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ORIGINAL PAPER

Analytical survey of arsenic in geothermal waters from sites in Kyushu, Japan, and a method for removing arsenic using magnetite

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Abstract The objective of this study was to survey the cation and anion contents of geothermal waters to gather fundamental information on geographical variations. Sixteen sites in hot spring areas on the island of Kyushu in Japan were studied. The study focused on the arsenic content of the samples. Very high arsenic concentrations (more than 0.1 mg/l) were detected in most of the geothermal waters sampled. High contents of boron and fluoride (more than 1.0 mg/l) were also detected in some samples. Arsenic removal was performed on a laboratory scale using columns packed with a magnetite-type adsorbent. The reduction of arsenic contamination to a concentration of less than 0.01 mg/l could be achieved in the early stages of adsorption (bed volume = 200).

Keywords Analytical survey · Arsenic removal · Geothermal water · Kyushu · Magnetite

Introduction

In Japan, there are many famous hot spring areas ("Onsen") located on a number of islands. These hot spring areas and spas are very popular as tourist destinations. In addition, there are currently (in 2009) 18 operational geothermal power plants, providing 0.2% of Japan's electricity supply. Because geothermal energy is a renewable resource with very low CO_2 emissions, electricity providers are planning to construct several geothermal power plants in the next 10 years, increasing the contribution from geothermal sources to around 1% of Japan's electricity supply.

For two millennia, water and steam from hot springs have been used for cooking by many people in Japan. There is also a tradition of bathing in spas and of drinking hot spring waters for medical purposes. In some geothermal waters, however, arsenic contamination is more than 10 μg/l higher than the limit set by the WHO Guidelines for Drinking-Water Quality (2008).

Arsenic is introduced into water by the dissolution of minerals and by concentration in groundwater (Choong et al. 2007). Geothermal water often contains relatively high contents of arsenic as a result of the leaching of arsenic from rocks, which occurs predominantly in the geothermal reservoir at high temperatures. Inorganic arsenic can occur in the environment in several forms. However, in natural waters, and, thus, in drinking-water, it is mostly found as trivalent arsenite or pentavalent arsenate. Drinking-water poses the greatest public health threat from arsenic (Henke 2009).

In the last decade, much research has been done on arsenic removal from contaminated groundwater,

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surface water, and soil using adsorption and ion-exchange technologies (Pande et al. 1997; Choong et al. 2007; Mohan and Pittman 2007; Henke 2009). Iron-based adsorbents such as zerovalent iron (Krishna et al. 2001; Zhang et al. 2004; Daus et al. 2004; Leupin et al. 2005; Bang et al. 2005; Tyrovola et al. 2006; Cornejo et al. 2008), iron (oxy)(hydr)oxides (Wilkie and Hering 1996; Thirunavukkarasu et al. 2003a; Sylvester et al. 2007; Zaspalis et al. 2007; Guan et al. 2008; Tuutijärvi et al. 2009), and their composites (Joshi and Chaudhuri 1996; Campos 2002; Katsoyiannis and Zouboulis 2002; Thirunavukkarasu et al. 2003b; Vaishya and Gupta 2004; Gu and Deng 2007; Mondal et al. 2008; Fierro et al. 2009) have frequently been used. Manganese (oxy)(hydr)oxides (Bajpai and Chaudhuri 1999), aluminum (oxy)(hydr)oxides (Gregor 2001; Xu et al. 2002; Hlavay and Polyák 2005), and titanium dioxides (Fostier et al. 2008) can also be used as arsenic adsorbents.

In this study, we survey the arsenic contents of geothermal water samples from 16 hot spring sites in Kyushu, Japan. We attempt to remove the arsenic on a laboratory scale by a column method packed with a magnetite-type adsorbent.

