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HYDROGEOCHEMICAL MODEL OF THE SODIUM SULPHATE SALT DEPOSIT WITHIN SHARI SALT MARSH-CENTRAL IRAQ SOURCE AND ORIGIN OF THENARDITE MINERAL

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Abstract

This study covers the examination of groundwater chemical analyses from the Hydrogeological System between Hemrin Anticline and Tigris River, surrounding the area of Shari Salt Marsh. The established Hydrogeochemical Model shed light on brines enrichment and Thenardite precipitation .

The physico-chemical processes that occurred within the groundwater of the 1st, 2nd and 3rd Hydrogeological Units and their interrelationships, could be considered as main direct factor affecting the hydrogeologic regime of brines enrichment and accumulation, followed by the effectiveness of the stream water and sheet runoff water during rainy seasons .

The main hydrogeochemical mechanisms that occurred within the hydrogeologic system are :-

1-Dissolution and leaching mechanisms.

2-Adsorption and ion exchange mechanisms.

3-Mixing and enrichment mechanisms, due to the following processes :

a-Molecular Diffusion Process, (causes a mixing at a contact front between two fluids).

b-Mechanical Dispersion Process, (causes a mixing due to irregular tortuous flow at different velocities).

c-Convection Transport Process, (Solute mixing due to bulk flow of groundwater and velocities).

4-Precipitation of salts hosted in Shari Salt Marsh, included (Thenardite, Halite, Gypsum).

الموديل الهيدروجيوكيميائي لترسبات ملح كبريتات الصوديوم في بحيرة الشاري – وسط العراق

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المستخلص

اعتمد هذا البحث على دراسة التحاليل الكيميائية للمياه الجوفية في النظام الهيدروجيولوجي بين طية حمرين و نهر دجلة ، حيث تشكل مملحة الشاري جزء حيوي من هذا النظام.وقد سلط الموديل الهيدروجيوكيميائي الضوء على اصل و مصادر المحاليل المشبعة بالاملاح لمملحة الشاري و ترسيبها، ومن ضمنها ملح كبريتات الصوديوم(معدن الثنردايت) والذي تكمن فائدته في صناعات الزيوت و الاصماغ و الزجاج .

العمليات الهيدروجيوكيميائية المؤثرة في النظام الهيدروجيولوجي هي :

١-عمليات الاذابة و الخلب : وفيها تتم عملية الاذابة والخلب على مكونات ترسبات النظام الهيدروجيولوجي

٢-عمليات الامدصاص و التبادل الايوني: وتتم بين ايونات المياه ومكونات الطبقات الحاملة للمياه في النظام الهيدروجيولوجي.

3– عمليات المزج والاغناء : وهذه العمليات ناتجة من :

ا- عملية الانتشار الجزيئي : وفيها يتم المزج والاغناء على جبهة تماس بين محلولين،المياه الجوفية ومياه التغذية(المياه المترشحة عن الامطار والجداول والينابيع ومياه نهر دجلة او المياه المتسربة بين الوحدات الهيدوجيولوجية).

ب-عملية التشتت(الانتشار) الميكانيكي : وفيها يتم المزج نتيجة الجريان المتعرج و بسرعات مختلفة المصادر والاتجاه.

ج- عملية النقل بالحمل: وفيها يتم المزج والاغناء بتراكيز الايونات نتيجة حركة المياه الجوفية على طول خط

٤-عمليات الترسيب: تترسب املاح المتبخرات من محلول الشاري المشبع و حسب ظروف الترسيب من ملوحة و درجة حرارة ، ومعدن الثنردايت احد هذه الأملاح .

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يمكن الاستفادة من معطيات البحث من المياه الجوفية في منطقة الدراسة في صناعة المياه المعبئة الخالية من الأملاح في ظل ظروف خطة طوارئ لإدارة أزمة الجفاف المحتملة الوقوع مستقبلا، مستفيدين من الناتج العرضي لعملية تقطير المياه الجوفية والمتمثلة بالحصول على املاح ذات نسبة عالية من كبريتات الصوديوم يمكن نقلها إلى مملحة الشاري لتكون مصدر إضافي لمكونات معدن الثنردايت في المملحة، وبنفس الوقت نضمن حماية للبيئة من خلال عدم تعريض البيئة للنفايات الصناعية الملحية الناتجة من عملية التحلية. وفي حالة الضرورة القصوى لاحتياج المياه الصالحة لشرب الإنسان في محافظة الانبار وفي ظروف استثنائية طارئة بسبب الجفاف ونقص الموارد المائية السطحية يمكن الاستفادة من المياه الجوفية من خلال عملية التحلية مع ضمان خزن النفايات الصناعية بشكل أكداس ذات تراكيز محددة يمكن التعرف على نوعية مكوناتها و تراكيزها لاستخدامها لاحقا اعتمادا على بحوث ودراسات متخصصة بهذا الشأن .

1-INTRODUCTION.

1.1-LOCATION AND PURPOSE :

The **Thenardite** mineral is precipitated in Shari Salt Marsh which is located within the low folded zone to the south of Hemrin Anticline and to the SE of Al-dor city (about 22 km) also to the NE of Samarra city (about 27 km).The purpose of this research is to determine the source and origin of the sodium sulphate salt deposit(Thenardite mineral) within Shari Salt Marsh.

1.2- GEOMORPHOLOGY :

Geomorphologically, the area can be divided into three major units. The first is the mountainous hilly unit represented by the southern limb of Hemrin Anticline .The elevation is ranged between (200-300) meter above sea level, Where the Fatha and Injana Formations are partially exposed. The second unit is the gently slope area , its elevation is ranged between (l00-200) meter(a.s.l.). This unit is formed of alluvial fans deposit and soils. The third unit is the flat plain unit, its elevation ranged between (60-100) meter(a.s.l.). The flat plain is formed of fluvial sheet- runoff sediments and eolian sediments . This area being dissected by ephemeral streams. Some of them poured in Shari Salt Marsh, which is classified as inland sabkha (ephemeral saline lake) formed in topographic depression, with intermittent inflow and high evaporation to inflow ratio .

The soil in the area are originally the product of the pedogenic processes taken place on the followings :

-Sediments of alluvial fans .
-Sheet run off deposits .
-Eolian sediments .
-Sediments of the stratigraphic units of Injana Formation.
-Evaporite deposits of some stratigraphic units of Fatha .Formation .

The area of Shari Salt Marsh is about (110 sq.km), located between the following coordinates ; see fig. (1).

