

By-Products Recovery from Solar Salt Operations

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ABSTRACT

The residual bitterns from seawater salt production contains large tonnages of various chemicals. The potential for these products has long been realized, but up to the present time no process has been sufficiently economical and low in cost to justify their production. However, a considerably improved process has recently been developed by Saline Processors, Inc. that should allow an economical production of various by-product chemicals from most seawater salt operations of 200,000 tons per year or larger. It consists of continued solar evaporation of the bitterns with a sequential brine flow in the ponds. Mixed salts are harvested in several groupings, and then treated by selective crystallization and flotation. Detailed flow sheets, equipment designs and economic estimates will be presented for the production of potassium sulfate, potassium chloride, sodium chloride, sodium sulfate, and concentrated magnesium chloride solution.

INTRODUCTION

Solar salt production is practiced in many areas of the world with a wide variety of plant sizes and technical complexity. In general these plants are located in direct relationship to the world's population distribution, with a bias toward inexpensive shipping to heavy population centers, and the availability of adequate seawater coastal sites or inland sources and pond locations. Wherever rock salt deposits occur with inexpensive mining or distribution costs they generally become the world's preferred salt source, but because of the extremely widespread occurrence of adequate inland brine or seawater sites, solar salt fills in the gaps left by local demand, especially for the more remote areas or where transportation costs are particularly favorable to major demand centers (i.e. the Mediterranean coast to Europe; Caribbean to the Eastern U.S. coast; Australia to Japan; and California (including Baja) to the Western U.S. coast). The larger the demand center, the larger the solar salt facility (with some limitation upon the site suitability), and thus the wide range in plant sizes, varying from small, somewhat primitive operations of 50,000 tons per year or less, to the very sophisticated operations of one to four million tons per year.

Considering the comparatively low value of salt, and the generally well placed locations of these solar salt plants for

marketing, it would appear logical that all such operations seriously consider the expansion of their facilities to also produce by-product salts from their residual brine or bitterns. The obvious potential value of various compounds in the bitterns has given rise to a great deal of research on developing methods for their recovery, but to date no salt operation in the world has found processing economics to justify the cost of the plant, except for one or two small isolated lime precipitation operations.

New technology developed by the Garrett Research group, however, for the Great Salt Lake (very similar to seawater bitterns) for the first time allowed such an operation to be economically and commercially possible. This was generally described in the Third Salt Symposium (7), but it is only now, with dramatic new improvements and simplifications in pond construction, cooling equipment, and potassium sulfate processing, that the technology is available for profitable operation on all salt plants down to 200,000 t per year in size. This recovery process is described here.

SEAWATER CHEMISTRY

The composition of seawater has been found to be remarkably consistent in all of the oceans throughout the world, but even so a number of authoritative analyses are

TABLE I
Sea Water Composition

A. Composition

Element	Concentration, ppm
Cl	18,980
Na	10,561
Mg	1,272
S	884
Ca	400
K	380
Br	65
C (inorganic)	28
Sr	13
B	4.6
F	1.4
Si	0.02 -4.0
C (organic)	1.2 -3.0
Al	0.16 -1.9
N (as nitrate)	0.001-0.7
N (organic)	0.03 -0.2
Rb	0.2
Li	0.1
P (as PO ₄)	> 0.001-0.10
Ba	0.05
I	0.05
Fe	0.002-0.02
Approximate Total	32,595.01
H ₂ O	= 967,404.99
ρ	= 1.025 or 63.99 lb/cu ft @ 15°C

B. Molal Composition

Element	Moles/1000 moles H ₂ O	Compound	Moles/1000 moles H ₂ O
Cl ₂	4.9848	MgSO ₄	0.5135
Na ₂	4.2773	MgCl ₂	0.4611
Mg	.9746	K ₂ Cl ₂	0.0905
S	.5135	Na ₂ Cl ₂	4.2773
Ca	.1859		
K ₂	.0905		
Br ₂	.0076		
C (inorganic)	.0434		
Sr	.0028		
B	.0079		

Element	Moles/1000m	Mole %
Mg	= .9746	61.74%
SO ₄	= .5135	32.53
K ₂	= .0905	5.73
Total	1.5786	100.00

C. Molal Composition Without CaCO₃ and CaSO₄

Ca	.1859 orig.	S	.5135 orig.
C	.0434 CO ₃ ppt.	Ca × .98	.1400 CaSO ₄ ppt.
Ca	.1425 after CaCO ₃ ppt.	S	.3735 after CaSO ₄ ppt.

Revised Composition, Moles/1000m H ₂ O		Moles/1000m	Mole %
MgSO ₄	.3735	Mg	.9746 67.7
MgCl ₂	.6011	SO ₄	.3735 26.0
K ₂ Cl ₂	.0905	K ₂	.0905 6.3
Na ₂ Cl ₂	4.2773	Total	1.4386 100.0

D. Typical Bittern Concentrations

		Solution Composition, moles/1000 moles H ₂ O				
°Be	Density, g/cc	Mg, Wt. %	MgSO ₄	MgCl ₂	K ₂ Cl ₂	Na ₂ Cl ₂
25.0	1.208	1.03	5.53	5.17	0.99	48.98
28.5	1.245	2.4	10.33	16.15	2.44	36.20
30.0	1.261	3.6	12.50	25.35	3.27	27.79
31.8	1.281	4.5	16.17	31.76	3.97	19.70
33.8	1.304	5.5	19.39	40.83	6.13	13.31
34.7	1.315	6.0	17.53	48.45	7.18	9.88
35.2	1.321	6.5	15.42	56.60	7.58	6.44
35.5	1.324	7.0	13.06	63.81	5.80	3.48
35.6	1.325	7.5	10.97	70.31	2.69	1.72

Data From "The Oceans", Sverdrup, Johnson and Fleming, Prentice Hall, Inc., 1942.

given for it. One of the older, widely used values is shown in Table 1, along with the molar values (section B), assuming that all sulfate is MgSO_4 and all sodium is NaCl . Since the calcium carbonate and calcium sulfate precipitate during the early stages of evaporation, the equivalent gypsum-free values are shown in section C. Although the precipitate is small, it still makes a considerable difference when the data is plotted on phase diagrams.

The salts present in seawater represent a complex mixture that is generally looked upon as a quinary system, considering only the five major components: sodium, potassium, magnesium, sulfate, and chloride. The innumerable minor elements have a fairly small influence on the phase chemistry, except during the early stages of evaporation, when a number of sparingly soluble salts crystallize. These compounds, such as calcium phosphate, silica, etc. also crystallize early, but are not present in sufficient quantity to be shown here. The major components are shown graphically in Figure 1, based upon fairly representative evaporation conditions in seawater salt plants throughout the world.

