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H. Gurbuz[a]; N. Yavasoglu[a]; A. N. Bulutcu[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, ISTANBUL TECHNICAL UNIVERSITY, MASLAK-ISTANBUL, TURKEY

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Recovery of Potassium Salts from Bittern by Potassium Pentaborate Crystallization

H. GURBUZ,* N. YAVASOGLU, and A. N. BULUTCU
DEPARTMENT OF CHEMICAL ENGINEERING
ISTANBUL TECHNICAL UNIVERSITY
80626 MASLAK-ISTANBUL, TURKEY

ABSTRACT

A new process for recovering the potassium content from bittern is developed in this study. In the process, the potassium content of bittern is crystallized as potassium pentaborate octahydrate by the addition of sodium pentaborate. The equilibrium conditions of potassium pentaborate octahydrate crystallization are examined as functions of the amount and concentration of sodium pentaborate solution and temperature. It is found optimum crystallization conditions are at 15°C by using a sodium pentaborate solution saturated at 25°C. At these conditions about 65% of the potassium content can be easily recovered as potassium pentaborate octahydrate, which is easily converted into any desired potassium salt.

Key Words. Potassium pentaborate; Bittern; Selective crystallization

INTRODUCTION

Potassium salts are one of the main constituents of NPK fertilizers. Bittern, which is the mother liquor of common salt production from seawater, can be regarded as a potential source of potassium salts, especially in countries where there is not another potash source. Several methods

* To whom correspondence should be addressed at Department of Chemical Engineering, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey. Telephone: 90-212-2856837. FAX: 90-212-2852925. E-Mail: KMGURBUZ@TR.ITU.BITNET

have been proposed for the production of potassium salts from bittern. These methods can be divided into three main groups:

1. Fractional crystallization methods by evaporation (1–4)
2. Selective precipitation or crystallization methods by the addition of a chemical which forms a sparingly soluble salt with potassium (5–7)
3. Salting-out crystallization methods by the addition of another water-miscible soluble solvent (8, 9)

There are many problems in reaching an economical feasible method to produce potassium salts from bittern. These problems were discussed in a previous study (10). Although fractional crystallization by evaporation is thought to be the best method, the solid phase obtained by this method is very complex in composition. The necessity of further treatment of the solid phase to obtain a desired product makes this method unfavorable. Selective precipitation by the addition of a chemical agent, such as dipycrylamine (5), sodium bismuth thiosulfate (6), or calcium perchlorate (7), is expensive since these chemicals cannot be recovered efficiently during the process. This is true also for salting-out crystallization by using methanol (8). However, the recovery of potassium salts by using this method were successfully performed when ammonia was used as a solvent (9).

Selective crystallization of a potassium salt from bittern by using a relatively cheap and easily recoverable chemical will provide an economical method. Potassium pentaborate is considered by many authors in their patents as an intermediate compound to obtain various potassium salts from KCl. Hackspill et al. (11) proposed a method to obtain any potassium compound from natural KCl by using H_3BO_3 with or without ammonia addition. They prepared not only potassium salts but also KOH and K_2CO_3 from the obtained potassium pentaborate. Newman (12) prepared potassium pentaborate from borax, sulfuric acid, and potassium chloride. In another patent, potassium pentaborate was prepared from borax, potassium chloride, and carbon dioxide (13). Almost all the previous studies dealing with potassium pentaborate crystallization depend on the use of a potassium salt, especially potassium chloride, as the potassium source. In the present study the recovery of the potassium content of bittern by selective crystallization of potassium pentaborate was the goal. Potassium recoveries in earlier studies were generally high since the potassium source was used as the solid form or as a saturated solution. However, bittern is dilute in potassium concentration and contains many other ions in a complex nature. The method suggested in the present study consists of the treatment of bittern with a sodium pentaborate solution to form potassium pentaborate, and crystallization of this salt at a constant temperature.

