

Geothermal Training Programme

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SCALING AND CORROSION MITIGATION IN OLKARIA IAU BY CONDENSATE - BRINE MIXING METHOD

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ABSTRACT

Monitoring and management of pH is an integral part in geothermal operations and utilization. At the Olkaria geothermal field, reinjection of geothermal wastewater from the power plants is a routine practice and an integral part of sustainable geothermal utilization. In order to safely and efficiently reinject the water without any problems of scaling or corrosion, the pH and temperature of the condensate need to be maintained within the design requirements so that it does not corrode the carbon steel components of the power plant or the casing of the cold reinjection wells. To achieve this, the pH of the wastewater is maintained within the required limits of 6.0 to 8.5. Current practice in Olkaria is treatment of the acidic condensate with sodium carbonate (Na₂CO₃). This method was introduced in the Olkaria field by the Sinclair Knight Merz company in 2001 in Olkaria II and later replicated in other plants that have come online since then. The suspected major concern with this method is side reactions from the impurities in the chemical, such as silicates and sulphides. In this study, an alternative method of pH modification in geothermal power plants is explored which is mixing the spent geothermal waters from the power plants with the separated waters (brine which has a higher pH than 8) before reinjecting into the cold reinjection wells. This approach assesses the scaling potential before and after mixing the fluids and how the pH changes upon mixing the condensate and brine in different mixing ratios, from 90% condensate and 10% brine to 50% condensate and 50% brine. This assessment is done using PHREEQC which is a geochemical modelling program code and the WATCH program. The PHREEQC program simulates the mixing of various fluids while assessing their scaling potential for silica, calcite and anhydrite. The results from the study show that mixing the geothermal wastewater from the power plant and the separated brine from the reinjection considerably lowers the calcite and silica scaling potential in the reinjection aquifers and also raises the pH of the fluid. Upon producing from the mixed fluid after heat up, the resultant fluid has low scaling and corrosion effect. The scaling potential of anhydrite is increased considerably but this does not pose any danger to geothermal operations.

1. INTRODUCTION

KenGen operates four conventional power plants in the Olkaria field: Olkaria I, II, Olkaria I additional unit and Olkaria IV. The Olkaria I additional unit was commissioned in two phases. The first unit was commissioned in October 2014 and the second unit in January 2015: each 75 MWe. The plant is a single flash condensing type with a Toshiba turbine and evaporative cooling towers. Each unit produces about 18,600 m³/h of condensate which is intermittently reinjected into the cold reinjection wells at a temperature from 37.3°C to 45°C (KenGen, 2012). The continuous condensate and brine reinjection is to sustain the geothermal reservoir by providing recharge and therefore limiting the pressure drawdown. The condensate generated at the plant is 550 t/h which is intermittently reinjected into well OW-801R1. The condensate is at very low pH due to dissolved acidic gases such as carbon dioxide and hydrogen sulphide. The amount of non-condensable gases at the plant is 1.503% wt and they are either emitted to the atmosphere through the gas extraction system or dissolved in the condensate. The pH of the condensate greatly depends on the amount of dissolved carbon dioxide and hydrogen sulphide.

Geothermal power generation involves production of electricity from steam which in turn generates more condensate which normally is acidic in nature. The pH of the condensate normally ranges from 2.5 - 3.0. The condensate is always in contact with the carbon steel components of the power plant installations and the components of the reinjection wells. The reinjection well casings and the condensate piping, the valves, the pumps, separators and liners are prone to corrosion and therefore failure. Natural geothermal waters are complex and often with high concentrations of dissolved solids. The chemistry of the geothermal fluid varies from one well to another and from one power plant to another, depending on factors such as well head pressure, hydrochemistry, flow rates, temperature, pH and the presence of solid particles suspended in the water (Gallup, 2011). The corrosiveness of the waters is largely elevated by the presence of corrosive species such as oxygen, hydrogen sulphide, carbon dioxide, ammonia, chloride and hydrogen atoms. Components such as oxygen and hydrogen sulphide can cause massive corrosion even in low concentrations (Gallup, 2011). Usually corrosion in geothermal installations occurs in the absence of oxygen. Corrosion in the presence of carbon dioxide occurs due to the formation and dissociation of carbonic acid which lowers the pH (Opondo, 2002). Scaling and corrosion occurs due to pressure drop, degassing, temperature changes and oxygen ingression.

To neutralize the acidic pH of the condensate (pH 2.5), sodium carbonate is added to raise the pH to 6.0. The sodium carbonate treatment method was first introduced in Olkaria II in 2001 by Sinclair Knight Merz. This was after a pilot study on the effectiveness of the neutralization of the condensate acidity with sodium carbonate. The sodium carbonate is injected at various points in the condensate flow line. Key areas where the condensate treatment is done is the cold reinjection water line, circulation line to the cooling tower and the cooling tower basin. This is done to: 1) prevent acid corrosion of the carbon steel components of the plant, reinjection well casings and liners, 2) balance the primary and the secondary gas emissions from the condenser, 3) prevent fouling/clogging of the cooling tower fills by the elemental sulphur which is also deposited in the condenser where the gases come in contact with oxygen. The deposition also occurs in the cooling tower distribution nozzles where there is a sudden temperature drop. Figure 1 shows the various points in the geothermal system where scale deposition takes place.

