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RECOVERY OF POTASSIUM FROM BITTERNS

by

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SUMMARY

Background

Seawater is potentially a vast and readily accessible reserve of potassium for fertilizer production. Potassium is not at present recovered from seawater commercially, since potash can be produced easily and cheaply from the extensive deposits of certain soluble salts that exist in some countries. However, Australia has no known deposits, and there is interest here in the development of a method for extracting potassium from seawater, or more particularly from the concentrated bittern which remains after the crystallization of sodium chloride by solar evaporation.

Objectives

An assessment was undertaken of the merits of possible lines of approach to potassium recovery, by reviewing published literature relating to all earlier processes or proposals. From this information, methods showing some economic promise were to be subjected to preliminary experimental investigation.

Summary of Work Done

From a study of the chemical literature, a review was prepared of possible methods for recovering potassium from bitterns.

An experimental study was made of the extraction of alkali metals by a 4: 1 mixture of Santophen-1 (a sterically-hindered phenol) and EHPA. This system, which is capable of operation at low pH, offered the possibility of a significant economic advantage over the use of the phenol alone, due to reduced alkali requirements.

It was found that the extractant showed an optimum potassium-sodium selectivity of about 9 when the final pH was 5. Selectivity was lower at high salt concentrations. The alkali metals could be completely stripped from the extractant by nitric acid solutions of pH below 2.

Magnesium was strongly extracted with the alkali metals from diluted bittern.

Conclusions

Using crystallization methods, complicated procedures would be required to produce a fertilizer-grade product from seawater bitterns. Economical operation could possibly be achieved if KCl-production were integrated into a comprehensive scheme for the recovery from seawater of NaCl, MgO and other saleable products.

No selective extraction procedure has yet proved wholly satisfactory. However, the experimental findings have shown sufficient technical promise to inspire confidence that it might ultimately be possible to extract potassium selectively from seawater bittern at a competitive cost.

Methods based on selective reagents of the dipicrylamine and phenolic-types are undoubtedly technically feasible, but they involve the consumption of alkali, and would not be economic at current market prices. It appeared that the use of di(2-ethyl hexyl) phosphoric acid (EHPA) in conjunction with a phenolic reagent might result in a worthwhile reduction in alkali requirements. Experimental results with Santophen-1-EHPA revealed several features which make the system unattractive for commercial application. In particular there were the interference of magnesium in potassium extraction, the required dilution of the bittern, and the quantity of alkali needed to establish the working pH in the presence of EHPA. In addition, relatively small losses of the costly reagents could become significant in view of the large volumes of brine to be treated.

The properties of some inorganic ion-exchange materials suggest application to potash recovery with attractive possibilities of low production costs. The realization of this potential would depend on the development of the ion-exchangers to satisfy practical criteria, such as adequate rates of exchange and selectivity in liquors of high salt-content. This development work might well require considerable time and effort, but a useful preliminary assessment could be obtained from a limited experimental investigation.

Recommendations

It is recommended that a preliminary experimental evaluation be made of certain inorganic materials as potassium-selective ion exchangers.

1. INTRODUCTION

This report is the result of a comprehensive survey of possible methods for the recovery of potassium values from seawater bittern.

At present, underground deposits of soluble salts of potassium are by far the major source of potash for world markets. Very extensive reserves of "sylvinite" (KCl plus NaCl) and carnallite ($KCl.MgCl_2.6H_2O$) exist in Canada and the USSR. These deposits are worked by conventional or solution mining techniques. The ores can be processed easily employing flotation or crystallization to produce a high grade KCl, containing at least 60% K_2O plant nutrient for fertilizer use. (Noyes, 1966).

The extraction of potassium from brines assumes a much smaller role in world production of potash. In addition to KCl and NaCl, natural brines contain much sulphate ion, and some magnesium and calcium. Evaporation of such solutions results in the precipitation of sodium and magnesium double salts with potassium, and it is not normally possible to crystallize pure KCl. However, by careful control of crystallizing conditions, three major plants in Israel, Utah and California currently produce KCl from brines. By-product salts make a significant contribution to the economy of these processes. (Noyes, 1966).

Although extraction processes have been operated from time to time, potassium is not now commercially recovered from seawater. The concentrated liquors remaining after the crystallization of common salt by solar evaporation of seawater, and generally referred to as bitterns, have a similar composition to the commercially worked natural brines, with the added complication of increased magnesium content. Proposed methods of potassium extraction from bitterns have been generally too complex to be competitive economically with the straightforward production of potash from sylvinite deposits. In Australia, no such deposits have been found, and all potash requirements are imported. Thus there is interest here in the development of possible methods which show some promise of economically extracting potassium from bitterns.

For this reason a review was undertaken of possible approaches based on earlier processes or proposals in the literature. Methods that appeared to have most potential were to be selected for preliminary investigation.

2. MATERIAL EXAMINED

In all tests the extractant used was a solution in trichlorethylene of:

a. Santophen-1 (4 chloro-2-benzylphenol) 1.0 M

and b. EHPA (di-(2-ethylhexyl) phosphoric acid 0.25 M

This solution is referred to as "Solution E" in the Experimental Section, 3.2.

An experimental sample of Santophen-1 was supplied by Monsanto Chemicals (Australia) Ltd.

The EHPA was a technical grade, supplied by Union Carbide (Australia) Ltd.

Aqueous solutions for the extraction tests were generally prepared by dissolving reagent grade salts in distilled water.