In the $Na_2O/B_2O_3/H_2O$ system, the solubility of the sodium pentaborate decahydrate is higher than the solubility of the other sodium borates. On the contrary, in the $K_2O/B_2O_3/H_2O$ system the solubility of the potassium pentaborate octahydrate is lower than of the other potassium borates (14). Since both of these salts are dissolved congruently, their solubilities can be examined as simple salts. Figure 1 shows the solubilities of these salts as functions of temperature. According to Fig. 1, potassium pentaborate octahydrate can be crystallized depending on the concentrations of potassium and pentaborate ions when a sodium pentaborate solution is added to a solution containing potassium ions. Other ions available in the solution are expected to depress the solubility of potassium pentaborate octahydrate.

Sodium pentaborate solution is prepared from borax and boric acid (or another acid stronger than boric acid, such as sulfuric acid, nitric acid, etc.) according to the reaction

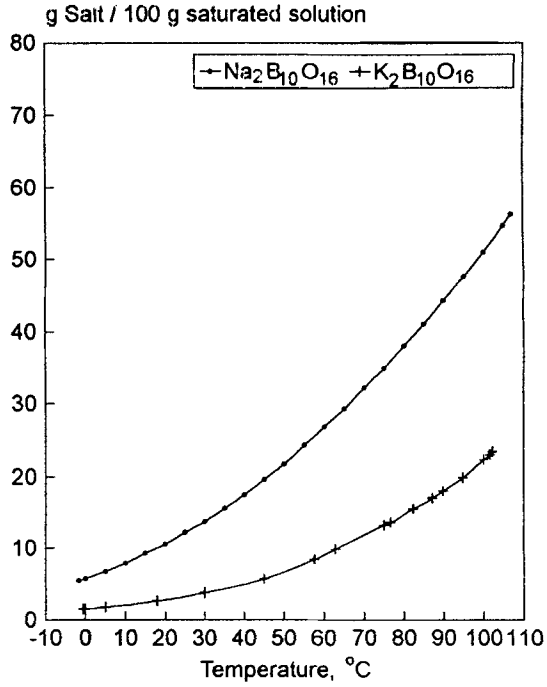

FIG. 1 Solubilities of $Na_2B_{10}O_{16}\cdot 10H_2O$ and $K_2B_{10}O_{16}\cdot 8H_2O$ in water as a function of temperature (15, 16).

$$Na_2B_4O_7 \cdot 10H_2O + 6H_3BO_3 + xH_2O \rightarrow Na_2B_{10}O_{16} + (19 + x)H_2O \quad (1)$$

Potassium pentaborate octahydrate crystals, which can be obtained from the treatment of bittern with the sodium pentaborate solution, can be easily converted into any desired potassium salt, for example, to K_2SO_4, according to the reaction

$$K_2B_{10}O_{16} \cdot 8H_2O + H_2SO_4 + 6H_2O \rightarrow K_2SO_4 + 10H_3BO_3 \quad (2)$$

If these reactions are compared with the reaction take place during boric acid production from tincal ore (Eq. 3), it is obvious that the suggested method is very similar to the boric acid production except that any desired potassium salt is obtained as a secondary product instead of sodium sulfate.

$$Na_2B_4O_7 \cdot 10H_2O + H_2SO_4 \rightarrow Na_2SO_4 + 4H_3BO_3 + 5H_2O \quad (3)$$

In both processes 4 mols of H_3BO_3 per mol of H_2SO_4 are obtained. The main advantage of the suggested process is the recovery of potassium from the bittern with an additional step in the boric acid production from tincal ore. In the crystallization of potassium pentaborate from bittern by using sodium pentaborate solution, the boron content of the mother liquor will increase. Therefore, boron in the mother liquor should be recovered before discharging this liquor. This can be achieved by various methods. These are:

1. Precipitating boron as practically insoluble magnesium metaborate, $Mg(BO_2)_2$, by means of magnesium available in the mother liquor of potassium pentaborate crystallization. Magnesium metaborate can be converted to boric acid and any desired magnesium salt by reacting with an acid (14).
2. Precipitating boron as calcium borate by lime addition to the mother liquor of potassium pentaborate crystallization, since the solubility of calcium borates is very low (14).
3. Recovery of boron from the mother liquor by solvent extraction. Solvent extraction methods using long-chain diol compounds are practised on an industrial scale for these kinds of solutions (17).
4. Recovery of boron by using boron-specific ion exchanger resins (18).

