



Equilibrium states of groundwater chemistry in coastal region of Kuwait

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ABSTRACT

Groundwater samples were collected along the coastal region of Kuwait to determine the geochemical nature of the ions and their thermodynamic states. The state of thermodynamic equilibrium predicts the nature of the reaction in the aquifer. The geochemical nature was determined by standard plots and ion ratios. The geochemical results of the groundwater samples were then studied with stability plots for silicate and carbonate equilibrium and later they were compared with the saturation states with the aid of geochemical model (PHREEQC). The samples reflect higher electrical conductivity values with greater values of Na and Cl ranging from brackish to hypersaline nature. The silicate stability plots with respect to major cations reflect that the samples were stable with respect to K-feldspar and kaolinite composition. The carbonate stability plots reflect the stability of the composition predominantly with respect to calcite and dolomite fields. Subsequently, the saturation states of silicates and the carbonate minerals were determined by using PHREEQC. The saturation index values indicate these samples were consistent with the observations made by plotting in the stability plots with minor variations. Though lithology plays a critical role the minor variations were mainly due to the consideration of temperature and the impact of the associated ionic species in the model. The variations were more significant in the carbonate mineral saturation as carbonates react and attain saturation faster than the silicate minerals. The study also infers that the “Common Ion Effect” governs the saturation of these carbonate minerals. Hence, the study reveals the fact that the carbonate minerals are more saturated than the silicate minerals in the groundwater and it is mainly governed by the lithology of the associated ions.

Keywords: Hydrogeochemistry; Stability plots; Saturation states; PHREEQC

1. Introduction

Coastal groundwater is a fragile environment acting as a buffer between a fresh and saline aquatic water bodies. In general coastal groundwater is brackish to saline in nature, especially in arid regions. In certain regions they are hyper-saline to acidic hyper saline in nature [1,2]. The geochemical nature of the coastal groundwater are generally affected by numerous factors like coastal land use [3–5], seawater intrusion [6,7], variation in the inflow of the river water [8], Submarine groundwater discharge [9,10], tidal influx [11,12], backwaters, lagoon and other coastal surface water bodies [13]. In a multi-layered aquifer system the

shallow aquifers are predominantly saline in nature [14,15]. The variation in lithology also governs the geochemistry of the coastal waters [16]. The brackish groundwater of the arid region is utilized for the various domestic and industrial purposes [17–19]. The geochemical variation in these waters may affect the utility. The normal variation in temperature triggers the change in pH apart from the nature of the host rock interaction and anthropogenic factors [20]. This change affects the thermodynamic states of ions and thereby alters their mobility and availability for reaction [21,22]. There are several computer aided programs like SOLMINQ, PHREEQC, WATEQ4F, EQNR3, etc., to determine the thermodynamic states of water. They calculate

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the ionic strength and the saturation states of water with respect to definite pressure, temperature, and concentration. Further, the shift in equilibrium governs the concentration of the resultant water and thereby changes in the state of equilibrium. Such hypothetical conditions by varying the temperature or external conditions can be simulated to understand the possible geochemical nature. The software CHIDAM and WATCLAST can plot the thermodynamic states for silicate minerals with respect to cations and silica in groundwater [23,24]. Coastal groundwater of Kuwait vary spatially with respect to their interaction with lithology, open sea, bay, and anthropogenic activities along the shore [14,19,25]. Drastic variation of temperature is observed in Kuwait with extremely hot summers and cold winters, which would affect the thermodynamic states of water seasonally thereby changing the water quality and the ions available of reaction. Hence this study aims to understand the thermodynamic equilibrium states and their variations with respect to temperature. The spatial variation of the saturation states were also been determined in this study.

