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RETENTION OF CHEMICAL TRACERS IN GEOTHERMAL RESERVOIRS

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ABSTRACT

This paper examines the advantages and disadvantages of chemical tracers for use in geothermal reservoir monitoring. Tracers are used to determine the magnitude of connectivity between injection and production wells in order to estimate the likelihood of premature fluid breakthrough. Even though chemical tracers are generally less environmentally sensitive than radioactivematerials, quantities injected need to be much larger to be distinguishable by chemical analysis. As a result, a non-equilibrium concentration of tracer material is injected into the reservoir, and the tracer is susceptible to retention within the reservoir by ion exchange, diffusion into the solids or immobile reservoir fluid, adsorption or dissolution. These various reactions lead to changes in the tracer concentration as the traced fluid flows through the reservoir, and therefore reduce the capability of the experiment to distinguish concentration changes due to purely mechanical effects. Experimental observations reported here show that substantial fractions of KI tracer were retained under reservoir conditions, even though it appears that the retained material was subsequently released into more dilute fluid. The result is an apparent "storage and release" mechanism that will distort the later response of a tracer breakthrough.

INTRODUCTION

A tracer is an identifiable substance that can be followed through the course of a process providing information on the pattern of events in the process or on the redistribution of the parts or elements involved. A tracer is a simulator. It must be similar in behavior to the substance which it has to trace, yet it must be sufficiently different to be identifiable. These are two contradictory conditions. The selection of a tracer is thus a search for a compromise.

In the management of geothermal reservoirs, tracers have become an important tool. They have provided valuable insight into the problem of short circuiting of waste water between reinjection and production wells Horne (1982a and b). Tracer tests provide a method of evaluating the nature of the fracture system (Fossum and Horne, 1982) and thus the potential for short-circuiting problems.

Tracers which have been used in geothermal reservoirs can be divided into two general groups: (1) chemical tracers; and (2) radioactive tracers. Chemical tracers are those which can be identified and measured quantitatively by general analytical methods such as conductivity, refractive index and elemental spectrometry. Radioactive tracers are detected by their emitted radiation, usually beta or gamma. Radioactive tracers present more severe licensing and safety concerns than chemical tracers and this study, therefore, investigated the use of chemical tracers only.

Tracers can be further subdivided into those which can be made part of the natural system and those which cannot. The first group includes radioisotopes of constituent elements in the reservoir fluids. These tracers only have to achieve equilibrium with their own non-radioactive kind. The second group of tracers includes most chemical tracers. This group has to establish equilibrium with every other kind present in the system. As a result, non-equilibrium processes such as dissolution, ion exchange, diffusion inside solids, and adsorption can occur between tracer and reservoir rock. These non-equilibrium processes will be of great importance in the field. These various types of reactions occur at a microscopic level and lead to changes in tracer concentration as the tracer fluid flows through the porous media.

This investigation was concerned with the characteristics of chemical tracer retention in reservoir rock. In most of the previous work done concerning tracer behavior in reservoirs, the retention parameter was not quantified and thus neglected in the interpretation of the tracer return. This investigation set out, therefore, to examine the magnitude of the retention problem, and to determine how it may affect the interpretation of tracer test results.

PREVIOUS WORK

Strum and Johnson (1950) studied the results of several tracer tests using brine, fluorescein dye, and a surface active compound. Their results verified the existence of directional permeabilities which had already been measured on core samples. Their findings are generally considered the first to illustrate the important use of tracers in verifying reservoir characteristics.

A comprehensive list of information obtainable from tracer tests was presented by Wagner (1974) who studied the results of twenty tracer programs conducted in petroleum reservoirs undergoing waterfloods, gas drives and water solvent injection operations.

The use of tracer tests in evaluating the short-circuiting problem found in geothermal reservoirs undergoing waste water reinjection was summarized in Horne (1982a and b). The nature of the fracture system at Wairakei was estimated by Fossum and Horne (1982) using the results of tracer tests performed by the Institute of Nuclear Sciences (McCabe, Barry and Manning, 1981).

The macroscopic processes of dispersion, diffusion and convection were considered by Horne and Rodriguez (1981); the present work is primarily concerned with the microscopic processes seen in tracer flow. Microscopic processes include adsorption, ion exchange, dissolution and diffusion inside solids. These processes are due to chemical or physical changes in the tracer and lead to tracer retention in the reservoir.

Vetter (1981) made an attempt to quantify radioactive tracer adsorption in porous media. This paper focuses on chemical tracers and the parameters causing their retention.

