

VOC and SVOC Remediation Using Thermally Enhanced Hydrolysis

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ABSTRACT: Hydrolysis is a water substitution reaction that aids in the breakdown of many organic molecules. While it has been long studied and used by chemists, hydrolysis has been underutilized by the environmental remediation community. Hydrolysis has been overlooked because its reaction rates, at ambient conditions, are in most cases too slow for efficient degradation of harmful organic compounds. In the last decade new subsurface thermal remediation technologies have been used to treat sites containing organic contaminants. These thermal treatment methods have opened up the possibility of utilizing the hydrolysis reactions as part of site treatment. Applicability of thermally enhanced hydrolysis for various contaminants, remedial optimization techniques, cost savings, and a remediation case study are discussed.

INTRODUCTION

During hydrolysis, an organic compound chemically reacts with water. The reaction takes place without regard to redox conditions, dissolved minerals, or the presence of soil microbes. The organic compound needs to be dissolved into water for the reaction to take place. The general hydrolysis reaction,



involves the exchange of some functional group X , on an organic molecule R , with the hydroxide group from water (Washington, JW. 1995).

Through the hydrolysis reaction, the organic compound either mineralizes or converts into another organic compound that is less toxic or less recalcitrant than its parent. The authors know of no common environmental contaminant for which hydrolysis is considered to be an unfavorable reaction. Hydrolysis tends to be important for chlorinated and other halogenated compounds, especially halogenated alkanes (Jeffers et. al. 1986).

Most hydrolysis reactions are considered pseudo first order reactions (Weintraub, 1986). Pseudo first order reactions are defined as systems where all but one of the reactants are in a supply so large that their concentrations can be considered constant. For compounds of environmental interest, only the concentration of the contaminant affects the reaction rate and therefore the reaction can be considered to be first order.

EFFECT OF PH

Three principal hydrolysis mechanisms for halogenated compounds have been identified (Morrison and Boyd, 1960): elimination by dehydrohalogenation, unimolecular nucleophilic substitution (S_N1), and bimolecular nucleophilic substitution (S_N2). Dehydrohalogenation and S_N2 are favored by higher pH; S_N1 is not pH-dependent. Therefore, the hydrolysis rates of some compounds increase with pH. Each unit increase

of pH will increase the concentration of the hydroxyl ion by a factor of ten and the hydrolysis rate will increase by a factor of ten if the hydrolysis reaction is pH-dependent.

The overall rate constant, k , for most hydrolysis reactions is described by:

$$k = k_B [OH^-] + k_N \quad (2)$$

where k_B is the rate constant for the base reaction, OH is the hydroxyl ion concentration, and k_N is the rate constant for the neutral pH reaction (Washington, JW. 1995). Equation 2 shows the dependence of the overall rate constant on pH. Depending on the pH of the system, one of the rate constants will become the dominant reaction. In basic solutions, the k_B rate constant will be multiplied by a high hydroxide ion concentration, thus increasing its effect on the overall hydrolysis rate. In neutral solutions the k_N reaction is usually dominant.

While pH does have an effect on the rate of hydrolysis reactions, there are few environmental situations where it can be taken advantage of. Because most environmental conditions are near a neutral pH the easiest and most effective control over hydrolysis comes from adjusting the temperature.

EFFECT OF TEMPERATURE

The pseudo first order hydrolysis reactions have a simple and constant relationship for the half-life of the reactant. A half-life is described as the time it takes for 50% of a reactant to be consumed by a reaction. In the case of a pseudo first order reaction, the half-life is described by:

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

where k is the reaction rate constant. The reaction rate constant describes how long it will take for a given amount of reactant to be consumed by the reaction. The k value is constant at any given temperature, but changes exponentially in relation to a change in temperature. This relationship is described by the Arrhenius Equation,

$$k = A \cdot e^{\frac{-Ea}{R \cdot T}} \quad (4)$$

where A is a constant specific to each reaction, Ea is the activation energy for the reaction, R is the universal gas constant, and T is the temperature of the system where the reaction is taking place. Exponents raised to a negative power return positive answers with values less than one. The larger the negative power, the smaller the positive result from the exponent. In order to increase the reaction rate constant, k , one must only reduce the size of the negative exponent. Of all of the numbers in the equation, only the temperature is variable. By increasing the value of temperature, the negative value in the exponent term will become smaller. This will in turn increase the value of the reaction rate constant.

