

Immobilization or Recovery of Chlorinated Hydrocarbons from Contaminated Groundwater Using Clathrate Hydrates: A Proof-of-Concept

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The objective of this study was to evaluate whether the formation of solid clathrate hydrates by certain chlorinated hydrocarbon compounds and water would be amenable to in situ immobilization and ex situ recovery of these contaminants from groundwater. Using help gases to enhance the formation of the solids, the melting points of clathrate hydrates of CCl_4 , 1,1-DCE, PCE, and TCE were measured at 1 atm pressure. CCl_4 hydrates had melting points between 16 and 20 °C; 1,1-DCE hydrates had lower melting points of between 11 and 13 °C. TCE and PCE hydrates could not be formed unless crystallizing seed material was introduced into the system. Concentrations of CCl_4 and 1,1-DCE in the hydrate phase and the aqueous phase after hydrate formation were determined from experiments in which the chlorinated hydrocarbon compounds existed as a separate dense nonaqueous phase liquid (DNAPL) or as dissolved species in water. Enrichment factors (C^H/C^A , where C is the concentration of the organic in the hydrate [H] and aqueous [A] phase) were between 200 and 500 for 1,1-DCE and CCl_4 , respectively. These experiments provided a proof-of-concept suggesting that the in situ immobilization or ex situ recovery of some common hydrophobic groundwater contaminants may be possible in a wide range of subsurface environments.

Introduction

Clathrate hydrates are solid crystalline "inclusion" compounds formed from mixtures of small nonpolar organic molecules and water. Under appropriate conditions of temperature and pressure, the water molecules form cage structures that contain the molecules of the nonpolar organic compound. There are three primary cage structures, or polyhedra, formed by hydrogen-bonded water molecules (Figure 1). The structure of the polyhedra depends on the size and chemical properties of the nonpolar organic molecule included in the cavities (1). In nature, these structures are typically further arranged into well-defined, three-dimensional crystalline solids.

The discovery of these structures in gas transmission lines (2) initiated an intense research effort to understand clathrate hydrate formation. Particular effort was directed at identifying

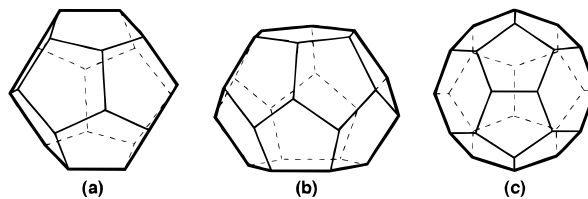


FIGURE 1. The three primary clathrate hydrate structures (1). (A) Pentagonal dodecahedron (12 pentagonal faces; average cavity diameter of 7.82 Å); (B) tetrakaidecahedron (12 pentagonal and two hexagonal faces, average cavity diameter of 8.66 Å); and (C) hexakaidecahedron (12 pentagonal and four hexagonal faces, average cavity diameter of 9.35 Å).

methods to reduce the formation of these structures because they clogged the porous media, thereby reducing oil recovery. Subsequent research discovered that trillions of cubic meters of natural gas was present as clathrate hydrates in the ocean floor and the permafrost regions of the earth (3). This estimate and more recent ones (1, 4) suggests that the majority of the fossil fuel in the world exists as clathrate hydrates. The enormous financial reward for developing technologies to recover this potential energy resource has further spurred applied and basic research of these structures (1–7). Most recently, research of clathrate hydrates has been directed toward evaluating the potential impact of global warming due to the dissociation of clathrate hydrates containing greenhouse gases (7). The melting of these structures would result in the release of enormous quantities of these gases that could further exacerbate global warming.