THE RETENTION EXPERIMENTS

The experimental apparatus consisted of an air bath, core holder, confining pressure system, water flow system, tracer flow system, temperature recording device, and cooling system. The confining pressure and water flow systems were designed and constructed by A. Sageev (Sageev, 1980). A schematic diagram of the apparatus is shown in Figure 1.

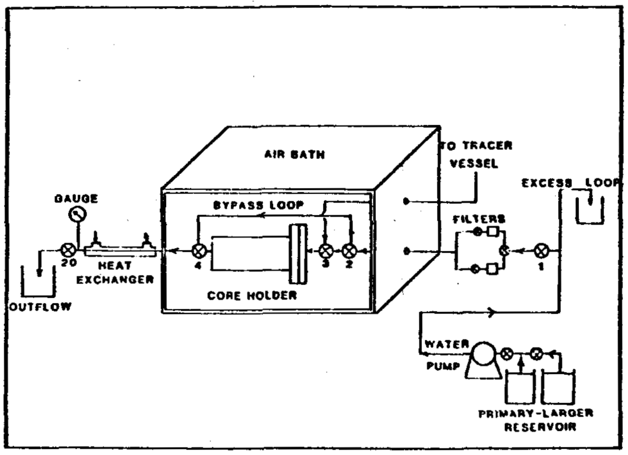

Figure 1 A schematic of the water flow systems

The core material was a volcanic andesite which was taken from the Los Azufres geothermal field, Mexico. Due to the extremely low permeability, the rock was crushed and sieved to various size fractions. A mixture of 40 to 140 mesh size was selected to be used. The mesh range was rinsed and washed several times before packing into the core holder. Porosity measurements were made with a Russell Volumeter.

The air bath houses the core holder which hangs from the ceiling to minimize vibration while the air bath is operating. In addition, the air bath houses the heating coils ahead of the core, the core bypass loop, flow lines, high temperature three-way valves, confining pressure line and thermocouples.

The assembled core holder is designed to withstand a maximum confining pressure of 4000 psig. The core plugs are sealed by "o" rings at both ends. The viton sleeve supporting the core material is rated not to exceed 350°F, setting an upper temperature limit on all the experiments. The viton sleeve is held in an aluminum perforated sleeve between the core plugs.

The viton sleeve is pressurized from the outside by the confining pressure system. A high pressure vessel is located outside the air bath and holds both oil and water. The water outlet is located on the lower end of the vessel while the oil outlet is on the upper end. Water was used in the confining chamber of the core holder to minimize the risk of contamination should a failure occur in the viton sleeve of the core holder. The pressure is applied by an Enerpac hand pump rated at 10,000 psig. The pump is oil operated.

The water flow system is comprised of the intake reservoir, water pump, excess flow loop, filters, and core bypass loop. The pump is capable of producing a maximum flow of about 1150 cc/hr at room conditions.

The core bypass loop was built into the water flow system so that the core could be isolated during specific parts of an experimental run. After tracer has been injected into the system, water flow is diverted through the core bypass loop, cleaning the system of chemical tracer from the down stream core plug to the outflow vessel. The result is that during the displacement of tracer, only tracer that has been in the core, and not the flow tubing, is collected and analyzed.

The tracer flow system consists of a gas system, tracer container, and a high pressure tracer vessel. A 2200 psig nitrogen bottle supplies gas to charge the high pressure tracer vessel. Nitrogen served as the displacement fluid driving chemical tracer through the core. All experimental runs were made with a gas pressure of 250 psig. The high pressure vessel is stainless steel and capable of holding 260 cc of chemical tracer under pressures up to 1000 psig. Before each run, the high pressure vessel is filled with tracers from the tracer container by gravity drainage.

Five thermocouples are scanned once every ten seconds by a Leeds and Northrup Speedomax Recorder which records temperatures in and around the core holder. Downstream of the core holder, outside the air bath, is a heat exchanger, pressure gauge rated to 800 psig, and a needle valve. The needle valve is used to regulate the downstream pressure. It is important to keep the pressure above 100 psig to prevent flash vaporization during the displacement of tracer from the core.

Chemical analysis to obtain tracer concentration was performed with Orion Model 94 single junction reference electrodes. Model 94-53 is iodide specific, and Model 94-35 is bromide specific. Ion specific electrodes allow for ion concentrations to be measured quickly and accurately. Estimated accuracy is ± 0.2 ppm. Measurements are read off the Orion Model 901 ionalyzer meter.

