Geochemistry and Isotope Study of Discharged Geothermal Fluids, NW Sabalan Geothermal Field, NW Iran

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ABSTRACT

Northwest Sabalan geothermal field is one of the four main high temperature fields in Iran that has practically been exploring and developing in the recent years. In the second stage of development and reservoir assessment, the discharged fluids from four wells, including NWS-6D, NWS-7D, NWS-9D and NWS-10D were analyzed. The water samples are classified as high chloride, neutral-pH and mature liquids that partially equilibrated with host rock. Chemistry of the waters also indicates that they are originated from an andesitic old hydrothermal system. The chemistry of deep aquifers charging wells is slightly different that can be due to presence of more than one aquifer with relatively different composition. Quartz geothermometers suggest the average temperature of 246°C, while cation geothermometers propose higher average temperatures; 257°C (K-Mg), 269 °C (Na-K), 279°C (Na-K-Ca), implying higher temperatures of aquifers at depth rather than adjacent area of boreholes. Gas (CO_2 and H_2S) and isotope (^{18}O) geothermometers represent much higher temperature ranges; 280°C-301°C and 299 °C, respectively. The δD and $\delta^{18}O$ isotope concentrations in the discharged samples of well NWS-6D (average of -69.8‰ and -7.9‰, respectively) indicate that charging water of geothermal system originate from higher elevations with lower humidity. Mineral saturation states of reservoir liquids display that amorphous silica is anticipated to be deposited in temperatures lower than 90°C, whereas super-saturation state of aquifers with regard to quartz will occur in temperatures lower than 240°C and will not cause serious problems during production. The deep aquifer liquid, however, is super-saturated with calcite in temperatures lower than 231°C and it is expected to give rise to scaling problems in the wells, even if the reservoir liquid is not super-saturated with regard to anhydrite and fluorite. Variation of saturation state trend of deep aquifers, charging each well along adiabatic boiling, can be considered as another sign of different chemical composition of deep multi-aquifer reservoir.

1. INTRODUCTION

Among the four systematic evaluated geothermal prospects in Iran, including Sabalan, Sahand, Damavand and Khoy- Maku areas, which all pertain to quaternary volcanism, Northwest Sabalan geothermal field was satisfactorily recognized as the highest potential reservoir for power generation. It lies in western slopes of Mt. Sabalan, approximately 20 km southeast of Meshkinshahr town, NW Iran (Figure 1). It is one of the fifth geothermal anomalies around Mt. Sabalan volcano that is determined by surface geothermal explorations and detailed MT geophysical surveys in 1998. It was also explored in detail through two developing stages in 2002 and 2008 by applying deep drilling of total 11 wells and also geological, geophysical and geochemical exploration methods, conducted by Renewable Energy Organization of Iran-SUNA. In order to assess the real production potential of the reservoir, various numbers of reservoir evolution methods, including completion tests, discharge tests and logging operations are executed alongside and after both exploration stages, in 2004 and 2011. The capacity of NW Sabalan geothermal field, therefore, was estimated to sustain 55 MWe power (SKM, 2005).
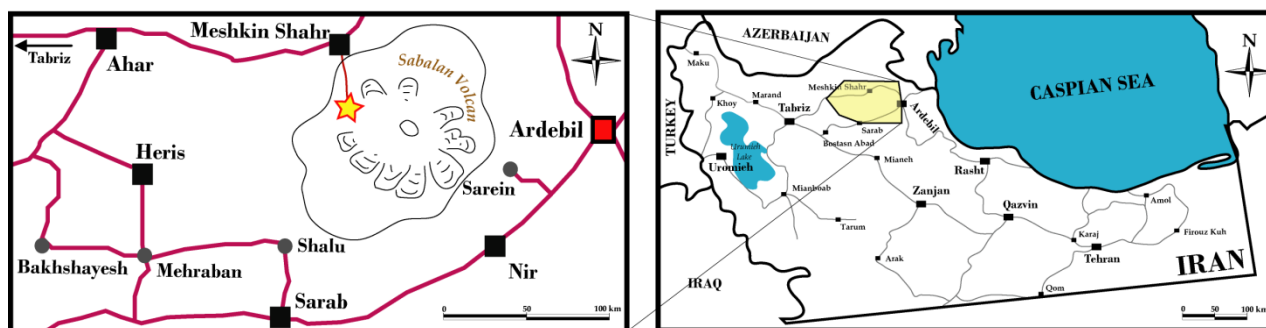

Figure 1: Schematic location of Northwest Sabalan Geothermal Field, NW Iran.

Sampling of discharged wells is one of the crucial parts of reservoir assessment procedure. In the second stage of field development and well testing in 2011, the discharged fluids of wells NWS-6D, NWS-7D, NWS-9D and NWS-10D were sampled and analysed for further interpretations. In this paper the chemistry of discharged fluids is examined to acquire the most realistic chemistry and temperatures of deep liquids, as a means of further detailed interpretation of reservoir characteristics.

2. GEOLOGICAL SETTING

Tectonically, Sabalan volcano lies on the south Caspian plate which underlies the Eurasian plate to the north and overlies the Iranian plate, producing northwestwardly compression. Mt. Sabalan where the NW Sabalan geothermal field is located is a

Quaternary (Pleistocene-Pliocene) andesitic volcanic complex that covers an area of approximately 2500 km square. Volcanic deposit of Sabalan volcano is characterized by predominant altered andesitic, dacitic and trachydacite and trachyandesitic lavas, pyroclastics, lahars, tuffs and domes. These volcanic deposits are formed in a sequence associated with structures of volcano and particularly the caldera formation. The date of these volcanic formations are estimated to range from 0.2 – 1.3 Ma, using K-Ar dating method (TBCE, 1978).

