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MODELLING THE GEOCHEMICAL EFFECTS OF GEOTHERMAL FLUID INJECTION IN THE OLKARIA GEOTHERMAL FIELD, KENYA

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ABSTRACT

Reinjection of used geothermal waters has become an integral part for sustainable geothermal utilization in the Olkaria geothermal field. The location of the field inside the Hell's Gate National Park requires an environmentally friendly way of disposing of separated brine and condensate. Additionally, increased production capacity has been proceeded over the years with increased reinjection. Despite the benefits mentioned, one of the major issues associated with reinjection is the possible loss of permeability due to scaling. In this study, the potential for scale formation in several hot reinjection wells in the Olkaria geothermal field was evaluated. The first approach assessed the potential of scale formation in reinjection wells prior to production using the WATCH speciation program to obtain the baseline data. The second approach using the PHREEQC geochemical model, simulated mixing of injected fluids and aquifer fluids to assess the scaling potential of the mixed fluid. The results from the two approaches were then compared for calcite, amorphous silica and anhydrite saturation in the geothermal fluid. The saturation state of the injected fluid with respect to calcite, amorphous silica and anhydrite at the temperature of reinjection was also assessed in the PHREEQC program using different databases. The results from this study did not only show both positive and negative geochemical effects of fluid injection in the Olkaria geothermal field, but they also showed some inconsistencies in the mineral thermodynamics properties in different PHREEQC databases. Despite these limitations, the confidence level for using the PHREEQC program in geothermal fluids was identified.

1. INTRODUCTION

In recent years, reinjection of used geothermal waters has become an integral part of sustainable geothermal utilization projects in the world (Kaya et al., 2011). The notable benefits associated with reinjection include: (1) provision of an environmentally friendly method of disposing separated geothermal brine and steam condensate, (2) recharging of the reservoir and providing the necessary pressure support. Pressure decline due to long term exploitation of the geothermal resource is a common observation in geothermal production wells (Axelsson, 2008). Despite these benefits, scale formation is the most problematic process associated with the reinjection and may result in loss of well



FIGURE 1: Map showing geothermal areas in Kenya (Ofwona, 2002)

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permeability (Serpen and Aksoy, 2005). Permeability loss will result in the inability to carry out reinjection into the reservoir. Although this is not the only challenge that is related to reinjection, a clear understanding of water-rock interactions and the chemistry of the geothermal fluid is important for a successful reinjection plan (Arnórsson, 2000).

The Olkaria geothermal area is a hightemperature geothermal system in Kenya located on the eastern segment of the East African Rift. (Figure 1). This field has been under exploitation since the early 80s. Most of the steam is used for power generation in the four main existing power plants and smaller wellhead units. The current installed capacity for geothermal power in Olkaria is 519 MWe (KenGen Database, 2016). Direct utilization has recently gained momentum with the current operation of a geothermal spa and usage in the Oserian greenhouses for horticulture farming. Initial decline in production capacity was observed 15 years after the commercial exploitation in the Olkaria East production field in the early 90s (Mwangi, 2000). This decline resulted in the drilling of six additional wells to maintain the production. Numerical studies carried out in the mid-80s suggested that re-injection into this field would reduce this decline rate and

hence reduce the required number of make-up wells. Currently, both cold and hot water reinjection is performed in the Olkaria geothermal field. Cold reinjection is used to dispose of cooling tower blowdown, which is the condensate from the power plants, whereas hot reinjection has been dedicated for disposing of the separated geothermal brine (Mariaria, 2011).

Studies have shown that various techniques can be employed to better understand the reinjection regime in geothermal systems. Chemical tracers for instance, have been used extensively over the years to study reservoir properties and thermal breakthrough in geothermal systems. Geochemical studies on the other hand, have mostly been focused on silica precipitation and its effects on the reservoir properties which contribute to permeability decrease. Several numerical modellings of the Olkaria geothermal area have been carried out over the years. In 2012, a review of the energy production capacity of the geothermal area was undertaken by a consortium composed of Icelandic consulting companies, such as Mannvit, Vatnaskil, Verkís and Iceland GeoSurvey (ÍSOR). This review was based on earlier studies done by Western Japan Engineering Consultants (WestJec). One of the highlights in this review was the need for a large scale reinjection strategy for sustaining the increased electricity generating capacity. (Axelsson et al., 2013). This plan is, however, hampered by lack of detailed research required for reinjection exploration.

The objective of this study is to model the possible geochemical effect of geothermal reinjection in the Olkaria geothermal system and assess the scaling potential of hot reinjection into Olkaria wells prior to production and during reinjection. A comparison of the two would enable evaluation of how mixing of fluids can modify saturation states and eventually affect the scaling potential in reinjection wells and in the receiving aquifer.

