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ARTICLE *in* ENVIRONMENTAL GEOLOGY · JANUARY 1993

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Received: 22 June 1992 / Accepted: 22 December 1992

Abstract Safe disposal of thermally spent geothermal brines that contain environmentally hazardous constituents is commonly obtained by reinjection. The reinjection process also serves to maintain reservoir pressure, enhance thermal recovery, and eliminate possible compactional subsidence. To avoid premature thermal breakthrough of reinjected fluids, tracer tests are employed for detection and evaluation of preferential path networks. In this paper some promising tracers that have not received much attention in geothermal reservoir studies are discussed, and a comprehensive tabulation of field sites of artificial tracer utilization is presented. Chemical and transport processes responsible for tracer retention by the formation of reservoir solids, as well as available tracer detection techniques, are emphasized.

Key words Geothermal brines — Artificial tracers — Hazardous dissolved solids

Introduction

Thermally spent geothermal brines contain high levels of environmentally hazardous dissolved solids and ions that cannot be discharged as surface waters because of potential contamination of irrigation or potable water supplies (Bowen 1973; Ellis 1978; Weres 1988). A common practice for the safe disposal of geothermal wastewater is by reinjection (Crittenden 1981; Horne 1982a). The reinjection process also serves to maintain reservoir pressure, enhance thermal energy recovery (Sarmiento 1986; Bodvarsson and Stefansson 1989), and eliminate possible compactional subsidence (Lindsey and Supton 1975; Tsang and others 1980). How-

ever, the effects of reinjection are complex, and they are not easily predicted, particularly in vapor-dominated geothermal reservoirs (Schroeder and others 1982; D'Amore and others 1987). Several uncertainties associated with reinjection exist, such as the permeability reduction due to silica and calcite deposition, the inducement of seismic events, and, of most importance, the reduction of discharge enthalpy and decline in steam production owing to premature breakthrough of cooled recharge fluid. There is ample field evidence indicating that rapid breakthrough of reinjected wastewater to the production zone is due to the highly fractured nature of geothermal reservoirs (see e.g., McCabe and others 1983; Gudmundsson and others 1984). A detailed investigation of natural reservoir structure and preferential flow paths is important prior to full-scale reinjection so that the reinjection wells can be located appropriately (Horne 1982b). The design of reinjection systems should be such that the advancing wastewater is reheated by heat conduction from the formation matrix before reentering into a production well. An optimum design of a reinjection scheme is case specific and requires careful utilization of appropriate field experiments.

Traditional reservoir-engineering geologic studies can establish the existence of fractures but cannot provide means of detection and evaluation of preferential path networks. Tracer tests, however, can accomplish this purpose successfully. Tracer tests are divided into single-well and multiwell tests. In single-well or injection-backflow tracer tests, a physicochemically characterized fluid is spiked with an artificial tracer, if natural tracers are not applicable, and is injected in the formation (Davis and others 1985). The injected fluid is allowed to remain in the reservoir for a desired time period before the injection well is produced. The physicochemical changes observed between the injected and recovered fluids provide information on the chemical interactions of the tracer or the dissolved constituents of the injected fluid with the formation matrix, on the natural fluid flow, on the reservoir structure, and on the heat-transfer mechanism among the formation solids and the injected fluid (Wright 1984; Adams 1985). Although injection-backflow tracer tests provide informa-

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tion about the reservoir in the immediate vicinity of the well, which can be used for preliminary field evaluation and for subsequent multiwell tracer test design (Kocabas 1986, 1989; Kocabas and Horne 1987), they have not been used extensively in geothermal systems. In multiwell tracer tests, at least one production well is used to monitor continuously or periodically the physicochemical properties and tracer concentrations of the produced geothermal fluid.

The first tracer identification at the production well represents the arrival of the reinjected fluid. If the produced tracer is recycled, the volume of the circulating fluid is estimated from the long-term tracer dilution. The tailing of tracer breakthrough curves observed in geothermal studies to a certain extent implies a multidimensional flow field, but most importantly indicates that the transport of tracers through fractured reservoirs is governed by dispersion along with mass transfer into zones of immobile liquid, as well as by equilibrium and nonequilibrium processes associated with tracer interactions with the solid formation and other soluble species present in geothermal fluids. Diffusion of tracers from fractures into porous matrix is virtually always an important transport mechanism, unless matrix porosities are very low, fracture spacings are extremely small, and/or fracture apertures are large (Grisak and Pickens 1980). For relatively short (tens of hours) tracer experiments, the fracture spacing and matrix diffusion are of minor importance (Małozzewski and Zuber 1985); thus, matrix diffusion cannot explain the observed skewness of tracer breakthrough curves. Mathematical modeling of these transport mechanisms, in conjunction with assumptions based on geological and geochemical information, is used to estimate fracture aperture and to predict thermal breakthrough of reinjected fluids (see e.g., Walkup and Horne 1985). Although for certain geothermal reservoirs there is evidence of direct correlation between the rate of tracer return and thermal breakthrough (Horne 1982a), this correlation is site specific, dependent on unknown reservoir composition and geometry and in certain situations may not be a useful relationship (Pruess 1990). Furthermore, rapid tracer returns do not necessarily indicate premature thermal breakthrough because the velocity of the thermal front is related to the formation solid surface area available for heat transfer (Pruess and Bodvarsson 1984).