Subsurface geology of the area is perceived from cores and cuttings of deep drilling wells. The first subsurface formation, shallower than around 300m in most wells, could be well judged from outcrops in the region and consists of terrace deposits (Dizu Formation). It is composed of a mixture of non-cemented and poorly sorted sediments. Its rounded clasts include predominantly non-hydrothermally-altered and relatively rounded andesite, trachyandesite and subordinate trachydacite. The subsurface volcanic formations in depth more than around 300m are composed of moderate to intense (Valhazir Formation) and intense hydrothermally altered (Epa Formation) andesitic pyroclastics and lavas deposits. They are also distinguished in boreholes by their different types of alteration including phyllic-argillic (Valhazir Formation) and propylitic (Epa Formation), suggesting that the hot neutral-pH fluids contribute in alteration process (SKM, 2003). These volcanic rocks are intruded by many diorite porphyry dikes, mainly in depth more than 1200m. The plutonic basement of Sabalan volcano (Miocene hornblende micro-monzodiorite porphyry) with an outcrop in 5-10km west of Sabalan is recognized in some wells in depth of 1000-2000 m. The surrounding intense contact metamorphic rocks which belong to formations deeper than 1500m are predominantly composed of biotite-garnet-hornfels. Based on occurrence of high temperature alteration minerals in cores taken from deepest part of the wells, reservoir temperatures are estimated around 240°C.

3. SAMPLING AND ANALYSIS

Good quality and satisfactory quantity of liquid and steam samples are key factors to have a reliable evaluation on characteristics of geothermal fluids. This can also guarantee the effectiveness of reservoir management in production stage. A total of 225 fluid samples were collected from the discharged wells; NWS-6D, NWS-7D, NWS-9D and NWS-10D, where a total of 20 two-phase samples were collected from webre separator on the wellhead. The analytical data of liquid samples includes Ca, Na, K, Mg, Li, Fe, Mg, Mn, B, Cl, F, SiO_2, SO_4, CO_2, H_2S, HCO_3, and NH_3 component concentrations in the liquid phase of webre and weir box samples. The steam samples were analysed for all gas components including CO_2, H_2S, He, H_2, Ar, O_2, N_2, CH_4 and NH_3. The liquid samples were mainly analyzed in site laboratory (NWS-7D, NWS-9D and NWS-10D), while the two-phase samples were analysed by chemistry laboratories of PNOC-EDC (NWS-6D, Manila, Philippines) and ISOR (NWS-10D and NWS-9D, Reykjavik, Iceland). The fluid samples of well NWS-6D also analyzed to acquire oxygen and hydrogen isotope values in PNOC-EDC's Chemistry and Isotope Laboratory in Manila, using Los Gatos Liquid-Water Isotope Analyzer.

In addition, through the approximately 530 days of discharging tests, a series of physical measurements were carried out to evaluate the production potential of wells and reservoir characteristics. Accordingly, it is estimated that the enthalpy of these wells varied from 1036 to 1225 kJ/kg in full discharge conditions and the average of wellhead pressure was 1 Kpa. The steam fraction of discharged fluids varied from around 7 to 15 kg/s, while the total mass flows ranged from 36 to 58 kg/s.

4. GEOCHEMISTRY

Chemical concentrations in the deep fluids at separator pressure are calculated with the aid of WATCH chemical speciation program, version 2.4 (Bjarnason, 2010). To choose valid analytical data, ionic balances were regarded, ranging from 0.01% to 4.36%, which indicate acceptable quality of thermal fluid analysis for speciation calculations.

4.1. Classification of discharged liquids

4.1.1 Cl-SO4-HCO3 ternary diagram (Giggenbach, 1991)

The Cl-SO_4-HCO_3 ternary diagram is a diagram for classification of natural waters based on the relative concentrations of the three major anions Cl^-, SO_4^{2-} and HCO_3^-. Since chloride does not take part in the host rock-related reactions, its concentration is independent of the rock-fluid equilibria. Such a conservative behaviour makes chloride a good tracer in geothermal investigations to define fluid types and also influence processes in depth. On the basis of this diagram several types of thermal water can be distinguished: mature waters, peripheral waters, steam-heated waters and volcanic waters. According to Giggenbach 1991, the chloride-rich waters are generally found near the upflow zones of a geothermal system, while high SO_4^{2-} steam-heated waters are usually indicate higher elevation parts of a field. Separation degree among data points for high chloride and bicarbonate waters may give an idea of relative interaction degree of the CO_2 charge fluid at lower temperature, and of the HCO_3^- concentration, increasing with time and distance from heat source. Figure 2 represents that all discharged samples collected from the wells plotted into domain with high chloride, neutral-pH and mature waters. This proposes that the thermal water originates from volcanic waters.

4.1.2. Na-K-Mg ternary diagram (Giggenbach, 1991)

The Na-K-Mg diagram is used to classify waters as fully equilibrated, partially equilibrated and immature waters. It can be used to predict the equilibrium temperature and also suitability of thermal waters for application of ionic solute geothermometers. It is pertinent to temperature dependence on the full equilibrium assemblage of potassium and sodium minerals that are expected to form after isocheimal recrystallization of average crustal rock under geothermal conditions (Giggenbach, 1991). It is essentially based on the temperature dependence of following reaction:

$$K-feldspar + Na^+ + K^+ = Na-feldspar + 0.8K-mica + 0.2chlorite + 5.4silica + 2K^+ = 2.8K-feldspar + 5.4silica + 16H_2O + Mg^{+2} \quad (1)$$
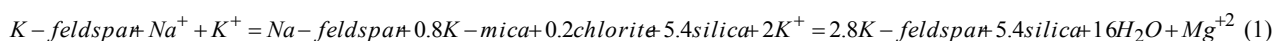
Figure 3 indicates that most of the samples plot in the partially equilibrated and mixed waters domain. The geothermometers applied in this geo-indicator, including K-Mg (Giggenbach, 1988)and Na-K (Giggenbach, 1984) show that the deep fluid temperatures range between 235-320°C and 285-335°C, respectively. Further explanation will be presented in "geothermometry" section.

4.1.3. Cl-B-Li ternary diagram (Giggenbach, 1991)

The Cl-Li-B triangular diagram and B/Cl ratio are useful to recognize the common origin of geothermal fluids. Since the alkali metal of Li are least affected by secondary processes, it may therefore be used as a tracer for the initial deep rock dissolution process and as a reference to evaluate the possible origin of two important conservative constitutes of geothermal waters; B and Cl. They are fixed in fluid phase and have not equilibrated with host rocks and are, therefore, the best geo-indicators of the origin of the geothermal system. Figure 4 shows that all the discharged samples have a high Cl content, indicating that they are mature and originated from relatively old hydrothermal systems and the fluid migrates from the old basement rock. The B/Cl ratio of the fluids is low and can be representative of andesite-hosted geothermal reservoir.