Some tests were carried out on a seawater bittern, Bl, whose principal ionic constituents were:

Ion	Concentration	
	g/l	g equiv/l
Sodium	71.0	3.1
Potassium	10.2	0.27
Magnesium	36.5	3.0
Chloride	186.2	5.2
Sulphate	50.4	1.05

3. EXPERIMENTAL PROCEDURE AND RESULTS

The investigation of methods of potassium recovery included a literature survey, and experimental work using a phenolic extractant. The results of the literature survey are reviewed below. An account of the experimental work is then presented.

3.1 Review of Possible Methods

Methods reported for the separation of potassium from brine solutions can be broadly divided into two groups. The first group comprises procedures in which crystallization under controlled conditions permits the separation of fractions containing a high proportion of KCl. The second group includes methods involving reagents which preferentially remove potassium from brine solutions.

3.1.1 Crystallization Procedures

The complex nature of brines, and of seawater bittern in particular, means that crystallization of KCl alone by evaporation is a difficult proposition.

Under equilibrium conditions during solar evaporation of bittern, much of the potassium crystallizes as a range of double salts such as glaserite ($Na_2SO_4 . 3K_2SO_4$) and carnallite ($KCl . MgCl_2 . 6H_2O$). Production of high-K_2O material from a series of these double salts cannot be accomplished readily.

However, it has been shown that equilibrium-imposed limitations can sometimes be avoided by crystallizing under metastable conditions of supersaturation. Some double salts, having inherently slow crystallization rates, can often be maintained in a state of supersaturation. Thus Wienert (1950) showed that KCl could be crystallized from a brine derived from glaserite, in which a high $MgSO_4$ content was sustained by preliminary precipitation of Na_2SO_4. In cooling the brine in two stages from 100°C, quite pure NaCl and KCl crops were obtained, although the liquor was sometimes supersaturated with respect to vanthoffite ($3Na_2SO_4 . MgSO_4$) and glaserite ($Na_2SO_4 . 3K_2SO_4$). Similarly, Garrett (1963) pointed out that by seeded crystallization of certain salts, it is possible to obtain a concentrated brine that is supersaturated with respect to langbeinite ($2Na_2SO_4 . K_2SO_4$) at 83°C. A large proportion of the potassium can then be crystallized as KCl by lowering the temperature to about 25°C.

Methods of this type might be applied to advantage to available bittern. Careful consideration of phase equilibria and crystallization rates could define possible favourable composition ranges. The practical feasibility of any proposed procedure would have to be established by a thorough experimental investigation, preferably using pilot scale equipment. Close control of bittern composition and crystallizing conditions would be necessary throughout. The likely heat requirements of these crystallization procedures constitute an economic drawback.

A crystallization process patented by Hadzeriga (1960) appears to be applicable to salt water bittern. The complexity of the procedure is offset economically by the almost complete utilization of all brine values, either as internal recycle reagents, or as saleable by-products. The steps of the proposed process are, briefly:

1. Solar evaporation of the brine to precipitate much of the NaCl.
2. Treatment with $CaCl_2$ solution (a by-product of step "6") to precipitate $CaSO_4$ as gypsum.
3. The production of sulphuric acid by ion exchange from gypsum. It is recommended that this acid be utilized in the treatment of phosphate rock, producing valuable phosphoric acid, with a gypsum tailing which can supplement the ion-exchange feed.
4. Evaporation of the sulphate-free brine from step "2" to crystallize "sylvinite" (KCl plus NaCl) and carnallite ($KCl. MgCl_2 . 6H_2O$), from which fertilizer-grade KCl can be produced by conventional methods.
5. Decomposition of the residual $MgCl_2$ brine by strong heating to yield finally an MgO calcine and a 14-16% HCl solution. The calcine can be converted to a high grade MgO product by further treatment.
6. Use of the HCl solution of step "5" to regenerate the acid form of the ion exchanger, with simultaneous formation of a $CaCl_2$ solution for step "2".

Further integration is possible by utilizing chlorine from NaCl-electrolysis in bromine recovery from the bittern. The process shows promise of economic operation where a market exists for each of the products NaCl, H_3PO_4, KCl, MgO and Br_2. Salutsky and Dunseth (1963, 1965) found that 90% of the potassium content of seawater could be precipitated at pH 9.5 as $KMgPO_4 . 6H_2O$, by the addition of trisodium phosphate. The precipitate also contained much calcium and magnesium in the form of water-soluble phosphates. The potassium could be brought into solution readily by treatment of the precipitate with a solution of ammonium salt, with simultaneous production of $MgNH_4PO_4 . 6H_2O$ which is a valuable fertilizer material. However, the remainder of the precipitate contained much phosphate which seems unlikely to be readily available as a plant nutrient and would be difficult to reconvert to trisodium phosphate for recycle. The cost of producing the original trisodium phosphate would weigh heavily against the economics of the process, even if wastage could be avoided.

Goodenough and Cooper (1965) patented a method for the recovery of potassium chloride from certain brines in which the magnesium content is almost entirely replaced by calcium by treatment with lime or slaked dolomite. The brine is contacted with ammonia under pressure which causes KCl to be precipitated preferentially. The process ultimately yields a KCl product of 94% purity, with a recovery of about 80%. The high magnesium and sulphate contents of seawater bittern would demand the use of excessive quantities of lime to adjust the bittern to a composition which would be acceptable for this process.