2. GEOLOGICAL SETTING AND GEOTHERMAL ACTIVITY

2.1 Geological outline

The Olkaria geothermal field (Figure 1) lies on the southern segment of the Kenyan Rift, which belongs to an Eastern African Rift System (EARS). This field, which has been classified as a high-temperature geothermal field, is among the 14 geothermal prospects that have been identified within the Kenyan Rift (Mwawongo, 2005). Macdonald and Scaillet (2006) noted that the Olkaria geothermal field is one of the 5 quaternary-recent volcanic complexes in Kenya and together with the Eburru volcanic complex, can be grouped as rhyolitic volcanic complexes, whereas Menengai, Longonot and Suswa are considered to be trachytic caldera volcanoes. Extensive studies of the geological setting of the Olkaria have been done in the past (Naylor, 1972; Odongo, 1993; Omenda, 1998; Lagat, 2004). The consensus from these studies is that the Olkaria geothermal field is a remnant of an old caldera. The occurrence of rhyolitic bodies along a north-south trending fissure strongly supports the existence of a north-south geological fissure in the area. Chorowicz (2005) clearly notes that volcanism along the EARS is strongly related to tectonics with normal faults being the main tectonic feature. The alignment of major volcanic centres along the Kenyan Rift (Figure 1) has been interpreted as surface manifestation of deep axial faults dissecting the inner graben with the Olkaria-Eburru lineament, displaying NS direction trend (Riaroh and Okoth, 1994). The Ololbutot fault zone and the Gorge farm area (Figure 2) have been characterized by substantial volcanic activity. Apart from the Ololbutot lavas, which represent the most recent volcanism, the rhyolitic flows are covered by pumice siliceous fall deposits and since the volcanic activity at Longonot predates volcanism in Olkaria, the present pyroclastic ash covering the area is thought to have originated from the Longonot volcano with some contribution from the Suswa volcano (Odongo, 1993). The subsurface geology based on cuttings from more than 200 drilled wells shows that four broad lithostratigraphic units can be identified based on age, tectono-stratigraphy and lithology as outlined by Omenda (1998). The formations are the Mau Tufts, Plateau Trachytes, Olkaria Basalts, and



FIGURE 2: Map of the Greater Olkaria complex showing major tectonic structures (Otieno, 2016)

Upper Olkaria Volcanics. The Olkaria field can further be divided into two units with reference to the formations: (1) the western sector which is characterized by the Mau tuffs and (2) the area east of the Olkaria hill, which has the plateau trachytes and Olkaria basalts as its signatures. The occurrences of different hydrothermal alteration minerals have been used to predict reservoir temperatures, fluid chemistry, permeability, and the evolutionary stage of the system. Omenda (1998) and Lagat (2010) summarized the common secondary minerals which occur in the Olkaria geothermal field. They include; calcium silicates, clays, oxides, silica minerals, zeolites, pyrite, fluorite, calcite, and albite. Further studies by Mibei (2012), identified four alteration zones in the Olkaria geothermal area. This was after correlating hydrothermal mineral assembles from three wells each belonging to three subfields: Olkaria East field, Olkaria North-East field, and the Olkaria Domes field.

2.2 Structural geology

The Eburru-Olkaria alignment was noted by Riaroh and Okoth (1994) as one of the three major alignments in the Kenyan Rift. A further examination revealed that the alignment does not always follow the general orientation of the Rift Valley, especially in sections where there is a change in direction. Studies on the structural pattern of the Olkaria geothermal area support the existence of several fault trends (Figure 2). These trends which include: NS, NW-SE, NNW-SSE, and ENE-WSW control the bulk fluid movement in the region (Omenda, 1998). The NS faults and fractures, which represent the latest tectonic event, are common in the axial region of the rift floor with vertical permeability indicated by strong fumarole activity. The most prominent is the Ololbutot fracture zone. The NW-SE trending faults on the other hand have been inferred from the alignment of the volcanic centres. The Suswa fault intersects the NNW rift faults whereas the ENE-WSW trending Olkaria fault has been interpreted as an old geothermal rejuvenated structure that cut through the geothermal field.

2.3 The history of utilization and the current status

The first research at the Olkaria geothermal field started between 1955 and 1959 when two exploratory wells, X-1 and X-2, were drilled, but failed to discharge. In the mid-1960s, the Olkaria area was considered as a promising geothermal prospect area after geophysical surveys had been carried out between Lake Bogoria (Figure 1) and Olkaria area. Funding from the United Nations Development Program (UNDP) supported more extensive geoscientific survey, which started in 1970. The geothermal resources were further confirmed by six exploratory wells, which were drilled between 1973 and 1976 (KPC, 1994). By 1981, the first 15MWe unit was commissioned in the Olkaria East field. Two more units were commissioned in 1983 and 1986 and the current installed capacity for Olkaria I is 45 MWe. Extensive exploration led to the discovery of additional resources in the Olkaria geothermal area. The Greater Olkaria geothermal area (GOGA) is divided into several fields based on the characteristics and location. These are; Olkaria East field, North-East field, Olkaria Domes, Olkaria South-East field, Olkaria Central field, Olkaria North-West field and Olkaria West field (Figure 3). The latter is owned by OrPower Inc, an independent power producer (IPP). With the exception of the Olkaria North-West Field, the other fields are operated by the mostly state owned Kenya Electricity Generating Company (KenGen). The Olkaria II power plant in the North-East Field was built in two stages; the first two units were built in 2003 with a capacity of 70 MWe and the third unit in 2010 with a capacity of 35 MWe.