Long. (43°30`00"-44° 30`00")
Lat.(34° 10`00"—35°00`00")

It's elevation ranged between (65-70) meter above sea level .The shape is oval elongated to the north-south direction The maximum length and width is (27 km) and (8 km) respectively . groundwater is discharged by artesian flowing wells or natural seepages

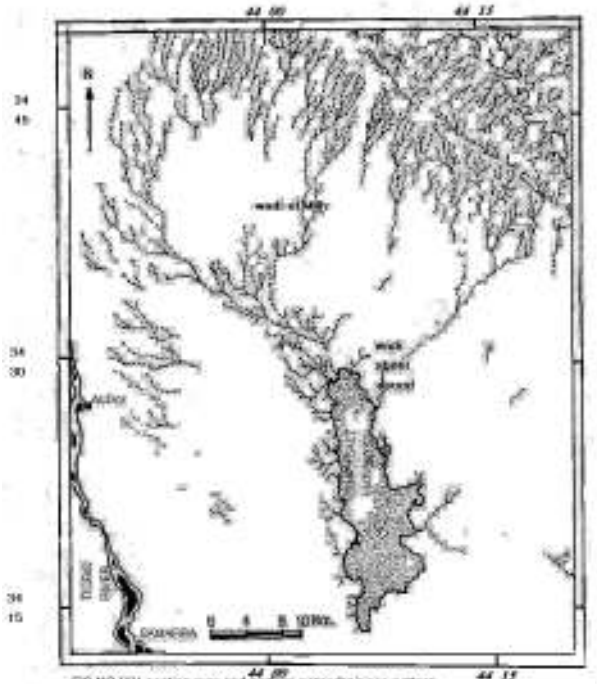

Fig. No-1: Location map and surface water drainage pattern

The Salt Marsh is seasonally replenished with surface water by ephemeralstreams and wash run off during wet season . The water depth in the salt marsh during the wet season exceeds onemeter in some places and becomes dry in the hot season except some area where the

3- CLIMATE CONDITION:

The information about the climatologic factors are derived from meteorological stations in Samarra and Baiji during long term period (1978-1987), ten years before the hydrogeochemical study.

RAINFALL:

The long term mean monthly rainfall recorded in Baiji and Samarra stations, range between (0.0- 33.73)mm and nbetween (0.0– 25.81)mm, respectively, see table (1).The rainfall might occur from October till June. The amount of rainy days are about (40) days with (10) days of thunder storms .

The rainfall intensity varies between (0.1-0.7) mm/min. for duration of about (60) minutes. The total amount of rainfall for each case varies from (5-20)mm. From the water balance calculation as reported in (Al-Forat Center for Studies and Design, Volume-1,1988); the mean annual rainfall on the area extends between Hemrin Anticline and the Tigris river is (170)mm.

EVAPORATION:

The mean monthly evaporation from free surface recorded in Baiji and Samarra stations range between (47.05-412.49)mm. and between (62.5-520.05) mm ,respectively, see table No.(1) The amount of evaporation that occurs from March to mid October is more exceeds than the amount of rainfall for the same period ,as shown in table No.(1) .

TEMPERATURE :

The mean monthly temperature recorded in Baiji and Samarra stations range between (9.08- 35.17)^{o}C, and between (9.43-35.4) ^{o}C ,respectively, see Table (1).

RELATIVE HUMIDITY :

The mean monthly relative humidity recorded in Baiji and Samarra stations range between (26.5-80.6) % and between (26.5-77.4) %, respectively, as listed in table No.(1).

WIND SPEED :

The mean monthly wind speed recoded in Baiji and Samarra stations range between (1.075-3.7)m/sec. and between(2.44- 4.65) m/sec, respectively. Wind speed may active and creates sand storm especially in dry season .

Finally, the meteorological factors indicate that the investigated area characterized by semi arid – arid climate .

1.4- GEOLOGY :

The regional geological section that exposed in the studied area is consist of the followings;

Age	Formation	Description
Quaternary	Recent deposits	Sabkha deposit.
		Eolian deposit.
		Gypsiferous soils and Gypcrete.
	Pleistocene deposits	Gravely Gypsiferous Clay.
		Sandy Gravel.
Pliocene	Bai Hasan Fn.	Conglomerates.
	Mukdadia Fn.	Peb.Sst & Cst.
Miocene	Injana Fn.	Sst. & Cst.
	Fatha Fn.	Gypsum/Anhydrite/ Halite & Marl.

CLIMATOLOGIC FACTORS	STATION	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
RAINFALL (mm)	Baiji	32.6	28.7	27.4	15.6	7.3	0.0	0.0	0.0	0.6	12.3	29.8	33.7
	Samarra	25.8	14.2	24.2	10.3	1.5	0.0	0.0	0.0	0.2	5.9	22.1	22.8
EVAPORATION (mm)	Baiji	49.2	74.9	124	193	296	368	412	386	279	182	84.0	47.5
	Samarra	67.4	103	148	256	376	478	529	496	380	243	118	62.5
TEMPERATURE (°C)	Baiji	9.0	11.0	14.7	21.1	27.1	32.1	35.1	34.0	30.6	23.3	15.1	9.8
	Samarra	9.4	11.0	14.9	22.1	28.1	32.8	35.4	34.3	31.4	23.7	16.3	10.5
RELATIVE HUMIDITY (%)	Baiji	78.9	70.9	63.1	50.5	37.8	29.1	26.5	29.6	33.6	48.9	67.1	80.6
	Samarra	76.3	64.3	59.6	46.6	36.5	27.2	26.5	29.0	29.0	44.4	64.0	77.4
WIND SPEED (m / sec)	Baiji	1.07	2.67	2.20	2.53	2.82	3.62	3.71	3.72	1.99	1.70	1.53	1.32
	Samarra	2.82	3.18	3.30	3.74	3.94	4.34	4.28	4.56	3.24	2.90	2.68	2.44

TABLE (1). Mean monthly rainfall, evaporation, temperature, relative humidity and wind speed in Baiji and Samarra station

More regional geological informations was explained in details by (Hamza ,et.al, 1999). The Thenardite mineral precipitated in topographic depression named Shari salt marsh (inland sabkha environment), which is located within the depositional basin of the Quaternary sediment ,where, these sediments originated to the materials of the geologic formations exposed in the southern limb of Hemrin Anticline formed after young Alpine Orogeny by water and wind activities (weathering and erosion) .These are :

-The sandy gravel originated mainly to Bai Hasan Fn. and partially to Mukdadia Fn.
- The sandy gravely Clay originated to Mukdadia Fn. and Injana Fn. ,partially to the Bai Hasan Fn.
- Gypsiferous soil and silty sandy Clay originated mainly to Fatha and Injana Formations, partially to the Mukdadia Fn. and to the re-worked materials of them .

The origin of Gypsum in soil is mainly of ;
1.Surface run off (ephemeral streams) as suspended , dissolved and bed loads.
2.The ephemeral sheet-run off over the exposed gypsum of the Fatha Formation and the weathered gypsum as suspended and dissolved loads.
- Gypcrete is commonly seen overlying the sandy gravel surface. It's thickness is less than one meter but increase locally to more than three meters . The Gypcrete according to Hassan and Jawadi , 1976, classified as ;
1.a fibrous type which is more common.
2.a spongy massive type found as lenses within the first type.
3.a powdery type which probably reworked .

Gypcrete originated mainly to Fatha Formation and partially to Injana Formation and their weathered reworked materials which is transported as suspended and dissolved loads as well as bed loads by stream and sheet flush run off.

The deposits are thick reddish sediments of rhythmic nature (thin bands). The bands are formed of red and dark brown mud passing upwards into salt crust then to eolian sediments.

Shari Marsh Deposits;

The sedimentary facies and environments in Shari Playa were explained by (Alrawi et.al,1998).

These deposits exceed 20 meters in thickness and may overly the sandy Gravel deposit (Jasim,1981). The brines within shari salt marsh originated to the Hydro-phiso-chemical processes occurred on the sediments by surface and groundwater activities, where the research treats this phenomena .

The salts which were sampled at the western side of Marsh analyzed by X-ray diffraction show the predominance of Halite, Thenardite and Gypsum with some traces of Calcite,(Al-Badri,et.al,1990).Finally, the mineralogy of evaporates minerals studied by (Jasim,et.al,1999).

