

EVOLUTION OF THE SALINE AND HYPERSALINE BRINES IN THE SOLAR PONDS FROM LAKE QUAROUN, FAIYOUM -EGYPT

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ABSTRACT

The net effect of evaporation ponds uses at EMISAL is to concentrate all the dissolved components. The basic principals of the evolution of the lake and pond brines are discussed here on the basis of the buildup of the dissolved components through evaporation as a major control on the brine composition. The salinity (Total Dissolved Solids) values , concentration of the major cations and anions (Ca^{+2} , Mg^{+2} , SO_4^{-2} , Na^+ and Cl^-), ions and molecular ratios ($\text{Mg}^{+2}/\text{Ca}^{+2}$, $\text{mMg}^{+2}/\text{mCa}^{+2}$, $\text{Na}^+/\text{Mg}^{+2}$, $\text{mNa}^+/\text{mMg}^{+2}$) are discussed. The type of Lake Quaroun water and fourth pond brine are detected.

INTRODUCTION

Beednell, (1905), and others referred to the Faiyoum Depression (1200 km²) as semicircular in outline and has 50 km in diameter. The lake surface area covers nearly 240 km². The lake is fed only by drainage water arising from the cultivated land in the Faiyoum depression. The lake receives more than 450 million m³. of drainage water every year (FWMP, 1999).

The investigated area centered at latitude 29° 26.5'N and at a longitude 30° 40.5' E. The area is hot and dry, rainfall is rare, the annual rain fall has been recorded as 10mm, but this value may change from one year to other (Samy , 2000).

The prevailing winds are relatively constant from north-northwest and may be changed to northeast , and ranges from 2.74 to 5.16 m/sec (through out the year and the average sunrise reaches 9.7 h/day (Al Kordy, 2003). The mean annual values of evaporation for II years 1982 to1992 is 6.9 m.m/m². /day (WYP, 1992), the hydraulic and water management research institute detected

the average values of the evaporation rate by 1947 mm/year (5.33 mm/ day), (HIR& WMI, 2004). By using evaporation coefficient of Lake Quaroun, the rate of evaporation ranged between 1.07- 8.8 mm/day (4.795 mm/day as average), (Abd Ellah, 1999, 2003). The mean average temperature during 2004 is 23.8°C, and the mean average relative humidity is 57.5%, (data from EMISAL records).

An area of about 5 km² was cut from natural bay at the southern coast of the lake, west of Shakshuk village. This area was divided into four successive evaporation ponds to prepare the suitable brine for salt extraction. These ponds were designed with adjusted depths to allow natural flow from one pond to the other. The water in the ponds is left to be evaporated to the required volume and concentration took place by solar energy only. The first pond has an area of about 2.1 million m² and its depth is about 1.7 m and receives water directly from the lake through pumping station. The total dissolved solids of this pond left to reach 80 g/L. The second pond has an area of about 1.05 million m². and its depth is about 1.8 m. In this pond

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EVOLUTION OF THE SALINE AND HYPERSALINE BRINES IN THE SOLAR PONDS FROM LAKE QUAROUN, FAIYOUM -EGYPT

the concentration rises to 140 g/l before into the third pond. The third pond has an area of about 1.4 million m², and its depth is about 2.35m. Here the brine is left to reach 250 g/l, before it flows to the fourth pond which

covers an area of about 0.6 million m² and its depth is about 2.8 m. The total dissolved salts in this fourth pond reaches to 350 g/l at outlet (Fig. 1).

