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# Study of the evaporation of Tunisian brine (Chott El Jerid) comparison between the sequences of crystallization experimental and theoretical

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## ABSTRACT

The evaporation of a Tunisian brine sample involving the system $Na^+$, $K^+$, $Mg^{2+}$/ $Cl^-$ $SO_4^{2-}$-$H_2O$ was studied under atmospheric pressure and at temperature room equal to 298 K. The selective densities of precipitation of halite (NaCl) and the co-precipitation of halite and sylvinite (KCl), and the co-precipitation of halite sylvinite and epsomite ($MgSO_4.7H_2O$), were determined. The sequence of crystallization determined experimentally has been compared with the theoretically sequence.

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## KEYWORDS

X-ray-diffraction;
Phase equilibria;
Vapour deposition;
Inorganic compounds;
Crystal fields.

## INTRODUCTION

Southern Tunisian's natural brines represent an important source of mineral salts with a high economic value. These salts are recovered by simple solar evaporation. Indeed, during isothermal solar evaporation it is possible to obtain mineral salts and to determinate the precipitations at the same time the sequences of the different salts as a function of the composition, and the density of the brine.

The present study was carried out in order to determinate the sequence of crystallization relating to the natural evaporation in order to develop an experimental work of the brine Chott El Jerid, located in south of Tunisia. The brine used in this study was drawn from the eastern part of Chott El Jerid on the road between Tozeur and Kebili (Figure 1).

## EXPERIMENTAL

### Evaporation of brine

Ten litters of brine of Chott El Jerid, was placed in a PVC thermostatic bath which was maintained at room temperature (around 298 K) and under atmospheric pressure. The solution is submitted to a continuous current of air so that the evaporation became easy. The ionic composition of the natural brines which has been studied is reported in TABLE 1.

### Sampling of solid and saturated solution

The evolution of the evaporation of brine was followed according to the density: The composition of liquid samples and solid phases was determinated by chemical analysis.

The solid phases formed constituting the precipi-

tated salts were separated by filtration. One of part is stocked in a small plastic bottle for protection from the atmospheric humidity witch served for RX and the other part was diluted two-fold with distilled water in order to avoid any further precipitation due to evaporation or a decrease in temperature. The concentrations of major ions in the liquid and in the solution of solid phases reported respectively in TABLE 2 and 3.

**Figure 1 : South of tunisia: geographical sites of Chott El Jerid.**

**TABLE 1 : Chemical analysis and density of the natural brine of Chott El Jerid.**

| Density | $Na^+$ (g $L^{-1}$) | $K^+$ (g $L^{-1}$) | $Mg^{2+}$(g $L^{-1}$) | $Cl^-$(g $L^{-1}$) | $SO_4^{2-}$(g $L^{-1}$) |
|---|---|---|---|---|---|
| 1.1416 | 105 | 9 | 12 | 197 | 12 |

## Analysis

The changes in composition of the brine were followed by analysis of the major element ($Na^+$, $K^+$, $Mg^{2+}$, $Cl^-$ and $SO_4^{2-}$). The $Mg^{2+}$ was determined by complexometric titration with EDTA[1,2]. The $Na^+$ and $K^+$ were analysed by flame spectrophotometric method[3,4]. A potentiometric titration was applied to the chloride ions[5]. $SO_4^{2-}$ ion concentration was determined gravimetrically[6,7]. The solid phases were identified by X-ray diffraction method and chemical analyses.

## RESULTS AND DISCUSSION

The analyse of the results was carried out respectively with the variation in the concentrations of different ions as a function of the density, the variation of density as a function of times and the variation of the conductivity of a solution as a function of the density.

## Variation of the concentration of major ions as a function of density

The concentrations of major ions in the liquid and in the solution of solid phases reported respectively in TABLE 2 and 3.

