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Hydrogeochemistry of the Kozakli Geothermal Field-Turkey

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ABSTRACT

The Kozakli geothermal field is located near the Kirsehir Massif, in the central part of Minor Asia. It is Paleozoic in age and composed of metamorphic schists, marble and granite.

The chemical composition of the geothermal fluid has been determined as mainly NaCl- (Ca) Cl (HCO_3) type with measureable amounts of SO_4.

Reservoir temperature of the system was estimated to be about 105°C -125°C at shallow depths (around 1000m.), while it was close to 200°C for depths of 2000 m-2500 m. This was estimated using the Giggenbach diagram and chemical geothermometers correlated with the geothermal gradient of the area.

Hot Springs of the Kozaklı geothermal field were estimated to not have reached equilibrium because of rapid circulation in the ground.

1. INTRODUCTION

Turkey is located on one of the major tectonic belts of the world known as the Alpine-Himalayan Tectonic belt. In addition to this, there are volcanic areas spread throughout the country. Therefore, the country has many hot springs with a variety of temperatures ranging up to 102°C. The hot springs are located mainly on major active fractures and volcanic areas one of which is the Kozakli geothermal field. The Kozakli geothermal field is located near the Kirsehir Massif, which is Paleozoic in age. This Massif is mainly composed of metamorphic schists, marble and granite, and forms the basement of the geothermal area covered by Tertiary volcanic-sedimentary units assumed to be cap rock. The younger units form a flat area with horizontal bedding covering large areas including a narrow valley presumably caused by a fracture on which geothermal manifestations appear.

The geothermal manifestation spreads throughout an area of about 1 km^2 including boiling hot springs, travertine and swampy areas formed by hot water emergence and leakage. The results of chemical analysis of hot and cold water samples have been evaluated for fluid – mineral equilibrium by using Watspec and Chiller computer programs, and for mixing models by mainly using Langelier-Ludwig, Silica - enthalpy and Giggenbach diagrams.

Molten magma, which is presumably the heat source of the geothermal system, was estimated to be at a depth of about 12,7 km. by using temperature gradient obtained from gradient holes of the area.

2. HYDROGEOCHEMISTRY

The geothermal manifestation spreads out about 1 km^2 including boiling hot springs, travertine and swampy areas formed by hot water emergence and leakage.

The hot springs roughly follow a trend within a valley NNW-SSW in direction. In this study 10 hot springs, 2 shallow hot wells and 2 cold waters, in total 14 samples, were collected in two periods, i.e. in the rainy and dry season, to capture the seasonal recharge effects. But there were no considerable differences in concentration between samples from these two seasons. The temperature of the springs and well samples are between 46°C and 93°C.

Table 1: Physical condition of the hot springs during sampling a) Dry season: 17/ 6 / 1996.

Spring no	T°C	pH orij.	pH(HNO3)	H_2SO_4	Chloro form	Discharge (lt/sn)
1	90-93	6.63-6.67	2.15	+*	+	15
2	79	6.55	1.95	+	+	1.5
3	71	6.55	2.15	+	+	0.75
4	46	6.98	2.12	+	+	0.3
5	69.5	6.48	-	+	+	0.5
6	72	6.60	-	+	+	0.07
7	78.3	6.60	2.02	+	+	0.01
8 (Down stream)	34.8	7.8	1.95	+	+	35-40
9	71	6.53	2.01	+	+	0.5
SSK-1	88	7.14	2.15	+	+	95
SSK-1 EŞ	85	6.70	2.1	+	+	-
DY(up stream)	21.5	8.20	2.13	-	-	-

* +: headline written in first cell of the column was added to the sample.

2.1. Methodology

Sampling was carried out with 250 cc. polyethylene bottles and samples were treated with some chemicals to prevent precipitation of some elements to be analyzed in the samples.

