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# Origin and Impacts of High Concentrations of Carbon Dioxide in Geothermal Fluids of Western Turkey

Jill Robinson Haizlip[1], Manon M. Stover[1], Sabodh K. Garg[2], Fusun S. Tut Haklıdır[3], and Nicholas Prina[1]

1-Geologica Geothermal Group, Inc. 5 3rd St. #420 San Francisco, CA 93105
2- Leidos 10260 Campus Point Drive, San Diego, CA 92121 USA
3- Bilgen University-İstanbul, TURKEY

e-mail: jhaizlip@geologica.net

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## ABSTRACT

Most explored and exploited geothermal systems located in Western Turkey have relatively high (>1% by weight) concentrations of non-condensible gas in reservoir fluids. The gas is typically 96-98% or greater carbon dioxide ($CO_2$) and is dissolved in the moderate temperature (200°C±50°C) liquid-dominated reservoirs. Carbonate-dominated metamorphic rocks including marbles, dolomitic marbles and calc-schists dominate reservoir rocks; the calcite in these rocks provides a large potential source of $CO_2$ when the calcite equilibrates with water. The dissolution of calcite to calcium and carbonate, bicarbonate, or water and $CO_2$ is accelerated by acidic conditions, temperature and depressed by salt concentrations. The $CO_2$ produces high-pressure, gas-driven geothermal systems. When the systems are produced, the $CO_2$ causes relatively deep two-phase conditions or boiling, requiring deep delivery of scale inhibitor and limiting pumping. When the $CO_2$ partitions into the vapor phase, it is removed from the reservoir and discharged to the atmosphere. Recharge (either from re-injected brine or meteoric water) is relatively low in $CO_2$. Without re-equilibration of recharge, reservoir $CO_2$ concentrations could decline if recharge mixes with reservoir fluids in the production zone. Understanding the source of $CO_2$ in these geothermal fluids, and monitoring $CO_2$ concentrations in reservoir fluids and in produced fluids is critical to managing and sustaining production and injection from these high-gas geothermal reservoirs.

## 1. INTRODUCTION

This paper focuses on the geothermal systems in Western Turkey in the Alasehir-Gediz and Menderes grabens and related horst blocks. Most geothermal systems in Western Turkey are characterized by moderate fluid temperatures ($150^0$C to $240^0$C), liquid-dominated, high in noncondensible gas (NCG) (>1 weight% in the reservoir and total flow) predominantly (>98% by volume in dry gas) carbon dioxide ($CO_2$) (e.g. Aksoy, 2015, Haizlip et al., 2013), moderate to low salinity and hosted in marine and lacustrine carbonate, meta-carbonates, marbles and calc-schist reservoir rocks (e.g. Simsek, 1985, Yilmazer et al., 2005). Calcite is the dominant carbonate mineral in most of these rocks. While stable isotopes of water indicate that the source of geothermal fluids in western Turkey is local meteoric water, carbon isotopes from geothermal $CO_2$ indicate that the $CO_2$ in geothermal fluids is from marine carbonate sediments (Yildrim and Guner, 2005, Haizlip and Haklidir, 2011, Simsek, 2003, and Aksoy et al., 2015) and there is no indication of magmatic $CO_2$ in the isotopes or in the geologic environment.

Geothermal geochemists working around the world have suggested that $CO_2$ concentrations in geothermal systems are the result of reactions between alteration minerals such as calcite and water (e.g. Arnorsson, 1986 and Giggenbach, 1980) whereas when there is reservoir vapor phase, gas-gas reactions can be important (D'Amore and Truesdell, 1984). Arnorsson (1986) suggests that when temperatures exceed $230^0$C, $CO_2$ concentrations in Icelandic geothermal systems are controlled by epidote + prehnite + calcite + quartz, but at lower temperatures, the control mechanism includes equilibrium with calcite.

Most geothermal systems in Turkey are below or near $230^0$C and there is no reported evidence of vapor phase in geothermal reservoirs in Turkey, supporting the conclusion that dissolution of calcite is producing dissolved $CO_2$. Although equilibrium with calcite is common in most geothermal reservoirs (Arnorsson, 1978), few geothermal reservoirs have the high gas concentrations observed in Turkey. $CO_2$ concentrations in geothermal systems in Western Turkey currently being developed for power generation range from approximately 0.015 to 0.034 kg $CO_2$ /kg $H_2O$ (Haizlip et al., 2013) relative to between 0.0005 and 0.01 kg $CO_2$ /kg $H_2O$ in most geothermal systems (Henley et al., 1984, Giggenbach, 1980). The high salinity Tuzla Geothermal System is an exception, with 0.005 kg $CO_2$ /kg $H_2O$ (Baba et al., 2004).

Additional physiochemical factors affecting initial reservoir $CO_2$ concentrations may include the dissociation (or association) of carbonic acid, temperature, salinity, or mineralogy. Other factors may involve the geologic setting such as the reservoir rocks and or the lack of of boiling.

The high $CO_2$ in Turkish geothermal fluids impact project efficiencies for production, injection and power generation in several ways. Previously discussed are the impacts of $CO_2$ on calcite scaling and the gas break-out (bubble point) pressure (e.g. Henley et al., 1994, Arnorsson, 1995, Serpen et al, 1999, Arkan et al., 2002, Tut-Haklidir et al., 2012, Haizlip et al., 2012) and $CO_2$ emissions (Aksoy et al., 2015).

This paper brings together some of the aspects of $CO_2$ generation previously discussed which may contribute to high gas concentrations in Turkish geothermal systems. We discuss some of the impacts of high NCG on the production and the exploitation of high-$CO_2$ Turkish geothermal systems and geothermal fluids and approaches to managing their impacts.

## 2. SOURCE OF HIGH $CO_2$ GEOTHERMAL FLUID

### 2.1 Chemistry of carbonate dissolution

The dissolution of calcite from carbonate reservoir rocks provide the source of $CO_2$ in accordance with the following reactions, which involve both the calcite mineral, and the state of the dissolved carbonate product. The dissolution of calcite is controlled by the reactions which control the solubility of calcite, such as the following reaction:

$$CaCO_{3(calcite)} = Ca^{+2} + CO_3^{-2} \qquad (1)$$

where the equilibrium constant $K_{calcite} = a_{Ca+2}*a_{CO3-2}$ (e.g. Arnorsson, 1990), $CaCO_3$= calcite, $Ca^{+2}$ = calcium ion, and $CO_3^{-2}$ = carbonate

The equilibrium constant for this reaction, $K_{calcite}$ is defined by the activities of the products (activities of calcium ($Ca^{+2}$), and carbonate ($CO_3^{-2}$) divided by the activity of the reactant, calcite, which is 1. Experimental data (Ellis, 1963) indicates that $K_{calcite}$ decreases with temperature and therefore the solubility and the dissolution of calcite increase at lower temperatures. Furthermore, at a constant temperature, $K_{calcite}$ increases with salinity suggesting that calcite is more soluble in saltier geothermal fluids, and $CO_2$ is less soluble in highly saline fluids (the salting-out effect).

