

## Chemical Study of free brine in solar salt works of Sfax Saline (E.S of Tunisia)

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A chemical study of free brine (salinity from 41 to 400 ‰) of the solar salt works of sfax saline (E.S of Tunisia) was carried out by measuring the following parameters: pH, temperature and density and the analysis of major (Na, K, Ca, Mg, Cl and sulphate) and minor elements (Li, Rb and Sr ). All analytical methods used in this work were adapted to these media of high salinity. Evolution of previous parameters and concentrations of the different elements investigated has been plotted as a function of concentration factor calculated on a basis of lithium content of seawater (coast of Sfax) and those of the brine of salt works.

### 1.INTRODUCTION

Solar Salt works of Sfax saline were installed on a little peninsula so-called "Ras-Sfax" (Sfax head) located in southern Sfax City. It is a platform about 1500 ha area, divided on several ponds along seacoast about 12 km (fig. 1). From the sea, water display into a series of ponds communicating between them by diagonal way through which the brine continuously flows by gravity or by pump and their concentrations were usually controlled by measure of densities.

After concentration, we obtained 25 – 26°B brine that is allowed into the crystallising pond where halite crystallises. Brines coming from crystallising pond (29.5 – 30.5 °B) were also evaporated to obtain magnesium brine.

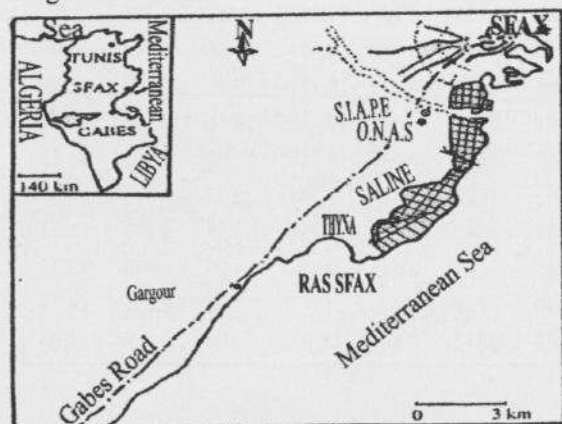


Figure.1: Location map of Sfax saline.

The objective of this study is to follow evolution of physical-chemical parameters and chemical composition of seawater during evaporation process. Factor "FC", used as a reference scale, was calculated on a basis of lithium content of seawater (coast of Sfax) and those of the brine of salt works.

### 2.SAMPLING AND EXPERIMENTALS METHODS

#### 2.1.Sampling

Waters from Sfax saline were sampled during two periods (May and November 1987). All the samples are free brines with the exception of those taken in the ponds of preparation of magnesium solutions that are interstitial brine. In addition, in the aim of discovering all salinity's field, some samples were obtained by evaporation in the laboratory.

#### 2.2Analytical methods

After filtration and acidification of sample brines, cations were analysed by Atomic Absorption spectrometry with flame (GBC 902). Chlorides and sulphides were analysed by liquid Chromatography method (HPLC). All analytical methods used were adapted to this media of high salinity.

### 3.RESULTS AND DISCUSSIONS

Some results of chemical analyses of the brine samples are presented in table I. The evolution of the pH and concentration (expressed in moles. kg<sup>-1</sup>) of several chemical species (Na, K, Ca, Mg, Cl, SO<sub>4</sub><sup>=</sup>, Rb and Sr) was plotted as a function of concentration factor.

#### 3.1. Physical parameters

##### 3.1.1. Temperature and density

Temperature, varying between 15 and 32 °C, increase with the increasing of water salinity and atmospheric temperature. Also, density increases from 1.024 to 1.310 from seawater to magnesium chloride brine. In the first stage of evaporate process the increase in density is due to evaporation, afterwards density was controlled by evaporation-salt precipitation antagonist effect.

##### 3.1.2. pH

The brines of Sfax saline show a gradual decreasing of the pH. It passed from 8.3 for seawater to 5.8 for magnesium chloride solutions (fig.2). This evolution, that correlated with the increase of salinity, was noted in several experimental studies (KRUMGALZ, 1980). And on natural systems (LANDRY and JACCARD, 1982). Others phenomena piles up to this of salinity effect and are responsible of local variations of pH for some brines samples. As an example we can mention photosynthetic activity (that decrease the CO<sub>2</sub> and make increase the pH) and bacteria activity responsible of gypsum sulphite reduction by liberate H<sub>2</sub>S that make increase the medium acidity. In most concentrated brines, biological activities is completely absent and the medium pH decrease with the increase of brines salinity.

