DUAL-GAS- TRACERS FOR SUBSURFACE CHARACTERIZATION AND NAPL DETECTION

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November 1994

Presented at the
Second Tracer Workshop
November 14-15, 1994
Austin, Texas

MASTER

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Dual-Gas Tracers for Subsurface Characterization and NAPL Detection

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Abstract

Effective design of in situ remediation technologies often requires an understanding of the mass transfer limitations that control the removal of contaminants from the soil. In addition, the presence of nonaqueous phase liquids (NAPLs) in soils will affect the ultimate success or failure of remediation processes. Knowing the location of NAPLs within the subsurface is critical to designing the most effective remediation approach. This work focuses on demonstrating that gas tracers can detect the location of the NAPLs in the subsurface and elucidating the mass transfer limitations associated with the removal of contaminants from soils.

Introduction

Soil and groundwater contaminated with organic compounds, such as carbon tetrachloride, trichloroethylene, perchloroethylene, machine oil, and gasoline, are widespread in both the government and private sectors. Attempts to clean up these toxins can be less successful than predicted because a non-aqueous phase liquid (NAPL) was not detected, the NAPL could not be effectively located, or mass transfer limitations slowed the remediation. Moreover, the distribution of the NAPLs and dense non-aqueous phase liquids (DNAPLs) in the pores of the soil as isolated droplets surrounded by water, as lenses, or as spreading films affects both their removal from the soils and their migration in the subsurface (Wunderlich *et al*, 1992). Therefore, a method for determining the location, size, and nature of these organic phases is a critical need in environmental remediation.

Historically, locating NAPLs and DNAPLs in the subsurface has been difficult. Often the appearance of a noticeable oil phase in a well was the only indicator that a NAPL or DNAPL was present. However, wells sample an exceeding small volume of the soil, making them an impractical method for locating NAPLs when drilling is expensive. Injecting and extracting tracers from adjacent wells permits sampling the large volume of soil between the wells. Tracer tests have been applied widely for elucidating the distribution of gas and liquid flow in soils and porous media, and partitioning tracer tests have been extensively used to estimate crude oil saturation in oil reservoirs, which is analogous to NAPL detection in an aquifer (Jin *et al*, 1995). Only very recently have researchers attempted to detect NAPL/DNAPLs in unsaturated soils with partitioning gas tracers (Whitley *et al*, 1995; Jin *et al*, 1995).

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Dual-Gas Tracer Technique

When gas tracers with different solubilities in water and NAPL phases flow through contaminated soils, the tracers will propagate at different velocities depending on their relative partitioning into the water and NAPL. The dual-gas tracer technique seeks to exploit these different rates of propagation. Figure 1 depicts the technique schematically, showing the retarded propagation of a partitioning tracer relative to an insoluble tracer. Selecting tracers that partition selectively into the phases of interest permits use of the relative rates of tracer transport to infer quantitative information about the amount, location, and relative geometry of those phases.

To detect NAPL/DNAPLs, two tracer gases that are identical except for their solubility in the NAPL/DNAPL, are injected into the soil. Analysis of the difference between the two tracers as they leave the soil reveals the location and amount of the NAPL/DNAPL. That information permits optimal placement of wells for remediation or, equivalently, determines the minimum number for effective remediation. In both cases, determining the location and amount of NAPL/DNAPLs greatly reduces the cost of remediation. For heat-enhanced soil remediation processes, success and cost effectiveness often hinge on whether the rate of removal of underground contaminants will be limited by their volatility or by slow diffusion processes. The difference in the elution of the two tracer gases from the soil also highlights the critical diffusion limitations in the soil. This information can then be used to select and properly design the most cost-effective remediation method.

Partitioning gas tracers for detecting NAPL/DNAPLs offer a cost-effective technique for sampling a large volume of soil. Because tracers are generally confined to the region between points of injection and withdrawal, a partitioning tracer method will give a positive result only if the NAPL/DNAPLs are present between the two wells. Accordingly, injecting the partitioning tracers in multiple wells surrounding the region of NAPL/DNAPL contamination permits identification of the spatial location of the NAPL/DNAPLs.

