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Aquifer Fluid Chemistry Characteristics for the Domes Geothermal Wellfield at Olkaria, Kenya

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Keywords

Phase Segregation Model, initial aquifer fluid, hydrothermal mineral assemblages, excess enthalpy, loss of circulation, geothermometers, pressure and temperature

ABSTRACT

The initial aquifer fluids feeding Olkaria Domes wellfield in Kenya have been modelled using the analytical data of the wellhead samples. The chemical composition of liquid water and vapour discharged were used to reconstruct the composition and species distribution in the initial aquifer fluid using the Phase Segregation Model at a temperature of 180°C in the case of wells with excess discharge enthalpy. The fluid enthalpy reveals that some of the wells have liquid enthalpy while the majority having “excess enthalpy” with the geothermometers indicating that excess enthalpy of well discharges is largely produced by phase segregation in producing aquifers or occurring by gravity under natural conditions. The measured pH was corrected for silica polymerization and subsequently used to calculate aquifer water pH and mineral saturation. The modelled fluids is characterized by Na-Cl-HCO₃ water type and it exposes the existence of a wide-ranging difference in composition with discharge wellhead waters showing a general increase in contents of most elements at surface conditions. As described in this paper, the results were further used to assess how closely they have approached equilibrium conditions with respect to various mineral-gas and mineral-solution reactions that may occur in the aquifer. The aquifer water is close to saturation with respect to calcite but under-saturated with fluoride except for the lowest temperature waters (~200°C). Aqueous carbon dioxide is either controlled by close approach to equilibrium with specific hydrothermal mineral assemblages or source controlled. Hydrogen and hydrogen sulphide show large scatter for their modelled concentrations in the initial aquifer fluid making it difficult to deduce the processes that govern them.

1.0 Introduction

Studies of discharged fluids from high-temperature reservoirs have supplied extensive information on the chemistry of aquifer fluids as well as their origin. A number of research studies have been carried out on the chemistry of fluids discharged from wells in high-temperature geothermal systems: to evaluate the process that control fluid composition (e.g. Arnórsson and Stefánsson, 1999); assess changes in fluid chemistry of producing fields by cold water recharge (e.g. Gudmundsson and Arnórsson, 2002), and; sources of some chemical constituents in the fluid (e.g. Giggenbach, 1992). Depressurization boiling in producing aquifers and wells in particular of high-temperature, liquid dominated geothermal systems causes cooling of the fluid and escape of gases. These affects the state of saturation of the liquid with respect to many minerals, hence causing precipitation or dissolution of some of them, depending on their kinetics, thus variation of fluid composition between intact aquifer fluid and wellhead where discharge samples are collected.

The sources of the main geothermal gases (CO₂, H₂S, H₂ and CH₄) are believed to be solidifying magma bodies, while nitrogen and argon are transmitted by recharging meteoric waters that have equilibrated with the atmosphere (Scott et al., 2011). Due to their relatively high abundance and reactivity, these components have long been used by reservoir scientists to characterize the physical nature of and manage production from hydrothermal systems (e.g. Ármannsson et al., 1982; Gudmundsson and Arnórsson, 2002) The concentrations of these gases in aquifer fluids are greatly affected by physical properties such as enhanced boiling and recharge, but are generally believed to be kept in close equilibrium with specific hydrothermal mineral assemblages (Scott et al., 2011).

The main objective of this study is to utilize analytical wellhead data to model initial aquifer fluid compositions and assess the state of gas- and mineral-solution equilibria in the aquifer of the Domes wellfield geothermal system and provide a baseline for future geochemical observations.
2.0 Geological Setting

Olkaria geothermal prospect is located on the floor of Kenya rift, south and west of Eburru and Mt. Longonot geothermal prospects, respectively. It is geologically situated within the Greater Olkaria volcanic complex. The surface geology has been described by MacDonald et al. (1987) as consisting of mildly peralkaline (comenditic) rhyolitic domes, lava flows, air fall pumices, and minor lake sediments, peripheral basalts and hawaiites. Quaternary comendites, pantellerites and an extensive cover of pyroclastic fall from the nearby Longonot and Suswa volcanoes envelop the surface to about 1400 m a.s.l.. It is marked by structurally controlled volcanic eruption centres of Quaternary age, with Olkaria hill, Gorge Farm area and the Oloolbutot fault zone being the most important volcanic centres. The Olkaria hill is not associated with an apparent caldera structure but an inference has been made with the presence of a ring of volcanic domes in the east and south, and a buried caldera in the southwest (Mungania, 1992; Clarke et al., 1990), bolstered by seismic wave attenuation studies (Simiyu et al., 1998).

