

Geochemical Modeling of Water-Rock Interaction in Uppermost Regional Aquifer in Arar Area

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Abstract

Geochemical modeling technique was used to study the chemical evolution of the Upper most regional aquifer in Wadi Arar area. This aquifer composed from limestone, dolomite and some scattered or interbedded anhydrite and gypsum. Karstic terrains are highly developed in the area. Geochemical calculations showed that the studied groundwater are supersaturated and undersaturated with carbonate and sulfate minerals respectively. Four flow paths were selected to determine the main chemical reactions thought to be responsible for the variation of chemical composition of the system under consideration and also to evaluate the amount of mass transfer of selected mineral phases. Many reaction path models have been identified, mainly calcite precipitation, de-dolomitization and cation exchange of Ca for Na for paths 11 and 12 (eastern parts) and calcite precipitation, dolomitization and cation exchange of the Na for Ca for the western parts, flow paths 2 and 5.

الخلاصة

استخدم أسلوب النمذجة الجيوكيميائية لدراسة التطور الكيميائي لنظام المياه الجوفية للمكمن الاقليمي الاعلى لمنطقة وادي عرعر. يتألف المكمن من الحجر الجيري والدولومايت مع وجود بعض الجبس والانهايديرايت المتناثر وتميز المنطقة بانتشار ظاهرة الكارست بشكل واضح. اوضحت الحسابات الجيوكيميائية ان المياه المدروسة هي في حالة فوق الاشباع بالنسبة للمعادن الكاربونية وتحت الاشباع بالنسبة للانهايديرايت والجبس. تم اختيار اربعة مسارات جريان لتحديد طبيعة التفاعلات الكيميائية المسيطرة على تباير نوعية مياه المكمن وكذلك حساب مقدار التحول الكتلي لاطوار معدنية مختارة. لوحظ وجود نوعين من التفاعلات الاول هو ترسيب الكلسايت وفك الدلمتة والتبادل الايوني للكالسيوم محل الصوديوم للمسارين 11,12 (الاجزاء الشرقية من المنطقة) والآخر هو الدلمتة وترسيب الكلسايت اضافة الى التبادل الايوني للصوديوم محل الكالسيوم في الاجزاء الغربية , المسارين 2 , 5.

Introduction

The studied area located in the Iraqi western desert, and covers 2407 Square mile (fig.1).

Karstification phenomena is the most prevailing ground shape in the area and play an important role in increasing the calcareous rocks porosity and controlling the flow direction. The area represents plain covered mainly by gravel,

sandstone, shale, dolomite, limestone and anhydrite in Um Erahduma Formation. Generally, wadi Arar is covered by Quaternary deposits including sand and sand dunes. From tectonic point of view, the area is a part from Al-Rutba-Al-Jazera subzone which belongs to the stable shelf.

This block is characterized by existence of faults of SW-NE trend as deduced from the geophysical studies [2].

Climatically, the area is characterized by hot desert conditions, the mean annual rainfall reach about 101.24 mm, while the evaporation rate reaches as high as 3266.39 mm [3]. According to this extreme condition, ground water form the main source for agricultural uses. Several hydrogeological studies such as [2, 4, and 5] were carried out; other studies dealing with various aspects specifically concerns on reconnaissance hydrological survey have been carried out.

These studies showed that Arar aquifer is characterized by the great spatial and temporal variations in its hydrochemical parameters. The present study aims to determine the chemical reactions thought to be responsible for the variations in the chemical composition along specific flow paths for the uppermost aquifer. The amount of mass transfer of selected mineral phases was evaluated as well.

Geologic and Hydrogeologic setting

Previous studies indicate that the uppermost Regional Aquifer are can be regarded as the main aquifer in the study area which extend in Um Er Radhuma, Tayarat, and Hartha formations [5, 2, and 4]. Because of its wide extension and thickness throughout the area, the aquifer is unconfined, with average thickness of about 75m. Faults, cavities; and karstification that found in the exposed rocks in the area play an

important role in controlling the ground water flow in this aquifer and its productivity. Water table map (fig.2) shows that the flow direction is from the south and southwestern to the north with significant change in hydraulic gradient [1]. Subsurface flow entering the studied area from Saudi Arabia in the south and southwest can be regarded as the prime source for recharging the aquifer system as well as the small quantities coming from the direct rainfall [3].

