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Extraction of High Purity Bischofite ($MgCl_2·6H_2O$) from Left Over-Resiudal Bittren, Lake Quroun, Egypt

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1 Introduction

The left-over (residual) brines often in industrial facilities is disposed back to the sea or in dump areas e.g. abundant salt mines in other cases. Dumping into the sea can harm marine organisms even if done on local and/or on a temporary basis since the residual brines have ion concentrations more than 70-90 times that of the original seawater concentration. In our case, it was found that it is impossible to dispose bittern into Lake Quaroun. This will definitely cause environmental impacts and affect more dangerously on the ecosystem and on the fishing productivity in the lake as compared with seawater because this lake is considered as a closed and isolated basin. Moreover it is against the Egyptian Environmental Authorities law of 2004. Many authors studied process of extraction high soluble salts from sea and sabkha brines as (Mnif, 1984; Mnif et al., 1998; Zayani et al., 1999; Fezei, 2011) and bittern from lakes as (Fezei, 2012; Elsheikh et al., 2009a,b) after extraction of anhydrous sodium sulfate (thenrdite), halite and epsomite ($MgSO_4.7H_2O$), magnesium chloride represents about 70% from a volume of left –residual bittern 150 thousand cubic meter annually riches with magnesium chloride , which constituent about 70% from total volume with valuable ions as Br , B and K . in the current methods for extraction high purity magnesium chloride (bishofite), must be removing boron ion firstly (boronization), the studied method it is not necessary to remove the boron firstly.

2 Experimental method and process description

The type of Lake Quaroun brine at 1.330 gm/cm^3 after extracting the anhydrous sodium sulphate assimilated to the quinary system Na^+ , Mg^{2+} , Cl^- , K^+ , SO_4^2 // H_20 .Several works were developed on the sabkhs brines (Mnif, 1984; Mnif et al., 1998; Zayani et al., 1999; Fezei, 2011), the investigations were extended to the modeling of phase diagram (Elsheikh et al., 2009a,b; Hammi et al., 2004; Elsheikh et al., 2008).

the Fractional Crystallization Method was used, where the bittern, evaporated at 35^{o}C and 25^{o}C respectively, temperature was adopted by thermostatic bath and were controlled by water circulation. the precipitated salts have been totally removed from bittern by filtration. The current method was started with a new 3 liter of the studied bittern sample. where at every step of evaporation liquid sample was taken to measure its density and ionic conductance as well as to determine its ionic composition by chemical analysis, but the salt phases, were totally removed from the brine solution to be tested by XRD and SEM.

3 Results and Discussion

Chemical composition of bittern are summarized in table 1. after bitten desulfated by calcium chloride solutions the solution containing magnesium chloride with smaller amounts of sodium chloride , potassium chloride and magnesium sulphate after this step , thus the solution may be suitable for magnesium chloride precipitated by dioxan as $Mgcl_2.6H_2O$.$C_4H_8C_2$. Chemical composition evolution of the studied bittern as in figure 1. It represents Isothermal of the Quinary system of Na^+ , Mg^{2+} , Cl^- , K^+ , SO_4^2 // H_20 at 35^{o}C, usually describe bittern equilibrium states, in this diagram ion percentage as expressed as follows:

$\%\ Mg = f\ Mg / D$

$\%SO_4 = f\ Mg / D$

$\%K_2 = f\ k_2 / D$

Where f = mole fraction

$D = f\ Mg + f\ Mg \mathrel{+}= f\ k_2$

Solid phases of carnalite and bishofite were detected by polarized microscope(pL) ,Scanning electron microscope (SEM) and energy dispersive X-Ray diffraction (EDX),

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Table 1 Ionic and salts composition of bittern(g/L)

SP.gr (1.330 g/cm^3)	T.D.S = 480 g/L
CO_3^{-2}	2.3
HCO_3^{-1}	3.2
SO_4^{-2}	57.4
CL^-	277.3
Ca^{+2}	-
Mg^{+2}	107.9
Na^+	5.9
Salts	
$MgCO_3$	3.2
$Mg(HCO_3)_2$	3.8
$MgSO_4$	72.
$MgCl_2$	359.9
NaCl	15.
others	26.090

The analytical methods are described as follows:
CO_3^{2-} : acid- base titration , K^+, B^{2-} : atomic absorption (Model GPC 932)
Na^+ : equivalent minus according to ion balance
Mg^{2+}: titration complex metrically with Ca^{2+} by using Eriochrom black T
Ca^{2+}: titration complex metrically by using muroxide.
SO_4^{2-} : by barium sulfate precipitation [10]
Cl^-: titration with silver nitrate using potassium chromate as indicator
XRD, SEM, EDX and Transmitted light microscope were used

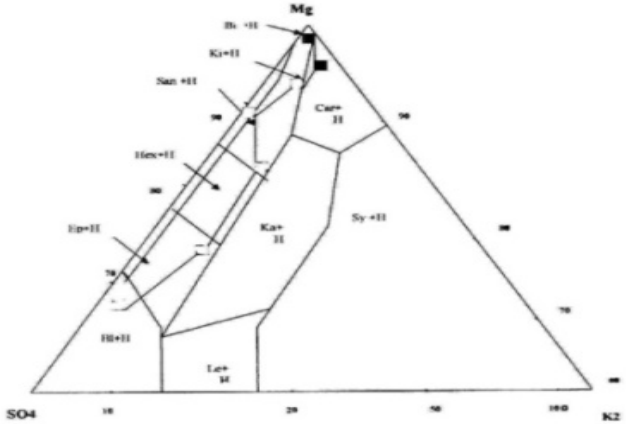


Fig .1. Isothermal of the Quinary system of Na^+ , Mg^{2+} , Cl^-, K^+, SO_4^2 // H_2O at 35°C.