Many different methods can be used to show the phase chemistry of evaporating seawater (11), but one of the most common is that of a Janecke diagram, shown in Figure 2. It assumes that all points are saturated with salt, and then merely records the molar ratio of the Mg , SO_4 and K_2 . The composition of the brine should remain constant on this plot until the bittern salts begin to crystallize. However, because of the previously mentioned influence of early gypsum and carbonates precipitation, there is actually a shift during the first stages of evaporation to a point that remains fairly constant throughout the salt crystallization period. This

point thus becomes the most meaningful starting point in examining solar evaporation and possible processing methods for a by-products operation. The diagram clearly shows what phases should be present at equilibrium, or in other words, if very long residence times and adequate seed and agitation are present for the solution to be in equilibrium with its salt phases. However, most of the compounds that can occur in this quinary system are comparatively slow to crystallize and are capable of being present with large supersaturations. Furthermore, there is a considerable difference between the rate of crystallization of the different phases, so it is rare in the course of an actual solar pond's operation that the phases coming down will be the ones predicted by the Janecke diagram. Consequently, it only serves as a rough guide on what to expect at different concentration levels, and considerable experience is necessary to know what phases actually will exist in the pond system, and what the actual brine concentration will be. Examples of the crystallization path occurring under different climatic conditions are shown in Figure 2, but even this is approximate, and the actual phase path can be expected to be considerably different for each pond location that is being examined.

A somewhat more useful general means of examining the phase relationships in the evaporation of quinary brines is shown in Figure 3, commonly referred to as an Autenreith chart. This phase diagram considers that the solution is always saturated with sodium chloride and some potassium salt, and that the primary variable is the magnesium chloride concentration. Magnesium sulfate, sodium chloride and the equivalent potassium chloride concentrations can be read

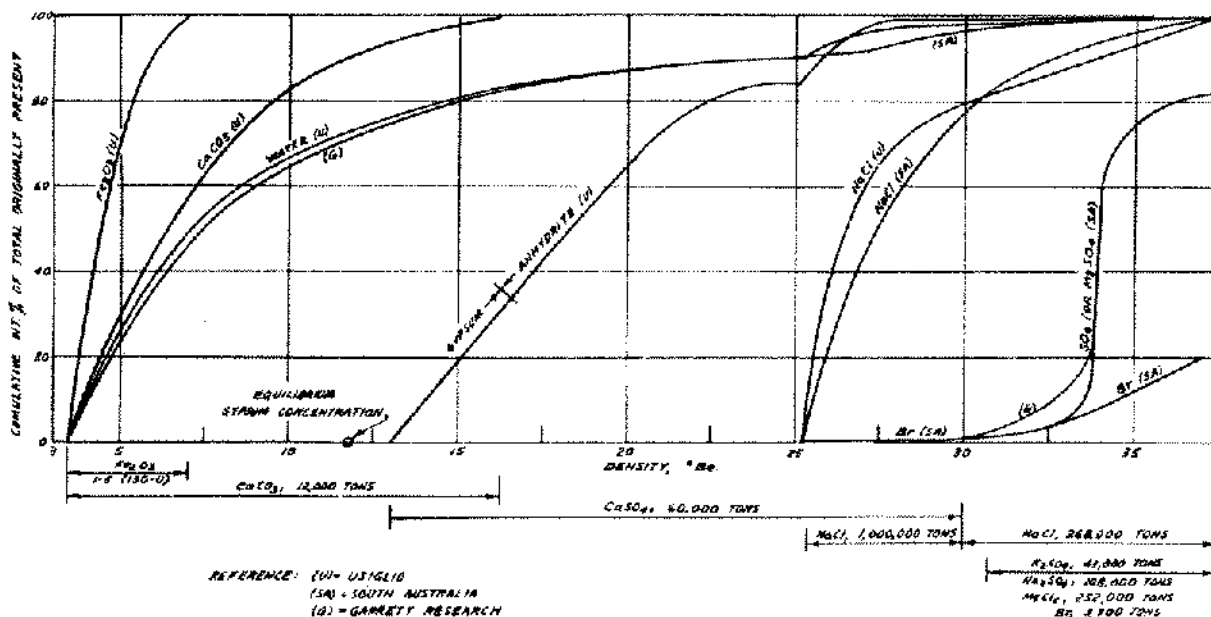


Figure 1. Deposition of salts during the evaporation of sea water at 25°C.

