

Thermodynamic Models: Application to the Brines of Chotts in Algerian North-Eastern Sahara

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Abstract

The Brines of chotts in Algerian Northeastern Sahara are highly concentrated solutions of mineral salts with a salinity that far exceeds that of the sea water (120 to 440 g/l). The first interpretation of data allows to specify the chemical facies of these brines from their chemical compositions. They have mainly a very marked sodic chlorinated character. Databases of the thermodynamic model PHREEQC v3 were used to determine the saturated state of the brines with respect to principal chemical species. They are more oversaturated with calcite than with gypsum. The saturated state compared to the halite is no longer reached. Indeed, we use the thermodynamic model PHREEQC v3 to calculate the mineral/solutions equilibria on the basis of different assumptions. The test of these assumptions shows that each one has its limits to simulate and control the thermodynamic behaviour of the brines.

Keywords: Thermodynamic model; Brines; Chotts; Northeastern Sahara

Introduction

The most famous works devoted to the study of the mineral / solutions interactions and the geochemical evolutions of salt and the brines in lakes' ecosystems, chotts and sebkhas, are the works of Ref. [1-15] about the geochemistry and mineralogy of brine in chott Merouane located in Algerian northeastern Sahara, and the work of Ref. [16] about the application of the Pitzer equation in the geochemistry of brine in chott El Jerid located in southern Tunisia. The thermodynamic models used in this work are applicable for brines where the ionic strength is less than 1 mol/l, which is not the case for our region where the ionic strength of the brines is greater than 1 mol/l. Therefore, a simulation of the geochemical evolution of brine using mathematical models will be necessary to verify the applicability of these models. For these purposes, databases of the thermodynamic model PHREEQC v3 (version 3.0 recently issued by the US Geological Survey) [17] have been used to determine the activity coefficients and the saturated state of the brines from the main chemical species. Considering the high concentration of the dissolved salt in the brines, the treatment of the results of the chemical analysis acquired during this research requires significant work. In order to evaluate the quality of the analysis results, a simple method based on the calculation of the ionic balance [18], is used. The results are therefore corrected by accepting an error of imbalances of an ionic balance lower than 10%. Nevertheless, this ionic balance provides information on the analytical quality only for the dominant chemical species in the solution. The chemical nature of the brines is influenced by the chemical properties of the drainage water, the severe climatic conditions, and by the human impact that can influence or accelerate the natural processes.

Materials and Methods

Study site

The Algerian Northeastern Sahara is a vast depression (-37 to 300 m above the sea level), partly occupied by the Gran Erg Oriental. It is defined by the boundary: the Saharan Atlas in the North; Saharan ridge and the Grand Erg Occidental in the West; the plateaux of Tademaït and Tinrhert in the South. This depression is opened in the North East over the Gulf of Gabes. It extends between 34° or 35° lat. N (of Chott) and 28° or 29° lat. N (the Tademaït) and for the longitude, 3°E (the Saharan Ridge) at 10° or 11°E (Figure 1). Chotts and sebkhas constitute

the lowest level. The chott that corresponds to the edge of the sebkha is composed of siliceous and/or gypseous sand and gypseous soils with gypseous crust at surface and subsurface. The shallow is characterized by the presence of a permanent water table, very little deep (1 to 5 m) in the chott, which is flush with the surface in the center of the sebkha.

Sampling protocol for solutions

The choice of sampling site is based on:

- their situation in the chott (1 to 3 m from the periphery)
- their contact with discharges (drainage water, for example)
- their depth with respect to the surface (without contact with the air)

Water samples were collected and analyzed per the protocol developed by A. Probst at the Laboratory of Mechanisms and Transfers in Geology (LMTG) in Toulouse [19]. The polypropylene sampling bottles were cleaned with hydrochloric acid (HCl) and then rinsed with distilled water and dried at 45°C in an oven. During sampling, the sample bottles were rinsed with a little sample before filling. The amount required for the analysis of the anions is taken without acidification. But, the dosage of the cations requires acidification beforehand. All samples once collected are stored in a cooler, and within a maximum of 12 hours placed in a fridge at 5°C. All manipulations are systematically performed with sterilized gloves (Figure 1).