3.1.2 Selective Extraction Procedures

Certain compounds have been shown to display a degree of selectivity for potassium over sodium. Several of these compounds have been applied with varying success to the recovery of potassium from large amounts of sodium.

In the discussion which follows, the compounds have been divided into three groups. However, it appears likely that in all cases the basic mechanism of selectivity is the same. The removal of alkali ions from aqueous solution is achieved when the hydration sphere of water molecules around the ion is replaced by a hydrophobic envelope. Because the potassium ion is significantly larger than the sodium ion:

1. the hydration sphere of the low field potassium ion is more readily displaced by the selective species,
2. the larger potassium ion is physically hindered from re-encounter with water molecules by the enveloping molecule(s) of the selective species.

Thus the chemical binding of potassium to the selective species is greatly assisted by a physical entrapping, or "cage", effect.

Methods Based on Dipicrylamine and Analogues

a. Precipitation of Potassium Dipicrylaminate

Dipicrylamine, or hexanitrodiphenylamine, (HDPA), forms water soluble salts of sodium and calcium when contacted with alkaline solutions. By contrast the potassium salt, KDPA, is almost insoluble (73 mg/litre at 0°C, 880 mg/litre at 25°C). It would appear that on formation of the KDPA ion pair, the bulky nitro groups of the aminate ion obstruct rehydration of the potassium ion and prevent its solvation. Thus KDPA is precipitated when an aqueous solution of NaDPA is added to a solution containing potassium. If the precipitate is separated and contacted with mineral acid, HDPA is regenerated with formation of a solution of the potassium salt of the mineral acid.

KDPA precipitation has evidently been employed in a Dutch commercial plant for potassium recovery from seawater. (Salutsky and Dunseth, 1962).

Butt et al, (1964), presented promising experimental data in support of a proposed process for the precipitation of potassium from seawater brines. These workers treated a brine initially three times the concentration of seawater (i. e. "3X", 10. 56 g Na per litre, 0. 38 g K per litre). The addition of a NaDPA solution diluted the liquor to 0. 5X, and precipitated KDPA at a reactant ratio NaDPA: K = 1. 64. When the precipitation was carried out at minus 0. 9°C to minimise KDPA solubility losses, they obtained 95% yields of KDPA, based on the initial potassium contents of the brines. The only significant impurity of the KDPA precipitate was calcium which appeared to be present as $CaCl_2$ (7-12 wt %). Where the final concentration of the liquor exceeded 0. 5X (for example 1. 00X, 1. 68X) the KDPA was increasingly contaminated by sodium.

Moyle (1957) reacted CaDPA solution with bittern (approximately 7. 5X), the final concentration being about 2. 25X. He obtained 66% recovery of potassium with a high level of sodium impurity (K: Na = 2. 5). These results, obtained at room temperature, and using a reactant ratio 1. 02, can be reconciled with those of Butt et al (1964).

Reagent losses are likely to be important economically. Losses can be minimized by low temperature operation, but cooling too, would be expensive. (This would not apply where the brine to be treated is a freezing desalination plant effluent). A disadvantage is the requirement that the bittern should be diluted to avoid sodium precipitation. It is noteworthy that a dipicrylamine precipitation process requires alkali (to obtain a water soluble salt of HDPA) and hydrochloric acid (to produce KCl with regeneration of HDPA), both in quantities at least equivalent to the KCl produced.

At current Australian market prices, (Anon 1966), the costs of lime and HCl total 88% of the value of KCl on the basis of chemical equivalents. Thus even before consideration of inevitable reagent losses in such a process, the economics of KCl production look unpromising.

b. Ion Exchange by Polymeric Analogues of Dipicrylamine

With the dipicrylamine precipitation method, reagent losses contribute significantly to production costs. Reagent solubility could be eliminated altogether by incorporating the active grouping of dipicrylamine into the structure of a polymer. Provided that the selective action of the grouping were not impaired thereby, the polymer could then be used as a cation exchanger. Skogseid (1947) patented a procedure for preparing such a polymer. A later patent (Skogseid, 1952) refers to its application in the recovery of potassium from seawater and brines. Bonhoeffer (1956) confirmed the potassium-selectivity of the polymeric material described by Skogseid. However, there appear to be no reports in the literature of any further developments in this field.

A cation exchange process of this type would also consume alkali and hydrochloric acid equivalent to the KCl produced. Slow rates of exchange might hamper the commercial application of an ion exchanger of this type. On the other hand the exchange rate could perhaps be improved by hydroxylating the polymer to make it more hydrophilic as observed by Gibson and Packham (1966).

c. Solvent Extraction of Potassium Dipicrylaminate

As a variant of the precipitation procedure, the potassium dipicrylaminate could in principle be extracted into a water immiscible solvent. Such a solvent extraction method could be adapted readily to a stepwise purification of a potassium-containing liquor.

Smit and Pummery (1962) developed a procedure for the extraction of caesium dipicrylaminate from fission-product waste liquors. The most satisfactory solvent was found to be nitrobenzene and their results indicate a high extraction coefficient for K^+ relative to Na^+ in this system. However, dipicrylamine has a low solubility in nitrobenzene, the maximum working concentration attainable being 0.025M. This low extractant concentration was tolerable for the recovery of relatively small amounts of caesium. For the large-scale treatment of bitterns, on the other hand, the necessary high organic:aqueous phase ratios or excessive dilution of the bittern would be unacceptable. Moreover reagent losses would be greater and far more important economically than in the caesium recovery context.