Accurate forecasting of fluid migration in geothermal fields, where thermally spent geothermal brines are reinjected, is particularly dependent on the type of tracer utilized. Since an ideal conservative tracer does not exist, a choice of a tracer with well-defined transport mechanisms that are easily incorporated into mathematical models should be employed. It should be mentioned that direct application of existing analytical solutions to tracer transport models may not be adequate in certain cases. For example, at an injection-extraction well pair, the produced fluid is pumped back into the injection well and tracer movement cannot be simulated accurately without taking into account the feedback due to recirculation (Kocabas and Horne 1988; Kocabas 1989; Chrysikopoulos and others 1990a). Therefore, interpretation of a tracer break-

through curve requires a complete knowledge of the stability and physicochemical retention processes of the employed tracer in conjunction with the most confident and precise mathematical description possible of the fundamental physical processes governing fluid flow.

The term tracer generally signifies a material whose properties or characteristics make it possible to follow the dynamic behavior of a flowing system. Tracers are categorized as either natural or artificial. Natural tracers are indigenous to the system under study, whereas artificial tracers are deliberately added. Natural tracers are stable or radioactive elements that occur naturally in the system being traced and should not be used as artificial tracers. The most frequently employed natural tracers as indicators of geothermal reservoir conditions are the environmental isotopes (e.g., H, ^2H , ^3H , ^{16}O , ^{18}O) and the atmospheric or radiogenic noble gases (e.g., He, Ne, Ar, Kr, Xe, ^{222}Rn). These elements serve to identify geothermal fluid ages, water sources, mixing processes, reactions between fluids and reservoir rocks, changes in reservoir temperature, interactions between adjacent producing wells, and the thermodynamic characteristics of geothermal reservoirs. There are numerous reviews and papers in the literature associated with applications of natural geothermal tracers, e.g., Ellis (1977), Kruger and others (1977), Mazor (1977), Panichi and Gonfiantini (1978), Andrews (1983), Hulston (1983), D'Amore and Truesdell (1984), Semprini and Kruger (1984), Mazor and Truesdell (1984), Semprini (1985), D'Amore and others (1987), to mention a few.

This paper presents a comprehensive review of artificial tracers applicable mainly to studies in liquid-dominated geothermal systems. Tracer physicochemical characteristics are discussed, and tracer detection techniques as well as criteria for choosing appropriate tracers are summarized. Tracers employed in geothermal investigations around the world, published in numerous reports, proceedings, and journal articles, are compiled in a tabular format. Some promising tracers that have not received much attention in geothermal tests and several recently developed tracers are also presented.

Tracer selection requirements

A satisfactory geothermal tracer should fulfill certain requirements associated with its conservation in the reinjected brine. Conservation of an artificial tracer in geothermal systems is difficult to ensure, owing to the complex chemical environment and high temperatures encountered. The tracer should be compatible with the chemistry of the geothermal fluid. It should not be lost in the reservoir by such processes as physical adsorption, chemisorption reactions, or ion exchange with the rock minerals. The tracer should not be susceptible to thermal degradation during transport through a high-temperature reservoir. It should be easily detectable in the fluid at the wellhead. The tracer should have a low background concentration in the geothermal fluid, preferably lower than

the minimum detectable level obtained by available detection techniques. Furthermore, for economic justification the tracer capital cost should be attractive, for environmental reasons the tracer should be nontoxic, and for practical purposes the tracer should be widely available. Moreover, a major consideration should be the tracer solubility limit; insoluble compounds are definitely undesirable. Selecting a suitable tracer that satisfies most of these criteria is not a trivial task.

Inappropriate tracer selection is not the only cause for tracer test failures. If an injection–production well pair interconnection is verified by interference testing, unsuccessful detection of a relatively conservative tracer at the observation well can be attributed to several factors. For example, high dilutions may reduce the tracer concentration below detection limits. Moreover, if the necessary prior information regarding the sampling frequency is unknown, a tracer response with a relatively sharp peak may be skipped completely when continuous monitoring is not employed.

Physicochemical tracer retention processes

Tracer retention by the formation of reservoir solids occurs mainly through sorption phenomena. Sorption is a general expression for processes, such as adsorption, physical adsorption, chemisorption, and ion exchange, which involve a selective uptake of one or more species contained in one phase by a second phase. Although sorption processes can take place at an interface between any two phases, here the second phase is assumed to be a solid. Sorption processes can be complex and depend on many variables, including temperature, pressure, solution pH, solution ionic strength, adsorbent surface charge, adsorbent sorptive capacity, and presence of species that compete for sorption sites.