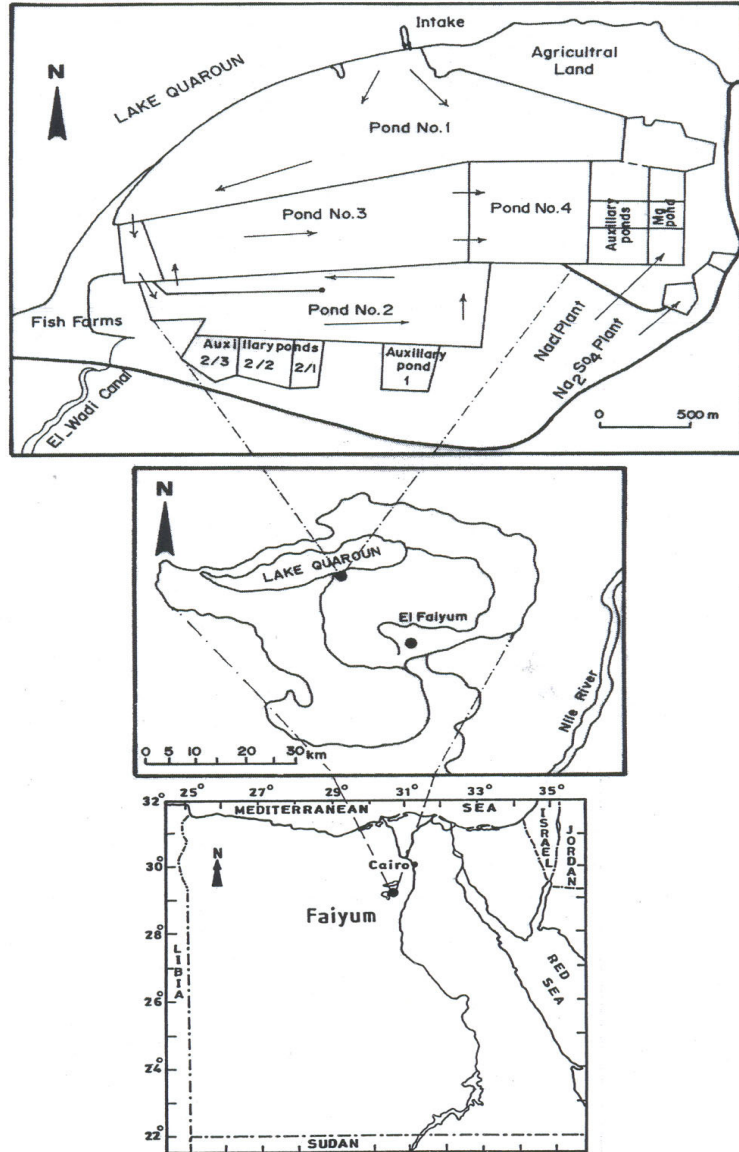


Fig. (1) Location of the area studied

The four successive solar evaporation ponds, EMISAL area commonly have initial composition that differs significantly from that of the sea water. The variety and abundance of minerals produced from an evaporating body of water depend on its initial composition. So the relationship between brine solutions and the associated minerals enable the formation of minerals and enhance the diagenetic processes to be closely delimited, as explained by Sherman (1963 and 1966); Kinsman (1966, 1969, 1974 and 1976); Butler (1969, 1970), Butler *et al.*, (1982); Evans *et al.*, (1969); Bush (1974); West *et al* (1979 and 1983); Ali and West (1983); Warren (1989); Ali and Osman (1993); Al-Kordy (2003); El sheikh (2004) and other authors.

Sampling and Analytical Procedures

The brine water samples from the lake and the other artificial four ponds were analyzed for the major anions and cations, mainly, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} and HCO_3^- . Calcium ions were determined in the brine water samples complex metrically using Muroxide as an indicator. Magnesium ion were determined in the brine water samples by subtracting the calcium ions value after determining both calcium ions and magnesium ions complex metrically using Eriochrom black T as an indicator. The sulphate ions were determined in the brine water samples by barium sulphate precipitation. The method was used by Dunk, *et al.*, (1969). Bicarbonate radical was analyzed by titration with O. In: HCl using methyl orange as an indicator. The chloride ions were determined in the brine water samples by titration with silver nitrate using potassium chromate as an indicator. The sodium ions were determined in the brine water samples by calculation the equivalent quantity of chloride ions and the quantity of remaining sulphate ions. The potassium ions were determined in the brine water samples by using atomic absorption (Perkin Elmer Analyst 800).

RESULTS AND DISCUSSIONS

1. Total Dissolved solids (salinity):

The salinity values of the ponds increase from the first pond to the fourth one. In Lake Quaroun water (pumping site) salinity attains value of about 34.9 g./l., in the first pond, salinity attains nearly 60.7 g./l. which is 1.73X the lake water salinity, this indicates moderately saline water. However, this increase of salinity attains its maximum value in the fourth pond, where the average salinity value is of about 357 g. /l. i.e. concentrated brine reached about 10.2 X the lake water salinity and about, 10.3X the Sea water salinity. In the other ponds, particularly the second and the third ponds, the average salinity value reaches of about 123 and 244g. /l. respectively. This reveals a hypersaline brine water which is about 3.51 and 6.98 X Lake Quaroun salinity and which is equivalent to 3.57 and 7.1 X the Sea water salinity (Fig. 2).