4.2. Aquifer chemistry

Subsequent to physical and chemical stability of the wells after discharge initiation, the daily collected samples were analysed. Despite slight differences in discharged water chemistry, the overall component concentrations and trends of each well through the discharge test were relatively similar and constant. Concentration of Cl ranges from around 1900 to 2200 ppm where SiO_2 concentration varies between 350-450 ppm. Discharged liquids are composed of about 1400-1600 ppm Na and 250-300 ppm K. The average concentration of Fe and Mg in both wells of NWS-6D and NWS-9D are measured and are around 0.15 and 0.17, respectively. The components measured in gas samples seem to be more scattered through time. The nearly high CO_2 concentrations range from 10000 ppm to 20000 ppm and H_2S concentration range from 80 ppm to 200 ppm.

Figure 5 shows that the concentrations of components such as SiO_2, Na and F in deep liquids, as a function of Cl fairly vary in different wells. It represents that the feeding aquifers charging in NWS-6D have slightly different chemistry. On the other hand, the well NWS-7D has shown also different chemistry, particularly in terms of B and F concentration. It indicates that aquifers feeding the wells NWS-6D and NWS-7D are chemically different from what charge the wells NWS-9D and NWS-10D. Such a chemical property could be related to presence of more than one aquifer with relatively different fluid composition in the deep levels. The assessment of the number and quality of aquifers in different wells can be accomplished by combining the logging and geology data of each well.

4.3. Geothermometry

The equilibrium between common minerals or mineral assemblages and a given water chemistry is temperature dependent. Geothermometers, therefore, are subsurface temperature indicators, derived from temperature dependent geochemical and/or isotopic composition of hot spring waters and other geothermal fluids under certain favorable conditions. Geochemical and isotopic geothermometers rely on the following assumptions: (i) there is equilibrium between liquid and minerals in the geothermal reservoir, (ii) the activity or activity ratio is controlled predominantly by temperature, and (iii) re-equilibrium has not occurred during ascent and discharge phases.

Figure 2: Comparative plot of relative Cl-SO₄-HCO₃ contents in discharged waters from NW Sabalan wells.

Figure 3: Na-K-Mg equilibrium diagram and geoindicator; representing equilibrium status of discharged waters from NW Sabalan wells.

Figure 4: Cl-B-Li ternary diagram; representing the origin of discharged waters from NW Sabalan wells.

Under such assumptions the temperature indicated by the geothermometer is not necessarily the maximum temperature of the water, but the temperature at which mineral and water phases are expected to be in equilibrium (Nicholson, 1993). Hence, comparing various types of geothermometers including solute, gas and isotope geothermometers with each other and especially with measured well temperature data is the best way to verify the real temperature of reservoir fluid.
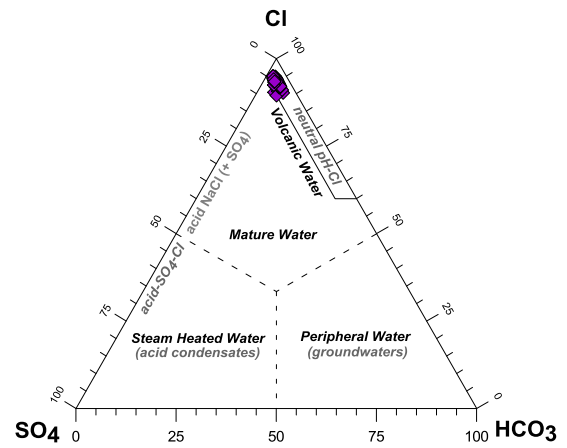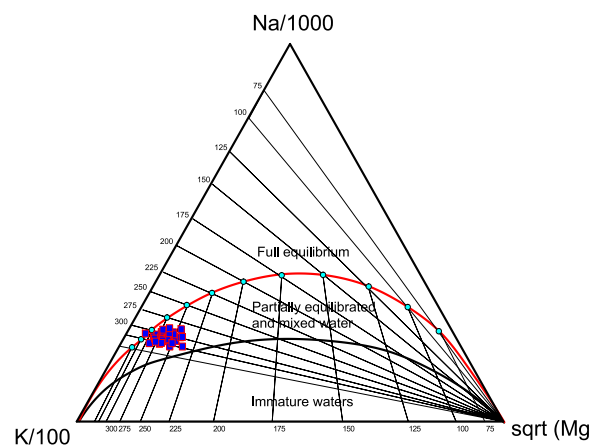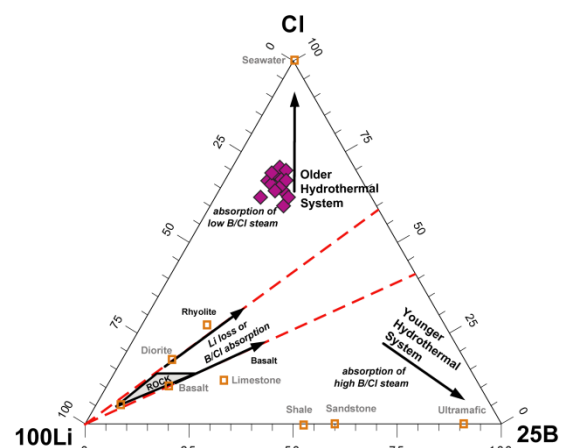
4.3.1. Solute Geothermometers

In geochemical studies, water chemistry and gas composition of geothermal fluids have proved useful in assessing the characteristics of geothermal reservoirs, both to estimate temperatures and to estimate initial steam fractions in the reservoir fluid (D'Amore and Celati, 1983; D'Amore and Truesdell, 1985).

