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Research Article

Hydrochemistry and Mineral Saturation of Thermal Spring in Ramsar Area, North of Iran

Mohamad Reza Ansari [1] and Sahar Sartipi Yarahmadi [2*]
[1]Assistant Professor of Geoscience department,
Parand Branch, Islamic Azad University (IAU), Parand, Iran.
[2*]M.Sc of Environmental department,
Tonekabon Branch, Islamic Azad University (IAU), Tonekabon, Iran.
*Corresponding Author: Sahar Sartipi Yarahmadi, Email: sartipi.sahar65@gmail.com

ABSTRACT:
Ramsar area is located across and between Alborze Mountain and Caspine Sea in North of Iran. About 30 spas are located south of the Ramsar and Sadatshar town. They are almost in between 20 to 70 m elevation. Paleozoic, Mesozoic and Tertiary rocks and alluvial deposit are exposed around the Ramsar area. In tertiary, acidic Plutonism was active and intrusion into the Paleozoic and Mesozoic formations. Quaternary and Alluvium deposits are exposed and extending on the Jurassic formations in Ramsar plain and have thickness lower than 10 m in show springs. The annual precipitation in the Ramsar region is 976 mm. There has not any proper Thermal spring management in Ramsar area yet. This could post some serious problem on improper management of Thermal spring sites, where its environment has been put into jeopardy. This study aims to provide a way to classify the Thermal springs in Ramsar area. The result of this study help in the classification of Thermal spring sites for official planning improvement of administration and sustainable development of natural resources of the area.The study makes use of the Department Applied Geosciences in Islamic Azad University and GIS data of a total of 9 Thermal springs in the attempt to set up a classification system of Thermal springs in Ramsar area. These data include surface temperature, conductivity, alkalinity, acidity, TDS, pH values, Ca, Cl, Fe, K, Mg, Mn, Na, SiO2, SO4 contents, their locations, usages and other relevant information.The surface temperature of Thermal springs are between 19^{o}C – 65^{o}C and SiO2 geothermometer shows estimated reservoir temperature range from 86 ^{o} C – 96 ^{o} C. Most of the water from these Thermal springs is relatively turbidness and their composition is sodium choloride. The Thermal springs in this area generally exhibit high SiO2 and Na content; strong smell of sulfur. In addition, there are 30 Thermal springs located in Ramsar area and that show high concentration of Cl, Ca, Na, K and Mg.There are two major criteria used in the classification system in this study, temperature and their usage. On the basis of temperature, there are three classes of Thermal springs in Ramsar area: hyperthermal spring (10 %, 50-99o C); thermal spring (80%, 30-50o C). There are 4 types of usage classification: swimming pools, Tourism, space heating and drying of organic materials. There is one class achieved on the basis of pH values, all of Thermal springs exhibit weak acids.

Keywords: Thermal spring, thermal water, chemical composition, classification

1. INTRODUCTION:
Ramsar area is located across and between Alborze Mountain and Caspine Sea in North of Iran. About 30 spas are located south of the Ramsar and Sadatshar town. They are almost in between 20 to 70 m elevation. Paleozoic, Mesozoic and Tertiary rocks and alluvial deposit are exposed around the Ramsar area. Quaternary and Alluvium deposits are exposed and extending on the Jurassic formations in Ramsar plain and is composed of fan and debris deposits and have thickness lower than 10 m in show springs. The annual precipitation in the Ramsar region is 976 mm. In tertiary, acidic Plutonism was active and intrusion into the Paleozoic and Cenozoic formations. (Fig. 1) Khazar fault is normally and longest fault in south of Caspine sea, and has NW-

SE trend, in junction locally fault with N-S trend and khazar fault thermal waters issue through these faults.(Ansari et al 2009)
There are increasing of usage of natural resources due to the population growth rate and convenient instruments used in everyday life. So there will be serious problems on sustainability and environment. Geothermal resources are one of natural resources, thus sustainable management and wise-used are needed. It is necessary to have information of all geothermal resources in this area. These data provided by BPJ programming (Bashgah Pazhooheshgaran Javan Islamic Azad university of Iran), investigation of thermal spring in Ramsar area. This paper will informs about thermal spring geological settings, geology, chemical characteristics of Thermal springs and some classifications of Thermal springs in Ramsar area.