In the presence of acid (represented by $H^+$ ions), the dissolution of calcite can produce $CO_2$ directly, according to the following reaction:

$$CaCO_{3(calcite)} + 2H^+ = Ca^{+2} + CO_{2(gas)} + H_2O \qquad (2)$$

where the equilibrium constant $K'_{calcite} = (a_{Ca+2}* a_{CO2})/(a_{H+})^2$ and $CaCO_3$= calcite, H+ = hydrogen ion, $Ca^{+2}$ = calcium ion, and $CO_2$= carbon dioxide, $H_2O$ = water. pH = -log $a_{H+.}$

The second equation includes the dissociation of dissolved $CO_2$. Arnorsson (1995) describes the relationship of the equilibrium constants of these reactions as follows:

$$K'_{calcite}*K_{H2CO3}*K_{HCO3-} = K_{calcite} \qquad (3)$$

where $K_{H2CO3}$ = the equilibrium constant for the first dissociation constant of dissolved carbon dioxide, also known as carbonic acid.The dissociation of $H_2CO_3$ produces bicarbonate ($HCO_3^-$) as follows:

$$H_2CO_3 = HCO_3^- + H^+ \qquad (4)$$

The second dissociation constant of carbonic acid, $K_{HCO3}$, produces carbonate ($CO_3^{-2}$) as follows:

$CO_3^{-2} + H^+ = HCO_3^-$ (5)

The equilibrium behavior of these reactions indicate that if $H^+$ increases (pH decreases), then at constant temperature, $a_{Ca+2}$ and $a_{H2CO3}$ must increase to maintain the $K_{calcite}$ at a constant value. Therefore, the addition of acid ($H^+$) will push the reaction (2) to the right dissolving calcite. This well-known principle is the chemical foundation for acidizing wells to increase well productivity by removing calcite and opening fractures in carbonates, removing fracture-filling calcite or carbonate scale which has been successfully practiced in Turkey for many years.

Furthermore, the equilibrium constant for reactions (2), like (1), decreases with temperature (Henley et al., 1984; Arnorsson, 1990), suggesting that calcite dissolution increases at lower temperatures (Table 1).

**Table 1: Values for the equilibrium constants for equations (1) and (2) as Log Kcalcite and Log K'calcite as defined by Arnosson (1990) data from Henley et al., 1984.**

| Temperature | 150 °C | 200 °C | 250 °C |
|---|---|---|---|
| log Kcalcite | -10.07 | -11.6 | -12.8 |
| log K'calcite | -6.45 | -8.05 | -9.26 |

As observed by many others (e.g. Arnorsson, 1978), most geothermal reservoirs are saturated with calcite. Observed reservoir chemistry from Turkish geothermal systems generally plots on the calcite equilibrium line (**Error! Reference source not found.**), from the equation of Ellis (1963). suggesting that the carbonate concentrations in these reservoir fluids are in equilibrium with calcite:

$$CaCO_{3(calcite)} + CO_2 + H_2O = Ca^{+2} + 2HCO_3^- \qquad (6)$$

where the equilibrium constant $K_{CHC} = (a_{Ca+2}* 2a_{HCO3})/(a_{CO2,g})$, where $a_{CO2,g} \approx P_{CO2}$ = partial pressure of $CO_2$.

This reaction (6) suggests that at constant temperature in equilibrium with calcite, $CO_2$ is controlled by $a_{Ca+2}$ and $a_{HCO3}$-, but $a_{HCO3}$- is controlled by the dissociation of dissolved $CO_2$ (carbonic acid, equation (4)) and pH. In geothermal fluids, other acids affect pH such as silicic acid, sulfuric acid and boric acid. Some Turkish geothermal fluids have relatively high concentrations of boron (~100mg/L) and/or sulfate (~500 mg/kg), suggesting other reactive acids affecting pH.