The most recent additions to the Olkaria geothermal field were done in 2014 when two power plants, each with 140 MWe capacity, were commissioned. The first power plant is the Olkaria I addition unit (AU) also in the Olkaria East field and the other one is in the Olkaria Domes where Olkaria IV power plant is located. Apart from the convection flash power plants, KenGen also generates electricity using wellhead technology. This technology allows the wells to be utilized and generate revenues in the short term. Usually in the construction of the conventional power plant those wells would be set to idle and would only be used to supply steam to the power plant once it has been commissioned.



FIGURE 3: Map showing the Olkaria geothermal sectors (KenGen Database, 2016)

2.4 Reinjection in the Olkaria geothermal field

Extensive geoscientific data has been obtained over the years in the Olkaria geothermal area. This data has revealed that the Olkaria geothermal field can sustain further production and therefore future expansion plans are ongoing. In order to be able to sustain future expansion, resource management programmes started in the mid-90s. As a result, a six-month injection and tracer test was carried out in the Olkaria East production field (Ambusso, 1994). The purpose of this test was to determine the effect of the injection on the production wells performance and to evaluate the possibility of implementing long term injection programmes in the field. This experiment was carried out after substantial pressure drawdown which was measured in the wells supplying steam to the Olkaria I power plant, ten years after commercial operations had started. The conclusion from this test was that commencement of reinjection prior to the onset of large drawdown in the reservoir leads to greater sustenance of well production.

The initial practise for disposal of used geothermal waters in the Olkaria Field was surface disposal, where geothermal brine was disposed of in surface ponds and left to percolate into the ground. However, due to environmental effects of such disposal and the need for geothermal resource management, a reinjection strategy was adopted in Olkaria. Currently both hot and cold reinjection is carried out in different sectors of the field. Cold reinjection is used to dispose of cooling tower condensate. Hot reinjection is preferred to minimize cooling of production wells and scaling process (Mariaria, 2011). Several hot reinjection wells are used at different sectors of the Olkaria geothermal field. In this study, the following hot reinjection wells will be considered in the modelling approach: the OW- 703 and OW-708, (located in the North East Field), OW-R3 (located in a buffer zone between the North-East Field and the East Field) and OW-911 (located in the Domes Field) (Figure 4). Apart from well OW-911 which was commissioned as a reinjection well in 2014, the other three wells have been used since 2003 when the Olkaria II power plant came online. The recent addition of the 140 MWe in the Olkaria East Field has seen a change in the reinjection regime such that the separated brine from wells with different chemical compositions is also being directed to the existing reinjection wells. The data considered for this study is prior to these changes which took place in 2014.



FIGURE 4: Location of hot reinjection wells in Olkaria (arrows show wells investigated during this study)

3. CHEMISTRY OF THE THERMAL FLUIDS IN THE OLKARIA GEOTHERMAL FIELD

3.1 Fluid classification

The chemical composition of the fluids in the Olkaria geothermal area have been routinely sampled and analysed at the Olkaria Geochemistry Laboratories over the years. The main purpose of those analyses is to understand the physical and chemical properties of the fluid, estimate subsurface temperatures, locate recharge zones and identify other reservoir processes such as mixing, boiling and cooling. The chemical composition of the discharge fluids is distinct between fields and also varies between wells located in the same field (Wambugu, 1996). This variability is attributed to the extent of water-rock interaction, boiling processes during the ascent of the geothermal fluid to the surface and possible mixing with colder fluids (Arnórsson et al., 2007).

The Cl-SO₄-HCO₃ diagram as specified by Giggenbach (1981) is based on the relative concentration of three major anions (Cl⁻, SO₄²⁻, CO₃²⁻). This diagram not only aids in classification of the geothermal waters, it also provides a good indication of mixing processes and helps isolate unsuitable fluids for application of geo-thermometry. The fluids in the Olkaria geothermal field can be classified as sodium chloride, sodium bicarbonate or a mixture of all those waters (Figure 5). The wells in the Olkaria East and North East Production fields have a near neutral sodium chloride water type whereas those derived from the central part of the field and in the Domes area are a mixture of chloride and bicarbonate rich. According to Ouma (2007), the Olkaria reservoir is a two phase liquid dominated reservoir which is overlain by a thin, steam dominated zone that is widest in the south and thinnest in the north. The top of the reservoir is further marked by impermeable basalts which act as the cap rock for the system.