According to the pumping tests results, the transmissivities of the aquifer range from 20-2100 m²/day while the average storage coefficient values was 3×10^{-5} [3].

Material & method

Twenty wells were selected to evaluate the chemical characteristics of the uppermost regional Aquifer (fig.1). Chemical data analyses that [1] included major cations and anions and cation-anion balance of less than ± 10 percent error were required for defining the hydrochemical facies.

The present study focuses on two major goals; the first is describing the water chemistry of the aquifer under consideration and then use the geochemical calculation to show the saturation state of the system being considered with specific minerals phase. Mass balance technique was used to predict mass transfer along a given evolutionary paths as suggested by Plummer 1984 [6].

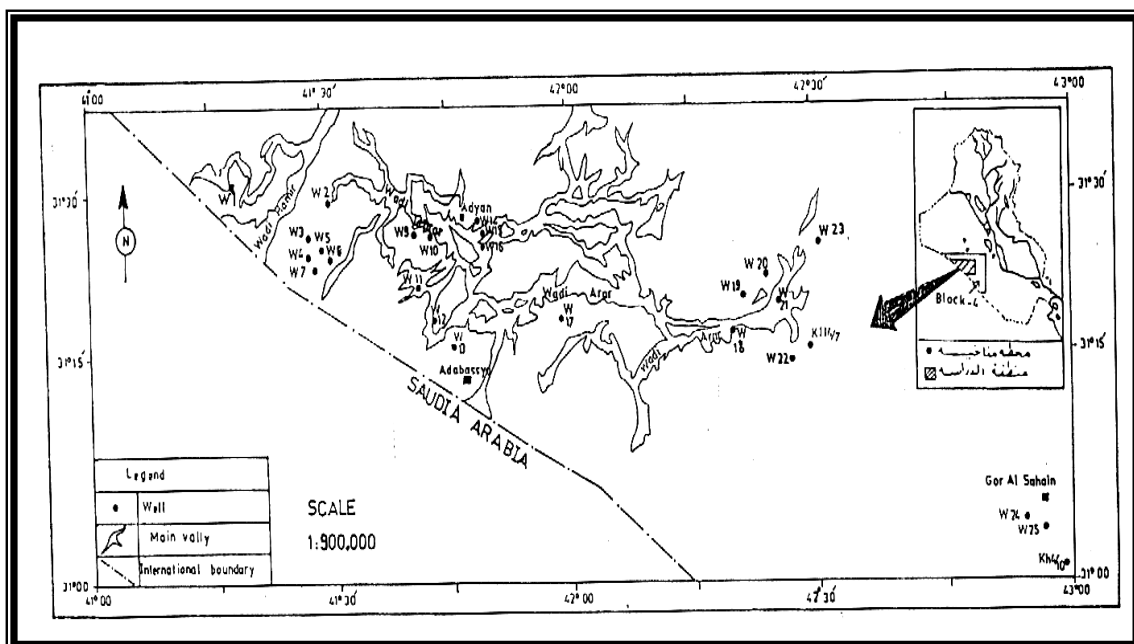


Fig (1) Location map of the study area

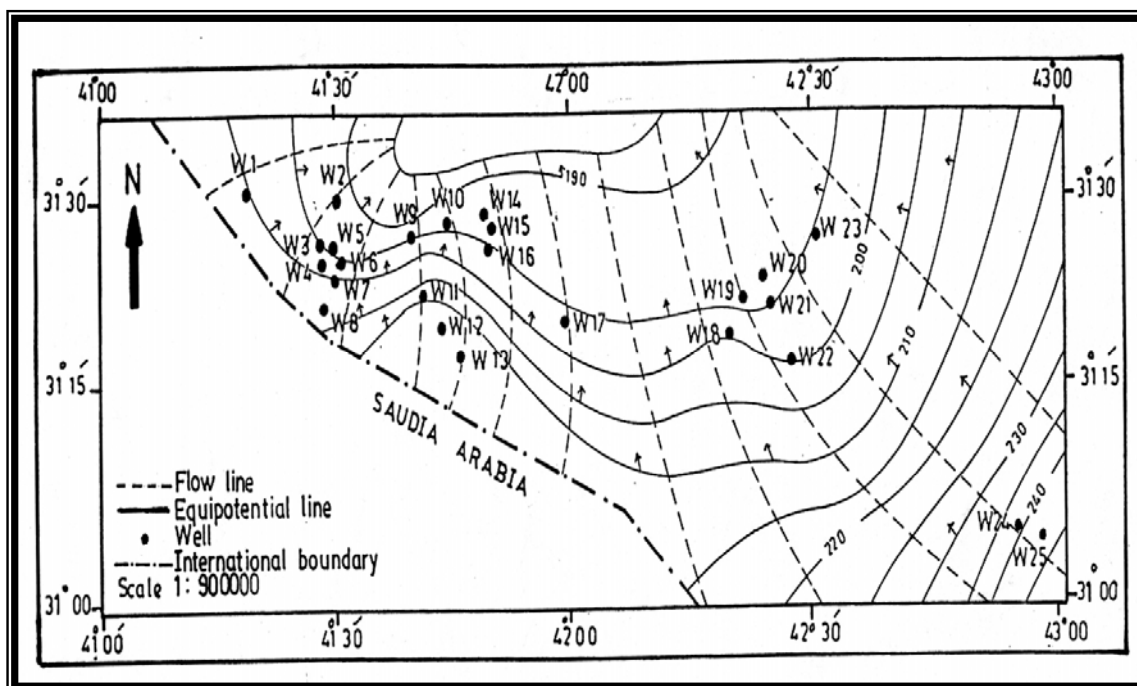


Fig.(2) :Water table map of the study area (modified from Idrotecneco-Consult Progetti, 1977)

Results and discussion

Results of pH, TDS and the concentration of the major ions, indicate that there are great spatial variations among the selected parameters, Table -1. Most of the selected samples are of the following ionic ratio:



This variation among the studied wells reflects variation in the controlling factors on hydrochemical behavior of the system under consideration. Indeed, the above variation of the analysed hydrochemical parameters along the flow paths reveal marked difference in the affecting factors such as precipitation and dissolution of the minerals consisting the aquifer matrix. To study these factors, geochemical modeling approach was used following the convention of [7].

Mineral Equilibrium

