

# Considerations on the Recovery of Potash from Sea Water Bitterns

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## ABSTRACT

### Practical and Theoretical Considerations in the Recovery of Potash from Sea Water Bitterns

*Sodium chloride is produced from the sea in many areas of the world where flat space for ponds is available and where solar evaporation is possible. However, with few exceptions, once the salt is obtained, the mother liquor is wasted back to the sea. This mother liquor contains about 1.2% by weight  $K_2O$  equivalent. As a raw material for potash production, this mother liquor compares favorably with other brines currently used for potash production (Dead Sea Works and Bonneville Operation at Wendover, Utah). However, potash recovery from sea water bitterns has resisted all attempts for its economical recovery.*

*Mainly using the tools given by the phase chemistry of the quinary system  $Cl^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{++}$ ,  $H_2O$ , brief practical and theoretical considerations for the recovery of potash from sea water bitterns are discussed.*

## INTRODUCTION

Currently, potash is produced in Canada, France, Germany, Israel, Italy, Poland, Russia, Spain, and the United States. Chile produces a relatively small quantity as a by-product of its sodium nitrate recovery.

About 97% of the total world production of potash comes from the processing of different ores, mainly sylvinit. The remaining 3% is obtained from natural occurring brines. These brines are the Searles Lakes in California; Wendover, Utah; and the Dead Sea.

Several lakes and well brines have received general attention as a source of potash. However, perhaps no other source of this valuable fertilizer has been studied for such long periods of time as sea water. Perhaps this is because sea water is available to most countries, and of course constitutes by far the greatest reserve of potash in the world.

Sea water contains only 0.05% potash equivalent ( $K_2O$ ), but evaporation may be carried on without major losses of potassium until a brine having about 2.3%  $K_2O$  is obtained. This brine compares favorably with other brines currently used for potash production (namely, the Dead Sea Works and Bonneville operation at Wendover, Utah).

In this paper we will briefly consider the recovery of potash from this almost inexhaustible source.

## I. POTENTIAL POTASH VALUE IN SEA WATER BITTERNS

Out of about 53 elements -- excluding the dissolved gases from the atmosphere -- there are only a few that may be considered as a "major" constituent. If we make a hypothetical combination

of these ions, sea water composition may be expressed as follows in percent by weight: (Kobe, 1957); (Harvey, 1960).

NaCl	2.74 %
MgCl <sub>2</sub>	.34 %
MgSO <sub>4</sub>	.23 %
CaSO <sub>4</sub>	.13 %
KCl	.07 %
Ca(HCO <sub>3</sub> ) <sub>2</sub>	.012%
MgBr <sub>2</sub>	.007%
	<hr/> 3.529%

The salinity shown above changes according to the ocean, the latitude, depth and other factors, but it may be considered as a good average composition of sea water.

Many different procedures have been proposed for the recovery of the several values from sea water (Tallmadge et al, 1964). As a result of the Saline Water Conversion Program, several aspects of the recovery of values from sea water have been studied (Salutsky et al, 1963; Weinberger et al, 1964).

The specific recovery of potassium values from sea water or its bitterns has been extensively studied. Of the several processes proposed, none have been operated on a large commercial scale. There are those using strictly physical-chemical processes (the Ballard process) (Tessler, 1951); (Hildebrand, 1918); (Niccoli, 1926, a); (Aravamuthan, 1961), and others where combinations of chemical and physical-chemical procedures are used (Niccoli, 1926, b); (Polucktoo, 1936); (Umano, 1956); (Bhavnagary et al, 1958 and 1959); (Hadzeriga, 1963); (Butt et al, 1964).

Our consideration here will be restricted only to the recovery of potash from the final sea water bitterns obtained by the solar sodium chloride producers.

The concentration of sea water by solar evaporation has been studied by many authors since the original work of Usiglio in 1849 (Clark, 1924). By this procedure, several different salts are obtained as evaporation progresses. After most of the calcium carbonate and gypsum are separated, a good crop of fairly pure sodium chloride crystallizes out.

Hence, sea water has been used for sodium chloride production since ancient times (Kaufmann, 1960), especially in those countries where solar evaporation was possible. Today there are many places in the world where this is still in practice and actually constitutes the major source of sodium chloride. For example, in the Middle East and Asia, with very few exceptions (small salt mining in Central China, Pakistan and Northern India), all the salt produced is obtained from the sea. The same applies for Australia, New Zealand, Africa, Central and South America. In the United States only about 5% of the total sodium chloride production comes from the sea.