Thus solvent extraction of potassium dipicrylaminate would not be commercially feasible.

Methods Based on Sterically-hindered Phenols. A number of phenols have been shown to exhibit some selectivity when applied to the liquor-liquid extraction of alkali metal ions.

The extraction process can be reduced to two steps:

1. formation of phenolate ion

$$PhOH_{org} + OH^-_{aq} \longrightarrow PhO^-_{aq} + H_2O$$

2. extraction of ion pair

$$PhO^-_{aq} + M^+_{aq} \longrightarrow (M^+_, PhO^-)_{org}$$

The smaller alkali ions lithium and sodium often display markedly different behaviour from potassium, rubidium and caesium in these extraction systems. Undoubtedly this phenomenon has a similar origin to the marked solubility differences observed for the corresponding dipicrylaminates.

It seems likely that during the formation of the alkali phenolate ion pair, the larger alkali ions lose their hydration spheres more easily. The larger alkali ions are then effectively prevented from contacting water molecules by a new "solvation sphere" incorporating large hydrophobic organic groupings. In this form, the ion pair is compatible with the organic phase. Of the phenols investigated to date (Brown et al, 1962; Horner et al, 1963; Keder et al, 1965) the most effective is sec butyl (α-methylbenzyl) phenol (BAMBP).

The solvates formed by BAMBP with caesium have been the subject of fundamental studies by Egan et al (1965) and Keder et al (1965). The most significant of their findings are outlined below:

a. Infra-Red Studies

Both groups recorded infra-red spectra for pure BAMBP, solutions of varying concentration of BAMBP in carbon tetrachloride, and similar solutions containing caesium-BAMBP solvates.

From the behaviour of absorption bands in the phenolic OH region, it would appear that with increasing concentration, the extent of hydrogen-bonding between different BAMBP molecules increases until in pure BAMBP there are essentially no unassociated molecules. When caesium ions are solvated by BAMBP in CCl_4 stronger hydrogen-bonding of phenolic OH-groups is possible, apparently linking different solvates. Where the ratio BAMBP: Cs exceeds 4: 1, there is no interaction between small amounts of dissolved water and other solutes in the CCl_4 phase.

b. Freezing-point Depression Measurements

Keder et al (1965) carried out freezing-point depression experiments on cyclohexane solutions of BAMBP, before and after titration with CsOH. The freezing-point depression data corresponded to unionized Cs^+, PhO^-. 3PhOH, which confirmed the indications of loading data that four molecules of BAMBP are involved in solvation of caesium. Where the ratio BAMBP:Cs was less than 4: 1, water was extracted with caesium.

c. Nuclear Magnetic Resonance Studies

In both investigations magnetic resonance spectra for BAMBP solutions were recorded.

The proton resonance shifts observed could be reconciled with the conclusions from the infra-red spectra, viz, that BAMBP becomes increasingly associated as its concentration is raised, and that enhanced hydrogen-bonding of phenolic OH groups results from the solvation of caesium.

Keder et al (1965) also studied the resonances due to the phenolic ring and observed that they were affected by solvation of alkali ions, particularly caesium. This suggests that the metal ion may interact with the II-electrons of the phenol ring.

BAMBP has been successfully employed in processes for extracting caesium from both fission product solutions (Horner et al, 1963) and pollucite ore liquors (Arnold et al, 1965).

There is little doubt that it would be feasible to apply a system based on BAMBP to the recovery of potassium from bitterns though it is clear that K-Na separation factors would be much lower than for Cs-Na. As with dipicrylamine-based processes however, alkali and acid consumption would make it very difficult to produce KCl at a competitive price. Thus at each extraction stage alkali is required to liberate phenolate ions, and acid is required to strip the organic extract.

Keder et al (1965) investigated the use of di(2-ethylhexyl) phosphoric acid (HA) in conjunction with BAMBP. It was found that efficient extractions could be achieved at considerably lower pH than by BAMBP alone. The extracted species was $Cs^+, A^-.4PhOH$ suggesting that the function of the di(2-ethylhexyl) phosphoric acid was to supply the anion which the phenol can only do at a high pH.

Methods Based on Inorganic Ion Exchange Materials. A reason for the relatively low content of potassium compared to sodium in seawater is the preferential absorption of potassium by some clays. By this mechanism, potassium derived from the weathering of rocks is removed from river waters before they flow into the sea.

The selectivity in the ion-exchange behaviour of certain clay minerals is also observed with several other crystalline inorganic materials (Darrer, 1962). Of these, high exchange capacities are exhibited by zeolites and a group of substances exemplified by zirconium phosphate.

a. Ion-exchange with Zeolites

Phillipsite and chabazite are natural silicates having a three-dimensional network structure.