Experimental

Figure 2 shows the apparatus used for conducting the tracer retention experiments. The soil was held in a 30 cm (12 in.) long column with an internal diameter of 88 cm (2 in.). Nitrogen was metered into the soil column with a Brooks 5850E mass flow controller. The nitrogen passed through a humidifier and then through a VICI 8-way Valve. The tracer was loaded into a 5 cm^3 sample loop at the VICI valve then injected by rotating the valve. The nitrogen flowed directly from the soil column into a sampling port on a Hewlett Packard gas chromatograph (GC). The GC injected a sample of the exit stream every six minutes onto a 30-m, Alltech Carbograph 1 capillary column. The ChemStation software running the GC automatically integrated the peaks for each tracer, and the peak areas were used for determining the concentration of the tracer gases.

The soil column was packed with 70/140 mesh Ottawa sand. The NAPL was mineral oil, added at the top of the vertically mounted soil column and allowed to infiltrate the soil. Nitrogen was metered through the column at 10 cm^3/min, which yielded one pore volume through the column every 25 minutes. SF$_6$ was the insoluble tracer and trichloroethylene (TCE) was the soluble tracer. For these preliminary experiments, TCE was used because it is soluble in both the NAPL and water phases and is easily separated and detected on the GC. TCE would never be injected as a tracer in a real application.

A suite of fluorinated gases with a wide range of solubilities were tested as tracers. A gas chromatograph with an electron capture detector can detect these tracers (SF_6, C_2F_6, C_2F_4, CHF_3, and others) at very low concentrations (as low as parts per billion).

Results

Figure 3 shows the tracer retention for separate experiments with NAPL saturations of 0, 2.1, 4.2, and 6.3%. As expected, the essentially insoluble SF_6 tracer was unaffected by the presence of the NAPL and eluted at one pore volume regardless of the NAPL saturation. The retention of the NAPL-soluble tracer increased monotonically with the amount of NAPL in a sandy soil.

Computer simulations of the retention of soluble and insoluble tracers confirmed that NAPLs retain soluble tracers. These calculations assumed local equilibrium between the tracers and the NAPL; this assumption neglects mass transfer limitations. Figure 4 compares the experimental and modeling results based on local equilibrium. The experimental results show the characteristic long, tailing tracer elution from the soil, which is a result of mass transfer limitations within the soil. These results demonstrate that the dual-gas tracer technique offers information on the nature and extent of mass transfer limitations, and that the model selected cannot appropriately address that issue. Mass transfer limitations can be eliminated by sufficiently slow flow. However, most soil remediation processes, including vapor extraction, are dominated by slow mass transfer after an initial transient period. The flow rate for this experiment was chosen to give a gas velocity comparable to those used in conventional soil vapor extraction (SVE) applications, 17 m/day (55 ft/day). Thus, flow velocities will need to be slower than those used during SVE if mass transfer limitations are to be avoided. If higher velocities are used, the interpretation of the tracer elution will require a model that accounts for finite mass transfer rates.

Figure 5 shows the effect of adding water to a sand column containing 6.3% mineral oil. After the addition of water, nitrogen was metered through the soil to reestablish gas flow. During this period, no mineral oil was observed leaving the soil. The addition of water decreased the retention of the soluble tracer. This effect can be explained by the distribution of the mineral oil in the pores of the soil. Because the mineral oil is a non-spreading NAPL, the oil forms lenses and may be surrounded by water films. The thickness of the water films depends on the location of the NAPL relative to the gas-occupied pores. The water films act as a barrier to the tracer, preventing its partitioning into the oil. The result is a decrease in the amount of tracer retained, as seen in the TCE elution curve.

