SELECTIVE RECOVERY OF BISCHOFITE FROM SEBKHA EL MELAH NATURAL BRINE

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Abstract--**Brines are high concentrated aqueous solutions frequently used as raw materials for the recovery of several salts, which are industrially useful and necessary in some agricultural applications. This paper deals with a six-stage process for the recovery of magnesium chloride hexahydrate (bischofite) from Sebkha El Melah natural brine (South of Tunisia). It is based on successive evaporation sequences to precipitate firstly sodium chloride and then potassium-magnesium double salts. After that, the mother liquor is cooled to remove magnesium sulphate heptahydrate (epsomite). This step is essential before precipitating the potassium-magnesium double salt $KCl.MgCl_2.6H_2O$ (carnallite). At the end of this step the recovered solution still contains sulphate ions which may disturb magnesium chloride extraction. In order to overcome this difficulty, a sulphate removal step has been advocated using calcium chloride solution. The treated solution becomes sulphate ion free and thus suitable to be used for bischofite preparation. The investigated procedure makes available the production of a magnesium chloride salt (purity upper than 90%) and various by-products, such as: halite (NaCl), gypsum ($CaSO_4.2H_2O$) and epsomite ($MgSO_4.7H_2O$).**

Keywords--**brine, isotherm evaporation, bischofite recovery, process.**

I. INTRODUCTION

In southern Tunisia there are many salt lakes which are considered as important material resources useful for industry and agriculture. They are called *sebkha* or *chott*, and they cover a large part of Tunisian land. The liquid raw material enclosed in these deposits is named brine and always assimilated to the quinary system: Na^+, K^+, Mg^{2+} / Cl^-, SO_4^{2-}//H_2O. These solutions are valuable and expected to play an important role in the economic sector.

To take advantage of this raw material, several works were developed. Besides the study of geological aspects and phase diagrams of the system representing the brines (Hajeri, 1979; Chaabouni, 1980; Guerfal, 1981; M'nif, 1984; Kalai, 1986; M'nif and Rokbani, 1998), investigations were extended to the modelling of phase diagrams (Chehimi 1997; Zayani, 1999; Zayani *et al.*, 1999; Hammi *et al.*, 2001; Hammi *et al.*, 2003a; Hammi *et al.*, 2003b; Hammi *et al.*, 2004a; Hammi *et al.*, 2004b) and extraction of interesting salts (Djebali *et al.*, 1998; M'nif *et al.*, 1998; Zayani and Rokbani, 2000; M'nif and Rokbani, 2000).

The present investigation pertains to the recovery of salts from aqueous salt solutions containing a plurality of water-soluble salts, such as the chlorides and/or sulphates of sodium, potassium, magnesium, etc. It is more particularly concerned with the recovery of magnesium chloride hexahydrate (bischofite) from the naturally occurring brine of Sebkha El Melah of Zarzis. The expected salt is used for fireproof materials, pharmaceutical products and for the preparation of specific cement pastes.

II. PROCESS DESCRIPTION

As shown in Fig. 1 the investigated process is mainly composed of six stages. The adopted flow sheet is principally supported by the previous works on natural brines (Janecké, 1907; Berthon, 1962; Cohen-Adad *et al.*, 2002; M'nif and Rokbani, 2004; Hammi, 2004) usually described using the oceanic quinary diagram Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}//H_2O. This useful graphic-tool is helpful in natural brines exploitation or valorization. In fact, it defines, during the system's evolution, the number, the nature, the composition and the relative quantity of different condensed phases that crystallize or disappear.

The first treatment step consists in evaporating at 35°C the raw brine (after being filtered). Simultaneously, a large part of sodium chloride (halite) is precipitated and removed.

In the second step of the process, the obtained mother liquor is further concentrated until a saturated magnesium salts solution. The precipitated salts may be said to consist essentially of sodium chloride and small amounts of magnesium-potassium double salt.

The third stage consists in maintaining the obtained saturated solution under magnetic stirring during four hours at 5°C and then removing the precipitated salt. This stage is devoted to partially desulphate the treated brine and slightly decrease its magnesium ions content which increases the evaporation rate in the following stage.

The fourth step consists in precipitating the potassium-magnesium double salt, carnallite ($KCl.MgCl_2$.