Phillipsite is found in deep sea sediments, and has a high K: Na ratio at its exchangeable cation sites despite the fact

that it is in equilibrium with seawater. (Rankama and Sahama, 1950). For equilibration with seawater bittern, chabazite would appear to have a K: Na selectivity coefficient of about 8 according to data reported by Barrer (1958). The exchange capacity of chabazite is cited as about 4 milli-equivalents per gramme.
The use of such zeolites for alkali metal separations has been limited to small scale radiochemical and analytical work. Their adaptation to large scale processing of bitterns is likely to be hampered by the low flowrates attainable in practice.
Recovery of adsorbed potassium from the exchangers may also present some difficulty.

b. Ion Exchange with Zirconium Phosphate and Related Materials

Zirconium phosphate (Kraus and Philips, 1956), zirconium tungstate (Crouch et al, 1957, Kraus et al, 1956a), zirconium molybdate (Kraus et al, 1956b), and ammonium phosphomolybdate (Smit, 1958) have been shown to display ion exchange selectivity within the alkali metal group. For these materials, exchange of ions is limited to the surface of the crystalline particles, but exchange capacities of several milli-equivalents per gramme are nevertheless attained. Separation schemes using zirconium phosphate and ammonium phosphomolybdate have been successfully scaled up for the recovery of caesium from fission product solutions (Amphlett et al, 1959, Healy and Davies, 1959, Smit et al, 1963).
Limitations on liquor throughput rates seem likely to be the only disadvantage met in applying these ion exchange materials to the recovery of potassium from bitterns, To offset this, the process would not require alkali, a significant advantage over the dipicrylamine and phenol-based methods.
From the published information (Skogseid, 1952, Smit and Pummery, 1962), it would seem feasible to recover potassium from bitterns by employing columns of ammonium phosphomolybdate (40-60 mesh). The necessary consumption of ammonium chloride regenerant, at least equivalent to the KCl produced, would make the process uneconomical. Alternative production of K_2SO_4, by elution with ammonium sulphate, is more attractive. However, the recovery of excess ammonium sulphate from the eluate would add to the cost of the product. It is possible that a mixed K_2SO_4-$(NH_4)_2SO_4$ product would be an acceptable fertilizer in some circumstances. The selectivity of zirconium phosphate for potassium over the other bittern components seems likely to be much impaired at high salt concentrations. (Amphlett et al, 1958, Baes, 1962). Low recoveries of potassium would result with undiluted bittern. Nevertheless, selective elution of sodium and potassium should be possible with hydrochloric acid of different strengths.

3.2 Solvent Extraction of Potassium Using a Mixture of Santophen-1 and EHPA

Keder et al (1965) showed that the selectivity for caesium of certain sterically-hindered phenols was retained in the presence of EHPA. The extraction of caesium into the organic phase was then possible at a much lower pH than with a phenol alone. Presumably the function of the EHPA was to provide an anion which could be extracted along with the phenol-solvated caesium ion. Whereas the phenol, a weak acid, requires a high alkali concentration before it can provide phenolate ions, the EHPA is highly dissociated at relatively low pH.

These workers also reported data which suggested that EHPA would permit potassium extraction at lower pH. If a substantial reduction in alkali requirements were to result from this measure, this would alleviate the major economic drawback noted in an earlier section in applying the phenolic reagents to the extraction of potassium. For this reason, it was decided to investigate the extraction of potassium from aqueous solution by phenol-EHPA mixtures.

3.2.1 pH Titrations

To obtain an indication of the optimum pH conditions for potassium-sodium separations using the Santophen-1: EHPA extractant, aliquots of the Solution E were titrated with 0.25N potassium hydroxide and 0.25N sodium hydroxide respectively.

The titration curves are shown in Figure 1.

The best separation should be achieved at about pH 5, before neutralization of sodium hydroxide becomes significant.

3.2.2 Extraction of Synthetic Brines

Effect of pH. These tests were conducted on synthetic brine solutions containing NaCl (0.065M) and KCl (0.0075M) with pH adjusted to the desired value by NaOH addition.

To ensure that extraction of alkali metal ions (M^+) was confined to species of the type $M^+, A^-.4PhOH$ (Keder et al, 1965), the alkali metal concentrations were intentionally low, since coextraction of water at higher concentrations leads to loss of selectivity.

The synthetic brine solutions were thoroughly contacted with Solution E and the two phases separated. The organic phase was stripped with 1N HNO_3 and analyses carried out on both strip solution and the extracted aqueous phase. The conditions of the tests and the results are given in Table 1. A plot of the extraction coefficients versus pH is shown in Figure 2. The extraction coefficients for sodium and potassium increased linearly up to pH 5.3, where 80% of the potassium was extracted.

Instead of sodium hydroxide, sodium carbonate was used to adjust the pH in one test, with no apparent effect on the values obtained for the extraction coefficients.

Effects of Na and K Concentrations. For these tests, a series of solutions was prepared in which the NaCl and KCl concentrations ranged from 0.05 to 2.0M and from 0.005 to 0.28M respectively. The solutions all contained NaOH at a concentration of 0.007N.

Each of these solutions was contacted with Solution E, and the separated organic phase stripped with 1N HNO_3. The test conditions and results are displayed in Table 2. In general, extraction coefficients decreased with increasing concentrations. Thus separation factors tended to decrease at higher concentrations.

3.2.3 Extraction of Seawater Bittern

Effect of Magnesium. A sample of the bittern B1 was diluted tenfold with distilled water and contacted with Solution E as before. A similar test was carried out with the diluted bittern, having an NaOH concentration of 0.007N.

Extraction coefficients for K, Mg and Na are given in Table 3.

The extractant displays no worthwhile selectivity for potassium over magnesium.

3.2.4 Acid Stripping of Organic Extract

Effect of pH. An alkaline synthetic brine was contacted with the organic extractant Solution E. The separated organic phase was divided into three portions which were treated with nitric acid solutions of pH 3, pH 2 and pH 1, respectively.

The results (Table 4) showed that incomplete stripping of the alkali metals is achieved above pH 2, unless large volumes of wash solution are used. A degree of preference for sodium was observed in stripping at pH 3.