RESULTS

The core dimensions were taken with a micrometer. The up stream measurements are taken 90° apart, while the down stream measurements are taken 120° apart to ensure accuracy around the core plugs. The porosity was measured with a Russel volumeter. The permeability was measured using pressure taps upstream and downstream of the core. The results are presented below:

Length of sand	=	15.348 cm
Diameter of sand	=	2.596 cm
Area of sand	=	5.293 cm^2
Volume of sand	=	81.237 cc
Weight of sand	=	126.5 g
Sand density (packed)	=	1.557 g/cc
Porosity	=	46.7%
Permeability	=	2.3 md

In order to quantify tracer retention under different conditions, it was necessary to analyze the water before and after it had been in the core for background concentrations of the traced ions (I, Br). The analysis of water before it had been through the core revealed trace amounts (< 0.5 ppm) of iodide and bromide.

The water background was analyzed after a three-day residence in the core at 300°F. The results are as follows:

	Concentration (ppm)
Iodide	0.26
Bromide	1.0
Bicarbonate	70.0
Calcium	19.0
Chloride	9.0
Magnesium	0.0
Potassium	4.5
Sodium	16.0
Sulfate (SO_4)	<4.0
Total Dissolved Solids	210.0

The total of the common salts equals one-half of the total dissolved solids. Some other salt must be present, perhaps silica. The low concentrations of iodide and bromide made it possible to select them as tracers. In addition, the water background analysis made it possible to account for tracer amounts in the material balance calculations.

In each of the experimental runs, complete saturation of the core with tracer was achieved by flowing three pore volumes (114 cc). It was assumed in all the calculations that as long as complete saturation of tracer in the core was achieved, the amount of tracer retained was not dependent upon the amount of tracer injected.

A summary of the experimental runs and results is presented in Table 1. The first three runs (#1, #2, #3) were made with potassium iodide at room temperature with a two-hour residence time. The results from Table 1 show that there was an increase in the amount of retention with an increase in tracer concentration. However, the percentage of tracer retained was so small (0.6% to 4.5%) that for all practical purposes, it can be assumed that retention is negligible under these conditions (two-hour residence, room temperature).

The next series of experimental runs (#4, #5, #6, #7, #8) were made under identical conditions (three-day residence, KI tracer, 300°F) but with the tracer concentration increasing from 10 ppm to 500 ppm. The objective of these runs was to test the effect of increasing tracer concentration on retention. The results expressed as a percentage retention are seen graphically in Figure 2. For the 20 ppm to 500 ppm runs, the percentage retention was quite constant, varying between 61.6% and 69.4%. The 10 ppm run showed a much smaller percentage retention of 30.6%. 10 ppm is much closer to the normal background at Los Azufres, which is around 1 ppm (Iglesias and Hiriart, 1981), and may be less of a perturbation to the iodide equilibrium of the system. The remaining experimental runs with KI were made using 10 ppm concentration of tracer. Run #9 was with potassium iodide for three-day residence at 300°F. This run followed runs #4-#8 which used increasing tracer concentration. The objective of run #9 was to go back to a low concentration of tracer to see if the microscopic processes causing retention were reversible. The pore volume was injected with 0.379 mg of tracer. At the end of the residence time, more tracer was produced (0.59 mg) than had been injected. Assuming that all the tracer had been produced from the previous run (#8), this shows that the retention was reversed.

To study the effect of residence time on tracer retention, runs #10 and #12 were made using 10 ppm potassium iodide at 300°F, but with residence times of one-day and two-hours, respectively. The results of these two runs, together with run #4 (three-day residence) are seen in Figure 3. Tracer retention increases with increasing residence time and appears to reach an equilibrium value given a long enough residence time.

The effect of temperature on retention is seen by comparing run #11 with run #4 and run #1 with run #12. These two comparisons do not show a consistent temperature effect.