2. Study area

Two major aquifers in Kuwait are the potential groundwater sources, the younger Kuwait group aquifer (KGA) deposited in the continental environment and the older Dammam Formation formed in the marine conditions. The Kuwait group aquifer is composed of the Ghar (predominantly represented by calcretised sandstone) and Fars (fossiliferous limestone and evaporites) formations deposited during Miocene, followed by the Dibdibbah (predominantly of gravelly coarse sand) formation formed during Pleistocene and then by recent sediments [26]. Dibdibbah formation serves as the prominent aquifer in KGA, followed by Fars aquitard then by Ghar formation. The KGA has a thickness of ~400 m in the north east and ~150 m in the south-western part of Kuwait. The piezometric surface varies from zero to 90 m with respect to the sea level, from the southwest to the coastal region respectively. The transmissivity varies from 10 to 200 m² d⁻¹, near the Bay and north eastern region respectively, with saturated thickness varying between 0 and 400 m. The Dammam Formation of Eocene is separated from the overlying KGA by a major unconformity. The Dammam Formation has a thickness varying between ~280 and 150 m, piezometric level ranging from a few meters to ~90 m with respect to the sea level [27]. The transmissivity varies due to the karstic nature of the formation and it's found to be higher in the south-western and southern part of Kuwait [28].

3. Methodology and analysis

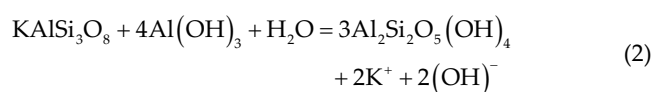
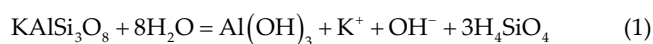
Groundwater samples were collected from 20 shallow bore wells along the coastal region of Kuwait (Fig. 1). The coastal region represents the open sea and the Bay. The groundwater samples were collected after well purging, before purging the screened interval of the well, the static water level of the well was measured. The pH, temperature, electrical conductivity (EC), dissolved oxygen (DO), and oxidation–reduction potential (Eh) were measured in the field. The aim of measuring these parameters on-site was to ensure that purging would extract a sufficient

quantity of water allowing representative groundwater sample to collect; and to provide on-site measurements of unstable parameters such as temperature and to compare with laboratory measurements to validate changes due to holding time and transport. The groundwater and seawater samples collected were analyzed using ion chromatography for major cations and anions (Na, K, Ca, Mg, Cl, and SO₄) (Method No. 4110); nutrients (NO₃, NH₃, PO₄) and silicate (H₄SiO₄) have been analyzed using a discrete analyser (Method No. 4130). Trace metals were analyzed using the Agilent 5100 ICP-OES Model equipment using the USPEA 200.7 procedure. These laboratory analyses were conducted in the Water Research Center's (WRC's) laboratory at KISR according to the procedures explained in the Standard Methods for the Examination of Water and Wastewater, 22nd edition. The silicate stability plots for Ca, Mg, Na and K were plotted using CHIDAM software [23] and the simulations by varying temperatures were determined by PHREEQC [29]. Saturation states of the minerals were obtained by determining the ratio between the ionic activity product and solution constant. Further variation in the composition of each groundwater sample was simulated for a range of temperatures between 19°C to 28°C. The saturation states, variation in pH, ionic strength and groundwater composition were recorded.

4. Results

The geochemical results show variation in groundwater composition, the maximum, minimum and the average composition of the groundwater samples are presented in Table 1. Greater variation in salinity was noted, the samples range from brackish to hypersaline and to acidic hyper salinity. The pH varies from acidic to alkaline conditions. Higher concentration of Cl was observed, followed by SO₄, HCO₃ and H₄SiO₄, but greater variation was observed with respect to Cl and SO₄ ions. Similarly, Na was observed to be predominant in cations followed by Ca, Mg and K. Range of variation was observed to be higher in all the cations. The concentration of ions governs the formation of saturation states apart from the environmental variables like temperature and pressure.

Kaolinite composition is achieved by the interaction of H₄SiO₄ with Al(OH)₃, initially, Al(OH)₃ referred as gibbsite and dissolved silica derived by the dissolution of feldspar at a definite pH. Subsequently with the further dissolution of feldspar enhances the Al in groundwater along with the dissolved silica concentration. Thus the colloidal association of the derived ions results in the compositional stability with kaolinite [30].



Breakdown of single feldspar releases K₂O and Na₂O in 1:1 ratio to SiO₂-CaO is released in 1:2 ratios to SiO₂.