Thermodynamic modelling

In the development of geochemical models, we can distinguish, with Ref. [20], the models that calculate the speciation of aqueous solutions and minerals. The theory of the thermodynamic equilibria

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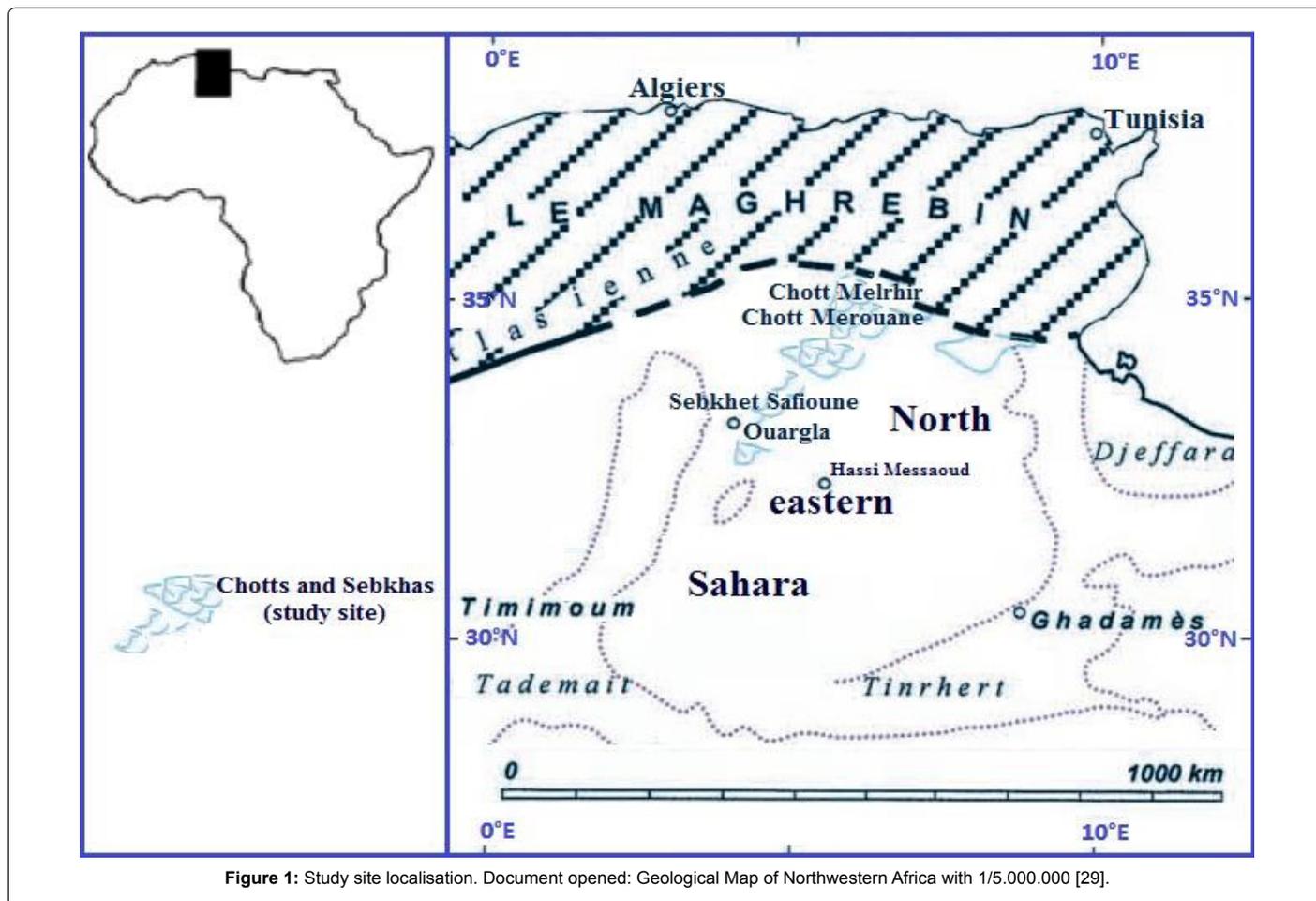