The last run (#13) was made using a different chemical tracer, sodium bromide, at 10 ppm for three-day residence at 300°F. The result was that 0.136 mg were retained, representing 35.9% of the amount injected. Comparing this result to potassium iodide (run #4) under identical conditions, the potassium iodide showed 30.6% tracer retention. Thus, it appears that both tracers have

TABLE 1

Summary of Experimental Runs

Run #	Tracer	Concentration (ppm)	Residence Time	Temperature (°F)	Mass of Tracer Into Core (mg)	Mass of Tracer Out of Core (mg)	Tracer Retained (mg)	Tracer Retained (%)
1	K1	10	2 Hour	Room	.379	.368	.011	2.9
2	K1	50	2 Hour	Room	1.895	1.81	.085	4.5
3	K1	500	2 Hour	Room	18.95	18.84	.11	0.6
4	K1	10	3 Day	300	.379	.263	.116	30.6
5	K1	20	3 Day	300	.758	.238	.52	68.6
6	K1	50	3 Day	300	1.895	.616	1.28	67.5
7	K1	100	3 Day	300	3.79	1.16	2.63	69.4
8	K1	500	3 Day	300	18.95	7.28	11.67	61.6
9	K1	10	3 Day	300	.379	.59	—	—
10	K1	10	1 Day	300	.379	.281	.098	25.9
11	K1	10	3 Day	Room	.379	.065	.314	82.8
12	K1	10	2 Hour	300	.379	.315	.064	16.9
13	NaBr	10	3 Day	300	.379	.243	.136	35.9

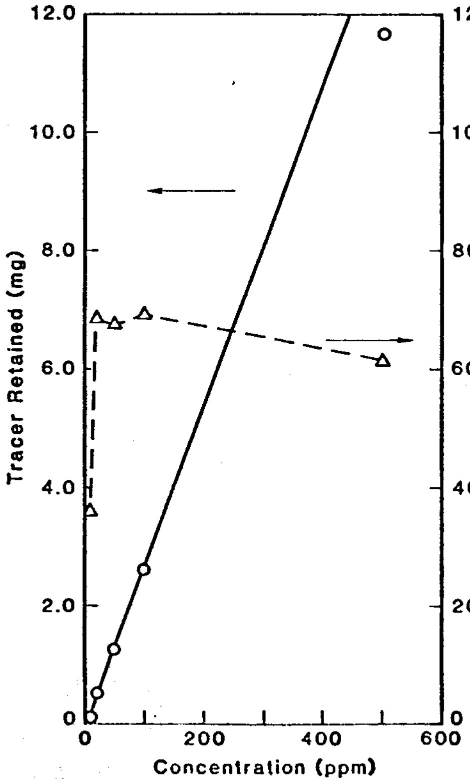

Figure 2 Potassium Iodide,
3 day Residence, 300°F

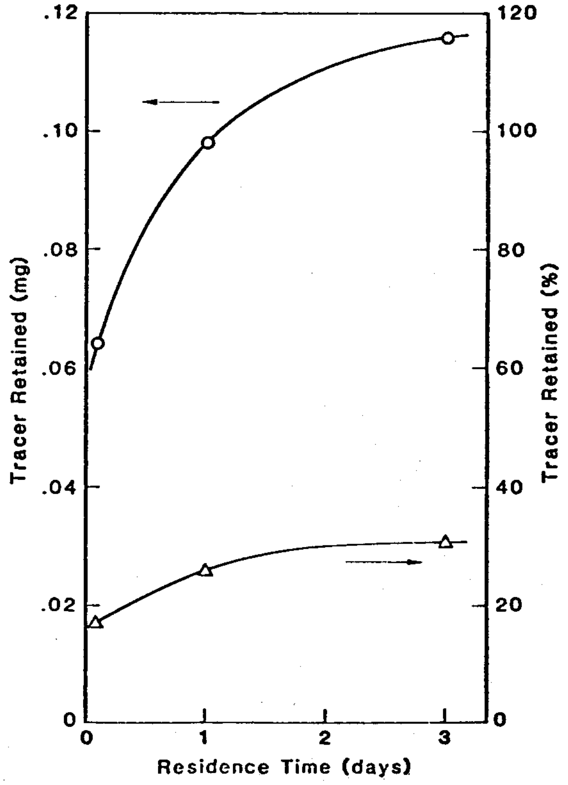

Figure 3 Potassium Iodide,
10 ppm, 300°F

similar degrees of retention under these circumstances.