FIGURE 5: The Cl-SO₄-HCO₃²⁻ ternary diagram for fluid classification in the Olkaria field

3.2 The geothermometry

The chemical composition of geothermal fluids is useful for estimating the subsurface reservoir temperatures. Several geothermometers can be used depending on the applications. One of the main assumptions when calculating the temperature using geothermometers is that the temperature dependent

chemical equilibria prevails in the source aquifer (D'Amore and 2000). Arnórsson, This assumption does not always hold. However, studies of mineral equilibria in geothermal aquifers indicate that quartz and alkali feldspar equilibria prevail in geothermal fluids with temperatures above 150-180°C. Therefore. the temperatures estimations based on quartz and Na-K geothermometers in high temperature reservoirs are valid. The application of the Na/K geothermometer solute as proposed by Fournier and Potter (1982) in the Olkaria geothermal field (Figure 6). indicates temperatures between 250 and 290°C for the East production field, while the Northeast production field indicates



FIGURE 6: Temperature distribution map in the Olkaria geothermal area calculated using Na/K geothermometers (Fournier and Potter, 1982)

temperatures slightly higher than the East production field. The Domes Production field waters show temperatures above 270°C for most of the wells. This information is comparable to the temperature estimates based on enthalpy chloride diagrams for the wells in Olkaria, which indicate a deep upwelling of fluid at 320-340°C, its cooling to 280°C before the onset of boiling and mixing in the North East and East production fields. In the Domes area, subsurface temperatures are closer to 330°C with reservoir boiling starting at this temperature without initial cooling.

4. THE DATABASE AND DATA HANDLING

4.1 Databases

4.1.1 Sampling and analysis

Samples discussed in this report have been classified into two: well discharge data (Table 1) and injected fluid data (Table 2). The well discharge data samples (Figure 7) were collected based on high-temperature sampling protocol described by Ármannsson and Ólafsson (2006). A Webre separator was connected along the two phase line and was used to sample liquid and steam phases. Sampling of the individual phases is made possible by adjusting the water level inside the Webre separator. A high water level is maintained during sampling the water phase and a low water level when sampling the steam phase. The recommended sampling pressure is usually close to the wellhead pressure. Both the sampling pressure and temperatures were recorded to be used in calculating the steam fraction.

Well	OW-703	OW-708	OW-R3
TDS	1430	1870	1930
рН/Т (°С)	9.34/20	9.72/20	9.56/20
В	2.73	1.81	2.3
SO4	21	38.8	39.2
CI	621.6	585.04	658.17
CO ₂	252.34	209.44	196.02
F	26.76	73.03	67.17
H_2S	64.6	31.45	21.25
SiO ₂	774	836	854
Са	0.077	0.348	0.176
Li	1.52	1.39	1.376
Na	528.1	538.3	523.5
к	106.7	112.2	95.7
Mg	0.036	0.019	0.04

TABLE 1: Chemical analysis for injected fluids (in mg/kg)



FIGURE 7: Two phase sampling of high temperature geothermal wells (Ármannsson and Ólafsson, 2006)

-				0
Туре	Method	Purpose	Sample type	Specification
physical	Filtration	Prevent interaction with suspended matter	Anions, cations	
	Airtight container	Prevent interaction with atmospheric air	Volatiles	Ru-raw untreated samples
	On-site analysis	Prevent reactions of reactive constituents	Reactive constituents	
Chemical	Base addition	Absorption of acid gases	CO ₂ , H ₂ S in steam	
	Acidification	Prevent adsorption on walls of containers	Cations	Fa- filtered acidified samples 0.8ml conc. HNO ₃ mixed with 200ml filtered sample
	Precipitation	Prevent a constituent from reaction to change the concentration of another	Sulphide to preserve sulphate	$\begin{array}{l} 2 \text{ ml } 0.2 \text{ M } \text{ZnAc}_2 \\ \text{added to sample in} \\ 100 \text{ ml volumetric} \\ \text{glass flask and 10 ml} \\ \text{to } 500 \text{ ml bottle} \\ \text{containing } 25 \text{ mg} \\ \text{SO}_4 \text{ to precipitate} \\ \text{sulphide} \end{array}$
	Dilution	Prevent polymerization and precipitation	Silica	Rd (1:10) 10ml of sample mixed with 90ml distilled water

TABLE 2: Sample preservation methods for geothermal fluids samples
(modified from Ármannsson and Ólafsson, 2006)

Several liquid phase samples were collected in different sampling bottles for the analysis of various components. Different methods of sample preservations were also used (Table 2). Steam samples on the other hand were collected using an evacuated double port glass flask containing 50 ml of 40% sodium hydroxide. The caustic solution dissolves the acidic gases (CO_2 and H_2S) while the residual gases fill up the head space in the gas flask.

The second dataset, which includes the chemical composition of samples from injected fluids, was sampled in a similar manner to one phase wells, however, the Webre separator was not used here. A cooling coil and appropriate sample preservation treatment was used. Sample preservation methods for both two phase fluids and liquid only phase are the same for all high-temperature wells described in this study.

