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Alkaline Dechlorination of Chlorinated Volatile Organic Compounds

Baohua Gu
Robert L. Siegrist

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Environmental Sciences Division

Alkaline Dechlorination of Chlorinated Volatile Organic Compounds

Baohua Gu and Robert L. Siegrist

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Prepared by
OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

The vast majority of contaminated sites in the United States and abroad are contaminated with chlorinated volatile organic compounds (VOCs) such as trichloroethylene (TCE), trichloroethane (TCA), and chloroform. These VOCs are mobile and persistent in the subsurface and present serious health risks at trace concentrations. The goal of this project was to develop a new chemical treatment system that can rapidly and effectively degrade chlorinated VOCs. The system is based on our preliminary findings that strong alkalis such as sodium hydroxide (NaOH) can absorb and degrade TCE. The main objectives of this study were (1) to determine the reaction rates between chlorinated VOCs, particularly TCE, and strong alkalis; (2) to elucidate the reaction mechanisms and by-products; (3) to optimize the chemical reactions under various experimental conditions; and (4) to develop a laboratory bench-scale alkaline destruction column that can be used to destroy vapor-phase TCE.

Batch experiments between TCE and NaOH were performed in both zero headspace extractors and Mininert micro-reaction vessels under varying experimental conditions (i.e., temperature, pressure, chemical reagents). Results indicated that TCE can be rapidly and completely degraded in NaOH at an elevated temperature. The half-lives for TCE degradation in 2 *M* NaOH at 40, 60, 80, and 100°C were 347, 49, 4, and 2.4 min, respectively. Degradation half-life of chloroform was on the order of a few seconds, much faster than that of TCE. The reaction of TCE with NaOH could be described by a pseudo-first order rate kinetics, and the estimated activation energy was about 85 kJ/mol. The reaction end products were identified to be primarily Cl^- and Na-glycollate by ion chromatographic analysis. Recovery of Cl^- was ~ 100% at a temperature above 80°C. Because both of these end products are non hazardous, this technique

offers a novel treatment technology to remove/destroy vapor-phase chlorinated VOCs in the off-gas when soil vapor extraction or air-stripping techniques are used to remediate VOC contaminated soils and groundwater. We have tested a prototype TCE destruction column in the laboratory. Results indicated that ~ 90% of TCE can be removed when TCE-contaminated gas (10 ppmv) is passed through the column. Therefore, we anticipate that this technology can be potentially commercialized and utilized for off-gas treatment during the soil vapor extraction or air-stripping processes. As a result, a patent has been filed with the U.S. patent administration. One environmental consulting firm (In-situ Fixation, Inc., AZ) has expressed great interest in this technology. We were also solicited for a full proposal by McClellan Air Force Base , California for a field-scale demonstration of this technology.

1. INTRODUCTION

Chlorinated volatile organic compounds (VOCs) such as trichloroethylene (TCE), trichloroethane (TCA), and chloroform are widespread contaminants in soil and groundwater in the United States including many U. S. Department of Energy sites such as the Paducah Gaseous Diffusion Plant, the Portsmouth Gaseous Diffusion Plant, the Savannah River Site, and the Hanford site, and the industrialized world (Siegrist and van Ee 1994). Because of its persistence in environmental media, numerous studies have been conducted on its chemical and biological degradation, adsorption/partitioning, and fate in these media (Wilson and Wilson 1985; Ball and Roberts 1991; Steinberg 1992; Ong and Lion 1991; Phelps et al. 1990; Pavlostathis and Jaglal 1991; Barton et al. 1992; Fan and Scow 1993). Many remediation technologies have been developed, such as biodegradation and vacuum/vapor extraction followed by adsorption with activated carbon (Brown 1992; Diguilio 1992; Hinchee 1994; Siegrist et al. 1995). Although these technologies each exhibited varying degrees of success, none of them has proven to be entirely satisfactory because of their low efficiency, the production of unwanted toxic by-products, or secondary waste-operation requirements (Fiorenza et al. 1991; Gibson et al. 1993; Siegrist and van Ee 1994). For example, biodegradation of TCE is a very slow process that requires specific conditions (e.g., adding nutrients) and a source of acclimated or specialized microorganisms (Fiorenza et al. 1991; Brown et al. 1993). Vacuum/vapor extraction followed by adsorption on activated carbon is effective and commonly used (Brown 1992; Hinchee 1994; Siegrist et al. 1995; West et al. 1995). Carbon adsorption is especially effective for the treatment of effluents with low VOC concentrations. However, the activated carbon has only limited capacity to adsorb TCE or other VOCs and is subjected to fouling (Gibson et al. 1993). Because the regeneration of carbon is relatively expensive, the process also generates large quantities of secondary hazardous waste (i.e., activated carbon with TCE), which must be disposed of promptly and properly to avoid TCE desorption and release (cf. Brown et al. 1993).

