

Disposal of Desalination Brine Effluents by Conversion to By-Products

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ABSTRACT

A process is described by which brines from the desalination of brackish water supplies can be converted to either useful products or waste materials which can be readily disposed of without environmental harm. The method involves (1) precipitation of the sulfate with calcium chloride, (2) exchange of chloride for bicarbonate by means of an amine liquid-liquid extraction system, and (3) recycling of the bicarbonate solution to the pretreatment (softening) step. The extraction system is regenerated with lime and carbon dioxide, producing calcium chloride as a product, some of which is used in step (1). In cases where the sodium bicarbonate production is greater than required in pretreatment, a second liquid-liquid extraction system, based on a carboxylic acid cation exchanger, is used to produce sodium carbonate for sale. Preliminary economic estimates indicate that such a process would become competitive with conventional disposal methods (solar ponds or wells) at a production level slightly above 5 mgd of water, and would be most attractive in cases where a high sodium carbonate requirement exists for pretreatment.

INTRODUCTION

Nature of the problem

The production of fresh water from saline sources involves the simultaneous production of a variable volume (depending on process) of concentrated brine. The extent of concentration of the brine is determined mainly by the concentration at which solids begin to precipitate from the solution. In seawater, the limiting concentration of brine is about two or threefold due to the precipitation of calcium sulfate and carbonates. As a consequence, considerable volumes of brine must be disposed of. At ocean sites this is not a major problem, although very large plants may give rise to some disturbances in the local ecology.

The problem of brine disposal at inland locations is considerably more complex. Brackish water supplies are generally considered to include water containing over about 1000–2000 ppm of total dissolved solids, and brackish water supplies now being utilized in desalination processes are largely in the 1000–5000 ppm range, (Loebel, 1963; MacRae, 1963). While the feed streams at inland sites generally contain much lower concentrations of dissolved solids, higher concentration factors are not necessarily obtainable without some form of pretreatment. This is because brackish waters are often at or near the saturation point with respect to the alkaline earth compounds which cause the scaling problems. The volume of waste brine may, therefore, be appreciable, and the absence of a nearby ocean requires the consideration of alternate methods of disposal.

This problem is compounded by the possibility that many of the future desalination installations in the United States will be inland sites, suggesting that inland brine disposal could become a headache of significant proportions.

Existing methods of inland brine disposal

At the present time there are four disposal methods, by which inland desalination brines can be handled. They are as follows:

1. Transportation to the ocean via pipeline or vehicle. This has been considered in connection with sewage disposal, and appears to be a possibility within a few hundred miles of the ocean (Federal Water Pollution Control Administration, 1967). From greater distances, removal of most of the water may be required.

2. Disposal in a river or other body. This method will probably be suitable only when the disposal volume is relatively small compared to the size of the river. This appears to represent an unlikely situation, since presum-

ably desalination plants will be attractive water sources only in areas without rivers or other large fresh water sources.

3. Deep well disposal. This appears to be the major disposal route for most inland sources, but is, of course, strongly dependent upon the existence of favorable local geological conditions. In many of the United States the geology is unfavorable, necessitating either very expensive wells, or high disposal costs for some alternate procedure, (Federal Water Pollution Control Administration, 1967).

4. Solar evaporation. If one considers only the reduction in volume obtainable by elimination of water, solar evaporation will in some areas be a very effective means to this end. Unfortunately, even in locations where solar evaporation is possible, annual weather cycles usually dictate the need for large water-tight storage ponds of many weeks' capacity to permit *continuous* daily acceptance of wastes.

Solar evaporation, however, is hardly a means for ultimate disposal, since the resulting solids must be stored or disposed of by one of the preceding methods. It could be readily combined with a process wherein evaporation is used only to concentrate the brine to the point of first solid precipitation, the brine then being fed to a conversion process.

ACKNOWLEDGMENT

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PROCESS OUTLINE

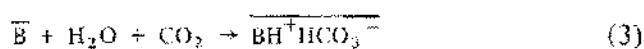
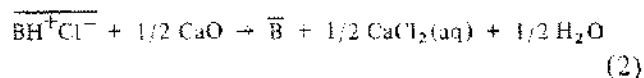
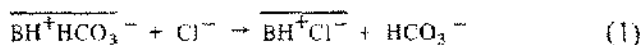
The process concept developed during this study involves a partial deionization of brine, sufficient to allow the recycle of the residual aqueous stream to the feed step. During the processing, the various components of the brine are largely converted to solid products or wastes as follows:

calcium, magnesium:	to calcium carbonate and magnesium oxide (waste)
sodium, bicarbonate:	to sodium carbonate (product)
sulfate:	to calcium sulfate (waste)
chloride:	to calcium chloride (product)

In cases where the sodium carbonate produced is equal or less than that required in the pretreatment (softening) step, the process consists of three major operations:

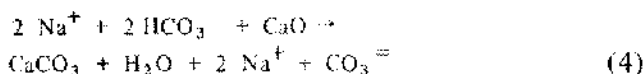
1. Precipitation of calcium sulfate with calcium chloride;
2. Exchange of chloride in the brine for bicarbonate ions by liquid-liquid extraction with an anion exchanging extractant.

The extractant is stripped with lime to produce calcium chloride, and regenerated with carbon dioxide. The reactions are as follows:



where B represents the base form of the extractant, and barred species denote those in the organic phase.

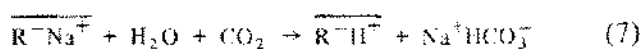
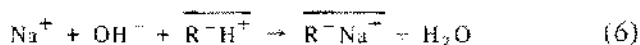
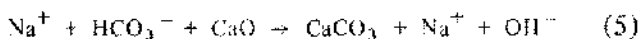
3. The bicarbonate solution is recycled to the pretreatment step, accompanied by an equivalent quantity of lime, which produces sodium carbonate in that step:



In cases where the excess sodium carbonate is produced, two additional steps are added after step 2 above:

2A. The bicarbonate brine is converted to a hydroxide solution with lime,

3A. The hydroxide solution is deionized by reaction with an acidic extractant, which is subsequently stripped with carbon dioxide to produce solid sodium bicarbonate. The reactions are:



The concept is built around two solvent extraction steps, the first of which exchanges the anions in the water (mainly chloride and sulfate) for bicarbonate ions. The second step converts the bicarbonate to carbon dioxide, picking up the cations (sodium and potassium) at the same time. The first extractant should be a weak base, presum-

ably an amine, and would be stripped with alkali. The second extraction system should be a weak acid, and would be stripped with carbon dioxide.

The concept envisions prior softening of the feed water, so that the desalination brine will contain only minimal concentrations of calcium and magnesium. If this is not done prior to desalination, such a step would probably be required here anyway in order to provide a simple means of eliminating these ions. Since one of the products of this system is sodium carbonate, a lime soda softening step has been assumed to be part of the desalination system.