Tracer arrival times are often overestimated by present numerical reservoir models (e.g., Adams and others 1989), possibly due to inaccurate estimation of flow parameters and inappropriate or no mathematical modeling of the tracer sorption processes. Tracer sorption onto geothermal formations is customarily assumed to be of minor importance, since moderate- and high-temperature reservoirs have little clay and organic-rich matter is relatively uncommon. Although several of the frequently employed geothermal tracers have been shown to sorb onto laboratory cores under standard conditions and high oxygen contents (Johns 1987), their sorption may be reduced at geothermal conditions. For example, iodide is expected to adsorb less at high temperatures; however, its exact sorption behavior in geothermal environments has not been fully explored. For a comprehensive representation of sorbing tracer transport in geothermal reservoirs, a retardation factor should be included in the governing partial differential equation. Furthermore, it is more realistic to assume that the retardation factor is spatially vari-

able. We borrow these concepts from the relatively mature field of groundwater research, where the distribution coefficient is no longer considered a position-independent constant (Durant and Roberts 1986; Roberts and others 1986), and the effects of spatially variable retardation on sorbing solute transport have been investigated (Chrysikopoulos and others 1990b, 1992). Borrowing from other fields is not uncommon in the geothermal industry; on the contrary, it has contributed to the maturity of geothermal reservoir simulation (Pruess 1990) and certainly will help future developments of other geothermal aspects.

Artificial tracers

The artificial tracers are divided into stable, radioactive, and reactive substances. The stable tracers are subdivided into chemical and activable tracers. Furthermore, the stable chemical tracers as well as the stable activable tracers are divided into inorganic and organic, whereas the stable chemical organic tracers are subdivided into fluorescent dyes and substituted aromatic acids. The classification of the artificial geothermal tracers is shown schematically in Fig. 1. Note that there are some overlaps in the categories (i.e., substituted aromatic acids and fluorescent dyes are both stable and reactive, depending on the temperature of the geothermal system).

Stable chemical tracers

Inorganic ionic tracers

Several ionic substances have been employed extensively as geothermal tracers. Inorganic ionic tracers are intro-

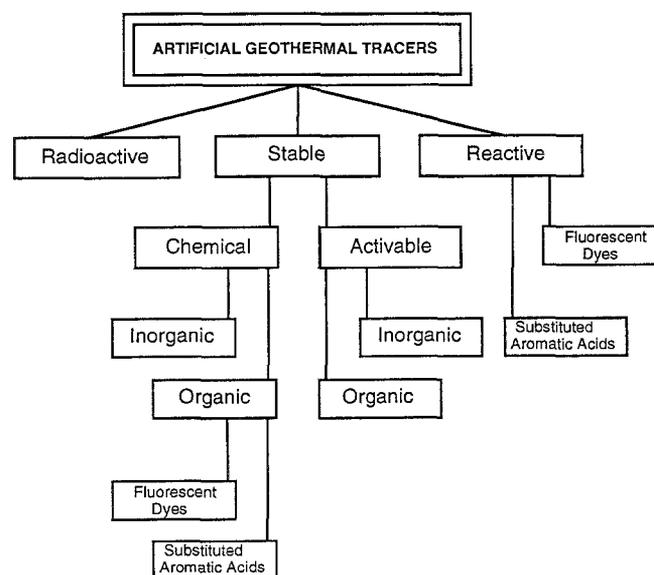


Fig. 1. Classification of artificial geothermal tracers.

Table 1. Properties of some alkali halides, associated halogen anions, and field sites of utilization

| Salt | Mol wt | Solubility (g/100 cc) ^a | Anion | Anion Conc. in Geothermal Fluids (ppm) ^b | Field sites ^c |
|------|--------|---|-----------------|---|--------------------------|
| NaF | 41.99 | 4.22 ¹⁸ | F ⁻ | ≤ 35 | |
| KF | 58.10 | 92.3 ¹⁸ –v.s. | F ⁻ | ≤ 35 | |
| LiCl | 42.39 | 63.7 ⁰ –130 ⁹⁵ | Cl ⁻ | ≤ 241,000 | a |
| NaCl | 58.44 | 35.7 ⁰ –39.12 ¹⁰⁰ | Cl ⁻ | ≤ 241,000 | |
| KCl | 74.56 | 23.8 ²⁰ –56.7 ¹⁰⁰ | Cl ⁻ | ≤ 241,000 | |
| NaBr | 102.90 | 116.0 ⁵⁰ –121 ¹⁰⁰ | Br ⁻ | 0.1–3,030 | a, c |
| KBr | 119.01 | 53.48 ⁰ –102 ¹⁰⁰ | Br ⁻ | 0.1–3,030 | b |
| NaI | 149.89 | 184 ²⁵ –302 ¹⁰⁰ | I ⁻ | ≤ 105 | a, c |
| KI | 166.01 | 127.5 ⁰ –208 ¹⁰⁰ | I ⁻ | ≤ 105 | b, d, e, f, g |

^a Data from Weast (1984) Superscripts indicate temperature in °C; v.s.—very soluble

^b Data from Tsai and others (1978) and Cosner and Apps (1978)

^c a, East Mesa, California (Capuano and others 1983; Adams 1985); b, Kakkonda, Japan (Horne 1982b, 1985); c, Raft River, Idaho (Downs and others 1982; Capuano and others 1983; d, Hatchobaru, Onuma, and Otake, Japan (Horne 1982b, 1985); e, Svartsengi, Iceland (Gudmundsson and others 1984); f, Klamath Falls, Oregon (Johnson 1984); g, Los Azufres, Mexico (Horne and Puente 1989)

duced into the hydrothermal fluids primarily in the form of moderately soluble common salts. However, ionic tracers exhibit potential reactivity and high natural background. Generally, anions tend to be more conservative than cations in natural subsurface systems (Wagner 1977; Stumm and Morgan 1981). Adams (1985) tested sodium, potassium, and lithium at the East Mesa geothermal system and observed that these monovalent cations undergo reversible adsorption. For this reason, stable inorganic cationic tracers have received less attention in geothermal studies.