Figure 1: Study site localisation. Document opened: Geological Map of Northwestern Africa with 1/5.000.000 [29].

is the most adequate concept to facilitate the identification of several variables in the determination of the relationship between the solution and the minerals [21]. The work of Debye and Hückel [22] is a major opening in the evolution of the thermodynamics of the electrolyte solutions. Indeed, we use the model PHREEQC v3 to calculate the activity coefficients and the mineral/solutions equilibria based on various assumptions:

- 1) The ion association model based on the extended Debye-Hückel function: the extent expression of the Debye-Hückel law is written for union i solution (Equation 1):

$$\text{Log } \gamma_i = -(A z_i^2 \sqrt{I}) / (1 + a_i^\circ B \sqrt{I}) + b \gamma_i \quad (1)$$

With: $b \gamma_i = 0.2$ or 0.3 : constant of error from the Debye-Hückel law; a_i° : the hard-core diameter, which is specific to each aqueous species i (in cm); z : the electric charge of i ; I : ionic strength; $A = 0.5092$ and $B = 0.3283$ in $t = 25^\circ\text{C}$: universal constants of the Debye-Hückel law [22].

- 2) The Ion-specific interaction model based on Pitzer's equations where the term $b \gamma_i$ is replaced by the sum of: $\sum \beta_{ij} m_j$; where m_j : the molality of the ion j ; β_{ij} : the characteristic coefficient of species pair i and j [23-25].
- 3) The Specific-ion Interaction Theory (SIT): The expression for a SIT parameter is the same as for a Pitzer's parameter [26].

In the case of the brines, the activity coefficients that take into account the influence of the concentration of various species in

the solution are easily calculated by the model of the specific ion interaction drawn up by Ref. [27]. In the conception of this model, ions remain unassociated and the ionic strength I of the solution is directly calculated from the molality of salt (Equation 2).

$$I = 0.5 \sum [E_i] z_i^2 \quad (2)$$

Where $[E_i]$ is the molality of the constituent E_i in the solution and z_i is the electric charge of E_i . The saturated state of the solution with respect to the minerals is expressed by the Saturation Index (SI) defined as the logarithm of the ratio between the Ionic Activity Product (IAP) and the solubility constant of the solid phase considered (K_s) (Equation 3):

$$SI = \text{Log}(\Omega) = \text{Log}(IAP/K_s) \quad (3)$$

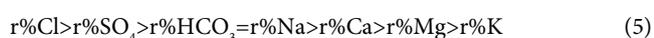
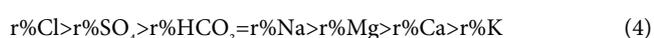
The sub-saturation of the solution relative to the mineral is characterized by a ratio less than 1 and therefore the mineral tends to dissolve. The saturation (or thermodynamic equilibrium) is characterized by a ratio equal to 1 and no change in the net quantity of the dissolved mineral precipitated and is therefore expected. Oversaturation is characterized by a ratio greater than 1, and consequently, the mineral tends to precipitate.

Results and Discussion

Chemical composition and facies

The Chemical analysis of the different ions allows to specify the geochemical facies of the brines. They generally include simple ions in

the solution, complex aqueous species and mineral species. The Table 1 summarizes the concentration of the dissolved salt in these brines under natural conditions. At average, they typically contain both chloride (6.04 mol/kgw) as the dominant anion and sodium (5.36 mol/kgw) as the dominant cation. The other dissolved elements have less significant concentrations relative to sodium and chloride; they are at average about 0.53 mol/kgw for sulphate and magnesium, 0.26 mol/kgw for calcium and of about 0.41 mol/kgw for potassium. The sulphate concentration is associated with evaporated formations (gypseous soils with gypseous crust). The total concentration of the dissolved elements can sometimes approach many hundreds of grams per liter (400 g/l); however, the water of the sea contains only 19 g/l of chlorides and an average of salinity of about 35 g/l. The Chemical facies of these brines are mainly chlorinated-sodium and rarely sodic-sulfated: (Equation 4 and 5)



r%: quantity in reaction in percent as milliequivalents per liter (meq/l).

