

## Brine-mixing of residual brines to obtain $\text{MgCl}_2$ salt: The case of El Mex solar , Egypt.<sup>1</sup>

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Storage of the residual brine for almost 110 years in a producing solar saline (El Mex) invites the investigations of the formation of  $\text{MgCl}_2$  salts through brine mixing. Nine sets of experiments were carried out, each involving two brines mixed together at five ratios (1: 1, 1:2, 1:3, 1:4, and 1:5) and their reverse, to form a total of 90 tests. Brines with specific gravities of 1.186, 1.218, 1.29, 1.239, 1.25, 1.261, 1.31, 1.311, and 1.32  $\text{g/cm}^3$  were chosen from the residual brine storage and halite crystallization ponds to conduct investigations. Two sets gave negative results. These were the mixing experiments of brines having specific gravities of 1.186 with 1.31, and 1.261 with 1.31  $\text{g/cm}^3$ . The other seven sets resulted in the formation of sodium chloride, potassium chloride, and magnesium chloride salts. Time required for their formation ranged between 15 to 30 seconds without manual stirring. With manual stirring, however, the precipitates increased in amount ( $\sim 60\%$ ) with an increase in crystal size. The formed salts were examined microscopically in order to determine the crystal faces, size homogeneity, agglomeration character (caking), and rates. They were also subjected to manual stirring for 5 to 10 seconds, mechanical stirring at 200 r/min and 500 r/min. for 5 and 10 minutes respectively in order to estimate the increase in size, segregation effect, and rates of formation. Products of all the steps were microscopically examined and documented.

Mineralogical investigations were done using XRD and microscopic examinations. The leftover brine (filtrate) was chemically analysed in order to determine its composition and suitability for washing the solar precipitated halite as a medium free of magnesium and potassium. Results indicate a 15% a reduction in loss and a lowering of magnesium content by 35% as compared with the regular procedure of washing. Results show that the production of pure  $\text{MgCl}_2$  and  $\text{KCl}$  is possible through this technique. Moreover, the obtained  $\text{NaCl}$  is of uniform size and of perfect cubes. Also, the process represents a step toward gaining pure valuable salts, with their wide industrial application, and in the meantime, helps to solve the problem of residual brine storage.

### 1. INTRODUCTION

Lake Maryut was once a depression and the Canopian branch of river Nile filled it. The lake was the source for fish and irrigation waters during the Roman times, with fertile lands surrounding it. Over time, the lake receives less feeders until the supplying branch was cut-off. Since then the Lake Maryut has been used as a saline. Since the industrial time of Mohamed Ali ( $\sim 1750$  yr.), part of the lake was cut-off for salt production, particularly for domestic and textile purposes. El Mex solar salt work is the oldest (founded in 1789), where it started production by 1805. In the late sixties, El Nasr Salines Co. (ENSC) was founded for salt production on a modern industrial scale, and now its production reaches 1.8 Mt./yr. (Fig. 1). The residual brines after halite precipitation are pumped to residual brine storage ponds, and left to evaporate with annual renewing by adding new residual brines.

Production of highly soluble salts through solar evaporations requires long time. This fact, combined with recent industrial modernisation, gives active push to test brine-mixing mechanism as to produce highly soluble salts. These salts gain increasing importance in industry of alloys and heat-resistant bricks required for furnace coating. The stored residual brines in one salina i.e. El Mex are millions of cubic meters in volume, which is one in addition to another three solar salt work salinas owned by ENSC. This article aims to form Mg and K salts through brine-mixing mechanism with emphasis on determining the optimum conditions for the process. Brine mixing occurred as a natural process in closed or semi-closed basin (1 and 2), developed by brine stratification process leading to pressure differences (1 and 3). The pressure difference will enforce the denser brine to move upwards and mix with the overlying lighter one (1 and 4).

