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APPLICATIONS OF GEOCHEMISTRY TO PROBLEMS
IN GEOTHERMAL INJECTION

by

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INTRODUCTION

During the past two years, the U.S. Department of Energy (DOE) has been conducting research into problems associated with the injection of spent geothermal fluids. Injection may cause degradation of permeability, channeling of injected fluids toward production wells, or environmental problems such as induced seismicity or aquifer contamination. Yet, injection is increasingly recognized as being necessary to help maintain reservoir pressure, to increase efficiency in the mining of heat, and to dispose of the large quantity of produced fluid.

As one part of DOE's injection research program, the Idaho Operations Office of DOE, UURI, and EG&G, Idaho have been jointly developing applications of geochemistry and hydrology along with injection-backflow testing of geothermal wells as a means of determining some of the effects of injection. Field experiments have been carried out at Raft River, Idaho and, with the participation of Republic Geothermal, Inc., at East Mesa, California. Supporting laboratory and interpretational work has been done at UURI and EG&G. This report presents some of the results obtained by UURI. Other important results have been reported by EG&G and Republic Geothermal, Inc. and are referenced herein.

Conventional reservoir engineering studies have, in the past, dealt mainly with interpretation of pressure transient effects in a reservoir. Present-day techniques can be used in many reservoirs to forecast with some reliability the probability, magnitude and timing of pressure interference among wells. However, forecasting fluid breakthrough from an injection well to a production well in geologically complex geothermal reservoirs is not presently possible with any reliability, and forecasting thermal breakthrough

is even more difficult. In addition, the chemical effects of injection are poorly understood at present, and it is not possible to predict beforehand the full range of scaling and aquifer plugging problems that may be encountered. Development of techniques to obviate problems in geothermal injection will require an interdisciplinary approach as well as both laboratory and field experiments.

PROJECT OBJECTIVE AND SCIENTIFIC APPROACH

The most important questions to be answered in injection are:

1. Will injectate from the injection well break through to the production well soon enough or in enough quantity to cause serious chemical or thermal degradation of the production well?
2. Will the well or adjacent formations become plugged as a result of injection? and,
3. Where should injection wells be sited?

Our objective is to develop techniques to answer these questions that are applicable to a broad range of geothermal systems. Our approach has been (1) to begin development of chemical tracers specifically designed for geothermal applications so that breakthrough of injectate can be detected early, and (2) to begin field and laboratory studies on the chemical interactions among reservoir fluids, reservoir rocks and injected fluids so that these interactions can be quantified and models developed for predicting any degradation (or enhancement) of permeability. Before our results to date are presented, I will discuss our objectives and approach in more detail.

Breakthrough

Breakthrough and production of injectate from a geothermal well can have negligible effects or, alternatively, the effects can be substantial and

highly undesirable. If injectate flows to a production well at too high a rate the chemistry of the produced fluids can be greatly changed and their enthalpy greatly decreased. On the other hand, a degree of hydraulic connection between injection wells and production wells sufficient to maintain production pressure through recharge of the dynamic reservoir system is desirable. What is needed, therefore, is establishment of a relatively slow recharge to the reservoir through injection so that the enthalpy and chemistry of the produced fluids remains relatively constant over periods measured in years, and only slowly begins to degrade as the heat of the entire system begins to be used up.

What are the potential approaches to predicting breakthrough from an injection well to a production well? In a broad manner, numerical hydrologic modeling of the reservoir can yield general information on fluid flow through the system. Physical scale modeling could conceivably be used to perform the same function, although physical models are generally limited in the complexities they can incorporate. Unfortunately, details of fluid flow in the real earth are not completely amenable to determination through numerical or physical modeling. This not due to any particular failing of the techniques themselves, but to the fact that the actual spacial variations in hydraulic properties, such as permeability and porosity, cannot be sufficiently quantified for a real reservoir, and these data are needed as input to the model. There is no known way to specify the details of the configuration of all the faults and fractures as well as the variations in intergranular porosity within and between aquifers from data that can be collected today.