Table.I: Chemical composition (mole/kg) of some brine of Sfax saline.

Sample	FC	T	Density	pH	Na	K	Mg	Ca (10 <sup>-2</sup> )	Cl	SO4	Li	Rb (10 <sup>-6</sup> )	Sr (10 <sup>-3</sup> )	Br (10 <sup>-3</sup> )
EM	1.00	17.5	1.020	8.3	0.560	0.012	0.065	1177	0.628	0.037	0.030	1.29	0.091	0.85
A1*	1.01	20.0	1.023	8.2	0.556	0.012	0.061	1565	0.645	0.039	0.030	2.54	0.091	0.89
A1	1.14	15.5	1.027	7.5	0.583	0.012	0.056	1181	0.634	0.032	0.034	1.19	0.090	1.26
A10*	1.38	22.5	1.038	8.1	0.707	0.015	0.083	2425	0.853	0.042	0.041	2.77	0.128	1.25
A10	1.47	15.0	1.037	8.3	0.773	0.016	0.077	1639	0.868	0.042	0.044	1.44	0.123	1.32
C21*	1.62	24.0	1.048	8.1	0.936	0.020	0.094	2796	1050	0.050	0.049	3.70	0.156	1.71
C21	1.87	18.2	1.048	8.4	0.987	0.026	0.118	2424	1204	0.062	0.056	1.82	0.181	1.92
C22	2.36	17.9	1.080	8.1	1.333	0.042	0.184	3525	1612	0.095	0.071	2.26	0.266	2.35
C22*	3.38	25.0	1.097	7.8	1.905	0.044	0.234	5368	2303	0.109	0.103	5.83	0.341	3.69
M1*	3.38	24.2	1.106	7.6	2.042	0.047	0.256	5885	2455	0.124	0.104	6.63	0.289	3.61
M1	3.69	19.6	1.098	7.9	2.041	0.042	0.219	3931	2378	0.118	0.114	5.00	0.327	3.82
M3	4.37	19.5	1.127	8.1	2.919	0.058	0.298	3441	3356	0.132	0.138	4.71	0.408	5.03
M3*	5.09	22.5	1.159	7.6	3.140	0.069	0.384	3786	3738	0.156	0.159	11.12	0.429	5.04
B12	6.35	19.0	1.159	7.9	3.682	0.077	0.390	3045	4195	0.163	0.203	8.92	0.468	5.55
PM6*	9.09	22.5	1.198	7.5	4.880	0.124	0.610	0.888	5785	0.257	0.304	21.60	0.489	7.50
PM6	11.40	19.8	1.207	7.7	4.289	0.132	0.687	1099	5417	0.240	0.371	10.46	0.470	8.35
TS9	13.27	20.8	1.228	7.4	3.985	0.205	1085	0.691	5776	0.413	0.435	24.16	0.394	11.61
TS18*	15.23	25.0	1.221	7.8	4.697	0.242	1114	0.877	6336	0.447	0.518	37.90	0.403	11.23
TS20	17.20	20.5	1.235	7.5	3.568	0.272	1338	0.555	5692	0.527	0.565	29.42	0.316	11.95
R1***	18.18	19.5	1.238	7.2	3.545	0.280	1494	0.474	5542	0.535	0.594	30.58	0.129	11.04
R25**	25.80	35.0	1.260	7.1	2.19	0.420	1961	0.335	5544	0.545	0.822	24.09	0.073	11.35
S4***	58.97	20.0	1.289	6.3	0.744	0.537	3219	0.140	6724	0.470	1877	77.27	0.001	14.74
L4	80.47	23.0	1.309	5.8	0.179	0.088	3815	0.153	6857	0.427	2502	50.00	0.006	15.08

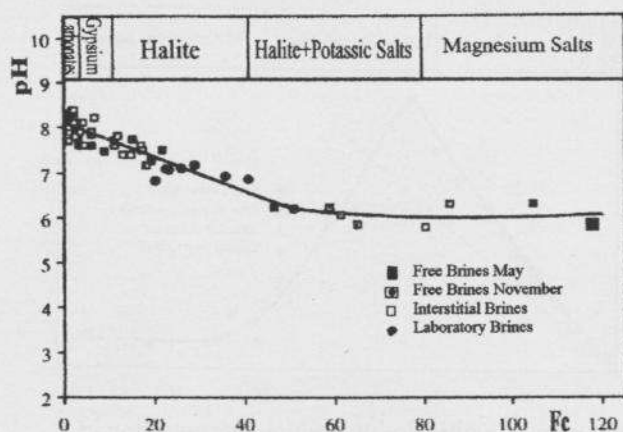


Figure 2: pH evolution in free brines as a function of concentration factor.