Conclusions

Experimental and modeling results show that partitioning tracers can detect the presence of NAPLs. In addition, the distribution of the NAPL as films, lenses, or as droplets surrounded by water affects the retention of the partitioning tracers. Finally, the well-known effect of mass transfer skewing the elution of the tracers form the soil was observed at interstitial flow velocities of 17 m/day (55 ft/day).

References

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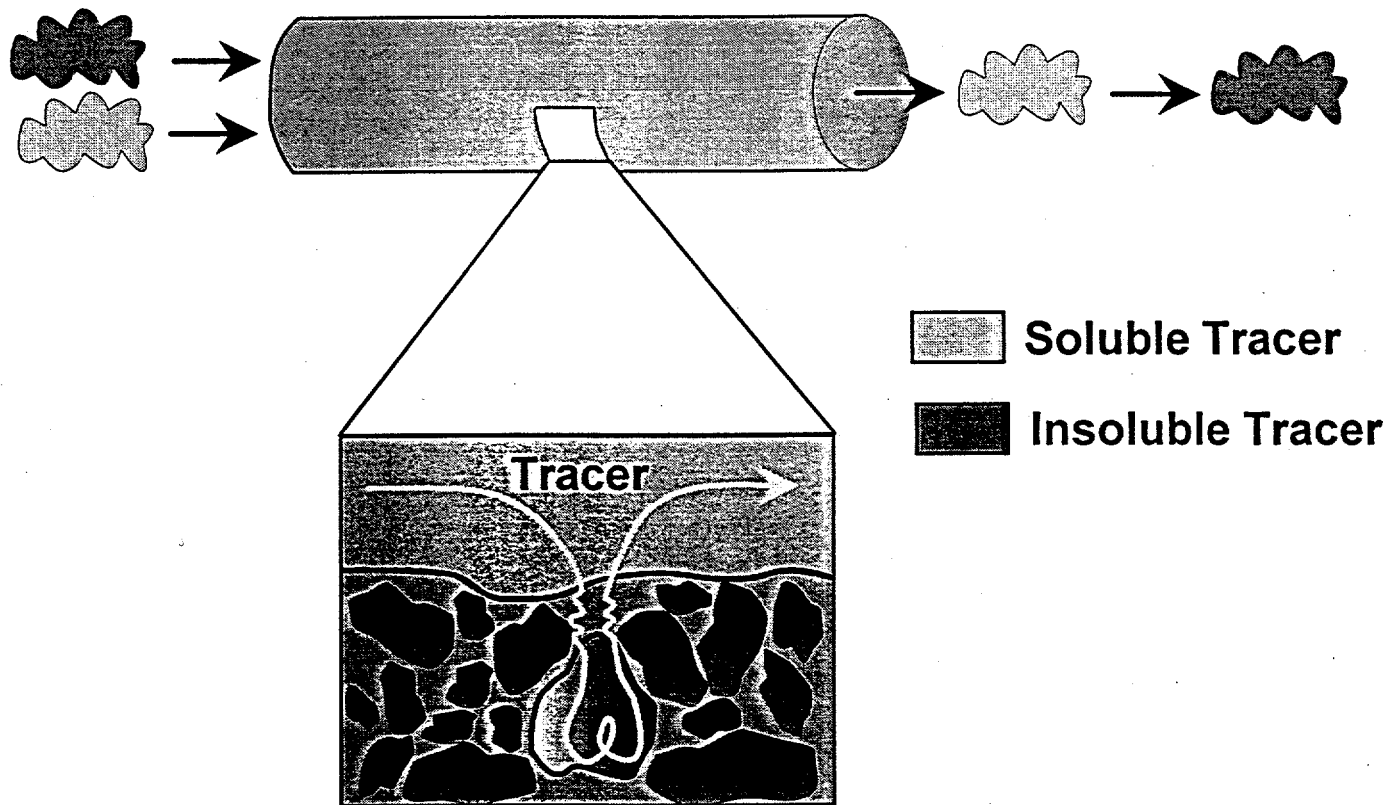
Soluble Tracer

