SF_6 -
A NEW NONRADIOACTIVE GEOTHERMAL TRACER

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SUMMARY - SF_6 is a nonradioactive inert gas, is readily available, is not naturally present in geothermal system, and can be detected at very low levels using an Electron Capture Detector (ECD) gas chromatograph suggesting that it has potential as a geothermal tracer. Two systems were designed and used successfully to inject 1 gm SF_6 into geothermal wells at Wairakei.

Separate injections were made into the steam and water reservoirs at Wairakei. Tracer injected into the hot water zone, primarily remained in that fluid. The velocities of the peak concentration were 3 - 6 m/hr for the steam and 9 - 12 m/hr for the water zones. The velocities of the "initial" return were 16 - 21 m/hr in both the steam and water zone experiments. The total return in the monitored wells was 34.9 % for the steam wells and 0.725 % for the water wells. Preliminary comparisons are made with ^{133}Xenon, ^{131}Iodine, Rhodamine WT and Fluorescein.

1. INTRODUCTION

SF_6 is an inert gas of low solubility. Solubility data for SF_6 is only available from 0 to 55°C (Wilhelm et al.1977). At 30°C solubility is 31 g/t ($3.9 * 10^{-6}$ molar), compared with 500 g/t ($6.89 * 10^{-5}$ molar), 1310 g/t ($5.4 * 10''$ molar) and 17 g/t ($1.1 * 10^{-5}$ molar) for xenon, carbon dioxide and nitrogen respectively. SF_6 should be injected sparingly because of its low detection level or the reservoir could build up a significant "background" concentration. The inertness of SF_6 and its low detection level has led to its use in atmospheric studies e.g. determining the movement of gases emitted by cooling towers or others industrial vapour discharges, (Clarkson and Hadfield, 1983). *As* it is absent from geothermal fluids it has potential as a tracer in the geothermal reservoir. This potential has been investigated by injection of SF_6 and other tracers into a number of wells in the New Zealand geothermal areas. Three experiments are reported here, all of which used wells from the Wairakei Production Area.

2. METHODS

2.1 Downhole Injection

Figure 1 shows the components of the downhole injection device. This consists of a sealed glass ampoule **(A)**, a steel holder for the ampoule (B) and inertia mechanism with a spike shaped striker (C) with which the ampoule is broken and the SF_6 released into the well when the device has been lowered to the desired depth. Ampoule **(A)** is 340 mm long and 28 mm O.D. with an approximate volume of 166 ml. At 1 atmosphere pressure and 25°C it contains 1 ± 0.2 gm SF_6. The steel holder (B) is constructed from 235 mm of steel tube (34 mm I.D. and 42.5 mm O.D.). **A** 50 mm long tapered solid steel cone is welded to the bottom end of the tube. Seventytwo 10 mm holes are located in 6 rows of 12 along the length of the tube. **A** small cone shaped anvil is located on top of the welded steel cone. The ampoule **(A)** sits on a spring which holds it just above the anvil when the device is at rest. The inertia mechanism (C) is from the Klyen MkII downhole fluid Sampler (Klyen, 1981). To operate the device the ampoule **(A)**, evacuated, filled with SF_6 and sealed by a glassblower, is inserted into the holder

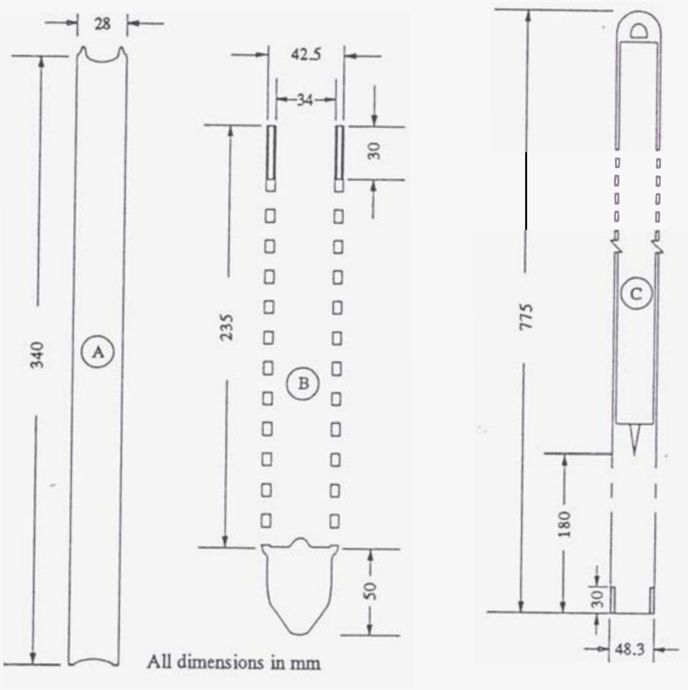

Figure 1 - Downhole injection device
A = ampoule
B = holder
C = inertia mechanism

(B) and held in place by means of thin copper wire that is tied round two "lugs" at the top of the ampoule and secured to the holder via the gaps between the holes in the holder (this prevents the ampoule from floating upwards and striking the inertia striker while the device is lowered down the well). The holder is then screwed into the inertia mechanism (C). The device is attached to a wire line winch and lowered down the drillhole to the depth at which it is desired to release the SF_6. At this point the wireline is jerked and the ampoule broken between the anvil and the striker. The device may be used in a closed drillhole with an internal downflow to convey the tracer into the reservoir or one into which fluid is being injected.

