THE SALT DEPOSIT THAT CAN BE PRECIPITATED FROM FREE BRINES OF SFAX SALINE (S. E OF TUNISIA)

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EXTENDED ABSTRACT

The saturation test realized on free brines of Sfax Saline vis-à-vis the principal evaporating minerals (carbonates, silicates, sulphates and chlorides) has been achieved by the SIMEQ and EQSEL programs which are based on the ion-specific interaction model developed by PITZER. The results that we obtained show that these solutions appear supersaturated or in equilibrium in relation to certain salts and in large part under-saturated in relation to others.

From observations on ponds, X-ray analyses and saturation tests realized on brines, we noticed that some minerals don't precipitate although their ion activity products greatly exceed their solubility product (Magnesia, Sepiolite,…). Others have crystallized although the equilibrium conditions were not achieved (Sylvite, Bischofite,…). This phenomenon of precipitation without equilibrium is linked to the physicochemical conditions, to the biological activities and to the sedimentary environment. The chemical composition of the environment is effected particularly by some element that can play the role of catalyst for the precipitation of certain minerals and of inhibitors for others. Morphological and hydrological conditions are also fundamental in the control of brine chemistry and the appearance of saline paragenesis.

The comparison of the saturation test results obtained by using the EQSEL and SIMEQ programs, show that the latter is more adapted to the prediction of paragenesis of neutral saline (in the case of the Sfax Saline) and give results without experimental errors. On the other hand, the EQSEL program appears to be more efficient in the prediction of the basic saline paragenesis.

Keywords: Brines, saturation test, evaporating minerals, ion-specific interaction model, ion activity product, solubility product, biological activities, catalyst, inhibitors, paragenesis

1. INTRODUCTION

During the evaporation of seawater various salts precipitate successively at the different saturation degrees. Minerals can precipitate when their activity products (I.A.P) in the solution reach their solubility products $K_{(P,T)}$. Therefore, the comparison of $K_{(P,T)}$ and (I.A.P) values of different salts that can be precipitated from seawater subjected to evaporation, permits us to know their saturation degree on the one hand and their succession in a normal evaporating sequence on the other hand. This sequence is in direct relation to the chemical composition of solutions and to their physicochemical parameters, to the solubility products of the minerals under consideration and to their kinetics of precipitation. Indeed, some minerals don't precipitate even though their ion activity products greatly exceed their solubility products; while others crystallize although their equilibrium conditions have not been met. This behaviour (over saturation without precipitation and precipitation without equilibrium), which is very frequent in certain evaporating domains is due in part to the presence of certain ions that inhibit or, on the contrary, accelerate the precipitation of a given mineral.
Since the studies realized by USIGLIO on the evaporation of the seawater [1], several models have been proposed with the aim of predicting the saline paragenesis that can be precipitated from seawater and their precipitation conditions [2,3]. Most of these models are based on an equilibrium between solutions and minerals susceptible to be formed by evaporation of a seawater, without calcium and carbonate (system: Na-K-Mg-Cl-SO_4-H_2O ; saturated in NaCl). The presence of the ion calcium in the system considerably modifies the sequence defined in the case of a system without calcium [3]. The application of models without calcium to the natural examples is possible in the case of a fractional crystallization (such as with the solar saltworks), but they cannot be considered when the concentrated brines react with the crystallized minerals (case of salt lakes)
The solar saltworks of Sfax saline [4] illustrate a model of fractional crystallization which demonstrates that during evaporative concentration of brines, crystallized phases keep their initial form and therefore are protected from the interaction with the mother brines. It results a lateral succession of evaporating faces in which all chemical elements participated very well by direct precipitation of a pure mineral or by co-precipitation with the other salts.

The objective of this survey is to know the saturation states of brines sampled in the Sfax saline in relation to the principal evaporating minerals.

2. SAMPLING AND EXPERIMENTAL METHODS

2.1. Sampling: Waters from Sfax Saline were sampled during two periods (May and November). All the samples are free brines with the exception of those taken in the ponds for preparation of magnesium solutions that are interstitial brine. In addition, with the aim of discovering the full salinity range, some samples were obtained by evaporation in the laboratory. Also, with the purpose of learning the chemical nature of deposits some sediments and salts were sampled in several ponds.