The first method is the most promising since it does not require the use of any additional chemical. A flow chart of our suggested process is given in Fig. 2.

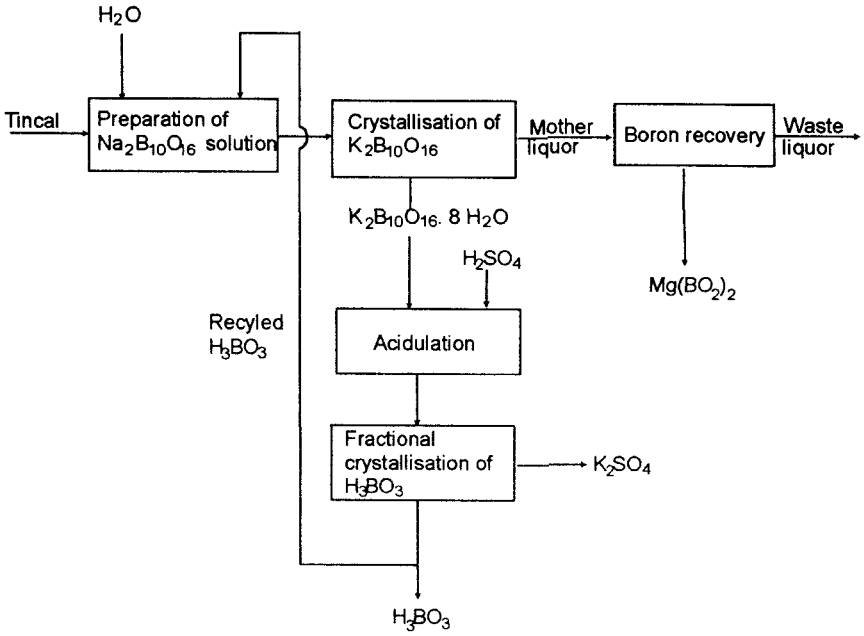

FIG. 2 Flow chart of the suggested process.

EXPERIMENTAL

Bittern remaining from common salt production in Çamalti Saltwork in Turkey was used for this study. A detailed analysis of this bittern is given in Table 1, in which the concentration ranges of various ions from different bitterns are also given for comparison. The other chemicals were of analytical grade. Distilled water was used in all experiments.

In the crystallization of potassium pentaborate, given amounts of bittern and sodium pentaborate solutions (or borax and boric acid mixtures) were introduced to a covered flask, and the flask was shaken in a thermostatted shaker-bath for a sufficient time to reach equilibrium. Then the mother liquor was separated from the solid phase by filtration and the composition of each phase was determined by chemical analysis. In order to prevent any possible alteration in equilibrium composition of the solid phase, the adhering mother liquor was not removed by any washing step.

TABLE 1
Analysis of the Bittern

Ingredient	Composition (g/L)	
	Camalti Saltwork	Various bitterns (10)
Na^+	56.0	44.5–67.0
K^+	12.0	8.9–14.3
Mg^{2+}	47.4	36.9–56.2
SO_4^{2-}	59.2	50.0–75.8
Cl^-	183.2	180–188.3
B^{3+}	0.0159	[a]
Density (g/cm^3)	1.2573	

[a] Boron content was not given in the literature.

In order to determine the optimum conditions of the crystallization of potassium pentaborate from bittern, the following three factors should be examined:

1. Amount of the sodium pentaborate which should be added to the given amount of bittern
2. Concentration of the sodium pentaborate solution
3. Crystallization temperature

Sodium and potassium were determined by using a Eppendorf Model Flame Photometer (19). Magnesium was determined by complexometric titration with a standard EDTA (ethylenediaminetetraaceticacid disodium salt) solution in the presence of eriochrome black T indicator (20). For the determination of sulfate, the classical barium sulfate method was used (21). Chloride was determined by titration with a standard $Hg(NO_3)_2$ solution in the presence of a mixed indicator solution consisting of diphenyl carbazone and bromphenol in ethyl alcohol (22). Boron was determined by titration of boric acid with a standard base in the presence of mannitol (23).

