ARTICLES

Characterization and Evaluation of the Confined Limestone Aquifer in Kuwait

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Abstract:

Al-Sulaibiya field is considered as the largest groundwater well field producing brackish water from the Dammam aquifer. The areal distribution of the TDS trend of some wells showed an increase in TDS towards the N-E direction and the trend size reached to ≈ 65 % in the eastern wells. However, this brackish groundwater is used mainly for irrigation, domestic purposes and blending with distilled water. The hydrochemistry of the groundwater of this field, was investigated and evaluated to recognize the prevailing geochemical processes in the aquifer, to determine the groundwater chemical and genetic types and to trace out the groundwater quality trends during the period of 1991-2005. Moreover, the source-rock deduction is carried out using the WATEVAL Program, and the chemical equilibrium of groundwater with respect to the minerals of aquifer matrix is assessed by calculating the saturation indices (S.I) using WATEQ4F. The collected groundwater chemical data were compiled, analyzed, plotted and interpreted using several computer programs such as SPSS, AQUACHEM, and Trend-Y-Tector, which have been utilized to achieve the objectives of the proposed study. The chemical analyses showed that the field is occupied by brackish groundwater whose salinity ranges from 3448 to 9460 mg/l. Moreover, it was found that the groundwater chemical properties of the study area are dominated by alkalies and strong acids, with the main groundwater chemical types being Na_2SO_4, $CaSO_4$, NaCl and $CaCl_2$. The main

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groundwater genetic types are $NaHCO_3$, $MgCl_2$ and $CaCl_2$. The chemical data revealed that the groundwater is exhibiting a simple dissolution or mixing process; in addition, to a reverse ion-exchange process. Generally, the groundwater exhibited an over-saturation with respect to calcite and dolomite and under-saturation with respect to anhydrite, gypsum and halite. Moreover, the P_{CO_2} ranges between 3.95×10^{-3} atm. and 5.65×10^{-3} atm., which represents a deep close environment system. The application of the mass-balance technique indicates that ion-exchange, reverse ion-exchange, dissolution of gypsum, calcite precipitation (dedolomitization), and the carbonate weathering are the prevailing geochemical processes in the Dammam aquifer of Al-Sulaibiya field.

1. INTRODUCTION

1.1 Location of the study area

Kuwait occupies an area of 17,818 sq km (6880 sq mi), and is located at the northwestern shore of the Arabian Gulf, between 28° 30' - 30°30' North latitudes and 46°30' - 48°30' East longitudes. The longest distance from north to south is 200 km (120 mi) and from east to west is 170 km (110 mi). It is an arid region, which is marked by very scarce rainfall, high temperatures and evaporation rates, and a lack of perennial surface waters (Alhumoud,2008).

Al-Sulaibiya field, located 20 km south of Kuwait Bay (Figure 1), is the first groundwater well field used for public water supply. Brackish groundwater of the study area is used mainly for irrigation, domestic purposes and blending with distilled water. The annual field production, which was 3.6 million m^3 in 1958 has increased to 16.3 million m^3 in 2007. The trend analysis of Al-Sulaibiya field production indicates a negative production rate, where a downward trend of 18% is detected. This means that the production from well field has been decreasing over pumping, and this is because the field is approaching its life expectancy (ME & W, 2009; Alhumoud, 2008).

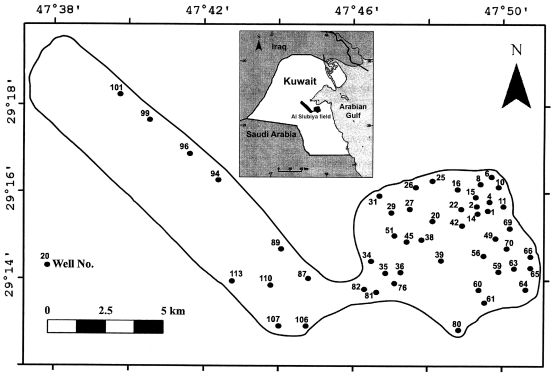

Figure 1- Location map of the selected water wells in Al-Sulaibiya field

1.2 Climate

Kuwait is a typical semitropical intercontinental area. The climate is extremely hot and dry in the summer and mild to cold in the winter. The rainfall is scarce and limited to the period from October to May. The annual precipitation has fluctuated during the period of 1990 to 2007. It reached its maximum value of 216.8 mm in 2004, where as the minimum recorded value was 61 mm in 2007. The 18 years average of total precipitation is 131.5 mm (Alhumoud, 2008; Al- Ruwaih et al., 2005). During the year, the evaporation process greatly dominates, increasing in the summer because of high temperatures, high wind speed and decrease in relative humidity. The very low average annual precipitation, the high rate of evaporation and the dry sandy nature of the top soil are the main cause of the scarcity of the natural water resources. Therefore, the main natural water sources in Kuwait are limited to the brackish groundwater (Al-Dhafeeri, 2009).

1.3 Geology of Kuwait

1.3.1 Topography

The State of Kuwait is located on the head of the Arabian Gulf. The topography of Kuwait is generally flat, with a gentle rise from sea level at the coast to an elevation of about 270 m in the southwestern

corner of the country. The landscape of Kuwait is a low relief desert with the ground surface generally featureless, gently undulating and is covered with sands and gravels. The main features are the Jal Az-Zor escarpment, Ahmadi ridge, Wadi Al-Batin and Wara hill. The Jal Az-Zor escarpment, which is located at the north of Kuwait Bay, is about 60 km in length with an elevation of 145 m above sea level. The Ahmadi ridge is located in the east and parallel to the coastline south of Kuwait City. It has an elevation of about 137 m above mean sea level. Wadi Al-Batin is a valley along the western border with 8 to 11 km long and relief of 70 m (a.s.l). The central part of Kuwait and the Neutral Zone are featureless with few wadis and little vegetation. The Arabian Gulf coast lies along the east of the country and sabkha (salty marsh land) has developed along the coast. In the northeastern part of the country a few barchan dunes up to 25 m,and of $\approx$ 20 m height are found (Omar et al.,1981;Al-Sulaimi&Al-Ruwaih, 2005).

1.3.2 General Stratigraphy

The stratigraphical column of Kuwait was mainly influenced by the stable shelf condition of the Arabian plate, causing the deposition of shallow water sediments and evaporites. The land surface is formed by sedimentary rocks and sediments ranging from Middle Eocene to Recent. The Dammam represents the oldest exposed sedimentary rocks. The Recent deposits of fine-grained beach sands cover the southern coast of Kuwait and the Neutral Zone. The Cenozoic (Tertiary-Quaternary) sediments are divided into two groups: the Kuwait Group and the Hasa Group (Figure 2). The Mesozoic (Late Cretaceous) sediments are characterized by carbonate rocks (Al-Sharhan & Nairn,1997; Al-Ruwaih, 2001).

A marked erosional unconformity surface separates the Kuwait Group from the underlying Hasa Group. The Hasa Group consists of mainly carbonate rocks, partly dolomitized in the lower parts and composed of anhydrite in the middle parts. The Hasa Group consists of three formations in descending order: Dammam, Rus and Radhuma formations, ranging in age from Middle Eocene to Paleocene (Al-Sulaimi et al.,1992). It underlies the whole State of Kuwait, and

consists of soft porous chalky limestone, hard crystalline dolomitic limestone and green shale at the base. The Dammam Formation dips gently towards the north and northeast.

