates the fact that at the same influent KCl-normality an increased feed-rate results in a decreased KOH-concentration (in the process-solution), while at constant feed-rate decreased influent KCl-normality decreases f, that is, increases the percentage of conversion.

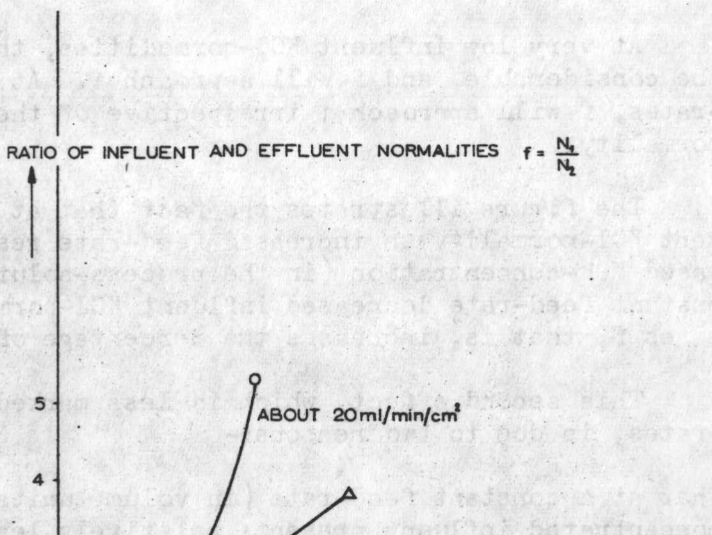
This second effect, which is less marked at lower feed-rates, is due to two reasons:-

1) That at a constant feed-rate (in volume units) a more concentrated influent presents relatively less chances for contact and exchange than a more diluted one.

2) That an increase in influent concentration means a decrease in influent volume. The interstitial volume of water stays constant; this results in an increased dilution of the KOH formed.

Both reasons tend to increase f at increasing influent concentration. This results in increased contamination by KCl, as is reflected in column IX of table 3.9. Regarding the discards, their total electrolyte contents is too small to assign any significance to eventual changes of composition.

FIGURE 3.7.
THE MUTUAL INFLUENCE OF FEED-RATES AND CONCENTRATIONS AT LOADING



### 3.2.7.7. Loading with KCl at Different Feed-rates

The results of series 3C, 3D and 3E in tables 3.10. and 3.11. and in fig. 3.7. serve to indicate the influence of the feed-rate. A decrease of the feed-rate of 1.34 N KCl from 20.3 to 8.4 ml/min/cm$^2$ results in an increase of the average KOH-normality from 0.58 to 0.70. This is due to the increased exchange at the longer residence times. This longer residence time would result in a smaller production per time unit, and the evaluation of an economic optimum would be required, if this method of operation were adopted for the final flowsheet.

### 3.2.7.8. The Equilibrium Curve for the Regeneration

An indication of the behaviour of the resin during regeneration with $Ca(OH)_2$ can be obtained from the equilibrium curve between the resin and regenerant solutions of different Cl' to OH' ratio's. To annul any influence of the volume on the equilibrium, solutions of $Ca(OH)_2$ and $CaCl_2$ of very nearly equal strength were prepared, and mixed in predetermined volume-ratio's. The number of meq in this (mixed) solution was equal to that in the resin, equilibrated with this solution. Equilibration was attained by occasional shaking during several hours in a thermostatic bath, kept at 19.7 - 20.2°.

The resin (Dowex-2, 8%) was prepared for the equilibration by cycling it several times between R-OH and R-Cl, and converting it finally into R-Cl, with a large excess of 2N HCl, washing and drying for several hours at 110-115°.

The $Ca(OH)_2$-solution contained 46.2 meq/l, the $CaCl_2$-solution 46.5 meq/l. The experiments and their results were as per table 3.12.

The data of the equilibrium are given in columns XII and XXII of the table. They have been represented in figure 3.8.

Table 3.12.

Data of the Equilibrium Curve for the Regeneration.

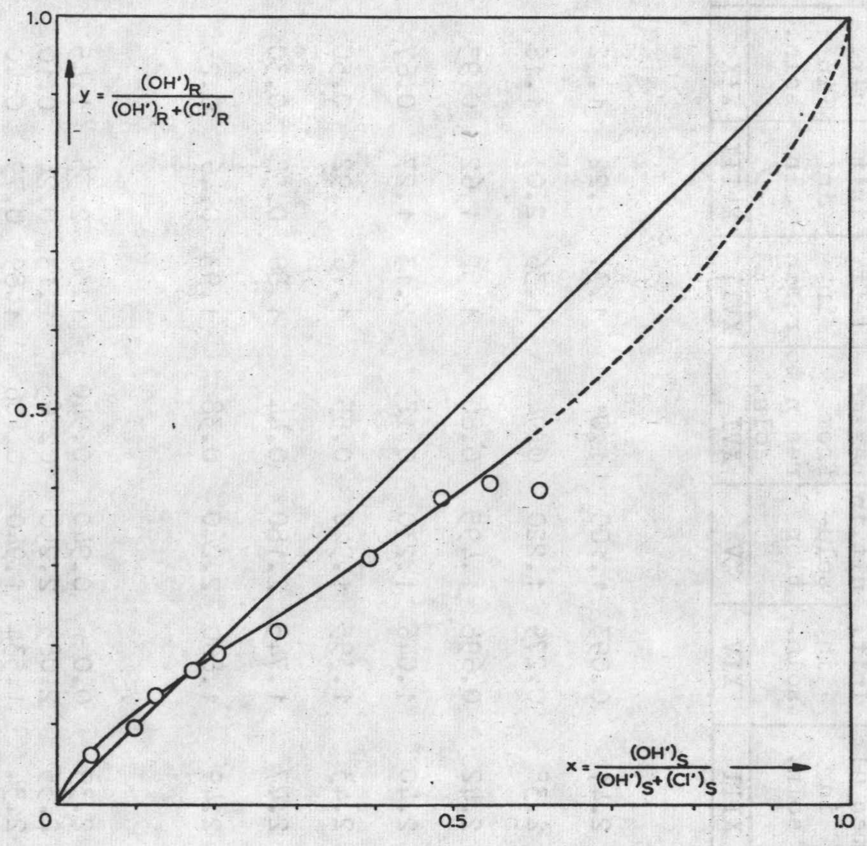
| Exp. No. | Resin weight (dry) mg | $CaCl_2$ soln. ml | $Ca(OH)_2$ soln. ml | Temp. °C | Sample ml | Acid ml req. for neutr. | $AgNO_3$ soln. ml | OH' meq/l in soln. | Cl' meq/l in soln. | Cl' + OH' meq/in solution |
|---|---|---|---|---|---|---|---|---|---|---|
| I | II | III | IV | V | VI | VII | VIII | IX | X | XI |
| | | | | | | HCl<br>0.1007N | | | | |
| | | | | | | | 0.0996N | | | |
| 4A1 | 631.4 | 2.00 | 48.00 | 19.8 | 10.00 | 2.61 | | 26.3 | | 48.3 |
| | | | | | 10.00 | | 2.22 | | 22.0 | |
| 4A2 | 627.0 | 6.00 | 44.00 | 20.0 | 10.00 | 2.30 | | 23.1 | | 47.5 |
| | | | | | 10.00 | | 2.45 | | 24.4 | |
| 4A3 | 631.4 | 15.00 | 35.00 | 19.8 | 10.00 | 1.84 | | 18.5 | | 48.4 |
| | | | | | 10.00 | | 3.01 | | 29.9 | |
| 4A4 | 628.3 | 22.50 | 27.50 | 19.7 | 10.00 | 1.33 | | 13.4 | | 48.0 |
| | | | | | 10.00 | | 3.48 | | 34.6 | |
| 4A5 | 629.2 | 30.00 | 20.00 | 19.8 | 10.00 | 0.98 | | 9.9 | | 48.7 |
| | | | | | 10.00 | | 3.90 | | 38.8 | |
| 4A6 | 627.1 | 37.50 | 12.50 | 19.8 | 10.00 | 0.59 | | 5.9 | | 49.5 |
| | | | | | 10.00 | | 4.38 | | 43.6 | |
| 4A7 | 629.4 | 40.00 | 10.00 | 19.7 | 10.00 | 0.50 | | 5.0 | | 49.8 |
| | | | | | 10.00 | | 4.50 | | 44.8 | |
| | | | | | | $H_2SO_4$<br>0.1004N | | | | |
| | | | | | | | 0.1000N | | | |
| 4A8 | 626.7 | 0.00 | 50.00 | 20.0 | 10.00 | 2.88 | 1.88 | 28.9 | 18.8 | 47.7 |
| 4A9 | 627.8 | 45.00 | 5.00 | 20.2 | 10.00 | 0.20 | 4.50 | 2.0 | 45.0 | 47.0 |
| 4A10 | 630.6 | 33.00 | 17.00 | 19.9 | 10.00 | 0.80 | 3.87 | 8.0 | 38.7 | 46.7 |

| $x=\frac{(OH')}{(OH'+Cl')}$ in solution ult. | Cl'+OH' meq ult. in soln. | Cl'meq init. in soln. | Cl'meq ult.in solution | Cl'meq passed from resin to soln. | Cl'meq left in resin | OH'meq init. in soln. | OH'meq ult. in soln. | OH'meq passed from soln.to resin | OH'+Cl' meq ult.in resin | $y=\frac{OH'}{OH'+Cl'}$ in resin ult. |
|---|---|---|---|---|---|---|---|---|---|---|
| XII | XIII | XIV | XV | XVI | XVII | XVIII | XIX | XX | XXI | XXII |
| 0.545 | 2.41 | 0.093 | 1.100 | 1.01 | 1.31 | 2.22 | 1.32 | 0.90 | 2.21 | 0.408 |
| 0.487 | 2.38 | 0.279 | 1.220 | 0.94 | 1.36 | 2.03 | 1.16 | 0.87 | 2.23 | 0.389 |
| 0.393 | 2.42 | 0.698 | 1.495 | 0.80 | 1.52 | 1.62 | 0.93 | 0.69 | 2.21 | 0.313 |
| 0.279 | 2.40 | 1.046 | 1.230 | 0.18 | 2.13 | 1.27 | 0.67 | 0.60 | 2.73 | 0.220 |
| 0.203 | 2.43 | 1.395 | 1.940 | 0.55 | 1.76 | 0.92 | 0.50 | 0.42 | 2.18 | 0.193 |
| 0.120 | 2.47 | 1.745 | 2.180 | 0.44 | 1.86 | 0.58 | 0.30 | 0.28 | 2.14 | 0.131 |
| 0.100 | 2.49 | 1.860 | 2.240 | 0.38 | 1.93 | 0.46 | 0.25 | 0.21 | 2.14 | 0.098 |
| | | | | | | | | | | |
| 0.606 | 2.39 | 0.0 | 0.940 | 0.940 | 1.36 | 2.35 | 1.45 | 0.90 | 2.26 | 0.398 |
| 0.043 | 2.35 | 2.085 | 2.250 | 0.165 | 2.13 | 0.24 | 0.10 | 0.14 | 2.27 | 0.062 |
| 0.171 | 2.34 | 1.534 | 1.940 | 0.406 | 1.89 | 0.79 | 0.40 | 0.39 | 2.28 | 0.171 |

FIGURE 3.8.

EQUILIBRIUM BETWEEN DOWEX-2-CHLORIDE AND AQUEOUS $Ca(OH)_2 + CaCl_2$ MIXTURES
TEMPERATURE 19.7°-20.2°; TOTAL CONCENTRATION IN THE SOLUTION 46.2-46.5 meq/l

VALUES IN BRACKETS DENOTE CONCENTRATIONS
SUBSCRIPTS: R = RESIN
S = SOLUTION



The data show "adsorbtion azeotropy", that is, a reversal of the selectivity at $x = y = 0.171$. On the whole, the deviation from the $45^\circ$ - line is rather small. These results are qualitatively in agreement with those of (118), where the same resin was equilibrated with mixtures of NaCl + NaOH at a total concentration of 100 meq/l. There, the curve cut the $45^\circ$ - line at $x = y = 0.25$.

Waterman and Weber found (119) that distribution curves often occur in the shape of hyperbolas. The occurrence of this form was verified in the present case. From known forms of distribution curves (such as in (118)) it was clear, that two hyperbolas would be required here, one below and one above the point of "azeotropy". The two hyperbolas might agree with the following formulas (119a):-

Below the point of azeotropy $$y = x + \frac{x(d-x)}{a_1+b_1x}$$

Above the point $$y = x + \frac{(d-x)\ (1-x)}{a_2+b_2x}$$

where $x = y = d$ is the point of azeotropy.

From the experimental x- and y-values, and with the technique of the "least sum of squares", lines forming part of two hyperbolas were drawn in the figure.

From the sum total of the experimental points in fig. 3.8. the impression was gained, that the point

$$(x=0.606; \quad y=0.398)$$

deviated from the general trend; this was probably due to inaccurate experimental results, and the point was not taken into consideration when calculating the hyperbola. It was

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(118) R.M. Wheaton & W.C. Bauman, Ind. Eng. Chem. 43 (1951) 1090.

(119) H.I. Waterman, Anal. Chim. Acta 18 (1958) 498; H.I. Waterman & A.B.R. Weber, J. Inst. Petr. 43 (1957) 315

(119a) H.I.Waterman, C.Boelhouwer & D.Th.A. Huibers, Process Characterisation (Amsterdam 1960) p. 114.

also found necessary to introduce a small correction in the experimental y-value of the point ($x=0.100$; $y=0.098$), and to equate its x- and y-values.

The degree of agreement between the hyperbolas and the experimental points may be considered satisfactory.

### 3.2.7.9. Regeneration at Elevated Temperatures

The solubility of $Ca(OH)_2$ in water decreases with increasing temperature, although the changes are small. Regeneration at a temperature different from that of the surroundings might have, however, other consequences, as follows. On decreasing the temperature, the equilibrium constant of the ion-exchange (note 9) would decrease(120), the viscosity of the solutions would increase, and the diffusion coefficients for both film- and particle - diffusion would decrease, all of which would tend to slow the exchange. An increase of temperature, which would have the opposite effects, might therefore be beneficial. Such an increase would be, however, limited, due to the limited stability of the resin-hydroxide, to about 40° (121).

One set of three cycles (series 3E) was carried out at increased temperature. The regenerant was heated by passing through a glass coil in a thermostatic bath. The column was fitted with thermometers at both inlet and outlet, and isolated externally with asbestos cord. The difference between top and bottom of the column amounted to 3°. The temperature stayed constant during the regeneration within 0.5°. The given values form averages between top and bottom. The loading and washing phase were carried out at ambient temperature.

(120) J.A.Kitchener, Ion Exchange Resins (London 1957)p.41
(121) F.K. Lindsay & J.S. d'Amico, Ind. Eng.Chem.43 (1951)1086

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Note 9: The average equilibrium constant, calculated from table 3.12., was found as $k = (OH')_R(Cl')_S/(Cl')_R(OH')_S=0.84$, the individual deviations from this value, however, might make the replacement of activities by concentrations somewhat doubtful (this, in contradiction to (108)).

The experimental results were as follows (table 3.13): -

Table 3.13

Regeneration at Elevated Temperatures

| Exp. No. | Temperature of regeneration, °C | Feed-rate ml/min/cm$^2$ | No. of meq Cl' removed from resin |
|---|---|---|---|
| I | II | III | IV |
| 3C1 | 19.0 | 20.1 | 399 |
| 3C2 | 19.4 | 21.4 | 390 |
| 3C3 | 18.2 | 18.0 | 402 |
| 3D1 | 16.3 | 17.9 | 359 |
| 3D2 | 18.1 | 16.4 | 387 |
| 3D3 | 16.0 | 17.0 | 388 |
| 3E1 | 35.8 | 16.6 | 392 |
| 3E2 | 35.8 | 16.4 | 383 |
| 3E3 | 35.8 | Not carried to completion * | |
| 3G1 | 11.6 | 20.8 | 388 |
| 3G2 | 14.4 | 23.3 | 368 |
| 3G3 | 12.0 | 23.0 | 356 |

* Explained below

The results indicate that increase of the temperature from 12° to 36° does not improve the regeneration. The number of meq Cl' removed from the resin (column IV) stayed on the same level, except for the variation around average values noted earlier. Due to oversaturation of the $Ca(OH)_2$ - solution by the heating, precipitation of the excess occurred on contact of this solution with the resin. The growing precipitate hindered the completion of cycle 3E3 due to untolerably low flow-rates.

### 3.2.7.10. Regeneration with a Chloride-containing Solution

Execution of the ion-exchange as described above would require very considerable amounts of water, because of the low solubility of the regenerant $Ca(OH)_2$. We saw that regeneration with 2 Q sufficed for our purpose. At a

$Ca(OH)_2$-solubility of 1.65 g/l (122), the regenerant requires per equivalent of $KHCO_3$ (= 100 g) 74.1/1.65 = 45 l of water, or 450 $m^3$/t $KHCO_3$, if we assume carbonation and dehydration efficiencies of 100%. As this amount of water would exclude the use of distilled water for the process, the influence of the impurities in tap water was investigated. Of these impurities, the influence of Cl' would probably be the most serious, due to its lowering the driving-force for the regeneration. An indication to this effect had, in fact, been obtained earlier in the preliminary experiments with the short columns (par. 3.2.6.).

Local (Haifa, Israel) tap water analyses yielded average Cl'- contents of 350 ppm, that is about 10 meq/l. A regenerant solution containing that amount of Cl', added as KCl, was prepared, and one set of experiments was carried out to ascertain the feasibility of such a regeneration (series 3F). Experimental results were as follows (table 3.14):-

Table 3.14.

Regeneration with Chloride - Containing Regenerant.

| Exp. No. | Feed-rate ml/min/cm$^2$ | Chloride meq/l | contents ppm | (OH')/(Cl') meq/meq | Meq Cl' removed from the resin |
|---|---|---|---|---|---|
| I | II | III | IV | V | VI |
| 3F1 | 22.6 | 9.7 | 344 | 4.85 | 213 |
| 3F2 | 21.8 | 9.7 | 344 | 4.85 | 190 |
| 3F3 | 20.6 | 9.7 | 344 | 4.85 | 234 |

Throughout these experiments, 2 Q of regenerant were used. The results indicate clearly that the amount of Cl' removed from the resin (column VI) is only about half of that when regenerating with a chloride-free solution. The presence

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(122) C.S. Hodgman, Handbook of Chemistry and Physics (Cleveland 1955) p. 1596.

of Cl', even in the small concentration indicated, lowers the driving force to such an extent that completeness of regeneration is not attained, and that the capacity of the resin is utilised to the extent of about 35% only, instead of 65% (or higher).

If no way were found to lower the water requirements of the process, and if a purity as high as indicated (with well below 350 ppm Cl') were mandatory, the problem of the technical possibility of execution, both in Israel and abroad, would arise.

### 3.2.7.11. Regeneration in the Presence of Solid $Ca(OH)_2$.

Of those methods which might result in economy of water during the regeneration, the use of a slurry of $Ca(OH)_2$ is one of the most evident.

Preliminary experiments with a short column (par. 3.2.6.) had indicated that the transport of such a slurry in downflow through the resin would result in clogging. To test the possibility of such a mode of operation, regenerations were carried out batch-wise, by stirring a mixture of resin and regenerant and withdrawing samples for analysis of Cl' after settling. The experiments were done in measuring cylinders, under intensive mechanical stirring.

The fresh resin (Dowex-2, 8%) was cycled several times between R-OH and R-Cl, and finally converted to resin-chloride with a large excess of HCl, washed and dried at 110°.

The time required for attainment of equilibrium, was determined as follows: Of the resin, 23.1214 g (85.1 meq) were mixed with 1.885 liter $Ca(OH)_2$-solution (45.2 meq/l) containing 85.2 meq. Several grams of solid $Ca(OH)_2$ were added. Experimental results were as follows (table 3.15) :-

Table 3.15.

Regeneration in the Presence of Solid $Ca(OH)_2$ -

Determination of Equilibration Time.

| Time since start | Volume of sample ml | Volume of $AgNO_3$-solution ( N = 0.0996) | Meq Cl'/l |
|---|---|---|---|
| I | II | III | IV |
| 15 minutes | 10.00 | 2.15 | 21.4 |
| 30 minutes | 10.00 | 2.20 | 21.9 |
| 45 minutes | 10.00 | 2.20 | 21.9 |
| 67 hours | 10.00 | 2.20 | 21.9 |

After 30 minutes equilibrium had been attained. In total, 21.9 x 1.885 = 41.3 meq Cl' were removed from the resin, yielding as equilibrium constant

$$K_{OH}^{Cl} = \frac{(Cl')r}{(OH')r} : \frac{(Cl')s}{(OH')s} = \frac{85.1 - 41.3}{41.3} : \frac{21.9}{45.2} = 2.19$$

(45.2 is the unchanged concentration of $Ca(OH)_2$).

This constant differs little from that given in(123) for a nearly identical resin (6% instead of 8% crosslinking), to wit : 1.95.

As the influence of solid $Ca(OH)_2$ would be greater if the number of meq OH' initially in the solution would be smaller than that of meq Cl' in the resin, the following experiments were done. Two equal amounts of resin (as R-Cl) were mixed each with equal volumes of regenerant solution, to one of which excess of solid $Ca(OH)_2$ was added. The results were as follows:-

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(123) W.C. Bauman & R. McKellar, US Pat. 2614099 (14.10.1952).

Table 3.16.

Regeneration in Presence of Solid $Ca(OH)_2$.

| Exp. No. | Resin weight | | $Ca(OH)_2$-soln. | | Excess $Ca(OH)_2$ | Time of equilib. minutes | Meq Cl' removed from resin |
|---|---|---|---|---|---|---|---|
| | mg | meq | vol., ml | meq | | | |
| I | II | III | IV | V | VI | VII | VIII |
| 4B2 | 10007.7 | 22.0 | 300 | 13.9 | none | 120 | 10.7 |
| 4B3 | 10006.2 | 22.0 | 300 | 13.9 | present | 120 | 13.9 |

These results show that the amount of chloride removed from the resin in presence of solid $Ca(OH)_2$ is greater than the amount, removed in absence of that solid. The increase is $(13.9-10.7)/10.7 \sim 30\%$. For the purpose of conservation of water, this value is quite low, although it is considerably higher than the "improvements" given in (74), which proposed an analogous method of operation.

### 3.2.7.12. One-Time Regeneration with Phenolic $Ca(OH)_2$-solutions.

We saw that in attempting to decrease the water requirements of the process, re-use of the regenerant solutions (containing Cl') did not have the desired result. Increase of the regenerant temperature had little influence on the outcome. Addition of excess $Ca(OH)_2$ decreased the water requirements but to a certain extent, while requiring operation with a slurry. The advantages of the simple percolation of clear solutions being evident, a way was sought to increase the solubility of $Ca(OH)_2$ by the addition of chemicals.

It is, for example, known, that $NH_4Cl$(124) and KCl(125) increase the solubility of $Ca(OH)_2$ in water, although they, on account of their Cl'- contents, would be unsuitable in this

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(74) N.W.Rosenberg & W.E.Katz, US Pat. 2884310 (28.4.1959)
(124) A.A.Noyes & E.S.Chapin, Z.physik. Chem. <u>28</u> (1899) 518-22.
(125) G.L.Cabot, J.Soc. Chem. Ind. <u>16</u> (1897) 417-19.

particular case, the required Cl'-concentrations exceeding the available OH'-concentrations several times. Better in this respect would be substances not containing Cl'-ions, known examples of which are saccharose (126) and glycerol (127). These substances suffer, however, from the serious drawback, that their recovery from aqueous solutions would be probably very costly.

It has been known for over three quarters of a century that phenol, $C_6H_5OH$, increases the solubility of $Ca(OH)_2$ in water. In fact, its use for this purpose was proposed in 1887 (128) and later for the caustification of $Na_2SO_4$ with $Ca(OH)_2$, and in 1910 (129) for the analysis of $Ca^{\cdot\cdot}$ in dolomites. Examination of phenol for our purpose indicated that it might have at least two desirable characteristics. Firstly, the increase of solubility of $Ca(OH)_2$ is considerable. The system $Ca(OH)_2$-$C_6H_5OH$-$H_2O$ at 25° has been described (130). It teaches us that in the presence of solid $Ca(OH)_2$ the maximum $Ca(OH)_2$-normality in a solution of 9.9 wt-% phenol is 1.28. In the presence of $Ca(C_6H_5O)_2 \cdot 3H_2O$, and in a solution of 40.7 wt-% phenol, the normality of $Ca(OH)_2$ is raised to 2.26. By way of comparison it may be remarked, that in pure water of 25° the normality of $Ca(OH)_2$ is 0.043.

As a second desirable characteristic, it seemed that phenol would be recoverable to a considerable degree by extraction, a method which requires relatively low amounts of energy. This expectation was based on the fact that streams of industrial origin, intended for discard, had been subjected successfully to dephenolation by extraction for many years, leaving no more than a few ppm phenol in the discard.

Preliminary one-time regenerations with a phenolic $Ca(OH)_2$-solution were carried-out, to test the suitability of this solution for our purpose. The solution was prepared by

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(126) F.K.Cameron & H.E.Patten, J.Phys. Chem. 15 (1911) 67-72
(127) W.Herz & M. Knoch, Z.anorg. Chem. 46 (1905) 193-6.
(128) W.W.Staveley, Brit.Pat. 17657 (1887); J. Soc. Chem. Ind. 7 (1888) 807-15
(129) L.Lindet & V.Brasart, Anal. Chim. Analyt. Appl. 15 (1910) 293-5.
(130) G.J.Van Meurs, Z. physik. Chem. 91 (1916) 313.

first saturating water with phenol, by cooling a clear, saturated, hot (47°) solution to room temperature, and drawing off the clear aqueous layer. The phenol used was chemically pure, confirming (according to its producer) to purity standard "DAB 6" of the German Pharmacopoeia. Phenol was determined analytically by the method of Koppeschaar (131), according to which it was precipitated as tribromophenol with excess bromine (from excess KBr + a known amount of standardized $KBrO_3$-solution, in presence of HCl) and the excess $Br_2$ determined iodometrically with excess KI and a standardized $Na_2S_2O_3$ -solution.

The phenol-water mixture contained 75.9 g phenol/l. This was then saturated with $Ca(OH)_2$ ("chemically pure" quality) by prolonged stirring. The clear filtrate contained 863 meq OH/l = 32.0 g $Ca(OH)_2$/l (OH' expressed as $Ca(OH)_2$), that is about 19.4 times the solubility in pure water.

With this phenolic $Ca(OH)_2$-solution, two batch regenerations of R-Cl were undertaken. The experimental results were the following (table 3.17.) :-

Table 3.17.

Batch Regeneration with Phenolic $Ca(OH)_2$-Solution.

| Exp. No. | Resin | | Regenerant Soln. | | Duration of stirring minutes | Resultant Soln. | | |
|---|---|---|---|---|---|---|---|---|
| | g | meq | meq OH | mg phenol | | meq OH' | meq Cl' | mg $C_6H_5OH$ |
| I | II | III | IV | V | VI | VII | VIII | IX |
| 4B5 | 10.0013 | 22.0 | 22.0 | 1935 | 35 | 7.6 | 17.4 | 453 |
| 4B6 | 20.0065 | 44.0 | 44.0 | 3870 | 60 | 12.0 | 38.2 | 918 |

It is remarkable that in both experiments the total amount of inorganic anions in the resultant solution (columns VII and VIII) exceeded the amount introduced (column IV), in 4B5 by 25.0 - 22.0 = 3.0 meq, and in 4B6 by double that amount, 50.2 - 44.0 = 6.2 meq. The excess in both cases was 0.3 meq/g

(131) W.Koppeschaar, Z. anal. Chem. 15 (1876) 233, in F.P. Treadwell & W.T.Hall, Analytical Chemistry (New York 1951) vol. II p.633.

resin, and resulted from chemical binding of $C_6H_5O'$-anions, as will be established finally at a later stage of the experimentation (see par. 3.2.8.). During these experiments 0.3/2.20 = 13.6% of the resin exchange capacity was taken up by $C_6H_5O'$ - anions. This accounted for 0.3 x 94~28 mg phenol/g resin. The total amount of phenol taken up by the resin was (in 4B5) (1935-453)/10.0013~148 mg/g, and (in 4B6) (3870-918)/20.0065, also 148 mg/g, of which 28 mg/g were thus exchanged, and 120 mg/g adsorbed, probably as undissociated molecules. This combined chemical binding and physical adsorbtion of phenol on Dowex-2 resin chloride has also been noticed elsewhere (132). On the other hand, a somewhat different resin (Amberlite IRA-400, containing $-CH_2N(CH_3)_3$ groups instead of $-CH_2N(CH_3)_2CH_2CH_2OH$) was said (133) to absorb phenol only physically, when in the chloride state. This result is somewhat doubtful, in view of the slight difference between the two types of resin.

The efficiency of the regenerant solution was measured, as formerly, by the amount of chloride, removed from the resin. These amounts were 17.4 meq/25.5 ml regenerant respectively 38.2 meq/51.0 ml (column VIII, table 3.17.). For the analogous removal of 400 meq Cl' from the resin (as in par.3.2.7.5., table 3.6.) 400 x 25.5/17.4 = 586 ml respectively 400 x 51.0/38.2 = 535 ml regenerant would be required. In comparison with a former regenerant consumption of 16-20 l (table 3.6.) a water saving of 95% or over would thus be effected. Regenerant efficiency, defined as meq Cl' removed per meq OH' introduced, would be 79% or higher, as compared with 45-58% (table 3.6., columns XVIII and XX).

Furthermore, it is beyond doubt that regeneration in a column (with this phenolic $Ca(OH)_2$-solution) would improve the regeneration still further, as compared with that of the batch experiments, due to the constantly fresh solution contacting the resin in the former case.

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(132) R.E.Anderson, & R.D. Hansen, Ind. Eng. Chem. 47 (1955) 71-5.

(133) A.Eaves & W.A.Munday, J. Appl. Chem. 9 (1959) 145-52.

To complete the picture of these batch experiments, the resin as obtained from the regeneration of 4B6 was loaded with 1.32 N KCl, after having been washed on a filter with water at room temperature(until the effluent showed no phenol) and dried by vacuum (at room temperature) and by gentle pressing between leaves of filter paper. Experimental results of the loading were as follows (table 3.18.) :-

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Table 3.18.

Batch - Loading after Regeneration with Phenolic $Ca(OH)_2$-Solution.

| Exp. No. | Resin meq $OH'$ | Resin meq $C_6H_5O'$ | Resin meq $Cl'$ | Loading soln. meq KCl | Duration of stirring, minutes | Resultant Solution meq $OH'$ | Resultant Solution meq $Cl'$ | Resultant Solution mg $C_6H_5OH$ |
|---|---|---|---|---|---|---|---|---|
| I | II | III | IV | V | VI | VII | VIII | IX |
| 4B6 (loading) | 32.2* | 6.0 | 5.8** | 44.0 | 45 | 6.5 | 34.2 | 285 |

* From column VIII of table 3.17., and from the calculated phenol-contents of the resin.

** By difference.

The loading efficiency, expressed as meq KOH formed per meq KCl introduced, was rather low, of the order of 15%. The major part of the KCl introduced remained unconverted. As the resultant solution contained (columns VII + VIII) 40.7 meq $OH' + Cl'$, it should contain about $44.0 - 40.7 = 3.3$ meq of phenol = 310 mg. The phenol contents of this solution, 285 mg, come very near to this value.

These preliminary experiments lead to the following conclusions: Regeneration with a phenolic $Ca(OH)_2$-solution saves very considerable amounts of water, at least 95% of that used formerly. The efficiency of the regenerant is increased about 1.7 times, implying that $2/1.7 \approx 1.2$ Q would suffice. The phenol adsorbed physically and present after the water wash is not removed in the subsequent loading. The reduced production of KOH is due probably to $C_6H_5O'$ - ions on the resin, and perhaps also to adsorbed $C_6H_5OH$ - molecules; of the $C_6H_5O'$ - ions, a part only is removed in the loading. The reduced production will be discussed in greater detail when considering cyclic experiments; it is of considerable importance in connection with the utilisation of the resin.

### 3.2.7.13. Regeneration with Phenolic $Ca(OH)_2$-solutions - cyclic experiments.

Cyclic experiments were carried out in the same column (of about 80 cm height) as before. The resin was converted to R-OH with the aid of diluted KOH and washed with water prior to the experiments.

A phenolic $Ca(OH)_2$-solution containing 31.6 g $Ca(OH)_2$ per liter (0.853 N) and 74.6 g $C_6H_5OH$/l (0.794 N) was used. Experimental results were as in table 3.19.

The amount of regenerant solution was kept constant in these experiments, irrespective of the production of KOH.

The exact amount of phenol, sorbed by the resin before experiment 4E1, was not known. In view of the previous regeneration with KOH, any phenol present would be physically adsorbed only. This is indicated by the absence of phenol from the loading effluent of 4E1 (column X). During these first cycles the amounts of phenol "led in" and "obtained" approached each other gradually. In 4E1, the difference between these two amounts was

$$1190 - (770 + 139) = 281 \text{ meq},$$

the 139 meq appearing in the loading effluent of the next cycle, 4E2; in 4E2, this difference was

$$1190 - (654 + 233) = 303 \text{ meq};$$

and in 4E3,

$$1190 - (985 + 169) = 36 \text{ meq only}.$$

For 4F1, no phenol balance could be drawn up, as the results of the next cycle, 4F2, proved to be unreliable, due to faulty analyses; for this reason, 4F2 was not included in the table.

## Table 3.19.

### Regeneration with Phenolic $Ca(OH)_2$-Solution - Successive Cycles

| Exp. No. | KCl - solution | | | Water | | Process solution | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Conc. g/l | No. of meq introd. | feed-rate ml/min/cm$^2$ | vol. ml | feed-rate ml/min/cm$^2$ | vol. ml | KOH meq | KCl meq | $C_6H_5OH$ meq(1) |
| I | II | III | IV | V | VI | VII | VIII | IX | X |
| 4E1 | 100.6 | 563 | 18.5 | 600 | 14.6 | 750 | 470 | 103 | 0 |
| 4E2 | 100.6 | 573 | 19.5 | 600 | 26.8 | 750 | 180 | 405 | 139 |
| 4E3 | 100.6 | 607 | 21.4 | 600 | 22.8 | 800 | 210 | 423 | 233 |
| 4F1 | 185.7 | 637 | 22.0 | 600 | 21.2 | 645 | 173 | 428 | 169 |

| Discards(2) | | Regenerant solution | | | Regeneration effluent(3) | | |
|---|---|---|---|---|---|---|---|
| KOH meq | KCl meq | OH meq | $C_6H_5OH$ meq | feed-rate ml/min/cm$^2$ | Cl meq | OH meq | $C_6H_5OH$ meq(1) |
| XI | XII | XIII | XIV | XV | XVI | XVII | XVIII |
| 2.1 | 0.2 | 1280 | 1190 | 20.3 | 398 | 868 | 770 |
| 3.5 | 1.5 | 1280 | 1190 | 18.7 | 254 | 967 | 654 |
| 3.7 | 1.2 | 1280 | 1190 | 17.5 | 224 | 1045 | 985 |
| 6.7 | 0 | 1280 | 1190 | 16.6 | 197 | 1057 | 1021 |

(1) As formerly, acidimetric milliequivalents: 1 meq = 94 mg.

(2) Any phenol-contents included in the "process solution" (column X).

(3) Including rinse-water.