The rate of hydrolysis increases markedly with temperature as described by the Arrhenius reaction. Heating the subsurface from ambient temperatures to 80°C will increase the hydrolysis rates of most organic compounds by a factor of over 1000. Heating to 100°C will increase hydrolysis by a factor of over 10,000. Heating can lead to dramatically fast and effective remediation of compounds that are subject to hydrolysis. The relationship between hydrolysis half-life and temperature is represented in Figure 1. The hydrolysis half-life is represented on a log scale.

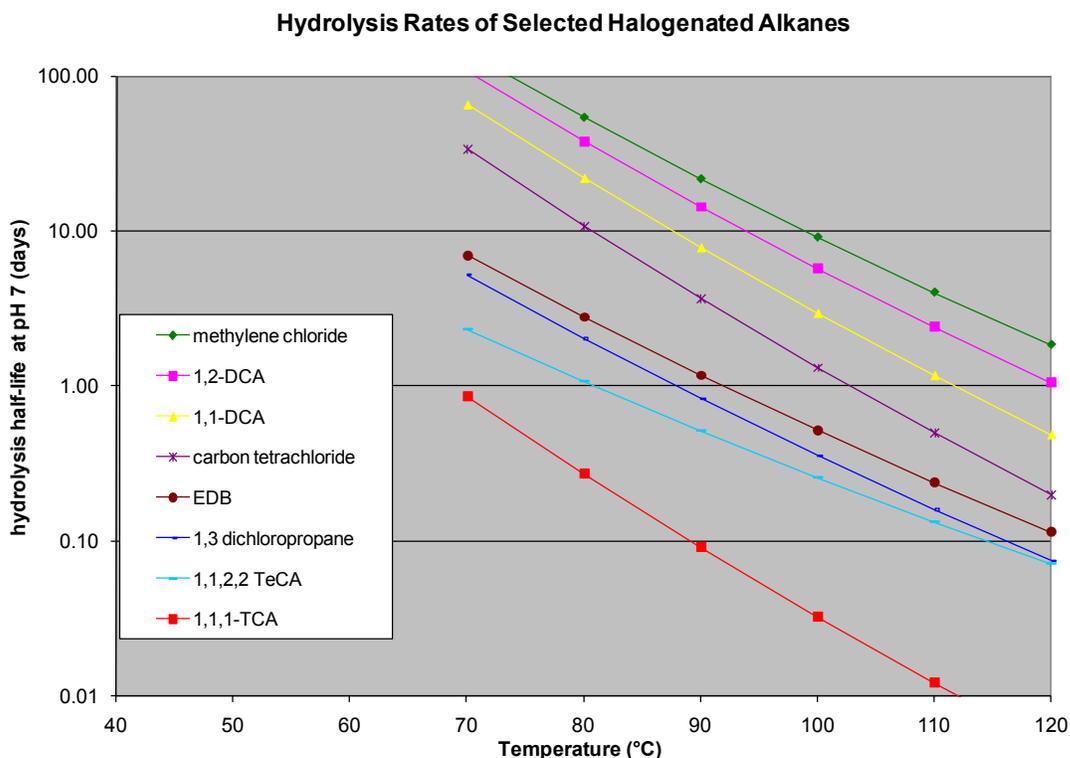


FIGURE 1. Hydrolysis half-life of common contaminants from 70°C- 120°C.

Because hydrolysis will only occur if the organic molecule is dissolved in water, it is important to increase the rate of contaminant dissolution. In the authors' experience, gentle boiling of the site can increase the rate of dissolution under hydrolysis conditions. Our experience is that the combined "desorption-dissolution-hydrolysis" half-life is generally about one week under boiling conditions, even if the hydrolysis half-life is a matter of hours.

If the hydrolysis rate is significant, the concentration of contaminant in the water-dissolved state will be near zero and that low concentration will increase the rate of contaminant dissolution. This dissolution will be on micro-scales, and therefore can be relatively fast.