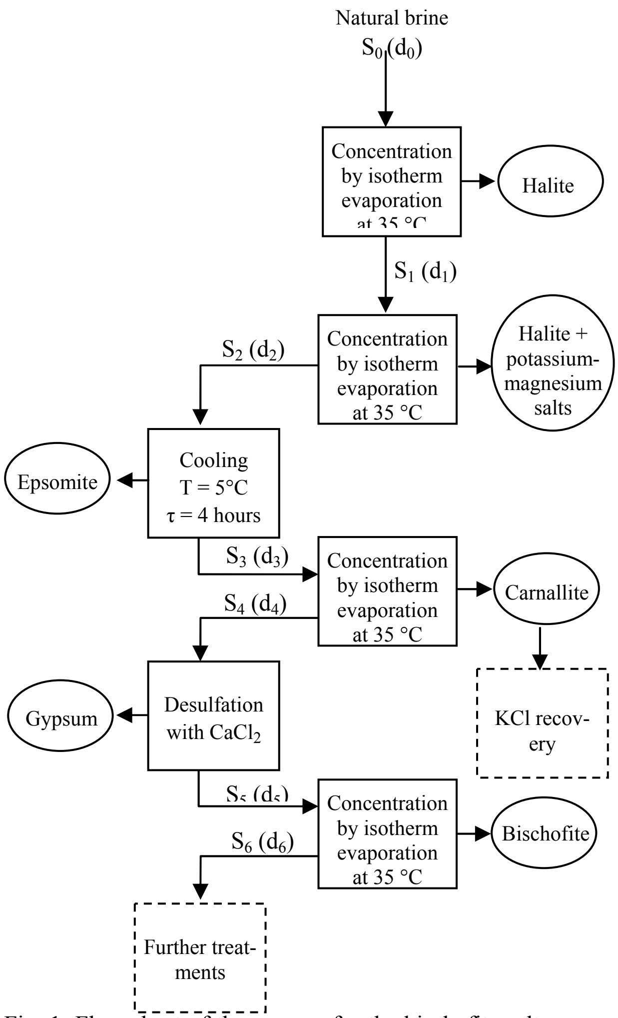

Fig. 1. Flow sheet of the process for the bischofite salt recovery from Sebkha El Melah natural brine.

$6H_2O$) and thus eliminating potassium ions or at least a considered quantity of this substance so that it will not be carried forward; in the subsequent process steps; with a sufficient amount to interfere with the production of an end product having good quality.

In the two last stages of the process the mother liquor leaving the carnallite precipitating step is desulphated by reaction with calcium chloride solution. After removing the calcium sulphate precipitate, the resulting brine; consisted predominantly of magnesium chloride together with residual potassium and sodium chloride; is further concentrated by isothermal evaporation at 35°C to precipitate the magnesium chloride salt.

III. EXPERIMENTAL

A. Chemicals

The principal raw material used in this work is Sebkha El Melah natural brine. Its density and chemical composition in major elements are given in Table 1. The only commercial reagent used in this work is calcium chloride dihydrate (99%) supplied by FLUKA.

B. Apparatus and analysis methods

All treatment stages of the process were performed at constant temperature (35°C) in a thermostatic bath, except the third stage which was carried out in a jacketed glass reactor where temperature (5°C) was controlled by water circulation and agitation was assured by magnetic stirrer.

The brines resulting from the different treatment stages of the process were chemically analyzed. The chemical analysis methods applied for sulphate, chloride, magnesium, and alkaline ions are respectively gravimetry, potentiometry (Titrino DMS 716 of mark Ω Metrohm), EDTA complexometry and flame atomic absorption spectroscopy (SAAF).

Furthermore, X-ray diffraction using a PHILIPS instrument (PW 3040 generator, 3050/60 θ/2θ) using Co K_α radiation (λ = 1.78901 Å) and TG-DTA analyses using a SETARAM SETSYS EVOLUTION apparatus were performed.

Also, the morphological nature of a solid sample was examined by Scanning Electronic Microscopy (SEM) using an ESM FEI Quanta 200 apparatus.

IV. RESULTS AND DISCUSSION

The natural brine, mother liquors resulting from the different treatment stages and all the recovered solids are noted respectively S_0, S_i, and Sd_i, where **i** is the number of the corresponding treatment stage. Their chemical compositions in major ions are gathered in Tables 1 and 2.