### 3.2. Chemical composition

In multistage evaporation, brines are transferred from one pond to another; every pond has a concentration level higher than that of the previous pond. Therefore, ionic concentration of solutions must be varied. These variations, sometimes very important, are controlled by several effects of which concentration by evaporation and impoverishment by precipitation are the most important.

#### 3.2.1. The major elements:

##### *a-The behaviour of sodium and the chloride ion:*

The concentration of sodium Sfax saline's brine evolves in a linear way in function of "FC", as long as the NaCl precipitation remains still relatively discrete ( $FC \leq 10$ ). The same behaviour is observed for the chloride ion, whose level increases in a linear way of FC till the stage of massive halite deposit, the first phase of its integration in saline paragenesis. In the brine under saturation with respect to NaCl, the evolution of the concentration in sodium and chloride ion explains the only evaporation effect. The biological effect, as well as the precipitation and re-dissolution phenomena are insignificant, as shown by the homogeneity of the contents detected in May and November, on the one hand and their place over the straight line that represents the evaporation effect ( $C_i = FC_i \cdot C_o$ ) on the other hand (figure 3 and 4). With the beginning of the massive precipitation of halite ( $FC \geq 13$ ), the fall of  $Na^+$  concentration is evidently

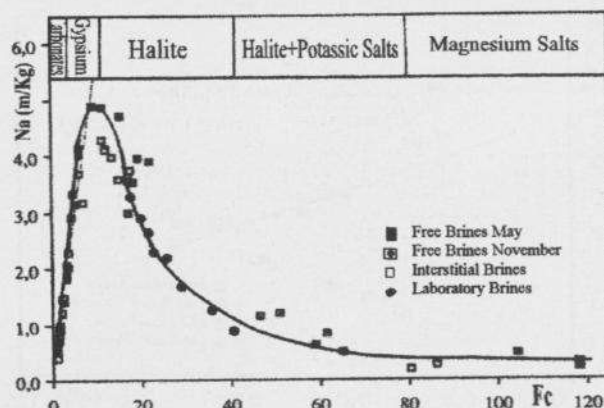


Figure 3: Evolution of Sodium concentration in brines of Sfax saline.

more marked than that of  $Cl^-$ . It should be pointed out that the almost totality of sodium of seawater takes part in the formation halite, while there remains some important quantities of chloride in the residual brine. The chloride ion, whose concentration continues to rise in the brine, serves as a compensatory ion for  $K^+$  and  $Mg^{++}$ . The connection  $Na/Cl$ , which is close to 0.8 in the initial solution, remains constant while the balance of the brine with NaCl has not been reached yet. With the beginning of the massive precipitation of halite, the relative fall of  $Na^+$  concentration is much more significant than that of the  $Cl^-$  with the fact that its concentration in the initial seawater is lower than that of  $Cl^-$ . As a result, the evolution takes place towards the chloride pole, as it remains balanced with the halite.

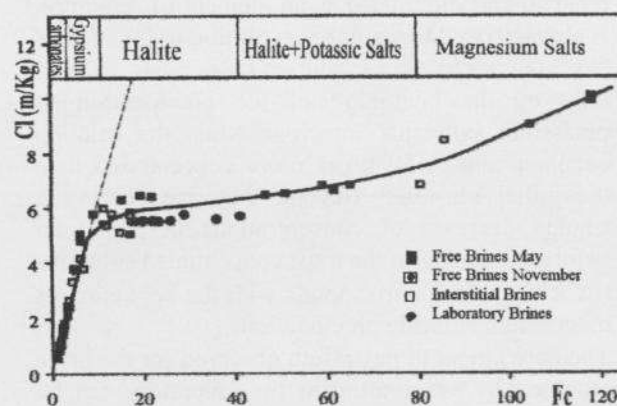


Figure 4: Evolution of chloride concentration in brines of Sfax saline.