EFFECT ON FIELD TESTS

Based on the preliminary results of these experiments it appears that about 60% of KI tracer is retained within the Los Azufres andesite sample, but may subsequently be released once the reservoir fluid is depleted of tracer. This "storage and release" mechanism would alter the tracer breakthrough profile such that the trailing edge of the tracer slug would be more dispersed than indicated by the normal dispersion transfer function used in Fossum and Horne (1982). This may account for the unexpectedly large dispersion (small Peclet number) in the analyses of Fossum and Horne (1982) or even for the observation of a double flowpath response. Dr. M. Manning of Institute of Nuclear Sciences, DSIR, Wellington, New Zealand (which conducted the Wairakei tracer tests) analyzed the response of Wairakei well WK 121 which showed a single, very strong response to tracer injection at WK 101, and suggested the holdup mechanism. We examined the response using the fracture flowpath model and confirmed Dr. Manning's results; despite the single, clearly defined peak, it is not possible to match the response with a single flowpath model, see Figure 4. The addition of a second flowpath improves the match (see Figure 5), but it is not until a third flowpath is added that the match becomes acceptable (see Figure 6). Figure 6 also shows the three individual components of the calculated response. Table 2 lists the inferred Peclet numbers and near arrival times for the single, double and triple flowpath models. Also listed are the "apparent" fracture apertures - these generally do not make physical sense since greater flow fraction is allocated to smaller fractures.

The results of this analysis for the WK 121 test are distinctly different from those reported in Fossum and Horne (1982) for WK 116, WK 76 and WK 108. In the latter three analyses the match obtained was satisfactory with only two flowpaths and the larger flow fraction is through the wider fracture (except for WK 76 where the flows are of similar size). In each of the three cases there is an indication of the second peak in the observed data. On the other hand the WK 121 shows a simpler response with a single discernible peak of substantial magnitude. It is therefore unsatisfying to attribute the complex three path model to this response.

TABLE 2

Inferred Flowpath Parameters WK 121

		Flow Fraction	Mean Time (days)	Peclet Number	Apparent Fracture (Aperture (mm)
Primary path	- single	1.00	2.95	9.98	12
	- double	0.63	2.56	20.27	8
	- triple	0.44	2.35	27.83	6
Secondary path	*- double*	0.38	4.57	6.75	17
	- triple	0.40	3.47	14.48	10
Tertiary path	- triple	0.16	6.97	4.74	26

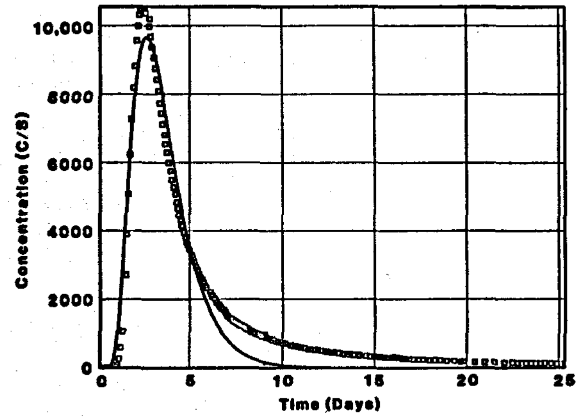

Figure 4 WK 121 response and single flowpath match

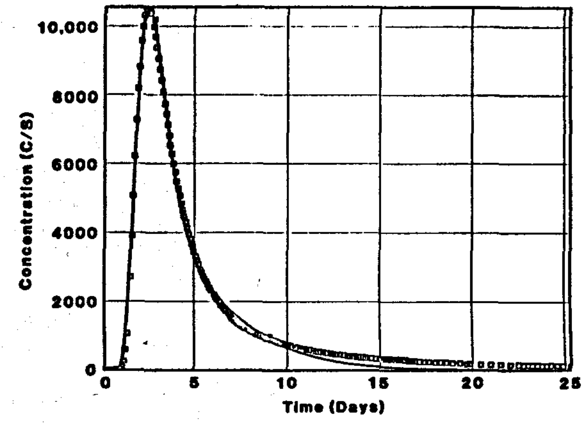

Figure 5 WK 121 response and double flowpath match

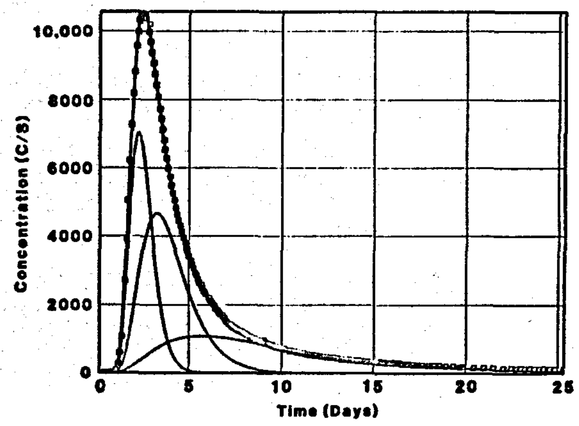

Figure 6 WK 121 response and triple flowpath match, 3 individual components indicated

Another explanation for the high concentrations in the WK 121 tracer response after the peak is the "retention and release" mechanism suggested by the experimental results. This is a more attractive model than multiple paths, particularly since the multiple path analysis results in greater flow through the smaller channels (which is a physically unreasonable result unless the narrowest paths are also the shortest). This "holdup" effect results in an underestimate of the Peclet number, and a consequent overestimate of the fracture aperture.

