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Estimation of Silica Scaling Temperatures of Kızıldere Geothermal Field Effluent, Turkey

SEVIL ARITÜRK

MAHMUT PARLAKTUNA
Department of Petroleum Natural Gas Engineering
Middle East Technical University
Ankara-Turkey

A computer program, SPECIATION, was developed to determine the detailed composition of an aqueous solution and the concentrations and activities of all species. Once the detailed composition of an aqueous solution is known, it is possible to determine the saturation level of the solution with respect to any mineral, which is silica for this study.

Three water samples from the Kızıldere geothermal field of Turkey were collected and the chemical analyses of these samples were used as input data in SPECIATION to determine their detailed composition for obtaining the silica scaling potential of the Kızıldere field effluent.

The analysis of the silica scaling studies indicate that the pH of the power plant effluent of the Kızıldere field increases due to boiling and loss of acid gases (mainly CO_2). This increase in pH results with an increase in the solubility of amorphous silica. As a consequence, the silica scaling danger of effluent is carried to lower temperatures, which makes the problem-free temperature range wider.

Keywords silica, scaling, geothermal, effluent, Kızıldere

Introduction

In the broadest sense, the geothermal energy is the natural heat of the earth. Leibowitz (1978) defined geothermal energy as the natural heat in the earth that is trapped close enough to the surface to be extracted economically. Geothermal systems occur most frequently in regions of active or recently active volcanism. They are also well known in active tectonic zones associated with plate convergence. Such systems are hot springs or reservoirs where hot flow waters approach the surface. Geothermal energy has received increasing attention as an attractive alternative energy source both from economic and environmental points of view. The applications vary from power generation, district heating, and hot water supplies to greenhouse heating, etc.

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Address correspondence to Mahmut Parlaktuna, Department of Petroleum Natural Gas Engineering, Middle East Technical University; 06531 Ankara-Turkey. E-mail: mahmut@metu.edu.tr

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While exploitation of geothermal energy appears desirable, there are still technical problems with the use of geothermal brines, including emission of H_2S, H_2 and CO_2 gases, and scaling due to calcium carbonate and silica depositions. The scaling, in particular, has been a major concern in geothermal power plants and is a primary deterrent to greater utilization in power generation.

At each stage of the geothermal utilization process, the natural hydrothermal fluids that may have been at thermal and chemical equilibrium within heated reservoir rocks can be exposed to substantial changes in temperature or pressure, which can affect the solubility of a variety of dissolved mineral species. A hydrothermal fluid is an aqueous solution containing as major components sodium, potassium, calcium, and chlorine. Other elements like magnesium, bromine, sulfur (as either sulfate or sulfide or both), strontium, and sometimes iron, zinc, carbonates (HCO_3 and CO_2), and NH_4 can be found.

Changes in fluid pressure can allow a change of state to take place: either boiling of the liquid or exsolution of dissolved gases. Boiling decreases both the volumes of the residual fluids and their temperature, thereby simultaneously increasing the concentration of the dissolved solids present and decreasing their solubility. Loss of dissolved gases (e.g., CO_2 and H_2S) from the fluid (with or without boiling) can also drastically affect the pH and therefore the solubility of both sulfide and carbonate minerals. Lowering of the fluid temperatures can decrease the solubility of dissolved silica or metal sulfide species and allow them to precipitate individually or together. Silica deposition has been encountered in virtually all high enthalpy, liquid-dominated, geothermal fields. The two forms of silica that are relevant to the silica deposition problem are quartz and amorphous silica. In short, the solubility of silica increases with temperature, decreases with salinity, and increases sharply with pH for alkaline fluids. The pH effect is very weak for neutral to acidic fluids.

Silica, being one of the two major scales found in geothermal systems, is abundant in nature and exists in large amounts in underground geothermal reservoirs. On the basis of geologic evidence, silica concentration is determined by the equilibrium solubility of quartz in hot reservoirs. The precipitation of silica is, however, dominated by the solubility of amorphous silica. When the hot brine is brought to the surface, it is either flashed or cooled while passing through a power plant system to release its available thermal energy. The dissolved silica in brine may then become supersaturated. Depending on the degree of supersaturation, the dissolved monomeric silica may nucleate, form polymers, and ultimately deposit as amorphous silica scale.

