

## Evaluation of Groundwater Hydrogeochemical Characteristics and Mixing Behaviour In Olkaria Geothermal Systems, Naivasha Kenya

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### ABSTRACT

The Olkaria geothermal field is recharged from precipitation in Aberdares Ranges and Mau forest that is heated before flowing into the overlying geothermal reservoirs via structures. Mixing ratios between cold and thermal waters will be estimated with Cl, Na and B concentrations since elemental concentrations may be derived from geothermal water. Hydrogeochemical features of ground and surface water samples are reviewed in the context of hydrogeological information. Hydrogeochemical characterization of thermal and non - thermal waters discharged from flowing artesian wells will be based on thermal waters with salinity, discharge temperatures and hydrochemical facies. Hydrochemical processes are characterized by analyzing ion ratios in various waters. Geothermal waters have high lithium and boron concentrations, probably due to exchange with smectite. The objective is to assess the hydrologic and geochemical connection between the fractured bedrock geothermal reservoir and the alluvial aquifer and provide an overall assessment on the origin of the thermal waters and geochemical processes giving rise to salinities of these waters as well as estimation of the subsurface reservoir temperatures. The temperatures of the deep geothermal reservoirs are estimated based on the Na-K-Mg geothermometry, while slightly lower estimates are obtained using silica geothermometers. Mixing of the waters provides evidence of groundwater flow paths that may be useful in investigations of thermal waters. Higher contents of some minor elements, such as water F, Si, B and Sr are probably derived from extended water rock interaction, and these elements can be regarded as indicators of flow paths and residence times. Elevated temperature, lithium, boron, chloride and silica indicate mixing may occur indicate geothermal activities.

### 1. INTRODUCTION

Geochemistry is the most important tool in determining the hydrodynamic nature of a geothermal system. The geochemical investigation of the thermal evolution fluids assumes a greater importance when cold water systems and the geothermal systems models are combined. Topographic head gradients drive cold water systems and Density differences between hot and cold fluids result in head differences for geothermal waters. Geothermal waters act as heat transfers medium in the geothermal system. Geothermal systems need at least four parameters to be fully delineated: recharge, heat source, cap rock and the conduits for water to reach the reservoir. Rain, wind, and insolation are atmospheric factor that govern reservoir recharge mechanisms. The cap rock system on top of the reservoir and density differences from the rising geothermal waters deters cold fluids from recharging the reservoir directly from its top. Only the deep circulation from a high topographic head is able to recharge the geothermal reservoir.

Surface waters percolate down the faults and fractures, the pathway to the geothermal reservoir. Water that ascends directly and relatively rapidly from the reservoir with little conductive cooling is likely to have chemical composition that reflects water rock equilibrium. Steam formation, degassing accompanied with changes in temperature and pressure lead to changes in the saturation state of water with respect to minerals. Kinetic factors in this state determine mineral precipitation or dissolution. When a well is discharged depressurization occurs in producing aquifers leading to extensive boiling. If pressure drop is sufficient extensive boiling occurs in reservoirs. The source of recharge waters, magmatic and metamorphic gases affect the chemical differences. Water rock interaction produces concentration of solutes at levels that corresponds to these high temperature geothermal waters of similar salinity. Temperature dependent mineral solution equilibria control concentration of these elements. Mineral-solution equilibria with respect to major elements except chloride, at least if the temperatures exceed 100 °C and in some cases at lower temperatures controls geothermal water compositions (Giggenbach, 1981; Arnosson et al., 1983). The interrelationships between these elements are used to identify particular water types with which the waters have been in contact (Ellis and Mahon, 1977). Giggenbach (1991) divides dissolved solids and gases in geothermal fluids into conservative and reactive components.

Reactive components tend to equilibrate with hydrothermal minerals that incorporate these compounds. These provide useful information on the physical state of geothermal systems. Conservative components include the rock with which the fluid has interacted with but also degassing magma and the recharging water. The residence time of the fluids in the rock and increase in temperature that increases the rate of fluid rock interactions determines the amount of interactions. A decrease in the concentration of Cl, boron and other conservative components in discharged water is a consequence of relative increase in water. Temperature dependent equilibria between alteration minerals in the reservoir rocks and gas ratios in the producing aquifer controls gas concentration in well discharges (Gudmunsson and Arnorsson, 2002). Boron isotopes are fractionated during mineral crystallization (Oi et al., 1989) and during hydrothermal alteration of rock (Spivack, 1985; Spivack et al., 1990; Leeman et al., 1992). Boron isotopic ratios are used to examine up flow zone systems (Leeman et al., 1992).