1 For the contamination (NO_2, NO_3, NH_3); the samples were treated with 3-4 drops of chloroform.

2 For the cations and SiO_2, samples were treated with nitric acid (HNO_3) until the pH of samples decrease down to 2.

3 Blank samples were collected to analyze cations and anions for each spring.

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Method of Analysis

Ions	Method
Na^+, Ca^{+2}, Mg^{+2}:	AAS
SO_4^{-2}, NO_2^-, NO_3^-, NH_3, B^+, SiO_2:	Spectro photometer
Cl^-, HCO_3^-:	Volumetric titration (potentiometer)
F:	Ion selector electrode

Table 1b: Rainy season: 2-3/11/1996.

Spring no	T °C	pH orij.	pH(HNO3)	H_2SO_4	Cloro fom	Discharge (lt/s)
1	90.05	6.43	2.05	+	+	15?
2A	66.5	7	1.96	+	+	1?
3	65.5	6.53	1.99	+	+	1.2
4	47.4	6.64	2.22	+	+	0.05
4A	60	6.43	2.22	+	+	1
5	69.3	6.56	2.15	+	+	0.1
6	71	6.60	2.17	+	+	0.5
7	75	6.50	2.22	+	+	0.2
8(Down stream)	32.5	7.73	2.12	+	+	≈25
9	75	6.4	1.70	+	+	0.8
SSK-1	86	7.0	019	+	+	95
SSK-1EŞ	79	6.86	1.85	+	+	
Ç (ÇAMUR)	53.5	6.79	1.97	+	+	1.5
DY(up stream)	12.1	8.70	-	-	-	

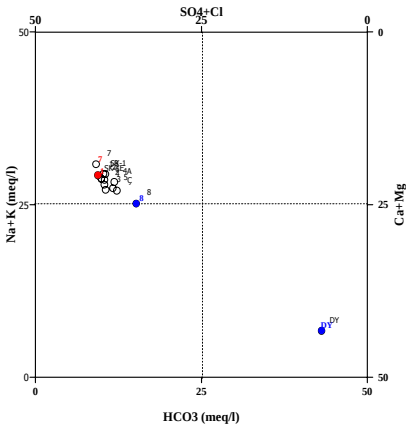

Figure 1: Langelier - Ludwig Diagram.

2.2. Evaluation of Kozaklı Geothermal Fluid Samples

In order to evaluate the Kozaklı Geothermal Field samples, the chemical type of the samples will first be classified. The chemical character of the Kozaklı samples can mainly be classified by three groups that are;

1. NaCl type, consisting of minor amounts of Ca, SO_4, HCO_3 ions.
2. $NaSO_4$ type, consisting of minor amounts of Ca, Cl ions.
3. $CaHCO_3$ type waters.

2.2.1. Langelier-Ludwig Diagram

This is one of the most important diagrams in order to evaluate geothermal fluids, including chemical type, mixing and to estimate reservoir rock type especially for low enthalpy fields.

As for the Kozaklı Samples, two diagrams are going to be discussed in this section (Fig. 1, 2). The first one is the Na+K – HCO_3 based type with the Ca+Mg – SO_4+Cl in opposite.

Most of the samples are located in the Na+K – Cl+SO_4 quadrangle indicating Na-Cl type water with some amount of SO_4. This type of water reveals that circulation has mainly taken place in reservoir rock which contains high amounts of Na - K bearing minerals. One sample (symbolized as DY) plots in Ca+Mg – HCO_3 quadrangle that is the sample collected from upstream representing local groundwater, flowing through the geothermal field. Another one plots on the boundary of Na+K – Ca+Mg, away from the cluster is sample number 8 taken from downstream. That clearly indicates mixing of the geothermal fluid with stream water. The plots show a roughly linear trend of the samples that are related to groundwater (Ca+Mg – HCO_3) corner, indicating the gradual mixing of hot spring samples with especially ground and presumably a little amount of stream water. Number 7 seems to be an end member of the geothermal reservoir fluid in from a chemical point of view. But the hottest spring of the field sampled is sample number 1. There seems to be a contradiction if we consider the hypothesis that the hottest one is the sample that reveals the most representative sample of the reservoir fluid. But sample number 7 seems to be the end member of geothermal fluid, since it plots in the NaCl corner.