Saturated state

Indexes of saturation in calcite, gypsum, anhydrite, sylvite and thenardite were calculated by using three thermodynamic models

(Table 2). Regarding the effect of the ionic strength on the solubility of the mineral salt, there is a slight increase in the solubility of calcite, gypsum and anhydrite because the ionic strengths are less than 6 mol/l. Apart from this ionic strength, the solubility of these minerals will augment with the increase of the ionic strength. Contrary to the halite and thenardite, the increase in the solubility of these two mineral salts is directly proportional with the ionic strength, except for the sylvite which has more than an ionic strength superior to 6 mol/l where the solubility becomes inversely proportional with the increase of the ionic strength. The results of the calculation of the mineral saturation indexes presented by the above three thermodynamic models are almost identical. The Thermodynamic modelling indicates that the brines are substantially saturated with respect to calcite than with respect to gypsum. Indeed, the calcite precipitation is controlled by the concentration of calcium ions. In the case of low concentrations of Ca, the precipitation kinetics of calcite control the concentration of the brines in Ca. In addition to this, when the gypsum dissolution is important, the precipitation of the kinetics of calcite has no significant influence on the concentrations of Ca. The state of thermodynamic equilibrium observed with halite is not reached. For the other minerals, the brines are more or less under-saturated with respect to sylvite and thenardite. The databases of three thermodynamic models used in the calculations show more or less significant differences between the measured values of the mineral saturation indexes. Taking into account the limited applicability of the

Sample	t (°C)	pH	Density	Ca (mol/kgw)	Mg	Na	K	Cl	SO ₄	HCO ₃
1	29.3	8.3	1.37	0.04	0.21	4.48	1.11	4.12	0.68	0.001
2	30.8	8.43	1.36	0.04	0.2	4.38	1.16	4.24	0.57	0.001
3	24.1	7.68	1.46	0.03	0.53	5.3	1.24	5.49	0.88	0.003
4	30.1	7.79	1.5	0.11	0.95	5.24	0.83	5.25	1.37	0.01
5	13.5	8.07	1.65	0.68	0.47	8.17	0.06	10.42	0.51	0.02
6	14	8.13	1.67	0.74	0.84	8.23	0.12	10.12	0.69	0.03
7	16	8.38	1.17	0.15	0.52	1.39	0.13	1.79	0.52	0.02
8	23.7	7.28	1.46	0.04	0.65	4.75	1.88	6.37	0.3	0.003
9	20.3	7.25	1.39	0.02	1.2	3.85	0.55	5.81	0.46	0.003
10	19.4	7.88	1.2	0.07	0.08	2.61	0.54	3.08	0.08	/
11	21.4	7.36	1.37	0.02	0.56	4.57	0.59	5.61	0.3	0.003
12	22.4	7.25	1.44	0.04	0.64	4.82	1.52	6.32	0.32	0.003
13	17.4	7.45	1.47	0.04	0.83	4.98	1.8	6.38	0.35	0.003
14	16.5	7.6	1.27	0.03	0.32	3.22	0.55	3.96	0.24	0.005
15	16	7.85	1.54	0.01	0.96	6.86	0.13	9.03	0.37	0.02
16	18	7.95	1.52	0.01	0.82	6.74	0.11	8.84	0.3	0.01
17	19	8.04	1.44	0.51	0.5	5.98	0.04	5.75	0.65	0.01
18	19.7	8.26	1.69	0.89	0.48	8.39	0.12	10.2	0.82	0.02
19	19.8	8.12	1.79	1	0.84	8.94	0.12	9.48	1.87	0.02
20	19.9	8.74	1.14	0.33	0.17	1.31	0.02	1.31	0.42	0.02
21	20	8.76	1.24	0.45	0.46	2	0.27	1.53	1.04	0.02
22	19	9.4	1.06	0.03	0.08	0.77	0.01	0.53	0.24	0.004
23	13.7	8.3	1.54	0.1	0.58	7.79	0.09	7.18	0.92	0.02
24	14.3	8.36	1.3	0.07	0.44	4.06	0.05	3.07	0.86	0.02
25	14.4	9.04	1.34	0.07	0.97	3.33	0.29	3.14	1.2	0.03
26	20	8.22	1.15	0.21	0.27	1.48	0.06	1.53	0.41	0.02
27	14	7.89	1.46	0.55	0.44	6.15	0.07	7.35	0.22	0.01
28	15	7.81	1.5	0.56	0.53	6.74	0.07	8.13	0.22	0.01
29	20.8	8.02	1.5	0.68	0.46	6.62	0.07	8.02	0.26	0.01
30	21.2	8.07	1.52	0.76	0.51	6.88	0.08	8.39	0.23	0.01
31	15.7	7.85	1.46	0.11	0.48	7.01	0.07	7.08	0.27	0.01
32	15.9	8.01	1.46	0.11	0.48	7.1	0.07	7.32	0.15	0.01
33	19	7.35	1.56	0.53	0.64	7.25	0.11	9.13	0.28	0.01