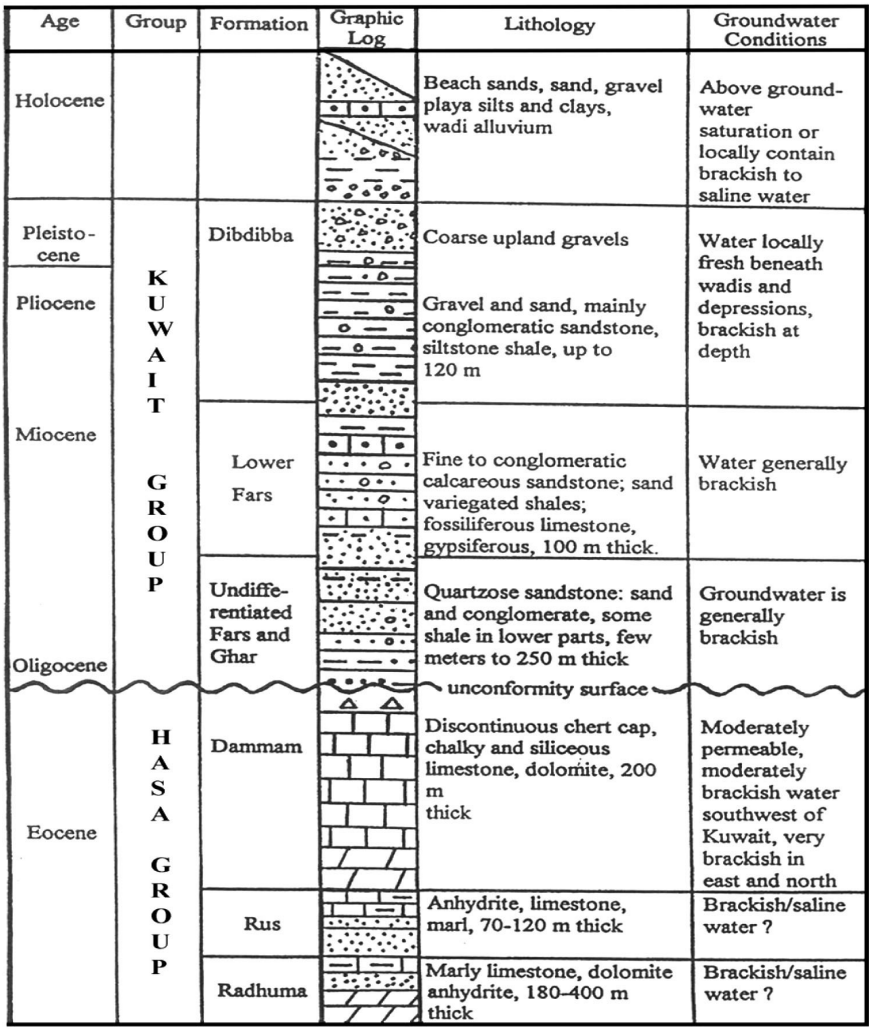

Figure 2- Lithostratigraphic representation of the Tertiary-Quaternary sediments of Kuwait (modified after Mukhopadhyay, 1995)

1.3.3 The Aquifer System in Kuwait

The most significant aquifer in Kuwait is the Tertiary-Quaternary system. Between the early 1950's and the early 1970's, the identification of two separate aquifers was made on the basis of gross lithology. These are the upper clastic sediments Kuwait Group and the lower Dammam Formation, which are separated by a confining layer of cherts and/or clay (Al-Ruwaih et al., 2005). The Eocene aquifer system, which starts from the Dahna area in Saudi Arabia, consists of two limestone formations, the Radhuma and Dammam. These two formations are separated by the anhydrite-bearing Rus Formation. This aquifer system is regionally confined, except in its recharge outcrop area in Saudi Arabia and in the discharge areas of the Arabian Gulf coast. The Dammam aquifer is isolated by confining layers. However, where these layers are absent, the Dammam aquifer comes into direct contact with the underlying Radhuma aquifer and the overlying Kuwait Group aquifer. Anhydrites of the Rus Formation together with the basal shale of the Dammam act as an aquitard, separating the underlying Radhuma aquifer from the Dammam aquifer. Based on lithology, hydraulic properties and karstification, the middle part of the Dammam Formation represents the main aquifer in Kuwait (Al-Alwadi &Mukhopadhyay,1995; Al-Sulaimi & Al-Ruwaih, 2004). The thickness of the aquifer varies from 120 m in southwestern corner of the country, to 280 m in Sabriya area in the north, while it reaches approximately 225 m in the synclinal area west of the Ahmadi ridge and more than 350 m to the east of it (Owen & Nasr, 1958; OBrein, 1952; Qabazared, 2001). The recharge of the Dammam aquifer occurs in the southern Iraqi desert, west of Kuwait and in Saudi Arabia (400 km of Kuwait), where the exposures of the Dammam aquifer cover 1200 km2 (Tleel,1973). However, this aquifer system was recharged mostly during ancient periods, while the modern current recharge is weak. The lateral outflow is directed Eastwards to the Arabian Gulf and Northward into Iraq (Mukhopadhyay et al., 1994). Disharge is indicated by terrestrial springs by upward leakage into the overlying aquifer and evaporation through coastal sabkhas (Senay,1981). The salinity of the Dammam aquifer increases from SW-

N-NE from brackish (3000 mg/l) to brine (> 150,000 mg/l). This increase in salinity may be attributed to the geometry of recharge and discharge of the aquifer system. In addition to the location of Kuwait at the edge of the Arabian Plate on the western of the Arabian Gulf synclinorium which hinders the groundwater movement and discharge.. Also may due to the decreasing of porosity and permeability along the SW-N-NE direction, in addition to the long distance that groundwater has to travel through the different geological units from recharge area to discharge (Talebi, 2003).

According to study conducted by Al-Ruwaih (1980) on Al-Sulaibiya field, the salinity were ranged from 3000 - 6000 mg/l, and that salinity increases as the water flows towards the NE direction. The mentioned study also identified four major groundwater chemical groups: NaCl, $CaCl_2$, Na_2SO_4 and $CaSO_4$. The NaCl and $CaCl_2$ types were present in the east and southeast, while the other two types Na_2SO_4 and $CaSO_4$ were found in the west and southwest. The total hardness of the water was from 1700 - 2000 mg/l during the period of 1965-1978. (Al-Ruwaih, 1996) stated that the salinity of the aquifer were ranged from 3500 mg/l to 7500 mg/l, and the total hardness ranged between 1500 - 3500 mg/l, during the period of 1975 - 1990.

The study also revealed that the Dammam aquifer showed a confined to semi-confined character. The aquifer transmissivity ranged from 45 to 90 m^2/d, with a storativity value of 2×10^{-4}. The piezometric levels of the Dammam aquifer in the study area ranged between + 15 and + 30 m (m.s.l.) in 1950s, but with increasing demand due to the population growth, the piezometric surface declined to a minimum of - 6 m in 1963, and - 67 m in 1978. The lowering of pizeometric levels indicates mining of groundwater resources, with an abstraction rates far in excess of any natural replenishment (Al-Ruwaih, 1996). In 1996, she also pointed out that the groundwater modeling of Al-Sulaibiya field predicted a continuous lowering of the piezometric level, especially in the eastern part of the field, to range between - 90 m to -115 m during the period from 1990 to 2000 as a result of the large number of wells and to the heavy over pumping. The calculated average drop of the predicted water level was found to be 1.5 m per annum.