Positions of the different solutions in the equilibrium diagram of the quinary system Na^+, K^+, Mg^{2+} / Cl^-, SO_4^{2-}//H_2O are represented in Fig. 2. The Janecke coordinates of the considered mixture points were calculated using the following expressions:

$$\%K_2 = \frac{100 \times n_{K_2}}{D}, \qquad \%Mg = \frac{100 \times n_{Mg}}{D},$$

$$\%SO_4 = \frac{100 \times SO_4}{D}, \qquad D = n_{K_2} + n_{Mg} + n_{SO_4}$$

with n_i is the mole number of the i entity.

As it was expected, the five first process stages involve the evolution of the brine until reaching the crystallization field of the bischofite ($MgCl_2.6H_2O$).

Table 2 exhibits chemical analysis results of the recovered solid phases. Mineralogical constitution of all recovered salts is confirmed by X-ray diffraction. It is confirmed that Sd_1 and Sd_2 are; as expected; composed of halite, Sd_3 is mainly epsomite, Sd_4 is carnallite including substantial amounts of halite and hexahydrite ($MgSO_4.6H_2O$), the chemically precipitated salt Sd_5 is almost pure gypsum and finally the target product Sd_6 is

Table 1. Brines ionic compositions (%)

	Density	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	H_2O
S_0*	1.24170	3.33	0.59	4.34	0.05	17.00	2.46	72.22
S_1	1.27885	1.61	0.86	5.86	0.00	18.29	3.27	70.11
S_2	1.30848	0.95	1.00	7.38	0.00	20.25	3.73	66.69
S_3	1.29017	0.82	0.92	7.04	0.00	20.19	1.92	69.11
S_4	1.34178	0.27	0.26	9.11	0.00	23.91	2.57	63.88
S_5	1.27420	0.13	0.15	7.26	0.00	20.33	0.16	71.96
S_6	1.35550	0.28	0.27	7.40	0.00	21.97	0.29	69.78

