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RECOVERY OF MAGNESIUM SALTS FROM BITTERNS BY FRACTIONAL CRYSTALLIZATION METHOD

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Abstract

The use of bittern in appropriate processes can yield magnesium, calcium, potassium and sodium salts, chlorine and bromine as well as sodium chloride. Recovery of such resources is considered very attractive in Iran. The hot weather and unlimited spaces available in the southern part of Iran make the process more feasible. Salt recovery from rejected bitterns of petrochemical plants in Mahshahr, is important because of economical point of view and environmental management. Due to increase in the use of magnesium salts and insufficient amount of magnesium-contained minerals, it is needed to recover it from seawater, brines produced from desalination plants and etc. Among different magnesium salts, magnesium chloride was selected. Different processes for the recovery of magnesium chloride from sea water and brines were proposed in the literature. In this study, the extraction of magnesium salts from this specific bittern was studied under atmospheric pressure and at 90°C temperature by fractional evaporation. The selective densities of precipitation of different salts were determined. The effect of pH and cooling on the purity of the product was studied. Two different process cycles were tested and the percentage of the purity and the efficiency of the magnesium salts produced, were compared. Under optimum condition, the efficiency of the extraction was near 85 percent and the purity of the product was more than 98 percent.

Key Words: Bittern; Magnesium; Crystallization; Recovery; Evaporation.

1. Introduction

The most of the world minerals resources are only enough for 100-150 years. Seawaters, brines and bitterns are considered important sources of several minerals such as sodium, magnesium, calcium, sulfur, chlorine, etc and recovery of minerals from them is considered to be a very attractive source of minerals. There are many factors that must be considered in evaluating the minerals recovery from the bittern, according to the literature, the main factors are:

- Product type: mixed salts or single element
- Separation methods
- Marketing, supply and demand
- Minerals concentrations in the bittern

Bitterns provide a source of very large volumes of recovered products, so careful evaluation of the local and international markets are required; also good selection of the recovered minerals or salts is needed as well as the appropriate separation method. These methods typically include precipitation, electrolysis, electrodialysis, adsorption, ion exchange, chelating, oxidation, chlorination, solvent extraction and evaporation [1].

Magnesium is the lightest of industrial metals employed in a large scale, on worldwide scale; %50 of the magnesium produced is used in the preparation of high quality aluminum alloys. Also, the magnesium salts are used in the water treatment, the paper industries, the production rubber and plastic, the refractory coating of the internal furnaces and in agriculture directly or indirectly. Accordingly, the separation and recovery of pure magnesium from very cheap resources is a vital process. Due to limited minerals resources in Iran, the production of some of the minerals and salts from seawaters and bitterns may be

beneficial [2]. The hot weather and the unlimited spaces available in the southern part of Iran make the process more feasible; it also minimizes the pollution problems associated with the bittern disposal. The aim of this investigation is to study the feasibility and amenability of finding an economic and effective method for selective separation of magnesium from the bittern. Due to the hot weather and the unlimited spaces available in the southern part of Iran for constructing of evaporation ponds, in this research, the evaporation and fractional crystallization method was selected.

The driving force for initiating of crystallization is super saturation of solution. Super saturation can be generated by cooling, evaporating, chemical reaction or by adding a third component to initial solution [3-5].

Due to the solubility curve of a composition with temperature a proper method for generating of super saturation is selected. In this investigation, for this purpose the evaporation of solution was done and the purification of product is studied by cooling and effluence of pH.

2. Analysis of feed

The bittern sample with containing about %63 of solid and density 1.268 g/cm^3 is extracted from an Iranian south part. For identify the composition of it and recognition the structure of crystal, XRF and XRD analysis was done. The result of this analysis is expressed in percentage of weight of existing ions in Table 1.

Table 1 Analysis of the bittern sample (%wt)

pH	Density at ambient temp. (g/cm^3)	Na^+	K^+	Mg^{+2}	Ca^{+2}	SO_4^{-2}	Cl^-
7	1.268	3.99	3.09	12.6	0.036	10.6	40.3

It is found from this data that, the most part of this bittern contains of Mg^{+2} and Cl^- ions with considerable impurities Na^+, K^+ and SO_4^{-2} and negligible Ca^{+2} .

Also, the result of XRD analysis is in accordance with structure crystalline of Bischofit ($MgCl_2.6H_2O$) and Halite (NaCl).