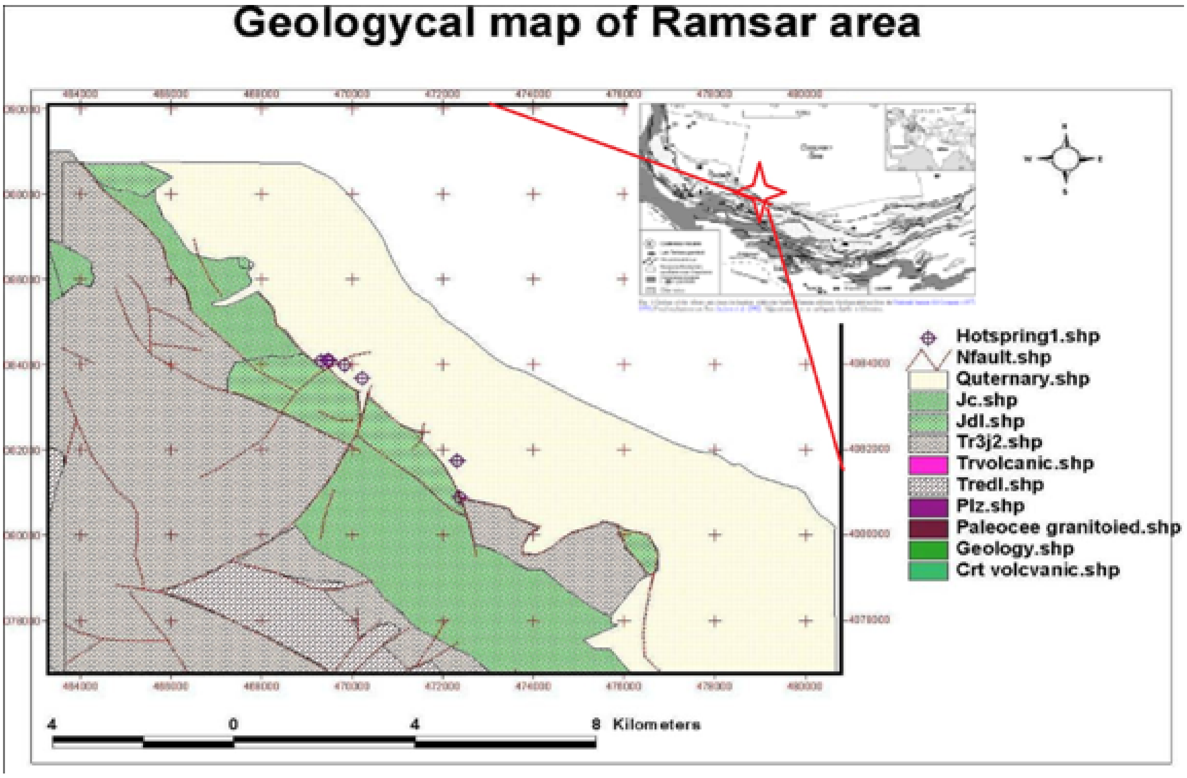


Figure1: Geological map of Ramsar area.

2.ANALYTICAL METHODS

Water samples were collected from thermal and cold springs on the Ramsar and Sadat shahr area in Alborz mountain. The fluid temperatures range of these springs are between 19° and 65 °C. Physicochemical parameters of the waters, such as temperature, pH and electrical conductivity (EC), were measured in the field, while calcium, potassium, magnesium, sodium, bicarbonate, sulfate and chloride ions were measured in the laboratory using standard titration and Inductively Coupled Plasma (ICP) methods.Trace elements Li, Cs, Rb and B, and Br were measured using ICP-MS. The water samples were analysed in ACME lab, In Canada. The mineral assemblages were analyzed by optical methods in combination with X-ray (powder) diffraction analysis at the Madar zamin Lab, In Iran.

3. CHEMICAL CHARACTERISTICS AND DISTRIBUTION

There are a total of 9 Thermal springs in Ramsar area. The assay of these Thermal springs consist of surface temperature, conductivity, alkalinity, TDS, pH values, H2S, Ca, Cl, Fe, K, Mg, Mn, Na, SiO2 and SO4 contents. The detail of some items is as follow;

3.1 Surface Temperature: The temperature measured from a total of 9 Thermal springs range between 19C and 65o C. The average temperature is 44 o C. The Standard deviation (SD.) is 9 and median (or 50th %) is 45 o C. The Thermal springs which, temperature are higher than 65o C mostly located in Ramsar town, probably related to the fault system.

3.2 Alkalinity (HCO3):A total of 9 assay of thermal water show HCO3 content ranging from 442.86 and7731.08 mg/l. The average is 1499 mg/l, with an SD. of 24.8 and the median value of 785.56 mg/l. Thermal springs in the Western part of this area have HCO3 content higher than the median values. It may have been cause by the chemical reaction while thermal water flows through wall rocks which shale is bearing coal lens, limestone, dolometic-limestone and dolomite.

3.3 TDS (Total dissolved solids):The 9 thermal water samples have TDS contents between 1356 and 16720 mg/l. The average is 11210.11 mg/l; the median is 13500 mg/l. Most of Thermal springs in this area have high TDS (>1,500 mg/l) especially those Thermal springs located near the junction of NW-SE and N-S faults in Ramsar area.