2.2 Surface injection

A 75 ml steel ampoule with valves on both ends (Figure 2) is purged with SF_6 at a known pressure and sealed. The ampoule is then attached to a "tee" on a gas line which is used to inject air from a compressor into the drillhole. A cylinder of dry nitrogen is connected to the end of the ampoule farthest from the "tee". A pressure of nitrogen greater than that in the air compressor is used to sweep the SF_6 from the ampoule into the main air line and thus it is carried down the drillhole (Figure 2a). Alternatively, a water blaster may be used in series with the ampoule to force the SF_6 through a narrow tube to the level at which the well permeability is located (Figure 2b).

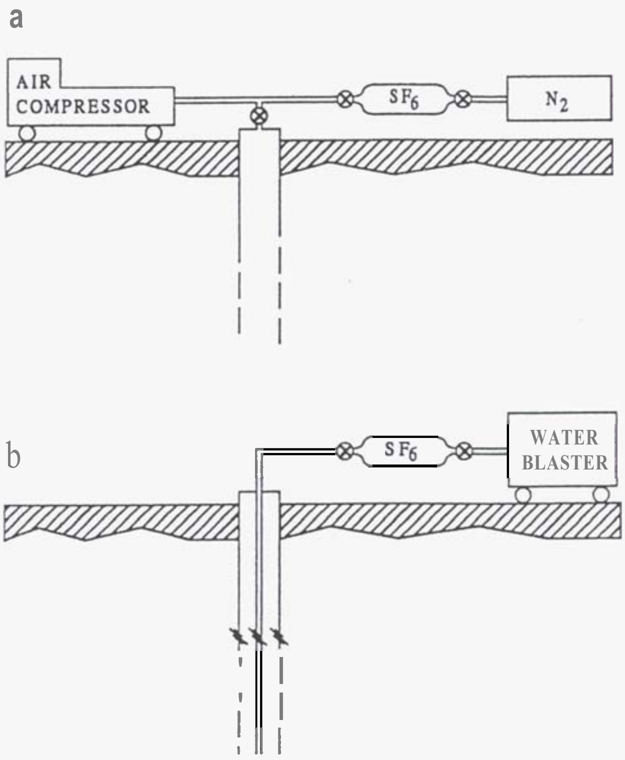

Figure 2 - Surface injection
a. into steam well "B"
b. into water well "A"

2.3 Sample Collection

As the SF_6 partitions almost completely into the vapour phase, the steam fraction of a discharging geothermal drillhole is collected for tracer analysis. If the well is under production and is equipped with a wellhead separator, the sample is collected from the separated steam line supplying the power station. Otherwise a 2 inch Webre 2 stage separator is used to obtain a steam sample from the two phase pipeline. The steam is condensed into an evacuated glass flask sealed with butyl rubber tubing to prevent contamination of the sample by either loss to the atmosphere or ingress of air. As SF_6 is adsorbed on to teflon the "Rotaflo" valves often used to sample geothermal gases cannot be used.

2.4 Sample Analysis

A Varian 3600 gas chromatograph fitted with an Electron Capture Detector (ECD) which has a ^{63}Ni source of 15mCi was used for Experiment 3. The carrier gas is a mixture of Methane and Argon in the ratio of 3:97. Separation is achieved with a 0.1 m 80-100 mesh Poropak T pre-column at room temperature followed by a 3 metre long 1/8 inch diameter column containing 45-60 mesh Molecular Sieve 5A. The carrier gas flow rate is 30 ml/min. The pre column, main column oven and detector temperatures are room temperature (c.22°C), 50, and 280°C respectively. The gas chromatograph can detect $2.8 * 10^{-17}$ moles ($4.1 * 10^{-15}$ g) of SF_6 or a concentration in the gas phase of $2.5 * 10^{-12}$ molar using a 0.25 ml sampling loop.

3. EXPERIMENTS

3.1 Experiment 1

Injection into well "B", a non-producing steam/gas well at Wairakei.

The aim of this experiment was to follow the tracer injected into the steam zone. Previous tests by Barry (1990) had shown that ^{133}Xe was detected in steam wells "1" and "2" but not in any of the wells drawing on a single water phase.

A 75 ml cylinder was filled with SF_6 gas at a pressure of 2.62 bA and a temperature of 15°C. This is equivalent to 8.22 millimoles of SF_6, or 1.2 gm SF_6. This was injected into the well at 1447 hours on 10 June 1991. The SF_6 was blown into the well by nitrogen and then forced down the well for 45 minutes by an air compressor (Section 2.2). Samples of steam were collected from two "dry steam wells "1", and "2". These samples were analysed on a Pye Unicam 500 gas chromatograph.