In this case we should consider the sampling conditions (Table 1-a, 1- b), i.e. that the discharge rate of these two samples are extremely different, number 7 is 0.01 lt/s and 0.2 lt/s, while number 1 is 15 lt/s both in dry and in rainy season.

Temperatures of these two samples are also different as number 1 is 90°C -93°C, while number 7 is 78,3°C -75°C for dry and rainy seasons, respectively.

Hence we can assume that sample number 7 has undertaken the steaming at the surface due to low discharge rate in a small pond.

As a result, the concentration of the water sample increases and plots (place looks like end member compare to cluster) closer to the end member position than number 1.

As for the diagram of Na+K – HCO3+SO4 based type with the Ca+Mg – Cl in opposite (Fig. 2) to leave the Cl ion alone to notice the percentage of Cl to HCO3+SO4 , it can easily be seen that the Cl concentration itself balances the HCO3+SO4 (it means that fluid contains approximately %50 Cl and %50 HCO3+SO4 in total anion) in geothermal fluid samples.

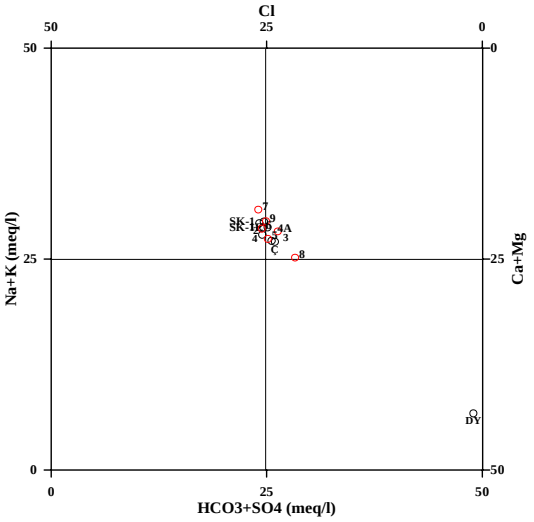

Figure 2: Langelier - Ludwig Diagram (Na+K)-HO_3+SO_4.

As a conclusion, from these two diagrams, hot samples are neutral- NaCl type water with minor amount of SO4 in general. So it can easily be assumed that the Kozaklı hot spring samples are quite deep geothermal type waters with minor amount of mixing with groundwater.

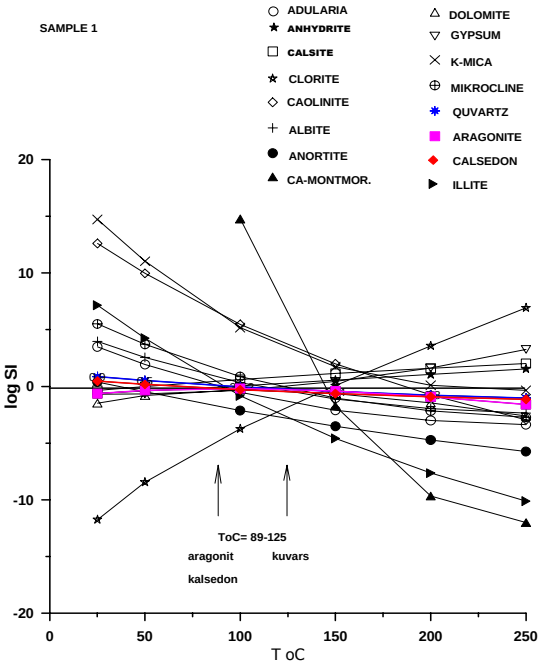

Figure 3: Saturation Index (SI).

The clustered pattern of the hot samples plot in NaCl quadrangle is presumably an evidence of the upflow zone of geothermal system.

