

PRELIMINARY ASSESSMENT OF HALOGENATED ALKANES AS VAPOR-PHASE TRACERS

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ABSTRACT

New tracers are needed to evaluate the efficiency of injection strategies in vapor-dominated environments. One group of compounds that seems to meet the requirements for vapor-phase tracing are the halogenated alkanes (HCFCs). HCFCs are generally nontoxic, and extrapolation of tabulated thermodynamic data indicate that they will be thermally stable and nonreactive in a geothermal environment. The solubilities and stabilities of these compounds, which form several homologous series, vary according to the substituent ratios of fluorine, chlorine, and hydrogen. Laboratory and field tests that will further define the suitability of HCFCs as vapor-phase tracers are under way.

INTRODUCTION

Tracers that can quantify the behavior of injected fluids in vapor-dominated geothermal systems are needed for reservoir management. In order to evaluate the mass recovery of the injectate, an ideal vapor-phase tracer should have the same concentration in the steam and liquid, regardless of the mass fraction of steam produced from the injected liquid. Unfortunately, only the isotopes of the elements of water even approach this behavior. Of these, deuterium and O-18 have multiple injection sources whose compositions vary with time. Thus, these are qualitative tracers. Tritium, which has been used frequently as a tracer at The Geysers, can be used to document breakthrough but cannot be used to differentiate multiple injection sources in a single tracer test. Consequently, there is a need for several new tracers that can be used to quantify the mass recovery of injected fluids on a field-wide basis. One such approach, which uses multiple tracers to tag each of several injection wells, was employed successfully at the Dixie Valley geothermal system (Adams et al., 1989).

In addition to the characteristics desired in a liquid-phase tracer such as inertness, detectability, and low toxicity, vapor-phase tracers are subject to potential degradation by the high oxygen content of the injection fluid and to more stringent environmental considerations because the steam may be released to the atmosphere. Thus, even if the high oxygen content of the injectate did not degrade the majority of organic compounds, their release into the atmosphere could still be prohibited.

Halogenated alkanes (HCFCs) provide an initial solution to the problem of effective vapor-phase tracers (Table 1). These compounds are completely nontoxic and chemically inert. However, the atmospheric interactions

of the most stable, least expensive, and best-characterized of these compounds with ozone has caused some uncertainty regarding their long-term use and availability. Although there are environmentally benign HCFCs known and more are under development, their availability will be low until some consensus is reached on which are the most acceptable to the manufacturing industries. We are currently investigating a variety of HCFCs in order to be ready to use those that will eventually become available. These compounds include the chlorofluorocarbons, the hydrofluorochlorocarbons, the hydrofluorocarbons, and the fluorocarbons. In this paper we discuss the extent of the HCFC thermochemical data set and present estimates of thermal stabilities and solubilities at reservoir conditions.

HISTORICAL DEVELOPMENT OF HCFCs

Although it seems unlikely, the criteria for refrigerants are similar to those for vapor-phase tracers. Refrigerants must be volatile at low temperatures, withstand cycling through a variety of temperatures in the presence of potentially degrading chemicals, and they must have very low toxicities because of their common household usage. Prior to the introduction of HCFCs, toxic, flammable, or unstable compounds such as methyl chloride, sulfur dioxide, ammonia, propane, or butane were used as refrigerants. In 1928, Thomas Midgley of Frigidaire Inc. was asked to develop nonflammable refrigerants with boiling points between -40° and 0°C, and with low toxicities, high thermal stabilities, and low chemical reactivities. Although this task was considered next to impossible, within three days Midgley had considered the elements of the periodic table that made up the individually unsatisfactory refrigerants and synthesized the first HCFC refrigerant. Using the same methodology, he developed the antiknock agent tetraethyl lead within a similar time period (Midgley, 1937).

TOXICITY

In general, the toxicity of a halogenated compound decreases rapidly with increasing fluoride content and slowly with decreasing molecular weight. The HCFCs currently in use have been tested by Underwriters Laboratory and were shown to be nontoxic at air concentrations greater than 20 volume percent for times of at least two hours (Downing, 1988). They are classified as noncarcinogenic and nonmutagenic, with extremely low acute and chronic toxicities.

Table 1. Status, ozone-depletion potential (ODP), and molecular formula of currently available and future HCFCs. The ODP is an arbitrary scale referenced to the compound R-11. Compounds that will be phased out under the Montreal Protocol (Mont. Prot.) are noted. The brominated compounds have not been considered as tracers because of their excessively high ODPs. na = not available.