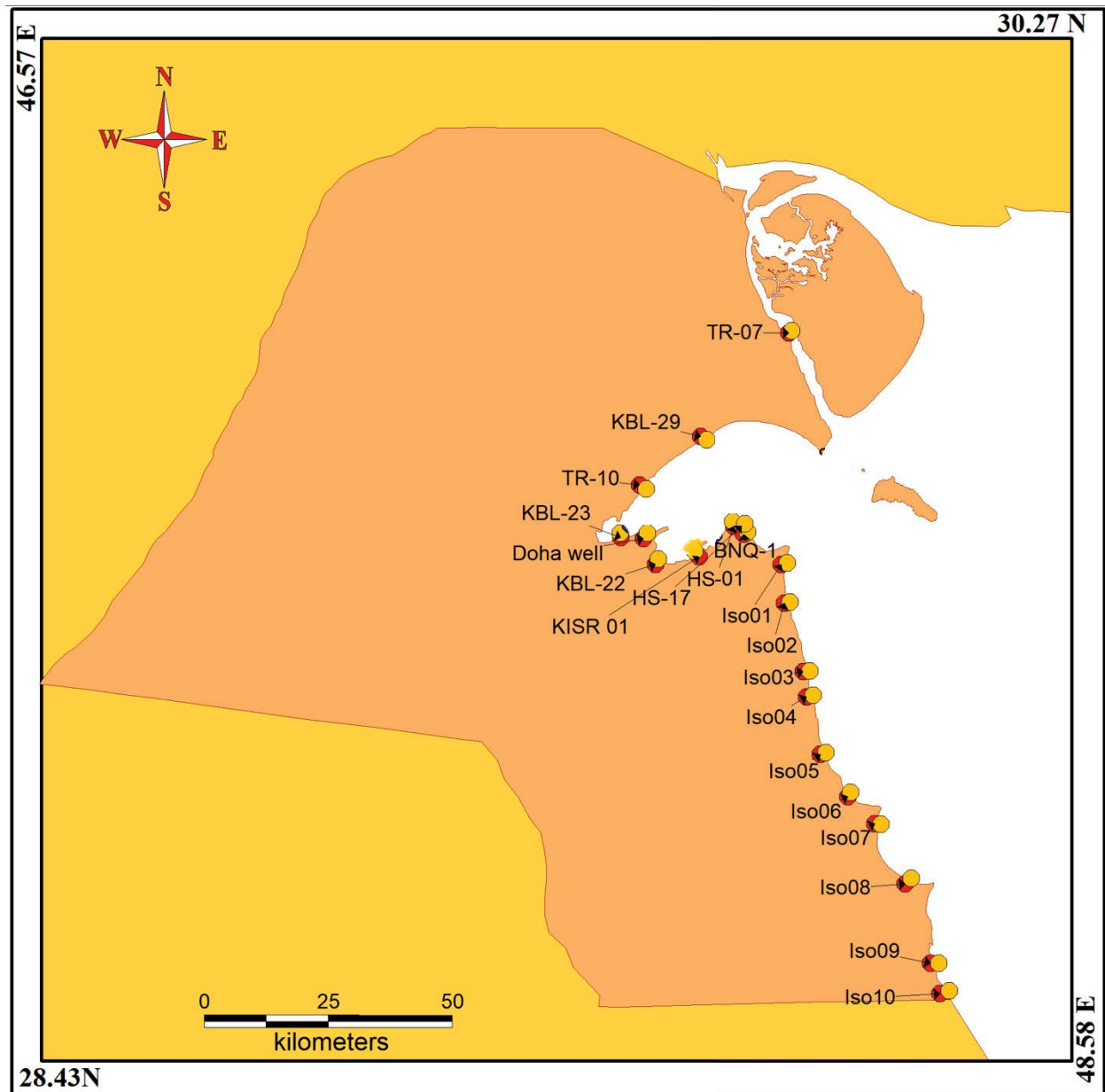
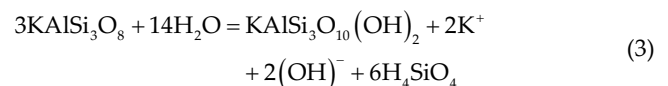


Fig. 1. Location of the groundwater samples collected for the study along the coastal region of Kuwait. All samples were collected from Kuwait group aquifer wells with depth less than 60 m.