Scaling in the turbine blades, corrosion of the cold reinjection wells, clogging of the cooling tower film pack due to elemental sulphur deposition and microbiological growth, and corrosion of the main steam line can lead to a plant shut down and have been experienced in the Olkaria I Additional Unit in the recent past. This is mainly caused by the low pH of the condensate circulating in the plant Corrosion mainly affects the steam and condensate pipeline and cold reinjection well OW-801R1. Corrosion has also been observed at the drain pots just before the scrubber and might be caused by corrosive carry overs due to inefficient separation of steam and brine





FIGURE 1: Areas of scale deposition in geothermal system (Tassew, 2001)

Some of the methods employed across the world to mitigate scaling and corrosion include the dilution of the brine with condensate. Mixing condensate with brine in predetermined fractions helps increase the pH of the resultant mixture, and maintain the temperature above the silica saturation temperature to avoid deposition in the well bore. This has been successfully implemented in Hellisheidi power plant in Iceland and has yielded positive results (Sigfússon and Gunnarsson, 2011). This, therefore is the approach evaluated for the Olkaria field. Instead of neutralizing the condensate with the sodium carbonate, it is mixed with the brine separated from the wells in the production field. The brine from Olkaria field is highly alkaline at pH of above 9 and a temperature above 150°C. The condensate on the other hand has a pH of 2.5 and a temperature of 45°C. Therefore the aim is to carry out a study on the viability of mixing the brine with the condensate to avoid scale deposition and the acid corrosion at the plant by raising the pH and mitigating the corrosion of the cold reinjection wells with the case study being Olkaria East field. The study therefore, focuses on the effects of injecting the mixed fluids in the production aquifers.

The objective is to investigate in detail the chemical composition of the brine and condensate and evaluate the possibility of scaling and corrosion by the fluids. This involves determining the best mixing ratios for the brine and condensate from the Olkaria IAU power plant and the separated brine from the representative well OW-703. OW-703 is an infield hot reinjection well located in the Olkaria North East field. The ideal mixing ratio will be achieved by mixing simulations at different ratios using the PHREEQC computer code program (Parkhurst and Apello, 1999). The reinjection well OW 703 is chosen as the representative hot reinjection well because its chemistry has remained stable over the years. The simulation also evaluates the ultimate temperature that prevents silica scaling in the reinjection wells and further scaling when production starts from the mixed fluids in the production aquifers. To evaluate the effect of the mixing, the mineral scaling potential and the pH of the fluids before and after mixing is assessed. The production well used in the simulation is OW-38A which has had scaling problems based on the monitoring data and is therefore an ideal well for a simulation of the

effects of the reinjection fluid. Results of the study will help with decision making when it comes to disposal of the wastewater and in the long run help prevent the corrosion and scaling in the geothermal system.

1.1 Geothermal power generation process

The geothermal power generation process starts at the production well where a two phase fluid of brine and steam is produced. The fluid is separated at the separator station at 10 bars pressure to get dry steam for power generation and the brine is reinjected back to the reservoir at a temperature of 150°C. Olkaria IAU and other power plants operated by KenGen are single flash cycle. The steam is channelled to the power plant along insulated steam pipes and combines with steam from other wells at the pressure control station, where the pressure of the steam is regulated to the turbine inlet pressure. The inlet pressure for Olkaria IAU is 4.2 bars. The turbine utilises saturated steam, the steam is therefore desuperheated using water to a temperature of 152.8°C. The steam is then admitted to the steam scrubber where all the impurities that might have passed the drain pots is removed so that the steam meets the minimum dryness requirement of 99.99%. For the purity and dryness of 99.99%, the concentration of silica, sodium and chloride is less than 0.1 ppm and the total dissolved solids (TDS) is less than 0.5 ppm (IAPWS, 2013). The steam is then admitted to the steam turbine at a pressure of 4.2 bars, temperature of 152.8°C and at a rate of 7.4 Kg/kWh. The steam pressure and its velocity rotates the turbine blades and shafts which is directly coupled to the generator to produce electricity. Once the steam has passed through the turbine, it condenses in the direct contact condenser at near vacuum conditions. This is done by spraying with cold water at 23°C from the cooling tower. The hot condensate is pumped through the hot well pumps to the cooling towers for heat rejection. The cooled condensate flows back to the condenser and sprays the incoming steam to create a new cycle. Excess hot condensate is the pumped to the reinjection wells using reinjection pumps. Figure 2 shows the schematic diagram of the geothermal power generation process.



FIGURE 2: Geothermal power generation process (modified from Ngomi, 2016)

1.2 Corrosion in Olkaria geothermal environments

Corrosion in high temperature geothermal installations mainly occurs in well casings, cold condensate injection pipelines of carbon steel material, wellhead equipment and first stage turbine blades. In power plants utilizing direct contact condensing turbines, the cooling circuit water has a pH (3-4) mainly as a result of acidic gases CO_2 and H_2S dissolved in the steam. Low pH condensate causes deterioration of the carbon steel. The condensate from the condenser is directed to the cooling tower where it falls into the basin and increases chances for the ingress of oxygen. Corrosion in the presence of oxygen is more severe (Kizito, 2002). The low pH in the condensate is due to conductive cooling along the steam pipelines which condenses the steam allowing for dissolution of CO_2 and H_2S . Olkaria geothermal power plants utilise direct contact condensing turbines where the low pH is a common challenge. Most of the corrosion occurring in the power plants and the steam condensate pipeline is mainly a result of the low pH. Two condensate reinjection wells were corroded in Olkaria and the corrosion occurred just below the master valve. Figure 3 shows corrosion in some of the cold reinjection wells in Olkaria.



FIGURE 3: Corrosion in condensate disposal wells in Olkaria field (KenGen, 2017)

Severe pitting corrosion in geothermal installations also occurs when air containing fluid is reinjected in the condensate reinjection wells under vacuum conditions. The corrosion that happens in the Olkaria installations vary from pitting, to localised/ general corrosion and crevices, however the corrosiveness of geothermal fluids depends greatly on the chemical composition of the fluid. This is because geothermal waters have a varied chemical composition, from waters containing strong acids to sulphur and halogen acids which actively corrode most common alloys and can even take out the protective scale on the surface such as metal oxide, calcite scales and silica scales (Opondo, 2002). Another major cause of corrosion in high temperature geothermal systems is corrosion by low pH due to acid sulphate waters (Corsi, 1986). Such cases have been reported in Philippines geothermal installations like Tiwi. Corrosion also can be caused by CO₂ rich waters as was reported in New Zealand where the CO₂ rich waters condensed during the ascent to the surface in near surface shallow waters In the presence of these, the rate of scaling and corrosion can be elevated and may hinder the operation of the power plants and operation of the production wells. In many or all geothermal installations, the production wells, steam and brine lines, injection lines and injection wells are susceptible to corrosion and scaling. (Ocampo et al., 2005)