(mol/kgw: mole per kilogram of water)

Table 1: Chemical compositions of brines in Algerian Northeastern Sahara (2009-2010).

Sample	I (mol/l)	SI Calcite			SI Gypsum			SI Anhydrite			SI Halite			SI Sylvite			SI Thenardite	
		IA	M-Pitzer	SIT	IA	M-Pitzer	SIT	IA	M-Pitzer	SIT	IA	M-Pitzer	SIT	IA	M-Pitzer	SIT	M-Pitzer	SIT
1	4.93	0.85	0.79	0.48	0.7	0.63	0.40	0.61	0.52	0.43	-0.42	-0.48	-0.71	-0.78	-0.67	-0.71	-0.48	-0.67
2	4.81	0.83	0.81	0.56	0.61	0.57	0.35	0.53	0.47	0.39	-0.41	-0.47	-0.69	-0.76	-0.64	-0.68	-0.55	-0.72
3	6.08	0.47	0.81	0.42	0.72	0.78	0.36	0.62	0.68	0.37	-0.08	-0.08	-0.48	-0.51	-0.35	-0.49	-0.13	-0.53
4	7.02	1.56	1.75	1.52	1.29	1.39	0.88	1.25	1.38	0.95	-0.12	-0.02	-0.61	-0.78	-0.57	-0.79	0.08	-0.49
5	7.68	2.62	2.76	2.69	1.92	2.69	1.38	1.85	2.78	1.47	0.83	1.08	0.36	-1.3	-0.96	-1.23	0.60	-0.56
6	8.26	2.64	2.12	2.87	2.04	2.73	1.46	1.98	2.87	1.55	0.87	1.17	0.30	-1.03	-0.65	-1	0.77	-0.46
7	3.46	2.39	2.36	2.20	1.23	1.06	1.09	0.89	0.66	0.89	-1.47	-1.49	-1.60	-1.96	-1.91	-1.87	-1.62	-1.47
8	5.83	-0.01	0.82	0.35	0.37	0.55	0.22	0.29	0.47	0.26	0.03	0.00	-0.40	-0.23	-0.05	-0.23	-0.62	-0.90
9	6.08	-0.76	0.17	-0.37	0.05	0.37	-0.05	-0.12	0.22	-0.09	-0.15	-0.08	-0.61	-0.78	-0.58	-0.82	-0.57	-0.82
10	2.97	/	/	/	0.24	0.17	0.23	-0.03	-0.15	0.10	-0.89	-0.96	-1.00	-1.11	-1.07	-1.01	-1.80	-1.65
11	5.21	-0.23	0.51	-0.03	0.01	0.25	-0.08	-0.15	0.09	-0.10	-0.15	-0.15	-0.48	-0.79	-0.64	-0.76	-0.67	-0.84
12	5.78	-0.08	0.77	0.25	0.37	0.57	0.22	0.26	0.47	0.23	0.02	0.01	-0.39	-0.32	-0.14	-0.31	-0.57	-0.84
13	6.15	-0.03	0.80	0.38	0.46	0.63	0.26	0.32	0.48	0.23	0.10	0.10	-0.37	-0.17	0.03	-0.18	-0.50	-0.83
14	3.98	0.57	0.94	0.49	0.21	0.23	0.14	-0.06	-0.09	0.01	-0.61	-0.66	-0.81	-0.95	-0.89	-0.89	-1.18	-1.09
15	6.92	0.02	0.42	0.65	-0.46	0.36	-0.62	-0.56	0.36	-0.59	0.54	0.71	0.04	-1.12	-0.83	-1.12	0.22	-0.51