As part of a major study of the stability of TCE (and other VOCs) in environmental media, we observed that a strong base such as sodium hydroxide (NaOH) can absorb and degrade TCE to form non hazardous by-products. The reaction resulted in a release of Cl^- anions. These preliminary observations prompted this exploratory research, supported by laboratory-directed research and development funds, because we anticipate that this chemical treatment methodology could lead to a new technique to destroy TCE from contaminated soils and groundwaters. Previous investigators (Brunelle and Singleton 1983) have reported that a strong base (KOH) and polyethylene glycol (PEG) can react and degrade polychlorinated byphenyls (PCBs) although no studies have been conducted on the interactions between a strong base and TCE or other chlorinated VOCs, particularly the "vapor-phase" treatment of VOCs. Many scientific questions remain to be answered, such as what are the reaction products and mechanisms and how do experimental conditions affect the degradation rates. Accordingly, our main objectives of this study were (1) to determine the reaction rates and kinetics between TCE and strong alkalis such as NaOH under varying experimental conditions; (2) to investigate the reaction by-products, mechanisms, and pathways between TCE and NaOH; (3) to study the similar reactions between other chlorinated VOCs (e.g., TCA, chloroform) and NaOH or other strong bases; and (4) to develop a laboratory bench-scale TCE-destruction column to remove/destroy vapor-phase TCE, which can be ultimately used to treat the chlorinated VOCs in the off-gas during soil vacuum extraction and groundwater air-stripping processes.

2. MATERIALS AND METHODS

2.1 MATERIALS

All chemicals used for this study were reagent grade. They include sodium hydroxide (NaOH) and potassium hydroxide (KOH) from VWR Scientific; sodium carbonate (Na_2CO_3) (Fisher), TCE, and chloroform from Baker; TCA, polyethyleneglycol (PEG), and TiO_2 from EM Science, Inc.

2.2 BATCH REACTIONS IN ZERO-HEADSPACE EXTRACTOR

Reactions between TCE and a strong base (2 *M* NaOH) were initially performed by using the zero-headspace extractor (ZHE) apparatus to prevent TCE volatilization losses. As shown in Fig. 1, the ZHE is essentially composed of a stainless steel cylinder and a piston. The upward movement of the piston is controlled by applying pressure at the bottom of the piston. The ZHE was initially filled with 120 mL NaOH solution, and headspace was eliminated by slowly applying pressure on the piston to move it upward. Pure phase TCE (10 µL) was then injected into the ZHE, and the sampling valve was immediately closed. The temperature was controlled by heating tape wrapped on the outside of the ZHE apparatus. The temperature of the reactant was estimated by a trial run with the same reactant at a desired concentration. This procedure was primarily to reduce opening of the sampling valve for temperature measurements during the experiment and to minimize VOC loss through the valve. However, final temperature of the reactant (at the end of batch experiment) was measured and recorded. Mixing of TCE and NaOH within the ZHE was achieved through the use of a Teflon coated magnetic stirring bar and by inverting the ZHE within the first 30 min of the heating period. At a given time interval, a NaOH/TCE sample was taken by slowly raising the piston so that no headspace was left in the ZHE as a result of sample withdrawal. An aliquot (0.1 mL) of sample was directly transferred into 3 mL of hexane to extract the residual TCE that had not reacted with NaOH, and ~4 mL of sample was transferred into a small glass vial which was then left open, allowing residual TCE to volatilize. These samples were then diluted 20 times before analysis by ion chromatography.