2.2.Analytical methods: After filtration and acidification of sample brines, cations were analysed by Atomic Absorption spectrometry with flame (GBC 902). Carbonates were analysed by potentiometry, chlorides and sulphides by liquid Chromatography (HPLC). Sediments and salts were analysed by X-ray diffraction methods.

3. RESULTS AND DISCUSSIONS

To test the saturation state of brines sampled in the solar saltworks of Sfax saline in relation to the principal evaporating minerals, we employed the SIMEQ [5] and EQSEL [6] programs which are based on ion-specific interaction models developed by PITZER [7].

The results obtained are compared to observations made on saltworks and to the X-ray analyses carried out on sediments and salts sampled in the different basins of the saline.

3.1. Carbonates

Since the seawater and up to the densest brines, the ion activity product of carbonated species is so important that (I.A.P) of these solutions invariably exceed the equilibrium constants of Dolomite, Calcite, Aragonite and Magnesia. The examination of the X-ray diagrams, realized on sediments, algae and salts showed the presence of weak quantities of Calcite, Aragonite and Dolomite and a total absence of the Magnesia. These results are difficult to interpret, but seem to be bound to the kinetics of precipitation of these minerals and to the biological activity of organisms that colonize the environment.

3.1.1. Dolomite

In the free brines of the Sfax saline, the values of the ion activity product of the Dolomite vary between $7.8\ 10^{-15}$ (in the sea water) and $1.5\ 10^{-10}$ (in the densest brines). These values, greatly superior to the thermodynamic solubility product of the Dolomite ($K_{dolomite} = 10^{-17.083}$), indicate a large saturation of the brines opposite to this mineral. Nevertheless, this over saturation is only theoretical and doesn't result in the chemical precipitation of the Dolomite. Indeed, as certain experimental studies at low temperature showed [8], the nucleation comes up against the kinetic barrier and it seems that the precipitation of the Dolomite is only possible if the growth of the germ is not blocked by the Mg^{++} ions. Such a condition is probably realized in the presence of organic compounds [9] or by the presence, in solution, of greatly absorbent ions (for example Li^{+}) that are able to catalyse the dehydration of the Mg^{++} ion, by reducing the water activity and therefore to accelerating the formation of Dolomite [10]. Other conditions, like the value of the ratio of Mg^{++}/Ca^{++} and the content of the carbonate ions are also necessary so that the formation of the Dolomite can take place in the environment. Indeed, concentrations in Ca^{++} must be weak to stop its competition from occupying the site of the Mg^{++} (a molar ratio of Mg^{++}/Ca^{++} slightly superior to 1 appears sufficient to permit Dolomite to precipitate). On the other hand concentrations of CO_3^{--} must be raised to precipitate an important quantity of magnesium carbonate. Under these conditions the small quantities of Dolomites detected, by X-ray, in sediments of the Sfax saline are due to the biological activity rather than to a chemical precipitation or a secondary transformation.

3.1.2. Calcite and Aragonite

The saturation test, done by the EQSEL program, on brines coming from Sfax saline, shows an over saturation of these solutions compared to Calcite ($pK_{calcite} = 8.406$) and Aragonite ($pK_{Aragonite} = 8.34$). Nevertheless, quantities of Calcite and Aragonite detected in the saline deposits (in sediments or in association with the Gypsum crust) are negligible and don't explain the high saturation of brines compared to these two carbonates. In addition, if the Calcite is present (even in weak proportion) in all post-Halite facies, the Aragonite is detected only in association with algae mats. Under normal conditions the Aragonite is an unstable mineral [9] and consequently its presence in the saline deposits is rather due to the biological activity than to the direct chemical precipitation from brines. The production of Calcium carbonate from aqueous solutions, using bacteria is a widely known phenomenon in nature and has been confirmed by laboratory studies (cultures of bacteria in artificial seawater [11]).