RESULTS AND DISCUSSION

In the first series of experiments, the amount of sodium pentaborate was changed whereas the concentration and the crystallization temperature were kept constant. These experiments were repeated with sodium pentaborate solutions saturated at 25, 35, and 70°C, and with the mixture of borax and boric acid, the composition of which fits the composition of a sodium pentaborate solution saturated at 105°C. In all of these experi-

TABLE 2
Crystallization of Potassium Pentaborate from Bittern by Using Sodium Pentaborate Solution Saturated at Approximately 25°C[a]

Expt.	Amount of $Na_2B_{10}O_{16}$ solution (g)	Amount of the obtained phases (g)		Composition of the obtained phases (wt%) Na^+	K^+	Mg^{2+}	B^{3+}	SO_4^{2-}	Cl^-	Density (g/cm³)
1	81.14[b]	Solid	3.05	0.17	12.88	0.17	18.12	0.00	0.53	
		Liquid	203.53	3.06	0.48	2.32	1.17	2.90	8.48	1.1861
2	109.07[b]	Solid	3.95	0.23	12.67	0.18	17.39	0.14	0.64	
		Liquid	230.54	2.99	0.37	1.94	1.29	2.44	7.56	1.1719
3	135.10[c]	Solid	5.72	1.03	8.60	0.70	12.48	1.27	2.64	
		Liquid	254.95	2.82	0.36	1.77	1.54	2.33	6.89	1.1629
4	162.42[c]	Solid	4.29	0.18	12.75	0.14	17.44	0.78	0.34	
		Liquid	283.53	2.72	0.31	1.64	1.72	2.17	6.48	1.1478
5	187.75[c]	Solid	5.41	0.25	12.27	0.19	16.63	1.13	0.55	
		Liquid	307.79	2.62	0.26	1.51	1.87	2.00	5.82	1.1375

[a] Amount of bittern = 125.73 g. Crystallization temperature = 25°C.
[b] Na = 1.372 wt%, B = 3.249 wt%.
[c] Na = 1.570 wt%, B = 3.830 wt%.

ments, the crystallization temperature was kept as 25°C. The experimental conditions and the results are given in Tables 2, 3, 4, and 5.

Figure 3 shows the compositions of the pure solid phases as functions of the $Na_2B_{10}O_{16}$/K weight ratio and of the concentration of $Na_2B_{10}O_{16}$

TABLE 3
Crystallization of Potassium Pentaborate from Bittern by Using Sodium Pentaborate Solution Saturated at Approximately 35°C[a]

Expt.	Amount of $Na_2B_{10}O_{16}$ solution (g)	Amount of the obtained phases (g)		Composition of the obtained phases (wt%) Na^+	K^+	Mg^{2+}	B^{3-}	SO_4^{2-}	Cl^-	Density (g/cm³)
6	54.53[b]	Solid	3.03	0.16	12.67	0.15	18.00	1.60	0.39	
		Liquid	176.84	3.69	0.52	2.56	1.09	2.94	10.29	1.2181
7	82.28[b]	Solid	9.88	1.05	4.19	3.09	12.59	1.49	2.70	
		Liquid	197.68	3.60	0.45	2.20	1.20	3.11	9.10	1.1521
8	111.53[c]	Solid	16.58	0.94	3.08	3.19	13.38	1.86	2.34	
		Liquid	220.12	3.22	0.23	1.83	1.40	2.63	8.11	1.1870
9	138.84[b]	Solid	20.57	0.68	3.99	3.28	14.43	0.84	1.63	
		Liquid	243.47	3.16	0.26	1.60	1.36	2.47	7.38	1.1547
10	166.13[c]	Solid	22.92	0.81	1.28	4.27	13.43	2.21	1.73	
		Liquid	268.67	3.11	0.18	1.47	1.77	2.27	6.64	1.1062

[a] Amount of bittern = 125.73 g. Crystallization temperature = 25°C.
[b] Na = 1.880 wt%, B = 4.360 wt%.
[c] Na = 12.175 wt%, B = 4.790 wt%.