1.3 Corrosion by CO₂ in geothermal power plants

In most geothermal installations, the pH of the geothermal fluid is largely controlled by dissolved acidic gases. Elevated concentrations of CO_2 have a greater effect on the pH of the geothermal fluid, especially the steam condensate. The most abundant in concentration of the carbonate species are dissolved CO_2 and HCO_3^- (bicarbonate) at a pH of 3.8 and 8.3, respectively. The concentration of carbon dioxide in high temperature geothermal fluid is mainly dependent on 1) the rate of CO_2 supply to the geothermal fluid from the magmatic sources and 2) equilibration with the mineral buffers in the field (Karingithi, 2002). In Olkaria the main mineral buffers are epidote+prehnite+calcite+quartz and epidote+grossular+ calcite+quartz. The Olkaria East CO_2 concentrations are mainly controlled by the equilibration with the mineral buffers above (Opondo, 2002). When the CO_2 dissolves in shallow ground water, it causes a reduction in the pH of the water especially when the buffering capacity of the water is low. The condensate pH is more affected by the CO_2 dissolution because it has no alkalinity to buffer the pH.

At high temperatures the solubility of CO_2 is low and the solubility decreases with increasing temperature and pH (Opondo, 2002). Carbon dioxide being a mild oxidising agent affects the pH of the system by the formation of carbonic acid through the following reaction:

$$\mathrm{CO}_{2}\left(\mathbf{g}\right) = \mathrm{CO}_{2}\left(\mathrm{aq}\right) \tag{1}$$

$$H_2 CO_3 = H^+ + HCO_3^-$$
(2)

$$HCO_3^- = H^+ + CO_3^{2-}$$
(3)

The H^+ ion produced during the process is the one responsible for the pH drop in the system. Corrosion by this species is majorly accelerated by the hydrochemistry, decrease in pressure of the fluid, temperature changes during fluid flow, presence of solid particles in the fluid which causes corrosion by abrasion, and oxygen ingression (Millero, 1986).

1.4 Corrosion by hydrogen sulphide

The presence of H_2S in a geothermal system is related to the volcanic activities or microbiological activities (sulphate reducing bacteria). H_2S causes sulphide deposition mostly because it combines with metals to form insoluble sulphides that deposit as scales (Axelsson, 2003). The most common sulphide deposits in geothermal systems are FeS (pyrrhotite) and FeS₂ (pyrite). H_2S can be oxidised in the presence of oxygen according to the equation below:

$$H_2S + O_2 = SO_4^{2-} + H^+$$
(4)

 H_2S can also readily be dissolved in water and partially dissociate according to the equations below. This dissociation is directly proportional to the partial pressures of the gases (Steijns et al, 1976).

$$H_2S(g) = H_2S(aq)$$
(5)

$$H_2S = H^+ + HS^- \tag{6}$$

$$HS^{-} = H^{+} + S^{-}$$
 (7)

The reaction leads to a production of H^+ which in turn lowers the pH of the system and can cause corrosion in the power plant installations and cold reinjection wells.

1.5 Mechanisms of hydrogen sulphide oxidation in cooling circuit water

Sulphur deposition occurs in geothermal power plants when there are prevailing conditions that favour the reaction, including a temperature range between 20 and 50°C, a pH of 5-8 and sulphide concentrations of 0.4-25 mg/kg (Giggenbach and Sewell, 1985). In these conditions, the dominant sulphur species is sulphate. The chemistry of the cooling circuit water largely depends on the presence of the sulphides (HS⁻ and H₂S), polysulphides (S²⁻₄,S²⁻₅), elemental sulphur, thiosulphate (S₂O³⁻₃) and sulphate (SO₄). Therefore, oxidation of sulphur to sulphate in geothermal environments proceeds as shown in the equations below:

$$2HS^{-} + H^{+} + O_{2} = 2H_{2}O + 2S$$
(8)

$$2HS^{-} + 2O_2 = H_2O + S_2O_3^{-}$$
(9)

$$2HS^{-} + 4O_2 = 2SO_4^{2-} + 2H^+$$
(10)

The rate of H₂S oxidation in the presence of oxygen is enhanced by an increase in the pH and temperature (Opondo, 2002)

Dissolved H_2S is usually formed by the sulphur reducing bacteria (SRB) under anoxic conditions (Millero, 1986) according to equation 11:

$$SO_4^{2-} + 2H^+ = H_2S + 2O_2 \tag{11}$$

H₂S is soluble in water and dissociates according to equations 12 and 13:

$$H_2S = H^+ + HS^-$$
(12)

$$HS^{-} = H^{+} + S^{2-}$$
(13)

The various forms of the sulphides are all dependent on the pH as well as the kinetics of the hydrogen sulphide reaction (Giggenbach and Sewell, 1985)

2. LOCATION AND GEOLOGICAL SETTING OF OLKARIA GEOTHERMAL COMPLEX

2.1 Location of Olkaria geothermal complex

The Olkaria high temperature geothermal field is located on the floor of the Kenyan rift, about 120 km to the North East of Nairobi and lies within the Hells Gate National Park. The resource is estimated to cover a surface area of about 204 km². The Olkaria geothermal complex is among the 14 prospects in the Kenyan rift system. Among the prospects, Olkaria, Eburru and Menengai are the main geothermal fields currently being exploited. The total estimated potential of the prospects is 10,000 MWe. Figure 4 shows the geothermal prospects and the fields in Kenya.