The water from the rift flank percolates deep into the hot geothermal field through faults. The chemical composition tends to acquire more chloride ions from water rock interactions to form the Na-Cl rich geothermal waters. The ionic concentrations of Na<sup>+</sup> and Cl<sup>-</sup> are low in the shallow wells but increase towards the deep geothermal wells. The hot water mixes with the shallow groundwater to form ionic concentrations of Na<sup>+</sup> and Cl<sup>-</sup>, which increase towards the deep geothermal wells. The geothermal

waters are sodium chloride type. The degree of separation between data points for high chloride and bicarbonate waters gives an idea of the relative degree of interaction of  $\text{CO}_2$  charged fluids at lower temperatures and the  $\text{HCO}_3$  contents increasing with time and distance travelled underground. The fluid in Olkaria West field contrasts sharply with that in the Olkaria East field and Olkaria Northeast field. In the Olkaria West field, the discharge is typically rich in bicarbonates (10,000 ppm) but the  $\text{Cl}^-$  content is very low (50-200 ppm). Comparatively, the bicarbonates-carbonate and  $\text{Cl}^-$  content of the Olkaria Northeast field wells are <1000 ppm and 400-600 ppm respectively. The Olkaria East fluid discharges have similar bicarbonates-carbonate concentration of <200 ppm as those in the Olkaria Northeast and relatively low deep reservoir  $\text{Cl}^-$  concentrations of 200-350 ppm as compared to Olkaria Northeast concentrations. Olkaria Central wells give deep reservoir  $\text{Cl}^-$  concentrations of 200-300 ppm except for well OW-201 that gives higher values in the order of 700 ppm. These wells produce waters with relatively high reservoir  $\text{CO}_2$  concentrations similar to those of Olkaria West field wells. Olkaria Domes wells discharge mixed sodium bicarbonate-chloride-sulphate type with low mean chloride concentrations of 181.5-269.9 ppm.

The Ca content of the geothermal water at Olkaria is low, 1-2ppm. Olkaria northeast field wells discharge sodium chloride waters, with chloride concentrations in the ranges of 400 – 600 ppm and bicarbonate concentrations < 1000 ppm. Olkaria west field wells discharge mainly sodium bicarbonate waters with concentrations about 10, 000 ppm and chloride concentrations ranging 50- 200 ppm while Olkaria central field wells discharge a mixture of sodium chloride and sodium bicarbonate waters. Olkaria domes wells discharge a mixed sodium bicarbonate-chloride-sulphate waters with mean chloride concentrations of 180-270ppm and Olkaria east wells discharge waters with chloride concentrations in the range of 200-350 ppm. Most of the samples approached calcite-solution equilibrium. The Total Dissolved Solids in well-discharged fluid is low in Olkaria geothermal system compared to most high temperature high-pressure geothermal system in the world. The Olkaria geothermal fields waters are dominantly sodium chloride with salinity range of 10 to 1200 ppm. Most Olkaria waters have a pH of 8.5 to 9.5 ranges. This implies limited pH buffer capacity and only a limited degassing of the water with respect to  $\text{CO}_2$  and  $\text{H}_2\text{S}$  is needed to raise the pH substantially (Karingithi, 2000;Karingithi, 2002).