The alkali halides are the most commonly used salts for groundwater and hydrothermal fluid tracing. Some properties of interest of the sodium and potassium halide salts, together with the geothermal fluid natural background concentration range of the associated anions, are given in Table 1. The concentration of fluoride is temperature-dependent due to fluid–mineral equilibria and exhibits the lowest background concentration in hydrothermal fluids. Unfortunately, fluoride is an unsatisfactory tracer in low-temperature environments because it is retarded considerably (Flühler and others 1982). Similarly, in low-temperature tracer environments, iodide displays retardation (Malcolm and others 1980) and is a less conservative tracer than either bromide or chloride (Davis and others 1980), but it is favorable in geothermal systems because of its relatively low natural background concentration and reduced sorption at elevated temperatures in the presence of low oxygen concentrations. However, it should be noted that iodide backgrounds may be higher in geothermal waters than in groundwater. Iodide is easily oxidized and transformed in the presence of organic matter (Bowman 1984); aerobic conditions and microbiological activity, however, do not prevail in geothermal systems. Bromide and chloride require injection of large quantities to assure tracer concentrations distinguishable from the natural background at the sampling locations. Introduction of rather high concentrations of salt solutions is not only undesirable due to the increased cost, but for the possible anomalous transport processes caused by density effects

and gravity segregation (Krupp and Elrick 1969; Rose and Passioura 1971). Furthermore, the halides are introduced into geothermal fluids in the form of salts (see Table 1); thus, cation geothermometry of the geothermal fluids may be hindered (Adams 1985).

Among the halides, iodide is recommended for geothermal tracer studies; bromide and chloride are useful only when their natural background concentrations are low. However, iodide may not be an ideal tracer since it has shown tendency to adsorb onto laboratory cores (Breitenbach and Horne 1982; Johns 1987). On the other hand, Adams (1985) reported that iodide behaved conservatively in the East Mesa field tests.

There are numerous detection and analytical techniques available for the analysis of inorganic ionic tracers. Ion selective electrodes (ISEs), which are portable and easy to use by relatively inexperienced operators, can be employed for economical and fast tracer detection. ISEs are sensors consisting of a natural electrode and a membrane that indicates a potential specifically proportional to the determinant activity. There are several types of membranes available (Koryta and Stulik 1983). The solid-state ISEs are suitable for the detection of halides. Detection sensitivity achievable by ISEs is of the order of 0.5 mg/l; however, other interfering ions present in the sample solutions may cause some bias on the observed measurements, or even hinder completely detection of the specific ion (e.g., Downs and others 1982; Gudmundsson and others 1984). Ion chromatography (IC) is another effective method for sensitive, specific, and precise analysis of ionic species. This method is more expensive and time consuming than ISEs, but it is more attractive than other complex analytical detection techniques. Ion chromatography is based on the principle of a differential distribution of sample components along a resin column, caused by the discriminative affinity of the various ions for the column resin, in conjunction with ion quantitation of the eluted species by a specific conductance detection system (Miller 1988). The detection sensitivity of IC is at least an order of magnitude greater than that of ISE.

Organic tracers

The two major categories of organic tracers are the fluorescent dyes and the substituted aromatic acids. Fluorescent dyes are organic substances whose molecules are capable of converting excitation energy caused by light into fluorescence. Because selective fluorescent dyes are inexpensive (Smart and Laidlaw 1977), relatively nontoxic (Clarke and Anliker 1980; Jensen and Kristensen 1989), and very easy to detect by spectrofluorometry or filter fluorometry at parts per billion levels if background fluorescence is negligible (Warner 1986), they have been used extensively as tracer substances in various types of groundwater/hydrologic studies (e.g., Smart and Smith 1976; Aulenbach and others 1978; Smettem and Trudgill 1983; Aldous and Smart 1988) and geothermal systems (see references cited in Table 2 below).

Fluorescent dyes are sensitive in various degrees to pH changes, salinity, and high chloride concentrations (Smart and Laidlaw 1977), exhibit photochemical (Tai and Rathbun 1988) and chemical (Feuerstein and Selleck 1963) decay, and are susceptible to adsorption losses onto sediment surfaces (Kaufman and Orlob 1956; Scott and others 1969) and ferric hydroxide deposits (Aldous and Smart 1988). Furthermore, at the elevated geothermal reservoir temperatures, most of the organic dyes are likely to break down and lose their fluorescent properties. Experimental studies have shown that rhodamine-WT and fluorescein in the presence of atmospheric oxygen appear very unstable at 200°C (Al-Riyami 1985); however, the degradation of fluorescein is suppressed at relatively high pH values (pH > 8.6) and low oxygen concentrations (Adams and others 1986a; Adams and Davis 1991).