16	6.64	0.15	0.45	0.73	-0.54	0.25	-0.65	-0.63	0.24	-0.61	0.48	0.63	0.02	-1.20	-0.93	-1.19	0.07	-0.58
17	6.4	2.38	2.81	2.30	1.78	1.91	1.38	1.63	1.77	1.37	0.07	0.16	-0.28	-1.90	-1.68	-1.82	-0.12	-0.59
18	8.16	2.85	/	2.83	2.20	2.78	1.56	2.20	2.96	1.72	0.84	1.10	0.33	-1.07	-0.73	-1.01	0.76	-0.42
19	9.34	2.57	/	2.62	2.53	2.86	1.76	2.54	3.10	1.89	0.82	1.22	0.18	-1.11	-0.72	-1.11	1.20	-0.21
20	2.79	2.91	2.89	2.66	1.52	1.31	1.37	1.22	0.94	1.2	-1.67	-1.70	-1.74	-2.84	-2.80	-2.72	-1.72	-1.57
21	4.68	3.07	2.85	2.74	1.88	1.55	1.6	1.60	1.21	1.45	-1.39	-1.40	-1.55	-1.77	-1.69	-1.67	-1.17	-1.08
22	1.28	1.81	1.68	1.6	0.49	0.34	0.41	0.14	-0.08	0.2	-2.34	-2.38	-2.37	-3.55	-3.54	-3.44	-2.10	-1.94
23	6.95	2.11	2.09	2.11	1.24	1.62	0.76	1.08	1.53	0.73	0.38	0.54	-0.06	-1.38	-1.13	-1.34	0.52	-0.33
24	4.87	2.19	2.13	1.88	1.03	0.87	0.72	0.74	0.52	0.56	-0.65	-0.67	-0.89	-2.11	-2.04	-2.03	-0.55	-0.63
25	5.68	2.43	1.93	2.12	1.10	0.96	0.76	0.80	0.63	0.6	-0.71	-0.67	-1.03	-1.32	-1.21	-1.3	-0.57	-0.7
26	2.89	2.53	2.57	2.31	1.29	1.12	1.17	0.99	0.76	1	-1.54	-1.57	-1.63	-2.37	-2.33	-2.26	-1.62	-1.48
27	6.31	2.08	2.84	2.14	1.44	1.81	1.09	1.26	1.67	1.07	0.31	0.40	-0.04	-1.44	-1.21	-1.35	-0.43	-1
28	6.71	1.98	2.79	2.15	1.43	1.91	1.06	1.30	1.85	1.08	0.48	0.60	0.08	-1.38	-1.11	-1.29	-0.25	-0.99
29	6.75	2.32	2.88	2.41	1.56	1.99	1.16	1.48	1.99	1.24	0.45	0.56	0.06	-1.50	-1.22	-1.4	-0.22	-0.97
30	7	2.34	2.79	2.47	1.57	2.02	1.13	1.51	2.07	1.23	0.54	0.67	0.12	-1.41	-1.12	-1.31	-0.19	-1.03
31	6.04	1.48	2.10	1.69	0.76	1.21	0.52	0.61	1.08	0.51	0.30	0.39	-0.05	-1.50	-1.27	-1.43	-0.16	-0.72
32	6	1.65	2.19	1.91	0.51	1.01	0.32	0.37	0.90	0.32	0.35	0.43	-0.01	-1.48	-1.24	-1.4	-0.38	-0.94
33	7.14	1.59	2.72	1.92	1.49	2.13	1.12	1.43	2.19	1.22	0.63	0.79	0.17	-1.21	-0.90	-1.14	0.07	-0.83

IA: Ion-association method; M-Pitzer: Pitzer specific-ion-interaction model; SIT: Specific ion Interaction Theory; I: Ionic strength.

