PROCEEDINGS, Thirty-Sixth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 31 - February 2, 2011
SGP-TR-191

DISTRIBUTION OF ARSENIC IN GEOTHERMAL WATERS FROM SABALAN GEOTHERMAL FIELD, N-W IRAN

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ABSTRACT

Distribution of Arsenic in geothermal waters in Sabalan area has been studied. In all samples concentration of As exceed the WHO limit for drinking water (10 µg/l) except one sample from Agh-su hot spring. Geothermal well fluids are sodium-chlorate type with extremely high As concentration (up to 3500 µg/l) in comparison with hot spring waters where concentration of As in the range of 0.8-890 µg/l. Concentrations of As are higher in the chloride hot springs than in the acid-sulfate features and increase with increasing temperature and salinity. Positive correlation As with Cl has been detected that is validate for most geothermal fields in the world.

As concentration in studied thermal waters is almost in range or rather lower than levels reported in geothermal waters from other parts of the world except the geothermal fields in Iceland and Hawaii where the As concentration is extremely low (< 0.001mg/l).

INTRODUCTION

Arsenic is one of the important trace components in geothermal systems which occur together with Hg, Sb, B, Li and F. Arsenic associated with geothermal waters has been reported in several areas, including hot springs from parts of the USA, Japan, New Zealand, Iceland, Kamchatka, France and Dominica (e.g. White *et al.*, 1963; Welch *et al.*, 1988; Criaud and Fouillac, 1989). Hot springs always contain considerable among of As produce an excess of fluid at the surface which usually drains unimpeded into the nearest catchments system. Using of these waters for drinking, stock watering and irrigation may have high As concentration in downstream of geothermal system (Webster, J.G., Nordstrom, D.K., 2003). In most active geothermal fields arsenic concentrations in the natural surface waters drainage can exceed 10 mg/l. The WHO (1993) limit for drinking water is 10 µg/l, for the protection of aquatic life of 19 µg/l and for stock watering and irrigation of 20 and 10 µg/l respectively.

Evaluation of As in natural waters can be useful for understanding the pollution problem, rock leaching and water-rock interaction (Webster, J.G., Nordstrom, D.K. 2003; Ballantyne 1988; Smedley, 2002).

Development of geothermal fields for power generation tends to increase the rate and volume of geothermal features reaching the surface. Sabalan geothermal field is a high temperature area under development which is rich in geothermal manifestation at the surface with a temperature in the range of 25–85°C. The geothermal springs are used as a swimming pools and hot spa both for local residents and tourists. Most of the hot springs has their outlet into the river. In this study, the data on the distribution of As in the main hot springs and deep reservoir wells of Sabalan geothermal field will be presented.

STUDY AREA

Mt. Sabalan geothermal field is one of the prospective area in NW-Iran for geothermal exploration which has been initiated by SUNA (Renewable Energy organization of Iran) since 1978 to constructing the geothermal power plant. The geothermal field is located in a Moil valley terraces set within the outer caldera rim of the Mt. Sabalan complex of NW Iran (Figure 1).

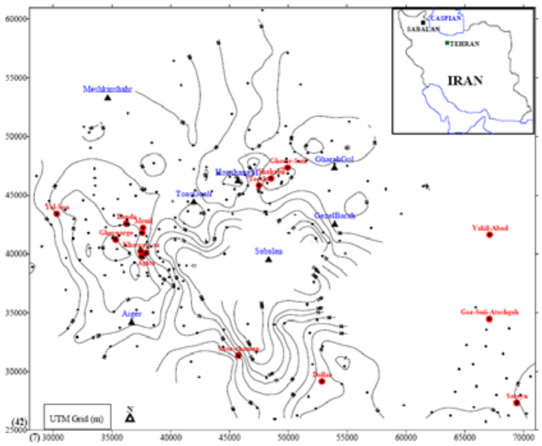

Figure 1: Map showing location of Sabalan geothermal field, hot springs, geographic feature and resistivity station (Bromley C., Khosrawi K., 2000)

Mt. Sabalan is a large stratovolcano and lies on the south Caspian plate, which underthrusts the Eurasian plate to the north. Exposed at the surface in the valley are altered Pliocene volcanism, an unaltered Pleistocene trachydacite dome (Ar-Ar dated at 0.9 Ma) and Quaternary terrace deposits. Caldera collapsing has caused a depression about 400m height and 12 km diameter. The lava flows consists of trachyandesite, andesite and dacite and pyroclastic deposits (Bogie et al, 2000; SKM, 2005).
The area is characterized by intensive geothermal manifestation at the surface which includes a hot springs, polls and geyser with temperature ranging of 28-83 ^{o}C.