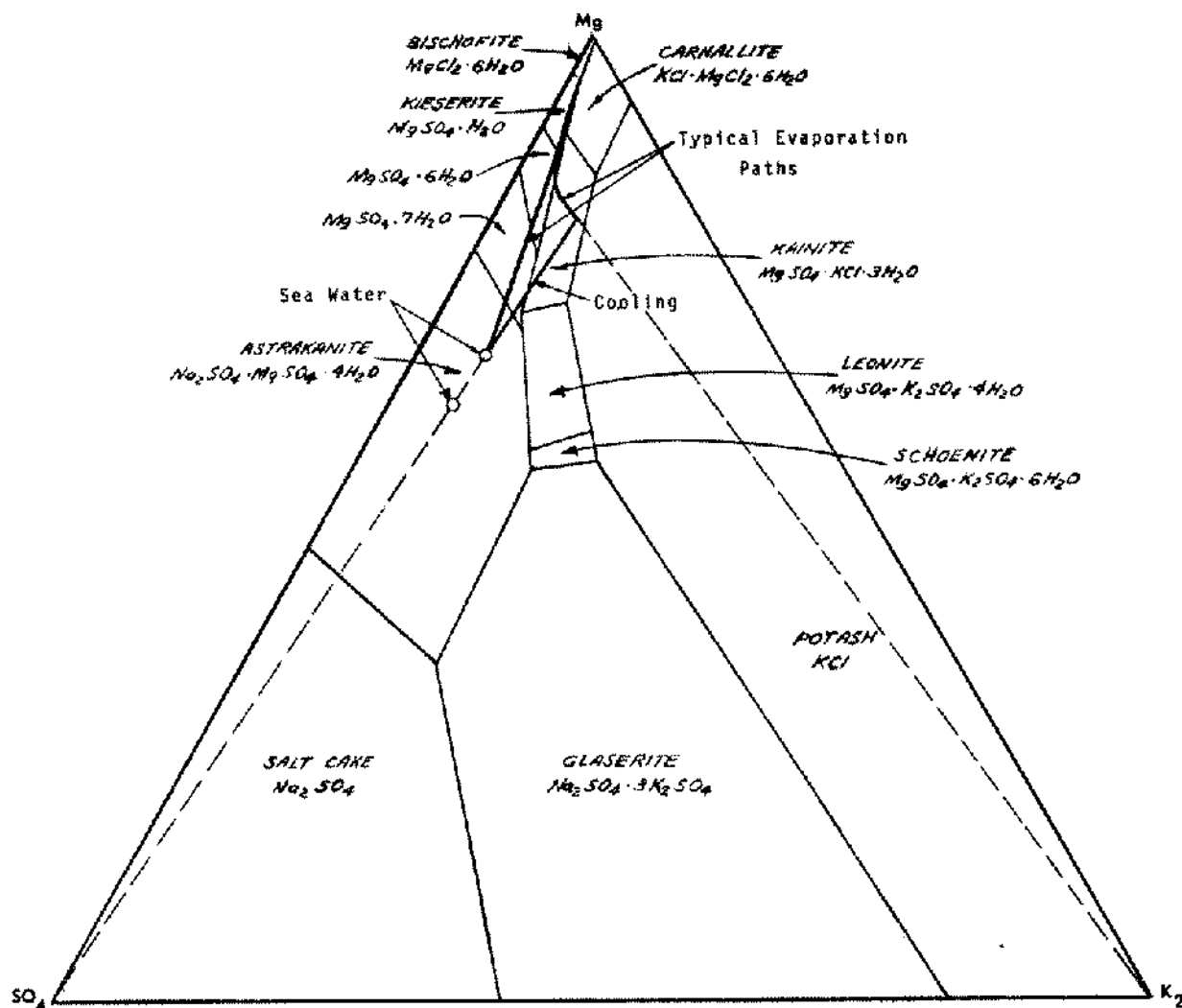


Figure 2. Diagram for the system $\text{Mg}-\text{K}_2-\text{SO}_4$ at 25°C . All points saturated with NaCl .

directly from the diagram. Furthermore, it shows to what extent metastable supersaturation may exist as fairly reproducible lines. It indicates how greatly the concentration may exceed that predicted on a Jancke phase diagram, and which phases may be actually precipitating. Unfortunately, however, in actual practice, the weather conditions and pond operation largely determine the actual path of crystallization, and it is rarely anywhere near Autenreith's indicated lines of saturation, or containing the compounds he predicts. Typical evaporation paths are shown in Figure 4 on this type of diagram, and in this form it is much more meaningful. However, it still must be cautioned that even with this improved plot each system will vary quite a bit in

practice. Individual locations will have their own specific characteristics, and usually will show quite different crystallization performance for the different periods of the year.

Data from a bitterns solar pond evaporation is most useful when plotted directly as concentration versus the extent of evaporation, which may be followed by either the brine's magnesium or magnesium chloride concentration. Many authors have attempted to correlate data as a function of density or $^{\circ}\text{Be}$, but as seen in Table 1D, once the $^{\circ}\text{Be}$ goes above about 30 (a density of 1.26), large changes in concentration occur with very small density changes. Furthermore, the correlations become totally erratic.

In Figures 4 and 6 it is seen that the first salt to crystallize

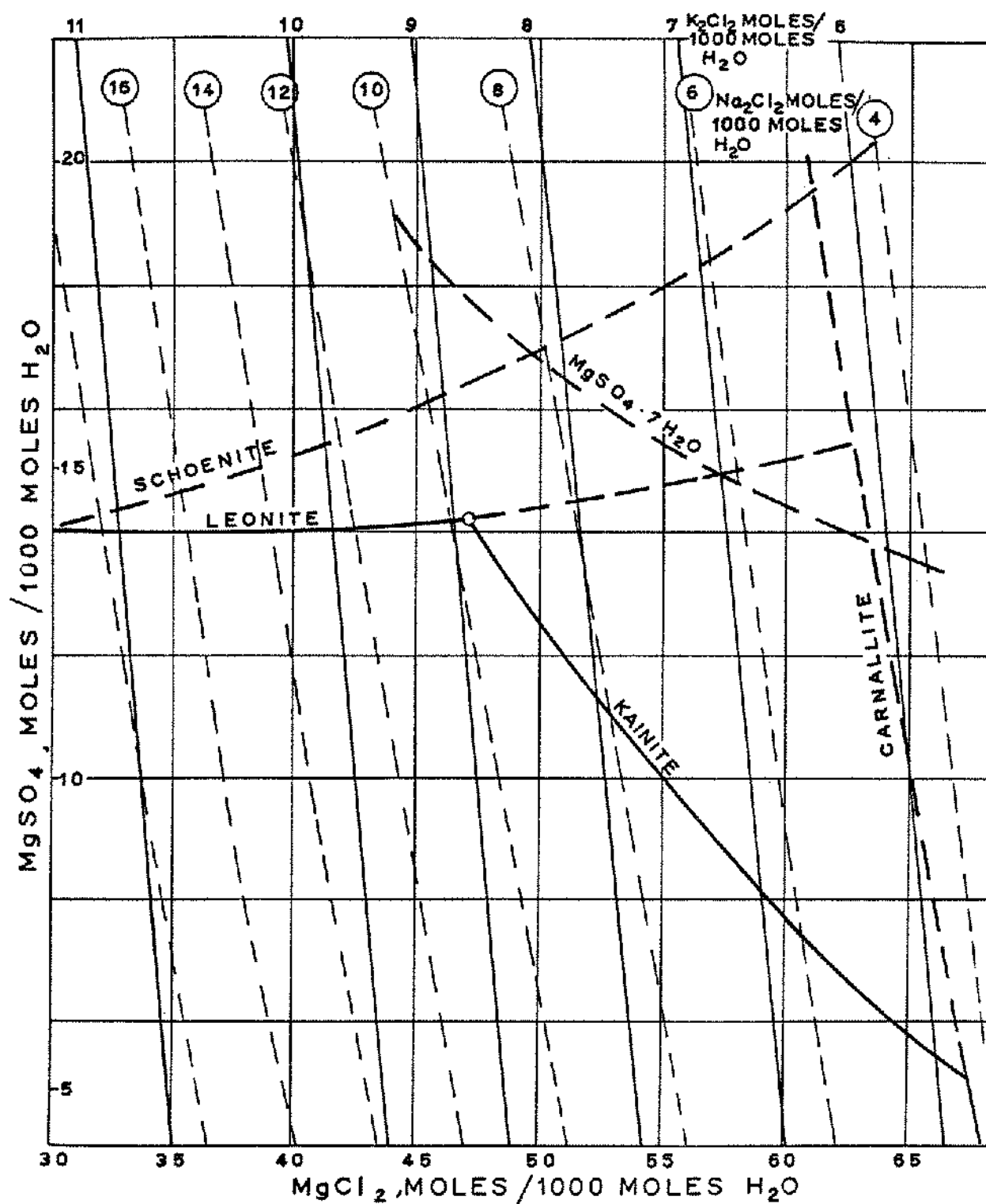


Figure 3. K-Mg-Na-Cl-SO₄ system at 25°C. Stable and metastable equilibrium.

