PROCEEDINGS, Tenth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford. California, January 22-24, 1985
SGP-TR-84

TRACER STABILITY AND CHEMICAL CHANGES IN AN INJECTED GEOTHERMAL FLUID DURING INJECTION-BACKFLOW TESTING AT THE EAST MESA GEOTHERMAL FIELD

Michael C. Adams

University of Utah Research Institute, Earth Science Laboratory
391 Chipeta Way, Suite C
Salt Lake City, Utah 84108
(801) 524-3422

ABSTRACT

The stabilities of several tracers were tested under geothermal conditions while injection-backflow tests were conducted at East Mesa. The tracers I and Br were injected continuously while SCN (thiocyanate), B, and disodium fluorescein were each injected as a point source (slug). The tracers were shown to be stable, except where the high concentrations used during slug injection induced adsorption of the slug tracers. However, adsorption of the slug tracers appeared to 'armor' the formation against adsorption during subsequent tests. Precipitation behavior of calcite and silica as well as Na/K shifts during injection are also discussed.

INTRODUCTION

The behavior of brine injected into a geothermal reservoir can have important effects on the longevity of a producing geothermal field. In order to investigate brine behavior, the injected fluid may be labeled with a tracer. To date, few tracers have been shown to be thermally stable as well as chemically inert in a geothermal reservoir. For this reason, injection-backflow experiments, conducted at the East Mesa, California geothermal field jointly by UURI, EG&G, Idaho and Republic Geothermal for the purpose of determining reservoir parameters, were used to test several possible tracers. These tracers were Br, I, SCN (thiocyanate), B (borax), and disodium fluorescein.

The injection-backflow technique (Wright et al., 1984) was used as a tool to collect chemical data during our tests. This technique consists of injecting chemically contrasting geothermal fluid (injectate) into a geothermal reservoir, and then withdrawing the injectate along with the reservoir fluid with which it has mixed. Chemical analyses of geothermally stable species are used to calculate the fraction of injectate (mixing fraction) in the recovered fluid. In addition, more complete chemical analyses of the recovered fluid provide data on the behavior of various naturally occurring chemical tracers, scale inhibitors, rock-water interaction, rates of natural reservoir fluid circulation and heat transfer processes.

This report describes the physical set-up of the injection-backflow tests, the observed tracer stabilities, and the fluid composition changes which occurred during the tests.

GEOLOGIC SETTING

The East Mesa geothermal field is located on the broad eastern bench (mesa) of the Imperial Valley, in southern California (Fig. 1). The geothermal reservoir occurs in up to four kilometers of Tertiary and Quaternary lacustrine and deltaic sediments. Permeability in these sediments is matrix dominated. Hydrologic flow is primarily horizontal, with faults providing the minor vertical component of permeability as well as the recharge of thermal fluids (Bailey, 1977).

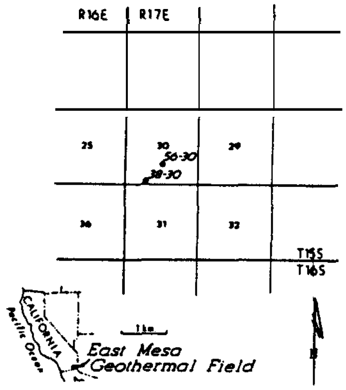

Figure 1. Location map of East Mesa geothermal field.

Two wells were chosen for injection-backflow experiments at East Mesa--Republic Geothermal, Inc. Wells 56-30 and 56-19. These wells were selected for comparative tests because their temperatures and fluid compositions differ and because they produce from different depths. Well 56-30 produces a 174°C sodium chloride fluid having a total dissolved solids (TDS) content of 1700 ppm from a depth of 1820 m. Well 56-19 produces a 126°C sodium chloride fluid having a TDS content of 4900 ppm from a depth of 910 m The well used to supply the injectate was Republic Geothermal, Inc. Well 38-30. Fluid from this well is similar in temperature and composition to that from Well 56-30. The two wells, 56-30 and 38-30, are believed, as a result of pressure-transient tests, to be in hydraulic communication (D. Michels, pers. comm., 1983). Average chemical analyses of fluids from these wells are listed in Table 1.

TABLE 1. AVERAGE CHEMICAL COMPOSITION IN MG/L OF FLUID FROM REPUBLIC WELLS 56-30, 56-19, AND 38-30.