![Figure 1. Map of the Kenyan rift showing the location of Olkaria geothermal field.](image)

3.0 Methodology

Analytical data of discharge fluid from nine wells were used in the study. Appropriate chemical data were selected based on ionic balance and the agreement between the quartz and Na/K geothermometer temperatures. Calculations were carried out with the help of the WATCH chemical speciation program (Bjarnason, 2010), with tolerance values of ≤ 10% and ≤ 20°C, respectively.

Corrections for pH for silica polymerization followed an iteration procedure that utilized WATCH program to incorporate analytical data and pH, assuming a liquid phase, water enthalpy and aquifer temperature (from geothermometers). Corrections were made on the assumption that measurements might have been delayed and that all dissolved silica in excess of amorphous silica solubility had polymerized at the time of pH measurement. Correct pH is rather essential in modelling aquifer chemical composition; speciation distribution is essential for geochemical interpretation and assessing the state of mineral-solution equilibria for minerals with pH dependent solubility, and also for mineral-gas equilibria involving CO$_2$(aq) and H$_2$S(aq) irrespective of their solubility dependency (Busey and Mesmer, 1977; Arnórsson et al., 1982; Tossell and Sahai, 2000; Gudmundsson and Arnórsson, 2005; Angcoy and Arnórsson, 2010).

Correction of pH followed an iteration procedure that utilized the WATCH chemical speciation program to incorporate water sample analytical data and pH, assuming a liquid phase (without gas phase), water enthalpy and aquifer temperature (from geothermometers). The initial aquifer fluids feeding Olkaria Domes well field were then modelled using the analytical data of the wellhead samples with, again, the aid of the WATCH chemical speciation program, based on the Phase Segregation Model (PSM), a model discussed by Arnórsson et al. (2007; 2010), and Arnórsson and Stefánsson (2005), where phase segregation occurred at a temperature of 180°C (equal to 10 bar-a) (Karingithi et al., 2010).

The stepwise approach of reinstating aquifer chemistry started with the calculation of the composition and speciation of the vapour and liquid at 180°C from the selected analytical wellhead data of the water and steam. This step used measured enthalpy, ambient temperature and corrected pH. The second step used the WATCH output from the first run to calculate initial aquifer composition and speciation distribution taking the average of Na/K and quartz geothermometer temperatures to represent the initial aquifer liquid temperature and enthalpy.

With the initial aquifer fluid concentrations, the WATCH speciation program was used to calculate individual species activities. The results of these modelled fluids were used to assess their saturation conditions, with respect to calcite, fluorite, quartz, chalcedony and amorphous silica when temperature drops. Considerations were also conducted on the concentrations of the reactive gases H$_2$S, H$_2$ and CO$_2$ in relation to their approach to equilibrium with respect to selected mineral-gas reactions.

Equilibrium constants have been used for mineral assemblages that potentially could control the concentrations of CO$_2$(aq), H$_2$(aq) and H$_2$S(aq) presented to assess to what extent mineral-reactive gas equilibria may be approached in the aquifer (Table 1). A consideration of the saturation state of the aquifer water for selected hydrothermal minerals has also been carried out for calcite and fluorite. The thermodynamic values and properties for CO$_2$(aq), H$_2$(aq) and H$_2$S(aq) were retrieved from Fernandez-Prini et al., (2003), Holland and Powell (1998) and Robie and Hemingway (1995), respectively, as summed up in Karingithi et al., (2010).
Such high HCO₃ values can either be high-temperature geothermal systems. Phenomenon uncharacteristic of a valid in the range 0-350°C at Psat. Unit activity was selected for all minerals and liquid water. That causes high CO₂ flux, the last case is water or high level of magma degassing indicative of peripheral origin of aquifer. Charge wellhead waters with a general increase in contents of most wide-ranging difference in composition between aquifer and discharge that may control gas aqueous CO₂, H₂ and H₂S concentrations. The equations are Table 1. Temperature equations for the equilibrium constants for mineral assemblage reactions that might correspond to H₂S in the alkaline medium of the NaOH-solution. The amount of SiO₂ in aquifer water varies from 216 to 614 mg/kg with an increasing to a range of 13-40% in the measured SiO₂ from the discharge fluids.