Clathrate hydrate formation results from the hydrophobic effect wherein the water molecules orient themselves around the nonpolar organic molecule to preserve their hydrogen bonding. Under the appropriate conditions of temperature and pressure, the hydrogen-bonded water molecules freeze and entrap the nonpolar molecules, forming solid clathrate hydrates. As dictated by Gibb's phase rule (1), the maximum temperature at a given pressure required to form clathrate hydrate is invariant for a three phase system (more specifically, degrees of freedom (F) = number components (water, organic compound) – number phases (liquid water, liquid or gaseous organic compound, solid clathrate hydrate) + 2, or $F = 2 - 3 + 2 = 1$). Therefore, if the temperature of the system is fixed, then the pressure above which clathrate hydrate formation will occur is also fixed. Similarly, if the pressure is fixed, the temperature below which clathrate hydrate formation will occur is also fixed. A schematic of a pressure–temperature phase diagram of a hydrate formation compound is presented in Figure 2A. As long as the pressure and temperature of a system lies in the region above the line, i.e., within the hydrate stability zone, the hydrates are stable; at conditions below the line, the hydrates are not stable and will eventually dissociate or melt. The PT phase diagram for the clathrate hydrate formation and stability depends on the size of the nonpolar guest molecule (1). Generally, at a given temperature, large molecules require lower pressures for the clathrate hydrate formation than smaller guest molecules (1).

There are almost 80 compounds that form the clathrate hydrates including several of the Light Non-Aqueous Phase Liquid (LNAPL) and some of the Dense Non-Aqueous Phase Liquid (DNAPL) contaminants in groundwater (5, 6). Therefore, a novel application for clathrate hydrates might be to use them to sequester or stabilize hydrophobic contaminants in the aquifer or to improve removal efficiency during ex situ treatment. However, since the temperature and pressure

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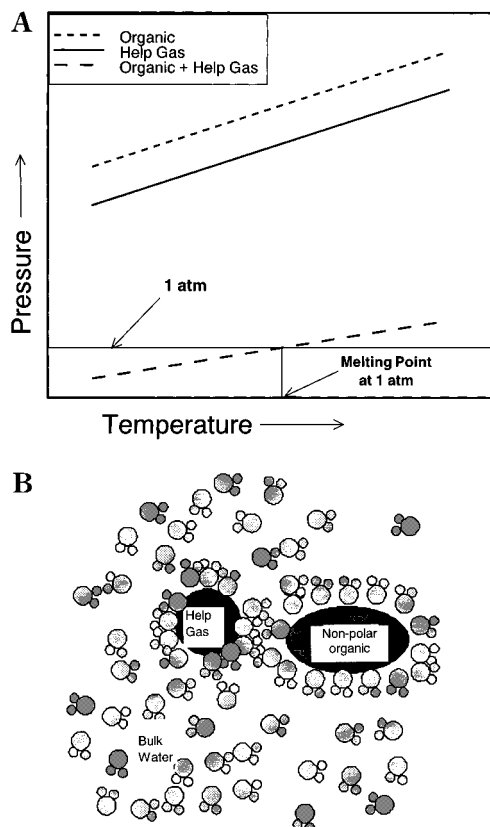


FIGURE 2. (A) Schematic of the pressure–temperature phase diagram for clathrate hydrates containing nonpolar organic compound with and without a help gas. (B) Schematic of the influence of help gases on hydrate formation.

conditions in the plumes are not appropriate for clathrate hydrate formation by the Non-Aqueous Phase Liquid (NAPL) contaminants, they remain as immiscible or dissolved liquids. If the NAPLs can be converted into solid clathrates, which are stable at or above the conditions prevalent in the plumes, the contamination of the plumes can be mitigated. One way to convert the NAPL molecules into clathrates stable at the conditions in the plumes is by the introduction of compound(s) which increase the hydrate stability zone. These compounds are also referred to as “hydrate formation promoters” or “help gases” because their inclusion in the clathrate lattices enhances the stability of the hydrate structure. As noted by Von Stakelberg and Muller (8), “in the presence of the *help gas* the upper limit of hydrate dissociation conditions can be raised so that it is virtually replaced by the size factor of the guest molecule”. Typical effect of the *help gas* on the hydrate stability zone is also shown (dashed line) in Figure 2a. It can be seen that in the presence of the *help gas*, at any given pressure, the hydrates are stable to a much higher temperature than in the absence of the *help gas*.