3.2 Experiment 2

Injection into a water well "A" at Wairakei

The aim of this experiment was to determine whether the tracer reached steam or water phase wells.

A glass ampoule containing 1.02 g SF_6 was lowered into "A" and broken at 705 m depth on 3 December 1991. A 60 t/h downflow of cold water carried the gas into the formations. Samples were collected from wells "1", "3" and "4" and analysed on a Perkin Elmer Sigma 4 gas chromatograph.

3.3 Experiment 3

Injection into well "A" at Wairakei

The purpose of this test was to compare results obtained using SF_6 tracer and ^{133}Xe tracer. This report gives the SF_6 results with brief reference to the ^{133}Xe data. The ^{133}Xe data used is from preliminary graphs drawn by Barry (pers comm.) on the November 1992 samples. Electicorp Production (ECNZ) supplied data for Rhodamine response in "3" from an October 1992 injection, and Fluorescein response in wells "3", "4" and "5" from a November 1992 injection. The iodine data for "3" is from preliminary spreadsheet data provided by McCabe (pers comm). June 1991 ^{133}Xe and ^{131}I data (Barry, 1991) is also used.

A 75 ml cylinder was filled with SF_6 gas at a pressure of 2.44 bA and a temperature of 15°C. This is equivalent to 7.64 millimoles of SF_6, or 1.116 gm SF_6. This was injected into "A" at 0831 hours on 10 November 1992. A water blaster forced the SF_6 through a 6.5 mm pipe whose lower end was located at a depth of 705 m (Section 2.2). The water was pumped for 30 minutes, three times that required to convey the SF_6 to the bottom of the tube. Samples of separated steam were collected from wells "3", "4" and "5".

The samples were collected in weighed evacuated glass ampoules sealed With either butyl rubber or surgical rubber tubing closed with clamps.

Analysis was carried out on 8 - 12 February 1993. This was caused by delay in the arrival and commissioning of a Varian 3600 gas chromatograph with an electron capture detector. The GC is now able to detect 2.8 x 10^{-17} moles (4.1 x 10^{-15} g) of SF_6 or a concentration in the gas phase of 2.5 x 10^{-12} molar.

The delay resulted in leakage of air into some of the ampoules; i.e. a high vapour pressure was measured (500 to 900 mbar) and oxygen was found in the vapour. These high pressures were limited to those ampoules with surgical rubber. However, as most of the pressures in these were under 1 atmosphere leakage out of the ampoule should not have occurred. However, many of the surgical rubber ampoules had very low SF_6 compared with the butyl rubber ampoules suggesting that some leakage outwards could have occurred. The leakage in would dilute the SF_6 and rake the detection limit.

4. WELL LOCATIONS and FEED ZONES POSITIONS

The location of the well head of each of the wells in which tracer was injected ("A" and "B") or in which return of the

