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THE POTENTIAL OF SF$_6$ AS A GEOTHERMAL TRACER

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Abstract—A novel application of gaseous sulphur hexafluoride (SF$_6$) tracer, in the evaluation of bulk water flow through an artificial geothermal reservoir, the Hot Dry Rock (HDR) reservoir at Rosemanowes quarry, south west England, is described. The potential advantages of SF$_6$ as a tracer, and details of its deployment and analysis are outlined. In a 52 h continuous borehole pumping test in the HDR reservoir, SF$_6$ and sodium fluorescein (NaFl) were injected simultaneously in a mass ratio of 7.5×10^{-7} SF$_6$:NaFl and analysed in production well waters. Resultant tracer response curves demonstrate conservation of the injected tracer mass ratio throughout the first 25 h of the test. However, substantial divergence of the curves beyond 25 h reflects significant tracer fractionation, most probably a consequence of selective diffusion and enhanced SF$_6$ residence times in some of the longer residence time flow paths of the system. These preliminary results clearly indicate the strong potential of SF$_6$ as a water tracer in this, and in related groundwater applications.

Key words—sulphur hexafluoride, SF$_6$, sodium fluorescein, NaFl, chemical tracers, geothermal reservoir evaluation, borehole pumping tests

INTRODUCTION

Conservative chemical tracers used to determine transport pathways must meet stringent performance criteria. Tracers for use in geothermal reservoir evaluation are required to retain their chemical integrity under temperature and pressure extremes, high concentrations of total dissolved solids (TDS) and large excursions in solution pH. The HDR ("Hot Dry Rock") geothermal research facility in the Carnmenellis granite at Rosemanowes Quarry, south west England, is a 2 km deep, artificial geothermal reservoir, characterised by widely spaced subvertical jointing and with a high geothermal gradient $\sim 34°C$ km^{-1} (Parker, 1989). Investigations of its flow characteristics (Kwakwa, 1988; Nazroo and Bennet, 1989; Richards *et al.*, 1989, 1994) have used principally sodium fluorescein (NaFl) and secondarily Br$^-$ (as NH$_4$Br) as routine tracers. Both are inert within the ranges of temperature ($<80°C$) and TDS (<250 mg l^{-1}) encountered in the Rosemanowes system. However, for high enthalpy geothermal systems with injection wells, characterised by much higher temperatures and salinities than at Rosemanowes, the value of NaFl and Br$^-$ would be severely limited; NaFl is susceptible to thermal degradation (Tester *et al.*, 1986), and for Br$^-$

increases in the natural background can result in substantially decreased measurement resolution. Therefore, we are currently investigating additional chemical tracers better suited to high temperature, high-TDS environments.

We describe briefly here some initial results from a preliminary borehole pumping test at Rosemanowes Quarry, involving NaFl used in conjunction with sulphur hexafluoride, SF$_6$, a tracer which would overcome the limitations of NaFl and Br$^-$ outlined above. SF$_6$ is a sparingly soluble gas with no known natural sources, manufactured for use in industry, and with a unique combination of properties which make it an ideal environmental tracer. It has an extremely low and constant atmospheric background, currently $\sim 3.0 \times 10^{-12}$ v/v, and it can be routinely detected in ambient air and at extreme aqueous dilutions $\sim 10^{-18}$ kg kg^{-1} (i.e. $\sim 10^{-17}$ molar) by electron capture gas chromatography (EC-GC). It is inert over a wide range of environmental conditions, non-toxic, inexpensive and safe to handle. One additional important aspect of SF$_6$ is its extremely low aqueous solubility (Willhelm *et al.*, 1977), which gives it the potential to delineate unsaturated zones underground, an application to which non-volatile tracers are unsuited. Large-scale tracer experiments with SF$_6$ are of currently increasing importance in the atmospheric and ocean sciences and are now becoming routine (e.g. Brown *et al.*, 1986; Watson and Ledwell., 1987; Wanninkhof *et al.*, 1985, 1987; Upstill-Goddard *et al.*, 1990, 1991; Watson *et al.*, 1991, Ledwell *et al.*, 1993). SF$_6$ has also been used as