3. 4 pH : The pH values of 9 Thermal springs show a range between 5.5 and 6, with an average of 5.8, the median value of 6. Most of Thermal springs are weak acid spring.

3.5 Ca, Cl, K, Mg and Na:The Ca content of thermal water has a range between 285948 and 3635254 µg/l. The average is 922999.7 µg/l with an SD, Of 319.23 and the median value of 726545 µg/l. One of the reasons of high Ca is flowing through mineralized veins related with Tertiary plutonism and carbonate units of thermal water in Ramsar region. The Cl content of thermal waters has an assay 16 to 62903 µg/l. The average is about 12636.7 µg/l, with an SD. of 155.06 and the median value of 8961 µg/l. Following Groundwater acts in 1991; standard drinking has Cl content less than 200 mg/l, brackish water has Cl content about 1,400– 3,000 mg/l and salty water has Cl more than 3,000 mg/l. Most of Thermal springs in this area have Cl content less than 200 mg/l.The K content of thermal water is between 6765 and 187925 µg/l. The average is about 51132.33 µg/l, with an SD. of 122.36 and a median value of 42012 µg/l. Most of thermal waters have medium K content. The Mg content of thermal water has arranged between 120886 and 893703 µg/l. The average is about 249722.4 µg/l., with an SD. Of 127.36 and the median value of 202128.The Na content of thermal water shows ranging from 35789 to 32600000 µg/l. The average is 6705330 µg/l, with an SD. Of 123.89 and the median value of 4942747 µg/l.The contents of Ca, Cl, K and Mg in thermal water are high concentration of these elements in some Thermal springs.

3.6 Fe (iron) : The Fe content of 9 Thermal springs has range from 754 to8849 µg/l. The average is 2287.33 µg/l, the SD is 138.334 and the median is 1311 µg/l. Most of them have Fe content higher than 1 mg/l; this value is the standard drinking water of Groundwater acts in 1991. To solve high Fe content in the water is to fill oxygen in to water, and related with infiltration mature water and interaction with mineralized and Alteration veins.

3.7 Mn (manganese) : The Mn content of 9 Thermal spring samples range from 37.43 to463.26 µg/l. The average is about 92 µg/l, the SD is 91.199 and the median value equals to 46.85 µg/l.

3.8 SiO2 (silica) : A total of 9 assay of thermal water show SiO2 content from 2.15 to 19 mg/l. The average is 4.6 mg/l, and a median value of 2.52 mg/l. Thermal springs have low SiO2 content in this area.

3.9 SO4 (sulfate) :The SO4 content of 9 Thermal springs has a range between 152 mg/l and 247.2 mg/l. The average is 204.13 mg/l, with an SD. of 8.06 and a median value of 216.71mg/l. The Thermal springs having high SO4 are mostly located in the spas.

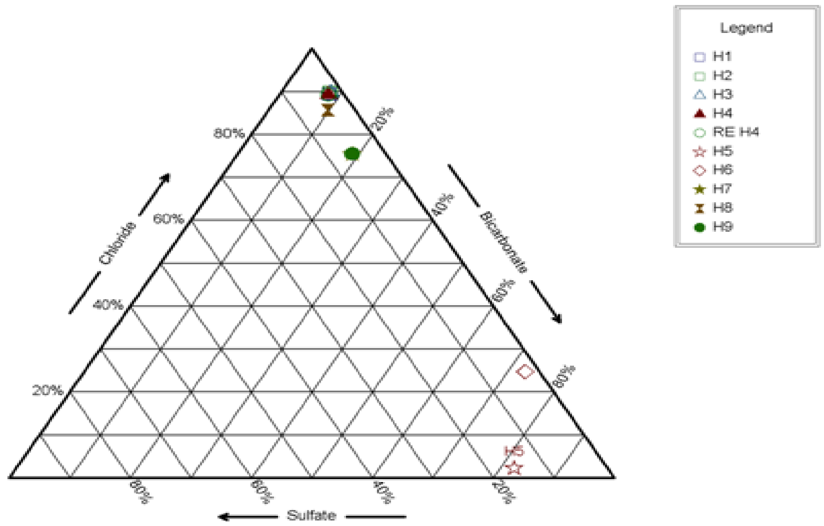


Figure 2 : Cl-SO4-HCO3 triangular diagram of thermal spring in Ramsar.

