

Hydrochemistry of the Damavand Thermal springs, North of Iran.

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Abstract: North part of Iran hosts a numerous of thermal springs around eastern part of Damavand dormant volcano. Thermal water composition of these springs are natural to weak acid and indicate that sulphate content varies from 95 to 1407 (mg/l), HCO₃ from 167 to 1257 (mg/l), chloride from 10 to 438 (mg/l), Calcium from 129 to 691 (mg/l), sodium from 18 to 229 (mg/l), silica upto 15 (mg/l). Ca is dominate cation and SO₄, HCO₃ are dominate anion, so, Cl- SO₄ -HCO₃ ternary diagram suggests the thermal waters are immature and classify in two type, in type1 Strabaku and Larijan thermal springs have Magmatic steam and steam-heated waters origin, in other hand, in type2 Ask thermal waters relate to Peripheral and shallow water origin, both type show a mixing of magmatic gases and volcanic steams with shallow ground water. Schoeller semi-logarithmic diagram confirm all the thermal waters have similar chemical characteristics to cold water. Because of waters immaturity, temperatures in the deep reservoir in Damavand area cannot be estimated clearly, Thus, Deep reserve temperature calculated by Quartz and Na-K geothermometers, so, Quartz geothermometer shown a range of reservoir temperatures from 53 °C to 94 ° and Na-K geothermometr, shown a range of reservoir temperatures from 232 °C to 265 °C.

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1. Introduction

Numerous thermal and cold springs are located in active volcanic regions all over the world, as a result of eruptive events, as well as obvious manifestations of long-lived hydrothermal systems. The temperature and rate of discharge of thermal springs depend on factors such as the rate at which water circulates through the system of underground channel ways, the amount of heat supplied at depth, and the extent of dilution of the heated water by cold ground water near the surface (Shakeri et al., 2008). These springs are frequently developed as spas and bathing facilities, improving social and economic well-being. Other useful applications of thermal springs in volcanic regions are related to direct application of heat production for domestic use, greenhouse heat supply, and power production. The applications depend on the discharge volume and temperature of geothermal resources (Wohletz and Heiken, 1992). Numerous studies have been conducted in active volcanic regions worldwide (Giggenbach, 1997a,b; Valentino et al., 1999; Varekamp et al., 2001). The geochemistry of thermal waters has been used by many authors as a useful tool for volcanic activity monitoring (e.g. Oskarsson, 1995; Shakeri et al., 2008). Extensive areas of Iran are made up of Tertiary volcanic rock in a long belt from Turkey to Pakistan. According to the geological information, geothermal resources are available throughout Iran in a variety of geothermal form and settings with thermal springs. One of the major tasks in the exploration of geothermal resources is to

estimate subsurface temperature in the reservoir from the geochemical composition of thermal springs. During the last few decades, various geochemical geothermometers applicable under different conditions have been developed (e.g. Fournier and Truesdell, 1973; Truesdell and Fournier, 1977; Fournier, 1977; Fournier and Potter, 1979; Arnorsson, 1983; Tonani, 1980; Fouillac and Michard, 1981; Giggenbach et al., 1983; Giggenbach, 1988; Giggenbach and Goguel, 1989; Kharaka and Mariner, 1989; Ahmad et al., 2002). The chemical composition of deep groundwaters can be used to explain the processes and precipitation of minerals, ion exchange, mixing) occurring during their generation at depth and/or during their rise to the surface. If chemical equilibrium between groundwater and rock is assumed to be attained in a deep-reservoir and the chemical re-equilibrium has not been attained during ascent, the temperature of the deep-reservoir can be estimated by applying geothermometers to the chemical composition of water outflowing to the surface (Hyeon-Su Choi et al., 2005). Damavand stratovolcano is one of the largest geothermal fields located in central Alborz Mountains of northern part of Iran about 150 km north-east of Tehran city. Several surveys are already carried out in this area (Davidson et al., 2004; Liotard et al., 2008; Jung et al., 1976; Brousse and Moine-Vaziri, 1982; Aftabi and Atapour, 2000; Mehdizadeh et al., 2002; Mirnejad et al., 2010; ENEL, 1983; Fotouhi and Noorollahi, 2000). The studies mainly focused on geological, petrological, environmental, geochemical, and

hydrothermal, hydrogeological and geothermal aspects of the area. The present study is aimed at defining the hydrochemistry of the thermal springs around the Damavand volcano, evaluation of geothermal fluids, estimating reservoir temperatures of the thermal waters. The final results can be used to plan future development of the geothermal resources on the Damavand area.