The effect of *help gas* was first reported in 1883 by DeForcand (9) who examined the clathrate hydrate formation of CH_2Cl_2 , CHCl_3 , CCl_4 , $\text{H}_2\text{C}=\text{CHCl}$, $\text{H}_2\text{C}=\text{CCl}_2$, $\text{ClHC}=\text{CCl}_2$, and other small fluorinated and brominated hydrocarbons. Von Stakelberg and co-workers (8, 10, 11) later determined the crystal structure and hydrate numbers. The studies of both DeForcand and Von Stakelberg and co-workers used H_2S as the *help gas* to promote hydrate formation at conditions above the freezing point of water and atmospheric gas pressure. From the results of their study, Von Stakelberg and co-workers concluded that the molecules of van der Waals diameter larger than 7 Å will not form hydrates even in the presence of the *help gas*. However, much later, Ripmeester and co-workers (12, 13) reported the formation

TABLE 1. Dissociation Temperatures of Some of the Constituents of the NAPLs at 1 Atm Pressure in the Absence and Presence of a Help Gas To Stabilize the Hydrates (5)

NAPL constituent	without help gas	with H_2S as help gas
CH_3Cl	+7.5	+16.3
CCl_4	no hydrate formation	+17.3
CH_3Br	+11.3	not measured
CH_3F	+3.7	not measured
$\text{C}_2\text{H}_5\text{Cl}$	no hydrate formation	+7.2
$\text{C}_2\text{H}_5\text{Br}$	no hydrate formation	+13.0
CH_2Cl_2	no hydrate formation	+14.0
CH_3I	no hydrate formation	+14.2
CH_3CHCl_2	no hydrate formation	not measured
$\text{CH}_2\text{ClCH}_2\text{Cl}$	no hydrate formation	+11.3

of double hydrates of several large organic molecules whose van der Waals diameter falls above the maximum diameter of the guest species proposed by Von Stakelberg. For example, with xenon as the *help gas*, Ripmeester and co-workers (12, 13) showed that clathrate hydrates of structure II and structure H are formed by large organic molecules such as benzene, cyclopentane, acetonitrile, neopentane, cycloheptane, cyclooctane, etc., whose molecular diameter is on the order of 9–10 Å. The structure H type hydrates involve the formation of another larger cavity (not shown in Figure 1) with 12 pentagonal and eight hexagonal sides (12, 13).

Examples of *help gases* or *hydrate formation promoters* are CO_2 , air, H_2S , noble gases (excluding helium and neon), etc. The effect of H_2S (the *help gas*) on the hydrate dissociation temperature at 1 atm pressure for some of the halogenated hydrocarbons are listed in Table 1 (5). It can be seen from the data in Table 1, the introduction of the *help gas* now enables the formation of the clathrate hydrates at 1 atm pressure and temperatures at or above those existing in the plumes. It should be noted that CCl_4 and larger molecules cannot form clathrate hydrates on their own since they can only occupy the large cavities of the clathrate lattice and require the help gas molecules to occupy the smaller cavity and stabilize the structure (5).

A simplified schematic diagram of how help gases promote clathrate hydrate formation in the presence of a hydrophobic compound is presented in Figure 2B. Water molecules in the liquid phase have weak connecting hydrogen bonds. These bonds form and break rapidly resulting in their somewhat random orientation. In the presence of a hydrophobic compound, the water molecules become appreciably more oriented such that the oxygen atoms are directed toward the hydrophobic compound. This orientation results from the dipole moment of the water molecules orienting themselves parallel to the water-organic interface. The introduction of a help gas into the system further organizes the water molecules. This organization is also due to the hydrophobicity of the gas. In localized regions where both the hydrophobic compound and the help gas exist, the highly organized water solidifies, forming clathrate hydrate structures containing the molecules of the help gas and the hydrophobic compound. A more detailed description of the role of help gases in clathrate hydrate formation can be found in Sloan (1).