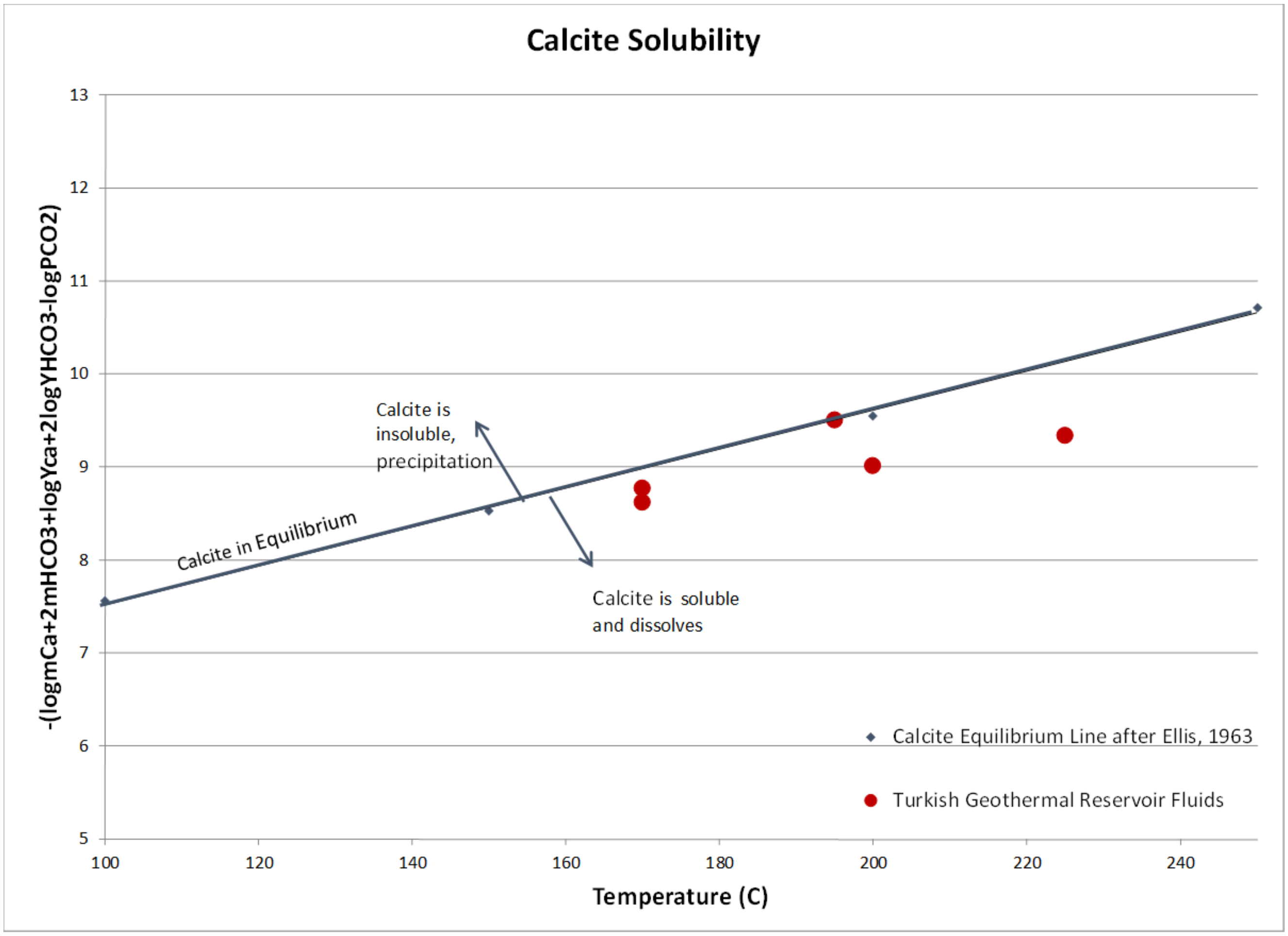

**Figure 1: Calcite Solubility based on the equation of Ellis (1963) for selected Turkish geothermal reservoirs with temperatures > 150C and gas from 1.5 to 3.5% in the reservoir. Reservoir concentrations from 2-phase samples corrected for steam loss and activity coefficients from the geochemical modelling program WATCH.**

### 2.2 Geochemical Modeling

Evaluation of the chemistry of complex geothermal fluids is simplified by using geochemical modelling programs such as WATCH (Arnorsson, et al., 1982, Bjarnason, 1994). In order to confirm calcite equilibrium, we ran fluid chemistry from several Turkish geothermal systems through WATCH to calculate the reservoir concentrations and activity coefficients as well as the equilibrium relative to calcite solubility.

Calcite solubility or saturation is estimated by WATCH using the saturation index. Scaling, or over saturation, is indicated if the saturation index for a mineral, SI >0 where:

SI = Q/K
Q = activities of products/activities of reactants in the solubility reaction (see reactions 1, 2, or 6) where the activity is the molar concentration times the activity coefficient, and
K= equilibrium constant for the solubility reaction.

SI is typically presented as log (Q/K). Q and K are calculated by WATCH. When log (Q/K)=0, the fluid is in equilibrium with the mineral.

Results (**Error! Reference source not found.**) indicate that most reservoir liquids are close to equilibrium with calcite within the variability of the geochemical data. This suggests that when the fluids flash during production and $P_{CO2}$ is reduced, the fluids will precipitate calcite. Equilibrium with calcite also suggests that the generation of $CO_2$ from calcite dissolution has stabilized. If undersaturated fluids such as injection water or groundwater enter the reservoir, the degree to which re-equilibrate depends on the reaction rate.

**Table 2: WATCH output results for Geothermal Fluids from Western Turkey: Reservoir Liquid Chemistry with no boiling. The equilibrium for calcite is represented as Log Q/K, which is 0 at equilibrium. Chemical analysis from samples of two-phase flow.**

| Reservoir T | | Ca+2 | | HCO3- | | H2CO3 | pH | PCO2 | Calcite |
|---|---|---|---|---|---|---|---|---|---|
| meas | WATCH: Qtz Geotherm | (mg/kg) | Y | (mg/kg) | Y | (mg/kg) | | bar(a) | LogQ/K |
| 186 | 214 | 5.4 | 0.40 | 987 | 0.77 | 16351 | 5.7 | 28.2 | -0.14 |
| 240 | 284 | 3.7 | 0.27 | 2434 | 0.68 | 50958 | 6.2 | 73.3 | -0.32 |
| 196 | 226 | 11.0 | 0.42 | 1155 | 0.79 | 47013 | 5.4 | 78.9 | 0.53 |
| 170 | 135 | 81.1 | 0.36 | 1765 | 0.75 | 42857 | 5.4 | 74.3 | 0.37 |
| 173 | 163 | 62.1 | 0.37 | 1685 | 0.75 | 42893 | 5.4 | 74.3 | 0.29 |
| 204 | 221 | 2.5 | 0.44 | 823 | 0.80 | 32026 | 5.6 | 53.0 | -0.61 |

## IMPACTS OF HIGH $CO_2$ ON PRODUCTION, POWER GENERATION, AND EMISSIONS

### 2.1 Effect of $CO_2$ on fluid phases

Carbon dioxide usually constitutes the dominant noncondensable gas in geothermal systems. Other gas phase components include hydrogen sulfide, hydrogen, methane, nitrogen, ammonia, argon and helium; if present in sufficient quantities, these gases can exert a significant effect on the phase behavior of reservoir fluid. In Turkish geothermal systems currently under development, $CO_2$ dominates all other gases (Table 2).

**Table 2: $CO_2$ concentrations as mole % in dry gas from Aksoy, 2015**

| Area | CO2 (as mole % in dry gas) |
|---|---|
| Alasehir-Akkecili | 98.6 |
| Kemaliye | 99 |
| Germencik | 98.3 |
| Salavatli | 98 |
| Yilmazkoy | 95.7 |
| Kizildere | 99.2 |

Therefore, to simplify present considerations, we assume that the NCG is purely $CO_2$. **Error! Reference source not found.** shows the phase behavior of water with a gas mass fraction of 1%. The presence of $CO_2$ in water substantially alters the phase behavior. In contrast with pure water, the two-phase region is a band bounded by $P_{max}$ (the boiling pressure) and $P_{min}$ (the condensation pressure). Note that $P_{min}$ is slightly higher than the saturation pressure for pure water. The presence of $CO_2$ greatly extends the range of reservoir temperatures for which the onset of two-phase behavior will occur in a geothermal reservoir.