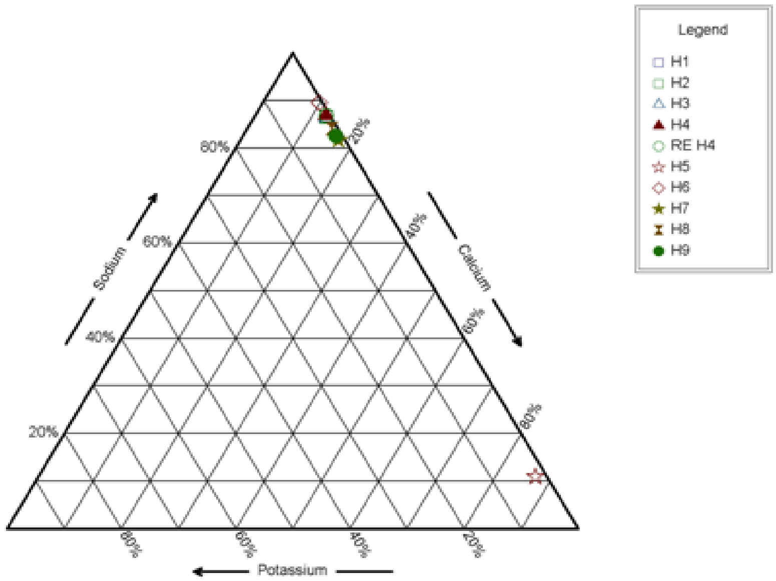


Figure 3 : Ca-Na-K diagram of thermal spring in Ramsar

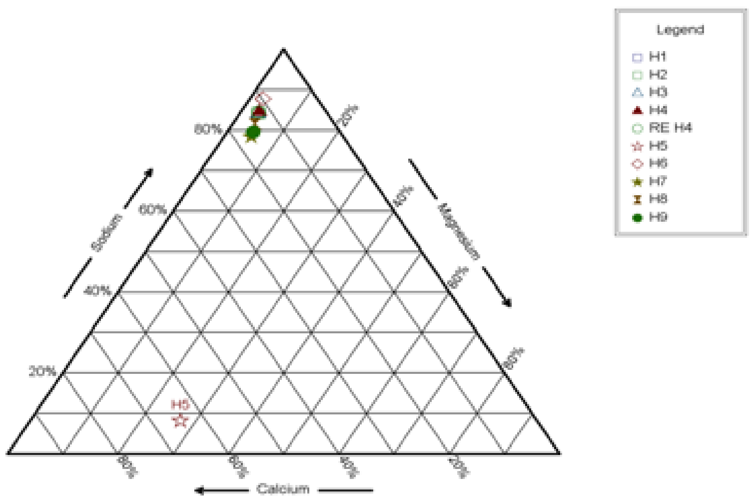


Figure 4 : Ca-Na-Mg diagram of thermal spring in Ramsar.

4. GEOTHERMOMETRY

Cl-SO4-HCO3 triangular diagram (Giggenbach, 1991) in Figure 2, Ca-Na-K equilibrium triangular diagram and Ca-Na-Mg equilibrium triangular diagram (modified from Hen,1959; Giggenbach, 1991 ; Arnorsson,S.2000) in Figure 3and Figure 4 present property of thermal water in the Ramsar area. Cl-SO4-HCO3 triangular diagram shows that some of thermal water are located near the bicarbonate region such as Safarod and Absiah thermal springs and they are known as (Peripheral Waters) due to absorobtion of deep CO2 and to the mixing with shallower water. Most of thermal water property is saline water and located near the Cl content also related with Mature water area. In Figure 3 and Figure 4 There are approximately 90% of total numbers of Thermal springs water samples show high Na content . On the basis of result from the chemical analysis of SiO2, Na, K, Ca and triangular geothermometers(Figure 5) were then calculated to estimate reservoir temperature (Fournier, 1981), (Giggenbach 1991). The estimated reservoir temperatures from the equations above are summarized in Table 1.Estimated temperature from triangular geothermometers (Giggenbach 1991), is approximately the same as the temperature obtained from quartz no stream loss , quartz maximum stream loss, where as Na-K-Ca geothermometer shows higher estimate temperature and the highest estimate temperature is Na/K and Na-K-Ca-Mg geothermometer, and triangular geothermometer is shown reservoir temperature between 100 ºc to 120 ºc .

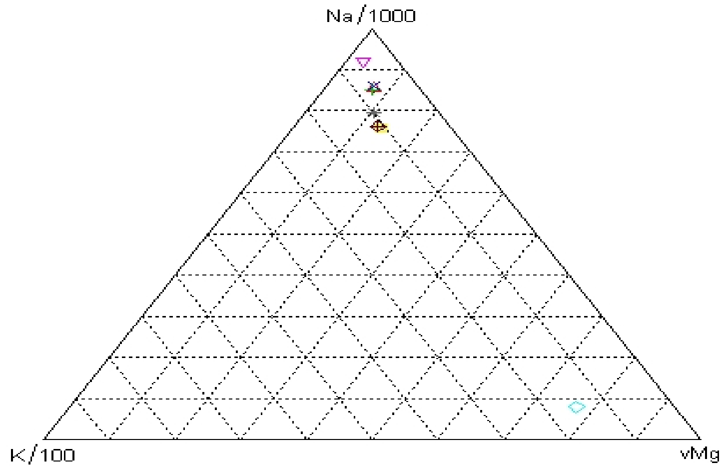


Figure 5 :Na/1000-K/100-√Mg diagram of thermal spring in Ramsar.