Insoluble Tracer

FIGURE 1: Two tracer gases, one partitioning and one non-partitioning, are injected simultaneously into the soil. The non-partitioning tracer is unaffected by the presence of NAPL, and its elution curve reflects only diffusion and dispersion of the tracer pulse. The partitioning tracer is absorbed by the NAPL, diffuses into it, and is slowly released back into the carrier gas. Retention by the NAPL delays its elution and gives the concentration curve a characteristic tail.
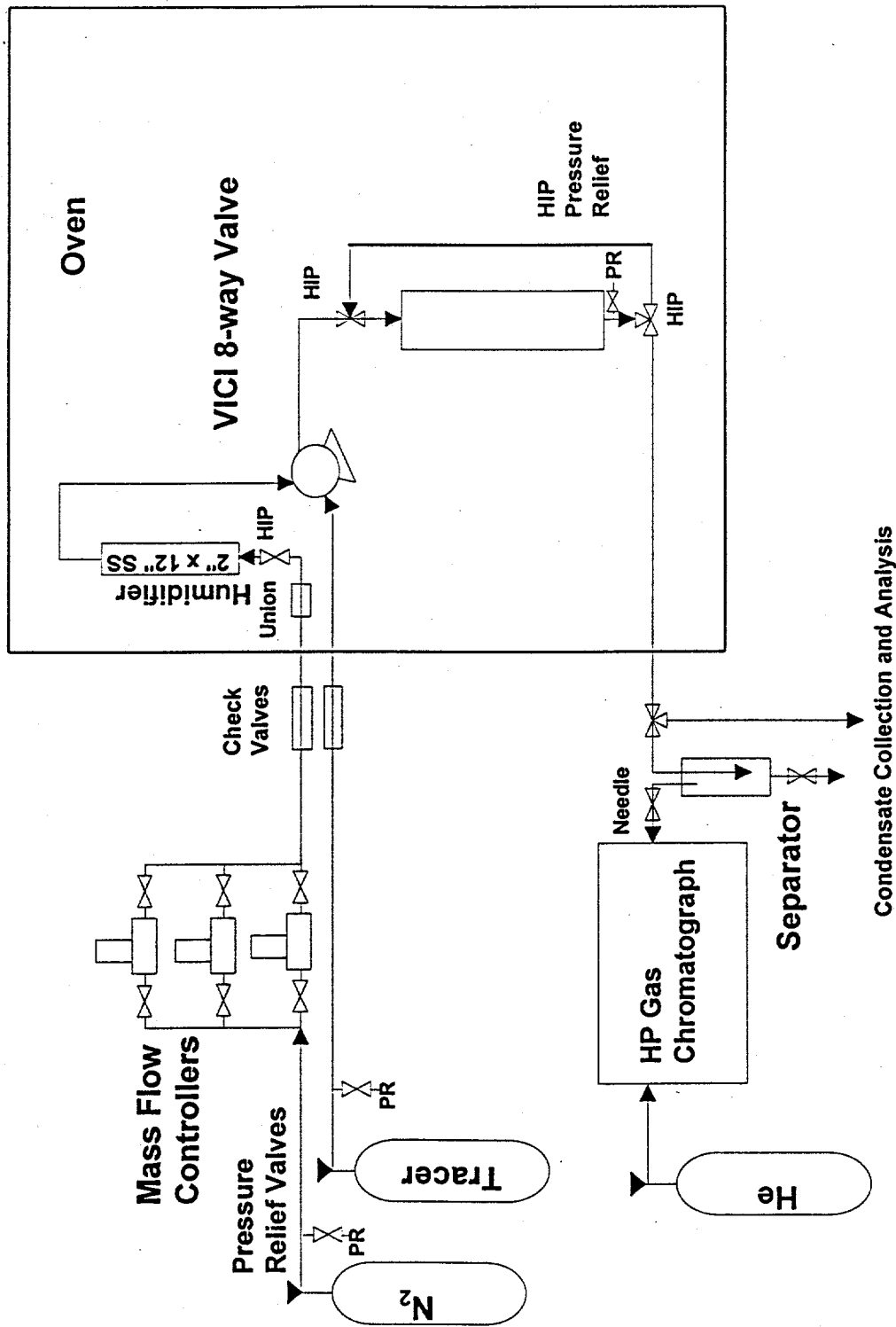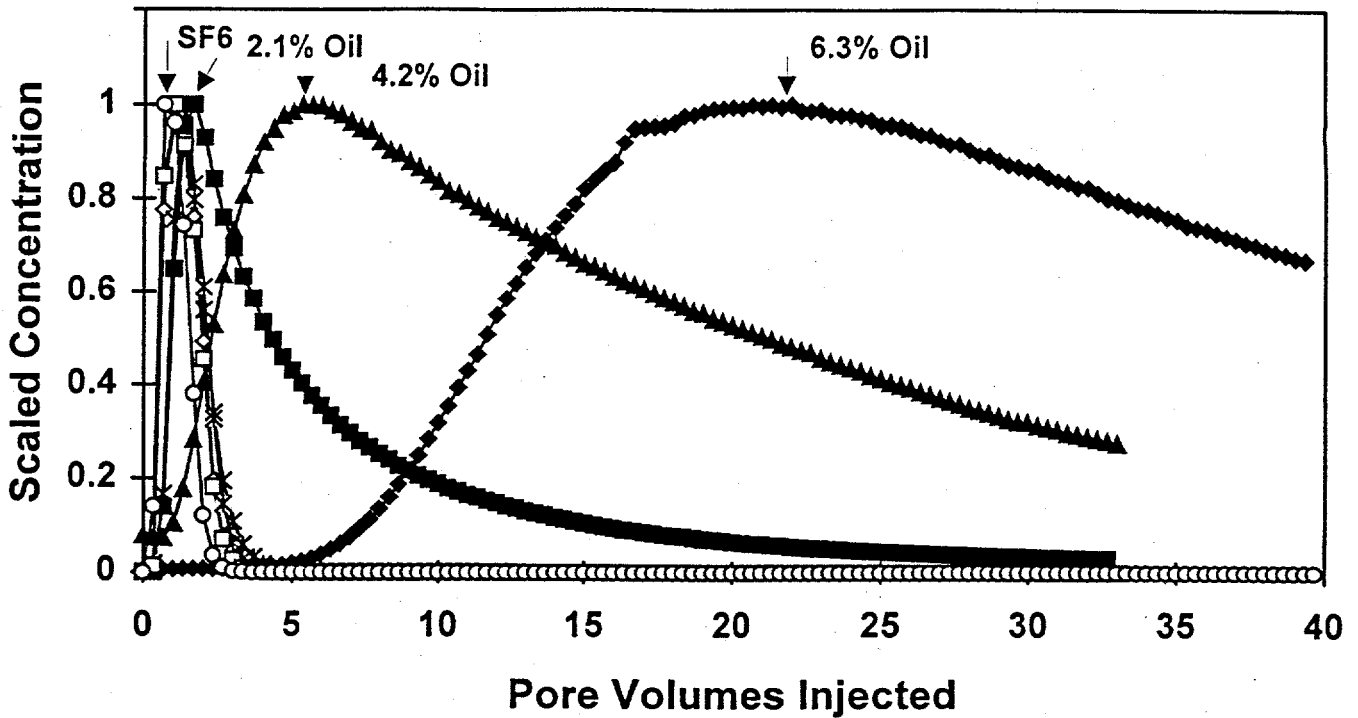
FIGURE 2: Dual Gas Tracer Apparatus