This project has been of an exploratory or early stage nature, and the experimental work has necessarily centered around the development of extractants suitable for use in the two extraction systems. The final proposed process, as it is discussed in this paper, represents therefore not a fully developed process, but rather one in which only the basic steps have been established. Further work will be needed to develop the data needed to define precisely the operating conditions.

EXPERIMENTAL METHODS

Materials

The primary amine Primene JM-T is a mixture of *t*-alkyl amines of average molecular weight equivalent to a total of about 21 carbon atoms, and was obtained from the Rohm & Haas Co. The compounds *N,N'*-bis-(2-ethylhexyl)-2-ethylhexanamidine and *N,N,N'*-tris-(2-ethylhexyl) guanidine were synthesized in this laboratory by methods described elsewhere. (Grinstead, Lingafelter, 1972.)

Chevron EEE is a naphthenic acid obtained from the Chevron Chemical Co., and has an equivalent weight of 226. The Sunaptic naphthenic acids are similar materials obtained from the Sun Oil Co. The "B" acid has an equivalent weight of 369, while the "C" acid has an equivalent weight of 460. Neotridecanoic acid is a branched chain carboxylic acid once obtained from Enjay Chem. Co., but which is no longer manufactured.

Chevron 3 is a high boiling aromatic hydrocarbon petroleum cut, obtained from the Chevron Chem. Co. The tridecanol used here is a commercial branched chain alcohol, obtainable from Union Carbide Corp. or Enjay Chem. Co. Priminox R-1M is an *N*-alkyl ethanolamine, where the alkyl is a tertiary alkyl group containing about 13 carbon atoms. Triton X-35 is mainly the *p*-octylphenyl ether of triethylene glycol, plus related materials. Both of the latter compounds are obtained from the Rohm & Haas Co.

EXPERIMENTAL RESULTS

Anion exchange systems — pH behavior

The major requirements placed on the compound utilized in this system are four:

1. It should be a sufficiently strong base to exist as the salt form in contact with natural waters (pH 7–8);
2. It should be capable of being stripped (i.e., converted to the free base) readily with calcium hydroxide.
3. It should exhibit preference for chloride and sulfate ions over bicarbonate, so that the efficiency of exchange is high;
4. It should prefer chloride to sulfate, in order to provide a simple means of separating these species.

Earlier work on amine systems in this laboratory has shown that of the simple aliphatic amines, only primary amines appear to fulfill requirement (1). In toluene/1M sodium chloride, primary amines exhibit apparent pK_a values in the range 7–8, (Davis and Grinstead, 1968), so that these materials are borderline in utility, but their pK_a values are strongly dependent upon the concentration of the brine being extracted.

Another potentially useful class of compounds, in terms of basicity, is the amidines, which we have studied in another project, and which have been determined to be at least one or two pK units stronger as bases, than aliphatic amines, (Grinstead and Jones, 1971). Ionic selectivities for these materials were found to be high for chloride over bicarbonate and sulfate. They were also readily regenerable with dilute bases, including ammonia.

For these reasons, a substantial effort was devoted to preparing and testing several members of the amidine family, as well as some members of the guanidines, a similar class known to be even more strongly basic than amidines.

Titration data showing the behavior of typical representatives of the various classes of compounds are shown in Figure 1. As anticipated, the guanidine compound lies highest in the pH field, indicative of its greater basicity. The amidine is intermediate in base strength, while the primary amine lies at the lowest pH. In each case the chloride curve is uppermost, indicating preference for chloride. Another way of saying this is that at a given pH, a greater fraction of the extractant is in the chloride form than the sulfate form. It follows that the degree of separation of the chloride and sulfate curves for a given compound is a measure of the degree of selectivity, and is seen to be least for the primary amine and most for the amidine. The formation of a third liquid phase in the case of some of the points of the amidine/sulfate systems leaves in some doubt the exact interpretation of this data, but the single point at 10% salt form provides this information.

Although both the amidines and guanidines exhibited much more desirable pH behavior and ionic selectivity than the aliphatic amines, considerable difficulty was experienced in maintaining the inorganic salts of the former two types of compounds in solution in the organic phase. For this reason these compounds were finally abandoned and the process was developed around the aliphatic amine Primene JM-T.

- 0.25 M $(\text{Eh})_3\text{G}$ in 30% Octanol 70% Chevron 3
 □ 0.25 M Eh_2EhA in Chevron 3 (crosshatched points contained three phases)
 ▲ 0.25 M Primene JMT in Chevron 3
 — in contact with 0.2 M NaCl Brine
 in contact with 0.1 M Na_2SO_4 Brine

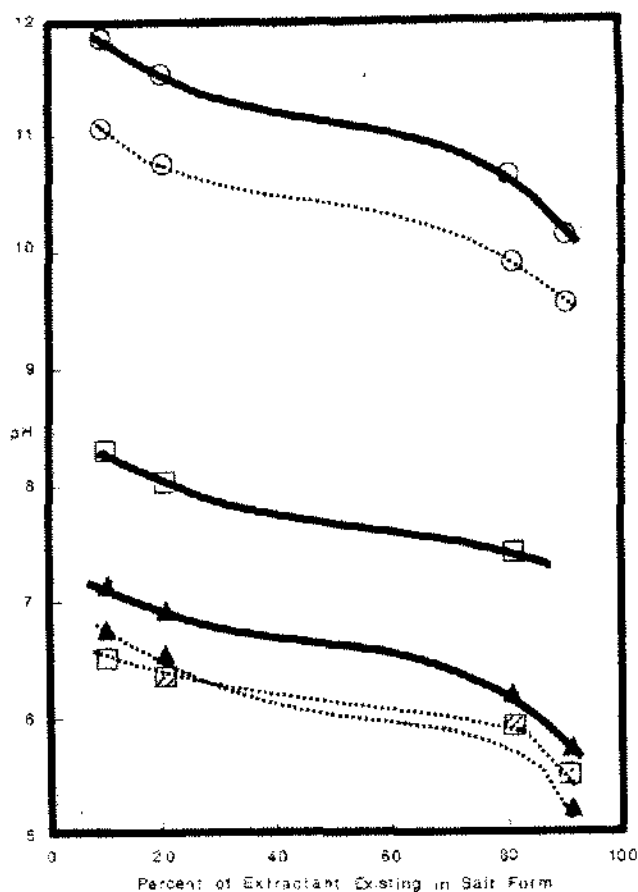
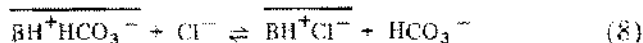


Figure 1. Titration Curves for Weak Base Extractants.