2.2.2. Saturation Index (SI)

This method is based on the fluid – mineral equilibrium and the equilibrium constant that can be calculated by temperature dependent equations. Hence we can assume that the evidences of SI reveal the reservoir conditions. The other meaning of this method is to be an alternative method to chemical geothermometers.

Sample 1 which has the highest temperature among the springs is used in LogSI=20, -20 diagram (Fig.3) to determine the mineral equilibrium state in between 25°C – 250°C.

The Geothermal fluid is oversaturated with k-mica, kaolinite, microcline, albite and adularia below the temperature of 90°C, in equilibrium between 90°C – 125°C and undersaturated above 125°C.

In the diagram in the Log SI = -3, +3 interval, Aragonite, Calcite, Dolomite, Anhydrite, Gypsum, Quartz, Adularia and Albite are roughly in equilibrium or close to equilibrium.

These minerals cut the saturation index axes between 89°C – 125°C which means that the last equilibration of the fluid was achieved in this temperature interval, i.e. it reveals that this is the last temperature state of the shallower reservoir temperature.

The dominancy of the Ca bearing minerals point out that the fluid has not reached to the deeper part well enough to dissolve the temperature dependent ions or has insufficient time to reach equilibrium with temperature dependent ions.

2.2.3. Activity Diagrams

Activity Diagrams are used to identify the chemical equilibrium between minerals and aqueous species.

In order to generate the diagram, a reservoir temperature of 105°C -110°C is calculated by chemical geothermometers and 100°C, 125°C and 150°C temperature intervals are selected to indicate the temperature effect on minerals. By considering the diagrams (Fig 4 a,b,c) it can be seen that muscovite stability area increases as the temperatures increases.

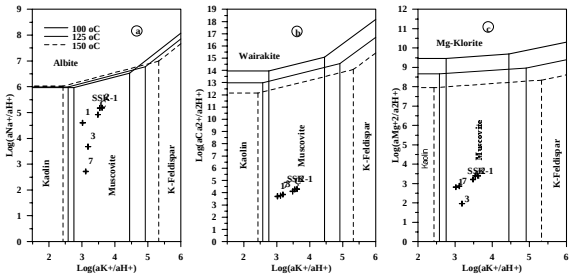

Figure 4: Activity Diagrams for Kozaklı Hot Springs(100, 125, 150 °C) Systems of a) Na2O-K2O-Al2O3-SiO2-H2O, b) CaO-K2O-Al2O3-SiO2-H2O, c) MgO-K2O-Al2O3-SiO2-H2O.

So the original reservoir fluid denotes that it is in equilibrium with muscovite at least in these temperature intervals. In Fig. 4-a, when the pH is directed to the alkaline side (decrease of H^+) the fluid tends to become stable towards the Albite and to K-Feldspar. In the reverse case, tends to Kaolinite side. Furthermore, in diagrams in Fig. 4-b and c tends towards Wairakite; K-Feldspar and Mğ-Chlorite; K-Feldspar respectively, in the reverse case the Kaolinite side in both diagrams b and c in view of pH conditions.

3. CHEMICAL GEOTHERMOMETERS

Chemical geothermometers are used in order to estimate the reservoir temperature. The important criteria for chemical geothermometer application to thermal spring are the pH, temperature and discharge rate of the spring.

Both silica and cation geothermometers are applied to the Kozaklı hot springs. Some of them give unreliable results such as either lower than spring temperature or extremely high temperature. These equations are based on geothermometers for chalcedony and quartz, which assume that these minerals used in geothermometers, are not in equilibrium with rock – water interaction in reservoir.

3.1. Giggenbach Diagram (Na-K-√Mg)

By considering the diagram presented in Figure 5, the Kozaklı hot springs plot in the immature water part, so using the chemical geothermometers is not reliable according to the theory used to establish the diagram. In this Na-K-√Mg diagram all the samples have not gained equilibrium with rock, presumably due to fast circulation of fluid through the rock fractures. This causes the water to be immature, considering the ion exchange processes that, equilibrium has not been reached yet with rock minerals because of circulation flow.