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## 2. INVOLVED BRINES

The involved brines in the brine-mixing experiments are from El Mex solar salt work salina, mainly from crystallization ponds and residual brines stored in residual brines storage pond (Fig. 1). Their concentration reaches: 23, 26.5, 27, 28, 29, 30, and 34 ( $^{\circ}\text{Be}$ ) corresponding to specific densities ( $\text{g}/\text{cm}^3$ ) 1.1985, 1.2237, 1.2288, 1.2393, 1.250, 1.2608, and 1.306 respectively. Moreover, a residual brine of 34  $^{\circ}\text{Be}$  (sp. gr. = 1.306  $\text{g}/\text{cm}^3$ ) was further evaporated by applying ultraviolet lamp with continuous monitoring the brine specifications. These brines will be considered as artificial brines, although those brines can exist in nature. The artificial brines were reaching  $^{\circ}\text{Be}$ : 34.1, 34.4, and 35, corresponding to specific densities ( $\text{g}/\text{cm}^3$ ). The characteristics of the involved brines are tabulated in Table 1. Three sets among the nine sets indicate negative results, these are set nos. 2, 3 and 4 of the following concentrations ( $^{\circ}\text{Be}$ ): 23, 30, and 34. The tested rates in each of the three sets were of 1: 1, as A to B and B to A in order to ensure that mixing will not produce salts.

## 3- PROCEDURE

The applied procedure in the executed experiments is based on:

- 1- Mixing is in a forward and reverse manner. Chosen rates are five in each direction.
- 2- Manual stirring is postponed until all observations of naturally formed salts are completed, and then gentle manual stirring for 10 - 15 seconds was applied.
- 3- Observations of the natural mixing include: a) thickness of mixing zone, b) time from mixing till appearance of a cloud, c) time from appearance till precipitation, d) weight of precipitates, e) description of crystal shape and size.
- 4- Mechanical stirring was applied (using 30 $^{\circ}$  wings glass rod) with speed of 200 r/min for 5 min and then 500 r/min for 10 min. The different speeds aim to define the optimum conditions.
- 5- The precipitate was then filtrated using mechanical pumps, where, the precipitate dried

in a furnace and x-rayed for mineral composition, whilst the filtrate was chemically analysed.

- 6- Mixing-brines preliminary experiments indicate agglomerated salts as chains with the presence of some organic relics. When the brine was treated by ethyl alcohol before mixing the agglomeration character disappeared.
- 7- The obtained salts were weight after being dry, and the values were documented in tables corresponding to each set.

Ten rates were chosen as five rates in both directions i.e. A to B, and B to A. A to B means addition of lighter brines on denser one in order to test the mixing effect, while the reverse is used to define optimum conditions.

### 3.1. Salt formation

The aim of preliminary experiments was to determine the saturation levels of the involved brines and their concentration differences. The former will help in predicting the formed salt type(s), while the second will reflect the yield amount and size uniformity as well. XRD and microscopic examination confirmed the mineralogy of the formed salts. The applied experiments indicate rapid formation of salt as a cloud within 15-30 seconds (Photo 1), using transparent plastic