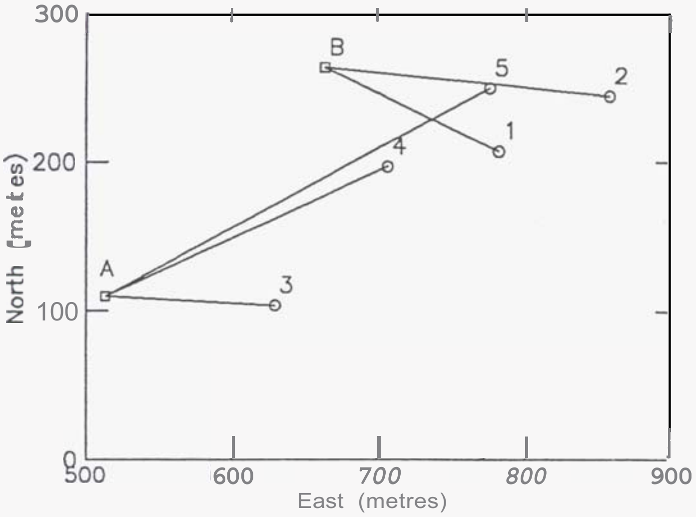

Figure 3 - Location of injection and sampled wells

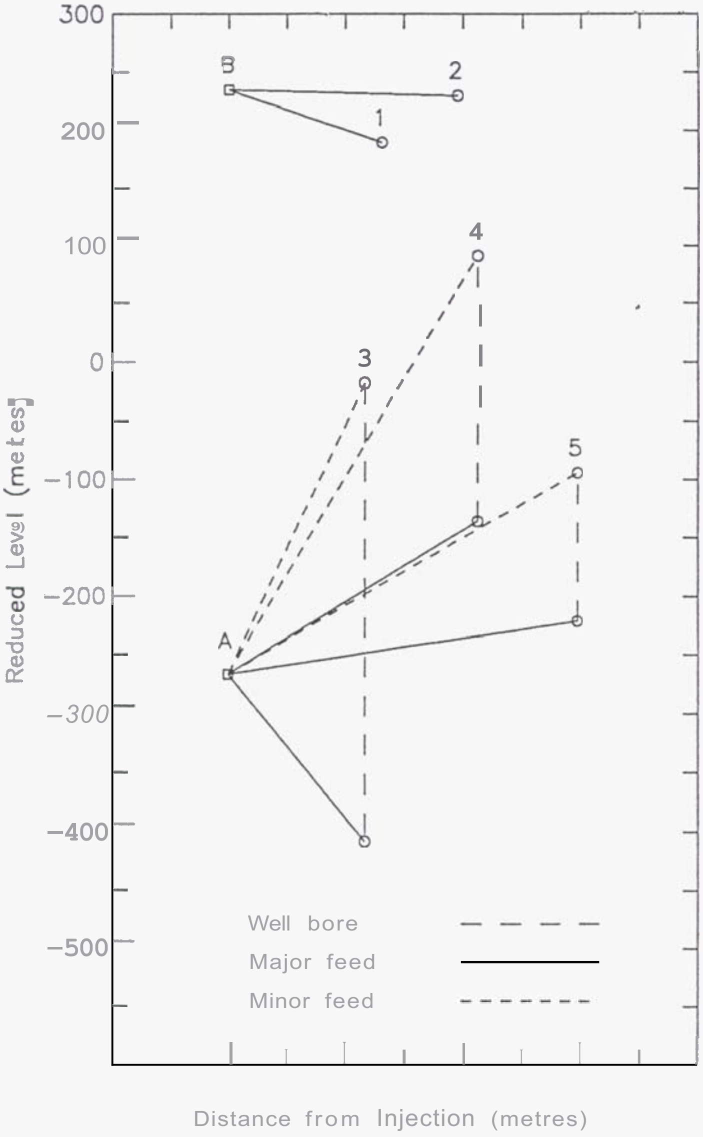

Figure 4 - Relation of injection points and feed zones.

injectate was found ("1", "2", "3", "4", and "5") are shown in Figure 3. A vertical section of all the wells is shown in Figure 4. In this figure the horizontal distances between each of the injection wells and the monitored wells is correct, as are the angles and distances between the points of injection and the feed zones in each of the receiving wells. As the direction from the injection wells to each of the monitored wells are different, then Figure 4 does not show the distances and angles between the monitored wells.

5. RESULTS

The concentration of SF_6 analysed in the vapour in the ampoule was converted into a concentration in the steam collected so that the number of grams of SF_6 discharged via each well could be calculated. The "normalised concentration" was also expressed in $kg^{-1} \times 10^{12}$; i.e.

$$\frac{gms\ SF_6\ per\ kg\ steam}{gms\ SF_6\ injected} * 10^{12}$$

The normalised concentrations of SF_6 in the steam are plotted versus time in Figure 5 (wells "1" and "2" in Experiment 1), Figure 6 (wells "3" and "4" in Experiment 3), and Figure 7 (well "5" in Experiment 3).

Table 1 lists the tracer velocity between the injection point in "B" (at RL +235 m, or 186 m depth) and the feed points of "1" and "2", and between the injection point in "A" (at RL -266 m, or 705 m depth) and the feed points of wells "3", "4", and "5".

In comparing tracers analysed in the vapour phase of the sample (SF_6 and ^{133}Xe) and tracers which were analysed in the collected water phase (^{131}Iodine, Rhodamine WT and Fluorescein) the results were normalised to total discharge i.e.

$$\frac{gms\ tracer\ per\ kg\ total\ flow}{gms\ tracer\ injected} * 10^{12}$$

6. DISCUSSION OF RESULTS

6.1 Experiment 2

Detailed analyses of these samples are not shown. The wells monitored were "1", "3", and "4". Tracer returns were found in "3" and "4" (both supplied predominantly by a single water phase. No tracer was detected in "1", a "dry steam" well. More detailed monitoring of injection into "A" was undertaken in Experiment 3 (below).