1.4 Objectives of the study

The main objective of this study was the investigation and evaluation of the groundwater chemistry of the Dammam aquifer of Al-Sulaibiya field. It was carried out in order to recognize the prevailing geochemical processes in the aquifer and to study the trends of groundwater quality changes during the period of 1991—2005. Moreover, to deduce the source-rock, and to assess the chemical equilibrium of groundwater with respect to the minerals of aquifer matrix. In addition, to reveal the groundwater chemical types and genesis.

2. METHODOLOGY

In this study, the geological and geochemical investigations of the Dammam aquifer were carried out.The investigation was mainly based on the chemical data collected from the Ministry of Electricity and Water (MEW) in Kuwait, for the period of 1991 - 2005, of Al-Sulaibiya field, as a case study. The chemical analyses of the major ions in the groundwater such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-} and Cl^{-}, expressed in mg/l were converted to equivalent per million (e.p.m.) by multiplying with an appropriate conversion factor according to mathematical formulas (Fetter,1994) and the % e.p.m. is calculated. Ion balance equation was applied to validate the accuracy of the chemical analyses, where $\pm$ 5% is acceptable (Seather & decaritat,1997). Well-known graphical methods such as Piper (Piper,1953), Durov (Durov,1948) and Sulin (Sulin,1948) diagrams have been used to plot the chemical data in order to determine the groundwater chemical types, groundwater genetic types and the prevailing geochemical processes. Several computer programs have been utilized, which include: WATEQ4F program to compute the saturation indices of the minerals with respect to a stated water composition (Ball & Nordstrom,1992);WATEVAL program (Hounslow,1995) to deduce the source-rock; Surfer for windows, to construct contour maps to show the distribution of salinity; SPSS program for statistical analyses of various hydrochemical characteristics; AQUACHEM package to carry out the graphical and numerical analysis of the geochemical data; and Trend-Y-Tector application to investigate the trend analysis of TDS in the study area.

3. GROUNDWATER CHEMISTRY

The results of the field and laboratory analyses of 139 groundwater samples from Al-Sulaibiya field were analyzed for the basic cations and anions, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}), sulfate (SO_4^{2-}) and bicarbonate (HCO_3^{-}). In addition to, temperature (^{o}C), electrical conductivity (EC) ($\mu S/cm$) at 25^{o} C, and pH. The chemical analyses are expressed in mg/l and data have been converted to e.p.m and % e.p.m., for the purpose of analyses and interpretation using different methods.

Field analyses of pH, EC, alkalinity and temperature are usually made at the time when the sample is collected using portable equipments. Some constituents, especially those involved in carbonate and redox reactions, will undergo changes upon reaching the atmosphere. Redox changes lead to difficulties such as precipitation of metals and thus, samples need to be stabilized to keep metal ions in solution (Hunt & Wilson, 1990; Seather & de - caritat,1997; Vanloon & Barefoot,1989).

The ion balance equation was used to validate hydrochemical analysis of standard inorganic constituents, where $\pm$ 5% is acceptable (Seather & de-caritat,1997).

3.1 Groundwater Chemistry of Al-Sulaibiya Field

Water chemistry term to the quantities of various solutes that are represented in a particular water sample, and make up its chemical composition. The results of the field and laboratory analyses of 139 groundwater samples from Al-sulaibiya field were interpreted to determine the groundwater chemical types, groundwater genesis,deduction of aquifer source - rock in order to identify the dominant geochemical processes operation in the aquifer and finally trace out the groundwater salinity trends.

3.1.1 Pipers Trilinear Diagram

Trilinear plotting technique developed by Piper (Piper,1953) is used to classify groundwater on the basis of chemistry, and to compare chemical trends among different aquifer systems with a view to getting

the picture of water quality at a glance. The Piper trilinear diagram is an effective tool in segregating the analyzed data for critical study with respect to sources of the dissolved constituents in the groundwater, modifications in the character of water as it passes through an area, and the related geochemical problems.

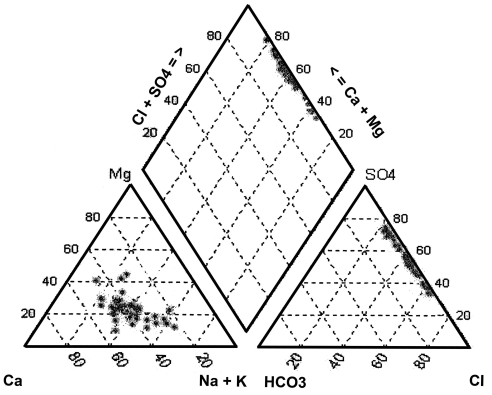

Figure 3- Piper diagram for the period 1991-2005

The Piper diagram has been utilized to plot the chemical analyses of Al-Sulaibiya field for the period of 1991-2005, only data of the years 2001-2005 is presented in Figure 3. It's clear from the Piper diagram that most of the groundwater samples of Al-Sulaibiya field during the study periods are located in sub-areas 1, 4 and 6 where the alkaline earths exceed alkalies, strong acids exceed weak acids and non-carbonate hardness (secondary salinity) exceeds 50% respectively. A few groundwater samples are located in sub-area 2 and 7; where the alkalies exceed alkaline earths and non-carbonate alkali (primary salinity) exceeds 50% respectively. Therefore, it's obvious from the chemical analyses that the groundwater chemical properties of the study area are dominated by alkaline earths Ca^{2+} and Mg^{2+} and by strong acids, Cl^{-} and SO^{2-}_{4}.

3.1.2 Expanded Durov Diagram

The groundwater samples of Al-Sulaibiya field have been plotted on the expanded Durov (Durov,1948) diagram as shown in Figures 4 and 5, for the period of 1991-1995 and 2001-2005. It's clear that some

groundwater samples are located on area 5, which indicates that the groundwater exhibits simple dissolution or mixing processes. However, the residual samples are located in area 8, which indicates that the Cl- ion is the dominant and there are no dominant cations. This suggests that reverse ion exchange of Na^{+}-Cl^{-} water is a prevailing chemical process (Lloyds & Heathcote,1985).

However; it's concluded from the plot of the chemical data of the period of 1991-2005 on the expanded Durov diagram, that the groundwater is exhibiting a simple dissolution or mixing processes, in addition, to a reverse ion-exchange process that operating the aquifer of the study area and explain its chemistry.

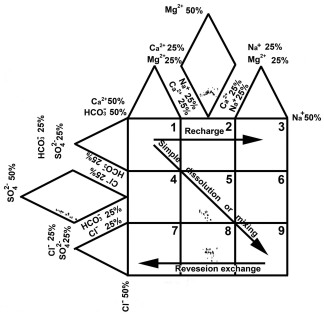

Figure 4- Expanded Durov diagram for the period 1991-1995

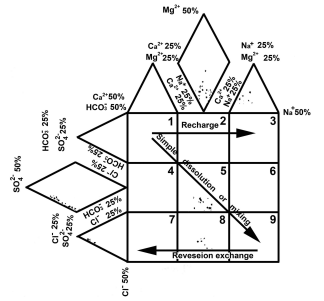

Figure 5- Expanded Durov diagram for the period 2001-2005

3.2 Sulin's Classification Graph

Sulins graph (Sulin,1948) is prepared for the genetic classification of water. The graph is divided into two main quadrants depending on Na^+/Cl^- ratio values. Water with ratio of $Na^+/Cl^- > 1$ is located in lower quadrant whereas water having ratio of $Na^+/Cl^- < 1$ is located in upper quadrant. A diagonal line with ratio of $Na^+/Cl^- = 1$ separates the two quadrants into four equal triangles each corresponding to a different genetic water type, while the coefficients $(Na^+-Cl^-)/SO_4^{2-}$ and $(Cl^--Na^+)/Mg^{2+}$ are used to identify each type of genetic waters. The upper quadrant contains the chloride group, Cl-Mg and Cl-Ca genetic types reflecting marine conditions, as an origin of formation, whereas the lower quadrant contains the Na^+ group, Na-SO_4 and Na-HCO_3 genetic types (terrestrial condition) reflecting the continental origin of formation of groundwater (Collins,1975).