Mineral - water relationships for the water samples analyzed were interpreted using the computer program **WATEQ4F** [8]. **WATEQ4F** calculates mineral saturation states for aqueous solution using the chemical analysis of the solution and the thermodynamic data for mineral phases used in this study in table (2). The saturation state for a given a mineral is expressed

as saturation index (SI), as given by Lee 1993, [9]

$$\text{SI} = \text{Log Iap}/\text{K}_{(t)}$$

Where:

Iap=ionic activity product

K (t)=mineral equilibrium constant

when SI>0, the specific mineral is oversaturated and precipitation is possible; when SI= 0, the specific mineral is in equilibrium with the solution and when SI<0, the specific mineral is undersaturated and dissolution is possible [9]. The Upper most regional aquifer matrix composed mainly from limestone, dolomite, calcite and some scattered sulfate minerals, hence the saturation indices of calcite, dolomite and sulfate mineral were calculated using **WATEQ4F** [9]. The calculated SI's ; were also presented in Table (2). Uncertainties of ± 0.1 for calcite and gypsum and ± 0.2 for dolomite would be impose on the studied system [9] and [10]

Generally, in the course of groundwater evolution, significant relationship between SO_4 and S.I of the selected minerals were observed (fig.3). For carbonate minerals, as SO_4 concentration increase, the Calcite and Dolomite SIs increase and exceeds the equilibrium limit whereas for Sulfate minerals, the increase of SO_4 concentration leads to less proportional increase of S.I but never reach equilibrium limit. General decrease in S.I's of these minerals along the flow

direction was also observed. The results of saturation state calculation of the studied wells are very useful for checking the compatibility of the calculated mass transfer "Models" for the selected flow path [10].