This trend of adsorbtion and desorbtion of phenol is also reflected in the mass-balance of Cl' and OH' for the individual cycles. See table 3.20. :-

Table 3.20

Regeneration with Phenolic $Ca(OH)_2$ - Solution (Mass Balance)

| Exp. No. | Loading + Washing | | | Regeneration + Washing | | | |
|---|---|---|---|---|---|---|---|
| | KCl meq in | Cl'+OH' meq out | $C_6H_5OH$ meq out | $Ca(OH)_2$ meq in | $C_6H_5OH$ meq in | Cl'+OH' meq out | $C_6H_5OH$ meq out |
| I | II | III | IV | V | VI | VII | VIII |
| 4E1 | 563 | 575 | 0 | 1280 | 1190 | 1266 | 770 |
| 4E2 | 573 | 590 | 139 | 1280 | 1190 | 1221 | 654 |
| 4E3 | 607 | 638 | 233 | 1280 | 1190 | 1269 | 985 |
| 4F1 | 637 | 608 | 169 | 1280 | 1190 | 1254 | 1021 |

On comparison of columns II and III, and V and VII, small differences will be noted. These are attributed to the transfer of electrolytes from one phase to the next, as was set out in par. 3.2.7.5. (table 3.8., and further). The differences between columns VI and VIII + IV (this last, of the next cycle) are of an altogether different order of magnitude, and could not serve for compensation of the small differences in the Cl' + OH' balance.

Thus, although absolute proof is lacking, there are strong indications that phenol is adsorbed and desorbed physically only in these cycles, and that any chemically bound phenol - as phenolate ion - is not removed. There are two further indications in the same direction :-

1) The small production of KOH (column VIII in table 3.19). The first cycle, 4E1, was preceded by KOH-regeneration, and should therefore not be taken into consideration. The other cycles show, however, a production roughly half of that in table 3.6., column XI. It is suspected that on continuation the production of KOH would become even lower. This is also indicated by the second point.

2) The equilibrium constant for the exchange of chloride by phenolate ions on Dowex-2(134), K = $(C_6H_5O'_R)\ (Cl'_S)\ /\ (C_6H_5O'_S)\ (Cl'_R)$, which was found to possess the value of 8.7. From the high value it follows that any phenolate ions, once "caught" by the resin, would be removed but with difficulty by chloride ions. This holds at least qualitatively in spite of the presence of a third species of ions on the resin - the hydroxide ions. A final indication of the correctness of this description will be given in par. 3.2.8.

This small production of KOH results in small loading efficiencies, i.e. a high ratio between incoming KCl-normality and outgoing KOH-normality, and therefore in considerable contamination of the process solution, up to 71% in 4F1. This value is very near to the limit of relative KCl-concentration, 75.1%, and would therefore allow but a very small precipitation-per-pass of subsequently formed $KHCO_3$.

### 3.2.8. The Drawbacks of Operation by Anion-exchange; Discussion of the Possible Uses of Cation-exchange

If the experiments with anion-exchange are regarded from the point of view of the economic and technical feasibility of the process, the following stands out :- Because of the ease of operation with clear solutions, we would prefer their use over that of slurries. Purely aqueous $Ca(OH)_2$-solutions, in an amount equimolar to the amount of the KOH formed (that is, 2 Q) suffice to execute the regeneration, i.e. to remove an amount of Cl' from the resin equal to that loaded in the first stage. This mode of operation suffers from a considerable expenditure of water, of the order of 450 $m^3$/t $KHCO_3$ or 800 $m^3$/t KOH, which water should moreover be of low chloride-contents, well below 350 ppm. These demands are so stringent that an economic realization of the present process in this way would be impossible.

By the use of phenolic $Ca(OH)_2$ as regenerant the water requirements of the process were lowered by more than 95% of their former value, at the same time even increasing the regeneration efficiency. The loading efficiency was, however, seriously impaired, by the exchange of phenolate ions for chloride ions on the resin.

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(134) S. Peterson, Ann. N.Y. Acad. Sci. 57 (1953) 144-58

We should therefore look for another method of operation which would retain the advantages of phenol without suffering from its drawbacks. Now, as $C_6H_5O'$-<u>an</u>ions cause the decrease of KOH-formation, the use of a <u>cation</u>-exchanger would circumvent this difficulty.

The reactions which would take place in case of the use of a cation-exchanger would be the following :-

Loading: $Ca_{\frac{1}{2}}\text{-R} + KCl \longrightarrow K\text{-R} + \frac{1}{2}CaCl_2$

Regeneration: $K\text{-R} + \frac{1}{2}Ca(OH)_2 \longrightarrow Ca_{\frac{1}{2}}\text{-R} + KOH$

The product, KOH, would be formed in the stage where $Ca(OH)_2$ was introduced. It is precisely this fact which has been the cause of disapproval of cation-exchange for the desired conversion; due to the low solubility of $Ca(OH)_2$ (0.045 N) a very dilute KOH-solution (0.045 N = 2.5 g/l, or less, because of incomplete conversion or dilution) would be formed (see for example (59)), which process would be devoid of any industrial interest.

This serious limitation can now be overcome with the aid of the former innovation, namely the use of phenol. Solutions of up to 2.26 N in $Ca(OH)_2$ can be prepared in this manner (130), and corresponding considerable KOH-concentrations might be expected (Note 10). On the other hand, cation-exchange ought to be exempt from the difficulties caused by phenolate anions, while retaining the advantages of the use of phenol addition.

Over and above this, cation exchange might be expected to produce a purer product than anion exchange, and this for the very same reason as that which disqualified its use until now. In <u>an</u>ion exchange, KOH was formed according to

$$KCl + R\text{-}OH \longrightarrow KOH + R\text{-}Cl$$

that is, in the stage where KCl was introduced, with the

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(59) Dow Chemical Co., Brit.Pat.662314(5.12.1951) page 1, lines 46 &c

(130) G.J. van Meurs, Z.physik.Chem <u>91</u> (1916) 313

<u>Note 10:</u> In the ensuing experiments, no such high $Ca(OH)_2$ concentrations were used, because of the observed viscosity of the solutions. The $Ca(OH)_2$-normality used was 0.68 -0.78. No higher-temperature experiments, such as might lower the viscosity of the regenerant, were carried out.

unavoidable contamination of KOH by KCl. In cation exchange, in contrast, due to inversion of the order of the reactions, no contamination of the KOH by chloride would be expected, as the relevant reaction is then

$$K\text{-}R + \tfrac{1}{2}Ca(OH)_2 \longrightarrow Ca_{\frac{1}{2}}\text{-}R + KOH.$$

The importance of this advantage could hardly be overestimated, not the least from the point of view of the commercial value of the product. Some $Ca(OH)_2$ (and eventually, $C_6H_5OH$, if used) might accompany the KOH produced; their removal, however, might be expected to proceed easily (Note 10a).

The use of cation-exchangers would also have the contributory advantage, that these resins would be more stable than anion-exchangers, chemically as well as thermally (Note 10b), and this, due to the chemical nature of the reactive groups. Also, the price of cation exchangers would be about half that of anion exchangers on a weight basis, and even less on an equivalent basis.

All these arguments made the use of cation exchangers for the present purpose a promising proposition. Experiments had to be carried out to verify these expectations.

## 3.3. Cation Exchange

### 3.3.1. Introduction

Experiments utilising cation-exchange were carried out to investigate the feasibility of this method for our purpose. Based on the arguments given at the end of the last paragraph (3.2.8.), cation-exchange was expected to give better results than anion-exchange : consumption of small amounts of water and delivery of a KOH-solution free of chloride, at reasonable loading and regeneration efficiencies.

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Note 10a: It is not clear whether pure KOH could not be produced by the present method, if concentration of the aqueous solution were carried out thermally and not by water-transfer. In this case it is possible, that removal of the phenol(e.g.by extraction) would leave a solution from which pure KOH were obtainable.

Note 10b: The cation-exchanging resins based on a sulfonated polystyrene - divinylbenzene skelet are stable until about 120° (134a).

(134a) F.C.Nachod & J.Schubert, Ion Exchange Technology (New York 1956) p. 24-5

As an industrial realization of this process might be envisaged in Sdom (Sodom), because of the proximity of the KCl plant, and as NaCl costs there little beyond manipulating expenses, the experiments with KCl were followed by comparative ones with NaCl. Using a considerable excess for the loading step, the suitability of NaCl as raw material for production of NaOH (and subsequently $NaHCO_3$ and $Na_2CO_3$) in this way was investigated.

An exploratory research of the influence of the following more important variables was conducted: the concentration of the influent KCl; its amount relative to the total resin capacity; the direction of loading, downflow or upflow; and the feed-rate of the KCl-solution. As regards the regenerant phenolic $Ca(OH)_2$-solution, variations in its feed-rate, amount and direction of flow were considered.

### 3.3.2. Choice of the Resin

There are commercially available mainly two kinds of cation-exchangers based on the poly-(styrene-divinylbenzene) "skeleton", depending on the chemical nature of the functional group attached. They are the sulfonic and carboxylic acid group resins. We preferred the former over the latter, as sulfonic acids are more highly dissociated (135).

Because of its availability at short notice, the analytical grade of Amberlite IR-120, a product of the Rohm & Haas Company, U.S.A., was taken for the present work. In accord with industrial practice, a product of "8% cross-linking" was used. The difference between "analytical" and "standard" grades of Amberlite Resins is, that the former have undergone several complete depletion and regeneration cycles in order to remove traces of fines and of intermediates left over from the production (136). This treatment would have little influence on the results, and was therefore not considered to disqualify this grade for the experiments.

To summarize : The experiments with cation-exchange were carried out on Amberlite IR-120, 8% cross-linked, analytical grade.

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(135) R. Kunin, Ion Exchange Resins (New York 1958) p.35

(136) The British Drug Houses, Laboratory Chemicals' Catalogue (Poole, 1958) p.330

### 3.3.3. Analysis of the Cations

The use of a cation-exchanging resin necessitated an analysis of the partaking cations. This can be seen from the equations representing this method :

$$\text{Loading} \quad : KCl + Ca_{\frac{1}{2}}\text{-}R \longrightarrow K\text{-}R + \tfrac{1}{2}CaCl_2$$

$$\text{Regeneration} : K\text{-}R + \tfrac{1}{2}Ca(OH)_2\ (C_6H_5OH) \rightarrow Ca_{\frac{1}{2}}\text{-}R + KOH(C_6H_5OH)$$

In principle, per reaction only one anion took part, in the loading Cl' and in the regeneration OH' (the presence of phenol or its ions did not change the picture, as set out below). Analysis for anions only would not give therefore an indication of the progress of each conversion.

Analysis of Ca•• was effected by titration with a standard solution of disodium ethylene diamine tetraacetate (EDTA, "versenate") in a buffered $NH_4OH$-$NH_4Cl$ medium, with Eriochrome Black as indicator (137). The use of this indicator and buffer, as recommended (137) for mixtures of Ca••+Mg••, instead of Murexide + 1% KOH, as recommended there for solutions containing Ca•• only, resulted from the observation (138) that the change of colour in the former case was easier to observe than in the latter, and that the analysis gave therefore higher reproducibility.

Potassium was determined indirectly, in two ways :-

1) By deducting the value of (Ca••) from that of the total anions, (Cl')+(OH')

2) By deducting (Ca••) from the total cation concentration, determined by conversion of all cations to H• with the aid of a hydrogen-resin after neutralisation of the initially present OH'.

The second way served only for confirmation of the results obtained in the first.

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(137) Kuang Lu Cheng, T. Kurtz & R.H. Bray, Anal.Chem. 24 (1952) 1640-1

(138) Israel Mining Industries, Analytical Laboratory, Unpublished results

In some cycles $K^{\cdot}$ was determined also directly as the tetraphenyl boron salt (138a). Phenol was found to increase the results by at most 2% relatively (138b). This direct determination served for confirmation only of the indirect, first mentioned, method.

In drawing up the balance of cations and anions, phenol did not interfere as it was expressed as undissociated $C_6H_5OH$. Any $(C_6H_5O)_2Ca$ present, for example, would on analysis for cations reveal all its $Ca^{\cdot\cdot}$, due to ionic dissociation according to

$$(C_6H_5O)_2Ca \longrightarrow 2C_6H_5O' + Ca^{\cdot\cdot} \quad ;$$

the $Ca^{\cdot\cdot}$ was then expressed as $Ca(OH)_2$. The same held for any $C_6H_5OK$ present. Phenol, on the other hand, was determined as set out above, in strongly acid medium, where the reaction

$$C_6H_5O' + H^{\cdot} \longrightarrow C_6H_5OH$$

proceeded to the right; any phenolate anions were reported as undissociated $C_6H_5OH$ only.

### 3.3.4. Preliminary Experiment with a Short Column (29 cm)

A glass column of 27 mm inner diameter was filled with 150 g Amberlite IR-120. The resin rested on a disc of sintered glass, and occupied approximately 29 cm of the height (Note 11).

A stopcock under the disc controlled the flow; downflow only was practiced.

The capacity of the resin was calculated as follows: The oven-dry (so called "free-flowing") resin contained approximately 4.25 meq/g (139). At an average moisture

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(138a) K. Sporek & A.F. Williams, The Analyst <u>80</u> (1955)347-54

(138b) Israel Mining Industries, Analytical Laboratory, Unpublished results

(139) T.R.E. Kressman, in C.Calmon & T.R.E. Kressman, Ion Exchangers in Organic and Biochemistry (New York 1957) p. 116

<u>Note 11</u>: This height resulted in a bulk density of $150/(29 \times \pi \times 2.7^2)\frac{1}{4} = 0.90$ g/ml.

contents of 46% as it was when packed (determined for each lot separately by the producer), the commercial resin (as long as it came from closed, original, containers) contained $4.25(1-0.46) = 2.3$ meq/g.

The total column capacity was thus $150 \times 2.3 = 345$ meq.

The resin was conditioned by cycling it once only in the $K^{\cdot}$ - $H^{\cdot}$ - cycle, with the aid of 2.7 eq KCl and subsequently 3.0 eq HCl. After thorough washing to a weakly acid effluent, conversion to calcium-resin was effected by passing slowly a phenolic $Ca(OH)_2$-solution containing 0.853 eq $OH'$/l and 74.6 g $C_6H_5OH$/l. The conversion was noted through the heat evolved; the "heat-front" moved progressively through the column. When it had reached the bottom, the pH of the effluent was 10. Another 100 ml regenerant were then passed. In all, 600 ml regenerant were used. The resin was then washed until a neutral, odourless effluent was obtained.

This resin was then loaded with 350 meq KCl at a low feed-rate, when 245 meq $Ca^{\cdot\cdot}$ (as $CaCl_2$) were removed from it. On regeneration with 683 meq of the aforementioned $Ca(OH)_2$-solution, containing 636 meq phenol, a solution of the following composition was obtained : 221 meq KOH (as 16.5 g/l), 353 meq $Ca(OH)_2$ (as 17 g/l) and 543 meq $C_6H_5OH$ (as 68 g/l). No chloride could be detected in this solution. No attempt was made to analyse all discards, or to establish a balance of materials.

This preliminary example showed that it was in principle possible to obtain a phenolic KOH-solution in this way, which solution would be quite free of chloride, and contain nearly all the phenol introduced. Little interference from phenolate ions was hence to be expected. This expectation was confirmed in the subsequent experiments.

## 3.3.5. Experiments with a Column 95 cm high

### 3.3.5.1. Setup of the Column

A longer column was set up for the execution of cyclic experiments involving the introduction of several variables. The same glass column as used in the anion-exchange experiments was taken here. Its inner diameter was 27 mm. 450 g Amberlite IR-120 were placed in this column after swelling in water. The resin rested on a perforated glass disc covered with a layer of 2 cm glass wool, and occupied some 95 cm of the height, this varying ± 10% depending on the state of the resin and its position in the cycle (note 12). The total capacity of the column was 2.3 x 450 = 1035 meq.

When passing solutions upwards through this column, satisfactory flow-rates could be achieved only after a filter had been placed above the resin to prevent its removal. This was achieved by placing a perforated porcelain filter disc, hand-ground to the proper diameter, between two rubber rings just above the resin top. These rings were made from rubber stoppers with large diameter borings.

The necessary flow rates were obtained by placing the reagent vessels on a platform 2½ m above the resin top. Vessels and stopcocks were all-glass, while the stoppers and tubing consisted of rubber.

The feed-rates were defined as in the anion-exchange experiments, that is, as the ratio of the volumetric flow, ml/min, and the cross-section area of the empty column, $cm^2$.

The resin was conditioned by converting it from hydrogen-resin to potassium resin (with the aid of 2200 meq KCl) and afterwards to calcium resin (with 2130 meq $Ca(OH)_2$ in phenolic solution). After thorough and prolonged washing and backwashing, experiments introducing several variables were carried out.

### 3.3.5.2. Loading in Down- and Upflow

At the start of each cycle, the interstitial space in the column is filled with water from the previous washing. The KCl-solutions used for the loading have specific gravities above that of water (note 13). If loading with a specifically heavier solution takes place from above (that is, in downflow), mixing due to this difference in specific gravities probably occurs, with resulting decrease of the degree of separation between formed $CaCl_2$ and unchanged KCl, and/or decrease of

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Note 12 : This height yielded a bulk density of 0.83 ± 0.08 g/ml

Note 13 : Specific gravities for KCl-solutions : 100 g/l -- 1.06 g/ml; 300 g/l -- 1.17 g/ml.

one or more of the concentrations. If this mixing occurs to any marked degree, then loading with the KCl-solution from below would lessen the undesirable effects mentioned.

The following experimental results were considered (table 3.21.):-

Table 3.21.

Loading Experiments by Cation Exchange

| Exp. No. | KCl - solution | | | | No.of meq $K^{\cdot}$ in loading + washing effluent | meq $K^{\cdot}$ loaded on the resin (calculated) |
|---|---|---|---|---|---|---|
| | Conc. g/l | Feed-rate ml/min /cm$^2$ | Direction of flow | No.of meq introd. | | |
| I | II | III | IV | V | VI | VII |
| 7A1 | 100.6 | 36.0 | down | 1038 | 358 | 680 |
| 7A2 | 100.6 | 16.6 | " | 1038 | 323 | 715 |
| 7A3 | 97.5 | 18.1 | " | 1026 | 303 | 723 |
| 7A4 | 97.5 | 23.9 | " | 1019 | 449 | 570 |
| 7A5 | 97.5 | 24.6 | " | 1960 | 1063 | 897 |
| 7A7 | 97.5 | 19.9 | " | 2026 | 1180 | 846 |
| 7A8 | 296.5 | 4.7 | " | 2068 | 1279 | 789 |
| 7A9 | 296.5 | 3.0 | " | 4156 | 3162 | 994 |
| 7A10 | 293.8 | 12.2 | up | 3938 | 3126 | 812 |
| 7A11 | 293.8 | 43.8 | " | 4048 | 3438 | 610 |
| 7A12 | 293.8 | 5.2 | " | 3938 | 2983 | 955 |

Since each loading experiment was followed by a regeneration, into which several variables were introduced as well, the variation around average values which was noted for the anion-exchange experiments would be even more marked in the present case.

As a criterion for the desired conversion, the amount of meq $K^{\cdot}$ loaded on the resin was taken. This amount was calculated (in table 3.21., column VII) from the difference of the number of meq $K^{\cdot}$ in the influent solution (column V) and that in the loading + washing effluents (column VI). The average of these amounts loaded on the resin was, for downflow (experiments 7A1-9) 777 meq, and for upflow (experiments 7A10-12) 792 meq.

Thus, although variation in the results was noted, the impression was gained that no important advantages should be expected from upflow as compared with downflow. As the latter mode of operation (downflow) could be carried out more simply than the former, it was applied in the flowsheet

### 3.3.5.3. Loading with KCl at Different Concentrations

Experiments were carried out at two levels of KCl-concentration : 97.5 - 100.6 g/l and 293.8 - 296.5 g/l.

Table 3.21. gives the results pertaining to these experiments. Part of the experiments at the higher concentration were executed at a lower feed-rate, so that the number of meq entering the column per time unit would be of the same order of magnitude as that number for the more diluted solutions.

The results of experiment 7A1, which was preceded by a total regeneration were not taken into consideration in this connection. The experimental results then indicate that at the higher concentration the tendency is noted for a more complete replacement of $Ca^{\bullet\bullet}$ by $K^{\bullet}$ during the loading. It will be shown below that this tendency was partly due to the influence of the feed-rate. Still, at about 100 g/l, (experiments 7A2-7)on the average 750 meq of $K^{\bullet}$ were loaded on the resin, while at 300 g/l (experiments 7A8-12) on the average 832 meq were loaded. These results would indicate higher concentration to be the more favourable way of operation.

From the point of view of the flowsheet, the more concentrated influent KCl-solution is advantageous for the ultimate separation between unchanged KCl and produced $CaCl_2$. This separation is required for economic operation aimed at recycling the unused KCl. The ternary system $KCl-CaCl_2-H_2O$ at 25° (140) shows that up to 44.7 g $CaCl_2$/100 g solution, a solution saturated with respect to KCl will be in equilibrium with solid pure KCl only. This solution will then contain 3.0 g KCl and 52.3 g $H_2O$ per 100 g solution, or, at a specific

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(140) W.B. Lee & A.C.Egerton, J.Chem.Soc. 123 (1923) 706-16; A.Seidell, Solubilities of Inorganic and Metalorganic Compounds (New York, 1940) vol. I p. 287

gravity of 1.485, 662 g $CaCl_2$/l and 47 g KCl/l. As long as the KCl-$CaCl_2$-solution contains less than 662 g $CaCl_2$/l (at 25°), water removal will result in precipitation of pure KCl only. As it will be desirable to have to remove as little water (per ton of KCl) as possible, operation with a KCl-solution as concentrated as the other factors would allow will thus be advantageous.

### 3.3.5.4. Loading with KCl in Different Amounts

In general, the amount of KCl used will have influence on the degree to which the resin is loaded. The ratio between the number of meq loading agent and the total resin capacity, expressed in meq, has been termed "symmetry ratio" (141), or $r_s$. The experimental results of table 3.21. illustrate the influence of three symmetry ratio's; $r_s = 1$, 1019-1038 meq (7A2 - 4); $r_s = 2$, 1960 - 2068 meq (7A5 - 8); and $r_s = 4$, 3938 - 4156 meq (7A9 - 12). The capacity of the resin equalled 1035 meq. At $r_s = 1$ (approximately), on the average 669 meq were loaded on the resin. When doubling $r_s$, the amount loaded increased sharply to an average of 844 meq. At the highest level tried, where $r_s = 4$, approximately the same amount (843 meq on the average) was loaded on the resin.

These results show that when loading at $r_s = 2$, the degree of saturation of the resin was 844/1035 $\doteq$ (say) 81%, as opposed to 669/1035 = less than 65% at $r_s = 1$. At $r_s = 4$, the degree of saturation was not increased over that, attained at $r_s = 2$. This was confirmed in the subsequent loading with NaCl, at $r_s = 10$ (par.3.3.5.9.), although the number of experiments with NaCl was limited.

The use of a greater excess KCl would result in a greater recycle of KCl from the ion exchange effluent to the influent solution. An economic optimum should have to be found from several sets of conditions. This optimum probably lies between $r_s = 1$ and $r_s = 2$.

### 3.3.5.5. Loading at Different Feed-rates

The feed-rate of the KCl solution was expected to have a very considerable influence on the amount of KCl loaded on the resin.

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(141) For example, R. Kunin & R.E.Barry, Ind.Eng.Chem. <u>41</u> (1949) 1270

The experimental results, as given in table 3.21., indicated this influence on the exchange. For the more concentrated KCl-solutions, an increase in the feed-rate resulted in a decrease in the amount of $K^{\cdot}$ loaded, at an approximately constant $r_s$ (7A9 - 12). Thus, at a feed-rate of 3.0 ml/min/$cm^2$ 994 meq were loaded (7A9); at 5.2 - 955 (7A12); at 12.2 - 812 (7A10); and at 43.8 only 610 (7A11).

The experiments for which $r_s \sim 2$ included two concentrations, and the data for each concentration were insufficient to draw conclusions as to the influence of the feed-rate.

The experimental results indicated that the time of residence of the KCl-solution in the exchanger was of major influence. The lower the feed-rate, the longer the residence time (the product of these two equalled the column height), and the greater the number of meq loaded on the resin. At relatively low feed-rates (up to 12.2 ml/min/$cm^2$, exp. 7A9-11), this relation was a straight line, indicating the direct proportionality of the two factors (residence time and amount loaded). This is in agreement with the generally accepted notion, that diffusion and not the chemical reaction controls cation-exchange for strongly dissociated exchangers.

### 3.3.5.6. The Amount of Regenerant $Ca(OH)_2$

The regeneration forms that phase of the cycle in which the product, the KOH-solution, is made. The first consideration governing the amount of regenerant $Ca(OH)_2$-solution is therefore its influence on the amount, and on the concentration, of the formed KOH.

Two experiments (7A1-2) were undertaken with 2040 meq $Ca(OH)_2$ (in phenolic solution), that is at $r_s \sim 2$. Their results, together with subsequent experiments, were collected in table 3.22.

Table 3.22.

Regeneration Experiments with a Cation Exchanger

| Experiment Number | Phenolic $Ca(OH)_2$ - solution | | | | | | Process solution | | | | | Discards | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Direction of flow | $Ca^{\cdot\cdot}$ normality | $C_6H_5OH$ g/l | Meq $Ca^{\cdot\cdot}$ introd. | g $C_6H_5OH$ introd. | Feed-rate ml/min/cm2 | Meq $K^{\cdot}$ | Meq $Ca^{\cdot\cdot}$ | g $C_6H_5OH$ | Vol. ml. | KOH g/l | Meq $K^{\cdot}$ | Meq $Ca^{\cdot\cdot}$ |
| I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII | XIII | XIV |
| 7A1 | down | 0.680 | 70.3 | 2040 | 211 | 24.0 | 588 | 1234 | 192 | 2750 | 12.1 | 36 | 141 |
| 7A2 | " | " | " | 2040 | 211 | 19.5 | 602 | 1159 | 178 | 2750 | 12.3 | 32 | 243 |
| 7A3 | " | " | " | 1020 | 105 | 12.0 | 454 | 323 | 74 | 1300 | 19.6 | 110 | 150 |
| 7A4 | " | " | " | 1156 | 119 | 6.8 | 492 | 369 | 88 | 1500 | 18.4 | 27 | 243 |
| 7A5 | " | " | " | 1326 | 137 | 11.0 | 702 | 318 | 104 | 1600 | 24.6 | 155 | 177 |
| 7A7 | up | 0.783 | 73.0 | 1292 | 121 | 4.4 | 758 | 232 | 89 | 1380 | 30.8 | 0 | 336 |
| 7A8 | " | " | " | 1265 | 114 | 4.4 | 698 | 210 | 79 | 1370 | 28.5 | 0 | 374 |
| 7A9 | " | " | " | 1276 | 119 | 4.2 | 885 | 82 | 88 | 1364 | 36.4 | 30 | 284 |
| 7A10 | " | " | " | 1292 | 120 | 29.3 | 619 | 316 | 86 | 1345 | 25.8 | 44 | 268 |
| 7A11 | " | " | " | 1253 | 117 | 9.4 | 640 | 315 | 86 | 1340 | 26.8 | 0 | 297 |
| 7A12 | " | " | " | 1331 | 124 | 3.2 | 827 | 153 | 89 | 1450 | 32.0 | 0 | 344 |

The composition of the several fractions in the regeneration effluent (exclusive of the subsequent washing) of experiment 7A2 was as per table 3.23. and fig. 3.9.

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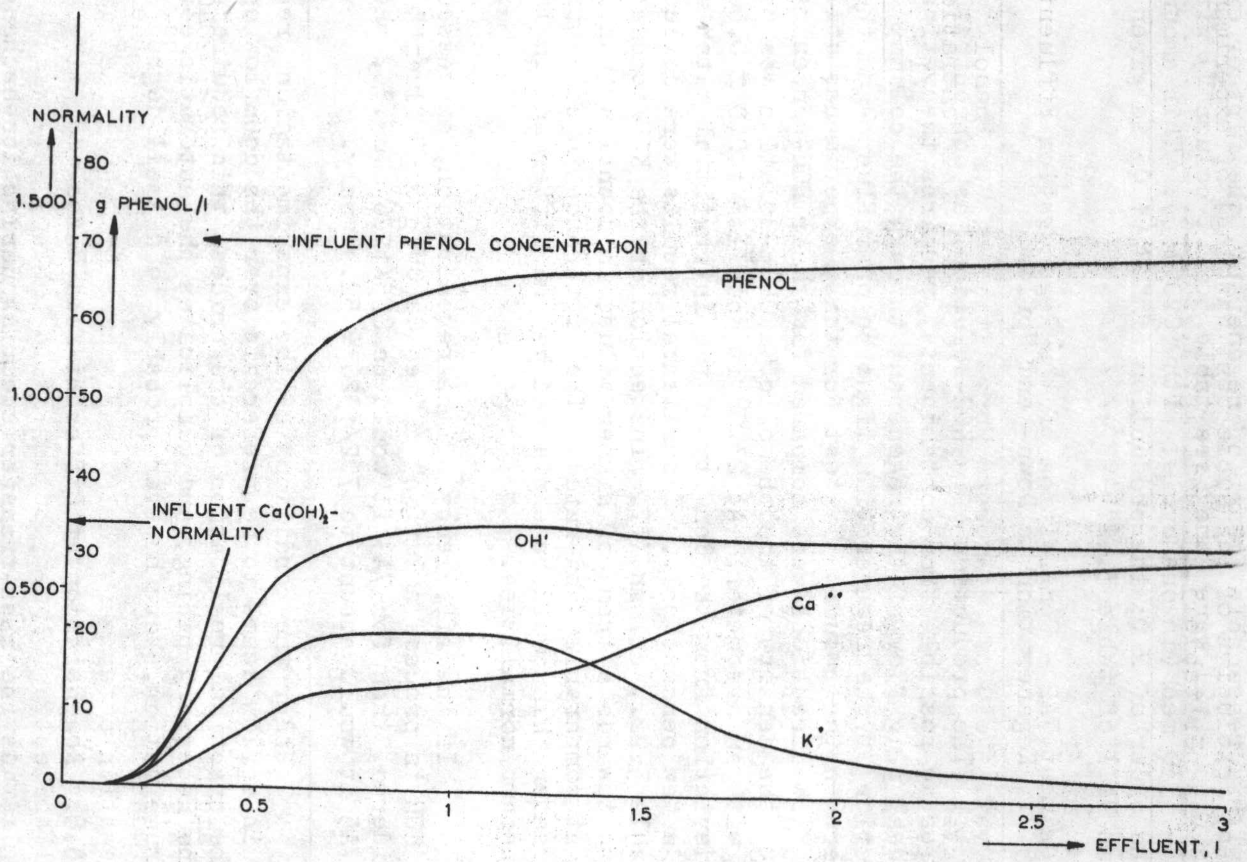
Table 3.23.

Experiment 7A2 - Composition of the Regeneration Effluent

| Total vol. collected ml | Vol. of fraction ml | Average Normalities | | | Phenol concentration g/l |
|---|---|---|---|---|---|
| | | $OH'$ | $Ca^{\cdot\cdot}$ | $K^{\cdot}$ | |
| I | II | III | IV | V | VI |
| 200 | 200 | 0.020 | 0.005 | 0.015 | 0.5 |
| 400 | 200 | 0.310 | 0.110 | 0.200 | 27.0 |
| 600 | 200 | 0.585 | 0.230 | 0.355 | 56.0 |
| 800 | 200 | 0.650 | 0.258 | 0.392 | 62.5 |
| 1000 | 200 | 0.682 | 0.280 | 0.402 | 65.7 |
| 1200 | 200 | 0.685 | 0.295 | 0.390 | 66.5 |
| 1400 | 200 | 0.673 | 0.353 | 0.320 | 67.0 |
| 1600 | 200 | 0.660 | 0.440 | 0.220 | 67.5 |
| 1800 | 200 | 0.655 | 0.515 | 0.140 | 67.7 |
| 2000 | 200 | 0.655 | 0.550 | 0.105 | 68.3 |
| 2200 | 200 | 0.655 | 0.573 | 0.082 | 68.7 |
| 2400 | 200 | 0.655 | 0.588 | 0.067 | 69.0 |
| 2600 | 200 | 0.655 | 0.600 | 0.055 | 69.5 |
| 2800 | 200 | 0.655 | 0.607 | 0.048 | 70.2 |
| 3000 | 200 | 0.655 | 0.613 | 0.042 | 70.5 |

At an influent $Ca(OH)_2$-normality of 0.680, the total amount of regenerant corresponded with 3 x 680 = 2040 meq. Table 3.23. and fig. 3.9. point to the fact, that for the KOH-production it would be of little value to continue the regeneration after about half that amount of $Ca(OH)_2$ had passed, as the $Ca^{\cdot\cdot}$-normality (between 1400 and 1800 ml "total collected volume", column IV in table 3.23.) was rising rapidly to its influent level, showing that the KOH-solution formed after this point would be dilute; the further the regeneration were carried, the more dilute the overall KOH - solution would be. Such a dilution would require either considerable recycle or increased demands on the subsequent dehydration section.

FIGURE 3.9.
EXPERIMENT 7A2 - THE REGENERATION



To approach the conditions of a regeneration carried out with a reasonable amount of regenerant, the further experiments (7A3 - 12) were done (see table 3.22., column V) with 1150 - 1330 meq (in one cycle, with 1020 meq). This amount was of the order of 2 Q; the production of KOH (1 Q) is given in column VIII of table 3.22.

### 3.3.5.7. Regeneration in Down- and Upflow

The production of a KOH-solution, as concentrated and as free as possible from contaminants, requires theoretically an ideal plug flow of the regenerant through the column. The direction of the regeneration might be of influence on the flow pattern in the column. To test for this, experiments utilising both flow-directions were compared for their KOH-concentrations. First, the density of the phenolic $Ca(OH)_2$-solution was determined with an areometer. At 23.0° it equalled 1.040 ± 0.005 g/ml. The deviation from the density of the interstitial water was thus a few percent only. Experimental results were collected in table 3.22., column XII. Inspection of the KOH-concentrations points towards a trend of higher values in downflow than in upflow at comparable feed-rates. The difference in concentrations is greater than could be explained by the difference in influent regenerant normalities.

If the efficiency of the regeneration, expressed as "meq KOH in process solution" / "meq $Ca(OH)_2$ in influent" were considered, then for 7A9 it would be 885/1276 = 69.3%, whereas for 7A5 it would amount to 702/1326 = 52.9% only.

Under the conditions of the experimentation, regeneration in upflow seems to be preferable over the downflow operation. In the practical realization of the process this requirement adds to the necessary piping, and complicates the automatic control instrumentation, both however probably to a small degree only.

### 3.3.5.8. Regeneration at Different Feed-Rates

As the mass-transfer occuring during ion-exchange phenomena is diffusion-controlled, the flow-pattern of the solutions in the column will have a marked influence on the results of the regeneration. This pattern is determined by the feed-rate of the solutions.

It is probable that an optimal feed-rate will exist, at which the concentration of the KOH-solution will be maximal. This can be seen in the following way. An increase in the feed-rate causes on the one hand increased mixing in the flow, due to the irregularly shaped interstitial channels, as a result of which the diffusion is increased, and thereby the diffusion-controlled mass-transfer. On the other hand, increased feed-rates of equal volumes of solutions result in decreased residence times, with less chances of contact between the ions in solution and the exchange-sites in the resin. These two causes have therefore opposite effects, the one favouring exchange and the other hindering it. Therefore, an optimal feed-rate will probably exist.

From the results of experiments 7A7-12 (table 3.22., column XII), the impression was gained, that such an optimal feed-rate was encountered in experiment 7A9. There, a maximum in the KOH-concentration was found. Both at lower and higher feed-rates, the KOH-concentrations found were smaller. It is very well possible, that further development of this process will require a more comprehensive evaluation of the degree, by which variations around average values influence the individual results. Here it will be seen, that repetition at equal feed-rates (experiments 7A7, 7A8) under otherwise very near conditions results in small differences only. This suffices for the present purpose.

It may happen that one of the two opposing factors is of such a magnitude as to overshadow completely the other. In this case a relationship without extremes may be found. For the loading experiments (par 3.3.5.5.) it was found that the degree of loading was directly proportional to the residence time. In view of the fact, that the hydrated radius of $K^{\cdot}$ is approximately half that of $Ca^{\cdot\cdot}$ (142), its rate of diffusion would be greater under otherwise equal circumstances; it is possible then that the rate of diffusion of $K^{\cdot}$ under the experimental circumstances was so great as to make the degree of loading dependent on the residence time only.