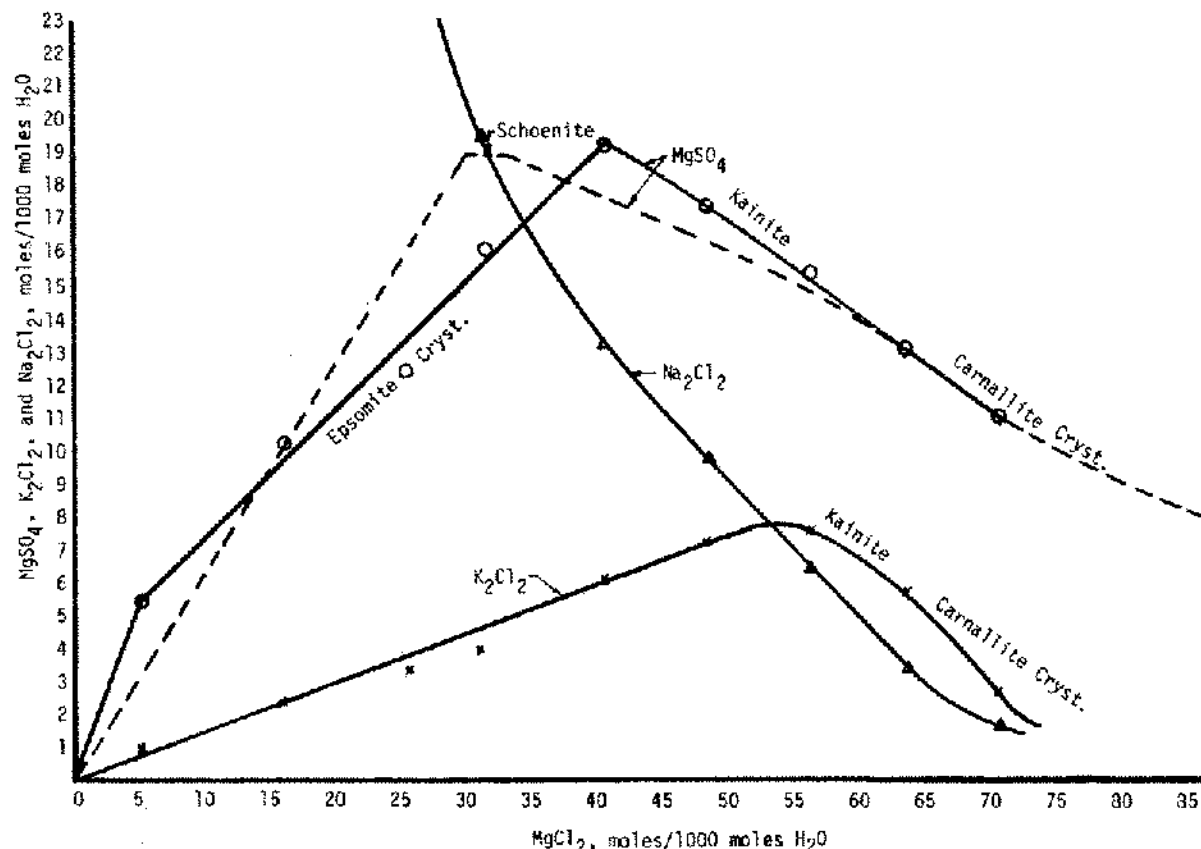


Figure 4. Actual data on an Autenreith-type plot. Experimental ponds (10' × 10') moderately cool summer weather.

is epsomite which usually occurs from about 29°Be onward. The first potassium salt to crystallize is kainite, although in some pond systems during portions of the year a small amount of schoenite will crystallize first. Leonite (the stable phase indicated by the phase diagrams) is essentially unknown in solar pond operation, as is astrakanite, which should come out instead of epsomite. Following the kainite field, and overlapping it to a very large extent, is carnallite, which continues to the end point of the evaporation. With many bitterns operations about 70% of the potash values crystallize as kainite, and 30% as carnallite. However, the variability between different solar pond locations is great, and actual data must be obtained for each operation. In all cases when evaporating bitterns in solar ponds the concentration of the potassium salts is not very high in any portion of the evaporating cycle, and the solid potassium is always in the form of various double salts, mixed with magnesium sulfate and sodium chloride.

GENERAL BY-PRODUCT PROCESSING METHODS

Because of the complexity of the brine system, dozens of seawater processing routes are possible, and literally hundreds of articles have been published on different processing methods (8, 12). To the present time, however, no known simple and economical processing method has been commercialized, other than with the very-similar-to-seawater bitterns at the Great Salt Lake. Some of the general processing methods are discussed in the following paragraphs.

Precipitation processes. The only bittern recovery method commercially practiced to date is that where the local value of the by-product chemicals is sufficient to warrant a rather drastic treatment of the brine. The principal example of this is the recovery of magnesia from seawater. If there is a good local demand for the magnesia, or export transportation is inexpensive and if inexpensive and good quality dolomite or limestone is available at a low price,