**TABLE 2 : Chemical analysis of saturated solution (concentrations expressed in molL$^{-1}$).**

| Times /days | Density | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | Probable solid phases |
|---|---|---|---|---|---|---|---|
| 0 | 1.1416 | 5.005 | 0.231 | 0.185 | 5.549 | 0.028 | - |
| 3 | 1.1838 | 5.120 | 0.246 | 0.146 | 5.655 | 0.038 | NaCl |
| 4 | 1.1852 | 5.100 | 0.222 | 0.122 | 5.022 | 0.035 | " |
| 6 | 1.1868 | 4.920 | 0.234 | 0.134 | 5.353 | 0.035 | " |
| 9 | 1.1870 | 4.852 | 0.241 | 0.141 | 5.292 | 0.037 | " |
| 10 | 1.1875 | 4.701 | 0.247 | 0.147 | 4.947 | 0.037 | " |
| 11 | 1.1879 | 4.654 | 0.251 | 0.151 | 4.905 | 0.036 | " |
| 13 | 1.1906 | 4.510 | 0.253 | 0.153 | 4.762 | 0.036 | " |
| 14 | 1.1955 | 4.465 | 0.281 | 0.181 | 4.746 | 0.038 | " |
| 16 | 1.2013 | 4.353 | 0.295 | 0.195 | 4.648 | 0.040 | " |
| 17 | 1.2026 | 4.342 | 0.304 | 0.322 | 4.645 | 0.041 | " |
| 20 | 1.2031 | 4.305 | 0.307 | 0.336 | 4.611 | 0.042 | " |
| 21 | 1.2043 | 4.358 | 0.314 | 0.358 | 4.672 | 0.045 | " |
| 23 | 1.2057 | 4.280 | 0.322 | 0.480 | 4.601 | 0.047 | " |
| 25 | 1.2061 | 4.287 | 0.377 | 0.491 | 4.664 | 0.048 | " |
| 29 | 1.2077 | 4.253 | 0.386 | 0.453 | 4.639 | 0.049 | " |
| 31 | 1.2082 | 4.235 | 0.402 | 0.600 | 4.637 | 0.050 | " |
| 34 | 1.2098 | 4.245 | 0.495 | 0.668 | 4.740 | 0.053 | " |
| 36 | 1.2119 | 4.269 | 0.498 | 0.725 | 4.767 | 0.062 | " |
| 37 | 1.2161 | 3.742 | 0.445 | 0.952 | 4.391 | 0.073 | " |
| 39 | 1.2192 | 3.538 | 0.670 | 1.259 | 4.408 | 0.072 | " |
| 40 | 1.2532 | 2.001 | 0.773 | 1.729 | 3.397 | 0.091 | NaCl + KCl |
| 43 | 1.3047 | 0.729 | 0.806 | 2.318 | 1.735 | 0.619 | " |
| 44 | 1.3069 | 0.478 | 0.637 | 2.640 | 1.315 | 0.418 | NaCl+KCl+ $MgSO_4.7H_2O$ |
| 47 | 1.3124 | 0.264 | 0.421 | 2.662 | 0.867 | 0.325 | " |

The Figure 2 representing the concentrations of different ions in the liquid at various densities reveals that at the beginning of the evaporation the number of moles of water decreases without any precipitation, and the brine becomes more concentrated.

At density between 1.1838 and 1.2192 there are simultaneous and rapid decreases in the concentrations $Na^+$ and $Cl^-$, which seems that it corresponds to crystallization field of the halite (NaCl) and this was confirmed by the X-ray diffraction spectra of the solid obtained.