Hence in water with biotite and feldspar, K_2O , Na_2O and CaO will be released into the groundwater. SiO_2 will be partly removed and partly fixed [31]. H_4SiO_4 obtained by the dissolution of feldspar is utilized for the formation of kaolinite from gibbsite. During this process, the migration of the groundwater composition is observed along the gibbsite–kaolinite interface. The composition is noted along the boundary until all the gibbsite is exhausted due to the reaction with silica and Al. Thus from then on the composition is observed to migrate to kaolinite stability field. Similarly, the composition is observed along the muscovite–kaolinite boundary till the stable kaolinite is exhausted by reacting with K, and Al derived from the dissolution.



The samples in the sodium stability plot falls in the kaolinite stability field. As dissolution of feldspars continues the value of $Si(OH)_4$ and $[Na^+]/[H^+]$ increases from gibbsite and the composition migrates to kaolinite field. The potassium stability plot indicates incongruent dissolution of K-feldspar stable with kaolinite. The variation of ion result in shift of kaolinite to K-feldspar (Fig. 2). The plots for Ca^{2+} shows representation in kaolinite field. In magnesium

Table 1
Maximum, minimum and average concentration of groundwater samples collected along the coast

Parameter	Unit	Groundwater ($n = 20$)		
		Min.	Max.	Average
EC	$\mu\text{S/cm}$	1,273	97,840	35,257
pH		7.06	8.26	7.48
HCO_3	mg/L	52	263	142
Na	mg/L	19	21,063	6,745
K	mg/L	4	864	256
Ca	mg/L	30	2,643	952
Mg	mg/L	2	2,279	781
SO_4	mg/L	31	4,272	2,930
Cl	mg/L	29	47,208	14,238
F	mg/L	0.07	4.97	2.77
H_4SiO_4	mg/L	1.50	44.23	15.14
NO_3	mg/L	0.00	617.49	82.79
TDS	mg/L	182	78,600	26,362

plot, samples were observed along the boundary of kaolinite–chlorite field. The solubility of silica and the variation of Mg^{2+} ions result in the change in compositional stability from kaolinite to chlorite (Fig. 2).

Almost all the groundwater samples collected adjacent to the coast fall in the albite stability field due to the higher concentration of Na. Subsequently, the samples with relatively lesser concentration of Na fall in the Na-montmorillonite field (Fig. 2). It is inferred from the ionic ratio that the Na concentration is higher than the Ca in groundwater. Thus, the sodic feldspar field exhibit a predominant display of the samples. The carbonate stability system is generally derived by relating the activity ratios of Ca and Mg to $\log\text{pCO}_2$. The major carbonate minerals are aragonite, calcite (CaCO_3), dolomite ($\text{Ca,Mg}(\text{CO}_3)$) and magnesite (MgCO_3). The vertical distribution of the field is between the two carbonate end members calcite and magnesite representing the regions with higher and lower Ca/Mg ratio respectively. Dolomite is intermediate between these two end members, the $\log\text{pCO}_2$ indicate variation along the horizontal direction considering the stability fields of brucite ($\text{Mg}(\text{OH})_2$) and carbonates (Fig. 2). The atmospheric $\log\text{pCO}_2$ value is designated as -3.75 [32], all the groundwater samples were noted to have a higher $\log\text{pCO}_2$ ranging from -2.8 to -1.8 , this is mainly due to the fact that they represent a closed system with lesser atmospheric interaction [33]. All the samples plot in the dolomite field due to the predominance of both Ca and Mg in the samples (Fig. 2). The trend indicates movement of composition of samples from calcite to hydromagnesite, with respect to changes in $\log\text{pCO}_2$ values.

4.1. Temperature simulations

The pH-REdoxEquilibrium Code (PHREEQC) was adopted to simulate the groundwater composition by varying the sample temperatures from 19°C to 28°C . The selected outputs of the simulation was considered for the

study like, pH, ionic strength, saturation index of predominant sulfate (anhydrite- SI_{An} ; gypsum- SI_{Gy}) and carbonate minerals (aragonite- SI_{Ar} , calcite- SI_{C} , dolomite- SI_{D} , magnesite- SI_{Mg}), halite (SI_{Ha}), forms of silica (quartz- SI_{Qtz} , silica amorphous- SI_{SiO_2} , chalcedony- SI_{Chal}), clinoenstatite (SI_{CE}) and forsterite (SI_{Fo}) minerals were considered.