After most of the sodium chloride has been crystallized out, a brine of a specific gravity of about 1.26 is obtained. This brine, with only very few exceptions, is disposed back to the sea. Typical composition of this brine, and again assuming hypothetical combination of the ions, is as follows: (Van Planch, 1958)

NaCl	12.5 %
MgCl <sub>2</sub>	8.7 %
MgSO <sub>4</sub>	6.1 %
KCl	1.9 %
MgBr <sub>2</sub>	.18 %
	<hr/> 29.38 %

In some cases this bittern is used for magnesia (Shreve, 1945) and bromine recovery (Faith et al, 1957) but not for potash production.

Further solar evaporation of this brine yields a complex series of different salts (Phillips, 1947). These solids containing as much as 12.9% K<sub>2</sub>O equivalent have resisted many attempts for its economical recovery.

Figure 1 gives an idea of the tonnages involved in an operation that produces one million tons of crude sodium chloride from sea water.

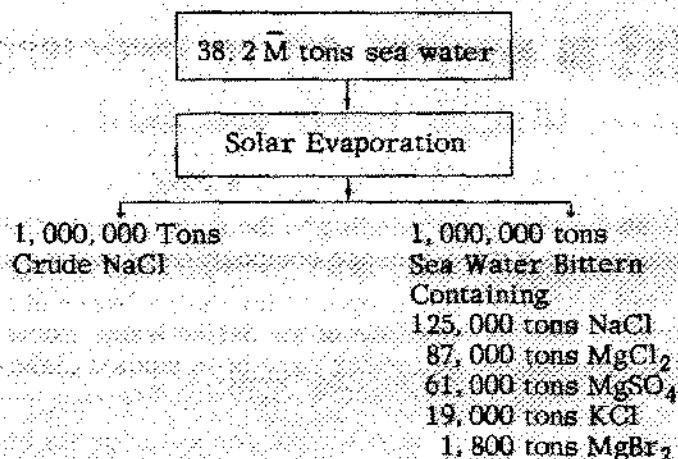


Figure 1

In the world there are few producers of one million tons sodium chloride from sea water. Those have a potential of less than 20,000 tons of potash, which is a relatively small amount for a potash producing country. However, for many potash importing countries it is a respectable tonnage. This is especially true when this tonnage has to be transported for many thousands of miles.

## II. THEORETICAL EXAMINATION OF SEA WATER BITTERNS

To some extent the final mother liquor from sodium chloride production in the Great Salt Lake has a similar composition to that of sea water bitterns. Table 1 compares these two brines with the ones used at Bonneville and the Dead Sea for potash production, assuming an hypothetical ions combination.

Table 1  
Brine Composition in Percentage by Weight

	Bonneville	Dead Sea	Great Salt Lake	Sea Water Bittern
KCl	1.2	1.0	2.1	1.9
MgCl <sub>2</sub>	1.2	12.1	2.7	8.7
MgSO <sub>4</sub>	.3	--	5.4	6.1
CaCl <sub>2</sub>	--	2.8	--	--
NaCl	24.0	7.0	18.4	12.1

We can see that both the Great Salt Lake and Sea Water bitterns compare favorably from the potassium content standpoint of those of Bonneville and Dead Sea.

Using the Janecke triangular representation of the quinary system  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{H}_2\text{O}$ , it is possible to predict the theoretical solids phases possible to obtain by evaporation of sea water bittern. Figure 2 shows the  $1/2 \text{Mg}^{++}$  corner of such representation at  $25^\circ\text{C}$ . Two