Under natural conditions the Calcite is thermodynamically more stable than the Aragonite and therefore its germs develop more quickly and reach critical size first. In the natural systems, the instability of the Aragonite can be explained by the kinetic factors. In general, this precipitation is more favoured at high temperatures and pressures [11]. The effect of certain ion, like Mg^{++} and $SO_4^{=}$, is not negligible and can favour the precipitation of the Aragonite, as compared to the calcite, even at low temperature. These two ions are inhibitors for the crystallization of the Calcite [12]. The duplicate role, played by the Mg^{++}

catalyst for the active precipitation and growth of Aragonite and inhibition for Calcite, is due to its adsorption on the active sites of the calcite germ, more than its adsorption on germs of the Aragonite. Therefore, Calcite can continue to precipitate when the concentration in Mg^{++} in the environment becomes negligible (Mg/Ca <<1) [12].

3.1.3. Magnesia

All solutions of the Sfax saline are extensively supersaturated compared to magnesia. The ion activity product (I.A.P) of this mineral varies between 3.7 10^{-8} and 13.3 10^{-4}. In spite of this large over saturation; the magnesia has not been detected in X-ray diagrams of sediments and salts coming from the Sfax saline. Thus, this saturation, which more and more elevated with increasing of brines salinity, is due to the increase of the magnesium content in solution.

In nature, the presence of magnesia is always assigned to the interaction between interstitial brines, rich in magnesium, and the primary Calcite [13].

3.2. Silicate minerals

In saline solutions, the contents in silica are understood between 0.1 and 2 mg/Kg. From the first view these contents are far from being controled by a solid phase. Nevertheless, the saturation test shows that the precipitation of a magnesium silicate (Sepiolite) is possible even from the most dilute waters.

In the diagram of the Figure 1, where the equilibrium curves of the amorphous Silica and the Sepiolite has been reported, we observe an under-saturation for amorphous Silica and an oversaturation, for most samples, in relation to the Sepiolite. This large oversaturation is due to the high contents of the magnesium ions in brines.

In the equilibrium diagram of Magadiite–Kenyaîte-Kanemite-Quartz-amorphous Silica (Figure 2), we again found the under-saturation of all samples compared to amorphous Silica. These same samples are under-saturated compared to the other silicate minerals considered in this study.

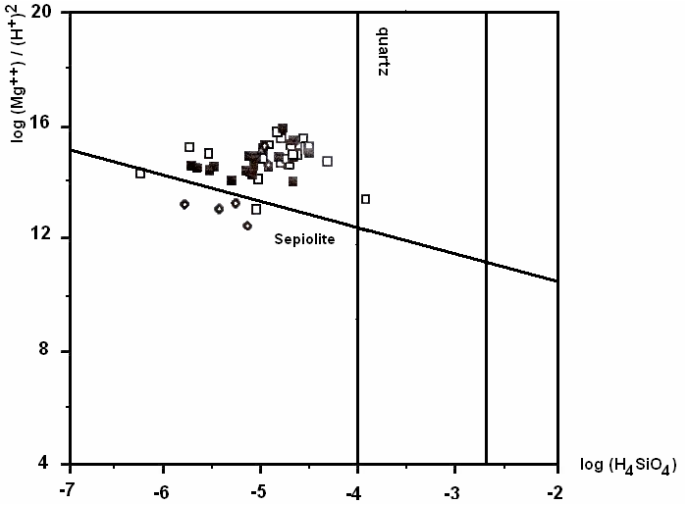

Figure 1: Saturation test of brine sampled in Sfax Saline opposite to Sepiolite, Quartz and amorphous Silica at 25 °C

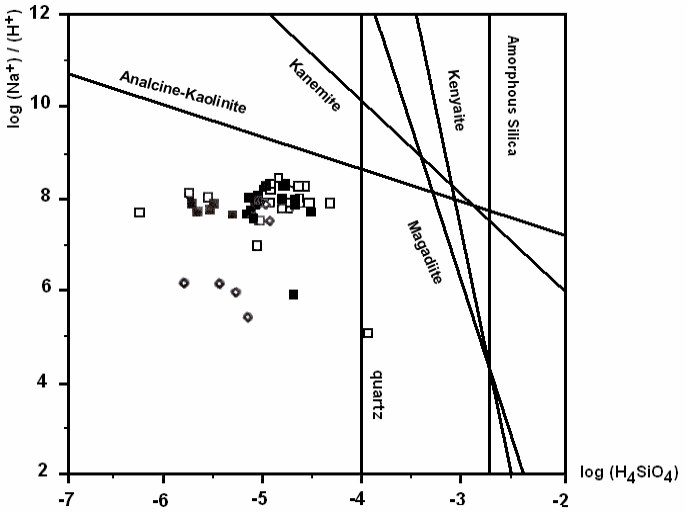

Figure 2: Saturation test of brine sampled in Sfax Saline vis-à-vis Magadiite, Kenyaïte, Kanermite, Quartz and amorphous Silica at 25 °C