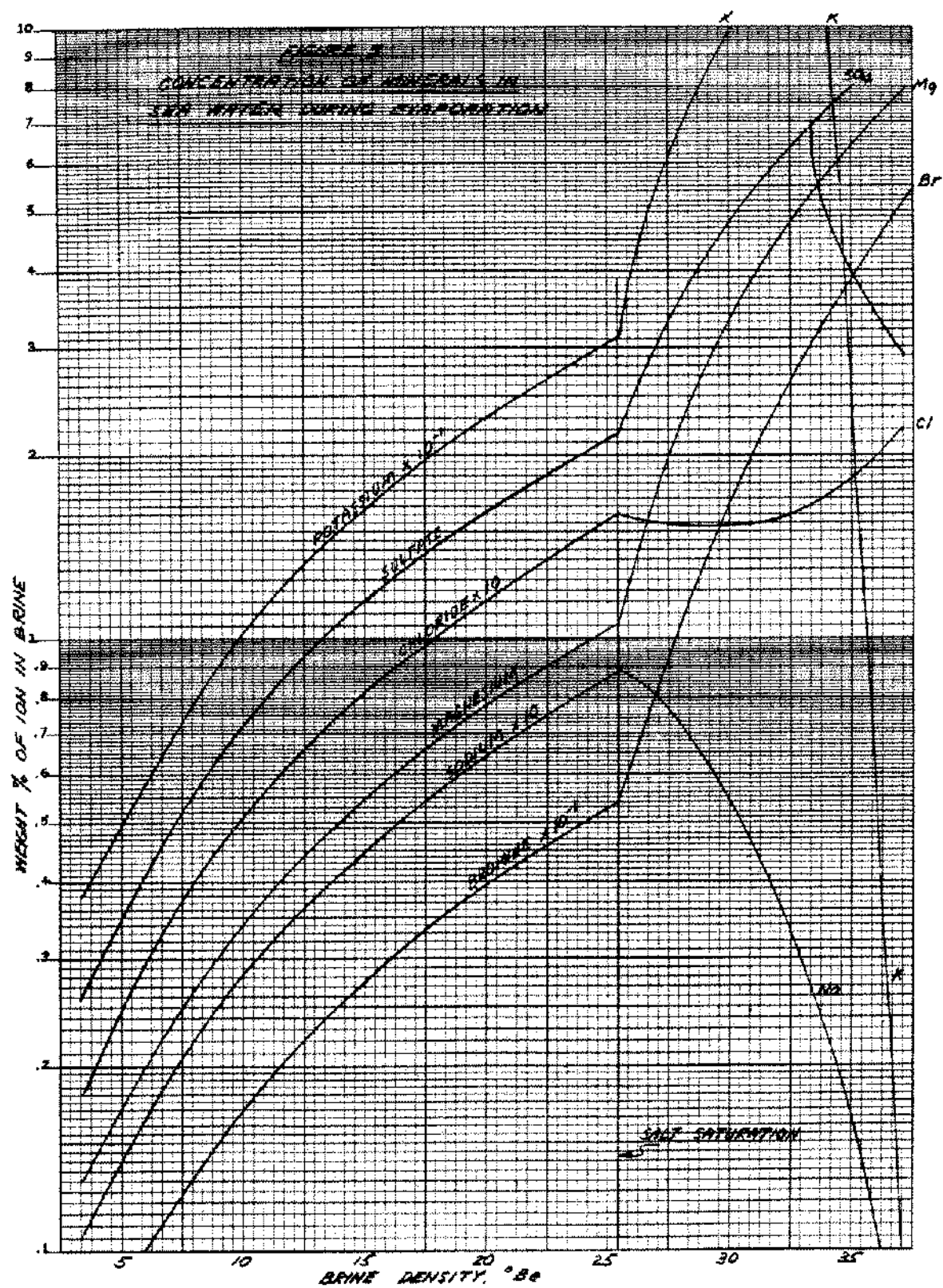


Figure 5. Concentration of minerals in sea water during evaporation.

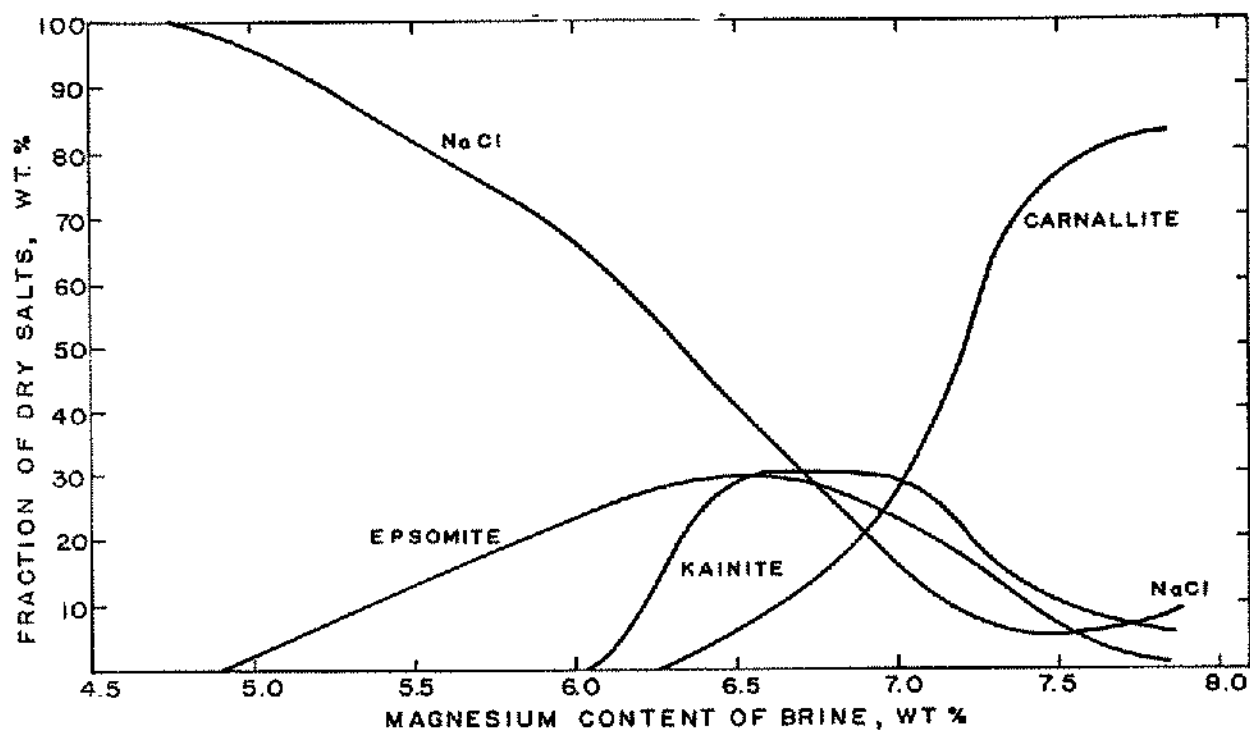


Figure 6. Typical salts composition during sea water evaporation.

magnesia can be recovered from seawater quite profitably. Since it is a well-known process and of only limited applicability, the details of the process will not be considered here. In a similar manner, in a very few locations where there is a demand for bromine and low cost chlorine exists, bromine recovery may also be economical. Many references adequately discuss these processes (9).

For the processing of seawater bitterns, one of the only examples of commercial by-product recovery is that currently practiced at the saltworks in Taiwan. Gypsum is harvested from some of the medium density seawater evaporative ponds (15 to 25°Be, before salt begins to crystallize) by hand-scraping the thin layer of gypsum that deposits. The yield per acre is very small, but the extensive use of cheap hand labor and the well-organized operation allows it to be practical for their local conditions. The residual bitterns are next precipitated in a cyclic process with lime to first recover additional gypsum, and then magnesium oxide. The final liquor is subjected to a plant evaporation-crystallization cycle to produce potassium chloride. The process is operated on a comparatively small scale, provides added income for the salt operation, and helps to meet the local demand for these products. Its economics, however, both there and on a general basis are very poor.

Cooling processes. There have been numerous reports on processes to cool bitterns so as to produce epsomite (or epsom salts— $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), mixed epsomite and potash salts (1, 2, 3) and glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). It is rela-

tively well-known that glauber salt and epsomite can be crystallized from brine, and in fact do occur naturally, such as in the South Pole, at the Caspian Sea, etc. Depending upon the bitterns concentration and temperature employed, various salts can be produced. The sulfate removal generally increases as the brine concentration increases, but pure compounds can only be recovered in comparatively small yields unless the system operates well into a metastable zone.

An example of cooling to produce a mixture of salts is that proposed in India (2) where bitterns were solar evaporated to 33.5°Be and then cooled to 12°C. Approximately a 55% magnesium sulfate yield was claimed, containing about 10% of the potash. These numbers appear optimistic, but even so, the bitterns are not sufficiently altered to prohibit sulfate double salts from crystallizing during the later stages of solar evaporation, and thus the complexity of the later separation problem is only slightly improved. Later Bhavnagary (1) indicated that 34 to 36°Be brine could be cooled metastably to 15°C or 0°C to produce relatively pure epsomite. It is thus apparent that by suitable manipulation of the brines between evaporation and a low temperature cooling cycle epsomite and various potash salts (kainite or carnallite— $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) can be produced individually or together, along with a residual magnesium chloride end liquor.