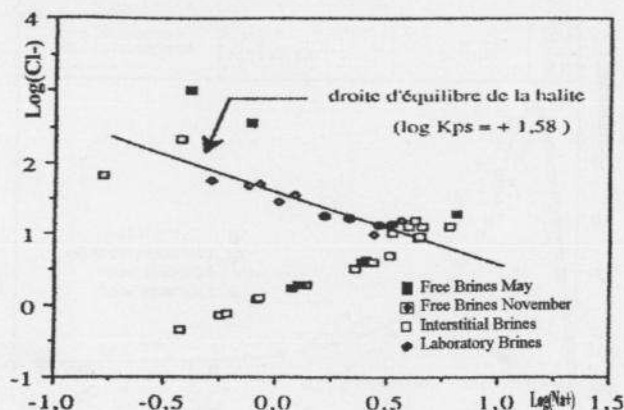


Figure.5: The brine's saturation test with respect to halite.

In the diagram of figure 5, where halite equilibrium line has been drawn, we observe a linear evolution of the logarithm of  $\text{Na}^+$  activity in function of that of the  $\text{Cl}^-$  activity. The distance from equilibrium line is not necessarily significant and could be explained by uncertainties in calculation of activities. In the most dense solutions, the dispersion of the values is due on the one hand to the low content in sodium of this brine, therefore the saturation is apparent and there is not precipitation of  $\text{NaCl}$  and on the other hand bordering on the application of PITZER Model (maximal ionic strength = 7) for the solutions as well concentrated as that of Sfax saline.

#### b) The potassium's behaviour:

The seawater (Sfax coast) contains almost 12 mmoles/Kg of potassium. This ion, considered as residual and often used as an element of reference, is characterised by its linear evolution in function of "FC" (figure 6). This evolution is seriously affected only by the beginning of the precipitation of potassium salts that intervene when the solution becomes almost 50 times more concentrated than the initial seawater. Beyond that, we observe a sudden decrease of concentrations in potassium before stabilising in the most concentrated solutions ( $\text{FC} \geq 80$ ); which corresponds with the beginning of magnesium chloride precipitation.

The enrichment in potassium observed for the brine obtained by evaporation in the laboratory can be explained only by pollution in the course of manipulation.

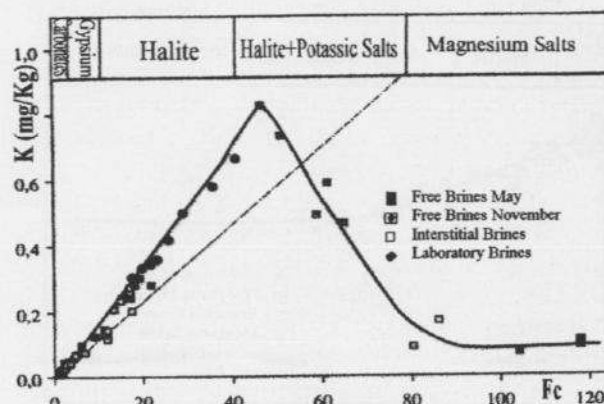


Figure.6: Evolution of potassium concentration in brines of Sfax saline.

#### c) The magnesium's behaviour:

Although it can be integrated in several evaporitic minerals, likely to take part in the first stages of evaporation (dolomite, sepiolite, and stevensite), the concentration of magnesium increases in a linear way as a function of "FC" (figure 7). This evolution is affected only on the brine coming out of the crystallising pond ( $\text{FC} \geq 30$ ), where the magnesium takes part largely in the formation of magnesium salt, that precipitate relatively late, compared to calcium, sodium and potassium salts. The reason is on the one hand the low concentration in  $\text{Mg}^{++}$  in the initial solution (compared with sodium) and on the other hand the large solubility of the most of the magnesium salts.

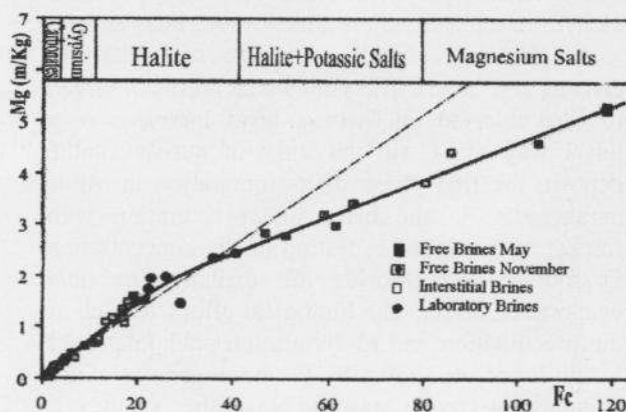


Figure.7: Evolution of magnesium concentration in brines of Sfax saline.