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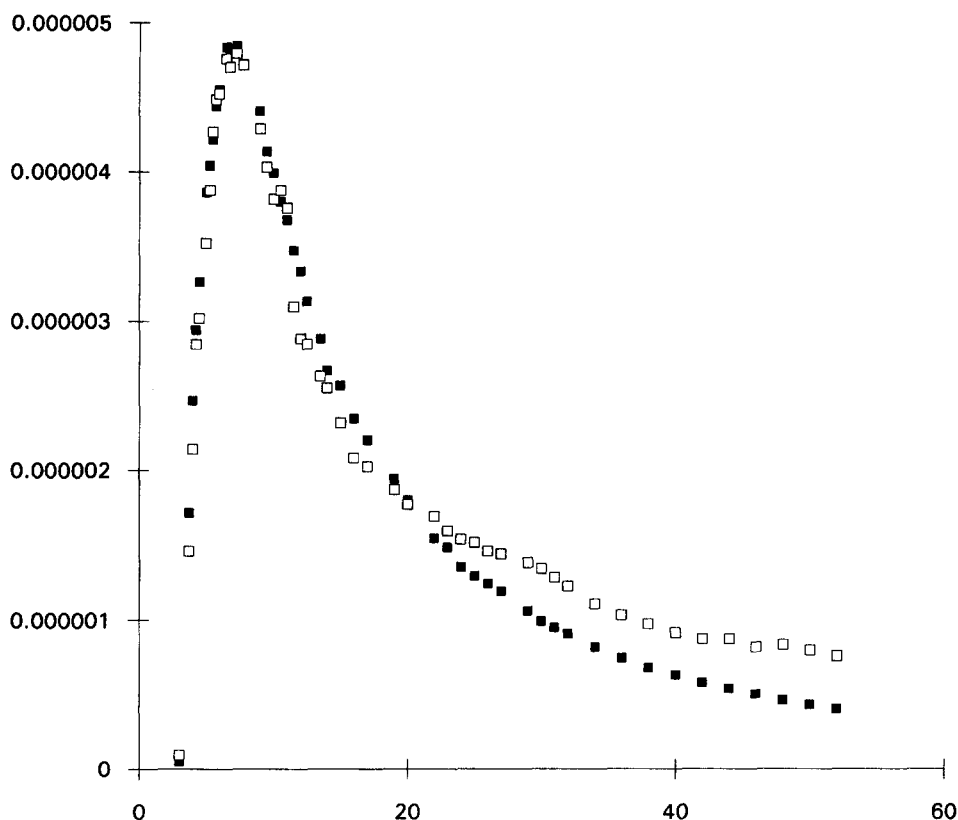
Fig. 1. Breakthrough–response curves from the joint NaFl/SF_6 tracer migration test at Rosemanowes Quarry, June 1989: □, SF_6; ■, NaFl.

a groundwater tracer (Biggin, 1991; Wilson and McKay, 1993), but as far as we are aware, its specific use as a geothermal tracer has not been reported previously.

In a borehole pumping test at Rosemanowes Quarry during June 1989, we simultaneously injected predetermined amounts of NaFl and SF_6 into the injection well (RH12) of the HDR system and monitored their concentrations in waters from the production well (RH15) over a period of 52 h. We added 50 cm^3 pure gaseous SF_6 to 20 cm^3 distilled water in a gas-tight, 100 cm^3 calibrated glass luer syringe fitted with a three-way polycarbonate stopcock. Following equilibration of the two phases by vigorous shaking for 3 min at ambient temperature (22.5°C), the gas phase was expelled via the stopcock and the procedure repeated twice more in order to ensure complete SF_6 saturation of the aqueous phase (Upstill-Goddard et al., 1990). The SF_6-saturated water was then completely expelled from the syringe, through 3 mm I. D. nylon tubing into the base of the hopper of a high pressure positive displacement dosing pump containing 1.0 kg NaFl dissolved in 10 kg tapwater. By avoiding all air contact, the procedure precluded measurable SF_6 losses, which would otherwise have modified the SF_6/NaFl ratio during injection. From the solubility of SF_6 in freshwater at

22.5°C, $3.74 \times 10^{-5}\,kg\,kg^{-1}$ (Willhelm et al., 1977), we estimate $7.5 \times 10^{-7}\,kg\,SF_6$ to have been injected. Therefore, the initial SF_6/NaFl mass ratio of the injection was 7.5×10^{-7}. The tracer mixture was pumped into the high pressure (9 MPa) borehole injection stream. The well system was subsequently operated on "open loop" circulation, continuously supplying the injection pumps with fresh make-up water (local stream water), which avoided the need for deconvolution of the effects of reinjecting the tracers after breakthrough in the production well. Immediately prior to the start of the tracer test, background levels of NaFl in injection well and production well waters were $\sim 4 \times 10^{-9}\,kg\,kg^{-1}$ and $\sim 5 \times 10^{-9}\,kg\,kg^{-1}$ respectively, consistent with natural levels of background fluorescence in the HDR reservoir supply water.

Because the HDR system contains water at elevated pressure, a significant potential for sample degassing can arise unless the appropriate caution is exercised during sample collection. For this experiment, a specially designed stainless steel branched sampling manifold was installed in line with the production well outlet and used in the collection of samples for SF_6 and NaFl. The design of the manifold facilitated the routine collection of SF_6 samples directly into 100 cm^3 glass syringes avoiding

all air contact, thereby precluding the potential for SF_6 degassing during sampling. SF_6 samples were subsequently cooled to ambient temperature and analysed by EC-GC within 1 h of collection, following routine headspace equilibration (Upstill-Goddard et al., 1990) Samples for NaFl were analysed immediately upon collection using a fluorimeter. Analytical precisions were better than $\pm 1\%$ for SF_6 and $\pm 5\%$ for NaFl for samples obtained after breakthrough.