3. Experiments

A specified amount of the bittern sample is heated at 90°C and atmospheric pressure in beakers inside the bath with temperature controller system with relative good accuracy of temperature control (±1ºC), after generating the super saturation condition of solution, the crystallization of bittern is started. The goal was to find the optimal condition of evaporation for recovery of magnesium salts.

For this purpose, 13 steps of evaporation of feed was done and in each step, the feed was evaporated in specified amount and in the same temperature (90°C), the decantation and filtration of it was done in another bath. At first, the participation of the sodium and potassium salts was occurred respectively due to the solubility of the sodium and potassium salts in comparative with magnesium salts.

After finding the proper step of evaporation for recovery of magnesium salts, the crystals of this step that were contained with sodium and potassium impurities, was separated and the purification of the filtrate (the main product) was done. The produced crystals of each stage are dried at 50°C in oven for 2 hours and then are analyzed.

The magnesium and calcium concentration of samples was determined by complexmetric titration with EGTA and sodium and potassium concentration was determined by flame photometry and chlorine was determined by Mohr method and sulfate was determined by gravimetric method. The pH of the samples was determined by pH paper (Merck type) and the density was determined by picknometer with high accuracy (with 4 decimals digit precision) [6-7].

4. Results

The results of analysis of the crystals of each stage of evaporation are reported in Table 2 in weight percentage.

According to these results, the produced crystals from 1 to 4 steps were concerned to halite salt (NaCl) with sulfate and other cations impurity. The amount of NaCl in mentioned

salt was %88.1 in average. So, these steps were proper for recovery of sodium chloride salt.

Table 2. Analysis of obtained crystals (%wt)

Step	Density at t=90°C (g/cm^3)	Na^+	K^+	Mg^{+2}	Ca^{+2}	SO_4^{-2}	Cl^-
1	1.2598	35.15	2.62	1.27	0.40	2.21	58.70
2	1.2729	32.06	2.63	1.51	0.40	3.05	60.72
3	1.2814	29.76	3.05	1.67	0.40	3.60	61.89
4	1.2996	28.46	3.26	2.42	0.40	4.15	61.95
5	1.3174	27.02	3.50	3.12	0.05	5.50	60.81
6	1.3346	26.99	3.81	3.26	0.05	7.66	58.22
7	1.3568	20.67	3.38	4.59	0.07	12.20	59.10
8	1.3781	19.20	3.03	4.45	0.07	16.01	57.24
9	1.3876	16.80	3.11	4.66	0.08	17.44	57.90
10	1.3938	16.04	3.32	4.52	0.08	19.34	56.69
11	1.3974	15.14	3.49	4.82	0.09	21.02	55.44
12	1.4077	14.78	3.62	6.00	0.10	22.53	52.92
13	1.4140	14.52	3.94	5.88	0.10	23.91	51.65

The produced crystals from 4 to 8 steps were concerned to potassium salt (K_2SO_4) with impurity of sulfate of other cations and small chloride of them. By further evaporation of sample from 9 to 13 steps, potassium chloride (KCl) or carnallite ($KCl.MgCl_2.6H_2O$) is precipitated [8].

Due to the importance of the recovery factor (the amount of magnesium content in filtrate to the amount of magnesium in initial feed) and the purification of product, the seventh step of evaporation (density=1.3568g/cm^3) was selected for separating of magnesium salts. The recovery of this step was %86 and the sodium and potassium impurity of the filtrate of this step (product) was about %3.14 and %2.99, respectively.

5. The purification process:

5.1.Effect of pH

The solubility of sodium and potassium salts was decreased in acidic pH and the participation of them was increased in comparison of neutralized pH. So, the seventh step of evaporation was done in acidic pH (pH=2), again [9]. The results of analysis of the crystal and filtrate of this evaporation were shown in Table 3 in mg.

Table 3 Analysis of crystal and filtrate of the seventh step of evaporation at t=90°C and different pH (mg)

pH	Na^+(mg)		K^+(mg)		Mg^{+2}(mg)		Ca^{+2}(mg)		SO_4^{-2}(mg)	
	Filtrate	Crystal	Filtrate	Crystal	Filtrate	Crystal	Filtrate	Crystal	Filtrate	Crystal
7	2847	14476	2711	2363	21784	3214	77	46	21986	8541
2	2398	15127	2507	2544	22221	3004	78	45	20643	9351

This table was shown that the purity of product in pH=2 was better than the pH=7 and the amount of impurity of sodium and potassium were decreased %15.8 and %7.5, respectively.