We believe that the best way to predict fluid breakthrough from an injection well to a production well is to observe breakthrough at its onset

and to monitor its growth. This can be done by labeling the injectate with tracers that will survive in the geothermal environment and then detecting them in extremely small quantities in the produced fluid. Studies in the Broadlands field have indicated that dilutions of the order of 10^8 can occur during propagation of fluid between two geothermal wells. Certainly it will be typical that at the onset of breakthrough, only a few parts per million of the injected fluid will be produced along with the reservoir fluid. This initial fluid has followed the fastest pathways between injection well and production well. Because of its small quantity, the overall chemistry and enthalpy of the produced fluid will not be perceptibly altered. However, injected fluid will eventually begin reaching the production well in increasing amounts along slower pathways. If injectate can be detected in produced fluids before degradation in well performance begins, then suitable precautionary steps can be taken.

A significant part of our injection research work to date at UURI has been in the testing of chemical tracers in geothermal environments. Prior to this work, little had been done to test or develop tracers specifically for geothermal use. The results of our work to date are reported in the discussion to follow.

Plugging

Injection wells are expensive, and for injection to be cost effective their life must be sufficiently long before workover or abandoning become necessary. Because the injected fluids will be out of chemical equilibrium with the natural fluids and reservoir rocks, chemical interactions are inevitable. These interactions can be either favorable or unfavorable. In the main, adverse chemical effects can be expected, especially if the fluids are

concentrated and degassed as a result of flashing. Both silica and calcite will be poised to precipitate and deposit.

Studies of the chemical effects of injection can be done in at least the following three ways, and each has merit and application:

1. Numerical modeling. Computer codes exist today that can help predict the nature of chemical interactions among injected fluids and reservoir fluids and rocks. These are equilibrium codes, however, and can not account for the kinetics of interactions. In addition, most of these codes lose reliability as the salinity of the fluid increases. Their results have limited application to the real world;
2. Laboratory experiments. In an autoclave, the geothermal environment can be simulated to a degree by adjusting temperature and pressure. Simulated injection fluids, reservoir fluids and reservoir rocks can be mixed and allowed to interact at geothermal temperatures and pressures for relatively long periods of time. Fluids can be periodically drawn off for analysis and eventually the entire contents of the autoclave can be examined chemically and mineralogically to see what changes have taken place;
3. Field experiments. The nature and extent of mineral precipitation can be determined by injecting a fluid into a reservoir, allowing a specified time for interaction and then withdrawing the fluid and noting changes in its chemistry.

Our approach has been a combination of all three methods, with emphasis to date on field experiments. During the coming year, laboratory and numerical modeling will be pursued to help understand and interpret results of the field experiments.

We have adapted as a practical tool for the collection of field geochemical data, the "injection-backflow" technique, which is described in detail in the following section. It is important to realize that this technique is simply a method of collecting data on chemical and other interactions that have taken place in the reservoir and that it is not an end unto itself. We believe that it is the only practical method to collect certain field data as two-well tests seldom achieve breakthrough.

Description of the Injection-Backflow Technique

The injection-backflow technique has been used to a limited degree in the petroleum and mining industries and in ground water hydrology, where it is referred to as the "huff-puff" or "push-pull" test (Drever and McKee, 1980; Pickens et al., 1981). Until now it has not been applied to geothermal problems. The technique consists of: (1) characterizing the chemical and physical properties of the native fluid prior to injection; (2) injecting a fluid having known chemical and physical properties, perhaps labeled with tracers, at a measured rate for a measured time; (3) allowing the injected fluid to remain in the formation for a quiescent period ranging from minutes to hours, days or months; (4) producing fluid from the well at a controlled, measured rate of backflow for a measured time; (5) characterizing the chemical and physical properties of samples of the produced fluid taken at specified intervals; and (6) interpreting the data in terms of chemical and physical processes in the reservoir.