* Raw material

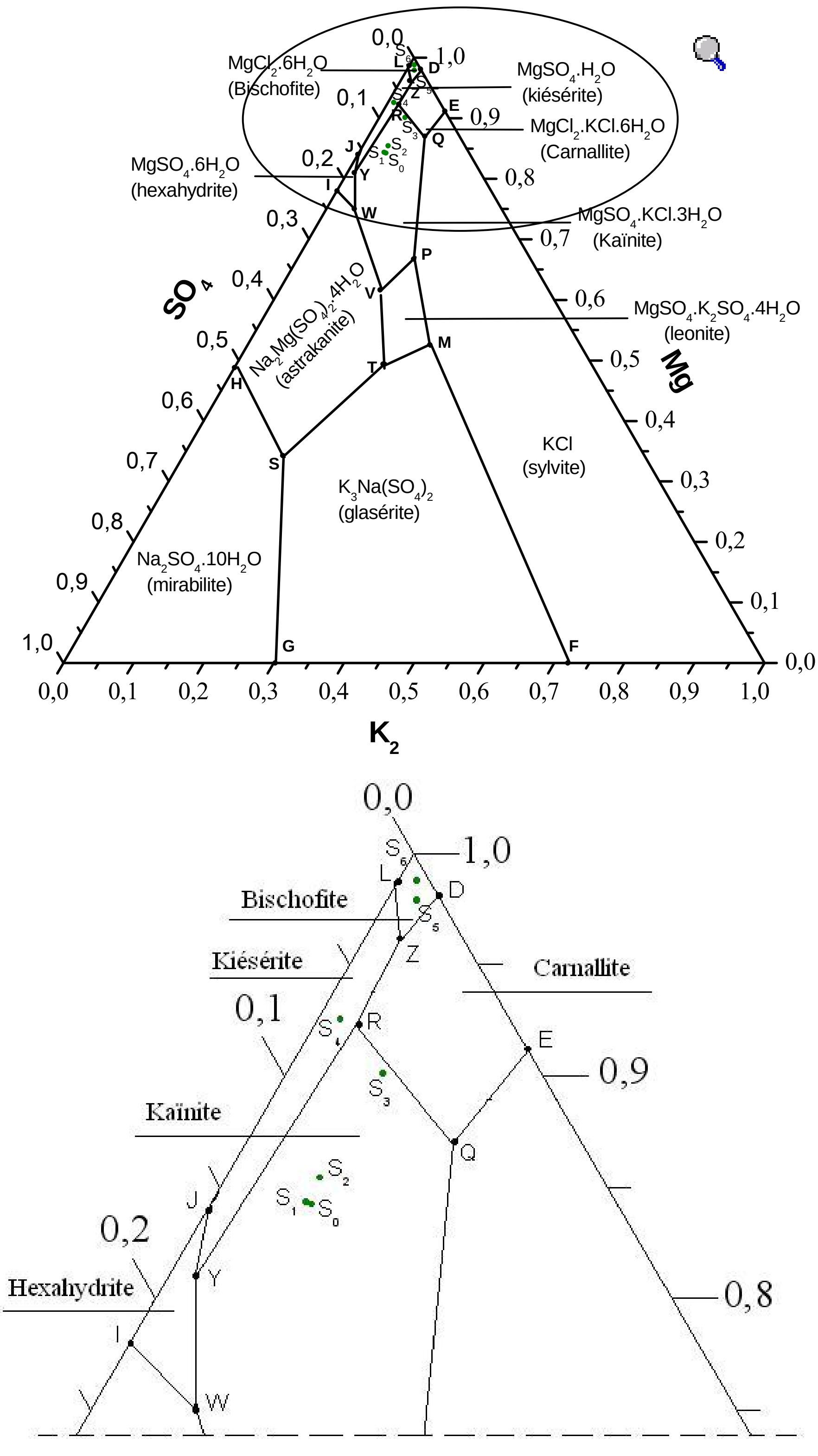

Fig. 2. 35°C isotherm of the System Na^+, K^+, Mg^{2+} / Cl^-, SO_4^{2-} // H_2O (NaCl saturated).

highly concentrated in bischofite. Figure 3 shows the diffractograms related to Sd_1, Sd_3, Sd_4 and Sd_6. Consequently, our predictions supported by the quinary diagram seem to be in agreement with the isothermal experimental results related to the three first steps.

However, in the case of Sd_4, carnallite salt contains hexahydrite instead of Kieserite ($MgSO_4.H_2O$). In addition, Sd_6 includes small quantity of carnallite.

In view of over-saturation and metastability phenomena; generally encountered in oceanic quinary sys