2.2 Geological setting of Olkaria

The Olkaria geothermal system is associated with an old central volcano which collapsed, leaving a large caldera of about 5 km in diameter defined by a ring structure and rhyolitic domes (Omenda, 1998). Rocks occurring on the surface are majorly quaternary comendites, pumice fall and volcanic ash deposits from late Pleistocene to Holocene. Trachytic flows appear in the southern part of the geothermal field below thick pyroclastics commonly associated with the Longonot and Suswa eruptive episodes (Omenda 1998). The complex is classified as remnant of an old caldera and is bounded by the Eburru complex to the North, to the east by the Longonot volcano , to the south by the Suswa volcanoes and to the west by the Western rift margin. The area comprises of many small active volcanic centres occurring either as steep sided domes formed as lavas and pyroclastic rocks or as thick lava flows of restricted lateral extent. Olkaria and Eburru are rhyolitic volcanic complexes, while Menengai, Longonot and



FIGURE 4: Kenya Geothermal prospects (Lagat, 2004)





Suswa are classified as trachytic caldera volcanoes. The geology is by dominated Pleistocene and Holocene structures. Holocene comenditic rhyolitic flows on the surface and basalts, trachyte and tuffs are common in the subsurface and basaltic dykes, syenitic, microgranitic and granitic intrusions are also common (Lagat, 2004). The litho-stratigraphic structure in the area is nearly horizontal (Muchemi, 1999). Based on rock cuttings and cores, the general litho-stratigraphy of the greater Olkaria complex can be divided into two: the western sector characterised by the Mau tuffs, and the east of Olkaria Hill which has the plateau and Olkaria basalts. Omenda (1998) discussed the formations of Olkaria in a sequence of Mau tuffs, plateau trachyte, Olkaria basalts and upper Olkaria volcanic formation. The Mau tuffs are unique to the western sector while the trachyte and basalts are unique to the eastern sector. Lagat (2010) further summarised the most common secondary minerals in the field as: calcium silicates, clays, oxides, silica minerals, zeolites, pyrites, fluorites, calcites and albites. Figure 5 shows the surface geology of the Olkaria complex

2.3 Structural setting of Olkaria

The dominant structures at Olkaria are the Ololbutot fault (N-S), the Gorge Farm fault (NE-SW), the Olkaria Fault (ENE-WSW) and the Suswa fault (NE-SW). An alignment of eruptive domes is prominent to the field, east of the probably demarcating a caldera rim which has been mapped elsewhere around the greater volcanic complex. Many other buried faults with similar trends have been inferred by analysis of drill cores and rock cuttings (Muchemi, 1999; Omenda, 1998). Figure 6 shows the structures in the Greater Olkaria Geothermal field



FIGURE 6: Olkaria structural map (Lagat, 2004)

2.4 Geothermal exploration and development in Olkaria

The electricity consumption in Kenya is projected to increase by 23% by 2018 (Mangi, 2017) and the main focus has been on renewable energy, especially geothermal energy to help meet the demand. Geothermal exploration and development in Olkaria began in the 1950s where two exploratory wells X-1 and X-2 were drilled but failed to discharge (Mangi, 2017). In 1972, the United Nations Development Programme (UNDP) intervened and in 1981 the first 15 MWe plant Olkaria I first unit was commissioned. Two more units were commissioned in 1983 and 1986, each 15 MWe. Currently KenGen's total capacity in the field is 533 MWe. This is derived from Olkaria I Additional Unit IV and V (140 MWe), Olkaria IV (140 MWe), Olkaria II (105 MWe), wellhead generators (83.3 MWe) and Eburru wellhead (2.5 MWe). Other plants in Kenya include Olkaria III which is privately owned and run by ORMAT. The plant generates 139.3 MWe. Another wellhead owned by the Oserian flower farm (the biggest flower farm in Kenya) generates 2 MWe. The Greater Olkaria geothermal field is divided into seven different fields according to the field characteristics and location. The seven segments are: Olkaria East, Olkaria North East, Olkaria North West, Olkaria Domes, Olkaria Central, Olkaria South West and Olkaria South East. Figure 7 shows the divisions of the greater Olkaria geothermal field.

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FIGURE 7: Olkaria geothermal field segments (Clarke, et al., 1990, modified by Lagat, 2004)

3. STUDY AREA

3.1 Olkaria East production field

The Olkaria IAU is located in the Olkaria East production field. The power plant receives steam from 26 production wells located in the East field with an average enthalpy of about 2600 kJ/kg and a depth of 3000 m. There are seven hot reinjection wells with depths varying from 600 m deep shallow reinjection wells to 1700 m deep reinjection wells. There are two cold reinjection wells OW- 801R1 and OW-801R2 at a depth of 600 -1500 m. The production wells production casing is at 1200 m depth while the reinjection wells are cased down to 270 m depth (Ng'ang'a, 2014). The wells have an average wellhead pressure of 10 bars. The fluid discharged from these wells are a dilute sodium chloride type (Otieno and Kubai, 2013). The field has a high chloride content of 200-350 ppm while the bicarbonate concentration in Olkaria ranges from 10,000 ppm in Olkaria West field to less than 10 ppm in the Olkaria East field (Wambugu, 1996). Figures 8 and 9 show the fluid classification and geothermometers of Olkaria East



FIGURE 8: Olkaria East geothermometers



FIGURE 9: Olkaria East fluid classification

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3.2 Reinjection in the East production field

Reinjection is a fundamental requirement in geothermal power plant operation. The main benefits of reinjection include:

- Disposal of the separated water from power plants and return water from the direct applications for environmental reasons;
- Additional recharge to supplement natural recharge, which is limited in some fields;
- Reinjection offers pressure support to reduce pressure decline due to mass extraction;
- To enhance the thermal extraction from the rocks;
- Offsetting the surface subsidence;
- Targeted reinjection enhances and revitalises surface features such as hot springs and fumaroles.