The average salinity of irrigation water is 0.79 g. /l. which is about 0.0226X Lake Quaroun salinity and about 0.0229X the Sea water salinity. In drainage water supply, average salinity attains 3.6 g./l. which is about 0.103X lake Quaroun salinity and about 0.104X the Sea water salinity. The salinity of the Dead Sea of about 322.6 g./l. (Nissenbaum, 1980) which is about 9.24 X Lake Quaroun salinity and about 9.37 X the Sea water salinity. Dardir (2000) and Al kordy (2003) revealed that the quantity of Lake Quaroun extracted by EMISAL Co. from the lake is 15 million³ and that the salt concentration in the lake about 34 g/L. So the salt mass extracted from the lake annually is calculated to be 510000 ton, this quantity if still in place and not extracted may lead to an increase in lake salinity by an amount equal to 0.523g/L This value is calculated under lake volume of equal about 976 million³. This results to decline the increasing salinity by about 69%.

EVOLUTION OF THE SALINE AND HYPERSALINE BRINES IN THE SOLAR PONDS FROM LAKE QUAROUN, FAIYOUUM -EGYPT

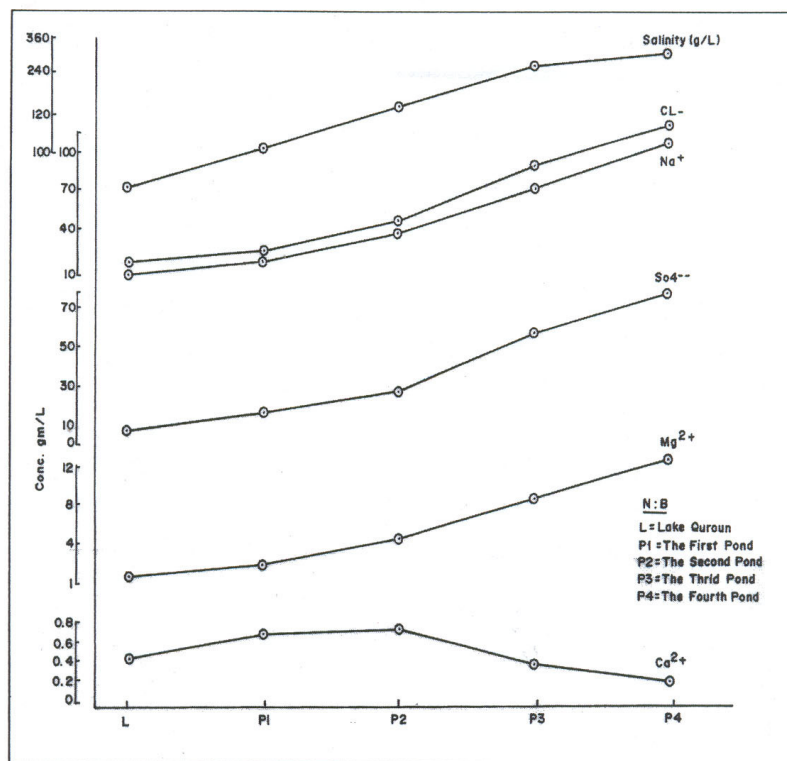


Fig. (2) The changes in salinity (g./l.) and the chemical composition of lake Quaroun water and the brines of the four hypersaline ponds

2- mMg²⁺To mCa²⁺ and Mg²⁺To Ca²⁺ Ratios:

The ratio values between molecular magnesium ion concentration to molecular calcium ion concentration in the various ponds increase from 4.5 in Lake Quaroun water to 182.9 in the fourth pond. The average values of mMg²⁺/ mCa²⁺ ratio range from 5.45 in the first pond , 10 in the second pond and 37.3 in the third pond. However, the mMg²⁺/ mCa²⁺ ratio values in the Sea water is 5.2. and in Lake Quaroun water 4.5.