Current Choices	ODP	Mont. Prot.	Molecular Formula	Future Choices	ODP	Molecular Formula
R-11	1	yes	CCl ₃ F	R-141b	0.081	CH ₃ -CCl ₂ F
R-12	1.9	yes	CCl ₂ F ₂	R-142b	na	C ₂ H ₃ ClF ₂
R-13	na	no	CClF ₃	R-134a	0.000	CH ₂ F-CF ₃
R-13B1	na	no	CBrF ₃	R-22	0.053	CHClF ₂
R-14	na	no	CF ₄	R-123	0.016	CHCl ₂ -CF ₃
R-21	na	no	CHCl ₂ F	R-124	na	C ₂ HClF ₄
R-22	na	no	CHClF ₂	R-125	0.000	C ₂ HF ₅
R-23	na	no	CHF ₃	R-152a	0.000	C ₂ H ₄ F ₂
R-112	na	no	CCl ₂ F-CCl ₂ F			
R-113	0.8	yes	CCl ₂ F-CClF ₂			
R-114	1	yes	CClF ₂ -CClF ₂			
R-114B2	na	no	CBrF ₂ -CBrF ₂			
R-115	0.6	yes	CClF ₂ -CF ₃			
R-116	na	no	CF ₃ -CF ₃			
R-C318	na	no	c-C ₄ F ₈			
1211	3.0	yes	CBrClF ₂			
1301	10.0	yes	CBrF ₃			
2402	6.0	yes	C ₂ Br ₂ F ₄			

Table 2. Critical constants of HCFCs. Data taken from Reid, Prausnitz, and Poling (1987). Tb = boiling point (K) at one atmosphere, Tc = critical temperature (K), Pc = critical pressure (Bars), Vc = critical volume (cc/mole), Zc = critical compressibility factor (PcVc/RTc), Ω = Pitzer's acentric factor, Dipm = dipole moment (Debyes), and na = not available.

Compound	Tb	Tc	Pc	Vc	Zc	Ω	Dipm
R-11	296.9	471.2	44.1	247.8	0.279	0.189	0.5
R-12	245.2	385.0	41.4	216.7	0.280	0.204	0.5
R-13	193.2	302.0	38.7	180.4	0.278	0.198	0.5
R-14	145.1	227.6	37.4	139.6	0.276	0.177	0.0
R-22	232.4	369.3	49.7	165.6	0.268	0.221	1.4
R-23	191.0	299.3	48.6	132.7	0.259	0.260	1.6
R-114	276.2	418.9	32.6	293.8	0.275	0.246	na
R-115	235.2	353.2	32.3	251.8	0.277	0.279	0.3
R-116	164.9	293.0	30.6	222.0	0.279	na	0.0
R-C318	267.2	388.5	27.8	324.0	0.279	0.356	na
R-218	236.5	345.1	26.8	299.8	0.280	0.325	na
SF ₆	209.6	318.7	37.6	198.8	0.282	0.286	0.0
R-141b	263.4	409.6	43.3	231.0	0.294	0.251	2.1
R-124	263.0	399.9	37.2	244.0	0.273	0.281	na
R-152a	248.2	386.7	45.0	181.0	0.253	0.256	2.3

HCFCs AS HYDROLOGIC TRACERS

The use of HCFCs as hydrologic tracers was first proposed by Thompson et al. (1974). The thesis of this study was that HCFCs had been used extensively and released to the atmosphere for at least 15 years, and therefore could be used to date groundwater qualitatively. Subsequent studies (Thompson, 1976; Thompson and Hayes, 1979) demonstrated a general correspondence of tritium ages with R-11 contents. However, in at least one instance in Texas complete drying of soil caused adsorption/desorption cycles which resulted in spurious enrichments and calculated ages that were too young (Russell and Thompson, 1983). Other uses of HCFCs as anthropogenic tracers include the evaluation of oceanic water-column ventilation rates (Wallace and Moore, 1985; Hammer and Hayes, 1978). HCFCs have also been used as purposefully introduced tracers to evaluate the diffusion parameters, tortuosity, and sorption-affected porosity of the unsaturated zone (Weeks et al., 1982; Kreamer et al., 1988), open-ocean dispersion and air-sea exchange properties (Watson and Ledwell, 1988), and the determination of true groundwater velocities (Ciccioli et al., 1980). These studies were possible because of the extremely low detection limits of one part per trillion that can be achieved with an electron-capture detector (Lovell and Watson, 1978; Thompson, 1976).