In the absence of thermodynamic data on the solubility of silicate minerals as a function of the quantity and the nature of dissolved salts, it was difficult to affirm their presence or their total absence in the paragenesis of Sfax saline. It is possible that the weak concentration of Silica in brines on the one hand, and the physicochemical conditions on the other hand are not favourable for the precipitation of these minerals.

3.3. Sulphates

3.3.1. Gypsum and Anhydrite

The waters of the Sfax Saline, that become enriched with calcium from the beginning of the evaporation processes, reach saturation quickly enough compared to gypsum and Anhydrite. The precipitation of these two minerals removes the largest part of the calcium to the free solution.

The values of the ion activity product, calculated on brines sampled in the saline, vary between $10^{-5.05}$ and $10^{-3.85}$. From this results we notices that only the waters of the first basins (FC < 2.5) are slightly under–saturated compared to Gypsum and Anhydrite. Nevertheless, on the bottom of basins, the Gypsum deposit appears only in basins where brines are about 3.5 times more concentrated than the initial seawater. This is not due to a nucleation problem, as in the case of carbonates, but it is due to the fact that in this concentration domain (2.5 ≤ FC ≤ 3.5), the saturation occurs only in the interface air water. The primary Gypsum crystals become progressively heavier and flow downwards under the effect of their own weight. Because of the importance of the water thickness, the saturation is not total and therefore crystals, initially formed, dissolve themselves before they reach the bottom of the basin.

The saturation of the saline solutions opposite to the Anhydrite is reached at the same time as their saturation opposite to the Gypsum (Figures 3 and 4). However, in the X-ray diagrams, achieved on all samples, only peaks corresponding to the diffraction stripes of Gypsum are present. Therefore, we can say that in the natural conditions the Anhydrite is an unstable mineral.

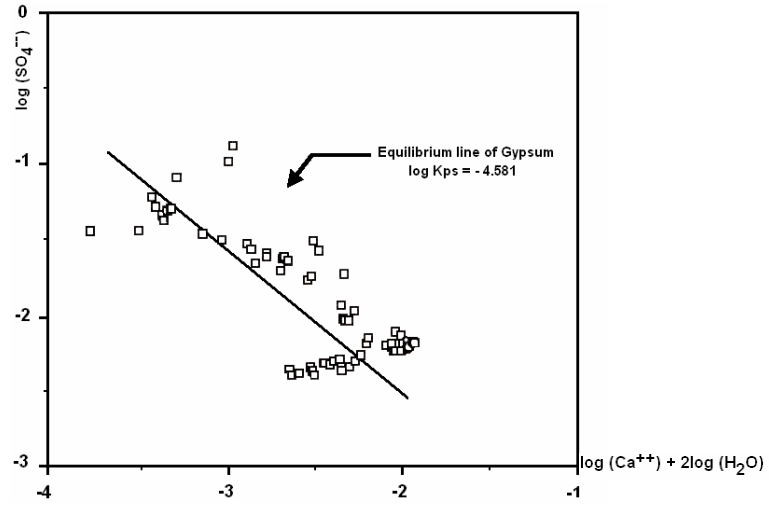

Figure 3: Saturation test of brines sampled in Sfax saline opposite to Gypsum at 25 °C