FIGURE 3: Tracer concentration vs. pore volumes injected for SF$_6$ and TCE with NAPL saturations of 0, 2.1, 4.2, and 6.3%. SF$_6$, the non-partitioning tracer, yielded approximately the same curve for each case (open circles, open squares, and open diamonds), and the retention of the partitioning tracer, TCE, in the absence of oil (*'s) is similar. Partitioning tracer retention increased monotonically with increasing NAPL phase (closed squares, closed triangles, and closed diamonds).
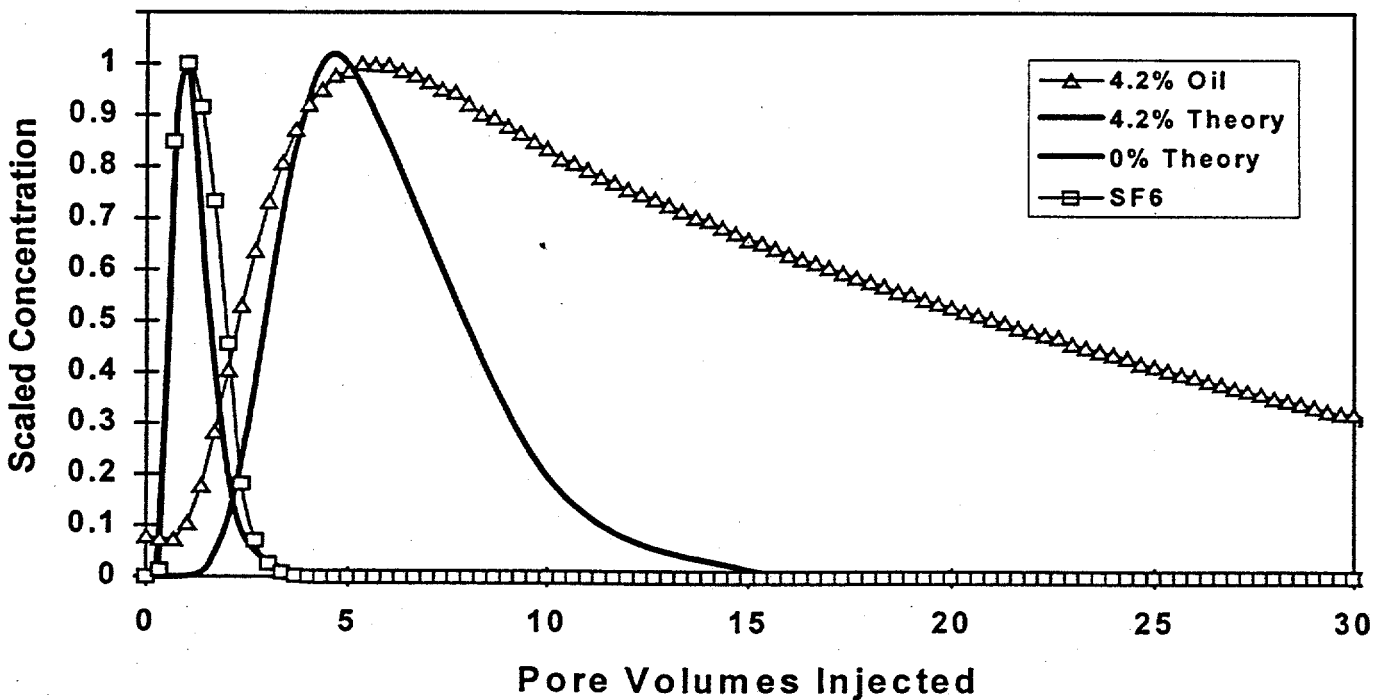