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(142) L. Wiklander, Kgl.Lantbruks Högskol Ann. 14 (1946) 1-171; R. Kunin, Ion Exchange Resins (New York 1958) p.27; $r_{K^{\cdot}} = 5.3$ Å, $r_{Ca^{\cdot\cdot}} = 9.6$ Å

### 3.3.5.9. Loading with NaCl (instead of KCl)

The present method of preparation of $KHCO_3$ and $K_2CO_3$ from KCl could be extended in principle to the analogous sodium-compounds as well. In view, however, of the very considerable difference in prices between $K_2CO_3$ and $Na_2CO_3$(143), it is uncertain whether the method, even if it were proved economic for the former, would prove to be so for the latter as well. On the basis of experimental results, this was calculated (see chapter 6) at a later stage.

The conversion of NaCl to NaOH (in phenolic solution) was carried out experimentally. In view of the fact that NaCl can be had in Sdom for the cost of handling only, a very considerable excess was taken in the loading experiments, $r_s \sim 10$. Also, in setting up the flowsheet, no treatment of the effluent NaCl-$CaCl_2$-solution for the recovery of NaCl was contemplated; this is detailed in chapter 5.

Using the same column (27mm x 95cm) as in the former experiments, two full cycles with a 5.470 N NaCl-solution (320.0 g/l) were carried out, after the resin had been regenerated with 1560 meq of $Ca(OH)_2$ and washed thoroughly to a neutral effluent. The experimental results were collected in table 3.24.

These results indicate clearly that a NaOH-solution could be produced in this way. Its concentration (table 3.24., column XIII) was comparable with that of KOH in former experiments (table 3.22., column XII); 23 g NaOH/l = 0.575 N, which would equal 32.2 g KOH/l. The amount of NaOH made (table 3.24., column IX) is of the same order as the amount of KOH (table 3.22., column VIII, exp. 7A7-9), and confirms the conclusions of par. 3.3.5.4., where it was found that loading at $r_s > 4$ would add little to the amount of alkali hydroxide produced subsequently.

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(143) Quarterly Report on Current Prices, Chem. Eng. News <u>38</u> (1960) No. 26; 64, 65 : $K_2CO_3$ 200 \$/t, $Na_2CO_3$ 34 \$/t; on a weight basis the price ratio is thus 5.9, on an equivalent basis 8.2.

Table 3.24.

Conversion of NaCl to NaOH by Cation Exchange

| Experiment number | NaCl - solution | | Phenolic $Ca(OH)_2$-solution | | | Phenolic $Ca(OH)_2$-solution | | Process solution | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Feed-rate ml/min/cm$^2$ | No. of meq introd. | Direction of flow | $Ca^{\cdot\cdot}$ normality | $C_6H_5OH$ g/l | Meq $Ca^{\cdot\cdot}$ introd. | Feed-rate$_2$ ml/min/cm | $Na^{\cdot}$ meq | $Ca^{\cdot\cdot}$ meq | $C_6H_5OH$ g | Vol. ml | NaOH g/l |
| I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII | XIII |
| 7C1 | 17.2 | 10940 | up | 0.703 | 61.2 | 1140 | 12.2 | 738 | 184 | 79 | 1400 | 21.1 |
| 7C2 | 3.5 | 9970 | up | 0.703 | 61.2 | 1355 | 7.8 | 816 | 92 | 91 | 1600 | 23.0 |

The amounts of $Ca(OH)_2$ and phenol found in the NaOH-solution (table 3.24., columns X and XI) are very similar to those of the KOH-solution (table 3.22., columns IX and X, exp. 7A7-9).

The decrease in regenerant feed-rate from 7C1 to 7C2 increased the concentration of NaOH made (column XIII), while the increase in the amount of regenerant increases the amount of NaOH (column IX). Even the higher amount of regenerant was still lower than 2 Q (1 Q = 816 meq in exp. 7C2).

### 3.3.5.10. The Balance of Materials

On making up the balance of materials, the agreement found per cycle was 96% or better in practically all the cases. Possible reasons for deviation from full agreement include:-

a) inaccuracies of the analyses;

b) differences in the resin state at comparable positions in the cycle, due to the variables introduced in the several cycles;

c) differences in the electrolyte- or phenol-contents in the resin at comparable positions in the cycle; as regards these, huge amounts of water would be required to remove the last small amounts from the resin, as was set out at the end of par. 3.2.7.5.

Experiment 7A3 may serve as a representative example (table 3.25.) :-

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Table 3.25

Experiment 7A3 - A Balance of Materials

| Loading + washing | Introduced | Obtained | Remained in resin | Left resin |
|---|---|---|---|---|
| Meq $K^{\bullet}$ | 1026 | 303 | 723 | |
| Meq $Cl'$ | 1026 | 1052 | | (26) |
| Meq $Ca^{\bullet\bullet}$ | 0 | 749 | | 749 |
| g $C_6H_5OH$ | 0 | 0 | | |
| Regeneration + washing | | | | |
| Meq $K^{\bullet}$ | 0 | 564 | | 564 |
| Meq $OH'$ | 1020 | 1037 | | (17) |
| Meq $Ca^{\bullet\bullet}$ | 1020 | 473 | 547 | |
| g $C_6H_5OH$ | $105\frac{1}{2}$ | $102\frac{1}{2}$ | (3) | |

Values in parentheses refer to materials other than exchangeable cations.

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Table 3.25. illustrates the points made above. The loading effluent discloses an "excess" of 26 meq Cl' over the influent, and the regeneration effluent - a similar "excess" of 17 meq OH'. As these two amounts cannot be ascribed to the former cycles, they should be attributed to inaccuracies of the analyses.

The difference between the amount exchanged in the loading and regeneration phases illustrates point (b) above, which referred to differences in the composition of the resin at comparable points in the cycle. The difference in phenol contents in the influent and the effluent illustrates point (c) made above. The phenol which remained in the resin (3 g) was found in the first fraction of the loading effluent of the next cycle. In subsequent experiments, removal of the phenol from the resin after the regeneration was improved by executing the washing partly in up- and partly in downflow. As a result of this, no phenol could be detected in the loading effluent ($KCl$-$CaCl_2$-solution) of the subsequent experiments.

## 3.4. Conclusions from the Cation-Exchange Experiments (144)

The summary of the experiments with anion-exchange (par. 3.2.8.) also contained a short exposition of the advantages to be expected from the change-over to cation-exchange while adhering to the use of phenol.

The cation-exchange experiments (section 3.3.) showed that these expectations were fulfilled. No chloride could be detected in the KOH-solution. This is a very considerable advantage, since it makes any steps for separation of the ultimate $KHCO_3$ from KCl superfluous, and yields directly a pure product. The KOH-solution did contain, as was expected, some $Ca(OH)_2$ and $C_6H_5OH$. As will be shown in the next chapter, separation between these materials was achievable by simple means. No interference from phenol was felt. After an initial saturation, the resin did not take up more phenol, and the amount in the influent equalled that in the effluent. Nor did phenolate anions influence the capacity of the resin adversely, this also being in accord with expectations.

The other substantial advantages of cation-exchange resins, enumerated at the end of par. 3.2.8., to wit the increased stability and the reduced price, could thus be exploited fully.

This wil be detailed in chapter 5, when the final flowsheet is set up.

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(144) The present application of phenol has been published :-
D. Araten
Phenol as Aid in the Carbonation of Alkali Metal Chlorides with Aqueous Calcium Hydroxide and Carbon Dioxide, Chem. & Ind. 1960 1301; D.Araten & O.Schaechter, Bull.Res. Council Israel 9A (1960) 238-9

# 4 - THE RECOVERY OF PHENOL

## 4.1. Introduction; the Mode of Operation

The cation-exchange experiments yielded a phenolic KOH-solution, containing some $Ca(OH)_2$.

In the preliminary description of the process it was set out that in order to apply water-transfer as the dehydration method, prior carbonation with $CO_2$ to $KHCO_3$ would be mandatory. The process also required carbonation for decomposition of any phenolates present to $KHCO_3$ and phenol. The basis for the latter was the difference between the dissociation constants for carbonic acid and phenol.(Note 14)

Carbonation should therefore precede any other step of phenol recovery. As a second step, $KHCO_3$ might be used to salt phenol out. No literature data were found about the system phenol-water-$CO_2$ (or carbonates).

Distillation of phenol from the aqueous solution would not be favourable as the azeotrope water-phenol contains (145) 90.8 wt-% of water. Absorption of phenol on ion-exchange resins would demand relatively great resin volumes because of the high phenol concentration. This method has been used for dilute phenol solutions (146). Desorbtion with alcohol, as described in this reference, would entail an additional separation. Desorbtion with water has been claimed to be possible (147).

Extraction of phenol with a suitable solvent might lead to the desired separation. Several solvents were examined and the "limiting conditions" for both concentrated and dilute phenol-solutions determined. The solvents examined include benzene and xylene, the petroleum ethers 60-90° and 140-180°, carbon tetra chloride, normal butyl acetate and normal butyl alcohol.

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<u>Note 14</u>: $CO_2$ as $H_2CO_3$, $pK_1 = 6.4$; $C_6H_5OH$, $pK = 9.9$ (reference 144a)

(144a) List of Tables Serving Laboratories, Royal Netherlands' Chemical Society (Amsterdam 1951) pp. 142, 145

(145) M. Lecat, Tables Azéotropiques (Bruxelles 1949) p. 220

(146) R.E.Anderson & R.D.Hansen, Ind.Eng.Chem. 47 (1955) 71

(147) Dow Chemical Co., Brit. Pat. 731335 (8.6.1955)

Recovery of the phenol from the solvent might be effected by one of the following methods:

a) Extraction with water at room temperature.

b) Extraction with water at a temperature above the critical mixing point (66°C) of water and phenol, say at 80°.

c) Extraction with an aqueous saturated solution of $Ca(OH)_2$.

d) Distillation of the solvent, in the case of high phenol-concentration and/or a low latent heat of vaporization. In this case, the presence or absence of azeotropes would have to be investigated.

## 4.2. Analyses

The analysis preferred for phenol was the bromatometrical method (131), as set out in par. 3.2.7.12. In the presence, however, of considerable amounts of bromine-consuming materials, as were used in the subsequent extraction experiments (xylene, for example), this method of analysis yielded unreliable results. There are two reasons for this :-

1) Deduction of blanc-values would result in the substraction of two large quantities to find their small difference, which procedure is not exact.

2) The blanc itself might depend on the duration of the experiment, the intensity of the light and other, unknown, factors.

Many methods for the analysis of phenol are known. It is evident, however, that for each solvent used subsequently, such a method would have to be standardized, which procedure would require a considerable amount of work. Moreover, the major part of this work would be fruitless, as of all solvents

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(131) W. Koppeschaar, Z.anal.Chem. 15 (1876) 233, in F.P. Treadwell & W.T. Hall, Analytical Chemistry (New York 1951) vol. II p. 633

tried only one or two would be chosen for the flowsheet. A proposal was then made (note 15) to evaporate the solvent in question by infra-red heating after binding any phenol present as potassium phenolate.

Experiments were carried out to test the suitability of this method. The amounts of phenol involved were determinated either bromatometrically prior to addition of the solvent, or else by formation of the solutions from analytically pure phenol (E. Merck A.G., Darmstadt, Germany). The purity of this material was not checked; its water contents (when taken from the closed, original vessel) was 1.5%.

To the phenol-containing solution, several grams of solid KOH (in excess) were added, then some water, when the solution was set to evaporate under infra-red heating. As low results (vide infra) were obtained, combined with a noticeable phenol-smell during heating, the water was replaced by 96% ethyl alcohol. Results of the experiments were as per table 4.1.

Table 4.1.

Bromatometrical Analysis of Phenol in the Presence of Solvents

| Exp. No. | Solvent | KOH-solvent added | Phenol - mg | | | Remarks |
|---|---|---|---|---|---|---|
| | | | introduced | Control of amount introduced | found | |
| 8N1 | normal butyl acetate | water | 5.86 | Bromatometrical analysis in presence of solvent | 4.67 | Phenol-smell noticed during evaporation |
| 8N2 | xylene | water | 214 | Brom.anal.in presence of solv.with deduction of "blanc" | 190 | |
| 8N3 | xylene | ethanol 96% | 214 | Idem | 212 | No smell noticeable |
| 8N4 | normal butyl alcohol | ethanol 96% | 100 | Synthesis from phenol A.R. | 92 | |
| 8N5 | normal butyl alcohol | ethanol 96% | 5 | Dilution of soln. of 8N4 | 9.8 | |

The results show that this method of analysis suffices for the present aim, namely, to distinguish between the suitability of the various solvents and to choose one for this process. In case the results of extraction of phenol for two or more solvents would be similar, a refinement of the procedure or changeover to some other method of analysis would be required.

## 4.3. Experiments and Results

### 4.3.1. Carbonation with $CO_2$

To simplify the initial approach, a solution similar to that of the ion-exchange effluent, containing, however, no $Ca(OH)_2$, was prepared. It contained 28.0 g KOH/l (0.500 N) and 66.2 g $C_6H_5OH$/l. Of this solution, 200 ml were placed in a separatory funnel, a thermometer was placed in the solution and a rapid $CO_2$-stream led in. The temperature of the solution, initially 23.5°, rose slowly, reaching 26.5° after 20 minutes, when turbidity appeared. After 44 minutes the temperature reached 27°, when the phenol-droplets started to coalesce. Gas was then led on the solution for another 16 minutes, when the funnel was closed and the phenol left to separate.

After 2 hours the separated phenol was drawn off. The aqueous solution was treated in a centrifuge, when small additional amounts of phenol were isolated. In all, about 2 g of raw phenol were thus isolated.

The aqueous solution was then placed in a bath of ice water, when its temperature dropped after 20 minutes to 2°. $CO_2$ was led in to ensure saturation. After 60 minutes the gas flow was stopped, the funnel closed and left for two additional hours in the ice-water bath. About one gram of raw phenol was thus isolated.

The aqueous phase contained 58.6 g phenol/l, and was 0.492 N to $K^{\cdot}$ as KOH.

There were thus removed $(66.2-58.6)/5 \sim 1.5$ g $C_6H_5OH$. An independent determination of the composition of the raw phenol disclosed that it contained some 75 wt-% $C_6H_5OH$, or some 2 g in all.

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Note 15: By Dr. A. Alon, Israel Mining Industries, Haifa.

The solubility of $C_6H_5OH$ in a $KHCO_3$-solution at 0°, under $P_{CO_2} = 1$ ata, 58.6 g/l, is somewhat lower than its solubility in pure water at that temperature, 63 g/l(148). A small salting-out effect of $KHCO_3$ (at 0°) is thus noticed.

## 4.3.2. Salting Out with $KHCO_3$

The flowsheet presents one electrolyte only which could be used for salting phenol out. This is $KHCO_3$, present in the aqueous solution. The carbonation-results at 0° indicated some salting-out effect. This had to be verified at room temperature, and for several $KHCO_3$-concentrations.

Aqueous solutions containing a known amount of $KHCO_3$ were saturated with phenol by adding solid $C_6H_5OH$ (chemically pure), introducing $CO_2$ and mixing strongly until a dispersion of the phenolic phase in the aqueous phase was reached. This took about 45 minutes. After about 1½ hour the phenolic phase had settled, when in the aqueous phase $K^{\cdot}$ as KOH and phenol were determined analytically. The temperature varied from 21.0-22.0°.

Results were as per table 4.2.

Table 4.2.

Salting-Out of Phenol by $KHCO_3$

| Exp. No. | K as $KHCO_3$ | | $C_6H_5OH$ | Remarks |
|---|---|---|---|---|
| | g/l | normality | g/l | |
| --- | 0 | 0 | 78 | Reference (148) (at 23.9°) |
| 8A1 | 49.2 | 0.49 | 61.1 | Aqueous phase from exp. in par 4.3.1. (interpolation) |
| 8B1 | 89.8 | 0.90 | 51.8 | |
| 8B2 | 133.6 | 1.34 | 43.5 | |
| 8B3 | 176.4 | 1.76 | 39.0 | |
| --- | 294 | 2.94 | 0 | Reference (148a); note 15a |

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(148) A.N.Campbell & A.J.R.Campbell, J.Am.Chem.Soc.59(1937)2481-8

(148a) A.Seidell, Solubilities of Inorganic and Metal Organic Compounds (New-York 1940) Vol.I, p.726

Note 15a: Compare with the solubility of $NaHCO_3$, 125.7 g/l=1.5N(148b)

(148b) A.Seidell, Solub.of Inorganic & Metal Organic Compounds (New-York 1940) Vol. I, p.1196

The results show that $KHCO_3$ has a marked salting-out influence on phenol in water. The final phenol-concentration was, however, still too high to limit phenol separation to this method.

The removal of phenol by salting out has the advantage of requiring little energy. This is even of greater importance if the subsequent demand for separation (between phenol and extractant) by distillation, is recalled; this is detailed in par. 4.3.5. Salting out, implies, on the other hand, the recycle of a part of the product $KHCO_3$, and thus an increase in the throughput of the solution, and therefore in the vessels and the piping, of the subsequent operations.

### 4.3.3. Extraction

The $KHCO_3$-solution after salting out still contained some 39 g $C_6H_5OH$/l. An attempt was made to recover this phenol by extraction into an organic phase. Assuming counter-current extraction, the distribution-coëfficients of phenol between aqueous phenol solutions and the extractant were determined under "limiting conditions".

Phenol solutions in aqueous $KHCO_3$ were prepared. The $C_6H_5OH$-concentrations were 65 g/l (as obtained from the ion exchange section), 1.9 g/l and 95 mg/l. This latter value (~ 100 mg/l) was arbitrarily considered as the maximum tolerable in the extraction effluent. For the extraction stage, the ratio of volumes of solvent to water was 1/100 or 1/50; for the back extraction it was 100 or 50 (note 16).

The phenol-rich extractant, as obtained in the "extraction stage", was stripped with water or an aqueous $Ca(OH)_2$-solution to recover the phenol. The extractant was considered to circulate between the "extraction" and "backextraction".

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Note 16: Where high extracted concentrations were encountered, concentrations in the aqueous media were determined anew after equilibration.

The distribution coëfficients K for the two processes were defined in the following manner:

For the extraction : $K_e = \dfrac{\text{g } C_6H_5OH\text{/l extractant}}{\text{g } C_6H_5OH\text{/l aqueous solution}}$

For the backextraction : $K_b = \dfrac{\text{g } C_6H_5OH\text{/l water (or aq. soln.)}}{\text{g } C_6H_5OH\text{/l extractant}}$

The product $r = K_e \times K_b$ then yields the $C_6H_5OH$-concentration in the aqueous stripper, divided by that in the original $KHCO_3$-solution. The value of r should at least be equal to 1.

The experiments were executed in stoppered separatory funnels. The volumes introduced were read off in measuring cylinders. Samples for analysis were withdrawn in pipettes. Analyses were carried out bromatometrically, with or without preliminary evaporation of the solvent, as set out below.

The experimental results were as in table 4.3. (page 120).

Table 4.3. demonstrates that for $CCl_4$ $K_e$ decreases with the concentration. The required $K_b$ was improbably high, for which reason this solvent was not investigated any further. The same holds for the two petroleum ethers. Benzene, in contrast, although showing a $K_e$ decreasing with the concentration, yielded at the arbitrarily fixed lower boundary of 100 mg/l a reasonable value for $K_b$.

Xylene showed the remarkable property of having a $K_e$ of approximately the same value at both high and low concentrations (note 17). If no intermediate minima in $K_e$ would occur, the line in the graph "aqueous phenol concentration"

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Note 17: This might be caused by a constancy of composition of the extracted species over the range of concentrations investigated, in which case the distribution law predicts a distribution coefficient independent of the concentration (149a)

(149a) G.H. Morrison & H. Freiser, Solvent Extraction in Analytical Chemistry (New-York 1957) p. 8.

versus "solvent phenol concentration" would be (approximately) a straight one. In general, such a form of distribution curve is preferable over a curved line rising steeply at higher aqueous phenol concentrations, since such a latter curve usually has a flat part at lower aqueous phenol concentrations, implying a considerable number of theoretical transfer stages for a given operating line.

n-Butyl acetate (further noted "nBuOAc") was taken for these experiments, as it has been used (149b, 150) in the so-called "Phenosolvan-Verfahren" for dephenolisation. The $K_e$-values obtained are strikingly high, especially at the lower concentration (expt. 8H6). As the equilibrium was approached by phenol transfer from the aqueous solution to the organic phase and not vice versa, the high value ($K_e = 48$) was regarded as not too optimistic. For an electrolyte-free solution, (150) gives the curve of $K_e$ versus the concentration of phenol in the aqueous solution from 1 mg/l (where $K_e = 23$) to 3000 mg/l (where $K_e = 28$), with an intermediate maximum of $K_e = 57$ at 28 mg/l. The resultant distribution curve, as logarithm of the aqueous phenol concentration versus the logarithm of the solvent phenol concentration, is approximately a straight line with a slope of about 45°.

In analogy with (150) it was assumed here, that no intermediate minima in the $K_e$-values between those of table 4.3., experiments 8C6 and 8H6, occurred. It follows then that any back-extraction for which the lowest distribution coefficient were 0.13 would yield a sufficiently concentrated phenol-solution.

On the other hand, such a concentrated phenol solution in nBuOAc as obtained, might, in the absence of a suitable backextractant, even be amenable to separation by distillation.

n-Butyl alcohol (further noted "nBuOH") was investigated here as it had been proposed for "water-transfer" (97b),

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(149b) R. Jauernik, Erdoel u. Kohle 13 (1960) 252-7

(150) A. Dierichs & L. Jaehn, Chem. Techn. (Berlin) 10 (1958) 408-12

(97b) A. Baniel, J. Appl. Chem. 8 (1958) 611-6; 9 (1959) 521-5

Table 4.3.

Extraction of Phenol from a $KHCO_3$-Solution with Various Solvents

| Extractant | Exp. No. | Temperature °C | $C_6H_5OH$ concentration in extractant g/l | $C_6H_5OH$ concentration in water g/l | Distribution coefficient $K_e$ | Minimal required distribution coefficient for backextraction $K_b$ |
|---|---|---|---|---|---|---|
| $CCl_4$ | 8C1 | 20.8 | 118 | 64.5 | 1.8 | |
| | 8E2 | 21.1 | 1.8 | 1.9 | 0.95 | |
| | 8H3 | 21.5 | 0.019 | 0.095 | 0.20 | 5.0 |
| Petroleum-ether 60-90° (1) | 8C4 | 20.0 | 6.8 | 65.0 | 0.10 | 10.0 |
| Petroleum-ether 140-180° (2) | 8C5 | 20.4 | 12.9 | 65.0 | 0.20 | 5.0 |
| Benzene (3) | 8C2 | 20.8 | 376 | 59.8 | 6.3 | |
| | 8E1 | 21.0 | 5.9 | 1.9 | 3.1 | |
| | 8H1 | 21.0 | 0.092 | 0.095 | 0.97 | 1.03 |
| Xylene (4) | 8C3 | 22.8 | 203 | 63.7 | 3.2 | 0.31 |
| | 8H9 | | 0.933 | 0.25 | 3.7 | 0.27 |
| n-Butyl acetate | 8C6 | 19.5 | 500 | 65.0 | 7.7 | 0.13 |
| | 8H6 | 17.0 | 1.34 | 0.028 | 48 | |
| n-Butyl alcohol (5) | 8C7 | 20.0 | 503 | 65.0 | 7.8 | 0.13 |
| | 8H7 | 21.0 | 1.81 | 0.129 | 14 | |
| | 8H8 | 21.8 | 6.70 | 0.168 | 40 | |

(1) The so-called SBP (Special Boiling Point fraction) 60-90°.

(2) The so-called White Spirits 140-180°.

(3) The system $C_6H_6$-$C_6H_5OH$-$H_2O$ was described (149), in the absence, however, of salts, except for some fragmentory data on KCl, $CaCl_2$ and $K_2SO_4$ at low concentrations.

(4) Conforming according to the producer, to the German Pharmacopoeia; consisting probably of a mixture of the three isomers.

(5) The fraction 116-118°/760 mm of the technical product.

(149) V. Rothmund & N.T.M. Wilsmore, Z.physik.Chem. <u>40</u> (1902) 623

which operation forms part of the present process. In experiment 8H8 (table 4.3.), the equilibrium was approached from a direction contrary to that of expt. 8H7, namely from a phenol-butanol mixture and an aqueous solution of $KHCO_3$ only. The differences in $K_e$-values between 8H7 and 8H8 may be due to the equilibrium not having been reached in the latter experiment.

Assuming no minima in $K_e$-values between the two concentrations, backextraction with $K_b \geqslant 0.13$ would yield a sufficiently concentrated phenol solution.

The similarity in the results between nBuOAc and nBuOH is remarkable.

### 4.3.4 Backextraction

Backextraction of the phenol was attempted only from those solvents for which (table 4.3.) the required $K_b \leqslant 1$. These solvents were benzene, xylene and nBuOAc. Backextraction from nBuOH was not attempted, for reasons to be discussed below (section 4.4.).

Experimental results were as per table 4.4. The $K_b$-values found differ from those of table 4.3., because of the different composition of the aqueous phase. The r-values in table 4.4. were found by multiplying the $K_b$'s by the proper $K_e$'s from table 4.3.

Table 4.4. demonstrates that backextraction of phenol from benzene with water (8F1) would result in a too low concentration ( r = 11.6%); the improvement due to the alkalinity of a $Ca(OH)_2$-solution (8J3) was smaller than expected (r = 17%), and still insufficient. $Ca(OH)_2$-slurry (8J2) improved the backextraction considerably, with the resulting $r > 1$; it is evident that working with a slurry would require more experimenting to establish details of the mode of operation, especially to prevent settling of and clogging by the slurry.

The backextraction from xylene with water was attempted at three temperatures. In view of the critical solution temperature of water and phenol (66°), extraction above this temperature might result in a higher phenol-concentration than at room-temperature. To minimise solvent losses at elevated temperatures, extraction was carried out in a separatory funnel closed with an Allihn condenser.

Table 4.4.

Backextraction of Phenol from Various Solvents with Water and Water-$Ca(OH)_2$-Mixtures

| Solvent | Extractant | Exp. No. | Temperature °C | $C_6H_5OH$ concentration | | Distribution coefficient $K_b$ | $r = K_b \times K_e$ |
|---|---|---|---|---|---|---|---|
| | | | | in solvent g/l | in extractant g/l | | |
| Benzene | Water | 8F1 | 21.1 | 332 | 40 | 0.12 | 0.116 |
| | Water | 8G1 | 21.5 | 13.3 | 6.1 | 0.46 | |
| | $Ca(OH)_2$-solution, 1.6 g/l | 8J1 | 20.0 | 13.3 | 10.0 | 0.75 | |
| | $Ca(OH)_2$-solution, 1.6 g/l | 8J3 | 21.3 | 332 | 58.3 | 0.18 | 0.17 |
| | $Ca(OH)_2$-slurry, 30 g/l | 8J2 | 21.0 | 13.3 | 16.3 | 1.2 | 1.16 |
| Xylene | Water | 8K3 | 20.0 | 214 | 42.5 | 0.20 | |
| | Water | 8K1 | 68.0 | 214 | 51.2 | 0.239 | 0.76 |
| | Water | 8K2 | 78.5 | 214 | 50.3 | 0.235 | |
| nBuOAc | Water | 8L2 | 17.0 | 0.586 | (too low to be determined) | 0 | |
| | Water | 8L3 | 80.0 | 0.586 | 0.268 | 0.46 | |
| | Water | 8K4 | 80.0 | 457 | 33.7 | 0.074 | 0.57 |
| | $Ca(OH)_2$-solution, 1.6 g/l | 8L4 | 18.5 | 0.586 | 0.07 | 0.1 | |
| | $Ca(OH)_2$-solution 1.6 g/l | 8K5 | 20.0 | 457 | 24.7 | 0.05 | 0.38 |

The funnel, placed in a thermostatic bath was shaken without disconnecting the condenser. Sampling was effected with heated Erlenmeyer bottles to collect the separate phases, and with heated pipettes to draw off samples. The results (8K3, 8K1 and 8K2) indicated a negligible influence of the temperature, with a resultant maximum value of r = 76%. This value was rather low.

Because of the experimental difficulties attendant on the lower boiling point of benzene (80°) as compared with the xylenes (138-143°), no high-temperature extraction from benzene was attempted.

When extracting from nBuOAc with water, the influence of increase of the temperature was marked (8L2 and 8L3). Still, the obtained r (57%) was too low to be of use. The results of backextracting with $Ca(OH)_2$ (8L4, 8K5) were also too low for the present purpose.

These experiments aimed at backextracting the phenol showed that in almost all cases the ultimate phenol solution which would be obtained would be more dilute than the initial one, thus necessitating an extra concentration. $Ca(OH)_2$-slurry might (8J2) form an exception to this statement, but then it would require special measures to prevent settling and clogging. If possible, operation with clear solutions only would be preferred.

## 4.3.5. Distillation

Of all solvents tried, only nBuOAc and nBuOH yielded a concentrated phenol-solution of 500 g/l, equalling approximately 50 wt-%. The former was distilled to investigate the possibility of separation between the phenol and the nBuOAc (note 17a).

A description of the complete ternary system $C_6H_5OH$-nBuOAc-$H_2O$ was not located. Neither was reference to the binary system $C_6H_5OH$-nBuOAc found. Azeotropic data for

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Note 17a: The following patents, describing this possibility, came to the attention of the author after completion of the work: W.Gey & R. Goerz, East German Pats. 12726 (11.2.1957) and 16266 (28.1.1959)

$H_2O$-$C_6H_5OH$ and $H_2O$-nBuOAc are known (151, 152). A solution of the following composition was prepared for the distillation (table 4.5.)

Table 4.5.

Composition of the Solution for Distillation

| Component | Concentration | |
|---|---|---|
| | g/l solution | g/kg solution |
| nBuOAc | 481 (by difference) | 502 |
| Phenol | 427 | 446 |
| $H_2O$ | 50 | 52 |

Specific gravity at 18° : 0.958

About 30 ml of this solution were subjected to distillation in a column filled with Raschig-rings and having 6 theoretical plates. A reflux-ratio of about 1 was employed. The first fraction came over at a head temperature of 91-94°. Separation of the distillate into two layers indicated that this fraction consisted of the heterogeneous azeotrope $H_2O$-nBuOAc, b.p. 90.2, 28.7 wt-% $H_2O$ (data from (152)). The volume of this fraction was 1.5 ml. The second fraction passed at a head-temperature of 119-126°, measuring 13.2 ml. This fraction consisted mainly of nBuOAc, b.p. 124.0 (153). Its composition was as given in table 4.6.

Table 4.6.

The nBuOAc-Rich Fraction of the Distillation

| Component | Concentration | |
|---|---|---|
| | g/l solution | g/kg solution |
| nBuOAc | 844.4 (by difference) | 976 |
| Phenol | 0.6 | 0.7 |
| $H_2O$ | 20 | 23 |

Specific gravity at 18° : 0.865

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(151) $H_2O$-nBuOAc: M.Lecat, Tables Azéotropiques (Bruxelles 1949) p.215 (this is a heterogeneous azeotrope)

(152) $H_2O$-$C_6H_5OH$ : idem, idem, p.220

(153) J.C.Brown, J.Chem.Soc. <u>83</u> (1903) 987

The heating capacity of the column employed was insufficient to obtain further fraction(s). At a pot temperature of 182° (i.e., the boiling point of phenol) top temperature did not surpass 130°, with no distillate coming over.

On cooling, the bottom product solidified. As its melting point turned out to be 27°, it consisted of phenol, contaminated probably by water.

The distillation yielded thus a fraction containing 11.2 g nBuOAc and only 8 mg phenol (along with 0.26 g water). This composition most probably does not reflect an azeotrope between phenol and nBuOAc, but rather entrainment of the former by the latter, indicating the possibility of separation by distillation.

The use of nBuOH instead of nBuOAc would not introduce any improvements. The high $K_e$ for nBuOH would make backextraction unfavourable. Separation by distillation between $C_6H_5OH$ and nBuOH would require far greater amounts of energy than in the case of nBuOAc, since firstly nBuOH dissolves greater amounts of water than does nBuOAc, and secondly such distillation would entail the volatilisation of the azeotrope $H_2O$-nBuOH, containing 42.4 wt-% water (154). As phenol would have to be separated from nBuOH, all the nBuOH would have to be evaporated, entailing sizeable heating expenses. (Formation of a zeotropic mixture of nBuOH and phenol has, however, been reported (155)).

On the other hand, any phenol not extracted previously would end up in the nBuOH used for water transfer.

### 4.4. The Method of Phenol Recovery

The phenolic KOH-solution is subjected to carbonation by gaseous $CO_2$. At $P_{CO_2} = 1$ ata this operation converts the phenolic potassium hydroxide to potassium bicarbonate and phenol. Under these conditions the solubility of phenol is reduced to 61.1 g/l. Also, any phenolic calcium hydroxide would be converted into calcium carbonate (which would precipitate) and phenol.

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(154) J.S.Stockhardt & C.M.Hull, Ind. Eng.Chem. 23 (1931) 1438-40
(155) M. Lecat, Tables Azéotropiques (Bruxelles 1949) p.113

Salting out with $KHCO_3$ to a concentration of 176.4 g/l lowers further the phenol solubility to 39.0 g/l.

nBuOAc extracts the remaining phenol and yields a solution of approximately 50 wt-%. This solution is separated by distillation; no azeotrope between phenol and nBuOAc is formed under atmospheric pressure.

# 5. FLOWSHEET FOR THE PROCESS

## 5.0 General Introduction

The present process for conversion of KCl into $KHCO_3$ and $K_2CO_3$ (and for the analogous sodium compounds) can be followed best with the aid of the concise scheme (see fig. 5.0). This scheme contains the proposed division of the process into sections. These sections will be dealt with one by one in the order of their numbers. The detailed treatment (par. 5.1. and further) follows the same sequence.

Section 1: A KCl-solution loads a cation-exchanging resin which is in the Ca-state. The reaction is

$$KCl + Ca_{\frac{1}{2}}\text{-}R \longrightarrow K\text{-}R + \tfrac{1}{2}CaCl_2$$

The effluent contains the excess KCl.

The resin is regenerated with a phenolic $Ca(OH)_2$-solution.

The reaction is

$$K\text{-}R + \tfrac{1}{2}Ca(OH)_2\ (+C_6H_5OH) \longrightarrow Ca_{\frac{1}{2}}\text{-}R + KOH\ (+C_6H_5OH)$$

Section 2: The lime required for the $Ca(OH)_2$ - solution originates from a lime kiln.

Section 3: The KCl - $CaCl_2$- solution is partly dehydrated by water-transfer, with the aid of NaCl as ultimate water-acceptor. Part of the KCl precipitates, and is recycled.