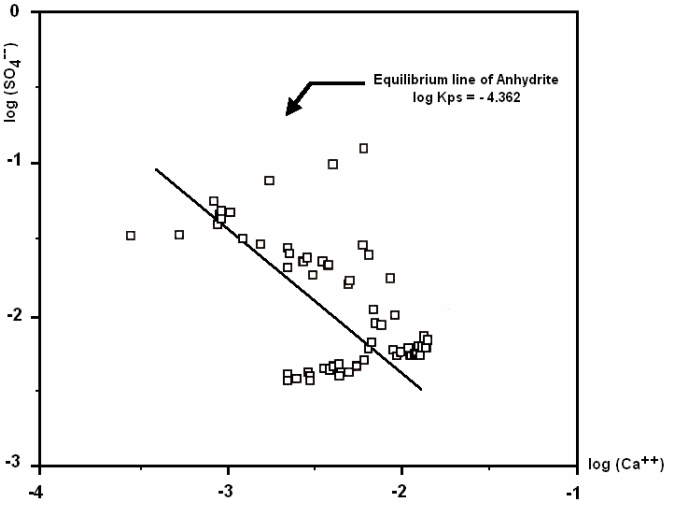

Figure 4: Saturation test of brines sampled in Sfax saline opposite to Anhydrite at 25 °C

The report of the data acquired on solutions of saline on a diagram concentration in NaCl versus Temperature (Figure 5), shows that the direct precipitation of the Anhydrite from the free brines cannot take place even in the densest solutions.

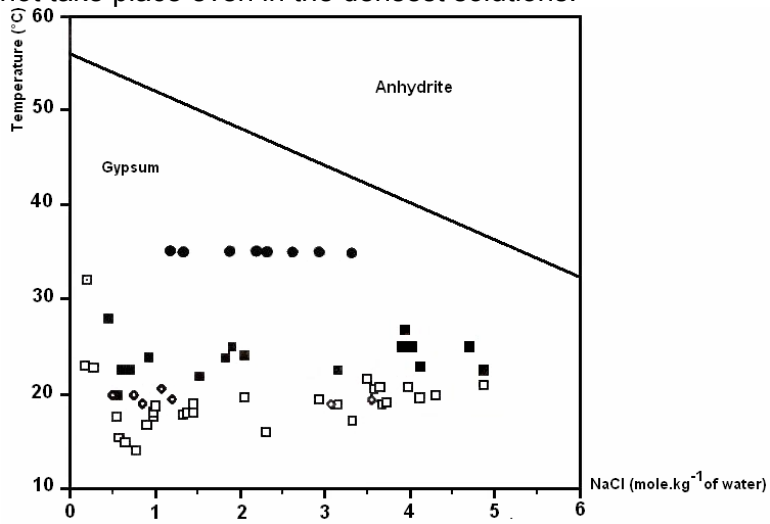

Figure 5: Transition temperature of Gypsum to Anhydrite versus Sodium Chloride concentration of the brines sampled in saltworks of Sfax Saline

3.3.2: Celestine:

In seawater, Strontium is considered a major element. Therefore, it can be associated with the sulphate ion (present in high concentration) to form a pure Strontium mineral. It is Celestine, whose solubility seems to be very dependent on the nature and the quantity of salts dissolved in the environment [14]. This solubility increases in presence of alkali and alkaline earth chlorides and decreases in presence of sulphates (effect of the common ion).

The saturation test realized on free brines of Sfax saline compared to the Celestine has been achieved by using the SIMEQ program [5]. The obtained values of the ion activity product vary from 10^{-10} to 10^{-8}. These values show an under-saturation of the brines compared to the Celestine. Consequently, the direct precipitation of Strontium sulphate ($SrSO_4$) cannot take place in the saltworks of Sfax Saline. Nevertheless, the results obtained from chemical analyses realized on samples coming from the Gypsum crust show that the contents in Strontium in this material vary from1 to 4 g/Kg. In addition, the examination of the X-ray diagrams achieved on the same samples shows the presence of this Celestine with the Gypsum crystals.

The report of the results, obtained on the free brines, in a logarithmic diagram (Figure 6), shows an evolution parallel to the equilibrium line right of the Celestine. This evolution indicates that the Celestine precipitates by formation of a solid solution with Gypsum.
In the nature the precipitation domain of this Celestine doesn't seem very definite. Some authors place it before [15] or on same domain [16] of Gypsum; others indicate a precipitation, during or after the halite domain [17]. Our analyses results are rather favourable to a precipitation of the Celestine at the same time as the massive Gypsum deposit. In absence of the precipitation of the Celestine, Strontium co-precipitate with calcium sulphate minerals, according to a distribution coefficient that could be used like a salinity indicator of the environment [4].