	Injection Wells		Supply Well
	Well 56-30	Well 56-19	Well 38-30
Na	585	1848	647
K	23	44	26
Ca	6	17	6
Mg	<0.5	2.7	(0.5
SiO_2	176	91	210
Sr	0.72	2.59	0.78
Li	0.45	1.99	0.61
B	0.98	8.38	n.d.[1]
Cl	519	2280	n.d.
F	2.3	2.3	n.d.
TDS	1760	4840	n.d.
pH	6.4	6.7	6.12
HCO_3	581	1120	n.d.
SO_4	171	33	n.d.
I	<0.1	0.5	<0.1
SCN	(0.5	(0.5	(0.5
Br	<0.2	2.2	n.d.

[1] n.d. = not determined

DESCRIPTION OF TESTS

Physical Set-up

Fluid from Well 38-30 was transported approximately 0.8 km in iron pipe to the 56-30 well site, where it was flashed at atmospheric pressure. Calcite scale inhibitor was added immediately prior to flashing. The flashed fluid was then transported via centrifugal pump to either the 56-30 or the 56-19 well head. The tracer solution, made up beforehand using fluid from Well 38-30, was injected into the flowline ahead of the centrifugal pump, using a positive displacement pump, at a rate of 0.06 to 0.12 l/s.

The flow rate of tracer injection was controlled manually. The flow rate of the total injected fluid was controlled by an automatic flow-control loop downstream of the tracer injection.

Test Parameters

The designation numbers and parameters for each of the tests at East Mesa are given in Table 2.

Before injection-backflow testing began, each injection well was flowed twice for at least one day to obtain samples for establishing the composition of the natural reservoir fluid prior to testing. These flow tests were designated 1(-30) and 2(-30) for Well 56-30, and 1(-19) and 2(-91) for Well 56-19. Tests 3(-30) and 3(-19) were injection-backflow tests conducted under identical conditions on each of the two wells. One high flow-rate (31.5 l/s) test and one high volume/high flow-rate test were run on Well 56-19. These tests have been designated as Tests 4(-19) and 6(-19), respectively. Eacn of these injection-backflow tests had a quiescent period of 12 hours between injection and backflow. For the last two tests, 4&5(-30) and 8&9(-19), tracer-spiked fluid was injected and left quiescent for 6.5 and 5.5 months, respectively, before backflow.

Chemical Tracers

The tracers used at East Mesa were anions chosen because our experience at Raft River (Capuano et al., 1983) had indicated that they may be conservative. These tracers were chloride, iodide, disodium fluorescein, thiocyanate (SCN), and boron as commercial borax ($Na_2B_4O_7 \cdot 5H_2O$). With the exception of Cl, the tracers were the sodium salt of the anion. Cl was obtained as LiCl so that the behavior of Li could also be evaluated. Tracer species used for each test are listed in Table 2.

TABLE 2. SUMMARY OF INJECTION-BACKFLOW TEST PARAMETERS

Test Designation	Injection Well	Quiescent Period	Tracers Continuous	Tracers Slug
1(-30)	56-30	n.a.[1]	n.a.	n.a.
2(-30)	56-30	n.a.	n.a.	n.a.
3(-30)	56-30	12 hr.	KCL	Borax
4&5(-30)	56-30	6.5 mo.	NaI	$Na_2FL.$[2], NaSCN
1(-19)	56-19	n.a.	n.a.	n.a.
2(-19)	56-19	n.a.	n.a.	n.a.
3(-19)	56-19	12 hr.	LiCl, NaI	$Na_2FL.$, NaSCN
4(-19)	56-19	12 hr.	NaBr	$Na_2FL.$, Borax
6(-19)	56-19	12 hr.	NaI	$Na_2FL.$, NaSCN
8&9(-19)	56-19	5.5 mo.	NaBr	$Na_2FL.$, Borax

[1] n.a. = not applicable

[2] $Na_2FL.$ = disodium fluorescein

Either one or two of the tracers, Br, I, and Cl, were continuously added to Well 38-30 fluid during each injection. In addition, disodium fluorescein and either B or SCN were injected at high concentrations for a period of five minutes during each injection as a point source or slug. The combination of tracers was based in part on analytical considerations. For example, titration of Br will also titrate SCN, so the sets used were Br + B and I + SCN. Continuous tracers were always Br or I, and slug tracers were consistently B or SCN.