**TABLE 3 : The concentrations of major ions in the solution of solid phases.**

| | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | $H_2O$ | Solid phases |
|---|---|---|---|---|---|---|---|
| $S_1$ | 47.07 | 0.00 | 0.62 | 47.38 | 2.77 | 3.38 | NaCl |
| $S_2$ | 47.20 | 0.00 | 0.29 | 45.73 | 2.97 | 5.02 | ″ |
| $S_3$ | 47.53 | 0.27 | 0.54 | 45.08 | 3.19 | 4.68 | ″ |
| $S_4$ | 47.46 | 0.00 | 1.16 | 48.92 | 0.55 | 2.17 | ″ |
| $S_5$ | 47.39 | 0.00 | 0.84 | 46.28 | 2.91 | 3.82 | ″ |
| $S_6$ | 49.28 | 0.00 | 0.89 | 47.20 | 3.32 | 0.85 | ″ |
| $S_7$ | 49.18 | 0.00 | 0.61 | 48.57 | 1.16 | 1.03 | ″ |
| $S_8$ | 48.30 | 0.00 | 0.62 | 46.45 | 2.72 | 3.10 | ″ |
| $S_9$ | 46.42 | 0.00 | 0.61 | 47.33 | 2.13 | 4.43 | ″ |
| $S_{10}$ | 46.35 | 0.00 | 0.93 | 46.04 | 2.08 | 5.45 | ″ |
| $S_{11}$ | 46.42 | 0.00 | 1.15 | 47.29 | 1.01 | 4.56 | ″ |
| $S_{12}$ | 48.05 | 0.00 | 0.62 | 46.81 | 1.64 | 3.59 | ″ |
| $S_{13}$ | 47.23 | 0.00 | 0.94 | 47.54 | 1.12 | 3.66 | ″ |
| $S_{14}$ | 46.28 | 0.32 | 0.96 | 45.96 | 3.83 | 4.25 | ″ |
| $S_{15}$ | 46.49 | 0.30 | 0.61 | 48.01 | 1.64 | 3.68 | ″ |
| $S_{16}$ | 46.82 | 0.29 | 0.88 | 47.99 | 1.06 | 3.42 | ″ |
| $S_{17}$ | 46.68 | 0.00 | 0.57 | 46.40 | 1.94 | 5.21 | ″ |
| $S_{18}$ | 46.54 | 0.30 | 0.90 | 45.95 | 2.02 | 5.12 | ″ |
| $S_{19}$ | 46.00 | 0.28 | 0.56 | 47.40 | 1.45 | 4.92 | ″ |
| $S_{20}$ | 47.47 | 0.28 | 1.14 | 47.19 | 2.05 | 2.78 | ″ |
| $S_{21}$ | 39.86 | 7.05 | 1.08 | 46.92 | 2.39 | 3.73 | NaCl+KCl |
| $S_{22}$ | 30.84 | 13.27 | 2.65 | 44.11 | 4.81 | 6.14 | ″ |
| $S_{23}$ | 2.08 | 8.14 | 8.71 | 10.23 | 5.74 | 62.12 | NaCl+KCl+ $MgSO_4.7H_2O$ |
| $Sj_{24}$ | 1.68 | 8.72 | 8.55 | 10.22 | 5.74 | 62.12 | ″ |

The concentration of $K^+$ increases at the density 1.2192 and then decreases.

The chemical analyses and the X-ray diffraction of the solid obtained at densities between 1.2192 and 1.3047 confirms the presence of KCl, for this purpose the field corresponds to a co-precipitation of halite and sylvinite (KCl).

The curve illustrating the variation in the concentration of $Mg^{2+}$ and the ion $SO_4^{2-}$ as function of the density, shows an ascending tendency at density equal to 1.3047 and decreases beyond this value. This result demonstrated that there is precipitation of a sulfate of magnesium salts as epsomite ($MgSO_4.7H_2O$) this was confirmed by the X-ray diffraction spectra of the solid obtained (Figure 3).

The evolution of the ratios of the $K^+/Na^+$ and $K^+/Cl^-$ ions as a function of density is represented in Figure 4, which shows an important increase at the density d = 1.2192 and which extends to the density d = 1.3047. This means that these fields corresponded to the co-precipitation of NaCl and KCl.