That WK 121 shows these effects where the earlier analyses did not is not explained, either the more rapid transport in WK 121 (2-3 days mean transport time as compared to 8-20 days for WK 116, 76 and 108) emphasizes the effect or the "second path" in the other three tests are also attributable to holdup. Further work is in progress in an attempt to quantify the process after which more extensive interpretation may become possible. One intriguing aspect of the holdup phenomenon is that it may be dependent on the surface area of the fracture, thus permitting this important parameter to be estimated.

CONCLUSIONS

An experimental apparatus was designed and built to investigate tracer retention on geothermal reservoir rocks at moderate temperature (300°F - 150°C). The effects of tracer type, concentration, residence time and temperature were evaluated. The following conclusions were reached.

1. An increase in tracer concentration produces an increase in retention.
2. An increase in residence time produces an increase in tracer retention.
3. The microscopic processes comprising retention are at least partially reversible.
4. Potassium iodide showed very similar retention values to sodium bromide under identical conditions.
5. The effect of temperature on retention was not consistent in the experiments.
6. Significant amounts of iodide and bromide tracers can be retained in reservoir rocks, and this effect must be considered in designing field tests.

It is not clear exactly where the tracer is retained. These experiments are continuing using a stainless steel core-holder assembly to determine whether the tracer is reacting with the viton sleeve in the present apparatus. This configuration will also permit higher temperatures.

The possible effects of tracer retention and release on field experiment interpretation were considered qualitatively, and this preliminary examination suggests that there is both a need and a significant advantage to quantifying the holdup mechanism. There is a delayed concentration enhancement in the response at well WK 121 which is not convincingly explained with the multiple flowpath model and is apparently the effect of a holdup of some kind.

ACKNOWLEDGEMENT

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REFERENCES

Fossum, M. P., and Horne, R. N., (1982), "Interpretation of Tracer Return Profiles at Wairakei Geothermal Field Using Fracture Analysis," Geothermal Resources Council Transactions, 6.

Horne, R. N., (1982a), "Geothermal Reinjection Experience in Japan," Journal of Petroleum Technology, 34, p. 495-503.

Horne, R. N., (1982b), "Effects of Water Injection into Fractured Geothermal Reservoirs - A Summary of Experience Worldwide," in Fractures in Geothermal Reservoirs, Geothermal Resources Council, Davis, Calif.

Horne, R. N., and Rodriguez, F., (1981), "Dispersion in Tracer Flow in Fractured Geothermal Systems," Proceedings, 7th Workshop on Geothermal Reservoir Engineering, Stanford, December 1981, SGP-TR-55, p. 103-108 (also submitted J. Geophysical Research, 1982).

Iglesias, E. R., and Hiriart, G. (1981), "Design of a Tracer Test for the Geothermal Field of Los Azufres, Michoacan, Mexico: Progress Report," Proceedings, 7th Workshop on Geothermal Reservoir Engineering, Stanford, December 1981, SGP-TR-55, p. 41-46.

McCabe, W. J., Barry, B. J., and Manning, M. R., (1981), "Radioactive Tracers in Geothermal Underground Water Flow Studies," Institute of Nuclear Sciences Report INS-R-298, DSIR, October 1981.

Sageev, A., (1981), "Design and Construction of an Absolute Permeameter to Measure the Effect of Elevated Temperature on the Absolute Permeability to Distilled Water of Unconsolidated Sand Cover," SGP-TR-43, Stanford University, Stanford, Calif., December 1980.

Strum, P. W., Johnson, W. E. (1951), "Field Experiments with Chemical Tracers in Flood Waters," Producers Monthly, Vol. p. 11-18.

Wagner, O. R., (1977), "The Use of Tracers in Diagnosing Interwell Reservoir Heterogeneities-Field Results," Journal of Petroleum Technology, 29, p. 1410-1416.

Vetter, O. J., (1981), "Evaluation of Well-to-Well Tracers for Geothermal Reservoirs, " LBL-11500, Earth Sciences Division, Lawrence Berkeley Laboratory, University of California, August 1981.