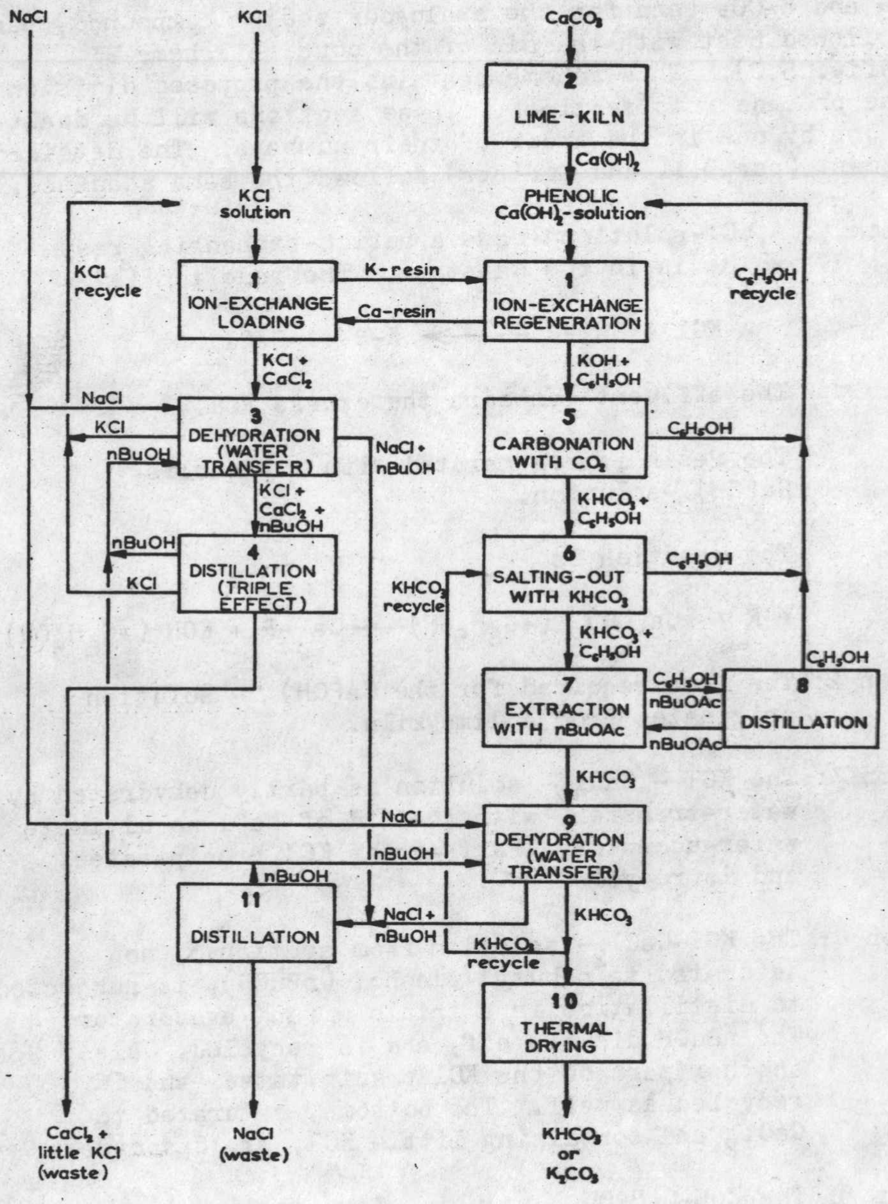
Section 4: The KCl-$CaCl_2$- solution from section 3, now saturated to n-butyl alcohol (nBuOH), is subjected to distillation in a triple effect evaporator. The nBuOH distils off, and is recycled. Also, another part of the KCl precipitates, and is recycled as well. The bottoms, saturated to $CaCl_2$ and containing little KCl, are discarded.

Section 5: The KOH-$C_6H_5OH$ - solution from section 1 is carbonated with gaseous $CO_2$. The potassium is converted into $KHCO_3$. Part of the phenol is liberated as a separate phase, and is recycled.

FIGURE 5.0.

CONVERSION OF KCl INTO $KHCO_3$ OR $K_2CO_3$

(CONCISE SCHEME)



Section 6: In the $KHCO_3$-$C_6H_5OH$- solution obtained, solid $KHCO_3$ is dissolved when an additional part of the phenol separates, and is recycled.

Section 7: The remainder of the phenol is extracted with n-butyl acetate (nBuOAc).

Section 8: The $C_6H_5OH$ - nBuOAc - mixture is separated by distillation; both chemicals are recycled.

Section 9: The now phenol-free $KHCO_3$- solution is wholly dehydrated by water transfer, with NaCl as the ultimate water-acceptor. Solid $KHCO_3$ precipitates.

Section 10: The solid $KHCO_3$ is dried of adhering liquid by low-temperature drying. Eventually, it is converted in the same operation into $K_2CO_3$.

Section 11: The NaCl-solutions obtained from the water-transfer operations (sections 3 and 9) are freed of the nBuOH (present to saturation) by distillation. The nBuOH is recycled, and the NaCl-solution is discarded.

The present flowsheet has been calculated for the production of 50 t $KHCO_3$/d (or the equivalent amount of $K_2CO_3$, $34\frac{1}{2}$ t/d). Unless otherwise stated, all quantities in this chapter are per day.

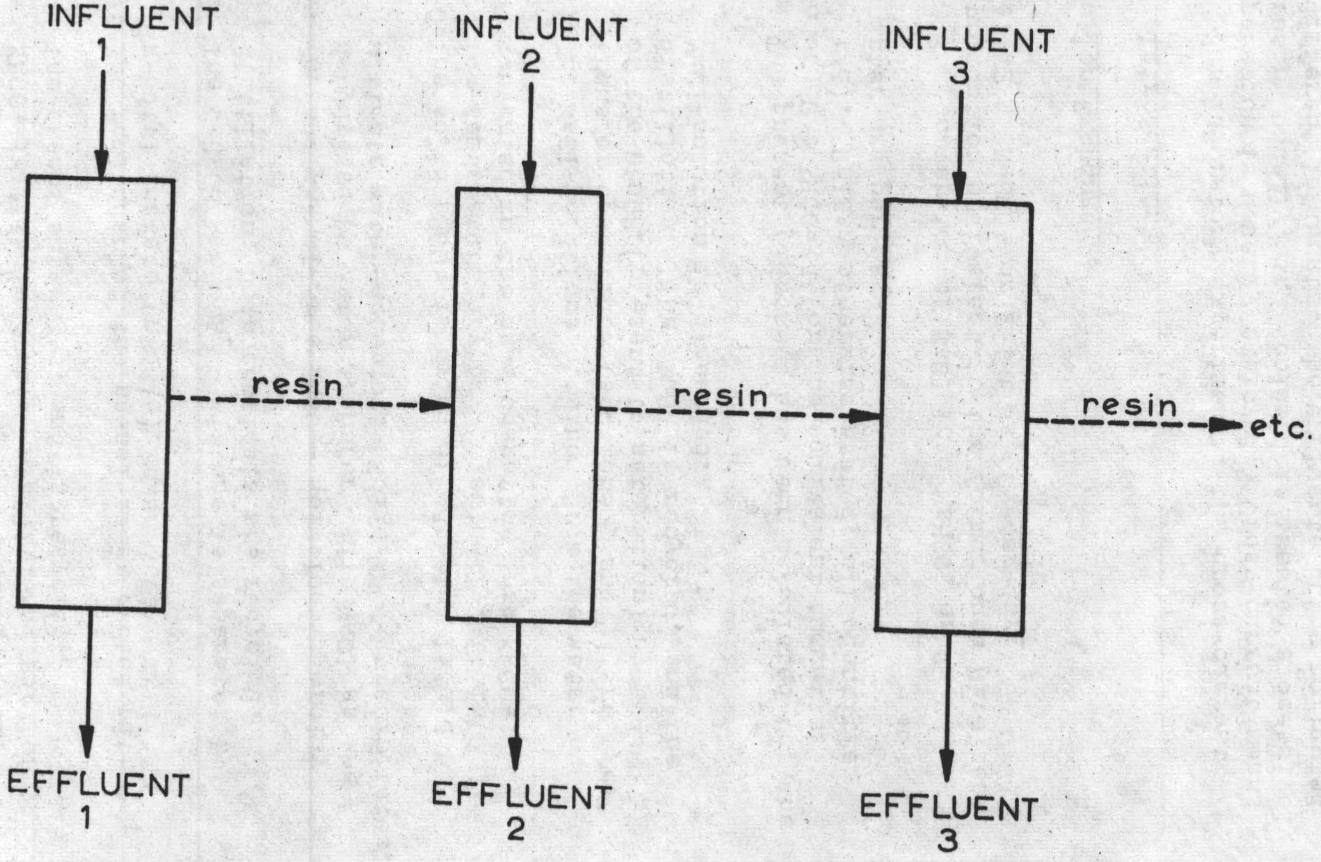
For conversion of NaCl into $NaHCO_3$ or $Na_2CO_3$, rates of production equivalent to the former ones have been taken, i.e. 42 t $NaHCO_3$ or $26\frac{1}{2}$ t $Na_2CO_3$ per day.

## 5.1. Ion Exchange

### 5.1.1. Introduction

For laboratory experiments, the cross-current mode of operation is usually employed. Cross-current means that the resin (usually, in a column) is treated successively with the different influents, the effluents being collected separately (see fig. 5.1.). One or more of these influents can be water, and the direction of flow may be either downwards (as depicted) or upwards. An advantage of this

FIGURE 5.1.
CROSS CURRENT ION EXCHANGE



method lies in the speed, with which results are obtained. A disadvantage is that a part of the effluents (and especially the washing effluents) is of low concentration.

Any industrial application would demand that the effluents be as concentrated as is compatible with the process, because of the costs of concentration (and eventual total dehydration). To achieve this, counter current has been proposed (156). This means a relative movement of the solutions and the resin in opposite directions (see fig. 5.2.). For actual technical operation, it is not necessary to move the resin through columns, as the same aim can be achieved by appropriate piping and valving. Although attrition may sometimes require the replacement of 50% of the resin per year (157), there are instances where actual movement of the resin has been executed, with a claimed low loss through attrition (158).

In the present flowsheet, the method by which the solutions are routed with the aid of multiple valves, and the resin rests immobile in the columns, has been preferred.

The necessary steps of the operation are the following:-

(1) Loading: $R\text{-}Ca_{\frac{1}{2}} + KCl \longrightarrow R\text{-}K + \frac{1}{2}CaCl_2$;

(2) Washing, to remove $CaCl_2$ and excess KCl ;

(3) Regeneration: $R\text{-}K + \frac{1}{2}Ca(OH)_2 \longrightarrow R\text{-}Ca_{\frac{1}{2}} + KOH$ (in phenolic medium);

(4) Washing, to displace the rest of KOH and to wash the resin free of $Ca(OH)_2$ and phenol.

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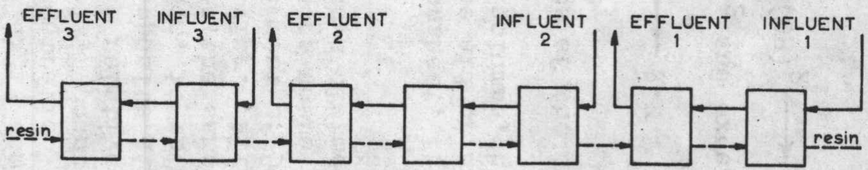
(156) S. Vajna, West German Patent 1.049.839 (5.2.1959)

(157) N.K. Hiester, R.K. Cohen & R.C. Philips, Chem.Eng. Progr. Symp. Ser.50 (1954) no 14, 23

(158) E.A. Swinton & D.E. Weiss, Austral. J. Appl. Sci. 7 (1956) no 1, 98

FIGURE 5.2.
COUNTER CURRENT ION EXCHANGE



## 5.1.2. Theoretical; equilibrium curves and operating lines

In analogy to other unit operations involving mass transfer, graphical treatment of ion exchange has been proposed, both according to the "McCabe-Thiele" method (159) as well as according to that of "Ponchon-Savarit" (160). The former method was used here.

Thus, the equilibrium line for the system Resin-KCl-$CaCl_2$ had to be determined, at the concentrations prevailing at loading and regeneration. This curve and the operating lines, would yield the number of theoretical stages.

This method of treatment has the drawback, that its applicability is limited to those cases (of mass transfer) where actual equilibrium exists. It cannot be applied to operations such as washing the resin, where equilibrium between the rinsing water and the interstitial electrolyte-solution never occurs. The washing steps of the process were, therefore, treated by assuming (in accordance with the concept of a theoretical stage) ideal mixing between the wash-water and the interstitial liquid, and "equilibrium", i.e. equality of concentration, between the "outgoing wash water" and the "outgoing interstitial liquid" obtained from each stage. After presetting the upper limit of electrolyte concentration encounterable in the interstitial liquid, and the lower limit desirable, the number of theoretical stages would then follow from the ratio of wash-water-volume to that of the interstitial liquid. Arbitrarily such volumes of wash water for steps (2) and (4) (see par. 5.1.1.) were chosen, as were equal with the required volumes of the reagent solutions in the steps preceding them ( (1) and (3) respectively), so that preparation of these reagent solutions could be limited to dissolving additional amounts of reagents (KCl respectively $Ca(OH)_2$) in the washing effluents. On finding a low, acceptable number of stages for each of these washing steps, the volumes chosen were kept to.

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(159 R. McNeil, E.A. Swinton & D.E. Weiss, J. Metals 7, AIME Trans. 203 (1955) 912-21

(160) P.W. Pfeiffer, Chem.Eng.Sci. 2 (1953) 45-52

### 5.1.3. Determination of the equilibrium curve

For the purpose of approximate determination of the number of theoretical stages, an equilibrium curve, determined at a concentration about half way between that at loading (4N KCl) and that at regeneration (0.7 N $Ca(OH)_2$), was used.

The following aqueous solutions were prepared :

KCl 2.32N

$CaCl_2$ 2.29N

Of these solutions, varying relative amounts (at a constant total volume containing 23 meq K + Ca) were equilibrated with 4.3 meq resin, partly as K-R and partly as $Ca_{\frac{1}{2}}$-R. This was done, to approach the equilibrium from both sides. Equilibration took place by shaking the samples occasionally in a thermostatic bath kept at 20.0 - 20.1°, for $2\frac{1}{2}$ - $3\frac{1}{2}$ hours.

The solutions were analysed for $Ca^{\cdot\cdot}$ with the aid of ethylene diamine tetra-acetate, disodium salt (EDTA), and their $K^{\cdot}$- contents determined from the balance of equivalents. This, in its turn, yielded the resin composition. Numerically, the results were as per table 5.1.(page 136)

The following example illustrates the calculation:-
Exp. 10A2

7.0 ml $CaCl_2$ 2.29N contained 16.0 meq Ca;

3.0 ml KCl 2.32N contained 7.0 meq K.

After the equilibration, the solution contained 14.1 meq Ca, and hence (16.0 + 7.0) - 14.1 = 8.9 meq K. The resin contained initially 0.9998 x 4.25 ~ 4.3 meq K; as the solution contained ultimately 8.9 - 7.0 = 1.9 meq K more than initially, the resin contained after equilibration 4.3 - 1.9 = 2.4 meq K, and thus 1.9 meq Ca.

The ultimate fractional composition in the solution was thus

$$X=\frac{(K^{\bullet})}{(K^{\bullet})+2\,(Ca^{\bullet\bullet})}=\frac{8.9}{23.0}=0.387$$ and in the resin

$$Y=\frac{(K^{\bullet})}{(K^{\bullet})+2\,(Ca^{\bullet\bullet})}=\frac{2.4}{4.3}=0.558$$

Inspection of table 5.1. reveals that for all values determined there was a preference of the potassium for the resin phase. At a resin composition of 0.837 (exp. 10A4, 10A5) the solution-composition approached and equalled that of the resin. It was therefore considered probable that the equilibrium curve would consist of two parts, one for $0 \leqslant Y \leqslant 0.837$ and one for $0.837 \leqslant Y \leqslant 1.0$. Due to lack of data, it would not be possible to trace the second part (for high Y-values); as result of the proximity of the "point of azeotropy" to 1.0, this second part would be very near to, if not actually coincident, with the $45^{\circ}$ - line.

The points conforming to the experimentally determined X and Y-values (table 5.1., columns XV and XVI) were noted in fig. 5.3.

In analogy with anion exchangers (par. 3.2.7.8.), the occurence of a hyperbolic form of the distribution curve, as found in many cases by Waterman and Weber (119), was considered in the present case. In analogy to fig. 3.8., there might occur two hyperbolas, having a common point X=Y=0.837 and conforming to the general formula of (119a) $y=x=\frac{x(0.837-x)}{a+bx}$.
The values of a and b were determined as described in par. 3.2.7.8., and the resultant curve drawn in fig. 5.3.

The agreement between the experimental points and the curve may be considered satisfactory.

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(119) H.I. Waterman, Anal. Chim. Acta 18 (1958) 498;
H.I. Waterman & A.B.R. Weber, J.Inst.Petr. 43 (1957) 315

(119a) H.I. Waterman, C. Boelhouwer & D.Th.A. Huibers Process Characterisation (Amsterdam 1960) p. 114.

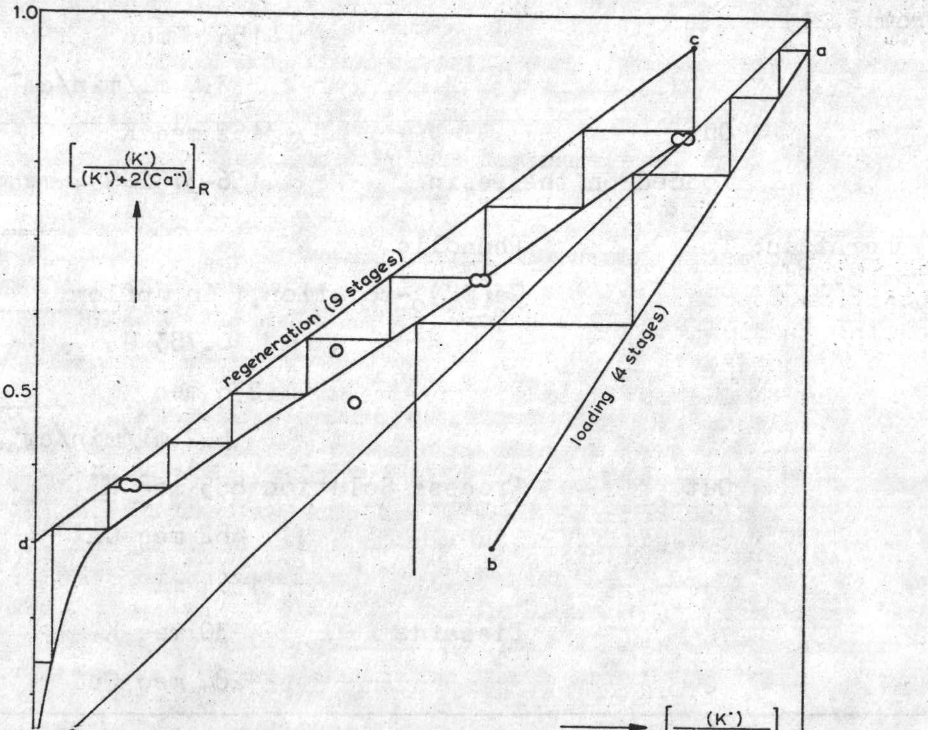
Table 5.1.

Determination of the Equilibrium Curve for Cation Exchange

| Exp. No. | Resin form | Resin weight mg | $CaCl_2$-soln ml | KCl-soln ml | Initial Composition of Soln. | | | Ultimate Composition of Soln. |
|---|---|---|---|---|---|---|---|---|
| | | | | | meq Ca | meqK | Total | meq Ca (analysed) |
| I | II | III | IV | V | VI | VII | VIII | IX |
| 10A1 | K-R | 999.5 | 10.0 | 0 | 22.9 | 0 | 22.9 | 20.3 |
| 10A2 | K-R | 999.8 | 7.0 | 3.0 | 16.0 | 7.0 | 23.0 | 14.1 |
| 10A3 | K-R | 1004.2 | 5.0 | 5.0 | 11.5 | 11.6 | 23.1 | 10.0 |
| 10A4 | K-R | 1005.8 | 2.0 | 8.0 | 4.6 | 18.5 | 23.1 | 3.9 |
| 10A5 | $Ca_{\frac{1}{2}}$-R | 1003.5 | 0 | 10.0 | 0 | 23.2 | 23.2 | 3.6 |
| 10A6 | $Ca_{\frac{1}{2}}$-R | 1003.8 | 0.0 | 7.0 | 6.9 | 16.2 | 23.1 | 9.7 |
| 10A7 | $Ca_{\frac{1}{2}}$-R | 1001.0 | 5.0 | 5.0 | 11.5 | 11.6 | 23.1 | 13.6 |
| 10A8 | $Ca_{\frac{1}{2}}$-R | 1001.1 | 8.0 | 2.0 | 18.4 | 4.6 | 23.0 | 20.1 |

| Ultimate Composition of Soln. meq K (calculated) | Initial Composition of Resin | | Ultimate Composition of Resin | | Ultimate Relative Composition | |
|---|---|---|---|---|---|---|
| | meq Ca | meq K | meq Ca | meq K | X Solution $\frac{(K^{\bullet})}{(K^{\bullet})+2(Ca^{\bullet\bullet})}$ | Y Resin $\frac{(K^{\bullet})}{(K^{\bullet})+2(Ca^{\bullet\bullet})}$ |
| X | XI | XII | XIII | XIV | XV | XVI |
| 2.6 | 0 | 4.3 | 2.6 | 1.7 | 0.114 | 0.395 |
| 8.9 | 0 | 4.3 | 1.9 | 2.4 | 0.387 | 0.558 |
| 13.1 | 0 | 4.3 | 1.5 | 2.8 | 0.568 | 0.652 |
| 19.2 | 0 | 4.3 | 0.7 | 3.6 | 0.831 | 0.837 |
| 19.6 | 4.3 | 0 | 0.7 | 3.6 | 0.845 | 0.837 |
| 13.4 | 4.3 | 0 | 1.5 | 2.8 | 0.580 | 0.652 |
| 9.5 | 4.3 | 0 | 2.2 | 2.1 | 0.411 | 0.488 |
| 2.9 | 4.3 | 0 | 2.6 | 1.7 | 0.126 | 0.395 |

# FIGURE 5.3.
## DETERMINATION OF THE NUMBER OF STAGES FOR CATION EXCHANGE



### 5.1.4. Choosing the operating lines

#### 5.1.4.1. The loading step

As basis for the calculations, the results of experiment 7A9 were taken. These results, taken from tables 3.21 and 3.22., are reproduced in table 5.2.

Table 5.2.

The Results of Experiment 7A9

| | | | |
|---|---|---|---|
| Loading :<br>(from 3:21) | In | KCl-solution | 296.5 g/l |
| | | | 4156 meq |
| | | | 3.0 ml/min/$cm^2$ |
| | Out | | 3162 meq K° |
| | Loaded on the resin | | 4156-3162=994 meq K° |
| Regeneration:<br>(from 3.22.) | In | Phenolic<br>$Ca(OH)_2$-solution, | in upflow |
| | | | 0.783 N |
| | | | 1276 meq |
| | | | 4.2 ml/min/$cm^2$ |
| | Out | Process Solution | 885 meq K° |
| | | | 82 meq Ca°° |
| | | | 1364 ml |
| | | Discards | 30 meq K° |
| | | | 284 meq Ca°° |

This experiment was chosen as a basis, because its results had demonstrated (par. 3.3.5.8.) the highest KOH-concentration encountered.

Loading was thus effected with 1045 ml = 4156 meq. As the loading effluent contained after 800 ml a concentration of K° over 3N, approaching steeply that of the influent KCl(3.98N), it follows that after such a volume had passed the column, the efficiency of loading rapidly approached zero. It may be assumed that practically all exchange of $Ca_{\frac{1}{2}}$-R for K-R had taken place before this volume had passed the column.

On loading with 800 ml, 800 x 300/74.6 = 3217 meq KCl were introduced.

In experiment 7A9, 994 meq K were loaded on the resin. The exact state of the resin before the experiment was not known; after loading it contained at least 994/1035 = 96% of its capacity as K-R. The relative composition of the resin, $Y_a$, was then at least 0.96. As loading was executed with pure KCl, $X_a = 1.00$. Hence point a (fig. 5.3.).

The resin circulates between the loading and the regeneration; its final Y- value for one step will of necessity equal its initial Y- value for the next. Hence, the two operating lines (for loading and regeneration) will be enclosed by two horizontal lines. The form of the equilibrium curve (see fig. 5.3.) results in a relatively high $Y_d$ (i.e. high fractional $K^{\cdot}$- composition in the resin after the regeneration with phenolic $Ca(OH)_2$) if a high utilization of the regenerant (i.e. a high $X_c$) and a still acceptable number of stages are required.

From these considerations, $Y_b$ ( $= Y_d$) = 0.30 is chosen. As the resin composition changes from 0.30 to 0.96, it takes on 1035 (0.96-0.30) = 683 meq. The excess "introduced" over "loaded" then amounts to 3217-683 = 2534 meq.

After loading, the interstitial liquid had a composition equal to that of the influent. In experiment 7A9, rinsing freed from the column 1733 meq KCl. Deducting from this the amount which was in the tubes under the resin ($38\frac{1}{2}$ ml = 153 meq), the resin was found to have contained (interstitially) 1733-153 = 1580 meq.

This amount of KCl was freed from the resin during the washing. The loading properly was then effected with 3217-1580 = 1637 meq KCl, of which 683 were loaded on the resin, and 1637-683 = 954 meq were passed during the loading stage. It is clear that an excess of KCl over the amount, loaded on the resin, is required in the influent as a driving force, to complete the reaction. The ratio of the two streams, "meq KCl in solution" / "meq resin" = 1637/1035 = 1.582, thus gives the slope of the operating line.

For point b (the lower end of the operating line for the loading), $Y_b = 0.30$ was chosen. $X_b$ follows from $1.582 = (0.96 - 0.30)/(1.00 - X_b)$, yielding $X_b = 0.583$. The number of stages for the loading step is then found to be 4.

### 5.1.4.2. The regeneration step.

$Y_d$ was chosen 0.30, as set out above. The incoming phenolic $Ca(OH)_2$ - solution was free of K° , hence $X_d = 0$. $Y_c$ should equal $Y_a$, and $X_c$ is chosen 0.85 so as to obtain a not too great number of stages at the price of an increased regenerant untilisation. From the slope of the operating line for the regeneration, $(0.96 - 0.30)/(0.85-0) = 0.776$, the number of meq $Ca(OH)_2$ for the regeneration proper is then $0.776 \times 1035 = 803$.

It was assumed that the number of meq $Ca(OH)_2$ left interstitially after regeneration was proportional to the number of meq KCl left interstitially after loading. Hence, this number of meq $Ca(OH)_2$ was $1580 \times 0.783/3.977 \simeq 310$. The total amount of $Ca(OH)_2$ is then 803 + 310 = 1113 meq = 1422 ml.

The number of stages for the regeneration is (say) 9.

Normality of the phenolic KOH - solution would be 638/(1422-270) = 0.593 N = 33.3 g KOH/l. This concentration is somewhat lower than that, obtained in experiment 7A9 proper (0.65N = 36.4 g KOH/l).

### 5.1.5. The washing steps.

### 5.1.5.1. Derivation of the equation

Let us use the following notation:

R = concentration of the KCl in the resin phase, g/l

$R_i$ = R in the resin stream entering stage no. n - i

n = number of theoretical stages

S = concentration of the KCl in the wash-water phase, g/l

$S_m$ = S in the wash water stream entering the stage m + 1

k = ratio of volume of wash-water or its ensuing solution to volume of solution in the resin phase (i.e., the interstitial solution); k is assumed constant.

Counter-current streams of resin and of wash-water are assumed.

Considerations of mass balance yield

for stage n: $R_o + kS_{n-1} = R_1 + kS_n$ (1)

for stages (n-1) + n: $R_o + kS_{n-2} = R_2 + kS_n$ (2)

for stages 1 + 2 + .... + (n-1) + n: $R_o + kS_o = R_n + kS_n$ (n)

Consideration of equilibrium yield

for stage n: $R_1 = S_n$ (n + 1)

for stage n-1: $R_2 = S_{n-1}$ (n + 2)

for stage 1: $R_n = S_1$ (2n)

Given are the following :

$R_o$ = 300 (concentration of the original KCl=solution)(2n + 1)

$S_0$ = 0 (washing is effected with pure water) (2n + 2)

$R_n = R_n$ (arbitrarily fixed) (2n + 3)

Insertion of equations (n + 1) to (2n + 3) into (1) to (n) then yields:

$300 + kS_{n-1} = S_n + kS_n$ (1)'

$300 + kS_{n-2} = S_{n-1} + kS_n$ (2)'

$300 + kR_n = S_2 + kS_n$ (n-1)'

$300 + 0 = R_n + kS_n$ (n)'

As $R_n \ll 300$, we may deduce from equation (n)'

$300 = kS_n$ (n)"

which, inserted in eq. (1)' to (n-1)' gives :

$kS_{n-1} = S_n$ (1)"

$kS_{n-2} = S_{n-1}$ (2)"

$kR_n = S_2$ (n-1)"

These equations yield:

$$S_3 = k^2 R_n \qquad (1)"'$$

$$S_4 = k^3 Rn \qquad (2)'"$$

$$S_n = k^{n-1} R_n \qquad (n-1)"'$$

Combining (n-1)'" with (n)" gives then

$$k^n R_n = kS_n = 300$$

or

$$k = \left(\frac{300}{R_n}\right)^{1/n}$$

In its general form, this equation becomes

$$k = \left(\frac{R_0}{R_n}\right)^{1/n}$$

This final, simple, equation connects the initial concentration of KCl between the resin-particles, the final concentration of the same, the number of theoretical stages and the volume ratios of wash-water and interstitial liquid.

For the washing following the regeneration, an entirely analogous equation holds. Instead of "300", the value of "29.0" should be used there, this being the concentration of the influent regenerant, expressed as g $Ca(OH)_2$/l.

### 5.1.5.2. The washing step after the loading

It is proposed to take a volume of wash-water equal to that used for the (preceding) loading step, i.e. (par. 5.1.4.1.) 800 ml (for 450 g of resin). Then $k = 800/395 = 2.03$ and $S_n$, the concentration of the KCl in the effluent wash-water, follows from equation (n)" .

$$S_n = 300/k = 300/2.03 = 148 \text{ g/l.}$$

Further: $2.03 = (300/R_n)^{1/n}$.

For $n = 12$, $300/R_n = 2.03^{12} = 4898$, $R_n = 300/4898 = 0.061$ g/l

$n = 11$, $300/R_n = 2.03^{11} = 2413$, $R_n = 300/2413 = 0.124$ g/l

$n = 10$, $300/R_n = 2.03^{10} = 1189$, $R_n = 300/1189 = 0.252$ g/l

The value for 11 stages was chosen arbitrarily.

### 5.1.5.3. The washing step after the regeneration

In analogy with the above, a wash-volume of 1430 ml (for 450 g of resin) was taken. Then $k = 1430/395 = 3.62$ and $S_n = 29.0/3.62 = 8.01$ g/l.

For $n = 5$ , $R_n = 29.0/3.62^5 = 0.047$ g/l

$n = 6$ , $R_n = 29.0/3.62^6 = 0.013$ g/l

The phenol-concentrations decreased proportionately, from 73.0 g/l in the influent to respectively 0.118 g/l and 0.033 g/l.

If the maximum tolerable losses of phenol would correspond to the (arbitrarily fixed) concentration of 0.1 g phenol/l, then 6 stages would be required here.

### 5.1.6. Summary - counter-current ion exchange (small scale).

A graphical representation of the quantities involved in the ion-exchange step, based on a total amount of resin as used in experiment 7A9, 450 g = 1035 meq, is given in figure 5.4.

It should be noted that the resin circulates through the successive steps loading-washing-regeneration-washing and back to loading.

The lengths of time involved in the different steps were calculated from the feed-rates used in experiment 7A9.

Loading is effected at 17.1 ml/min, and hence takes 800/17.1 = 46.8 min. Washing at 30 ml/min, takes 800/30 = 26.7 min. Regeneration, executed at 23.9 ml/min, takes 1422/23.9 = 59.5 min. The last washing step, executed at the same feed-rate as the regeneration preceding it, takes therefore the same time. As, during the regeneration, the first 270 ml effluent (consisting of pure water) are returned to the wash-water influent stream, which occupies 270/23.9 = 11.3 min, actual production of phenolic KOH takes only 59.5 - 11.3 = 48.2 min.

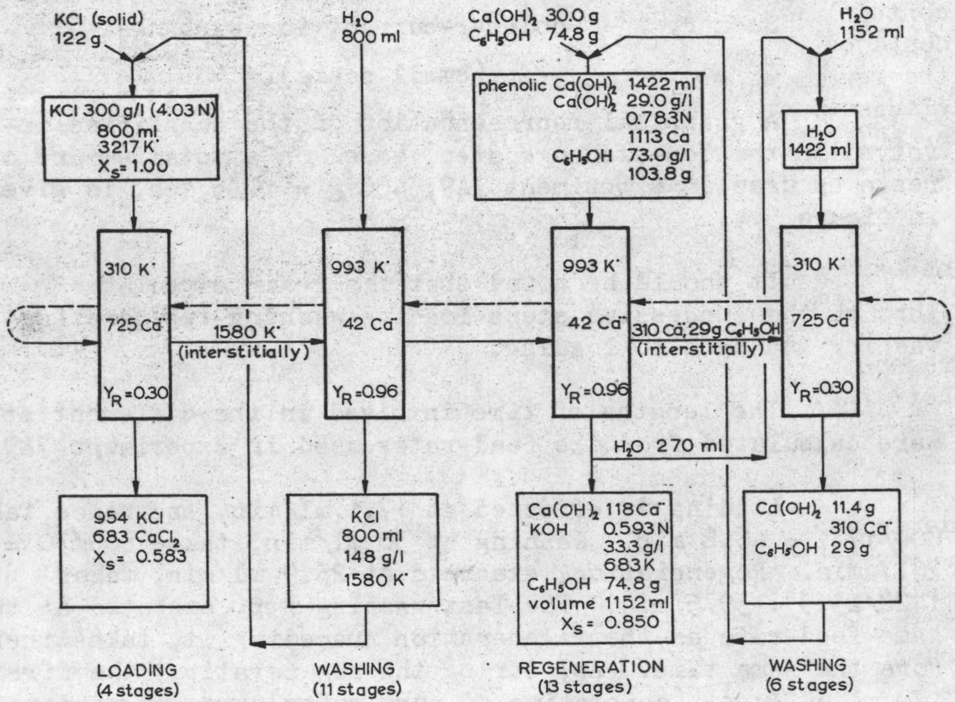
The total cycle takes 46.8 + 26.7 + 2 x 59.5 = 192.5 min = 3.21 hours.

## FIGURE 5.4.

## ION-EXCHANGE FLOW SHEET (COUNTER-CURRENT)

BASED ON THE LABORATORY-COLUMN OF 450 g = 1035 meq OF AMBERLITE IR-120; UNDIMENSIONED FIGURES REFER TO MILLIEQUIVALENTS. E.g.: $310\ Ca^{\cdot\cdot} = 310$ meq OF CALCIUM.

THE REQUIRED KOH IS OBTAINED IN A PHENOLIC MEDIUM IN THE REGENERATION STEP.



## 5.1.7. Discussion of the water requirements of the ion exchange

For reasons of availability or economy, a decrease of the water requirements of the ion exchange section might be required.

A review of the flow-sheet (fig. 5.4.) discloses, that the water requirements of this part of the process consist of two amounts:

(a) For the loading

(b) For the regeneration

The amount needed for regeneration could be lowered if a more concentrated $Ca(OH)_2$ - solution would be suitable for this process. Theoretically, a phenolic $Ca(OH)_2$ - solution containing at the most 83.6 g $Ca(OH)_2$ /l (and 406.9 g phenol/l) could be prepared (161). Whether this solution would execute the regeneration satisfactorily is open to question. Its high viscosity would probably require special precautions for the promotion of the flow. No experiments were taken at this concentration.

For this reason, decrease of the amount of water necessary for the regeneration will not be considered here.

Any decrease in the volume of wash-water after regeneration would require supplementing the difference between this volume and that needed for the regeneration; hence, no saving would result.

The loading stage consumes an amount of water which depends on the concentration of the KCl. As 300 g/l approaches saturation (20°- 300 g/l, 30°- 318 g/l, after (162)) only a raise of temperature might permit some saving of water. This point was not investigated experimentally. It thus appears that there is only one way of decreasing the water-requirements of the process. This can be seen as follows.

Consider two cases:

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(161) G.J. van Meurs, Z.physik. Chem. 91 (1916) 313

(162) R. Paris & P. Mondain-Monval, Bull.Soc.Chim. (5) 5 (1938) 1142-7.