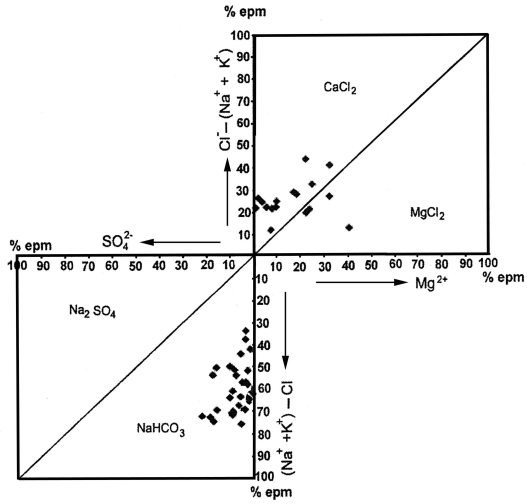

Figure 6- Sulin's classification of Al-Sulaibiya field, 2001-2005

The Sulin's concept has been applied to the chemical data of Al-Sulaibiya field for the studied period. It's found that most of the groundwater samples are located on $CaCl_2$, $NaHCO_3$ and $MgCl_2$ quadrant as shown in Figure 6. The presence of three genetic water types, may present and explain the nature of the shallow marine

environmental deposits of the limestone aquifer of the study area that has been mixed and interacted with water of meteoric origin infiltrated on the out crop part of the aquifer, and reached the main aquifer in Kuwait through seepage process (Al-Ruwaih,1993).

4. GEOCHEMICAL MODELING

The geochemical models are techniques used to estimate chemical reactions in groundwater system, such as dissolution and precipitation of solids, ion-exchange and sorption by clay minerals (Talebi, 2003). According to Plummer (1984), the geochemical models are divided into two general types. The first one refers to Forward models, and the second one refers to Inverse models.

Table (1)
Thermodynamic speciation calculations
for Al-Sulaibiya Field (1991-2005)

Well No.	Anhydrite	Calcite	Dolomite	Gypsum	Halite	PCO_2
Period 1 (1991-1995)						
1	-0.500	0.365	0.319	-0.282	-4.666	3.71E-03
2	-0.306	0.376	0.098	-0.088	-4.506	4.68E-03
4	-0.340	0.384	0.153	-0.123	-4.308	3.29E-03
6	-0.456	0.194	0.077	-0.237	-4.817	6.06E-03
8	-0.510	0.355	0.103	-0.291	-4.491	6.93E-03
10	-0.628	0.472	0.490	-0.410	-4.581	3.72E-03
11	-0.732	0.313	0.055	-0.514	-4.574	5.68E-03
14	-0.366	0.388	0.189	-0.148	-4.877	4.82E-03
15	-0.801	0.043	-0.344	-0.583	-4.494	8.72E-03
16	-0.669	0.340	-0.005	-0.451	-4.663	7.63E-03
20	-0.212	0.275	-0.140	0.007	-5.085	6.96E-03
25	-0.544	0.219	-0.182	-0.325	-4.925	4.94E-03
26	-0.439	0.234	-0.130	-0.220	-4.885	7.93E-03
27	-0.648	0.185	-0.165	-0.430	-4.691	7.02E-03
29	-0.492	0.283	-0.034	-0.273	-4.879	6.06E-03
30	-0.373	0.319	-0.048	-0.154	-4.942	7.05E-03
31	-0.451	0.383	0.159	-0.232	-5.048	5.34E-03
34	-0.409	-0.118	-0.859	-0.190	-4.699	8.04E-03
35	-0.343	0.216	-0.192	-0.125	-4.620	6.45E-03

Cont. Table (1)
Thermodynamic speciation calculations
for Al-Sulaibiya Field (1991-2005)

Well No.	Anhydrite	Calcite	Dolomite	Gypsum	Halite	PCO_2
36	-0.411	0.398	0.165	-0.192	-4.809	4.45E-03
38	-0.375	0.499	0.345	-0.156	-4.815	3.72E-03
39	-0.481	0.239	-0.142	-0.262	-4.671	7.00E-03
42	-0.421	0.302	0.021	-0.203	-4.615	5.55E-03
45	-0.422	0.378	0.147	-0.203	-4.855	4.50E-03
49	-0.382	0.439	0.308	-0.164	-4.494	4.54E-03
51	-0.385	0.367	0.121	-0.166	-4.998	5.05E-03
56	-0.382	0.377	0.169	-0.164	-4.665	5.64E-03
59	-0.273	0.444	0.295	-0.055	-4.375	4.26E-03
61	-0.417	0.327	0.062	-0.199	-4.486	5.58E-03
63	-0.321	0.090	-0.403	-0.104	-4.251	1.01E-02
65	-0.491	0.603	0.636	-0.273	-4.670	3.37E-03
69	-0.336	0.339	0.048	-0.118	-4.538	5.91E-03
70	-0.211	0.222	-0.152	0.006	-4.128	6.71E-03
76	-0.450	0.273	-0.059	-0.232	-4.776	5.75E-03
80	-0.464	0.269	-0.026	-0.246	-4.843	6.08E-03
81	-0.401	0.262	-0.061	-0.183	-4.723	8.52E-03
82	-0.452	0.238	-0.127	-0.233	-4.785	5.38E-03
87	-0.303	0.714	0.686	-0.084	-5.125	2.64E-03
89	-0.262	0.402	0.026	-0.043	-5.149	7.08E-03
94	-0.358	0.338	0.029	-0.139	-5.153	6.61E-03
96	-0.411	0.518	0.357	-0.192	-5.173	4.53E-03
99	-0.402	0.339	0.003	-0.184	-5.122	7.02E-03
101	-0.387	0.430	0.222	-0.168	-5.126	5.47E-03
106	-0.514	0.564	0.423	-0.295	-5.256	4.25E-03
107	-0.394	1.036	1.362	-0.175	-5.118	1.11E-03
110	-0.284	1.014	1.279	-0.065	-5.148	1.51E-03
113	-0.303	0.302	-0.127	-0.084	-5.253	8.42E-03
Mean	**-0.424**	**0.361**	**0.110**	**-0.205**	**-4.784**	**5.65E-03**
Period 2 (1996-2000)						
1	-0.335	-0.025	-0.644	-0.117	-4.487	2.67E-03
2	-0.248	0.333	0.030	-0.030	-4.523	5.04E-03
4	-0.302	0.288	-0.014	-0.085	-4.208	4.57E-03
6	-0.311	0.798	0.995	-0.093	-4.444	2.47E-03