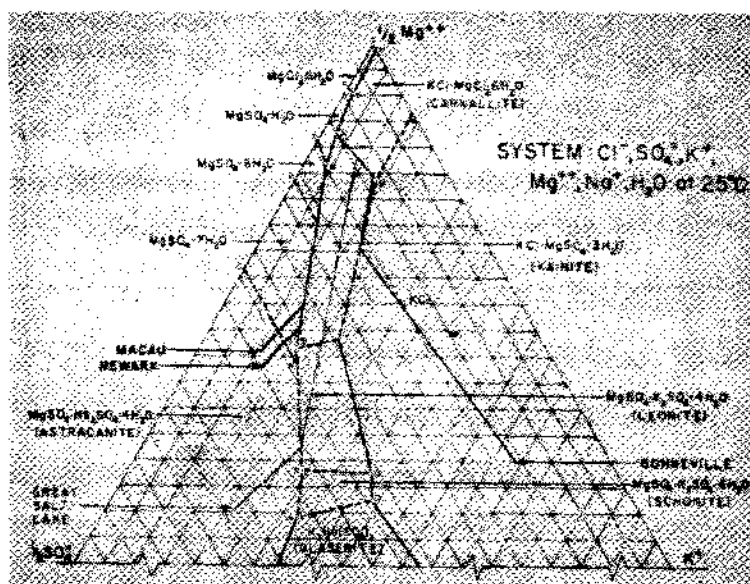


Figure 2. Corner of  $1/2 \text{ Mg}^{++}$  of the Quinary System  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{H}_2\text{O}$  at  $25^\circ \text{C}$ .

typical and similar sea water bitterns are plotted: one from Macau (northeast of Brazil), and another from Newark (San Francisco Bay). As a matter of comparison, Great Salt Lake and Bonneville brines have also been included in Fig. 2.

In a previous presentation (Hadzgeriga, 1964, b), the different theoretical phases which might be obtained upon evaporation at  $25^\circ \text{C}$ . of the Great Salt Lake brine were calculated. This showed that a series of complex solid phases containing the potassium might present difficulties for potash recovery.

We can see in Fig. 2 that Great Salt Lake brine, as well as sea bittern, lies in the astrakanite field. This means that the first salt, in addition to halite, to crystallize out upon evaporation at  $25^\circ \text{C}$ ., in both cases will be astrakanite ( $\text{MgSO}_4 \cdot \text{NaSO}_4 \cdot 4 \text{H}_2\text{O}$ ). However, as evaporation continues, the Great Salt Lake brine theoretically should enter into the field of leonite ( $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4 \text{H}_2\text{O}$ ), and this will be the first obtainable potassium containing salt. Sea water, however, crosses a small section of the epsomite field ( $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ ) and then reaches a crystallization path limiting the several fields of magnesium sulfates and kainite ( $\text{KCl} \cdot \text{MgSO}_4 \cdot 3 \text{H}_2\text{O}$ ). Therefore, for sea water evaporation, kainite should be the first obtainable potassium containing salt.

The successive theoretical solid phases obtained from sea water bittern and Great Salt Lake are as follows:

<u>Sea Water Bittern</u>	<u>Great Salt Lake Brine</u>
Astrakanite	Astrakanite
Epsomite	Leonite
Epsomite + kainite	Kainite
Hexahydrate + kainite	Carnallite
Kieserite + kainite	Kieserite + carnallite
Kieserite + kainite + carnallite	Kieserite + carnallite + bischoffite
Kieserite + carnallite	
Kieserite + carnallite + bischoffite	

Of course, all these solid phases are contaminated to various extents with halite ( $\text{NaCl}$ ).

Calculations were made on the sea water bittern to see what kind of theoretical solid phases could be obtained upon solar evaporation at  $25^\circ \text{C}$ . From the standpoint of potash recovery, it was

assumed that astrakanite and part of the epsomite could be segregated before kainite will begin to crystallize. Kainite plus some carnallite and the hydrates of magnesium sulfate will constitute the potash "ore" obtained. The overall composition is shown in Table 2 as compared with the equivalent material obtained from the Great Salt Lake (Hadzeriga, 1964, b).

Table 2  
Theoretical Composition of Solid Phases  
Obtained by Evaporation at 25°C.

Great Salt Lake		Sea Water Bittern
34.0%	NaCl	18.3%
13.0%	KCl	20.4%
10.2%	K <sub>2</sub> SO <sub>4</sub>	---
23.9%	MgSO <sub>4</sub>	40.0%
3.3%	MgCl <sub>2</sub>	1.4%
15.6%	H <sub>2</sub> O (crystallization)	19.9%
100.0%		100.0%

It can be seen that the K<sub>2</sub>O equivalent in the Great Salt Lake material is 13.7%, and is very close to the 12.9% from the sea water bittern. However, the total sulfate content in the Great Salt Lake solids is 24.7% SO<sub>4</sub><sup>=</sup> against 31.9% SO<sub>4</sub><sup>=</sup> in the solids from sea water bittern. The difference of NaCl content is also remarkable. In spite of this, it is the belief of the author that the general beneficiation problems of both of these solid phases -- if obtained as predicted theoretically -- are very much alike.