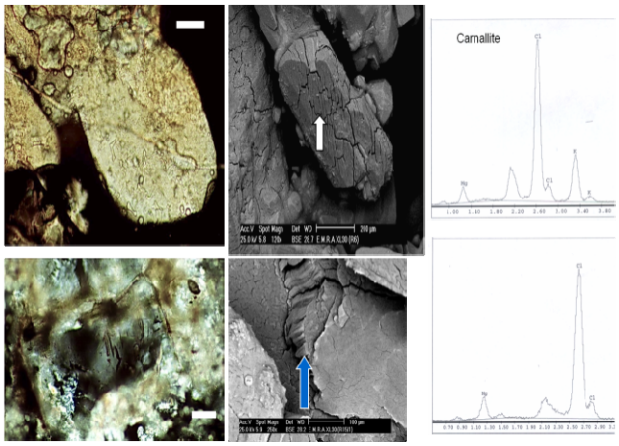


Fig. 2. Photomicrograph , SEM and EDX pattern of solid crystals separated of carnallite and bischofite at 35, 25ºC, Bar is250µ.

Fig. 2 .

The solids phases precipitate at first step of treatment by adding calcium chloride solutions (desulfation) are pure

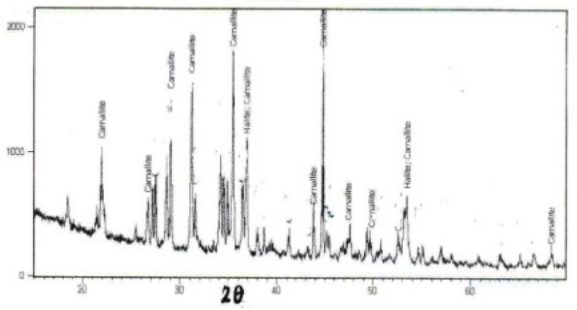


Fig.3 XRD Pattern of Carnalite extracted

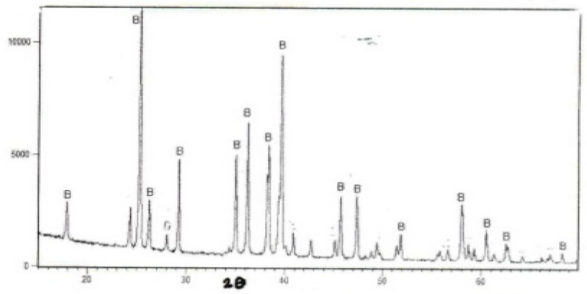
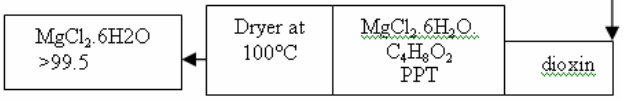


Fig. 4. XRD pattern of bischofite after drying at 100 C° 4-Material balance of flow diagram.

Carnalite ppt.

In let	evaporator	Out let
Sp.gr =1.33g/cm3 Q = 20m^3/h 26.6t/h	35°C	1.33 g/l 15.39 m3/h 20.9 t/h
$MgCl_2$=7.18 ton/h	2 t/h	5.18 t/h
KCl= 0.5 t/h	0.3 t/h	-
NaCl= 0.3 t/h	0.3 t/h	0.3 t/h
$MgSO_4$= 1.44 t/h	1.44 t/h	1.44 t/h
H_2O = 10.4 t/h	2.89t/h	7.51t/h

KCl - $MgCl_2.6H_2O$



gypsum, the second step precipitate carnallite (KCl . $MgCl_2.6H_2O$) containing little amounts of halite , third step bischofite precipitated by dioxan as ($MgCl_2.6H_2O.C_4H_8O_2$) including minor amounts from sodium , potassium and sulfate ions, the final product , bischofite ($MgCl_2.6H2O$) by drying at 100 C^0 to obtained high purity more than 99.5%, when treating one litter from bittern, 160 grams of this salt will be recovered. i.e. the yield of this process 45%.

5 Conclusions

This study contribution to extraction of magnesium chloride hexahydrate salt from left – over residual bittern at Egyptian salts and mineral Co.Fayioum,Egypt .In this study three step process based on isothermal evaporation

and chemical precipitation was preformed , by this processes we obtained high quality from magnesium chloride hexahydrite, higher than 99.5%. all separated salts besides end products are useful.

KEY Words: Bishofite , Carnalite, Hexahydrite, waste residual bittern, lake Quaroun

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