During the experiment, $\sim 4 \times 10^3 \, m^3$ of water was injected into the reservoir. Water flow rates measured at the injection and production wellheads were $77.4 \, m^3 \, hr^{-1}$ and $70.2 \, m^3 \, hr^{-1}$ respectively. The average outlet temperature from the HDR reservoir was $< 40°C$; typical temperatures in the main flowpath were between 20°C (injection well RH12) and 35°C (production well RH15) (Nichol, 1989).

Figure 1 shows the background corrected breakthrough–response curves of SF_6 and NaFl during the experiment. For comparative purposes, tracer concentrations have been converted to their "response functions", by ratioing them to their corresponding concentration in the initial injection. Inspection of the curves therefore facilitates a direct comparison of the two tracer histories. These results show essentially identical behaviour for the two tracers during the first 25 h of the experiment, thus indicating a conservative behaviour for gaseous SF_6 tracer over this time scale. The characteristic forms of the response curves are typical for rock matrix tracer migration experiments (e.g. Eikenberg et al., 1991) and the mean breakthrough and peak response times, 3.25 hr and 7.25 hr respectively for both tracers, are similar to those determined previously with NaFl in the Rosemanowes HDR formation (Camborne School of Mines, 1987, 1988). Interestingly, despite their initially closely coherent behaviour, there is substantial evidence for increased tailing of SF_6 with respect to the NaFl breakthrough curve from about 25 h. Similar effects have been observed with other tracer pairs in comparable experiments (Carter et al., 1959, Eikenberg et al., 1991). This result most probably reflects enhanced residence times for SF_6 in some of the longer residence time flowpaths, due to selective diffusion into stagnant or near-stagnant zones of fracture fluid or the bulk rock matrix. Mass recovery curves for the two tracers, constructed by integration of the pulse breakthrough curves, are shown in Fig. 2. Mass recovery of NaFl with time is similar to that found in previous tracer experiments in the Camborne HDR system (Camborne School of Mines,
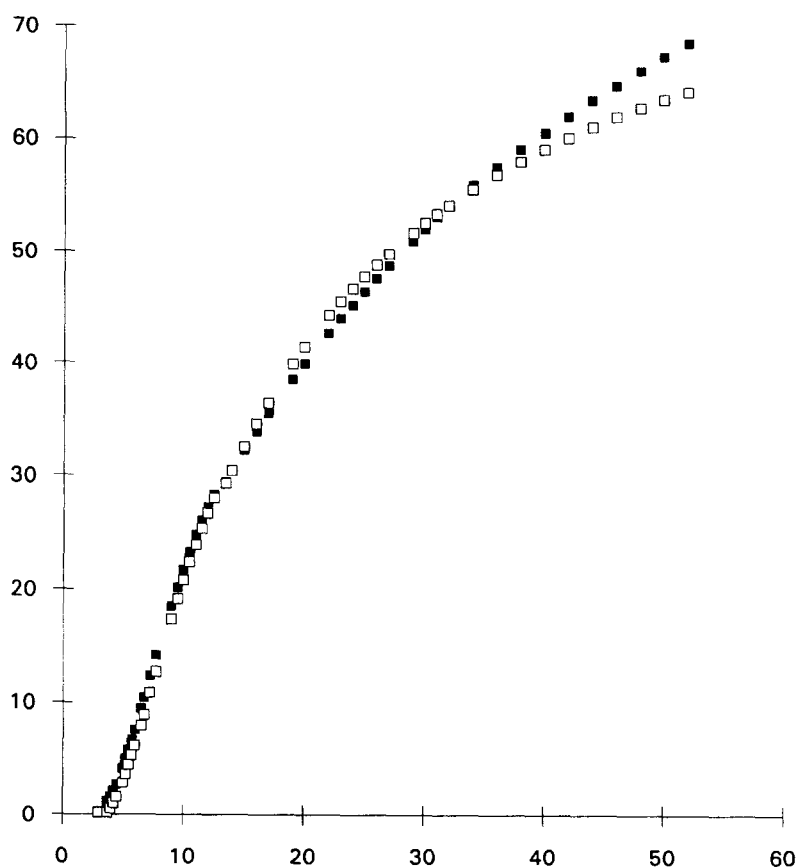
Fig. 2. Tracer mass recovery curves from the joint NaFl/SF_6 tracer migration test at Rosemanowes Quarry, June 1989: ■, SF_6; □, NaFl.

1987, 1988). Unfortunately, because of a technical problem with the SF_6 analyses, the experiment was terminated after 52 h. Further experiments of this type are therefore necessary in order to compare and interpret the long-term response and mass recovery behaviour of the two tracers.

The results of the initial borehole pumping tests for SF_6 presented here are extremely encouraging because they clearly demonstrate the strong potential of this tracer in applications of this type, and also in related applications such as the routine monitoring of groundwater migration through aquifers for example (Biggin, 1991; Wilson and MacKay, 1993). Of particular importance from both environmental and economic standpoints, the results of this pilot study demonstrate that relatively large scale high resolution experiments involving extremely small amounts of SF_6 should be possible routinely. We hope to carry out additional detailed pumping tests involving SF_6, and we confidently predict that SF_6 will find increasing use as a tracer in the geo- and hydrosciences.

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