# ALCOHOL TRACER TESTING AT THE MATSUKAWA VAPOR-DOMINATED GEOTHERMAL FIELD, NORTHEAST JAPAN

Daisuke Fukuda<sup>1</sup>, Mikihiro Asanuma<sup>1</sup>, Yasuyuki Hishi<sup>1</sup>, and Koichi Kotanaka<sup>2</sup>

<sup>1</sup>JMC Geothermal Engineering Co., Ltd. (Geo-E) 101-1 Hosoyachi, Ukai Takizawa, Iwate, 020-0172, Japan e-mail: fukuda@geothermal.co.jp

<sup>2</sup>Tohoku Hydropower & Geothermal Energy Co., Inc. 1-7-25 Chuo-dori Morioka, Iwate, 020-0021, Japan

### ABSTRACT

A series of water injection was practiced in the Matsukawa vapor-dominated geothermal field, northeast Japan, and the necessity of a tracer test emerged to evaluate the returns of injected water. Because production wells produced superheated or saturated steam, vapor-phase tracers (sulfur hexafluoride and hydrofluorocarbons) and two-phase tracers (alcohols) were examined in terms of their practical use. We selected the alcohols because (1) they were significantly soluble in water and thus handled simply during injection, sampling and analysis, and (2) they were expected to boil and flow as with injected water in the reservoir.

Five tracer tests were conducted on the four production wells from 2000 to 2003, and the returns of tracers were successively detected for each test. The results of the tests using mixed solutions of ethanol and i-propanol showed variation in the ethanol/i-propanol ratios and different peak times between the alcohols, which may depended on the difference in volatility and the mechanism of twophase flow in the vapor-dominated reservoir. The tracer test using mixed alcohol may have potential to give some information about the boiling process of injectate and properties of two-phase flow in the reservoir.

### **INTRODUCTION**

#### **The Matsukawa Geothermal Field**

The Matsukawa Geothermal Power Station is located in the Hachimantai volcanic area, Iwate prefecture, northeast Japan (Figure 1). The station started power generation in October 1966 with 9.5 MWe as the first commercial geothermal power station in Japan. The capacity has been increased gradually up to 23.5 MWe by June 1993.



Figure 1. The location of the Matsukawa field.

The geothermal field is in a valley and the production wells are distributed along a stream (Figure 2). The productive fractures are found in a Miocene formation composed mainly of dacitic lapilli tuff and sandy tuff, and around the southeastern boundary of a dioritic body intruding into the Miocene. The cap rock of the reservoir is composed of andesitic lava and welded tuff covering the productive formation.

The field has contained over 10 production wells and one re-injection well (Figure 2). Although almost all of the production wells had been producing superheated steam, a couple of them started production of saturated steam following water injection. Therefore, monitoring of the returns of injected water became important for the reservoir management.

## **Injection History**

One re-injection well (MR-1) and three production wells (M-6, M-13 and M-14) were used for water injection and tracer tests. The re-injection well was used for long-term injection and the three production wells were used for short-term injection tests. Steam condensate, stream water, brine and their mixture were injected. Long-term injection has been carried out at well MR-1 for 15 years (from March 1988 to July 2003). The range of injection rates were from 10 t/h to 130 t/h. Short-term (less than nine months) injection were conducted on wells M-6 and M-13. Fluid was injected at the average rates of 20 t/h for well M-6 (from February to October 2000), and 40 t/h for well M-13 (from October to November 2002). The test at well M-6 was terminated when increased brine production was observed in well M-8. At well M-14, injection was conducted only during drilling and tracer was injected at the end of the drilling before the start of production.

# **Monitoring of Injected Water**

Chemical and physical monitoring clearly detected the returns of injected waters in some cases of the short-term tests: e.g. (1) changes in chemical composition of steam, (2) decrease in steam temperature and (3) beginning of brine production. The monitoring for the long-term injection lacked noticeable signs of returns except during the primary period of injection. It was especially difficult to detect the injection flow toward the relatively new wells which started production after the beginning of the injection, because the reservoir conditions around the wells could have been changed by the long-term injection.