Reinjection can also have negative consequences, such as cooling of the production wells or a cold front breakthrough due to mixing along direct flow paths such as open fractures. Silica scaling in surface pipelines and injection wells in high temperature geothermal fields is also a risk since after flashing the separated fluid becomes supersaturated with silica and silica precipitates from the fluid. Calcium carbonate scaling is also commonly associated with reinjection operations. This results in the clogging of aquifers next to the injection wells by the precipitating silica. Reinjection is a common practice in Olkaria geothermal field. In Olkaria East field, the average downhole temperature is 250°C. Temperature taken at the depth of 1000-1500 m indicate a higher temperature of 280°C in the north of the East production field while lower temperature less than 220°C are recorded at the central part of the East production field in the area around the OW 201 to OW 204 wells as shown by the contours in Figure 10. The central part of the EPF is believed to be associated with the Olol Butot fault which is a conductor of the cooler fluids. Many wells in the East and North East production fields are at a temperature of about 240°C. The reinjection well OW-R3 has a temperature of less than 220°C,



FIGURE 10: Temperature contours at 1000-1500m in Olkaria Geothermal field to show the temperature variations (Mwawongo, 2004)

probably due to down flow of cooler fluids from shallow aquifers in the fields (Mwawongo, 2004). The OW-R3 well is located in the buffer zone of Olkaria North East and East production fields to stabilise the pressure in the EPF. The well is an infield reinjection well connected to the production wells OW-720, OW-728, OW 713, OW 718, OW 719 and OW-726. The infield reinjection strategy is a fundamental feature as reinjection within the production field results in higher reinjected fluid recovery (Axelsson, 2004). The brine reinjection from one field to another is permitted in the Olkaria reinjection set up. Therefore OW-R3 in the East production field reinjection well in the North east production wells as listed above. OW-703 is also an infield reinjection well in the North East production field connected to the production wells OW-716, OW-714, OW-725 and OW-705. OW-703 has the effect of the Ol-Butot fault which is a cooler fluid conductor. From tracer tests the OW-R3 has connections with the OW- 25, OW- 30 and OW- 29 wells (Mwawongo, 2004).

4. METHODOLOGY

4.1 Sampling and analysis

Sampling and analysis were done according to the procedures by Ármannsson and Ólafsson (2006). The power plant samples were sampled from the condenser outlet at a temperature of 45°C. Analysis of H₂S was done in the field by titrating with 0.001 M HgAc₂ with dithizone as the indicator. 5 ml of NaOH was put in 250 ml beaker and 5 ml of acetone added. In the mixture 1 ml of sample was added and titrated with mercuric acetate. The cation samples were filtered and treated with 0.8 ml concentrated HNO₃ to fix the ions to avoid its precipitation and prevent adsorption on the walls of the sampling container during storage. To prevent the sulphide from oxidising and increasing the concentrations of the sulphate 2 ml of zinc acetate is added in the 100 ml sample to fix the sulphide. One sample was collected for the chloride, CO₂ and pH measurements. Silica from the steam condensate required no dilution because it is in lower than 100 ppm concentrations. The anions were analysed using Ion chromatography (IC). The cations were analysed using Inductively Coupled Plasma Optic Emission Spectrum (ICP-OES). The Olkaria IAU condensate chemistry and the discharge chemistry for OW-38 can be seen in Table 1-2.

	Condensate chemistry						
Parameter	Unit 4	Unit 5	Units 4 & 5				
			mixed				
Tref	45.0	45.0	45.00				
TDS	412.0	616.5	970.00				
pH @20°C	2.8	2.9	2.84				
SO ₄	105.4	128.4	234.34				
Cl	0.1	0.4	0.48				
CO ₂	14.3	33.0	46.52				
F	0.3	0.5	0.80				
SiO ₂	0.4	0.6	1.01				
Ca	0.2	0.9	1.07				
Na	3.5	33.5	37.08				
Κ	0.1	0.7	0.77				
Mg	0.0	0.2	0.21				

TABLE 1: Olkaria IAU condensate chemistry

SP	5.37
WHP	5.86
Temp (°C)	161
Enthalpy	2662
TDS	849
pН	8.2
SiO ₂	514
Cl (ppm)	299
SO ₄ (ppm)	163
CO_2 (ppm)	115
$H_2S(ppm)$	2.38
Na (ppm)	391
K (ppm)	70
Ca (ppm)	2.17
Mg (ppm)	0.118
F	94
Li	1.4
Mmol/100moles I	H ₂ O
$\overline{CO_2}$	72
H_2S	5.1
CH ₄	0.02
H_2	4.4
N_2	8.22

TABLE 2: Discharge chemistry for OW-38(SP: sampling pressure, WHP: well head pressure, TDS: total dissolved solids)

The condensate data was obtained from the Olkaria I Additional Unit power plant. Olkaria IAU units IV and V have slightly different chemistry and required that the condensate from the two units were mixed using PHREEQC to attain a composition that would be used to dilute the brine from the reinjection wells. The condensates were mixed in the ratio 1:1 and a reaction temperature of 45°C. The mixed condensate was then heated up in WATCH to a temperature of 150°C to simulate the hot reinjection conditions in Olkaria. The pH of the mixture was obtained from PHREEQC. The output from WATCH was then used as input file in PHREEQC to carry out the mixing of brine from the OW R3 and OW 703 wells.

The well discharge samples were collected based on high temperature sampling methods described by Ármannson (2006). The chloride was analysed using the argentometric titration method where the sample is titrated with 0.1 M AgNO₃ and potassium dichromate as the indicator to a permanent orange colour preceding a brick red colour. Silica analysis was done using a spectrophotometric method where the absorbance of the β -molybdic acid complex is measured at a wavelength of 410 nm. The major cations were analysed using a flame photometer. Total carbon dioxide was analysed by a titrimetric method by adding AgNO₃ prior to analysis to remove the hydrogen sulphide that may be present in the sample. Sulphate was analysed using an indirect spectrophotometric method with barium chromate and bromophenol blue. The sample is precipitated prior with the zinc acetate to eliminate possible interferences from the bicarbonate and the sulphide. After the sample preparation it was analysed in the UV-Vis spectrophotometer at an absorbance of 385 Nm

4.2 Calculation of deep liquid composition

The geochemical interpretations are based on the results of samples collected at the surface. A clear and better understanding of the reservoir fluid chemistry can be achieved by re-calculating the surface fluid chemistry back to the reservoir conditions. The approach is based on two assumptions: a one phase

liquid inflow only and excess enthalpy in the reservoir, or assuming a two-phase fluid in the reservoir, liquid and vapour. Mass conservation is a key factor in this calculation as indicated by equation 14:

$$m_i^t = m_i^v X + m_i^{iq} (1 - X)$$
 (14)

Where m_i^t is the total concentration of the ith component and m_i^{lq} and $m_i^{\nu}x$ are the concentrations of the liquid and the vapour phases respectively while x is the steam fraction.