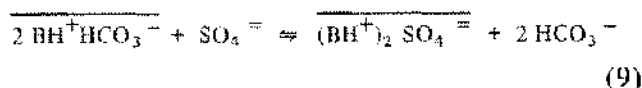
In Figure 2 titration curves are shown for JM-T in Chevron 3, a high-boiling aromatic hydrocarbon diluent, at both 1M and 0.25M extractant concentrations. Little preference for either inorganic ion is exhibited at either concentration, but there is a pronounced effect of extractant concentration on the location of the titration curve. At the 1M level the extractant can be seen to exist in the salt form to the extent of about 50% at pH 7.5, which should be adequate for its use as the anionic extractant.

Anion exchange system—exchange data

The major reaction of interest in the anion exchange system is the exchange of bicarbonate ions in the extractant for chloride and sulfate ions in the brine;



and



The equilibria which apply in this system accordingly involve all three ions in both phases. In order to simplify the study of these equilibria, we chose to study the simpler two-ion systems, principally the chloride-bicarbonate system, since this one represents most of the exchange which actually occurs. Experiments were also done on the sulfate-chloride and sulfate-bicarbonate systems.

The experiments were run at 1.0 N and 0.3 N aqueous ionic strength and the systems containing bicarbonate were saturated with 1 atmosphere of carbon dioxide. Under these conditions, the organic phase, which was 1M Primene JM-T in 25% tridecyl alcohol in Chevron 3, was approximately 50% in the salt form. Thus, the active capacity of the extractant was about 0.5 M.

Chloride-bicarbonate system. The data for the chloride-bicarbonate system are plotted in Figure 3. The coordinates used are the equivalent percent (based on normality) of the ions in each phase that are chloride ions. The graph shows that when plotted in this fashion, the equilibrium constant for the exchange is relatively near unity, as well as being independent of the total ionic strength. That is, the extractant exhibits little preference for either ion.

Chloride-sulfate exchange. The equilibrium data for

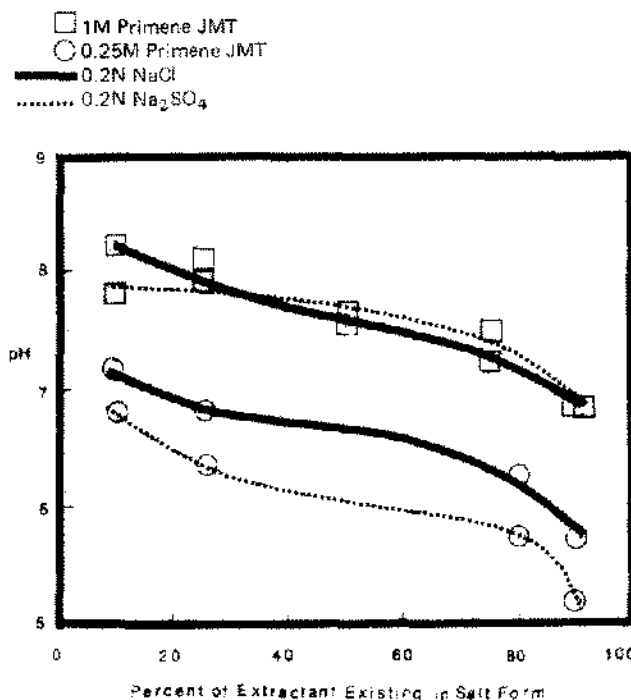


Figure 2. Titration Curve For Weak Base Extractant Primene JMT in Chevron 3

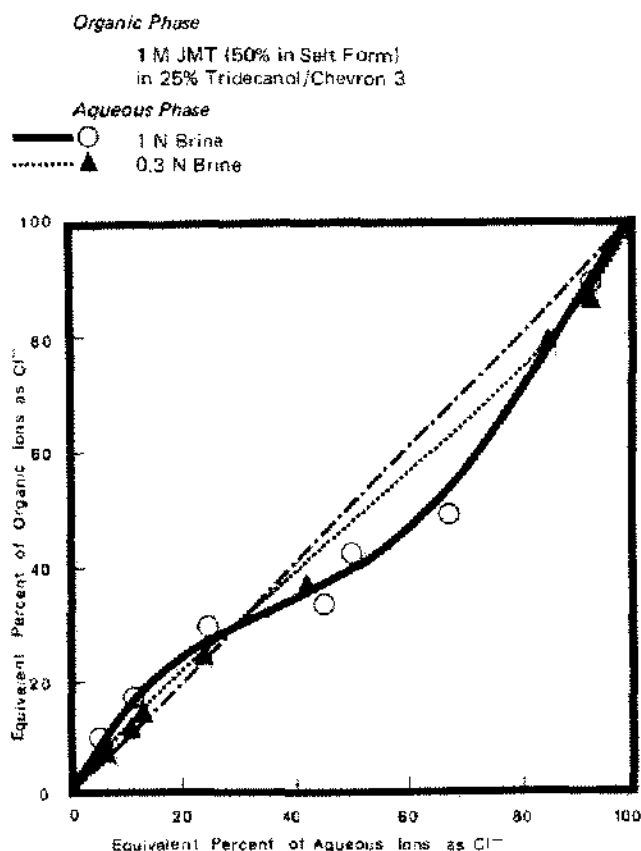


Figure 3. Chloride-Bicarbonate Equilibrium For Primene JMT and Brine Systems.

this reaction are plotted in Figure 4. The coordinates used are the percent of ions in each phase that are chloride ions. The curves indicate a preference for chloride over sulfate. However, as with the sulfate-bicarbonate exchange this preference is strongly influenced by the total ionic strength in the aqueous phase.

As will be seen later in the section on process design, the sulfate-chloride equilibria become most important in the region of high chloride to sulfate ratios. Accordingly, some additional data were obtained for this equilibrium and are shown in Figure 5. The first point in the high chloride/sulfate region is shown for the 0.3 N and 1.0 N brines of Figure 4, and in addition, points are shown for ionic concentrations varying from 0.2 N (about 12,000 ppm sodium chloride) to 0.7 N (about 100,000 ppm sodium chloride). As the data in Figure 4 suggested, the dependence of the exchange on ionic strength is confirmed. Interestingly, the data at 0.2 N show that sulfate is actually preferred to chloride in this region. From the standpoint of process usefulness, we can conclude that in systems where extraction of sulfate is desired, it will be necessary to work at relatively low brine concentrations, while if complete rejection of sulfate is desired, high brine concentrations are to be preferred.