1.5 HYDROGELOGIC CONDITION:

The hydrogeologic system within the area of investigation is defined by the regional depositional basin of Upper Miocene–Quaternary Age.The basin is composed of Injana Formation, Mukdadia , Bai Hasan Formations and Quaternary sediments. According to the properties of the formations sediments, the hydrogeologic system divided into:-
1-First Hydrogeologic Unit(water bearing horizons of Quaternary and may be of Bai Hasan deposits):
These water bearing horizons are

mainly composed of sandy Gravel and/or conglomerates. The first hydrogeologic unit is characterized by unconfined-semi unconfined conditions with local bank storage condition exists along side left bank of Tigris river down stream of Al-Dor City, and of unconfined perched condition to the east and south direction of Shari salt marsh.

2-Second Hydrogeologic Unit(water bearing horizons of Injana and Mukdadia deposits):

These horizons are mainly composed of sandstones and pebbly sandstones . The second hydrogeologic unit is characterized by semi-confined to confined conditions.

3-Third Hydrogeologic Unit(water bearing horizons of Fatha deposits):

These horizons are mainly composed of fractured gypsum. This unit is characterized by semi-confined to confined condition.

The general pattern of groundwater flow in the area restricted between Tigris river and Hemrin anticline is to the south west direction, slightly deflected to the south (Shari Salt Marsh direction), recharged from rain water at the SW flank of Hemrin anticline. Another pattern of flow exists from Tigris river downstream of Al-dor city. The discharge zones are Tigris river (upstream of Al-dor city) and Shari Salt Marsh, see Fig. No.(2).

The static water levels reach the maximum rise during the water surplus period (Jan, Feb, Mar, and Apr.), while the maximum declines are occurred during the water deficit period (Jun.-Oct.) .The mean of the static water level fluctuation is (0.7)meter ranged between (0.1-4.3) meter in the First Hydrogeologic Unit, while the mean value of static water level fluctuation is (1.56)meter ,ranged between (0.2-4.6) meter in the Second Hydrogeologic Unit .

The statistical interpretation on the specific capacities values, show that the hydrogeologic system is influenced by large dewatering mechanisms, on the other hand the productivity of the First Hydrogeologic Unit is more than the productivity of the Second Hydrogeologic Unit .

Hydrogeologically, the area of investigation is divided into three districts based on the recharge and discharge boundaries, groundwater divide and flow direction. These are ;-

-District-1:Al-Fatha—Al-Alam District .
-District-2:Hemrin –Shari Salt Marsh District .
-District-3:Al-Dor—Samarra—Shari Salt Marsh District .

The groundwater flow through recharge area is (1446000) cubic meter/year,(27115000) cubic meter/ year,(2628000) cubic meter / year ,in the Districts D-1, D-2 and D-3, respectively.

The groundwater flow through discharge area is 2446000 cubic meter / year (towards Tigris river), 6515000 cubic meter/year and 487000 cubic meter/year (towards Shari marsh) , from the Districts D-1,D-2 and D-3, respectively .

The groundwater flux (m/day) through the districts D-1 ,D-2 and D-3 ranged between (0.0018-0.0077) m/day (0.0077-0.049) m/day and (0.0025-0.0063)m/day ,respectively .

The groundwater pore velocity (m/day) through the districts D-1 ,D-2 and D-3 ranged between (3.01-12.90) m/day, (5.93-37.76) m/day and (0.903-2.259) m/day, respectively .

More details about the hydrogeologic conditions are reported in (Ahmed etal., 1990) .

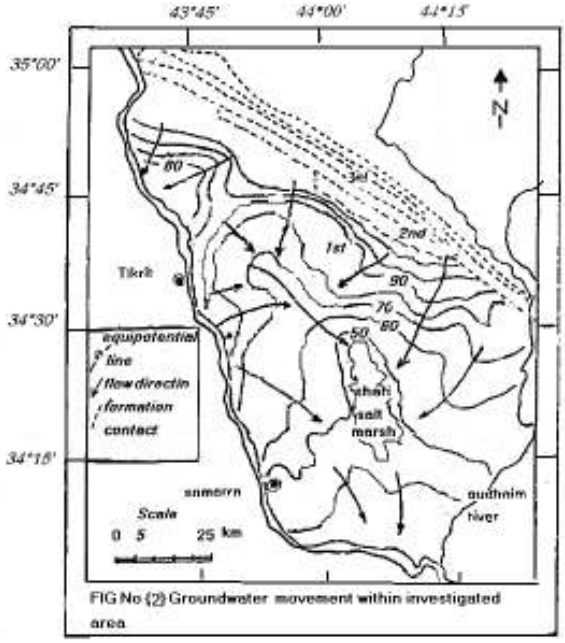

Fig No-3: Groundwater movement within investigated area

1.6-HYDROCHEMICAL CHARACTERISTICS :

The physical and bio-chemical monitoring system which were performed on the groundwater of the investigated area (e.g, groundwater and air temperatures, color, turbidity, and density as well as Biochemical Oxygen Demand) indicate that the hydrogeologic system is influenced by climatic condition and man activities as well as biologic activities (existence of an aerobic bacteria).

The reduction-oxidation potential and BOD_{20} values indicate that the groundwater may contaminated by another source of water (such as connate oil field water). Low percent of Hydrogen Sulphide concentration was observed in the groundwater . The origin of Hydrogen Sulphide may be from the leakage mechanisms through fractured zones or as a result of reduction-oxidation reaction in the presence of anaerobic bacteria. .

The groundwater is classified as neutral to slightly alkaline water, slightly brackish to brackish water except for the water of spring No. (S-1) which is of salty water.The distribution map of Total Dissolved Solids (TDS), shows that the TDS concentrations increase with the direction of groundwater flow .

The groundwater polluted by Nitrate ion ,especially, in the area of intensive agricultural activities, where the existence of nitrate ion concentration in the groundwater originated to the artificial pollution (fertilizations and putrefaction of organic materials).The different patterns of major ions (K ,Na ,Ca ,Mg ,Cl, SO_4,HCO_3 and CO_3) fluctuations indicate that the hydrogeologic system are of hydrodynamic condition influenced by climatic condition, where, mthese constituents originated to different sources as interpertated in the hydrogeochemical processes in another item of this study .

The groundwater is hydrochemically classified into two groups ,these are :-

1-Sulphate group of:
Ca –Sulphate family .
Na-Sulphate family .
Mg-Sulphate family .
2-Chloride group of:
Na-Chloride family .

The hydrochemical ratios (rNa/rCl, rSO_4/rCl) ,show that the groundwater is of meteoric origin except for the water of spring No. S-1 is of oil field water origin .

More details about the hydrochemical characteristics of the groundwater within area study were reported in (Ahmed etal.,1990) .

1.7-SEDIMENTS IN THE HYDROGEOLOGIC SYSTEM:

Based on the chemical composition and the degree of alteration of the minerals making up the rocks, the

sediments in the hydrogeologic system are classified as :-

RESISTATE SEDIMENTS :

A rock composed principally of residual minerals not chemically altered by the weathering of the parent rock (e.g. sandstones and conglomerates).

