

In situ redox potential measurements as a monitoring technique for hot spring water quality

Seiichiro Ioka¹ · Hirofumi Muraoka¹ · Kazuo Matsuyama^{2,3} · Kazuo Tomita^{2,4}

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Abstract Previous studies on the redox potential of hot springs have indicated that redox potential sensors display a more heightened sensitivity to the $\text{HS}^-/\text{SO}_4^{2-}$ redox couple, and that redox potential is not related to many different redox couples. However, previous studies have not focused on long-term, continuous measurement of hot spring aquifers. Therefore, three continuous in situ redox potential (Eh) measurements, each lasting approximately 1 month, were conducted using a platinum electrode in a 32 °C hot spring aquifer. Measured Eh values were −353, −343, and −329 mV in the three monitoring campaigns. The chemical properties of water sampled from the aquifer indicate that S^{2-} concentrations ranged from 0.04 to 0.19 mg/L and Fe concentrations were below the quantification limit (<0.003 mg/L). Comparison of measured Eh values and those calculated using $\text{HS}^-/\text{SO}_4^{2-}$ and $\text{S}^{2-}/\text{SO}_4^{2-}$ redox couples show an agreement within 0.02–0.05 V. This indicates the effectiveness of long-term, continuous, in situ redox potential measurements as a monitoring technique for hot spring aquifers.

Keywords Water monitoring · In-situ · Redox potential · Hot spring aquifer

Introduction

Japanese hot spring resorts, known as onsen, are famous throughout the world. The definition of onsen in Japan requires that the water is above 25 °C or that the concentration of several chemical components is above a predetermined level (Ministry of the Environment 2016). For example, if total sulfur (HS^- , $\text{S}_2\text{O}_3^{2-}$ and H_2S) concentration in groundwater at 20 °C is above 1 mg/kg, the groundwater is called a hot spring. Hot springs in Japan are classified into three types by their discharge pattern: natural hot springs; artesian hot wells; and non-artesian hot wells, where the hot water in a non-artesian hot well is pumped up. There are approximately 25,000 hot springs in Japan and approximately 130 million people visit onsen hotels each year (Yanagisawa et al. 2015). Onsen, therefore, play an important role in the economy in Japan. In addition, binary cycle plants that use hot springs for small-scale geothermal electrical power generation have recently been developed in Japan and other countries (Leland et al. 2015; Bertani 2016). Thus, the owners of Japanese onsen resorts must be aware of any change in the chemical properties and discharge quantities of hot springs. In particular, to ensure sustainable use of hot spring resources, owners frequently conduct monitoring campaigns of onsen water quality.

The monitoring of hot spring chemical properties in Japan usually includes temperature, electrical conductivity, and pH (Ministry of the Environment 2015). In addition, estimation of the redox potential (Eh) in hot spring aquifers and deep groundwater in Japan showed that the redox reaction of iron sulphide/sulphate ions is dominant,

✉ Seiichiro Ioka
ioka@hirosaki-u.ac.jp

¹ North Japan Research Institute for Sustainable Energy, Hirosaki University, 2-1-3 Matsubara, Aomori 030-0813, Japan

² Tokyo Electric Power Services Co., Ltd., 9F, KDX Toyosu Grandsquare, 7-12, Shinonome 1-chome, Koto-ku, Tokyo 135-0062, Japan

³ Present Address: Geothermal Research Institute Co., Ltd., Parkside Square, 2-1-5 Shinjyuku, Shinjyuku-ku, Tokyo 160-0022, Japan

⁴ Present Address: Nittetsu Mining Consultants Co., Ltd., 2-3, Shiba 4-Chome, Minato-ku, Tokyo 108-0014, Japan

although concentrations of SO_4^{2-} , S^{2-} , and H_2S in the groundwater are generally below the detection limit and have only been measured successfully once (Hokari et al. 2014). Thus, this estimation needs to be examined more thoroughly.