The order of saturation states regarding the minerals considered are as follows:

$$\text{SI}_{\text{D}} > \text{SI}_{\text{C}} > \text{SI}_{\text{Ar}} > \text{SI}_{\text{Mg}} > \text{SI}_{\text{Qtz}} > \text{SI}_{\text{Chal}} > \text{SI}_{\text{Gy}} > \text{SI}_{\text{An}} > \text{SI}_{\text{SiO}_2} > \text{SI}_{\text{CE}} > \text{SI}_{\text{Ha}} > \text{SI}_{\text{Fo}}$$

The state of saturation with regard to sulphate, carbonate and silicates show the following order:

$$\text{Sulphate minerals: } \text{SI}_{\text{Gy}} > \text{SI}_{\text{An}}$$

$$\text{Carbonate minerals: } \text{SI}_{\text{D}} > \text{SI}_{\text{C}} > \text{SI}_{\text{Ar}} > \text{SI}_{\text{Mg}}$$

$$\text{Silica minerals: } \text{SI}_{\text{Qtz}} > \text{SI}_{\text{Chal}} > \text{SI}_{\text{SiO}_2}$$

$$\text{Fe silicates: } \text{SI}_{\text{CE}} > \text{SI}_{\text{Fo}}$$

The trend of saturation were observed to be the same in all samples except for the SI of carbonates which varied in samples 10, 13, 14, 16, 17 and 20 (Table 2). These samples located along the southern flanks of the bay reflected higher saturation states of magnesite than the calcite and aragonite. The trend of variation in these saturation states were simulated from 19°C to 28°C . The data reveals that the saturation states of carbonate minerals, halite, and Fe-silicates increases with temperature. The decrease of saturation states was observed for different forms of silica, gypsum, pH and ionic strength of the samples. Anhydrite was observed to be sensitive with respect to temperature as most of the samples showed a decrease in saturation from 21°C – 24°C (Table 2). The SI_{C} and SI_{Ar} (calcium carbonates) show similar behaviour in most of the samples with an increase in saturation state with increase in temperature, but certain location HS-01, KBL-23 and TR-07 show a decrease in saturation with increase in temperature. These samples have pH values >7.5 and Mg >850 mg/L. This condition favors the available HCO_3 and Ca to combine with Mg and form Ca, Mg carbonates (dolomite and magnesite) when temperature increases. The formation of this mineral is governed by the selected association of Ca to HCO_3 than to SO_4 at certain temperature. This is mainly due to the phenomenon referred as ‘‘Common Ion Effect’’. This temperature depends on the composition of the groundwater and the atmospheric pressure. The temperature simulation study also reveals that a decrease in pH is observed with increase in temperature and this process changes the availability of HCO_3 in groundwater and thus its capacity to associate with ions to become saturated.

4.2. Spatial variation of saturation index

The saturation states of the minerals considered were compared to sampling location in the study area (Fig. 3).