Waters in high-temperature geothermal systems are often alkali chloride solutions at a pH within 1 to 2 units of the neutral water pH for the temperature. Steam separated from a well discharged at atmospheric pressure contains most of the gases originally dissolved in deep hot water, with CO_2 making up over 80% of the total gases. Steam formation from the water phase causes concentration of salts and depletion of gases, and the loss of acidic gases causes a rise in the water pH. That is why the pH of deep hot water is usually lower than that measured in a cooled water sample.

From the separate analyses of vapor and liquid phases separated from the discharge at a known pressure, the composition of the deep hot solution can be calculated in terms of ionic and molecular species. The steam fraction in the discharge and the concentrations of gases can be calculated.

Kızıldere Geothermal Field

Turkey is located on an active tectonic belt and has young graben systems and volcanic activity, suggesting a promising geothermal energy potential. There are four main geothermal regions in Turkey: Western Anatolia, the North Anatolian Fault Zone, and the areas affected by upper Tertiary-recent volcanic activity localized mainly in Eastern Anatolia and Central Anatolia.

The Kızıldere field was found in 1968. It is located 45 km west of the city of Denizli. It is the first developed field in Turkey. It is a high-temperature, hot-water dominated geothermal field having reservoir temperatures of 170–212°C. There is also natural steam and several hot springs with temperatures between 30–100°C (Figure 1) (Şimşek, 1985a).

The Kızıldere field is located in Büyük Menderes graben, which is part of an active tectonic belt. The reservoir is a marble quartzite formation at a depth of approximately 600 m from the surface. The field has two reservoirs on top of each other. The upper reservoir has lower temperature and lower permeability and the lower reservoir has just the opposite. The second reservoir is the main producing zone. The presence of a third reservoir is very likely, which is very important, particularly for increasing the well production (Figure 2) (Şimşek, 1985b).

At its initial state, the Kızıldere geothermal field was a hot-water dominated field having reservoir temperatures above 200°C. Table 1 gives the composition of Kızıldere geothermal fluid (ENEL, 1989).

A single-flash power plant of 20.6 MWe capacity was put into operation in February 1984 by the Turkish Electricity Authority to produce electricity. It is the first commercial geothermal power plant and is the only field utilized for electricity production in Turkey. Its net contribution to an interconnected system is 17.8 MWe.

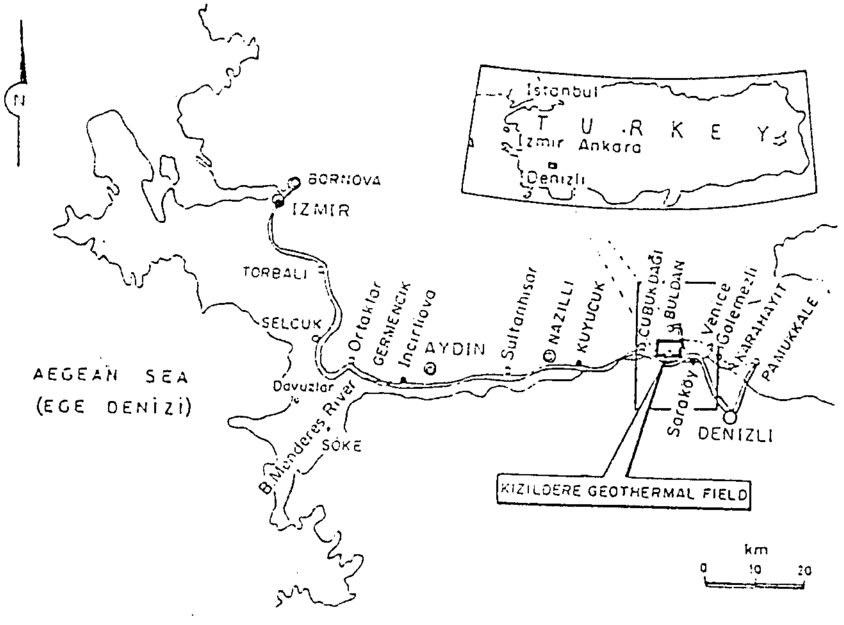

Figure 1. Location map of the Kızıldere geothermal field (Şimşek, 1985a).