### 4.2 Reactive Gases Composition

The concentrations of H₂S, H₂ and CO₂ in the initial aquifer fluid are presented in Table 2. The equilibrium constants for mineral assemblage reactions that might control these gases are given in Table 1. Reactive gas species, H₂S, H₂ and CO₂, provide information on the physical state of geothermal reservoirs such as temperature and steam-to-water ratio (Arnórsson, 2000). Two mineral assemblages were selected for CO₂ concentrations. Apart from three samples showing a scatter closely matching with the assemblages (see Figure 2), they are generally higher departing in average from 0.3 to 0.4 SI units with reference to clinozoisite-calcite-quartz-prehnite and clinozoisite-calcite-quartz-grossular mineral assemblages, respectively. The CO₂ concentrations displayed are considerably high and this can be attributed to a high flux of this gas from the magmatic source that hinders its close approach to local equilibrium with the mineral assemblages under consideration.

Three mineral assemblages were selected for H₂S, and in general, aquifer water show that the content of this gas is low relative to equilibrium of the assemblages, with an average departure of -1.0, -0.7 and -0.5 SI units, respectively. Further assessment, nonetheless, of waters from the aquifer separately reveals that three of samples relate closely to the assemblages. It is more likely that the relatively low amount of H₂S is due to oxidation or contamination of samples with atmospheric air. Although O₂ was not detected in these waters, as reported in the discharge data, it may have been present initially but destroyed upon sample storage by reaction with H₂S in the alkaline medium of the NaOH-solution.

### 4.0 Results

#### 4.1 Chemical Composition of Aquifer Fluids

The modelled aquifer chemistry exposes the existence of a wide-ranging difference in composition between aquifer and discharge wellhead waters with a general increase in contents of most elements at surface conditions due to steam separation. The equations are Table 1. Three mineral assemblages were selected for H₂S, and in general, aquifer water show that the content of this gas is low relative to equilibrium of the assemblages, with an average departure of -1.0, -0.7 and -0.5 SI units, respectively. Further assessment, nonetheless, of waters from the aquifer separately reveals that three of samples relate closely to the assemblages. It is more likely that the relatively low amount of H₂S is due to oxidation or contamination of samples with atmospheric air. Although O₂ was not detected in these waters, as reported in the discharge data, it may have been present initially but destroyed upon sample storage by reaction with H₂S in the alkaline medium of the NaOH-solution.

### Table 2. Calculated initial aquifer fluid composition from wet-steam wells, alongside enthalpy, aquifer temperature and pressure; chemical concentrations are in mg/kg.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>LogK(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CO₂</td>
<td>(2 \text{CO}_2 + \text{cal} + 3 \text{qtz} = 3 \text{gro} + 1/2 \text{H}_2\text{O} \ l + \ \text{C}_0\text{aq})</td>
<td>-1.449-40536/(T^2)-2135.9/(T) + 0.0065639T + 0.000029625T + 0.000002683T + 0.00004064T + 0.1398</td>
</tr>
<tr>
<td>2. CO₂</td>
<td>(2 \text{H}_2\text{O} + 1/2 \text{qtz} + \text{H}_2\text{O} \ l = \text{pre} + \ \text{C}_0\text{aq})</td>
<td>-0.897+7251.5/(T^2)-1710.6/(T) + 0.004188T + 0.00000787T + 0.00000073T + 0.00000094T + 0.00000005</td>
</tr>
<tr>
<td>3. H₂S</td>
<td>(2 \text{H}_2\text{O} + 1/2 \text{pyr} + 1/2 \text{pyrr} + 3/2 \text{qtz} + )</td>
<td>13.659+555082/(T^2)-9256.6/(T) + 0.03608T + 0.00000286T + 0.00000002T + 0.00000008T + 0.00000001T + 0.1041</td>
</tr>
<tr>
<td>4. H₂S</td>
<td>(2 \text{H}_2\text{O} + 1/2 \text{pyr} + 1/2 \text{pyrr} + \text{H}_2\text{O} \ l = \text{mag} + \text{H}_2\text{S} \text{aq})</td>
<td>13.589+90215/(T^2)-9024.5/(T) + 0.04188T + 0.00000297T + 0.00000002T + 0.00000005T + 0.00000001T + 0.1041</td>
</tr>
<tr>
<td>5. H₂S</td>
<td>(2 \text{pyr} + 1/2 \text{mag} + \text{H}_2\text{O} \ l = \text{em} + \text{H}_2\text{S} \text{aq})</td>
<td>14.340+630124/(T^2)-9605.6/(T) + 0.09488T + 0.00000007T + 0.00000002T + 0.00000001T + 0.1041</td>
</tr>
<tr>
<td>6. H₂S</td>
<td>(1/2 \text{pyrr} + \text{H}_2\text{O} \ l = 1/2 \text{pyr} + 1/2 \text{mag} + )</td>
<td>-1.654+95546.8/(T^2)-621.8/(T) + 0.01257T + 0.00000007T - 0.060T + 0.00000001T + 0.1041</td>
</tr>
<tr>
<td>7. H₂S</td>
<td>(2 \text{semi} + 1/2 \text{pyrr} + 1/2 \text{qtz} + \text{H}_2\text{O} \ l = \text{em} + \text{H}_2\text{S} \text{aq})</td>
<td>-1.544+115109/(T^2)-752.3/(T) + 0.0000586T + 0.00000007T - 0.532T + 0.00000001T + 0.1041</td>
</tr>
<tr>
<td>8. H₂S</td>
<td>(2 \text{mag} + \text{H}_2\text{O} \ l = 3 \text{hem} + \text{H}_2\text{S} \text{aq})</td>
<td>-2.257-116652/(T^2)-10006/(T) + 0.000121T + 0.00000007T - 0.788T + 0.00000001T + 0.1041</td>
</tr>
</tbody>
</table>
Saturation state versus aquifer temperature of calcite and fluorite minerals for Olkaria Domes waters. Figures 2, 3 & 4. State of equilibrium between calculated concentrations of dissolved CO$_2$, H$_2$S and H$_2$ in the aquifer water of Olkaria wells with several minerals assemblages.

