

Application of ethanol as a geothermal tracer: a field test in the Los Azufres geothermal field, Michoacan, Mexico

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Abstract

The thermal decomposition rate of ethanol, rhodamine WT and fluorescein was determined from laboratory data obtained under conditions of temperature and pressure that simulated a geothermal reservoir. It was found that ethylic alcohol had better thermal stability than rhodamine and fluorescein.

Using data obtained from de-ionized water experiments after 168 hours and 200°C of temperature, the rhodamine WT and fluorescein presented a degradation of 99.4% and 99.7%, respectively, while for the ethanol the degradation percentage under the same conditions was only of 44.6%. According to this, ethylic alcohol can be used as a conservative tracer up to about 250°C, while rhodamine WT and fluorescein can be used only at less than 200°C, and only where the transit return time is expected to be less than 7 days.

Ethanol was used as a conservative tracer in a field test in the southern zone of the Los Azufres geothermal field. The highest concentration was detected in a monitoring well in the steam phase 15 days after the injection, and in the liquid phase, or brine, 34 days after the injection. This suggests that alcohol fractionates preferentially in the steam phase and moves or migrates twice as fast than it does in the liquid phase. The tracer speed can be calculated in 176 m/day in the steam phase and 77.5 m/day in the brine. The ethanol presents good enough characteristics to be used as a tracer in both phases in geothermal environments.

Keywords: Tracers, Los Azufres, Ethylic alcohol, Ethanol, Fluorescein, Rhodamine.

Uso del etanol como trazador geotérmico: prueba de campo en Los Azufres, Michoacán, México

Resumen

Se determinó la velocidad de descomposición térmica del etanol, la rodamina y la fluoresceína a partir de datos de laboratorio obtenidos bajo condiciones de presión y de temperatura que simulan las de un yacimiento geotérmico. Se encontró que el alcohol etílico presenta una mayor estabilidad térmica que la rodamina y la fluoresceína.

Empleando los datos obtenidos de experimentos con agua de-ionizada después de 168 horas y a 200° C de temperatura, la rodamina y la fluoresceína presentaron una degradación del 99.4% y del 99.7%,

respectivamente, mientras que para el etanol el porcentaje de degradación en las mismas condiciones fue de sólo el 44.6%. Consecuentemente, puede usarse alcohol etílico como un trazador confiable hasta unos 250° C, mientras la rodamina y la fluoresceína pueden utilizarse sólo a menos de 200° C y únicamente donde el tiempo de retorno esperado sea menor de 7 días.

Se empleó etanol como trazador en una prueba de campo en la zona sur del campo geotérmico de Los Azufres. La máxima concentración se detectó en un pozo monitor en la fase de vapor 15 días después de la inyección, y en la fase líquida o salmuera la máxima se detectó 34 días después de la inyección. Esto sugiere que el alcohol se fracciona preferentemente en la fase de vapor y que se mueve o migra el doble de rápido que en la fase líquida. La velocidad del trazador puede calcularse en 176 metros por día en la fase de vapor y en 77.5 metros por día en la salmuera. El etanol presenta características suficientemente buenas para usarse como trazador en las dos fases en ambientes geotérmicos.

Palabras clave: Trazadores, Los Azufres, alcohol etílico, etanol, fluoresceína, rodamina.

1. Background

During the last 15 years, tracer tests have been carried out in different geothermal fields of the world. For instance, in Wairakei, NZ, fluorescent tints, inert gases, organic compounds and radioactive isotopes have been proven (Bixley *et al.*, 1995). In the case of fluorescein it was proven that these tracers are not significantly degraded in periods of two weeks and at temperatures up to 230°C (Bixley *et al.*, 1995).

The kinetics of the rhodamine WT decay was studied by Rose and Adams (1994) and it was used like a tracer by them in the well 3-1 of Steamboat Hill. Also halogenated alkenes as vapor tracers were tested by Adams *et al.* (1991) in the low pressure area of the Southeast Geysers geothermal field. Two tracers, R-12 and R-13, were injected into the NCPA well C-11. Tracer was found in 38 of the 44 production wells monitored during the 51-days test.

In Ahuachapan, El Salvador, between 1987 and 1990 five tests were carried out using I-131 in wells AH-2, AH-5 and AH-29; the injected concentration was equal to 0.8 curies and the radioactive recovery was 25% in well AH-1. The maximum concentration was detected only 20 days after the tracer was injected, although the detection started two days after the test started (Mc Cabe *et al.*, 1990).

Research on aromatic acids as geothermal tracers has also been carried out at the UURI (Adams *et al.*, 1992).

This activity is important because knowing the direction of fluid displacement in the reservoir improves locating injection wells and estimating injection fluid rates. It makes it possible to estimate if the arrival of the injected liquid is too fast so that it could diminish the fluid enthalpy cooling down the system.

In the Mexican geothermal field of Los Azufres, six tests using inorganic and radioactive tracers were carried out between August 1983 and July 1987. The tests were done in wells located both in the northern and the southern sectors. The tracers were KI (iodine of potassium) and iridium 192 (Horne and Gutiérrez, 1989). The first test was carried out with KI in well AZ-8 and the second one with Ir-192 in well AZ-7. According to the test analysis, the tracers could not be detected—probably because the tracer was not appropriate or the tracer return was at such low concentrations to avoid detection.