SAMPLING

The geochemical study is based on discharge water samples collected from the discharge brine line of two production wells (NWS-1 and NWS-4) and samples collected from seven main hot springs. Discharge water samples were collected in May and June 2004 for well NWS-1 and in September 2004 for well NWS-4. Fifteen samples from hot springs were collected during 2009 year. The sampling locations can be seen in Figure 1. Samples were untreated and included acidified water. All chemical analyses (Cl, HCO_3, SO_4, Ca, B, CO_2 Li, Na, K, Ca, Mg and SiO2) were carried out in the laboratory of SUNA.

ARSENIC IN GEOTHERMAL WATERS

The chemical composition of studied thermal waters is given in Table 1.
The discharge geothermal waters from two productional wells (NWS-1 and NWS-4) are Na-Cl type and can be classified like Cl-rich geothermal waters with Cl concentration of 2460-2750 and Na concentration of 1413-1600 mg/l, whereas Mg is present only in trace (0.1-0.23 mg/l) (SKM, 2005; Strelbitskaya and Radmehr, 2010). Temperature of these waters is 223 and 226 ^{o}C respectively. Cl -rich geothermal waters are formed by the interaction of geothermal fluids with the host rock and dilution with low salinity water at depth (White and Muffler, 1971). The concentration of As in these waters is 3.5 and 3.6 mg/l respectively that is three times more than in the studied hot springs.

Hot springs

There are several hot springs with temperatures ranging from 28 to 82 $^{\circ}$C within Sabalan geothermal field. The chemical composition of these waters has been described in detail by Khosrawi, K.; (1996); Bogie, I (2002); Yousefi, H., (2004); Haeri, A (2010) and S.Porkhial (2010). According to water chemistry geothermal waters can be classified into two main types:

1. **Neutral Cl-SO_4 waters:** these waters can be a mixture of alkali chloride water and acid sulphate water, or can arise from the oxidation of H_2S to SO_4 in alkali-chloride water or dissolution of S from rock followed by oxidation (Ellis., Mahon 1978).
Gheynargeh, Malek-su, Ilando and Khosrow-su hot springs are typically neutral Cl-SO_4 waters with temperatures from 28 to 82 ^{o}C. These hot springs have higher concentration of Cl (263-1337 mg/l) in comparison with acid-SO_4 waters and sulfate (89-309 mg/l) and relatively high concentrations of Mg (11-15 mg/l). The As concentrations in these waters are in the range of 1 to 890 µg/l that are higher than in acid-SO_4 waters.

2. **Acid –SO_4 waters**. These waters arise from the oxidation of H_2S to SO_4 near the surface and most of its composition is dissolved from surface rock (Ellis., Mahon 1978). Acid –SO_4 waters include Moil (pool), Moil 2 and Agh-su hot springs with temperature ranging from 28 to 43 °C. These waters have pH 3-4. They are high in SO_4 (up to 530 mg/l) and have low concentration of Cl (from 1.19 to 6.9 mg/l). Concentration of As in these waters is 0.8-660 µg/l.

GENERAL TRENDS

The concentration of As in thermal fluids mainly will be depend on the thermal sources at depth and subsequent hydro-chemical evolution of water chemistry along its pathway up to the surface. According to Ellis and Mahon's (1964), As in geothermal fluids is derived mainly by host rock leaching and could be derived from the wall rock similar to chloride. Both elements remain in the fluid during sub-surface boiling and phase separation. The

As/C1 ratio can be used as a tool to trace the effects of geothermal fluid dilution, concentration or mixing within a geothermal field. Many thermal waters show linear trends of As vs C1 that suggesting mixing with cool meteoric ground waters on their way to the surface (Webster, J.G., Nordstrom, D.K., 2003). The concentration of As in the studied hot springs are plotted as a function of Cl concentrations and temperatures in Figure 2. Analyses of As in hot springs reflected a positive correlation between As and Cl that suggest that they have similar origin.