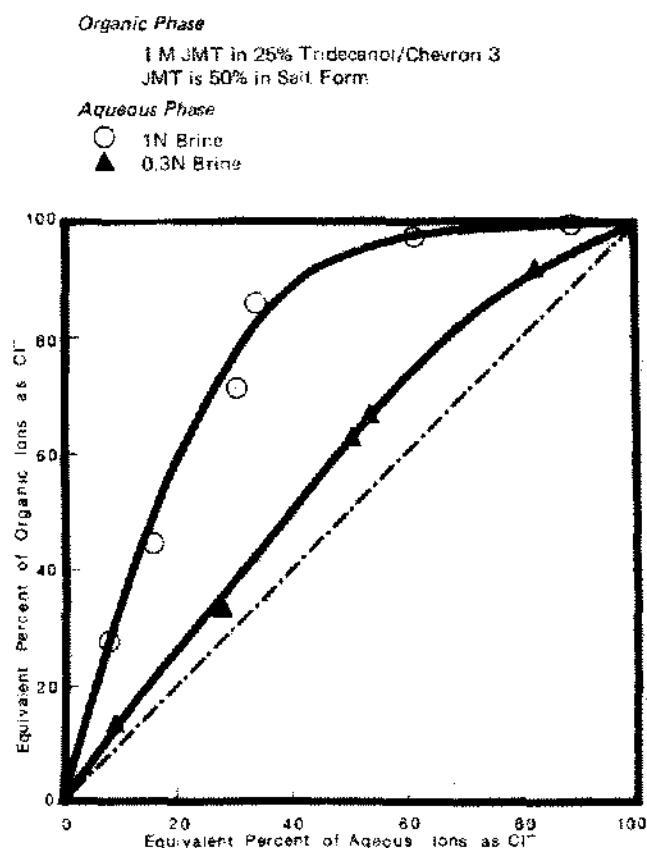


Figure 4. Chloride-Sulfate Equilibrium For Primene JMT and Brine Systems.

Anion exchange system: solubility losses in the aqueous phase

The distribution of the extractant Primene JM-T into various aqueous systems during contact with the organic phase was determined by a colorimetric method based on the fact that the highly colored picrate ion will extract into chloroform in the presence of a high molecular weight amine cation. Determination of JM-T was made on a number of aqueous phases of ionic concentrations in the range 0.3 to 1.2 normal, which had been equilibrated with 1M JM-T with 25% tridecanol in Chevron 3. The amine losses so determined were in the range of 20–40 mg/liter (20–40 ppm).

In addition the soluble distribution loss of the free JM-T base was determined by contact with the same aqueous phases, after adding sufficient sodium hydroxide to convert all of the organic salt to the free base. No detectable amine was found in the aqueous phase. The amine level was therefore less than 3 mg/liter, which is the detection limit of the analytical method used.

Cation exchange systems

The extraction system in this case must meet two requirements:

1. It must be sufficiently strong acid that dilute (1 M) sodium hydroxide will convert it to the sodium salt;
2. It must be a sufficiently weak acid that carbon dioxide in the presence of saturated sodium bicarbonate will convert it from the sodium salt back to the free acid. The pH of such an aqueous system is about 7.8, and thus at this pH the acid extractant must be mainly in the free acid form.

These requirements are filled rather well by most high molecular weight carboxylic acids. Titration curves of several of these are shown in Figure 6. For comparison, some titration curves are also shown for a somewhat stronger acid, bis-(2-ethylhexyl) phosphoric acid. As a reference point a calculated titration curve for carbon dioxide ($pK_a = 6.4$) is also shown in the figure.

The carboxylic acids all behave as considerably weaker acids than carbonic acid, with a considerable variation among them. The effect of the additive, Triton X-35, on Naphthenic EEE is to raise the titration curve at the high pH end. More information on the effect of additives is shown in Figure 7, based on Sunaptic B as the acid component. It can be seen that, compared to the case with no additive present, the Triton X-35 lowers the curve while the other additives raise it. The reasons for this are probably numerous, but since the measured pH is determined

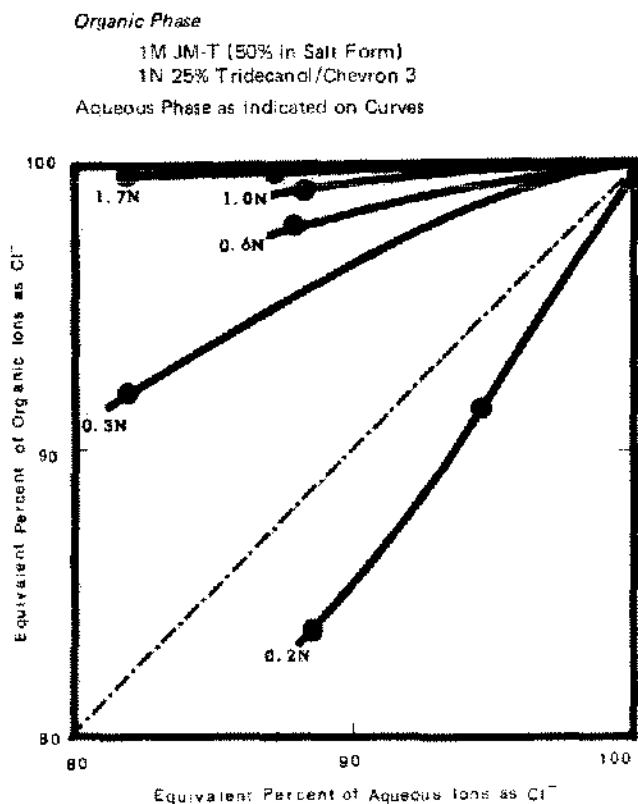


Figure 5. Chloride-Sulfate Equilibrium For Primene JM-T and Brine Systems.

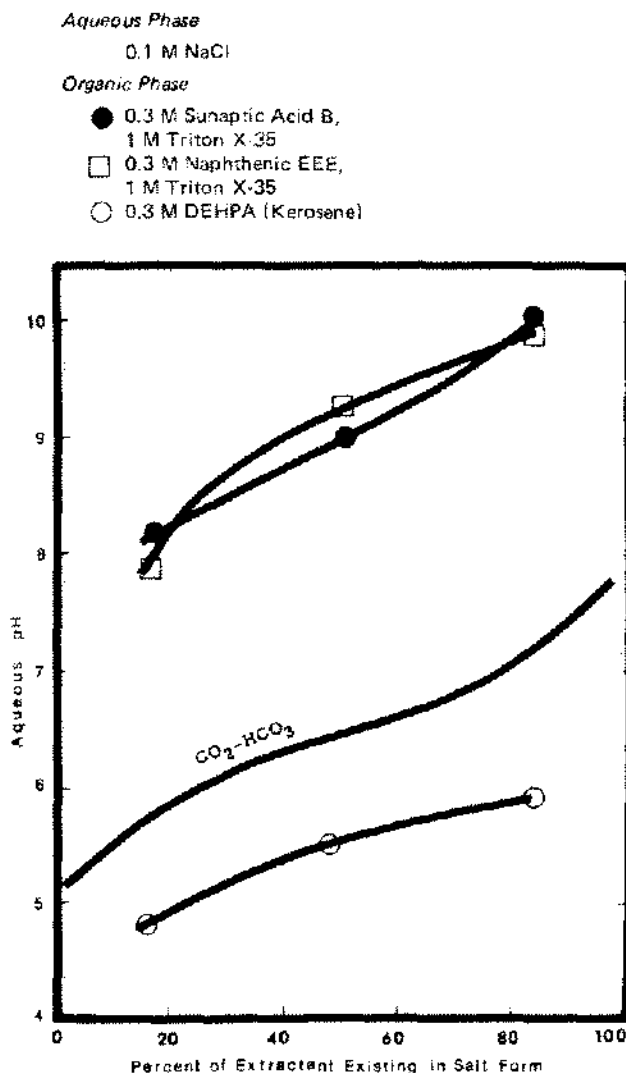


Figure 6. Titration Curve for Weak Acid Extractants in Chevron 3 Diluent.