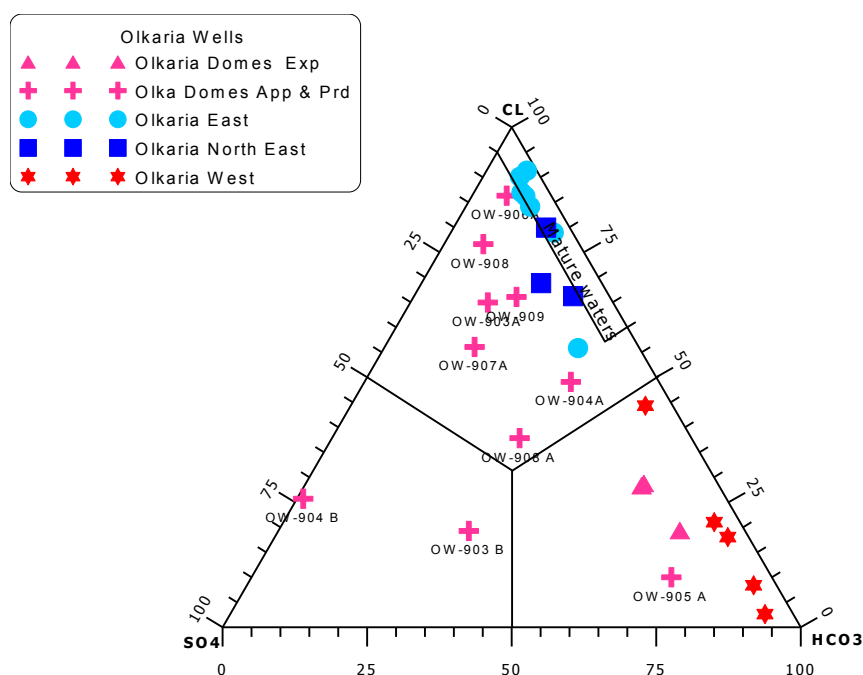
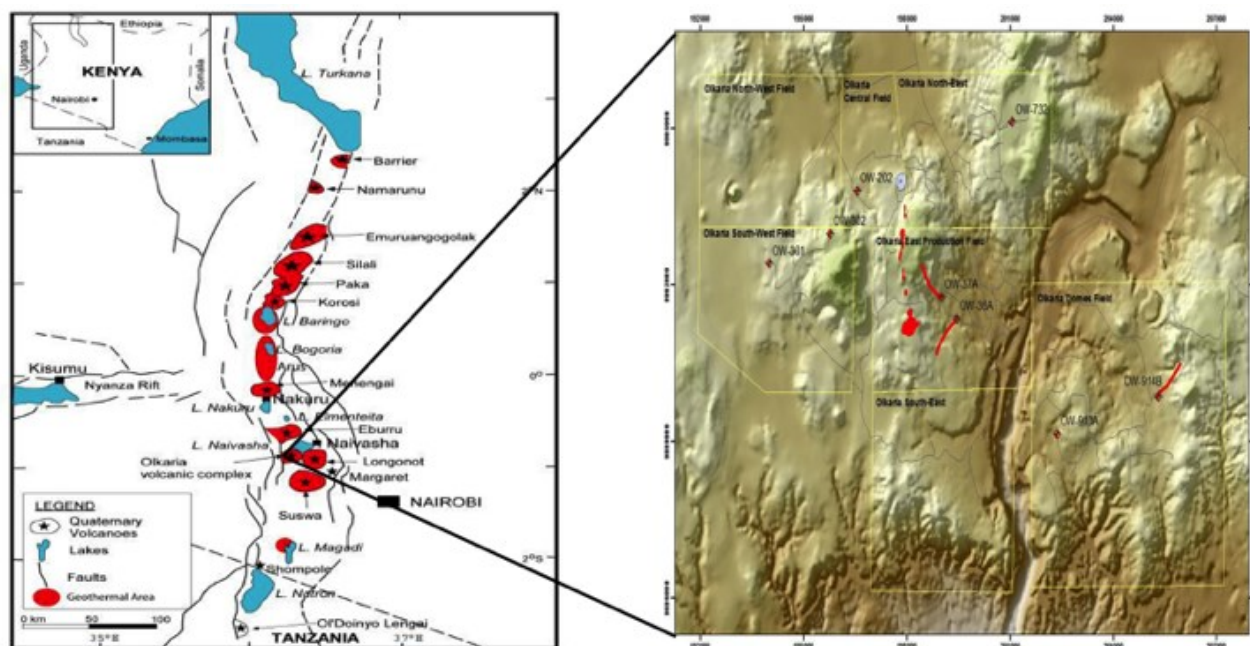