TABLE 4
Crystallization of Potassium Pentaborate from Bittern by Using Sodium Pentaborate Solution Saturated at Approximately 70°C[a]

Expt.	Amount of $Na_2B_{10}O_{16}$ solution (g)	Amount of the obtained phases (g)		Composition of the obtained phases (wt%) Na^+	K^+	Mg^{2+}	B^{3+}	SO_4^{2-}	Cl^-	Density (g/cm³)
11	30.80[b]	Solid	11.99	1.35	4.20	3.64	14.31	1.41	3.62	
		Liquid	144.20	4.45	0.62	2.93	0.94	4.08	2.28	1.2407
12	51.56[b]	Solid	39.25	1.89	1.06	3.75	12.10	1.98	4.32	
		Liquid	137.63	4.76	0.54	2.23	0.95	3.61	11.13	1.2194
13	92.98[b]	Solid	64.74	1.83	0.95	3.34	12.94	0.97	3.55	
		Liquid	153.46	4.90	0.45	1.70	1.08	3.50	10.20	1.2035
14	125.97[b]	Solid	98.62	2.21	0.86	2.97	12.63	1.45	3.61	
		Liquid	152.80	5.45	0.38	1.22	1.18	3.12	9.52	1.1962

[a] Amount of bittern = 125.73 g. Crystallization temperature = 25°C.
[b] Na = 3.618 wt%, B = 8.495 wt%.

solution. These compositions were calculated from the wet solid phase compositions given in Tables 2, 3, 4, and 5. In these calculations chloride was accepted as the key constituent, since it does not precipitate under the working conditions. According to Fig. 3(A), reasonably pure potassium pentaborate octahydrate can be crystallized from the bittern in a wide

TABLE 5
Crystallization of Potassium Pentaborate from Bittern by Using Sodium Pentaborate Solution Saturated at Approximately 105°C[a]

Expt.	Amount of $Na_2B_{10}O_{16}$ solution (g)	Amount of the obtained phases (g)		Composition of the obtained phases (wt%) Na^+	K^+	Mg^{2+}	B^{3+}	SO_4^{2-}	Cl^-	Density (g/cm³)
6	16.37[b]	Solid	9.68	1.81	7.65	1.48	11.51	2.12	5.28	
		Liquid	132.34	4.66	0.48	3.36	1.21	4.42	13.40	1.2585
7	19.70[b]	Solid	14.04	1.94	5.61	2.39	11.43	1.75	5.34	
		Liquid	131.32	4.83	0.38	3.32	1.15	4.32	13.33	1.2661
8	26.23[b]	Solid	34.02	4.06	1.53	3.57	8.90	2.52	9.01	
		Liquid	117.87	5.27	0.70	2.87	0.85	4.42	13.45	1.2593
9	32.81[b]	Solid	38.19	2.17	1.16	3.63	11.10	1.78	5.00	
		Liquid	120.29	5.58	0.69	2.74	0.83	4.43	13.35	1.2543
10	40.86[b]	Solid	53.43	2.39	1.02	3.46	10.58	1.88	5.28	
		Liquid	113.13	6.63	0.74	2.77	0.95	4.71	14.75	1.2512

[a] Amount of bittern = 125.73 g. Crystallization temperature = 25°C.
[b] Na = 6.137 wt%, B = 14.408 wt%.