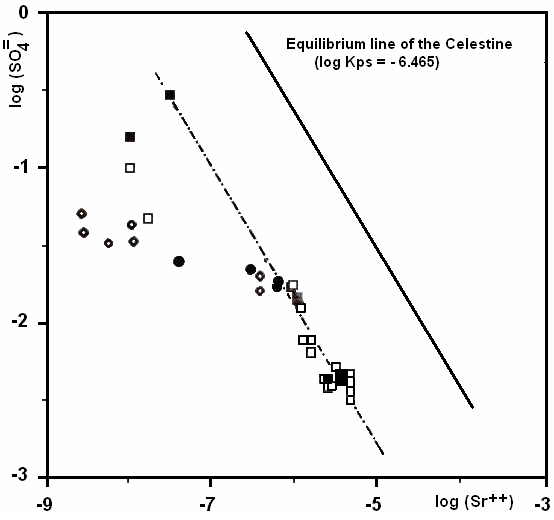

Figure 6: Evolution of the brines sampled in saltworks of Sfax with respect to the equilibrium with the Celestine

3.3.3. Kieserite, Hexahydite and Epsomite.

All these three minerals are magnesium sulphates that differ only by the number of water molecule in their chemical formulas. The studies, concerning the kinetics and precipitation conditions of these salts and their relative stability either rare more non-existent. This absence can be justified, as these minerals are very soluble; therefore their presence is limited in the nature. The brines of Sfax saltworks, that reach a very advanced stage in seawater evaporation, are supersaturated compared to these three sulphates.
The chemical analyses carried out on the free waters as well on salts crystal, coming from storage basins of magnesium brines, confirm the precipitation of one or several magnesium sulphates. Besides that, the X-ray analyses show the presence of these salts well, but the knowledge of their exact formulas was very difficult to us because of the partial dehydration that can occur during the preparation of samples or even during contact of the X-ray with the crystalline powder.

3.3.4. Polycationic Sulphates

Out of the seven-polycationic sulphates salts tested, only the Polyhalite and the Glauberite are susceptible to precipitate from the free brines of Sfax saltworks. Nevertheless, none of these two minerals has been detected in the paragenesis of the saline. This is expected because these sulphates, frequently described in saline deposits of present or fossil evaporative basins [13,18], always have a diagenetic origin, resulting from the reaction of Magnesium brines with the mineral phases that are precipitated from the beginning of the evaporation processes. Thus, the absences in the mineralogical assembly of Sfax saline are due to the fact that saltsdeposits in saltworks is protected against the interaction with the mother brines.

3.4. Chlorides

The first phase of the integration of chloride ion to the saline paragenesis of Sfax saltworks takes place in the crystallisers. The chloride minerals of the saline are represented especially by the halite and to a lesser degree by potassium and magnesium salts.

3.4.1. Halite

The precipitation of the halite occurs only when the solution becomes almost 10 times more concentrated than the initial seawater [4]. This precipitation, that begins discreetly in basins before salting tables (PM basins) reaches their maximum in the crystallisers. At this stage we observe one massive precipitation of the halite with a yearly average thickness in excess of 20 cm.

During the massive precipitation of halite, we observe that the fall of Na^+ concentration is more marked than that of Cl^-. This evolution is due to the fact that almost all of the sodium in brines takes part in the formation of halite, while there remains some important quantities of chloride in the residual solutions. The chloride ion, whose concentration continues to rise in the brines, serves as a compensatory ion for K^+ and Mg^{++} [4].

In the diagrams of Figure 7, where halite equilibrium line has been drawn, we observe a linear evolution of the logarithm of Na^+ activity as a function of that of the Cl^- activity. The distance from equilibrium line is not necessarily significant and could be explained by uncertainties in calculation of activities. In the densest solutions, the dispersion of the values is due on the one hand to the weak content of sodium of this brine, therefore saturation is apparent and there is no precipitation of NaCl and, on the other hand, bordering on the application of PITZER Model (maximal ionic strength = 7) for the solutions as highly concentrated as that of Sfax saline.