For more accurate and more sensitive tracing of injectate in the vapor-dominated reservoir, two-phase and vapor-phase tracer tests were considered as the best method. Accordingly, we selected alcohols as the two-phase tracers. This paper presents the basic results of five tracer tests conducted from 2000 to 2003 in the Matsukawa field.

# SELECTION OF TRACERS

hexafluoride hydrofluorocarbons Sulfur  $(SF_6)$ , (HFCs, R-23 R-134a) e.g. and and hydrochlorofluorocarbons (HCFCs, e.g. R-12 and R-13) have been used extensively as vapor-phase tracers at The Geysers, California, U.S.A. (Adams et al., 1991a, b and 2001; Adams, 1995; Beall et al., 1994, 1998; Voge et al., 1994) and Wairakei, N.Z. (Glover and Kim, 1993). The potential of alcohols as two-phase tracers were reported by Adams (1995) and Adams et al. (2000), although their practical use

in the field had not been tested sufficiently. Lovelock (2001) showed the usefulness of alcohols in tracer flow testing, where i-propanol was used at temperatures up to  $225 \,^{\circ}$ C.

Based on these previous studies, we examined the use of  $SF_6$  and HFCs as vapor-phase tracers, and alcohols (e.g. methanol, ethanol, i-propanol and n-propanol) as two-phase tracers. Alcohols were selected because of the properties discussed below. HCFCs were excluded since they are ozone depleting substances.

## <u>Thermal Stabilities and Detection Limits of SF<sub>63</sub></u> <u>HFCs and Alcohols</u>

Adams et al. (2000) reported that  $SF_6$  and methanol showed high stability (< 5% decay) at temperatures up to about 300 °C, pHs of 3 to 7 and for durations of up to two weeks. Ethanol and n-propanol showed decay of 10-20%. R-134a, one of HFCs, showed 10 -50% decay at temperatures up to 290 °C and durations up to 19 days (Adams et al., 2001).

Sulfur hexafluoride and HFCs are detectable in the order of ppb to ppt using a gas chromatograph (GC); in contrast, our detection limits of alcohols are 0.03 to 0.1 ppm using a GC. Therefore,  $SF_6$  is superior to alcohols in terms of thermal stability and detection limit.

## **<u>Physical Properties of SF<sub>6</sub></u>**, **HFCs and Alcohols <u>Related to Injection, Sampling and Analysis</u>**

Despite their theoretical advantages,  $SF_6$  and HFCs have some disadvantages for injection and sampling. It is difficult to inject the all of the gas into formations from the surface. For example, in order to optimize the injection of  $SF_6$  gas tracer, Glover and Kim (1993) employed a downhole injection method in which a glass ampoule containing  $SF_6$  was broken at the desired depth during water injection. Furthermore, vapor-phase tracers do not always follow the same path as the injected water, which takes time to boil in the reservoir (Adams, 1995).

Also,  $SF_6$  and HFCs are collected into specially sealed and evacuated flasks containing an alkali solution, as used for general steam sampling. This is not suitable for frequent sampling, e.g.: once an hour to several times a day for more than 10 wells. In contrast, alcohols have advantages as two-phase tracers:

- 1) The vapor pressures are similar to that of water;
- 2) Alcohols are miscible or significantly soluble in water;
- 3) Several alcohols with different saturated vapor pressures are available: e.g. methanol, ethanol, n-propanol and i-propanol.

Being liquid at atmospheric temperature and pressure, alcohols are injected easily using a simple

pump as is the case with liquid-phase tracers. Since alcohols are miscible or significantly soluble in water and their vapor pressures are similar to that of water, it is expected that alcohols boil and flow in the vapordominated reservoir as the injected water. Being condensed at atmospheric temperatures, alcohols are collected quite easily into screw-cap bottles as steam condensate. Furthermore, it is possible to use different alcohols at the same time for the different wells, or mix them to take advantage of their different vapor pressures for investigating the boiling process of the injected water.

In addition to the advantages mentioned above, we have developed a direct-injection method for alcohol analysis by modifying an existing gas chromatograph. This technique shows greater sensitivity than the head-space gas chromatographic method used in tracer flow testing (Lovelock, 2001). For these reasons, alcohols were employed as tracers at the Matsukawa field, even though SF6 and HFCs are more thermally stable and detectable as shown by the results of previous studies. We also thought that alcohols would not decay significantly at the temperatures found in the Matsukawa field (< 260 °C), unlike the result of the experiments at the high temperature up to 300 °C by Adams et al., (2000).