PROPERTIES OF AVAILABLE HCFCs AND THEIR ALTERNATIVES

Although there is a broad base of thermodynamic data for HCFCs, these data primarily relate to refrigerant conditions. Thus, the data base is restricted to the pressure-temperature-volume relationships and heat capacities of the anhydrous liquid or gas (Martin, 1959). However, the critical constants of a majority of the compounds are known (Table 2), allowing the estimation of compressibility factors and fugacity coefficients. Because of the corrosion potential of water in a refrigeration system, some data also exist on their solubility in water to temperatures of 100°C (Table 3). The solubility data were extrapolated to higher temperatures by transforming the Henry's Law constants (K_h) to volatility ratios (VR), which represent the ratio of the molal concentration in the gas to that in the liquid. It has been shown empirically that $\log(\text{VR})$ is an approximately linear function of temperature (Drummond, 1981). The compressibility factors required for the transformation of K_h to VR were calculated from the critical constants listed in Table 2 using the three-parameter corresponding states correlation of Lee and Kesler (1975).

The solubilities of HCFCs in water, extrapolated to geothermal conditions, are shown in Fig. 1. The measured solubilities of hydrogen and carbon dioxide, which are common geothermal gases, are shown for reference. The solubility behavior of the HCFCs follow a consistent trend with composition. Those containing hydrogen (R-22, -23, and -31) are the most soluble. Compounds that contain only chlorine and fluorine (i.e., R-12 and -13) are intermediate in solubility, with the solubility being proportional to the number of chlorine atoms in the molecule. Gases that contain only fluorine (i.e., R-14, -116, -218, -C318, and SF_6) are sparingly soluble, with the solubility decreasing as the molecular weight increases.

Table 3. Literature sources for solubility data of HCFCs.

Compound	Formula	Literature Sources
R-11	CCl_3F	3, 4
R-12	CCl_2F_2	2, 3, 4
R-13	CClF_3	2, 3, 4
R-14	CF_4	1, 2, 3
R-22	CHClF_2	2, 4
R-23	CHF_3	2, 4
R-31	CH_2ClF	4
R-114	$\text{C}_2\text{Cl}_2\text{F}_4$	5
R-115	C_2ClF_5	2, 4
R-116	C_2F_6	1, 3
R-C318	$\text{c-C}_4\text{F}_8$	3
R-218	C_3F_8	1
-	SF_6	3

1. Wen and Muccitelli (1973)
2. Parmelee (1953)
3. Park et al. (1982)
4. Numerous sources listed in the compilation of Wilhelm et al. (1977)
5. Stepakoff and Modica (1973)

The stabilities of HCFCs have been tested under various conditions, some of which were similar to those found in geothermal environments. The test conditions ranged from repeated flow cycles through a high-temperature (up to 700°C) compartment (Snider, 1967; Callighan, 1969) to static experiments in sealed quartz vials containing oils, metals, metal oxides, water, or oxygen (Norton, 1957; Parmelee, 1965; Kvalnes and Parmelee, 1957). The experiments with oxygen and water are particularly pertinent because oxygen is absorbed from the atmosphere in the cooling tower and has the potential to degrade many organic compounds.

The stabilities of HCFCs also vary as a function of their compositions. In general, the stability of these compounds is directly proportional to fluorine saturation and inversely proportional to hydrogen saturation. For example, temperatures that will induce 1% decay per year in substituted methanes with one, two, and three fluorines are 298°, 498°, and 538°C, respectively. In contrast, a compound that contains two fluorines but also one hydrogen will decay 1% per year at 250°C. A comparison of decay rates for a substituted methane that contains two fluorines and either two chlorines (R-12) or one chlorine and one hydrogen (R-22) is shown in Fig. 2. These decay curves are based on the experimental data of Norton (1957). In these experiments, oxygen and water had little effect and were grouped with data for the pure compound, indicating that these HCFCs are not likely to be affected adversely by oxygenated injectate.

APPLICATION OF HCFCs AS GEOTHERMAL TRACERS

Although the HCFCs appear to have excellent potential as vapor-phase geothermal tracers, little data exist for these compounds under actual geothermal injection and

reservoir conditions. Two separate approaches are currently being used to produce these data.

The first approach involves the laboratory simulation of a geothermal environment. Strict control of variables in the laboratory will allow the determination of specific properties of the HCFCs, such as their thermal stabilities and solubilities. These tests are currently being conducted at UURI in a laboratory specifically designed for this purpose.

The second approach is to perform field tests. Field tests address the variables inherent in the practical application of HCFCs as tracers, which include the injection of the tracers and the sampling and analysis of production fluids. A field test that will take place in early 1991 is

planned for the underpressured region of the Southeast Geysers. This test will inject R-12 and -13 simultaneously into NCPA well C-11. At least 10 production wells will be monitored.