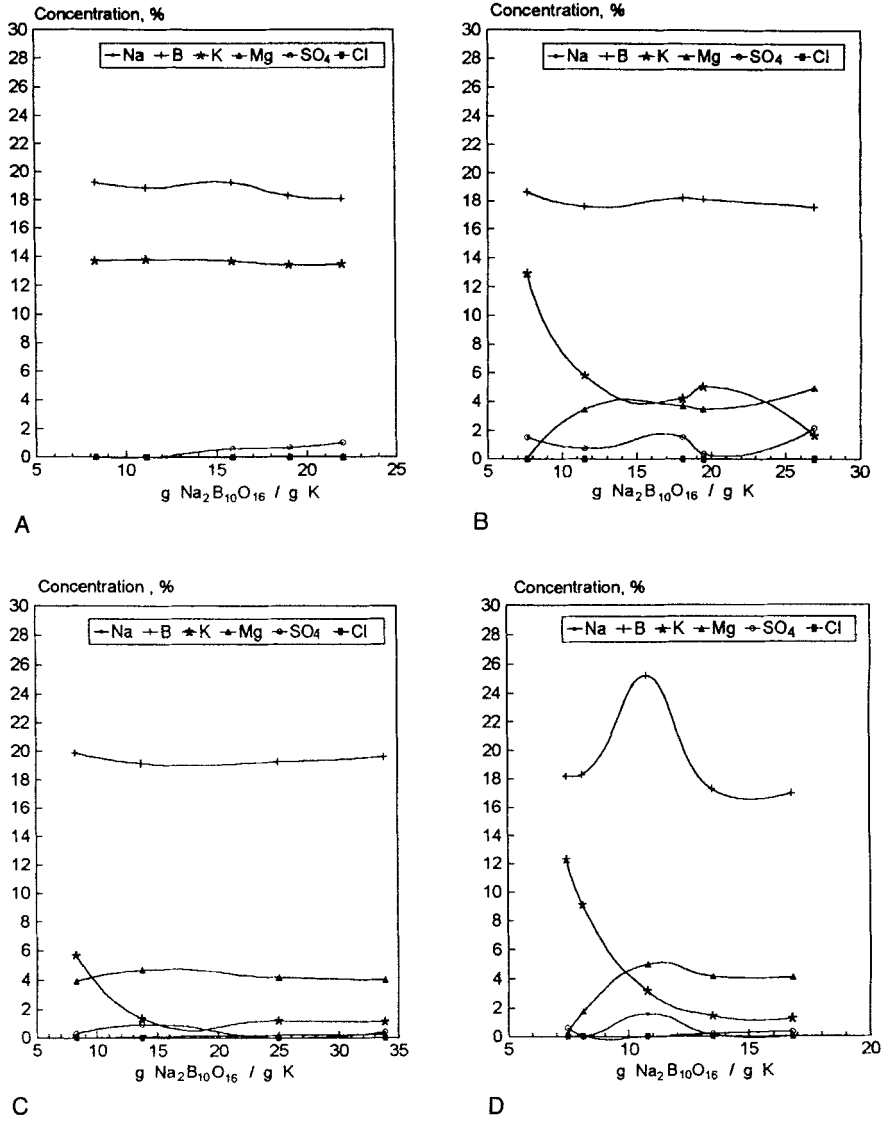

FIG. 3 Composition of pure solid phase as a function of $Na_2B_{10}O_{16}$ amount. (A) With $Na_2B_{10}O_{16}$ solution saturated at 25°C. (B) With $Na_2B_{10}O_{16}$ solution saturated at 35°C. (C) With $Na_2B_{10}O_{16}$ solution saturated at 70°C. (D) With solid $Na_2B_{10}O_{16}$.

range of the $Na_2B_{10}O_{16}$/K weight ratio when the crystallization is carried out at 25°C by using the $Na_2B_{10}O_{16}$ solution saturated at 25°C.

From Figs. 3(B), (C), and (D) it is clear that when the crystallization is performed by using more concentrated $Na_2B_{10}O_{16}$ solutions, the pure potassium pentaborate can only be obtained at a $Na_2B_{10}O_{16}$/K weight ratio smaller than 8. For higher ratios magnesium borate begins to precipitate and the purity of the product decreases.