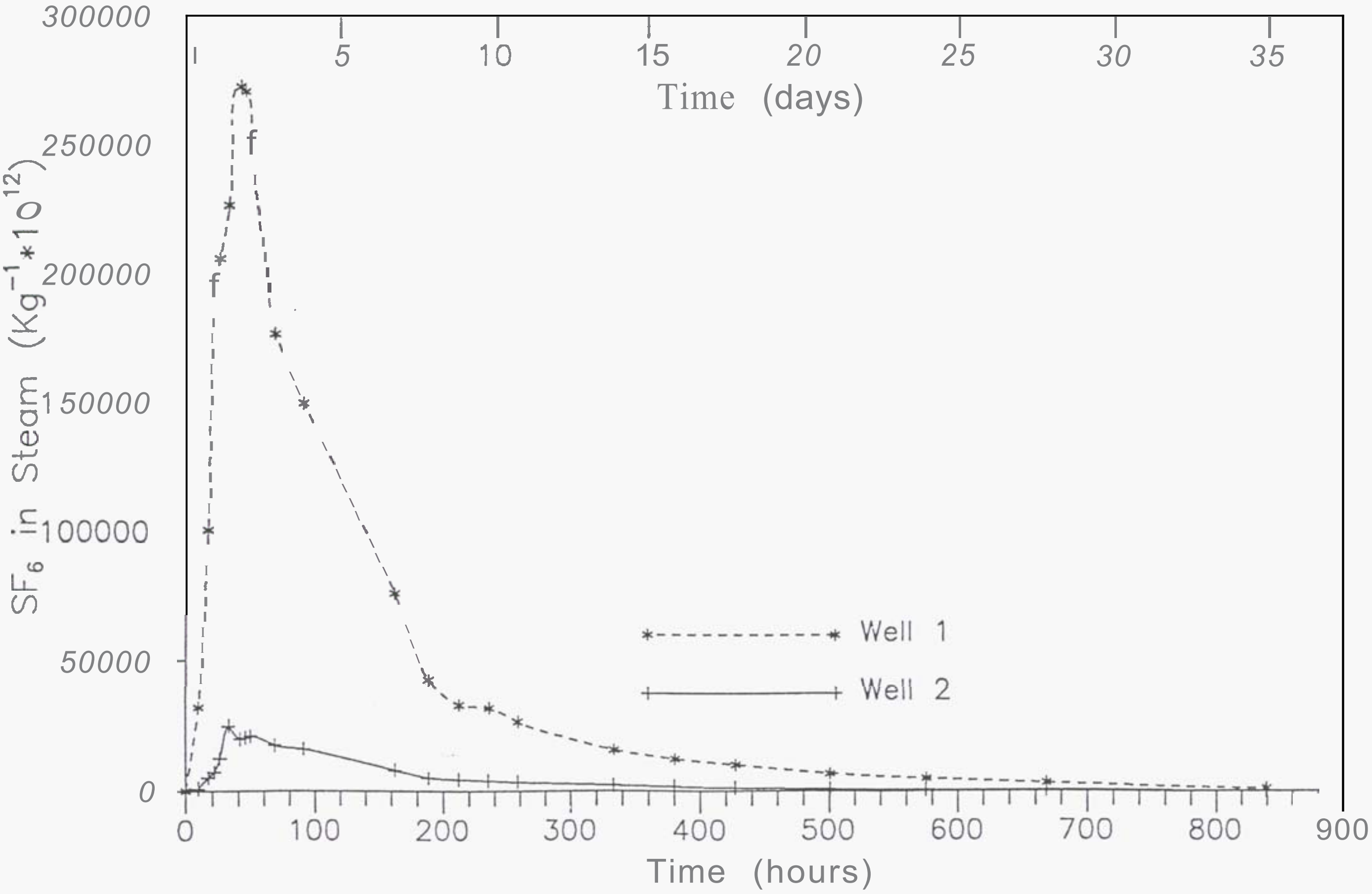

Figure 5 - Experiment 1 - tracer response in wells "1" and "2".