4.1.2 Analysis and results

Results of chemical analyses of water, steam and (condensate) wells' samples are presented in Table 3. Sampling and analysis of those samples were performed according protocol described by Ármannsson and Ólafsson (2006).

Well	OW-703	OW-708	OW-911	
WHP bar-g	8.39	2.41	4	
SSP bar-g	4.94	0.69	2.2	
Enthalpy (Kj/kg)	1257	1323	1484	
Tref (0C)	271	246	226	
TDS	2642	1165	1120	
рН @20°С	9.2	9.31	9.4	
В	1.2	2.6	1.14	
SO4	24	129	69.2	
CI	884	507	239.5	
CO ²	216.5	261	444.36	
F	83	33	70.28	
H ₂ S	1.42	0.26	13.6	
SiO ₂	886	379	618.5	
Са	0.2	0.04	1.32	
Li	1.51	1.5	1.358	
Na	710	505	461.5	
к	176	79	64.47	
Mg	0.1	0.2	0.225	
gas values in mmoles/100moles H2O				
CO2	246.2	314	360.4	
H ₂ S	4.3	0.3	2.6	
CH₄	2.7	0	0.9	
H ₂	18.3	0	0.2	
N ₂	4.5	15.1	10.7	
O ₂	0	0	0.6	

TABLE 3: Water and gas analysis of discharge wells

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The atomic absorption spectrometer (AAS) was used for analysis of major and minor cations (Na, K, Li, Ca, and Mg). Silica and boron analysis were carried out using spectrophotometric methods while fluoride was determined using ion selective electrode. The titration method with pH adjustment from 8.2 to 3.8 using 0.1 N HCl was used to obtain the concentrations of the total inorganic carbon (DIC) in the analysed water and steam. The H₂S concentration in water and steam was determined by titration using mercury acetate titrant and dithizone as a colour reagent. For determination of chloride, titration with silver nitrate and potassium chromate indicator was used. The liquid phase component values were reported in parts per million (ppm). The residual gases (CH₄, H₂ N₂ and O₂) in the steam were determined by gas chromatography. The gas concentration values are reported in mmoles per 100 moles steam for each gas component (Table 3).

4.2 Data handling

The first step in data handling involved using the analytical results from the separated water and gas samples from well OW-703, OW-708 and OW-911 to calculate the aquifer deep fluid composition using the WATCH speciation program version 2.4 (Bjarnason, 2010). The conductive cooling and adiabatic boiling simulations calculated the mineral

saturation indices of anhydrite, calcite, and silica. They were considered as the baseline data prior to reinjection. The reference temperature used for simulation was the measured downhole temperature. The degassing coefficient representing the completeness of degassing when the fluid boils was 1, 0.5 and 0.1 with 1 representing equilibrium degassing while 0.1 indicating little degassing

The second step involved mixing of reinjected fluid with the aquifer fluid. This mixing simulation was done using the geochemical model PHREEQC version 3.7 (Parkhurst and Appelo, 2013). The output from the mixing simulation was then used as an input for boiling simulation using the WATCH speciation program. Results of this simulation revealed the scaling potential of the minerals assessed in the first step. The saturation state of the injected fluid with respect to calcite, anhydrite and amorphous silica was also assessed using the same version of the PHREEQC geochemical program.

4.2.1 Calculation of aquifer fluid composition

The computation of the aquifer deep fluid composition was done using the WATCH speciation program version 2.4 (Bjarnason, 2010) and discharge data (samples' pressure, temperature, pH, and chemical composition) obtained at the surface (Table 4). The basic assumption

TABLE 4: Variation in log K value for different minera	ıls
in different databases in the PHREEQC program	

LOG K VALUES IN DIFFERENT DATABASES			
	PHREEQC.DAT	MINTEQ.V4.DAT	PITZER.DAT
Calcite	-8.48	-8.48	-8.406
Anhydrite	-4.36	-4.36	-4.362
SiO2(a)	-2.71	-2.74	-2.71
Chalcedony	-3.55	-3.55	-3.55
Quartz	-3.98	-4	-3.98

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when performing those calculations is the conservation of mass and enthalpy.

The enthalpy conservation is described by:

$$h^{t} = Xh^{\nu} + (1 - X)h^{l} \tag{1}$$

where h^t is the total enthalpy of the fluid, h^v and h^l are the enthalpies of the vapour and liquid phases respectively and X is the steam fraction which is obtained by:

$$X = \frac{h^t - h^l}{h^v - h^l} \tag{2}$$

The conservation of mass for the i-th component is defined as:

$$m_i^t = X m_i^v + (1 - X) m_i^l$$
(3)

where m_i^t is the total concentration of the i-th component in the total fluid, m_i^v and m_i^l are the i-th component in the vapour and liquid phases, respectively.