The goals of this work were to evaluate whether the formation of clathrate hydrates would be amenable to in situ immobilization or ex situ recovery of chlorinated hydrocarbon compounds from contaminated groundwater. The in situ stabilization technology would involve injecting a help gas into an aquifer that would immobilize (stabilize) the targeted chlorinated hydrocarbon compound as solid clathrate hydrates in the aquifer. Once the help-gas injection is terminated, the contaminant is expected to remain as an immobile solid phase provided the temperature in the system

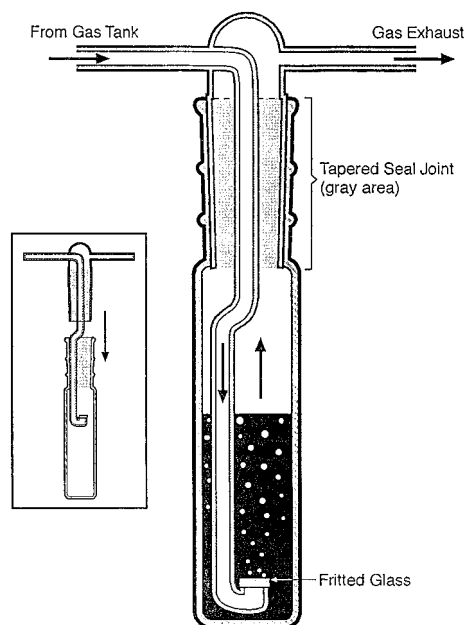


FIGURE 3. Schematic of the gas-bubbling reaction vessel.

did not exceed the hydrate's melting point. With the in situ remediation approach, there would be some concern of decreasing the permeability of the aquifers due to the formation of the solid clathrate structures. This would generally be a function of the concentration of the organic in the aquifer. At very low concentration of the organic (on the order of ppm) in the aquifer, the formation of the clathrate hydrates should have no impact on the aquifer permeability. The ex situ recovery technology would treat a waste stream, such as the waste stream from a groundwater pump-and-treat operation.

For the in situ option, experiments were conducted to determine whether clathrate hydrates of selected chlorinated hydrocarbon compounds could be formed with help gases under temperature and pressure conditions existing in subsurface groundwater. Our approach was to form clathrate hydrates of carbon tetrachloride (CCl_4), dichloroethylene (DCE), trichloroethylene (TCE), and perchloroethylene (PCE) existing as a dissolved species or as a separate dense nonaqueous phase liquid (DNAPLs). Two help gases, H_2S and xenon, were evaluated. Once formed, the dissociation temperatures of the clathrate hydrates were measured at 1 atm; the approximate pressure at the top of a water table. The enrichment and separation factors of dissolved chlorinated hydrocarbons were also measured to provide a measure of the separation efficiency of this technique for the ex situ application.

Materials and Methods

Melting Point Experiments. The first set of experiments were designed to provide the melting points (dissociation temperatures) of various hydrates containing chlorinated hydrocarbon compounds formed in the presence of either H_2S or xenon gas. A single sample of the chlorinated-hydrocarbon/water/help gas was used for the melting point determination of each chlorinated-hydrocarbon/help gas system (i.e., the melting points tests were not duplicated). The procedure used in these experiments was based on the one presented by Sloan (1). The gas-bubbling reaction vessel (ACE Glass Inc.) used in these experiments is shown in Figure 3. This reaction vessel consisted of two glass pieces: a chamber for holding the chlorinated hydrocarbon compounds and water and an inside piece for sealing the chamber and delivering and venting the help gas. The fritted delivery tube associated

with the inside piece introduced the gas as small bubbles, and the vent tube ensured that the experiments were conducted at 1 atm. In a typical experiment, the chamber was filled with about 10 mL of the chlorinated carbon compound and about 40 mL of deionized water. The entire assembly was then placed in a temperature-controlled water bath cooled to 5 °C. The help gas was then bubbled through the vessel for about 1 min, which was a sufficient amount of time for clathrate hydrate formation to occur. The gas inlet and outlet lines were then closed with plastic tube clamps, and the gas-bubbling reaction vessel was shaken vigorously to ensure complete mixing of its contents.

