

Recovery of Epsomite and Sylvite from Seawater Bittern by Crystallization

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ABSTRACT

The concentrated seawater bittern from the fabrication of halite contains about 13% epsomite and 2% sylvite, the extraction of which is made difficult by the presence of magnesium chloride, halite and other salts. A continuous process for the recovery of epsomite and sylvite from seawater bittern has been developed.

In the developed method for the recovery of epsomite the crystallization is effected by solar evaporation of seawater bittern to a specific gravity of 1.30 to remove halite, followed by dilution of the concentrated bittern with 5% volume of fresh water to prevent the coprecipitation of halite, magnesium chloride and sylvite with the epsomite, then surface cooled to crystallize epsomite 96 + % pure.

For the recovery of sylvite, the desulfated bittern from the epsomite plant is solar concentrated to 1.31 specific gravity to remove halite and then to about 1.36 to recover carnallite with 18% sylvite. The carnallite is decomposed with water removing magnesium chloride and simultaneously crystallizing sylvite, and some halite, due to common-ion effect. The sylvinite salt containing 55% sylvite is leached by hot solution and filtered hot to separate halite, then surface cooled to crystallize sylvite 97 + % pure.

Up to 70% of the magnesium sulfate and 85% of the sylvite are recovered as high-grade marketable products.

INTRODUCTION

From the standpoint of an ore reserve, it can be said that seawater contains a low grade ore which necessarily has to be concentrated by evaporation of the molecules of water present in it. Because of very favourable weather conditions in many areas of the world, it seems reasonable to think of solar evaporation as the most economical process for the concentration.

Seawater bittern is obtained as a by-product from the

salt industry and saline water conversion plants. However, with few exceptions, these rich ores are wasted back to the sea.

Some interesting separation methods for recovering several chemicals from seawater have been proposed (Salutsky, et al., 1963; Weinberger, et al., 1964; Tallmadge, et al., 1964; Garrett, 1969; De Pree, 1969; Glassett, 1970; and Burns and Roe, 1971), but none of them to the date have been broadly successful.

The specific recovery of epsomite and magnesium chloride from seawater bittern has scarcely been studied (Galimberti, 1932; Rafols, et al., 1964; Grinstead, 1968; Glassett, 1970; Fernández, 1972).

The specific recovery of potassium values from seawater and its bittern has been extensively studied, but of all the methods proposed, none have been operated on commercial scale (Hildebrand, 1918; Johnstone, 1922; Niccoli, 1926; Tessler, 1951; Bhavnagary, et al., 1959; Hadzeriga, 1963; Kenat and Sadam, 1965; Salutsky, et al., 1966; Hadzeriga, 1966; Block, et al., 1968, and Georgy, 1968).

Most of the known methods for the recovery of salts from seawater and seawater bitterns have been widely reviewed in the given literature, consequently this paper is devoted only to a new developed technology for the recovery of epsomite and sylvite, which for the first time promises a practical solution for the exploitation of seawater bittern from halite plants.

The seawater bittern as a source of chemicals

Three solar evaporation experiments were made simultaneously. The temperature variation was between 26 and 45°C. Chemical analysis of the solid and liquid phases and the determination of the optical properties of the solids under a polarized microscope made possible to trace the approximate crystallization pattern for natural solar evaporation of seawater bittern. This pattern is shown in

TABLE I
Dynamic Crystallization Pattern for Seawater
and Great Salt Lake Bittern

Seawater Bittern	Great Salt Lake Bittern (Hadzeriga, 1966)
Calcium Carbonate	
Gypsum	
Halite + Gypsum (traces)	Halite
Halite + Epsomite + Schoenite (traces)	Halite + Schoenite
Halite + Epsomite + Schoenite (traces)	Halite + Schoenite + Epsomite
Halite + Epsomite + Kainite	Halite + Epsomite + Sylvite
Halite + Hydrates of Magnesium Sulfate + Carnallite	Halite + Hydrates of Magnesium Sulfate + Carnallite
Halite + Hydrates of Magnesium Sulfate + Carnallite + Bischofite	Halite + Hydrates of Magnesium Sulfate + Carnallite + Bischofite

Table I and compared with the crystallization pattern for Great Salt Lake bittern.

The dynamic equilibrium data presented in Table I are somewhat different from the static equilibrium results reported by Van't Hoff, 1903 and D'Ans, 1933; these discrepancies are due mainly to dynamic mixing and temperature fluctuation.

Cooling experiments made with Great Salt Lake Bittern (Done, 1938 and Glassett, 1970) consistently crystallized mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). However, when the same experiments were carried out with seawater bitterns always crystallized epsomite. This shift from mirabilite to epsomite is caused by a higher concentration of magnesium and lower concentration of sodium in the seawater bitterns when compared with bittern from Great Salt Lake. These differences are shown in Table II.

The sylvite concentration in seawater bittern compares favourably with those bitterns from Great Salt Lake in Utah; Bonneville in Utah, and the Dead Sea in Israel (Table II), all three are being used for sylvite production. However, sylvite recovery from seawater or seawater bittern has resisted all attempts for its economical recovery.

The near absence of sulfate in the bitterns from Bonneville and Dead Sea makes the recovery of sylvite and other chemicals easier. As for the small differences in composition between bitterns from seawater and Great Salt Lake, have already been mentioned above.