A comprehensive evaluation of several common fluorescent dyes in low-temperature tracing environments has been presented by Smart and Laidlaw (1977). It was suggested that rhodamine-WT, lissamine-FF, and amino-G-acid are the most advantageous among the fluorescent dyes considered and that they can be used simultaneously without interference. Aldous and Smart (1988) have found that dyes with sulfonic functional groups are suitable for

fields where ferric hydroxide deposits are present. Thompson and others (1974) reported results from tracing experiments through a porous medium where fluorescein dye was unsuccessful. These findings and associated conclusions are suitable for groundwaters and to various degrees may not be valid for geothermal fluids.

Fluorescein, rhodamine-B, and rhodamine-WT are the only dyes reported that have been used in geothermal applications; the field sites are listed in Table 2. These fluorescent dyes have been selected primarily for their relatively higher detection sensitivities (see Table 2). Fluorescein is used mainly as a drug and cosmetic dye under the official Food and Drug Administration name D&C Yellow No. 8 (Colour Index 1971). Rhodamine-B [D&C Red No. 19 (Colour Index 1971)] is considered potentially carcinogenic and should not be used in groundwaters. Rhodamine-WT is a patented fluorescent dye developed exclusively for water tracing (Stryker 1968). Fluorescent dyes suffer from several formation-retention processes in low-temperature environments due to sorption in soils. At the elevated temperatures of geothermal reservoirs, sorption of selective fluorescent dyes may be of less importance. For example, fluorescein was shown to be unsusceptible to sorption processes in field experimental studies at Dixie Valley where the reservoir temperature was 243°C and the duration period of the test 2.5 months (Adams and others 1989), whereas rhodamine-WT appeared to suffer from adsorption and/or thermal degradation at Svartsengi where the temperature was 235°C and the test lasted one month (Gudmundsson and others 1984). The thermal degradation rate of a fluorescent dye at a given temperature certainly can be measured experimentally. Adams and Davis (1991) measured the kinetic parameters of fluorescein at temperatures up to 290°C, and they concluded that the dye decays less than 10% at temperatures below 210°C during a one-month time period. If the thermal degradation rate of a nonsorptive fluorescent dye is sufficiently low, it can be used successfully in high-temperature geothermal fields by applying appropriate correction factors to the observed tracer concentrations. It should be noted that the correction for decay requires that more than one tracer be in-

Table 2. Some properties of a few fluorescent dyes and field sites of utilization

| Dye | CI No. (generic name) ^a | Chemical formula | Mol wt | Detection limit (µg/l) ^b | Field applications ^c |
|--------------|------------------------------------|--|---------|-------------------------------------|---------------------------------|
| Fluorescein | 45350 (acid yellow 73) | C ₂₀ H ₁₀ O ₅ Na ₂ | 376.276 | 0.29 | a, b, c, d, e, f, g, i |
| Rhodamine-B | 45170 (basic violet 10) | C ₂₈ H ₃₁ N ₂ O ₃ Cl | 479.017 | 0.010 | a |
| Rhodamine-WT | | C ₂₉ H ₂₉ N ₂ O ₅ Na | 508.548 | 0.013 | e, h |

^a CI—Colour Index, a five-digit constitution number that uniquely identifies the dye structure (Colour Index 1971)

^b Readings with a Turner-111 filter fluorometer at 10% in excess of background fluorescence for distilled water or 1 scale unit (Smart and Laidlaw 1977)

^c a, Raft River, Idaho (Downs and others 1982; Capuano and others 1983); b, Hatchobaru, Japan (Horne 1982b, 1985); c, East Mesa, California (Capuano and others 1983; Adams 1985); d, Palinpinon I, Philippines (Urbino and others 1986); e, Klamath Falls, Oregon (Gudmundsson and others 1983; Johnson 1984); f, Dixie Valley, Nevada (Adams and others 1989); g, Cornwall, England (Batchelor 1986); h, Svartsengi, Iceland (Gudmundsson and others 1984); i, Fenton Hill, New Mexico (Tester and others 1986)

jected simultaneously, a procedure that is commonly employed with reactive tracers.

Substituted aromatic acids designate a large class of compounds consisting mainly of organic molecules such as benzoic acid and phenylacetic acid (Adams and Moore 1985; Adams and others 1986b). Substituted aromatic acids have low background concentrations in geothermal fluids, low toxicity at tracer concentrations, and excellent detectability at parts per billion to parts per trillion levels by GC-MS (gas chromatography-mass spectrometry) or by the relatively less expensive GC-EC (gas chromatography with electron capture detector). The usefulness of substituted aromatic acids as geothermal tracers has been demonstrated by Adams and others (1989) in tracing experiments at Dixie Valley, a geothermal reservoir consisting primarily of gabbro and altered basalts, where fluorescein, benzoic, benzenesulfonic, and 4-ethylbenzenesulfonic acid were injected, but only benzoic acid and fluorescein were detected in a production well.