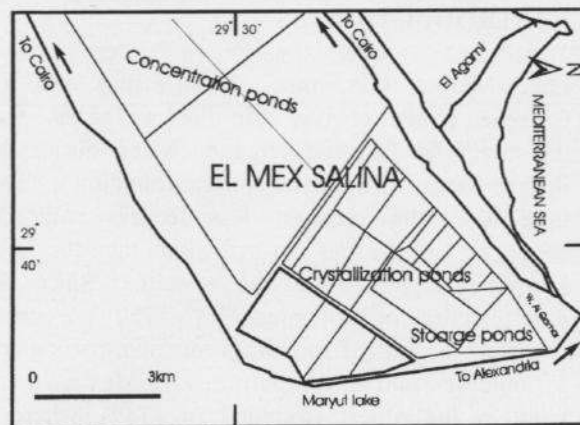


Fig. 1. Location map of El Mex solar salt, work salina

**Table 1 Involved brines characteristics (El Mex solar salt work salina).**

Set no.	1		5		6		7		8		9	
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
$^{90}\text{Be}$	26.5	34.1	26.5	35	27	34.4	27	34	28	35	29	35
Sp.gr. (g/cm <sup>3</sup> )	1.223	1.307	1.223	1.320	1.228	1.309	1.228	1.306	1.239	1.320	1.250	1.320
TDS (g/l)	358.1	482.1	358.1	444.3	339.7	432.8	339.7	429.3	352.8	444.3	368.4	444.3
pH	7.13	5.8	7.13	5.75	6.98	5.76	6.98	5.8	6.90	5.75	6.82	5.75
$\text{SO}_4^{2-}$	42.1	82.67	42.1	44.97	27.29	52.44	27.29	55.87	37.59	44.97	48.79	44.97
$\text{Cl}^-$	190.6	248.7	190.6	267.3	189.7	246.0	189.7	237.1	192.2	267.3	195.8	267.3
$\text{Mg}^{2+}$	26.50	83.21	26.50	84.49	20.94	69.33	20.94	62.73	28.57	84.49	38.46	84.49
$\text{Na}^+$	91.33	44.85	91.33	331.02	93.38	48.21	93.38	54.94	84.02	33.02	71.49	33.02
$\text{K}^+$	5.234	12.93	5.234	8.895	6.378	12.93	6.378	14.96	8.746	8.895	11.88	8.895

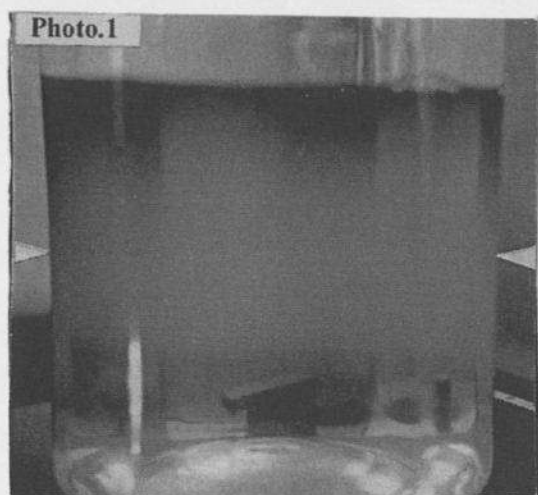


Photo 1: Cloud formation after mixing. Arrows indicate the mixing zone.

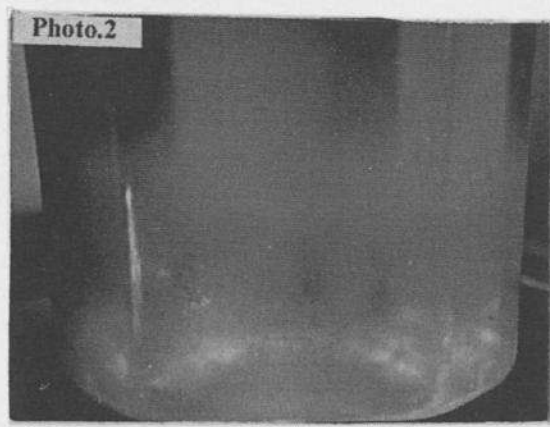


Photo 2: Precipitation of crystals seen as a dense shower

jar, while after 20-30 seconds more a shower of precipitation started till final precipitation (Photo 2).

#### 4. MECHANICAL STIRRING

After applying manual stirring a rapid increase the amount of precipitated salts occurred. This result lead for further mixing experiments of the two brines through applying mechanical stirring in two stages, the first through 200 r/min for 5 minutes, followed by 500 r/min for 10 minutes. Upon applying 200 r/min effect, a cone started to form to suspending the precipitated crystals. A remarkable increase in amount and size of the crystals after stirring was recorded. A remarkable feature concerning the crystal shape perfection of halite and sylvine was always recorded after mechanical

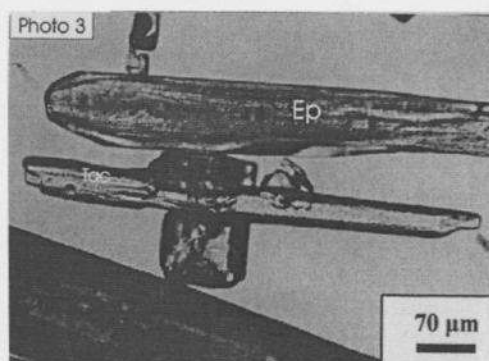


Photo 3: Corroded edges of epsomite (Ep.) and tachydrate (Tac.) after mechanical stirring.



stirring. Most of the crystals were either damaged totally and/or partially corroded. As for Mg salts i.e. tachydrate ( $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ ) and epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), different patterns of corroded edges were recorded. Photo 3 illustrates the corroded effect occurring in Tachydrate and epsomite, where edges and/or middle parts of the crystals are abraded till almost breaking into smaller pieces.