Table 1: estimated reservoir temperature from 9 type of geothermometer .

	1	2	3	4	5	6	7	8	9
	Qtz no	Qtz Max	Chalcedony	α-Ciristobalite	Na-K	Na-K-Ca	Na-K-Ca-Mg	Mg-Li	Na-Li
H1	88.744˚c	91.219˚c	57.929˚c	38.66˚c	<150˚c	95.318˚c	>350˚c	38.347˚c	38.347˚c
H2	88.868˚c	91.327˚c	58.061˚c	38.781˚c	<150˚c	94.391˚c	>350˚c	38.71˚c	50.304˚
H3	93.248˚c	95.14˚c	62.72˚c	43.044˚c	<150˚c	95.462˚c	>350˚c	39.109˚c	50.821˚c
H4	92.005˚c	94.059˚c	61.396˚c	41.832˚c	<150˚c	92.125˚c	>350˚c	38.386˚c	48.489˚c
H5	85.9˚c	88.737˚c	54.914˚c	35.809˚c	278.41˚c	`	<0˚c	13.571˚c	181.85˚c
H6	83.558˚c	86.7˚c	52.436˚c	33.6˚c	<150˚c	94.081˚c	>350˚c	55˚c	41.647˚c
H7	94˚c	96˚c	63˚c	44˚c	<150˚c	99.543˚c	>350˚c	55˚c	41.647˚c
H8	94.551˚c	96.272˚c	64.11˚c	44.03˚c	<150˚c	195˚c	>350˚c	47˚c	75˚c
H9	91.4˚c	93.5˚c	60.7˚c	41˚c	<150˚c	107˚c	>350˚c	45˚c	78˚c

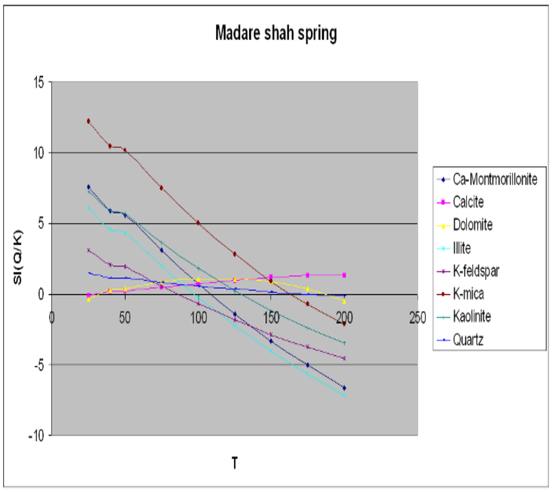
1)Fournier (1977); 2) Fournier (1977); 1) Fournier (1977); 2) Fournier (1977);5) Fournier & potter (1982); 6) Fournier (1973).

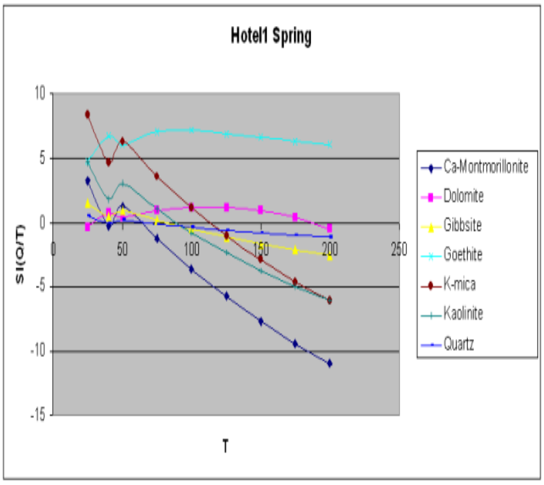
4.1 Mineral saturation and estimated subsurface temperatures