In February 1992, production tests were performed to verify the connection between wells AZ-8 (injector) and AZ-46 (producer) (Fig. 1). During this stage, 10 to 225 tons per hour (t/h) of liquid were injected in the well AZ-8. After 21 days of maximum injection, response was noticed at well AZ-46 (Fig. 2). The injection

well AZ-8 is 1330 m deeper than the production well and the horizontal distance between them is 2630 m. An average flow speed between both areas could be estimated at around 124.8 m/day. Assuming that the flow takes place in a plane defined by both wells, a pressure gradient of 0.054 bar/m was calculated. Applying Darcy's law in two dimensions, a global permeability of 11 Darcys was deduced ($\sim 1.16 \times 10^{-11} \text{ m}^2$). On the basis of the above-mentioned facts, it was deduced that the fluid transport in this area is conditioned by faults and fractures oriented E-W (Suárez, 1996).

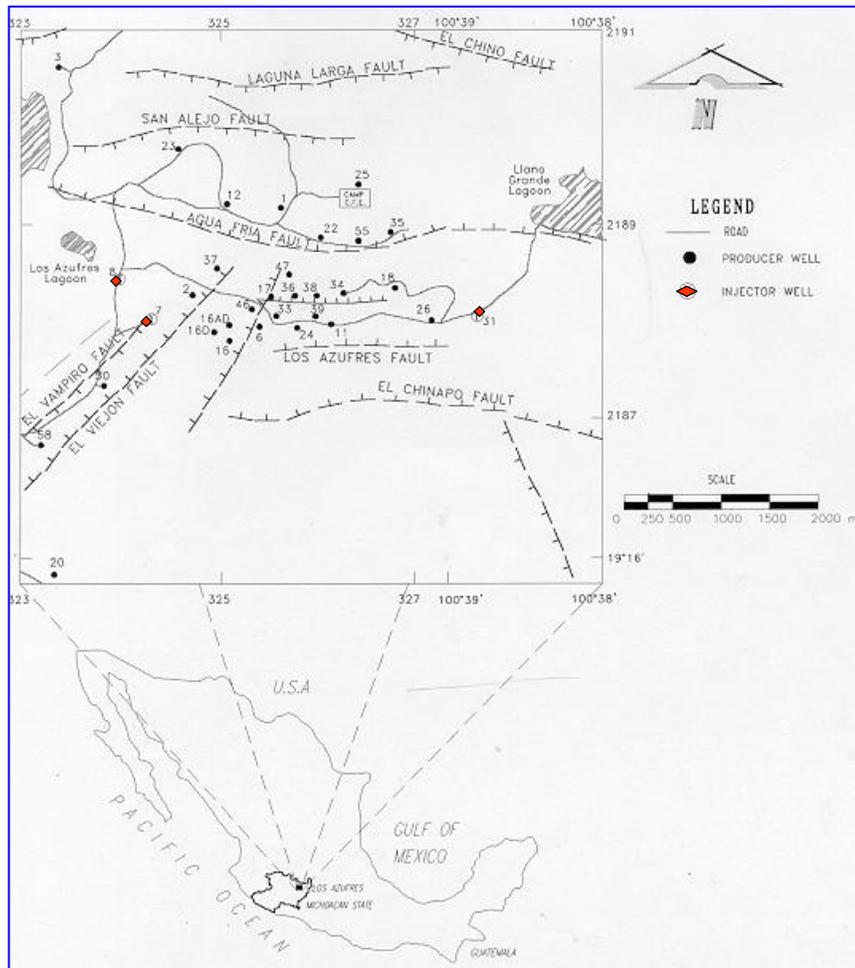


Fig. 1. Map of the Los Azufres geothermal field showing location of wells in the south zone.

of Los Azufres. This made the use of tracers necessary to confirm if the chemical changes were due to the influence of injected fluids. To confirm this, we decided to test ethanol as a tracer in the geothermal reservoir.

The objectives of the tests included:

- To accurately know the type and amount of interaction between extraction and injection zones to define some geo-hydrological aspects of the system and to establish the mass balance between extraction and injection fluids.
- To know the relative amounts of injected fluid that every well is receiving.
- To define preferential trajectories between producing and injection wells.
- To verify if the injection is cooling the reservoir.
- To find out the most appropriate tracer for the typical temperatures existing in Mexico's geothermal fields.

2. Objective of the tests

Tracers have become an important tool for understanding geothermal reservoirs, because with them we can determine underground water speed, flow direction, porosity, etc. However, it is important first to know their thermal stability—to determine the magnitude of their degradation when they are subjected to high temperatures, as in geothermal conditions.

In the present work, experiments were carried out simulating reservoir conditions using ethanol, rhodamine and fluorescein as tracers, determining their behavior and their changes in the laboratory under varying temperatures and time conditions. The tracer studies were carried out at the Mexican Institute of Electrical Research (IIE).

In addition to the above-mentioned studies, an increment of some chemical constituents in the separated water and in the gases was observed in most production wells of the southern zone

Some parameters, such as porosity, permeability, flow speed and effective distances traveled by fluids, could also be indirectly estimated.

3. Tracer types

A tracer is a simulator. It must be very similar to the substance that it has to trace in every respect that is of importance in the tracing process. It must also be very different so as to be identifiable. These are two contradictory conditions. Thus the selection of a tracer is a compromise. For the tracer not to influence the process itself, it must be used in quantities as small as possible (Vetter and Zinnow, 1981).

Tracers can be classified as natural and artificial. The natural ones, such as N₂ of atmospheric origin, are introduced into the injection wells together with the brine. It can be clearly observed how the nitrogen content increases in the samples of gases taken from production wells located near the injectors (Hirts, 1995). This phenomenon was observed in the Los Azufres field, for example, at wells AZ-6 and AZ-16AD located to the east of injectors AZ-8 and AZ-7.