Size, mechanical stirring speed, and hardness of the crystal itself might control this character. Upon applying 500 r/min for 15 minutes partial and/or total disintegration of the crystals was observed. Applied speed and time represent the maximum range for mechanical stirring due to total disintegration of the formed salts.

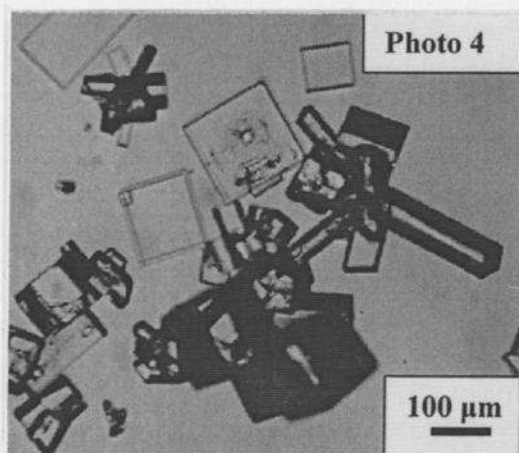


Photo 4: Fibro-radiating pattern. Halite crystals are the nuclei.

## 5. TEXTURES

The following is a description of the formed salt types and their textures according to their abundance:

### 5.1. Halite ( $\text{NaCl}$ )

An experiment was executed in order to test the stages of formation of halite crystal from involved brines in the brine-mixing experiments. The experiment was based on slow evaporation of the brine through the incident light from the microscope, where the brine itself was saturated enough to precipitate halite leading to formation of a hopper texture. Another texture described as

fibroradiating was also detected, where cubic halite is the nucleus tachydrate crystals radiating out (Photo 4). Tabular halite is rarely found in nature, and does occur whenever halite is precipitated in a short time.

### 5.2. Tachydrate ( $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ )

Tachydrate is as prismatic crystal soft crystal, here also a bending character is clearly seen (Photo 5), and the smaller disintegrated crystals will display a fibro-radiating texture. The nuclei could be a halite crystal or a disintegrated part of it.

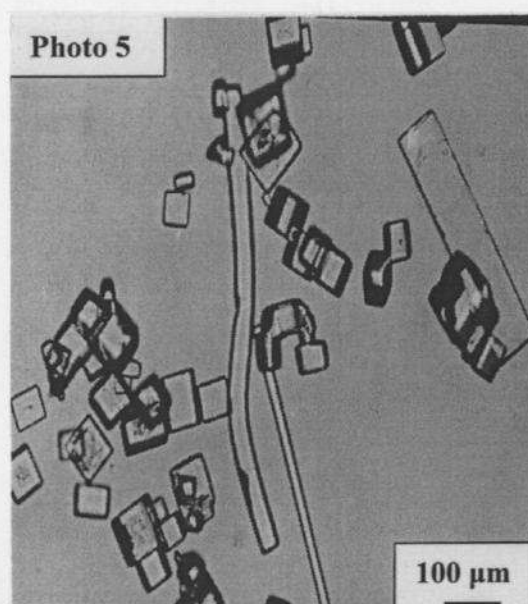


Photo 5: Bend tachydrate crystal due to the mechanical stirring effect.

### 5.3. Sylvine ( $\text{KCl}$ )

Sylvine crystals can be easily differentiated from halite by its low relief. This character helps in estimating the ratios of both halite and sylvine. The relative ratio of halite and sylvine is variable since both are succeeding in sequence of crystallization. Sylvine always display cubic texture, mostly in solitary habit and displaying more or less uniform size.

### 5.4. Epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ )

Epsomite is found variable quantities as will be discussed in the Geochemistry section. Always seen as large bipyramidal crystals, though in some other

Table 2  
Physical and Chemical characteristics of set no. 9 and results of different rates of mixing.