2. Geologic setting

The Alborz Mountain Range is a 600 km long and 100-km-wide east–west trending fold and thrust belt that stretches across northern Iran and south of the Caspian Sea (Fig. 1). The bedrock consists of a Paleozoic–Mesozoic passive-margin sedimentary sequence with few volcanic rocks, overlain, in the south, by Tertiary volcanics and sediments. The Alborz is seismically active as it accommodates near 25% of the whole Arabian–Eurasian convergence in Iran (Vernant et al., 2004). Recent fault movements are mainly reverse with range parallel sinistral component (Jackson et al., 2002) although sense of the strike-slip offsets was just the opposite before ca. 5±2 Ma (Axen et al., 2001; Mirnejad et al., 2010). According to (Sengör et al., 1993; Zanchi et al., 2006), the Alborz range results from different tectonic events, which occurred during two major orogenic cycles: (1) the Late Triassic (Cimmerian) demise of the Paleotethys and collision of the Iranian block with Eurasia; and (2) the post-Neo-Tethys, intraplate deformation related to the convergence of the Arabian and the Eurasian plates. The final closure of Neo-Tethys and suturing of the Afro-Arabian and Iranian plates are recorded in the Zagros orogenic belt, part of the Alpine–Himalayan orogenic belt that extends from Europe, through Iran, to western Pakistan (Stöcklin, 1968; Braud and Ricou, 1971; Berberian and King, 1981; Bina et al., 1986; Alavi, 1994; Agard et al., 2005; Mirnejad et al., 2010).

2.1. Damavand Volcano and Related Thermal Springs

Damavand volcano, located in the central part of Alborz Mountains in North of Iran, is a large composite cone that consists of mainly trachyandesite lava flows, and subordinate pyroclastic materials (Davidson et al., 2004). The immediate basement to Damavand volcano in the Alborz Mountains are a folded and thrust-faulted passive-margin sedimentary sequence of carbonate, siliciclastic, and volcanic rocks. Young normal faulting attributed to transtension has been documented in central Alborz (Ritz et al., 2006) and around the Damavand (Hassanzadeh et al., 2006; Omidian, 2007; Mirnejad et al., 2010). Paleozoic, Mesozoic sedimentary rocks, Quaternary volcanic- pyroclastic rocks and alluvial sequence of shale, sandstone, marl, carbonate formations and with alluvial deposits are exposed and

extending on the Jurassic formations around the Damavand volcano. Jurassic deposits are composed of sandstone, silt, shale bearing coal lens, marl, and limestone and dolomite units. Thus, normal and thrust faults cause, thermal and cold springs issue through these rocks and structures. Some spas and thermal springs such as Strabaku thermal springs, Ask e Zagh thermal spring, Ask e Sar e Pol thermal spring, Ask e Nadali thermal spring, Ask e Pashnak thermal spring, Larijan thermal spring and Polor cold spring are located around east and north-east side of the Damavand volcano. Haraz River is located east-northeast wards of Damavand volcano and recharge by surface and ground water derived from Alborz Mountains.

3. Material and Methods

Water samples from thermal springs were collected from most of the springs for chemical analysis and physicochemical parameters i.e., 2009-2010. Strabaku, Ask and Larijan thermal springs could be approached during the first sampling time. Collected water samples were stored in pre-cleaned, 60 mL HDPE bottles with screw caps, after being filtered through 0.45 µm cellulose nitrate membrane filters. Samples for elements analysis were acidified to pH<2 with ultrapure nitric acid. Physico-chemical parameters such as temperature, pH and electrical conductivity were determined 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 in the ACME lab (Vancouver, Canada). Chemical analysis of major, trace (Li, F, Cs, Rb and B) and Rare earth elements in waters was performed within 30 days after sample collection using ICP-AES and ICP-MS in the ACME lab (Vancouver, Canada). The results of the chemical analyses are presented in Table 1.