For non-volatile components which do not go into the vapour phase, the Xm_i^{ν} is equivalent to zero, hence the concentration of such components in the total aquifer fluid is defined by:

$$m_i^t = (1 - X)m_i^l \tag{4}$$

For components such as hydrogen and methane, which partition completely into the vapour phase, their concentration in the total aquifer fluid is derived using:

$$m_i^t = X m_i^v \tag{5}$$

4.2.2 Simulation of mixing using the PHREEQC program

The PHREEQC program is a hydro-geochemical tool used for simulation of a variety of reactions and processes in natural waters and also in laboratory experiments. The PHREEQC is a speciation program that can be used to calculate saturation indices, the distribution of aqueous species, and the density and specific conductance of a specified solution composition. In order to simulate mixing in the program, specific KEYWORDS such as solution and mix are used. They allow data to be inserted into the input and database files.

The first step for the mixing of injected fluid with aquifer fluid involved defining the aqueous composition of the solution. For instance, SOLUTION 1, represented the injected fluid composition and SOLUTION 2, the aquifer fluid composition. The keyword MIX was used to assess the effects of mixing, between the injected fluid and aquifer fluid, on speciation and mineral saturation state. Various mixing ratios between injected and aquifer fluid were used. These were 1:1, 0.3:0.7 and 0.7:0.3. Those ratios were chosen to simulate how mixing of different amounts of solutions will affect the final mixture concentrations.

5. MINERAL SATURATION STATES

In order to determine the state of equilibrium of specific minerals in the aquifer fluid composition at a reference temperature, it becomes important to calculate the aqueous speciation for the same. The WATCH speciation program allows for the calculation of individual aqueous activities. From these activities, the reaction quotient, Q, for individual minerals can be obtained. In thermodynamics terms, the activity describes the behaviour of aqueous species. A comparison between the reaction quotient, Q,

and the equilibrium constant, K, allows for the determination of the mineral state of equilibrium in a system.

The relationship between the logarithm ratio of the reaction quotient, Q, to the equilibrium constant, K, gives the saturation index (SI) of a particular mineral, and is expressed by the equation below

$$SI = \log\left(\frac{Q}{K}\right) \tag{6}$$

Hence, the determination of mineral saturation states is based on activities of various aqueous species and their mineral solubility. SI = 0 implies a state of equilibrium, while, SI < 0 and SI > 0 denotes water undersaturation and supersaturation with respect to minerals, respectively.

As previously mentioned, only three minerals were considered for assessing the mineral saturation states. These are 1) anhydrite, 2) calcite 3) amorphous silica. The choice for these minerals was mostly governed by the chemical analysis data available, which did not include chemical data for aluminium and iron. It was therefore not possible to establish the level of saturation in the geothermal fluid with respect to pyrite, despite the fact that it is a common alteration mineral observed during borehole logging. Amorphous silica on the other hand has occasionally shown signs of being problematic within the Olkaria field especially on surface installations such as steam pipelines, hence the consideration. Anhydrite has not been known to pose a threat with reinjection. However, there was a need to confirm this fact.

5.1.1 Anhydrite and calcite saturation

Mineral deposition from boiling fluid largely occurs as a response of cooling and degassing (Arnórsson et al., 2007). Unlike amorphous silica, which has prograde solubility, the solubility of anhydrite and calcite decrease with increasing temperatures (retrograde solubility). This means that undersaturation occurs during cooling. Calcite is known to have a pH dependent solubility, which decreases with increasing pH.

The dissolution of calcite is defined by:

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \tag{7}$$

whereas the reaction quotient Q, is given as,

$$Q = aCa^{2+} aCO_3^{2-}$$
(8)

The dissolution of anhydrite is given as,

$$CaSO_4 = Ca^{2+} + SO_4^{2-} \tag{9}$$

whereas the reaction quotient is defined as,

$$Q = aCa^{2+} aSO_4^{2-}$$
(10)

Results of the WATCH adiabatic boiling of the aquifer fluid from OW-703 shows that the fluids in the well are saturated with respect to calcite at temperatures of about 180°C and above (using a degassing coefficient of 1). The highest saturation level is attained at temperatures of 250°C after which there is a substantial decrease to undersaturation at temperatures below 180°C. (Figure 8). The onset of boiling either in the wellbore or in the feeding aquifer may be taken to be the cause of this sharp rise in the saturation state. Upon boiling, the fluid pH will rise as a result of degassing and eventually increase the solubility of calcite which is reflected in the saturation state (from the supersaturated state until it reaches an undersaturated state). Similar findings were reported by Wambugu (1996) where the saturation peak

indicates the first level of boiling, which further implies that effective boiling in the well would take place in the feeding aquifer.