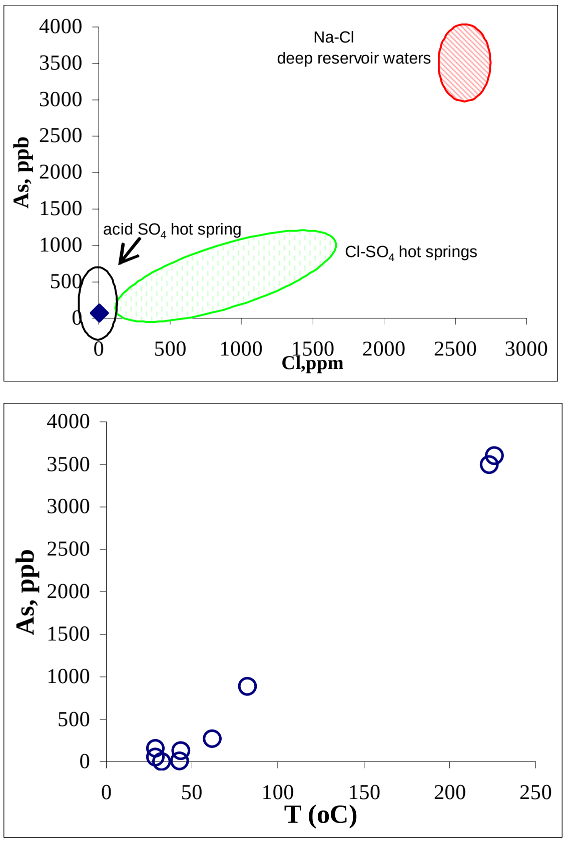

Figure 2: The relationship between As, Cl and T^{o}C in studied hot springs.

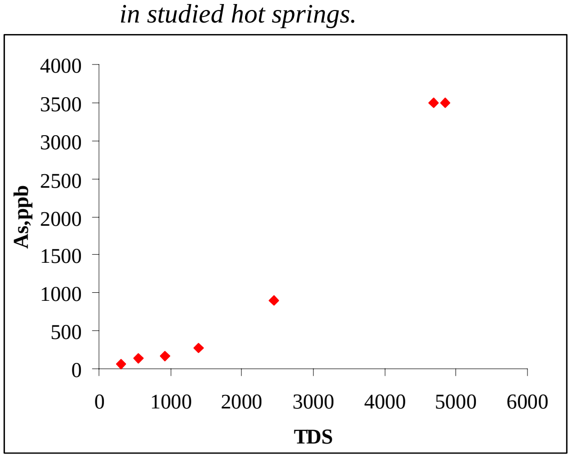

Figure 3: The relationship between As and total dissolved solid (TDS) in studied hot springs.

The close geothermal association between Cl and As concentration has been confirmed for most geothermal fields. For example, linear trends between As and Cl were identified in Yellowstone geothermal waters (Stauffer R. and Thompson J, 1984).
The As concentration tends to be increased with increasing temperature (Figure 2). Increasing temperature will lead to increasing of rock dissolution and leaching As from host rock in the fluid. The As concentration increases with temperatures increasing from 0.8 to 890 µg/l at t < 100 ^{o}C to 3600 µg/l at higher temperatures. Positive correlation As with salinity have also been detected (Figure 3).

DISCUSSION

Results show that significant As concentration with range of 0.8-3600 µg/l occur in thermal fluids through out the study area. Seven of the samples from hot springs exceed the WHO drinking water guideline for As (10 µg/l).

Geothermal wells. Significant concentration of As (3.5 mg/l) detected in studied production wells. Using this water for power generation requires substantial amounts of water to be extracted. During the separation of steam and bore water in geothermal power generation, As is retained in the waste bore water. Re-injection of thermal waters is necessary to prevent contamination of cold waters (Webster & Nordstrom 2003).

Hot springs. The As concentration in studied hot springs ranging from 0.8-890 µg/l. Maximum concentration of As (up to 890 µg/l) detected in Gheynargeh boiling hot spring, minimum in Ag su (0.8 µg/l). Significant concentration of As (130-270 µg/l) are noted in some hot springs such as Khosrow su, Ilando and Malek su. This high concentration of As can affects the area surrounding these springs. These hot springs have their outlet into the river. Mixing of these waters with cold water can increase the As content in the river water. Therefore additional investigation are needed to detect where the highest risk of mixing between thermal waters of high As concentration and cold surface waters occur and investigate how this mixing process affects humans in the area in the long term.

COMPARISON OF THE DATA WITH OTHER GEOTHERMAL FIELDS

The results show that concentration of As in discharged water from the wells of Sabalan geothermal field is around 3.5 mg/l, that substantially can be compared with values detected in geothermal wells from Waiotapu NZ geothermal field (2.1-3.9 mg/l), Wairakei, NZ (1-5 mg/l) and extremely higher than the values detected in the geothermal waters from Hawaii which As concentration is in the range of <0.01-0.07 mg/l (Table 2). Arsenic concentrations reported in geothermal wells from geothermal fields in OhaakV Broadlands, NZ (5.7-9 mg/l), Los Azufres, Mexico (5-24 mg/l), El Tatio, Chile (45-50 mg/l) are higher than detected in this study. Differences in As concentrations in geothermal fluids from different geothermal fields may be related to the fact that basaltic rock have relatively low As concentration -0.05-0.2 mg/kg compared to around 1 mg/kg for rhyolites (Arnorsson, 2003).