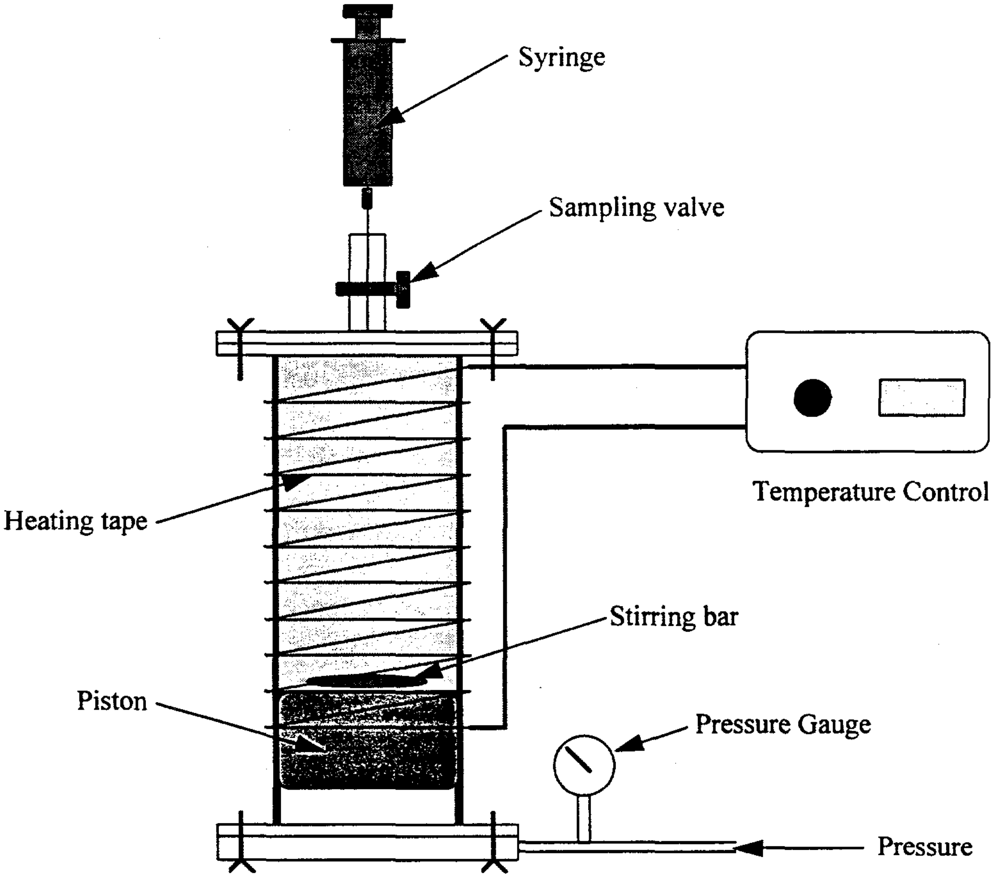


Fig. 1. Schematic representation of a zero-headspace extractor (ZHE).

Different chemical reagents and reactants were also tested for their effectiveness to degrade TCE (or other chlorinated VOCs) at varying temperatures. These chemicals include KOH, Na_2CO_3, PEG, and TiO_2. One of the batch experiment was performed with ^{14}C-labeled TCE to assess the mass-balance and to evaluate the volatilization loss of TCE during the course of batch experiment that used ZHEs.

2.3 BATCH REACTIONS IN MININERT MICRO-REACTION VESSELS

A major problem of using ZHEs for batch experiments is that there is a significant time-lag to raise the temperature of ZHE during the initial heating period using a heating tape. For example, if the desired reaction temperature is 100°C, the fluid in the ZHE takes about 25–30 min to reach that temperature with the heating tape. Because reactions between chlorinated VOCs and strong alkalis are strongly temperature dependent (as will be discussed later), the reaction rate cannot be accurately determined because of these initial temperature variations. An attempt was made by directly injecting VOC into the heated NaOH solution in ZHE (at a desired temperature) but was unsatisfactory because of the design of the injection/sampling valve, which lead to a significant volatilization loss of VOCs at the time of injection, especially at a high temperature.