Wells OW-708 and OW-911 reflect a different picture when compared to well OW-703. Fluids in well OW-708 (Figure 9) are undersaturated with respect to calcite from the reservoir temperatures all the way to atmospheric conditions. It can therefore be said, that calcite scaling prior to reinjection in this well does not seem to pose a risk. Fluids in well OW-911 (Figure 10) on the other hand, are supersaturated with respect to calcite throughout the boiling process from the aquifer temperatures of 226°C. At temperatures of around 200-240°C the solubility of carbon dioxide is relatively low and the degassing is rapid. Stratigraphy data for this well indicates a presence of calcite. The presence of platy calcite has been documented in well OW-911A (Njathi, 2012) and is indicative of a boiling system similar



to well OW-911. Calcite scaling in the Olkaria field has been well documented for well OW-202 in the Olkaria Central field (Opondo, 2015).



FIGURE 9: Calcite saturation curve for fluids from well OW-708 after adiabatic boiling

FIGURE 10: Calcite saturation curve of fluids from well OW-911 after adiabatic boiling

Anhydrite scaling in geothermal fields may also pose problems in production wells and is thought to be as a result of mixing of deeper high calcium brines with shallower sulphate rich fluids (Brown, 2013). The fluids in all the three wells under consideration are undersaturated with respect to anhydrite.

5.1.2 Silica saturation

Silica exists in a variety of forms such as quartz, amorphous silica, and chalcedony. Quartz is the most stable and common form of silica in geothermal systems. The solubility of quartz in geothermal reservoir conditions determines the concentrations of dissolved silica in the brines. The difference in solubility between quartz and amorphous silica allows for the exploitation of geothermal systems

limiting silica scaling (Brown, 2013). The deep fluid is saturated with respect to quartz and undersaturated with respect to amorphous silica. Adiabatic boiling of the reservoir fluid has two effects; 1) it increases concentration of silica due to steam loss, 2) lowers solubility of silica due to a drop in temperature as the pressure decreases. The dissolution of solid silica is given as:

$$SiO_2 + H_2O = H_4SiO_{4(aq)}$$
(11)

The reaction quotient is given as:

$$Q = aH_4SiO_{4(aq)} \tag{12}$$

The pH dependence of silica solubility can play an important role in determining the temperature of injecting fluids. The solubility of amorphous silica increases with increased pH as silicic acid becomes dissociated.

The first order dissociation of weak silicic acid can be expressed as:

$$H_4 SiO_{4(aq)} = H^+ + H_3 SiO_4^-$$
(13)

For most dilute geothermal fluids, the pH value of the residual flashed waters is alkaline (1-2.5 pH units above neutral) and in this pH range the solubility of silica is strongly dependent on pH (Henley, 1983). This would further imply that flashed waters from 250-290°C reservoirs may not reach saturation as is the situation in well OW-708. (Figure 11), where the fluid is undersaturated with respect to amorphous silica.

The pH of geothermal water following steam separation in wellhead separators is a function of composition and temperature and is strongly dependent on the gas removal during single stage and multistage steam separator (Henley, 1983).

The current practice in the operation of production wells in the Olkaria geothermal field is to operate them at temperatures higher than that of amorphous silica saturation to minimize the risk of scaling. With this in mind, both wells OW-703 and OW-911, which are at potential risk of

scaling need to be operated at temperatures no lower than 150 and 160°C, respectively (Figures 12 and 13). This approach, however, limits the amount of energy than can be extracted from the geothermal fluid upon reaching the surface.

5.2 Effects of fluids mixing

Simulations for mixing was done using the PHREEQC program as discussed earlier. Prior to simulating the effect of mixing of injected fluid with aquifer fluid, the chemical composition of the injected fluid at 158°C was obtained using the PHREEQC program. The input data was the chemical analysis results acquired during sampling of injection fluid at the point of reinjection. The results based on the three different databases are comparable, except for the concentration of carbon dioxide. The reason for this variation can be attributed to inconsistencies in the mineral thermodynamics properties in different PHREEQC databases. (Table 4). This variation also affects the pH values (Table 5). Additionally, the





FIGURE 12: Amorphous silica saturation curve for fluids from well OW-911

state of mineral saturation for calcite, anhydrite and amorphous silica at the point of injection was assessed using the three databases used (Table 6).

It is important to emphasize that the limitations in the number of phases, components, and species contained in the pitzer.dat and phreeqc.dat databases could not allow comparison of the saturation level for amorphous silica with the minteq.v4.dat, without modifications of the database, which was not done during this study.

For the simulation of mixing, three different mixing ratios were assumed between the injected fluid and the aquifer fluid: 1) 1:1 ratio, 2) 0.3:0.7 ratio, and 3) 0.7:0.3 ratio.