- *Silica geothermometers:*

Increased solubility of quartz and its polymorphs at elevated temperatures has extensively been used as an indicator of reservoir temperatures (Fournier and Potter, 1982). The assumption that should be considered when the silica geothermometers are applied is that silica dissolved at high temperature at depth remains metastable in the solution and does not precipitate when the thermal waters rise to the surface, like what happens in high-temperature well discharge.

In geothermal systems above 180°C, the silica concentration in the form of H_4SiO_4 that is a weak acid is controlled by the equilibrium with quartz, while at lower temperatures the equilibrium with chalcedony becomes more significant. Solubility reactions for silica minerals can be expressed as follows:

$$SiO_{2,solid} + 2H_2O = H_4SiO_4^0 \qquad (2)$$
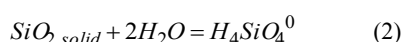
Analysis of silica in aqueous solution yields total silica concentration, which includes both un-ionized $H_4SiO_4^0$ and disassociated (ionized) $H_4SiO_4^0$; $H_3SiO_4^-$ that forms fluids with pH of higher than 10. Regarding the maximum pH of discharged fluids of the wells; 7.3 (NWS-6D), 7.2 (NWS-7D), 7.2 (NWS-9D) and 7.7 (NWS-10D), the silica concentrations in the samples are undissociated silicic acid ($H_4SiO_4^0$) and the quartz geothermometer is valid. The quartz geothermometers used to estimate the aquifer temperatures in this study are Fournier (1977) and Fournier and Potter (1982). Accordingly, the average temperature for the deep aquifer using quartz geothermometer equation of Fournier (1977) ranges from 237.0 to 246.3 °C (average of 244.3°C), where quartz geothermometer using equations of Fournier and Potter (1982) that applies silica concentrations in water in equilibrium with quartz after adiabatic boiling to 100 °C (atmospheric pressure) ranges from around 247.0 to 250.5 °C (average of 248.2 °C) for various wells (table1). The subtly higher temperature (around 3 °C) of the deep aquifers charging well NWS-6D can also confirm the relatively different composition of its reservoir in proportion to other wells.

Cation geothermometers:

A commonly used geothermometer where geothermal waters are known to come from high-temperature resources is the ratio of sodium to potassium (Na/K). The ratio decreases when temperature increases and accordingly the cation concentrations (Na^+, K^+) in solution are controlled by temperature-dependent equilibrium reactions with feldspars (albite and K-feldspar) that have often been described as exchange reactions. The main advantage of this thermometer is that it is less affected by dilution and steam separation than quartz geothermometer provided, since there is little Na^+ and K^+ in the diluting water compared to the reservoir water. The exchange reaction is expressed as:

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+ \qquad (3)$$

Figure 5: Concentration of SiO_2, Na and F as a function of Cl in deep aquifers of NW Sabalan wells.

In this paper the equation suggested by Arnórsson et al., (1983) and (Giggenbach et al, 1988) is used to find the most realistic temperature of further deep aquifer. As it is presented in table 1, the average temperature of the thermal deep aquifer in wells ranges from 264.3°C to 276.0°C (average of 270.9°C) when Na-K geothermometer proposed by Arnórsson et al (1983) is applied. On the other hand, the temperature of reservoir varies from 260.5 to 273.3°C (average of 267.4°C), using the geothermometer proposed by Giggenbach et al, (1988). These temperatures may represent the source of thermal aquifer in the deeper levels. There are some discrepancies between quartz and Na/K temperatures. It is commonly observed that the Na/K temperatures are higher than quartz temperatures. Although it can be affected by another equilibria (i.e. not albite and K-feldspar) controlling Na/K ratio as geothermometer. The other common explanation is that the Na/K equilibrium re-equilibrates slower than quartz and thus has more valid temperature for the deep liquid temperatures.
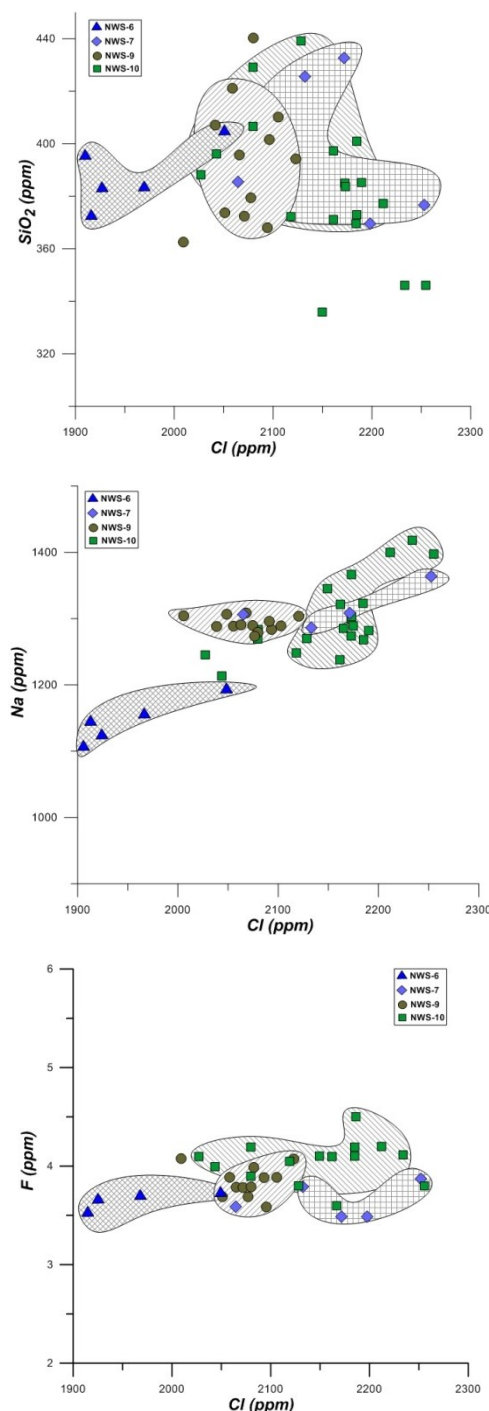
The Na-K-Ca geothermometer is developed and empirically calibrated by Fournier and Truesdell (1973). The main advantage of this geothermometer in comparison with quartz and especially Na-K geothermometer is that it does not yield high and misleading results, specifically for cold and slightly thermal, non-equilibrated waters, whereas high calcium fluids may provide an anomalously high temperature using Na-K temperature. The discharged fluids from the NW Sabalan wells produce temperatures ranging from 271.5°C to 287.9°C (average of 279.0°C), using Na-K geothermometer. As it is shown in table 1, this temperature is higher than average temperatures calculated by Na-K geothermometers which can be associated with high concentration of carbon dioxide in the fluids.