To accurately determine the reaction rate between VOCs and NaOH at a given temperature, the batch experiments were repeated with micro-reaction vessels equipped with Mininert valves and triangular magnetic stirring bars (Supelco, Inc.). The Mininert valve prevents VOC loss through volatilization during VOC injection and sampling at a given temperature. Experimental procedures include the following steps. The vials were first filled with NaOH (with no headspace) and heated to the desired temperature in a water bath (Na_2SO_4 was added to the water bath to raise the boiling point of water). The total volume of the vial, ~7 mL, varied slightly among each individual vial. The actual volume was determined gravimetrically before the batch experiment for each vial. At the desired temperature, 3 μL pure-phase TCE was rapidly injected into the vial through the septum of the Mininert valve, and the valve was closed immediately. At a given time interval, an aliquot (20 μL) of sample was withdrawn and mixed with 4 mL hexane for

VOC analysis. The vial was then transferred to a cold water bath and left open to allow residual VOC to volatilize as the temperature of the vial decreased. This experiment was repeated at different time intervals until enough data points were collected. By-products or end products such as Cl^-, glycollate, dichloroacetate, and monochloroacetate (for TCE degradation) were determined by ion chromatography after appropriate dilutions.

2.4 ANALYSIS OF VOCS AND BY-PRODUCTS

The concentrations of TCE (or other VOCs) in hexane were analyzed by gas chromatography (GC) (Hewlett-Packard, 5890 Series II) through the use of an electron capture detector on an HP-5 fused-silica column (0.32 mm × 50 m) (Hewlett Packard Co., Wilmington, Del.). A 1–2 μL aliquot of the hexane extract was directly injected into the GC column; the concentration was determined in reference to TCE standards prepared in hexane (Gu et al. 1995).

Cl^- anions in NaOH were determined by an ion chromatograph equipped with an ED-40 electrochemical detector (Dionex, Calif.). The mobile phase was 1.8 m M Na_2CO_3 and 1.7 m M $NaHCO_3$, and the flow rate was at 1.5 mL/min with a sample loop of 20 μL. The sample was diluted 20 fold (in most cases) before it was injected into the column. The detection limit for Cl^- was ~0.01 mg/L. Na-glycollate, monochloroacetate, dichloroacetate, or Na-formate (formed by degradation of chloroform) were determined similarly by the liquid chromatography with a Rezex ROA analytical column (Phenomenex, Calif.) operated at 85°C. The mobile phase was 0.005 M H_2SO_4, and the flow rate was at 0.5 mL/min. Samples were directly injected into the column via a 20 μL (or 50 μL for formate determination) sample loop. The detection limit was about 20–50 mg/L for these organic compounds.

2.5 VAPOR-PHASE DESTRUCTION OF TCE

A vapor-phase destruction column was designed for rapid dechlorination of TCE or other chlorinated VOCs in an air stream (Fig. 2). This chemical treatment system consists of an alkaline solution recirculation pump, a heating unit, and a reaction column with packed stainless steel interlocks to increase the areas of contact between chlorinated VOC vapor and the heated base. Upon contact of chlorinated VOCs with the base, chlorinated VOCs are absorbed and subsequently dechlorinated; cleaned vapor can be then released to the atmosphere. System pressure and temperature were monitored; the off-gas sample was taken through the sampling valve by using Tedlar bags or by on-line monitoring with a flame ionization detector.