Reaction - Path Models

Models describing the mass transfer and distribution of elements between aqueous solution, solid, and gas phases are often described as reaction path models. This geochemical process includes mineral dissolution and precipitation, fluid mixing, sorption, and ion exchange. The "path" refers to the evolutionary changes in the composition and abundance of modeled phases, including the aqueous phases, through the course of the simulation [9]. Also the modeling approach can be used to predict the amount of mass transfer between the solid and liquid with certain thermodynamic and chemical constraints. This approach is relied on the mass balance calculation concept which exactly account for the observed changes in the chemical composition between initial and final waters. The mass balance method can be expressed by the following form:

Initial Solution Composition + "Reactant Phases" → Final Solution Composition + Product Phases"

Some degree of uncertainties due to analytical errors and inaccuracy of thermodynamic data can be inherent in this approach. Therefore, no unique solution can be obtained through the modeling process. However, this technique is the best way for eliminating the mass balance models appeared to be incompatible with constraints imposed on the system [11]. The elimination process is very useful in limiting the possible chemical reaction and showing the additional data required to reduce the modeling uncertainties [7].

In the present study "NETPATH" program developed by (12), was used to study the geochemical evolution of the Upper most regional aquifer in Wadi Arar area, along selected flow path (Fig 1) using the mass transfer of the selected minerals. However, it should be mentioned that model selection was limited to those found to be compatible with WATEQ4F results. The following paragraph summarizes the best models accounted for the observed changes in ground water composition along the studied flow paths.