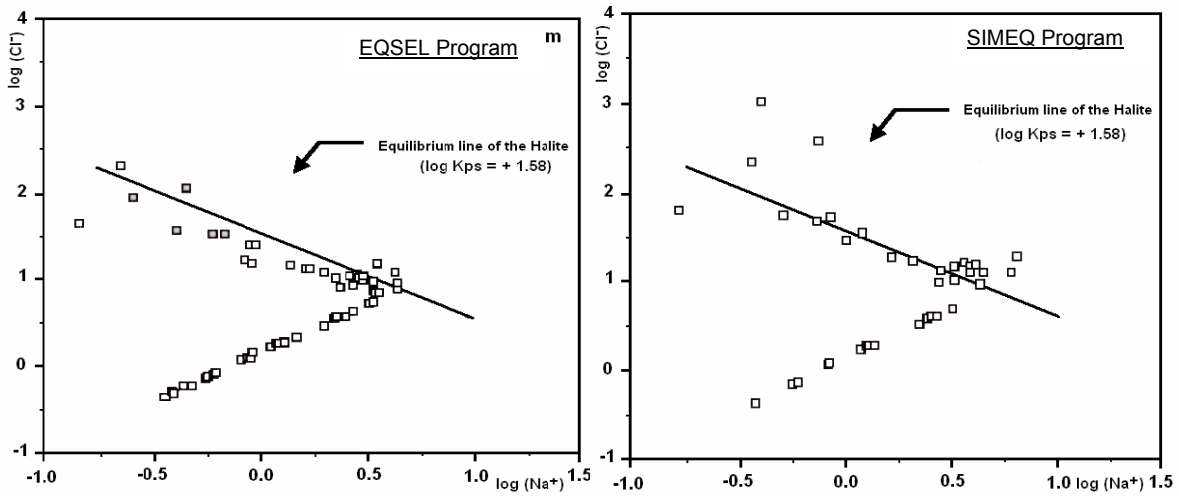

Figure 7: Evolution of the brines sampled in saltworks of Sfax with respect to the equilibrium with the Halite

3.4.2. Sylvite

The precipitation of Sylvite intervenes at a very advanced stage of evaporation processes rarely reached in natural conditions. Even though the saturation is reached theoretically, the precipitation of the Sylvite is not always obvious because of the competition by other potassium salts like the Carnallite ($KMgCl_3\ 6H_2O$).

Like the Halite, the saturation test of the Sylvite, realized on brines coming from the solar salts works of Sfax saline was carried out by two programs (EQSEL and SIMEQ). The results obtained concerning potassium and chlorine activities have been reported on a logarithmic diagram (Figure 8), where a Sylvite equilibrium line has been drawn. From this representation we observe a linear evolution of the logarithm of K^+ activity in relation to the Cl^- activity. The (K/Cl) ratio is constant until the saturation of brines opposite to the Sylvite was reached (salinity ≈ 315 ‰). The final evolution takes place towards the chloride pole, as it remains balanced with the Sylvite.

For the most concentrated samples, the dispersion of the values of the ion activity products is justified for the same reasons that we indicated for halite and particularly those concerning the application of the PITZER model for the solutions as highly concentrated as that of Sfax solar saltworks.