TABLE II
Composition of Bitterns from Bonneville, Dead Sea,
Great Salt Lake and Seawater Bittern Used in This Study

Components	Seawater	Great Salt Lake (Glassett, 1970)	Bonneville Dead Sea (Hadzeriga, 1966)
NaCl	14.5	18.4	24.0
MgCl ₂	8.3	2.7	1.2
KCl	1.9	2.1	1.2
MgSO ₄	6.0	5.4	0.3

After all the calcium carbonate, calcium sulfate, and 83% of the halite has been crystallized out from seawater by solar concentration, a bittern of a specific gravity of about 1.26 is obtained. The composition of the bittern used in this study, assuming a hypothetical combination of the ions, is shown in Table III. This bittern with few exceptions is placed back in to the sea. In some cases, as in Spain, it is used for recovering some epsomite, bischofite, and bromine, but not for the production of potassium salts.

Further concentration of seawater bittern yields complex series of different salts (Table I). These salts have resisted many attempts for economical recovery.

Figure 1 shows the quantity of different chemicals that could be recovered from the bittern of a one million ton halite salt plant from seawater. If all these products are sold at the present world price, the value would be quite large.

Desulfation of seawater bitterns

When seawater is evaporated, CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and halite are the first salts deposited. Up to 96% of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 83% of the halite may be recovered as high-grade product by solar evaporation of seawater to a specific gravity of 1.26. On further evaporation, a complex mixture of halite, sylvite, and double salts of potassium, sodium, and magnesium begin to crystallize; recovery of marketable products becomes difficult and inefficient. However, in the absence or near absence of sulfate, the bittern may be readily processed to recover high-purity sylvite and bischofite with excellent efficiency.

Sulfate may be removed from seawater by (1) cooling to crystallize the sulfate as epsomite, (2) precipitation of the sulfate as gypsum by addition of CaCl_2 , and (3) removal of sulfate as BaSO_4 with BaCl_2 . The addition of CaCl_2 or BaCl_2 is very effective, but is uneconomical unless a source of very low cost CaCl_2 or BaCl_2 is available.

SCOPE OF THE INVESTIGATION

The main objectives of the present investigation were:

1. To devise and to demonstrate in the laboratory and pilot plant a simple crystallization process for the separa-

TABLE III
Composition of the Seawater Bitterns
Used in This Study

Components	Composition, % Wt. Sp. Gr. 1.26	Composition, % Wt. Sp. Gr. 1.28	Composition, % Wt. Sp. Gr. 1.30
NaCl	14.50	6.87	3.25
MgCl ₂	8.32	12.15	14.81
KCl	1.91	2.66	3.40
MgSO ₄	6.00	7.15	7.95
MgBr ₂	0.18	—	—

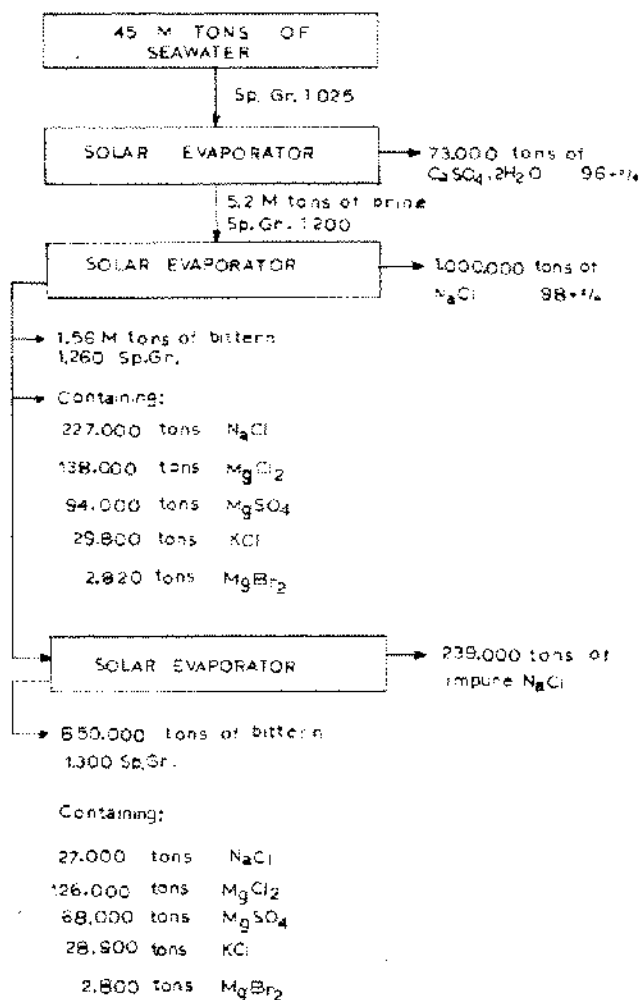


Figure 1. The Seawater Bittern from Halite Plants as Source of Chemicals.

tion and recovery of high purity epsomite and sylvite from sea bittern.