5.2. Effect of cooling

The purification of product that was generated by evaporation, is possible with different physical and chemical processes i.e. use of barium chloride or calcium chloride for decreasing of sulfate and use of sodium sulfate for decreasing calcium or the extraction of salts with

inorganic solvents because of different solubility of them. Most of these processes are expensive and complicated. The common physical processes, is based on difference of solubility of different salts in different temperatures in water that are simpler and cheaper than the chemical processes [10].

Due to the above description and primary studies of bittern, the process that is shown in figure 1 was selected.

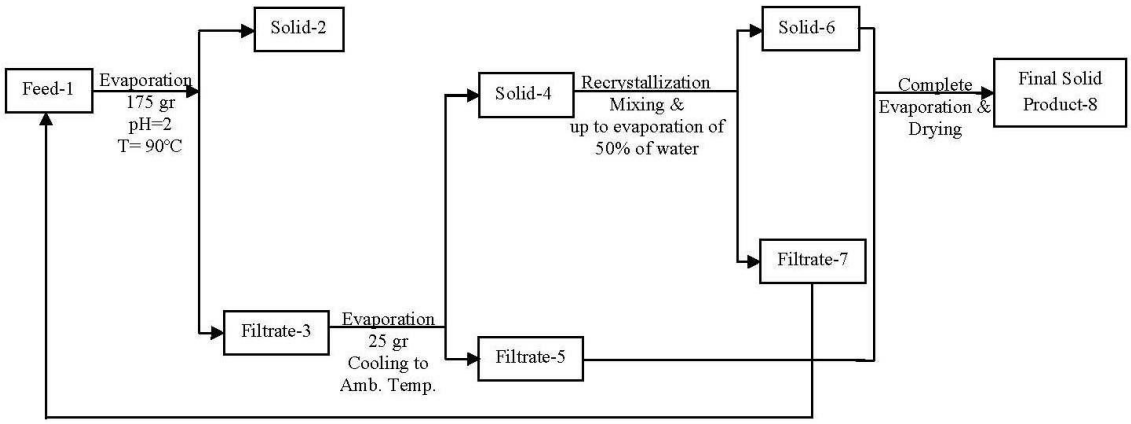

Figure 1. Steps of different production & purification of product

This process cycle was done 3 continuously. The analysis result of the different steps was presented in Table 4.

Table 4. Analysis of ions concerning to evaporation cycle figure 1(mg)

No. of Sample	Density (g/cm^3)	Na^+(mg)	K^+(mg)	Mg^{+2}(mg)	Ca^{+2}(mg)	SO_4^{-2}(mg)
1	1.2531	19043	5287	25502	136	32007
2	-	15121	2510	3001	44	9340
3	1.3568	2411	2503	22228	79	20655
4	-	1740	1980	8958	38	15075
5	1.3976	318	294	12792	37	3414
6	-	15	14	3278	8	927
7	1.4118	1540	1699	5147	26	12673
8	-	290	241	15642	43	2895
9	1.3409	20236	6724	30250	155	42600
10	-	15035	3075	3553	49	11573
11	1.3933	3842	3311	25992	97	28640
12	-	2958	2634	10465	41	19388
13	1.4135	552	469	14783	48	6432
14	-	30	28	3750	8	1035
15	1.3741	2433	2419	6112	28	17097
16	-	477	421	17784	52	4390
17	1.3906	21089	7464	31244	162	46866
18	-	15372	3423	3740	55	13458
19	1.4019	4344	3648	26532	102	29853
20	-	3452	2856	10751	49	20488
21	1.4154	621	614	15116	47	7166
22	-	38	33	3866	10	1079
23	1.3838	3125	2563	6430	36	17703
24	-	552	521	18111	54	4754
25	1.3980	21982	7605	31560	170	47408
26	-	15651	3524	3791	58	15644
27	1.4071	4899	3739	26714	109	30175
28	-	3879	2911	10819	53	20951
29	1.4188	709	660	15320	51	7456
30	-	42	36	3890	10	1096
31	1.3944	3560	2658	6409	41	18020
32	-	626	573	18464	57	4860

Numbering of continuous cycles was based on the first cycle. According to this table, the loss of magnesium in different stages of repeating of this cycle in comparison of the total magnesium of the same step was %11.8, %11.7, %12.11 and %12, respectively.