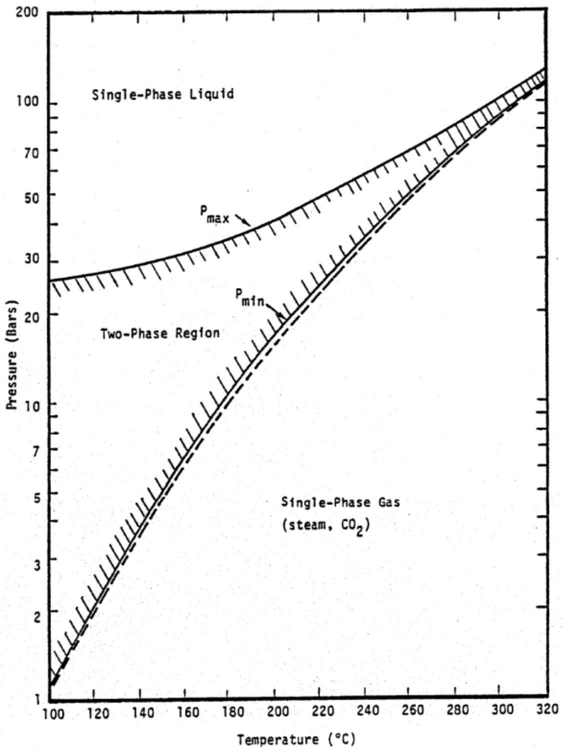

**Figure 2: Illustration of placement of figure and Phase diagram for water with a CO2 mass fraction of 1 %. The dashed line is the saturation line for pure water. From Pritchett et al., 1981**

When geothermal fluids boil (flash) or transform from single phase to two-phase conditions, almost all of the $CO_2$ partitions into the steam (vapor) phase, although this process is not always instant (e.g. Arnorsson, 1995, Henley and Singers, 1982). Distribution $CO_2$ between the vapor phase and liquid phase at geothermal flash temperatures (125$^0$C to 250$^0$C) as shown by distribution coefficients (m $CO_2$ -vapor/m $CO_2$ -liquid, Giggenbach, 1980) range from approximately 2500 at 125$^0$C to approximately 100 at 250$^0$C. The gas concentration in the steam phase is based on both the distribution coefficient and the amount of steam relative to the total flow (%steam) generated. Therefore, concentration of gas (as weight % gas/steam + gas) in the initial flash is proportional not only to the amount of gas but to the reservoir temperature or enthalpy and the %steam generated by flashing.

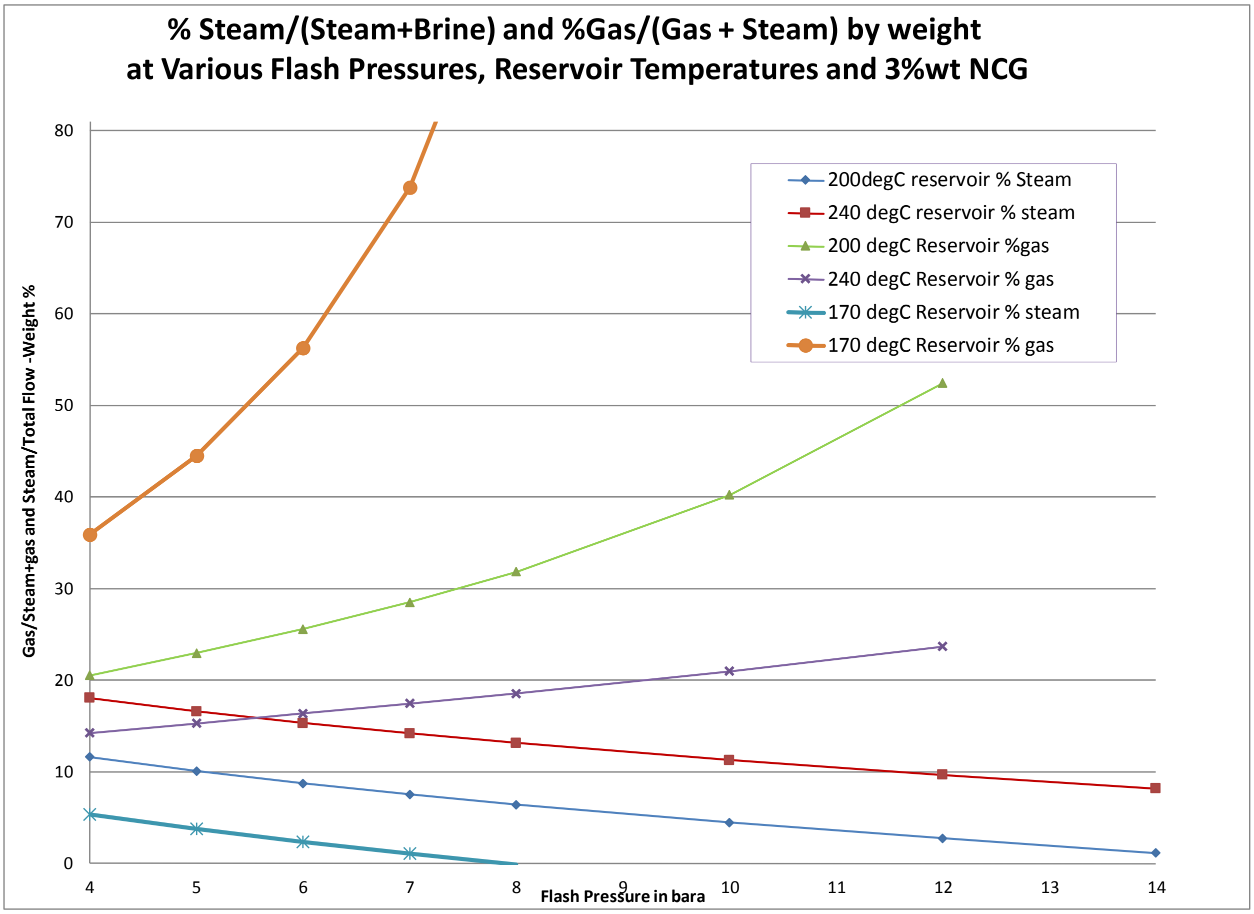

**Figure 3: Gas/Steam +Gas and % steam at the first flash/separation of geothermal fluids at 170°C, 200°C and 240°C assuming a concentration of 3wt % $CO_2$ in unflashed reservoir liquid and single stage flash at various pressures.**

Given constant $CO_2$ concentrations in reservoir fluids, at lower the reservoir temperature or enthalpy of the total flow less steam is in the first flash, and the higher gas/steam. Though there are some indications that $CO_2$ is present at lower concentrations in lower temperature reservoirs (Haizlip and Tut, 2011; Arnorsson, 1986), there is no clear correlation between temperature and reservoir $CO_2$ between different fields in Western Turkey. The concentration of $CO_2$ in the steam can be manipulated during project design by changing the flash pressure. Since almost all of the gas partitions into the vapor phase, most of the total mass of $CO_2$ will flow into the power plant with the steam from the first flash, distribution coefficients (discussed above) suggest that at higher flash temperatures, more gas remains in the liquid, producing $CO_2$ in the steam of the second flash, if there is one.