After clathrate hydrate formation at 5 °C, the temperature of the water bath was increased at a rate of about 1 °C per 24–48 h. During each 24- to 48-h equilibration period, the hydrate cell was shaken periodically. At the end of the equilibration period, the contents of the hydrate cell were visually examined for the presence of the hydrates. The temperature at which all visible hydrates in the cell disappeared was defined as the hydrate melting point and is the same as that presented by Sloan (1). In these experiments it was very easy to identify the hydrates since they are present as a white crystalline material in the reaction vessel.

Enrichment Factor and Separation Efficiency Experiments. Experiments were also conducted to determine the concentration of the chlorinated hydrocarbon compounds in the hydrate phase. After forming the clathrate hydrates at 5 °C using the above procedure, the solutions were vacuum filtered through a 0.45 μm filter that was precooled to ~ 3 °C. The solid hydrate phase was then permitted to melt at room temperature. The aqueous and organic phases of the melted hydrates were separated using a separating funnel and both phases were weighed. The enrichment factor was calculated using the following equation

$$\text{enrichment factor} = C^{\text{H}}/C^{\text{A}} \quad (1)$$

where C^{H} is the concentration (wt %) of the chlorinated hydrocarbon compound in the hydrate and C^{A} is the saturation concentration (200 ppm for 1,1-DCE and 800 ppm for CCl_4) in the aqueous phase.

Two experiments were conducted to evaluate the separation efficiency of this technique for waste stream recovery of dissolved chlorinated hydrocarbon compounds. Hydrates were formed by bubbling Xe into solutions containing 50 and 200 ppm of CCl_4 in water. The hydrates were allowed to settle to the bottom of the gas-bubbling reaction vessel, and then a sample of the aqueous liquid (upper phase) was collected. The concentrations of the initial (C_i) and final (C_f) CCl_4 solutions were determined by extracting into hexane and then analyzing by gas chromatography using a UV detector and standard stock solutions for calibration. The separation efficiency was calculated using the following equation:

$$\text{separation efficiency (\%)} = [C_i - C_f] \cdot 100 / C_i \quad (2)$$

As with the case of the melting point determination tests, the separation efficiencies reported are also based on single point determinations.

Results and Discussion

Melting Point Experiments. The first experiment was designed to duplicate experiments reported by DeForcand (9). The help gas was H_2S , and the nonpolar organic compound was CCl_4 . The measured melting point at 1 atm was between 19 and 20 °C (Figure 4). This melting point is 2 °C greater than that reported by DeForcand (9) and Jeffrey and McMullan (5). The slightly greater melting point in our study was likely due to the inclusion of air into the hydrates,

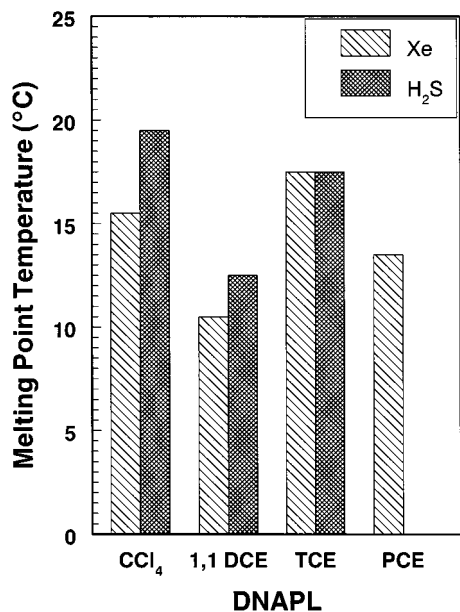


FIGURE 4. Melting points (or dissociation temperatures) at 1 atm of clathrate hydrates formed in the presence of H₂S and Xe (*TCE and PCE hydrates required seed material for formation; no experiment was conducted to form PCE hydrates with H₂S).

which has been shown to increase the melting point (5). Since our experimental system was designed to simulate aquifer conditions, no attempt was made to eliminate air. Also, the inclusion of air could be beneficial to the formation of clathrate hydrates of the chlorinated hydrocarbons in the aquifers because it would increase the hydrate melting points even more.