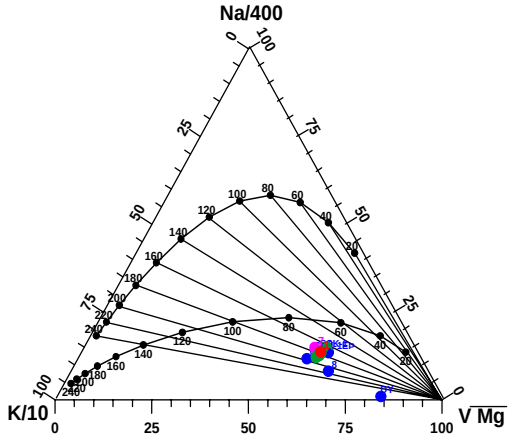

Figure 5: Giggenbach Diagram (Na-K-√Mg).

However, if one considers that if that the water could reach even partial equilibrium; it could be assumed that, as the trend of the samples indicates, that the reservoir temperature could reach 180°C.

3.2. Enthalpy – Silica Mixing Diagram

Another estimation method of reservoir temperature is Enthalpy - Silica Mixing Diagram by using silica concentrations and temperature of springs sampled (Fig.6).

The samples plotted on the graph are scattered due to the difference of physical conditions of well samples and springs during sampling, such as high discharge rate, forming of small ponds, leakage, etc. The mixing lines have been drawn by connecting the sample DY representing groundwater and hot water samples (Fig..6). There is an accumulation of samples symbolized by 2A, 3, 5, 6, 7, SSK-1EŞ are acceptable for representing the reservoir character. Hence we can assume that, the intersecting point of this line and the silica dissolution curve reveal the last equilibrium of silica with rock and the projection of this point on the enthalpy line gives the reservoir temperature as 124,7°C.

But in a broader sense one can assume that the reservoir temperature is between 101°C – 128,5°C according to this diagram.

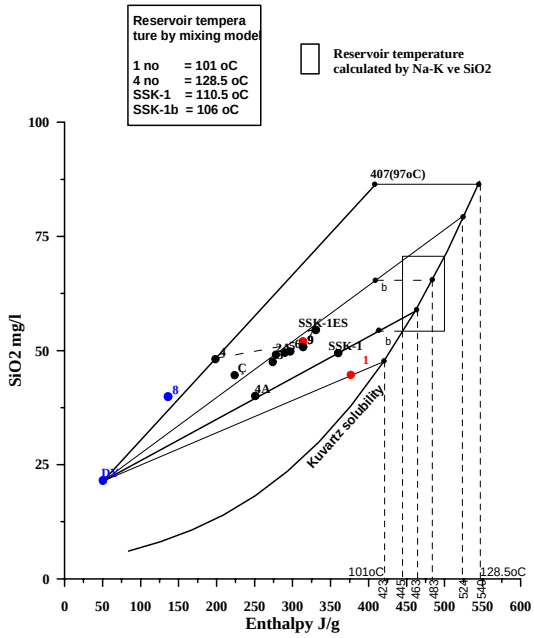

Figure 6: Enthalpy - Silis Mixing Diagram (Fournier, 1977).

3.2.1. Reservoir Temperature and Depth Estimation

The temperature gradient of the area has been estimated as 0.2°C/10 m. by using data obtained from gradient wells with a depth of about 100 m. On the other hand, the heat source has been assumed to be granite by considering regional geology. One can establish a linear graph in temperature and depth axes by using the temperature gradient of the area and by assuming the temperature of the granitic magma to be around 900°C. The reservoir temperatures can be estimated to be around 105°C -125°C at shallow depths (around 1000m.), while close to 200°C for depths of 2000 m-2500 m, by putting the estimated chemical geothermometers on the graph.