Previous studies on redox potential in hot springs have been conducted in Taiwan (Chen and Sung 2009) and Iceland (Stefánsson et al. 2005). The results from Taiwan confirmed that redox potential sensors displayed a more heightened sensitivity to the $\text{HS}^-/\text{SO}_4^{2-}$ redox couple in hot springs. On the other hand, the measurements from Iceland indicated that redox potential in natural waters was not related to many redox couples. However, these studies did not focus on long-term, continuous, in situ measurement. Thus, the purpose of this study is to conduct this type of redox potential measurement using a platinum electrode in a hot spring aquifer to examine the relationship between redox potential values and redox couples.

Site description

The study site, Minami-Izu Town, is located on the southern peninsula of Izu, Shizuoka Prefecture, in Japan (Fig. 1). Minami-Izu Town has an annual mean temperature of 16.6 °C and receives annual precipitation of 1778 mm. Izu peninsula is located south of Mt. Fuji and approximately 100 km southwest of Tokyo, on the Philippine Sea Plate. In the study area, there are many high temperature (approximately 100 °C) hot springs originating from approximately 150 m depth, and correspondingly many onsen resorts (Yanagisawa et al. 2013). The chemical characteristics of hot springs at approximately 100 °C include Cl^- concentrations of approximately 10000 mg/L and Na^+ concentrations of approximately 4000 mg/L (Noda and Abe 1985). The origin of the hot springs water is a mixture of local surface water and deep geothermal brine

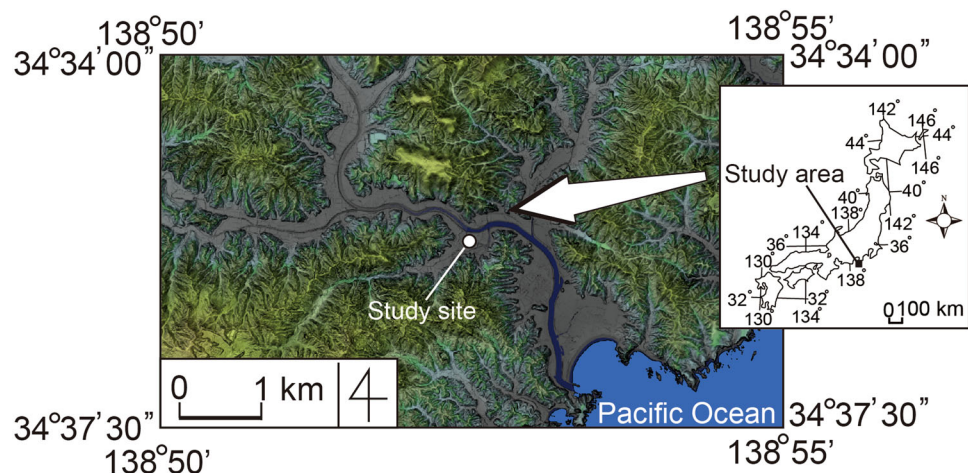
interpreted as a seawater intrusion (Mizutani and Hama-suna 1972). The geology of the site consists of alternating layers of agglomerate and tuff from 10 to 50 m depth and the same layers interbedded with andesite from 50 to 150 m depth (Okubo et al. 1983).

Methodology

This study analyzed a discontinued hot spring well that is now used as a monitoring well (Fig. 1). The monitoring well is 30 m deep and made of steel pipe with an inner diameter of approximately 0.07 m. The screens of the monitoring well are placed 25–30 m below ground level (mbgl) at the site. The water level of the monitoring well varied from approximately 2.60 to 3.01 mbgl during the monitoring campaign, which involved three slightly different durations: (1) 26 days; (2) 30 days; and (3) 28 days.

Physicochemical groundwater parameters [temperature, pH, dissolved oxygen (DO), and oxidation–reduction potential (ORP)] were measured in situ using a multi-probe (model W-22XD, Horiba Ltd. Kyoto, Japan) at the screen depth (approximately 28 mbgl). The accuracy of the multi-probe was ± 1.0 °C for temperature, ± 0.1 for pH, and ± 0.2 mg/L for DO. The pH electrode was calibrated with buffer solutions prepared from powder reagents of pH standard solutions (Code No. 150-4 and 150-7, Horiba Ltd. Kyoto, Japan). The DO electrode was calibrated using a standard solution of sodium sulfite (Code No. 192-03415, Wako Pure Chemical Industries, Ltd., Osaka, Japan). The ORP electrode was verified against an ORP standard solution made from the powder of an ORP electrode solution (Code No. 160-51, Horiba Ltd. Kyoto, Japan). The pH, DO, and ORP electrodes were again verified at the end of the monitoring campaign using the same standard solutions. The DO electrode showed no changes over the duration of the study period; however, the pH electrode at