Several parameters in the field experiment can be controlled. Among these are: injection rate and duration; quiescent period duration; production rate and duration; tracer composition; duration of tracer injection (continuous vs. slug injection); and, in some cases, chemistry and temperature of the

injected waters. Increasing the injection rate increases subsurface pressure and may cause new zones of uptake to open. By increasing the total volume of water injected, a larger volume of reservoir around the injection well can be interrogated.

Once injection is completed, the injectate may be left in the reservoir for any desirable quiescent period, to allow the injectate to interact with the reservoir fluids and rocks. The extent of such interaction will depend, among other things, on the difference in chemistry between the reservoir and injected fluids, the temperature, the kinetics of the reactions, the area of contact and the duration of the quiescent period. Some reactions such as adsorption/desorption and ion exchange may be relatively fast, but others such as mineral precipitation or dissolution may require long periods even at elevated temperatures. By characterizing the chemistry of the injected and recovered fluids, one can obtain useful information on chemical processes in the reservoir. An additional phenomena that may become manifest through the quiescent period is movement of the injectate due to natural fluid circulation in the reservoir.

After quiescence, the well is backflowed, and complete chemical analyses, including analysis of tracer concentrations, are performed. Production of a volume equal to two to six or more times the injected volume appears to be necessary in order to recover most of the injectate.

It is important to note that during the injection-backflow test, pressure, flow rate and temperature of fluids can be measured in the injection well, the supply well and in surrounding monitor wells. These data allow reservoir engineering analyses to be done in conjunction with the geochemical analysis made possible by the injection-backflow technique.

Applications to Reservoir Analysis

In our field experiments to date, we have been able to demonstrate that injection-backflow testing can provide information on:

1. The behavior of various chemical tracers in the reservoir;
2. The chemical interactions of the injected waters with the reservoir fluids and rocks;
3. The behavior and effectiveness of scale inhibitors in the reservoir;
4. The presence of natural circulation of reservoir fluids;
5. The nature of the subsurface flow of injected fluids, i.e. porous media flow vs. channeled flow due to fractures; and
6. The transfer of thermal energy between reservoir rocks and injected fluid.

Conventional reservoir pressure-transient testing provides information on (5), but essentially no information on the other items.

The reasoning and approach to our research are summarized in the diagram of Figure 1. Let me explain this diagram in some detail.

1. Injection-Backflow (Huff-Puff). So discussed previously, this procedure consists of injecting a known fluid into a formation along with a tracer, allowing a quiescent time in the reservoir and then removing and analyzing the fluid. The rationale for this will become apparent as we go along.
2. Reactivity of Tracers. Little is known about the behavior of chemical tracers in the geothermal environment. Tracers suitable for use in groundwater hydrology have been identified, but there are little data on how they behave at high temperatures in saline solutions, where the environment is much more chemically reactive. A significant portion of our work has been directed at quantifying behavior of the most commonly used chemical tracers. We have stayed away from radioactive tracers such

INJECTION-BACKFLOW FIELD EXPERIMENTS

Injection - Backflow Procedure

↓
Measure Reactivity of Tracers

↓
Identify Conservative Tracers

↓
Quantify Mixing of Injected Fluid with
Reservoir Fluid in Recovered Samples

↙
Quantify Chemical
Changes Due to
Injection

- Mineral Precip./Dissol.
- Kinetics of Reactions
- Test Scale Inhibitors
- Test Applicability of
(Equilibrium) Chem. Codes
- Test New Tracers

↘
Quantify Hydrologic
Parameters of Flow
Around Well

- Porous vs. Fracture
- Permeability Anisotropy
- Natural Fluid Movement
- Heat Transfer

Figure 1.

as tritium because of environmental concerns and because tritium contamination of a reservoir can render useless other experiments to obtain the age of reservoir water using concentration of natural tritium.