by the species actually in the aqueous phase, the shifting of curves is probably mainly due to the relative effect of the additive on the distribution of the salt and acid forms of the extractant. That is, an additive which helps to solvate the salt form of the extractant in the organic phase to a greater extent than the acid form will reduce the aqueous concentration of the salt form to a greater extent. The acid/salt ratio in the aqueous phase will now be increased as a result, and a lower pH will be observed. Thus, it appears that the Triton X-35 stabilizes the acid form.

Solubility losses of extractant to aqueous phase

The final aqueous phase leaving the cation extractant system will be very low in ionic strength, and will contain some cationic extractant dissolved in it. In order to obtain an estimate of this loss we contacted a solution of 0.65 M Sunaptic B (middle cut) in a diluent consisting of 25%

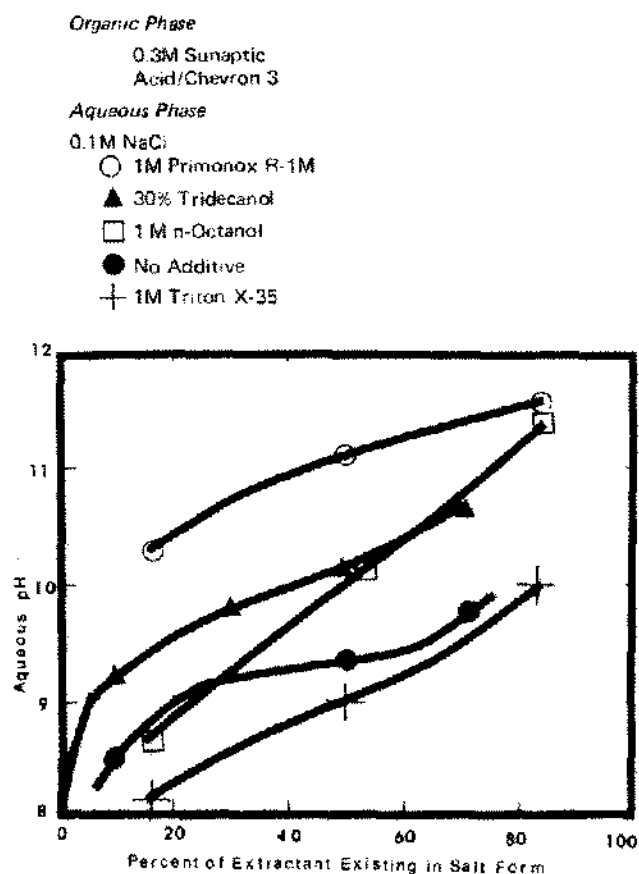


Figure 7. Titration Curves for Weak Acid Extractant.

Priminox R-1M and 75% Chevron 3 with 0.010 M sodium chloride (585 ppm) containing sufficient sodium hydroxide to convert the acid to the extent of 50% to the sodium salt form. After separation of the aqueous phase, it was found to contain 0.015 M naphthenic acid. Contact of the aqueous phase with a fresh sample of the organic phase entirely in the free carboxylic acid form resulted in an aqueous concentration of 0.014 M, nearly the same. Following this contact, the aqueous phase was acidified with a stoichiometric quantity of hydrochloric acid, and again contacted with fresh organic phase in the free carboxylic acid form. The residual naphthenic acid concentration in the aqueous phase was found to be only 0.0003 M.

The initial concentration 0.015 M represents the sodium salt of the naphthenic acid, and represents the loss in a contractor in which the conversion of the free naphthenic acid to the salt form occurs to the extent of about 50%. The final concentration of 0.0003 M represents essentially the soluble loss due to the free acid only, and indicates the limit obtainable provided a second contact is made on the effluent water after addition of sufficient hydrochloric acid to neutralize any naphthenic salt in the aqueous phase.

Regeneration of the organic extractant system. One ex-

periment was performed to check the ability of carbon dioxide to regenerate the extractant system. A 0.65 M Sunaptic B system at the 50% conversion point, was equilibrated with 0.3 M aqueous sodium bicarbonate in the presence of one atmosphere of carbon dioxide. The resulting organic phase was found to be regenerated to 90% of its free acid form, while the aqueous phase was increased to about 0.9 M sodium bicarbonate, quite close to the solubility limit of this salt. Thus, the equilibrium clearly allows a roughly saturated sodium bicarbonate solution to coexist with an extractant system in the acid form. If a reactor is then fed with the sodium form of the extractant, and an atmosphere of carbon dioxide is maintained, and if a saturated solution of sodium bicarbonate is also present, then solid sodium bicarbonate will precipitate continuously, and can be recovered by continuously circulating the aqueous slurry through a filter system. The organic phase can also be continuously drawn off at a level of something like 90% regeneration.

PROCESS DESIGN

Brine systems

Five brines were chosen to demonstrate the application of this process concept. These brines were chosen because they represented a variety of compositions, and because they have been the subject of a detailed study in a previous OSW project, (Legros, et al., 1970). In that study, the costs of water supply, pretreatment, reverse osmosis desalination and brine disposal by deep well injection or solar evaporation were developed, and subjected to a systems analysis to determine the optimum degree of water recovery in the desalination step. Generally, the analysis indicated that this optimum point was at relatively high recovery because of the high cost of disposal. The analyses were not carried beyond the 98% recovery level, although in most cases the overall processing costs were still dropping as recovery increased.

The brines chosen are those expected from desalination of brackish waters from Midland, Texas; Clinton, Oklahoma; Gallup, New Mexico; Minot, North Dakota; and Arkansas City, Kansas. The compositions of the water supplies are listed in Table I.