The tracers will be injected from pressurized cylinders at a constant rate. The production well fluids will be sampled using evacuated flasks that contain cadmium chloride, a method that is similar to conventional gas sampling. No special equipment or ports are needed. The purpose of the cadmium chloride is to precipitate hydrogen sulfide, which can interfere with the analysis. The analytic method, developed at Thermochem, is performed on a gas chromatograph equipped with an electron capture detector. Detection limits as low as 0.1 parts per billion can be achieved using this method.

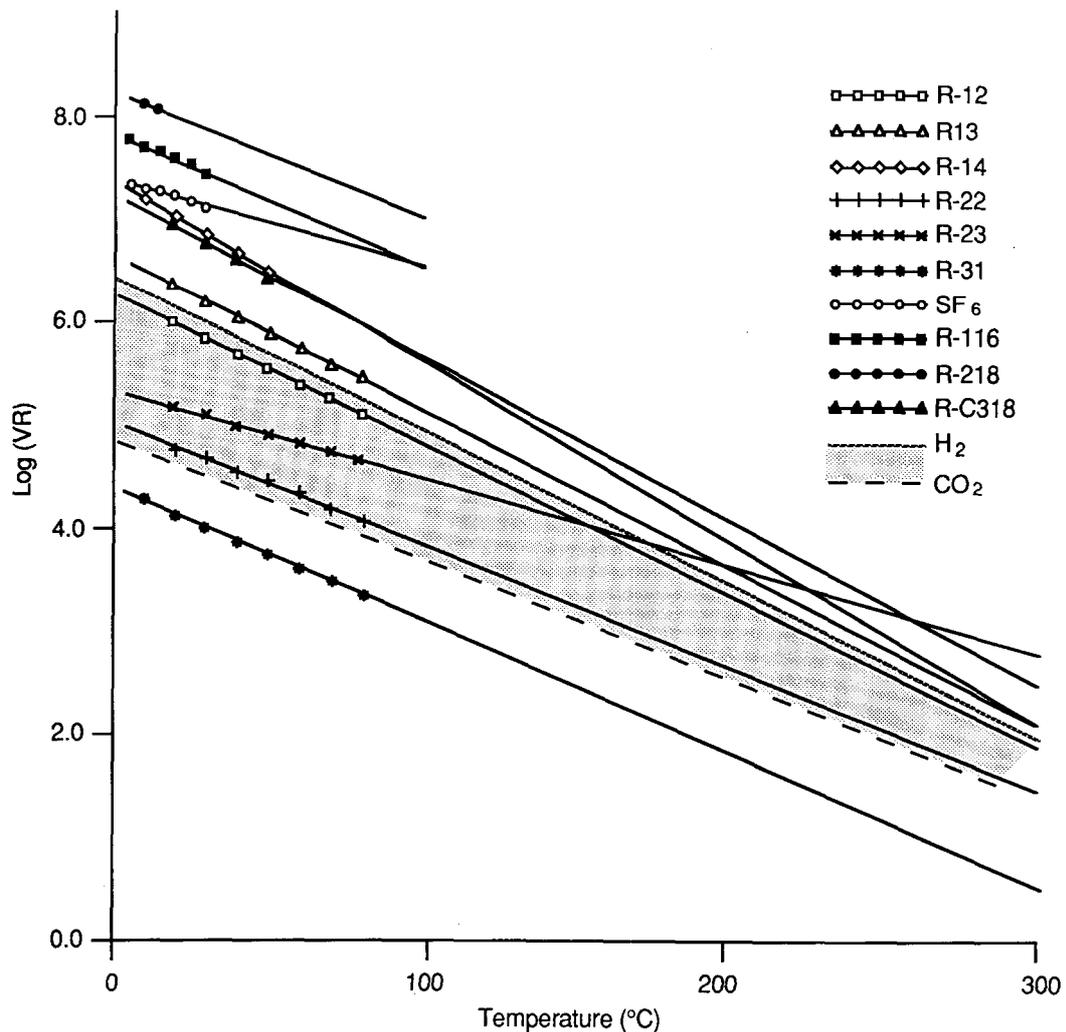


Figure 1. Temperature variations of the volatility ratios (VR) of the HCFCs. VR is defined as the ratio of the molal concentrations in the steam and liquid phases. The shaded area represents the VR region of common geothermal gases (Drummond, 1981). The data sources for the HCFCs are listed in Table 3. The symbols represent measured values, while the solid lines are extrapolations. The lines for H₂ and CO₂ represent measured values throughout the temperature range. Note that the shallow slopes of R-23 and SF₆ will not converge to zero at the critical point of water, indicating that the solubility data for these compounds may be of poor quality.