There are two reasonable approaches to testing tracers. First, one could perform laboratory tests on candidate tracers in an autoclave at geothermal temperatures and pressures. We have used this technique on selected tracers in the past and have plans for further autoclave tests. Second, one could test the tracers in situ by injecting them into the earth and recovering them later to see what reactions, if any, took place, i.e. whether any of the tracer was removed from solution. This is the injection-backflow technique, and is the only reasonable way to test tracers in situ. It should be obvious that use of a tracer in any kind of multi-well, flow-through test would not produce reliable data on tracer reactivity. In flow-through tests, if no tracer is detected in the effluent, one does not know whether the tracer has been removed through reaction, whether it occurs in the produced fluid in concentrations too low to detect, whether the pumping time was too short to allow fluid to be propagated through the flow system, or whether there is no hydrologic connection between injection and production wells.

2. Conservative Tracers. The main objective of the exercise in (1) is to identify tracers which do not degrade in the geothermal environment and which do not react with reservoir rocks or fluids. The identification of conservative tracers is key to our further work, as described below.

Chemical reactivity of a tracer will probably be a site-specific phenomenon, although generalities can probably be made about the most likely conservative tracers under specified conditions. We have developed

techniques to identify conservative tracers and have described them in several papers and reports.

3. Mixing. Once one or more conservative (non-reactive) tracer has been identified, a whole host of possibilities open up for pertinent measurements and interpretations on reservoir behavior using injection-backflow testing. This is because the concentration of conservative tracer in the recovered fluid allows one to quantify the amount of injectate in the sample. Because one can chemically characterize both the native reservoir fluid and the injected fluid by sampling and analyses before the injection-backflow test, one can then quantify chemical changes to the injectate as a result of being injected into the reservoir. One can also describe the physical mixing process of the two waters in the reservoir, and from this acquire hydrologic information.
4. Chemical Changes. With the ability to quantify chemical changes to the injectate due to residence in the reservoir, one can
 - (a) interpret the data in terms of precipitation and dissolution of minerals (plugging problem)
 - (b) test the effectiveness of scale inhibitors (plugging problem)
 - (c) test new tracers against the known behavior of conservative ones (tracer development)
 - (d) determine the kinetics of observed chemical reactions in situ, which provides valuable reactionate data, and
 - (e) test chemical modeling codes, which are all presently equilibrium codes, for their applicability to reservoir calculations.
5. Hydrologic Parameters. By quantifying fluid mixing at depth one can interpret the data in terms of fluid flow parameters in the immediate vicinity of the wellbore. We have demonstrated that it is possible to:

- (a) determine the style of fluid flow, i.e. fracture flow vs porous media flow;
- (b) estimate the permeability anistropoy of the formation;
- (c) measure heat transfer rates between the reservoir rocks and the injected fluid.

Please note that all of these things become possible through use of conservative tracers with the injection-backflow technique, which is the only practical way we know of to obtain in situ data on reservoir chemical behavior. Another suggested field technique is flow-through or doublet well testing. But, using flow-through tests, one cannot quantify chemical reactions because one cannot identify the portion of injectate in the recovered solution since there is no way to establish conservation of the tracer. Also, most flow-through tests take far too long to be practical.

DESCRIPTION OF FIELD TESTS

We have been involved in cooperative field experiments with EG&G, Idaho at two geothermal fields, Raft River, Idaho and East Mesa, California. At East Mesa, Republic Geothermal, Inc. has been an additional experimenter. UURI's role in these field experiments has been in the areas of tracer development, geochemistry and geophysics, whereas EG&G's role has been in project management, hydrologic field measurements and hydrologic data interpretation.

The Raft River site was chosen for field experiments only a few months before the field was abandoned by DOE and sold. The imminent sale of this site was one of the reasons for choosing it. However, the abundance of publically available information on the field, including information on the orientation and distribution of fractures in the reservoir, and the availability of fluids of contrasting chemistry made the Raft River field particu-

larly well suited for field testing. East Mesa and Republic were chosen after a formal solicitation was issued for a second field experimental site with an industrial partner who could contribute technically to the project.