### **METHOD**

### **Tracer Injection**

For a well with negative wellhead pressures, tracers were injected directly from metal barrels at the wellhead. For wells with positive wellhead pressures, a pump was used. The injection took less than 25 minutes for a negative wellhead pressure and 20 to 45 minutes for the positive ones. Methanol, ethanol, i-propanol, n-propanol and mixtures of these were used. These solutions were diluted to 60% because of the inflammability of alcohols. In order to make detection easier, about 100 kg to 3,000 kg of alcohols were used per test (Table 1). Water injection continued during tracer tests at the rates ranging from 10 t/h to 40 t/h.

### Sampling

Cooling coils were connected to the steam lines and 100 ml of condensates were collected into screw-cap bottles. Samples were treated with 0.1 ml of 5% zinc acetate solution to precipitate  $H_2S$  to protect the GC column. Sampling for a well was done within 10 minutes. Sampling continued for one to more than six months. About 10 production wells were sampled

approximately once an hour at the beginning of tests, twice a day after three days, once a day after a weeks, and once several days after a few weeks.

# <u>Analysis</u>

The analyses were performed on a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector. Separation was achieved with a 3 m x 3 mm column containing 80/120 mesh Carbopack, and the carrier gas of nitrogen. Samples and calibrators (1-5  $\mu$ l) were injected into the GC directly by an auto injector. Alcohol concentrations were calculated by comparing peak area values of samples and calibrators. The detection limits were 0.03 ppm for ethanol, i-propanol and n-propanol, and 0.1 ppm for methanol in the steam condensates.

# **RESULTS AND DISCUSSION**

Five tracer tests were conducted on the four wells from 2000 to 2003. The basic results are summarized in Table 1. The returns of tracer were detected for each test, and then injector-producer pairs were determined (Figure 2). To compare quantitatively the returns of various tracer materials injected in various amount, the normalized tracer-production rates were used for drawing return curves. The normalized tracer-production rates were calculated by dividing the tracer-production rate (g/h) by the number of kilograms of tracer material injected. Since an area under a return curve shows the recovery of a tracer, the degree of connectivity between an injectors and a producer can be inferred by the normalized return Results from the individual tests are curves. presented below.

### Tracer test on well MR-1

Water injection into well MR-1 has continued for 15 years (1988 to 2003) at injection rates ranging from 10 t/h to 130 t/h. On 6 August 2000, the first twophase tracer test was conducted to determine the flow paths from well MR-1. The mixed solution of 770 kg ethanol and 130 kg i-propanol was injected directly from metal barrels to the wellhead in eight minutes under negative pressure. Tracer returns were found in production wells M-1, M-5 and M-12 (Figure 3). The tracer first arrived at well M-1 in 30 hours, and then at wells M-5 and M-12 in 120-150 hours after tracer injection (Table 1). The highest recovery in well M-12 indicated the strongest return from well MR-1. The returns lasted for more than two months, which indicates that the alcohols were stable long enough for evaluation of tracer returns in the field.



Figure 2. Well locations and flow paths of tracers. Well MR-1 is the only re-injection well in the field.

Injection well	Injection date / tracer	Production well	Recovery (%)		Initial detection time (h)	Tracer velocity (m/h)
MR-1	6-Aug-00	M-1	ethanol	1.5	30	7
			i-propanol	2.5		
	ethanol: 770 kg	M-5	ethanol	5.1	145	3
	+		i-propanol	3.3		
	i-propanol: 130 kg	M-12	ethanol	24	121	3
			i-propanol	17		
MR-1	13-May-03	M-5	i-propanol	-	192	3
	i-propanol: 3,200 kg	M-8	i-propanol	-	1,510	0.2
	+	M-12	i-propanol	> 6.8	96	3
	toluenesulfonate: 100 kg		toluenesulfonate	> 6.2	171	1.6
		M-15	i-propanol	-	1,850	0.2
M-6	12-Sep-00	M-8	n-propanol	73	10	39
	n-propanol: 1,530 kg	M-13	n-propanol	9.1	49	5
M-13	24-Oct-02	M-6	methanol	18	-	-
	methanol: 710 kg		ethanol	9.8	45	6
	+ ethanol: 680 kg					
M-14	18-May-01	M-7	i-propanol	0.08	17	32
	ethanol: 650 kg	M-11	ethanol	0.30	4	61
	+ i-propanol: 1,290 kg		i-propanol	0.24		

Table 1. Results from tracer tests at the Matsukawa geothermal field.