4. Results and Discussion

Chemical and physical composition data of all samples are given in Table 1. The discharge temperature of the thermal springs of Damavand area varies from 25 to 60 °C while that of the thermal waters of Strabaku have ranges from 31 to 33 °C. Ask thermal springs have almost the same temperature (25 and 32 °C). Larijan hot spring, discharge boiling water with about 60 °C, respectively. All the thermal waters in the area are neutral and/ or weak acidic and have pH values in the range between (5.5- 6.8). These springs have EC values in the range 1100–4000 mS/cm. The analyses show that SO₄ (101–1407 mg/l), HCO₃ (167–1257 mg/l) and Ca (129–691mg/l) are the dominant anion and cation, respectively. Cl (10–438 mg/l), Sodium (18–230mg/l) and potassium (3–29 mg/l) are also significant. On the basis of their chemistry, anion variation such as SO₄ and HCO₃, the

Damavand thermal spring waters can be divided into two groups.

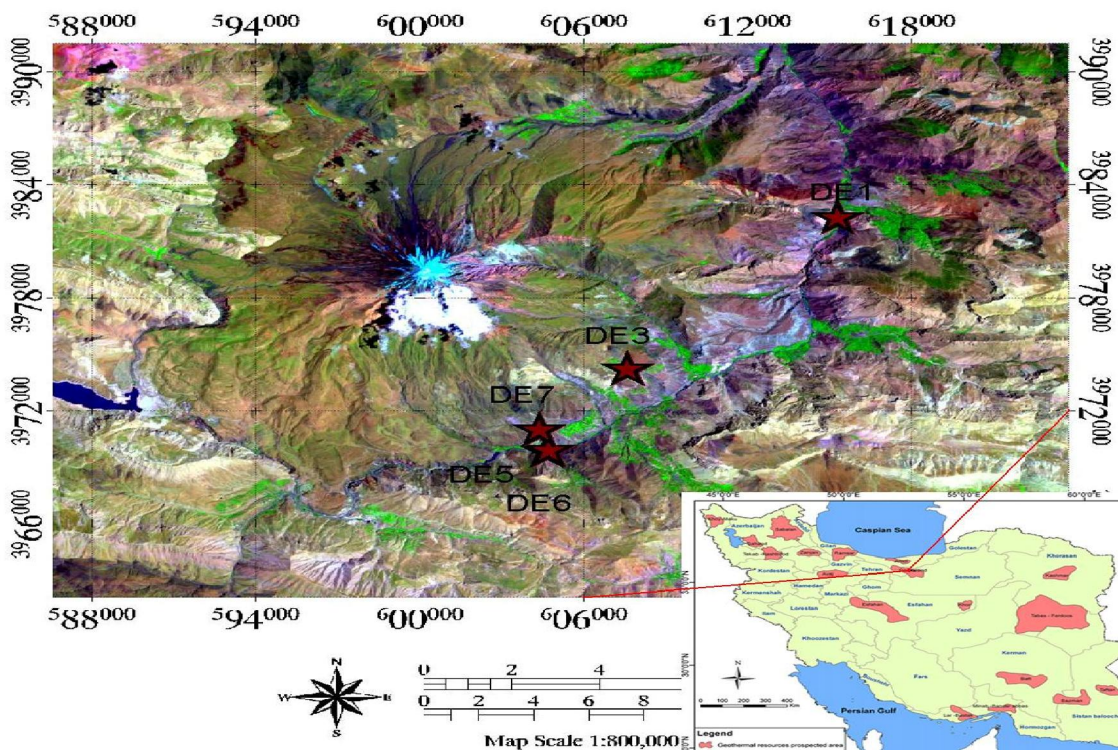


Fig. 1 Landsat RGB color (4, 3, 1) image of Thermal spring around eastern part of Damavand Volcano, with Geothermal resources map of Iran (Yousefi, 2004). DE1 (Strabaku springs), DE3 (Larijan Spring), DE5, DE6, DE7 (Ask springs).