In addition, the amount of NCG in the initial flash is significant, a portion of the total pressure is gas and the temperature of the brine discharge is less than if the total pressure is only determined by saturated water pressure. For example, if the first flash produces 25% steam at 8 bara, then the vapor pressure is actually only 7.2 bara and the brine temperature is 166$^0$C rather than 170$^0$C if the steam constituted the full 8 bara of pressure and the brine enthalpy declines from 720.8 kJ/kg to 703.3 kJ/kg.

### 2.2 Gas Breakout (Bubble point), calcite scale mitigation and pumping

In addition to high $CO_2$, Turkish geothermal systems are characterized by calcite scaling in production wells when reservoir liquid begins to transform into a two-phase fluid (Parlaktuna and Okandan, 1989, Satman, 1999, Arkan et al., 2000, Haklidir-Tut et al., 2011). Calcite scaling occurs when changes occur in the physiochemical conditions in the reservoirs in equilibrium with calcite (and most geothermal systems are; Arnorsson, 1995). The effect of high $CO_2$ in reservoir fluids on calcite scaling is therefore:

1) the dissolution of calcite can increase calcium and carbonate concentrations in the initial reservoir liquid,
2) high concentrations of dissolved $CO_2$ cause the gas breakout depth two-phase conditions (or bubble point) to occur at greater depths in a well (Haizlip et al., 2012).

As discussed previously, when fluid pressure falls below the minimum total pressure (water pressure + gas pressure) or "gas break out pressure" or "bubble point", the geothermal fluid is transformed from single phase to two-phase. When the fluid transforms from single phase (liquid) to two-phase (vapor (gas and/or steam) +liquid), $CO_2$ partitions from the liquid phase into the vapor phase. When the concentration of dissolved $CO_2$ decreases in the liquid, the loss of $CO_2$ forces the carbonic acid dissociation (equations 4 and 5) in the opposite direction, pH rises and calcite becomes super-saturated and precipitates (scales) from the liquid (equation 2 goes to the left) and calcite precipitates (scales) in accordance with the reactions described above. The pressure at which gas breakout occurs is highly dependent on the concentration of $CO_2$, and dependent, but less so on the temperature (**Error! Reference source not found.**).

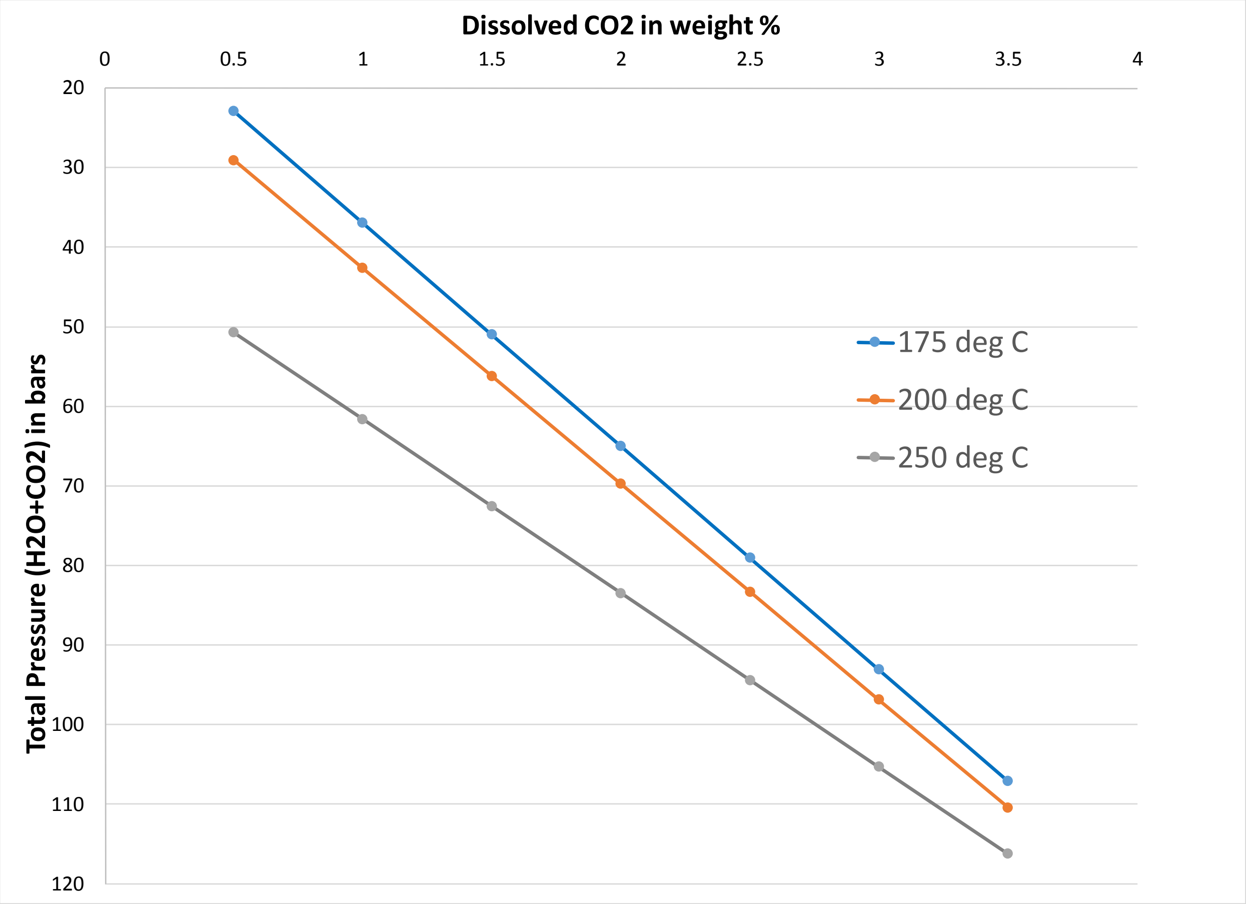

**Figure 4: Total Pressure or Total Minimum Pressure (liquid) or Gas Break-out Pressure or Bubble Point= pressure required to maintain gas in solution or to maintain reservoir conditions as a single liquid phase. Total Minimum Pressure (liquid) = PH2O, Pressure of water at saturation temperature + PH2O, Pressure of dissolved gas based on mole fraction x Kh (Henry's law constant) (Henley et al., 1984).**

At pressures below the gas break-out pressure, or, in a flowing well, above the depth of the gas break-out pressure, calcite scaling potential rises significantly. The depth of gas breakout is affected by the gas concentration and temperature which control gas break-out pressure and wellbore dynamics such as flow rate. As the gas breakout pressure increases, the depth of potential scaling also increases.