Raft River, Idaho

Injection-backflow testing was conducted on well RRGP-5 (Figure 2). This well has been hydrofractured and the near-well flow regime is believed to be dominated by one major fracture (Dolenc et al., 1981). Thermal water produced from RRGP-5 is of the sodium chloride type with 1400 ppm TDS and a temperature of 145°C. The fluid is produced from fractures in the Precambrian basement. Well RRGE-3, which was used as the supply well, is located approximately 2400 m from RRGP-5. Water produced from RRGE-3 is higher in salinity (4700 ppm TDS), and, therefore, compositionally distinct from water encountered in the reservoir around RRGP-5. Because of this compositional difference many of the elements in the fluids could be used as natural tracers.

Table 1 summarizes the test program conducted at Raft River. During the first test (2A-1), tracers were injected for sufficient time to fill the well-bore but not enter the formation. Approximately 96% of the injected tracers were recovered, indicating excellent operational control. Two series of parametric tests were then conducted in conjunction with the evaluation of various tracers. First, the effect of increasing the volume of injected fluid was studied (tests 2A-2, 2C and 2D). Flow was held at 150 gpm and backflow was initiated as rapidly as possible after the completion of injection. The second series of tests (4A, 4B, 4C, and 4D) investigated the effect of varying quiescent time between injection and backflow. The final test (5) was a long-term injection test to determine if tracer breakthrough could be obtained at well RRGE-1, nearby. No breakthrough was achieved.

Figure 2. Raft River well field locations.

TABLE 1
Summary of Raft River Tests
(flow rate = 150 gpm)

<u>No.</u>	<u>Injection Time (hrs.)</u>	<u>Quiescent Time (hrs.)</u>	<u>Backflow Time (hrs.)</u>
2A-1	1	0	1
2A-2	2	0	10.4
2C	46.5	0	110
2D	96.5	0	231
4A	0.3	27.5	8
4B	0.3	2.2	10.5
4C	0.3	12	8.5
4D	0.3	50	48.5
5	376	80	120

TABLE 2
Summary of East Mesa Tests

<u>No.</u>	<u>Injection (hrs)</u>	<u>Injection (gpm)</u>	<u>Quiescent Time</u>	<u>Backflow (hrs)</u>	<u>Backflow (gpm)</u>
Well 56-30					
3(-30)	11.5	300	12 hrs.	67	300
4(-30)	12	300	~6 mos.	43	300
				51	450
				46	370
Well 56-19					
3(-19)	12.5	300	11 hrs.	53.3	300
4(-19)	7.4	500	13 hrs.	25	500
				20	400
6(-19)	14.5	500	12 hrs.	39	500
				9	450
8(-19)	7.3	500	~6 mos.	140	400

East Mesa, California

At East Mesa the reservoir occurs in clastic deltaic and lacustrine deposits of Tertiary and Quaternary age (Coplen, 1976). Hydrologic flow in the area is generally intergranular, with faults contributing to vertical permeability and recharge.

Two East Mesa wells, 56-19 and 56-30, approximately 1600 m apart, were selected for injection-backflow testing (Figure 3). Waters from these wells have distinctly different compositions. Water flowing from 56-19 has a temperature of 126°C and is sodium chloride in character, with a TDS of up to 5800 ppm. Well 56-30 discharges a hotter (174°C), less saline (2200 ppm TDS) sodium chloride water. The supply well, 38-30 is located only 600 m from well 56-30 and draws water of a composition similar to well 56-30.

Table 2 summarizes the test program at East Mesa. Injection-backflow testing was initiated in each well after a series of flow tests (not shown on Table 2) designed to yield standard reservoir engineering data. Two tests, 3(-30) and 4(-30), were run on 56-30 using essentially the same flow rate and injection time, but with large differences in the quiescent periods (12 hrs. vs. ~6 months). Four tests, 3(-19), 4(-19), 6(-19) and 8(-19), were run on 56-19, with the final test having a ~6-month quiescent period. Results of these tests are discussed below.