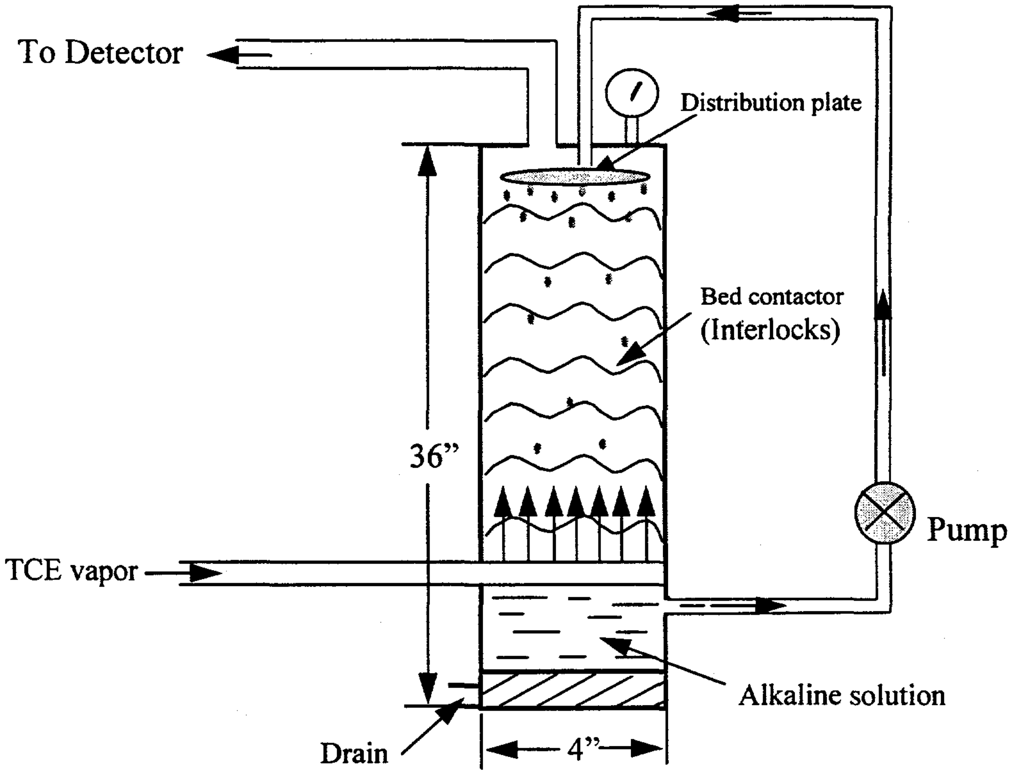


Fig. 2. Illustration of the alkaline destruction column.

The destruction column was made with a stainless steel column (4in. diam. × 36in. length). The length of the packed bed that was in contact with the alkaline solution was ~ 24in. with a total volume of about 5 L. Two system configurations were used: (1) TCE (10 mg/L, Scotty Specialty Gases, Inc.) vapor mixed with N_2 was passed through the destruction column; the alkaline solution was recirculated within the column, as shown in Fig. 2. The incoming vapor concentration (before reaction) and outgoing vapor concentration (after reaction) were collected frequently and analyzed by GC. (2) The contact bed, or interlocks, were completely immersed in alkaline solution so that no recirculation of NaOH solution was necessary during the operation. In addition, a relatively stable reaction temperature can be maintained because the whole system is bathed in the alkaline solution. The off-gas was sampled with a Tedlar-bag, and TCE in the off-gas stream was measured by injecting 50 μL of off-gas directly into the GC column.

3. RESULTS AND DISCUSSION

Our initial batch experiments were performed in ZHEs. However, as has been described above, the reaction rates between TCE and NaOH cannot be accurately determined because of an initial slow heating period of ZHE with a heating tape. These experiments were later improved by using the Mininert micro-reaction vessels so that reactions can be initiated at any given temperature, and the reaction kinetics can be precisely determined. Therefore, the first part of this discussion will focus on these batch experiments performed in Mininert micro-reaction vessels. Results of the batch experiments performed in ZHE will only be briefly discussed (Sect. 3.4–3.6).