Fig.1: Classification of geothermal water using CL-SO4-HCO3

Depleted  $\text{CO}_2$  levels of the geothermal waters indicate boiling in less than 400 m based on reservoir fluid of 200-250°C and boiling curve with depth. Boiling and  $\text{CO}_2$  loss in the upper parts of the system lead to the attainment of equilibrium with secondary minerals in the hot reservoir fluids at temperatures between 200 and 250°C. This equilibration is accompanied with mixing between the geothermal water and cold ground water. Elevated  $\text{CO}_2$  levels outside the geothermal field depict mixing prior to boiling. Spatial distribution of temperature and Cl concentrations demonstrate the mixing of cold groundwater with upwelling geothermal waters along the main tectonic fractures. The chloride concentration varies between 50 or 100 and 1100 ppm, being lowest in OW304D and highest in OW10. In the Olkaria West field the chloride concentrations are quite low (100–200 ppm) except in well OW-305 that discharges water (530-750 ppm) similar to that discharged from the wells in the Olkaria East and Olkaria Northeast fields (Wambugu, 1995). Olkaria East and Olkaria North east wells tend to be highest in chloride. The observed highest chloride concentrations in water from wells in Olkaria East and Northeast could be the consequence of up flow of deep high-temperature geothermal fluid. Chloride concentrations decrease with increasing discharge enthalpy. Steam loss and consequent loss of mass as vapour to produces heat loss and increase in chloride content in the liquid phase. The gas/steam ratio is usually between 0.001 and 0.003 in steam from wells. Heat flow from the rock may also contribute to progressive boiling in the Olkaria East field well discharges. The Olkaria wells discharged water is generally high in bicarbonate concentrations except in the East production field. The high bicarbonate together with the pH causes  $\text{CO}_2$  partial pressures to be higher than atmosphere pressures. Such degassing tends gives high pH readings and low carbonate carbon concentrations to cause calcite supersaturation. Upon extensive boiling calcite saturated water becomes oversaturated to deposit in the wells. The Ca content of well discharges becomes lower than that of the parent aquifer water as a result. Calcite deposition of this kind leads to low values for calculated calcite saturation index values.



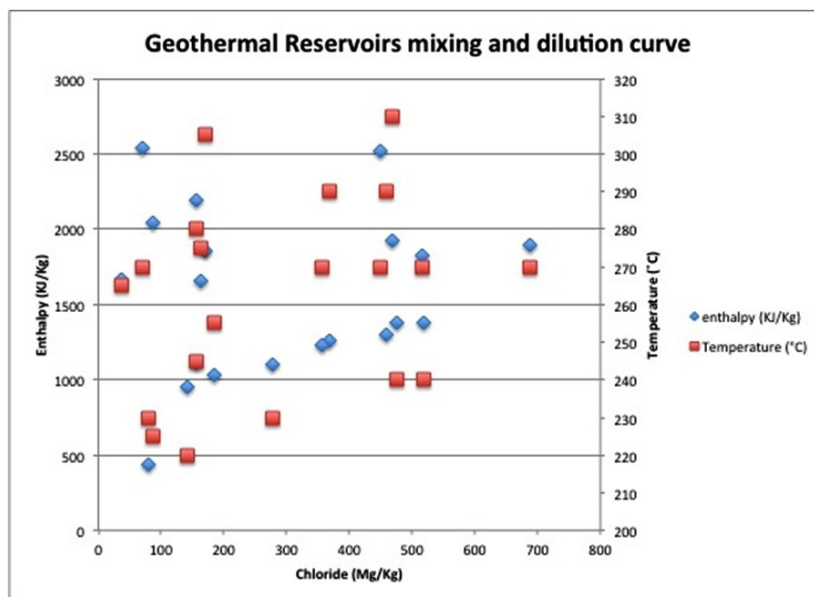
Processes of mixing, boiling and cooling usually have a significant influence on the final composition of the geothermal fluids. Reliable gas geothermometers results are calibrated to account for the composition of the mineral buffers that these gases tend to equilibrate with. The CO<sub>2</sub> gas geothermometer temperatures are erroneously high due to high flux of CO<sub>2</sub> from the magmatic heat source, and lack of equilibration between CO<sub>2</sub> and the respective mineral buffer. The solute geothermometers most often yield comparable aquifer temperatures in the range 184°C to 310°C In Olkaria geothermal wells (Karingithi, 2000).

Nineteen well data were re-analyzed after chemical sampling. The sampling techniques employed were those of Nehring and Truesdell (1977), in which separate liquid water and steam fractions were collected from condensers attached to well head separators. Table 1 lists the sampling conditions of the wells and separators during the flow tests. Unstable chemical species were taken to KenGen geochemistry laboratories and analyzed soon after collection. The remaining major and trace constituents were analyzed independently.