Artificial tracers, as the name suggests, are substances industrially manufactured and ready to be injected.

According to the necessary amount for a given job, tracers can be divided into two groups: chemical and radioactive. Tracers can also be classified as chemical and isotopic. The chemical ones, in turn, can be classified as organic and inorganic.

Chemical tracers are those that have to be identified by general analytical methods such as conductivity, refractive index, elemental spectrometry, etc., while radioactive tracers are detected by their emitted radiation—usually beta or gamma. The amount of a tracer to be used is determined by the detection limits of these methods. Liquid scintillation counters for beta-radiation and gamma spectrometers are by many orders of magnitude more sensitive than other more conventional determination methods and instruments (Hirts, 1995).

The isotopic tracers are of two types: radioactive and stable. Radioactive tracers require specialized personnel and sophisticated equipment, besides environmental formalities and compulsory requirements, which imply higher costs.

Inorganic tracers have some advantages over the radioactive ones. For example, they are easily determined, but it is necessary to use relatively higher quantities than for organic tracers, and some of them also react with geothermal fluids.

A good geothermal tracer should have good chemical stability, not react with the rock, and not exist in a natural form in the reservoir. It must be not expensive or toxic and be easy to handle.

4. Determination of tracer degradation

The experiment consisted of making a solution of 20 liters of distilled water and a tracer such as rhodamine (2.5 ppm), 2000 ppm of ethanol (ethylic alcohol at 96°) and fluoroscein (2.5 ppm). From that solution, 500 ml of fluid were separated. This amount of fluid was kept with no abrupt temperature changes. From the remaining solution, we took 600 ml that were introduced into the Cement Curing Test Cylinder in the

laboratory. This solution was placed inside the oven and heated to different temperatures (100°C, 150°C, 200°C, 250°C), for specific times (12, 24, 48, 72, 120 and 168 hours).

At the beginning of the experiments, a sample of 600 ml was placed inside the cell and exposed to a temperature of 200°C for 12 hours. Once the test was initiated, variations of pressure and temperature were carefully controlled every hour. Once the time of the experiment elapsed, the equipment was switched off and let to cool down at ambient temperatures. Then the cell was taken out from the oven and the sample was quantified. Next 100 ml of solution were separated and put in a plastic bottle and labeled with the following data: code of the experiment, initial volume (V_i), final volume (V_f), Temperature (°C), Time (T), and Net (content in the bottle).

Later on, the remaining solution was placed again in the cell and the 200°C experiment continued for 24 hours. The separation process was repeated. Using the same procedure, the solution was subject to the same temperature for different periods, up to 168 hours. The following experiments were carried out, varying the temperature at 250 and 150°C, for the same periods of 12, 24, 48, 72 and 168 hours.

After that, the samples obtained from the different stages of each experiment were analyzed in the chemical laboratory of the Los Azufres field. The concentrations for each substance are shown in Table 1 and in the figures 2, 3 and 4.

Sample No.	Time (hours)	T (°C)	Ethanol (ppm)	Rhodamine (ppb)	Fluoroscein (ppb)
Series to 150°C					
A1	12	150	1,603	673.10	1306.1
A2	24	150	1,577	609.59	1032.4
A3	48	150	1,539	471.98	744.3
Series to 200°C					
B1	12	200	1,688	694.27	1488.6
B2	24	200	1,631	577.83	1149.8
B3	48	200	1,579	450.81	769.7
B4	72	200	1,359	355.54	470.1
B5	120	200	1,318	165.00	135.3
B6	168	200	1,109	14.91	8.5
Series to 250°C					
C1	12	250	1,702	260.27	366.7
C2	24	250	1,533	37.67	64.3
C3	48	250	1,293	0.00	3.5
C4	72	250	1,015	0.00	0.0

Table 1. Thermal behavior of ethanol, rhodamine and fluorescein tracers.

According to Table 1, concentrations are quite distinct for each tracer (rhodamine, fluorescein and ethanol). In the A series (at 150°C), the original concentration of ethanol (2000 ppm) went down to 1603 ppm after 12 hours, and to 1539 ppm after 48 hours. In the B series (at 200°C), the concentration decreased to 1688 ppm in 12 hours and to 1109 ppm in 168 hours (seven days). In the C series, the concentrations are not so low (1702 ppm) in short times (12 hours), but they drop to 1015 ppm after 72 hours.

The general behavior of the ethanol is plotted in Figure 2, and a preliminary conclusion is that it seems to be more stable at high temperatures (250°C) than at low temperatures (150°C) for a short period of time (12 hours), which is contrary to what one could expect. However, for more prolonged times (1, 2 or more days), the thermal stability of ethanol is higher at low temperatures.