### III. THE RECOVERY OF POTASH FROM SEA WATER BITTERN

In observing Table 1, we can see that the main difference between Bonneville and Dead Sea brines and those of the Great Salt Lake and sea water bittern is the sulfate content. Upon solar evaporation, Bonneville brines yield sylvinite which is easily treated by flotation to recover potash. Dead Sea brine yields carnallite, which after proper leaching with water gives an impure sylvinite from which potassium chloride is produced by flotation or crystallization.

Table 2 showed that the theoretically predicted solid phases obtainable by evaporation at 25°C. from either the Great Salt Lake brine or sea water bittern are more complex because of the great amount of sulfates present. In these calculations none of the factors found in operating solar evaporation ponds have been considered. Variation of temperature during a particular day and during a season, supersaturation, etc., may play an important role in changing the composition found theoretically. This aspect of evaporating a brine was studied by several authors, principally by Autenrieth, Borchert, Karsten and Valiashko. Dynamo-polythermal evaporation and "solar equilibrium" concepts were introduced which compared the composition of salts obtained under natural conditions and those obtained by calculation from equilibrium diagrams (Borchert, 1964), (Karsten, 1950).

As mentioned before, a number of different processes have been proposed for the recovery of potash from sea water. It is out of the scope of this presentation to discuss in detail all these procedures. However, it is very interesting to note that the Bhavnagary-Gadre-Rao proposal is in a pilot plant state at the Central Salt Research Institute at Bhavnagar using the residual brine from the Kandla Salt Works (European Chemical News, 1963).

In connection with the potential production of potash from sea water bittern, the author had studied this subject as it would be applicable to the Bombay area. The process for such recovery was using the method illustrated in Fig. 3 (Hadzeriga, 1963 and 1964, a).

### SIMPLIFIED FLOWSHEET SEA WATER

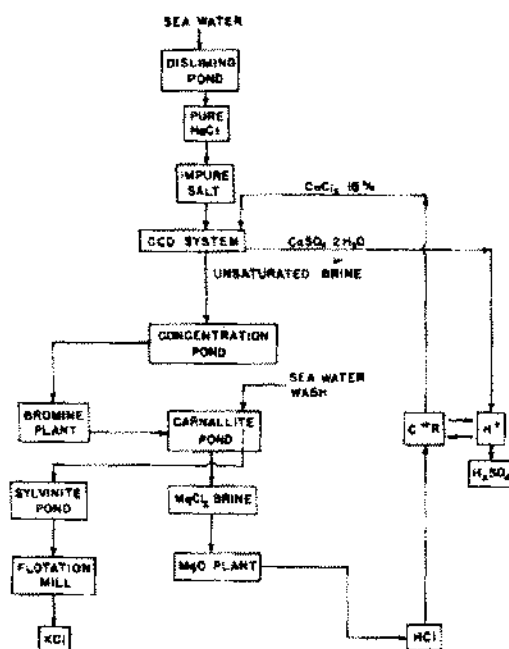


Figure 3

The conclusions are somehow discouraging. First of all, the quantity of mother liquor available in the Bombay area is quite small. Actually, the bittern from seven different producers of sodium chloride will have to be put together in order to have a production of 4,000 tons a year of potassium chloride.

Second, the land for ponds, plant site and other facilities has to be leased from the Indian Government at a very high price. The lease of 740 acres amounted to more than 25% of the total annual operating cost.

In spite of these factors and because the commodities produced (potash, magnesium oxide and sulfuric acid) are highly priced in India, the plant operation of a 4,000 tons of potash is not quite out of the question. But it is necessary to remark here that the potash sales amounted to only 21.5% of the total annual manufacturing cost. Therefore, what actually paid the manufacturing cost was the sale of magnesium oxide and sulfuric acid.

This case led us to think that under present circumstances, and in spite of the relatively large salt production in India (Thakore, 1960), recovery of potash from sea water bittern could be profitable only if the other values present in the bittern are also recovered, namely, magnesium and sulfate compounds, and bromine.

### CONCLUSIONS

Even though sea water bitterns are more valuable from the K<sub>2</sub>O equivalent content than Bonneville and Dead Sea brines, at the present it is believed that potash production alone would not pay for an operating plant. It will also be necessary to recover and market the other products present in the bittern.

Much larger solar salt producers, with a proportionally greater residual bittern, will considerably improve the overall economics and the recovery of potash from sea water bittern may become a reality in the future.

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