The values of the magnesium ion concentrations to the values of the calcium ion in the various saline and hypersaline ponds showed increases from the lake water , which attains a value of 2.73 to the third pond, where the Mg²⁺/Ca²⁺ ratio is 23. During

May the value of the Mg²⁺/Ca²⁺ ratio increase to its maximum value in the first pond to reach 3.7. , whereas in the second pond its value increases to reach maximum value during March and April. Yet in the third pond the Mg²⁺/Ca²⁺ ratio value increases to reach its maximum value during May and June. This is probably due to the precipitation of calcium carbonates and sulphates during March to June. The plotting of the magnesium ion concentration (m mole/kg) against Mg²⁺ / Ca²⁺ (mole ratio) of each of the lake water, the first, the second and the third ponds brine on the diagram of Butler (1969) , reveals that the main evaporite precipitation in the first , the second and the third ponds are hydrous calcium sulphate

(gypsum) in contact with brines and not anhydrite i.e. in the stable field of gypsum where magnesium ion concentration (m.mole/kg) around 180 (m.mole/kg), particularly in the second and the third ponds, (Fig. 3). The plotting of the Mg^{+2} / Ca^{+2} ratios against the salinity (g. /l.) of the first, the second and the third ponds on the diagram of Folk and Land (1975). (Figure 4) shows that the precipitation of the carbonates of the first, the second and the third ponds located in the aragonite and high Mg calcite zone.

Kinsman (1966, 1969, 1974 and 1976) indicated that gypsum will probably always

be the first calcium sulphate mineral to precipitate from natural solution under each surface climatic condition. The plotting of specific gravity against chlorinity of the brines of the first , the second and the third ponds on the diagram of Miller (1961) which was used by Butler , (1969 , 1970) Butler *et al.*, (1982), and Osman (1986) and El sheikh (2004) shows that gypsum is the stable calcium sulphate mineral in contact with the brines of chlorinitis (chloride ion concentration) less than 145‰ and anhydrite at chlorinities greater than 145‰ (Fig. 5).

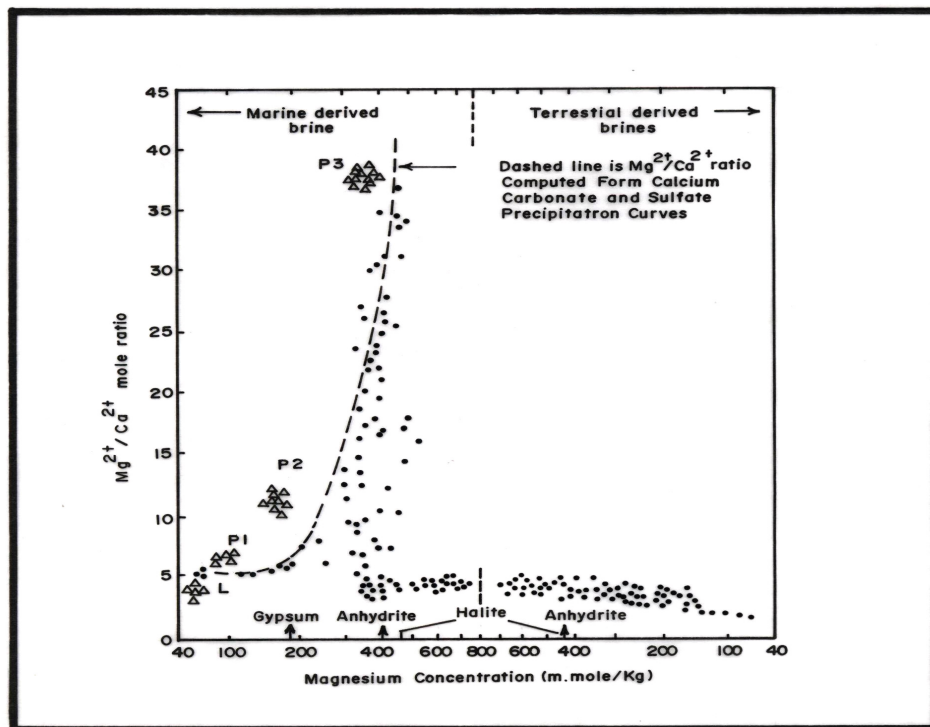


Fig. (3): Mg^{+2} / Ca^{+2} ratio as a function of Mg concentration for Abu Dhabi sabkha (Butler 1969) used for comparison with brines from the various saline and hyper saline ponds in the present study.