2. To determine the optimum variables of the developed process shown in Figures 4, 5 and 6, consisting of:

- Solar evaporation of the bittern from a halite plant to remove halite and to raise the magnesium concentration.
- Surface cooling to remove the sulfate ion and to crystallize and recover epsomite.
- Water dilution to prevent coprecipitation of halite, bischofite and sylvite.
- Solar evaporation to remove additional halite and some sulfate ion.
- Additional evaporation to recover carnallite.
- Decomposition of carnallite to recover sylvinite.
- Leaching of the sylvinite to separate the halite from the sylvite.
- Surface cooling to recover sylvite.

These two objectives have been met by the investigation summarized in this paper. The process outlined in the objectives was found to work efficiently.

EXPERIMENTAL WORK

General considerations

The evaporation steps were conducted in four large rectangular solar evaporation ponds. The evaporation proceeded under natural conditions with the temperature of the bitterns varying between 26 and 45°C.

The bitterns and their salts were harvested in the ponds by suction pumps and conveyed through plastic pipes to plastic lined thickeners. The thickened slurries were conveyed by centrifugal pumps to leaf-type filters and the solid crystalline salts were dried in direct-fired rotary driers.

The laboratory cooling steps were conducted by placing measured quantities of bitterns into a large rectangular cabinet cooled by an ammonia plant. The temperature was decreased in a stepwise manner. After each temperature increment, the bittern was separated from the salt by suction filtration within the cold atmosphere of the freezer cabinet. The bitterns were maintained at each temperature a minimum of 15 minutes; this time was varied up to several hours. The plastic containers that held the bittern samples being cooled were covered with sheets of plastic to reduce evaporation during cooling.

The ionic composition of the liquid and solid phases was determined as follows: Ca^{++} and Mg^{++} volumetrically with E.D.T.A.; K^{+} and Na^{+} by flame photometry; $\text{SO}_4^{=}$ and $\text{CO}_3^{=}$ by ordinary gravimetric methods, and Cl^{-} volumetrically with silver nitrate. These procedures are outlined by Rafols (1969).

The identification of the solid phases was done with a microscope under polarized light.

Seawater bittern tests without dilution

The test was begun by cooling 10 liters of 1.30 specific gravity bittern in a stepwise manner to 10°C, 5°C, 0°C, -5°C, and -10°C. The small crop of crystals obtained at 10°C consisted mainly of halite. The larger crop of crystals obtained at the other temperatures consisted of a mixture of epsomite, halite, sylvite, and magnesium chloride. The results are summarized in Figure 2. It is important to observe that mirabilite did not form at any temperature.

The test was repeated for different cooling periods and it was observed that the total recovery increases to a maximum with increasing cooling time, and then levels off.

Tests were also conducted with bitterns of specific gravity 1.26 and 1.28, but the epsomite salts recovered were too contaminated to be of marketable value, in addition the recuperation was inefficient. Only the most promising

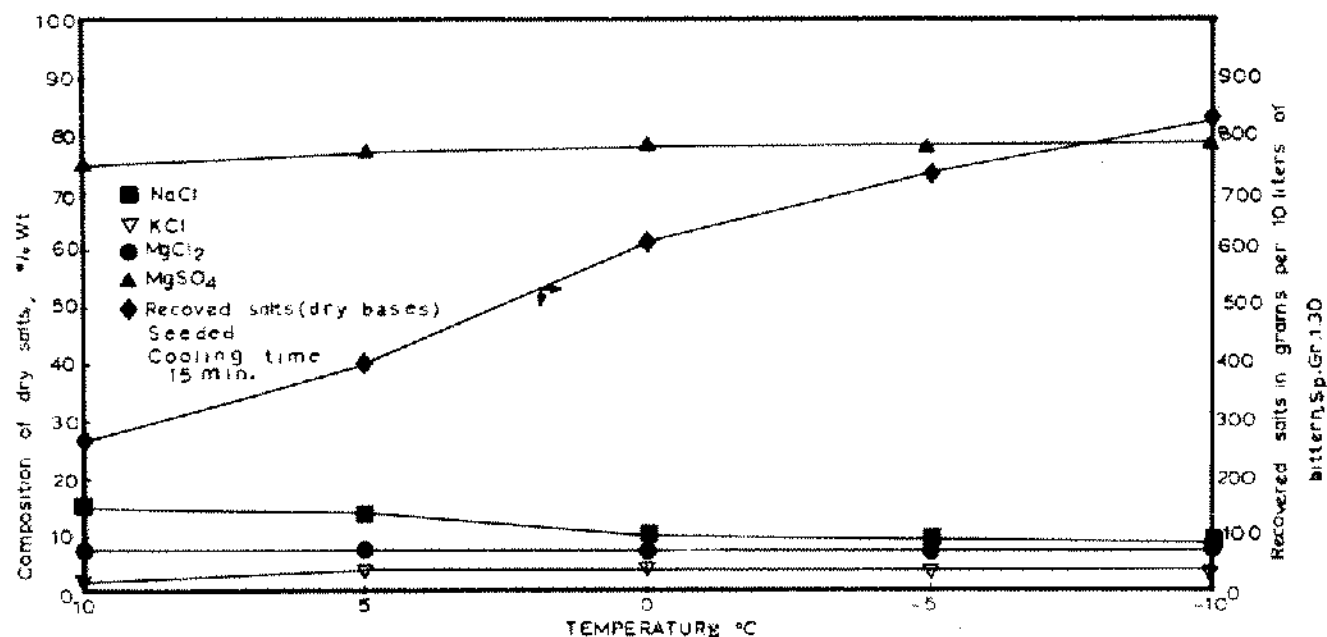


Figure 2. Composition and Amount of the Dry Salts Recovered from Seawater Bittern by Cooling Without Dilution.

results obtained with 1.30 specific gravity bittern are presented in order to save space.