(a) The wash-water volume succeeding the loading has the same volume as the loading influent. Then no KCl could be used for water transfer from the $KHCO_3$-solution, the dehydration of which could then be accomplished by water transfer to NaCl or by thermal evaporation. As the second method requires considerable amounts of energy, the first would be preferred, resulting in a loss of the water to the process.

(b) The wash-water volume succeeding the loading is smaller than that of the loading influent. The KCl could be used for transfer of a volume of water equal to the difference between the wash-water volume and the loading volume. This difference would then represent the water savings.

It need hardly be said that these considerations hold only for the loading and not for the regeneration step.

The possibility of lowering the wash-water volume preceding the loading will be considered, on the basis of the derived equation $k = (R_o/R_n)^{1/n}$.

Consider such a change in k that $k_2 = k_1/a$ (where $a > 1$). Then, at a constant number of theoretical stages ($n_2 = n_1$), we find

$$(R_o/R_{n2})^{1/n_1} = (R_o/R_{n1})^{1/n_1} . (1/a)$$

where $R_{n2}$ represents the final value $R_n$ in the second case.

Then $R_{n2} = R_{n1} . a^{n_1}$

For $n_1 = 11$ (as taken above) then $R_{n2} = R_{n1} . a^{11}$

which yields ($a$ being $> 1$) impossibly high final $R_n$ - values.

On the other hand, consider $R_n$ constant and change n:

$$k_2 = (R_o/R_{n1})^{1/n_2}$$

$$k_1 = (R_o/R_{n1})^{1/n_1}$$

from which follows $n_1/n_2 = \log k_2/\log k_1 = 1 - \log a/\log k_1$. Consider such a small change that $a = 1.5$. Then we find $n_1/n_2 = 1 - (\log 1.5/\log 2.03) = 0.43$, or (as $n_1 = 11$) $n_2$ = approximately 26 stages.

For increased changes in a, $n_2$ increases much more; for $a$ = 2 nearly 400 stages are found, while for the limiting case ($a = 2.03$) an infinite number of stages results.

Although it is obvious that the most economical solution of this problem would require a detailed analysis and balancing of investments (in additional stages) versus availability and operating costs of more water, it will be assumed for the sake of the preliminary cost-price calculating based on this flowsheet, that the volume of the wash-water succeeding the loading cannot possibly be decreased.

The amounts in fig. 5.4. will, therefore, be adhered to.

### 5.1.8. Ion exchange-industrial scale

The technical scale of operations as calculated in the present flow-sheet is based on laboratory experiments. No semi-technical or technical experimentation was done on the ion-exchange. It goes without saying that this will have to be done as the process progresses to technical realization.

The considerable experience gained with ion-exchange operations in particular, and with liquid - solid contacting in general, indicate that no insurmountable difficulties would be encountered on the engineering side. In order to decide, however, whether such relatively expensive experimentation should be undertaken, a calculation as the present one, based on laboratory scale experiments, is indispensable.

The amount of resin required, follows from that, used in the laboratory experiments. There 0.450 kg of resin yielded 1152 ml 0.593 N KOH in a cycle of 192.5 minutes.

For a daily production of 28 t KOH we therefore need:

$$\frac{28 \times 10^6}{(1.152 \times 0.593 \times 56.1) \times 60 \times 24} \times 0.450 \times 192.5 =$$

= 43910 kg, say 44 t of resin. The volume of this amount is 44/0.918 = 47.9 (say 48) $m^3$; 0.918 is the bulk density of the resin, as obtained in the laboratory experiments (450 g occupied 490 ml).

The volumes of the solutions involved are as follows:

For 1.152 x 33.3 = 38.36 g KOH, 240 g KCl were led in (fig. 5.4.) (note 18). A daily production of 28 t KOH will then need 28 x 240/38.36 = 175.2 t KCl/d. As a solution of 300 g/l, its volume will be 175.2 x $10^3$/300 = 583.9 $m^3$/d, weighing 583.9 x 1.174 (163) = 685.7 t, of which 175.2 t KCl and 510.5 t water.

Stream (1) : 175.2 t KCl (300 g/l), 510.5 t water : 583.9 $m^3$ (all streams are given on a daily basis; their numbering corresponds with that used in the general flowsheet).

The volume of wash-water following on the loading is 510.5 $m^3$.

Stream (2) : 510.5 t = 510.5 $m^3$ of water.

This wash-water leaves the resin, containing 1.580 x 74.6/240 = 0.49 g KCl per g KCl loaded, i.e. with 175.2 x 0.49 = 86.0 t KCl. This effluent contains 86.0/(86.0 + 510.5) = 14.4 wt% KCl, thus occupies 596.5/1.094 (163) = 545.1 $m^3$ and contains 86.0 x $10^3$/545.1 = 157.8 g/l.

Stream (3) : 545.1 $m^3$ = 596.5 t ; 86.0 t KCl (157.8 g/l), 510.5 t water.

The loading effluent contains 954 meq KCl/3217 meq KCl introduced, or 954 x 175.2/3217 = 51.6 t KCl. This stream also contains 683 meq $CaCl_2$ per 240 g KCl introduced, i.e. 0.683 x 55.5 x 175.2/240 = 27.7 t $CaCl_2$. The total

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Note 18: This amount does not represent the total KCl required as raw material. Part of the 240 g is not converted, and recovered subsequently and recycled.

(163) C.S. Hodgman, Handbook of Chemistry and Physics (1957) p. 1896 (extrapolated)

weight is thus 510.5 t water + 51.6 t KCl + 27.7 t $CaCl_2$=589.8 t, the volume (at an assumed specific gravity of 1.14 after(163)(164)) 589.8/1.14 = 518 $m^3$. The concentrations are : for KCl 51.6 x $10^3$ / 541.8 = 95.2 g/l, for $CaCl_2$ 27.7 x $10^3$/518 = 53.5 g/l.

Stream (4) : 518 $m^3$ = 589.8 t ; 51.6 t KCl (95.2 g/l), 27.7 t $CaCl_2$ (53.5 g/l), 510.5 t water.

Regeneration is executed with a phenolic solution of $Ca(OH)_2$.

For 38.36 g KOH, 1.113 x 74.1/2 g $Ca(OH)_2$ were needed (fig. 5.4.). Hence we shall require 1.113 x 37.05 x 28/38.36 = 30.1 t $Ca(OH)_2$. In the same way, 103.8 x 28/38.36 = 75.8 t phenol are needed. The total volume of the regenerant will be 1422 x 28/38.36 = 1038 $m^3$. At a specific gravity of 1.04 as determined experimentally its weight is 1038 x 1.04 = 1080 t, of which 1080-105.9 = (say) 974 t water. Concentrations are: for $Ca(OH)_2$ 30.1 x $10^3$/1038 = 29.0 g/l, for phenol 75.8 x $10^3$/1038 = 73.0 g/l.

Stream (5) : 1038 $m^3$ = 1080 t ; 30.1 t $Ca(OH)_2$ (29.0 g/l), 75.8 t phenol (73.0 g/l), 974 t water.

The amount of slaked lime which has to be added, is 30.0 x 28/38.36 = 21.9 t $Ca(OH)_2$; the balance comes from washing the resin.

Stream (6) : 21.9 t $Ca(OH)_2$.

This slaked lime requires 21.9 x 56.1/74.1 = 16.6 t of CaO.

Stream (7) : 16.6 t CaO

Slaking of this lime demands 21.9 - 16.6 = 5.3 t water.

Stream (8) : 5.3 t water.

The major part of the phenol comes from recycle. It consists of 74.8 x 28/38.36 = 54.6 t.

Stream (28) : 54.6 t phenol.

The balance of the phenol, 75.8 - 54.6 = 21.2 t, comes with the wash-water following the regeneration. This solution also contains the balance of $Ca(OH)_2$, i.e. 30.1 - 21.9 = 8.2 t, as well as the 974 t water. The total weight is 1003 t, occupying (say) 1003 $m^3$.

Concentrations are then : $Ca(OH)_2$ 8.2 x $10^3$/1003 = = 8.2 g/l, phenol 21.2 x $10^3$/1003 = 21.2 g/l.

Stream (29) : 1003 $m^3$ = 1003 t; $Ca(OH)_2$ 8.2 t (8.2 g/l); phenol 21.2 t (21.2 g/l); 974 t water.

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(163) C.S.Hodgman, Handbook of Chemistry and Physics (1957) p. 1896 (extrapolated)

(164) International Critical Tables (New-York and London,1926) vol. III p.72.

The amount of influent wash-water is 974 t = 974 $m^3$.

Stream (30) : 974 t = 974 $m^3$ water. Of this amount, 270 x 974/1422 = 185 $m^3$ of water are recycled.

Stream (10) : 185 $m^3$ = 185 t water.

The amount of additional water which has to be supplied is thus 974 - 185 = 789 t.

Stream (31) : 789 t = 789 $m^3$ water.

The composition of the process-solution is as follows : It contains 28 t KOH (in phenolic solution), 0.118 x 37.05 x 28/38.36 = 3.2 t $Ca(OH)_2$, 74.8 x 28/38.36 = = 54.6 t phenol and 789 t water. Total weight is (say) 875 t. At an assumed specific gravity of 1.03 (note 18a) its volume is 875/1.03 = 850 $m^3$.

Concentrations are : KOH 28 x $10^3$/850 = 33.0 g/l ($\sim$ 0.59 N), $Ca(OH)_2$ 3.2 x $10^3$/850 = 3.8 g/l, phenol 54.6 x $10^3$/850 = 64.3 g/l.

Stream (11) : 850 $m^3$ = 875 t; KOH 28.0 t (33.0 g/l), $Ca(OH)_2$ 3.2 t (3.8 g/l), phenol 54.6 t (64.3 g/l), water 789 t.

The amount of solid KCl (stream (49) ) will be determined at a later stage (in section 4) when the recycled amounts of KCl will be calculated.

## 5.2. Section 2: Lime Kiln

The kiln has to supply (stream (7) ) 16.6 t CaO/d. This requires burning of theoretically 100.1 x 16.6/56.1 = = 29.6 t $CaCO_3$, say 30 t $CaCO_3$.

Stream (9) : 30 t $CaCO_3$.

To account for fines and losses, the amount quarried has to exceed this quantity by about 2/3 (166). Thus, about 50 t limestone have to be quarried (daily).

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Note 18a: Approximately that of a KOH-solution as present; aqueous phenol solutions have a specific gravity very near to 1.0 (165).

(165) F.H. Rhodes & A.L. Markley, J.Phys.Chem. 25 (1921) 527-34.

(166) Private communication from Dr. N. Ben-Ya'acov, Fertilizers and Chemicals Ltd., Haifa.

The kiln supplies dilute $CO_2$ (about 25% - note 19), which can be used for partial carbonation of the phenolic potassium hydroxide.

The amount available is composed of two parts : from the dissociation of $CaCO_3$ proper, 44 x 30/100.1 = 13.2 t; and from the flue gases, 6.3 t.

Stream (12) : 19.5 t $CO_2$.

## 5.3. Section 3 : Concentration of the KCl-$CaCl_2$-solution by water transfer

### 5.3.1. Mode of operation

Loading the resin yields an effluent containing potassium chloride and calcium chloride. It is economically necessary to recover at least a part of the potassium chloride before rejecting the solution. Examination of the system KCl-$CaCl_2$-$H_2O$ (to be discussed in detail later) yields that partial dehydration of this loading effluent will precipitate pure KCl until the $CaCl_2$-concentration will amount to nearly 45%, when only 3% of KCl will have remained in the solution (the percentages are in weight and based on the solution obtained).

It is now proposed to execute this dehydration by water transfer as far as possible, that is, until the partial water vapour pressure of the solution will be near to that of the ultimate dehydrant of the water transfer agent. As it was shown above that the KCl required for the process could not serve for water-transfer purposes (par. 5.1.7.), NaCl available cheaply and abundantly in Sdom will be used for this purpose.

It should be pointed out at this stage that the water transfer was not executed experimentally. The suitability of any particular solvent for the process was thus not ascertained. As alcohols with a $C_4$- and $C_5$-chain have been shown to exhibit generally more or less favourable water-transfer characteristics, it was assumed that for the purpose of a preliminary economic analysis the choice of normal butanol would be sufficiently justified.

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Note 19: Local practice utilises 120 kg fuel oil per ton burnt lime, and 40% excess air.

It goes without saying that future development of the process will have to ascertain this point experimentally.

### 5.3.2. Construction of the equilibrium lines (note 20)

Data necessary for construction of the equilibrium line between aqueous NaCl-solutions and normal butanol (nBuOH) are known (167).

As the substance transferred from the one stream to the other is water, the data plotted are weight ratios between water and NaCl respectively water and nBuOH, as proposed by (168).

An exact determination of the equilibrium line for the system KCl-$CaCl_2$- $H_2O$ - nBuOH would require extensive experimental work. The procedure was simplified by considering the potassium chloride present in terms of calcium chloride. In other words, the amount of KCl was regarded as an additional amount of $CaCl_2$ causing the same decrease of the partial water vapour pressure (p.w.v.p.). This method is justified if it is considered that the influence of $CaCl_2$ on the p.w.v.p. is at all concentrations considerably higher than that of KCl. This is illustrated by fig. 5.5., constructed with the aid of (169) and (170). Hence, the calculation could be limited to the equilibrium line between an aqueous $CaCl_2$-solution and nBuOH. This line was calculated with the data of (171) and plotted analogously to that above.

For conveniency, both lines were set out on the same graph. See fig. 5.6.

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<u>Note 20:</u> The calculations have been carried out for a reference temperature of 20°. It is assumed that the results will not be influenced considerably when operating at higher temperatures, such as encountered in Sdom.

(167) A. Baniel, J.Appl.Chem. 9 (1959) 523
(168) R. Blumberg, Brit.Chem.Eng. 5 (1960) 172-3
(169) International Critical Tables (New-York & London, 1928) vol. III p.295
(170) International Critical Tables (New-York & London, 1928) vol. III p. 298
(171) R. Blumberg & J. Mashall, Israel Mining Industries - Unpublished

FIGURE 5.5.

THE PARTIAL WATER VAPOUR PRESSURE OF AQUEOUS SOLUTIONS OF KCl AND $CaCl_2$ AT 20°

(VARIOUS SOURCES, SEE INTERN. CRIT. TABLES III 295, 298)

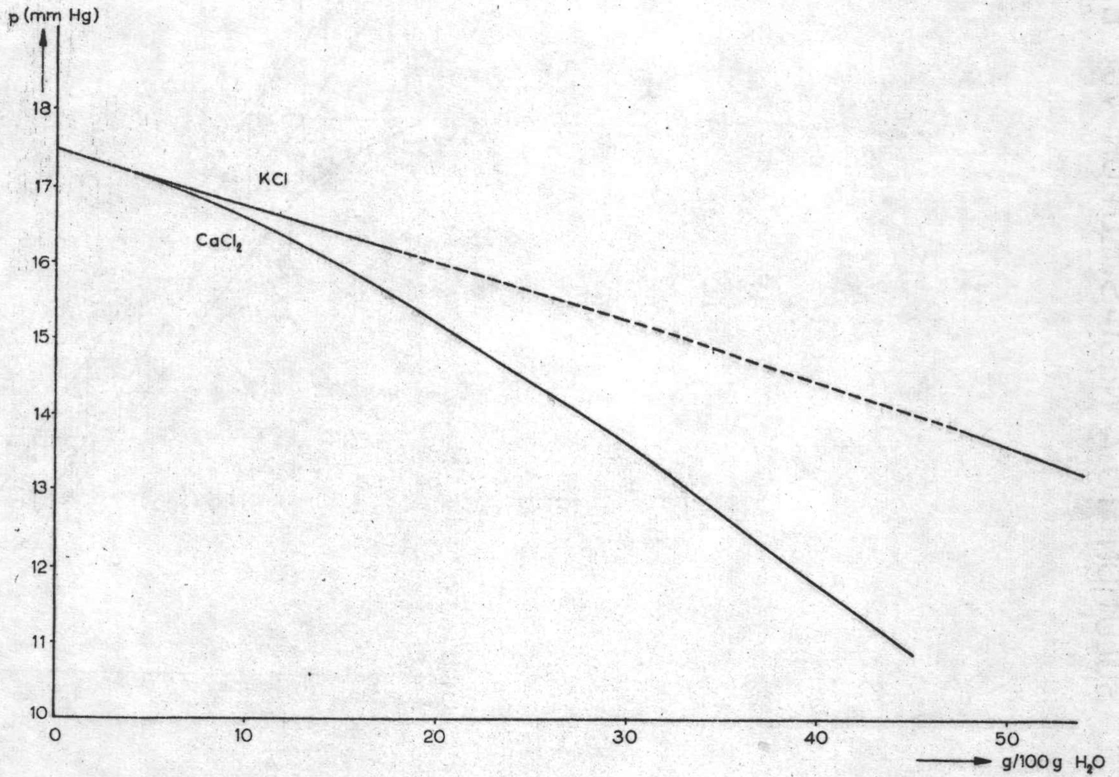
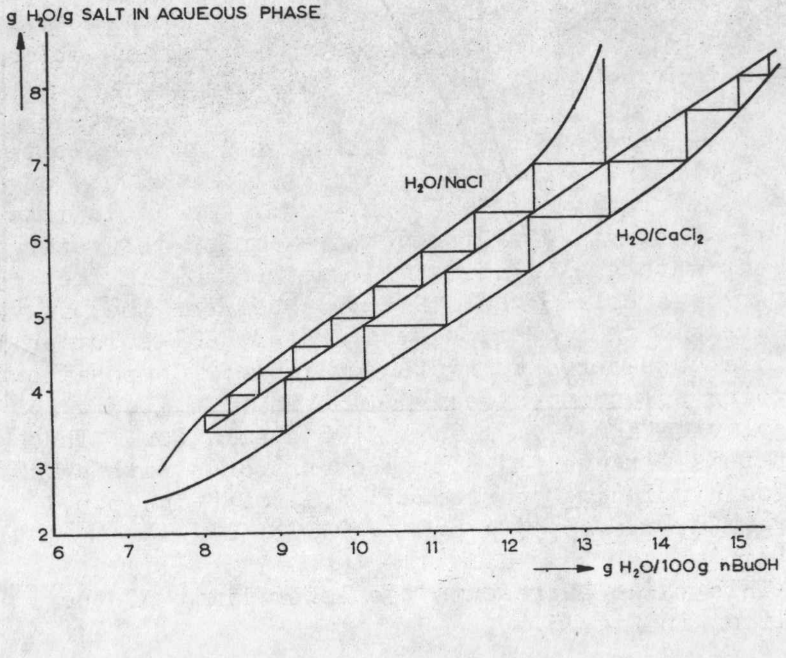


FIGURE 5.6.

EQUILIBRIUM LINES AND OPERATING LINES IN THE WATER TRANSFER FROM A $CaCl_2$-SOLUTION TO A NaCl-SOLUTION VIA nBuOH.



### 5.3.3. Operating lines

All possible operating lines in fig. 5.6. will be limited by two horizontal lines. The upper value corresponds with the concentration of the incoming $CaCl_2$-solution (including KCl expressed as $CaCl_2$). The lower value corresponds with the concentration of the outgoing $CaCl_2$-solution (including KCl).

Stream (4) contains 51.6 t KCl/510.5 t water = = 10.11 g KCl/100 g water. This concentration lowers (fig. 5.5.) the p.w.v.p. to 16.74 mm., i.e. by 17.50-16.74 = = 0.76 mm.

Stream (4) also contains 27.7 t $CaCl_2$/510.5 t water = 5.42 g $CaCl_2$/100 g water, lowering the p.w.v.p. to 17.06 mm, i.e. by 17.50-17.06 = 0.46 mm. The total decrease is 0.76 + 0.46 = 1.22 mm, corresponding to a p.w.v.p. of 16.28 mm, i.e. a total $CaCl_2$-concentration of 12.40 g/100 g $H_2O$ or 100/12.40 = 8.07 g $H_2O$/g $CaCl_2$. This is the upper limit of the operating lines.

The lower limit of the operating lines is found by trial and error. The actual concentrations of KCl and $CaCl_2$ should (a) be compatible with those of the system $KCl-CaCl_2-H_2O$ (fig. 5.7.); (b) have such a combined p.w.v.p. that its difference from that of a saturated NaCl-solution leaves a usable driving force for the dehydration.

An arbitrary decrease of the p.w.v.p. due to the $CaCl_2$ is then chosen, yielding (table 5.4.) a p.w.v.p. of the mixture. Saturation to KCl is assumed. As it is intended to execute the last stage of the dehydration of the water transfer agent with a saturated solution of NaCl in the presence of excess solid, the difference between the p.w.v.p. of the mixture and that of such a saturated NaCl-solution in "case No.1" is considered sufficiently large. Composition of the outgoing solution (stream (44) ) is thus 10.3 g KCl/100 g solution and 17.4 g $CaCl_2$/100 g solution. The p.w.v.p. of this mixture (13.63 mm) corresponds with a $CaCl_2$-concentration (including "converted" KCl) of (fig. 5.5.) 29.7 g/100 g $H_2O$, i.e. 3.37 g $H_2O$ /g $CaCl_2$.

This value represents the lower limit of the operating lines in fig. 5.6.

## TABLE 5.4.

The Partial Vapour Pressures of Aqueous KCl-CaCl$_2$ - Mixtures

| Case No. I | Decrease of p.w.v.p. by CaCl$_2$ mm II | P.w.v.p. of CaCl$_2$-soln. mm III | CaCl$_2$ concn g/100g water (from fig.5.5.) IV | CaCl$_2$ concn g/100g water + CaCl$_2$ V | KCl concn g/100g mixture (from fig.5.7.) VI | CaCl$_2$ concn g/100g mixture VII | KCl concn g/100g mixture (corrected from fig.5.7.) VIII |
|---|---|---|---|---|---|---|---|
| 1 | 2.80 | 14.70 | 23.0 | 18.8 | 9.3 | 17.5 | 10.3 |
| 2 | 3.10 | 14.40 | 25.0 | 20.0 | 9.0 | 18.7 | 9.5 |
| 3 | 2.50 | 15.00 | 21.3 | 17.6 | 10.4 | 16.2 | 11.2 |

| CaCl$_2$ concn g/100g mixture (corrected by calcul.) IX | KCl concn g/100g water X | P.w.v.p. of KCl soln mm XI | Decrease of p.w.v.p. by KCl mm XII | Sum of decreases of p.w. v.p. mm XIII | P.w.v.p. of mixture mm XIV | Remarks XV |
|---|---|---|---|---|---|---|
| 17.4 | 14.2 | 16.43 | 1.07 | 3.87 | 13.63 | P.w.v.p. of saturated NaCl = 13.60 mm. (172). |
| 18.6 | 13.2 | 16.50 | 1.00 | 4.10 | 13.40 | |
| 16.1 | 15.4 | 16.34 | 1.16 | 3.66 | 13.84 | |

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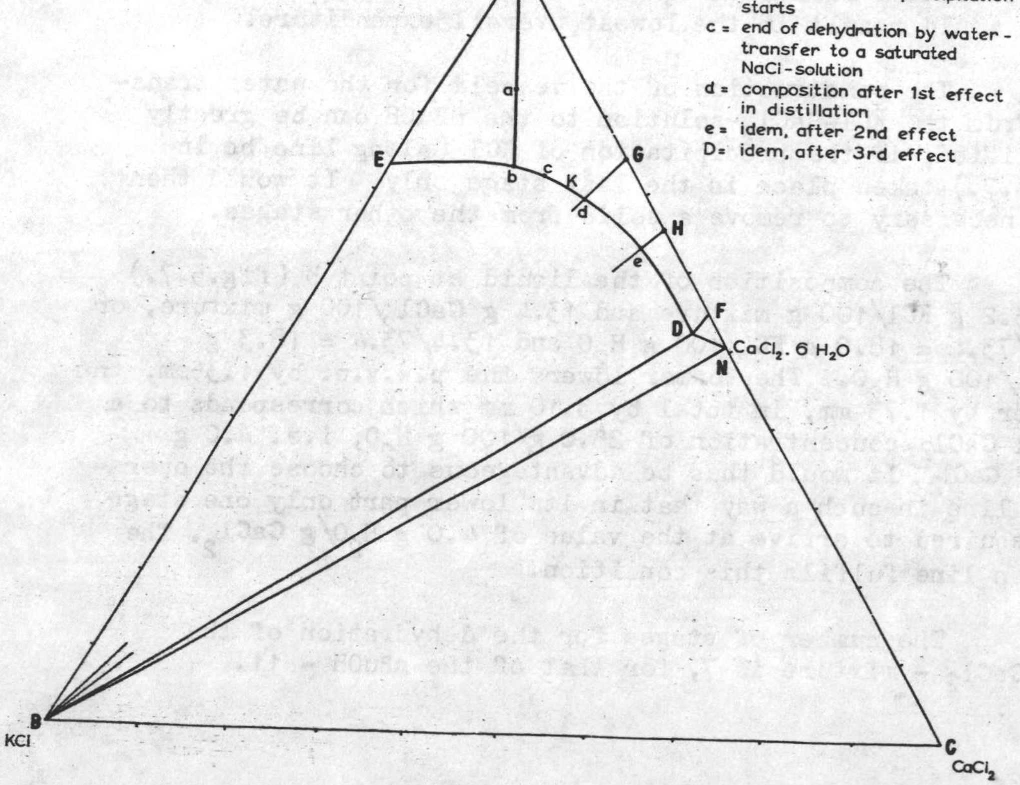
(172) International Critical Tables (New-York and London 1928) vol. III p.370

FIGURE 5.7.
THE SYSTEM KCl-$CaCl_2$-$H_2O$
25°
(g/100g solution)

W.B. LEE & A.C. EGERTON
J. CHEM. SOC. (LONDON)
123 (1923) 706



Between these limits, many operating lines (for both sides of the water transfer) are possible. If a high utilisation (i.e. small inventory) of the water transfer agent (here: normal butyl-alcohol) is required, then the upper limit of the operating line should be near to the $H_2O$ /$CaCl_2$ equilibrium line. If a small number of stages is required, the operating line should be as far as possible from both equilibrium lines. If required, dehydration of the nBuOH with NaCl might be executed in a single stage, resulting in less equipment. Salt consumption would be higher than with multiple stages, as in the latter case a diluted salt-solution would be obtained.

The correct choice of the operating lines demands, strictly speaking, that for several cases the final calculation be made, including costs of chemicals, equipment, operating, the influence on subsequent stages of the process, etc. It has been determined that a single operating line near to the $H_2O$/$CaCl_2$-equilibrium line at the upper limit, but approximately equidistant from both equilibrium lines in its middle portion, would result in the lowest overall expenditure.

The construction of the vessels for the water transfer from the KCl-$CaCl_2$-solution to the nBuOH can be greatly simplified, if the precipitation of KCl (along line bc in fig.5.7.) takes place in the last stage only. It would then be unnecessary to remove a solid from the other stages.

The composition of the liquid at point b (fig.5.7.) is 13.2 g KCl/100 g mixture and 13.4 g $CaCl_2$/100 g mixture, or 13.2/73.4 = 18.0 g KCl/100 g $H_2O$ and 13.4/73.4 = 18.3 g $CaCl_2$/100 g $H_2O$. The former lowers the p.w.v.p. by 1.35mm, the latter by 1.75 mm, in total by 3.10 mm which corresponds to a total $CaCl_2$ concentration of 25.0 g/100 g $H_2O$, i.e. 4.0 g $H_2O$/g $CaCl_2$. It would thus be advantageous to choose the operating line in such a way that in its lower part only one stage is required to arrive at the value of 4.0 g $H_2O$/g $CaCl_2$. The chosen line fulfils this condition..

The number of stages for the dehydration of the KCl-$CaCl_2$ - mixture is 7, for that of the nBuOH - 11.

### 5.3.4. Composition of the outgoing streams

The outgoing stream (44) contains 10.3 g KCl/100 g solution and 17.4 g $CaCl_2$/100 g solution. As no $CaCl_2$ has precipitated, we have in total 27.7 x $10^6$ x 100/17.4 g solution = 159.2 t solution, containing (besides the 27.7 t $CaCl_2$) 159.2 x $10^6$ x 10.3/100 g KCl = 16.4 t KCl.

At a specific gravity of 1.24 (173), the volume of the solution is 159.2/1.24 = 128.3 $m^3$, and the concentrations are 128 g KCl/l and 216 g $CaCl_2$/l.

The amount of KCl that has precipitated is 51.6 - 16.4 = 35.2 t (stream (45) ).

The KCl-$CaCl_2$-stream dissolves some nBuOH, the exact concentration of which is not known. If the solubility of nBuOH is assumed to be equal to that in an aqueous solution containing the same number of moles NaCl, and if we assume further, that the decrease of solubility of nBuOH by NaCl is a linear function, then the solubility of nBuOH is found as follows: (44) contains 128 g KCl/l = = 1.72 M; 216 g $CaCl_2$/ = 1.95 M; in total 3.67 M, which would equal 215 g NaCl/l ~ 19 g NaCl/100 g solution = = 23.5 g NaCl/100 g $H_2O$. Here, solubility of nBuOH is then (from (167) and unpublished data) 31 g/l.

Assuming this value to hold in the present case, the total amount of nBuOH dissolving is: 31 x 128.3/1000 ~ 4.0 t. Correction of this amount for the now corrected volume, yields an amount of 4.1 t nBuOH dissolved.

### 5.3.5. Composition of the nBuOH streams

The amount of water transferred to the nBuOH is 510.5 - 115.1 = 395.4 t. The alcohol has an incoming hydration (fig. 5.6.) of 8.0 g $H_2O$/100 g nBuOH, and an outgoing hydration of 12.85 g $H_2O$/100 g nBuOH, i.e. a difference of 4.85 g $H_2O$/100 g nBuOH. For 395.4 t $H_2O$, 395.4 x 100/4.85 = 8150 t nBuOH are needed. These enter (stream (50) ) with 8150 x 8.0/100 = 652 t $H_2O$, and leave (stream (51) ) as 8150 - 4.1 = 8146 t with 1047 t $H_2O$.

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(173) W.B.Lee & A.C.Egerton, J.Chem. Soc.(London) 123 (1923) 706-16

The volume of (50) will be (at a specific gravity of 0.825 for a 7.4 wt-% $H_2O$ -solution (174)) 8802/0.825 = 10670 $m^3$. The volume of (51) will be (spec.grav.(for 11.4 wt-% $H_2O$) is 0.830 (174)) 9193/0.830 = 11080 $m^3$.

The ratio of volumes in the extraction of water from the KCl-$CaCl_2$- solution to the nBuOH is thus initially volume (4)/volume (50) =518/10670 ~ 1/21, and changes gradually to its final value of volume (44)/volume (51) = 131.7/11080 ~ 1/84.

Mutual contamination in this extraction is unavoidable. Some KCl and $CaCl_2$ will dissolve in the nBuOH. For this reason the dehydration of the nBuOH from this water-transfer cannot be combined with the dehydration of that from the $KHCO_3$ -stream.

Dehydration of the nBuOH will take place with a NaCl-solution. The concentration of the latter will on the one hand determine the concentration of the former. On the other hand, the amount of NaCl will be determined by the amount of nBuOH returning from the distillation and requiring dehydration. Therefore, the NaCl-requirements will be calculated in section 9 (water transfer from the $KHCO_3$ -solution), par.5.9.4.

## 5.4. Section 4: Distillation of nBuOH and water and precipitation of KCl.

The incoming stream(44) corresponds to point c of fig.5.7.(except for its nBuOH-contents). To recover as much KCl as possible, evaporation until point D (or near to it) is required. This evaporation also serves to recover the nBuOH.

The evaporation is carried out in multiple effect distillation columns. The first column serves to distil the nBuOH off.

### 5.4.1. Composition of the distillates.

Unpublished research of the Israel Mining Industries' Laboratories has indicated that unless considerable fractionation is applied, the distillation of nBuOH from its aqueous solution does not yield its azeotrope, but a mixture containing considerably more water.

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(174) Y.D.Wad & A.G. Gokhale, J.Ind.Inst.Sci. 4 (1921) 17-25

It is now assumed that the composition of the vapour-phase will be such as to correspond with higher water-contents, i.e. with a higher boiling point of the solution than that of the azeotrope. For this boiling point, 95.0° was taken, corresponding (175) to a vapour-phase composition of 16.5 mol-% nBuOH, or 1.24 g $H_2O$/g nBuOH (the azeotrope boils at 92.3 (176).

The nBuOH - $H_2O$ mixture distilling (stream (52) ) will hence contain (approximately all) the nBuOH, 4.1 t, and 4.1 x 1.24 = 5.1 t water. After condensation and cooling this mixture will separate into two layers, with a total volume of approximately 11 $m^3$.

In addition to this mixture a stream of pure water is obtained as well from this distillation. The final composition of the mixture (point D, fig. 5.7.) contains 52.4 g $H_2O$/44.6 g $CaCl_2$ = 32.6 t $H_2O$/27.7 t $CaCl_2$ (no $CaCl_2$ precipitates). The excess water, 115.1 - (5.1 + 32.6) = 77.4 t is obtained free from salts (stream (53) ).

### 5.4.2. Composition of the bottom

The bottom (stream (46) ) (or rather, combined from the multiple effects) contains 32.6 t $H_2O$, 27.7 t $CaCl_2$ and 3.2 g KCl/44.6 g $CaCl_2$ (fig. 5.7.) i.e. 2.0 t KCl. This amount represents an irrecoverable loss.

At a specific gravity of 1.485 (173) the bottom's volume is 62.3/1.485= 42 $m^3$. The concentrations are :
KCl, 2.0 x 1000/42= 47.6 g/l; $CaCl_2$, 27.7 x 1000/42= 660 g/l.

### 5.4.3. Amount of KCl recycled; final KCl needs of the process

The amount of KCl precipitating in the distillation is 16.4 - 2.0= 14.4 t (stream (47) ). Any liquid adhering to this precipitate is neglected at this stage.

The total KCl - recycle (stream (48) ), from the water transfer (stream (45) ) and from the distillation, amounts to 35.2 + 14.4 = 49.6 t.

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(175) J.S.Stockhardt & C.M.Hull, Ind.Eng.Chem. 23(1931)1438-40
(176) International Critical Tables (New-York,1928) Vol.III,318
(173) W.B.Lee & A.C. Egerton, J.Chem.Soc.(London) 123 (1923) 706-16

The total KCl - requirements of the process (in stream (1) ) are 175.2 t. Hence, there must be supplied (stream (49) ) 175.2 - (49.6 + 86.0) = 39.6 t. (The 86.0 t are from the diluted KCl - solution, stream (3) ). Stream (49) represents the requirements of the process as regards KCl as raw material.

## 5.5. Section 5: Carbonation of the Phenolic Potassium Hydroxide Solution

The incoming stream (11) contains the phenolic solutions of potassium and calcium hydroxide. By carbonation with $CO_2$ the potassium compound is converted to $KHCO_3$, the calcium precipitates as $CaCO_3$, and part of the phenol separates as a distinct phase.

The amount of $CO_2$ required is as follows :-

For bicarbonation to $KHCO_3$ 28.0 x 44/56.1 = 22.0 t;

For carbonation to $CaCO_3$ 3.2 x 44/74.1 = 1.9 t;

in total 23.9 t.

Of this, the lime kiln supplies (stream (12) ) 19.5 t only, and these as a diluted gas, with which the carbonation cannot be completed. An additional, concentrated amount becomes available from the decomposition of the $KHCO_3$ (in the final stage) to $K_2CO_3$. From 50 t $KHCO_3$, 44 x 50/2 x 100.1 = 11.0 t $CO_2$ (stream (13) ) can be obtained. This, together with that available from the lime kiln (19.5 + 11.0 = 30.5) suffices, as follows from the overall reaction

$$2KCl + CaCO_3 \longrightarrow K_2CO_3 + CaCl_2.$$

Alternatively, if $KHCO_3$ would be the desired end product, the extra, concentrated, $CO_2$ (stream (32) ) would have to be drawn from some other source (note 21).