The Resistates in the hydrogeologic system is represented by the water bearing horizons of Injana, Mukdadia, Bai Hasan and/or Quaternary sediments . Some of these sediments are consolidated and contain cementing materials deposited on the grains surfaces and within the porous among grains. This cementing material is usually deposited from water that has passed through the rock at some past time and can be re-dissolved like SiO_2 ,$CaCO_3$ and secondary Gypsum. In general the resistate sediments in the hydrogeologic system are permeable to water and may easily receive and transmit solutes acquired by water from other type of rocks.

HYDROLYZATE SEDIMENTS :-

A rocks composed principally of relatively insoluble minerals produced during the weathering of the parent rocks (e.g.clays and claystones). The hydrolyzate sediments in the hydrogeological system is represented by the aquitards and aquicludes of Injana,Mukdadia and Quaternary sediments .In the hydrolyzate sediments the particles normally are very small and the circulation of water through the material is greatly impaired and include a large proportion of clay minerals with large cation exchange capacity,where, these sediments are porous but do not transmit water because of small openings and poorly connected .

EVAPORITES SEDIMENTS: -

A rocks produced as a result of evaporation of the water in which they were dissolved soluble minerals (e.g. Gypsum,Halite, Anhydrite and Thenardite). The highly soluble nature of evaporates causes high dissolved-solids concentrations. Gypsum and Anhydrite are the least soluble of the rocks considered as evaporite. Gypsum can transmit water through solution channels as in (Limestone & Dolomite) does . The composition of natural brines is usually closely related to the evaporite deposits . The evaporates in the hydrogeological system is represented by Fatha Formation which is located in the recharge zone .

2-INFLUENCE OF RAIN & SURFACE WATER ON THE CHEMICAL COMPOSITION OF SHARI SALT SOLUTION :

The processes of rocks weathering are influenced by temperature , amount and distribution of rainfall .Certain of the major ionic constituents of natural water are influenced more strongly than others by climatic effects.Climate characterized by alternating wet and dry seasons may favour weathering reactions that produce larger amount of soluble inorganic matter at some seasons of the year. During the dry season, the water table drops to a lower level and the high temperature causes the evaporation of soil moisture then the water at lower static water level rises up by capillary action from the zone of saturation towards aeration zone. The continuous evaporation causes increasing of ions concentrations and leads to precipitate salt again .

During the wet season, the effectiveness of water as a solvent in weathering process of rocks is also increased by the ability of this cohesive liquid to wet mineral surfaces and penetrate into small opening .

In the process of weathering, the exposed surfaces of these rocks may

develop noticeable efflorescence of salts by evaporation of water between rainy periods . Heavy rainfalls wash away these deposits and at the same time the layer of leach sediment at the surface also may be stripped away .

The texture of the weathered residum varies with:-

- the nature of the parent rocks .
- the dominant weathering process .
- the maturity of the end product .

In the investigated area which is classified as semi arid to arid region, the soils are usually not fully leached, and the surplus solutes may accumulate near the surface. The insoluble detritus is mechanically removed by water running off the exposed rock surfaces, then, fresh surfaces containing soluble and insoluble materials are exposed for future weathering .

The rate of water movement is rapid in the vallies during run off and/or flushed water after rain period. The direct run off has a considerably higher dissolved solids content than the original rain.The base flow has greater dissolved solids content. The solute concentration of stream water at high flow rates may be dilute. The reactions among water, solutes and suspended matter are significant. Thecation-exchange capacity of stream sediments can be large and the ions carried on exchange positions of suspended particles could be a significant part of the total load.

In the hydrogeologic system, the Sulphate occurrences are in evaporite sediments. Calcium Sulphate as Gypsum ($Ca\ SO_4.2H_2O$),or Anhydrite ($CaSO_4$), Sodium Chloride as (Halite).The amount of Sulphate, Chloride, Sodium and Calcium brought to the semi-closed basin by flush and stream runoff after leaching process of Ca, SO_4 from the parent rock (Gypsum) & it's weathered result (Gypcrete and Gypsiferous soils), and leaching process of Na, Cl from Halite content of Fatha Formation through out the flowing spring (Ain Al-Milh) under high pressure in deep seated strata. The spring Ain Al-milh is located closed to Hemrin border and flow out around the absolute elevation of (200) meter a.s.l.

Spring salty water of sodium chloride type drain to ephemeral stream passed over the sediments of the investigated area, some of this water in rainy periods is directly mixed with rain water forming surface run off, poured in Shari Salt Marsh .In dry season the spring water percolated to the water bearing horizons of the hydrogeologic system .

The influence of surface water on the hydrogeologic system is explained in fig-3, which shows the general hydrological interrelationship network within system .

3-HYDROGEOCHEMICAL PROCESSES:

The water chemical quality represented by major ions (K,Na,Ca,Mg,Cl,SO_4,HCO_3 and CO_3)in the groundwater of the hydrogeologic system originated to different hydrogeochemical mechanisms. These mechanisms are :-

1-Dissolution mechanism on the minerals composition of the sediments .
2-Adsorption and ion exchange mechanism .
3-Leachate mechanism on the soils and sediments .
4-Mixing mechanism from another sources of water.

3.1- DISSOLUTION MECHANISM :

The source of most dissolved ions in the groundwater of the studied area is the minerals assemblage in rocks near the land surface .The purity and crystal size of minerals,the rock textures & porosity,

the regional structure, the degree of fissuring and the length of previous exposure time, might influence the composition of water passing over and through the rocks.

The dissolution mechanism that occurred between water and sediments within the studied area includes the reversible solution and deposition reactions like:

NaCl (solid crystalline material)---→Na + Cl

$CaSO_4$ (solid crystalline material) - -→ Ca + SO_4

Reaction among aqueous species or complexes :

Ca +SO_4----→ $CaSO_4$ (aq.).

The chemical equation representing the dissolution of gypsum inthe recharge area of exposed formation is :

$CaSO_4.2H_2O = Ca + SO_4 + 2H_2O$

Where, the infiltrated water to the aquifer sediments of 1st and 2nd hydrogeologic units can be simultaneously in equilibrium with two or more solids having a common ion such as:

$CaSO_4 + HCO_3 = CaCO_3 + H + SO_4$

3.2-ADSORPTION & ION EXCHANGE MECHANISM:

Cation exchange equilibria have a considerable influence on the sodium and calcium concentrations in the most of the groundwater within the studied area. The exchangeable cations on mineral surfaces in aquifer sediments of 1st and 2nd hydrogeologic units provide a major reservoir of ions added to the