FIGURE 4: Comparison of experimentally observed tracer retention and predictions with a local equilibrium model. Non-partitioning tracer, open squares vs. no retention prediction, solid line; partitioning tracer at 4.2% oil saturation vs. predicted retention.
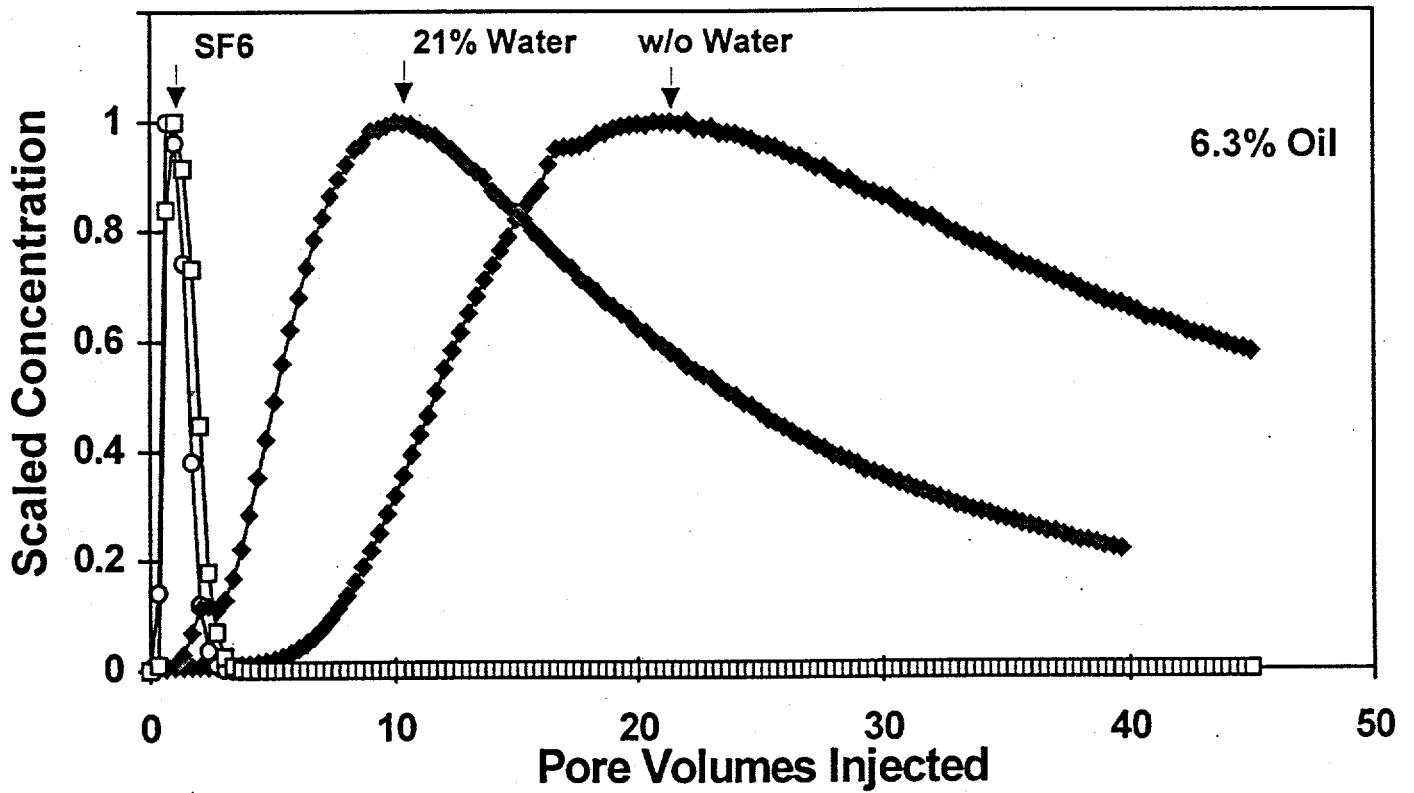
FIGURE 5: Retention of the partitioning tracer by 6.3% oil saturation (dark diamonds) is reduced when water is subsequently added (light diamonds), forming a mass transfer barrier between the tracers and oil lenses.