 TABLE 5: Injected fluid chemistry after simulation in

PHREEQC using a reaction temperature of 158°C

Component	OW-703	OW-708	OW-R3
pH/°C in different databases			
pitzer.dat	8.31	8.59	8.46
minteq.v4.dat	7.83	8.19	8.07
phreeqc.dat		8.44	
Ca	0.08	0.38	0.18
CI	622.86	586.34	659.37
F	26.81	73.19	67.32
к	106.90	112.41	95.91
Li	1.52	1.39	1.38
Mg	0.04	0.02	0.04
Na	529.23	539.35	524.63
SO4	21.02	38.85	39.25
SIO ₂	361.44	390.36	398.76
CO ₂	252-257	209-213	196-199

The results for the mixed fluid composition obtained from PHREEQC program was then used as an input in the WATCH speciation program and adiabatically boiled using the downhole measured temperatures as the reference temperature.

Results obtained after adiabatic boiling show that mixing of injected fluid with aquifer fluid in the Olkaria geothermal field has an effect on the saturation state of the fluids with respect to calcite, amorphous silica and anhydrite. The fluids however remain undersaturated with respect to anhydrite.



FIGURE 13: Amorphous silica saturation

curve for well fluids from well OW-703

wells	databases	calcite	anhydrite	Amorphous silica
OW-703	1) pitzer.dat	undersaturated	undersaturated	N/A
	Minteq.v4.dat	undersaturated		supersaturated
OW-708	1) pitzer.dat	supersaturated		N/A
	phreeqc.dat	ي equilibrium	undersaturated	N/A
	Minteq.v4.dat	undersaturated		undersaturated
OW-R3	1) pitzer.dat	ي equilibrium	undersaturated	N/A
	2) Minteq.v4.dat	undersaturated	undersaturated	undersaturated

TABLE 6: Saturation states for injection fluids for calcite, anhydrite and amorphous silica at the point of injection

N/A implies that this phase was absent in the chosen database during simulation

The mixing ratio affects the saturation state of the mixed fluid. Fluids in well OW-703 display a slight departure of calcite saturation compared with the initial aquifer saturation state (Figure 14). The mixing causes an increase in the saturation state of calcite with 0.7:0.3 ratio being nearest to that of the aquifer. The effect of mixing of fluids in well OW-703 with respect to amorphous silica, shows that mixing lowers the saturation state of the fluids to a point where it is not seen as a risk during production (Figure 15).



mixed fluids in well OW-703 after adiabatic boiling

FIGURE 15: Amorphous silica saturation curve after adiabatic boiling of mixed fluids in well OW-703

A similar scenario is seen in fluids in wells OW-708 (Figure 16 and 17) and OW-R3 (Figure 18 and 19). The reason for these changes can be attributed to the change in pH. The injected fluid, which is alkaline with pH values above 9, has both a positive and negative effect on mixing with the dilute neutral aquifer fluid. An increase in the pH value at the aquifer increases solubility of silica whereas the pH dependance solubility of calcite is favoured at low pH values. This would cause the increased solubility of calcite.



6. CONCLUSIONS

The assessment for potential scale formation in hot reinjection wells OW-708, OW-703 and OW-911 in the Olkaria field prior to production show that the fluids from the three wells are undersaturated with respect to anhydrite. Furthermore, fluids from well OW-708 are undersaturated with respect to both calcite and amorphous silica. Fluids from well OW-911, on the other hand, are supersaturated with respect to calcite and the well has a higher risk of scaling compared to well OW-703, which reaches

supersaturation at temperatures above 160°C. The current practice to minimize silica scaling is to operate them at temperatures above that of amorphous silica saturation. With this in mind, well OW-703 and OW-911 need to be operated at temperatures above 150°C and 160°C respectively.

Comparison of the saturation states prior to injection and as a result of mixing of injected fluid with aquifer fluid confirm that mixing of fluids as a result of reinjection in the Olkaria geothermal field has both positive and potentially negative impacts. However, since only mixing of injected fluid and aquifer fluid was simulated in this study, additional of other equilibrium phases to the model may change the outcome, especially when incorporated with residence time of the fluid in the aquifer. Consideration of mixing with other fluids recharging the system may equally change the outcome of the model.

Based on the study, the following recommendations should be considered:

- The limitations in the databases within the PHREEQC program may require comparison with other geochemical modelling programs, which can incorporate the high-temperature conditions common in geothermal reservoirs.
- The practise of converting production wells with low production capacities to reinjection wells should be done with caution and should additionally incorporate thermodynamic information from geochemistry to aid in decision making.
- Well OW-911 should be closely monitored as it poses a risk of calcite scaling problems.
- The absence of aluminium and iron chemical analysis data from the sampled fluids excluded the assessment of possible formation of metal scales such as pyrite, which is a common alteration mineral in the Olkaria geothermal field. Therefore, it will be prudent to routinely analyse the fluids for these components together with other trace elements.
- More studies on how mixing of reinjected fluids with other fluids can modify the mineral saturation indices in the reinjection well and receiving aquifer should be carried out in the Olkaria geothermal field. These studies should also include both thermodynamics and kinetics studies to be able to complement reservoir data on reinjection and also build up the information database, which is helpful when carrying out numerical models.

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