4. CONCLUSIONS

The Kozaklı Hot Springs have likely not reached equilibrium because of the rapid circulation in the subsurface. The indications for this are the plots of the samples on a Giggenbach diagram, mixing models and most of the calculated reservoir temperatures that are not comparable with the discharge temperature of springs, in spite of some of them being near boiling temperature with high discharge rate on the surface.

Reservoir temperature estimate is about 100°C -125°C and 150°C -200°C at around 1500 m. and 2500 m, respectively. This is found by correlating chemical geothermometers and graphics with temperature gradient of the field.

These conclusions reveal that Kozaklı Hot Springs result from infiltration of meteoric water into the rocks, bearing dominantly alkali elements; presumably granitic in composition or rock groups in the deeper part, with rapid circulation.

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Table 2: Chemical Composition of Kozaklı Geothermal Fluids.

KOZAKLI SAMPLES (2-3/11/1996) in mg/l

Sample No:	ToC	pH	Na	K	Ca	Mğ	CO_3	HCO_3	Cl	SO_4	F	Fe	B	SiO_2	NO_3	NO_2	PO_4	NH_3	NH_4	Al*
1.00	90.00	6.43	422.50	19.00	230.00	23.00	14.70	370.76	592.02	458.11	10.40	0.42	2.95	44.64	-	0.00	-	0.38	0.40	0.37
2A	66.50	7.00	437.50	20.00	248.00	25.00		418.03	623.92	488.86	11.40	0.39	3.33	49.10	-	0.05	0.27	0.13	0.13	0.25
3.00	65.50	6.53	400.00	22.00	260.00	26.00	-	424.56	570.75	475.20	11.20	0.23	4.81	47.53	0.38	0.02	0.29	0.14	0.15	0.25
4.00	47.40	6.64	400.00	20.00	245.00	24.00	-	394.67	563.66	422.24	12.50	0.03	2.04	48.11	0.95	0.02	0.28	0.06	0.07	0.25
4A	60.00	6.43	410.00	19.00	244.00	23.00	-	436.58	506.94	417.11	12.50	0.44	3.55	40.06	5.48	0.05	0.28	0.37	0.39	0.25
5.00	69.30	6.56	392.00	21.00	244.00	24.00	-	442.56	549.48	403.45	13.70	0.04	2.27	49.50	2.79	0.11	0.29	0.19	0.20	0.25
6.00	71.00	6.60	415.00	20.00	239.00	24.00	-	394.67	563.66	418.82	14.50	0.22	2.62	49.79	0.74	0.15	0.30	0.23	0.25	0.25
7.00	75.00	6.50	467.00	20.00	223.00	22.00	-	346.85	574.29	446.16	14.70	0.16	1.51	51.99	1.09	0.22	0.29	0.14	0.15	0.30
8.00	32.50	7.73	220.00	17.00	165.00	20.00	-	340.87	283.60	232.47	7.97	1.23	1.64	39.89	43.76	0.07	0.27	0.24	0.25	0.25
9.00	75.00	6.40	427.50	18.00	228.00	23.00	-	382.71	545.93	432.45	15.30	0.92	1.59	50.78	1.09	0.09	0.30	0.36	0.38	0.25
SSK-1	86.00	7.00	425.00	17.00	227.00	23.00	-	388.69	542.39	410.28	14.10	0.56	2.12	49.44	-	0.02	0.26	0.24	0.25	0.25
SSK-1EŞ	79.00	8.86	402.50	17.00	228.00	23.00	-	376.74	549.48	454.70	14.30	3.16	2.80	54.54	-	0.04	0.26	0.25	0.26	0.25
Ç	53.50	6.79	387.50	24.00	258.00	24.00	-	466.47	531.75	410.28	13.90	0.03	1.54	44.58	19.21	0.01	0.28	0.42	0.45	0.26
DY	12.10	8.70	12.60	5.00	75.00	7.50	11.76	257.18	3.55	27.53	1.79	0.85	0.08	21.53	61.95	0.11	0.27	0.49	0.51	