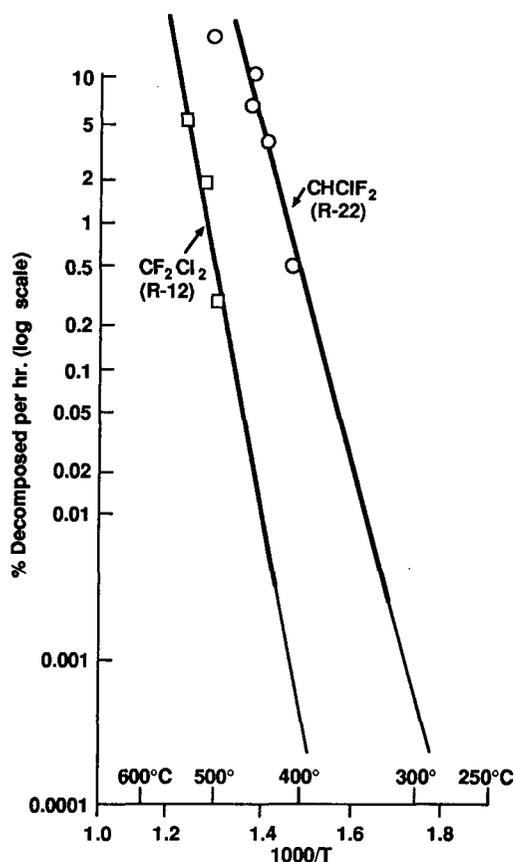


Figure 2. Decay rates of two HCFCs, R-12 and -22. The hydrogen-containing compound, R-22, is representative of the new generation of HCFCs. Up to one percent each of water and oxygen were included in the experiments that produced these data. Data from Norton (1957).

Several chromatographic scans of steam from The Geysers were performed in late 1989 to measure the background levels the HCFCs that are commonly found in the atmosphere, which include R-12 and -13. Background concentrations in these samples were below detection.

CURRENT AND FUTURE AVAILABILITY OF HCFCs

Although HCFCs are nearly ideal for use as vapor-phase tracers, their use as industrial chemicals has been criticized because they influence the steady-state concentration of ozone in the stratosphere. This effect is due to the presence of chlorine or bromine in the molecule. For example, R-11, which contains 3 atoms of chlorine per molecule, has been assigned an ozone-depletion potential (ODP) of 1.0. Brominated compounds, which are widely used as fire extinguishing

agents, have ODPs which range from 3 to 10 (Table 1). In contrast, compounds with similar properties, but which contain hydrogen in addition to chlorine and fluorine, have ODPs as low as 0.016. Compounds on only hydrogen and fluorine pose no threat to the ozone layer and have an ODP of zero.

Because of the suspected ozone degradation from the HCFCs currently in use, new compounds with similar properties are being developed for use as refrigerants at breakneck speed. The candidates that can perform as replacements are listed in Table 1 under the heading of future choices. Of these, R-123 and -134a are on the EPA inventory of existing chemicals (i.e., grandfather clause) and can be produced without extensive toxicity testing. The others are not grandfathered and production will be delayed until testing is completed. Most of the new compounds have passed preliminary toxicity tests, but the complete tests are still in progress and won't be finished until the mid-1990's. Despite these potential delays, plants are already being built to produce many of the new compounds on the assumption that they will pass the toxicity tests.

SUMMARY

Halogenated alkanes (HCFCs) possess many of the characteristics required for vapor-phase tracers. These compounds are very stable and nontoxic, and are available in a wide variety of compositions. HCFCs consist of various combinations of hydrogen, chlorine, and fluorine on a saturated carbon skeleton. In general, the stabilities of HCFCs are increased by the addition of fluorine atoms to the molecule, while solubilities are increased in proportion to the number of chlorine or hydrogen atoms. The ozone-depletion potential decreases with decreasing chlorine content and is zero for compounds with no chlorine.

Stability data exist for some HCFCs in environments similar, but not identical, to those believed to occur in vapor-dominated geothermal systems. These data indicate that HCFCs may be sufficiently stable for use as tracers. Tests are currently under way to determine their stabilities under simulated and actual geothermal conditions. The results of our analytic development for field tests indicate that a detection limit as low as 0.1 parts per billion can be achieved.

The costs of HCFCs vary as a function of their use by the manufacturing and refrigeration industries. Cost and availability will vary during the next few years as new HCFCs are developed to replace those with high ozone-depletion potentials. We expect that many of the new compounds will be useful as vapor-phase tracers.

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