Cont. Table (1)
Thermodynamic speciation calculations
for Al-Sulaibiya Field (1991-2005)

Well No.	Anhydrite	Calcite	Dolomite	Gypsum	Halite	PCO_2
8	-0.298	0.664	0.694	-0.080	-4.359	2.77E-03
10	-0.301	0.298	-0.062	-0.083	-4.651	5.25E-03
11	-0.333	0.037	-0.524	-0.115	-4.628	9.77E-03
14	-0.334	0.325	0.022	-0.115	-4.660	3.69E-03
15	-0.292	0.392	0.152	-0.074	-4.714	3.83E-03
16	-0.392	0.375	0.127	-0.173	-4.677	4.11E-03
18	-0.412	0.273	-0.057	-0.194	-4.611	5.30E-03
20	-0.406	0.224	-0.197	-0.187	-5.043	5.84E-03
22	-0.337	0.744	0.868	-0.119	-4.444	2.35E-03
25	-0.406	0.280	-0.067	-0.187	-4.783	5.55E-03
26	-0.332	0.318	-0.067	-0.113	-4.940	5.95E-03
27	-0.366	0.399	0.113	-0.148	-4.985	4.81E-03
29	-0.478	0.466	0.315	-0.260	-4.847	2.47E-03
31	-0.464	0.585	0.504	-0.245	-4.981	2.08E-03
34	-0.463	0.473	0.336	-0.245	-4.615	2.09E-03
35	-0.397	0.523	0.398	-0.178	-4.704	2.44E-03
36	-0.381	0.642	0.629	-0.163	-4.877	2.12E-03
38	-0.411	0.641	0.634	-0.193	-4.892	2.08E-03
39	-0.381	0.568	0.360	-0.162	-4.869	4.24E-03
42	-0.359	0.565	0.486	-0.141	-4.647	2.38E-03
45	-0.407	0.305	-0.084	-0.189	-4.851	7.91E-03
49	-0.359	0.444	0.299	-0.141	-4.347	2.81E-03
51	-0.323	0.392	0.051	-0.104	-5.107	4.20E-03
56	-0.371	1.102	1.589	-0.152	-4.652	5.59E-04
59	-0.276	0.538	0.476	-0.060	-4.036	2.14E-03
61	-0.399	0.168	-0.226	-0.181	-4.415	1.04E-03
63	-0.376	-0.858	-2.286	-0.159	-4.161	2.26E-03
64	-0.291	0.179	-0.244	-0.074	-4.031	3.61E-03
65	-0.494	0.349	0.105	-0.276	-4.653	4.57E-03
69	-0.341	0.555	0.462	-0.123	-4.390	3.66E-03
70	-0.274	0.308	-0.016	-0.057	-4.048	6.67E-03
76	-0.416	0.320	0.001	-0.197	-4.899	4.06E-03
80	-0.452	0.282	-0.032	-0.233	-4.919	5.53E-03
81	-0.502	0.327	0.060	-0.288	-4.618	3.93E-03

Cont. Table (1)
Thermodynamic speciation calculations
for Al-Sulaibiya Field (1991-2005)

Well No.	Anhydrite	Calcite	Dolomite	Gypsum	Halite	PCO_2
82	-0.592	0.490	0.378	-0.374	-4.757	2.52E-03
87	-0.397	0.308	-0.064	-0.179	-5.071	6.18E-03
89	-0.276	0.534	0.341	-0.057	-5.066	3.80E-03
94	-0.272	0.523	0.333	-0.053	-5.253	3.96E-03
96	-0.289	0.517	0.326	-0.070	-5.188	7.03E-03
99	-0.250	0.485	0.280	-0.030	-5.074	5.35E-03
101	-0.278	0.508	0.368	-0.060	-5.057	5.16E-03
106	-0.361	0.423	0.157	-0.142	-5.213	5.59E-03
107	-0.354	0.588	0.455	-0.135	-5.000	3.01E-03
110	-0.302	0.735	0.727	-0.083	-5.185	2.49E-03
113	-0.373	0.777	0.812	-0.154	-5.070	1.82E-03
Mean	**-0.363**	**0.418**	**0.190**	**-0.144**	**-4.728**	**3.95E-03**
Period 3 (2001-2005)						
1	-0.204	-0.261	-1.067	0.014	-4.666	1.11E-02
2	-0.129	-0.902	-2.405	0.088	-4.351	2.95E-02
4	-0.207	-0.076	-1.018	0.010	-4.093	7.58E-03
6	-0.205	-0.010	-0.600	0.013	-4.604	5.92E-03
8	-0.146	0.110	-0.459	0.071	-4.482	3.53E-03
10	-0.272	-0.216	-0.988	-0.054	-4.519	1.06E-03
11	-0.055	0.210	-0.212	0.163	-4.700	7.32E-03
14	-0.368	0.290	0.028	-0.150	-4.747	3.11E-03
15	-0.143	-0.141	-0.970	0.075	-4.538	6.72E-03
16	-0.242	0.036	-0.615	-0.024	-4.724	4.34E-03
18	-0.096	0.140	-0.342	0.122	-4.786	4.00E-03
20	-0.284	0.013	-0.672	-0.066	-5.013	5.94E-03
22	-0.475	0.118	-0.481	-0.257	-4.653	3.35E-03
25	-0.632	0.088	-0.456	-0.413	-4.757	3.54E-03
26	-0.333	0.541	0.476	-0.114	-4.864	2.37E-03
27	-0.332	0.101	-0.386	-0.113	-4.808	4.75E-03
30	-0.207	0.140	-0.309	0.011	-5.008	4.92E-03
31	-0.493	-0.089	-0.385	-0.274	-4.772	7.45E-03
34	-0.727	0.097	-0.447	-0.509	-4.643	2.63E-03
35	-0.257	-0.876	-2.465	-0.038	-4.485	9.96E-03
36	-0.740	-0.098	-0.839	-0.522	-4.494	4.25E-03

Cont. Table (1)
Thermodynamic speciation calculations
for Al-Sulaibiya Field (1991-2005)

Well No.	Anhydrite	Calcite	Dolomite	Gypsum	Halite	PCO_2
38	-0.396	0.661	0.870	-0.177	-4.970	1.50E-03
42	-0.219	0.197	-0.362	-0.001	-4.924	3.88E-03
45	-0.121	0.546	0.398	0.097	-4.973	1.50E-03
49	-0.367	-0.078	-0.820	-0.149	-4.418	7.19E-03
51	-0.256	-0.017	-0.672	-0.037	-5.047	7.73E-03
56	-0.237	0.001	-0.765	-0.018	-4.717	7.14E-03
59	-0.410	-0.138	-0.722	-0.192	-4.660	7.73E-03
61	-0.393	-0.316	-1.408	-0.175	-4.766	1.08E-02
63	-0.319	0.288	0.286	-0.101	-4.435	3.40E-03
64	-0.224	0.513	0.439	-0.007	-4.315	2.87E-03
65	-0.427	0.052	-0.493	-0.209	-4.276	5.52E-03
70	-0.217	0.174	-0.502	0.001	-4.151	7.56E-04
80	-0.459	-0.043	-0.960	-0.240	-4.947	8.48E-03
81	-0.811	-0.378	-1.087	-0.592	-4.735	1.12E-03
82	-0.737	0.191	-0.179	-0.518	-4.975	2.01E-03
87	-0.758	0.274	-0.033	-0.539	-5.075	4.57E-04
94	-0.090	0.148	-0.431	0.129	-5.229	7.17E-03
96	-0.309	0.441	-0.021	-0.090	-5.144	3.77E-03
99	-0.209	0.589	0.024	0.010	-5.223	4.61E-03
101	-0.227	0.828	0.948	-0.008	-5.159	3.11E-03
106	-0.376	0.359	0.114	-0.157	-5.124	3.48E-03
107	-0.187	0.341	0.104	0.032	-5.034	4.02E-03
110	-0.252	0.205	-0.287	-0.033	-5.191	3.30E-03
113	-0.250	-0.034	-0.848	-0.031	-5.216	1.06E-02
Mean	**-0.329**	**0.089**	**-0.467**	**-0.110**	**-4.765**	**5.46E-03**