Pond or plant leach or conversion of bittern salts. The method that has perhaps most often been studied and tested

for the production of values from bittern salts is that of dissolving or converting the crude mixture of salts into something else. Obviously there are literally hundreds of methods by which this may be done, and there is an equally large number of literature references on the subject. They all suffer from being complex, usually require a great deal of energy (for heating and cooling), need considerable recycling of brine and solids, and the yields are usually poor. This results in high capital and operating costs, and consequently, these procedures have never led to a commercially successful operation.

With brines somewhat similar to seawater bitterns one plant of this type, however, was constructed but it shut down very quickly because of the poor economics (10). In another somewhat trivial example, a dry lake brine has a composition which crystallizes sylvinite until 90% or so of its potash content is gone, and then crystallizes "bittern salts". These are decomposed in the ponds to produce additional crude sylvinite, which is harvested along with the other product. The conversion is primarily only on the carnallite, so both the yield and quality are poor, but it does allow some additional production relatively inexpensively.

Flotation processes. The first process with somewhat more general economic potential was recently developed by the Garrett Research and Development Company, and later noted by others. It involves the solar evaporation of bitterns with some sequential segregation of the crystallizing salts so that a kainite-rich fraction may be isolated and harvested separately. The harvest salts are taken into a processing plant, and after suitable crushing, grinding and washing, given a flotation separation to produce a kainite-rich product. This material can be converted into schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), and it in turn partially leached or reacted with KCl to produce potassium sulfate. This process has the potential of being relatively simple and inexpensive, and quite effective low-cost flotation reagents have been developed. With pure salt fractions or on salts crystallized in experimental ponds good separation, yields, and efficiencies were obtained. However, when the process was applied to bittern salts from a large experimental or commercially operated solar pond it was found that the liberation size for the kainite was exceedingly small. Either poor yields and purities would have to be accepted, or else very expensive grinding and a delicate slime separation step from the finely ground solids would be required. Also, the kainite fraction usually does not represent more than about 70% of the potash in the bitterns, and much of this kainite is intermingled with carnallite. Thus, the method does not allow a good versatility in the processing of bitterns, and the total recovery from the ponds is low. It does, however, represent a significant advance in the technology of processing bitterns, and in some instances could be successfully applied.

A further development on the above process made it much more economically attractive. It has been found (5)

that the crude kainite salt as harvested from the ponds, together with any schoenite that may also have been crystallized, and the carnallite from the later stages of evaporation can be very simply, rapidly, and completely converted into schoenite in an initial crystallizer stage. The schoenite then can be readily floated from the residual salts, with a very high yield and with comparatively high purity. Since the schoenite is a product crystallized under plant conditions with good crystal growth and quality control, it represents an essentially pure component with no liberation problem, and flotation yields and costs are excellent. This process has been commercialized on a large scale with Great Salt Lake Brines.

IMPROVED GARRETT PROCESS

Process requirements. Products: Several factors become immediately apparent in considering the possible production of by-products from seawater bitterns. On the positive side, as seen by Table 2, the potential dollar value of the salts contained in the brine is great, being two to 3.5 times the value of the salt produced in the parent saltworks. However, only potassium sulfate (it is the preferred form of potassium, selling for twice the price of potassium chloride) and sodium sulfate (salt cake) have markets large enough to guarantee their being saleable. For the additional salt (NaCl) to be saleable, it must be of the same purity and quality as the main plant's salt, and if markets are limited, it may only be able to substitute for part of the basic salt production.

At some locations all of the magnesium may be sold, but this cannot be predicted for the general case. $MgSO_4$ has essentially no market, and even though $MgCl_2$ brine has a large market, it is only where shipping is favorable to the world's few magnesium metal operations, or for the small amounts needed for agriculture or miscellaneous uses. MgO has an excellent market, but could only be sold for the occasional situation when a refractory (brick) operator needs new capacity, or if produced speculatively by the salt maker, by risking a high capital operation in a very competitive market. It is unlikely that any bromine can be sold at all.

It thus can be summarized that a high value can be obtained for the bittern by-products only if: 1) all of the potash can be produced as K_2SO_4 , and 2) all of the remaining sulfate can be produced as Na_2SO_4 . If the bittern salt ($NaCl$) and any of the magnesium or bromine can be sold they would considerably add to the profitability of the operation.

Plant Size: The next dominant factor in considering a bitterns operation is the fact that even for the largest saltworks the by-product tonnage is modest. This means that the plants will be at a competitive disadvantage to the normal very large plants producing these products from other

TABLE 2

Quantity and Potential Value of Seawater Bittern Salts.
Theoretical Quantities for a Salt Production Rate of 200,000 Tons Per Year,
Based Upon 24.5 to 28.5°Be Brine—a 70% Salt Yield.

Product	Est. \$ Per Ton*	Tons Per Yr.	Est. Value Per Yr., \$	Value at 85% Yield, MM \$
Potassium Sulfate	94	9,700	900,000	0.8
Sodium Sulfate	45	24,600	1,100,000	0.9
Magnesium Chloride	40**	56,800	(2,300,000)	(1.9)
Sodium Chloride	7	85,700	(600,000)	(0.5)
Bromine	500	660	(300,000)	(0.3)
Total, $K_2SO_4 + Na_2SO_4$			\$2,000,000	1.7
Total, $NaCl + K_2SO_4 + Na_2SO_4$			\$2,600,000	2.2
Total, $MgCl_2 + NaCl + K_2SO_4 + Na_2SO_4$			\$4,900,000	4.2
Basic Salt Production	7	200,000	\$1,400,000	

*FOB works, Chem. Marketing Reporter, May 1, 1978.

**Probably only partially saleable, but priced as crude, 28% $MgCl_2$ brine.

sources. It necessitates that the bitterns process require only a modest capital investment, produce high yields of quality products, and have low operating costs. Furthermore, since many saltworks are in somewhat isolated locations, and/or do not have highly skilled chemical plant operators, the process must be simple to run.

Process design. The ability to realize these objectives was made possible for the first time in the Garrett Research (now Saline Processors, Inc.) process for the Great Salt Lake. However, this is a very large plant, and even though it should point the way toward what is needed for a seawater bitterns operation, a direct copy would probably not be economical considering the smaller-sized bitterns production. Thus, considerable cost improvement was needed, and based upon three separate new developments, it appears possible for the first time to economically recover by-products from seawater. These innovations are discussed below.

Pond construction. It is imperative that bitterns solar evaporation ponds be as close to leak-free as possible, and generally much tighter than salt ponds. In many locations this poses no problems, but for those areas where the soil is not adequate, an inexpensive, reliable pond lining is required. Saline Processors, Inc. has recently developed just such a lining system based upon a simple additive and application method that can be used at any pond location. It should allow all salt plants to inexpensively install leak-free, durable bitterns evaporation ponds. The pond area is very small compared to the main salt crystallizing area.