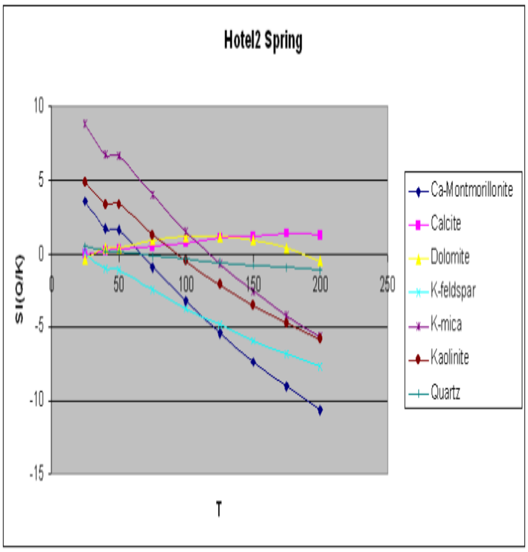
Mineral equilibrium calculations are important to predict which minerals may precipitate during the extraction and use of the waters. A saturation index of zero indicates that thermodynamic equilibrium exists with the solid phase of the relevant mineral. A negative (-) or a positive (+) index indicates undersaturation and oversaturation, respectively. Mineral saturation indices of hydrothermal minerals, which are possibly present in the reservoirs of the geothermal systems, were calculated at outlet temperature and pH by the PHEERQCi computer code.

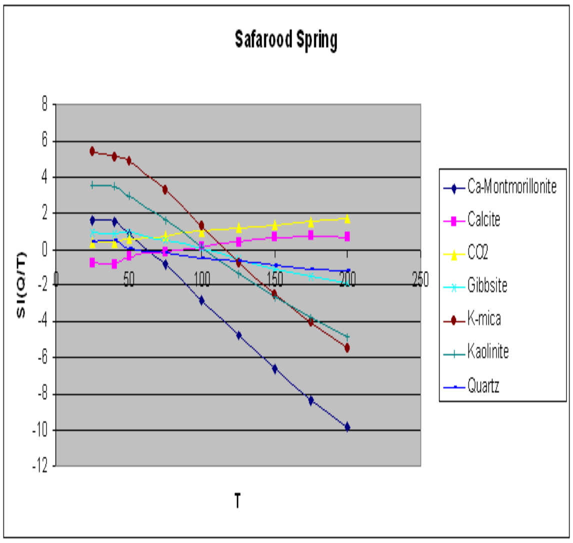
In these thermal springs we see that Hematite is undersaturated at outlet temperature and pH values for all of the waters in the study area.

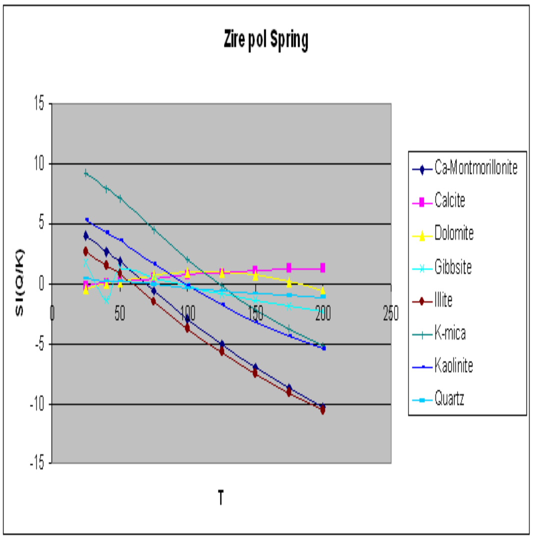
Calcite, Aragonite , Dolomite , Albite , Illite , Ca-montmorillonite , Quartz , Gibbsite , K-Feldspar , Kaolinite , Barite minerals are mostly oversaturated or undersaturated in all springs. Siderite , Alonite , Strontanite are over saturated in Abesiah and Hotel1 spring : Due to high Fe^{2+} concentration and abundance of CO_2 in fluid, and dissociation of CO_2 and occur mixing process and rising adiabatic at near surface , Siderit is oversaturate only in Abesiah spring. Interaction between water and mineral vein solves stransium and due to high CO_2 create Strontanite in Abesiah spring. Combination of Sulphate with K^+ and Al lead to form Alonite in Hotel 1 spring. In the studied water samples, the absence of gypsum may be a result of Ca-montmorillonite precipitation Saturation indices can be used as geothermometers by plotting temperature versus Saturation Index (SI) diagrams. Ansari (2009) proposed that if the SI with respect to several minerals converges to zero at a particular temperature, this temperature corresponds to the most likely mineral solution equilibrium temperature or at least the equilibrium temperature of that particular water. Fig. 5 shows the SI with respect to selected hydrothermal minerals versus temperature for the thermal waters of the Ramsar geothermal area. SIs was initially calculated by using the PHEERQCi computer code at outlet temperature and measured pH. Temperature was then changed iteratively and the saturation indices recomputed. Saturation indices for each mineral were then plotted versus temperature and trend curves depicted. Crossing of the lines for several minerals below (conductive cooling) or above (rising or boiling adiabatic) the zero may indicate admixtures of waters at various temperatures, on the other hand, crossing in some point, indicate plurality of mixing process. We are suggesting 70º to 150ºC temperature for thermal source of Ramsar.