Table 1: Chemical and physical composition data of Thermal springs from Damavand area.												
Spring name	PH	EC	HCO ₃	Cl	SO ₄	k	Na	Mg	Ca	Fe	SiO ₂	Temp
		μs/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	(oC)
Larijan	6.5	1100	167.77	10.64	330.45	3.13	18.85	24.05	129.26	0.9	42	60
Strabaku1	6.1	2700	671.11	166.6	902	13.69	110.58	77.82	444.8	1.5	24	33
Strabaku 2	6	4000	915.15	283.68	1404.8	21.51	165.53	83.9	691.38	1	32.5	32
Strabaku 3	5.5	4000	658.91	383.6	1395.7	21.51	165.53	94.85	637.27	0.65	33	31
Strabaku 4	6.2	4000	686.36	383.68	1406.8	21.51	165.53	84.51	654.3	1.75	33	32
Ask e Nadaali	6.6	3160	1256.8	426.5	101.8	27.3	229.9	3655	376.6	1.2	17.5	28
Ask e Zagh	6.7	3002	1134.7	437.9	98.9	27.3	229.9	67.4	322.6	0.91	15	25
Ask e Sare Pol	6	3111	1238.5	400.7	95.5	29.3	211.5	51.6	370	1.04	16.5	32
Ask e Pashnak	6.8	2600	793	117	106	28	215	731	680	0.5	26.7	31
Polor	7	78	13	0.75	10	5	32	*	*	*	*	5
*: not measured												

The first group consists of waters from near the Damavand volcano and issue through the quaternary volcanic rocks and includes the Strabaku1, Strabaku2, Strabaku3 and Strabaku4 thermal springs and Larijan hot spring. Their waters have EC in the 1100– 4000 μs/cm range, and pH from 5.5 to 6.5.

SO₄ is the dominant anion in this group; major cations are Ca, Mg, Na and with lesser amounts of K. The waters in this group have the highest measured

spring temperatures (31–60 °C). The second group , most of springs includes Ask e Zagh, Ask e Pashnak , Ask e Sar e Pol, Ask e Nadali thermal springs occurs at Jurassic carbonate rocks excepted Ask e Nadali thermal spring which issue in columnar basaltic rocks . Their waters EC and pH range from2600 to 3160 μs/cm and from6to 6.8, respectively. As in the first group, the main anion is HCO₃; the main cations are Ca ,Mg and Na.

4.1. Water Chemistry

The Piper triangular diagram (Fig. 2) shows the major cations and anions are used to investigate the chemistry of thermal waters. Ca is the dominant cation in all cases except two Mg-rich samples (Ask e Pashnak and Ask e Nadali). The relative concentrations of the main anions show that these thermal waters can be classified into two chemical types, i.e. HCO₃ type and SO₄ type. Therefore, most samples range in composition from Ca-HCO₃ or Mg-HCO₃ to Ca-SO₄. These Ca and /or Mg rich compositions are typical of comparatively evolved waters circulating mainly in carbonate and altered volcanic rocks. The relative proportion of Cl, HCO₃ and SO₄ are reported in the diagram Cl-HCO₃-SO₄ (Fig. 3) proposed by (Giggenbach, 1991). This diagram shown all of water samples are immature and haven't deep circulation, enough time for water-rock interaction and dissolution the element into the aquatic system, so, not in equilibrium with the host rock. Most Strabaku and Larijan spring samples plot in the field corresponding to Magmatic steam and steam-heated waters (Fig. 3). Typically these waters are weakly acidic or natural and S due to the absorption of magmatic vapor's by the shallow circulating groundwaters. The proportion S in these waters depends upon the composition of the original magmatic vapour (Giggenbach, 1997a, b; Shakeri et al., 2008). An H₂S smell is also noted in the thermal springs and sulphur deposits, so an input of S-bearing gases from below and subsequent oxidation of reduced-S species to sulfate, as observed in high-temperature geothermal areas (e.g. Giggenbach, 1988, Giggenbach, 1997 a; Giggenbach, 1997 b; Ahmad et al., 2002). In all the thermal waters of Strabaku and Larijan area, SO₄ is the dominant anion and it ranges from 330 to 1407 (mg/l), while HCO₃ varies from 167 to 915 (mg/l), could also explain the transition from HCO₃ to SO₄ waters. The varying SO₄/ HCO₃ ratios of the Ca-rich waters have ranges (1.3-2.1) and could be attributed to the relative with Magmatic steam and steam-heated waters (Fig.3). At Ask area in all the thermal waters HCO₃ is the dominant anion and it ranges from 117 to 426 (mg/l), while SO₄ varies from 95 to 106 (mg/l) and the varying SO₄/ HCO₃ ratios of the Ca and /or Mg-rich waters have ranges (0.064-0.087) and fall into Peripheral and shallow water field and could be attributed to circulation of shallow water in sedimentary and volcanic rocks.