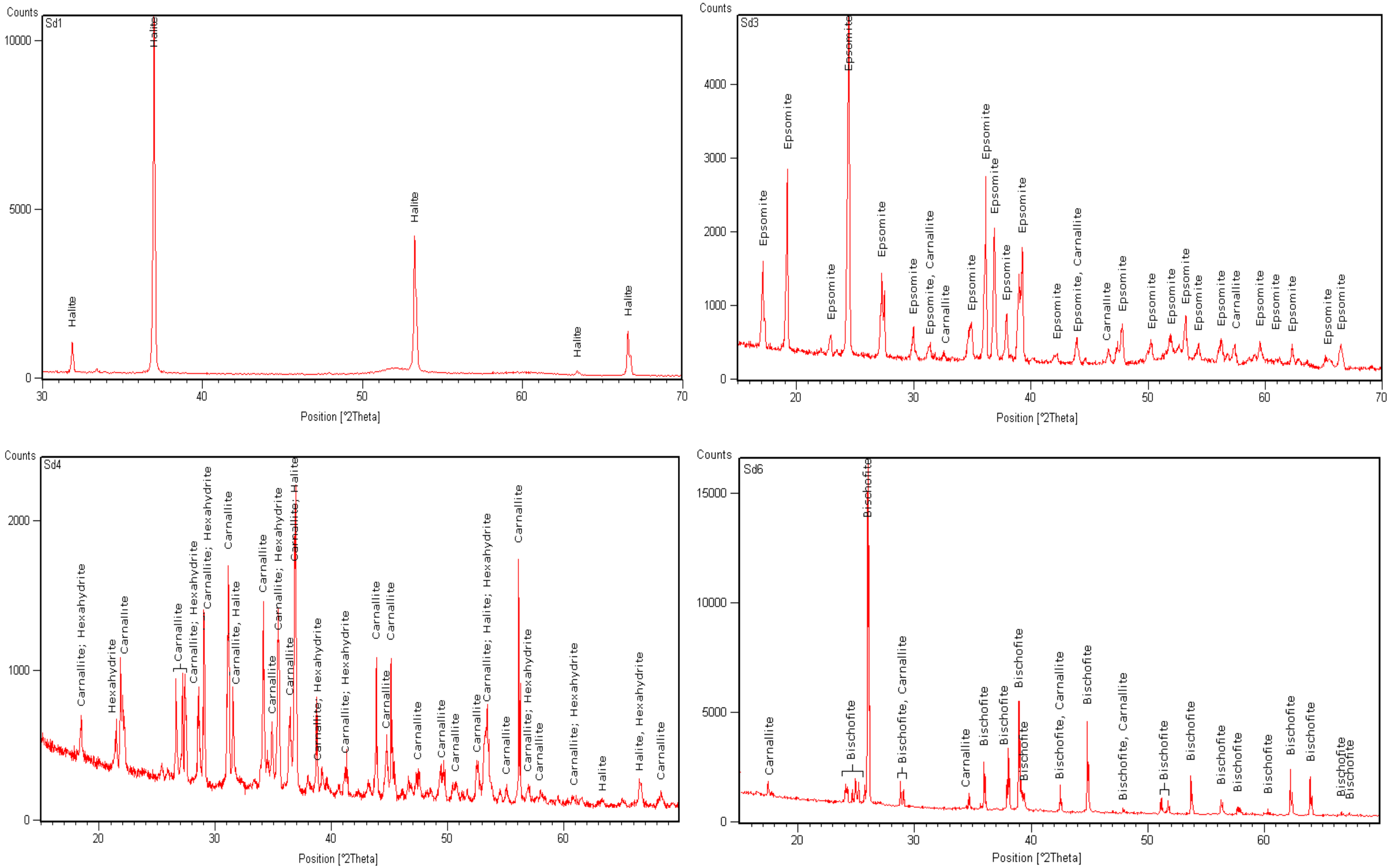

Fig. 3. X-ray diffraction patterns of the recovered salts Sd_1, Sd_3, Sd_4 and Sd_6

Table 2. Salts ionic compositions (%)

	Density	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	H_2O
Sd_1	1.27885	36.3	0.35	0.88	0.00	55.70	2.39	4.39
Sd_2	1.30848	35.1	0.41	1.26	0.00	53.88	2.47	6.88
Sd_3	1.29017	2.56	0.40	9.16	0.00	1.73	34.02	52.13
Sd_4	1.34178	5.46	11.4	7.86	0.00	37.41	4.43	33.44
Sd_5	1.27420	3.81	1.22	1.47	20.29	2.02	50.80	20.39
Sd_6	1.35550	2.97	4.28	10.78	0.16	33.95	1.40	46.45

tems; the mentioned differences between the predictable and experimental results (Sd_4 and Sd_6) are expected.

Figure 2 clearly shows the existence of the advocated phenomena of supersaturation and metastability. Indeed, the path S_3S_4 which is normally the carnallite crystallization path must cross the crystallization field of this mineral (QRZDE). However this path is out from the carnallite field and it crosses two juxtaposed fields which are Kainite and the kieserite. In other words the solutions are geometrically located in a given field and are in equilibrium with a salt belonging to another domain. Accordingly, a such situation is better described if it is taken into account the metastability phenomenon. Therefore, the considered liquors are rather supersaturated solutions.

The previous observations allow the comprehension of the experimental results and particularly the divergence encountered between predictable salts and those experimentally obtained (Sd_4, Sd_6).

Eventually, the experimental data are summarized as follow: the two first by-products (Sd_1, Sd_2) are considered to be halite (NaCl) containing less than 5% impurities coming from impregnating solution. The other by-products (Sd_3, Sd_4, Sd_5) are essentially composed of epsomite ($MgSO_4.7H_2O$), carnallite ($KCl.MgCl_2.6H_2O$) and gypsum ($CaSO_4.2H_2O$), respectively. Also, they contain NaCl, hexahydrite and some ions from the coating solution.

The desired product, which is collected from the last process stage, is basically made of bischofite of purity more than 90% (undesired substances are mainly carnallite and ions from impregnating solution). Its morphology is represented by Fig. 4 which shows the hygroscopic character of this kind of salt.