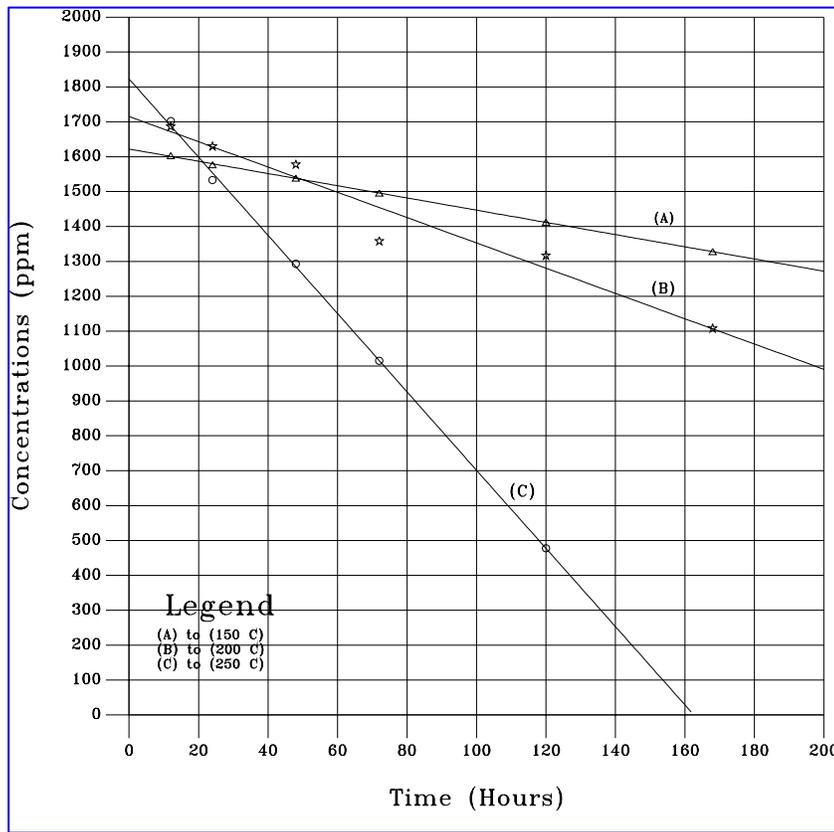


Fig.2. Decay of ethanol in de-ionized water at 150°C, 200°C and 250°C.

and rhodamine. This is because the decay and/or loss of alcohol were consistently smaller than those for rhodamine or fluoroscein. Particularly in the B series after 168 hours and at 200°C, the rhodamine and the fluoroscein presented a degradation of 99.4% and 99.7%, respectively, while for the ethanol the degradation percentage in the same series B, was only 44.6%. For the maximum temperature (250°C), rhodamine and fluoroscein practically disappear after 48 hours, but the ethylic alcohol only loses 35.4% of its original concentration, and 49.3% after three days (Table 2).

On the other hand, the rhodamine tracer presents in the series A concentrations from 673 to 472 ppb, while in the series B concentrations from 694 to 15 ppb, and in the series C from 260 to 0 ppb (Fig. 3).

Fluoroscein presents concentrations in series A ranging from 1306 to 744 ppb, while in the B series concentrations from 1489 to 8.5 ppb are observed, and in the series C concentrations are from 367 to 0 ppb (Fig. 4).

The degradation of each substance is presented in Table 2. It was calculated as the loss of concentration for each one (ethanol, rhodamine and fluoroscein) from the original concentration (2000 ppm, 2.5 ppm and 2.5 ppm, respectively), and expressed as a percentage of this.

According to those results, it is possible to say that when tracer tests are carried out under the previously described conditions, alcohol ethylic presented better thermal stability than fluoroscein

Temperature	Time elapsed	% of Degradation of Original Concentration of		
		Ethanol	Rhodamine	Fluoroscein
150°C	48 hours	23.1	81.1	70.2
	72 hours	32.1	85.8	81.2
	168 hours	44.6	99.4	99.7
200°C	48 hours	21.1	82.0	69.2
	72 hours	35.4	100	99.9
250°C	48 hours	35.4	100	99.9
	72 hours	49.3	100	100

Table 2. Degradation of the tested tracers.

5. Analytical techniques

Colorimetric technique

Gases chromatography is the advisable analytical technique to analyze organic substances using a flame ionization detector. In 1996, this technique was not available at the Los Azufres laboratory, and therefore a

colorimetric technique was used to determine the presence of ethanol in liquids. This technique is used by some police institutions to detect alcohol contained in blood, and also was used to determine alcohol in geothermal brine, giving satisfactory results. Solutions having well-known ethanol concentrations were prepared providing the corresponding calibration curves. The estimated detection limit is high, approximately 30 mg of ETOH/100 ml of water (300 ppm), but it was good enough for these tests (Fig. 5). The technique is based on the oxidation of alcohol to give acetic acid by the dichromate potassium method, according to the following reactions:

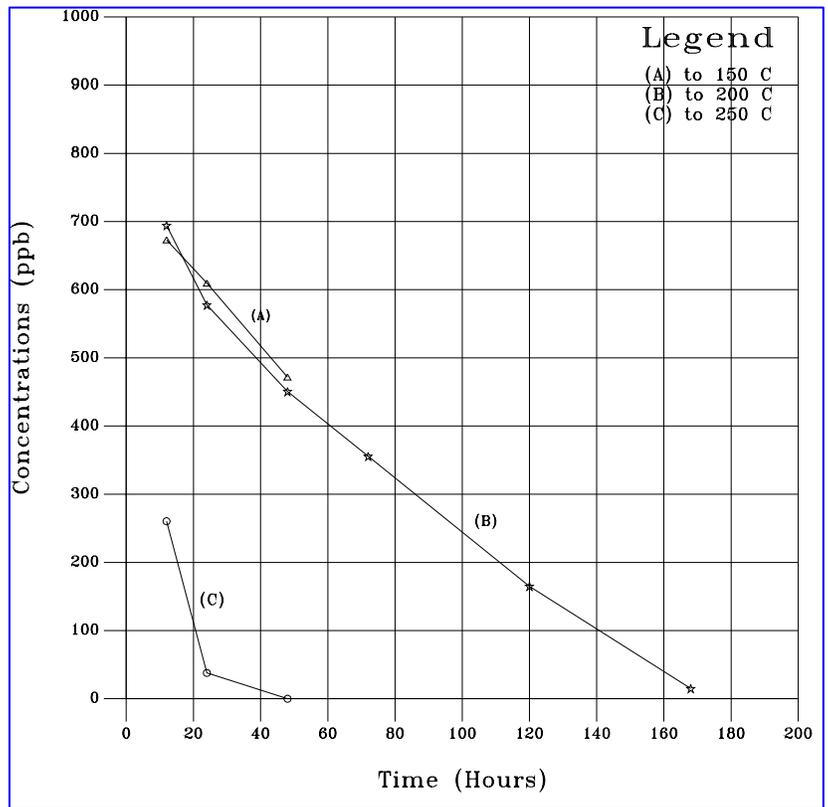
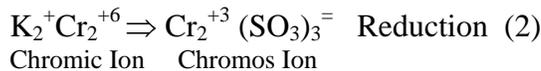
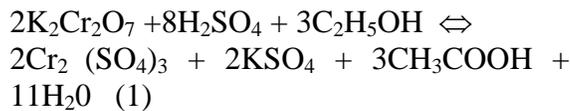
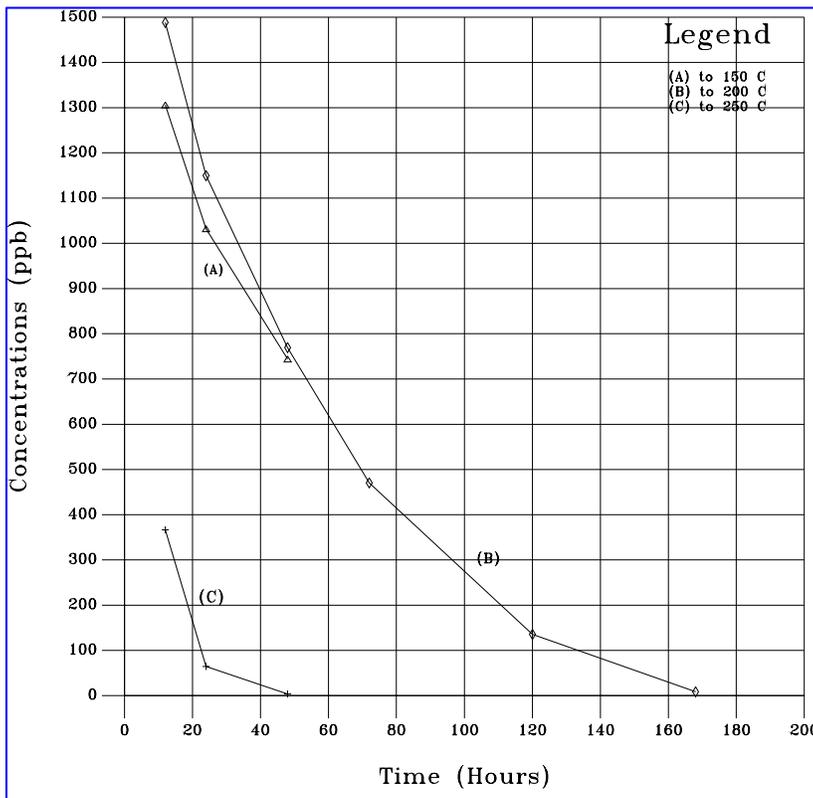


Fig. 3. Decay of rhodamine in de-ionized water at 150°C, 200°C and 250°C.



Reagents

To prepare a solution oxidizer:

- potassium dichromate = 4.165 g
- distilled water = 200 ml
- sulfuric acid = 250 ml

It is appraised to 1000 ml and stored in an amber recipient.

Saturated solution with potassium carbonate: The solution gets ready in distilled water with continuous agitation until no more is dissolved.

Witness Solution: A milliliter of the solution oxidizer is diluted in 4 ml of distilled water.

Fig. 4. Decay of fluorescein in de-ionized water at 150°C, 200°C and 250°C.

Standard Solution: 0.187 ml of ethanol is dissolved in 100 ml of distilled water.

This produces a solution with a concentration of 150 mg of ETOH/100 ml of water (1500 mg/l). If 1 ml of alcohol is dissolved in 100 ml of water the concentration would be 8000 ppm.

Procedure

Inside the Conway camera, 2 ml of mixture oxidizer, 1 ml of solution saturated with potassium carbonate and 1 ml of the solution-problem are placed in the external compartment. The camera is covered and let to spin round, in order to mixing perfectly the solution-problem with the potassium carbonate. The mixture is left at ambient temperature during 12 hours or, in a hurry, the mixture is put in a stove at a temperature between 80-85°C during 30 minutes. A target is prepared using the same treatment as for the samples. The boxes are taken out of the stove and 1 ml of solution from the interior of the Conway box is mixed with 4 ml of previously prepared distilled water. The readings are made in the spectrophotometer at 440 nm, gauged with distilled water.