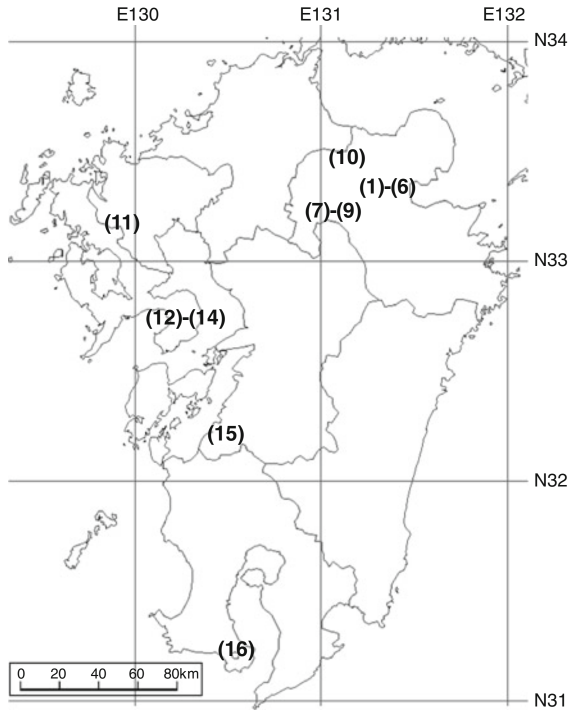

Fig. 1 Map of geothermal waters sampling sites in Kyushu, Japan

Materials and methods

Analytical survey of geothermal waters in Kyushu, Japan

Kyushu (area: 36,732 km^2; latitude: 33.45° to 30.58° N; longitude: 129.33° to 132.05° E; maximum altitude: 1,791 m above sea level) is an island located in southwestern Japan.

We took samples directly from the following hot spring areas in Kyushu: six sites at Beppu (1–6), three sites at Kuju (7–9), and one site at Takeda (10) in Oita; one site at Ureshino (11) in Saga; two sites at Unzen (12–13), and one site at Obama (14) in Nagasaki; one site at Hinaku (15) in Kumamoto; and one site at Ibusuki (16) in Kagoshima. A map of the sampling sites is shown in Fig. 1.

During January to March in 2008, we collected 1 l of geothermal water directly from the fountainhead at each sampling site using a ladle. Samples were transported to the laboratory within 8 h of sampling and kept at 25°C. Before filtration, the pH values were measured using a pH meter (Horiba model D-25). Samples of volume 10 cm^3 were filtered using a cellulose acetate membrane filter (Millipore GSWP, 0.22 μm) to measure the cation and anion concentrations. We measured the concentrations of Li^+, B^{3+}, Na^+, Mg^{2+}, Si^{4+}, K^+, and Ca^{2+}, and of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, and SO_4^{2-}. Metal concentrations were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Shimadzu model ICPS-7000) and anion concentrations were measured by an ion chromatograph (Compact IC 761, Metrohm). The total arsenic concentrations (As^{3+} and As^{5+}) were measured by atomic absorption spectroscopy (AAS; Shimadzu model AA-6800 or SPCA-6210) with a hydride vapor generator (HVG-1; Anezaki et al. 1999).

Removal of arsenic from geothermal waters

Preparation and characterization of magnetite

$FeCl_2·4H_2O$ (1.8 g) and $FeCl_3·6H_2O$ (5.0 g) were each dissolved in 20 cm^3 of deionized water. The molar ratio of ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}) was 1/2. The aqueous solutions were mixed and aqueous sodium hydroxide solution was added to the mixture until the pH was 12. Magnetite was washed with deionized water and dried at 323 K in an electric oven. The magnetite was ground for the adsorption experiments. The characteristics of the magnetite crystal structure were observed using a powder X-ray diffraction meter (40 kV and 20 mA, CuKα, Rigaku model XRD-DSC-X II). The BET surface area was determined from the adsorption isotherms of N_2 at 77 K using an automatic specific surface area/pore size distribution measurement apparatus (Bel Japan model BELSorp-mini II).

Adsorption experiment using a batchwise method

The magnetite (20 mg) and aqueous arsenic solution (10 cm^3) were mixed and shaken at 25°C for 12 h. The arsenic concentration was analyzed by AAS. The amount of arsenic on the adsorbent, q (mmol/g), was determined by:

$$q = \frac{(C_0 - C) \cdot L}{w} \quad (1)$$

where C_0 and C are the initial and equilibrium concentrations in the aqueous phase (mmol/l), respectively, L is the volume of aqueous solution (l), and w is the weight of adsorbent (g).

Adsorption experiment using a column method

The chromatographic operation was also conducted using a column system. Granulated magnetite (wet volume 1.5 cm^3) and glass wool were packed into the column in the form of a sandwich. The geothermal water sample from Hachoubaru (pH = 8.0) was introduced into the column (flow rate: 0.2 cm^3/min) using a dual-plunger pump (Flom model KP-11). The effluent was collected with a fraction collector (Advantec model CHF122SA), and the arsenic concentration in the effluent was measured by AAS.

The bed volume (B.V.) was calculated by:

$$\text{B.V.} = vt/V \quad (2)$$

where v is the flow rate of the feed solution (cm^3/min), t is the supply time of the feed solution (min), and V is the wet volume of the adsorbent (cm^3).