Due to extensive steam flashing in the wellbore during production, chemical concentrations do not represent the chemical composition of the reservoir fluids. The weight of liquid water,  $X$  \*liquid flashing at the separator pressure (Table 1) was calculated from the relationship  $H = X * h_{\text{liquid}}^* + (1 - X) \times H_{\text{steam}}^*$  (1). Where  $H$  is the reservoir enthalpy, and  $H_{\text{liquid}}^*$  and  $H_{\text{steam}}^*$  are the enthalpies of liquid water and steam at the separator pressure. In addition to production from flashing, steam may also originate in the reservoir. Non-volatile chemical species remain in liquid water and volatile species are contained in the coexisting steam phase. The proportions of steam and liquid in the reservoir are related to the reservoir enthalpy by the expression,  $H = X \times h_{\text{liquid}} + (1 - X) \times H_{\text{steam}}$  (2). In which the liquid water and steam enthalpies are for the temperature and pressure of the reservoir. The reservoir enthalpy can be calculated from equation 1 using the measured separator liquid-water fraction and data for  $H_{\text{liquid}}^*$  and  $H_{\text{steam}}^*$  at the separator pressure (Keenan et al 1969). The liquid fraction in the reservoir was calculated from equation (2) and  $h_{\text{liquid}}$  and  $H_{\text{steam}}$  values using reservoir temperatures based on the Na/K geothermometer. The concentration of a non-volatile chemical species,  $C$ , in the liquid-water phase of the reservoir can then be calculated from the relationship  $C = C^* X \frac{H_{H_2O}}{X_{H_2O}}$  (3). Where  $C^*$  is the concentration in the flashed liquid. The relationship assumes no chemical precipitation during flashing and no corrosion in the well bore.

Mixing and equilibrium conditions between solutes and alteration minerals characterize the chemistry and composition of geothermal water; however, the kinetics of leaching process determines the groundwater composition (Opondo, 2006). Mixing of water components dissolves or precipitates mineral and may lead to changes in fluid composition depending on kinetic factors. Changes in pressure have much lesser effect on mineral dissolution than temperature changes (Manning, 19994, Rimstidt, 1997).

The chemical composition of mixed water can be used for temperature estimation in a mixing model discharged from wells (Arnórsson 1985). The enthalpy-chloride mixing model is very useful mixing model that takes into account both mixing and boiling processes in determining models of fluid movements and hydrology by considering chloride concentration and enthalpy. Steam and cold waters generally have low chloride contents and very different enthalpy values. Boiling moves the liquid from a point representative of the 265°C geothermal liquid towards higher chloride contents and lower enthalpies (Fournier (1979). Conductive heat loss of a deep hot water decreases its enthalpy, but its chloride concentration remains unchanged. Addition of cold waters decreases both enthalpy and chloride (Montalvo and Tenorio 2009).



**Fig. 3: Enthalpy–Chloride mixing model**

The high enthalpy and high chloride is interpreted as showing that this well draws its waters from near source of hot chloride geothermal fluids and mixes with shallow ground waters to form the bulk of the Olkaria geothermal waters. Boiling processes predominantly form most of the Olkaria geothermal waters. The reservoir in the Greater Olkaria geothermal area is liquid-dominated in terms of volume; however, steam zone caps the liquid reservoir in the Olkaria East production field. The wells OW 309, OW 714, OW 719 are in a state of equilibrium and can be in either direction. Dilution in the well OW 307 and Dilution occurs in the formation around well OW 301, OW 304D, OW 306, and OW 505. Steam gain occurs in wells OW 19, OW 308, OW 901, OW 902, and OW 903. Conductive heat gain occurs in OW16, OW 19 and OW 25. Conductive heat gain and evaporation occurs in well OW 10, and evaporation occurs solely in OW 15. Enthalpy chloride diagrams have been used to predict salinity, boiling, underground temperatures and mixing relationships.

Silica enthalpy mixing model is based on the assumption that no conductive cooling has occurred after mixing. The calculated temperature of hot water component is too high. It is also assumed that no silica deposition takes place before or after mixing and that quartz controls the solubility of silica in hot water. Mixing occurs deep in hydrothermal system. The recognition of mixing is especially difficult if water-rock re-equilibration occurred after mixing (whether complete or partial) is more likely if the temperatures after mixing is well above 110°C to 150°C or if mixing takes place in aquifers with long residence times. Enthalpy of steam at 100°C is 2676J/g (Henley et al. 1984). The mixing line cannot be derived from the process of mixing hot and cold water, because any mixture would be on or due to the mixing line. Some indications of mixing are the variation in the ratio of relatively conservative elements that do not form solutes during movement of water through rock.