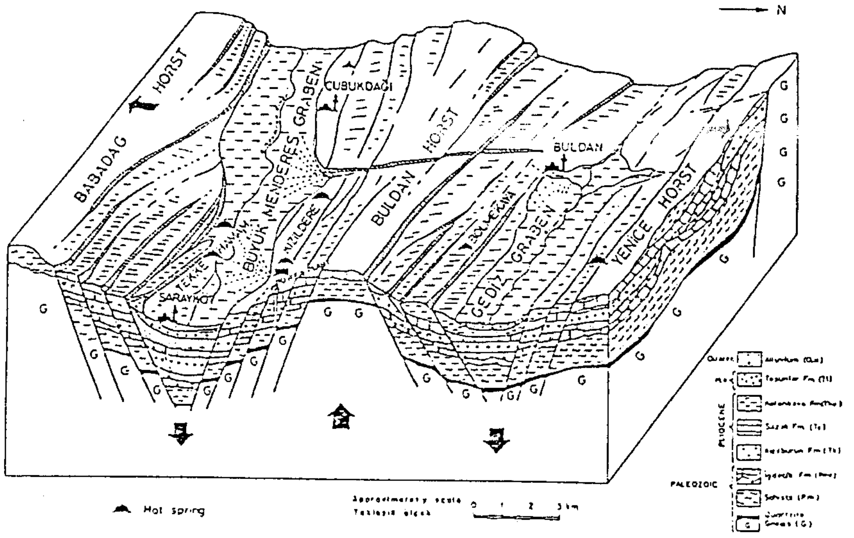

Figure 2. Block diagram of the Sarayköy-Buldan area (Şimşek, 1985b).

Table 1
Possible concentration ranges of
the Kızıldere Geothermal Fluid (ENEL, 1989)

Compounds	Concentration range (ppm)
Silica	239–463
Carbonate (total)	2040
Chloride	100–207
Boron	35
Sulphide (total)	<0.1
Fluoride	15.4–18.0
Sulphate	321–707
Sodium	1025–1480
Potassium	116–158
Magnesium	0.011–67.8
Calcium	0.12–93.2
Ammonia	0.17–0.20
Aluminum	0.08–0.75

The steam is separated from the mixture at the surface and utilized in the power plant. The water is drained to the Büyük Menderes River. The steam transmitted from each well is collected and admitted in a main pipe, which feeds the steam to the main separator (Okandan & Polat, 1985).

The main separator separates the final liquid drops and sends the complete dry steam to the turbine at a certain flow rate, absolute pressure, and temperature. The turbine extracts the noncondensable gases from the steam and sends them to the

Table 2
Chemical composition of Kızıldere field effluent

Elements (mg/kg)	KD-13 separator discharge	Pool discharge	Heat exchanger discharge
PH/°C field	9.85/90.8°C	9.88/85.5°C	7.70/51.6°C
PH/°C laboratory	9.54/23.5°C	9.59/23.5°C	7.67/23.9°C
Silica	271.7	263.4	183.3
Total carbonate	1893.1	1920.9	2530.0
Boron	33.3	33.3	36.7
Sulphide	1.02	1.02	0.68
Fluoride	23.6	31.7	21.3
Sulphate	825.3	1029.0	692.6
Sodium	1233.0	1314.0	1069.0
Chloride	36.0	37.5	18.3
Potassium	136.3	148.2	123.0
Magnesium	3.402	1.944	1.458
Calcium	0	0	0
Ammonia	11.22	22.35	11.51
Aluminum	0.0	0.0	0.0
Arsenic	0.197 ppb	0.224 ppb	0.152 ppb
Iron	0.069	0.044	0.065
TDS	4468	4803	4688

dry-ice plant while sending the pure steam to the generator with a 20.6 MWe output capacity. The generator produces electrical energy of 17.8 MWe from this steam.