Figure 5 & 6. Saturation state versus aquifer pH of calcite and fluorite minerals for Olkaria Domes waters.

Figure 7 & 8. Saturation state versus aquifer pH of calcite and fluorite minerals for Olkaria Domes waters.

The H$_2$ concentrations in these calculated aquifer fluid displays a considerable scatter showing no relations compared to CO$_2$ and H$_2$S, with respect to the three assemblages selected. On average, the departure of H$_2$ from mineral equilibrium with assemblages 6, 7 and 8, are in the magnitude of -0.05, -0.4 and 1.2 respectively. However, a single sample shows a close relationship with the saturation is dependent on several factors, largely the measured pH of water samples, and the analyzed concentration of total carbonate carbon, also in water samples and the selection of aquifer water temperature. Errors in these parameters are considered also to be the cause of the observed relationship between the degree of calcite saturation and pH.

4.3 Calcite and Fluorite Saturation

The ion activity product for calcite (Q) in aquifer waters of individual wells is scattered around solubility constant for calcite. The average departure from equilibrium is 0.07 log (Q/K) units and the standard deviation 0.62 log (Q/K) units. However some samples depart much from saturation, in particular wells OW-901 and OW-903A. The graph for fluorite shows that the aquifer waters of the lowest temperature are very close to being fluorite saturated but hotter waters are undersaturated. In all of the aquifer waters considered for the present study, the dominant fluoride species is F$. The other important F species is HF but it only constitutes a small fraction of the dissolved F in all cases. The fluoride concentrations in the various aquifer waters are very variable. In view of this, the data on the F species and the data for calcite, it is concluded that most of the aquifer waters modelled here are truly fluorite under-saturated.

LogQ values for calcite change from under-saturation to over-saturation with increasing aquifer water pH. This change is not considered to be real, but an artefact reflecting an error in the calculated aquifer water pH. Equilibration between aqueous solution and calcite is rapidly attained, certainly at the high temperatures of the Olkaria reservoir. The value calculated for aquifer water calcite
5.0 Conclusion

The initial aquifer fluids feeding Olkaria Domes wellfield have been modelled successfully using the analytical data of the wellhead samples on the basis of Phase Segregation Model (PSM) taking the phase segregation to occur at a temperature of 180°C (equals to 10 bar abs.). Some of the wells at the wellfield have liquid enthalpy, but the majority have “excess enthalpy”. Geothermometer results indicate that excess enthalpy of well discharges is mainly produced by phase segregation in producing aquifers or occurring by gravity under natural conditions. The result of these modelled fluids was done to assess how closely they have approached equilibrium conditions with respect to various mineral-gas and mineral-solution reactions that may occur in the aquifer.

The modelled aquifer chemistry is characterized by Na-Cl-HCO₃ water type with a wide-ranging disparity in composition between aquifer and discharge wellhead waters with a general increase in contents of most elements at surface conditions. The high CO₂ concentration is attributed to a high flux of this gas from the magmatic source that hinders its close approach to local equilibrium with the mineral assemblages. The low H₂S concentration is probably due to oxidation or contamination of samples with atmospheric air. The large scatter of the H₂ data points must, at least partly, be a reflection of the stoichiometry of the reaction involved. From the data on the F-species and the data for calcite, most of the aquifer waters are truly fluorite saturated, but the majority have “excess enthalpy”. The data for calcite, most of the aquifer waters are truly fluorite sulfate and calcite are not considered to be real, but an artefact reflecting an error in the calculated aquifer water pH.

References