Seawater bittern test with dilution

The test was begun by diluting 10 liters of seawater bittern of specific gravity of 1.30 with 5% volume of fresh water, and then cooling it stepwise to 10°C, 5°C, 0°C, -5°C and -10°C. The small crop of salts obtained at 10°C were principally epsomite plus some halite and magnesium chloride. The salts recovered at the other temperatures were nearly pure epsomite. The results are presented in Figure 3.

The test without dilution shows that it is more efficient to desulfate bitterns by cooling without dilution, but the epsomite recovered is too contaminated by other salts to be a marketable product. About 80% by weight of the sulfate originally present in the bittern may be recovered as epsomite, by cooling the bittern to -10°C.

General description of the process for desulfating seawater bittern and recover epsomite

The choice of the cooling method for desulfation of seawater bittern to prepare it for the recovery of sylvite was made on the basis of the results obtained in the course of this investigation. These results proved: a) that to prepare the bittern for sylvite recovery it was only necessary to remove 70% of the sulfate ion present in the bittern; b) Cooling the seawater bittern to -5°C removes about 70% of the sulfate ion and c) The sulfate ion could be recovered as high grade epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), the value of which may defray the cost of freezing.

A question often arises regarding the choice of surface

cooling instead of vacuum cooling. Actually vacuum cooling is efficient only to a terminal temperature of about 5°C and it is impossible to cool below 0°C by this method. To remove 70% of the sulfate ion present in the seawater bittern it is necessary to cool the bittern to -5°C. Therefore the surface cooling system was chosen.

In brief, the process comprises a concentration of the seawater saltfield bittern from a specific gravity of 1.26 to 1.30 in solar evaporation ponds. This step raises the magnesium concentration and reduce the sodium and sulfate. The bittern with a specific gravity of 1.30 is diluted with 5% volume of fresh water to prevent coprecipitation of halite and sylvite with the epsomite and then cooled to -5°C.

The cooling system for desulfating and recovering epsomite salt from seawater bittern is shown in Figure 4. About 70% of the sulfate present in the bittern is recovered as epsomite by cooling the bittern from 30°C to -5°C. To cool 1,000 liters per hour of 1.30 specific gravity diluted bittern, and to crystallize 120 kg of epsomite requires about 35,000 kcal of refrigeration. About 65% of the refrigeration is provided by the ammonia plant and the rest 35% is recovered through heat exchange from the desulfated bittern before it is conveyed to the carnallite plant.

Four heat exchangers and two ammonia coolers are used. The heat exchangers and coolers are home made. Each unit consists of an insulated 4.5 m long and 10 cm diameter tube with a 7.5 cm tube in the inside. The bittern flows through the inner tube, which is equipped with rotating scraper to prevent the salts from building up in

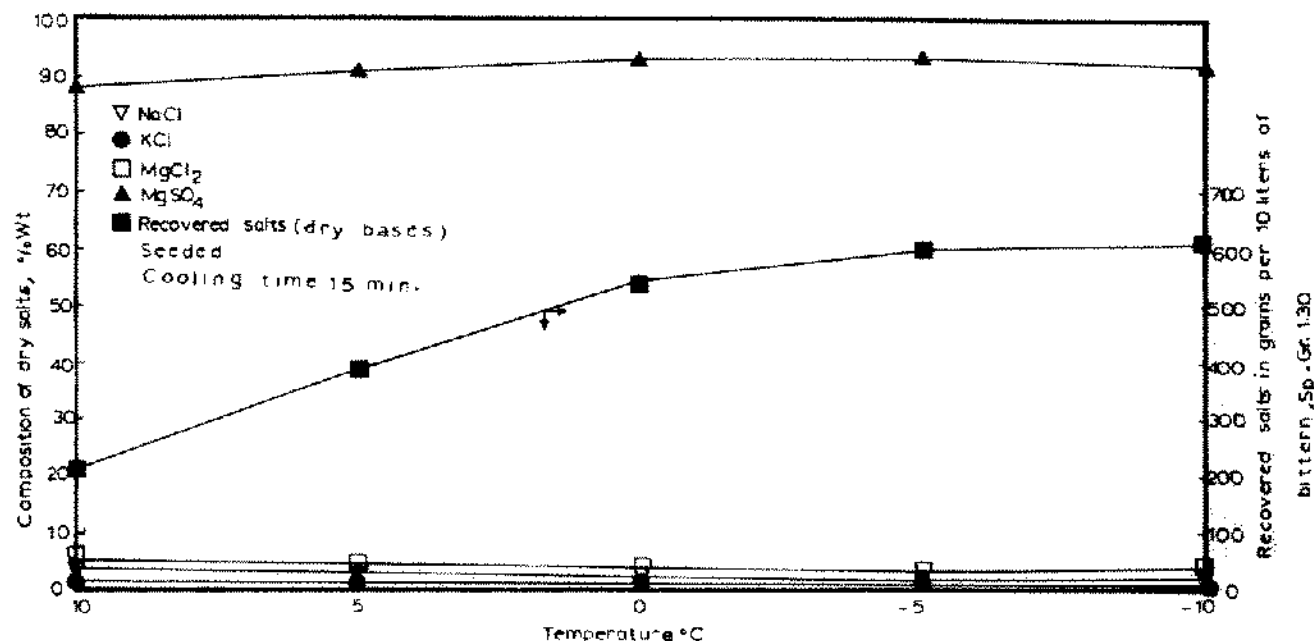


Figure 3. Composition and Amount of the Dry Salts Recovered from Seawater Bittern by Cooling with Dilution.

the tubes and at the same time to improve heat transfer and increase crystal growth.