Sampling Procedure

Fluid sampled during all experiments was cooled below 40°C prior to sampling to prevent evaporative cooling loss. Sample intervals varied from one minute to eight hours, and were determined by the rate of change of electrical conductivity and/or fluorescence of the test fluid. The samples were analyzed for the tracer suite or for a multi-element suite, consisting of Na, K, Mg, Fe, SiO_2, Sr, Li, B, HCO_3, SO_4, Cl, F, TDS, pH and the relevant tracers. Ca was not analyzed by us for a majority of the samples due to contamination, discovered after the tests, from black phenolic resin caps used on the sample bottles. However, a concurrent investigation by Republic Geothermal, Inc. (Michels, 1983) on calcite scaling during injection has provided reasonable coverage of Ca concentrations during the tests. These values are included along with our chemical data in a companion report which documents all analyses (Adams et al., 1984).

Detection limits, estimates of analytical precision, sample preservation methods, and a more comprehensive explanation of the analytic techniques used can be found in Kroneman et al. (1984).

RESULTS

Calculation Procedures

The fraction of injectate present in each backflow sample was calculated from the relationship:

$$X_i = \frac{C_i - C_R}{C_I - C_R} \quad , \quad (1)$$

where X_i = fraction of injectate in the ith sample of the recovered fluid,

C_i = concentration of conservative tracer in the ith sample of the recovered fluid,

C_R = concentration of conservative tracer in the reservoir fluid, and

C_I = average concentration of (conservative) tracer in the injected fluid.

The expected concentrations of other species were then predicted from the relationship:

$$C_{pi} = X_i C_I + (1-X_i)C_R \quad , \quad (2)$$

where C_{pi} = predicted concentration based on assumption of conservative behavior.

The actual and predicted concentrations were plotted against cumulative volume. These comparisons are shown for selected elements in Figures 2 to 5.

The total mass of tracer recovered was also determined and compared with the mass of tracer injected to help evaluate whether or not the tracer had undergone reaction in the reservoir, i.e. whether or not the tracer was conservative. The mass of tracer recovered (M) was calculated using the equation (Capuano et al., 1983)

$$M = \sum_{i=0}^{n} 1/2\ (T_{i+1} - T_i)\ (C_I X_i + C_I X_{i+1}) R_i \quad (3)$$

where T_i = relative collection time of the ith sample;

R_i = average flow rate during time interval T_i to T_{i+1}, and

n = number of samples.

Fluctuations in the chemistry of the injectate or reservoir fluid can result in an injectate fraction somewhat greater than one or less than zero. In these cases $C_I X_i$ is replaced by C_I or 0, respectively, in Equation 3.

DISCUSSION

Conservative Species

The species which behaved conservatively in our experiments were Cl, Br, I, disodium fluorescein, and SO_4. Two criteria were used for deciding if a species behaved conservatively. The first criterion was complete recovery of the injected species mass. Complete recovery was indicated by a value close to 1.00 for the ratio of recovered to injected mass (recovery ratio). Recovery ratios for Cl, Br, I, disodium fluorescein, and SO_4 ranged from 0.91 to 1.03. The second criterion was concordance of the actual recovery concentrations of a species with concentrations predicted from a species already shown or assumed to be conservative. This criteria was based on the initial assumption that Cl was conservative. Evidence for the validity of this assumption has been given by Cicciolf et al. (1980), who showed that the chromatographic retention time of the Cl ion was equal to that of pure water, within analytic error. The stationary phase materials used were limestone and sand.

Nonconservative Species

The most reactive species tested were the slug tracers SCN and B, and the common scaling species Ca and SiO_2. Other species, such as Na, K, and Li, reacted to a lesser extent.

Slug Tracers

The recovery ratios for the slug tracers are listed in Table 3, and recovery plots for SCN and B were shown in Figure 2. The predicted slug-tracer recovery curves are based on the conservative behavior of disodium fluorescein as inferred from its recovery ratios. These curves are more dependable than the recovery ratio because they depend on the easily measured ratio between the slug tracers. Inspection of these curves shows that, contrary to its recovery ratio, no net gain of SCN is indicated for Test 6(-19). The curves for Tests 3(-19) and 4(-19), however, are in agreement with the recovery ratios. The slug recovery for Test 3(-19) was spread out over 3 injection volumes. The data suggest that this is not a chemical phenomenon, but rather a hydrologic complication.