Fig. 1 Study area and location of the monitoring site, drawn using KASHMIR 3D



the end of the second monitoring campaign showed pH values 0.3 higher than the pH standard solutions. Thus, when pH values from the second monitoring campaign were used to evaluate calculated Eh, the pH value was corrected to the in situ measured pH value, -0.3 . In addition, the ORP electrode readings at both the start and end of the monitoring campaigns were within ± 20 mV of the known oxidation–reduction potential value of the ORP standard solution. The accuracy of the multi-probe for ORP was, therefore, ± 20 mV.

Measured ORP values were converted into measured Eh values using the following equation:

$$\text{measured Eh} = \text{measured ORP} + 206 - 0.7(t - 25) \text{ mV} \quad (1)$$

where Eh denotes the ORP value measured using a hydrogen electrode normalized to the reference electrode; measured ORP is derived using Ag/AgCl (in 3.33 mol/L KCl) as the reference electrode (model W-22XD, Horiba Ltd. Kyoto, Japan); and t is the measured water temperature.

The hot spring water was sampled after removing the multi-probe at the end of each monitoring campaign. Standing water within the piezometer was removed for water sampling. Hot spring water samples were then collected by slowly lowering a dedicated and pre-cleaned PVC bailer (model DIK-687A, Daiki Rika Kogyo Co. Ltd., Saitama, Japan). First, water samples for field measurements of sulfide ions (S^{2-}) were collected in a 25 mL glass vial. Second, water for alkalinity measurement was collected in 100 mL polyethylene bottles and unfiltered splits were sent to the laboratory for testing. Third, filtered (model DISMIC-25_{HP}, 0.2 μm pore size polytetrafluoroethylene (PTFE) filter; Advantech Toyo Kaisha, Ltd., Tokyo, Japan) splits were taken for laboratory measurement of cations and anions. Subsamples of the filtered water were acidified to $\text{pH} < 2$ using ultrapure nitric acid, and were then used for the analysis of Fe, Mn, Sr, Ba, and Si in 100 mL polyethylene bottles. Non-acidified splits were retained in 100 mL polyethylene bottles for cation (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) and anion (F^- , Cl^- , Br^- , NO_3^- , and SO_4^{2-}) analysis.

Field measurements of S^{2-} were made using a portable colorimeter (model DR890, Hach Company, Loveland, Co, USA) and the methylene blue method (Method 8131, Hach Company), which indicates total sulfides (sum of H_2S , HS^- , and S^{2-} species). Concentrations of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , Br^- , NO_3^- , and SO_4^{2-} were analyzed by ion chromatography with conductivity detection on a DX-320 instrument (DIONEX Co., now Thermo Fisher Scientific Inc., MA, USA). Concentrations of Fe, Mn, Sr, Ba, and Si were measured by inductively coupled plasma atomic emission

spectrometry (Optima 7000DV, PerkinElmer Inc., MA, USA). Alkalinity was determined in the laboratory using an 876 Dosimat Plus instrument (Metrohm AG, Herisau, Switzerland) with N/50 H_2SO_4 , and is presented in terms of HCO_3^- concentration (in mg/L of water).

Analytical precision (i.e., coefficients of variation for triplicate measurements) was within 3 % for Na^+ , NH_4^+ , K^+ , Ca^{2+} , F^- , Cl^- , Br^- , SO_4^{2-} , Fe, Mn, Sr, and Ba; 4 % for Mg^{2+} ; and 7 % for Si. The error in charge balances between cations and anions was less than ± 2 % for all samples. The charge balance for groundwater samples was calculated using the aqueous speciation code from the PHREEQC database (Parkhurst and Appelo 2013) and its default thermodynamics database (phreeqc.dat). The activities of groundwater samples were also calculated using the PHREEQC thermodynamics database (phreeqc.dat).