Due to the constant evaporation amount in different steps of cycle, the negligible changes of loss of magnesium and also, yield of it, is occurred. Also, the system goes to the steady state condition with increasing of repeat of these steps and therefore the results were fixed, relatively.

The amount of Mg/Na for main products with No. 8, 16, 24 and 32 were 53.9, 37.3, 32.8 and 29.5, and the amount of Mg/K for them were 64.8, 42.3, 34.8 and 32.2, resp.

The reason of this decreasing was concerned to further remaining of sodium and potassium ions in product. Due to the constant evaporation amount in each step, the further sodium and potassium impurity was added to initial feed with recycling filtrate that was affected in the purity of the main product after finishing each cycle [11].

The product with No. 32 was near to steady state condition in comparison to the other product. The XRF analysis of it was reported in Table 5.

Table 5. Analysis of ions concerning in final product No. 32 (%wt.)

Ion	Na^{+}	K^{+}	Mg^{+2}	Ca^{+2}	SO_4^{-2}	Cl^{-}
Concentration, (%wt.)	0.001	0.004	18.1	0.41	0.09	54.1

The purity of the product was more than 98 percent of magnesium salt and the efficiency of the extraction was near 85 percent. The analysis TGA (Thermo gravimetric Analysis) was resulted the similar crystalline structure of the product and the Merck type of sample (Figures 2 and 3).

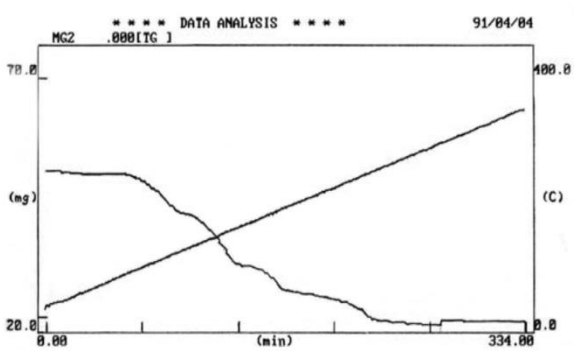

Fig. 2 The thermal profile of product (No. 32)

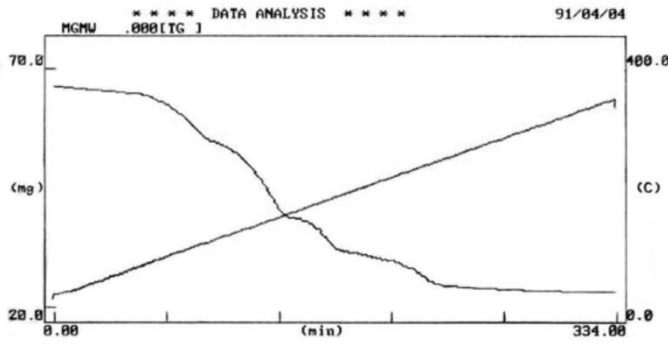

Fig.3.The thermal profile of $MgCl_2.6H_2O$ (Merck type)

6. Conclusion

Due to the huge amount of rejected bittern from Mahshahr petrochemical plants and limited minerals resources in Iran, the recovery of magnesium salts from bitterns becomes beneficial. Among different magnesium salts, magnesium chloride was selected. Different processes for the recovery of magnesium chloride from sea water and brines was proposed by researchers and reported in the literature. In this study, due to the hot weather and the unlimited spaces available in the southern part of Iran for constructing of evaporation ponds, the evaporation and fractional crystallization method was selected. The effect of pH and cooling on the purity of the product was studied. According to the results, by evaporating of bittern in pH=2 which had density 1.3568g/cm^3, the most of sodium and potassium impurity was participated and the loss of magnesium was about %12.6 in this step. After this step, the evaporation of filtrate was continued to density 1.3976g/cm^3. The system was optimized. By cooling and crystallization of produced solid, the efficiency of the extraction was near 85 percent and the purity of the steady product that produced from repeating 4 process cycle, was more than 98 percent in Mahshahr bittern under optimum condition.

The analysis TGA (Thermo gravimetric analysis) was resulted the similar crystalline structure of the product and the Merck type of sample.

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