Set No.(9)		A → B										B → A									
Ratio of Addition		1 <sub>A</sub> :1 <sub>B</sub> (9/1) (200/200) ml		1 <sub>A</sub> :2 <sub>B</sub> (9/2) (100/200) ml		1 <sub>A</sub> :3 <sub>B</sub> (9/3) (100/300) ml		1 <sub>A</sub> :4 <sub>B</sub> (9/4) (50/200) ml		1 <sub>A</sub> :5 <sub>B</sub> (9/5) (50/250) ml		1 <sub>B</sub> :1 <sub>A</sub> (9/6) (200/200) ml		1 <sub>B</sub> :2 <sub>A</sub> (9/7) (150/300) ml		1 <sub>B</sub> :3 <sub>A</sub> (9/8) (100/300) ml		1 <sub>B</sub> :4 <sub>A</sub> (9/9) (50/200) ml		1 <sub>B</sub> :5 <sub>A</sub> (9/10) (50/250) ml	
Results		S*	F*	S*	F*	S*	F*	S*	F*	S*	F*	S*	F*	S*	F*	S*	F*	S*	F*	S*	F*
Physical Properties	Be <sup>o</sup>		30.8		30.9		31.0		31.2		31.3		29.9		30.6		30.8		31.1		31.2
	Sp.Gr.(g/cm <sup>3</sup> )		1.2700		1.2711		1.2722		1.2742		1.2748		1.2601		1.2670		1.2702		1.2730		1.2745
	T.D.S. (gl)		397.357		398.047		403.011		411.133		415.477		389.876		392.962		410.26		412.062		416.286
	Color	Less		less		less		less		less		less		less		less		less		less	
	Insoluble	0.016		—		—		0.012		0.098		0.033		—		0.011		0.034		0.061	
	Mixing zone	2.5 cm		1.9 cm		1 cm		8 mm		6 mm		2.5 cm		3.5 cm		2.3 cm		1 cm		8 mm	
	Wt. (gm)	7.605		—		—		15.34		6.523		10.20		—		5.769		8.860		5.529	
	Crystal Shape	C+P		C+P		C+P		C+P+FR		C+P		C+P+FR		C+P		C+P+F		C+P+FR		C+P	
Ion Concentration	CO <sub>3</sub> <sup>2-</sup>	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	HCO <sub>3</sub> <sup>-</sup>	—	0.488	—	0.488	—	0.610	—	0.411	—	0.488	—	0.488	—	0.488	—	0.366	—	0.488	—	0.366
	SO <sub>4</sub> <sup>2-</sup>	18.011	62.110	—	55.614	—	56.379	35.545	62.012	27.103	54.321	0.732	52.110	—	50.412	0.991	59.011	28.334	59.341	36.70	60.351
	Cl <sup>-</sup>	46.52	221.110	—	230.872	—	236.535	33.382	237.211	39.35	246.110	59.98	221.581	—	230.441	59.55	237.181	38.64	239.110	32.11	243.11
	Ca <sup>++</sup>	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Mg <sup>++</sup>	4.481	73.611	—	79.991	—	85.067	8.879	86.525	6.898	87.713	0.423	67.411	—	78.505	0.392	86.741	7.23	86.280	9.546	90.191
	K <sup>+</sup>	0.324	12.00	—	10.9	—	10.9	0.305	11.8	0.332	12.0	0.228	10.8	—	12.0	0.446	11.4	0.270	11.5	0.179	11.7
	Na <sup>+</sup>	30.112	26.982	—	20.673	—	13.259	21.64	13.036	25.25	12.789	38.31	34.936	—	18.177	38.09	11.389	24.77	13.657	20.23	9.172
	Others	0.536	1.056	—	0.509	—	0.260	0.328	0.138	0.977	2.056	0.290	—	—	2.939	0.520	3.938	0.710	1.686	1.177	1.396
	Total	100.0	397.357	—	398.047	—	403.011	100.0	411.133	100.0	415.477	100.0	389.876	—	392.962	100.0	410.26	100.0	412.062	100.0	416.286
	NaCl	61.55	—	—	—	—	—	43.01	—	51.17	—	77.39	—	—	—	82.62	—	49.97	—	51.41	—
	MgSO <sub>4</sub> .7H <sub>2</sub> O	20.20	—	—	—	—	—	40.97	—	31.66	—	5.917	—	—	—	5.242	—	34.50	—	42.98	—
	KCl	5.168	—	—	—	—	—	5.023	—	5.632	—	5.435	—	—	—	4.554	—	5.548	—	0.324	—
	K <sub>2</sub> SO <sub>4</sub>	0.527	—	—	—	—	—	0.562	—	—	—	—	—	—	—	—	—	—	—	—	—
	KMgCl <sub>3</sub> .6H <sub>2</sub> O	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	MgCl <sub>2</sub> .12H <sub>2</sub> O	10.00	—	—	—	—	—	10.10	—	10.30	—	10.91	—	—	—	6.754	—	9.239	—	4.018	—
	Others	0.536	—	—	—	—	—	0.328	—	0.977	—	0.290	—	—	—	0.520	—	0.716	—	1.177	—
	Total	100.0	—	—	—	—	—	100.0	—	100.0	—	100.0	—	—	—	100.0	—	100.0	—	100.0	—