Wellbore simulation (Garg et al., 2004) can evaluate the depth of gas breakout at various wellhead pressures or mass flow rates. Simulation of a typical Turkish well construction and reservoir temperature (approximately 175 $^0$C) variable $CO_2$ concentrations of 1.5, 2.75 and 3.5%wt, and a reservoir pressure at the median gas concentration (**Error! Reference source not found.**) relates gas breakout (bubble) depth to $CO_2$ concentrations and, to a lesser extent flow rate. Although the assumptions in this calculation (reservoir pressure and productivity index are applicable for all the NCG in %wt) are not entirely true, it shows that $CO_2$ concentrations are the primary influence on depth to gas breakout and therefore maximum depth of scaling.

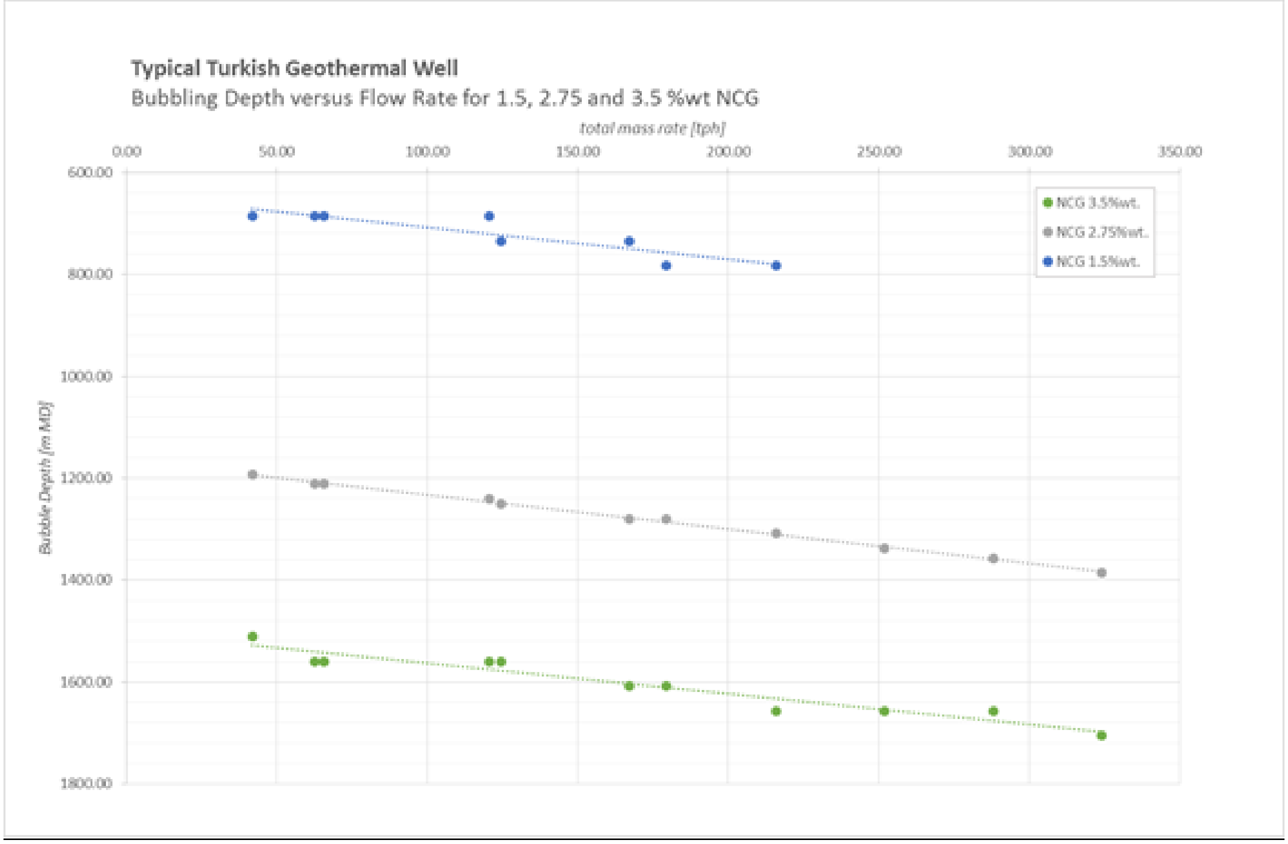

**Figure 5: Wellbore simulations of Mass flow rate versus the Depth of Gas Break-out Pressure or Bubble Point; pressure required to maintain gas in solution or to maintain reservoir conditions as a single liquid. Simulations using a typical wellbore construction, reservoir temperature of 175°C, average reservoir pressure at three levels of CO2 in reservoir liquid: 1.5% (blue dots), 2.75% (grey dots) and 3.5% (green dots).**

Fortunately, the Turkish geothermal producers have developed reliable methods for managing calcite scale using downhole chemical inhibitors (e.g. Parlaktuna and Okandan, 1989, Osborn et al., 2008, Tut-Haklidir et al., 2011). These chemical inhibitors need to be delivered below the depth that calcite scaling could occur: below the depth of gas breakout. For some wells where the main feed zone is at the bottom of the well, delivering chemicals below this depth is a challenge. In wells for which the gas breakout depth is below the main entry at a given flow rate, the potential for scaling in the reservoir may require the flow rate to be curtailed in order to lower the gas breakout depth (bubble point) below the feed zone (**Error! Reference source not found.**).

Because the high $CO_2$ concentrations produce deep gas breakout pressures and high total pressures, most wells are flowed artesian. Pumping of most these fluids before they are allowed to flash with conventional geothermal downhole pumps is difficult. The deep gas breakout requires a deep pump setting, and the high pressure requires a large pump. In order to maintain single phase production using downhole pumps, the pump would have to maintain pressure above the gas breakout pressure (**Error! Reference source not found.**) and be set below the bubble point depth. Even with 2% CO2, this would require pressures of 65 to 85 bar and set depth, depending on flow, permeability and well construction, below 1000m. Therefore, few Turkish fields have used downhole geothermal pumping and single phase production.

### 2.3 Well testing

For high NCG geothermal wells, applying the traditional Lip Pressure method (James, 1962) for estimating total mass flow and enthalpy of a two-phase flow stream can provide confusing results even when the gas correction (James, 1970) or modified gas correction (Grant 1982) is applied. The correctness of the enthalpy calculated by the Lip-Pressure method are dependent on the correctness of the NCG ($CO_2$) concentration values, and the total flow is dependent on obtaining representative enthalpies.