Figure 3. Normalized tracer-return curves from the first MR-1 tracer test in 2000

In contrast to the case of the test on well M-14 as described later, the peak concentrations of ethanol and i-propanol were detected simultaneously in each production well, although the alcohols had different vapor pressures. Furthermore, because well M-1 and M-12 had been producing water, a large part of tracer may have moved as a liquid and then boiled finally near or in the wells.

As Figure 4 shows, the ethanol/i-propanol ratios of samples taken from well M-1 was smaller than that of the tracer, although the ratios of samples from wells M-5 and M-12 were equal to that of the tracer. Since ethanol is more volatile than i-propanol, steam enriched in ethanol may have been generated and then escaped to a fracture disconnected to well M-1. In consequence, the residual tracer flowing into well M-1 may have become depleted in ethanol.

The second test on well MR-1 was conducted on 13 May 2003 with more two-phase tracer (3,200 kg of ipropanol) and a liquid-phase tracer (100 kg of toluenesulfonate) injected almost simultaneously. The returns of i-propanol were observed in wells M-5, M-8, M-12 and M-15 (well M-1 was shut in at this time). The additional detection of i-propanol in wells M-5 and M-8 can be attributed to the more mass of ipropanol and the change of injection depth observed by well logging before the test.

The only toluenesulfonate return was only seen in well M-12, although wells M-8 and M-15 had been producing brines during the test. This observation indicates that the two-phase tracer spread more widely than the liquid-phase tracer did. As shown in Figure 5, the return curves of i-propanol and toluenesulfonate are close together and thus indicate the tracer recoveries are similar (M-12 was shut in 30

days after tracer injection due to a periodic inspection). This observation suggests that a large part of the i-propanol moved together with toluenesulfonate as liquid phase to well M-12.



Figure 4. Relationship between ethanol and ipropanol concentrations in samples taken from well M-1, M-5 and M-12. The correlation line for well M-1 (broken line) differs from the line indicating the ethanol/i-propanol ratio of the tracer (solid line).



Figure 5 Normalized i-propanol and toluenesulfonate returns from well MR-1 to well M-12 during the second MR-1 test in 2003. Well M-12 was shut in 30 days after due to a periodic inspection.

#### Tracer tests on wells M-6 and M-13

Short-term injection including tracer tests was conducted on well M-6 for nine months in 2000. Four to six months after the injection, well M-8 showed decreases in NCG concentration and wellhead temperature, an increase in steam flowrate, and the beginning of water production (Figure 6). These chemical and physical changes indicate the obvious breakthrough from well M-6 to well M-8. In contrast, well M-13 had been producing superheated steam during the injection, and the only decrease in NCG concentration was seen. These observations revealed the strong connectivity between wells M-6 and M-8.



Figure 6. Chemical and physical changes in wells M-8 and M-13, showing decrease in steam temperature and NCG concentration and increase in steam flowrate, and the beginning of water production in well M-8 after injection. In contrast, M-13 showed only the decrease in NCG concentration.

On 12 September 2000, 1,560 kg of n-propanol was injected over a period of 20 minutes into well M-6, and then the returns of the tracer were detected in wells M-8 and M-13 (Table 1, Figures 2 and 7). The tracer return at well M-8 showed the short period for the first arrival (10 hours) and the extremely high recovery (73%) of the mass injected. As with the chemical and physical changes, the tracer test

suggested the strong connectivity between wells M-6 and M-8.

Short-term injection including a tracer tests was conducted on well M-13 for a months in 2002. On 24 October 2002, a mixture of 710 kg methanol and 680 kg ethanol was injected over a period of 45 minutes into well M-13. The returns of the alcohols were observed only in well M-6; the tracer may have flowed in a same path indicated by the return from well M-6 to well M-13 in the previous test on well M-6.