Fluid Sampling and Analyses

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 used and selected samples were further analyzed

Figure 3. Location map of the East Mesa geothermal field.

for a multi-element suite, consisting of Na, K, Mg, Fe, SiO_2 , Sr, Li, B, HCO_3 , SO_4 , Cl, F, TDS, and pH. Ca was not analyzed by us at East Mesa in the majority of the samples because of 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. All analytical chemical data are given in Adams et al. (1984).

Sample Collection and Preservation. Samples were collected at the geothermal sites from ports in the piping systems (Fig. 4). Both flashed and unflashed fluids were sampled using a stainless steel tubing that had been cut to a 45° angle and sealed in the sample port with the end of the tubing in the center of the pipe. The external tubing coils were immersed in ice water to bring the samples approximately to ambient temperature.

The samples were vacuum or pressure filtered through a 0.45μ membrane filter. Pressure filtering is preferred because it is less likely to cause exsolution of gases or evaporation of the sample. pH was determined on the cooled, unfiltered sample immediately after collection. Alkalinity was determined at the collection site on a pressure-filtered aliquot. The remainder of the filtered sample was collected in plastic bottles which had been precleaned by soaking in 20% nitric acid and then rinsing thoroughly with demineralized water. Samples collected for inductively coupled argon plasma (ICP) spectrometry were stabilized with 20% nitric acid (v/v) whereas samples collected for SO_4 analysis were preserved with 1 or 2% hydrochloric acid (v/v).

Black bakelite or phenolic-resin caps contain a significant amount of readily leachable calcium and should not be used on sample bottles. It was found that molded polypropylene caps without paper liners were suitable.

Figure 4. Sampling Apparatus.

Sample bottles may be linear or conventional polyethylene or polypropylene.

The frequency of sampling was determined by the rate of change in one or more selected variables associated with fluid chemistry that could be easily monitored in the field. Sampling rate varied from one sample per minute to one sample per two hours. On-site monitoring was done with both an in-line fluorometer to measure the concentration of the organic dyes (disodium fluorescein or rhodamine-B) used as tracers and an in-line conductivity meter to measure specific electrical conductance, a quantity related to the total amount of dissolved solids. I, Cl, and alkalinity were also measured during backflow to help determine the sampling frequency.

Selection of Analytical Methods. The analytical methods chosen for the chemical determinations were based primarily on three factors: accuracy, precision and cost effectiveness. In many cases, more than one analytical method could be used. Wherever possible, each of the several different methods was evaluated. The preferred methods and associated sample preservation techniques are summarized in Table 3 (Kroneman et al., 1985).

As shown in Table 3, most of the major and minor elements of the waters were determined by ICP spectrometry. A comparison of analytical data for Na, K, and Ca indicate that the precision of the determinations by ICP techniques is substantially better for Na and K and only slightly less for Ca than by atomic absorption (AA) spectrometry. Because of the large number of elements that can be determined simultaneously, and the high levels of accuracy and precision possible by ICP techniques, this method was preferred to single-element techniques. A more complete discussion of the accuracy and precision of ICP spectrometry has been presented by Christensen et al. (1980). A detailed discussion of the preferred techniques for each of the species

TABLE 3. METHODS OF GEOTHERMAL WATER ANALYSIS.