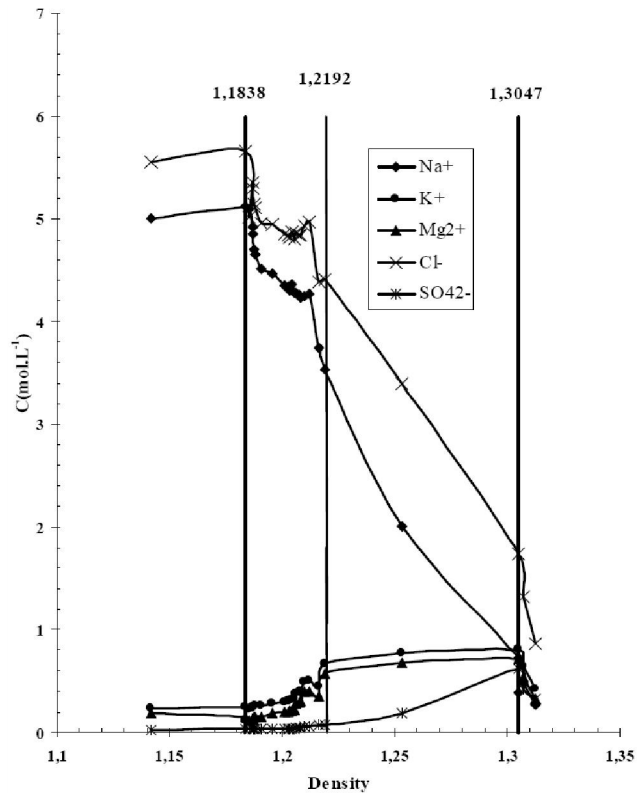


**Figure 2 : Variation in the concentrations of different ions as a function of the density.**

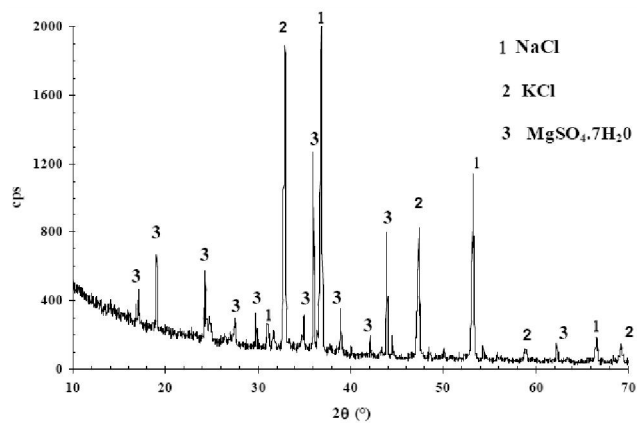


**Figure 3 : XR diffraction of salt $S_{23}$.**

## Variation of density as a function of times

The variation of density as a function of times which is given in Figure 5 presents three parts. This corresponds to the changes of the number and nature of the equilibrium phases. In fact, according to the results of chemical analysis and X-ray diffraction of solid phase, these breaks coincide with:

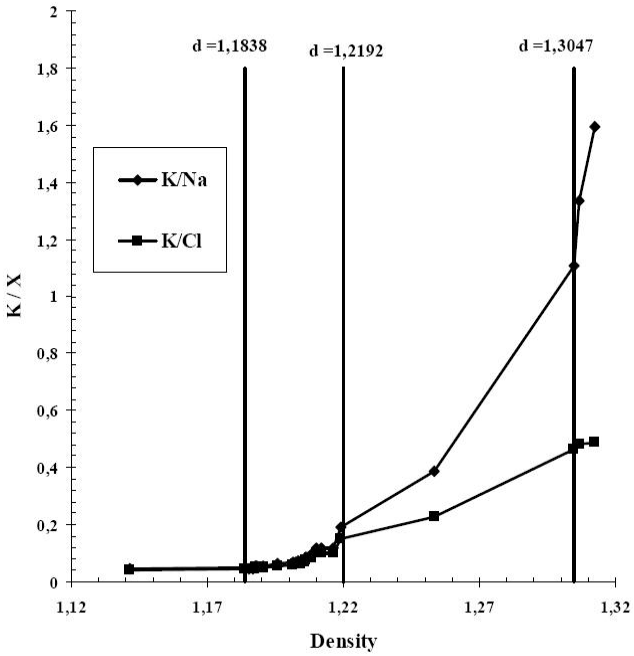


**Figure 4 : Variation of frations $K^+/X$ ($X= Na^+, Cl^-$) as a function, of density.**

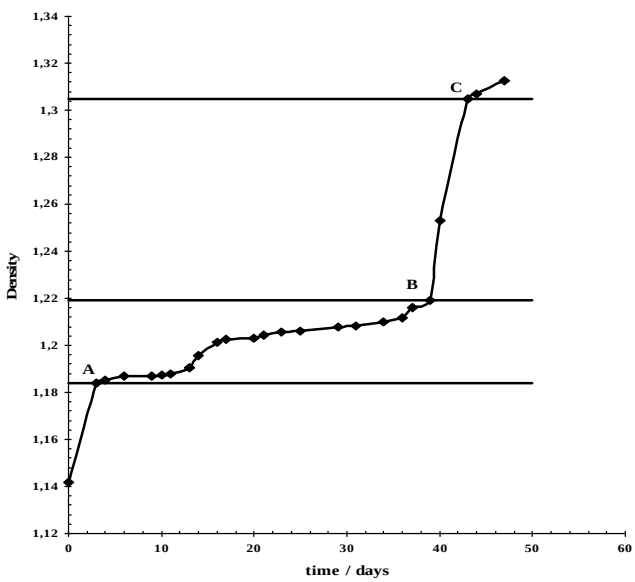


**Figure 5 : Variation of density as a function of time.**

Break A: firstly there was precipitation of halite NaCl which continues to point B.

Break B: then there was precipitation of KCl. Co-precipitation of NaCl and KCl continues from point B to point C.

Break C: Beginning of precipitation of a magnesium sulfate salt $MgSO_4.7H_2O$.