The hydrate melting point temperatures with H₂S as the help gas were also measured for 1,1-DCE and TCE, and these results are shown in Figure 4. The melting point of the 1,1-DCE clathrate hydrates was between 12 and 13 °C. Clathrate hydrates of TCE could not be formed even after 48 h of equilibrating at 5 °C, repeated bubbling with H₂S, and repeated mixing of the phases. The reason that TCE would not form hydrates is not known; however, it may be due to the fact that TCE has a larger molecular size than either 1,1-DCE or CCl₄. The larger molecule may not easily form the nuclei to promote rapid clathrate hydrate formation (i.e., the larger molecule may have precluded the formation of the cage-like structure to initiate the primary nucleation of the clathrate hydrates). TCE hydrates formation was achieved by introducing clathrate hydrate seed crystals to the system by adding a small quantity of tetrahydrofuran (THF) (approximately 5 wt % of the TCE to the liquid phases) and then introducing H₂S gas. The TCE hydrates formed very rapidly, <1 min, and the melting point of these hydrates was between 17 and 18 °C. The use of clathrate hydrate seed crystals to promote hydrate formation rates is reviewed by Sloan (1). The encapsulation of TCE in the clathrates in the presence of THF was concluded from the precipitation of the white solids to the bottom of the reaction vessel; simple THF/H₂S clathrates are translucent, lighter than water, and float to the surface. No attempt was made to form PCE hydrates using H₂S gas.

Although the use of H₂S in these experiments permitted comparison to previous results, it is not an especially good gas for environmental remediation purposes because it is highly toxic. Xenon is another help gas that has been shown to form similar hydrate structures as H₂S, S1 hydrates, composed of pentagonal dodecahedron and tetrakaidecahedron, Ripmeester et al. (12, 13). The similar chemical behavior of these two help gases in hydrate formation has

TABLE 2. Separation Efficiency and Enrichment Factors Achieved by Forming Hydrates in Solutions Containing Dissolved Chlorinated Hydrocarbons

chlorinated hydrocarbon	aqueous concn (ppm)	enrichment factor ^a (dimensionless)	separation efficiency ^b (%)
1,1-DCE	200	200	
CCl ₄	800	500	
CCl ₄	200		94
CCl ₄	50		72

^a Enrichment factor is defined by eq 1. ^b Separation efficiency is defined by eq 2.

been attributed to their near identical size, approximately 4.6 Å, Sloan (1). Xenon has also been shown to form hydrates with several large organic (12, 13).

Xenon was used as a help gas to form hydrates of 1,1-DCE, CCl₄, TCE, and PCE (Figure 4). The melting points were generally the same or slightly less than those reported hydrates formed with H₂S. Neither PCE or TCE hydrates could be formed without nucleating the system with THF clathrate crystals. Once the THF was introduced into the system as described above for the H₂S/TCE experiment, clathrate formation was rapid. The melting point of the TCE hydrate formed with Xe was identical to that formed with H₂S, between 17 and 18 °C. The melting point of the PCE hydrate was between 13 and 14 °C.

No specific correlation could be made between the molecular size, number of chlorine atoms, and the dissociation temperatures in Figure 4. For example, an increase in the molecular size between 1,1-DCE and CCl₄ results in an increase in the dissociation temperature, but PCE which is larger than CCl₄ has a lower dissociation temperature. Similarly, although the increase in the number of chlorine atoms from 1,1-DCE to TCE results in an increase in the melting point temperature, the PCE system was found to have a lower dissociation temperature than TCE. The variation in the results could be due to the differences in the relative ratios of the help gas to the chlorinated hydrocarbon required to form the stable clathrate hydrate lattices. However, no attempt was made to determine the stoichiometric numbers of the help gas and the chlorinated hydrocarbon molecules in the clathrates.