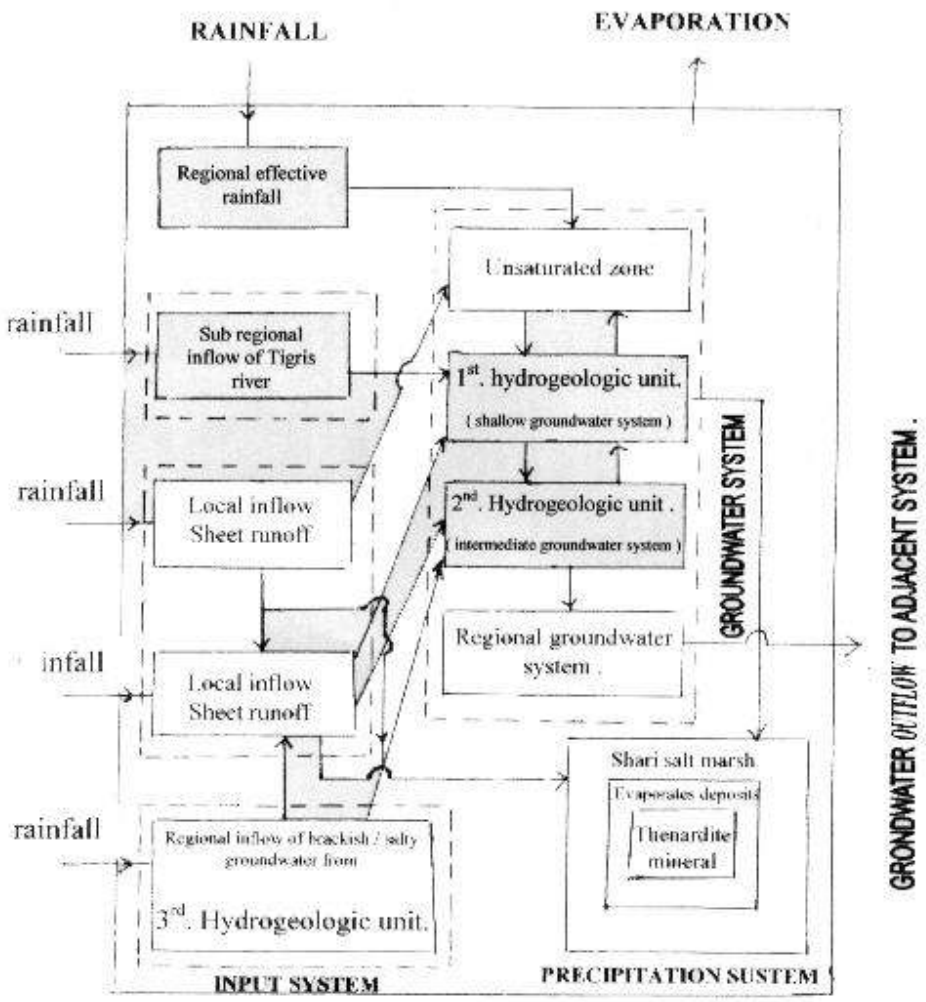

Fig -4: General Hydrogeological interrelation ship network for THENRDITE Precipitation

composition of the water coming in contact with. These reflects the results of exchanges between water and solid surfaces The groundwater contact with sediments includes clays, a cation composition altered by ion exchange reactions as explained in the following reaction;

$$Na_2X + Ca \longrightarrow CaX + 2Na$$

sediment water sediment water

3.3- LEACHATE MECHANISM :

The sources of Sulphate, Calcium, Sodium, Chloride, Magnesium and Carbonate in the groundwater of the studied area resulted by the leaching processes occurred on the exposed evaporites sediments (Gypsum, Halite of Fatha Formation, Gypsiferous soils and Gypcrete), while in resistate sediments the above mentioned ions present in unaltered mineral grains as an impurity in the cement materials. The soluble salts go into the groundwater of the studied are readily & usually are rather quickly removed from coarse grain sediment after environmental changes, where Leaching process depends on the rate of groundwater velocity and reaction rate. The rate of water movement is slow in groundwater and soil environment, which gives a considerable time for completion slow reactions, where, the water velocity and reaction rates affects on the concentration of ions in solution quantitavely and qualitatively .

3.4- MIXING MECHANISMS :

The mixing mechanism rules of groundwater within the studied area explained by three solute transport processes. The physico-chemic processes that contribute to transport are :

-Molecular Diffusion Process .
-Mechanical Dispersion Process.
-Convection Transport Process .

The molecular diffusion is a physical process depends upon the kinetics properties of the fluid molecules. This process causes a mixing at a contact front between two fluids .

The mechanical dispersion is mixing of contaminants in flowing groundwater occurs mainly because of irregular tortuous flow within which the water moves at different velocities,(Gupta, A,D and Poojith, N,O,D , 1982) .

The convection transport refers to solute transport due to the average bulk flow of the groundwater and the mean velocities are usually computed from Darcy"s law divided by the effective porosity .

3.4.1-MIXING MECHANISM DUE TO DIFFUSION PROCESS:

Primatively, the replenishment of the aquifer by rain water and surface water (represented by Tigris river water) affects on major ions concentrations (dilution case), but these waters have ability to dissolution and leachate the ions from their minerals caused enrichment in ions concentrations of groundwater. On the other hand the chemical composition of rain water and river water may add low percent concentrations of these constituents to the groundwater .

The mixing of rain, irrigation and river water is occurred after leaching sediments and soils during infiltrated processing till reaching the groundwater level, then dispersed within groundwater. The solutes may accumulate in soil and groundwater of hydrogeologic basin within interior drainage, where, the solute can not escape or mixed, because of restricted geologic boundaries making perched or pocket saline water in closed drainage basin .

Mixing may occur by membrane effects when two aqueous solutions of different solute concentrations are separated by a semi-permeable memb-

rane. The water molecules tend to pass through the membrane into the more concentrated solution by osmosis pressure .

Springs waters namely (S-1 , S-2 & S-3) affect on the quantity and the quality of the groundwater, especially, the water come out from springs are flow on and percolated through the covered sediments of First Hydrogeologic Unit .

The discharge of spring water that replenished the hydrogeologic system is of about (332 m^3/day), while the quantity of total dissolved solids that enter the hydrogeologic system is of about (6.87ton/day), where, the percentage of NaCl salt as calculated from hypothetical salt combination is (87%) from the total dissolved salts .

In localities near Al-Milh valley ,where, the water of spring No.(S-1) has entered the aquifers , the advancing salt –water front commonly carries higher proportions of Cl to SO_4 and Na to Ca than it"s characteristic of groundwater . The effectiveness of spring water is obviously observed in the water points, located in the vicinity of spring, more detailed was discussed in Ahmed ,et.al, 1990 .

Finally ,the mixing of groundwater of the Fatha Formation may directly occured by under ground leakage through the fractures along side Hemrin flank to the hydrogeologic system.

3.4.2-MIXING MECHANISM DUE TO MECHANICAl DISPERSION PROCESS :

Geologic and hydrogeologic data indicated that permeable sandy Gravel or Conglomerates deposits of limited areal extent existed between shallow depths which cuts into interbedded sandstones and claystones of Mukdadia and Injana Formations. It is reasoned that if there is appreciable tortuous flow of groundwater into the buried gravel and sand deposits. The water in the hydrogeologic units would be a mixture of water. This suggestion is proved by plotting of the chemical constituents of the groundwater on the tri-linear diagram as shown in fig.(4) for the representative water points of First, Second Hydrogeologic Units and Spring water . This plotting show that the groundwater is mixed and of same source except for water of Spring No.1 is of another origin (same as of oil field water)

3.4.3- MIXING MECHANISM DUE TO CONVECTION TRANSPORT PROCESS :

The distribution maps of chloride, sulphate and TDS, indicate increasing of their concentrations towards shari salt marsh and surrounding area which represents the discharge zone of the hydrogeologic basin. These phenomena coincide with the groundwater movement, this means that the groundwater enriched in their concentrations with the flow direction.

The chloride concentration related to NaCl, indirectly, reflects sodium concentration in the groundwater. The sulphate concentration related to $CaSO_4$, indirectly reflects calcium concentration in the groundwater. Total Dissolved Solids concentration represents all cations and anions concentration of the groundwater.

Depend on the abovementioned facts; Auther explains the enrichment of groundwater components that affects on the accumulation of ions composed Sodium Sulphate solution as shown in table(2).The data in table shows positive correlation between groundwater pore velocity and the enrichment of chemical constituents. .