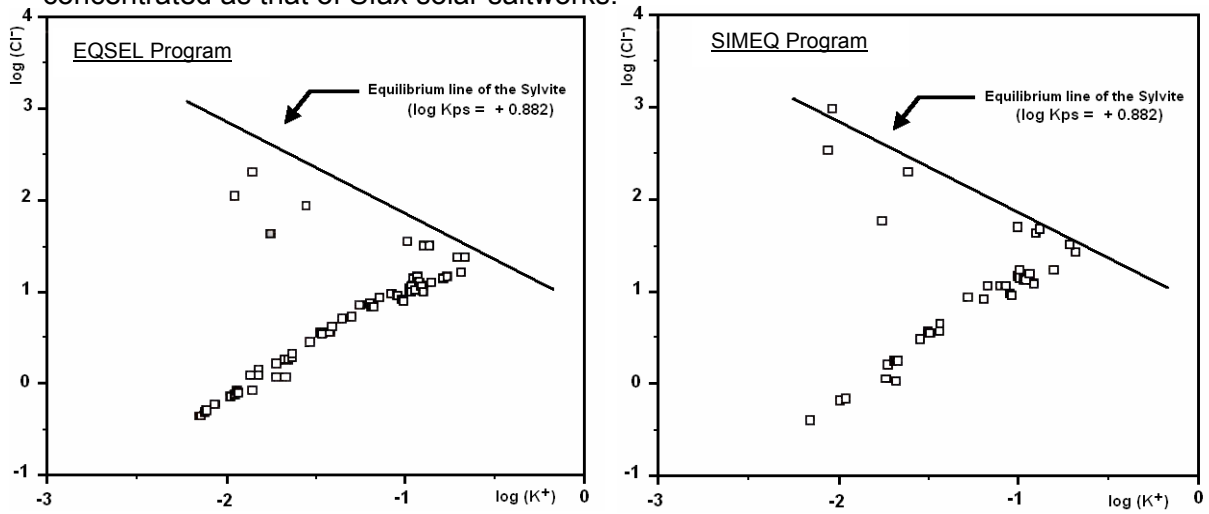

Figure 8: Evolution of the brines sampled in saltworks of Sfax with respect to the equilibrium with the Sylvite

In the last stages of the evaporation processes, brines deposit other potassium and magnesium salts. We can mention particularly Carnalite, Leonite, Basanite, Kainite, Hexahydrite, Picromerite, Bishofite and Starkeyite that have been detected by X-ray diffractometry. With the exception of the Picromerite, the saturation of the brines compared to these salts is verified from saturation tests realized while using the EQSEL and SIMEQ programs.

Concerning the other more soluble salts like, Chloromagnesite and Tachydydrite, it will be necessary to wait for the higher concentrations of brines, before their precipitation begins.

4. CONCLUSION

The Saturation tests carried out on brines of Sfax saline permits us to define the list of evaporating minerals susceptible to precipitate from seawater submitted to the evaporation.

The first event with reference to the evaporative concentrations of free brines of Sfax Saline, which are developed in neutral saline, is the precipitation of carbonates that takes place when the initial solution is almost 1.5 times more concentrated. The nature and quantity of these carbonates, mainly alkaline earth, are a function of the chemical composition of the initial solution and particularly of its concentration in carbonate, Magnesium and Calcium. The precipitation of Aragonite is limited to basins where algae mats proliferate.

The Gypsum precipitation takes place in a domain of concentration variable from a concentration factor of 3.7 to a concentration factor of 11.8. In this concentration domain, the Sulphate content continues to increase while the content of Calcium decreases. The Halite, that is a main mineral of saline the paragenesis characteristic of systems evolving in neutral concentrated saline way does not start to crystallize unless the initial volume is reduced to one tenth.

In the magnesium brine basins, we have a complete mineralogical assembly that regroups in addition to Halite, the potassium and magnesium salts namely: Carnalite, Leonite, Basanite, Kainite, Hexahydrite and Starkeyite. We were surprised by the absence of Sylvite in this assembly, but it was noticed that this mineral can be formed only under unstable equilibrium conditions, particularly from oversaturated solutions.

From the observations realized on saltworks, X-ray analyses and saturation tests, we noticed that certain minerals do not precipitate despite the fact that their ionic activity exceeds the widely solubility products (Magnesia, Sepiolite,…). Others, crystallized although the equilibrium conditions are yet to be achieved (Sylvite, Bishofite,…). This precipitation equilibrium is linked to physicochemical conditions, biological activity and the entire sedimentary environment. The chemical composition of the environment intervenes particularly as a result of the effect of some ions that can play the role of catalyst for the precipitation of some minerals and an inhibitor for others. Therefore, many factors (crystallization, biological reduction, oxidation…) work at the same time and push the saline towards concentration. Morphological and hydrological conditions are also fundamental in the control of the chemical in the brines and therefore of the occurrence of saline paragenesis.

The comparison of the saturation tests results obtained by using the EQSEL and SIMEQ programs, show that this last is more adapted to the prediction of the paragenesis characteristic of neutral concentration saline (in the case of the Sfax Saline) and give results without experimental error. On the other hand, the EQSEL program appears to be

more efficient in the prediction of the paragenesis characteristic of basic saline concentrations.

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