To mitigate an over or under estimation of the enthalpy and total mass rate when testing high gas liquid-dominated geothermal systems, enthalpy can be calculated from the measured downhole temperature of single phase liquid flow (from the dynamic survey), assuming that the total discharge enthalpy is approximately equal to the enthalpy of reservoir liquid prior to gas-breakout. This assumption can be validated by calibrating the wellbore simulator with the dynamic survey. The steam fraction for atmospheric flash is then calculated using the total discharge enthalpy and the enthalpy of steam and brine at atmospheric conditions and the steam mass flow rate is then calculated from the mass flow rate of liquid (from the weir box) and the steam fraction.

In **Error! Reference source not found.** 3, the calculated enthalpy values are shown for a 'typical' Turkish geothermal well completed in a moderate temperature, high $CO_2$, liquid dominated geothermal system. The enthalpy is calculated with three (3) different methods for non-condensible gas content ranging from 2.25 wt.% to 3.25 wt.% $CO_2$. Enthalpy calculations with the lip pressure method are dependent on the $CO_2$, concentrations; the results in Table 3 suggest that incorrect or inaccurate NCG content values have impact on the enthalpy. Therefore, downhole dynamic surveys during two-phase testing provide an important method for estimating enthalpy whether or not lip pressure is measured.

**Table 3 Comparison of Enthalpy Calculations for a Typical Turkish Well with High Gas Content**

| | **Enthalpy (kJ/kg)** | | |
|---|---|---|---|
| **$CO_2$ content (wt.%)** | **Lip Pressure Method + Gas Correction (R. James 1970)** | **Lip Pressure Method + Gas Correction (M. Grant, 1982)** | **Enthalpy of Liquid Water at Measured Liquid Temperature ≈Total Enthalpy** |
| 2.25 | 769.2 | 750.3 | 714.8 |
| 2.75 | 735.5 | 732.7 | 714.8 |
| 3.25 | 675.9 | 715.9 | 714.8 |

### 2.4 Changes with production (and injection)

In some geothermal systems, the NCG content of the fluid discharged from wells changes dramatically with time (Truesdell et al., 1995). In geothermal systems where boiling occurs in the formation, NCG could decrease in reservoir liquid because NCG fractionates preferentially into the produced vapor phase, reducing *in situ* NCG content of remaining liquid or increase in produced fluids with excess steam.

Boiling in the reservoir Turkish geothermal systems has not been documented. However, changes in the $CO_2$ content of the discharged fluids could occur as a result of the mixing of injection water or groundwater recharge. Injection water or waste brine is depleted in $CO_2$, as a result of boiling. Groundwater is also low in $CO_2$. Injection into the production reservoir and/or the influx of recharge water with lower $CO_2$ concentrations from the lateral boundaries into the production zone could reduce in $CO_2$. As an example, Garg et al. (2015) used a 3-D numerical model to predict the discharge characteristics of deep wells at the Kizildere geothermal field; the computed results indicated a significant lowering of the $CO_2$ mass fraction as a result of the mixing of the low-$CO_2$ injected water and influx from boundaries with the in situ reservoir fluids.

### 2.5 $CO_2$ Emissions

Although not a focus of this paper, a clear impact of high $CO_2$ concentrations in Turkish reservoir fluids is $CO_2$ emission to the atmosphere. For reasons discussed above, most geothermal systems are produced after flashing in the well. After the flashed, two-phase fluids are produced and the steam flows through the turbine or heat exchanger, the associated gas is typically discharged to the atmosphere. Emission estimates provided by Aksoy et al. (2015) range from 900 to 1300 g/kWh.

Preventing $CO_2$ emissions by pumping, may work in some systems with low gas, particularly if the wells are design for pumping. Other ways to manage $CO_2$ emissions involve re-injection of $CO_2$, requiring re-absorption of the $CO_2$ by the fluids either chemically or with pressure, other uses of $CO_2$ such as industrial or greenhouses, or minimizing emissions by changing the flash pressure. It is also possible that changes in reservoir fluid chemistry through carefully managed injection could reduce in $CO_2$ without damaging reservoir temperatures.

## 3. CONCLUSIONS

The source of $CO_2$ in Turkish geothermal fluids are probably related to the readily available source of calcite in the carbonate reservoir rocks. However, in the reservoir, as in geothermal reservoirs around the world, calcite ($CaCO_3$) and the geothermal fluids appear to be in equilibrium. Therefore, the high $CO_2$ concentrations are probably related to a combination of physiochemical factors affecting initial reservoir $CO_2$ concentrations such as: moderate temperatures, a source of acid (H+), high calcium concentrations, possibly low salinity, and a readily available source of $CaCO_3$.

Given the tendency of $CO_2$ to partition into a vapor phase, boiling of geothermal fluids reduces high $CO_2$ concentrations n the liquid phase. The liquid-dominated geothermal systems do not indicate signs of deep reservoir boiling though a few shallow aquifers boil and produce low temperature fumaroles. The single phase to two-phase transition in a flowing well causes calcite scaling.

The impacts of the high $CO_2$ in production for geothermal power generation includes:

- at high reservoir pressures, two-phase conditions occur more readily;
- total minimum pressure for maintaining single phase, or the gas breakout pressure or bubble point are directly related to CO2 concentrations;
- gas breakout (bubble point) which affects the depth of boiling and therefore the maximum depth of calcite scale is deeper,
- gas breakout depth is also affected by mass flow;

- well testing using lip pressure often gives mixed results and enthalpy of liquid water before the bubble point from donhole dynamic temperature surveys can be used;
- downhole pumping is limited by the high and deep gas breakout pressure;
- the flash or separation pressure required to obtain a specific discharge brine temperature into the power plant is higher;
- gas concentrations in steam can be very high at low steam fractions; and
- injection or groundwater breakthrough may lower gas concentrations over time.

Appropriate project design can mitigate these impacts as follows:

1. Measure $CO_2$ and brine chemistry in reservoir fluids through appropriate two-phase sampling of the vapor phase during well testing before wellfield, gathering system and power plant design.

2. Balance project design parameters such as inlet flash pressure, wellhead pressure, to manage high $CO_2$.

3. Reservoir modelling to predict likelihood of $CO_2$ declines allows for design to focus on the likely $CO_2$ concentrations over the project life. These models must be based on real well data and updated after production and injection begins. Design the production and injection accordingly and modify as needed to maintain production and manage $CO_2$ sustainably.

4. Include $CO_2$, gas/steam measurements and other geochemical monitoring as part of reservoir monitoring during production and injection in order to manage both the reservoir and $CO_2$ impacts.