The distribution maps of Cl, SO_4 and TDS (Figs. No.5, 6and 7) show that the water of spring No. S-1 makes deterioration case on the groundwater,

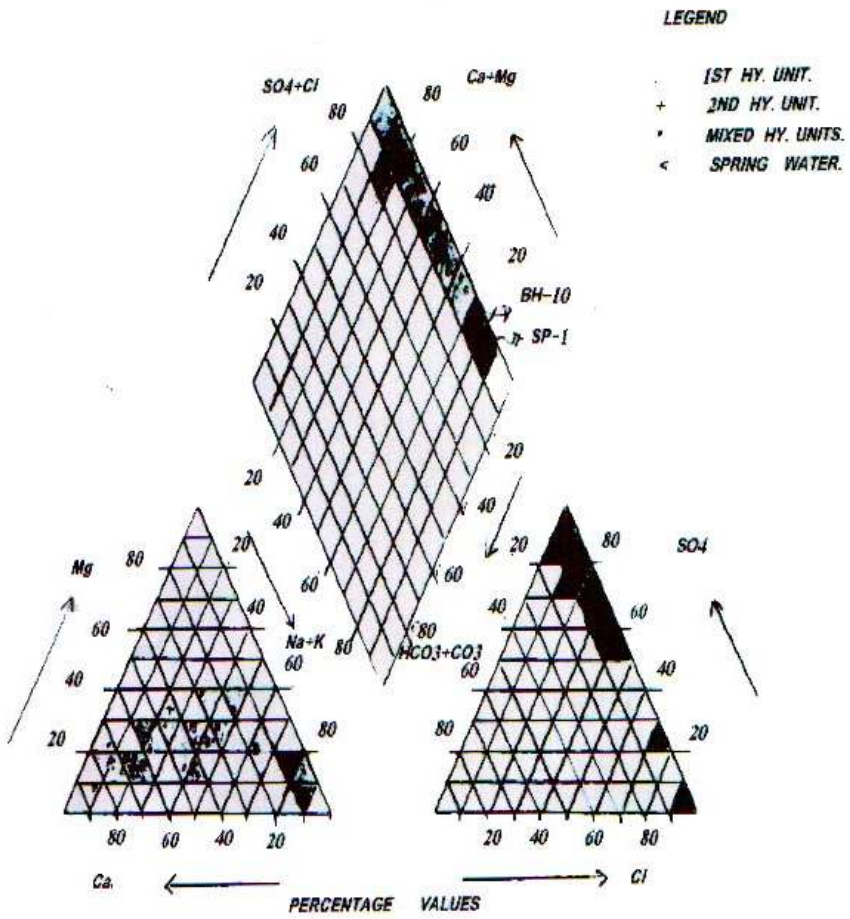

Fig -4: Chemical Water analyses plptted on PIPER DIAGRAM for the groundwater types of 1st 2nd mixed Hydrogeologic Units and spring

where this spring adds (1.83-3.11) ton/day for sodium, (3.11-5.23) ton/day for sulphate and (5.3-9.01) ton/day for TDS. In the system, the deterioration that occurred on the groundwater surrounding spring No.S-1 is 25 meq/l, 13 meq/l and 500 mg/l for SO4 ,Cl and TDS, respectively . The data in table (2), show that the concentrations of SO_4, Cl and TDS in District No. 1 ,initiated by 37 meq/l,15 meq/l and 2000 mg/l, respectively, while the same components initiated by 12 meq/l, 2meq/l and 1500 mg/l, respectively, in the District No.2 ,where the recharge zone of both districts is the same .

Table-2: Groundwater Pore Velosity and SO_4, CL, TDS concentration

Dist-rict	*Groundwater PoreVelocity m/day*	*SO4 ion meq/l*			*Cl ion meq/l*			*TDS mg/l*		
		Fr.	*To*	*En.*	*Fr.*	*To*	*En.*	*Fr.*	*To*	*Enrich-ment*
D-1	*3.01-12.9*	*37*	*80*	*43*	*15*	*50*	*35*	*2000*	*8000*	*6000*
D-2	*5.23-37.7*	*12*	*88*	*76*	*2*	*51*	*49*	*1500*	*8000*	*6500*
D-3	*0.9-2.2*	*32*	*70*	*38*	*2*	*50*	*48*	*2000*	*7500*	*5500*

4-HYDROGEOCHEMICAL FACIES AND SALTS :

The groundwater within the hydrogeological system classified as Sulphate water group . This group includes Calcium- Sulphate and Sodium Sulphate families. Calcium-Sulphate family of Na-Mg-Ca ; SO_4 type represent the area of recharge and perched zones ,while the Mg-Na-Ca ; Cl-SO_4 type represents the area of transition zone .

Sodium-Sulphate family of Mg-Ca-Na ; Cl-SO_4 or Ca-Mg-Na ;Cl-SO_4 types represent the area of discharge zone (area surrounding Shari Salt Marsh). Here, good phenomenon supported us to solve the faced problem for the salt genesis that occurred in the Shari Salt Marsh. The salts combination that are calculated from the chemical analyses of groundwater samples show the presence of Na_2SO_4 , $CaSO_4$,$MgSO_4$ salts and the absence of $CaCl_2$,which indicates the meteoric origin and the groundwater saturated by sulphate ions .

The percents of Na_2SO_4 , $CaSO_4$ and $MgSO_4$ in the groundwater are ranged between (0.0-30.3) meq% , (8.38-71.6)meq% and (6.02-39.93) meq% , respectively . While the percents of NaCl are ranged between (5.84-48.36) meq%. More details in Ahmed, et.al, 1990.

The plotting data of [(Na+K)-Cl] meq% upon (SO_4) meq% in SULIN GRAPH (Collins, 1975) see fig.(8), shows that 82% of groundwater points in the First Hydrogeological Unit of the investigated area plotted in the zone of Na2SO4 salt .

This result gives good idea for the existence of $NaSO_4$ in the Shari Salt Marsh, where the hydrogeologic indicators refers that the groundwater seeps and drained to the salt pan.

5-HYDROGEOCHEMICAL PROCESSES WITHIN SHARI SALT MARSH :

Shari Salt Marsh is inland closed basin have short lives in a geologic sense, and has important salts and saline accumulations contain small exposures of evaporite sediments present in it's surrounding edges and accumulation of Glaubrite colloidal salts within it's boggy materials .

Closed basin of Shari becomes saline owing to evaporation of water and continued influx of solutes .In hot season the groundwater in the bog sediments of Shari basin is confined all reactants and products in an inert closed basin which allows the reactions to proceed in mineralization, till solution reaches the degree of saturation for each salt to precipitate . In rainy season the groundwater mixed with surface runoff water, where, the movement of reactants and products in and out is unrestricted and some variables may changed slowly. The system may not attain a true saturation. The saturation may occur lately.

5.1- SHARI SOLUTION :

Shari solution is completely uniform mixtures in which each dissolved particles is surrounded by solvent molecules (water molecules) and has no direct contact with other like particles except as permitted by migration electrical charge, or may be neutral .

SODIUM: Sodium is the most abundant member of the alkali-metal group. When Na has been brought into solution, it tends to remain in that status. Because of the high Na concentration that can be reached before any precipitate is formed, the Na content of Shari solution may reach high limit concentration of brines in closed system.