4. CONCLUSIONS AND RECOMMENDATIONS

For the sake of continuity, discussion of published methods for potassium recovery has been included with the description of the methods in the previous section. The principal conclusions are briefly reiterated below:

4.1 Crystallization Procedures

The methods proposed for crystallizing KCl from seawater bittern are necessarily more complex, and therefore more expensive, than those applicable to the simpler brines obtained from soluble salt deposits.

The processes operating under conditions of supersaturation require heating and cooling stages. Other approaches involve preliminary removal of large quantities of interfering ions such as magnesium and sulphate, which would also be costly. At best, these procedures would produce a material having a composition comparable to the sylvinite ore deposits.

Thus, potash produced from seawater by crystallization procedures could be marketed at a competitive price only if several byproducts were produced for which the demand were sufficient to make the overall operation economical.

It is not considered that crystallization processes warrant investigation unless adequate markets could be demonstrated for magnesium salts and bromine as well as KCl and NaCl. Even then a careful economic appraisal would be essential.

4.2 Selective Extraction Procedures

Each of the approaches discussed below is largely successful in separating potassium from solutions containing a considerable excess of sodium. At present, none of the procedures could be applied economically to the large-scale production of potash fertilizer from seawater bittern. On the other hand, the promise of these approaches could well be brought to commercial realization by future technical developments, or even by altered economic conditions.

4.2.1 Methods Based on Dipicrylamine and Analogues

The dipicrylamine precipitation method has been studied thoroughly. The inherent simplicity of the process, and the single-stage production of a high-grade product are attractive features. At today's prices, the process would not be economic, due to excessive reagent costs (for acid, alkali and make-up dipicrylamine) and the need for large volumes of low-salt water for dilution.

Potassium extraction using a polymeric analogue of dipicrylamine appears to be quite a promising approach. Costly solubility losses of dipicrylamine would be thereby eliminated. Although economic operation would still be difficult in the face of current acid and alkali prices, the development of such ion exchangers in a form that is useful commercially would be a worthwhile long-term project.

4.2.2 Methods Based on Sterically-Hindered Phenols

Solvent extraction procedures employing phenols are subject to the same economic disadvantages as the dipicrylamine precipitation process. Production costs would be high in view of the acid and alkali consumed, and the phenol lost through solubility in the aqueous phase.

The experimental work discussed in greater detail in Section 4.3 showed that the use of EHPA in conjunction with a phenol did not result in a worthwhile reduction in alkali consumption. Moreover, co-extraction of magnesium was an added complication.

4.2.3 Methods Based on Inorganic Ion Exchange Materials

Published results of extraction experiments with ammonium phosphomolybdate and zirconium phosphate, in particular, suggest that their potassium-sodium selectivities could be utilized in recovering potassium from seawater. It is likely that these ion exchange materials could require chemical and physical modification before they would be suitable for commercial application.

It is recommended that a short preliminary experimental investigation be carried out to assess whether or not practical potassium separations can be effected from seawater.

4.3 Solvent Extraction Using a Mixture of Santophen-1 and EHPA

The tests indicated that 4:1 Santophen-1:EHPA solutions in trichlorethylene can be used to extract alkali metals from aqueous solutions. At pH 5, a potassium-sodium selectivity of about 9 is attainable. The alkali metals can be stripped efficiently from the extract by treatment with nitric acid solutions of pH 2 or less. However, in applying this system to the extraction of potassium from seawater bittern, optimum selectivity would not be obtained unless:

1. magnesium (and probably calcium) were first removed,
2. the bittern salt concentrations were lowered by dilution (at least threefold).

These requirements could not be met in commercial operation, and further work with this system is not warranted.

It seems likely that magnesium is extracted as a co-ordination complex with EHPA alone. (Baes, 1962). Thus the undesirable extraction of magnesium from bittern might be greatly reduced if EHPA were replaced by some other organic electrolyte which does not have this complexing ability.

The need for dilution of the bittern might be avoided by using higher phenol concentrations and higher organic:aqueous volume rations. However, solvent extraction processes of this type are economically unattractive with the current market values of potassium salts. This is because the steps inherent in such processes are:

1. stripping of the loaded organic phase - this requires acid at least equivalent to the alkali metals extracted.
2. regeneration of extractant by treatment of the stripped organic phase - this requires alkali approximately equivalent to the acid consumed in the stripping stage.

The cost of alkali and acid required would make potassium recovery unprofitable even without the inevitable losses of organic reagents. Thus unless the value of potassium salts rises markedly, further investigation of solvent extraction systems of this type is not justified.

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TABLES 1 to 4

FIGURES 1 and 2

TABLE 1: EXTRACTION OF ALKALI METAL IONS FROM SYNTHETIC BRINES - EFFECT OF pH

Test Conditions:		
	Organic phase	1M Santophen-1 0.25M EHPA in trichlorethylene solvent
	Aqueous phase	0.0075M KCl 0.065 M NaCl with variable alkali concentration
	Phase ratio	Organic: Aqueous = 1:1 by volume
	Contact time	10 minutes

Test No.	Normality of base	Final pH	Extraction Coefficient E_a^o		Extracted %		Separation Factor, E_{Na}^K
			K	Na	K	Na	
2	0.007[a]	3.9	0.35	0.045	26	4	7.8
4	0.014[a]	4.5	0.82	0.088	45	8	9.4
5	0.028[a]	5.3	2.3	0.25	70	20	9.2
6	0.057[a]	5.5	5.0	0.65	83	39	7.8
6A	0.08[a]	5.5	5.2	0.93	84	48	5.6
7	0.014[b]	4.1	0.72	0.082	42	8	8.8

a. base = NaOH

b. base = Na_2CO_3

TABLE 2: EXTRACTION OF ALKALI METAL IONS FROM SYNTHETIC BRINES EFFECT OF Na AND K CONCENTRATIONS

Test Conditions:

Organic phase	1M Santophen-1 0.25M EHPA in trichlorethylene solvent
Aqueous phase	Variable NaCl and KCl 0.007N NaOH
Phase ratio	Organic: Aqueous = 1: 1 by volume
Contact time	10 minutes

Test No.	Initial Molarity Aqueous Phase		Final pH	Extraction Coefficient E_a^o		Separation Factor E_{Na}^K
	KCl	NaCl		K	Na	
2	0.005	0.05	3.9	0.35	0.045	7.9
9	0.12	0.80	2.6	0.026	0.0077	3.4
10	0.28	2.0	2.8	0.030	0.0072	4.2
11	0.03	2.0	3.4	0.071	0.0098	7.2

TABLE 3: EXTRACTION OF METAL IONS IN DILUTED BITTERN - EFFECT OF MAGNESIUM

Test Conditions:
Organic phase 1M Santophen-1
0.25M EHPA in trichlorethylene solvent
Aqueous phase Bittern B1 - tenfold dilution
0.0033 g equivalents/litre K
0.035 g equivalents/litre Na
0.034 g equivalents/litre Mg
Phase ratio Organic: Aqueous = 1: 1
Contact time 15 minutes

Test No.	Normality of NaOH	Final pH	Extraction Coefficient E_a^o			Separation Factors	
			K	Na	Mg	E_{Na}^{K}	E_{Mg}^{K}
3	-	3.0	0.058	0.0072	0.050	8.1	1.1
3A	0.007	3.1	0.12	0.019	0.23	6.3	0.5

TABLE 4: ACID STRIPPING OF ALKALI METAL IONS FROM ORGANIC EXTRACT - EFFECT OF pH

Test Conditions:

Organic phase	1M Santophen-1 0.25M EHPA in trichlorethylene solvent, loaded by contact with alkaline synthetic brine.[a]
Aqueous phase	Acid strip solution with variable pH
Phase ratio	Organic: Aqueous = 1:1 by volume
Contact time	10 minutes

Test No.	Acid	Initial pH	No. of Washes	Milli-Equivalents	
				Na Stripped	K Stripped
12-1	HNO_3	3	5	0.22	0.064
12-2	HNO_3	3	10	0.22	0.13
13	HNO_3	2	2	0.19	0.14
14	HNO_3	1	1	0.17	0.14
15	H_2SO_4	1	1	0.17	0.14

a. In each case, the loading of the organic extract was accomplished under conditions as for Test No. 2 (See Table 1).