Calibration curve for ethanol

To prepare the calibration curve, standard measures of 50, 100, 150, and 200 mg of ETOH/100 ml of water were prepared. In this range of concentrations a regression coefficient r equal to 0.99 was observed. This value indicates good fit with a linear model. At concentrations higher than 300 mg this fitting is not preserved. The resulting equation from the calibration curve is (Figure 5):

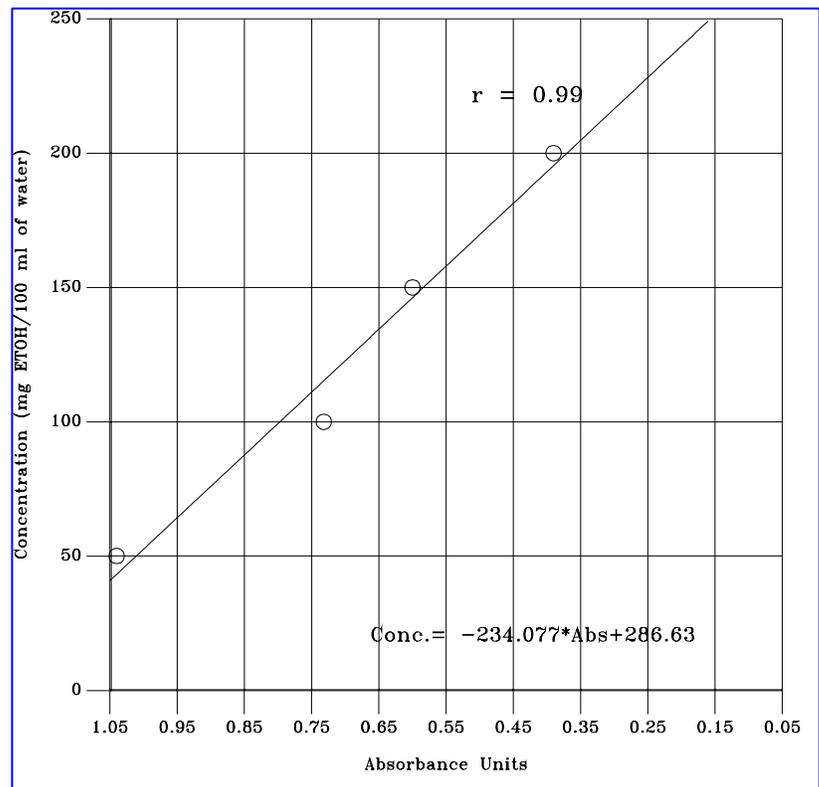


Fig. 5. Calibration curve for ethanol.

$$\text{Conc. ETOH} = -234.077\text{ABS} + 286 \quad (4)$$

The colorimeter used to prepare the curve was a Spectronic 21, Bausch & Lomb, from the chemistry laboratory of the Los Azufres geothermal field.

Calibration curve for rhodamine

For the rhodamine calibration curve, patterns from 1 to 85 ppb were prepared. These standards were analyzed using a fluor-meter (Turner, Model 111), with automatic temperature compensator, obtaining a correlation coefficient of 0.99 (Figure 6). It was found out that the detection limit for rhodamine is 8 ppb.

Calibration curve for fluorescein

For this calibration curve, standard measures from 2 to 100 ppb were prepared. These standards were analyzed using the same fluor-meter used for rhodamine. The corresponding correlation coefficient was equal to 0.998, indicating a very good linear fit. The minimum detectable concentration is 2 ppb (Fig. 7).

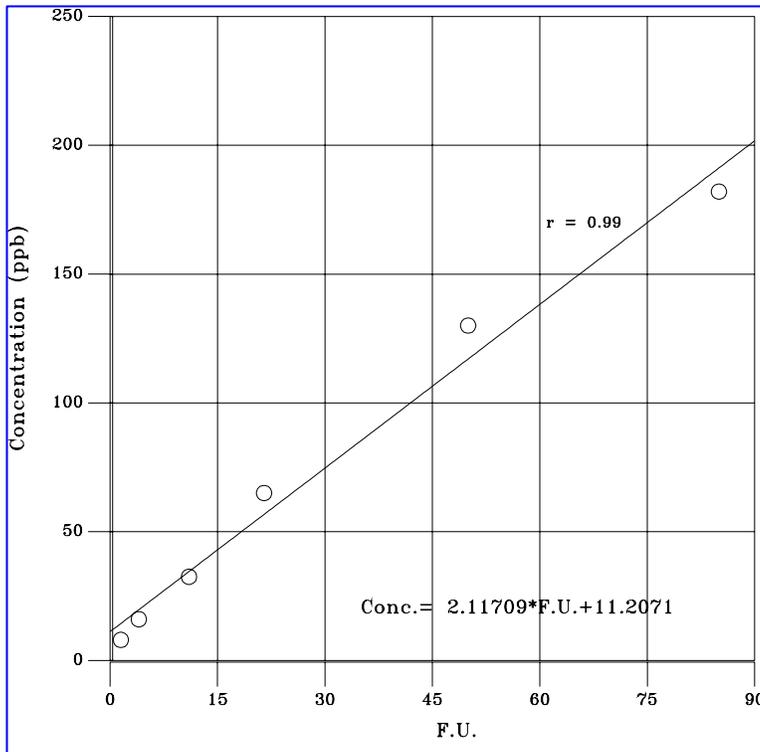


Fig. 6. Calibration curve for rhodamine.

6. Field test with ethanol

In accordance with the above-mentioned characteristics, ethanol was selected as an organic tracer and was tested in the Los Azufres geothermal field (Sámamo and Tello, 1996). This tracer was injected in the well AZ-8 (Figure 8). The feeding zone of this well is located at depths of 2040 m. The ethylic alcohol was injected directly into the wellhead, and the injection rate of brine was kept at 84 t/h during the test. Wells AZ-46, AZ-2, AZ-37, AZ-16D and AZ-33 were used as monitors (Fig. 1).