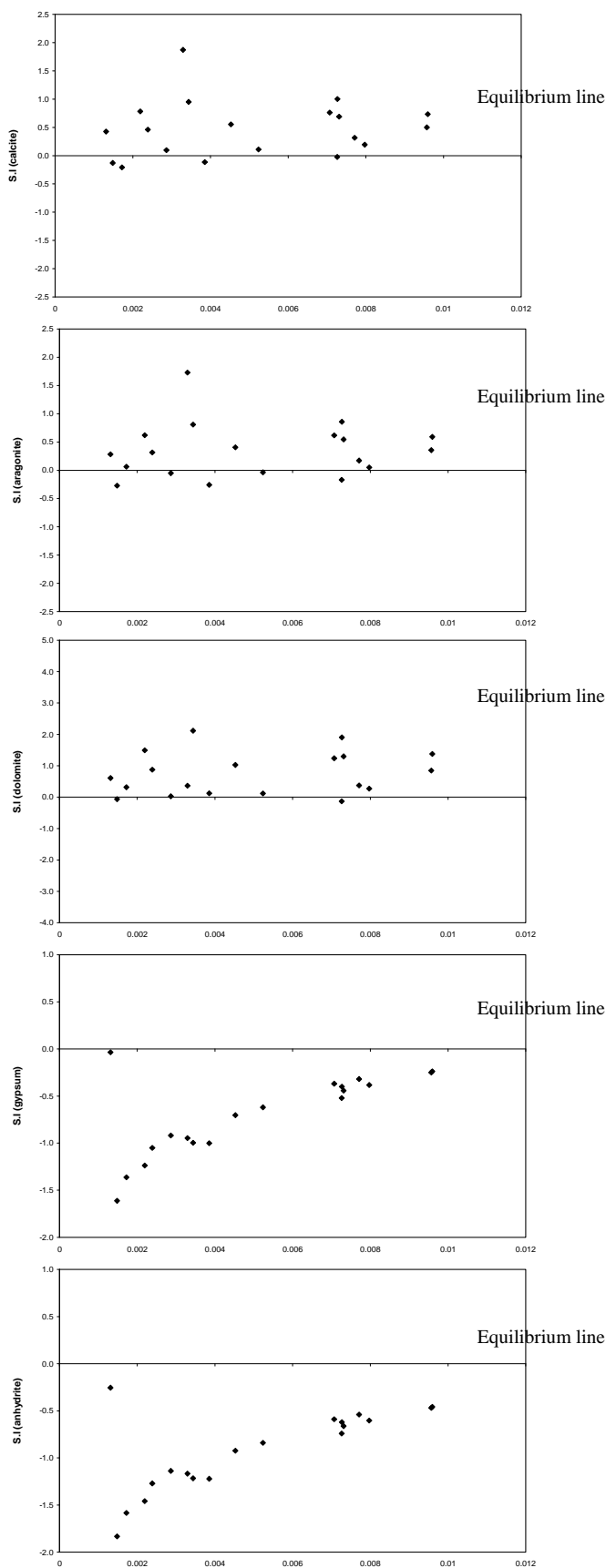


Fig.3: The relationship between saturation indices and the selected minerals with sulfate concentration (Results of this study)

Mass Transfer Results:

The amount of mass transfer of the selected minerals in (m mol 1 kg_{H₂O}) are presented in table (3) indicating, in general, for flow path 2 dissolution of calcite, dolomite, gypsum, and cation exchange of sodium for calcium. In the flow path 5, dolomite, gypsum and halite were precipitated while calcite is dissolved with the cation exchange of calcium for sodium. At flow path 11, dolomite and gypsum were dissolved whereas calcite, halite are precipitate as well as continues cation exchange of sodium for calcium. For flow path 12, the most unique model indicates calcite, gypsum and halite precipitation and dolomite dissolution with cation exchange of calcium for sodium.

According to the mentioned flow paths models, there are significant differences in the model output and their compatibility with the observed chemical and thermodynamic constraints, and hence in the calculated mass transfer of the selected minerals phases. Also, the results show calcite dissolution and dolomite, gypsum and halite precipitation in the southern part of the area whereas the flow path 1 exhibit dissolution and precipitation of these minerals with variable degree, while gypsum and anhydrite precipitate along the studied flow path. Indeed, the karstification phenomena exist in the area

support the continuous dissolution of sulfate and carbonate minerals. Based on the above results, there is substantial difference in the observed reactions in addition to the factors responsible for the groundwater variations mainly, due to the aquifer lithological variation in the study area.

Conclusions

A great temporal and spatial variation among the selected hydrochemical parameters of the Uppermost regional aquifer in Wadi Arar area was observed. This was attributed to the chemical reactions responsible for these variations. Two mains reaction found to be the most controlling factor on chemical compositions of the considered groundwater in Wadi Arar area.. The first is the incongruent dissolution of dolomite, which controls the chemistry of the less mineralized water, the second reaction is dolomitization and calcite precipitation. As the groundwater flows toward the discharging areas, its composition would be changed due to the variable degree of precipitation and dissolution of the existed mineral phases as well as the cation exchange process characterizing the considered aquifer.

Table (1): Results of water chemical analyses for the study area wells [1]