SPECIES ^a	SAMPLE PREPARATION ^b		ANALYTIC TECHNIQUES	DETECTION LIMITS ^e (mg/l)	PRECISION (RPD %)
	Filtered ^{b,c}	Preservation ^b			
Na	Yes	20% HNO ₃	ICP ^d	1	0.7
K	Yes	20% HNO ₃	ICP	2	1.0
Ca	Yes	20% HNO ₃	ICP	0.2	1.2
Mg	Yes	20% HNO ₃	ICP	0.5	4.5
Fe	Yes	20% HNO ₃	ICP	0.1	1.9
B	Yes	20% HNO ₃	ICP	0.1	2.1
SiO ₂	Yes	20% HNO ₃	ICP	1	1.0
Sr	Yes	20% HNO ₃	ICP	0.01	0.9
Li	Yes	20% HNO ₃	ICP	0.05	1.2
Cl ⁻	No	None	Mohr Titration	2	0.9
F ⁻	Yes	None	Specific Ion Electrode ^f	0.1	2.8
SO ₄ ⁼	Yes	1% HCl	Gravimetric	2	1.8
HCO ₃ ⁻ , CO ₃ ⁼	Yes	None	H ₂ SO ₄ Titration	1	1.4
I ⁻	No	None	Specific Ion Electrode ^f	0.1	2.8
I ⁻	No	None	Titration	0.5	1.6
Br ⁻	No	None	Titration	0.5	1.6
SCN ⁻	Yes	None	Colorimetric	0.2	2.3
pH	No	None	pH electrode ^b	±0.1	g
TDS	Yes	None	Gravimetric or fluorometric	5	0.5
Na ₂ Fluorescein	Yes	None	Colorimetric or fluorometric	0.02	g
Rhodamine-B	Yes	None	Colorimetric or fluorometric	0.02	g

a. For ions, analytical method is ion-specific; otherwise method gives total element.

b. Completed immediately after sample collection.

c. 0.45 μ membrane filter.

d. ICP = Inductively Coupled Argon Plasma Spectrophotometry.

e. The detection limit is defined as the point at which precision is approximately ± 100% of the given value with a confidence level of 95%. At ten times the detection limit the precision is ± 10% (Christensen et al., 1980).

f. Method of additions.

g. Not determined.

commonly determined in our injection research efforts is presented in Kroneman et al. (1985).

The tracers, I, Br and thiocyanate (SCN) were each analyzed by several different methods. I was analyzed by ion chromatography (INEL¹ and Chemical Criteria), titration (ESL² and UBTL³), and specific ion electrode (on site and ESL). In the absence of interferences, titration is the most accurate method followed in turn by specific ion electrode and ion chromatography. Because the titration involves an oxidation - reduction reaction, it cannot be used if other tracers that will interfere are present. At East Mesa, SCN was present with I so the specific ion electrode was used for I.

Br was analyzed by titration and ion chromatography. Titration is the preferred method because it is more accurate.

SCN was analyzed colorimetrically and by ion chromatography. The colorimetric method developed at ESL is preferred because it is more accurate and precise, and is about one-tenth the cost of ion chromatography.

Calculation Procedures

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

$$X_i = \frac{C_i - C_R}{C_I - C_R}$$

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

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

¹ Idaho National Engineering Laboratory
² Earth Science Laboratory
³ Utah Biomedical Test Laboratory

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:

$$C_{pi} = X_i C_I + (1-X_i) C_R$$

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

The actual and predicted concentrations were plotted against cumulative volume.

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)

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

where T_i = relative collection time of the i th 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.

RESULTS--TRACER DEVELOPMENT

Besides mixing, several other processes can affect tracer concentrations in the recovered solution. These include tracer gains or losses as a result of adsorption or desorption, ion exchange, mineral dissolution or precipitation, and, in the case of the organic dyes, disodium fluorescein and rhodamine-B, thermal instability. Because of the higher reactivity of waters and rocks at high temperatures in geothermal systems, tracers used successfully in ground water injection can be affected substantially by these processes. Prior to this research, essentially no work has been done to develop non-isotopic tracers specifically for the geothermal environment.