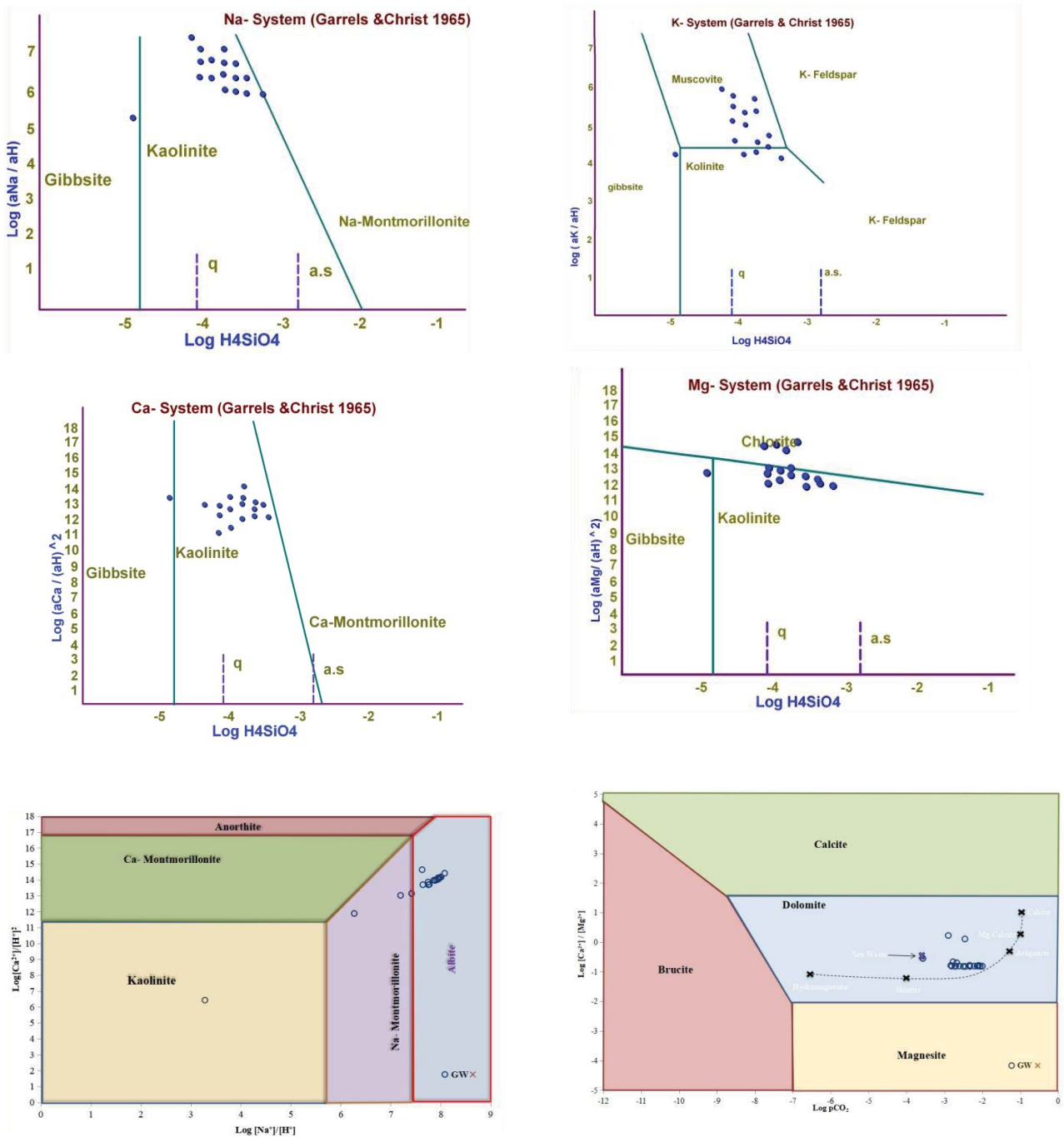


Fig. 2. Thermodynamic states of the groundwater samples observed in the different stability plots group aquifer wells with depth less than 60 m.

The trend of the saturation states predominantly remains the same. The SI_{Mg} is nearly saturated in all the samples located in the coast adjacent to the open sea. The coastal samples adjacent to the southern part of the bay show under saturation of magnesite. Further, the SI_{An} shows under saturation in the coastal samples adjacent to the bay but samples adjacent to the open sea show near saturation. This variation is mainly due to variation in the groundwater composition [19,23,25]. Though the trend of the saturation

states of minerals remain the same minor variations are observed at specific locations due to the compositional variability in the groundwater.

4.3. Common ion effect

The composition of groundwater play a major role in determining the saturation states of minerals. As the availability of ions play a significant role in saturation

Table 2

Summary of the trend of saturation states of minerals obtained by simulating the temperature variation from 19°C to 28°C though PHREEQC model

Sam	pH	IS	Sulphate		Carbonates			Hal	Silica			Silicate	
			Anh	Gyp	Ara	Cal	Dol		Mag	Qtz	Si	Cha	CE
Iso 01	↓	↓	25(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 02	↓	↓	21(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 03	↓	↓	21(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 04	↓	↓	21(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 05	↓	↓	23(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso06	↓	↓	22(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 07	↓	↓	23(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 08	↓	↓	26(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 09	↓	↓	23(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Iso 10	↓	↓	23(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
BNQ-1	↓	↓	21(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
HS-17	↓	↓	23(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
HS-01	↓	↓	24(↓	↓	↓	↑	↓	↓	↓	↓	↑	↑
KISR 01	↓	↓	↑	↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
KBL -22	↓	↓	21(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
Doha well	↓	↓	25(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
KBL-23	↓	↓	26(↓	↓	↓	↑	↓	↓	↓	↓	↑	↑
TR-10	↓	↓	24(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
KBL-29	↓	↓	21(↓	↑	↑	↑	↓	↓	↓	↓	↑	↑
TR-07	↓	↓	26(↓	↓	↓	↑	↓	↓	↓	↓	↑	↑