The flow of bittern is countercurrent to the cold desulfated bittern in the annular space and the four heat exchangers are operated in series. Ammonia is the refrigerant in the annular space of the coolers. The bittern passes through the heat exchangers and coolers and is discharged to the insulated plastic lined thickener.

The thickened slurry is conveyed by a centrifugal pump to a leaf-type insulated filter, where the epsomite is filtered and washed with cool water.

The washed epsomite salt from the filter is discharged into a rotary drier and dried at 70°C. The composition of the dried epsomite is presented in Table IV.

The filtrate and washings from the filter are combined and pumped through the (1a) heat exchanger to the solar evaporator. In this way no magnesium sulfate is lost by dilution. The overflow from the thickener is pumped through the three heat exchangers in countercurrent with the feed. The desulfated bittern is conveyed to the carnallite plant.

TABLE IV
Composition of the Epsomite Salt
Recovered from Seawater Bittern

Components	Composition, % Wt.	
	Industrial Grade	Technical Grade
MgSO ₄ ·7H ₂ O	96.10	99.00
MgCl ₂ ·6H ₂ O	1.50	0.20
NaCl	2.20	0.08
KCl	0.20	0.00

Recovery of carnallite from seawater bittern

The partially desulfated seawater bittern obtained from the epsomite plant is readily amenable for recovering sylvite and magnesium chloride hexahydrate by a combination of solar evaporation and fractional crystallization.

The system for recovering the carnallite is shown in Figure 5. The bittern from the epsomite plant is concentrated in a solar evaporation pond to a specific gravity of 1.31. Between the specific gravity interval of 1.21 and 1.26 no crystals form. By continuing the evaporation to the specific gravity of 1.31 a crystal crop of halite contaminated with sulfate, magnesium and sylvite is obtained. The bittern is conveyed to a second evaporation pond and evaporated to about 1.36 specific gravity, yielding a crop of carnallite. The carnallite and bittern are conveyed to a thickener. The thickened slurry is conveyed by a centrifugal pump to a leaf type filter, where the carnallite salt mixture is separated from the bittern. The filtrate and the overflow from the thickener are conveyed to a solar evaporation pond in the bischofite plant. An approximate analysis of the carnallite salt mixture and residual bittern are shown in Table V.

The sylvite concentration in the carnallite salt mixture as shown in Table 5 compares favorably with carnallite from the Dead Sea and other sources at present being used for potash production. The carnallite residual bittern is very rich in bischofite.

Decomposition of carnallite

In order to produce marketable sylvite from carnallite (KCl·MgCl₂·6H₂O), the magnesium chloride should be