Figure 4 shows potassium recovery in the solid phase as functions of the $Na_2B_{10}O_{16}$/K weight ratio and of the concentration of the $Na_2B_{10}O_{16}$ solution. As can be seen from Fig. 4, potassium recovery increases with increasing concentration of $Na_2B_{10}O_{16}$ solutions for $Na_2B_{10}O_{16}$/K ratios below 10. Increasing the amount of $Na_2B_{10}O_{16}$ also increases the potassium recovery gradually up to a $Na_2B_{10}O_{16}$/K weight ratio value of 8–10. Above this value, another compound, magnesium borate, begins to precip-

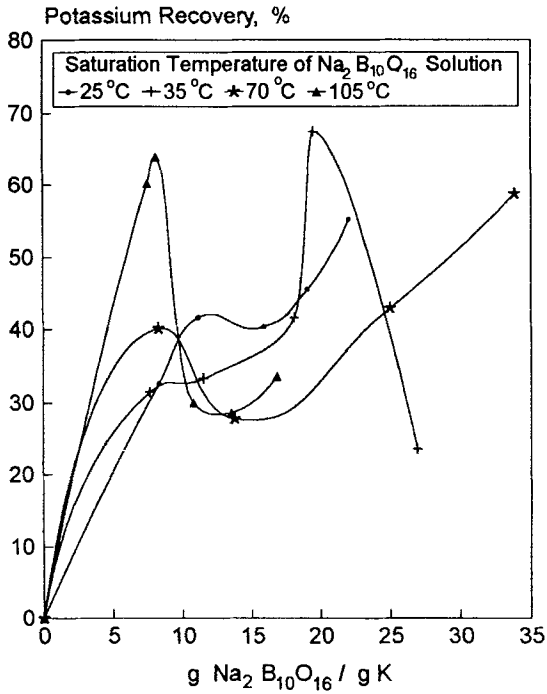

FIG. 4. Potassium recoveries in the solid phase as functions of the $Na_2B_{10}O_{16}$/K weight ratio and of the concentration of $Na_2B_{10}O_{16}$ solution.

itate and, depending on this, the purity of the potassium pentaborate decreases.

From the point of view of potassium recovery and product purity, a $Na_2B_{10}O_{16}$ solution saturated at 25°C is the most convenient for the crystallization of potassium pentaborate from bittern. Although a reasonably pure potassium pentaborate octahydrate can be obtained in a wide range of $Na_2B_{10}O_{16}$/K weight ratios by using a $Na_2B_{10}O_{16}$ solution saturated at 25°C, and the potassium recovery increases with an increasing amount of it, the optimum $Na_2B_{10}O_{16}$/K weight ratio also depends on the Mg/B ratio in the mother liquor. Figure 5 shows the Mg/B atomic ratio in the mother liquor versus the $Na_2B_{10}O_{16}$/K weight ratio. Because it was suggested that the boron content of the crystallization mother liquor could be recovered by precipitating $Mg(BO_2)_2$, the Mg/B atomic ratio of the mother liquor should be kept higher than 0.5. Since 5.24 g $Na_2B_{10}O_{16}$ per gram

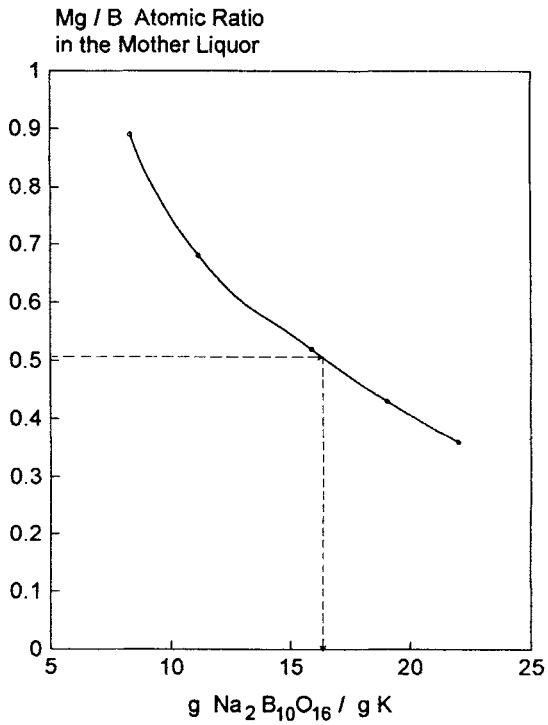

FIG. 5 Mg/B atomic ratio in the mother liquor as a function of $Na_2B_{10}O_{16}$/K weight ratio.