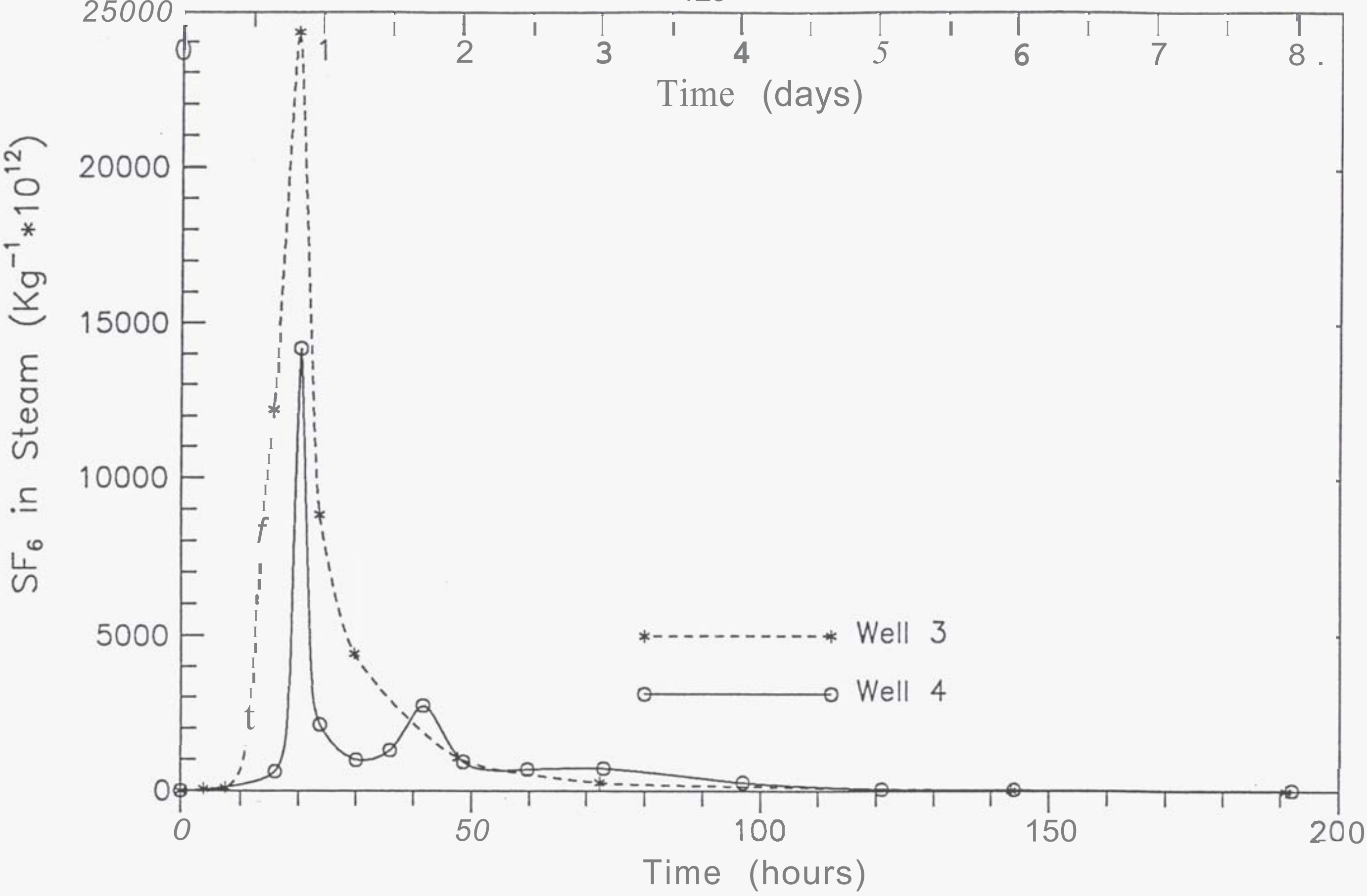

Figure 6 - Experiment 3 - tracer response in wells "3" and **"4".**

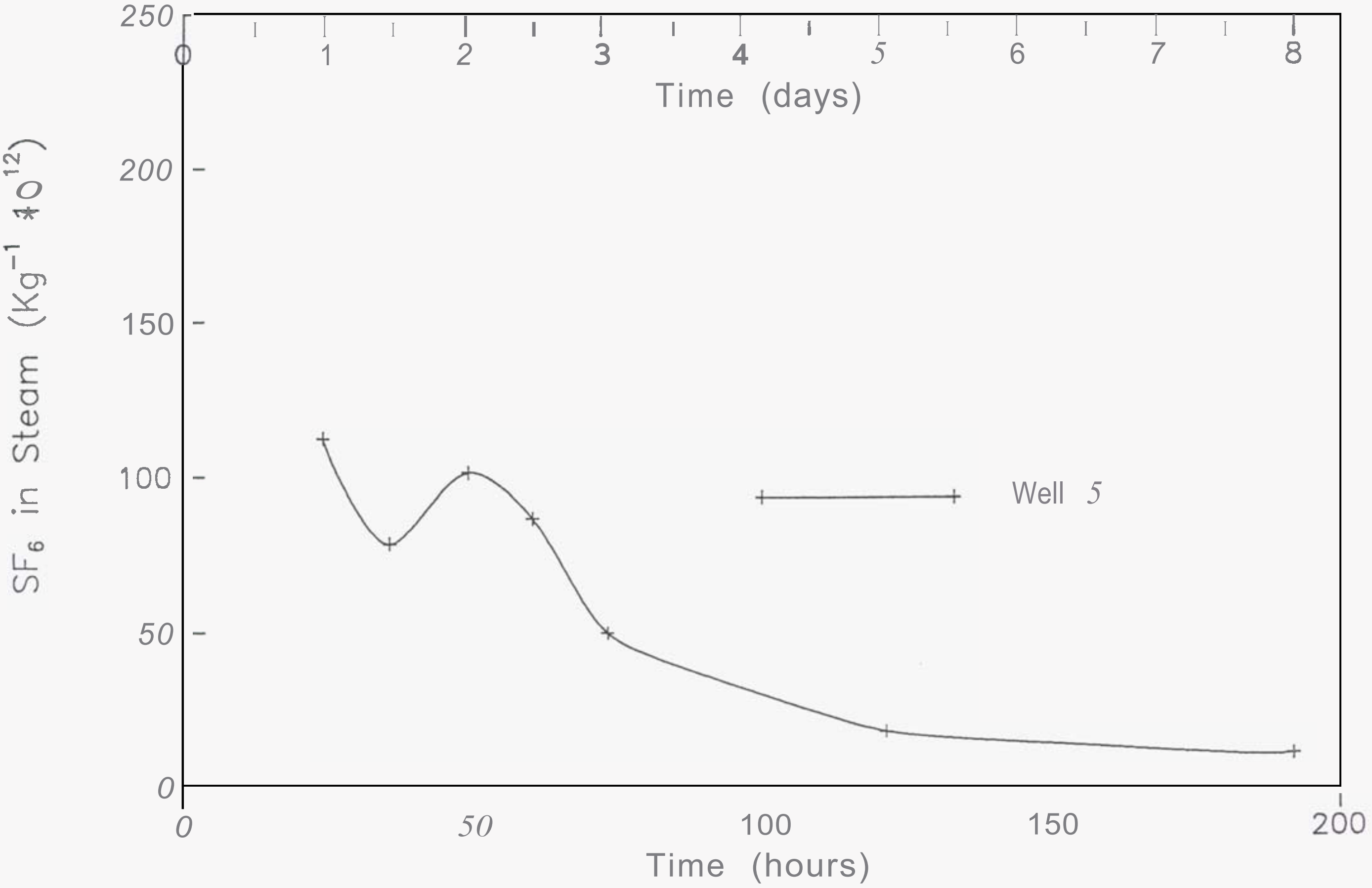

Figure 7 - Experiment 3 - tracer response in well "5".

6.2 Experiments 1 and 3

6.2.1 Curve Shapes

In experiment 3 the response curves for wells "4" and "5" (Figures 6 and 7) show a second high peak. This has not been noted with any of the other tracers used. However the fact that both wells are in approximately the same direction from injection well "A" (Figure 3) whilst well "3" that does not show the second peak is in on a bearing 27 to 30 degrees different to the former wells. This suggests that the second peak may be real. Errors have not been determined for these samples. However in Experiment 1 duplicate samples were collected at each sampling time and the average deviation from the mean was ± 1.9% and ±2.5% for wells "1" and "2" respectively.

TABLE 1: Tracer flow distance, direction, and flow rates (m/hr)

Well (feed zone)	Tracer	Time *hours*	Direct distance *metres*	Direct bearing -degrees *from* vertical	Direct speed *m/hr*
"1"	initial	7.9	138	109°	17
	peak	42			3.3
"2"	initial	9.1	195	91°	21
	peak	32			4 to 6
"3" (major)	initial	10.4	184	140°	18
	peak	20			9
"3" (minor)	initial	10.4	274	25°	26
	peak	20			14
"4" (major)	initial	15.8	249	59°	16
	peak	20			12
"4" (minor)	initial	15.8	415	31°	26
	peak	20			21
"5 (major)	peak	24	300	81°	12.5
"5" (minor)	peak	24	343	*60°*	14

6.2.2 Tracer Velocities

It is difficult to determine the initial tracer arrival time unless a more detailed or continuous sampling regime is followed. The "initial" time used in our calculations is obtained by extrapolating the first three data points on the leading edge of the tracer response curve for each well. insufficient data points are available for "5". The "peak" time is taken from the sample with the highest concentration of the tracer for each well. The tracer velocities have been determined for the direct flow path between injection and feed point.