EVOLUTION OF THE SALINE AND HYPERSALINE BRINES IN THE SOLAR PONDS FROM LAKE QUAROUN, FAIYOUUM -EGYPT

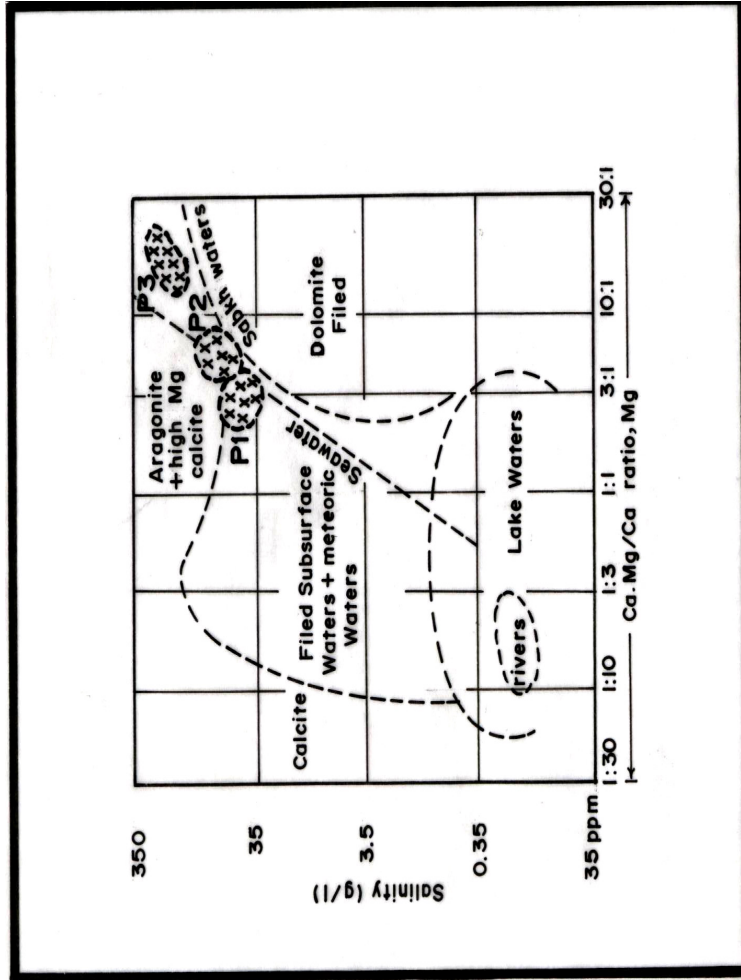


Fig. (4): Plot of salinity (g./l.) against Mg/ Ca ratio of the brines from the first, the second and the third ponds on the diagram of Folk and Land (1975).