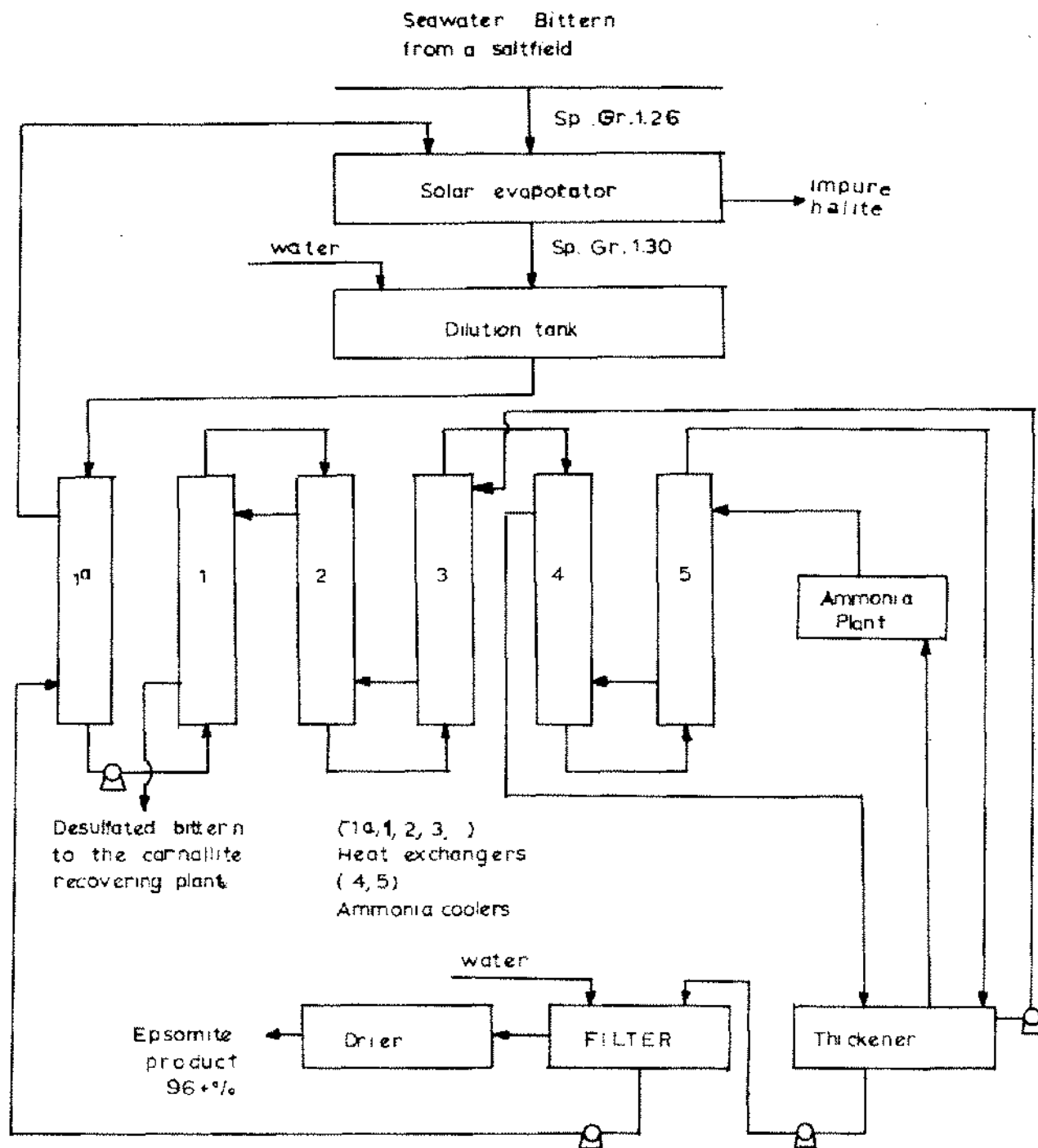


Figure 4. Flow Diagram of the Process for Desulfating Seawater Bittern and Recovering Epsomite.