The slug tracers SCN and B lost up to 36% of their injected mass in some tests, but behaved conservatively in others. It is hypothesized here that SCN and B were irreversibly adsorbed onto formation minerals due to the extremely high concentration present during the injection of the slug, and that the formation was armored by the first slug injection such that slug tracers in subsequent tests were not detectably adsorbed. The reasoning for this is as follows: the

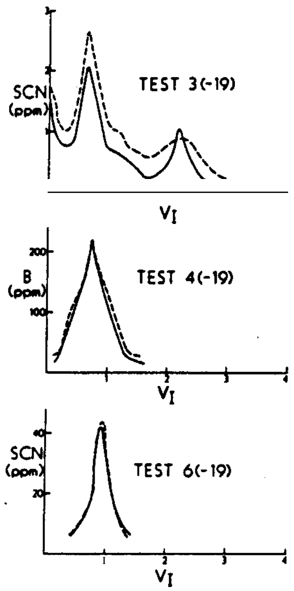

Figure 2. Recovery curves of slug tracers used on Well 56-19. Dashed lines are predicted concentrations and solid lines are measured concentrations. V_I = volumes of injectate recovered.

TABLE 3. RECOVERY RATIOS OF SLUG TRACERS

Test	Recovery Ratio
3(-30)	0.69 (E)
4(-30)	0.64 (SCN)$_1$
3(-19)	.91 (I), .96 ($Na_2FL.$)^1
4(-19)	.96 (Br), .93 ($Na_2FL.$)
6(-19)	.98 (I), 1.03 ($Na_2FL.$)

[1] $Na_2FL.$ = disodium fluorescein

slug tracers SCN and B each lost approximately 35% of their injected mass during the first test (3(-19), 3(-30)) of each well whereas no slug tracer (mass) was lost during the second (4(-19)) or third (3(-19)) test of Well 56-19. If the SCN and E adsorbed at all concentrations except where the formation minerals were armored, then SCN would have been adsorbed during Tests 6(-19). This would have occurred because the volume of injectate was doubled during Test 6(-19) and the slug was injected at the leading edge of the injectate. Thus unarmored minerals would have been encountered by the slug tracers. Since SCN was not lost during Test 6(-19). and the slug was continuously diluted during injection, it must be concluded that the lack of adsorbtion was due to the lower concentrations of SCN at the greater distance from the wellbore.

An apparent exception to the hypothesis that adsorption will not occur once the near-wellbore formation is armored is the 36% loss of SCN during Test 4&5(-30), which was the second injection-backflow test of Well 56-30. Adsorption during this test, however, occurred over a 6-month quiescent period. Moreover, the injected fluid drifted away from the wellbore during this test such that unarmored minerals were encountered. Thus, the adsorption kinetics are slow but detectable at concentrations below those of slug injection.

Ca and SiO_2

During the injection-backflow tests at East Mesa both Ca and SiO_2 were lost during injection. Recovery curves for Tests 6(-19) and 3(-30) are shown in Figures 3 (Ca) and 4 (SiO_2). Test 6(-19) is representative of all tests on Well 56-19, as the parameters tested had little effect on the precipitation of Ca and SiO_2.

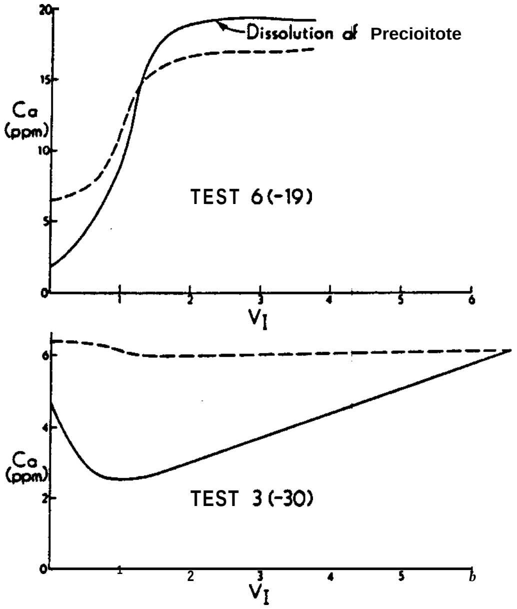

Figure 3. Recovery curves contrasting Ca behavior in Wells 56-19 and 56-30. See Fig. 2 and text for explanation.

Inspection of the recovery curves in Figures 3 and 4 shows that, in most cases, minerals that precipitated during injection were then dissolved after the unmixed body of injectate had been recovered. The only Case where this did not occur was the precipitation of Ca during Test 3(-30). During this test aqueous Ca concentrations were reduced to as low as 30% of the injected concentration. In addition, reservoir Ca concentrations did not return to the background values of 6.0 ppm until 6.5 injection volumes had been recovered. The prolonged precipitation of Ca from the reservoir fluid in Well S6-30 may have been due to the attainment of critical nucleation size or may simply be related to the degree of supersaturation in the fluid.