The earlier study (Legros, et al., 1970) included a lime soda softening step to remove calcium and magnesium, followed by sulfuric acid addition to destroy bicarbonates and carbonates. We have assumed the same pretreatment conditions. Since no data were available for the compositions of the resulting brines, however, we have assumed that the reverse osmosis unit would be operated to produce product water of 500 ppm of total dissolved solids, and that all ionic species would be distributed in the same proportions between product and brine; that is, no preferential rejection would occur in the osmosis step. This is

TABLE I
Brackish Water Compositions
Concentrations in ppm

	Clinton	Gallup	Minot	Midland	Arkansas City
Ca ⁺⁺	260	12	33	76	131
Mg ⁺⁺	149	13	2	75	28
Na ⁺ & K ⁺	117	893	1478	149	275
SO ₄ ⁻	1209	509	400	222	216
Cl ⁻	53	770	1781	255	441
HCO ₃ ⁻	204	408	460	—	234
CO ₃ ⁻		45			

*as sodium

not strictly true, as it is known that divalent ions are rejected to a greater degree than monovalent, and the brine will therefore contain a greater proportion of these ions. However, we believe this is probably not a major problem and for the purposes of demonstrating the applicability of the process under study, the assumptions should be adequate.

A second factor which influences the brine compositions in this study is the fact that all water contained in the brines is recycled to the feed step, and eventually appears as product water. Thus the water recovery in all cases is essentially 100%. The designation of "recovery" in this study thus reflects only the actual split in brine versus product water in the desalination unit, rather than the ultimate recovery of feed water. The use of the term here is mainly to identify the corresponding case in the earlier systems study for comparison.

Since some dissolved salts are recycled with the final brine, some adjustments are required in the sulfate, chloride, and sodium concentrations in the feed to the softening step to reflect the steady state conditions which would exist. Since none of the calcium or magnesium is recycled in the dissolved condition, however, no adjustments were required in the pretreatment conditions.

Finally, we have neglected the minor constituents in the waters, since they have little effect on the mass balances which are the main consideration in this study.

Overall process description

Based on the considerations in the preceding section, the basic process flow diagram for this concept has been developed and is presented in Figure 8. This flow scheme shows the incorporation of pretreatment and the proposed disposal concept to a desalination process. This is the general process and in specific applications, one or more of the steps may not be necessary.

There are eleven major steps in the process:

1. Lime-soda softening pretreatment with H₂SO₄ and alum addition.

2. Desalination.
3. CaSO₄ precipitation.
4. Cl⁻ extraction by exchange with HCO₃⁻.
5. Stripping of Cl⁻ from extractant.
6. Conversion of HCO₃⁻ to OH⁻ by precipitation of CaCO₃.
7. Sodium extraction.
8. Sodium stripping with CO₂ to make Na₂CO₃.
9. Organic removal.
10. Calcination of CaCO₃ to make CaO and CO₂.
11. CO₂ purification.

The pretreatment and desalination steps are included to show their relation to the disposal process, which accepts the desalination brine from the desalination unit at the calcium sulfate precipitation step. This precipitation is accomplished by addition of calcium chloride to the brine, which effectively replaces most of the sulfate with chloride. The solubility of calcium sulfate was determined by assuming the final solutions to be a sodium chloride brine of the same total ionic strength (Marshall & Slusher, 1968). The chloride is then extracted by exchange with bicarbonate ions from the Primene JM-T.

Depending upon the ionic strength of the brine at this point, variable amounts of the residual sulfate will be extracted. The organic phase leaving the system will consist mainly of the chloride salt, plus some sulfate salt. We have assumed that the extraction would be carried out so as to replace about 90% of the bicarbonate in the organic phase with the chloride and sulfate salts.

The organic phase is stripped with a slurry of lime in calcium chloride, producing calcium chloride. Any coextracted sulfate or unused bicarbonate ions are also removed.

A portion of the calcium chloride brine containing the precipitated solids is returned to the calcium sulfate precipitation step, and all solids are removed at this point. The remaining calcium chloride brine becomes available as a by-product.

The JM-T is converted to the bicarbonate salt form by introducing carbon dioxide into the bottom of the extraction column. The CO₂, as well as the lime, required for stripping the extractant, is obtained from calcining the solids obtained in the lime soda pretreatment. The carbon dioxide is purified in a standard scrubber-stripper process.

The brine leaving the anion extraction step will be primarily a solution of sodium bicarbonate, but will contain some carbon dioxide in addition to minor amounts of sulfate and chloride. We have arbitrarily assumed a 90% extraction of chloride.

There will also be present a small amount of the extractant in the salt form, e.g., the Primene JM-T cation. In order to recover as much as possible of the dissolved extractant, the pH of this brine will be raised by the addition of a small amount of lime, precipitating the carbon