Blue indicates the decrease of saturation with increase in temperature and the ochre indicates the vice versa. The “24(“ indicates the decrease and increase of saturation sates with the adjacent value reflects the temperature with lowest value of anhydrite saturation.

states, Ca and HCO₃ are the common ion for the carbonate minerals (calcite, aragonite and dolomite). Ca is the common ion for both the carbonate and the sulphate minerals considered. The exponential variation was noted in SI dolomite and anhydrite. Hence, it is observed that there is a decrease in the saturation states of the carbonate minerals, when there is an increase of sulfate mineral saturation, due to the dual role of “Ca” a common ion. Though the greater concentration of certain ions like SO₄, Na and Cl are observed their saturation states are not obtained due to the solution composition, availability of other ions and the pressure (P) – temperature (T) conditions. The variation of saturation index of gypsum and anhydrite in saline conditions were attempted in the CaSO₄-NaCl-H₂O system by (1955) [34] and the study concluded that the mineral transition temperature is decreased by the enhancement of groundwater salinity. The equilibrium temperature of gypsum–anhydrite in NaCl solution was estimated by [35], their transformation in saline aqueous solution was determined by [36]. Laboratory studies were reported with regard to CaSO₄ system [37] and CaSO₄-Na₂SO₄-H₂O system by [38]. The transformation of gypsum to anhydrite was studied by (1937) [39] in CaSO₄-H₃PO₄-H₂O the system, with the interplay of MgCl and NaCl. The study inferred that anhydrite and gypsum cannot co-exist in Na₂SO₄ waters. The CaSO₄-H₂SO₄-H₂O system shows that simultaneous precipitation of both the salts anhydrite and gypsum do not alter their field of stability [40] studied the CaSO₄-NaCl-H₂O system

and concluded that a minimum value of 0.75 is required for the activity of brine water to form the calcium sulfate deposits. The activity of brine water with CaSO₄ varies between 0.90 and 0.96 for a change in temperature of 25°C to 70°C. Similarly, it is to be noted that the silica at lower temperatures is comparatively more saturated with quartz, silica and chalcedony. At higher temperatures, the clinoenstatite and forsterite show an increase in saturation. There is a decrease in pH with temperature, as the silica dissolution is favoured in alkali environment [41,42]. Later the dissolved silica is associated with cation to form clinoenstatites and forsterite. Hence it is inferred that the variation in temperature governs the pH and the dissolution of minerals.

5. Conclusion

The study on the thermodynamic states of groundwater samples show that the coastal groundwater are predominantly stable with the kaolinite field as reflected by the silicate stability plots. The saturation index of the minerals observed in the study are in the following order, SI_D > SI_C > SI_{Ar} > SI_{Mg} > SI_{Qtz} > SI_{Chal} > SI_{Gy} > SI_{An} > SI_{Sio2} > SI_{CE} > SI_{Ha} > SI_{Fo}. The temperature simulation from 19°C to 28°C, shows an increase in saturation sates with temperature in clinoenstatite, forsterite, dolomite, magnesite minerals. Except for three samples the saturation index of calcite and aragonite were observed to increase with temperature. The anomaly

was due to the pH and Mg concentration in these samples. pH, ionic strength, saturation index of gypsum and silica decreased with increase in temperature. Anhydrite showed a mixed behaviour with most of the low saturation states observed around 21°C–24°C. Ca being the common ion for both the carbonate and the sulphate minerals, tend to be more associated with the Ca, Mg carbonates like dolomite and magnesite. The saturation states are governed by the availability of ions and the P-T conditions. The anhydrite and gypsum saturation states are also inferred to be affected by the salinity, presence of H₂S and the pH of the groundwater. The spatial variation of the saturation indices show that the samples adjacent to the open sea are more saturated than the samples adjacent to the bay, especially with respect to anhydrite. Though higher concentration of certain ions are observed in the samples they do not tend to saturate either due to the non-availability of the associated ions or due to P-T conditions. This study provides a key understanding on the nature of water to form precipitates or scales on the pipe line either during the extraction or during transportation when there is a variation in temperature.

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