As shown in the Schoeller semi-logarithmic diagram (Fig. 4), cold and thermal waters with similar chemistry give similar peaks. It is clearly seen that the thermal waters have similar chemical characteristics to cold water, In Larijan and Strabaku area thermal spring water have $Ca > (Na+Mg+K)$ and $SO_4 > (HCO_3 + Cl)$ and in Ask area thermal spring water

have $Ca > (Na+Mg+K)$ and $HCO_3 > (SO_4 + Cl)$ excepted Ask e Pashnak and Ask e Nadali springs have $Mg > (Na+ Ca +K)$ and $HCO_3 > (SO_4 + Cl)$. The cold water (Polor cold spring) show similar chemical characteristics from thermal waters.

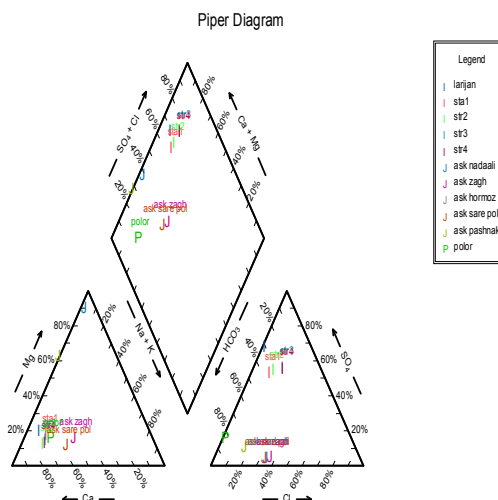


Fig. 2 Distribution of thermal spring waters from Damavand area in Piper triangular diagram.

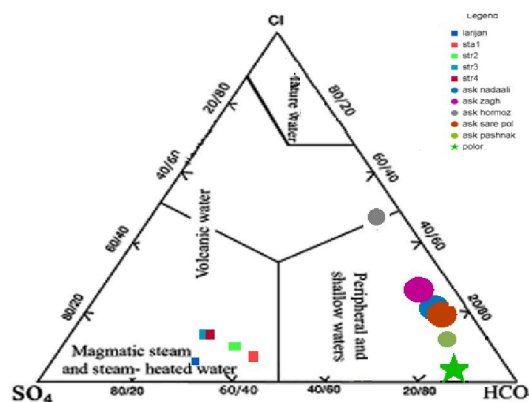


Fig.3 Triangular plot of Cl-HCO₃-SO₄ of thermal spring waters from Damavand area.

As seen in Fig. 4, Larijan and Strabaku thermal waters are depleted in Na+k and Cl and are enriched in SO₄ with respect to cold water, Ask thermal waters are depleted in Na+k and Cl and are enriched in HCO₃, so, the increase of HCO₃ could be explained by the reaction between the dissolved carbon dioxide and host rock that form HCO₃. Variation of element concentrations relative to that of chloride, in geothermal systems chloride can be regarded as a chemically conservative ion (Motyka et al., 1993; Shakeri et al., 2008). Showing the concentration of ions or elements relative to chloride will reveal the changes in the concentration of ions (Shakeri et al., 2008). The relations of the chemical

components in thermal water samples from the study area are presented in Figs. 5. The concentrations of these major ions, EC and temperature were plotted against Cl, which is regarded as the chemical conservative for thermal waters from the study area. The good positive correlations (up to 0.6) between Cl and K, Na, HCO₃ is indicate to similarity of chemical origin, However, there is a poor negative correlation

between Cl and Ca, SO₄, respectively, due to the high proportions of vary magmatic gases and volcanic steams derived from Damavand volcano. Ca and SO₄ have good positive correlations (not shown) and shown similarity in chemical origin or relatively between volcanic gases and hydrothermal alteration of volcanic and sedimentary rocks.