In August 14, 1996, five hundred liters of ethylic alcohol were injected in well AZ-8, at a rate of 45.5 liters per minute. The injection lasted 11 minutes, beginning at 18:42 hours and concluding at 18:53 hours (Tello, 1997).

The concentration of injected ethanol in the well can be calculated as follows:

Quantity of ethanol (tracer): 500 liters in 11 minutes, or 45.5 liters per minute

Dissolvent agent (geothermal brine): 84 t/h, or 1400 liters per minute

Concentration of ethanol in injected brine: $45.5 / 1400 = 0.0325$, or 3.25 l / 100 l of brine.

Considering that if 1 liter of ethanol diluted in 100 liters of water is equivalent to 8000 ppm, 3.25 liters has to be equivalent to: $3.25 \times 8000 = 26,000$ ppm. Therefore, the ethanol concentration presented at the moment of tracer injection and mixing with 84 t/h of separated water was 26,000 ppm.

Sampling in the monitoring wells began 12 hours after the tracer was injected. As shown in Figure 1, the monitor wells cover practically all the possible routes for the fluids, under the assumption that the injected fluids migrate from west to east through faults and fractures existing in the zone.

Due to alcohol volatility, samples of separated water and condensed vapor were

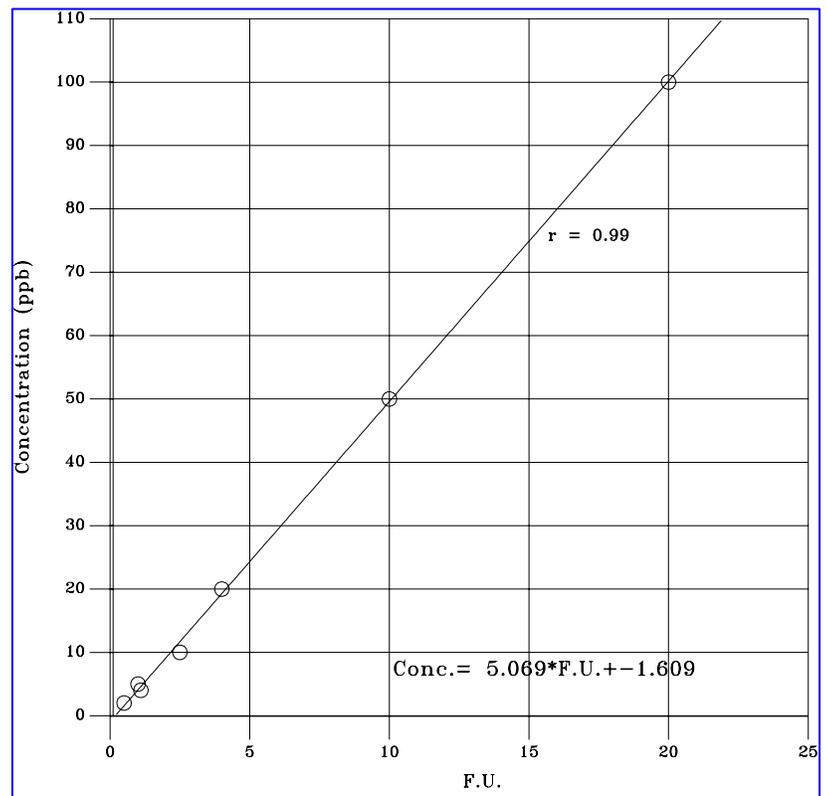


Fig. 7. Calibration curve for fluorescein.

taken at each monitor well. The sampling was done every 12 hours, including weekends, during three months. A total of 334 samples of separated water and 444 of condensed vapor were taken (Table 3).

WELL	SEPARATED WATER	CONDENSED STEAM
AZ-2	89	89
AZ-16AD	89	89
AZ-33	67	88
AZ-37	0	89
AZ-46	89	89
SUBTOTAL	334	444
TOTAL	778	

Table 3. Samples of separated water and condensed vapor.

There was no flame ionization detector in the Los Azufres laboratory at that time. The colorimetric technique is not enough sensitive to analyze low concentrations because its lowest limit of detection is 300 ppm. No ethanol could be detected in those 778 samples from the colorimetric method (Tello, 1997).

Therefore, 24 samples from the well AZ-46 (12 from separated water and 12 from condensed water) were selected and sent to an external

laboratory able to read concentrations up to 1 ppb by using the gas chromatography method with an ionization flame detector. These samples covered a period of two months after the injection, from August 19 to October 17.

7. Results of the analyses and conclusions

Table 4 presents the results of the analyses made on these 24 samples from the well AZ-46 (Tello, 1997). The highest concentrations of ethanol were detected in the steam phase in sample 3, taken 15 days after the injection, and in the liquid phase in samples 7 and 8, taken 34 and 39 days after the injection started, respectively (Figure 9).

The fact that the highest concentration of ethanol in the steam phase occurred 15 days after the injection, while the maximum one in the liquid phase or brine occurred 34 days later, suggests that alcohol fractionates preferentially in the steam phase and moves or migrates two times faster than in the liquid phase.

Considering that the distance from the injector well AZ-8 to the monitoring well AZ-46 is about 2630 m, it can be estimated that the tracer traveled at an average of 176 m/day in the steam, equal to 77.5 m/day in the brine. Thus, an average fluid speed of 126.7 m/day is very similar to the fluid velocity value of 124.8 m/day obtained by production tests. The percentage of recovered tracer at the well AZ-46 was 3%.