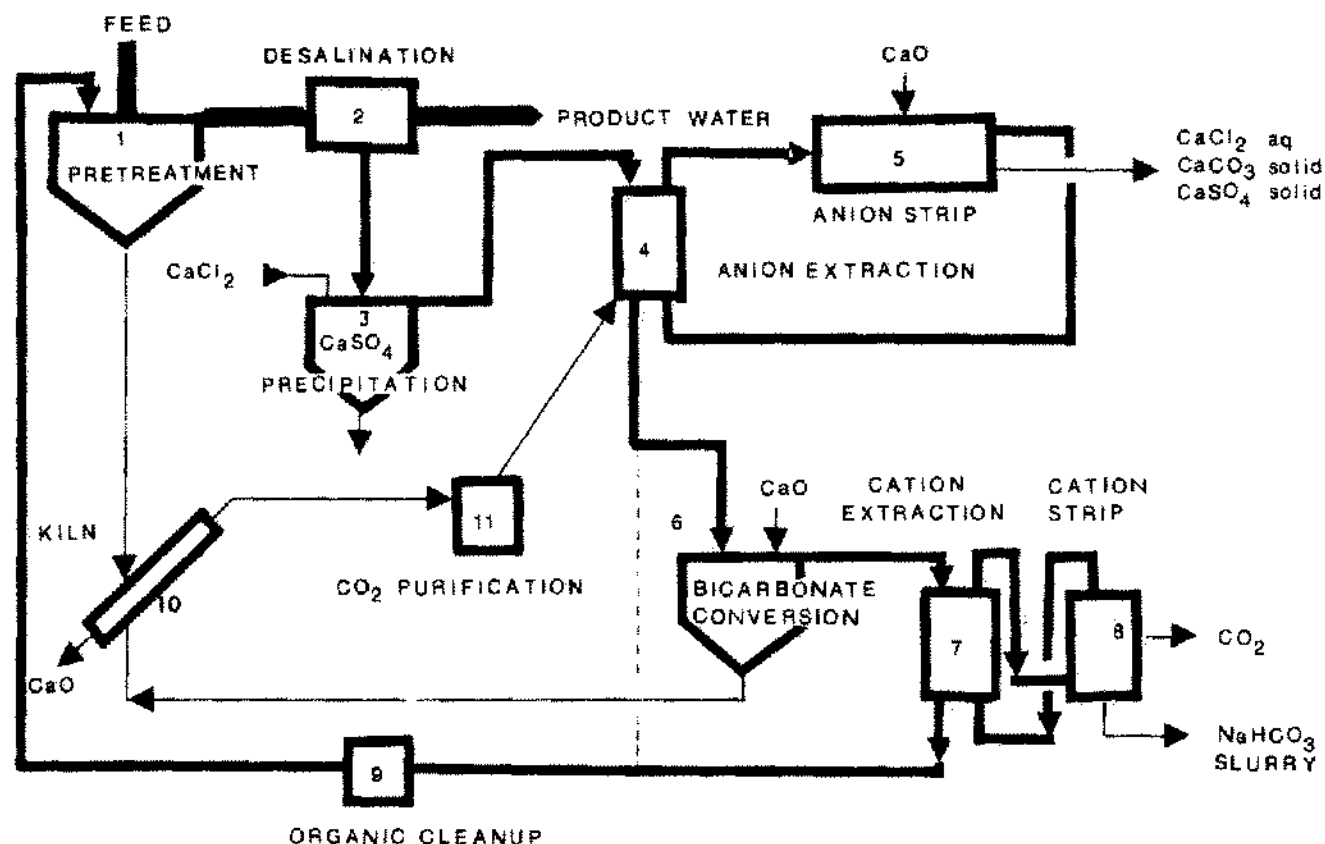


Figure 8. Schematic of Final Brine Treatment and Disposal Process.

dioxide as calcium carbonate. The pH of the resulting bicarbonate solution, which will be in the range of 8 to 8.5, is now high enough to convert the Primene JM-T cation to the free base in which form it is much less soluble in the aqueous solution and will phase out as an immiscible liquid phase. A coalescing state is then used to collect the extractant at this point for recycle. Solid calcium carbonate precipitated at this point will be retained with the aqueous stream and returned to the lime soda step with the bicarbonate solution.

Since the aqueous phase is mainly sodium bicarbonate, it is recycled to the lime soda softening step, where the addition of a mole of lime converts the bicarbonate to carbonate, and provides the carbonate needed in this step. In cases where more bicarbonate is available than is required here, a portion of the bicarbonate brine is treated by the carboxylic acid extractant system to produce solid sodium bicarbonate and, ultimately, sodium carbonate.

In order to treat the bicarbonate/sulfate brine by the second (cation) extractant step lime is first added to convert bicarbonate to hydroxide. This sodium hydroxide solution is now fed to an extraction step with the cation extractant where the sodium hydroxide is eliminated, forming the sodium salt of the carboxylic extractant. The extractant is then regenerated by contact with carbon di-

oxide at one atmosphere in a second contactor. Here the carbon dioxide and the sodium salt of the extractant react to form sodium bicarbonate and the free acid extractant, the latter being returned to the brine contact stage. Since the aqueous phase was a saturated sodium bicarbonate solution the additional bicarbonate formed precipitates as a solid, is filtered and the filtrate recycled to the extractant contactor. The wet sodium bicarbonate is calcined to sodium carbonate, the carbon dioxide and water being recycled to the bicarbonate precipitation step.

In order to eliminate all extractant from the aqueous phase for recycle to the lime soda step, we have specified an active charcoal treatment step for the recycled solution. The charcoal would be removed and disposed of in the lime kiln.

Recovery of extractants and cleanup of final aqueous phase

In cases where only the anion exchange system is used, the coalescing stage is included after the extraction train to recover the JM-T which is phased out of the aqueous solution by the addition of lime. The stage can perform an additional function of entrainment elimination, which is accomplished by conducting the mixing with the organic phase in excess. Under these conditions, the aqueous

phase is dispersed in the organic phase, with the result that entrainment is mainly of aqueous in organic, rather than vice versa. We have assumed that the organic remaining in the aqueous phase emerging from this stage will be essentially the amount of the hydrocarbon diluent which actually dissolves in the aqueous phase, plus about 10 ppm of entrainment. This is a somewhat optimistic assumption, but as the cost figures will show, this is a negligible factor, and even a several fold increase in entrainment would not present a significant cost.

Discharge of the final aqueous phase to the environment, or recycle back to the feed water section will probably require treatment to remove dissolved and entrained organic materials from the extraction systems. The most common method for accomplishing this task, and one which is standard in water treating practice, is the use of activated carbon. The valuable characteristic of active carbon adsorption is its great versatility; i.e., its ability to pick up a wide variety of organic materials from aqueous solution. The two materials which will be present in the final aqueous phase from this process will be the hydrocarbon diluent and the carboxylic acid extractant. The solubility of the Chevron 3 diluent has been determined in earlier work in this lab to be in the range of 20 ppm (Grinstead and Jones, 1971) while the soluble loss of the former in the form of the undissociated acid was determined in this study to be about 3×10^{-4} M under typical operating conditions, or about 100 ppm. Added to this will be a certain amount of physically entrained organic phase, the amount depending upon the operation of the extraction system.

We expect that this entrainment would be in the range of 10 ppm, but could be as high as 50–100 ppm.

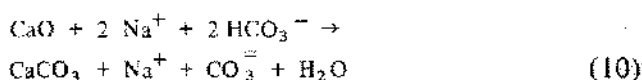
Considerable information exists in the literature on the use of activated carbon for organic adsorption, most of it pertaining to the type of material found in natural water systems. We believe that the highly hydrophobic nature of the organics to be encountered in this system makes these materials considerably easier to remove than naturally occurring types, which are often rather polar and hydrophilic materials. More useful data relating to this type of material has been published by the Federal Water Pollution Control Administration in a study of the adsorption of pesticides and other biochemically resistant materials (Morris and Weber, 1966). Data from the study indicate that absorption of such materials as alkyl phenols, DDT, phenoxy herbicides, etc. readily occurs to the extent of 30% or more by weight of the carbon, in equilibrium with concentration as low as 1 ppm in the aqueous phase. The use of powdered activated carbon has been accordingly proposed in the final cleanup of the treated water from the brine operations. This treatment would be expected to produce a quite clean effluent, which would probably be suitable for either recycle or discharge.

In the case of recycle of the sodium bicarbonate brine

to the feed water system, it has been assumed that the carbon would be retained with the aqueous solution, and be sent to the calciner with the lime sludge soda.

Direct recycle of sodium bicarbonate

Since sodium carbonate is required in the lime soda softening step for most brines, the simplest means of supplying this from the products of this process is simply to return the bicarbonate brine to the pretreatment step with the addition of an equivalent of lime. The reaction



shows that the result is the addition of one-half mole of sodium carbonate plus a mole of calcium carbonate, so that the main difference in the operation of the lime soda unit is the presence of an additional quantity of insoluble calcium carbonate. In those systems where appreciably more sodium carbonate is available than is required by the lime soda step, we have included the carboxylic acid extraction step and applied it to that fraction of the bicarbonate brine which is not required by the softening step.