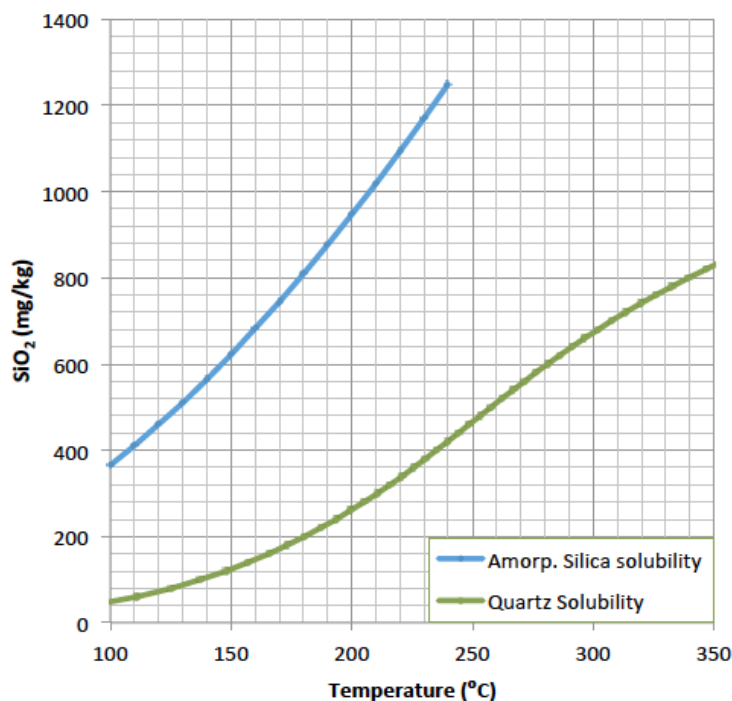
## 5. CHEMICAL GEOTHERMOMETRY

Geothermometry can be used to elucidate chemical reactions in the zone of depressurization around wells. Boiling or cold water recharge induces cooling. Many geothermometers components react slowly upon cooling (Karingithi, 2009). Geothermometers take advantage of specific mineral-solute reactions that are slow to re-equilibrate at cooler temperatures, especially under conditions where the fluid is effectively separated from the minerals that control the equilibria (Fournier and Potter, 1982; Giggenbach, 1980, 1981; Arnórsson et al. 1983).

Reservoir temperatures calculated using K/Na ratio function is based on thermodynamic properties (Arnórsson et al. 1983). K/Na ratio chemical geothermometers give aquifer temperature values ranging from 199-275°C with an average value of 245°C in Olkaria East, the temperatures range is from 215-302°C with an average value of 270°C in the Olkaria Northeast, temperatures indicate minimum values of 180-264°C with an average value of 245°C the Olkaria West field (Wambugu, 1996).

The aquifer water closely approaches equilibrium with quartz geothermometers temperature calculated based on Fournier et al (1982) quartz geothermometry. Amorphous silica controls silica solubility at low temperature and quartz at high temperature. At low temperature quartz is less soluble and amorphous silica is more soluble. Quartz solubility and amorphous silica are a function of temperature at the vapour pressure of solution. The temperature is reflected in the low-albite, calcite and microcline hydrothermal minerals. Olkaria East wells Quartz geothermometry indicate aquifer temperatures range from 172-272°C with an

average value of 245°C. The Olkaria Northeast wells have values ranging from 195-304°C with an average value of 266°C whereas Olkaria Central field give values ranging from 186-259°C. In Olkaria Domes field, the highest mean solute equilibrium temperatures of 242°C, 238°C and 232°C in well OW-903, OW-901 and OW-902 respectively.



**Fig 4: Solubility of Quartz and Amorphous silica based on Olkaria data**

Some wells like OW-305 and OW-301 give comparable temperature values from the two geothermometers and they are taken to indicate proximity to up flow region. Wells OW-304D and OW-307 in Olkaria West field and towards wells OW-708, OW-704 and OW-724 in Olkaria Northeast field could be recharge zones of the geothermal system.