Table 2: Ionic strength and saturation indexes (SI) of mineral salts in brines of chotts and sebkhas in Algerian Northeastern Sahara (2009-2010). calculated by three thermodynamic models: IA, M-Pitzer and SIT.

ionic association model for the highly concentrated solutions [28]. It is estimated: 21, 24, 9 and 12% of aberrant values under or overestimated SI Calcite, SI Gypsum, SI Anhydrite and SI Sylvite calculated by the SIT method against respectively 45, 24, 57 and 63% calculated by the Pitzer's method except for halite, where it is estimated that the values of aberrant are 0% under or overestimated SI Halite calculated by the method of Pitzer against 84% calculated by the SIT method. This leads us to deduce that the calculation with the specific ion interaction theory SIT is satisfactory.

The saturation indexes of thenardite are not calculated by the ionic association model; however, in the activity diagrams, the equilibrium state simulated by different thermodynamic models shows that:

- i) For the saturation with respect to the gypsum and with respect to calcite, points are organized, more or less in accordance with the straight equilibrium solubility product of gypsum K_{sp} (gypsum) and of calcite K_{sp} (calcite) drawn up by the method of Pitzer against that of the other methods. When saturation is reached, the concentrations of Ca and SO_4 are conditioned by their solubility products (Figures 2 and 3) [29-31].
- ii) For the saturation with respect to halite, it will not be well reached if the concentrations of sodium and chloride increase;

therefore, their precipitation can only be obtained for higher concentration factors (Figure 4).

The equilibrium straight line of the solubility product of gypsum:

$$\text{Log } K_{sp} (\text{gypsum}) = \text{log } a_{Ca} + \text{log } a_{SO_4} + 2\text{log } a_w = -4.58$$

The equilibrium straight line of the solubility product of calcite:

$$\text{Log } K_{sp} (\text{calcite}) = \text{log } a_{Ca} + \text{log } a_{CO_3} = -8.36$$

The equilibrium straight line of the solubility product of halite:

$$\text{Log } K_{sp} (\text{halite}) = \text{log } a_{Na} + \text{log } a_{Cl} = 1.56$$

Conclusion

The results obtained during this research project show that the brines of chotts and sebkhas in the Algerian Northeastern Sahara are characterized by a high concentration of about 290 g/l at average, a state of oversaturation with respect to calcite and more or less with respect to gypsum. Speciation and thermodynamic modelling of these brines differ according to the used model. This model depends mainly on the thermodynamic database with which the calculations are performed.

Taking into account the limited applicability of the ionic association model for highly concentrated solutions, the specific ionic

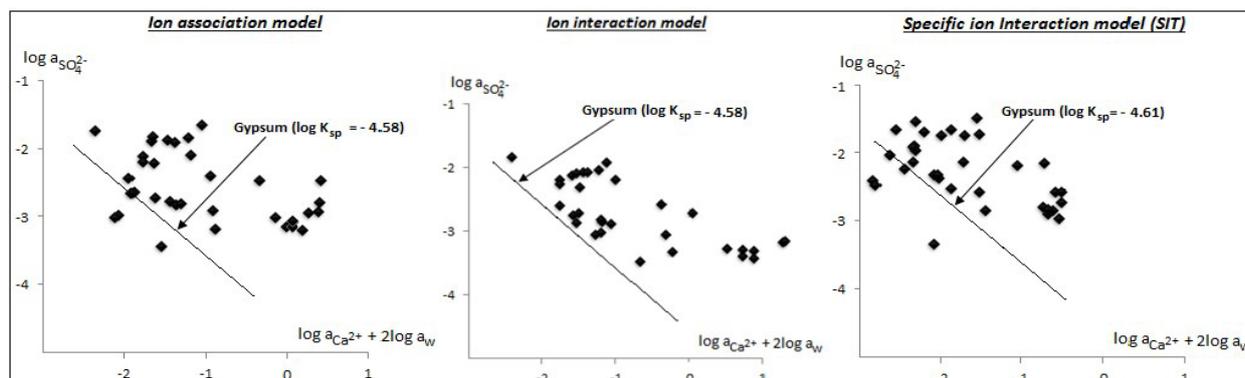


Figure 2: Brine equilibrium relative to gypsum.