**d) The behaviour of calcium and sulphate:** In spite of its large participation in the formation of the carbonates, that precipitate from the beginning of the evaporation, the contents in calcium show a linear relation as a function of "FC", even with the emergence of the first crystal of gypsum on the borders of the pond. Then, they suddenly decrease with massive store of the gypsum crust (FC = 4). In addition, we noticed that for the same factors of concentration, the contents in calcium, detected in November, were much lower than that measured in May (figure 8). The last fact could be explained by the precipitation of the calcium minerals (through chemical way or biological activity) favoured by physical and chemical conditions propitious to this time of the year. Another possible explanation, for the contents detected in May, is the provision in calcium, resulting from the destruction of the gypsum crust by the bacteria. The sulphate content does not appear to be much affected by the precipitation of gypsum. The general evolution is an increase from the initial solutions till mother brines (FC  $\geq$  25). In the detail, we can note during the beginning of the gypsum's precipitation, a light bending in the curve  $SO_4^{2-}$  versus FC (figure 9). Consequently, the concentration by evaporation is most important and the contents continue to grow till a factor "FC" equal to 25. The contents in  $SO_4^{2-}$  decrease lightly and remain always between 0.4 and 0.6 moles/Kg. This decrease is probably due to the precipitation of the sulphates salts relatively more soluble (magnesium sulphate).

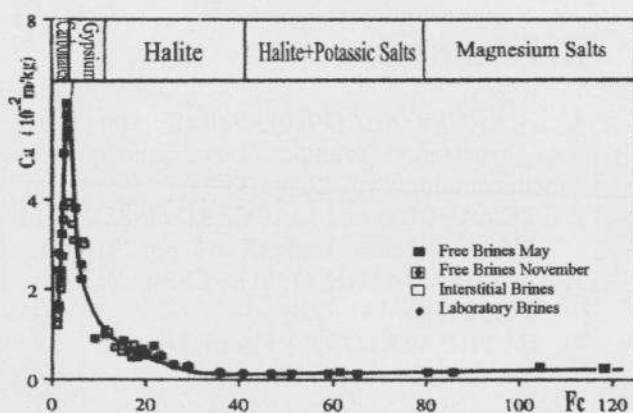


Figure 8: Evolution of calcium concentration in Brines of Sfax saline.

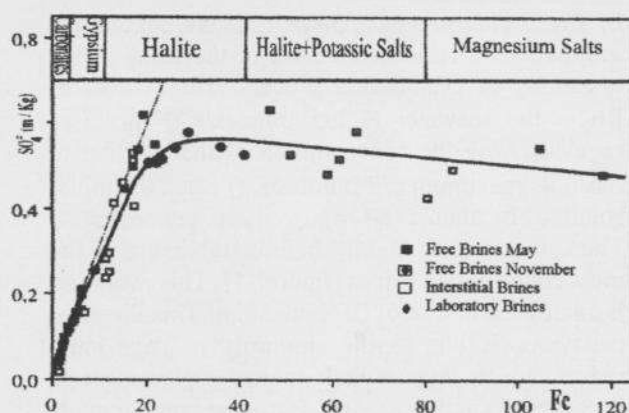


Figure 9: Evolution of sulphate concentration in brines of Sfax saline.

### 3.2.2. The minor elements

**a)- The lithium's behaviour:** In the free brine of Sfax Saline, the lithium piles up in solution during the concentration of the water by evaporation. The content in lithium varies from 30  $\mu$ moles/Kg in the seawater to 4087  $\mu$ moles/Kg in the most concentrated brine. This ion is not involved in any minerals of saline paragenesis that precipitate gradually from the evaporation of the brine till we reach a salinity of 320 %.

The molar link Mg/Li varies from 2500 in the initial water to 1100 in the most concentrated solutions (figure 10). Because of this, till a factor concentration of 40, the geochemistry of lithium is not linked to that of the magnesium whose content is controlled by the store of magnesium sulphate. In the densest brine, the link Mg/Li becomes constant and witnesses the co-precipitation of  $Li^+$  with the magnesium salts thanks to the similarity in their ionic radius.