Results and discussion

Analytical survey of geothermal waters in Kyushu, Japan

Tables 1 and 2 show the cation and anion concentrations, the pH values, and the electrical conductivities of the geothermal waters, and the temperatures of the sampling site fountainheads. The arsenic concentrations in most of the samples were over ten times the value specified by the WHO Guidelines for Drinking-Water Quality, despite the wide range of pH values. The sample from Hachoubaru (site no. 7), had a particularly high arsenic concentration, 3.23 mg/l, because the steam used for geothermal power generation, which is pumped up from a depth of below 1,500 m, has a high temperature (160°C) and pressure (0.59 MPa).

High levels of boron (WHO Guidelines value = 0.5 mg/l) and fluoride (WHO Guidelines value = 1.5 mg/l) were also detected in some geothermal waters: site nos. 7, 11, 14, and 16 for boron, and site nos. 7 and 11 for fluoride. Arsenic, boron, and fluoride all have to be removed from geothermal waters before the waters can be used for cooking or drinking.

Removal of arsenic from geothermal waters

Because the X-ray diffraction (XRD) pattern of the magnetite was identical to that in the XRD database (Ohe et al. 2005), the magnetite could be prepared by the co-precipitation method described. The specific surface area of the magnetite was 94.3 m^2/g.

Figure 2 shows the effect of pH on the adsorption of arsenic on magnetite. The maximum adsorption of arsenic was obtained at pH 7. This indicated that magnetite can be used for arsenic removal from geothermal waters, because the pH values of most geothermal waters are within the range pH 3–9.

Figure 3 shows the adsorption isotherm of arsenic with magnetite. From linear regression based on the Langmuir adsorption equation (C_{As}/q_{As} vs. C_{As}), arsenic adsorption was seen to progress via the adsorption of a single adsorbate onto a corresponding site on the surface of the adsorbent. The maximum amount of arsenic adsorbed was found to be 0.95 mmol/g.

Table 1 Cation concentrations, pH values, and electrical conductivity (E.C.) of geothermal waters

Site no.	Site name	Prefecture	pH	E.C. (S/m)	Element concentration (mg/l)							
					As	Li	B	Na	Mg	Si	K	Ca
1	Umi-jigoku	Oita	3.8	0.404	0.21	6.0	<0.01	1,242	12.7	214	288	39.9
2	Yama-jigoku	Oita	7.9	0.647	0.97	13.1	<0.01	954	4.8	145	220	24.0
3	Kamado-jigoku	Oita	7.2	0.646	1.36	12.6	<0.01	1,480	2.4	203	280	42.0
4	Chinoike-jigoku	Oita	2.6	0.424	<0.01	4.4	<0.01	595	27.2	98.0	128	54.6
5	Shiraike-jigoku	Oita	7.1	0.151	<0.01	0.7	<0.01	198	3.1	39.0	30.9	47.2
6	Oniyama-jigoku	Oita	7.9	0.641	0.88	13.4	<0.01	1,324	4.8	232	326	37.8
7	Hachoubaru	Oita	8.0	0.754	3.23	9.8	33.9	1,501	0.3	328	229	16.8
8	Komatsu-jigoku	Oita	5.9	0.016	0.24	<0.01	0.1	1.3	1.6	19.1	1.0	4.8
9	Sujiyu	Oita	7.1	0.019	0.20	<0.01	0.4	3.0	0.9	17.0	2.0	3.3
10	Ganiyu	Oita	6.3	0.138	0.33	0.6	1.5	34.0	316	75.7	83.3	3.4
11	Ureshino	Saga	8.5	0.221	0.32	1.2	10.7	39.7	0.8	58.5	15.0	5.1
12	Unzen	Nagasaki	2.6	0.372	0.14	<0.1	0.8	1.9	13.3	96.1	6.7	59.3
13	Unzen-kojigoku	Nagasaki	3.9	0.159	0.21	<0.1	0.1	1.1	3.2	33.0	2.4	8.5
14	Obama	Nagasaki	7.9	1.394	0.55	4.7	14.9	207	148	107	156	141
15	Hinagu	Kumamoto	8.0	0.268	0.11	0.8	1.5	31.1	3.5	15.4	5.2	68.7
16	Ibusuki	Kagoshima	6.8	0.980	0.39	1.9	6.1	131	27.0	91.9	138	258