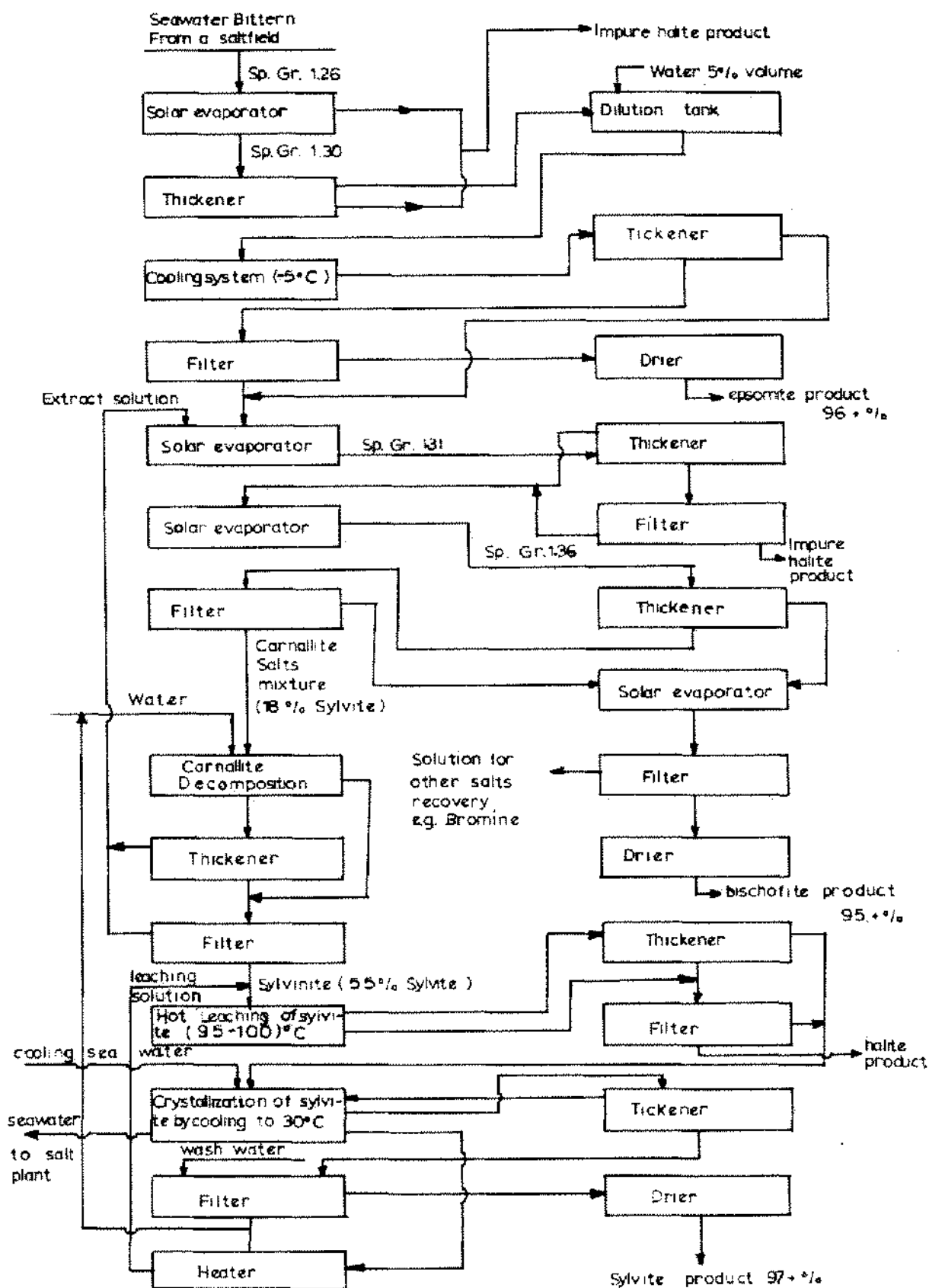


Figure 5. Flow Diagram of the Process for the Recovery of Epsomite, Sylvite and Bischofite from Seawater Bittern by Crystallization.

TABLE V

Composition of the Carnallite Salt Mixture and Carnallite Bittern Obtained by Solar Concentration of Seawater Bittern from the Epsomite Plant

Components	Composition, % Wt. Carnallite Salt Mixture	Composition, Grams/liter Carnallite Bittern
KCl	18.66	3.25
NaCl	12.25	2.96
MgCl ₂	31.15	340.10
MgSO ₄	2.98	5.25
CaCl ₂	0.30	32.50
H ₂ O	34.60	—

removed first, by making use of the equilibrium that exists between carnallite, sylvite and halite in its saturated solution. Such a solution is much richer in magnesium chloride than in sylvite, the actual ratio at 30°C being about 7.8. Then solutions of a system containing magnesium chloride, and sylvite at lower ratio are in equilibrium with sylvite and halite only, and may decompose carnallite salts. Some magnesium sulfate is present in the carnallite salt mixture, but it does not affect the decomposition process.

The decomposition steps are illustrated in Figures 5 and 6. The carnallite salt mixture from the filter is discharged by gravity into a countercurrent three stage extractor. Fresh water at 30°C is brought into contact with the carnallite salt in such quantities that the resulting solution contains most of the magnesium chloride and magnesium sulfate present in the carnallite salt mixture. About 55% by weight of water was necessary for complete decomposition of the carnallite salt. In each stage the carnallite salt is contacted with a solution containing magnesium, potassium sulfate and sodium chloride. As carnallite dissolves in each stage, sylvite and halite crystallize out, until at the first stage the extract composition has reached about the 7.8 ratio.

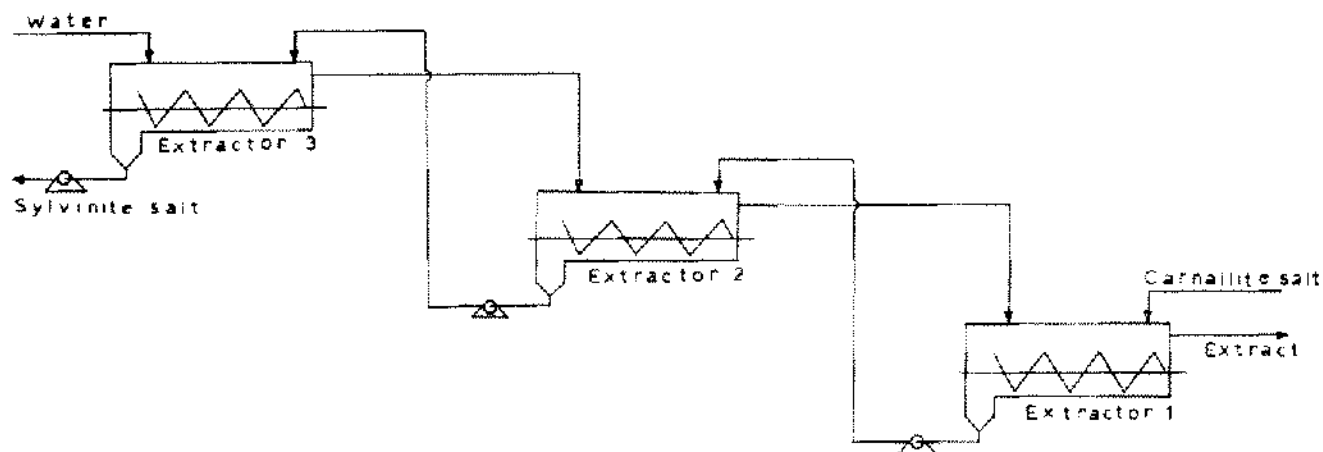


Figure 6. Flow Diagram for the Recovery of Sylvinite by Decomposition of Carnallite.

The extract solution is discharged into a thickener. The slurry together with the sylvite salt from the extractor are conveyed to a leaf-type filter, where the sylvite is separated from the bittern. The filtrate and overflow from the thickener are passed back to the evaporation pond. In this way no potassium is lost.

The decomposition of carnallite salt is carried out in the extractor shown in Figure 6, consisting of three rectangular vessels equipped with spiral stirrers. The purposes of the stirrers are to lift the crystals formed through the solution and to convey them to the pump. In this manner the crystals grow while they are freely suspended in the liquid and therefore are very uniform in size.

The extract solution contains about 24% of the sylvite present in the carnallite, and about 0.9 liter of extract solution is produced per kg of carnallite decomposed.