Hot water discharged from the separator is at 140°C and just before being released to the Büyük Menderes River, it is left in a settling pool. The discharge of the residual water into the Menderes River is a big problem when we consider the fact that for each ton of separated steam there are nearly 9 tons of water to dispose of.

The disposal of the discharged water from the separator to the river may create environmental problems due to its boron content, namely, 30 ppm of boron, and the Büyük Menderes River is used for irrigation purposes downstream from the discharge of the power plant. Since the maximum allowable boron concentration is < 1 ppm in the river, the high concentrations of dissolved solids, and especially the high boron and fluoride concentration, make it unsuitable for domestic use or for irrigation. Nowadays a total of 1000 tons/h of geothermal fluid is obtained from 8 production wells and 20% of this consists of steam, which is being utilized in the generation of electricity, while 80% of the water is given to the Büyük Menderes River.

In order not to preclude any further development of the field, it is necessary to find suitable solutions for a correct use and development of the geothermal resources. It is also obvious that a solution to this problem may be useful to the development of other areas in Turkey that have fluid characteristics similar to those of the Kızıldere field.

The applicable method in the world is the reinjection into the geothermal reservoir of the spent water obtained after separation at the wellhead. This is one of the essential conditions for generating a larger quantity of electrical energy than the one presently allowed by the existing power plant. However, some precipitation problems may arise during production and reinjection. From the chemical investigation of water and scales it is clear that calcium carbonate will most likely be precipitated from the discharge water just after the steam separation. There appears to be a high risk of siliceous deposits from the water by cooling. Precipitation of silica is not expected until supersaturation, with respect to amorphous silica, is exceeded.

In the present study, fluid samples from the Kızıldere power plant effluent have been collected and analyzed. A computer program has been developed to calculate aqueous speciation and pH of the effluent at different temperatures. The silica scaling conditions from these samples have also been estimated.

Results and discussion

The computer program was utilized to study the silica scaling potential of the Kızıldere power plant effluent. Three water samples were collected after steam was separated from produced fluid. The reason for sampling after steam separation is that both reinjection and/or low temperature applications will be carried out by using the effluent of the power plant after steam separation, and the chemistry of these samples should be studied to determine their silica scaling potential. The sampling sites are separator discharge of well KD-13, settling pool, and heat exchanger discharge. The results of chemical analysis of the samples are tabulated in Table 2.

Figure 3 shows the silica content of the samples. The silica concentrations of the samples at sampling temperatures are plotted with the solubility curves of different types of silica. The solubility curves are obtained from Equations (1)–(5) as function of temperature at near neutral pH (≈ 7.0). These equations are valid only for reservoir temperatures $< 250^\circ\mathrm{C}$ (Fournier, 1989).

$$\text{Quartz}: \quad t(^\circ C) = \frac{1309}{5.19 - \log S} - 273.15 \tag{1}$$

$$\text{Chalcedony}: \quad t(^\circ C) = \frac{1032}{4.69 - \log S} - 273.15 \tag{2}$$

$$\text{Alpha-Cristobalite}: \quad t(^\circ C) = \frac{1000}{4.78 - \log S} - 273.15 \tag{3}$$

$$\text{Opal-CT}: \quad t(^\circ C) = \frac{781}{4.51 - \log S} - 273.15 \tag{4}$$

$$\text{Amorphous Silica}: \quad t(^\circ C) = \frac{731}{4.52 - \log S} - 273.15 \tag{5}$$

where S is silica concentration in mg/kg.