Well No	Cations				Anions			
	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	Cl ⁻	SO ₄ ⁻²	HCO ₃ ⁻	NO ₃ ⁻
	ppm epm	ppm epm	ppm epm	ppm epm	ppm epm	ppm epm	ppm epm	ppm epm
W1	143	106	-	-	907	452	262	-
	7.15	8.83	-	-	25.91	9.41	4.29	-
W2	48	34	92	-	71	173	217	-
	2.4	4.33	4	-	2.02	3.6	3.55	-
W3	164	52	92	-	204	375	165	1
	8.4	4.33	4	-	5.82	7.81	2.70	0.030
W5	144	59	115	-	266	312	174	12
	7.2	4.91	5	-	7.6	6.5	2.85	0.19
W8	203	78	117	-	199	611	142	6
	10.15	6.5	5.08	-	5.68	12.72	2.32	0.09
W9	112	115	74	-	150	520	205	20
	5.6	9.58	3.21	-	4.28	10.83	3.36	0.32
W10	69	25	-	-	39	202	128	-
	3.45	2.083	-	-	1.11	4.20	2.04	-
W11	146	54	78	-	138	417	156	2
	7.3	4.5	3.39	-	3.44	8.68	2.55	0.032
W12	336	81	72	-	146	993	105	1
	16.8	6.75	3.31	-	4.12	20.68	1.72	0.016
W13	-	-	-	-	110	-	200	-
	-	-	-	-	3.14	-	3.27	-
W14	224	82	92	-	160	710	150	30
	11.2	6.83	4	-	4.57	14.79	2.45	0.48
W15	224	86	71	-	120	960	120	20
	11.2	7.16	3.06	-	3.42	14.37	1.96	0.32
W16	376	96	102	-	180	1100	170	30
	18.8	8	4.43	-	5.14	22.41	2.78	0.48
W17	85	36	68	6	103	265	112	-
	4.25	3	2.95	0.153	2.94	5.52	1.83	-
W18	310	110	148	8	148	1120	123	-
	15.5	9.16	6.43	0.205	4.22	23.2	2.01	-
W20	384	126	63	-	133	1375	138	-
	19.2	10.5	2.73	-	3.8	28.64	2.26	-
W21	280	108	98	24	149	1020	134	-
	14	9	4.26	0.615	4.25	21.25	2.19	-
W22	307	113	-	-	168	1032	132	-
	15.35	9.41	-	-	4.8	21.5	2.16	-
W23	563	151	85	563	135	1950	183	-
	28.15	12.56	3.69	28.15	3.85	40.25	3	-
W24	404	151	97	-	215	1416	77	-
		12.53	4.21	-	6.19	29.5	1.26	-

Table (2): Results of Thermodynamic Speciation Calculation

Well No.	SATURATION INDICES				
	Calcite	Aragonite	Dolomite	Gypsum	Anhydrite
W1	0.951	0.807	2.117	-0.996	-1.215
W2	-0.130	-0.273	-0.065	-1.613	-1.833
W3	0.093	-0.51	0.027	-0.918	-1.138
W5	0.460	-0.316	0.087	-1.050	-1.270
W8	0.551	0.407	1.025	-0.703	-0.923
W9	-0.114	-0.258	0.122	-1.001	-1.221
W10	0.207	0.063	0.314	-1.363	-1.583
W11	1.087	1.728	3.669	-0.947	-1.167
W12	0.761	0.617	1.239	-0.369	-0.589
W13	0.108	-0.036	0.117	-0.620	-0.890
W14	-0.025	-0.169	-0.134	-0.521	-0.741
W15	0.315	0.172	0.373	-0.320	-0.540
W16	0.782	0.619	1.495	-1.283	-1.458
W18	0.193	0.049	0.270	-0.383	-0.603
W20	0.499	0.355	0.846	-0.250	-0.469
W21	0.689	0.545	1.299	-0.443	-0.663
W22	1.002	0.858	1.904	-0.401	-0.621
W23	0.425	0.281	0.609	-0.036	-0.255
ncW24	0.734	0.590	1.374	-0.239	-0.458

+ Supersaturation (Precipitation)

- Undersaturation (Dissolution)

Table (3): (mmole/kgH₂O) results of the amount of mass transfers for studied flow paths.

Flow Path	WELL No.	Calcite	Dolomite	Gypsum	Halite	Ca/Na Exch.
2	3,2	-2.344	-0.736	-8.273	-3.774	3.781
5	10,12	4.436	-2.142	-8.537	-3.174	-0.156
11	22,20	-0.464	0.387	3.809	-0.795	-2.0133
12	24,21	-2.762	1.868	-4.117	-1.860	1.893

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