Giggenbach (1988) proposed a temperature equation for the K-Mg geothermometer which its calibration was based on calculated equilibrium constant for the following reaction:

$$2.8K - feldspar + 1.6water + Mg^{+2} = 0.8K - mica + 0.2cholorite + 5.4quartz + 2K^{+} \tag{4}$$
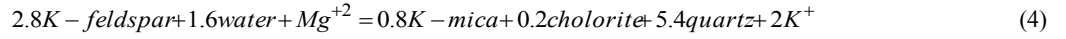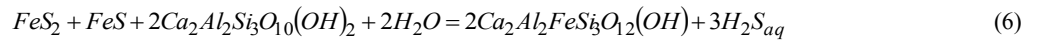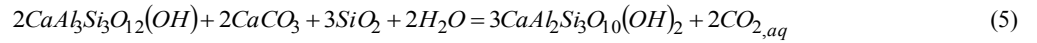
Despite the restricted amount of analysis for Mg concentration in NW Sabalan discharged fluids, K-Mg geothermometer shows 249°C and 264.7°C for the wells NWS-6D and NWS-7D respectively (average of 256.8 °C). The different result achieved by K-Mg and Na-K geothermometer is referred to variable intensity of equilibrium in two reactions. Generally, the K-Mg geothermometer responds more quickly than the Na-K ratio to temperature decrease in upflow zones. Accordingly, the K-Mg geothermometer tends to produce lower temperature than the Na-K geothermometer.

- *Gas Geothermometers*

In many high-temperature geothermal fields, the gas content of geothermal discharges (fumaroles and wells) like CO_2, H_2S, H_2, N_2, NH_3, and CH_4 is used to obtain information about the source of the fluid and its temperature. Gas geothermometers are on assumption of specific gas-gas or mineral-gas equilibria or/and distribution of isotope ratios among gaseous species (Arnórsson et al., 2007). The assumptions of specific chemical equilibria provide the thermodynamic data required for calibration of gas geothermometers. When using gas geothermometry, it is important to consider several factors; a) aquifer temperature may affect the gas composition of a geothermal fluid, b) gas concentrations at equilibrium depend on the ratio of steam to water of the fluid, c) the flux of gaseous components into geothermal systems from their magmatic heat source may be very significant and influence how closely gas-gas and mineral-gas equilibria are approached in specific aquifers (D'Amore and Arnórsson, 2000).

The CO_2 and H_2S geothermometers are based on mineral-gas equilibria and the temperature equations for the thermodynamic data for the following reactions are:

$$2CaAl_3Si_3O_{12}(OH) + 2CaCO_3 + 3SiO_2 + 2H_2O = 3CaAl_2Si_3O_{10}(OH)_2 + 2CO_{2,aq} \tag{5}$$

$$FeS_2 + FeS + 2Ca_2Al_3Si_3O_{10}(OH)_2 + 2H_2O = 2Ca_2Al_2FeSi_3O_{12}(OH) + 3H_2S_{aq} \tag{6}$$

Q in the gas geothermometry equations represents the gas concentrations in log mmol/kg. The equations were:

For TCO_2 (Arnórsson et al., 1998)

$$T(^{\circ}C) = 4.724Q^3 - 11.068Q^2 + 72.012Q + 121.8 \tag{7}$$

For TH_2S (Arnórsson and Gunnlaugsson, 1985) that can be applied for all the waters in the range of 200-300°C and Cl > 500 ppm

$$T(^{\circ}C) = 246.7 + 44.8Q \tag{8}$$

Gas geothermometry results imply that H_2S geothermometers changing from 269.1°C to 277.1°C (average of 274.2°C) is fairly well correlated with Na-K geothermometer (279°C), while CO_2 geothermometer represents temperatures ranging from 287.3°C to 308.9°C (average of 301.8°C) which is higher than all the other gas, solute and solute thermometers (table 1). The reason behind this increase can be explained by high CO_2 concentrations in the deep liquid, the reason that is also supposed to affect the application of Na-K-Ca geothermometer in estimation of NWS reservoir temperatures.

- *Oxygen isotope geothermometer*

Isotopes are chemical elements with different atomic mass, but the same atomic number (protons) and identical chemical behaviour but different physical properties. Similar to other chemical elements, isotope exchange reactions can achieve equilibrium in the natural system and they are temperature dependent. When steam separates from hot water, isotopes fractionate in natural water-rock systems. The exchange reactions may be between gases and steam phase, a mineral and gas phase, water and a solute. Lighter isotope elements (helium, hydrogen, oxygen, carbon, sulphur) have larger fractionation. Simplicity of sample collection and preparation, ease of isotope measurements and well-understood isotopic equilibrium constants constrain the number of isotope exchange processes applied in isotope geothermometry studies.

The isotopic compositions of both the steam and water in a well sample may be determined from the total discharge, whose steam and water fraction is known. Isotopic fractionation factors are generally symbolized by α. The general expression for fractionation between two components A and B is as follows:

$$1000\ln_{AB} = \delta_A - \delta_B \tag{9}$$

where δ_A and δ_B designate the respective isotopic ratios in compounds A and B (Arnórsson, 2000).

In this study the oxygen isotope geothermometer defined based on exchange reaction 21 (Lloyd, 1968), which consider $\delta^{18}O$ values in aqueous SO_4 and liquid water (sulphate-water oxygen isotope geothermometer) is used:

$$S^{16}O_4 + H_2{}^{18}O = S^{16}O_3{}^{18}O + H_2{}^{16}O \tag{10}$$

The Kinetic for this reaction is fast, even at low temperature, so re-equilibrium upon change in temperature occurs rapidly. For this reason, this isotopic reaction does not constitute a useful geothermometer. On the other hand, unified isotopic equilibria are generally not observed in geothermal system. The different isotope geothermometers, therefore, yield different temperature values (Arnórsson, S., 2000). As it is presented in table 1, the oxygen isotope geothermometer gives an average temperature of 299.1°C for discharged samples of well NWS-6D that is considerably higher than solute and gas geothermometers.