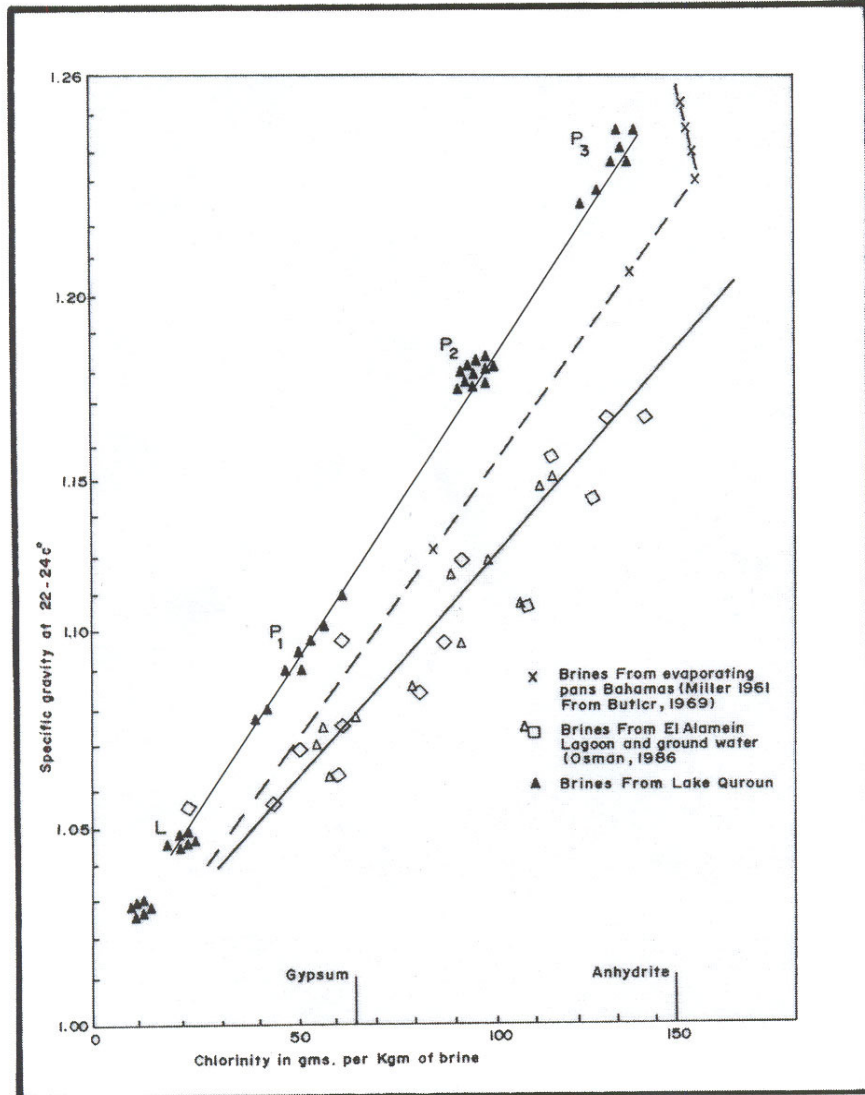


Fig. (5): Water brines from Quaroun Lake (L) and the various ponds (P1, P2 and P3) compared to data from Bahamas from Butler, (1969) and El Alamein lagoon (Osman, 1986). Notice change in brine specific gravity with increasing brine concentration. Gypsum precipitates at chlorinity 65‰, sp.gr. 1.085. Gypsum – Anhydrite equilibrium at chlorinity 145‰, sp. gr. 1.186.

3- Na^+ / Mg^{+2} and $m Na^+ / m Mg^{+2}$ Ratios:

The sodium to magnesium ratio values slightly increases with an average value of 7.53 in the lake brine to 8.4 in the fourth pond brine. The average value of Na^+ / Mg^{+2} ratio are 7.96, 8.25 and 8.37 respectively in the first, the second and the third ponds. Obviously there are enrichment in the concentration of the sodium ions and the magnesium ions particularly in the fourth pond. The molecular sodium ion concentration to molecular magnesium concentration ratios (mNa^+ / mMg^{+2}) ratio values increase from 7.9, 8.36, 8.6 and 8.9 respectively in the lake water, the first, the second and the third ponds. Its value is 8.9 in the fourth pond, this is probably due to the precipitation of halite and sodium sulphate salts with excess Mg^{+2} ions content.

4- Type of lake Quaroun water brine:

Harvie *et al* (1980) and Hardi (1984, 1991) postulated models for experimental evaporation of Sea water and Dead Sea water. Applying these models to Lake Quaroun water evaporation. The author concluded that the calcium ions concentration in the lake water is much higher than the alkalinity. i.e. $Ca^{+2} > CO_3^{-2} + HCO_3^-$, after 80% of the initial water has been lost by evaporation and essentially all the carbonates has been precipitated in the first and second ponds. The sulphate ions concentration in the lake water are much higher than the calcium ions, i.e. $SO_4^{-2} > Ca^{+2}$, the gypsum precipitation removes nearly all the calcium ions from the solution, thus the path of the solution composition tend toward chloride brine. Thus the type of the lake water brine is SO_4^{-2} and Cl^- as major anions and Mg^{+2} and Na^+ as major cations.

The postulated flow diagram of the lake water (Fig. 6) shows the various saline and hyper saline ponds, the calcium ions removed from the solution in the first pond as low-Mg calcite, in the second pond as low and high Mg- calcite. Almost calcium ions removed in the third pond as gypsum and high Mg-

calcite. Finally the type of the brine of the fourth pond is Cl^- , Na^+ , Mg^{+2} and SO_4^{-2} brine.

5- Brine of The Fourth Pond:

The brine type of the fourth pond is Cl^- , Na^+ , Mg^{+2} and SO_4^{-2} as mentioned above, and as indicated in the flow diagram (Fig.6). Quinary diagram was used by (Hamzaoui *et al*, 2000) for brines of Na^+ , K^+ , Mg^{+2} , Cl^- , SO_4^{-2} / H_2O , composition, consequently two natural brines (El Adhibate and Dead Sea) brines are applied on the Quinary diagram. We employed the composition of the fourth pond on the above mentioned Quinary diagram (Fig. 7). The result is that the brines of the fourth pond fall in the area number 6 which is the Thenardite precipitation field.

SUMMARY AND CONCLUSIONS

The present study offers example to understanding the evolution of the brines geochemistry in the artificial saline and hypersaline solar ponds.