## REFERENCES

Aksoy, N., Solak Gok, O., Mutlu, H., and Kılınc, G., 2015, "CO2 Emission from Geothermal Power Plants in Turkey", *Proceedings World Geothermal Congress 2015*, Melbourne, Australia, 19-25 April 2015.

Arkan, S., Akin, S. and Parlaktuna, M. (2002) "Effect of Calcite Scaling on Pressure Transient Analysis of Geothermal Wells*", Proceedings, 27th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, January 28-30, 2002, SGP-TR-171.

Arnorsson, S., 1978; "Precipitation of calcite from flashed geothermal waters in Iceland", *Contributions to Mineral Petrology*, Vol., 66, p. 21-28.

Arnorsson, S., Sigurdsson, S., and Svavarsson, H., 1982; "The Chemistry of Geothermal Waters in Iceland I. Calculation of Aqueous Speciation from 0-Degree-C to 370-Degree-C", *Geochimica et Cosmochimica Acta*, Vol., 46, p. 1513-1532.

Arnorsson, S., 1986; "Chemistry of Gases Associated with Geothermal Activity and Volcanism in Iceland. A Review", *Journal of Geophysical Research*, Vol., 91, p. 12,261-12,268.

Arnorsson, S., 1995; "Calcium Carbonate Depaosion From Geothermal Fluids: Causes, Operational Problems and Their Solution", in *Scaling Problems and Treatment of Separated Water Before Injection*, p. 79-94.

Bjarnason, J.O., 1994; "The Speciation Program WATCH, version 2.1" Orkustofnun, Reykjavik, Iceland.

Baba, A., Deniz, O., Ozcan, H., Erees, S.F., and Cetiner, S.Z., 2007, "Geochemical and radionuclide profile of Tuzla geothermal field, Turkey", *Environ Monit Assess*, DOI 10.1007/s10661-007-0045-0.

D'Amore F. and Truesdell, A.H., 1985; "Calculations of geothermal reservoir temperatures and steam fractions from gas compositions", *Transactions* Geothermal Resources Council Annual Meeting, 1985, Vol. 9

Drever, James. I., 1988, The carbonate System and pH Control in *The Geochemistry of Natural Waters*, Prentice Hall, Inc., Englewood Cliffs, New Jersey 07632, pages 48-75.

Ellis, A.J., 1963, Solubility of Calcite in Carbon Dioxide Solutions, *American Journal of Science*, V. 257, p. 259-267.

Garg, S.K., Pritchett, J.W., Alexander, J.H. (2004). A new liquid hold-up correlation for geothermal wells. *Geothermics* 33, 795-817.

Garg et al, 2015, "Reservoir Simulation and Kizildere Geothermal Field", *Proceedings World Geothermal Congress 2015*, Melbourne, Australia, 19-25 April 2015.

Guney, A. and Fusun S. Tut Haklidir, T. Akin, and A. Alpagut Bukulmez, 2011, Short Term Flow Testing at Kizildere-Impact of Deep Wells, *Proceedings:*36th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, January 31-February 2, 2011, SGP-TR-181, p. 80-85.

Haizlip, J. R., Tut, F. (2011) High Noncondensible Gas Liquid Dominated Geothermal Reservoir Kizildere, Turkey, Geothermal Resources Council *Transactions*, Vol. 35, October 23-26, 2011.

Haizlip, J.R., Guney, A., Tut Haklidir, F.S. Garg, S.K., 2012, "The Impact of High Noncondensible Gas on Well Performance", Kizildere Geothermal Field, Turkey, *PROCEEDINGS, 37th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, January 30 - February 1, 2012 SGP-TR-194.

Haizlip, J.R., Tut Haklidir, F., and Garg, S.K., 2013, "Comparison of Reservoir Conditions in High Noncondensible Gas Geothermal Systems", *PROCEEDINGS, 38th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, February 11-13, 2013 SGP-TR-198.

Henley, R.W., A.H. Truesdell and P.B. Barton, 1984, Fluid-Mineral Equilibria in Hydrothermal Systems, Reviews in Economic Geology, American Society of Petroleum Engineers, Vol. 1.

Henley, R.W. and Singers, W.A., 1982, "Geothermal gas separation in conventional cyclone separators", *New Zealand Journal of Science*, Vol. 25, p. 37-45.

Osborn, W.L., Demirci, N., Gülgör, A., Erkan, B. and Yildirim, N. (2007) Carbonate Scale Inhibition in a High-Gas Geothermal Well, Germencik, Turkey, Geothermal Resources Council *Transactions*, Vol. 31, 2007.

Parlaktuna, M., and Okandan, E., 1992, "The use of chemical inhibitors for prevention of calcium carbonate scaling", *Geothermics*, Vol. 18, p. 241-248.

Pritchett, J. W., Rice, M.H., Riney, T.D. (1981), Equation-of-state for water-carbon dioxide mixtures: implications for Baca reservoir. S-Cubed, La Jolla, California (DOE Report No. DOE/ET/27163-8).

Satman, A., Ugur, Z. and Onur, M. 1999, "The effect of Calcite Deposition on Geothermal Well Performance", *Geothermics*, Vol. 28, p. 425-444.

Simsek, S., 1985, "Geothermal Model of Denizli-Sarakoy-Buldan Area", *Geothermics* Vol. 14, No 2/3 p 393-417.

Simsek, S., 2003, "Hydrological and isotopic survey of the geothermal fields of the Buyuk Menderes Graben, Turkey", *Geothermics*, Vol. 32, p. 669-678.

Truesdell, A.H., Lippmann, M.J., Quijano, J.L., and D'Amore, F., 1995; "Chemical and physical indicators of reservoir processes in exploited high-temperature, liquid-dominated geothermal fields", *Proceedings* 1995 World Geothermal Congress, Florence, Italy.

Tut Haklidir, F. S., Taylan A., Guney, A., and Alpagut-Bukulmez, A., 2011, Short Term Flow Testing at Kizildere-Impact of Deep Wells, *Proceedings:36th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, CA, January 31-February 2, 2011, SGP-TR-181, p. 869-875.

Yildrim, N. and Guner, I. N., 2005, "Geochemical Properties and Determination of Turnover Time by Using $^{14}$C Isotope, in Kizildere and Tekkehamam Geothermal Field of Turkey", *Proceedings* World Geothermal Congress 2005, Antalya, Turkey, 24-29 April 2005.

Yılmazer S., Pasvanoğlu S., and Vural S., 2005, "The Relation of Geothermal Resources with Young Tectonics in the Gediz Graben (West Anatolia, Turkey) and Their Hydrogeochemical Analyses", *Proceedings* World Geothermal Congress 2010 Bali, Indonesia, 25-29 April 2010.