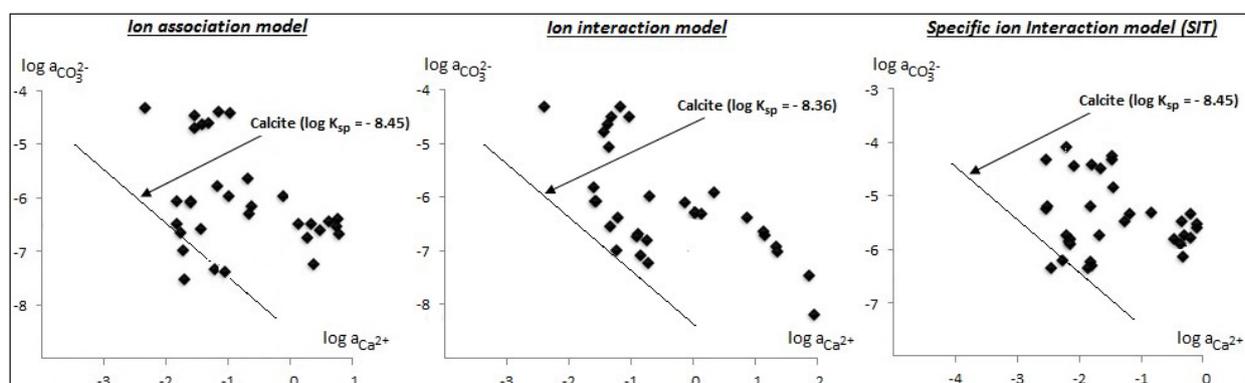


Figure 3: Brine equilibrium relative to calcite.

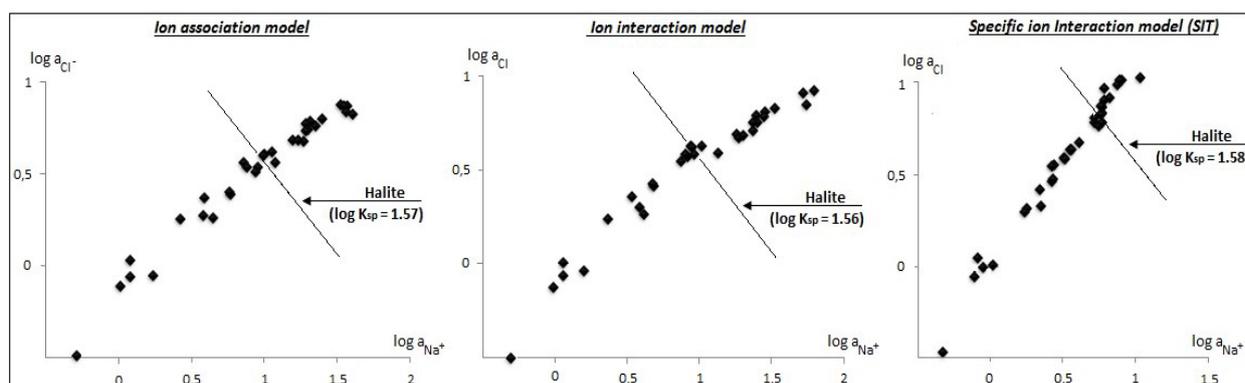


Figure 4: Brine equilibrium relative to halite.

interaction model drawn up by Pitzer was compared with that of the Specific ion Interaction Theory. It is generally observed that the SIT model involves more parameters and it is more or less satisfactory, in its field of application, compared to that of Pitzer. However, the diagrams of the activity of halite show that there are points over the equilibrium straight line, which is important, i.e., none of these three models will work. This paragraph highlights the fact that there is no more ideal modelling tool. Each one has its advantages and limitations, but still modelling remains a valuable tool to simulate and control the thermodynamic behaviour of the brines. Therefore, the modeler should

primarily select the best model relative to the study site, depending on the data available, the objectives of the modelling, etc.

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