If hydrolysis is the primary mechanism for contaminant destruction, it is most cost-effective to heat the site to the boiling point of water. The increase in heating cost is more than compensated by the increase in reaction rates and shorter treatment times.

An exception to the above rule applies to a few compounds with relatively low volatility and non-hazardous hydrolysis progeny. For these compounds, it may be most

cost-effective to rely on hydrolysis alone to treat the site, with no vapor extraction. Examples include the fumigants dichloropropane and trichloropropane which have the progenies propylene glycol and glycerol, respectively (Washington, JW. 1995, Ellington, JJ. et. al. 1987). For these compounds, heating to 80-90°C without vapor recovery may provide the most cost-effective treatment.

Thermally enhanced hydrolysis is generally the most cost-effective remediation method for halogenated alkanes and many fumigants and pesticides. A listing of common compounds with their hydrolysis half-lives at 100°C is shown in Table 1.

TABLE 1. Hydrolysis half-lives at pH 7.

Compound	Half-life at 15°C (years)	Half-life at 100°C (days)	pH Effect	Hydrolysis Product	Resource
chloroform	8019	117	7.1+	mineralizes	Jeffers, et al 1989
bromoform	3089	43	pH++	mineralizes	Washington, 1995
dichlorofluoromethane	973	22	6.0+	mineralizes	Jeffers, et al 1996
1,1,2-TCA	479	39	pH++	DCE	Jeffers, et al 1989
1,2-DCA	306	6	-	ethylene glycol	Jeffers, et al 1989
1,1-DCA	285	3	-	acetaldehyde	Jeffers, et al 1989
methylene chloride	266	9	-	formaldehyde	Taylor, 2001
carbon tetrachloride	206	1	-	mineralizes	Jeffers, et al 1989
1,2,3-trichloropropane	192	3	-	glycerol	Ellington, et. al. 1987
1,1,1,2-TeCA	178	5	pH++	TCE	Jeffers, et al 1989
1,2-dichloropropane	78	0.8	-	propylene glycol	Washington, 1995
EDB	9	0.5	-	ethylene glycol	Weintraub, et al 1986
1,3-dichloropropane	8	0.4	-	propylene glycol	Jeffers, et al 1989
1,1,1-TCA	6	0.03	-	1,1-DCE	Jeffers, et al 1989
1,1,2,2-TeCA	1	0.3	pH++	TCE	Jeffers, et al 1989

##+ = The neutral and alkaline reactions are equal at the stated pH. Higher pH accelerates hydrolysis.

pH++ = Alkaline dominant, a unit increase in pH will increase the hydrolysis rate by a factor of 10.

- = Change in pH in the range of 5 to 9 pH does not significantly change the rate of hydrolysis.

Seven half-lives are required for a 99% conversion

Ten half-lives are required for a 99.9% conversion



An electrical resistance heating (ERH) remediation presently operating in Annapolis, Maryland, USA provides a good example of the impact of hydrolysis. The compound of concern is 1,1,2,2-tetrachloroethane (TeCA), which hydrolyzes to trichloroethylene (TCE). Conversion of TeCA to TCE is beneficial for the following reasons:

- TCE has 12 times greater volatility and therefore 12 times greater extraction rate than TeCA.
- When the ERH remediation is complete, residual TCE biodegrades much more quickly than TeCA. Some experts have estimated that TCE biodegrades about 10 times faster than TeCA.

- TCE is generally considered to have less health risk than TeCA. The US Agency for Toxic Substances and Disease Registry (ATSDR) attributes three times greater cancer risk to TeCA than to TCE.

The Annapolis site is located in the loading dock area of a Navy Exchange department store. The lithology consists of:

- Clean fill from surface to 10 feet below grade surface (ft bgs) (0-3 m).
- Dense fine sand with interbedded silt layers from 10 to 40 ft bgs (3-12 m).
- Sandstone from 40 to 65 ft bgs (12-20 m), with a very hard iron cemented layer from 50 to 65 ft bgs (15-20 m).
- Slightly more permeable clayey silt deeper than 65 ft bgs (20 m).
- The water table is located at 60 ft bgs (18 m).