Results

Physicochemical parameters

The in situ temperature of the hot spring water was approximately 32°C during the three monitoring campaigns. The in situ pH values during each campaign were 8.31, 8.53, and 8.37, respectively, indicating weakly alkaline water. The in situ DO concentrations were 0.01, 0.00, and 0.00 mg/L, respectively, indicating anoxic conditions (Bradley et al. 2008) in the hot spring aquifer. The in situ measured Eh was -353 , -348 , and -329 mV, respectively (Fig. 2), which indicates very reducing conditions (Christensen et al. 2000; Clark 2015). The measured Eh values decreased to -300 mV in approximately 7 days and showed relatively little drift after that.

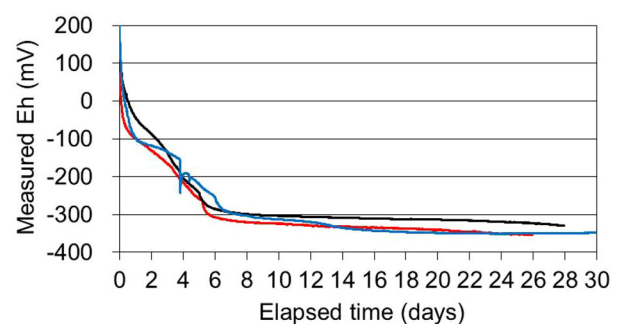


Fig. 2 In situ measured Eh in the hot spring aquifer over three periods of approximately 1 month. Red denotes the first campaign, blue denotes the second campaign, and black denotes the third campaign

Table 1 Chemical composition of hot spring water samples

Sampling campaign	First campaign	Second campaign	Third campaign
F ⁻	2.97	2.98	2.93
Cl ⁻	352	376	385
Br ⁻	1.13	1.20	1.21
NO ₃ ⁻	<0.01	<0.01	<0.01
SO ₄ ²⁻	27.1	28.4	28.4
S ²⁻	0.12	0.19	0.04
HCO ₃ ⁻	139	136	135
Na ⁺	261	266	275
NH ₄ ⁺	<0.02	<0.02	<0.02
K ⁺	10	11	11
Mg ²⁺	0.592	0.596	0.446
Ca ²⁺	22.3	24.8	26.9
Fe	<0.003	<0.003	<0.003
Mn	0.009	0.010	0.008
Sr	0.145	0.139	0.152
Ba	0.014	0.013	0.014
Si	18.8	17.9	19.9

Hot springs water quality

The chemical composition of hot springs water samples are shown in Table 1. The hot springs water is of the type Na-Cl, in which Na⁺ is the dominant cation and Cl⁻ is the dominant anion. The Na⁺ and Cl⁻ concentrations were always above 260 and 350 mg/L, respectively. The SO₄²⁻, S²⁻, and Mn concentrations were detected as redox-related species although Fe, NO₃⁻, and NH₄⁺ concentrations were below the quantification limit. The dominant redox related species was sulfur as Mn concentrations were below 0.01 during the monitoring campaigns.

Discussion

The measured Eh values were plotted against those calculated using two redox couples for interpretation of the monitoring results. The HS⁻/SO₄²⁻ and S²⁻/SO₄²⁻ were selected as redox couples because the dominant redox related species in the hot springs water was sulfur. The plot of measured Eh vs. calculated Eh is shown in Fig. 3. The symbols used and their meanings are shown in Table 2. Log *K* values were calculated at the in situ temperature of 32 °C using the Rxn program of Geochemist's Workbench, version 9.09 (Bethke and Yeakel 2011) and with the PHREEQC thermodynamic database. The plot utilized ion activities evaluated using the PHREEQC and the analytical results shown in Table 1. The bold in line Fig. 3 represents the locus of the points expected if all the calculated redox couples were in internal equilibrium and if each of the