The thermal stability of a large collection of substituted aromatic acids in distilled water at molecular oxygen concentrations typical of geothermal fluids and temperatures ranging from 125 to 250°C has been investigated through batch laboratory experiments by Adams and others (1986a,b). It was concluded that, over the experimental duration period of one week, the sulfonated, methylated, and carboxylated groups remained relatively stable at 250°C. Among this large selection of substituted aromatic acids, several compounds may be proven to meet most criteria of promising geothermal tracers. Possible disadvantages of these organic compounds, however, are their susceptibility to thermal decay in the presence of molecular oxygen and their vulnerability to microbial degradation. At geothermal reservoir conditions, molecular oxygen concentrations are low and microbial growth practically nonexistent; therefore, care must be taken only to exclude oxygen from reinjected fluids and to pretreat the collected liquid samples appropriately to avoid tracer biodegradation during the delay time until instrumental tracer concentration measurement. Although most of the previously described substituted aromatic acids are negatively charged at typical pH values of natural groundwaters (Adams and others 1986a) and hence can be considered relatively nonsorptive, their interactions with solid formations at geothermal conditions have not yet been investigated in a thoroughly quantitative fashion. However, Adams and others (1986a) indicated that several substituted aromatic acids are not expected to sorb at high temperatures.

Stable activable tracers

Activable tracers are readily available stable elements, which, in conjunction with activation analysis, yield an excellent detection sensitivity at extremely low tracer concentrations. An activable tracer must meet the requirements of conservative geothermal tracers as well as the necessary parameters demanded by the activation analysis technique. These additional parameters are: a large natural

isotopic abundance, large neutron activation cross sections, a product radionuclide with appropriate gamma radiation for measurement by gamma-ray spectrometry, and a product radionuclide with an optimum half-life. The half-life of the product radionuclide should be long enough to permit a distinguishable counting rate after a cooling period between the end of irradiation and measurement of the activity. The quantity of the stable element used for geothermal tracing is dependent upon the expected tracer dilution and the neutron flux available. The higher the neutron flux, the smaller the quantity of stable element required. Clearly, activable tracers require convenient neutron irradiation facilities for the activation analysis. It is therefore troublesome if there is no access to a nearby neutron source.

The technique of neutron activation analysis is a unique combination of nuclear and chemical processes selected to optimize the precision and accuracy of trace-element analysis. A sample is irradiated by neutrons, and both quantitative determination and qualitative identification of the tracer elements are achieved by detection and measurement of the induced radioactive products (Kruger 1971). For simplicity, the comparator radioactivation analysis is frequently employed (e.g., Chrysikopoulos and Kruger 1986a). This method requires only relative measurements, and it is based on identical irradiation and counting treatment of the standards and samples (Kruger 1971; Robertson and Carpenter 1974).

An optimization analysis, based on chemical composition of geothermal effluents and activable tracer requirements, suggested stable ^{51}V , ^{59}Co , ^{115}In , and ^{164}Dy isotopes as potential activable tracers (Chrysikopoulos and Kruger 1986b). The thermal neutron activation products of these potential activable tracers, together with relevant nuclear properties, are given in Table 3. Indium is considered to be an excellent activable tracer because of its unique combination of good detection sensitivity (see Table 3) and low background concentration in geothermal fluids, less than 100 ppb (Cosner and Apps 1978). Furthermore, indium has only two naturally occurring isotopes, ^{113}In and ^{115}In , with isotopic abundances of 4.3% and 95.7%, respectively (Lederer and Shirley 1978), also, the induced product of the reaction $^{115}_{49}\text{In}(n, \gamma)^{116\text{m}}_{49}\text{In}$ has a half-life of 54.12 min and provides adequate radiation measurement at concentrations far below chemical tracers.

The majority of activable tracers can not be used as simple cationic tracers because at the pH of most geothermal fluids they hydrolyze with rapid formation of reversible hydrolysis products. Therefore, to enhance conservation of activable tracers in geothermal fluids it is necessary to chelate the metal isotopes to ensure geochemical stability and mobility, as well as to prevent hydroxide precipitation. The organic ligands ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) can serve this purpose well, because they have low-molecular-weights and form water-soluble complexes with most metal ions.

Activable tracers have been used frequently in hydrological investigations in both subsurface (Schmotzer and others 1973; Behrens and others 1977) and surface (Kruger

Table 3. Properties of some potential activable tracers

| Target nuclide | | | | Product nuclide | | | | |
|----------------|----------------------------------|-------------------|---------------------------------|--|------------------------------|------------------------|------------------------------------|-------------------------------|
| Element | Conc. in geothermal fluids (ppb) | Target isotope | Isotopic abundance ^a | $\sigma_{(n,\gamma)}$ (barns) ^{a,b} | Product isotope ^c | $T_{1/2}$ ^a | Major- γ (MeV) ^a | Sensitivity (ng) ^d |
| V | <5 ^e | ⁵¹ V | 0.997 | 4.88 | ⁵² V | 3.75 m | 1.434 | 50.424 |
| Co | 14–18 ^f | ⁵⁹ Co | 1.000 | 19 | ^{60m} Co | 10.47 m | 0.059 | 0.896 |
| In | <100 ^e | ¹¹⁵ In | 0.957 | 70 | ^{116m} In | 54.12 m | 1.294 | 0.237 |
| Dy | <2,000 ^e | ¹⁶⁴ Dy | 0.281 | 900 | ¹⁶⁵ Dy | 2.33 h | 0.095 | 0.041 |