To more investigate this product, thermogravimetry-differential thermal analysis (TG-DTA) was performed and the result was compared with that obtained for a commercial bischofite (MC6). As shown in Fig. 5, great similarity of thermal behaviours is noted. In particular, the TG-DTA thermogram of each compound shows the succession of five endothermic peaks corresponding to five thermal decomposition stages and a total weight loss of 64% when the compound is heated between 50 and 700°C.

Finally, it should be noted that the resulting mother liquor S_6 remains rich in magnesium and chloride ions; therefore it can be further treated to recover from it more magnesium chloride salts.

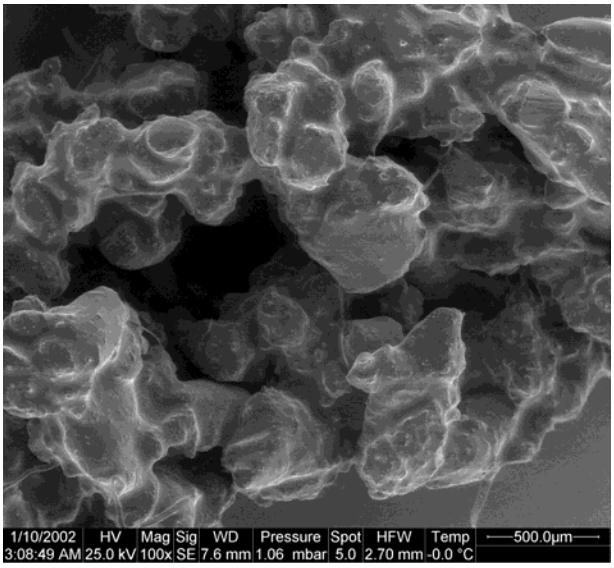

Fig. 4. SEM image of Sd6 salt.

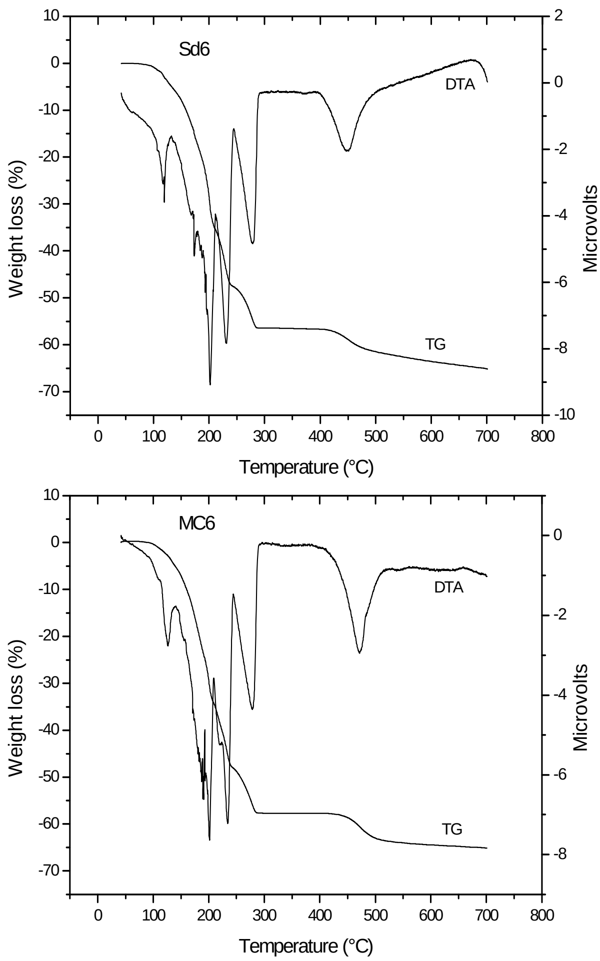

Fig. 5. TG-DTA thermograms of the commercial and the experimentally obtained bischofite.

V. CONCLUSIONS

The present work is a contribution to the valorisation of Sebkha El Melah natural brine. To perform this task, two main unit operations are experienced, firstly isothermal evaporation and crystallization and then chemical precipitation. To characterize the handled phases many techniques are used: potentiometry, complexometry, gravimetry, X-Ray diffraction and SEM. In this way magnesium chloride salt, the bischofite ($MgCl_2.6H_2O$) of purity higher than 90% is extracted. As a result of the implementation of the different treatment stages, various by-products are formed. Also, it has to be mentioned that the final resulting mother liquor remains rich in magnesium and chloride ions, thus it can be subjected to further treatments in order to make more magnesium chloride salt.

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