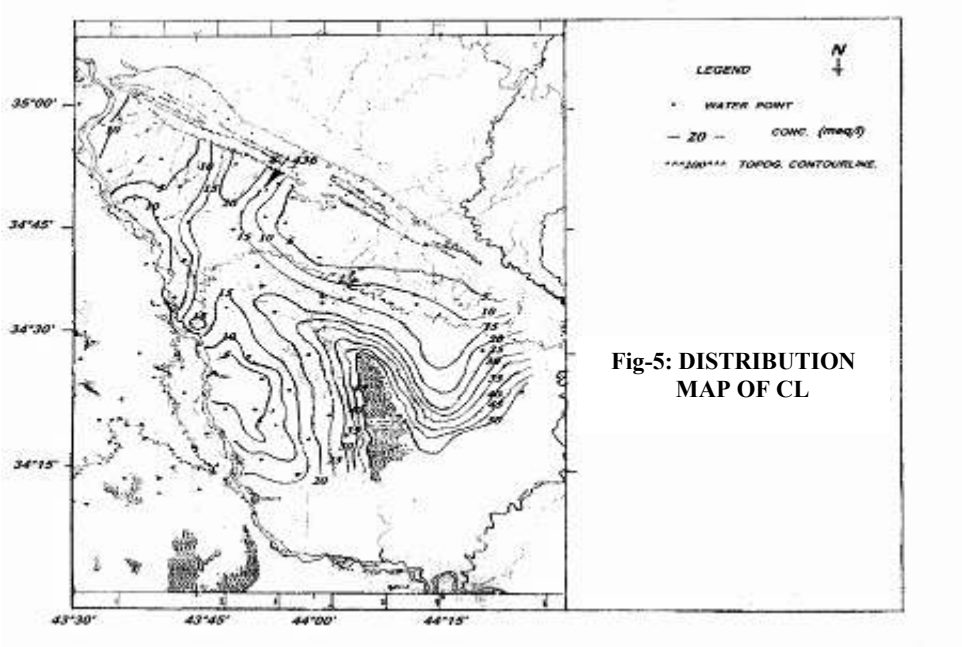

Fig-5: DISTRIBUTION MAP OF CL

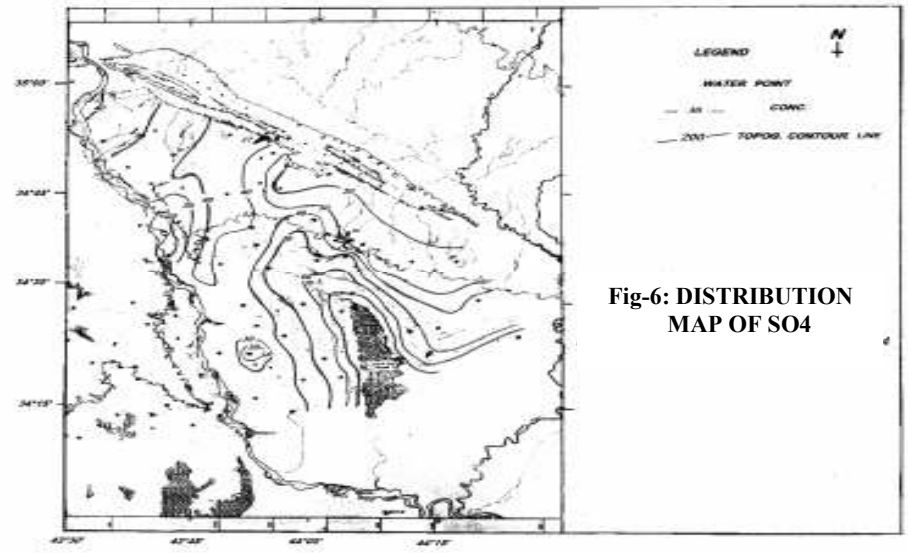

Fig-6: DISTRIBUTION MAP OF SO4

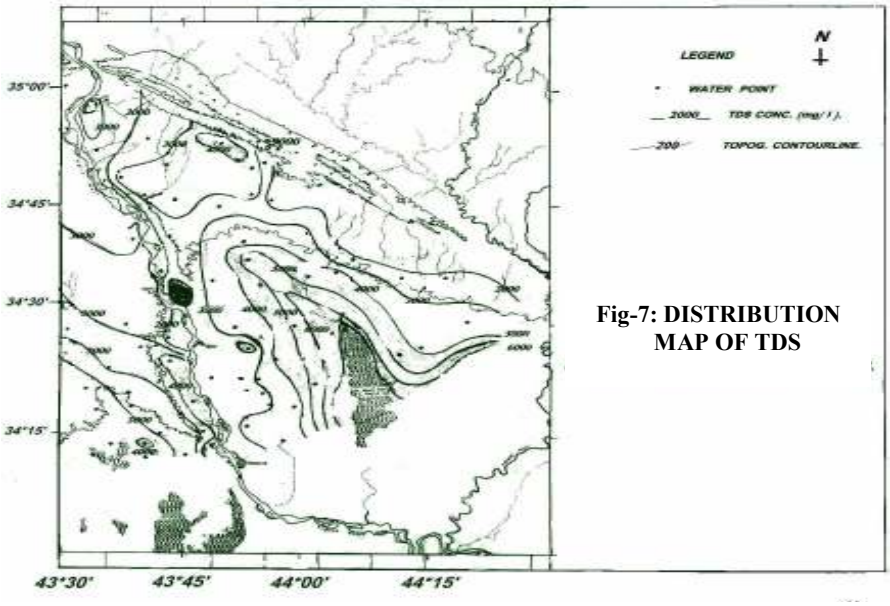

Fig-7: DISTRIBUTION MAP OF TDS

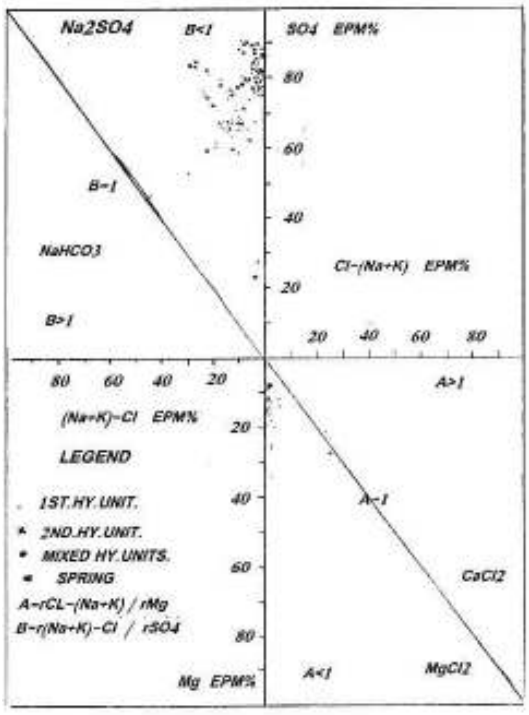

Fig-8:Genetic Classification of the groundwater on SULIN GRAPH

CHLORIDE: The chemical behaviors of chloride is not significantly enter into Redox potential, is not adsorbed on mineral surface, plays few vital biochemical rules and can form complexes with a few of the positively charged ionic species of natural water, such complexes are weak .Hence, and because of the abovementioned behaviors, the chloride may reach high limit concentration of brines in closed system such as Shari Salt Marsh, resulting by leaching then enrichment.
CALCIUM: Calcium ions are relatively large (ionic radius is 0.99 A^o). The charged field around the ion is therefore not as intense as those of smaller divalent ions .Calcium ions do not have a strongly retained shell of oriented water molecules surrounding them in solution . The usual dissolved form can be simply represented as the ion Ca^{++} .