Table 2 Anion concentrations and fountainhead temperatures of geothermal waters

Site no.	Site name	Fountainhead temperature (°C)	Element concentration (mg/l)					
			F	Cl	Br	NO_2	NO_3	SO_4
1	Umi-jigoku	98	0.53	1,193	4.0	<0.2	1.6	468
2	Yama-jigoku	80	1.20	1,927	8.2	<0.2	1.9	342
3	Kamado-jigoku	90	1.32	2,220	8.6	<0.2	1.7	276
4	Chinoike-jigoku	78	0.61	938	3.6	<0.2	1.7	576
5	Shiraike-jigoku	95	0.11	100	1.1	<0.2	3.0	187
6	Oniyama-jigoku	98	1.64	1,861	7.5	<0.2	3.8	329
7	Hachoubaru	160°C at 0.59 MPa	3.76	1,914	9.3	<0.2	<0.2	204
8	Komatsu-jigoku	98	<0.04	101	<0.1	<0.2	2.9	13.8
9	Sujiyu	60	<0.04	10.6	<0.1	<0.2	<0.2	40.1
10	Ganiyu	38	<0.04	197	<0.1	17.5	<0.2	333
11	Ureshino	53	9.23	215	<0.1	<0.2	<0.2	12.5
12	Unzen	94	<0.04	13.3	<0.1	<0.2	<0.2	1,081
13	Unzen-kojigoku	90	<0.04	8.2	<0.1	<0.2	<0.2	279
14	Obama	98	1.27	5,382	4.9	<0.2	<0.2	324
15	Hinagu	44	1.09	726	2.2	<0.2	<0.2	7.6
16	Ibusuki	72	<0.04	3,549	6.4	<0.2	<0.2	107

Figure 4 shows the breakthrough profile of arsenic from the geothermal water samples. The arsenic was slowly adsorbed, with breakthrough at B.V. = 200. It was clear that, to keep the arsenic concentration below 0.01 mg/l, arsenic removal using a column operation should stop before B.V. = 200.

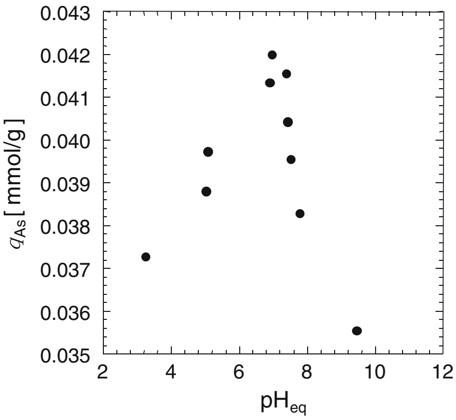

Fig. 2 Effect of pH on arsenic adsorption with magnetite

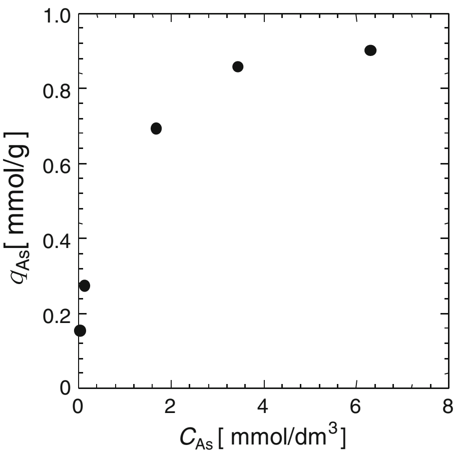

Fig. 3 Adsorption isotherm of arsenic with magnetite

Conclusion

We surveyed 16 sites in hot spring areas in Kyushu, Japan, to measure the cation and anion concentrations in the geothermal waters. Most of the geothermal water samples contained very high levels of arsenic, more than ten times the value given in the WHO Guidelines for Drinking-Water Quality. High levels of boron and fluoride were also detected in some geothermal waters. These results show that arsenic, boron, and fluoride have to be removed from geothermal waters prior to using the waters for cooking or drinking.

The magnetite could be successfully prepared by the alkali precipitation method. The adsorption of arsenic on magnetite increased with pH. The highest adsorption was obtained in the neutral pH region. The column operation was conducted on a laboratory scale using granulated magnetite. The reduction of arsenic concentrations to less than 0.01 mg/l was obtained up to bed volume (B.V.) = 200.

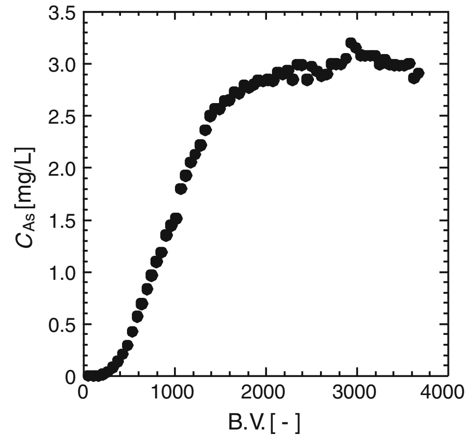

Fig. 4 Breakthrough profiles of arsenic from geothermal waters

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