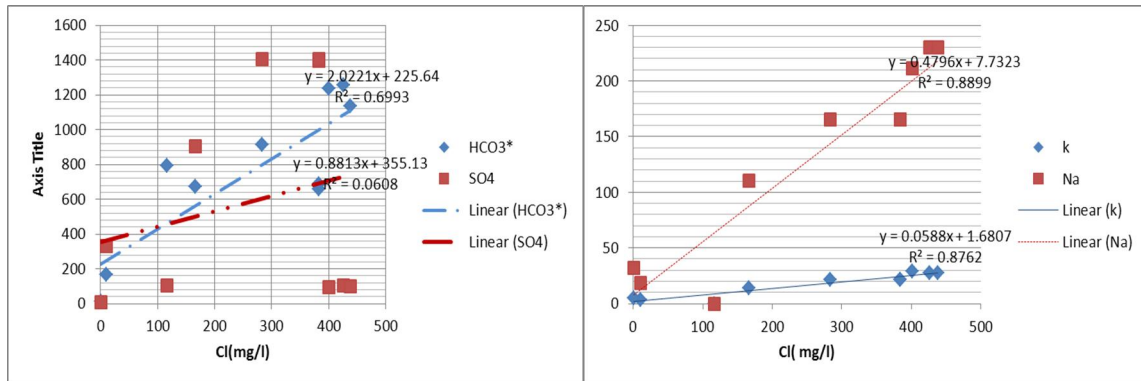


Fig.4 Schoeller semi-logarithmic diagram of cold and thermal waters in Damavand area.

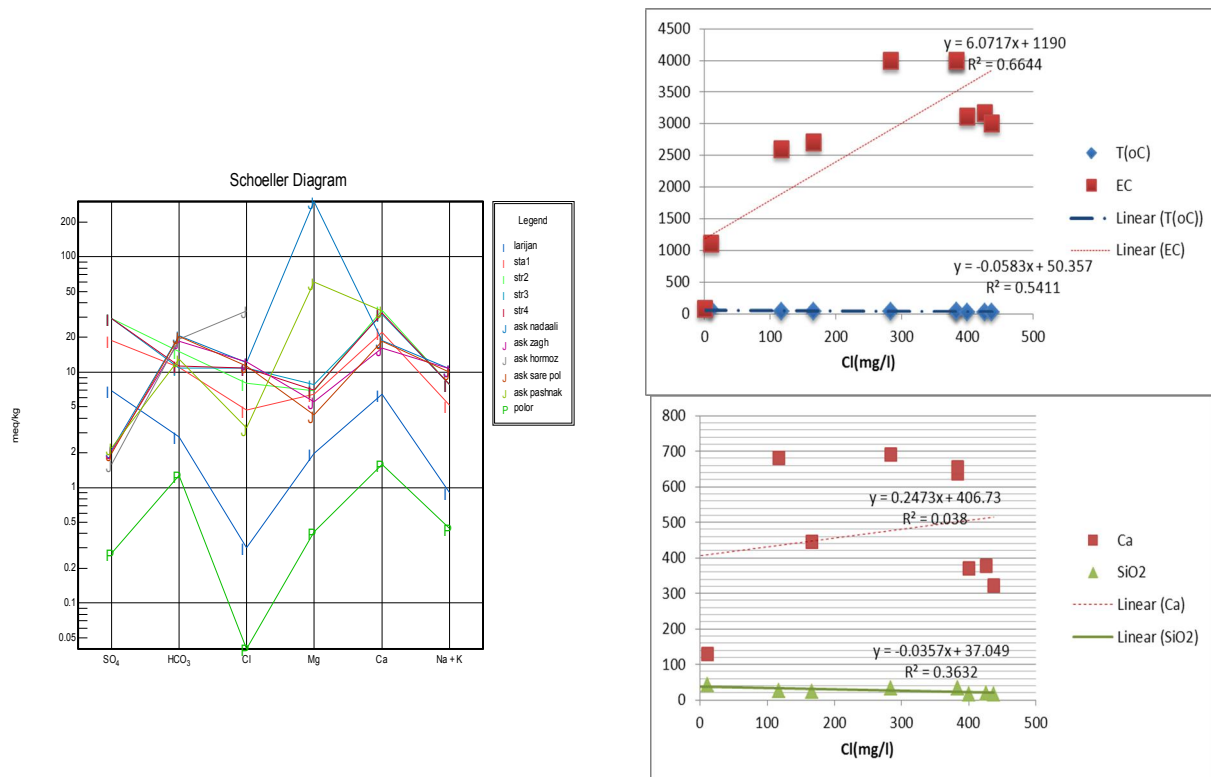


Fig.5 Relations between various ions, EC and temperature versus chloride from cold and thermal water springs in Damavand area. (Values in mg/l).