As observed from Figure 3, the silica content of the samples collected during this study is very close to the solubility curve of the amorphous silica. If only the temperature dependence of the silica solubility of amorphous silica is taken into account, the sample taken from the heat exchanger discharge is on the solubility curve. A few degrees of cooling are required for the samples KD-13 separator discharge and pool discharge to reach the saturation condition. However, a change in silica solubility of samples due to change in pH is expected. Therefore the change in pH of samples with temperature should be known in order to study the effect of pH on the silica deposition potential of Kızıldere field. The computer program SPECIATION was utilized for the samples collected, and the change in pH of each sample is tabulated in Table 3 and plotted in Figure 4. The

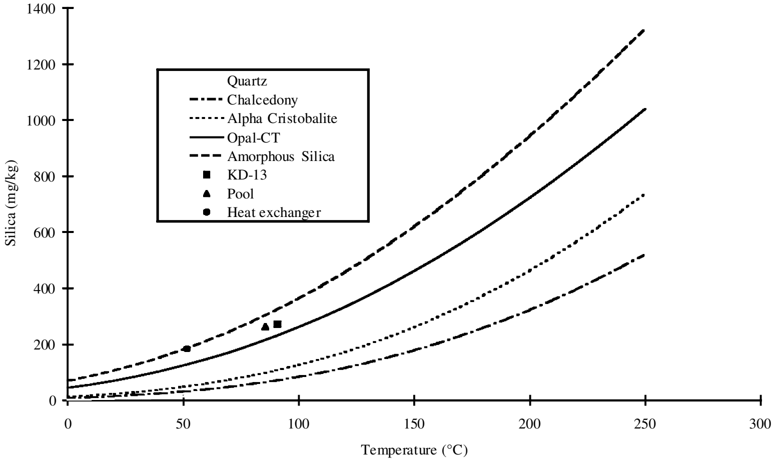

Figure 3. Initial state of silica concentration at sampling conditions.

Table 3
Change in pH of samples with temperature

Temperature (°C)	KD-13 separator discharge	Pool discharge	Heat exchanger discharge
33	9.56	9.58	7.67
35	9.59	9.61	7.68
40	9.61	9.63	7.68
45	9.63	9.65	7.69
50	9.66	9.68	7.69
55	9.68	9.70	7.70
60	9.70	9.72	7.71
65	9.73	9.75	7.71
70	9.76	9.78	7.72
75	9.79	9.81	7.73
80	9.82	9.84	7.74
85	9.85	9.87	7.75
90	9.88	9.90	7.76
95	9.91	9.93	7.77
100	9.95	9.97	7.78

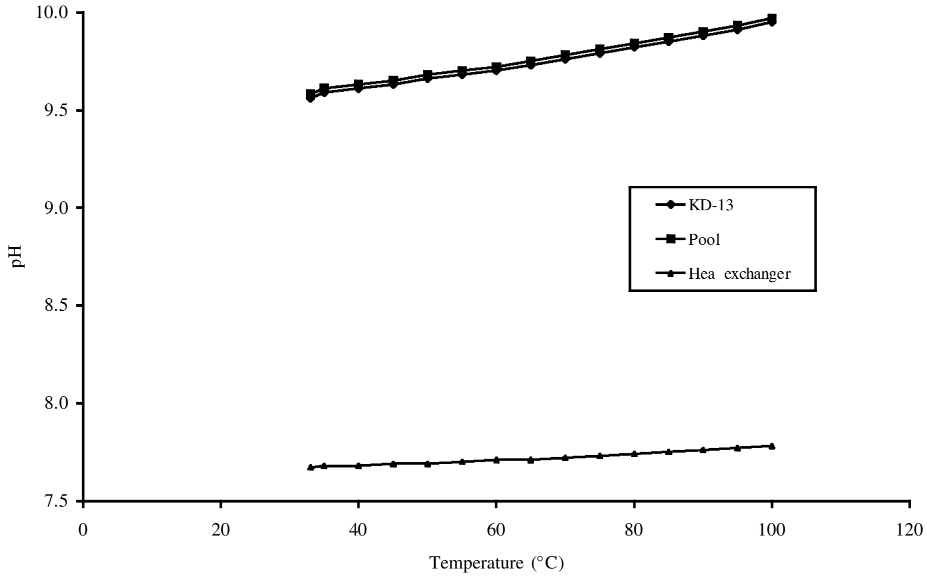

Figure 4. Change in pH of samples with temperature.

pH of the samples increases with temperature. It was assumed here that at the temperatures of sampling all of the dissolved gases left the fluid into the steam phase, therefore there will be no change in pH due to loss of acid gases and the only effective parameter is temperature.