## Variation of the conductivity of a solution as a function of the density

The values of the conductance saturated solutions measured during the evaporation of brine from Chott El Jerid according to their densities given in Figure 6 shows three changes, defining three fields of crystallization.

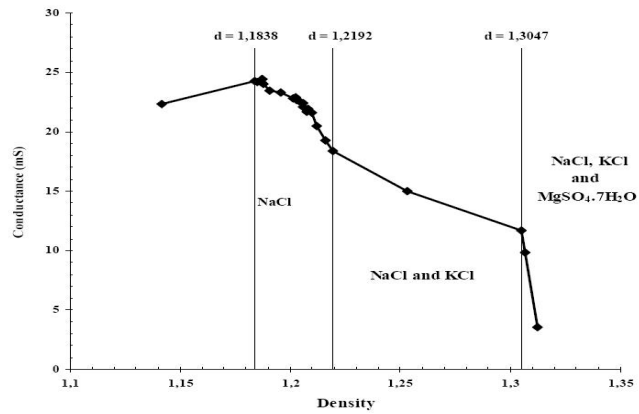


**Figure 6 : Variation in the conductivity as a function of the density.**

The values of the densities of these changes are those obtained by the study of the variation in the concentration as a function of the density.

The results of this study show that the sequence of crystallization of the Chott El Jerid

brine at 298 K and under atmospheric pressure comprises four steps:

- d < 1.1838 : Concentration of brine
- 1.1838 < d < 1.2192 : Precipitation of NaCl
- 1.2192 < d < 1.3047 : Co-precipitation of NaCl and KCl
- d > 1.3047 : Co-precipitation of NaCl, KCl and $MgSO_4.7H_2O$

The viscous aspect of the saturated solution obtained at end of evaporation is due to the concentration of ions $Mg^{2+}$ present in the solution remaining.

## Comparative study between experimental and theoretical paths

The comparison between the experimental crystallization sequence obtained for the Chott El Jerid brine during evaporation and theoretically (S0-S1-S2, Figure 7) determined from the diagram of the quinary system representative of brine[8]. Shows that there is concordance between the two first steps of crystallization. From the third step, the brine does not evolve in the same way for both sequences. The theoretical sequence provides the précipitation of double salt $KClMgSO_4.3H_2O$ (kainit), while experimentally, the

$MgSO_4.7H_2O$ (epsomite) was harvested. This difference is probably due firstly to the kinetics of precipitation kainit which is very slow compared to epsomite[9], and secondly it is also significant to note that the epsomite $MgSO_4.7H_2O$ was formed apart from its stable field of existence. That seems to indicate that the crystallisation field of this salt has a metastable space extension, which partly covers the space reserved for the kainite $KClMgSO_4.3H_2O$ (Figure 7)[10-12].

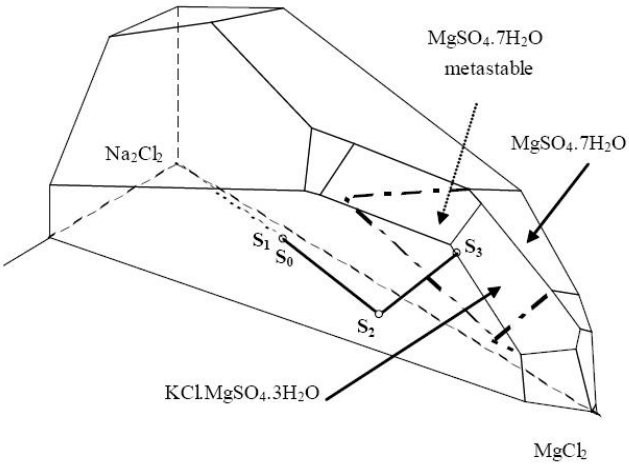


**Figure 7 : Field of crystallization of NaCl: theoretical path of the brine: domain metastable $MgSO_4.7H_2O$.**

## CONCLUSION

In the present work, a study was made concerning evaporation of brine from a naturel saumure of Chott El Jerid situated in the south Tunisian. The brine was subjected to evaporation in the laboratory under conditions as close as possible to the natural conditions.

The densities at the beginning of crystallization of NaCl, KCl and $MgSO_4.7H_2O$ salts were determined.

The comparison between the sequences of crystallization experimental obtained for brine Chott El Jérid in the course of its evaporation and that determined theoretically from the diagram of the system representative of brine shows there is concordance between the two first stages of crystallization and at the third stages, there is difference. This is due to metastability and to the kinetics of formation of the epsomite which is faster than that kainite.

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