Sodium sulfate production. In the Third Salt Symposium, Garrett Research suggested the use of a $NaCl$ - $MgSO_4$ metathesis reaction to produce Na_2SO_4 from bittern salts. Considerable development was done on this process, and reactions similar to potassium sulfate production were found to be effective. Astrakanite or vanthoffite was first

produced, and this compound was converted into Na_2SO_4 . The method worked well, but the process was complex and had only modest yields per pass. Its economics were not as favorable as desired for smaller sized plants.

To overcome this problem a much simpler process has been developed. It involves the cooling of seawater brine at a concentration such that only glauber salt ($Na_2SO_4 \cdot 10H_2O$) crystallizes, and then producing salt cake (Na_2SO_4) by "salting out" with the salt- $MgSO_4 \cdot 7H_2O$ mixture that remains behind from the later schoenite flotation step. The end liquors are recycled, allowing a complete conversion of the sulfate to potassium and sodium sulfates. By removing part of the sulfate ion in this manner (from the cooling step), no sulfate contaminates the salt ($NaCl$) until about 32.5°Be, and thus through the recycling action, all of the bitterns salt ($NaCl$) may be recovered at the same quality as the regular salt, and at about the same production rate per unit area as the main salt ponds.

In most seawater studies cooling of bitterns has been shown to yield only a contaminated epsomite ($MgSO_4 \cdot 7H_2O$). However, glauber salt can be crystallized instead if the brines are less concentrated, as seen in Figure 7. Rapid cooling through the intermediate temperatures, and heavy seeding to allow metastable operation at the end point are required. Normal salt pond end liquor (28.5°Be) would be used, with temperatures of about -5°C for optimum yields and process efficiency. Cooling and crystallizing at these temperatures is normally difficult and expensive, and the equipment tends to foul rapidly. However, new techniques have recently been developed that greatly improves the operation. Fouling can be essentially eliminated, and the energy requirements kept very low. Salt cake by this process should allow a favorable profit, even with small plants and competitive pricing.

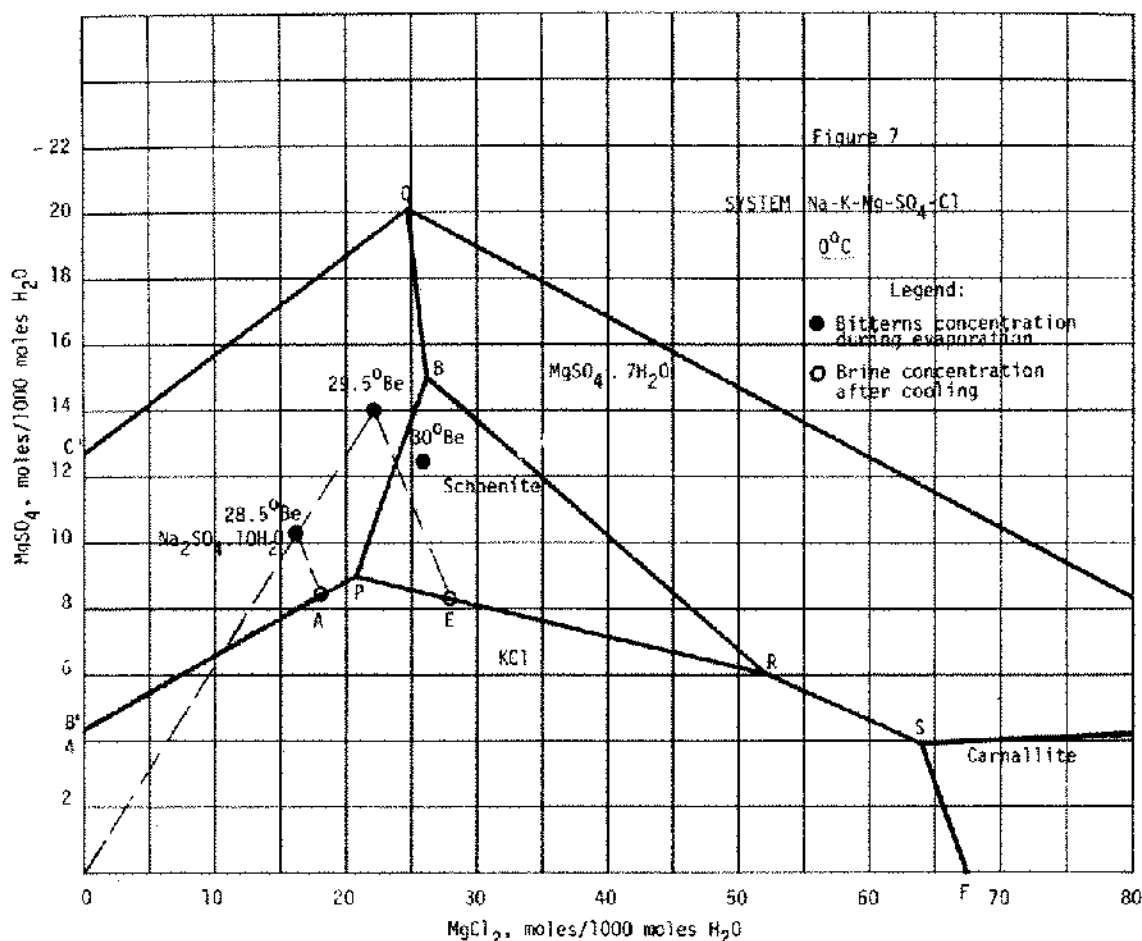


Figure 7. Diagram for the system Na-K-Mg-SO₄-Cl at 0°C.

Potassium sulfate production. The Great Salt Lake process requires either a second expensive parallel operation to produce potash (KCl) (4), or the purchase of KCl, unless much lower K₂SO₄ yields per pass, with considerable additional brine recycling requirements to the solar ponds is experienced. In this new process, however, the initial sulfate removal allows the first potash salt coming out of the treated bitterns in the ponds to be sylvinite (see Figure 2) which can be harvested separately. Its processing can still be largely along with the mixed potash salts, so little extra expense is involved, and yet the K₂SO₄ yields are high. The total flow sheet for the process is shown in Figure 8.

PROCESS ECONOMICS

In order to examine the economic potential of the process a capital and operating cost estimate has been made for a 200,000 tons per year salt plant. Using this new process the production quantities and value of the products are those shown in Table 2, after applying an 85% yield factor. The

capital and operating costs, and the general economics for a plant of the type shown in Figure 8, with a separate sylvinite (carnallite) handling step, is estimated in Tables 3 and 4. The analysis assumes that the plant works on a three shift, seven day per week basis. It is also assumed that area for the solar ponds for the bitterns and all of the general service and support facilities are available. For simplicity, the strong magnesium chloride end liquor has been considered to be sold as a 28% MgCl₂ solution, and no bromine recovered. The evaporating conditions are assumed to be those of only moderately high temperatures and evaporation rates.