After knowing the pH of samples with temperature the following equation can be utilized to calculate the solubility of amorphous silica as the function of temperature and pH:

$$m_{SiO_2(total)} = m_{H_3SiO_4}((10^{-pH} \times \gamma_{H_3SiO_4}/K_1) + 1) \tag{6}$$

where $m_{SiO_2\ (total)}$ is the solubility of silica (moles/l), $m_{H_3SiO_4}$ is the molal concentration of H_3SiO_4 (moles/l), $\gamma_{H_3SiO_4}$ is the activity coefficient of H_3SiO_4, and K_1 is the first dissociation constant of silicic acid dissociation.

All of the variables of Equation (6) are obtained from program SPECIATION as the function of temperature (Arıtürk, 1997). Activity coefficients are the functions of ionic strength of sample as well as temperature and are obtained by an extended Debye-Hückel equation. Dissociation constants of the reactions considered in the program SPECIATION are functions of temperature and the equations used to calculate them are taken from Arnorsson et al. (1982).

The solubility of silica of the samples at the given temperature and calculated pH obtained from Equation (6) are compared with the amorphous silica solubility curve, which is given by Equation (5) as the function of temperature at near neutral pH (Figures 5–7). The thick solid line shows the concentration of silica measured at the laboratory.

Analysis of Figures 5–7 indicate that with an increase in pH of solution the solubility of amorphous silica increases, in other words the silica scaling potential of solution is carried to lower temperatures compared to that of a solution with

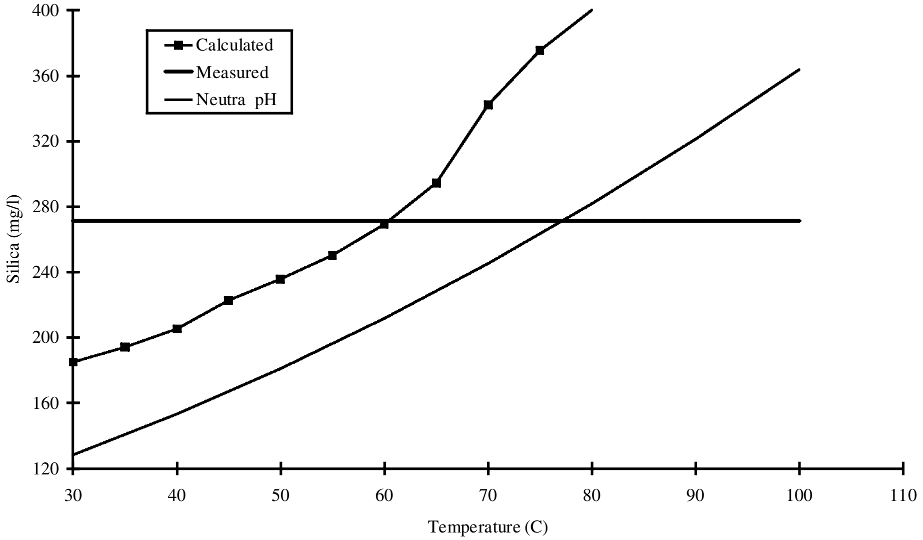

Figure 5. Amorphous silica solubility of the sample from KD-13 separator discharge as a function of temperature and pH.