TABLE 6
Effect of Crystallization Temperature on Potassium Recovery[a]

Expt.	Crystallization temperature (°C)	Amount of the obtained phases (g)		Composition of the obtained phases (wt%) Na^+	K^+	Mg^{2+}	B^{3+}	SO_4^{2-}	Cl^-	Density (g/cm³)
20	20	Solid	5.80	0.24	11.26	0.16	17.20	0.70	0.56	
		Liquid	255.59	2.77	0.27	1.84	1.48	2.41	7.05	1.1603
21	15	Solid	6.95	0.22	11.20	0.15	17.39	0.09	0.53	
		Liquid	253.85	2.83	0.20	1.85	1.12	2.35	7.05	1.1640
22	10	Solid	7.69	0.51	10.28	0.32	15.41	0.84	1.28	
		Liquid	254.41	2.81	0.17	1.84	1.27	2.27	7.05	1.1670

[a] Amount of bittern = 125.73 g. Amount of $Na_2B_{10}O_{16}$ solution = 135 g. Concentration of $Na_2B_{10}O_{16}$ solution: Na = 1.34 wt%, B = 3.19 wt%.

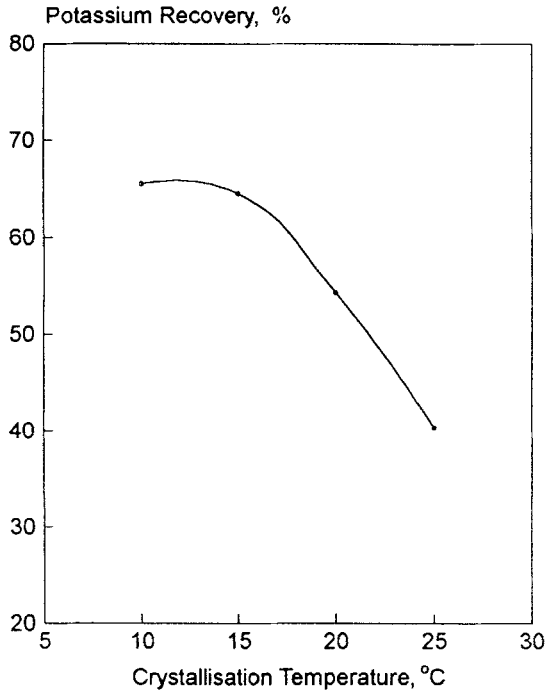

FIG. 6 Potassium recovery in the solid phase as a function of crystallization temperature.

of potassium is theoretically necessary for the stoichiometric conversion of potassium ion to potassium pentaborate, in the given conditions an almost 300% excess of sodium pentaborate is used. According to Fig. 5, the respective $Na_2B_{10}O_{16}/K$ weight ratio is 16. Under these conditions, potassium recovery is of the order of 45%. In order to increase the recovery, the crystallization temperature should be decreased. Table 6 shows the experimental results obtained at crystallization temperatures of 20, 15, and 10°C. According to these results, potassium recovery in the solid phase is given in Fig. 6 as a function of the crystallization temperature.

Figure 6 implies that the crystallization of potassium pentaborate octahydrate should be carried out at 15°C. Because there is no big difference in the recoveries obtained at 15 and 10°C, the former is accepted as the most suitable. Under these conditions, the atomic ratio of Mg/B in the mother liquor is 0.61.

CONCLUSION

The potassium content of seawater bittern is recovered as the intermediate compound potassium pentaborate octahydrate by the reaction crystallization of bittern with sodium pentaborate solutions. Maximum purity of potassium pentaborate is obtained by using a sodium pentaborate solution saturated at 25°C. Cooling the reaction mixture to 15°C gives 65% recovery of the potassium content. This recovery is higher than conventional solar evaporation methods (1–4) which are very complex. The simplicity of the process is another positive feature of the proposed method. When the recovery obtained by the present work is compared to the 80% recovery which is the maximum value obtained up to the present time (9), the results seem very promising. This process also has the possibility of recovery the magnesium content of bittern by magnesium metaborate precipitation.

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