Injection-backflow testing allows one to determine the behavior of various tracers in the reservoir in ways not possible with flow-through or two-well testing. Reduction of tracer concentration in response to water-rock reactions can greatly alter a breakthrough curve from a two-well tracer test and confound interpretation based on that curve. Also, in a two-well tracer breakthrough test, when no tracer is detected in the recovery well, one does not know if the fluid reached the recovery well in amounts sufficient for tracer detection, if the fluids reached the recovery well at all or if the tracer was removed by reaction with reservoir fluids or rocks.

One means of studying tracer behavior is to use a conservative tracer, that is, one which is relatively unaffected by chemical processes in the reservoir. The extent of various effects on other tracers can be estimated by comparing the recovery concentration curves of conservative and nonconservative tracers.

Raft River

At Raft River, nine artificial tracers were investigated: I, Br, SCN, Mg, Li, K, B (as borax), disodium fluorescein and rhodamine-B. The reactivity of the anion tracers, I, Br and SCN, and the dye tracers, disodium fluorescein and rhodamine-B were tested through comparison with Cl, a tracer known to be conservative. Of the anion tracers, Br appears to be the least reactive. Iodide, the most commonly used groundwater tracer, was lost due to reactivity upon its first usage (test 2A-2), whereas later tests indicate complete recovery and even additional recovery of I from the earlier loss (test 4C). SCN, with 87% recovery, is slightly reactive. Recovery of the organic dyes disodium fluorescein and rhodamine-B, 91% and 100%, respectively, suggests that they are thermally stable up to the test temperature of 122°C. Their adsorbing properties are untested because of an earlier dye injection that went unmonitored which could have filled all adsorbing sites.

East Mesa

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 Cl, I, disodium fluorescein, SCN, and boron (as borax). 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.

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 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.

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 criterion was based on the initial assumption that Cl was conservative. Evidence for the validity of this assumption has been given by Ciccioli 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.

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.

The recovery ratios for the slug tracers are listed in Table 4, and recovery plots for SCN and B were shown in Figure 5. The predicted slug-tracer recovery curves for B and SCN were calculated on the basis of conservative behavior. 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

Figure 5. Recovery curves of slug tracers.

TABLE 4. RECOVERY RATIOS OF SLUG TRACERS

Test	Recovery Ratio
3(-30)	0.69 (B)
4(-30)	0.64 (SCN)
3(-19)	.85 (SCN), .96 (Na ₂ FL.) ¹
4(-19)	1.02 (B), .93 (Na ₂ FL.)
6(-19)	1.15 (SCN), 1.03 (Na ₂ FL.)

¹ Na₂FL. = disodium fluorescein

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 so that slug tracers in subsequent tests were not detectably adsorbed. The reasoning for this is as follows: the 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 SCN and B 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 adsorption 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 the slug injection.

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 aluminosilicates. As a result of our work, Na and K have been shown to be unsuitable tracers for the East Mesa system. The cation Li was also evaluated, and was shown to be conservative 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 tested 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.

The behavior of Sr, HCO_3 , F, Mg and Fe was also examined. Recovery plots of 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.

RESULTS--WATER/ROCK INTERACTION

East Mesa

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 6 (Ca) and 7 (SiO_2). Test 6(-19) is representative

of all tests on Well 56-19, as the parameters tested at this well site had little effect on the precipitation of Ca and SiO_2 .

Inspection of the recovery curves in Figures 6 and 7 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 56-30 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. 8; 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.

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 con-

Figure 6. Recovery curves contrasting Ca behavior in Wells 56-19 and 56-30. Dashed lines are predicted concentrations and solid lines are measured concentrations. V_I = Volume of injectate recovered.

Figure 7. Recovery curves contrasting SiO₂ behavior in Wells 56-19 and 56-30. See Figure 3 and text for explanation.

Figure 8. Normalized concentration of calcium vs. recovered fraction of injection volume (from Michels, 1983).

sidered 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 aluminosilicates have been predicted by theory and empirical data (e.g., Fournier and Truesdell, 1973). As shown in Figure 9, 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 9. Recovery curves contrasting behavior of Na and K in Well 56-19.

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