The aim of Forward model is to predict water compositions and mass transfers that result from hypothesized reactions (Plummer,1992). The Inverse geochemical model deduces the chemical changes that take place as water evolves along a flow path (Plummer et al.,1994). The typical Inverse modeling approach is a grouping of speciation modeling and mass-balance modeling (Parkhurst & Plummer,1993).

In this study, the Inverse speciation model has been applied to determine the thermodynamic speciation calculations of the ground-

water of the study area for the periods of (1991-1995), (1996-2000) and (2001-2005) (Table 1); using WATEQ4F Program (Ball & Nordstrom,1992), in order to determine the degree of saturation of groundwater with respect to certain minerals. In addition, a mass-balance model using WATEVAL program proposed by Hounslow (Hounslow,1995) has been applied to deduce the source-rock in order to investigate the major geochemical processes that influence the groundwater chemistry of Al-Sulaibiya field.

4.1 Speciation modeling

The saturation state of water is an important concept because it can be used to better understand the chemical history of the groundwater. Saturation state of any solution with specific mineral phase can be calculated as follows (Plummer,1992):

$$\mathrm{S.I} = \log(\mathrm{IAP}/\mathrm{K_{sp}}) \qquad (1)$$

Where:

S.I = Saturation Index.

IAP = Ion Activity Product.

K_{sp} = Solubility Product.

If S.I > 0, the solution is saturated with the mineral and the precipitation is possible, if the S.I < 0, the solution is under-saturated with the mineral and the dissolution occurs, whereas if S.I = 0, the solution is in equilibrium with the specified mineral.

4.2 Langelier Index

The Langelier index is the saturation index (S.I.) for calcite. Any solution contain Ca^{2+} and CO_3^{2-} will have an IAP = $[Ca^{2+}]$ $[CO_3^{2-}]$ from solution. In the case of calcite, the S.I. may be expressed in different manner, it may be written as:

$$\mathrm{S.I.} = \mathrm{pH}_{\text{ of solution}} - \mathrm{pH}_{\text{ at which calcite precipitates}} \qquad (2)$$

When written in this form the S.I. is usually known as Langelier index. Thus, Langelier index = S.I. (calcite) = log IAP / K_{sp} =

$pH_{of\ solution}$ - $pH_{at\ which\ calcite\ precipitates}$. If the langelier index is positive, the solution is oversaturated, with respect to calcite, and if it is negative, it is undersaturated with respect to calcite (Hounslow,1995). The degree of saturation or under-saturation of groundwater with respect to some minerals has been calculated for the Dammam aquifer of Al-Sulaibiya field, during the periods of 1991-1995, 1996-2000 and 2001-2005 respectively; and the results are displayed in Table 1. The results of the thermodynamic speciation calculations of the studied periods of 1991-1995, 1996-2000 indicated that the groundwater showed a negative saturation index values for anhydrite, gypsum and halite, which demonstrates that the groundwater was under-saturated with respect to these minerals. On the other hand, the saturation index of calcite and dolomite have positive index values, which means that the groundwater was oversaturated with respect to calcite, and dolomite. The results of the saturation index of anhydrite, dolomite, gypsum and halite for the period of 2001-2005 indicate that the groundwater was under-saturated with respect to these minerals. While, the groundwater was oversaturated with respect to calcite, which might be precipitated. The average partial pressure of carbon dioxide (P_{CO_2}) of the groundwater for the studied periods ranges between 3.95 x 10^{-3} atm. and 5.65 x 10^{-3} atm. which is found to be greater than the P_{CO_2} of the Earth's atmosphere ($10^{-3.5}$), and revealed that the aquifer is being charged with carbon dioxide through the soil zone, and suggested a deep closed environmental system (Appelo & Postma,1994; Stigter et al., 1998; Hadi & Al - Ruwaih, 2005; Hadi & Al-Ruwaih, 2008).

Table 2 summarizes the mean saturation indices and the Pco2 values of Al-Sulaibiya field

Table (2) The mean saturation indices and Pco2. of Al-Sulaibiya Field

Studied periods	Anhydrite $CaSO_4$	Gypsum $CaSO_4.2H_2O$	Halite NaCl	Calcite $CaCO_3$	Dolomite $CaMg(CO_3)_2$	P_{CO_2}
1991-1995	-0.424	-0.205	-4.784	0.361	0.110	5.65E-03
1996-2000	-0.363	-0.144	-4.728	0.418	0.190	3.95E-03
2001-2005	-0.329	-0.110	-4.765	0.089	-0.467	5.46E-03

4.3 Source-Rock Deduction

A mass-balance technique using WATEVAL program (Hounslow,1995) has been utilized to deduce the source-rock of the Dammam aquifer of Al-Sulaibiya field, in order to identify the main geochemical processes that influence the groundwater chemistry. The most common chemical reactions are gypsum dissolution, calcite precipitation, dedolomitization, ion exchange and silicate/carbonate weathering.

Hounslow's approach (Hounslow,1995) was applied to 139 groundwater samples of the Dammam aquifer in which the pH values of the groundwater samples were checked and found to be ranged from 6.3 to 8.2 with an average value of 7.3.

5 RESULTS AND DISCUSSION

5.1 Dissolution and Precipitation

The progressive dissolution of minerals as groundwater moves downgradient in aquifer will result in increases in the TDS content of the water. This effect is noticeable in sedimentary rocks, because of the occurrence of highly soluble minerals such as gypsum, anhydrite and halite. The ratio of HCO_3^-/ (sum anions) indicates the minerals dissolution rates in the aquifer, which is according to Hounslow (1995) if HCO_3^-/ (sum anions) is < 0.8, it reveals gypsum dissolution and if the ratio > 0.8, it indicates silicate or carbonate weathering.However it is found that the ratio of HCO_3^-/ (sum anions) of all groundwater samples of the study area is < 0.8, which suggests that the gypsum and anhydrite are dissolving minerals in the aquifer of the study area. This finding is supported by the results of the thermodynamic speciation calculations obtained previously. Furthermore, the calcite precipitation is a common process in aquifers. The chemical process involved is as follow according to Hounslow, 1995:

$$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3\,(s)} \qquad (3)$$

The $CaCO_3$ will precipitate when ($[Ca^{2+}]$ $[CO_3^{2-}]$ / K_{sp}) > 1, where Ksp is the solubility product for calcite.