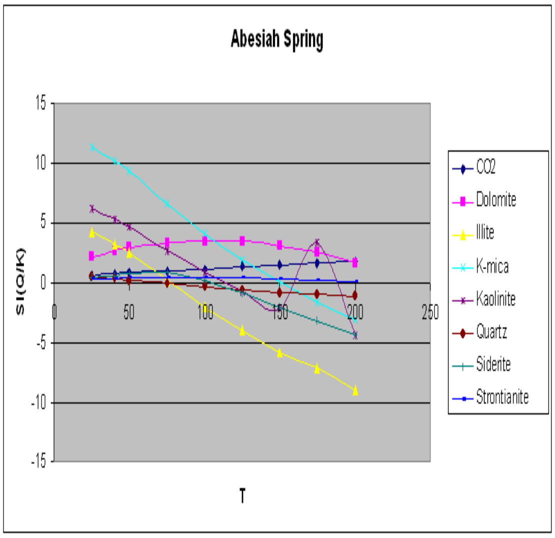


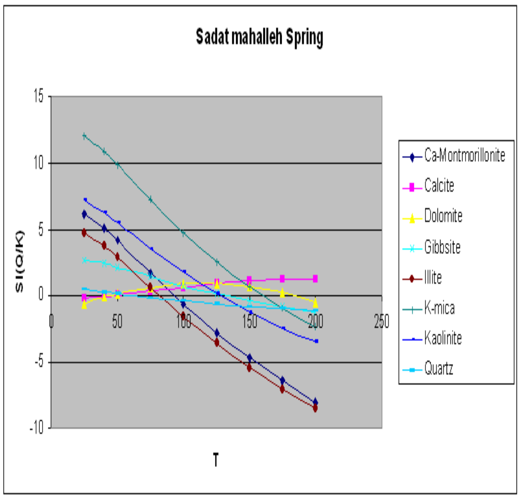


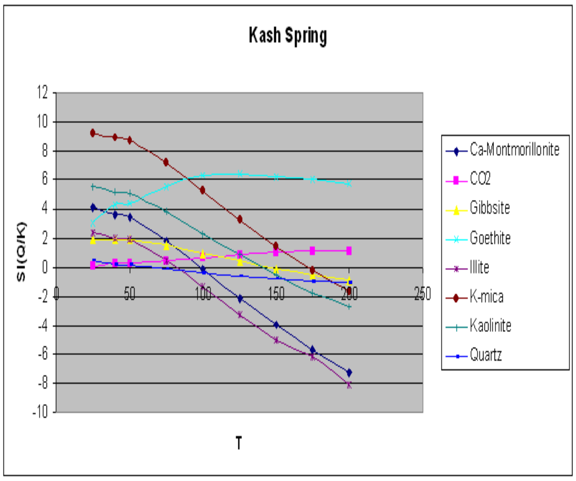

Hotel2 Spring
SI(Q/K)
T
Ca-Montmorillonite
Calcite
Dolomite
K-feldspar
K-mica
Kaolinite
Quartz


Safarood Spring
SI(Q/T)
T
Ca-Montmorillonite
Calcite
CO2
Gibbsite
K-mica
Kaolinite
Quartz


Zire pol Spring
SI(Q/K)
T
Ca-Montmorillonite
Calcite
Dolomite
Gibbsite
Illite
K-mica
Kaolinite
Quartz


Abesiah Spring
SI(Q/K)
T
CO2
Dolomite
Illite
K-mica
Kaolinite
Quartz
Sidente
Strontianite


Sadat mahalleh Spring
SI(Q/K)
T
Ca-Montmorillonite
Calcite
Dolomite
Gibbsite
Illite
K-mica
Kaolinite
Quartz


Kash Spring
SI(Q/K)
T
Ca-Montmorillonite
CO2
Gibbsite
Goethite
Illite
K-mica
Kaolinite
Quartz

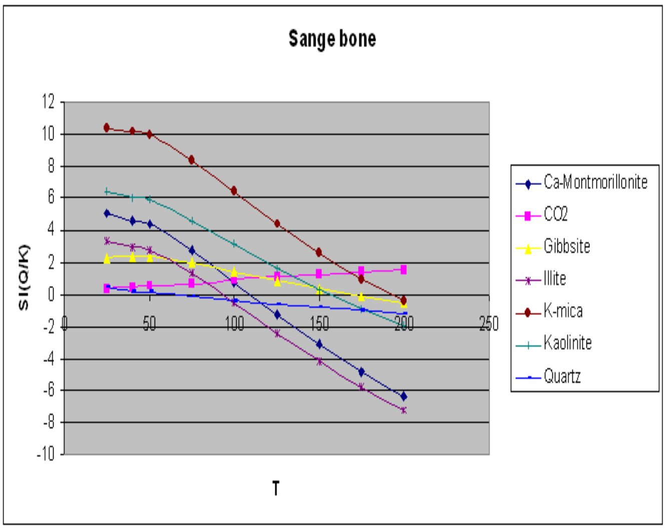


Figure 5: Mineral equilibrium diagrams for the hot water Ramsar area; the saturation index was calculated with: PHEERQCi.