Table 2: Calculated reserve temperatures of the thermal spring's water in the Damavand area, Iran

Springs	Lrijan	Strabaku1	Strabaku2	Strabaku3	Strabaku4	Ask e Nadali	Ask e Sare Pol	Ask e zagh
T SiO ₂ (quartz, no steam loss) ^a	94	71	83	84	84	59	57	53
T SiO ₂ (quartz, max steamloss) ^a	95	76	86	87	87	65	63	60
T SiO ₂ (chalcedony) ^c	63	39	52	52	52	26	24	20
T α -cristobalite	44	23	33	34	34	10	5	8
T Na-K ^c	265	236	241	241	241	232	247	232
T Na-K-Ca ^d	16	46	54	55	55	77	79	80
T Na-K-Ca-Mg ^b	< 0	>350	>350	>350	>350	>350	>350	>350

5. Estimation of Reserve Temperatures

Chemical composition of the spring's water is used to estimate the reservoir temperature. For this reason the solubility and exchange reactions of various solid phases must be taken into account. Several geothermometry techniques, which were summarized by (Arnorsson, 2000), have been developed to predict reservoir temperatures in geothermal systems during the past three decades. In this study, solute geothermometry techniques were applied to the thermal spring's water of the Damavand area. Some of the geothermometers (i.e. Quartz, amorphous silica, α -cristobalite and Chalcedony, Na-K, Na-K-Ca and Na-K-Ca-Mg etc.) give unreasonable geothermometry temperatures. Some of them are lower than the measured surface temperatures or much higher than possible. Discarding these results, the rest of the calculations yield reservoir temperatures between 53 and 265°C shown in Table 2. Comparing the measured reservoir temperature most of the Na-K-Ca-Mg geothermometry results are generally too high to be reservoir temperatures. The temperatures obtained from silica, Na-K geothermometers are more reasonable than those of the other cation geothermometers. Quartz geothermometers (Fournier, 1977), shown a range of reservoir temperatures from 53 °C to 94 °C and 60 °C to 95 °C and Na-K geothermometr (Arnorsson et al., 1983), shown a range of reservoir temperatures from 232°C to 265°C were obtained for thermal springs in the Damavand area, respectively Table 2. However, it can be concluded that all of the observed chemical geothermometry results in the Damavand area show that the reservoir temperatures of thermal waters increase towards flank Damavand volcano such as Larijan thermal spring or increase rate of mixing and dilution between the cold groundwater and hot water at some of springs such as Ask and strabaku area.

6. Conclusion

Thermal springs around Damavand volcano occur in an area of Quaternary volcanic and Mesozoic sedimentary rocks. Chemical analyses of thermal waters show that concentrations of the major

ions belong to SO₄, HCO₃ and Ca. Also, they can be divided into two groups. The first group consists of waters from near the Damavand volcano and issue through the quaternary volcanic rocks have measured spring temperatures (31–60 °C), EC in the 1100– 4000 μ s/cm range, and pH from 5.5 to 6.5 and SO₄ is the dominant anion in this group; major cation are Ca. The second group, this thermal springs occurs at Jurassic carbonate rocks, Their waters EC and pH range from 2600 to 3160 μ s/cm and from 6 to 6.8, the main anion is HCO₃ and the main cation are Ca, Mg. Different plots of water chemistry suggest thermal and cold springs are immature water and not in equilibrium with the host rock. The high SO₄ content, relatively low HCO₃ content indicate to mixing the Magmatic steam and steam-heated waters with shallow cold groundwater, in other hand the high HCO₃ content, relatively low SO₄ content indicate to circulation of Peripheral and shallow water in sedimentary and volcanic rocks.

Elements component indicate that the two types of analysed water have similar origin and the difference in concentration is related to dilution of thermal water with almost shallow fresh groundwater. Deep reserve temperature calculated by Quartz and Na-K geothermometers, so, Quartz geothermometer shown a range of reservoir temperatures from 53 °C to 94 ° and Na-K geothermometr, shown a range of reservoir temperatures from 232°C to 265°C were obtained for thermal springs in the Damavand area. Chemical geothermometry results in the Damavand area show that the reservoir temperatures of thermal waters increase towards flank Damavand volcano such as Larijan thermal spring or increase rate of mixing and dilution between the cold groundwater and hot water at some of springs such as Ask and strabaku area.

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