TeCA at concentrations of up to 169 mg/kg were detected from 10 to 66 ft bgs (3-30 m), with the highest concentrations generally observed in the iron cemented sandstone layer. The ERH system was designed to treat from 10 to 70 ft bgs (3-21 m).

The site pH is unusually acidic, ranging from 4.8 to 5.2 pH. TeCA hydrolysis is via the dehydrohalogenation mechanism and is directly proportion to the concentration of the hydroxyl ion (OH⁻). Therefore, the site pH could be expected to slow the hydrolysis rate by a factor of 100, although the pH would have no effect on the desorption and dissolution steps required for the complete conversion process. The project team considered adjusting the site pH to a more favorable range but elected instead to collect interim boring soil samples to check that the rate of hydrolysis was acceptable for cost-effective site remediation.

Data collected to date indicates that the acidic site concerns may have been unfounded. Conversion of TeCA to TCE appears to be progressing at an acceptable rate. Recovered vapor data is depicted below:

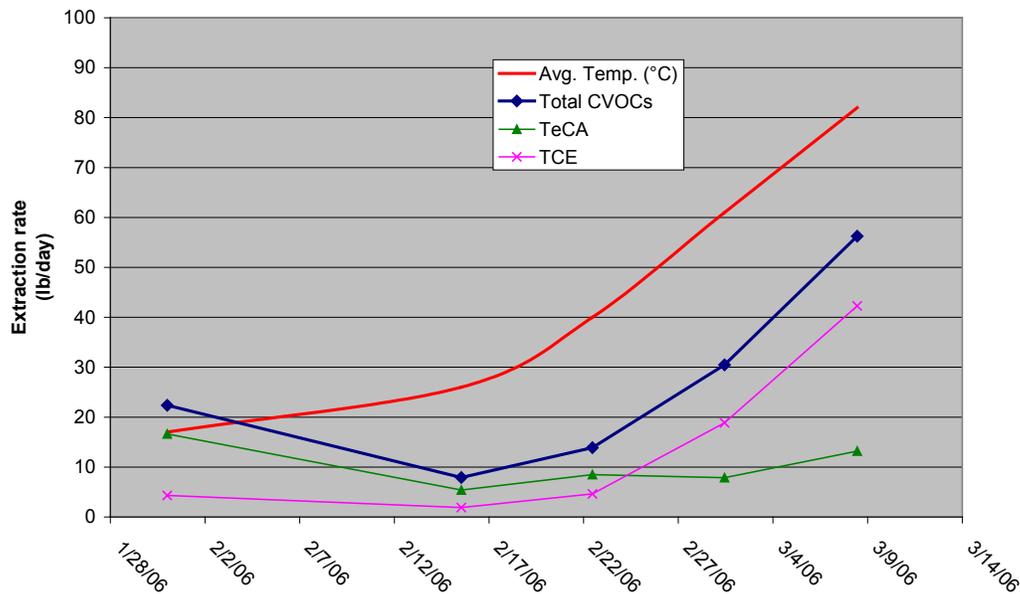


FIGURE 2. Vapor extraction with temperature.

This data suggests that the conversion of TeCA to more volatile TCE is significant and is accelerating as the site temperature increases.

Soil samples were collected from the interim boring were non-detectable for CVOCs and indicated that the soil chloride concentrations increased from 9 mg/kg to an average of 128 mg/kg. Higher chloride concentrations were found at depths that had higher initial concentrations of TeCA.

Site data suggests that hydrolysis is rapidly converting very recalcitrant TeCA to TCE and that the ERH system is removing the more volatile TCE from the site soils.

CONCLUSIONS

Hydrolysis is a chemical process that is very limited at ambient conditions, but that can be greatly beneficial at increased temperatures. This process is not only accelerated by increased temperature, it can also be improved by adjusting the pH of a system. Further research into the effects of increased temperature and pH needs to be pursued. With improved predictions on hydrolysis behavior, more efficient thermal remediation can be applied to many sites contaminated with harmful organic compounds.

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