Table 1: Solute, gas and oxygen isotope geothermometers of NW Sabalan discharged geothermal fluids and the reference temperature applied geochemical speciation calculations

	T_{q-1}	T_{q-2}	T_{NaK-1}	T_{NaK-2}	$T_{Na-K-Ca}$	T_{K-Mg}	T_{CO2}	T_{H2S}	$T^{18}O$	Ref. T
NWS-6D	246.3	250.5	268.0	263.3	271.5	249.0	305.0	269.1	299.1	235
NWS-7D	243.9	247.8	264.3	260.5	278.7	-	305.7	277.1	-	230
NWS-9D	243.9	247.8	275.4	272.5	278.1	264.7	308.9	274.1	-	230
NWS-10D	243.0	246.9	276.0	273.3	287.9	-	287.8	276.5	-	223
Mean	*244.3*	*248.2*	*270.9*	*267.4*	*279.0*	*256.8*	*301.8*	*274.2*	*299.1*	*229.5*

T_{q-1}: Fournier, 1977; T_{q-2} : Fournier and Potter, 1982;, T_{NaK-1} : Arnórsson et al, 1983; T_{NaK-2} : Giggenbach et al, 1988; T_{NaKCa}: Fournier and Truesdell, 1973; T_{KMg}: Giggenbach et al, 1988; T_{CO2} : Arnórsson et al , 1998;, T_{H2S} : Arnórsson and Gounnlaugsson, 1985; T_{18O} : Lloyd, 1968

4.4. Stable isotopes of O & H

Isotopic techniques have become essential part of studies related to the main geothermal development stages. The interpretations derived from isotopic studies are strengthened if complemented and combined with other chemical results. Among the various isotopes, the variations in stable isotopes of oxygen, hydrogen and carbon provide the most useful information. In this study both hydrogen and oxygen isotope values of eight webre liquid samples discharged from well NWS-6D are used.

Geothermal systems, where the isotopic content of the geothermal waters is somewhat lower than that of the local precipitation, are influenced dominantly by processes such as boiling, mixing, steam heating-surface evaporation and water-rock interaction. The arrow to the right in figure 6 shows how the water-rock interaction at high temperatures resources can change oxygen content of geothermal fluid, which is referred to as an "oxygen shift". The oxygen content exchanged between host rocks, which have relatively heavy isotopic ratios compared to the water, and water result in oxygen shift. The exchange process is greatly accelerated at the high temperature geothermal fields, where less oxygen shift is anticipated in low to intermediate temperatures resources. Since there is much more hydrogen in water than in volcanic rocks, hydrogen is less affected by this water-rock interaction and the deuterium value of thermal water, therefore, still characterizes that of the original source. However, occurrence of hydrous minerals can make a slight "deuterium shift" (Ellis and Mahon, 1977).

One of the main aspects of geochemistry of geothermal fluids is determination of the recharge area in a geothermal system. Craig (1963) verified the isotopic characteristics δ^2H and $\delta^{18}O$) of precipitation related to latitude and altitude as well as continental impacts. He suggested that samples from higher latitudes and elevation or those from further inland have progressively lighter isotopic values than lower latitudes and sea. This is basically due to preferential behaviour of the heavier isotopes in removing from the precipitating clouds. To evaluate the origin of waters charging a geothermal system, the deuterium excess (d) is defined as $\delta D-8*\delta^{18}O$. It is a good indicator when oxygen shift is not observed and can show the relative humidity at source area of participation (Johnsen et al, 1989). Figure 7 shows a linear relationship between $\delta^{18}O$ and the d values, where the deuterium excess is relatively variable and lies mostly in the range from -9‰ to -6‰. Accordingly, the source waters originate from identical region and with low humidity. Furthermore, it could be deduced that the origin of the thermal waters can be traced up to the higher elevations.
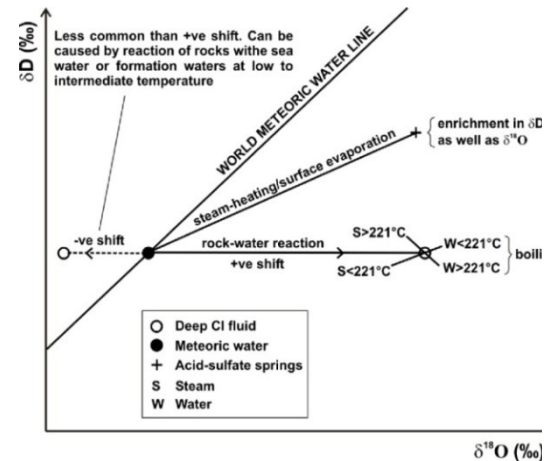

Figure 6: Schematic trends in isotopic signatures of meteoric water and geothermal fluids with active processes (Nicholson, 1993)
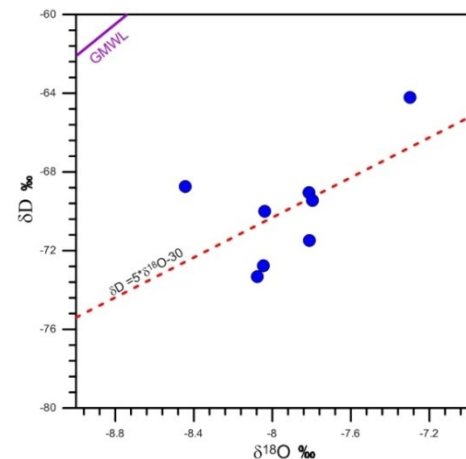

Figure 7: Relationship between δD and $\delta^{18}O$ of discharged liquids from well NWS-6D, NW Sabalan geothermal field

5. SCALING POTENTIAL

Evaluation of solid scales' potential of reservoir fluids, using chemistry of discharged geothermal samples is one of the main aims of geochemistry investigations. It is very well understood and experienced that calcite and amorphous silica are most troublesome scales in the utilization of geothermal resources, particularly in high temperature wells. Other types of deposition accompanying

them include metallic sulphides and silicates, anhydrite and fluorite. With respect to calcite and amorphous silica, they don't influence production procedure due to their small amounts of deposition. . According to Corsi, (1986), scale deposition can be divided into three main types including deposition from a single phase fluid (injection pipelines), deposition from flashing fluid (wells, separators, two phase-pipelines) and deposition by steam carryover (separators, steam lines and turbines).