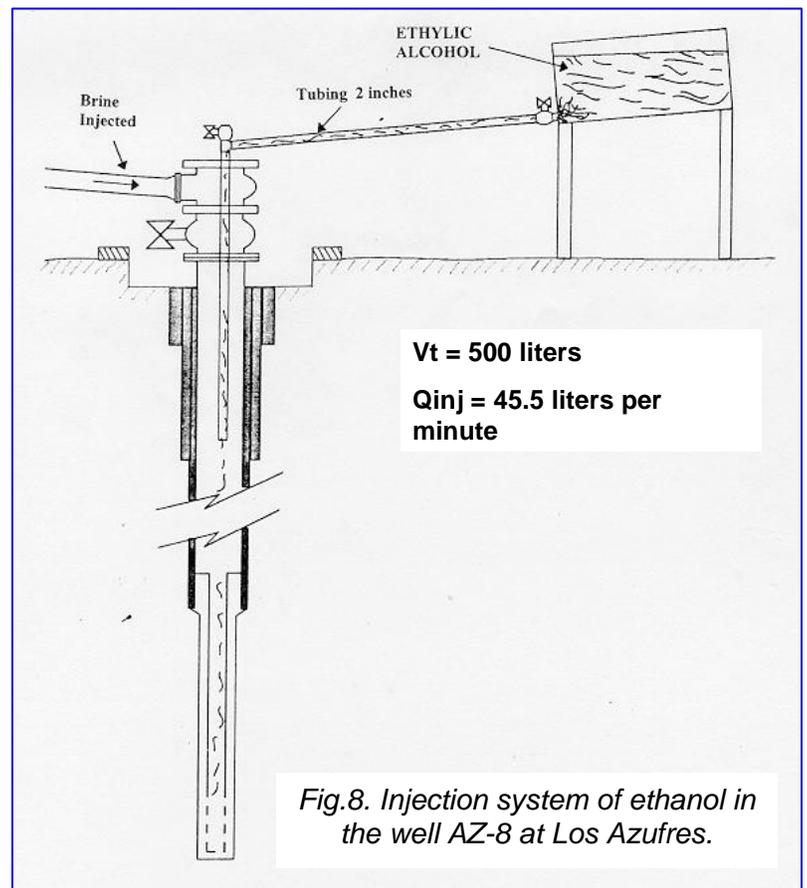


Fig.8. Injection system of ethanol in the well AZ-8 at Los Azufres.

The percentage of recovered tracer at the well AZ-46 was 3%.

From the results of this tracer analysis, it is possible to conclude that ethanol presents good enough characteristics (chemical, thermal, and physical) to be used as a tracer in both phases in geothermal environments.

SAMPLES		ETHANOL (ppm) IN:	
No.	Date	Condensed steam	Separated brine
1	19/08/96	0.39	0.22
2	24/08/96	0.42	0.26
3	29/08/96	5.48	0.34
4	03/09/96	0.74	0.31
5	08/09/96	0.19	1.72
6	13/09/96	0.37	0.94
7	18/09/96	0.57	5.03
8	23/09/96	0.21	5.07
9	28/09/96	0.19	0.9
10	03/10/96	0.51	0.31
11	12/10/96	0.95	0.35
12	17/10/96	0.54	0.26

Table 4. Analyses of ethanol by gases chromatography using flame ionization detector on samples form well AZ-46.

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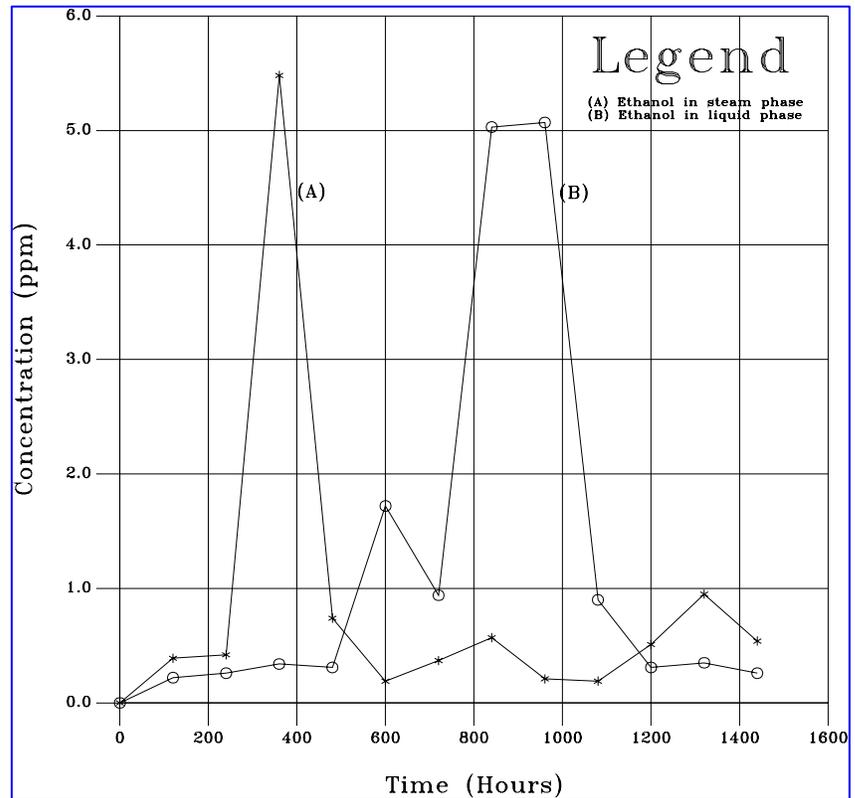


Fig. 9. Ethanol return curves in both phases steam and brine in samples from the monitoring well AZ-46.

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