The diagenetic changes involving precipitation from concentrated brines or reaction between brines and the original sediments are reflected in the brine chemistry. Chemical analyses of Lake Quaroun water, the first, the second, the third, and the fourth ponds. The study revealed that, magnesium, sodium, and chloride ion concentrations, in general increase with the increase of salinity from the first to the fourth pond. However calcium and bicarbonate ions show decrease with increase of salinity. This is probably due to the precipitation of calcium carbonate and hydrous calcium sulphate in the second and third ponds which led to depletion of calcium and bicarbonate ions in the third and fourth ponds. The degree of supersaturation of these the ionic concentrations from the first and the second ponds are: $Cl^- > Na^+$ brines varies with respect to total salinities and precipitation of sulphate minerals (gypsum, glouberite, thenardite (Na_2SO_4), allenite ($MgSO_4 \cdot 5H_2O$) and leonhardite ($MgSO_4 \cdot 4H_2O$)), carbonate

minerals (calcite, high Mg. calcite and aragonite) and chloride minerals (halite). The average salinity values of successive solar ponds increase from 60.7 g/l. in the first solar pond , which is 1.73 X the Lake Quaroun water salinity, this indicates moderately saline water . However, this increase of salinity attains its maximum value in the fourth pond, where the average salinity value is of about 357 g/l. This reveals concentrated water, which is of about 10.2 X

the lake water salinity. In the second and the third ponds, the average salinity value is of about 123 and 244 g/l. respectively. This reveals hypersaline brine which is of about 3.51 and 6.98X Lake Quaroun salinity respectively. EMISAI Co. extracted around 8.34 million tons of salts out from lake Quaroun (from 1986-2004), if this quantity is still in Lake the salinity would have increased by 8 g/L more than actually present (i.e \approx 43 g/L).

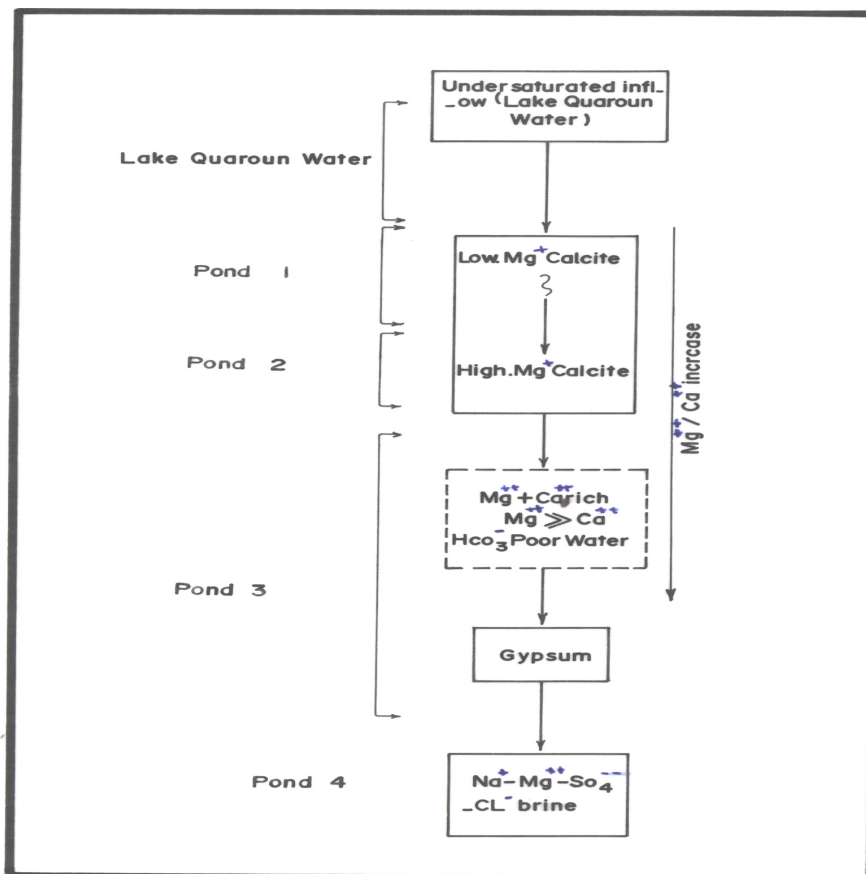


Fig. (6): Flow diagram of Lake Quaroun water and the various four saline ponds.