In solutions where sulphate concentrat-ion exceeds 1000 mg/l more than half of calcium could be present in the form of $CaSO_4$ ion pair ($CaSO_4$ aq.), (Collins, 1975). In a solution containing 2500 mg/l of chloride ion and about 1500 mg/l of sodium ion , the equilibrium concentration of calcium ion would be near 700 mg/l ,(Hem,1970) .
SULPHATE: Sulphate is a complex ion, but displays a strong tendency to form farther complex species .The most important of these in natural water chemistry are associations of the type $NaSO_4$ and $CaSO_4$ ion pairs. At 25^{o}C, the sulphate concentration would be about 1480 mg/l ,in the absence of Na ion and Cl ion , and in the presence of 2500 mg/l of Na +Cl ,the sulphate would be 1800 mg/l . Magnesium and Sodium Sulphates are highly soluble, and water containing large amounts of these components with little Calcium ion concentration can attain sulphate concentration in excess of 100000 mg/l, (Hem,1970) .

5.2- EVAPORATION AND SATURATION:

The surface of a body of water in contact with the atmosphere at standard pressure and temperature is rigidly maintained by inter molecular forces, as shown by the surface tension of water, which is 72.2 dynes/cm at 25^{o}C, a value higher than that of most liquids (Hillel,1990).

Water molecules are able to pass through this surface. This process tends to produce mutual saturation near the interface. Rates of water evaporation are functions of the characteristics of the system .These are:-
1-The total area of interface.
2-The rate of molecules which transported away from the interface .

The continuity of evaporation from the water interface needs continuous heating reaches 590 Calorie /gm of water at 15^{o}C . In closed basins, water can escaped only by evaporation, the residual water can be expected to change

in concentrations of chemical composition, and the particles unite form aggregates that will settle out of the solvent by gravity as a result of reaching saturation limit for solution in the marsh.

These particles is the products of chemical reactions ,which are controlled by temperature and the degree of saturation for each constituents .The wide range of particles sizes considered as a colloidal diameter ($5A^o$-$2000A^o$) may retained in suspension,(Hem,1970) .

5.3- SALTS PRECIPITATION AND CONDITIONS :

The saline deposits are formed by the precipitation of salts from concentrated solutions or brines. Because concentration is brought about by evaporation, the saline deposits have been termed evaporites. The common order of evaporite depositions in a basin have complex solution such as Shari Salt Marsh; is Gypsum-Anhydrite (Calcium Sulphate), followed by Magnesium Sulphate salt , followed by Sodium Sulphate salt, then by Halite (Sodium Chloride salt), finally ,by Potash salt .

Gypsum will begin to precipitate at 30^oC and at a salinity 3.35 times that of normal sea water,(TDS=115000 mg/l), (Hem,1970).

When the solution becomes 4.8 times as saline as normal sea water (water volume is reduced to about 1/5 of the initial volume by evaporation TDS=170000 mg/l), direct precipitation ,of Anhydrite is taken place at 34^oC of solution temperature .Hence, whether gypsum and anhydrite will form depends on both temperature and gross salinity .

Magnesium and Sodium Sulphate salts will begin to precipitate at a salinity of (5-7) times than that of normal sea water (TDS=175000-250000) mg/l, at 20^oC of solution temperature (Collin's, 1975).

Halite (Sodium Sulphate) will begin to precipitate at (32 - 48.4) ^oC and at salinity of about (250000-350000) mg/l, (Pettijon, 1969).

Finally, when the mineralized water becomes of super saline environment (TDS=500000) mg/l, Potassium salts will begin to precipitate. Usually, the common order of evaporites deposition as mentioned above may not be taken place, consequently, because evaporites deposition can be stopped in a basin by a change in climatic regimen, such as:

1-Direct rainfalls on basin and surface runoff brought by streams see fig. (9).

2-Temperatures and evaporation which may vary between day and night ,also between cold and hot seasons .These factors affect on the gross salinity of the complex solution in basin, which may formed another condition to precipitate another salt.

These variations caused a precipitation of different salt in Shari basin, such as ;Na_2SO_4, $MgSO_4$, $CaSO_4$, NaCl and may be $Ca[HCO_3]_2$, or KCl, partially or completely .The salts in Shari Marsh taken place as a mixture of crystallized salts or colloidal accumulation of salts suspended in solution or settle down according to specific gravity of each salt .The precipitation may occur within the boggy clayey sandy sediments of Shari basin , where, the distribution of salts concentrations in basin depend on the degree of solute saturation and the head of surface water (complex solution) within the basin. Here, it is necessary to mentioned that (Habib,et.al,2000) achieved study on the labouratory condition of salt component separation from the solution of Shari Salt Marsh.

6-CONCLUSION:

The Hydrologic transport mechanisms of sodium and sulphate ions that formed Thenardite Mineral is explained in the Hydrogeochemical model see fig.No.9.

The main results that abstracted from this research are :

1-Sodium and Sulphate ions are dissolved and leached from the rocks forming the hydrogeologic system within it`s recharge area and become a part of groundwater components**.**

2-The groundwater is a fluid mobile media hosted sodium and sulphate ions which transported as chemical loads with flow direction under the effectiveness of groundwater pore velocity and dispersion law, accompanied with different types of hydro-geochemical mixin mechanisms.

3-The groundwater and it`s components is out from subsurface system then entered surface system represented by sabkha environment in which sodium sulphate precipitates as Thenardite mineral.

STRATEGY AND GROUNDWATER MANAGEMENT:

According to the conclusion of this research; the following environmental conservation management can be deduced in case of intense future Drought Crisis (deficit in rainfall and/or surface water deficit in Tigris and Euphrates rivers) .This Plan can be classified as strategic emergency plan for drought prevention or minimization and mitigation of drought impacts. The project plan needs the following requirements:

1-Groundwater Production:

The production of groundwater is achieved by:

1-Drill many shallow water wells with depth of drilling not exceeds (100) meters.

2-The water wells will be drilled in the area restricted between Hemrin Anticline and Tigris river including the surrounding area of Shari Salt Marsh.

3-The distances between wells are not less than 1 kilometers.

4-The number of drilled wells depend on the required quantity needed to solve the drought crisis.

5-Installing pump system and piping with storage tank for each water well.

2-Groundwater Softening :

A pilots or small factories can be used for softening the groundwater from it`s chemical components ,where, the TDS values ranged between (2000-8000) mg/l ,using the distillation method to produced bottled fresh water for human use.

3 -Environment Conservation :

The chemical residue from the distillation process containing sodium and sulphate ions can be used for Thenardite separation as by products, or may collected and dumped inside Shari Salt Marsh to be additional source for sodium sulphate salt in the Marsh.

The three abovementioned requirements give the followings:

1-Suitable drinking water for human uses during the period of the drought crisis.

2-Source of industrial salts.

3-Prevent the environment from pollution.

Finally, this emergency plan can be generalized to other hydrogeologic system in Iraq, after determination of elements that can be concentrated as by product materials resulting from softening process, where, the chemical residue must be dumped as stockpiles contaainning high concentration percent of some salts and trace elements .

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