## 6. DISCUSSIONS

Olkaria field well water discharges are low in total dissolved solids when compared to most high-temperature geothermal fields in the world. A general rise in solutes is probably due to steam loss and increase in water-rock interaction. Hydrogeochemical analyses show the trend of heat flow anomalies and predict reservoir temperatures that can be used to create a geothermal model. Under normal circumstances conservative elements are low in cold water but much higher in geothermal waters. Chlorine (Cl) and boron (B) behave as mobile elements in geothermal waters meaning they are not incorporated into any secondary minerals. These constituents mixing involve simple lowering of concentrations. Reactive elements are differentiated based on temperature differences and oxidation states. Oxidation is assumed to occur in the shallower depths.

As the deeper hotter fluids ascend to the surface and mixes with shallower ground waters, much modified water composition emerges. Mixing, boiling and cooling processes have significant influence on the final composition of the geothermal fluids. Changes in enthalpy could influence changes in chloride and changes in chloride could also be inversely related to changes in sulphates. The depletion of hydrogen sulphide gas or diminishing contribution of the deeper reservoir fluid to reservoir processes influences sulphates concentration changes. These two processes cause sulphate concentration to increase and chlorides would most likely decrease. Other than Olkaria East production field various parts of the Olkaria field aquifer water are relatively rich in bicarbonate. Low chloride enthalpy implies most of the waters are undergoing phase changes into steam from boiling water. The mixing models should be applied with great care in geothermometry as the model results are very sensitive to the estimated mixing proportions. High peak at some wells indicate that high temperature values are associated with hot geothermal fluid up flow. Parameters thought to provide significant indication of the boiling, mixing and phase separation processes are used in the assessment of the reservoir changes. These parameters from solute and gas geothermometry temperatures, gaseous concentration of carbon dioxide, hydrogen sulphide, hydrogen and nitrogen and solute concentrations of silica, sulphate, chloride and the enthalpy of the well discharge. The calculated quartz equilibrium temperatures depend on the model selected in accounting for the excess enthalpy in the well discharges. Heat flow from the aquifer rock to the fluid contributes to vaporization of the water to give high values for quartz equilibrium temperatures, particularly in the East production field. Partial segregation of the water and steam phases in the depressurization zone is assumed responsible and the dominant process accounting for the excess enthalpy. Mixing of fluid in wells from different aquifers leads to Na/K temperatures becoming higher than the quartz equilibrium temperatures, particularly if the hotter component in the mixture had higher salinity. The Na/K geothermometer tends to preserve deep equilibrium ratios of Na/K. High temperature tends to increase dissolution but give low Na/K values. Almost equal quartz and Na/K temperature show that the low surface temperature is as a result of cooling rather than mixing with cold groundwater. Well water subjected to a certain degree of mixing and extensive boiling cause calcite-saturated water to become supersaturated, hence the deposition of calcite mineral.



Contribution to well flow from several aquifers of significantly different temperatures causes  $H_2S$  temperatures to be higher than any solute geothermometer temperature, particularly if the deeper, hotter aquifer is rich in steam. High  $H_2$  temperatures compared with those of  $H_2S$  are indicative of the presence of equilibrium steam in the aquifer beyond the zone of depressurization. Phase segregation in the aquifer is the most important process generating excess enthalpy well discharges. Some reaction may be expected to occur, depending on kinetic factors that would affect different geothermometers to a different extent (Arnorsson and Gunnlaugsson, 1985).

## 7. CONCLUSIONS

The relationship between concentrations of elements can be used to identify particular waters in a geothermal system and to predict rock type with which the waters have been in contact. The water rock interaction can indicate flow paths and residence times. Changes with time in the fluid compositions provide valuable information on the response of exploited reservoir to cold recharge and production load factors. The chemical composition of mixed water can be used for temperature estimation in a mixed model. Geothermometers based on dissolved silica content and the solubility of different silica species can be used to determine the temperature of water-rock interaction processes at depth in a rising fluid before its discharge and locate levels of producing horizons in the wells. Amorphous silica controls silica solubility at low temperatures. The high enthalpy encountered in newly drilled wells in Olkaria East implies scales could form during utilization of geothermal fluids in power production and direct uses applications. Olkaria Domes water is very variable, mixed sodium bicarbonate, sodium chloride water and sodium sulphate waters do exist.  $T_{NaK}$  are mostly higher than  $T_{qtz}$  suggesting possible removal of silica and there are relatively high levels of  $CO_2$  in Olkaria Domes for example around OW-914 and OW-905A.

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