5. CLASSIFICATION OF THERMAL SPRING.

There are many criteria to classify Thermal springs such as temperature, pH, chemical composition etc. These criteria depend on purpose or object of classification. The object of these classifications is to sustainable management and development.

5.1 Temperature Classification: There are 3 types of Thermal springs classified by surface temperature as follow;The 7 data of springs in Ramsar indicated that Thermal springs (80%) are thermal springs, where as 1 Thermal springs (10%) are hyperthermal springs.

5.2 pH Classification: Thermal springs in Ramsar have1 classes on the basis of pH. These are weak acid spring . (pH = 4–6).

5.3 Usage Classification: There are 3 types of this classification: Electric power generation plant, swimming pool and Tourism, House heating and Greenhouses. There are approximately 13% of Thermal springs used in tourism purpose. The Electric power generation plant of Thermal springs in Ramsar is approximately 70%, where 17% of Thermal springs in this area use to House heating and Greenhouses. It is useful to know status of all Thermal springs, if sustainable development of geothermal are needed.

6. CONCLUSION

Most of Thermal springs in Ramsar are classified in sodium chloride; some of them are calcium sulfate water. In the thermal water generally exhibits strong smell of sulfur and high SiO2 contents. The surface temperature is between 19oC – 65oC. The SiO2 geothermometer shows estimated reservoir temperature range from 86 o C – 96o C. here are two types of Thermal spring classification system; temperature and geothermal usage. On the basis of temperature, there are three classes of Thermal springs in Ramsar: 10 % of Thermal spring is hyperthermal spring (50- 99o C) and 80% show thermal spring (30-50o C). The last classification is geothermal usage. They are classified in 3 types: There are approximately 13% of Thermal springs used in tourism purpose. The Electric power generation plant of Thermal springs in Ramsar is approximately 70%, where 17% of Thermal springs in this area use to House heating and Greenhouses. Extremity, suggestion to exploration to deep(reservoir > 1000 m depth), is essential for assessment of deep reservoir potential and identifying the up flow zone. The present discharge may be used for direct heat uses viz. spa, greenhouse cultivation, food industry and tourist attraction. So, this study evaluates and assesses the hydrogeological and hydrogeochemical properties, chemical geothermometers, and the state of mineral saturation of the thermal springs in Ramsar geothermal fields. The heat source is probably a high geothermal gradient resulting from a young tectonic regime. Occurrence of the thermal springs is spatially related to the young normal faults. Meteoric waters recharge the reservoir rocks, are heated at depth with increasing geothermal gradient, and circulate to the surface through the fractures and faults by convection, emerging as springs.

Different plots of water chemistry suggest thermal and cold springs are mature water and in equilibrium with the host rock. The high Cl content, relatively low HCO_3 content and moderate temperature indicate that the most probable mechanism for low Mg content is mixing with shallow cold groundwater. Conservative elements indicate that the analysed water has similar origin and the difference in concentration is due to dilution of thermal water with almost shallow fresh groundwater, not affecting the elements, proportions. Also, the constant ratios of the conservative elements with respect to Cl concentration indicate that thermal waters have been diluted by shallow waters of meteoric origin. The results demonstrate that thermal waters have reached chemical equilibrium with the host rocks. Therefore, because of the maturity and slightly acidity of the thermal waters, the temperatures inferred from geothermometer data are reliable. High Cl concentration and slightly acid springs and other evidences, are indicative of a mature hydrothermal water system in Ramsar area.

The saturation indices (SI) of waters at outlet temperature and measured pH indicate that all of the waters are oversaturated with respect to Hematite. Calcite, Aragonite , Dolomite , Albite , Illite , Ca-montmorillonite , Quartz , Gibbsite , K-Feldspar ,K-mica , Kaolinite , Barite minerals are mostly oversaturated or under saturated in all springs. Siderite, Alonite , Strontanite are over saturated in Abesiah and Hotel1 spring. Mineral saturation states show that Quartz (Quartz and Qartz steam loss) minerals are most likely to cause scaling during the extraction and use of waters. Results obtained from chemical geothermometers, and the use of ternary diagrams and mineral equilibrium diagrams indicate reservoir temperatures between 83.558°C to 96.279°C. Results showed that geothermal fluids of 83.558°C to 96.279°C may be obtained from springs in the study area. This fluid can be used in an integrated system which includes district and greenhouse heating, spas, fishing and swimming pools and power production.

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