Figure 7. Normalized n-propanol returns from well M-6 to wells M-8 and M-13.

#### Tracer test on well M-14

The water and tracer injection into well M-14 was conducted during its drilling, using a drilling pipe set close to the main fracture. Well M-14 has been a production well and the aim of the test was to evaluate interference with the surrounding wells before start of production. Being located in the highest-temperature upflow zone, well M-14 and the two neighboring wells, M-7 and M-11, have been producing superheated steam.

On 18 May 2001, a mixed tracer of 650 kg ethanol and 1,290 kg i-propanol was injected into well M-14 with a pump in five minutes. The returns were found in wells M-7 and M-11 (Table 1, Figures 2, and 8). The tracer first arrived at well M-11 in four hours and then at well M-7 in 17 hours. The returns lasted for only two days and the recoveries were quite small (< 0.5%), which means the more than 99% of tracer was missing. It is possible that most of the tracer and injected water flowed downwards in the vapordominated region because of the difference in density between steam and water. As Figure 8 shows, the peak concentration of ethanol was detected earlier than that of i-propanol in well M-11. This time difference of peak concentrations was reflected in the ethanol/i-propanol ratios of M-11 samples. Figure 9 shows that the samples collected from well M-11 contained ethanol excessively compared to the tracer at the beginning of return. The ratio of samples approached and then became equal to that of the tracer 14 hours after tracer injection.



Figure 8. Normalized ethanol and i-propanol returns from well M-14 to wells M-7 and M-11. Well M-11 shows the difference in peak time between the alcohols.

The time difference of peak concentrations and the change in the ethanol/i-propanol ratios can be explained as follows:

- 1) The injected fluid containing tracer moved slowly when it was liquid under the vapor-dominated condition.
- 2) The fluid was heated and more ethanol vaporized faster than i-propanol because ethanol is more volatile than i-propanol. As a consequence, ethanol-rich steam was generated.
- 3) Since steam moves faster than water in a vapordominated region, the ethanol-rich steam flowed ahead of the residual fluid.
- 4) Then the fluid was kept heated and more ipropanol began to vaporize. As a result, the ethanol/i-propanol ratio approached that of the tracer. Finally whole fluid flowing to M-11 evaporated, and the ethanol/i-propanol ratio became equal to that of the tracer.



Figure 9. Relationship between ethanol and ipropanol concentrations of samples taken from well M-11. The ethanol/ipropanol ratio of the tracer injected was shown as solid line. Samples contained excess ethanol compared to the tracer's ratio at the beginning of return. The ratio of samples approached and then became equal to that of tracer 14 hours after tracer injection.

### **CONCLUSIONS**

A series of water injection was practiced in the Matsukawa vapor-dominated geothermal field, and the tracer test using vapor-phase or two-phase tracers was requested for evaluation of injectate returns. We selected alcohols as the two-phase tracer because they were expected to boil and flow as injected water in the reservoir. Five tracer tests were conducted on the four wells, and the returns were successfully observed for each tests.

Results from the first test on well MR-1, in which a mixed tracer of ethanol and i-propanol was used, showed that the ethanol/i-propanol ratios of samples taken from well M-1 were lower than that of the tracer and samples from wells M-5 and M-12. Since ethanol is more volatile than i-propanol, ethanol-rich steam may have been generated and escaped to a fracture disconnected to well M-1. A liquid-phase tracer (toluenesulfonate) was used together with i-propanol for the second test on well MR-1. The observation indicated that i-propanol spread more widely than the liquid-phase tracer did.

The results from the test on well M-6 showed the high recovery in well M-8 that is consistent with the chemical and physical changes after water injection.

The tracer test using a mixed tracer of ethanol and ipropanol were conducted on well M-14. The returns showed that the peak concentration of ethanol was detected earlier than that of i-propanol in well M-11, and the samples collected from well M-11 contained excess ethanol compared to the tracer at the beginning of return. The observations indicates that ethanol-rich steam was generated soon after tracer injection, and then the steam arrived first at well M-11.

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