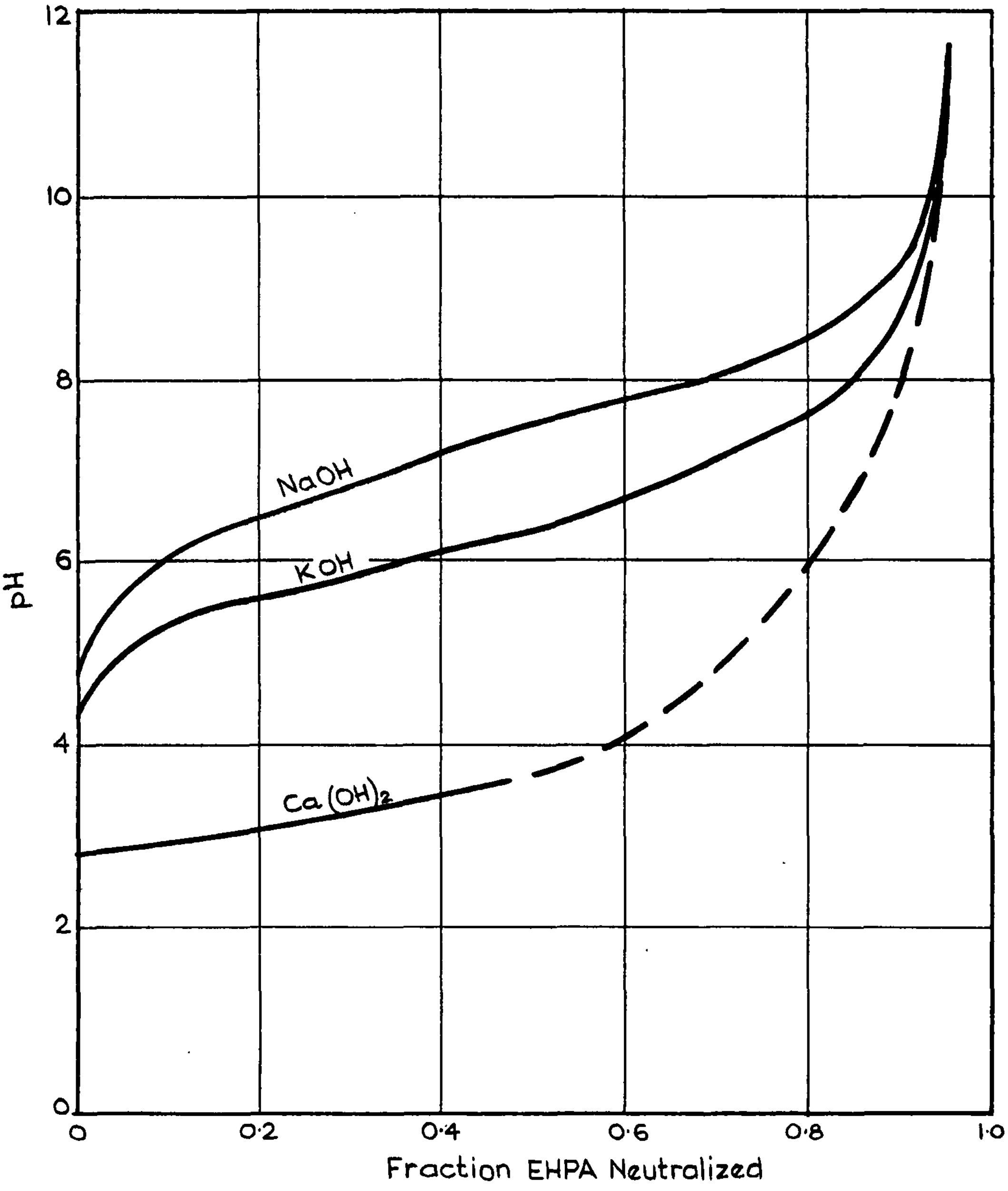

FIG. 1: pH TITRATIONS - SOLUTION E VERSUS ALKALIS

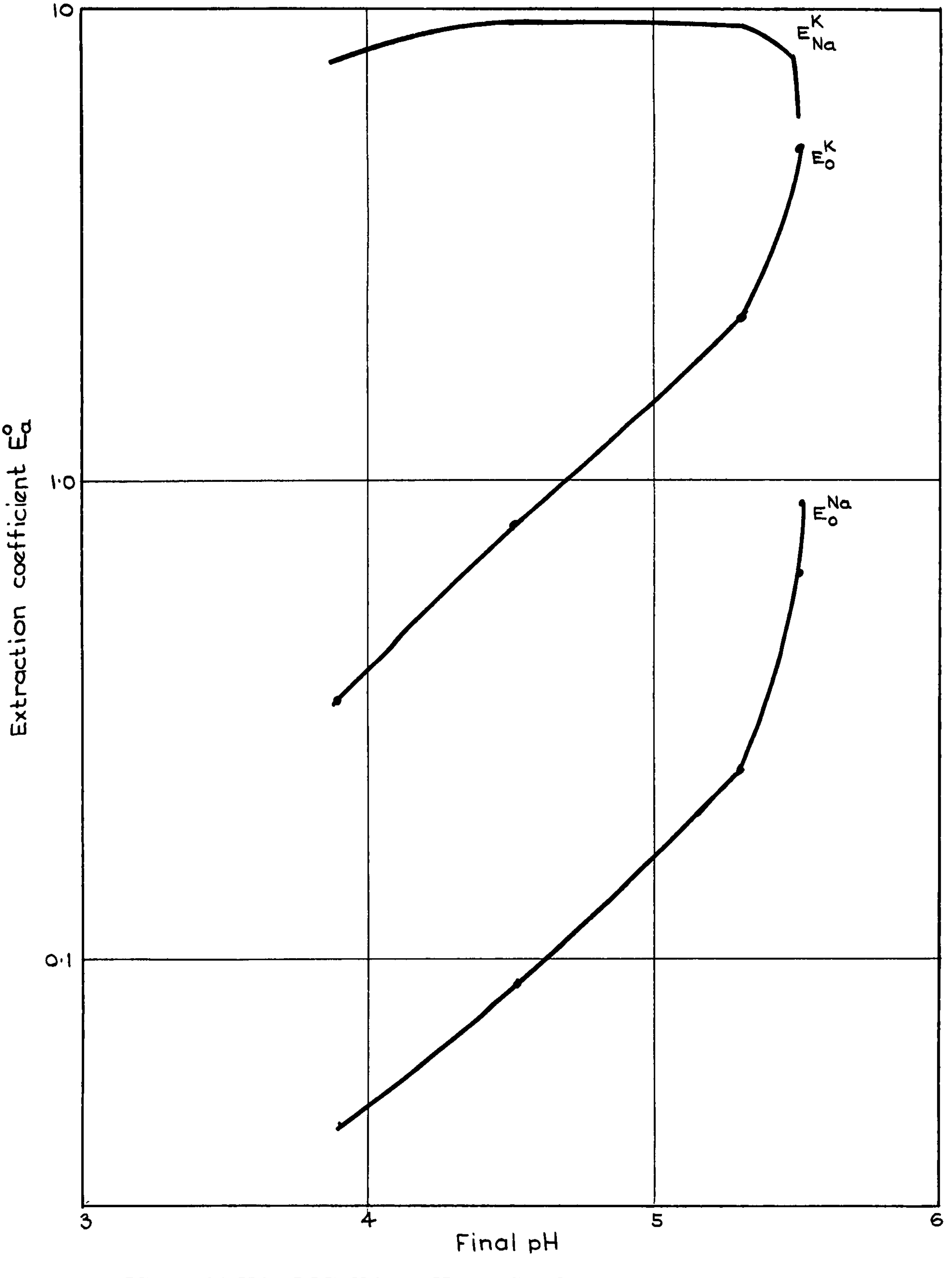

FIG. 2: ALKALI METAL EXTRACTION WITH SOLUTION E