The carnallite decomposition system was designed to decompose 250 kg of carnallite salt per hour, yielding 70 kg of sylvinite salt.

The approximate composition of the salt crystals (sylvinite) and extract solution are summarized in Table VI. The results show that the concentration of sylvite has raised from 18% to about 55%.

Recovery of sylvite from sylvinite salt by leaching and crystallization

The recovery of sylvite from sylvinite (KCl-NaCl) is based upon the temperature solubility relationships of the sylvite and halite. For sylvite the solubility increases rapidly as the temperature raises, however the solubility of halite is only slightly more soluble in hot than in cold water. In the presence of sylvite the solubility of halite actually was found to decrease slightly at higher temperature. These results are shown in Table VII.

The sylvinite leaching system is shown in Figure 5. The sylvinite salt from the decomposition of carnallite is conveyed to a countercurrent three stage extractor, externally heated to keep the temperature at 100°C. A solution

TABLE VI
Composition of the Salt Mixture (Sylvinite) and
Extract Solution Obtained by Decomposition of Carnallite

Components	Composition, % Wt. Sylvinite Salt Mixture	Composition, Grams/liter Extract Solution
KCl	55.15	51.25
NaCl	30.80	41.13
MgCl ₂	2.95	295.40
MgSO ₄	0.90	84.15
H ₂ O	10.45	—

TABLE VII
Solubility of Halite and Sylvite in the System Halite-
Sylvite-Water at 35°C and at 100°C

Components	Composition, gr. 35°C	Composition, gr. 100°C
KCl	177	349
NaCl	290	275
H ₂ O	1,000	1,000

at 100°C with a composition about that shown in Table VIII is brought into contact with the sylvinite salt. The extractor is kept close to reduce water losses by evaporation. A plastic lined thickener is used for solution separation and the halite is separated by filtration. Both the thickener and filter are insulated and kept at 100°C by external heating.

The filtrate from the halite filter and overflow solution from the thickener at 100°C are cooled in tubular heat exchangers. The cooling system is similar to that shown in Figure 4, but using seawater as coolant. The solution is flowing through the inner tubes which are equipped with rotating scraper ribbons to keep the sylvite crystals from building up in the tubes. The residence time in the cooling system is dictated by the sylvite crystal size desired.

The cooled solution and salts from the heat exchangers and coolers are conveyed to a thickener. The slurry from the thickener is conveyed by centrifugal pumps to a filter, where the sylvite is filtered and washed.

The overflow solution from the thickener and filtrate from sylvite filter are pumped through the heat exchangers in countercurrent with the feed, then passed to a heater, heated to about 100°C and reused.

The concentration of magnesium chloride and sulfate in the extract solution from the leaching process increases somewhat and this increase in turn decreases the solubility of halite and sylvite; for this reason some solution must be bled off. The bleed is returned to the decomposition plant. In this way no potassium or magnesium is lost. Some make-up water is needed to cover the losses by evaporation and bleeding. This water is added as washing water to the filter.

The sylvite plant was designed for treating 100 kg of

sylvinite salt per hour, yielding about 50 kg of sylvite. The sylvinite leaching system is the same as that used for carnallite decomposition shown in Figure 6.

To cool 500 liters of sylvinite leaching solution per hour and to crystallize 56 kg of sylvite salt requires about 20,000 Kcal of refrigeration. 14,000 Kcal are provided by seawater and the remaining 6,000 Kcal are recovered through heat exchange from the sylvinite cooled solution before it is reheated and reused.

The composition of the washed and dried sylvite salt and equilibrium solution obtained by leaching the sylvinite salt is presented in the Table VIII.

TABLE VIII
Composition of Sylvite Salt and Equilibrium Solution

Components	Composition, % Wt. Sylvite Salt Mixture	Composition, Grams/liter Equilibrium Solution (35°C)
KCl	97.24	161.45
NaCl	1.76	262.20
MgCl ₂	0.50	25.66
MgSO ₄	0.10	5.10
H ₂ O	0.32	—

In the overall operation was recovered about 85% of the sylvite (KCl) from the total quantity present in the feed bittern.

The choice of surface cooling instead of vacuum cooling, which is commonly used in similar crystallization problems, was made based on the results of experimental research on potassium chloride crystallization carried out by the author. This research proved that it was possible to recover high-purity sylvite with excellent efficiency in the form of very uniform crystals by surface cooling.

The choice of crystallization instead of flotation for the separation of sylvite from halite was made on the basis that crystallization offers the advantages of being simpler, cheaper and producing better product as far as purity and crystal size is concerned.

Recovery of bischofite from seawater bittern by solar evaporation

The residual bittern from the carnallite solar ponds with a specific gravity of 1.36 is further evaporated to a specific gravity of 1.75 bringing about the crystallization of bischofite. Because of the very low vapor pressure of the bittern a suitable climate is necessary. The bischofite separated from the bittern by filtration and dried at 70°C was 95 + % pure.

CONCLUSIONS

It has been shown in this study that in spite of the very complex phase chemistry of seawater bittern, a simple

crystallization method may be employed for the efficient recovery of high purity epsomite and sylvite.

From the results presented in this work it is quite evident that the process developed offers enough incentive to utilize it for the recovery of epsomite and sylvite salts from seawater bittern.

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