^a The nuclear data have been adapted from Lederer and Shirley (1978)

^b $\sigma_{(n,\gamma)}$ —thermal neutron cross section (barn = 10^{-24} cm²)

^c *m* stands for metastable (decay by γ -radiation from an excited state to the ground state)

^d Corresponds to the minimum total tracer mass in the sample necessary to obtain 60 cpm after 10-min irradiation in thermal neutron flux of 5.0×10^{12} n/cm²-s and 30-min delay time until measurement; (ng = 10^{-9} g)

^e Cosner and Apps (1978)

^f Tsai and others (1978)

and Channell 1970; Navada and others 1981) flows. Employment of activable tracers in geothermal systems has not yet been reported. However, Chrysikopoulos and Kruger (1987) have shown through batch laboratory experiments that chelated indium is a reliable activable tracer for low- to moderate-temperature geothermal systems. Indium chelates of EDTA and NTA are degraded at and above 200°C through a metal dissociation mechanism. Furthermore, EDTA is more favorable than NTA because indium liberation is inversely proportional to the magnitude of the metal ligand formation constant. Moreover, some preliminary results of chelated indium adsorption onto graywacke indicated that tracer sorption losses may be insignificant. Laboratory experiments do not fully represent field situations, because the chemistry of geothermal fluids is temperature dependent (Kacandes and Grandstaff 1989). Therefore, care is necessary in applying laboratory results to actual geothermal systems.

Radioactive tracers

Radioisotopes are available in wide selections according to material property, radiation energy, and half-life. The half-life of a convenient radioactive tracer must be at least three to five times the expected average hydraulic residence time of the geothermal reservoir under investigation. To ensure geochemical stability and mobility in subsurface tracer applications, as well as to prevent hydroxide precipitation of certain cationic radioactive tracers, organic ligands are commonly employed. Some useful organic ligands that serve this purpose, together with their chemical, and thermal stability properties have been presented in the previous section. The major drawback of radioactive tracers is the safety hazard to the operators, population, and environment. Although reasonable precautions may be taken for the use of radioactive tracers in subsurface reservoir testing, the public reaction has generally been one of fear and mistrust. Because of the potential radiation hazards of radioactive tracers, local, state, and federal reg-

ulations prohibit their field applications in many countries worldwide.

Radioactive tracers are easy to measure by their emitted gamma or beta radiation with great sensitivity and negligible interference. Continuous measurement is achievable with an on-line radiation monitoring system, but most frequently measurements are taken at regular time intervals by collecting a small aliquot and counting its radioactivity under standardized conditions.

Radioactive tracers have been used extensively in groundwater (e.g., Meyer and others 1981; Pickens and Grisak 1981), flood runoff (e.g., Pilgrim 1978), soil cores (e.g., White and others 1984), and petroleum reservoirs (e.g., Heisler 1988; McIntyre and others 1988; Allison and others 1991) to mention a few of the many applications. The most commonly employed radioactive tracers for subsurface investigations together with their type of radiation and half-life are listed in Table 4. Among all possible radioactive tracers available, according to the literature, only ³H, ⁸²Br, and ¹³¹I have been used in geothermal reservoir studies; the field sites of their utilization are cited in Table 4.

Tritium, in the form of tritiated water, is considered the best tracer available for vapor-dominated geothermal fields, but it should not be used as an artificial tracer because tritium injection interferes with natural tritium studies. Tritiated water travels with the same velocity and changes phases like normal water. Tritium emits low-energy β -particles (0.018 MeV) and can be easily transported and handled without radiation hazards. Tritium is less expensive than most radioisotopes, but it is more difficult to measure because its low radiation energy requires sophisticated detection equipment. The measurement of tritium in water samples is obtained by gas-proportional or liquid-scintillation counting, with detection limits 2 and 10 TU, respectively (Florkowski 1981; Jouzel and Merlivat 1981), where TU is the tritium unit and represents one tritium atom in 10^{18} atoms of hydrogen or an activity of 3.19 pCi/kg of water. The detection sen-

Table 4. Properties of some radioactive tracers and geothermal field sites of utilization

| Radionuclide | Type of radiation | $T_{1/2}$ ^a | Field applications ^b |
|-------------------|-------------------|------------------------|---------------------------------|
| ³ H | β^- | 12.3 y | a, b |
| ⁵¹ Cr | γ | 27.8 d | |
| ⁶⁰ Co | β^-, γ | 5.27 y | |
| ⁸² Br | β^-, γ | 35.4 h | c, d |
| ⁸⁵ Kr | β^-, γ | 10.7 y | |
| ¹³¹ I | β^-, γ | 8.04 d | c, e, f, g |
| ¹⁹² Ir | β^-, γ | 72.2 d | h |
| ¹⁹⁸ Au | β^-, γ | 2.70 d | |

^a Lederer and Shirley (1978), (h-hour, d-day, y-year)

^b a, Ahuachapan, El Salvador (Einarsson and others 1975); b, The Geysers, USA (Gulati and others 1978); c, Fenton Hill, New Mexico (Tester and others 1982); d, Wairakei, New Zealand (McCabe and others 1983); e, Wairakei and Broadlands, New Zealand (McCabe and others 1983; McCabe and Barry 1985); f, Tongonan, Philippines (PNOC 1981); g, Palinpinon I, Philippines (Urbino and others 1986); h, Los Azufres, Mexico (Horne and Puente 1989)

sitivity can be increased to 0.1 TU if the aliquots are enriched by gas chromatography (Hoy 1968), thermal diffusion (Verhagen 1967), and electrolysis (Taylor 1981; Florkowski 1981).