N.D.= Not Determined

S\* = Salt

F\* = Filtrate

C\* = Cube

Fib.\* = Fibrous

FR\* = Fibro-radiating

P\* = Prismatic

cases it is found as radial pattern with nuclei of fragmented halite. Epsomite is rather easily corroded through mechanical stirring but it is relatively harder than tachydrate.

## 6- CHEMICAL CHARACTERISTICS

The filtrate and salts were analysed for  $\text{CO}_3$ ,  $\text{HCO}_3$ ,  $\text{SO}_4$ , K, Na, Cl, Ca, and Mg. Consequently salt combinations were calculated according to hypothetical salt combination. The obtained calculations are based on solar evaporation. Recalculations according to the determined observations concerning rates were executed. The recalculations were made and data are tabulated in Table 2 as an example. There are some gaps in the table columns due to lack data (not enough salt was formed). Figure 2 represents an example of the relation between tachylidrite and halite where both patterns show consequent formation of both minerals in a sequence order.

The obtained weights of the different salts in set no. 9 are appreciable, particularly with epsomite, sylvine, and tachylidrite. In some cases epsomite amounts more than 30%, sylvine 5%, and tachylidrite 15% of the total of precipitated salts. The total is about 50% of the formed salts. These figures were not reached in many former trials indicating possibility of applying the author's technique to obtain Mg-salts first, and gained weight second. The previous examples of plotting chemical characteristics will help understanding the saturation limits and consequently anticipate the salts to be formed.

## 7- CONCLUSIONS

The experiments of mixing-brines from El Mex solar salt work proved the following facts:

- 1- Possibility of forming magnesium salts as Epsomite and Tachylidrite has been proven.
- 2- The involved brines in the experiments represent actual valid brines, either from the crystallization ponds of halite or from the stored non-used residual brines. This will offer the chance to get use of these brines to produce valuable salts.
- 3- The applied different combination of brines and rates are definite approach towards defining the maximum and minimum limitations to produce viable economic salts. Some weights were

reaching a yield of almost 30 grams per liter of which  $1/4$  belongs to epsomite and  $1/5$  to tachydrate. This gives a promising probability concerning the expected weight of the product since in one salina millions of cubic meters are available.

- 4- Results of mechanical stirring with two different speeds and times indicates that crystals were disintegrated and/or worn during the process. This will homogenize the variable sizes, grinding them down to more or less uniform finer size. All magnesium salts are affected by the disintegration process, which turns them into easily dissolved smaller prisms and/or cubes.
- 5- The purity of the formed salt types is high which is another economic character leading to lesser amount of washing needed for purifying and upgrading of the salt.
- 6- The results of chemical analysis of the filtrate indicate a lesser amount of Mg, used in Mg-salt formation, where this left-over volume can be directed for washing of naturally produced salt through solar evaporation.

## REFERENCES

1. O.P Raup, brine-mixing: additional mechanism for the formation of basinal evaporite, Amer. Assoc. Petrol. Geologists Bull., v.54, no. 17 2246-2259 (1970).
2. L.T.Briggs Quantitative aspects of evaporite deposition: Michigan Academic, SCI, paper, v.43 115-123, (1957).
3. R.S -Schmalz, Deep-water evaporite deposition: A genetic model. Amer. Assoc. Petrol. Geologists Bull., v.35, no. 4 798-823 (1969).
4. D.E Garrett The geochemistry and origin of potash deposits. In P Symp. On Salt: Northern Ohio Geol. Soc., v. 1 211-222 (1970).