The maximum amount of Ca precipitation in

Well 56-30 occurred at least 0.6 injection volumes away from the wellbore (Fig. 4) (Michels, 1983). However, the maximum Ca precipitation during Well 56-19 tests occurred adjacent to the wellbore. Thus it appears that, unlike the behavior of Ca in Well 56-30, the scale inhibitor failed to prevent near-wellbore precipitation in Well 56-19.

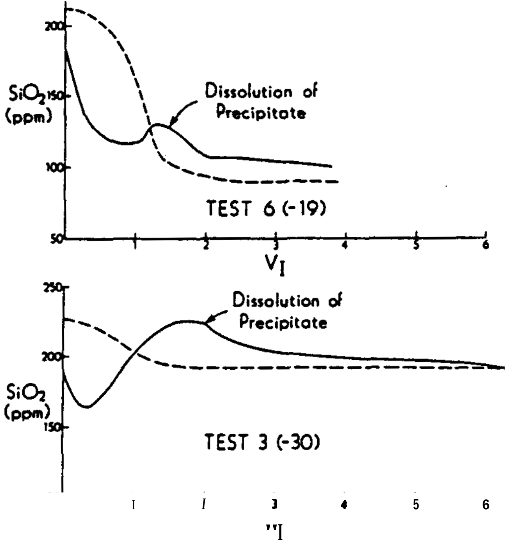

Figure 4. Recovery curves contrasting SiO_2 behavior in Wells 56-19 and 56-30. See Fig. 2 and text for explanation.

Although up to 50% of injected SiO_2 was lost during injection in both wells, recovery of this species differed between the two wells. Recovery of the silica precipitate in Well 56-30 was rapid and complete, i.e. no silica from the injected fluid was left in the well. Recovery of the silica precipitate in Well 56-19, however, occurred somewhat later than in Well 56-30 and was incomplete. Up to 20% of the injected silica was left in Well 56-19.

It has been suggested by Fournier (1981) that chalcedony should be considered as the equilibrium SiO_2 polymorph for geothermal systems with temperatures below 180°C. Despite this generalization, the predicted quartz geothermometer temperatures for the three East Mesa test wells are in close agreement with their measured temperatures of 174°C and 126°C. The recovery curves for Well 56-19, however, display flat minimums where concentrations are in agreement with chalcedony equilibrium; this occurs despite the abundant quartz in the East Mesa reservoir rock.

Na/K

Temperature-induced shifts in the Na/K and Na/Ca ratios of a fluid co-existing with alkali-bearing alumino-silicates have been predicted by theory and empirical data (e.g., Fournier and Truesdell, 1973). As shown in Figure 5, these shifts occurred in the fluid injected into Well 56-19. The Na-K-Ca (-Mg) geothermometer temperatures (Fournier and Truesdell, 1973; Fournier and Potter, 1979) were calculated from chemical analyses of the recovered fluid. Although these predicted temperatures are not valid due to the precipitation of calcite during the tests (Fournier and Truesdell, 1973), the similarity between the predicted and measured temperatures demonstrates that the ion ratio shifts were of the proper magnitude and direction for decreasing fluid temperatures.

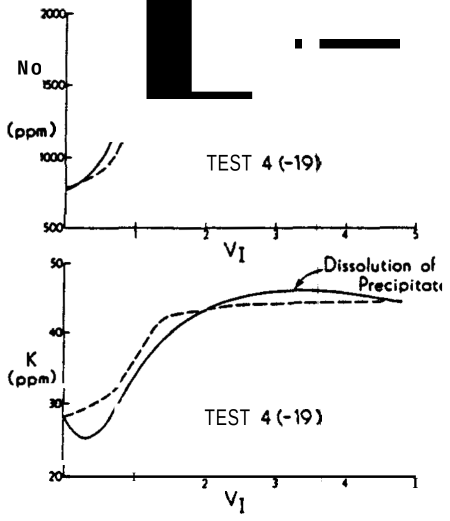

Figure 5. Recovery curve contrasting behavior of Na and K in Well 56-19. See Fig. 2 and text for explanation.

Cation vs Anion Tracers

Our choice of tracers for these tests was based on the assumption of preferential occurrence of cation exchange rather than anion exchange in reservoir rock alumino silicates. As mentioned above, Na and K were shown to be unsuitable tracers for the East Mesa system. The cation Li was also evaluated, and was shown to be cdnservative when used as a tracer in Test 3(-19). However, a few tenths of a ppm out of the 100 ppm of Li injected was lost during Test 3(-19). This is clearly shown by the elevated background concentrations of Li during Test 4(-19), which was performed immediately after Test 3(-19). The tracer B was compared in a similar manner, and no elevated background concentrations were found. Thus, although some cation tracers may lose less than one hundredth of their injected concentration, extensive flow may be required to clear the reservoir of their presence.