There was some concern about the long-term stability of the clathrate hydrates should this approach be used for the in situ immobilization of the chlorinated hydrocarbon molecules in the aquifers. The stability was tested by forming CCl₄ hydrates in the presence of the help gas Xe and holding the system at a temperature of 12 °C and 1 atm pressure for a period of two months. During the entire period, the hydrates remained stable. This result suggests that, in principle, the hydrates once formed could remain at the bottom of the aquifer as long as the temperature does not go above the hydrate stability zone.

Enrichment Factor and Separation Efficiency Experiments. To evaluate the applicability of this process for ex situ applications, the enrichment factor (eq 1) and the separation efficiency (eq 2) were determined using aqueous solutions of dissolved CCl₄ and 1,1-DCE (Table 2). The enrichment factor for the hydrates formed in a 200-ppm 1,1-DCE solution was 200. The enrichment factor for the hydrates formed in an 800-ppm CCl₄ solution was 500. Thus, the hydrates concentrated 1,1-DCE by a factor of 200 and CCl₄ by a factor of 500 for these experimental conditions. Stated differently, 18% (wt) and 43% (wt) of the hydrates were comprised of 1,1-DCE and CCl₄, respectively. The separation efficiency of CCl₄ at 200 ppm was 94%, and at 50 ppm was 72% (wt) (Table 2). Stated differently, 94% (wt) and 72% (wt) of the dissolved CCl₄ was transferred to the hydrate phase in 200 and 50 ppm CCl₄ solutions.

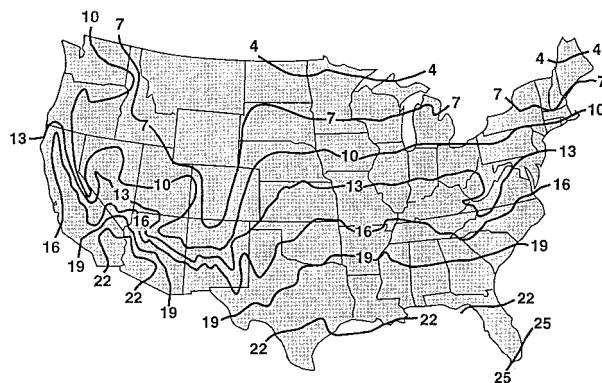


FIGURE 5. Approximate groundwater temperatures (°C) at depths between 10 and 25 m (14).

These rather large separation efficiency values and enrichment factors indicate that this may be an efficient waste stream treatment process (Table 1). Much higher values could very likely be achieved if a better hydrate-liquid separation process was developed. An important attribute of this process in an ex situ application is that it is not dependent on another separation medium, such as activated carbon. It is also not dependent upon volatilization, such as vapor stripping, which requires recovery of the vapor phase. Instead it simply involves forming the hydrate and then separating the liquid and solid phases.

Conclusions

The objective of this study was to evaluate whether clathrate hydrates of four chlorinated hydrocarbon compounds could be formed at 1 atm with melting points that are above the ambient temperature of most groundwaters. The four organic compounds evaluated, CCl_4 , 1,1-DCE, PCE, and TCE, are among the most common groundwater contaminants found throughout the U.S. This work showed that, depending on the identity of the help gas, CCl_4 hydrates had melting points between 16 and 20 °C and 1,1-DCE hydrates had melting points between 11 and 13 °C. To put these temperature values into context regarding the in situ application of this technology, a map of the average groundwater temperatures in the U.S. (14) is presented in Figure 5. Regions with temperatures greater than the melting points would not be suitable for this technology. This figure suggests that CCl_4 hydrates would remain stable in most aquifers in the U.S., whereas 1,1-DCE hydrates would be stable in only the cooler regions of the U.S.