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Note 21: The flue-gases of the lime-kiln would not serve for the present purpose, since total carbonation requires that at least part of the $CO_2$ be concentrated.

The amount of $CaCO_3$ precipitating (stream (14) ) is 100.1 x 3.2/74.1 = 4.3 t. It is discarded. Any liquid adhering to it is neglected at this stage.

The concentration of the phenol in the aqueous phase after carbonation drops to 61.1 g/l (par. 4.3.1.). The amount that has separated equals
$(64.3 - 61.1)\ 850 \times 1000/10^6 = 2.7$ t (stream (15) ).
This amount, together with the water it contains, is recycled.

The outgoing $KHCO_3$ - solution (stream (16) ) contains the following:-

$KHCO_3$ 28.0 x 100/56.1 = 50.0 t; phenol, 54.6 - 2.7 = 51.9 t; water, 789 t. Setting the final phenol concentration at 61.1 g/l, the volume will be 851 $m^3$, indicating a specific gravity of about 1.04. $KHCO_3$ - concentration is then 58.8 g/l.

## 5.6. Section 6: Salting out of Phenol

To recover the phenol in stream (16), its solubility is decreased by salting out with solid $KHCO_3$. From the point of view of energy - expenditure, this step advantageously precedes that of the extraction, as the latter method requires distillation to separate the extractant from the phenol, which requires sizeable amounts of steam.

Strictly speaking, several cases of differing extent of salting out (including no such operation) together with the respective requirements of extraction and distillation, should be calculated totally, and their costs compared. For the present preliminary analysis, this has not been done.

In the presence of 176.4 g $KHCO_3$/l, phenol concentration drops to 39.0 g/l (par. 4.3.2.). To attain this, $(176.4 - 61.1) \times 851 \times 10^3/10^6$ = (say) 100 t of $KHCO_3$ have to be recycled (stream (17) ). The amount of phenol staying in solution is $39.0 \times 851 \times 10^3/10^6 = 33.2$ t. The amount of phenol which separates (stream (18) ) is thus 51.9 - 33.2 = 18.7 t.

The outgoing stream (19) contains:-

$KHCO_3$, 150.0 t (176.4 g/l);

phenol, 33.2 t (39.0 g/l);

water, 789 t.

Its weight is 972 t, its volume 851 $m^3$.

## 5.7. Section 7: Extraction of Phenol

The final stage in the recovery of phenol from the $KHCO_3$ - solution consists of extraction with normal butyl-acetate (nBuOAc). This solvent forms a solution containing 500 g phenol/l (par. 4.3.3, exp.8C6). For 33.2 t phenol, the volume of the $C_6H_5OH$ - nBuOAc is then $33.2 \times 10^6/500 \times 10^3 = 66.4$ $m^3$. This mixture contains 5% of water (par. 4.3.5.), and has a specific gravity of (say) 0.95.

Let now a = weight of pure nBuOAc

b = weight of mixture of nBuOAc, phenol and water.

Then $b = a + 33.2 + 0.05\ b$

Also, $b/66.4 = 0.95$

giving $b = 63.0$ t; $a = 26.6$ t; $0.05\ b = 3.2$ t.

The entering nBuOAc - stream (21) should contain not only the amount necessary for the extraction, but the losses to the $KHCO_3$ - solution as well.

The solubility of nBuOAc in an aqueous $KHCO_3$ - solution of 176 g/l was established (177) at 0.35 ml nBuOAc/100 ml $KHCO_3$ - solution. This results (for an approximate $KHCO_3$ - solution volume of 843 $m^3$) in $3.5 \times 0.882 \times 843/10^3 = 2.6$ t nBuOAc (note 22).

Thus, the entering nBuOAc - stream (21) contains $26.6 + 2.6 = 29.2$ t. At a specific gravity of 0.882 (178)

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Note 22: Research aimed at lowering this amount should be one of the first aims of any further development of this process. The losses might perhaps be decreased by using higher homologues of the solvent.

(177) Israel Mining Industries' Analytical Laboratory, unpublished results.

(178) C.D.Hodgman, Handbook of Chemistry and Physics (1957) p. 713

its volume is 33.1 $m^3$. This nBuOAc-stream contains water, as cooling of the nBuOAc - $H_2O$ azeotrope obtained in the top of the subsequent distillation, yields two phases. The nBuOAc - phase, saturated with water, is added to the pure nBuOAc obtained from a lower stage in the distillation, and the combined streams are recycled to the extraction.

The amount of water in the nBuOAc - phase (stream (24) ) is small (of the order of 0.1 t) and will be neglected here.

The phenol-loaded extractant (stream (22) ) contains 26.6 t nBuOAc, 33.2 t $C_6H_5OH$ and 3.2 t water. Its total weight is 63.0 t, its volume is 66.4 $m^3$.

Concentrations in this solution are: $C_6H_5OH$, 500 g/l; water, 3.2 x $10^3$/66.4 = 48.2 g/l; nBuOAc, 26.6 x $10^3$/66.4 = 401 g/l.

The extracted $KHCO_3$ - stream (20) contains very little phenol, 28 mg/l (par. 4.3.3., exp. 8H6). It comprises the following : water, 789 - 3.2 = 786 t; $KHCO_3$, 150.0 t; and some $C_6H_5OH$. At a specific gravity of circa 1.11 (interpolated from (179) and (180)) the volume is 936/1.11 = 843 $m^3$. Hence the phenol-contents are 28 x 843/$10^3$ = 23.6 (say 24) kg. These represent the losses inherent in the process (excluding any eventual losses in the distillation, due to decomposition, reaction with any fragments of the nBuOAc, etc.).

The concentration of $KHCO_3$ is 150 x $10^3$/843 = 178 g/l.

The ratio of volumes in the extraction is initially volume (19)/volume (22) = 851/66.4 = 13/1, and finally volume (20)/volume (21) = 843/33.1 = 26/1.

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(179) International Critical Tables (New-York, 1928) vol. III p. 90

(180) A. Seidell, Solubilities of Inorganic and Metal-Organic Compounds (New-York, 1940) vol. I, p. 727

## 5.8. Section 8: Distillation of the $C_6H_5OH$-nBuOAc mixture

### 5.8.1. Distillation

The separation of $C_6H_5OH$ from nBuOAc is feasible by distillation. Two products distill over, an azeotrope nBuOAc - $H_2O$ at the top (b.p. 90.2; composition 28.7 wt-% water (181) ) and pure nBuOAc at some lower point (b.p. 126 (178) ). Phenol, free from the ester, is obtained as bottoms.

A part of the top is condensed only and returned as reflux to the column. No experiments as to the reflux-ratio were executed; arbitrarily a ratio of 1:1 has been chosen. The rest of the top is cooled. The nBuOAc-phase is combined with the pure nBuOAc - stream and recycled to the extraction.

The top-product (stream (23), after deduction of the reflux) contains the 3.2 t water, and (100 -28.7) x 3.2/28.7= = (say) 8.0 t nBuOAc.

Phase separation yields two streams:-

Aqueous, containing x ton water + y ton nBuOAc;

Solvent, containing v ton water + z ton nBuOAc.

The following then holds:-

$$x+v = 3.2$$

$$y+z = 8.0$$

$y/x = 5/1000$ (=solubility of nBuOAc in water (177))

$v/z = 8/1000$ (=solubility of water in nBuOAc (177))

This gives:
$$\left.\begin{aligned} x &= 3.14\ \text{t} \\ y &= 16\ \text{kg} \end{aligned}\right\}\ \text{stream (25)}$$

$$\left.\begin{aligned} v &= 64\ \text{kg} \\ z &= 8.0\ \text{t} \end{aligned}\right\}\ \text{stream (24)}$$

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(181) M. Lecat, Tables Azéotropiques (Bruxelles 1949) Tome I, p. 215

The remainder of the solvent, not obtained in the top, exits at a somewhat lower point. It comprises (stream (26) ) 26.6 - 8.0 = 18.6 t.

The two nBuOAc - streams are combined, and form 26.6 t. To the combined stream, the make up of nBuOAc (2.6 t) is added (not depicted in the flow - sheet).

The value of the solvent in the discarded aqueous stream (16 kg, at a value of 0.13 \$/lb (182)) is 0.13 x 16/0.459 ~ 4.6 \$. Unless pollution control requires it, recovery is probably not economic.

The volume of the water in the discarded aqueous stream (3.2 $m^3$) is very small in comparison with the total water requirements of the process (about 1200 $m^3$).

The bottom of the distillation is formed (stream (27) ) by 33.2 t $C_6H_5OH$. It is recycled as a liquid, containing little water.

### 5.8.2. Balance of the phenol

Phenol is recovered in the following streams:-

(15) 2.7 t (saturated with water).
(18) 18.7 t ( " " " ) } stream (28)
(27) 33.2 t (containing little water)
(29) 21.2 t (as a dilute solution).

Total 75.8 t.

Except for eventual losses of phenol (as set out in the end of paragraph 5.7.) the process contains no inherent source by which $C_6H_5OH$ might be lost, save for the very small amount in the $KHCO_3$ - stream (24 kg).

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(182) Chem. Eng. News, Quarterly Report on Current Prices <u>38</u> (1960) no. 26, 58

## 5.9. Section 9: Dehydration of the $KHCO_3$ by water-transfer

### 5.9.1. Mode of operation

Dehydration of the potassium bicarbonate by water transfer instead of by conventional means is favourable from the point of view of energy. Heating is unnecessary, and no application of vacuum (to prevent untimely decomposition) is required.

It is proposed to use NaCl as dehydrant. This cheaply and abundantly available material (in Sdom) makes it possible to dehydrate $KHCO_3$ solutions completely and to effect precipitation, which operation needs only be followed by centrifugation to separate adhering liquid.

In analogy with many other mass-transfer operations, the water-transfer is executed counter-currently. The diluted $KHCO_3$-solutions encounter the nBuOH in its wettest state. The saturated $KHCO_3$-solution, emerging from the last stage, is mixed in an additional stage with nBuOH in its dryest state (having been contacted with a saturated NaCl-solution) to effect precipitation of $KHCO_3$. This extra stage is represented in the figure of equilibrium and operating lines by a single point.

The wet nBuOH is dried counter-currently by a NaCl-solution of increasing concentration, and finally by saturated NaCl, whence it is returned to the $KHCO_3$-dehydration.

### 5.9.2. Equilibrium and operating lines; number of stages

The equilibrium line for the system NaCl - nBuOH - $H_2O$ has been described - par. 5.3.2.

For the equilibrium line $KHCO_3$ - nBuOH - $H_2O$ three points are available (183) (table 5.5.):-

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(183) Unpublished data, Israel Mining Industries' Laboratories

Table 5.5.

Equilibria $KHCO_3$ - nBuOH - $H_2O$

| $KHCO_3$, concentrations in $H_2O$ | | | |
|---|---|---|---|
| solution as prepared * | g $KHCO_3$ /100 g $H_2O$ | g $H_2O$ /g $KHCO_3$ | g $H_2O$/100 g nBuOH in organic phase |
| saturated | 39.23 | 2.546 | 13.4 |
| 1.0 : 0.25 | 31.40 | 3.185 | 18.2 |
| 1.0 : 1.0 | 19.61 | 5.10 | 24.4 |

* volumes saturated solution: volumes of water

These data are plotted in fig. 5.8.

The operating lines terminate at points determined by the concentrations of the incoming streams.

$KHCO_3$ enters (stream (20) ) at 150 t/786 t $H_2O$ = = 19.1 t/100 t $H_2O$, i.e. 5.23 g $H_2O$/g $KHCO_3$. $KHCO_3$ leaves the system as a saturated solution (with excess solid $KHCO_3$, which plays no role any more in the system). At 30° this solution contains 38.9 g $KHCO_3$/100 g $H_2O$ (184) = 2.57 g $H_2O$/g $KHCO_3$. Point a is chosen thus that its "$H_2O$/100 nBuOH" - value is as high as possible, to ensure a high nBuOH - utilization without incurring too many stages. Point b is chosen thus, that its "$H_2O$/100 nBuOH" - value, which will of necessity equal that of the second operating line, will result in a reasonable number of stages in both operations.

A thorough analysis, requiring a complete calculation for a number of cases, was not considered necessary for this preliminary analysis.

The number of stages for the water-transfer from the $KHCO_3$ to the nBuOH - stream is thus $4\frac{1}{2}$ (say 5) + 1 (additional for separation of solids) = 6.

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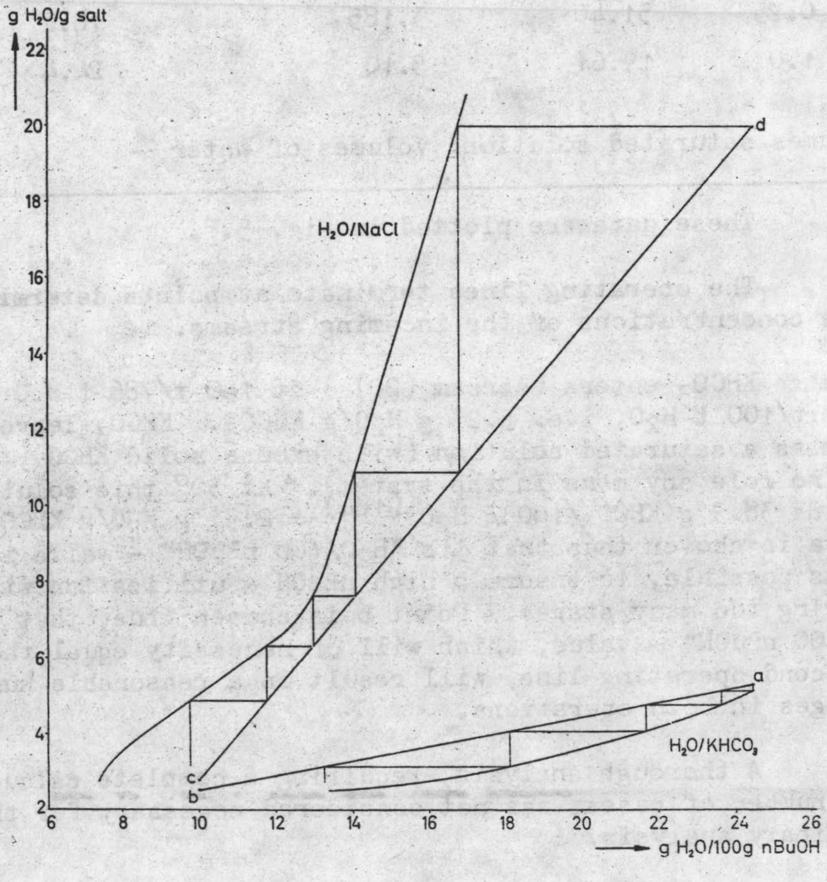
(184) International Critical Tables (New-York and London, 1928) Vol. III p. 240.

FIGURE 5.8.
EQUILIBRIUM AND OPERATING LINES IN THE TRANSFER OF WATER FROM A $KHCO_3$-SOLUTION TO NaCl-SOLUTION VIA nBuOH



As the nBuOH enters the $KHCO_3$ - dehydration, coming from the saturated NaCl-solution, its initial "g $H_2O$/g NaCl"-value is equal to that of such a saturated NaCl-solution, to wit 2.76. Its hydration after contact with the saturated $KHCO_3$ - solution in the additional stage, "g $H_2O$/100 g nBuOH", is equal to that of b. Hence c. The outgoing nBuOH has a hydration, "g $H_2O$/100 g nBuOH" which must equal that of a; its "g $H_2O$/g NaCl" - value is chosen so that a low concentration of the outgoing NaCl-solution (i.e., a low comsumption of NaCl per unit of water transferred) is not obtained at the price of a too high number of stages.

Once more, a detailed, complete analysis was not executed here.

The number of stages for the nBuOH dehydration is then $4\frac{1}{2}$ (say 5) + 1 = 6 stages.

### 5.9.3. Composition of the influent and effluent streams

The weight of the water to be transferred is (from the flowsheet) 786 t, except for that amount adhering to the crystals, 2 wt-% = 0.02 x 150 = 3 t. The water-concentration in the dried nBuOH is that of the equilibrium line NaCl-nBuOH-$H_2O$ (assuming equilibrium to have been established), 7.4 g $H_2O$/100 g nBuOH (= 6.89 wt-%). The water concentration in the wet nBuOH has been chosen (see fig. 5.8.) as 24.5 g $H_2O$/100 g nBuOH (= 19.7 wt-%). The difference is 24.5 - 7.4 = 17.1 g $H_2O$/100 g nBuOH. Thus, (786 - 3) x 100/17.1= = 4606 t nBuOH are needed here.

The nBuOH enters the $KHCO_3$ - dehydration with 342 t water, leaves with 1128 t water. Stream (42) : 4606 t nBuOH + 342 t $H_2O$ (6.9 wt-%); at a specific gravity of 0.823 this is (say) 6000 $m^3$. Stream (43) : 4606 t nBuOH + 1128 t water (19.7%); at a specific gravity of (say) 0.845 this is (say) 6800 $m^3$.

The amount of nBuOH lost on the solid $KHCO_3$ is quite small (it will be calculated below). A more considerable amount is lost to the NaCl-solution; this loss is however recovered and recycled.

The solid $KHCO_3$ - stream (38) comprises 150 t (any solubility of $KHCO_3$ in the nBuOH is neglected), wetted with 3 t water, which is saturated to nBuOH. The nBuOH-solubility in a saturated $KHCO_3$-solution is 14.4 g/l (185), the total nBuOH amount on the $KHCO_3$ crystals is of the order of 43 kg.

This emerging $KHCO_3$ - stream is divided into two. A part (stream (17) ) is recycled (100.0 t) to the salting-out operation (section 6). The balance (stream (39) ), 50.0 t $KHCO_3$, comprises the production of the plant.

The amount of salt, needed for the water-transfer here, follows from the final NaCl-concentration (point d, fig. 5.8.), 20 g $H_2O$/g NaCl; 783/20 = 39.2 t NaCl are required (stream (70) ). The total amount leaving is 39.2 t NaCl + 783 t $H_2O$ = 822 t, i.e. 797 $m^3$ (at a specific gravity of 1.032). NaCl-concentration is 49.2 g/l. Assuming that nBuOH-solubility in a NaCl-solution varies linearily between pure water and a saturated NaCl-solution (70.0 g/l and 10.0 g/l, respectively (186) ), this solubility is (at 5 g NaCl/100 g $H_2O$) 62 g nBuOH/l solution; i.e. 797 x $62/10^3$ = 49.4 t.
Thus stream (71) : 783 t $H_2O$, 39.2 t NaCl (49.2 g/l), 49.4 t nBuOH (62 g/l).
It is further assumed, that addition of the nBuOH changes the specific gravity but little. The total weight of the solution being 872 t, its volume is (say) 872 $m^3$, giving an amount of nBuOH of 872 x $62/10^3$ = 54.1 t. This results in a total weight of 876 t, say 876 $m^3$, dissolving 54.3 t nBuOH.

### 5.9.4. The NaCl- and nBuOH - streams for sections 3 and 9

As was pointed out in par. 5.3.5., the amounts of NaCl and nBuOH are interdependent. For the sake of simplicity it is now assumed, that the wet nBuOH returning from the two distillations (sections 4 and 11) is in its totality returned to section 3 (water transfer from the KCl-$CaCl_2$-solution). The NaCl-requirements of section 9 ($KHCO_3$-dehydration) are considered constant, and its nBuOH-losses are considered to

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(185) Israel Mining Industries Analytical Laboratory, unpublished results

(186) Israel Mining Industries, unpublished data

be made up by solvent dehydrated in section 3. The flow-sheet depicts the more probable state, which is, however, more complicated to calculate. Both methods yield the same overall NaCl-consumption.

See fig. 5.9.

Let NaCl in (72) = a

nBuOH in (73) = b

c = extra water (over the amount which should be transferred in (73) )

nBuOH-losses in the distillation (Sect. 11) = 0

Ratio nBuOH/$H_2O$ from the distillation (sect. 11) equalling that ratio from the former distillation (sect. 4), to wit $H_2O$/nBuOH = 1.24 (in wt/wt).

Then, $H_2O$ in (57) = 1.24 (54.3 + b) = 67.4 + 1.24 b. (59) is calculated, and added to (51) to give the influent for the solvent-dehydration in section 3.

The water-balance yields:

$395 + c = 468 + 1.24\ b$, whence

$$1.24\ b + 73 = c \qquad (5.1.)$$

The amount of water being 395 + c, that of NaCl is (395 + c)/8.07 (from fig. 5.6.) = 49.0 + 0.124 c. Thus,

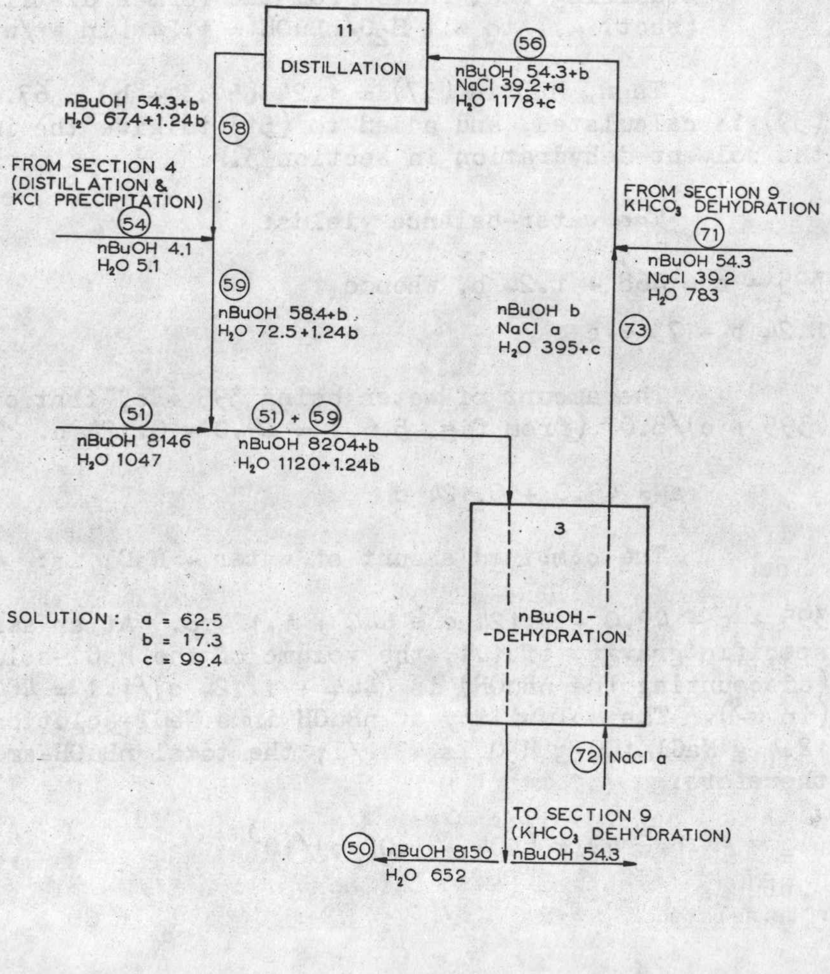
$$a = 49.0 + 0.124\ c \qquad (5.2.)$$

The combined amount of water + NaCl is:

395 + c + 49.0 + 0.124 c = 444 + 1.124 c. At an assumed specific gravity of 1.1, the volume of the NaCl-solution (discounting the nBuOH) is (444 + 1.124 c)/1.1 = 404 + 1.02 c (in $m^3$). The solubility of nBuOH in a NaCl-solution of 12.4 g NaCl/100 g $H_2O$ is 49 g/l; the total nBuOH-amount is therefore:

$$b = 49 \times (404 + 1.02\ c)/10^3 \qquad (5.3.)$$

FIGURE 5.9.
CALCULATION OF THE NaCl-CONSUMPTION
(ALL QUANTITIES IN TONS; BASIS = 24 HOURS)



Solution of the equations (5.1.) to (5.3.) gives:

a = 61.9 t; b = 25.0 t; c = 104 t.

| | | |
|---|---|---|
| Hence stream (72) | 61.9 t NaCl. | |
| (73) | $H_2O$ | 499 t |
| | NaCl | 61.9 t |
| | nBuOH | 25.0 t |
| (56) | $H_2O$ | 1282 t |
| | NaCl | 101.1 t |
| | nBuOH | 79.3 t |
| (57) = (58) | nBuOH | 79.3 t |
| | $H_2O$ | 98.4 t |
| (59) | nBuOH | 83.4 t |
| | $H_2O$ | 103.5 t |
| (51) + (59) | nBuOH | 8229 t |
| | $H_2O$ | 1551 t |

The total NaCl-requirements of the process are then (70) + (72)= 39.2 + 61.9 = 101.1 t (stream (55) ).

### 5.10. Section 10 : $KHCO_3$-drying (and eventual conversion to $K_2CO_3$)

The wet $KHCO_3$-crystals (stream (39) ) are dried in a rotary furnace. A gentle heating suffices for this operation. If conversion to $K_2CO_3$ is required, heating to about 160° is necessary. By cooling the effluent vapours, a separation between $H_2O$ + nBuOH on the one hand (stream (41) ) and $CO_2$ on the other hand (stream (13) ) is obtained. The latter is then used for the carbonation in section 5.

The entering (stream (39) ) 50.0 t wet $KHCO_3$ yield then (stream (40) ) either 50.0 t dry $KHCO_3$ or 50 x 138.2/ / (2 x 100.1) = 34.5 t $K_2CO_3$. Further, 1 t $H_2O$ (in the case of non-decomposition) respectively 1 + 18 x 50.0/(2 x 100.1) = = 5.5 t $H_2O$ (if converted) are obtained, as well as 14 kg nBuOH, in stream (41). If conversion takes place, stream (13) consists of 44 x 50.0/(2 x 100.1) = 11.0 t $CO_2$.

## 5.11. Section 11: nBuOH-distillation

The NaCl-solutions obtained from both water-transfer operations are saturated with nBuOH (stream (56) ). This nBuOH has to be recovered before discarding the brine.

For the sake of simplicity it has been assumed in the present preliminary analysis, that the most economic method of this recovery is by direct distillation with closed steam. Although this operation requires the heating of considerable volumes of brine, part of this heat can be recovered subsequently in heat exchangers. Any other method, such as for example extraction of the nBuOH with a suitable solvent and the separation by distillation between that solvent and nBuOH, might incur smaller heating requirements, but would complicate the flowsheet, as it would necessitate additional operations and equipment. As stated in former sections, a complete, detailed calculation for several possibilities was not executed for the present preliminary analysis.

By taking the required column dimensions, a brine containing less than 100 kg of nBuOH can be obtained. This amount has been taken arbitrarily as the maximum permissible nBuOH-losses. The distillate, stream (57) = (58) then contains all (or very nearly all) the nBuOH obtained from the water transfer operations (stream (56) ), i.e. 79.3 t, along with the water accompanying it, 98.4 t. On cooling, two phases are obtained. As the aqueous phase contains still 7 wt-% nBuOH, it is not discarded; both phases are dehydrated by NaCl (as set out in par. 5.9.4.).

The bottoms of the distillation, stream (60), contain the brine, 101 t NaCl and 1282 - 98 = 1184 t water, i.e. a 7.9% NaCl-solution (about 83 g/l, spec. grav. 1.055 (187) ). The total weight is thus 1285 t, the total volume 1285/1.055 = 1218 $m^3$.

The water contained in this brine is the largest source of loss of water in the process.

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(187) C.D. Hodgman, Handbook of Chemistry and Physics (1957) p. 1909.

## 5.12. Balance of Materials

### 5.12.1. Partial Balance, for Entering and Leaving Materials.

The balance of materials is made up for each material entering or leaving. The numbers in brackets denote the stream number.

KCl

In: 39.6 t (49)

Out: 2.0 t (46)

37.4 t (The equivalent of 50.0 t $KHCO_3$ (40) is 50 x 74.6/100.1 t KCl)

Total: 39.4 t

Stream (46) represents the losses of KCl inherent in the process; they amount to some 5.1% of the incoming KCl.

$Ca(OH)_2$

On the basis of calcium

In: 21.9 t (6), from 30 t $CaCO_3$(9)

Out: 3.2 t , the equivalent of 4.3 t $CaCO_3$ (14)

18.5 t , the equivalent of 27.7 t $CaCl_2$ (46)

Total 21.7

On the basis of hydroxyl

In: 21.9 t (6)

Out: 3.2 t (from (14) )

18.5 t the equivalent of 50.0 t $KHCO_3$ (40)

$(1\ Ca(OH)_2 \longrightarrow 2\ KOH \longrightarrow 2\ KHCO_3)$

Total 21.7

NaCl

In: 101.1 t (55)
Out: 101.1 t (60)

Thus, the NaCl-consumption is 101.1/50 = 2 t NaCl/t $KHCO_3$, which corresponds to a ratio of NaCl/KCl = 2.56.

$H_2O$

In: 5.3 t (8)
789 t (31)
510.5 t (2)

Total 1305 t

Out: 3.1 t (25)
1.0 t (41)
4.5 t equivalent to 50.0 t $KHCO_3$ (40)
77.4 t (53)
32.6 t (46)
1184 t (60)

Total 1303 t (or $m^3$)

The water-consumption of the process (except for cooling purposes) is somewhat smaller than this total, as stream (53), consisting of pure water, is returnable to the process. The consumption thus amounts to
1303 - 77 = 1226 $m^3$ per 50 t $KHCO_3$, or
24.5 $m^3$/t $KHCO_3$ = 35.6 $m^3$/t $K_2CO_3$.

### 5.12.2 The Complete Balance

A complete account of all streams in the flowsheet is given in table 5.6.

TABLE 5.6.

The Balance of Materials - Streams of Materials in tons per day

| Stream number | KCl | KOH | $KHCO_3$ | $K_2CO_3$ | $CaCO_3$ | CaO | $Ca(OH)_2$ | $CaCl_2$ | $CO_2$ | $C_6H_5OH$ | n-$C_4H_9OCOCH_3$ (nBuOAc) | n-$C_4H_9OH$ (nBuOH) | NaCl | Water | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 175.2 | | | | | | | | | | | | | | |
| 2 | | | | | | | | | | | | | | 510.5 | 686 |
| 3 | 86.0 | | | | | | | | | | | | | 510.5 | 511 |
| 4 | 51.6 | | | | | | | | | | | | | 510.5 | 597 |
| 5 | | | | | | | | 27.7 | | | | | | 510.5 | 590 |
| 6 | | | | | | | 30.1 | | | 75.8 | | | | 974 | 1080 |
| 7 | | | | | | | 21.9 | | | | | | | | 21.9 |
| 8 | | | | | | 16.6 | | | | | | | | | 16.6 |
| 9 | | | | | | | | | | | | | | 5.3 | 5.3 |
| 10 | | | | | 30.0 | | | | | | | | | | 30.0 |
| 11 | | 28 | | | | | | | | | | | | 185 | 185 |
| 12 | | | | | | | 3.2 | | | 54.6 | | | | 789 | 875 |
| 13 | | | | | | | | | 19.5 | | | | | | 19.5 |
| 14 | | | | | | | | | 11.0 | | | | | | 11.0 |
| 15 | | | | | 4.3 | | | | | | | | | | 4.3 |
| 16 | | | 50.0 | | | | | | | 2.7 | | | | | 2.7 |
| 17 | | | 100 | | | | | | | 51.9 | | | | 789 | 891 |
| 18 | | | | | | | | | | | | | | | 100 |
| 19 | | | 150 | | | | | | | 18.7 | | | | | 18.7 |
| 20 | | | 150 | | | | | | | 33.2 | | | | 789 | 972 |
| 21 | | | | | | | | | | 0.024 | 2.6 | | | 786 | 936 + 2.6 |
| 22 | | | | | | | | | | | 29.2 | | | | 29.2 |
| 23 | | | | | | | | | | 33.2 | 26.6 | | | 3.2 | 63.0 |
| 24 | | | | | | | | | | | 8.0 | | | 3.2 | 11.2 |
| 25 | | | | | | | | | | | 8.0 | | | 0.064 | 8 |
| 26 | | | | | | | | | | | 0.016 | | | 3.14 | 3.2 |
| 27 | | | | | | | | | | | 18.6 | | | | 18.6 |
| 28 | | | | | | | | | | 33.2 | | | | | 33.2 |
| 29 | | | | | | | | | | 54.6 | | | | | 54.6 |
| 30 | | | | | | | 8.2 | | | 21.2 | | | | 974 | 1003 |
| 31 | | | | | | | | | | | | | | 974 | 974 |
| 32 | | | | | | | | | | | | | | 789 | 789 |
| 38 | | | 150 | | | | | | 11.0 | | | | | | 11.0 |
| 39 | | | 50.0 | | | | | | | | | 0.030 | | 3 | 153 |
| 40 * | | | 50.0 | | | | | | | | | 0.014 | | 1 | 51 |
| 40 ** | | | | 34.5 | | | | | | | | | | | 50.0 |
| 41 * | | | | | | | | | | | | | | | 34.5 |
| 41 ** | | | | | | | | | | | | | | 1 | 1 |
| 42 | | | | | | | | | | | | | | 5.5 | 5.5 |
| 43 | | | | | | | | | | | | 4606 | | 342 | 4948 |
| 44 | 16.4 | | | | | | | | | | | 4606 | | 1128 | 5734 |
| 45 | 35.2 | | | | | | | 27.7 | | | | 4.1 | | 115.1 | 163 |
| 46 | 2.0 | | | | | | | | | | | | | | 35.2 |
| 47 | 14.4 | | | | | | | 27.7 | | | | | | 32.6 | 62.3 |
| 48 | 49.6 | | | | | | | | | | | | | | 14.4 |
| 49 | 39.6 | | | | | | | | | | | | | | 49.6 |
| 50 | | | | | | | | | | | | | | | 39.6 |
| 51 | | | | | | | | | | | | 8150 | | 652 | 8802 |
| 52 = 54 | | | | | | | | | | | | 8146 | | 1047 | 9193 |
| 53 | | | | | | | | | | | | 4.1 | | 5.1 | 9.2 |
| 55 | | | | | | | | | | | | | | 77.4 | 77.4 |
| 56 | | | | | | | | | | | | | 101.1 | | 101 |
| 57 = 58 | | | | | | | | | | | | 79.3 | 101.1 | 1282 | 1462 |
| 59 | | | | | | | | | | | | 79.3 | 98.4 | | 178 |
| 60 | | | | | | | | | | | | 83.4 | | 103.5 | 187 |
| 70 | | | | | | | | | | | | | 101.1 | 1184 | 1285 |
| 71 | | | | | | | | | | | | | 39.2 | | 39.2 |
| 72 | | | | | | | | | | | | 54.3 | 39.2 | 783 | 876 |
| 73 | | | | | | | | | | | | | 61.9 | | 61.9 |
| | | | | | | | | | | | | 25.0 | 61.9 | 499 | 586 |

* in case $KHCO_3$ is the product

** in case $KHCO_3$ is converted to $K_2CO_3$

## 5.13. Conversion of NaCl into $NaHCO_3$ and $Na_2CO_3$

### 5.13.1 Introduction

It has been pointed out earlier that the method of carbonation proposed in the present thesis need not necessarily be limited to the potassium compounds, but could be extended to the analogous sodium compounds as well. NaCl, cheaply and abundantly available in Sdom (Sodom), would then serve both as raw material and as dehydration agent of the $NaHCO_3$ made. Eventually, $Na_2CO_3$ could be obtained.

The present paragraph describes a flowsheet for the production of 42 t $NaHCO_3$ per day. This is equivalent with the 50 t $KHCO_3$ per day of the former paragraphs. The methods of calculation are quite analogous to the former ones, and will not be repeated here. Reference to the parallel sections of the $KHCO_3$ - flowsheet should be made.

All quantities are <u>per day</u>, unless otherwise stated.