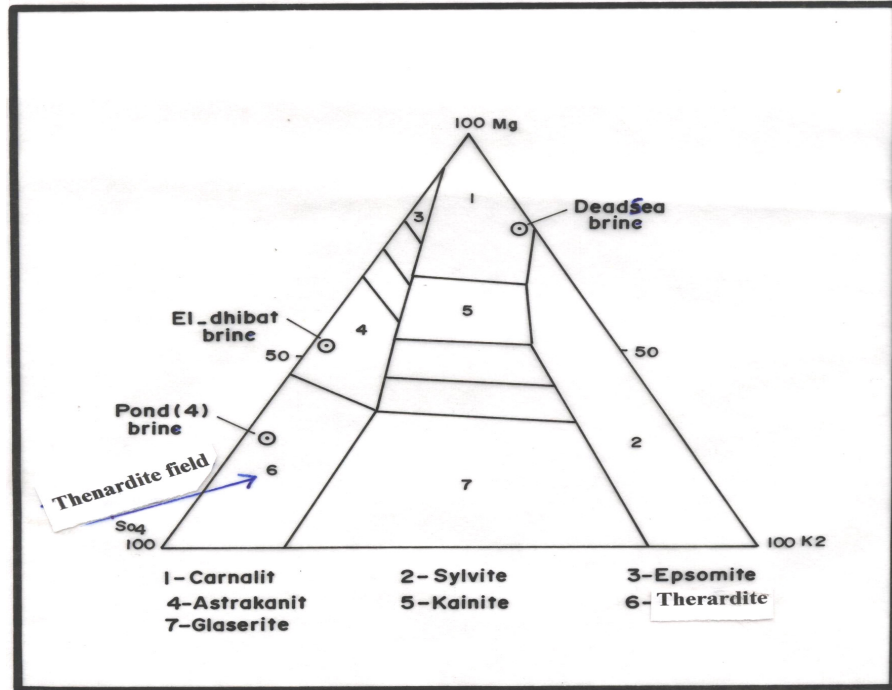


Fig. (7): Plotting the fourth pond brine compared with Dead Sea brine and El- dhibat brine on Quinary diagram , Na^+ , K^+ , Mg^{+2} , Cl^- , SO_4^{-2} , / H_2O (Hamazawi *et. al.* 2000).

The ion and molecular ratio values reveal the type of mineral precipitation, such of these ratios are $\text{m Mg}^{+2} / \text{m Ca}^{+2}$, $\text{Cl}^- / \text{SO}_4^{-2}$ and $\text{m Na}^+ / \text{m Mg}^{+2}$. The $\text{m Mg}^{+2} / \text{m Ca}^{+2}$ ion concentration ratio values in the various ponds increase from 4.5 in the lake water to 182.9 in the fourth pond water , while the average value of $\text{m Mg}^{+2} / \text{m Ca}^{+2}$ ratio values range from 5.45 in the first pond , 10 in the second pond and 37.3 in the third pond . The values of the $\text{Mg}^{+2} / \text{Ca}^{+2}$ ratio increases to its maximum value in the first pond to reach 3.7 during May . However in the second pond this ratio increases to reach maximum value during March and April, but in the third pond the $\text{Mg}^{+2} / \text{Ca}^{+2}$ ratio increases to reach maximum values during May and June. This is due to precipitation of calcium carbonates and sulphates (gypsum) during March and June, in the first, the second and the third ponds.

The $\text{Cl}^- / \text{SO}_4^{-2}$ ratio values in the various ponds, show that the $\text{Cl}^- / \text{SO}_4^{-2}$ ratio value increases from the lake water (1.35) to the fourth pond water (1.83). This reflects the excess of chlorinities (chloride ion concentration) during precipitation of gypsum from March to July. This is due to precipitation of calcium carbonates and sulphates (gypsum) during March and June, in the first, the second and the third ponds. The averages $\text{m Na}^+ / \text{m Mg}^{+2}$ ratio values increase from 7.9, 8.44, 8.6 and 8.9 respectively in the lake water, the first, the second, and the third ponds. This is due to precipitation of halite and sodium sulphate salts with excess of Mg^{+2} ion content. From the postulated flow diagram of Lake Quaroun water, the type of the brine of the fourth pond is Cl , Na , Mg and SO_4 brine. The brine type of the fourth pond falls in the area of the

thenardite precipitation field on the Quinary diagram.

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EVOLUTION OF THE SALINE AND HYPERSALINE BRINES IN THE SOLAR PONDS FROM LAKE QUAROUN, FAIYOU M -EGYPT

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