TCE and PCE hydrates could not be formed at 1 atm by simply bubbling help gases into the system; their formation required the introduction of a crystallizing seed material, THF. The need to use a seed material compromises the application of this approach for in situ remediation of TCE and PCE contaminated groundwater. It is possible that at the higher static pressures existing below a water table, that TCE- and PCE-hydrates may form without the introduction of seed materials. Similarly, higher static pressures would be expected to increase the melting points of CCl_4 and 1,1-DCE above those measured in these experiments at 1 atm.

A casual, yet important, observation was made during these experiments; that is, the hydrates containing chlorinated hydrocarbons settled to the bottom of the reaction vessel. Hydrates formed with only gas and water were lighter than water and rose to the water-air interface. It suggests that these organic-containing hydrates will settle to the bottom of a plume, thereby increasing the hydrostatic pressure head and increasing the stability of the hydrates.

Finally, the settling of these hydrates suggests that they will be less inclined to move with groundwater flow and more inclined to remain immobilized in the aquifer.

Hydrate formation may also provide a means to separate dissolve chlorinated hydrocarbon compounds from wastewater streams, such as those generated from pump-and-treat remediation technologies. Enrichment factors of between 200 and 500 were obtained using rather unsophisticated solid-liquid separation techniques (single-pass filter membrane). Certainly, several other hydrophobic compounds could also be concentrated by this technique.

These results suggest that the in situ immobilization of some common hydrophobic groundwater contaminants via clathrate hydrate formation may be possible in a rather wide range of environments. The remediation process would involve bubbling a help gas into the plume for a short contact time, less than a minute. This process may be a simple and passive solution to a very complicated environmental remediation problem.

No attempt was made in these studies to optimize this process for remediation purposes. Also for remediation applications different types of help gases should be evaluated since neither gas used in this study, H_2S or Xe , is especially practical for in situ applications (Xe is expensive and H_2S is potentially lethal). A possible help gas is CO_2 , which will help minimize the safety concerns as well as reduce the cost of the immobilization process. However, this may come at an expense of the range of the clathrate hydrate stability.

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Literature Cited

- (1) Sloan, E. D. *Clathrate Hydrates of Natural Gas*; Dekker: New York, 1990.
- (2) Hammerschmidt, E. G. *Ind. Eng. Chem.* **1934**, 26(8), 851-55.
- (3) Kuustaa, V. A.; Hammerschmidt, E. C.; Holder, G. D.; Sloan, E. D. *Handbook of Gas Hydrate Properties and Occurrence*; DOE Report No. DOE/MC/19239-1546, 1983.
- (4) Monastersky, R. *Sci. News* **150**, 298.
- (5) Jeffrey, G. A.; McMullan, R. K. *Prog. Inorg. Chem.* **1967**, 8, 43-108.
- (6) Jeffrey, G. A. *Inclusion Compounds*; Academic Press: London, 1984; Vol. 1, pp 135-90.
- (7) Englezos, P. *Ind. Eng. Chem. Res.* **1993**, 32, 1251-73.
- (8) Von Stakelberg, M.; Muller, H. R. *Z. Electrochem.* **1954**, 58, 25.
- (9) DeForand, R. *Ann. Chim. Phys.* **1883**, 28, 5.
- (10) Von Stakelberg, M.; Meinhold, W. *Z. Electrochem.* **1954**, 58, 40.
- (11) Von Stakelberg, M.; Fruhbuss, H. *Z. Electrochem.* **1954**, 58, 99.
- (12) Ripmeester, J. A.; Tse, J. S.; Ratcliffe, C. I.; Powell, B. M. *Nature* **1987**, 326, 8, 135.
- (13) Ripmeester, J. A.; Ratcliffe, C. I. *J. Phys. Chem.* **1990**, 94, 8773.
- (14) US-EPA (United States-Environmental Protection Agency) *Protection of public water supplies from groundwater contamination*; Cincinnati, OH, U. S. Environmental Protection Agency: EPA/625/4-85/016, 1985.

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