The total enthalpy of the geothermal system is considered and is given by equation 15:

$$h^{t} = h^{v}X^{v} + h^{l}(1 - X)$$
(15)

in which h^t , h^v , and h^l are enthalpies of the system, vapour and liquid, respectively. The steam fraction X is given by the following equation:

$$X = \frac{h^{t} - h^{lq}}{h^{v} + h^{lq}}$$
(16)

The WATCH program by (Bjarnason, 2010) is then used to calculate the aquifer fluid composition from the data collected at the surface. In this case, the brine collected from the OW- 38A well at 161°C is recalculated back to reservoir conditions by heating it to 240°C and boiling it adiabatically in WATCH. In this project the main aim of calculating the deep liquid using WATCH is to get the saturation states of various minerals that are scale forming in production aquifers, before and after mixing with the diluted brine from OW-703.

4.3 Simulation of mixing using PHREEQC modelling programme code and WATCH

PHREEQC is a reaction path computer code program used for simulating a variety of reactions in natural waters. It is used for the speciation of chemical components, batch reaction, one dimensional transport and inverse geochemical modelling. In this project, PHREEQC is used to carry out fluid mixing, calculate saturation indices of the scale forming components anhydrite, calcite and silica, which are the most common scaling minerals in geothermal installations. The program is used to calculate the temperature effects on the various reactions using the Van't Hoff equation because it is critical in determining the possibility of mineral precipitation.

The brine discharge data was obtained from the hot reinjection well OW-703 located in the Olkaria North East production field (Table 3).

TABLE 3: OW 703	Separated	water chemistry
	-	

Parameter	Conc. in ppm
WHP	5.9bars
SP	6.00bars
Temp	162°C
Enthalpy	1355Kj/Kg
TDS	2642
pH@20°C	8.6
SiO ₂	886.01
Cl	884.01
SO_4	24
CO_2	216.48
H_2S	1.42
Na	710.01
Κ	176
Ca	0.2
Mg	0.1

Mixing of the separated brine from OW 703 with condensate was done in the PHREEQC computer code program. The condensate composition was heated up to 240°C to simulate the reservoir conditions and then mixed with the brine from well OW-703 in the ratios of 0.1:0.9, 0.2:0.8, 0.3:0.7, 0.4:0.6 and 0.5:0.5. After mixing, the resultant fluids were heated up to 240°C again to simulate the reservoir conditions in the field. Table 4 shows the brine composition after mixing.

Ratio	pН	Temp(°C)	В	CO3 ²⁻	Ca	Cl	F	K	Mg	SO ₄	SiO ₂	Na	H ₂ S
0.9:0.1	3.12	56.33	1.42	50.02	0.50	87.75	0.36	17.95	0.10	107.20	89.20	87.93	0.25
0.8:0.2	3.86	67.66	1.26	77.23	0.47	175.25	0.32	35.52	0.10	97.96	177.88	157.32	0.39
0.7:0.3	5.98	78.99	1.10	104.44	0.43	262.76	0.28	53.09	0.10	88.73	266.57	226.70	0.53
0.6:0.4	6.50	90.32	0.95	131.64	0.40	350.28	0.24	70.66	0.10	79.49	355.26	296.10	0.67
0.5:0.5	6.88	101.65	0.79	158.84	0.37	437.78	0.20	88.23	0.10	70.26	443.95	365.49	0.81

TABLE 4: Brine condensate mixture composition (ppm)

The mixed fluid was boiled down in WATCH from the heat up temperature of 240°C down to 120°C. The mineral scaling potential was then evaluated for calcite, anhydrite and amorphous silica. The temperature and pH changes during boiling were also evaluated and tabulated in Table 5.

Mixing ratios	pН	Temp.	Calcite	SiO2(a)	Anhydrite
0.9:0.1	3.12	56.33	-9.6	-0.3	-3.6
0.8:0.2	3.86	67.66	-7.9	-0.1	-3.5
0.7:0.3	5.98	78.99	-3.6	-0.01	-3.5
0.6:0.4	6.50	90.32	-2.7	0.04	-3.5
0.5:0.5	6.888	101.6	-2.1	0.08	-3.5

TABLE 5: Mineral precipitation potential during mixing

The brine mixture has a potential to precipitate only amorphous silica when mixed in the ratios 0.6: 0.4 and 0.5:0.5. All the other minerals are under-saturated for all the ratios.

The injected fluid can be of great impact in the production aquifers. It can cause mineral precipitation and thus sealing off the permeable zones. Therefore, to determine the effect of reinjecting the condensate-brine mixture into the production aquifer, the condensate-brine mixture was then mixed with production fluid (brine) from well OW-38A which is a production well located in the Olkaria East production field and its brine is reinjected in the same field. The mineral scaling potential of the well was assessed before incursion of the condensate-brine mixture. This was done by heating up the well discharge chemical composition in PHREEQC to 240°C then boiling it in WATCH from 240°C to 120°C. The brine from OW-703 which was mixed with condensate and the brine from OW-38A were mixed in the ratio 1:1. The PHREEQC output of the mixture was adiabatically boiled in WATCH in steps of 20°C from 240°C to 120°C. The mineral scaling potential for calcite, silica and anhydrite were evaluated and the pH changes recorded during the adiabatic boiling process.

The evaluation of the mineral saturation potential involved all potential scale forming phases and also considered the adiabatic boiling of the aquifer fluid (total discharge), adiabatic boiling of the separated water and adiabatic boiling of the separated water and condensate mixtures. The results of these simulations are discussed below.