5.1. Silica scaling potential

It has been realized that aqueous silica concentrations in high-temperature geothermal resources are controlled by close approach to equilibrium with quartz (Gunnarsson and Arnórsson et al., 2000). Silica scales are found nearly in all geothermal installations, where it can be controlled by maintaining the temperature above the solubility level for amorphous silica, as one of the main design criteria for most geothermal plants. Due to boiling of thermal fluid in the well and the afterward cooling, mostly in surface installations, silica solubility in

Figure 8: Relationship between deuterium excess (d=δD-8 δ¹⁸O) and δ¹⁸O of discharged liquid from well NWS-6D, NW Sabalan geothermal field

water decreases resulting in immediate quartz supersaturation state of discharged waters, while the formation rate of quartz is slow. It cause a safe temperature zone for quartz scaling, so that when only some 25% of the water convert into steam, which is usually possible by a 100°C temperature drop in discharged water, no scaling and relevant choking danger will threaten the surface installations in practice. Reservoir water of 240°C has thus to be separated above 140°C to avoid silica scaling. Other problematic aspect of silica scaling, which is more troublesome in productive geothermal reservoir where temperature exceeds 250°C is silica scaling in formations due to reinjection of waste water into the injection wells. Amorphous silica, deposited around the well bore cause reduction in formation permeability and subsequently the injection capability of the well (Hauksson and Gudmundsson, 1986). The higher the reservoir temperature, the higher the temperature of reinjected water into the formation needs to be.

The most representative samples of discharged water of each well are used to obtain the most realistic deep aquifer chemistry. Using the highest measured temperature in the wells as the reference temperature (Table 1), deduced from logging operations, the composition of feeding aquifers and their changes during the adiabatic boiling are calculated by WATCH 2.4. The calculated activity product (Q) and equilibrium constant (K) of reaction 2 are also applied to demonstrate super-saturation state of silica minerals (amorphous silica, chalcedony and quartz). Figure 9 shows that amorphous silica is anticipated to be deposited in temperatures lower than around 90°C, while quartz will form in temperatures lower than around 220°C in well NWS-10D. The well NWS-9D is expected to deposit amorphous silica in temperatures lower than 120°C and deposit quartz in temperatures lower than 240°C.

The commonly adapted methods to reduce or eliminate deposition of amorphous silica in surface installations, maintaining steam separation pressures (and consequently temperatures) above amorphous silica saturation state are the best methods ever applied. On the other hand, the same temperature limitation should be applied in injected waste water temperature. This method that is called "hot injection" method, pumps waste water from geothermal production wells and he water from steam separators to the injection wells. Since the wells NWS-6D, NWS-7D and NWS-10D are located in the same drilling pad (pad D) and are expected to produce the main load of power plant in the future, temperatures of 90°C can be considered as the criteria temperature for silica scaling, so that the injected water temperature should not exceed 90°C. This practice limits the amount of heat that can be extracted from the discharged geothermal waters. To optimize the production, therefore, numerous methods are suggested and executed efficiently in various fields. All these methods are examined to alter two main factors, affecting silica saturation state of water; reservoir temperature, and water salinity or the overall water composition. Direct infiltration, chemical treatment, evaporation, silica polymerization and storage in effluent ponds are the most applicable methods to alleviate silica scaling problems in geothermal plants.

5.2. Calcite scaling potential

Despite silica minerals that represents prograde solubility through cooling, calcite has retrograde solubility. Therefore, it becomes over-saturated in geothermal fluids when boiling happens in the well and becomes under-saturated along cooling on the surface. Many researchers have accordingly reported that calcium carbonate, in the crystalline forms of calcite and/or aragonite is the major scale-forming mineral in many geothermal systems. When boiling takes place in the geothermal wells, water converts rapidly into steam (flashing) and the consequent degassing (CO_2 loss from the liquid phase into a gas phase) results in pH rise. Consequently, carbonate minerals tend to deposit in boiling point of the well, where the extent of degassing and cooling determines whether boiling causes initially calcite saturated water to become over or under-saturated. In other word, temperature and pH play an important role to identify the possibility of minerals precipitation from solution. The kinetics of the precipitation reaction and fluid composition, in terms of salinity and dissolved CO_2 in the deep liquid are also effective in degree of over-saturation and the amount of minerals precipitated from solution (Arnórsson, 1989). Calcite precipitates from brines according to the following reaction:
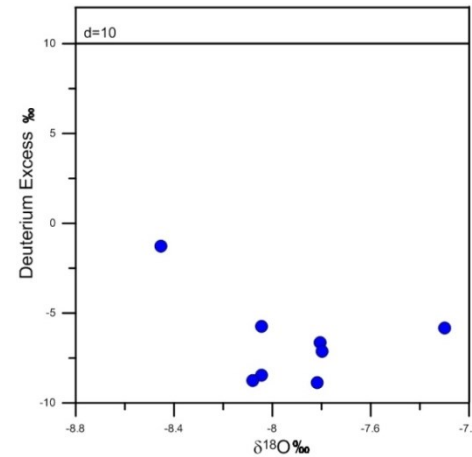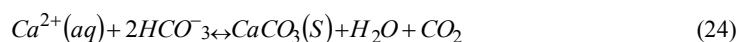
$$Ca^{2+}(aq) + 2HCO^{-}_{3} \leftrightarrow CaCO_3(S) + H_2O + CO_2 \qquad (24)$$

Most of the geothermal liquids at reservoir temperature of 140-240°C are typically close to be calcite-saturated. Calcite scales are primarily found over a 200-300 m long section in the well above where flashing occurs, but are not found much lower or higher that section. Since the quantity of dissolved carbonates at higher-temperature (>260°C) reservoirs' liquids is less than moderate to high temperature reservoirs, usually the calcite scaling is not a problem in such production wells. At temperatures above 300°C, especially in highly saline water, more complex minerals can form scales, mainly metal sulphides, silicates and oxides (Thorhallsson, 2005).