Reactive tracers

Reactive tracers are temperature-sensitive chemically reacting compounds by which the rate of thermal drawdown of a geothermal formation can be measured directly. A reactive tracer is injected into a geothermal reservoir, and concentration–time behavior of the tracer or reaction product is detected at a near by production well, followed by evaluation of tracer conversion or reaction completion. At a later time, when some thermal drawdown has been attained, subsequent reactive-tracer experiments will probably lead to a reduced conversion to the reactant. Thus, the rate of thermal drawdown can be measured by analyzing the decay product, since a reactive tracer undergoes an irreversible, first-order reaction that is controlled by the residence time and the temperature of the system (Robinson 1985; Batchelor 1986; Tester and others 1986, 1987). The effective reservoir temperature can be obtained when two tracers with different thermal degradation rates are used simultaneously by monitoring the change in the ratio of the tracer concentrations (Adams and Davis 1991). The technique used by Adams and Davis (1991) also is capable of providing a conservative return profile.

In addition to the requirements associated with the conservation of an artificial tracer in geothermal reservoirs, a reactive tracer should possess specific reaction kinetic parameters so that the reciprocal of the first-order rate constant at the highest formation temperature equals the average residence time of the tracer. Furthermore, the proposed rate law for the actual reaction mechanism should predict accurately the behavior of the reactive tracer at various geochemical conditions, otherwise a new rate

law must be derived for each set of field conditions that may be encountered (Robinson 1985). In field situations where reaction rates may be very fast or very slow, reactive tracers will not provide any useful information on the thermal drawdown of a reservoir (Robinson 1985). The theoretical development of reservoir analysis using reactive tracers as well as the treatment of experimental reactive tracer data have been reported by Tester (1985), Robinson (1985), and Tester and others (1986, 1987).

Appropriate reactive tracers that have been proposed for use in geothermal reservoirs at 70–125°C are ethyl acetate, ethyl propionate, and isopentyl acetate; at 150–200°C, ethyl pivalate, and acetamide (Tester 1985); and at temperatures greater than 200°C fluorescein is suitable as a reactive tracer (Adams and Davis 1991). Reactive tracers have been used at the Rosemanowes site in Cornwall, England (Batchelor 1986), Fenton Hill hot dry rock reservoir in New Mexico, USA (Tester and others 1986), and Dixie Valley in Nevada, USA (Adams and others 1989). The results of these tests indicate that reactive tracers should be a better means of evaluating thermal drawdown than measuring the temperature decrease in the extracted fluid. Although organic compounds have a stronger tendency for sorption than inorganic substances, many organic tracers at certain conditions have been shown to move at the same velocity as water (i.e., Ciccioli and others 1980; Malcolm and others 1980). Thus, among the proposed reactive tracers, several may be nonsorptive in geothermal systems.

Summary

Most types of artificial tracers applicable for use in geothermal reservoirs have been reviewed. Inorganic halide tracers have received much attention in geothermal studies because they exhibit low reactivity and good detectability. Organic tracers such as fluorescent dyes and substituted aromatic acids have low background concentration, good detectability, and low toxicity at dilute concentrations, but in certain circumstances they may suffer from thermal degradation and/or sorption losses. Several radioactive tracers for geothermal applications can be selected from the available radioisotopes, which can be incorporated into a wide variety of organic and inorganic compounds. Although many radioactive tracers have excellent detection sensitivity at extremely low tracer concentrations, it is difficult to get permits for them because of public perceptions. On the other hand, stable activable tracers offer a reasonable compromise between retaining the advantages of radioactive tracers without the possibility of creating health and environmental hazards, such as those that may occur with the introduction of highly radioactive materials into the reinjected geothermal fluid, but the measurement of activable tracers in the fluid at the wellhead requires laborious procedures. Finally, reactive tracers are excellent for direct measurement of thermal drawdown of a geothermal formation, but the analysis of reactive tracer data

requires experimentally derived correction factors. Clearly, there is no single substance currently available that is an ideal geothermal tracer under all field conditions. However, most geothermal operators are satisfied with a knowledge of the injection–production flowpath directions and velocities. Further research is needed to identify all possible compounds that can be classified as unique, environmentally acceptable tracers for geothermal reservoir studies.

Acknowledgments The author is indebted to Charalambos Papelis, Lewis Sempirini, and Robert Johns for their contributions to this paper. Appreciation is extended to Dr. L. J. Patric Muffler for his helpful suggestions.

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