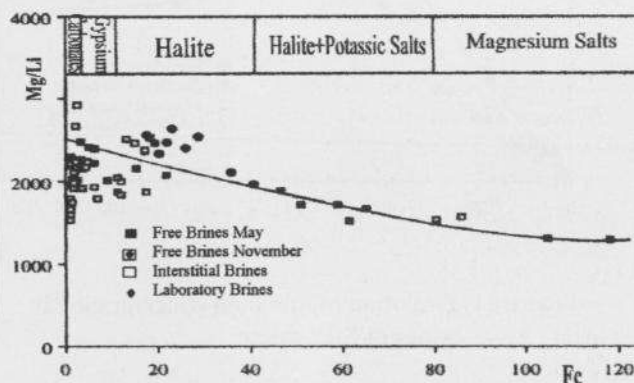


Figure 10: Evolution of molar link (Mg/Li) in brines versus F.C.

b) *The rubidium's behaviour*: Like the lithium, the rubidium is a residual element in the brine at the beginning of evaporation process. The content of Rb in the seawater ( $1.295 \mu\text{moles/Kg}$ ) increases regularly with the concentration of the solution to reach its maximum ( $77 \mu\text{moles/Kg}$ ) when the initial solution is almost 60 times more concentrated. Then, it decreases lightly before stabilising in the most concentrated brines (figure 11). This evolution is analogous to that of the potassium. This identical behaviour is due to the similarity in their ionic radius, which favours their mutual replacement in the crystal networks. In fact, the rubidium is generally associated to potassium minerals carnallite and sylvite and it forms no mineral of rubidium alone.

c) *The strontium's behaviour*: In the Sfax Saline's solutions, the general evolution of the strontium concentration (figure 12) shows a certain similarity with that of calcium, in spite of the fall of  $\text{Sr}^{++}$  intervenes late compared with that of  $\text{Ca}^{++}$ . This fact suggests that the precipitation of the minerals of strontium, if it ever takes place, intervenes at the same time with that of the gypsum and not before, as thought by some writers (HERRMANN, 1961) or during the store of halite (USDOWSKI, 1973).

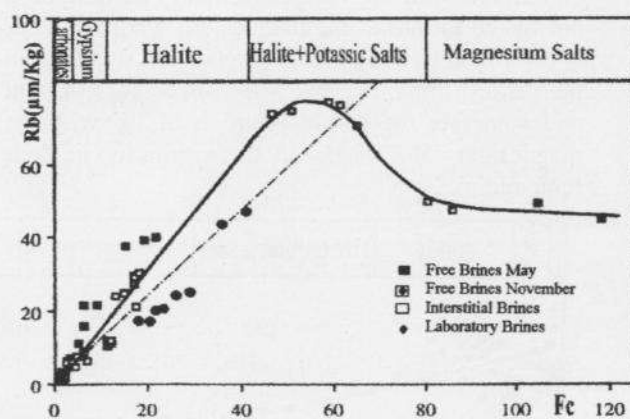


Figure 11: Evolution of rubidium concentration in brines of Sfax saline.

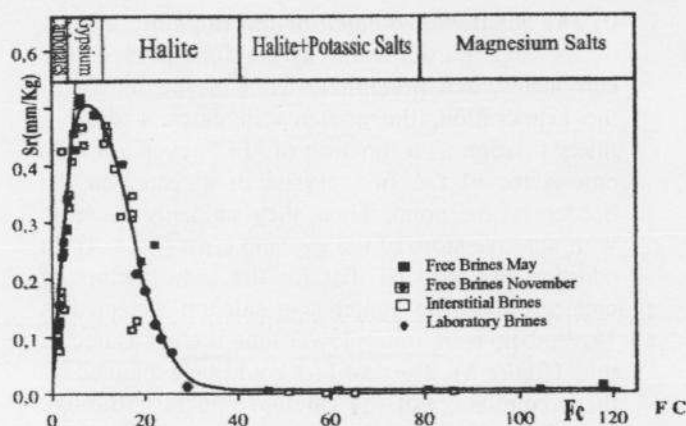


Figure 12: Evolution of strontium concentration in brines of Sfax saline.

## CONCLUSION

Chemicals studies carried out on the free brines of Sfax saline that allow as to follow the evolution of physical parameters and chemical concentrations of major and minor elements in seawater evaporated. In the first stage of evaporate process, the increasing of ions concentration is due to evaporation; in contrast in the most concentrated brines the evolution of several elements was controlled by evaporation-salt precipitation antagonist effect.

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