Applying the deduced reference temperatures from logging surveys, the chemistry of each well's representative sample has been entered into WATCH 2.4 and deep aquifer composition and consequent activity product (Q), and equilibrium constant (K) of reaction 24 are obtained. Calcite saturation state of deep liquid phase of every sample, including K and Q, are calculated during the adiabatic boiling and are plotted in figure 10. It shows that the deep liquid is generally super-saturated at lower temperatures than reference temperature and under-saturated in temperatures more than reference temperature (see reference temperature in Table1). It also displays that although the boiling temperature of the wells NWS-6D and NWS-7D is slightly different (233°C and 231°C, respectively), the calcite saturation trend through adiabatic boiling is similar. On the other side, the well NWS-10D behaves differently in terms of super-saturation state/trend, when it is compared with the other three wells, while the boiling temperature is not far from what other wells have indicated. Figure 6b also implies that the boiling temperatures range between 231-233°C, while the reference temperature applied for calculating saturation indices are different; 223-235°C (Table 1). Accordingly the whole deep liquid can be considered to be super-saturated with calcite in temperatures lower than 231°C.

There are some limited but thoroughly effective methods to cope with calcite scaling in geothermal wells. The efficiency of each method depends directly on production state of plant. When the plant is managed to produce constantly, conducting "Calcite Inhibition System" is the most and economical method in a mid-long term period to prevent economical and technical aspects of calcite scaling in the wells and consequent interruption in production. Otherwise, periodic mechanical cleaning (drilling) and chemical treatment (acidization) methods could be meticulously evaluated, in order to be conducted each or both at the same time, to remove the scaled carbonates in the wells.

5.3. Other minerals' scaling potential

Calcite and Quartz are the only minerals that can cause problem during production. Assessments indicate that the reservoir fluids never reach to saturation state through adiabatic boiling. Anhydrite and fluorite are examples of safe minerals in NW Sabalan geothermal field that their saturation states are plotted in figure 11. It indicates that the deep liquid is always under-saturated at all temperature and never meets over-saturation state. Therefore, such minerals will never cause problems in the wells and surface installations, though it is expected to accompany calcite and silica scaling in minor quantities in form of clay minerals.

6. CONCLUSION

Classification diagrams for natural water indicate that the liquids discharged from high temperature wells in NW Sabalan geothermal field is chloride, neutral-pH and mature waters that are partly equilibrated with host rocks. Chemistry assessment of deep aquifer shows that the wells NWS-6D
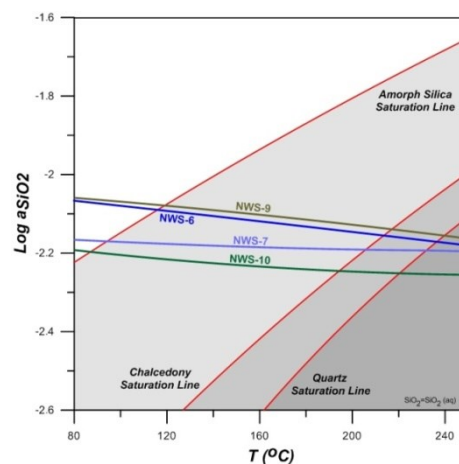

Figure 9: Silica saturation states of NW Sabalan reservoir liquids
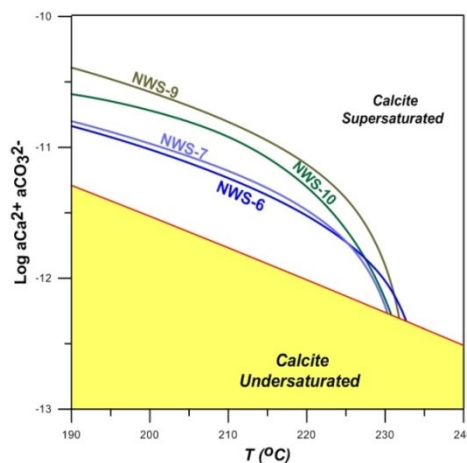

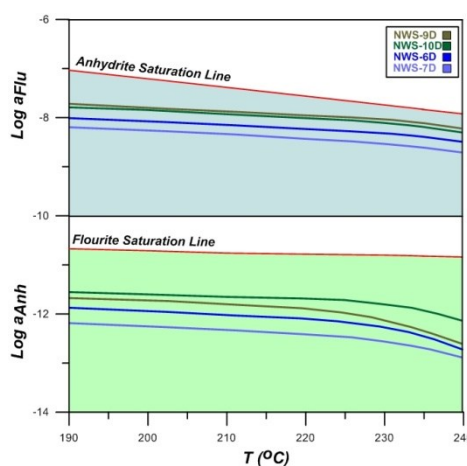Figure 10: Calcite saturation states of the NW Sabalan reservoir liquids

Figure 11: Anhydrite and fluorite saturation states of NW Sabalan reservoir liquids

is relatively different from the rest. Chemical geothermometers applied for all wells suggest a temperature range of 244-248ºC for the liquids in the wells, where a temperature range of 256-301ºC is estimated for deeper parts of the reservoir. Isotope chemistry of discharged samples indicates that an identical source of water has been charging the reservoir, originating from a higher elevation area with lower humidity. The calculated minerals saturation indices of reservoir fluids shows that the aquifer fluids are under saturated with regard to amorphous silica in temperatures lower than around 90°C and is in under saturation state with regard to calcite in temperatures higher than 231°C. The liquids are not supersaturated in terms of other secondary minerals such as anhydrite and fluorite. The difference in chemistry of discharged fluids and the consequent calculated chemistry of deep thermal liquids all indicate that each well can be charged by more than one aquifer in depth, having various chemical characteristic. Further logging and geological data can shed light on thorough characteristic of NW Sabalan geothermal reservoir.

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