Chemicals used and produced

The quantities of materials produced and consumed were calculated for each of the five desalination brines under study, and are shown in Table II. The Clinton case is perhaps the one in which the production and consumption of chemicals is most nearly in balance. A small amount of lime is required, but the rather large requirement for soda ash in the pretreatment step is entirely made up from that produced in the disposal process. As a result of the balance in the soda ash, the second solvent extraction system is not required.

The Gallup and Minot cases, in contrast, produce a considerable excess of soda ash, and utilize the second (cation) extraction system. Considerable calcium chloride is also produced and a substantial amount of lime is required. Both the Midland and Arkansas City cases produce small net amounts of soda ash, although they are, in general, nearly in balance with respect to the major chemicals.

PRELIMINARY ECONOMIC ESTIMATES

The cost of installing and operating the processes developed as cases 1 through 6 have been estimated according to conventional procedures, assuming a Southwest U.S. location, and for both 1 mgd and 5 mgd plant sizes. Costs for the solvent extraction steps were estimated as in an earlier study (Grinstead, Davis, and Snider, 1969). Capital estimates are summarized in Table III. Credits, where shown, are based on two items: 40% calcium chloride brine, valued at \$41/ton (100% basis), and sodium carbonate (soda ash), valued at \$31/ton.

TABLE II
Chemicals used and produced (lb./1000 gallons feed water)

Location Recovery per pass	Clinton 93%	Clinton 98%	Gallup 98%	Minot 90%	Midland 97%	Arkansas City 98%
CaO	Consumption	17.2	16.8	26.2	48.7	4.8
	Production	<u>14.4</u>	<u>13.4</u>	<u>18.5</u>	<u>32.1</u>	<u>4.3</u>
	Net Consumption	2.8	3.4	7.7	16.6	0.5
Na ₂ CO ₃	Consumption	5.5	10.6		2.3	3.7
	Production	<u>5.5</u>	<u>10.6</u>	<u>14.4</u>	<u>26.6</u>	<u>5.6</u>
	Net Consumption	--	--	(14.4)	(26.6)	(1.9)
CaCl ₂	Consumption	10.0	10.0	8.3	9.0	--
	Production	<u>10.2</u>	<u>11.2</u>	<u>15.9</u>	<u>29.7</u>	<u>1.39</u>
	Net Consumption	(.2)	(.3)	(7.6)	(20.7)	(3.4)
H ₂ SO ₄	Consumption	.332	.664	.771	3.076	.144
Alum	Consumption	.17	.17	.17	--	.17
KMnO ₄	Consumption	--	--	--	.114	--
	Waste Production	15.3	16.9	9.04	13.5	3.8

Numbers in parentheses indicate a negative consumption; i.e., a net production

TABLE III
Comparison of economics of brine disposal methods
in \$ per 1000 gallons product water

Location	Clinton, Okla.	Clinton, Okla.	Gallup, N.M.	Minot, N.D.	Midland, Texas	Arkansas City, Ark.
Water Recovery per Pass	98%	98%	98%	90%	97%	98%
1 MGD	Processing Cost	1.03	1.04	1.59	2.01	0.78
	Credit: Na ₂ CO ₃	--	--	0.22	0.40	--
	CaCl ₂	--	0.01	0.16	0.43	--
	Net Cost	1.03	1.03	1.21	1.18	0.78
	Conventional Process Cost	0.57	0.61	0.40	0.38	0.32
5 MGD	Cost	0.48	0.49	0.75	1.09	0.30
	Credits: Na ₂ CO ₃	--	--	0.22	0.40	--
	CaCl ₂	--	0.01	0.16	0.43	--
	Net Cost	0.48	0.48	0.37	0.26	0.30
	Conventional Process Cost	0.37	0.44	0.27	0.22	0.19

The cost included the cost of the pretreatment as well as the disposal of the brine. In four cases, a credit is claimed for the excess CaCl_2 and Na_2CO_3 produced in the process, over and above that required internally. The net cost of operation is then compared to the costs developed in the earlier systems study (Legros, et al., 1970) for pretreatment and disposal.

For the 1 MGD plants, this process is considerably more expensive than the conventional one. However, for the 5 MGD plants, the costs are quite comparable in one of the Clinton systems (98% recovery) and in the Minot case.

It will be noted that we have assumed a lime cost of \$20 per ton, instead of the \$15 used in the earlier study. However, the net lime costs in the proposed process are small except in the case of Minot (17¢/M gal) and the Gallup (8¢/M gal). The change leads to our estimates being about 4¢/M gal higher for Minot and 2¢/M gal higher for Gallup. Neither of these differences are very significant.

The more favorable comparison of the proposed process for larger throughputs is largely a result of the fact that it is a high capital, low raw material process. Only raw materials costs are shown which involve actual external inputs, so that, for example, no soda ash raw materials costs are incurred.

The usual advantages of increasing scale in reducing capital and labor charges are realized, as the table shows. The conventional process, on the other hand, includes considerable volume-independent raw materials costs in the pretreatment step. Although the same advantages of scale apply, because of these raw materials costs the total cost is not nearly so sensitive to scale as the proposed process. It can be anticipated that at production rates somewhat larger than 5 mgd, the proposed process would, in general, be more economical as a disposal method than the conventional process, provided, of course, that credits for the products could still be obtained. In Midland, Texas, and Clinton, Oklahoma, where significant credits are not involved, this restriction would not, of course, apply.

One interesting point which the data of Table III show is the effect of increasing the recovery of water from the brine. The estimated cost of the proposed process is the same for either 93% or 98% recovery per pass. At first glance, this seems unexpected, since the process treats 7% of the feed in the first case, and only 2% in the second. However, a large part of the capital is associated with either the pretreatment step which treats roughly the same quantity of water in both cases, or in other operations (e.g., the lime kiln, extraction process, calcium sulfate precipitator) which depend more on the solids content of the brine than on its volume. Thus the cost of the disposal step itself is not likely to decrease further with further recovery.

On the other hand, the conventional process for Clinton brine increases several cents per 1000 gallons in raising the recovery from 93% or 98%, mainly due to a sharp increase in pretreatment cost to get above the 93% recovery point.

It appears, then, that the type of desalination brine to which the proposed process could be most effectively applied are those such as Clinton, Oklahoma, where a considerable soda ash requirement exists, and in which this requirement can be provided by the process. Less promising are cases such as Gallup, New Mexico, and Minot, North Dakota, where soda ash is produced, but is not required. Although a potential credit is thereby created, the processing costs are also greater, due to the additional extraction step and additional lime requirements. As a result, the net processing costs are brought into the same region as for the conventional process, but depend upon establishment of the by-product credit.

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