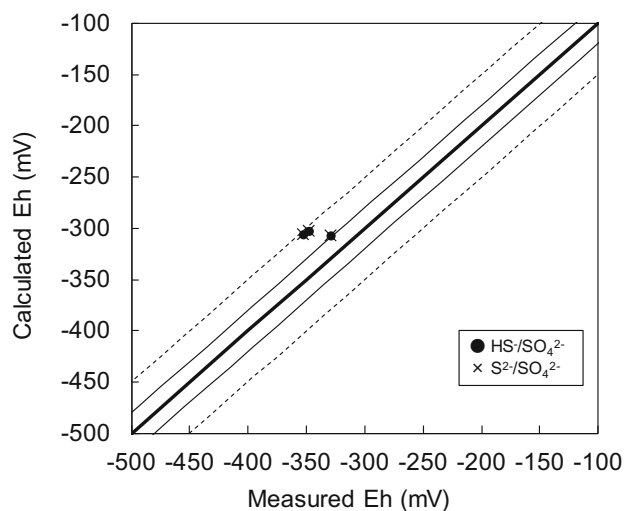


Fig. 3 Plot of in situ measured Eh vs. Eh calculated using the redox couples listed in Table 2. The symbols used in the plot and their meanings are listed in Table 2. The *two solid lines* represent the precision range (± 20 mV) for the ORP electrode used in this study. The *two dashed lines* represent a range of ± 50 mV

calculated Eh values matched the measured Eh. The two solid lines in Fig. 3 represent the ORP precision (± 20 mV) of the multi-probe used in this study. The disagreement between the data points and the line revealed that internal equilibrium was not attained. However, Stefánsson and Arnórsson (2002) reported that Eh calculated from different redox couples are within 0.02–0.04 V of measured Eh for saline geothermal fluids (Cl > 500 ppm), suggesting that such fluids are closer to an overall redox equilibrium than dilute geothermal fluids (Cl < 175 ppm). The hot

Table 2 Redox couples and log *K* values for Eh calculation and symbols used in Fig. 3

Symbols	Redox couples	Log <i>K</i> at 32 °C
●	HS ⁻ /SO ₄ ²⁻	SO ₄ ²⁻ + 9H ⁺ + 8e ⁻ = HS ⁻ + 4H ₂ O Log <i>K</i> = 32.6386
×	S ²⁻ /SO ₄ ²⁻	SO ₄ ²⁻ + 8H ⁺ + 8e ⁻ = S ²⁻ + 4H ₂ O Log <i>K</i> = 19.9240

springs water in this study has Cl > 350 mg/L but not Cl > 500 ppm. Thus, the two dashed lines in Fig. 3 represent the ORP values ±0.05 V (50 mV), taking into consideration the results of Stefánsson and Arnórsson (2002).

The Eh values calculated using the sulfur redox couples did not correlate well with the measured Eh values from the first and second monitoring campaigns, suggesting that internal equilibrium of HS⁻/SO₄²⁻ and S²⁻/SO₄²⁻ redox couples was not attained. However, the two values agreed within ±50 mV. This difference is smaller than results from previous studies comparing calculated and measured Eh values (Lindberg and Runnells 1984; Stefánsson et al. 2005).

In the third monitoring campaign, the measured Eh value agreed to within approximately ±20 mV with the HS⁻/SO₄²⁻ and S²⁻/SO₄²⁻ redox couples. This result suggests that these redox couples are related to the Eh value of the hot springs water. The chemical composition of the hot springs water showed that the dominant redox related species was sulfur and that Fe, NO₃⁻, and NH₄⁺ concentrations were below the quantifiable limit during the monitoring campaigns. In addition, previous studies of long-term, continuous, in situ redox potential measurements of groundwater that is not hot springs water reported that sulfur redox couples are related to measured Eh values (Auqué et al. 2008; Ioka et al. 2011). These results support the existence of the relationship between measured and calculated Eh values.

Furthermore, the good agreement between the measured Eh value and that calculated using sulfur redox couples is of significant interest because the sulfur redox reactions are slow (Kaasalanien and Stefánsson 2011). Thus, additional in-depth experiments are required to clarify the reasons behind this relationship between measured and calculated Eh values, which may involve local equilibrium of sulfur redox couples.

Conclusions

In this study, we measured in situ Eh values for a duration of approximately one-month using a platinum electrode, and performed chemical analysis of each water sample three times to monitor hot springs water quality. Our results showed that measured in situ Eh values were consistent within 0.02–0.05 V with those calculated for HS⁻/SO₄²⁻

and S²⁻/SO₄²⁻ redox couples using both thermodynamic data and chemical analysis data. This indicates the effectiveness of long-term, continuous, in situ Eh measurements as a monitoring technique for hot spring aquifers.

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