### 5.13.2 The flowsheet

#### Section 1: Ion Exchange

Table 3.24. Summarizes the laboratory-scale experiments pertaining to the conversion

$$NaCl + Ca_{\frac{1}{2}}\text{-}R \longrightarrow Na\text{-}R + \tfrac{1}{2}CaCl_2 \qquad \text{and}$$

$$Na\text{-}R + \tfrac{1}{2}Ca(OH)_2 \quad (+C_6H_5OH) \longrightarrow Ca_{\frac{1}{2}}\text{-}R + NaOH \quad (+C_6H_5OH)$$

Complete analogy at equal normality for this conversion and the parallel one for potassium is assumed.

The following is then found:

(1) NaCl, 101.5 t; water, 279 t; total stream 380.4 t = 317 $m^3$

(2) 279 $m^3$ water.

(3) 31 t NaCl (assumed 10 wt-% on the water, i.e. 107.1 g/l(188))

(48) Recycled NaCl = 0

(49) Raw material NaCl = 101.0 - 31.6 = 70.5 t.

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(188) C.D. Hodgman, Handbook of Chemistry and Physics (1957) p.1909

(4) NaCl, 41.3 t; $CaCl_2$, 27.7 t; water 279 t. This stream is discarded.

The following streams need not be considered any further: (44) to (48), (50) to (53), (72) and (73).

Due to analogy of the regenerations, the following streams remain unchanged: (5) to (10), (12), (28) to (31).

(11) 20 t NaOH (of the same normality as formerly KOH); 3.2 t $Ca(OH)_2$; 54.6 t $C_6H_5OH$; 789 t water. The volume is 850 $m^3$.

## Section 2: Lime Kiln

This passes unchanged from the $KHCO_3$ - flowsheet

Section 3 & Section 4 which served for KCl-recovery are dropped altogether.

## Section 5: Carbonation

(12) 13.2 t $CO_2$ from the lime kiln

(13) $CO_2$ from $NaHCO_3$ - decomposition to $Na_2CO_3$, 11.0 t.

The carbonation will yield the following

(14) $CaCO_3$, 14 t (discarded)

(15) $C_6H_5OH$, 2.7 t (recycled)

(16) $NaHCO_3$, 42 t; $C_6H_5OH$, 54.6 - 2.7 = 51.9 t; water, 789 t.

The volume is 851 $m^3$.

## Section 6: Salting Out

It is assumed that at equal molarities, $NaHCO_3$ and $KHCO_3$ have equal salting-out properties.

(17) Recycle of $(176.4 \times 84/100.1 - 49.3) \times 851/10^3 = 84.1$ t $NaHCO_3$ is then required.

(18) Separated phenol = 18.7 t.

(19) Process solution : $NaHCO_3$, 126.1 t ; $C_6H_5OH$, 33.2 t; water, 789 t. The volume is 851 $m^3$.

## Section 7: Phenol-Extraction

It is assumed that at equal molarities, nBuOAc will dissolve in equal amounts in $NaHCO_3$ and $KHCO_3$-solutions.

(21) Required nBuOAc = 29.2 t.

(22) Loaded extractant: nBuOAc, 26.6 t; $C_6H_5OH$, 33.2 t; water, 3.2 t. The volume is 66.4 $m^3$.

(20) Phenol-free process solution : $NaHCO_3$, 126.1 t; $C_6H_5OH$, 24 kg (28 ppm); water, 786 t; in all 855 $m^3$.

## Section 8: $C_6H_5OH$ - nBuOAc - Distillation

passes unchanged from the $KHCO_3$ flowsheet.

## Section 9: $NaHCO_3$ - Dehydration by Water Transfer.

For the dehydration of $NaHCO_3$ by water transfer using NaCl as ultimate dehydrant, an appropriate difference of vapour pressures of the aqueous solutions is required.

From published data (189) a comparison between $NaHCO_3$ and $KHCO_3$ can be made. The amount of water transferable per g of NaCl from a saturated solution of $NaHCO_3$, is more than double that amount for $KHCO_3$, to wit 25 as compared with 11 g. This ratio does not yet yield sufficient data for the construction of an equilibrium curve. By assuming, however, that the number of stages for the $NaHCO_3$ - dehydration is equal to that required for the $KHCO_3$ - dehydration, the results will be conservative. This is the more so if the greater solubility of $KHCO_3$ as compared with $NaHCO_3$ is considered (Note 23).

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(189) A. Baniel, J.Appl.Chem. 9 (1959) 522

Note 23 : $NaHCO_3$, 1.13 gmol/1000 g $H_2O$; $KHCO_3$, 3.32 gmol/1000 g $H_2O$; both at 20° (190).

(190) International Critical Tables (New-York, 1928) vol. IV pp. 237, 240.

(191) R.M. Caven & H.J.S. Sand, J. Chem. Soc. 99 (1911) 1359-69.

Thus, in analogy with par. 5.9.2., 6 stages are needed for the $NaHCO_3$-dehydration with nBuOH as well as for the nBuOH-dehydration with NaCl.

The dried and wet nBuOH-streams, (42) and (43) respectively, remain unchanged.

(38) Solid $NaHCO_3$ : 126.1 t ; + 3 t water and some 40 kg nBuOH.

(39) To the ultimate drying: 42.0 t $NaHCO_3$ , with 1 t water and 14 kg nBuOH.

The difference between (38) and (39) forms the recycled $NaHCO_3$ , (17).

### Section 10 : $NaHCO_3$ - Drying (and Eventual Conversion to $Na_2CO_3$).

Gentle heating suffices for drying. Conversion to $Na_2CO_3$ is effected already at 100-105° (191).

Composition of the nBuOH- , water- and $CO_2$-streams ( (41) and (13) ) is unchanged.

(40) Product : 42.0 t $NaHCO_3$ or 26½ t $Na_2CO_3$.

### Section 11 : nBuOH - Distillation.

In analogy with par. 5.11 it has been assumed that distillation would be the most favourable method of nBuOH-recovery.

The distillate (stream (57) ) contains all the nBuOH, 54.3 t, together with 1.24 x 54.3 = 67.3 t water.

The bottoms (stream (60) ) consist of 39.2 t NaCl and 783-67.3 = (say) 716 t water, i.e. a 5.2 wt-% solution (specific weight 1.035, about 52 g/l (192)).

The volume is thus 730 $m^3$.

The water-loss of this operation, 730 $m^3$, is considerably lower than that for the $KHCO_3$ - flowsheet (1184 $m^3$), even if the differences in weights of daily production (50 t $KHCO_3$; 42 t $NaHCO_3$) is considered.

This smaller water-loss is due to the simplification eliminating the recovery of NaCl from the NaCl-$CaCl_2$-stream.

### 5.13.3. The Complete Balance

A complete account of the streams of materials for the conversion of NaCl into $NaHCO_3$ or $Na_2CO_3$ is given in table 5.7.

(192) C.D. Hodgman, Handbook of Chemistry and Physics (1957) p. 1909.

## TABLE 5.7.

**The Balance of Materials - Streams of Materials in tons per day.**

**Remark:** Stream-numbers appearing in the $KHCO_3$-flowsheet but absent in the present one, are non-existent for $NaHCO_3$ - production.

| Stream Number | NaCl | NaOH | $NaHCO_3$ | $Na_2CO_3$ | $CaCO_3$ | CaO | $Ca(OH)_2$ | $CaCl_2$ | $CO_2$ | $C_6H_5OH$ | $n\text{-}C_4H_9OCOCH_3$ (nBuOAc) | $n\text{-}C_4H_9OH$ (nBuOH) | Water | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.5 | | | | | | | | | | | | 279 | 381 |
| 2 | | | | | | | | | | | | | 279 | 279 |
| 3 | 31 | | | | | | | | | | | | 279 | 310 |
| 4 | 41.3 | | | | | | | 27.7 | | | | | 279 | 348 |
| 5 | | | | | | | 30.1 | | | 75.8 | | | 974 | 1080 |
| 6 | | | | | | | 21.9 | | | | | | | 21.9 |
| 7 | | | | | | 16.6 | | | | | | | | 16.6 |
| 8 | | | | | | | | | | | | | 5.3 | 5.3 |
| 9 | | | | | 30.0 | | | | | | | | | 30.0 |
| 10 | | | | | | | | | | | | | 185 | 185 |
| 11 | | 20 | | | | | 3.2 | | | 54.6 | | | 789 | 867 |
| 12 | | | | | | | | | 19.5 | | | | | 19.5 |
| 13 | | | | | | | | | 11.0 | | | | | 11.0 |
| 14 | | | | | 4.3 | | | | | | | | | 4.3 |
| 15 | | | | | | | | | | 2.7 | | | | 2.7 |
| 16 | | | 42. | | | | | | | 51.9 | | | 789 | 883 |
| 17 | | | 84.1 | | | | | | | | | | | 84.1 |
| 18 | | | | | | | | | | 18.7 | | | | 18.7 |
| 19 | | | 126.1 | | | | | | | 33.2 | | | 789 | 948 |
| 20 | | | 126.1 | | | | | | | 0.024 | | | 786 | 912 |
| 21 | | | | | | | | | | | 29.2 | | | 29.2 |
| 22 | | | | | | | | | | 33.2 | 26.6 | | 3.2 | 63.0 |
| 23 | | | | | | | | | | | 8.0 | | 3.2 | 11.2 |
| 24 | | | | | | | | | | | 8.0 | | 0.064 | 8.0 |
| 25 | | | | | | | | | | | 0.016 | | 3.14 | 3.2 |
| 26 | | | | | | | | | | | 18.6 | | | 18.6 |
| 27 | | | | | | | | | | 33.2 | | | | 33.2 |
| 28 | | | | | | | | | | 54.6 | | | | 54.6 |
| 29 | | | | | | | 8.2 | | | 21.2 | | | 974 | 1003 |
| 30 | | | | | | | | | | | | | 974 | 974 |
| 31 | | | | | | | | | | | | | 789 | 789 |
| 32 | | | | | | | | | 11.0 | | | | | 11.0 |
| 38 | | | 126.1 | | | | | | | | | 0.04 | 3 | 129 |
| 39 | | | 42 | | | | | | | | | 0.014 | 1 | 43 |
| 40 * | | | 42 | | | | | | | | | | | 42 |
| 40 ** | | | | 26.5 | | | | | | | | | | 26.5 |
| 41 * | | | | | | | | | | | | | 1 | 1 |
| 41 ** | | | | | | | | | | | | | 5.5 | 5.5 |
| 42 | | | | | | | | | | | | 4606 | 342 | 4948 |
| 43 | | | | | | | | | | | | 4606 | 1128 | 5734 |
| 46 = 4 | | | | | | | | | | | | | | |
| 49 | 70.5 | | | | | | | | | | | | | 70.5 |
| 55 | 39.2 | | | | | | | | | | | | | 39.2 |
| 56 | 101.1 | | | | | | | | | | | 79.3 | 1282 | 1462 |
| 57 =59 | | | | | | | | | | | | 54.3 | 67.3 | 124 |
| 60 | 39.2 | | | | | | | | | | | | 716 | 755 |
| 70 =55 | | | | | | | | | | | | | | |
| 71 | 39.2 | | | | | | | | | | | 54.3 | 783 | 876 |

* in case $NaHCO_3$ is the product

** in case $NaHCO_3$ is converted to $Na_2CO_3$

# 6. THE MANUFACTURING COSTS

## 6.1. Introduction

In the present chapter, the manufacturing cost of $K_2CO_3$ from KCl, and of $Na_2CO_3$ from NaCl, as described in the foregoing chapters, is given. The calculations have been based on the carbonates and not on the bicarbonates, as the market for the latter is rather small.

Costs and prices are given in local currency, Israel Pounds (shortened IL). The rate of exchange is as follows: For imports, 1 US $ = 1.80 IL (thus, 1 IL = 0.556 US $ = 2.11 Dutch Florins). For exports the same rate of exchange prevails, except that for each US $ of the added value in foreign currency of the product, a premium of 0.85 IL per $ is paid to the producer.

Customs' duties on industrial apparatus amount to 10% of their value.

Apparatus have, as far as possible, been calculated as produced from mild steel. An average cost of 1.2 IL per kg manufactured apparatus, including the labour required, has been taken.

Investments in the lime-kiln and in the steam-generating equipment have not been taken into the total investment, as these two sums were accounted for in the respective prices of the two commodities.

The calculations have been carried out in the kg (mass) - m - sec - $^{o}C$ system of units. The unit of heat (and of energy in general) is the joule (J), having the dimension kg x $m^2/sec^2$. The unit of power is J/sec = watt (W). Thus, specific heats are given in J/kg x $^{o}C$, latent heats of evaporation in J/kg, and heat transfer coëfficiënts in $J/m^2$ x sec x $^{o}C$, (equal to $W/m^2$ x $^{o}C$). Specifications for motors have been converted to HP, in conformance with commercial usage.

## 6.2. Equipment

The investment in equipment is as below. The plant has been divided into sections, as set out in fig. 5.0. (paragraph 5.0.).

MS = mild steel
CI = cast iron
C = concrete
StSt = stainless steel
PFE = polyfluoroethylene

## SECTION 1 : ION EXCHANGE.

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit cost IL | Total cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| 1/1 | 30 | Ion exchange column | 1600 l resin | h = 1.20, r = 0.75 | MS | 530 | 15,900 | |
| 1/2 | 30 | Head tank | 0.012 $m^3$/sec; 5' | v = 3.6 $m^3$ | MS | | 17,200 | |
| 1/3 | 30 | Sump tank | Interstitial v = 1.1 $m^3$ /column | v = 2 $m^3$ | MS | | 12,000 | |
| 1/4 | 30 + 6 | Centrifugal pump | h = 5 m, q = 0.012 $m^3$/sec<br>g = 1200 kg/$m^3$ | 2 HP | CI | 1,200 | 43,200 | |
| 1/5 | 1 | KCl - silo | 1 day; g = 770 kg/$m^3$ | 52 $m^3$ | MS | | 8,350 | |
| 1/6 | 1 | KCl-recycle belt conveyor | 49.6 t/d | | | | 1,500 | |
| 1/7 | 1 | KCl-screw-feeder | 39.6 t/d | | MS | | 2,000 | |
| 1/8 | 1 | KCl elevator | h = 10 m | | | | 2,500 | |
| 1/9 | 1 | Tank for dilute KCl | 545 $m^3$/d; 30' reserve | 12 $m^3$ | MS | | 1,220 | |
| 1/10 | 1 | KCl solution mixing tank | 583.9 $m^3$/d; 20' mixing | 10 $m^3$ | MS | | 1,310 | |
| 1/11 | 1 | Stirrer for 1/10 | | 1.5 HP | | | 600 | |
| 1/12 | 1 | Tank for conc'd KCl | 583.9 $m^3$/d; 1 cycle's storage | 80 $m^3$ | MS | | 8,900 | |
| 1/13 | 1 | Water tower | 1490 $m^3$/d; ½ day | 700 $m^3$ | C | | | 20,000 including erection |
| 1/14 | 1 + 1 | Pump for 1/13 | h = 12 m, q = 1490 $m^3$/d | 5 HP | CI | 2,000 | 4,000 | |
| 1/15 | 1 | Phenolic $Ca(OH)_2$-sol'n mixing tank | 1038 $m^3$/d, 30' | 25 $m^3$ | StSt 316 | | 2,400 | |
| 1/16 | 1 | Stirrer for 1/15 | d of vessel 3 m | 5 HP | MS/PFE | | 1,500 | |
| 1/17 | 1 | Conveyor belt for CaO | 16.6 t CaO/d | | | | 1,500 | |
| 1/18 | 1 | Phenol recycle tank | 54.6 t $C_6H_5OH$/d; 1 cycle | 10.5 $m^3$ | StSt 316 | | 20,000 | |
| 1/19 | 1 | Phenolic $Ca(OH)_2$ sol'n reservoir | 1038 $m^3$/d; 1 cycle | 139 $m^3$ | StSt 316 | | 79,000 | |
| | | TOTAL: | | | | | 223,100 | 20,000 |

## SECTION 2 : LIME BURNING

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit cost IL | Total cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| | 1 | Lime kiln | 30 t $CaCO_3$/d | | | | 200,000 | including erection and accessories. |

SECTION 3 : KCl - $CaCl_2$ - DEHYDRATION AND KCl - PRECIPITATION BY WATER-TRANSFER.

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit Cost IL | Total Cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| 3/1 | 7 | Vessels for KCl-$CaCl_2$-dehydration | 0.13 $m^3$/sec; 30" | 4.3 $m^3$ | MS | | 3,000 | |
| 3/2 | 7 | Mixers for 3/1 | d of vessel 1.76 m | 2 HP | MS | 600 | 4,200 | |
| 3/3 | 7 | Settlers | 0.13 $m^3$/sec; 60" | 7.8 $m^3$ | MS | | 4,400 | |
| 3/5 | 1 | Basket centrifuge for KCl | 35.2 t KCl/d | 1.5 $m^2$ | MS | | 10,000 | |
| 3/6 | 1 | Surge tank for wet nBuOH | | 2 $m^3$ | MS | | 350 | |
| 3/7 | 1 | Surge tank for wet nBuOH | | 2 $m^3$ | MS | | 350 | |
| 3/8 | 1 | Surge tank for KCl-$CaCl_2$-sol'n from ion-exchange | | 2 $m^3$ | MS | | 350 | |
| 3/9 | 1 | Head tank for KCl-$CaCl_2$-sol'n prior to distillation | | 2 $m^3$ | MS | | 350 | |
| 3/10 | 11 | Mixing vessels for nBuOH-dehydration | 0.13 $m^3$/sec; 30" | 4.3 $m^3$ | MS | | 4,700 | |
| 3/11 | 11 | Mixers for 3/10 | d of vessel 1.76 m | 2 HP | MS | 600 | 6,600 | |
| 3/12 | 11 | Settlers | 0.13 $m^3$/sec; 60" | 7.8 $m^3$ | MS | | 7,000 | |
| 3/15 | 1 + 1 | Pump for wet nBuOH | 110 kg/sec; h = 4 m | 10 HP | CI | 5,000 | 10,000 | including standby for 3/17 |
| 3/17 | 1 | Pump for dried nBuOH | 105 kg/sec; h = 4 m | 10 HP | CI | | 5,000 | standby included in 3/15 |
| 3/18 | 1 | Silo for NaCl | 101 t/d = 131 $m^3$/d; $\frac{1}{2}$ day | 64 $m^3$ | MS | | 9,220 | |
| 3/19 | 1 | Screwfeeder for NaCl | 61.9 t/d | | | | 1,000 | |
| 3/20 | 1 | Tank for NaCl-sol'n | 545 $m^3$/d, 2 hours | 45 $m^3$ | MS | | 4,130 | |
| | | TOTAL : | | | | | 70,650 | say 70,700 |

MS = mild steel
CI = cast iron
C = concrete
StSt = stainless steel
PFE = polyfluoroethylene

SECTION 4 : nBuOH - DISTILLATION AND KCl-PRECIPITATION.

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit cost IL | Total cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| 4/1 | 1 | First column | 0.375 kg/sec; g = 0.622 kg/m$^3$ | r = 0.44, h = 6.0 (except reboiler) | MS | 1,720 | | |
| | | Reboiler (internal) | A = 37.0 m$^2$; $\overline{\Delta t}$ = 10° | r = 0.44, h = 3.0; 80 tubes 2" | MS | 8,810 | 10,550 | (say) |
| 4/2 | 1 | Second column | As 4/1 | As 4/1, h = 4.0 m | MS | 1,180 | | |
| | | Reboiler (internal) | As 4/1 | | MS | 8,810 | 10,550 | (say) |
| 4/3 | 1 | Third column<br>Reboiler | As 4/2 | | | | 10,000 | |
| 4/4 | 1 | Slurry-to-feed heat exchanger | Q = 176,000 J/sec; k = 1000 J/m$^2$ x °C x sec; $\overline{\Delta t}$ = 50.5 | 3.5 m$^2$ | MS | | 800 | |
| | | Vessel + mixer | | | MS | | 1,000 | |
| 4/5 | 1 | 3rd effect overhead-to-feed heat exchanger | Q = 360,000; k = 2000; $\overline{\Delta t}$ = 38.6 | 4.7 m$^2$ | MS | | 1,700 | |
| 4/5a | 1 | 3rd effect overhead cooler | Q = 270,000; k = 1500; $\overline{\Delta t}$ = 42 | 4.3 m$^2$ | MS | | 1,700 | |
| 4/6 | 1 | nBuOH-$H_2O$-condenser | Q = 160,000; k = 2000; $\overline{\Delta t}$ = 31 | 2.6 m$^2$ | MS | | 1,100 | |
| 4/7 | 1 | nBuOH cooler | Q = 53,000; k = 1000; $\overline{\Delta t}$ = 43 | 1.3 m$^2$ | MS | | 600 | |
| 4/8 | 1 | Steam ejector | | | | | 400 | |
| 4/9 | 1 | Condensate cooler | Q = 304,000; k = 1000; $\overline{\Delta t}$ = 39 | 7.8 m$^2$ | MS | | 2,800 | |
| 4/10 | 1 + 1 | Feed pump | 1.89 kg/sec; h = 15 m | 1 HP | CI | 400 | 800 | |
| 4/11 | 1 | Centrifuging filter | 0.167 kg/sec; capacity 0.5 kg/m$^2$ x sec | 0.35 m$^2$ $\sim$ 4 ft$^2$ | MS | | 10,000 | |
| 4/12 | 1 | Feed heater (to b.p.) | Q = 165,000; k = 2000; $\overline{\Delta t}$ = 27.7 | 3.1 m$^2$ | MS | | 1,300 | |
| | | TOTAL : | | | | | 52,750 | say 52,800 |

SECTION 5 : CARBONATION OF THE PHENOLIC KOH-SOLUTION.

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit Cost IL | Total Cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| 5/1 | 1 | Carbonation Reactor | 0.0316 kmol $CO_2$ absorbed/ $m^3$ x sec; | r = 0.4 m; h = 1.6 m | StSt 316 | 6,000 | | |
| | | Mixer (radial turbine) | | d = 0.4 m; motor 5 HP | | 2,300 | | |
| | | Settling section | | | StSt 316 | 27,400 | 35,700 | |
| 5/2 | 1 | $CO_2$ gas holder | 25.2 t/d; 1 hour | 560 $m^3$ | MS | | 50,000 | |
| 5/3 | 1 | KOH-solution surge tank | | 2 $m^3$ | StSt 316 | | 2,000 | |
| 5/4 | 1 + 1 | KOH-solution pump | 10.1 kg/sec; h = 12 m | 2 HP | StSt | 2,000 | 4,000 | |
| 5/5 | 1 + 1 | $KHCO_3$-solution pump | 10.3 kg/sec | 2 HP | StSt | 2,000 | 4,000 | |
| 5/6 | 1 + 1 | Phenol-solution pump | Smallest suitable available | 1.2 HP | Stoneware | 600 | 1,200 | including standby for 6/4 |
| 5/7 | 1 | $CaCO_3$ rotary drum filter | 0.05 kg/sec | 1 $m^2$ | | | 10,000 | |
| 5/8 | 1 + 1 | $CO_2$ blower | 9.33 $m^3$/min = 400 $ft^3$/min | | CI | 3,000 | 6,000 | |
| 5/9 | 1 | Recycle pump for wash-water | | 1 HP | CI | | 400 | |
| | | TOTAL : | | | | | 113,300 | |

SECTION 6 : SALTING OUT OF PHENOL.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6/1 | 1 | Mixing vessel | 851 $m^3$/d; 300" | 3 $m^3$ | StSt 316 | | 12,000 | |
| 6/2 | 1 | Mixer for 6/1 | | 1 HP | MS/PFE | | 1,600 | |
| 6/3 | 1 | Settler | 851 $m^3$/d; 15' | | StSt 316 | | 19,000 | |
| 6/4 | 1 | Phenol pump | 0.24 kg/sec; h = 8 m | 1.2 HP | Stoneware | | 600 | standby included in 5/6 |
| 6/5 | 1 | $KHCO_3$ - sol'n pump | 972 t/d; 8 m | 2 HP | CI | | 1,200 | |
| 6/6 | 1 | Conveyor belt for $KHCO_3$ | | | | | 1,500 | |
| 6/7 | 1 | Intermediate $KHCO_3$-storage with screw-feeder | 100 t/d; ½ h | 2 $m^3$ | MS | | 2,000 | |
| | | TOTAL : | | | | | 28,300 | |

SECTION 7 : EXTRACTION OF PHENOL.

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit Cost IL | Total Cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| 7/1 | 6 | Mixing vessel | 0.0099 $m^3$/sec; 30" | 0.35 $m^3$ | StSt 316 | | 6,600 | |
| 7/2 | 6 | Mixer for 7/1 | | 1 HP | | 1,600 | 9,600 | |
| 7/3 | 6 | Settler | 0.0099 $m^3$/sec; 13' | 9 $m^3$ | StSt 316 | | 57,000 | |
| 7/5 | 1 | $KHCO_3$-sol'n (phenol-free) pump | | 2 HP | CI | | 1,200 | |
| 7/6 | 1 | nBuOAc pump | 0.34 kg/sec, h = 20 m | 2 HP | CI | | 1,200 | |
| 7/7 | 1 | nBuOAc surge tank | | 2 $m^3$ | MS | | 350 | |
| | | TOTAL : | | | | | 75,950 | say 76,000 |

SECTION 8 : DISTILLATION OF THE nBuOAc - PHENOL MIXTURE

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 8/1 | 1 | Distillation column | 5 t/h | s = 0.44 $m^2$, h = 5 m | Graphite | | 4,500 | |
| | 1 | Reboiler | Q = 0.36 x $10^6$ J/sec;<br>k = 1000; $\overline{\Delta t}$ = 20° | A = 18.2 $m^2$ | Graphite | | 15,000 | |
| 8/2 | 1 | Overhead (Azeotrope) condenser | Q = 0.23 x $10^6$ J/sec;<br>k = 500; $\overline{\Delta t}$ = 56.8 | A = 8.1 $m^2$ | MS | | 6,100 | |
| 8/3 | 1 | Overhead (Azeotrope) cooler | Q = 2 x $10^4$ J/sec;<br>k = 500; $\overline{\Delta t}$ = 15.4 | A = 2.6 $m^2$ | MS | 3,150 | | |
| | 1 | Phase separator | 10' | v = 0.08 $m^3$ | MS | 50 | 3,200 | |
| 8/4 | 1 | nBuOAc-to-feed heat exchanger | Q = 0.15 x $10^6$ J/sec;<br>k = 500; $\overline{\Delta t}$ = 24 | A = 12.5 $m^2$ | MS | | 3,450 | |
| 8/5 | 1 | nBuOAc-cooler | Q = 25600 J/sec;<br>k = 500; $\overline{\Delta t}$ = 15.8 | A = 3.3 $m^2$ | MS | | 2,000 | |
| 8/6 | 1 | nBuOAc surge tank | | 2 $m^3$ | MS | | 350 | |
| 8/7 | 1 | $C_6H_5OH$-to-feed heat exchanger | Q = 6700 J/sec;<br>k = 500; $\overline{\Delta t}$ = 3.5 | A = 3.8 $m^2$ | Graphite | | 2,100 | |
| 8/8 | 1 | $C_6H_5OH$-cooler | Q = 66000; $\overline{\Delta t}$ = 46.6 | A = 2.9 $m^2$ | Graphite | | 1,800 | |
| 8/9 | 1 | Phenol pump | | 1.2 HP | Stoneware | | 600 | |
| 8/10 | 1 | Feed pump | | 1.2 HP | Stoneware | | 600 | |
| | | TOTAL : | | | | | 39,700 | |

## SECTION 9 : $KHCO_3$ DEHYDRATION BY WATER-TRANSFER

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit Cost IL | Total Cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| 9/1 | 7 | Mixing vessels for $KHCO_3$ dehydration | 0.0791 $m^3$/sec; 30" | 2.7 $m^3$ | MS | | 1,500 | |
| 9/2 | 7 | Mixers for 9/1 | As 3/2 | 2 HP | MS | 600 | 4,200 | |
| 9/3 | 7 | Settlers | 60" | 5.0 $m^3$ | MS | | 2,200 | |
| 9/5 | 1 | $KHCO_3$-sol'n surge tank | | 2 $m^3$ | MS | | 350 | |
| 9/6 | 1 | Centrifuge for $KHCO_3$-crystals | 150 t/d | 6.1 $m^2$ = 70 $ft^2$ | | | 20,000 | |
| 9/7 | 1 | Recycle pump for sat'd $KHCO_3$ sol'n | | small capacity | MS | | 300 | |
| 9/8 | 1 + 1 | Pump for dried nBuOH | 62.3 kg/sec; 5 m | 5 HP | CI | 4,000 | 8,000 | including standby for 9/1 |
| 9/9 | 1 | Surge tank for dried nBuOH | | 2 $m^3$ | MS | | 350 | |
| 9/10 | 1 | Pump for wet nBuOH | 65.6 kg/sec | 5 HP | CI | | 4,000 | standby included in 9/8 |
| 9/11 | 6 | Mixing vessels for nBuOH-dehydration | 0.080 $m^3$/sec; 30" | 2.7 $m^3$ | MS | | 1,300 | |
| 9/12 | 6 | Mixers for 9/11 | As 9/2 | 2 HP | MS | 600 | 3,600 | |
| 9/13 | 6 | Settlers | As 9/3 | 5.0 $m^3$ | MS | | 1,900 | |
| 9/15 | 1 | Conveyor belt for NaCl | As 6/6 | | | | 1,500 | |
| 9/16 | 1 | Surge tank for wet nBuOH | | 2 $m^3$ | MS | | 350 | |
| | | TOTAL : | | | | | 49,550 | say 49,600 |

### SECTION 10 : $KHCO_3$-DRYING (OR EVENTUALLY, DECOMPOSITION TO $K_2CO_3$)

| Item | Quantity | Designation | Data for sizing | Size, dimensions | Materials of construction | Unit Cost IL | Total Cost IL | REMARKS |
|---|---|---|---|---|---|---|---|---|
| - | 1 | Drying furnace | | | | | 33,000 | |

### SECTION 11 : nBuOH-RECOVERY FROM THE NaCl-SOLUTION (BY DISTILLATION)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 11/1 | 1 | Distillation column | Overhead: 79.3 t nBuOH/d; 98.4 t $H_2O$/d; 1 m/sec | A of cross section 4.12 $m^2$ | MS | 2,600 | | |
| 11/2 | 1 | Reboiler | Q = $3.61 \times 10^6$ J/sec; 12 ata steam | A = 79 $m^2$ | Steel shell copper tubes | 7,100 | 10,000 | |
| 11/3 | 1 | Overhead to feed heat exchanger | Q = $3.14 \times 10^6$ J/sec; $\overline{\Delta t}$ = 33.1 | A = 190 $m^2$ | MS | | 18,100 | |
| 11/4 | 1 | Overhead cooler | $0.45 \times 10^6$ J/sec; $\overline{\Delta t}$ = 19.2 | A = 47 $m^2$ | MS | | 6,600 | |
| 11/5 | 1 | Bottom-to-feed heat exchanger | $1.16 \times 10^6$ J/sec; $\overline{\Delta t}$ = 6.4 | A = 353 $m^2$ | MS | | 26,500 | |
| 11/6 | 1 | Feed pump | 1463 t/d; h = 10 m | 3 HP | CI | | 1,500 | |
| 11/7 | 1 | Overhead return pump | 2.17 kg/sec; h = 10 m | ½ HP | CI | | 300 | including overhead from section 4, stream (54) |
| 11/8 | 1 | Feed tank | | 2 $m^3$ | StSt 316 | | 600 | |
| 11/9 | 1 | Bottoms sump tank | | 2 $m^3$ | StSt 316 | | 600 | |
| | | TOTAL : | | | | | 64,200 | |

## 6.3. The Physical Plant Cost; Required Investments.

| Section No. | Operation | Investment, IL | |
|---|---|---|---|
| | | not erected | erected |
| 1 | Ion exchange (apparatus) | 223,100 | 20,000 |
| | (automatization) | 200,000 | |
| 2 | Lime kiln | | 200,000 * |
| 3 | KCl-CaCl$_2$-dehydration | 70,700 | |
| 4 | nBuOH-distillation & KCl-precipitation | 52,800 | |
| 5 | Carbonation | 113,300 | |
| 6 | Salting out | 28,300 | |
| 7 | Phenol-extraction | 76,000 | |
| 8 | nBuOAc-distillation | 39,700 | |
| 9 | KHCO$_3$-dehydration | 49,600 | |
| 10 | KHCO$_3$-drying or -decomposition | 33,000 | |
| 11 | nBuOH-distillation | 64,200 | |
| | Cooling tower | | 20,000 |
| | nBuOAc-recovery (note 24) | 50,000 | |
| | Total | 1,050,700 | 40,000 |

(* not included in the total investment, but contained in the price of the lime)

Note 24. It has been calculated that the nBuOAc-losses in the KHCO$_3$-stream, as found experimentally, would result in an expenditure of 1.2 million IL of a total annual production cost of 5.9 million IL. This is prohibitively high and unnecessarily wasteful. Moreover, the influence of dissolved nBuOAc on the subsequent water-transfer from KHCO$_3$ might be disastrous.

It is now assumed, that recovery of this nBuOAc from the KHCO$_3$-solution prior to water-transfer is possible. Extraction with a solvent insoluble in water, and subsequent separation by distillation, will probably not represent insurmountable difficulties. It goes without saying that future development of the process will require experimental verification of such a nBuOAc-recovery.

The required investment in extraction-- and distillation - equipment is assumed to amount to 50,000 IL (not erected). The steam-requirements of the distillation are taken as 4 t/d. The make-up of cooling water, as calculated without this operation, will be influenced to a negligible degree only.

Additional Investments:

Resin: 44 t = 48 $m^3$ (par 5.1.8.); 48 $m^3$ = 1345 $ft^3$, at 21 $/$ft^3$ (223) cost 56,400 IL.

nBuOH: The total amount in circulation is

| | | |
|---|---|---|
| (42) | 4606 t | |
| (50) | 8150 t | |
| total | 12156 t | |

The number of stages is (7 + 11) + (7 + 6) = 31. At $1\frac{1}{2}$ minute per stage, the amount present is 12156 x 31 x $1\frac{1}{2}$/60 x 24 = 393 t; with the amounts in distillation, 395 t are required. At 1335 IL/t (including duties), they cost 527,000 IL.

nBuOAc: 29.2 t are in circulation, in the extraction and the distillation. 6 stages equal 9 minutes, say 12 minutes; there are required 29.2 x 12/60 x 24 = 0.25 t. At 1400 IL/t its cost is 350 IL.

Phenol: The hold-up time is estimated at $\frac{1}{2}$ h, requiring 54.6/48 = 1.2 t; at 1400 IL/t the cost is 1680 IL.

The total investment in the resin and the "solvents" is 585,500 IL.

The total investment is then as follows:-

| | | | | |
|---|---|---|---|---|
| Working capital | | | | 760,000 IL |
| Fixed capital | | | | |
| Installation, not erected | 1,050,700 | | | |
| same, erected | | 4,202,800 | | |
| Additional installations, erected | | 40,000 | | |
| Total erected installations | | | 4,242,800 | |
| Cation exchange resin, solvents (not erected) | | 585,500 | | |
| Same, in plant | | | 622,600 | |
| Physical plant cost | | | | 4,865,400 IL |
| Total investment | | | | 5,625,400 IL |

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## 6.4. Utilities

**Water for the reaction:**

| Stream | Function | Amount, $m^3$/day |
|---|---|---|
| 2 | KCl - washing | 511 |
| 8 | Lime - slaking | 5.3 |
| 31 | $Ca(OH)_2$-$C_6H_5OH$-washing | 789 |
| | Total | 1305 |
| Subtract: 53 | Recycled water from thermal KCl-precipitation | 77.4 |
| | Net daily requirement | 1228 $m^3$ = 24.6 $m^3$/t $KHCO_3$= = 35.7 $m^3$/t $K_2CO_3$. |

**Water for cooling:**

In circulation there are 2952 $m^3$/day. The daily make-up is estimated at 60 $m^3$.