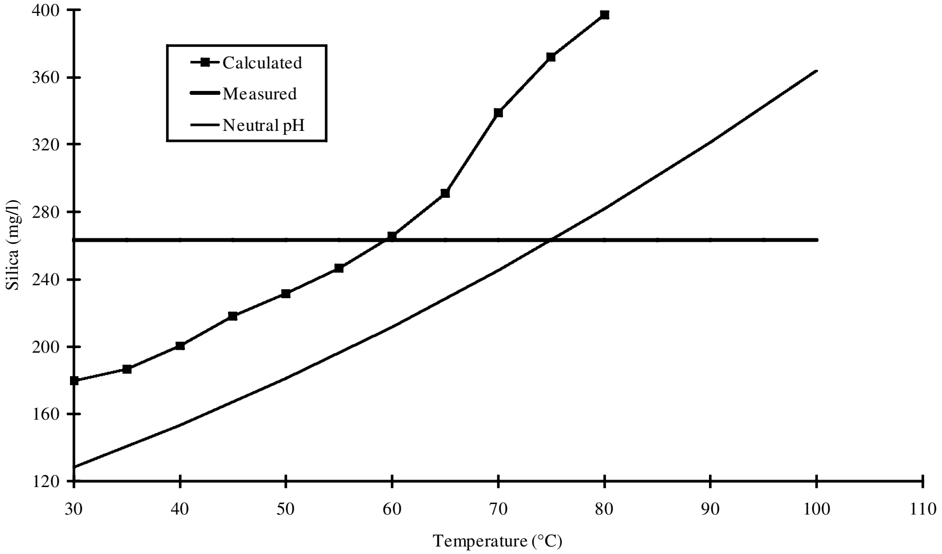

Figure 6. Amorphous silica solubility of sample from pool discharge as a function of temperature and pH.

neutral pH. Table 4 gives the temperatures at which the samples from the Kızıldere field become saturated with amorphous silica by using calculated pH as well as without considering pH effect. There is a considerable difference between the solubility temperatures of samples from the KD-13 separator discharge and the pool discharge, which have pH values of higher than 9. On the other hand, there is only 1°C difference for the sample from the heat exchanger discharge since its pH is close to neutral.

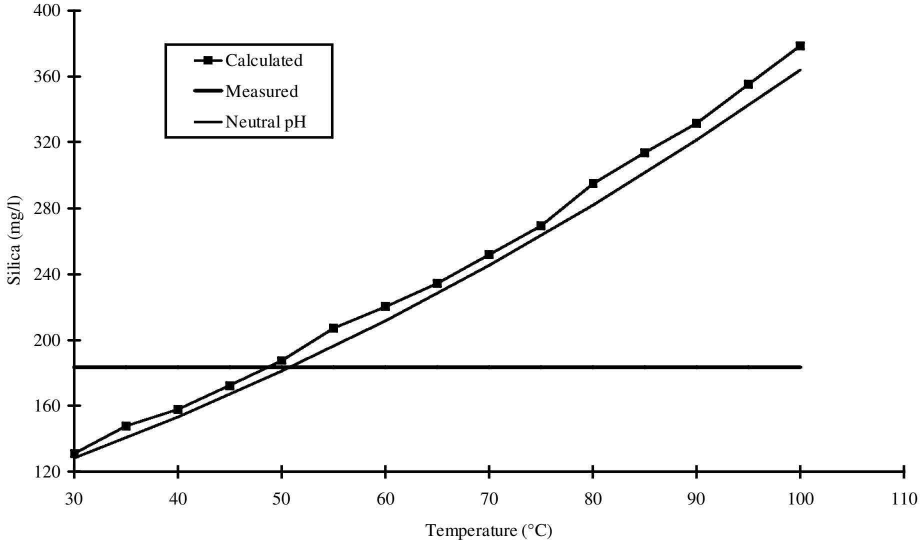

Figure 7. Amorpous silica solubility of the sample from heat exchanger discharge as function of temperature and pH.

Table 4
Temperatures at which the samples from
the Kızıldere field are saturated with amorphous silica.

Sample name	With neutral pH (°C)	With calculated pH (°C)	ΔT (°C)
KD-13 separator discharge	78	60	18
Pool discharge	75	58	17
Heat exchanger discharge	50	49	1

Conclusions

The following conclusions can be drawn from the results of this study:

1. A computer program, SPECIATION, was developed to determine the detailed composition of an aqueous solution and the concentrations and activities of all species.
2. Once the detailed composition of an aqueous solution is known, it is possible to determine the level of the solution with respect to any mineral, which is silica for this study.
3. Three samples from the Kızıldere geothermal field have been collected and their silica scaling conditions were determined as the functions of temperature and pH.
4. The silica deposition danger of an aqueous solution is carried out to lower temperatures if it is alkaline ($pH > 8.5$).

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