The calcite will precipitate when either Ca^{2+} or CO_3^{2-} is increased, so that the solubility product is exceeded, or if the solubility product is reduced. Also, calcite will precipitate when increasing the Ca^{2+} ion concentration by dissolving soluble calcium mineral such as gypsum ($CaSO_4.2H_2O$). This process is called dedolomitization (Hounslow,1995). The Langelier index, which is an indication of calcite precipitation, has been computed for all the groundwater samples of the study area during the selected study period, showed positive values ranging from 0 to 1.2, which revealed that the groundwater is oversaturated with respect to calcite, which in turn might be precipitated in the system.

5.2 Dedolomitization

Dedolomitization may occur in aquifers containing limestone and dolostone. In its simplest form, dedolomitization is the replacement of dolomite by calcite according to the following reaction (Hounslow, 1995):

$$Ca^{2+}{}_{(aq)} + CaMg(CO_3)_{2\,(s)} \rightarrow 2CaCO_{3\,(s)} + Mg^{2+}{}_{(aq)} \quad (4)$$

Back et al. (1983) and Langmuir (1971) pointed out that the dedolomitization is a result of dissolution of calcite, dolomite, gypsum and precipitation of calcite.

The reaction is initiated by Ca^{2+} / Mg^{2+} ratio > 1. The high ratio of Ca^{2+} / Mg^{2+} is achieved by the introduction of dissolved gypsum or anhydrite into the aquifer. Richter & Kreitler (1986) suggested that dedolomitization is indicated by a ratio of $(Ca^{2+} + Mg^{2+}) / SO_4^{2-}$ approaching one. By the application of this concept to the study area, it is found that the calculated values of $(Ca^{2+} + Mg^{2+}) / SO_4^{2-}$ for the groundwater samples are within the range of 0.8 to 1.2, revealing the occurrence of the dedolomitization process in the aquifer. Figure 7 shows a systematic increase of Mg^{2+} and Ca^{2+} concentrations, which indicates dolomite and gypsum dissolution, and calcite precipitation in the aquifer system. This may explain the saturation condition with respect to calcite and slight undersaturation with respect to dolomite in the study area.

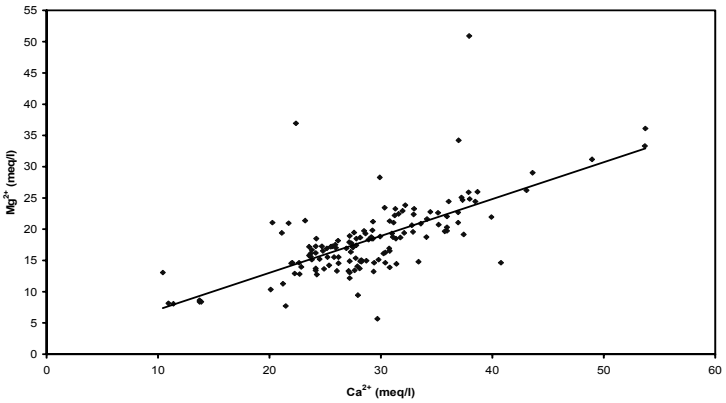

Figure 7- The relationship between calcium and magnesium of the study area.

5.3 Cation Exchange

The ratio SiO_2/ [(Na^+K^+)-Cl^-] < 1 indicates the conditions cation exchange in the aquifer. The results showed that most of the groundwater samples of the study field fall within the range of cation exchange ratios which is less than one. Thus, it's indicated that the cation exchange is taking place as one of the chemical processes operating within the Dammam aquifer.

The reverse Ion exchange requires the presence of clay with exchangeable calcium and a water higher in sodium than the clay-exchange equilibrium concentration. Ion exchange can be represented simply by the following reaction (Appelo & postma,1994):

$$2Na^+_{(aq)} + Ca - Clay \rightarrow Na_2 - Clay + Ca^{2+}_{(aq)} \qquad (5)$$

The result is often expressed in meq/l of Na^+/ Cl^- < 1. However, most of the groundwater samples of the study area, for the studied periods shows Cl^- > Na^+ which suggests that reverse Ion exchange process is likely to occur in the aquifer.

5.4 Mode of Weathering

Weathering is caused by the interaction of rocks with the

atmosphere and hydrosphere. The HCO_3^-/SiO_2 ratio can indicate the dominant mode of weathering. Silica will not be released by dissolving carbonate, while silicate weathering will release a considerable amount of silica in water. Hounslow(1995) found that waters with $HCO_3^-/SiO_2 < 5$ showed dominantly silicate weathering, while waters with $HCO_3^-/SiO_2 > 10$ suggested dominantly carbonate weathering. It is found that some of the groundwater samples of the study area show the ratio $HCO_3^-/SiO_2 > 10$, indicating a carbonate weathering. Few groundwater samples represented a silicate weathering as the ratio $HCO_3^-/SiO_2 < 5$. The remaining samples are ambiguous or uncertain. However, carbonate weathering represents 27% of the groundwater samples of the study field.

In addition, the ratio $Mg^{2+} / (Ca^{2+} + Mg^{2+}) < 0.5$ indicates limestone-dolomite weathering. However, it's found that the ratio of $Mg^{2+}/ (Ca^{2+} + Mg^{2+})$ for most of the groundwater samples of the study area are within the range of 0.26 to 0.57, indicating that limestone-dolomite weathering is operating in the aquifer with 95.7%. Table 3 summarizes the major geochemical reactions affecting the groundwater chemistry of the Dammam aquifer of the study area.

As indicated in Table 3, the sovereign reaction in this aquifer is the gypsum dissolution with a percentage of 100%, followed by the limestone-weathering process (95.7%) and the calcite precipitation (94%), which supports the existence of gypsum dissolution process. The dedolomitization process is also supporting the previous two reactions operating in the aquifer. In addition, the cation exchange and the carbonate weathering processes are occurring in the aquifer, but not in the same importance of the previous reactions, where 50% of the samples showed cation exchange, 27% of the samples exhibited carbonate weathering and 25% of the samples exhibited reverse softening.

Table (3)
Major geochemical reactions of Al-Sulaibiya Field during 1991-2005

S. No.	Chemical reactions	Index	Range	Percentage % of samples
1	Gypsum dissolution	HCO_3^-/ (sum anions)	< 0.8 (sulfate high)	100 %
2	Limestone-dolomite weathering	$Mg^{2+}/(Ca^{2+}+Mg^{2+})$	< 0.5	95.7 %
3	Calcite precipitation	Langelier indices	Positive	94 %
4	Reverse ion exchange	Na^+ / Cl^-	< 1	77.7 %
5	Dedolomitization	$(Ca^{2+} + Mg^{2+})/SO_4^{2-}$	> 0.8 < 1.2	54 %
6	Cation exchange	$SiO_2/ [(Na^+ + K^+)-Cl^-]$	< 1	50 %
7	Carbonate weathering	HCO_3^-/ SiO_2	> 10	27 %
8	Reverse Softening	$Na^+ / (Na^+ + Cl^-)$	< 0.5	25%

5.5 Groundwater Quality Trends

Statistical trend analysis offers an objective tool to detect and estimate changes in water quality. Because of the variety of tests nowadays available to analyze a water quality data record, each with its own capacities and underlying assumptions, considerable judgment is required to select the appropriate test. Oslo and Paris Commission (ICES,1999) proposed three trend detection methods in a suite. The idea is to take the benefits of all methods, because there is not one method which is always the best. The starting method is the Mann-Kendall test (MK), it is the most simple method which robust in detecting monotonic downward trends. When this method dont detect significant monotonic trends, it is possible that a non-linear trend exists. Then a smoother will be used because it is most

powerful in detecting non-linear trends. This so called Trend-Y-Tector application decides whether there is a significant trend or not (ICES,1999).