5. RESULTS AND DISCUSSION

5.1 Scaling potential in the production aquifers of OW-38A

The mineral scaling potential in the production aquifers of well OW-38A located in the Olkaria East was evaluated by adiabatically boiling in WATCH to 120°C to predict the baseline scaling tendencies in the well fluid before mixing with the separated water and condensate mixture during production. From the results, there is a high potential for calcite scaling in the wellbore. Calcium carbonate scale usually forms due to emission of CO₂ from the liquid during boiling. Evolution of CO₂ can also occur due to a pressure drop in the well and in steam piping where there are bends. When the fluid pressure drops the fluid experiences a substantial increase in pH due to degassing. Calcium scale precipitates faster at high temperatures due to reduced solubility. The well fluid is under-saturated with respect to anhydrite and super-saturated with respect to amorphous silica at temperature below 140°C. When the temperature of the fluid decreases due to a pressure drop, the concentration of silica increases in the brine phase. The silica in the brine become unstable and therefore precipitates as amorphous silica. Sometimes the silica reacts



FIGURE 12: OW-38A scaling potential in production aquifers

with available cations such as Fe, Na or Ca to form silicate deposits in the geothermal installations (Ocampo et al., 2005). The well therefore should be operated at temperatures above 160°C to avoid amorphous silica scaling. Figure 12 shows the production aquifer scaling potential of well OW-38A

5.2 Scaling potential in reinjection well OW-703

The mineral scaling potential assessment was done for the hot reinjection well OW-703 prior to mixing with the condensate. From the simulation results, the well has a potential of precipitating silica at temperatures below 180°C. On the other hand, there is a high risk of calcite scaling in the well at temperatures above 180°C with the highest saturation level reached at a temperature of 240°C because of the rapid decrease to under-saturation. Boiling increases degassing which produces fluids that are oversaturated with respect to minerals whose solubility decreases with increase in pH (Arnórsson et al, 2007). The boiling causes the rapid increase in the solubility of calcite. Figure 13 shows the mineral saturation in the well OW-703 in the production aquifers

5.3 Scaling potential of separated brine and condensate mixtures

The solubility of some scale forming minerals such as calcite, amorphous silica and anhydrite is majorly dependent on the pH. Degassing of water upon boiling affects the mineral saturation state of the scale forming minerals. To try to mitigate this phenomenon, the separated brine and the condensate from the power plant was mixed in various ratios and the possibility of mineral precipitation determined in PHREEQC. The pH and the resultant temperature of the mixtures were recorded. It's important to consider the temperature and pH change during mixing to ensure it is within the permissible reinjection requirement limit that mitigates the scaling and corrosion, especially in the cold reinjection wells. From



FIGURE 13: OW-703 scaling potential

heating up

the results of mixing the two fluids, the mixture has the potential to precipitate only silica at ratios of 0.5:0.5 and 0.6:0.4 as seen in Figure 14. Increasing the injected separated water proportion in the mixture increases the saturation index of calcite of the mixed fluid.

5.4 Mineral saturation state in reinjection aquifers - effect of fluid mixing

The separated water and the condensate mixture was adiabatically boiled in steps of 20°C from 240°C to 120°C to mimic the reinjection reservoir conditions in the WATCH speciation programme. All the mixing ratios gave temperatures that were less or equal to 100°C and therefore were heated up in PHREEQC before the boiling process. Generally, anhydrite (Figure 15), amorphous silica (Figure 16), and calcite (Figure 17) are under-saturated in the mixed fluid. The saturation index of anhydrite is lowered by increasing the separated water in the mixture as indicated in Figure 15. The ratios of 0.5:0.5 and 0.6:0.4 have a potential to precipitate calcite at temperatures above 200°C as observed in Figure 17. Increasing the injected separated water proportion while lowering the condensate proportion in the mixture increases the saturation index of calcite of the mixed fluid upon boiling. On the other hand, amorphous silica scaling potential is increased by the increasing proportion of the separated water in the mixed fluids as observed in Figure 17. The increase in separated water from well OW-703, increases the concentration of silica in the mixture which upon boiling increases the saturation index.

Mixing the separated water – condensate mixture with the production well (OW-38A) brine to simulate extreme situations when all the reinjection fluid would replace the deep aquifer fluid during production was also done. Therefore, the two ratios with high potential to precipitate the minerals and less or no potential to precipitate any of the minerals were chosen for the mixing simulations. The ratio 0.8:0.2 (80% condensate and 20% separated waters) was used because it gave a pH of 3.9 which is considered corrosive to the carbon steel materials used in the power plant and a temperature of 67.5°C with no potential to precipitate minerals. On the other hand, 0.6:0.4 gave a pH of 6.5 which is an acceptable limit for reinjection practices in Olkaria and a temperature of 90.3°C with indications of calcite scaling upon boiling.



FIGURE 15: Anhydrite scaling potential of the condensate and separated water mixtures

FIGURE 16: Silica scaling potential of the condensate and separated water mixtures



FIGURE 17: Calcite scaling potential of the condensate and separated water mixtures

FIGURE 18: Anhydrite scaling potential as a result of condensate and separated water mixture in production and reinjection aquifers

5.4.1 Scaling potential 60% condensate: 40% separated water mixture

The condensate and brine mixed in the ratio 0.6:0.4 gave a resultant pH of 6.5 and temperature of 90.3°C. To evaluate the scaling tendencies of the fluid once it gets to the reinjection aquifers in the field, the mixture was heated up to a temperature of 240°C in PHREEQC to mimic the reservoir conditions and the output was boiled adiabatically in WATCH fro m 240°C to 120°C. The potential of mineral precipitation was evaluated for calcite, anhydrite and silica. Mixing the separated water with the condensate lowers the scaling potential of amorphous silica and calcite in the reinjection well OW-703 as seen in Figures 18 and 19. In well OW-703 after mixing with the condensate, there is a possibility of calcite scaling at temperatures above 220°C.