Other Species

The behavior of Sr, HCO_3, F, Mg and Fe were also examined. Recovery plots of species Sr and HCO_3 were not included in this report because their behavior mimics that of Ca and the plots would be redundant. Concentrations of F and Mg were too low to give reliable recovery data, and thus were also deleted.

Concentrations of Fe were found to be dependent on the flow history of the test, and were thus the result of contamination from the well casing.

CONCLUSIONS

Chemical losses and gains occurred in the injected fluids during the injection-backflow tests conducted at East Mesa. Three mechanisms were found to account for these chemical changes in the tracer-labeled fluid injected at East Mesa; irreversible adsorption, reversible adsorption, and mineral precipitation. Irreversible adsorption occurred when highly concentrated solutions of SCN or B were injected as point sources. Up to 36% of the injected mass of these slug tracers was lost upon the first exposure of the reservoir rock to these compounds. In subsequent short-duration tests, SCN and B were conserved due to armoring of the adsorbing sites.

Reversible adsorption (including ion exchange) was detected for the monovalent cations Na, K, and Li. The effect of this mechanism was to change the shape of the recovery curve and temporarily raise the background concentration of these species in the reservoir fluid. Thus, the use of a cation tracer is not advisable.

Mineral precipitation of calcite and silica was extensive during the tests conducted at East Mesa. Concentration of SiO_2 and Ca were reduced by one-half at 0.5 injection volumes of recovery. During the short-term test of Well 56-30, Ca continued to be lost until 6.5 injection volumes were recovered. This behavior is a function of the degree of supersaturation or the critical size of nucleation.

The silica polymorph that precipitated during the tests was metastable with respect to the reservoir fluid. Silica precipitated during these tests was partially dissolved by reservoir fluid during the recovery stage of each test.

ACKNOWLEDGEMENTS

The author wishes to thank Don Michels for his ideas and his calcium data, and Mike Wright and Joe Moore for discussions and review of this paper. Funding for this study was provided by U.S. Dept. Energy under contract number DE-AC07-80ID12079.

REFERENCES

Adams, M. C., Kroneman, R. L., and Yorgason, K. R., 1984, Chemical analyses of water sampler collected during East Mesa injection-backflow testing: in prep.

Bailey, T. P., 1977, A hydrogeological and subsurface study of Imperial Valley geothermal anomalies, Imperial Valley, California: University of Colorado, M.S. Thesis, 100 p.

Capuano, R. M., Adams, M. C., and Wright, P. M., 1983, Tracer recovery and mixing from two geothermal injection-backflow studies: 9th Workshop on Geothermal Reservoir Engineering, Stanford University, p. 299-304.

Ciccioli, P., Cooper, W. T., Hammer, P. M., and Hayes, J. N., 1980, Organic solute-mineral surface interactions: A new method for the determination of groundwater velocities: Water Resources Res., v. 43, p. 217-223.

Fournier, R. O., 1981, Application of water chemistry to geothermal exploration and reservoir engineering: In Rhybach, L., and Muffler, L. J. P.: Geothermal Systems: Principles and Case Histories: John Wiley & Sons, N.Y., p. 109-144.

Fournier, R. O., and Potter, R. W. II, 1974, Magnesium correction to the Na-K-Ca chemical geothermometer: Geochim. Cosmochim. Acta, v. 43, p. 1543-1550.

Fournier, R. O., and Truesdell, A. H., 1973, An empirical Na-K-Ca geothermometer for natural waters: Geochim. Cosmochim. Acta, v. 37, p. 1255-1275.

Kroneman, R. L., Yorgason, K. R., and Moore, J. N., 1984, Preferred analytic methods for water samples collected during injection-backflow testing: in press.

Michels, D. E., 1983, Disposal of flashed brine dosed with $CaCO_3$ stale inhibitor; What happens when the inhibitor is exhausted: 9th Workshop on Geothermal Reservoir Engineering, Stanford Univ.. p. 317-321.

Wright, P. M., Capuano, R. M., Adams, M. C., and Moore, J. N., 1984, Uses of geochemistry with injection-backflow testing in geothermal reservoir studies: GRC Transactions, vol. 8, p. 349-354.