For both experiments the "initial" velocities are remarkably similar for the major (or only) feed zones. "1" and "2" velocities are 17 and 21 m/hr whilst "3" and "4" velocities are 18 and 16 m/hr. This suggests that the steam and water phases move through the ground at approximately the same speed. Within the accuracy of the data (limited by the frequency of sampling) there appears to be no significant difference in the velocities. If this is true then it would support a directional fracture flow rather than a more diffuse porous medium flow. In the latter case the average velocity for a two dimensional flow would be in proportion to (distance)". Thus a velocity of 18 m/hr for "3" would mean a velocity of 8 m/hr for "4" compared with the determined value of 16 m/hr. High calculated velocities are obtained from the minor feed zone paths in the wells which are (a) further from the injection point and (b) less likely to contribute to the flow, than the major feed zones. The "peak" velocities are obviously less than the "initial" velocities. There is a large difference between the steam (3.3, and 4 to 6 m/hr) and the water (9, 12, and 12.5 m/hr).

6.2.3 Yield

Graphs Figures 5 to 7 were drawn with a "spline" curve joining all points whilst the yields were calculated by obtaining the area under the "curve" assuming straight lines between each sample data point.

The amount of tracer reaching the sampled wells in the steam zone injection (Experiment 1) is quite high i.e. "1" = 31.16% and "2" = 3.74% , a total yield of 34.9% equivalent to 0.419 g SF_6. This is similar to the total of 82% found for ^{133}Xe in 1990 (Barry, 1991). However injection into the water zone (Experiment 3) gave a much lower yield consistent with other liquid tracers i.e. "3" = 0.27%; "4" = 0.45%; "5" = 0.011% of the SF_6 injected giving a total yield of 0.725% which represents 0.008 g SF_6 (see Table 2).