It is seen that even though this salt plant is very small, the bitterns operation can be attractive. It is quite likely that other capital costs would be required for support facilities, and that not all of the salt or MgCl₂ could be sold. However, there is considerable margin for error with the 20% rate of return shown. The basic consideration is that the plant is very small, turning out only 35,000 tons per year of K₂SO₄ + Na₂SO₄ products, and thus, with the process

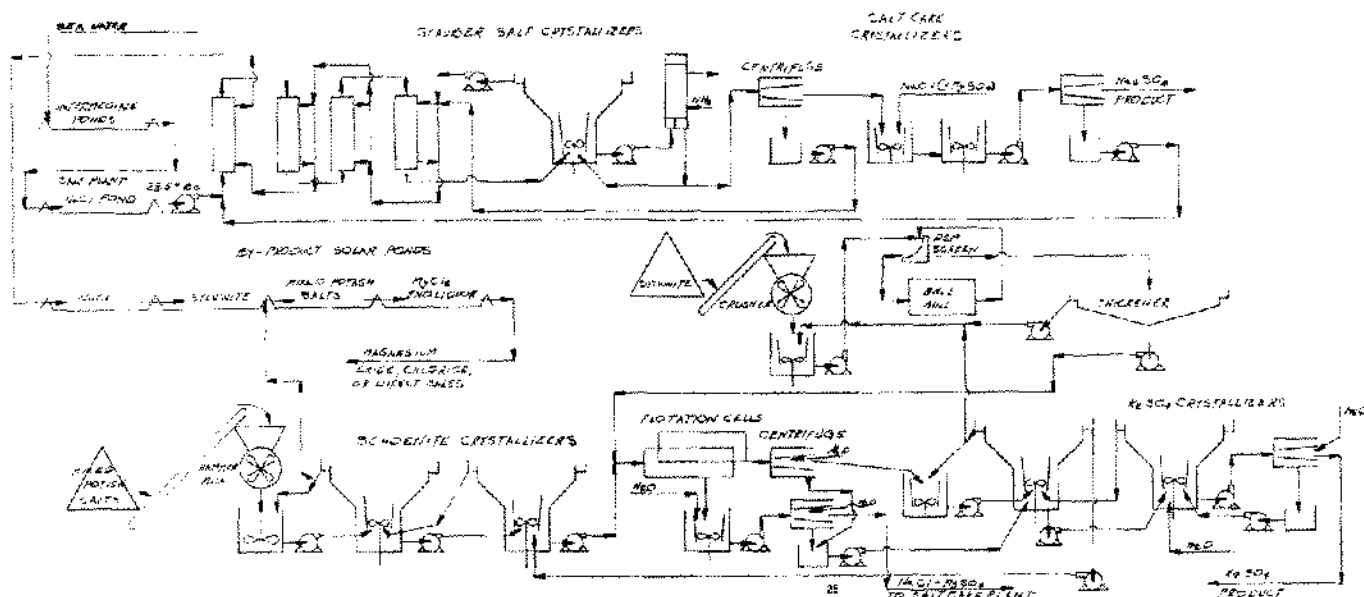


Figure 8. Saline Processors, Inc., Seawater bitterns by-product plant.

TABLE 3

Capital Cost Estimates.
10,000 t/yr K₂SO₄, 25,000 t/yr Na₂SO₄ Production.

		Purchased Price, U.S., 1,000 \$	
A. K₂SO₄ Plant			
1. Dump Pads, Stacking Conveyors, Reclaim Conveyors	30	3. Glaubers Salt Crystallizer, Ammonia Cooling System, Controls, Pumps	100
2. Hammer Mill	10	4. Salt Cake Crystallizers, Controls, Pumps	50
3. Repulp Tank, Agitator, Pump, Screen	10	5. Na ₂ SO ₄ Centrifuge, Receiver, Conveyor	30
4. Schoenite Crystallizers, Pumps, Controls	75	6. Dryer, Dust Collector, Conveyors, Elevator, Storage Bin, Loader	60
5. Conditioning Tank, Flotation Cells, Receiver Tanks, Pumps; Sylvinite System	150	Sub-Total	\$340
6. Schoenite and Tailing Salts Centrifuges, Receivers, Repulp Tanks	60	Total Plant Cost (× 3) = \$1,020,000	
7. K ₂ SO ₄ Crystallizers, Pumps, Controls	80	C. Auxiliary Facilities	
8. K ₂ SO ₄ Centrifuge, Receiver, Conveyor	25	1. Solar Ponds, Pumps, Piping	100
9. Dryer, Dust Collector, Conveyors, Elevator, Storage Bin, Loader	60	2. Harvesting Equipment	100
Sub-Total	\$500	3. Steam, Power Plant	100
Total Plant Cost (× 3) = \$1,500,000		4. Buildings (Office, Storage)	100
B. Na₂SO₄ Plant		5. Miscellaneous	80
1. Brine Pumps, Piping, Storage Tanks	50	Sub-Total	\$480
2. Heat Exchangers, Controls, Pumps	50	D. Working Capital, Start-up Expense, Engineering, Contingency	
			300
		E. Total Investment	\$3,300,000

shown, must be quite inexpensive. Operating costs such as harvesting and flotation reagents must be carefully controlled, but these are basically well known factors for a modern processing operation. The plant must be operated as a chemical plant, with the attendant close monitoring and control of process variables, but this again should not be prohibitively demanding or costly.

SUMMARY

Although very complex phase chemistry and chemical engineering operations are involved, it has been shown that a comparatively simple processing method can be employed for the economical recovery of by-products from seawater bitterns. The process first employs the cooling of bitterns to

TABLE 4
Operating Costs, Profitability,
10,000/yr K_2SO_4 , 25,000/yr Na_2SO_4 Production.

Operating Cost	Cost/year, 1,000 \$		
Labor			
3 Operators/shift $\times 4 = 12$ @ \$10,000/yr			120
4 Maintenance men @ \$10,000/yr			40
2 Chemists @ \$14,000/yr			28
2 Harvesting Operators @ \$10,000/yr			20
1 Engineer			20
1 Manager			30
Utilities			
Fuel			260
Water			20
Maintenance Materials, 3% of Capital Cost			90
Insurance, 1% of capital			30
Reagents and Supplies			40
Pond Operation (paid to salt plant)			10
Miscellaneous			100
Depreciation, 15 years			200
	Total \$1,000		
	$Na_2SO_4 + K_2SO_4$	$NaCl + Na_2SO_4 + K_2SO_4$	$MgCl_2 + NaCl + Na_2SO_4 + K_2SO_4$
Profitability			
Gross Profit, M \$	700	1,200	3,200
Net Profit after 50% Taxes, M \$	350	600	1,600
Simple After Tax Rate of Return, % of \$3,000,000 Capital	11.7	20.0	53.0

produce glaubers salt followed by evaporation of the remaining bitterns to produce harvestable potash salts. These salts are then treated by flotation and two rather simple double decomposition crystallization steps. Salting out is used to convert the glauber salt to salt cake with salt and epsomite. The economics to produce potash (K_2SO_4) and salt cake (Na_2SO_4) as major products is shown to be excellent even for salt plants as small as 200,000 tons per year.

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