Generally, the scaling potential in well OW-703 is substantially lowered by mixing the separated water with the condensate from the power plant. In well OW-38A, mixing reduces the calcite saturation index up to a temperature of 220°C, above which the saturation index begins to increase as seen in Figure 18. Calcite scaling in the well is highest at temperatures above 220°C with SI>1 (supersaturated). From this we can deduce that mixing the production fluid with the separated water - condensate mixture increases the calcite saturation index of the mixed production fluid and diluted brine in the well at temperatures above 220°C. The solubility of calcite decreases with increasing temperature and that is why the precipitation increases at this temperature due to increased degassing in the well bore. Therefore, mixing in this case only reduces the saturation index but does not mitigate the scaling in the aquifer. The amorphous silica saturation index in OW-38A increases at temperatures above 160°C in the mixed condensate - separated water and production fluid mixture in the aquifers as observed in Figure 19. A reduction in the saturation index occurs at temperatures below 160°C. This therefore suggests that mixed condensate-separated water can mitigate silica scaling in the well if it is operated at temperatures above 160°C. All the fluids are under-saturated with respect to anhydrite, although the mixing raises The anhydrite saturation index increases due to the increased sulphate the saturation index. concentrations in the condensate which further undergoes boiling in the aquifers. Figures 19 and 20 show the silica and anhydrite scaling potentials.

5.4.2 Scaling potential of 80% condensate: 20% separated water mixture

Simulation was carried out for the mixture of 0.8 condensate and 0.2 separated water. This mixture gave a pH of 3.9 and a temperature of 67.5°C. The pH is below the required reinjection pH limits in Olkaria which is >6.0. The mixture therefore, was heated up in PHREEQC to 240°C to simulate the reservoir conditions and adiabatically boiled in WATCH from 240°C to 120°C in order to predict the scaling potential upon reinjection. The effect of the 80% condensate with 20% brine mixture in the production aquifer was evaluated by mixing it with brine from production well OW-38A. The OW-703 fluid has a potential to precipitate amorphous silica at temperatures below 160°C as observed in Figure 21. Upon mixing with the condensate, the saturation index of amorphous silica is substantially lowered and the separated water - condensate mixture becomes under-saturated with respect to amorphous silica. When the condensate – separated water mixture reacts with the OW-38A fluid, there is an increase in the amorphous silica saturation index at temperatures above 180°C. The saturation index then reduces from temperatures below 180°C. This therefore suggests that the separated water-condensate mixture can only mitigate the scaling in the well if operated at temperatures below 180°C, otherwise the scaling risks are increased with the mixed fluid incursion into the production aquifers. Both the production well OW-38A and reinjection well OW-703 are under-saturated with respect to anhydrite and therefore reinjecting the diluted brine does not pose any danger of anhydrite precipitation. Calcite precipitation will occur when the injected fluid mixes with the fluid in well OW-38A as the mixed condensate and brine provides conducive conditions for calcite precipitation. Calcite has pH dependent solubility and it increases with decreasing temperature but decreases with increasing pH. Boiling increases degassing which produces fluids which are oversaturated with respect to minerals whose solubility decreases with an increase in pH (Arnórsson et al., 2007). The brine from the production well increases the pH and calcium concentration, hence it precipitates from the fluid due to over-saturation. Figures 21, 22 and 23 show the mineral saturation state of mixing 80% condensate and 20% separated water



FIGURE 19: Calcite scaling potential as a result of condensate and separated water mixture in production and reinjection aquifers

FIGURE 20: Silica scaling potential as a result of condensate and separated water mixture in production and reinjection aquifers





FIGURE 22: Calcite scaling potential as a result of condensate and separated water mixture in production and reinjection aquifers

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FIGURE 23: Silica scaling potential as a result of condensate and separated water mixture in production and reinjection aquifers

6. SUMMARY

- The Olkaria East production field discharges dilute sodium chloride water with a high chloride content of 200-350 ppm. The bicarbonate content of the field is below 1000 ppm while the CO₂ concentration in the field is 10,000 ppm in the western part and 10 ppm and below in the eastern part of the field. The average temperature according to Na/K and quartz geothermometers is 230-260°C;
- Olkaria I additional unit power plant has two units with varying chemistry because they are fed by steam from different separator stations. Unit 5 seems to have carry overs as indicated by the high sodium and silica concentrations. Mixing condensates from these two units results in an overall increase in silica, sodium and CO₂ concentrations in the resultant condensate;
- Well OW-703 has calcite scaling potential at temperatures above 220°C and silica scaling at temperatures below 180°C. The well therefore needs to be operated at temperatures that will lower the scaling potentials of the two minerals;
- Well OW-38A, used as a representative well for the production field, has a high potential for calcite scaling and may precipitate silica at temperatures below 140°C;
- Mixing the condensate and separated water may result in silica precipitation if the mixing ratio is lowered below 70% condensate and 30% separated water.

7. CONCLUSIONS

The assessment of the scaling potential in the production aquifers before production in well OW-38A show that the fluid has a potential to precipitate calcite. The condensate – separated water mixture only reduces the saturation index of silica and calcite at certain temperatures but does not completely mitigate the scaling in the wells. The mixture lowers the scaling potential at temperatures below 160°C, above which the saturation index for calcite and silica increases in the production aquifers.

Reinjection well OW-703 reaches over-saturation with respect to silica at temperatures below 160°C. The well therefore needs to be operated at temperatures above 160°C which is above the amorphous silica saturation temperatures to mitigate scaling in the well. The well has a potential to precipitate calcite at temperatures above 160°C with the highest saturation state above 220°C after which there is a rapid decrease to under-saturation with respect to calcite. This is because boiling causes degassing and a rapid increase in the solubility of calcite. OW-703 requires to be operated at a minimum temperature of 160°C to mitigate the possible scaling in the well;

Injecting the separated water – condensate mixture in the reinjection aquifers lowers the scaling potential for calcite and silica substantially. Increasing the separated water proportion in the mixture increases the calcite and silica saturation indices. Mixing the condensate and separated water substantially lowers the scaling potential of calcite and silica when the proportion of the condensate is kept higher than the separated water proportion. The ideal proportion for mixing the fluids is 70% condensate and 30% separated water. On the other hand, the saturation index for anhydrite is increased but does not pose any major challenge because it still remains under-saturated. This method therefore can be a solution to pH modification instead of the current chemical dosing.

8. RECOMMENDATIONS

- Further simulations including more reinjection and more production wells need to be carried out with the inclusion of condensate from other plants due to distinct chemistry in the plants;
- The modelling should include design aspects especially in Olkaria where cold reinjection is done at the periphery of the production field;
- Financial aspects need to be considered for the project considering the changes in design of the condensate pipeline

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