Table 2: Arsenic in hot springs and wells at various geothermal fields (Webster, J.G., Norstrom, D.K. 2003)

Field	**As mg/l**
Hot springs:	
Yellowstone Nat. Park, US	0.16 - 10
Wairakei, NZ	0.23 - 3.0
Waiotapu, NZ	0.71 - 6.5
OhaakVBroadlands, NZ	1
Valles Caldera, New Mexico	0.021 - 2.4
Lassen Volcanic National Park, California	up to 27
Los Azufres, Mexico	0.001 - 4.0
Mt Apo, Philippines	3.1 - 6.2
Tamagawa, Japan	2.3 - 2.6
Japan (national survey)	0.001 - 9.5
Salton Sea, USA	0.03 - 12
Kamchatka, Russia	2.0 - 3.6
Phlegraean Fields, Italy	0.012 - 5.6
Iceland	0.001 - 0.048
Well fluids	
Wairakei, NZ	1.0 - 5.2
Waiotapu, NZ	2.1 - 3.9
OhaakVBroadlands, NZ	5.7 -9.0
Hawaii	<0.01 - 0.07
Los Azufres, Mexico	5.1 - 24
El Tatio, Chile	45 - 50

The concentration of As in studied hot springs is ranging from 0.0008 to 0.89 mg/l that is higher than the values reported in hot springs from Iceland (0.001-0.048 mg/l) and lower than corresponded in hot springs in geothermal fields from Kamchatka, Japan, Philippines, California and NZ.

CONCLUSION AND RECOMENDATION

Distribution of Arsenic in thermal waters of Sabalan geothermal field has been studied. Results show that high As (up to 3.5 mg/l) concentration occurs throughout the studied are.
Deep production wells have significant As concentration (3.5 mg/l). Therefore re-injection of thermal waters is necessary to prevent contamination of cold waters.

Concentration of As in studied hot springs ranging from 0.8 to 890 µg/l. Neutral Cl-SO_4 hot spring is rich in As (up to 890 µg/l) than in acid sulfate features with As concentration up to 66 µg/l. As concentration tends to be increased with increasing temperature. Positive correlation As with Cl concentration and TDS has been noted. Due to high As concentration (up to 890 µg/l) in hot springs which exceed the WHO level for drinking water (10 µg/l), irrigation (10 µg/l) and protected aquatic live (19 µg/l), there is a risk of contamination of cold water by arsenic. Mixing of thermal waters with cold water can increase the As concentration in the cold water due to flooding during rain season, therefore monitoring of river water is recommended.

Totally As concentration in studied thermal waters is almost in range or rather lower than levels reported in geothermal waters from other parts of the world except the geothermal fields in Iceland and Hawaii where the As concentration extremely low (< 0.001mg/l). These fields include basaltic rock which usually is low in As in the fluids than fields associated with andesitic volcanism.

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Table 1. Chemical composition of studied thermal waters, ppm

springs	TDS	pH	T	Cl	B	Fe	As	SO_4	HCO_3	Na	K	Ca	Mg
Pool(Moil)	458	4.8	43	1.19	0.3	0.72	0.01	560	22.5	63.53	28.8	92.38	23.8
Moil2	313	3.05	28.7	6.62	0.1	0.56	0.66	298	0	25.63	10.4	43.45	10.6
Ag-su	209	3.2	32.3	6.25	0.55	0.09	0.0008	162	0	20	13.5	30.8	4.5
Malek-su	559	5.9	43.5	263	0.92	0.1	0.13	89.5	172	204	42.8	33	15.8
Ilando	918	5.9	28.7	390	0.77	0.025	0.16	283	176	328	36.7	75.8	19.6
Khosraw-su	1398	6.62	62	836	2.87	0.019	0.27	249	127	508	49.5	58.8	11
Gheynarjeh	2456	6.5	82.5	1337	83.56	0.017	0.89	309	261	875	117	92.25	11.2
Well NWS-1	4854	8	226	2605	22	0	3.5	119	98	1524	279	16	0.17
Well NWS-4	4680	8.5	223	2500	21	0	3.6	109	73	1413	269	27	0.2