The TDS values of the groundwater samples of Al-Sulaibiya field from 1995 to 2005 have been taken as the input data and are subjected to the Trend-Y-Tector application. The trend analysis for well nos. 2, 4, 20,36 are plotted in Figure (8). The areal distribution of the TDS trend size of the same wells are presented in Figure 9. Both Figures showed an increase in TDS towards the N-E direction, where the trend size reached to? 65 % in the eastern water wells. The salinity ranged from 3448 to 9084 mg/l in 1995, and from 3623 to 9460 mg/l in 2005. It is clear that there is an increase in groundwater salinity over the years, mostly in the N-E of the study area.

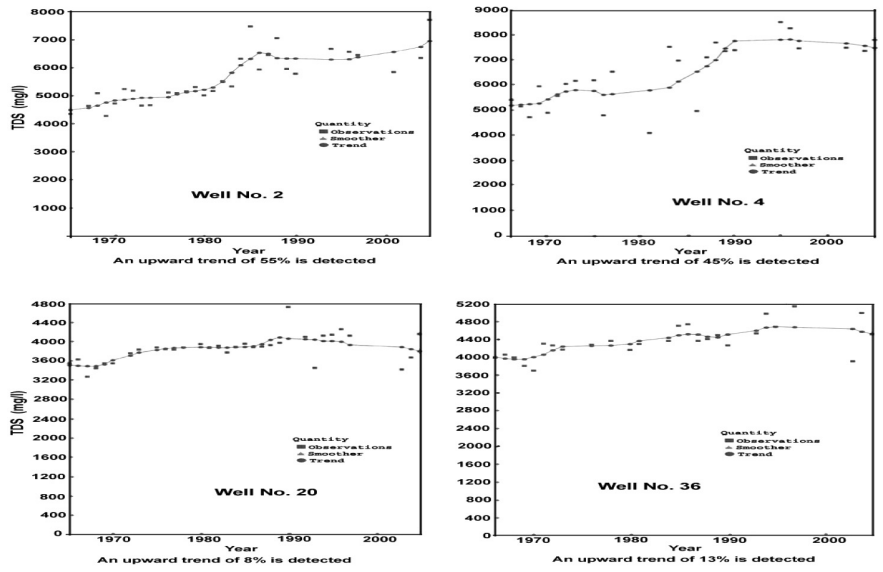

Figure 8- Trend analysis of TDS by Lowess- smoother method

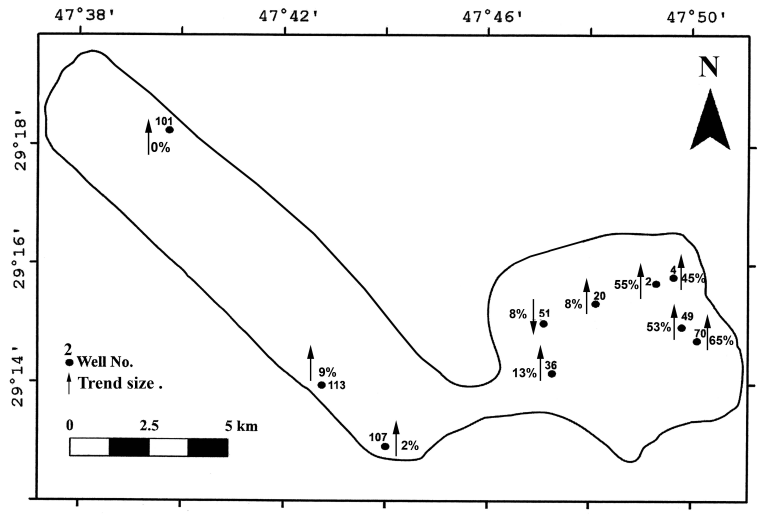

Figure 9- Trend analysis of TDS by Lowess-smoother method

6. CONCLUSION AND RECOMMENDATIONS

The aquifer system in Kuwait is mainly divided into two main aquifers: the Kuwait Group and the Dammam aquifers. Thus, the groundwater production is mainly derived from Dammam aquifer. The groundwater salinity of the Dammam aquifer ranges from brackish (2500 mg/l) in southwest to brine (> 150,000 mg/l) in northeast of Kuwait.

In this study, the groundwater chemistry of the Dammam aquifer of Al-Sulibiya field was investigated through the analysis of water samples collected during the period from 1991 to 2005.

The chemical analyses of groundwater samples collected from the Dammam aquifer of the study area show that the aquifer is occupied by a brackish groundwater with a TDS range between 3448 and 9460 mg/l, and gradually increases toward north and northeast. The increase in salinity has been attributed to a number of factors including dissolution processes, connate water, possible saline intrusion and upwelling of saline water due to over pumping within the well field. The main groundwater chemical types recognized based on the most

dominant cations and anions concentration are: Na_2SO_4, $CaSO_4$, NaCl and $CaCl_2$. Three main groundwater genetic types: $NaHCO_3$, $MgCl_2$ and $CaCl_2$ are present in the aquifer and exhibit a continental-marine environment interaction.

The alkalinity ranges between 45 and 170 mg/l, and the total hardness (as $CaCO_3$) is from 1624 to 3632 mg/l indicating a very hard groundwater due to the nature of the aquifer sediments. The computed saturation indices indicated that the groundwater is under-saturated with respect to gypsum and anhydrite, and over-saturated with respect to calcite and dolomite, due to the dissolution and precipitation processes. The calculated mean values of the partial pressure of carbon dioxide (P_{CO_2}) of the groundwater in the Dammam aquifer, ranges between 3.95×10^{3} atm. and 5.65×10^{-3} atm., which is greater than the P_{CO_2} of the Earth's atmosphere, suggesting that the Dammam aquifer represents a deep closed environmental system with respect to CO_2. The application of the mass-balance technique indicates that ion-exchange, reverse ion-exchange, dissolution of gypsum, calcite precipitation (dedolomitization), limestone-dolomite weathering and the carbonate weathering are the prevailing geochemical processes in the Dammam aquifer of Al-Sulaibiya field.

The spatial distribution of the groundwater salinity indicated an increase in groundwater salinity from SW to NE, where the range of salinity in 1995 was from 3448 to 9084 mg/l, and increased slightly to be ranged from 3623 to 9460 mg/l in 2005. The change of the groundwater salinity of the Dammam aquifer downgradient from SW-N-NE in the study area may be attributed to the geometry of the recharge and the discharge of the aquifer system and the environmental deposition, where the infiltrated recharge water is mixed with the prime water of the aquifer material. Moreover; the long distance that the groundwater has to travelling from the recharge to discharge area. The trend analysis of Al-Sulaibiya field production indicates a negative production rate of 18%, mainly due to the fact that the field is approaching its life expectancy, and to the increase of TDS in NE wells, and the construction of new emergency water wells. Due to the heavy exploitation of the Dammam aquifer since 1954, the salinity is

found to increasing with time, especially in NE area, and the water level is also expected to decline. Accordingly, it is recommended to install a regular monitoring system for groundwater quality, water level measurements and production and it is also recommended to decrease pump rate in the eastern area of the aquifer of Al-Sulaibiya field to counteract the continuous lowering of piezometric level and deterioration of water quality.

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