**Steam:**

| Section | Function | t/day |
|---|---|---|
| 4 | Triple effect evaporation | 37.4 |
| 8 | nBuOAc - distillation | 13.9 |
| 11 | nBuOH - distillation | 142.0 |
| | nBuOAc - recovery | 4.0 |
| | Total daily requirement | 198 t |

**Electricity:**

A load of 1000 kW is assumed, resulting in a consumption of 24,000 kWh/day.

**Fuel:**

1.3 t/day are required for the decomposition of $KHCO_3$ to $K_2CO_3$. The amount required for steam-generation is not included, as it is contained in the price of the steam.

## 6.5. Cost Sheet for the Process

A cost sheet for the process, based on the data calculated above, is given below.

|  | Unit | Price, IL/unit | Amount/year | Amount/t $K_2CO_3$ | Costs per year |  | Costs per ton $K_2CO_3$ |  | % |
|---|---|---|---|---|---|---|---|---|---|
| 1 Raw Materials |  |  |  |  |  |  |  |  |  |
| Potassium Chloride | ton | 74.- | 13,070 | 1.15 | 967,180 |  | 85.0 |  |  |
| Calcium Oxide (lime) | ton | 25.- | 5,480 | 0.48 | 137,000 |  | 12,0 |  |  |
|  |  |  |  |  |  | 1,104,180 |  | 97.0 | 21.3 |
| 2 Chemicals |  |  |  |  |  |  |  |  |  |
| Sodium Chloride | ton | 1.- | 33,360 | 2.93 | 33,360 |  | 2.93 |  |  |
| Water (reaction) | $m^3$ | 0.06 | 405,240 | 35.7 | 24,310 |  | 2.14 |  |  |
| Make-up |  |  |  |  |  |  |  |  |  |
| Cation-exchange resin | kg | 1.28 | 6,600 | 0.58 | 8,450 |  | 0.74 |  |  |
| n-Butyl alcohol | t | 1335.- | 132 | 0.0116 | 176,220 |  | 15.5 |  |  |
| n-Butyl acetate | t | 1400.- | 7.9 | 0.0007 | 11,090 |  | 1.0 |  |  |
| Phenol | t | 1400.- | 7.9 | 0.0007 | 11,090 |  | 1.0 |  |  |
|  |  |  |  |  |  | 264,520 |  | 23.3 | 5.1 |
| 3 Services |  |  |  |  |  |  |  |  |  |
| Water (cooling) | $m^3$ | 0.06 | 19,800 | 1.74 | 1,190 |  | 0.10 |  |  |
| Steam | t | 14.- | 65,340 | 5.73 | 914,760 |  | 80.25 |  |  |
| Fuel | t | 75.- | 430 | 0.0377 | 32,250 |  | 2.83 |  |  |
| Power | kWh | 0.04 | 7,920,000 | 695 | 316,800 |  | 27.80 |  |  |
|  |  |  |  |  |  | 1,265,000 |  | 111.0 | 24.4 |
| 4 Total Variable Costs |  |  |  |  |  | 2,633,700 |  | 231.3 | 50.8 |
| 5 Manpower: 4 Supervisors + 20 Labourers |  |  |  |  |  | 543,500 |  | 48.7 | 10.6 |
| 6 Maintenance: 4% of "Erected Equipment" |  |  |  |  |  | 169,700 |  | 14.9 | 3.3 |
| 7 Amortisation: 10% of Physical Plant Cost |  |  |  |  |  | 486,500 |  | 42.7 | 9.4 |
| 8 Interest: 5% of Physical Plant Cost + 10% of Working Capital |  |  |  |  |  | 319,300 |  | 28.0 | 6.1 |
| 9 Overhead: 75% of Manpower + Maintenance |  |  |  |  |  | 534,900 |  | 46.9 | 10.2 |
| 10 General Costs: Management 2% of Turnover |  |  |  |  |  | 91,000 |  | 8.0 | 1.8 |
| Sales 1% of Turnover |  |  |  |  |  | 45,500 |  | 4.0 | 0.9 |
| Royalties |  |  |  |  |  |  |  |  |  |
| Insurance 1% of Physical Plant Cost |  |  |  |  |  | 48,700 |  | 4.3 | 1.0 |
| 11 Costs in Bulk Ex Plant Sdom |  |  |  |  |  | 4,872,800 |  | 428.8 | 94.0 |
| 12 Bags and Bagging |  |  |  |  |  |  |  | 10.0 | 2.2 |
| 13 Transportation to Haifa |  |  |  |  |  |  |  | 12.0 | 2.6 |
| 14 Loading Costs (including Port Taxes) |  |  |  |  |  |  |  | 5.0 | 1.1 |
| 15 Costs F.O.B. Haifa |  |  |  |  |  |  |  | (say) 456.0 | 100 % |

A calculation of the rentability of the process in terms of turnover-ratio's and pay-out times before and after taxes presupposes a knowledge of the ultimate selling price. This has not been determined in the present case.

The costs f.o.b. Haifa thus amount to 456 IL/t. It is estimated that of this sum, 135 IL represent foreign currency expenditure, equal to 135/1.80 = 75 \$. To cover production costs, the price f.o.b. Haifa would have to be 196 \$, the equivalent of which in local currency would then be

$$75 \times 1.80 + 121 \times (1.80 + 0.85) = 456 \text{ IL.}$$

This f.o.b. price is thus below the f.o.b. price in U.S. plants, 200 \$/t.

For export to the East through the port of Elat, a similar price would hold.

The cost of the saved \$ in terms of IL is in this case the following. The cost of the product (per ton) is 75 \$ + 321 IL. The saved dollars cost therefore 321/(200 - 75)= = 2.57 IL/\$, which value may be considered reasonable (note 25).

Increase in the scale of operations by a factor of 10 would result in a cost f.o.b. Haifa (or Elat) of some 320 IL/t. At a foreign currency expenditure of 60 \$/t, the product costs 60 \$ + 212 IL, the foreign equivalent of which is 140 \$/t, that is very considerably below U.S. f.o.b. prices.

The conversion of KCl into $K_2CO_3$ via KOH and $KHCO_3$, with the aid of cation - exchange and water - transfer, therefore seems a promising proposition. This conversion is executable both chemically as well as technologically, and yields a product competitive with $K_2CO_3$ from other sources.

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Note 25: The actual cost of the saved \$ is lower, since the c.i.f. price of imported $K_2CO_3$ would be higher than 200 \$ by the costs of transportation, maritime insurance etc.

| | Unit | Price IL/unit | Amount/year | Amount/t $Na_2CO_3$ | Costs per year | | Costs per ton $Na_2CO_3$ | | % |
|---|---|---|---|---|---|---|---|---|---|
| 1 Raw materials | | | | | | | | | |
| Sodium Chloride | ton | 1.- | 36,200 | 4.14 | 36,200 | | 4.14 | | |
| Calcium Oxide | t | 25.- | 5,480 | 0.63 | 137,000 | 173,200 | 15.65 | 19.8 | 5.6 |
| 2 Chemicals | | | | | | | | | |
| Water (reaction) | m | 0.06 | 354,090 | 40.5 | 21,250 | | 2.43 | | |
| Make-up | | | | | | | | | |
| Cation exchange resin | kg | 1.28 | 6,600 | 0.75 | 8,450 | | 0.97 | | |
| n-Butyl alcohol | t | 1335.- | 23.1 | 0.00264 | 30,840 | | 3.52 | | |
| n-Butyl acetate | t | 1400.- | 7.9 | 0.0009 | 11,090 | | 1.27 | | |
| Phenol | t | 1400.- | 7.9 | 0.0009 | 11,090 | 82,720 | 1.27 | 9.5 | 2.7 |
| 3 Services | | | | | | | | | |
| Water (cooling) | m | 0.06 | 9,240 | 1.06 | 560 | | 0.063 | | |
| Steam | t | 14.- | 36,300 | 4.15 | 508,200 | | 58.1 | | |
| Fuel | t | 75.- | 430 | 0.049 | 32,250 | | 3.69 | | |
| Power | kWh | 0.04 | 7,920,000 | 905 | 316,800 | 857,810 | 36.20 | 98.1 | 27.6 |
| 4 Total variable costs | | | | | | 1,113,730 | | 127.4 | 35.9 |
| 5 Manpower : 4 supervisors + 20 labourers | | | | | | 543,500 | | 62.2 | 17.5 |
| 6 Maintenance : 4% of "erected equipment" | | | | | | 129,300 | | 14.8 | 4.2 |
| 7 Amortisation : 10% of physical plant cost | | | | | | 340,700 | | 39.0 | 11.0 |
| 8 Interest : 5% of physical plant cost + 10% of working capital | | | | | | 180,300 | | 20.6 | 5.8 |
| 9 Overhead : 75% of manpower + maintenance | | | | | | 505,000 | | 57.7 | 16.3 |
| 10 General costs : Management 2% of turnover | | | | | | 11,900 | | 1.4 | 0.4 |
| Sales 1% of turnover | | | | | | 6,000 | | 0.7 | 0.2 |
| Royalties | | | | | | | | | |
| Insurance 1% of physical plant cost | | | | | | 34,100 | | 3.9 | 1.1 |
| 11 Costs in bulk ex Sdom | | | | | | 2,864,530 | | 327.7 | 92.4 |
| 12 Bags and bagging | | | | | | | | 10.0 | 2.8 |
| 13 Transportation to Haifa | | | | | | | | 12.0 | 3.4 |
| 14 Loading costs | | | | | | | | 5.0 | 1.4 |
| 15 Costs F.O.B. Haifa | | | | | | | (say) | 355.0 | 100 % |

## 6.6. Cost Sheet for $Na_2CO_3$-manufacture

A cost sheet for the conversion of NaCl into $Na_2CO_3$ via NaOH and $NaHCO_3$ is given on page 198. The methods of calculation are analogous to those for $K_2CO_3$. The relevant balance of materials was set out in paragraph 5.13.3.

The manufacturing costs of $Na_2CO_3$ would thus be 355 IL/t, f.o.b. Haifa or Elat. Increase of the scale of operations by a factor of 10 might decrease the costs further to about 250 IL/t. This latter value would, however, still be about 4 times the price of this commodity on the international market, 34 $/t.

It follows that although conversion of NaCl into $Na_2CO_3$ by ion exchange and water transfer is possible chemically and technologically, this conversion would not result in a product able to compete with Solvay soda-ash as available today.

## Appendix: The System KCl - $KHCO_3$ - $H_2O$

### A. 1. The Solubility of $KHCO_3$ at 20°

The exact solubility of $KHCO_3$ in water, at 20° and under $P_{CO_2} = 1$ ata, seems to have been open to doubt; it is given as 33.2 ± 10% g $KHCO_3$/100 g $H_2O$ (225).

Determination was carried out by saturation of distilled water with $KHCO_3$ ("Analytical Reagent" quality) and stirring by bubbling gaseous $CO_2$ through the solution. A wash-bottle for gases was used as container, and was placed in a thermostatic bath at 20.0 ± 0.2°.

Saturation was continued for several hours, and checked by renewed sampling. Analysis of $K^{\cdot}$ was carried out gravimetrically as the tetra-phenyl boron salt (226), while $CO_3''$ and $HCO_3'$ were determined volumetrically by standard procedures. Results were as per table A1.

Table A1

Analysis of a Saturated $KHCO_3$ - solution

| Ion | % = g/100 g solution | eq/100 g solution |
|---|---|---|
| $HCO_3'$ | 13.7 | 0.2245 |
| $CO_3''$ | 0.75 | 0.0250 |
| $K^{\cdot}$ | 9.77 | 0.2499 |

$CO_3''$ was converted to equivalents on the basis of 2 eq/g-ion. The difference between the sums of anion- and cation-equivalents is 0.16%, i.e. well below the experimental error. Taking the average value, 0.2497 eq/100g solution, the solubility of $KHCO_3$ (including $K_2CO_3$ expressed as $KHCO_3$) is 25.0 g $KHCO_3$/100 g solution, or 33.3 g $KHCO_3$/100 g $H_2O$.

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(225) International Critical Tables (New-York 1928) Vol. IV p. 240

(226) K. Sporek & A.F. Williams The Analyst 80 (1955) 347-54

## A.2. The system $KCl-KHCO_3-H_2O$

Precipitation of pure $KHCO_3$ from a solution containing both $KHCO_3$ and KCl, by isothermal water-transfer, is limited by the initial concentration of KCl. The maximum KCl-concentration at which the solution is in equilibrium with pure solid $KHCO_3$ only, had to be determined. This system has been described (227), but in view of the uncertainty of $KHCO_3$-solubility, as mentioned earlier, redetermination was considered necessary. This was done at 20.0 ± 0.2°.

The method utilised was Bancroft's "zero method" (228). To a solution in equilibrium with excess solid $KHCO_3$ and under $P_{CO_2} = 1$ ata increasing KCl - amounts were added under intensive stirring, and the Cl'-contents determined by standard procedure.

The solution was found to attain saturation with respect to KCl at 251 g KCl/l. It then contained 9.21 g $K_2CO_3$/l and 104.6 g $KHCO_3$/l, and its specific gravity was 1.220. Expressing $K_2CO_3$ as $KHCO_3$, the composition of the solution was as per table. A2..

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(227) R.Paris & P.Mondain - Monval, Bull.Soc.Chim.
[5] <u>5</u> (1938) 1142-7
in A.Seidell, Solubilities of Inorganic Compounds
(New-York 1940) Vol. I, p. 730

(228) W.D.Bancroft, J.Phys.Chem. <u>6</u> (1902) 178-84

## Table A2

### Composition of the Solution Saturated to $KHCO_3$ and $KCl$

(20.0 ± 0.2°)

| | g/l | g/100 g $H_2O$ | | Mol-% |
|---|---|---|---|---|
| | | Found | From (227) | |
| $KCl$ | 251.0 | 29.4 | 29.29 | 75.1 |
| $KHCO_3$ | 104.6 | 13.8 | 15.22 | 24.9 |
| $K_2CO_3$ | 9.21 | | | |

Specific gravity : Found 1.220

From (227) 1.218

# English Summary.

The chlorides of potassium and sodium are widely spread in nature. Their industrial application as such is rather limited, and conversion to the (bi)carbonates yields important raw-materials for other processes.

This thesis describes a new method for conversion of KCl into $KHCO_3$ and $K_2CO_3$ via KOH, and of NaCl into $NaHCO_3$ and $Na_2CO_3$ via NaOH. The scheme of the conversion is as follows: KCl in aqueous solution is turned into KOH with the aid of a cation-exchanging resin; $Ca(OH)_2$ serves as source of OH'-ions. The reactions are the following:-

Loading: $KCl + Ca_{\frac{1}{2}}\text{-}R \longrightarrow K\text{-}R + \frac{1}{2}CaCl_2$ (R- is the skeleton of the resin)

Regeneration: $K\text{-}R + \frac{1}{2}Ca(OH)_2 \longrightarrow Ca_{\frac{1}{2}}\text{-}R + KOH$.

When using anion-exchangers for this aim, KOH would be formed in the loading step, as follows:-

$KCl + R\text{-}OH \longrightarrow R\text{-}Cl + KOH$

and contamination of the product by chloride would be inevitable. For this reason cation-exchangers were preferred here.

The small solubility of $Ca(OH)_2$ in pure water would have two undesirable effects:-

1. The process would consume much water;

2. When using cation-exchangers, a very diluted KOH-solution would be obtained. Both difficulties were overcome by the addition of phenol, $C_6H_5OH$, to the regenerant. The concentration of $Ca(OH)_2$ was increased in this manner from 0.044 N to 0.78 N, while the expenditure of water was decreased proportionally. A KOH-solution 0.6 N, free of Cl', and containing some $Ca(OH)_2$ and $C_6H_5OH$, was obtained.

Carbonation with gaseous $CO_2$ converts the potassium into $KHCO_3$; the calcium precipitates as $CaCO_3$, and is separated. By decreasing the dissociation of the phenol, part of it forms a separate phase, and is recycled to the process.

Further recovery of phenol takes place by salting out with $KHCO_3$, while the last amounts are extracted by n-butyl acetate. Phenol and this solvent do not form an azeotrope at atmospheric pressure, and separation through distillation is therefore possible.

The $KHCO_3$-solution so obtained is dehydrated through "water-transfer", where the water is extracted with n-butyl alcohol, which in its turn is dried with a saturated NaCl-solution, and recycled. From the diluted NaCl-solution so formed, the contained n-butyl alcohol is recovered by distillation prior to discard of the brine.

This water-transfer yields solid $KHCO_3$, which is dried by gentle heating and eventually converted to $K_2CO_3$.

The conversion of NaCl into $NaHCO_3$ and $Na_2CO_3$ proceeds analogously.

The raw materials of this process are thus KCl (or NaCl), $Ca(OH)_2$ and $CO_2$ (from $CaCO_3$), and NaCl for the water transfer.

For a plant at Sdom (Sodom), Israel, near the present KCl-plant, a calculation of the manufacturing costs shows that $K_2CO_3$ can be produced economically according to the process above. In comparison to the usual method of preparing $K_2CO_3$, namely electrolysis of KCl to KOH followed by carbonation with $CO_2$, the proposed method has the advantage that it can be carried out economically on a small scale, while the energy-requirements per ton $K_2CO_3$ are smaller.

From the low price of $Na_2CO_3$, produced by the Solvay-method, it was suspected that $Na_2CO_3$ made according to the present process would have a higher manufacturing cost. A calculation verified this suspicion.

Potassium bicarbonate cannot, as is known, be produced by the Solvay-method, as a result of its high solubility. The process described opens, however, a new route for conversion of the chlorides of potassium and sodium into their (bi)carbonates, with the aid of cation-exchangers, and with a clear solution of calcium hydroxide and $CO_2$. Phenol, used for increasing the solubility of the $Ca(OH)_2$, is recovered without marked losses. The raw materials, KCl, NaCl and $CaCO_3$ are to be found in many parts of the world, as a result of which the possibilities of application are considerably enhanced. *

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* D.Araten, Chem. & Ind. 1960 1301.

# Nederlandse Samenvatting.

Kalium- en natrium-chloride komen verspreid in de natuur voor. Hun industrieële toepassing als zodanig is echter beperkt, en omzetting in de respectievelyke (bi)-carbonaten levert belangryke grondstoffen voor andere processen.

Dit proefschrift beschryft een nieuwe methode ter conversie van KCl via KOH in $KHCO_3$ en $K_2CO_3$, en van NaCl via NaOH in $NaHCO_3$ en $Na_2CO_3$. Het schema van de conversie is als volgt : KCl in waterige oplossing wordt met behulp van een kationenwisselaar omgezet in KOH; als bron van de OH-ionen dient $Ca(OH)_2$. De reacties zyn de volgende :-

Belading : $KCl + Ca_{\frac{1}{2}}\text{-}R \longrightarrow K\text{-}R + \frac{1}{2}CaCl_2$ (R- is het skelet van het ionenuitwisselhars)

Regeneratie : $K\text{-}R + \frac{1}{2}Ca(OH)_2 \longrightarrow Ca_{\frac{1}{2}}\text{-}R + KOH$.

By het gebruik van anionenwisselaars voor dit doel zou KOH in de beladingsstap als volgt gevormd worden :-

$KCl + R\text{-}OH \longrightarrow R\text{-}Cl + KOH$

en contaminatie van het product met chloride zou onvermydelyk zyn.
Om deze reden is aan kationenwisselaars de voorkeur gegeven.

De geringe oplosbaarheid van $Ca(OH)_2$ in zuiver water zou twee ongewenste resultaten hebben :

1e. Het proces zou veel water kosten;

2e. By het gebruik van kationenwisselaars zou een zeer verdunde KOH-oplossing verkregen worden.

Beide moeilykheden zyn overwonnen door middel van toevoeging van fenol, $C_6H_5OH$, aan het regeneratie-middel. Hierdoor is de concentratie van $Ca(OH)_2$ van 0.044 N op 0.78 N gebracht; het water-verbruik werd evenredig verminderd terwyl een 0.6 N KOH-oplossing verkregen werd, vry van Cl', en verontreinigd met $Ca(OH)_2$ en $C_6H_5OH$.

By carbonatie met gasvormig $CO_2$ gaat het kalium over in $KHCO_3$; het calcium slaat neer als $CaCO_3$, en wordt afgescheiden. Door het terugdringen van de dissociatie van fenol wordt een gedeelte ervan afgescheiden als aparte fase, en gerecirculeerd.

Een verdere terugwinning van fenol heeft plaats in de daarop volgende uitzouting met $KHCO_3$, terwyl de laatste resten door middel van normaal butyl-acetaat geëxtraheerd worden. Fenol en dit oplosmiddel vormen by atmosferische druk geen azeotroop. Scheiding door middel van destillatie is dan ook mogelyk.

De verkregen $KHCO_3$-oplossing wordt ontwaterd door middel van "water-overdracht", waarby het water geëxtraheerd wordt met normaal butyl-alcohol, die op zyn beurt gedehydrateerd wordt met een verzadigde NaCl-oplossing, en gerecirculeerd. Uit de ontstane verdunde NaCl-oplossing wordt - voor het wegwerpen - opgeloste n-butyl alcohol teruggewonnen door destillatie.

By deze "water-overdracht" wordt vast $KHCO_3$ verkregen, dat door geringe verhitting gedroogd wordt, en eventueel omgezet in $K_2CO_3$.

De conversie van NaCl in $NaHCO_3$ en $Na_2CO_3$ verloopt geheel analoog.

De grondstoffen voor het proces zyn dus KCl (respectievelyk NaCl), $Ca(OH)_2$ en $CO_2$ (uit $CaCO_3$), en NaCl voor de water-overdracht.

Voor een bedryf dat in Sdom(Sodom),Israel zal liggen, naast het bestaande KCl-winnings bedryf, toont een kostprysberekening aan, dat $K_2CO_3$ volgens het hierboven beschreven proces economisch produceerbaar zal zyn. Ten opzichte van de gebruikelyke bereidingsmethode van $K_2CO_3$, namelyk electrolyse van KCl tot KOH, gevolgd door carbonatie, heeft de voorgestelde methode de voordelen, op kleine schaal nog economisch uitvoerbaar te zyn, en tevens een geringer energie-verbruik per ton $K_2CO_3$ te hebben.

De lage prys van $Na_2CO_3$, dat volgens het Solvay-procedé gemaakt wordt, deed vermoeden, dat het volgens het hierboven beschreven proces gemaakte $Na_2CO_3$ een hogere kostprys zou hebben. Berekening bevestigde dit vermoeden.

Kaliumbicarbonaat kan, zoals bekend, niet volgens het Solvay-procedé gemaakt worden, vanwege de hogere oplosbaarheid. Het beschreven proces opent echter een nieuwe weg, om met behulp van kationenwisselaren de chloriden van kalium en natrium in waterige oplossing met behulp van een heldere oplossing van calcium hydroxide en met koolzuur in de respectievelyke (bi)-carbonaten om te zetten. Fenol, gebruikt om de oplosbaarheid van het calcium hydroxide te verhogen, wordt teruggewonnen zonder noemenswaardige verliezen. De grondstoffen, KCl, NaCl en $CaCO_3$ zyn op vele plaatsen ter wereld aanwezig, waardoor een bredere toepasbaarheid van de voorgestelde werkwyze mogelyk is.*

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* D.Araten, Chem. & Ind. 1960 1301.

# תקציר עברי

כלורידים של אשלגן ונתרן מופיעים בטבע במקומות רבים. שמושם התעשיתי בתור שכאלו הנו מוגבל. המרתם אל (דו) פחמות נותנת חמרי גלם חשובים לתהליכים אחרים.

התיזה הנוכחית מתארת שיטה חדשה להמרת הכלורידים של אשלגן ונתרן דרך הֲמֵימָה אל דוּ-פַּחְמָה וּפַּחְמָה. אופן ההמרה הוא כדלקמן: תמיסת כלוריד האשלגן מומרת בעזרת שרף מחליף קטיונים אל מימת האשלגן; כמקור ליוני הידרוקסיל משמש סיד כבוי. התגובות הן הבאות:

הטענה: $KCl + Ca_{\frac{1}{2}}\text{-}R \longrightarrow K\text{-}R + \frac{1}{2}\,CaCl_2$

(R- הוא השריג של השרף)

שחזור: $K\text{-}R + \frac{1}{2}\,Ca(OH)_2 \longrightarrow Ca_{\frac{1}{2}}\text{-}R + KOH$

בזמן השימוש במחליפי אניונים למטרה זאת היתה מימת האשלגן נוצרת בשלב השחזור, כדלהלן:

$$KCl + R\text{-}OH \longrightarrow R\text{-}Cl + KOH$$

וזיהום התוצר בכלוריד היה בלתי נמנע. מסיבה זאת מועדפים כאן מחליפי קטיונים.

המסיסות הנמוכה של מימת הסידן במים טהורים היתה גורמת לשתי תוצאות בלתי רצויות:

א) התהליך היה יקר מבחינת השימוש במים.

ב) בשימוש במחליפי קטיונים היתה מתקבלת תמיסה מהולה ביותר של מימת האשלגן.

נמצא שעל שני הקשיים אפשר להתגבר על ידי הוספת פֶּנוֹל למשחזר. כך הועלה ריכוז מימת הסידן מ-0.044 נורמאלי אל 0.78 נורמאלי; השימוש במים הוקטן באופן יחסי. מתקבלת תמיסת מימת האשלגן 0.6 נורמאלית, חפשית מכלוריד ומזוהמת במימת הסידן ובפנול בלבד.

על ידי פִּיחְמוּת (קָארְבּוֹנָאצִיָה) עם דו-תחמוצת פחמן גזית הופך האשלגן לדו-פחמה; הסידן שוקע כפחמה, ומופרד מהתמיסה. על ידי הקטנת ההִתְפַּרְדוּת (הדיסוציאציה) של הפנול מופרש חלק ממנו כפאזה נפרדת, המושב לתהליך.

השבת פנול נוספת מתבצעת על ידי המלחה משקיעה ("סוֹלְטִינְג אָאוּט") עם דו-פחמת אשלגן. את שאריות הפנול האחרונות ממצים בעזרת בּוּטִיל-אָצֶטַט נוֹרְמָאלִי. פנול וממיס זה אינם יוצרים אָזֵיאוֹטְרוֹפּ בלחץ אטמוספֵירי, כך שהפרדה אפשרית בדרך זיקוק.

מתמיסת דו-פחמת האשלגן המתקבלת מוצאים המים על ידי תהליך "העברת מים", שבו ממצים את המים בעזרת בוטאנול נורמאלי. את הכהל מייבשים בעזרת תמיסה רווייה של כלוריד הנתרן ומשיבים אותו לתהליך. מתוך התמיסה המהולה של כלוריד הנתרן משיבים את הבוטאנול על ידי זיקוק טרם הזרמתה לשפכין.

ב"העברת המים" הזאת מתקבלת דו-פחמת אשלגן מוצקת. על ידי חמום קל מייבשים אותה, או הופכים אותה לפחמה.

המרת כלוריד הנתרן לדו-פחמה ולפחמה ניתנת לביצוע בדרך דומה.

חמרי הגלם לתהליך זה הם כלוריד האשלגן (או הנתרן), סיד כבוי ודו-תחמוצת הפחמן (מתוך אבן גיר), וכלוריד הנתרן להעברת המים.

עבור מתקן שיפעל בסדום, ליד מפעל האשלג, מראה חשבון התמחיר שפחמת האשלגן ניתנת לייצור בדרך זאת באופן כלכלי. ביחס לתהליך המקובל לייצור פחמת האשלגן, דהיינו אלקטרוליזה של הכלוריד למימה ופיחמות, יש לשיטה המוצעת כאן היתרונות של אפשרות בצוע כלכלי בקנה מידה קטן וכן תצרוכת יותר קטנה של אנרגיה לטון תוצר.

על יסוד המחיר הנמוך של פחמת הנתרן המיוצרת בתהליך סולויי ניתן לשער, שפחמת נתרן המיוצרת בתהליך המוצע תהיה יקרה יותר. החישובים אימתו השערה זאת.

אין, כידוע, אפשרות לייצר פחמת אשלגן בתהליך סולויי בגלל מסיסותה הגבוהה. התהליך המוצע, לעומת זאת, פותח דרך חדשה להמיר את הכלורידים של נתרן ואשלגן בתמיסה מימית אל (דו) - פחמותיהם, בעזרת תמיסה צלולה של סיד כבוי ודו-תחמוצת הפחמן. פנול, הנצרך כדי להגביר את מסיסות הסיד, מושב ללא הפסדים ניכרים. חמרי הגלם, הכלורידים של האשלגן ונתרן, וכן אבן גיר, נמצאים במקומות רבים בעולם, מה שמרחיב את אפשרות השימוש בשיטה המוצעת. *

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* D. Araten, Chem. & Ind. 1960 1301

D. Araten

## Stellingen

1. Uit de gegevens van Korf en Shatrovskaya is een meer economisch procedé voor de bereiding van natrium-sulfaat af te leiden, dan het tot nog toe gebruikelijke.

   D.M.Korf & L.P. Shatrovskaya
   Zhurnal Obschei Khimii (J.Gen.Chem.USSR)
   10 (1940) 1232-4
   Chem.Abstr. 35 (1941) 2782
   Gegeven in
   A.B.Zdanovskii, Ye.I.Lyachovskaya & R.E.Shleimovitsh
   Spravotshnik Eksperimentalnich Dannich po Rastvorimosti Mnogokomponentnich Vodno-Solevich Sistem
   (Handboek van Experimentele Gegevens over de Oplosbaarheid van Meer-Komponentige Water-Zout Systemen)
   Leningrad 1954, deel II, pag. 790:-

   t = 25°

| Gewichts-% in de Oplossing | | | | Vaste Fase |
|---|---|---|---|---|
| HCl | $H_2SO_4$ | NaCl | $Na_2SO_4$ | |
| 0 | 10.58 | 12.75 | 19.31 | NaCl + $Na_2SO_4$ |
| 0 | 8.43 | 14.40 | 16.90 | " |
| 0 | 7.25 | 16.61 | 13.35 | " |
| 0 | 3.04 | 21.12 | 10.50 | " |
| 0 | 1.57 | 21.53 | 8.94 | " |
| 0 | 8.53 | 5.15 | 25.5 | $Na_2SO_4$ + $Na_2SO_4 \cdot 10H_2O$ |
| 0 | 4.54 | 12.03 | 17.31 | " |
| 0 | 1.54 | 14.4 | 15.10 | |

2. Het verdient aanbeveling, de bereiding van natrium-sulfaat (uit natrium-chloride en zwavelzuur) en die van fosforzuur (volgens het Israel Mining Industries' procedé) te combineren.

   A.Baniel, R.Blumberg & A.Alon
   Brit. Chem. Eng. 4 (1959) 223-4
   Anoniem, Chem. Engng 67 (1960) no. 8, 81

3. By de concentratie van waterige oplossingen zonder indampen heeft de methode, voorgesteld door Baniel, de voorkeur boven die, voorgesteld door Schaufelberger.

   A.Baniel
   J.Appl.Chem. 8 (1958) 611-6

   F.A.Schaufelberger
   United States Patent 2,780,530 (5.2.1957)
   Chem.Abstr. 51 (1957) 7073f

4. De methode van Scribner en Reilley, om op grond van polarografische gegevens de omstandigheden van reductie met behulp van amalgamen en tevens de aard van het amalgaam te kiezen, is onvolledig, en kan derhalve tot foutieve resultaten leiden.

   W.G.Scribner & C.N.Reilley
   Anal.Chem. 30 (1958) 1453

5. By de titratie van calcium in aanwezigheid van fosfaat heeft de methode van Ince en Forster de voorkeur boven die van Cimerman, Alon en Mashall.

   A.D.Ince & W.A. Forster
   Analyst 85 (1960) 608-9

   Ch.Cimerman, A.Alon & J.Mashall
   Anal.Chim.Acta 19 (1958) 461-6

6. De experimentele resultaten van Frangiskos en Smith bewyzen de juistheid van de theoretische gevolgtrekkingen van Gaudin wat betreft het chemische karakter van verkleining van mineralen.

   A.M.Gaudin
   Mining Engineering 7 (1955) 561-2

   A.Z.Frangiskos & H.G.Smith
   International Mineral Dressing Congress (Stockholm 1957) I:2 pp. 1-15

7. Het gebruik van geconcentreerde kunstmeststoffen ("high-analysis fertilisers") brengt met zich mede, dat er in de aarde gebrek kan ontstaan aan calcium, zwavel en sporen-elementen ("trace elements"), die in minder geconcentreerde kustmeststoffen wel aanwezig zyn. By de economische beschouwing van het gebruik van dergelijke geconcentreerde kustmeststoffen moet men rekening houden met de kosten van toevoeging van de ontbrekende stoffen.
   G.L.Terman & J.Silverberg
   Farm Chemicals <u>1960</u> no.3 (March) pp.2-4
   H.V.Jordan & H.M.Reisenauer
   SOIL, The Yearbook of Agriculture 1957
   The United States Department of Agriculture
   (Washington D.C. 1957) pp.107,110.
8. By het aangeven van capaciteiten van ionenuitwisselaars verdient de gewichtsbasis de voorkeur boven de volumebasis .
9. De door Stern onopgeloste moeilykheden, ondervonden by het neerslaan van basisch strontium chloride, rechtvaardigen ernstige twyfel aan de mogelykheid, zyn proces ter conversie van natrium chloride en water in natrium hydroxide en zoutzuur chemisch uit te voeren.
   Het valt te betreuren dat de samenvattingen van dit werk, zowel in de Iowa State College J.Sci. als in Chem.Abstr., van deze moeilyheden geen enkele vermelding maken.
   H.Stern
   Production of Sodium Hydroxide by Ion Exchange
   Ph.D.Thesis, Iowa State College (1950)
   Iowa State College J.Sci. <u>25</u> (1951) 358-60
   Chem.Abstr. <u>45</u> (1951) 6896e
10. Het werk van de Wereld Gezondheidsorganisatie (WHO) en dat van de Voedsel- en Landbouworganisatie der Verenigde Naties (FAO) dient beter gecoordineerd te worden,
11. Door het oprichten van instituten, belast met het vertalen van Russische natuurwetenschappelyke vakliteratuur in het Engels (of in andere Westerse talen) wordt, op lange termyn beschouwd, verkwisting van tyd, van geld en van wetenschappelyke arbeidskrachten veroorzaakt. Dit kan voorkomen worden indien Westerse natuurwetenschapsbeoefenaars zich een beperkte kennis van de Russische taal eigen maken.
   Anoniem, Chem.Eng.News <u>37</u> (1959) no. 31, 70
   Anoniem, Chem. & Ind. <u>1958</u> 1487.
12. Voor Israeli's die zich naar het buitenland begeven om een studie voor ingenieur of middelbaar technicus te volgen, verdient het aanbeveling de keuze van een opleiding in Nederland ernstig te overwegen.

David, son of Yehuda Araten and Hannah de Leeuw, was born in Amersfoort, the Netherlands on May 27th, 1928. At the age of 5 he came with his parents to (the then called) Palestine. He studied at the Beth Hasefer Hareali Haivri (Reali School, Principal Dr. A. Biram), in Haifa, from 1934 to 1946, with a two-year break (1943-4) at the Technion Secondary Vocational School (Principal Dr.G.Aharoni).

In 1946 he passed the High School Certificate Examination, as well as the British Matriculation Examination. In 1947 he started his studies at the Department of Chemical Technology of the Technical University of Delft. At the outbreak of Israel's war he enlisted for service, and resumed his studies after demobilization late in 1949. In 1953 he passed the propadeutic examination, in 1956 the candidate's examination, and in 1957 the final ("ingenieurs-") examination (M.Sc.Chem.Eng.). For this grade he worked for over a year under the guidance of Prof. Ir.J.G.Hoogland on "Hydrogen Peroxide by Reduction of Oxygen with the aid of Cadmium Amalgam".

In 1952 he married Miss Hannah Ida Kaufman, and has two daughters.

On completion of his studies he returned to Israel, and has since been working at the Research Laboratories of Israel Mining Industries in Haifa. The experimental work executed there forms the basis of the present thesis.