Table 2: Percentage Yield of SF_6 Tracer

Well	Yield (%)
"1"	31.16
"2"	3.74
Total from "B"	34.90
"3"	0.266
"4"	0.448
"5"	0.011
Total from "A"	0.725

6.2.4 Comparison of Peak Concentrations for different tracers

Only an approximate comparison can be made as the tracers were not injected at the same time. However there has probably been only small changes in the hydrology over the past two years. The ^{133}Xe data is from preliminary results obtained by Barry (pers com) at the same time as the SF_6 Experiment 3 was conducted. The ^{131}I data is from McCabe results from November 1992 together with earlier data from June 1991. The Rhodamine WT and the Fluorescein data was obtained in October and November 1992 respectively, both these sets of data were made available by ECNZ.

The SF_6 and ^{133}Xe normalised concentrations in the total discharge were calculated from the steam values multiplied by steam fraction for each well; i.e. "3" = 0.136; "4" = 0.194; "5" = 0.122. The liquid tracers values in total discharge were obtained by multiplying the water values by the respective water fractions; i.e. "3" = 0.762; "4" = 0.714; "5" = 0.782. **N.B.** The values have been calculated using the highest analysed value; i.e. there could be some higher values that were not detected due to the frequency of sampling. For the steam wells "1" and "2" the steam fraction = 1. All the maximum normalised concentrations in total discharge are shown in Table 3.

6.2.4.1 Experiment 1: Wells "1" and "2"

These wells show extremely high concentrations of SF_6 and excellent agreement with Barry's data from 1990.

6.2.4.2 Experiment 3: Well "3"

The peak response occurs at approximately 20 hours after injection for all tracers.

The similarity of the normalised concentration values for total discharge in Table 3 for SF_6, Iodine, and Rhodamine suggest that the SF_6 was totally dissolved in the liquid water phase as it left "A" and stayed dissolved until steam formation occurred as pressure was reduced in the well bore of "3". The Xenon (1.3 - 1.4 times the others) could indicate that some steam formation occurred prior to the entry to "3", carrying Xenon which entered "3" at a possible upper feed zone (RL - 18 m). However this is difficult to envisage as the SF_6 does not show similar behaviour and SF_6 is approximately 6% as soluble as Xenon at 45°C (high temperature data is available for Xenon (Potter and Clynne, 1978) but not for SF_6). More accurate fluorescein data would probably show good correlation with the other tracers (see footnote to Table 3).

TABLE 3: Normalised Concentrations in Total Discharge for Peak Concentration (in $Kg*10^{12}$)

Well	Tracer				
	SF_6	Xe	I	Rh	Fl
Steam wells in Experiment 1					
"4"	275000	[270000]			
"5"	25000	[26600]			
Water wells in Experiment 3					
"1"	3300	4750 (2800)	3500 (2250)	'3650	'34300
"2"	2750	1300 (960)	(650)		'3300
"3"	22	58 (15)	(24)		'840

[ ]	is calculated from June 1990 data (Barry, 1990)
( )	is calculated from June 1991 data (Barry, 1991)
+	October 1992
*	November 1992 - these values are probably an order of magnitude too high due to bore water samples being compared with fluorescein standards prepared in distilled water (K L Brown pers comm)

6.2.4.3 Experiment 3: Well "4"

If the basic dilution in the liquid phase (calculated to total discharge) is taken as the Iodine value (650), then both the Xenon (1.5 times) and SF_6 (4 times) are less diluted. This would agree with the higher enthalpy discharge of "4" and probable stem feed to the well. Both the main feed zone (RL - 136 m) and a possible steam feed (RL + 91 m) are above the injection level in "A" (RL - 266 m). Some steam (plus SF_6 and Xe) separation has occurred in the country and the steam, enriched in the gases, has reached "4" and the higher enthalpy fluid discharged by the well has thus a higher gas concentration (less dilution) than the iodine concentration which travels only in the liquid phase.

The SF_6 is less diluted as it partitions more easily into the steam phase than the Xenon (see above) but it is surprising that there is a factor of more than 2 between them.

6.2.4.3 Experiment 3: Well "5"

This well shows only a low concentration of any of the tracers (approximately 1% of "3"). The difference between the different tracers is probably not significant or reliable at this level.

7. CONCLUSIONS

1. SF_6, although a gas, when dissolved in liquid at depth, acts as a "liquid" tracer with similar dilution as Iodine and Rhodamine.

2. For wells that have a steam and liquid feed a greater normalised concentration of SF_6 is found in the discharge than for Iodine which is transported solely in the liquid.

3. "Initial" tracer velocities are 16 to 21 m/hr in both the steam and water phases.

4. "Peak " tracer velocities are 3 to 6 m/hr in the steam phase and 9 to 12 m/hr in the water phase.

5. The steam injection gave 40 to 50 times the percentage yields (returns) than the water phase injection.

8. ACKNOWLEDGEMENTS

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