3.1 REACTION KINETICS BETWEEN TCE AND NaOH IN MININERT MICRO-REACTION VESSEL

On the basis of our preliminary studies with ZHEs, we first determined the chemical degradation of TCE in NaOH at an elevated temperature (Fig. 3). Experimental results indicated that TCE was rapidly degraded at 100°C. After about 10 min, no detectable amounts of TCE were left in the solution phase. On the other hand, we observed a rapid increase in Cl^- concentration in NaOH by ion chromatographic analysis. These results demonstrate that TCE can be rapidly and completely dechlorinated under the given conditions, as evidenced by the stoichoimetric release of Cl^- in solution (Fig. 3). In other words, each mole of TCE released 3 moles of Cl^- into the solution. Note that the initial TCE concentration ($C_0 = \sim 4.81$ mmol/L) were calculated because a known amount of pure-phase TCE was injected into the vial. Obtaining this initial value experimentally (at $t = 0$) is difficult because of a rapid reaction between TCE and NaOH at an elevated temperature.

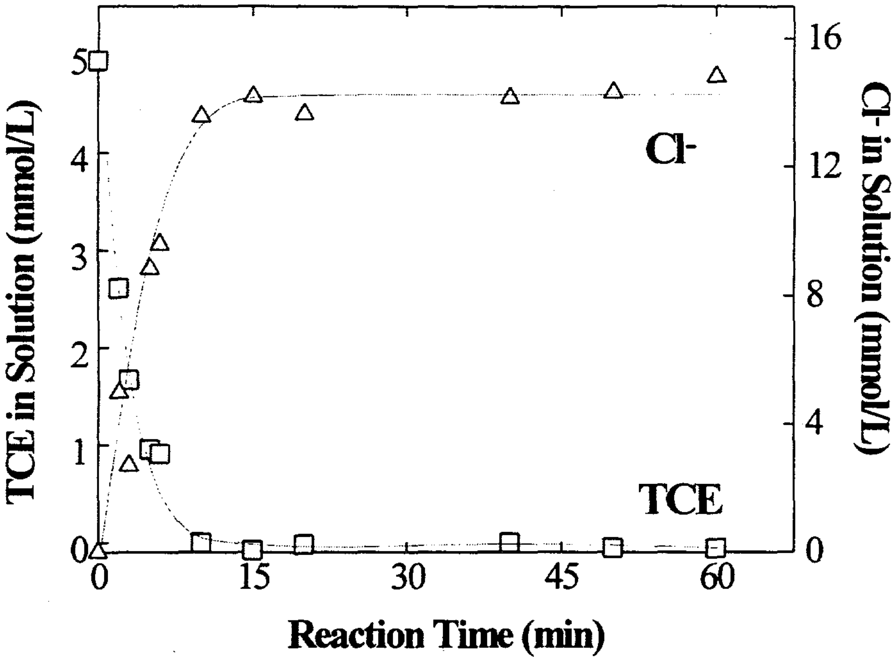


Fig. 3. Reaction kinetics between TCE and *2 M* NaOH at 100°C and by-product (Cl⁻) formation.

The reaction between TCE and NaOH is strongly temperature dependent (Figs. 4–6). At a low temperature, TCE degraded at a reduced rate as indicated by a relatively slow decrease in TCE concentration and a slow increase in Cl^- concentration. Although ~60% of TCE was degraded at 40°C after about 7 h (Fig. 6), < 15% of Cl^- was dechlorinated from TCE in comparison with that observed at 100°C (Fig. 3). These observations suggest that TCE was not completely dechlorinated at a low temperature; some intermediate products must be formed during the reaction, as will be discussed in Sect. 3.2.

The reaction rate between TCE and NaOH may be expressed as:

$$\frac{d[TCE]}{dt} = -k'[TCE][OH^-]^n \ , \tag{1}$$

where k' is the theoretical rate constant between TCE and OH^-, brackets represent the concentration of the reactant(s) and n is the hypothetical order of rate law involving OH^-. However, because OH^- concentration is in large excess, we can reasonably assume OH^- concentration is a constant, $[OH]_0$, throughout the reaction. Therefore, although the true rate law may be the third order or else, we can rewrite Eq. 1 as

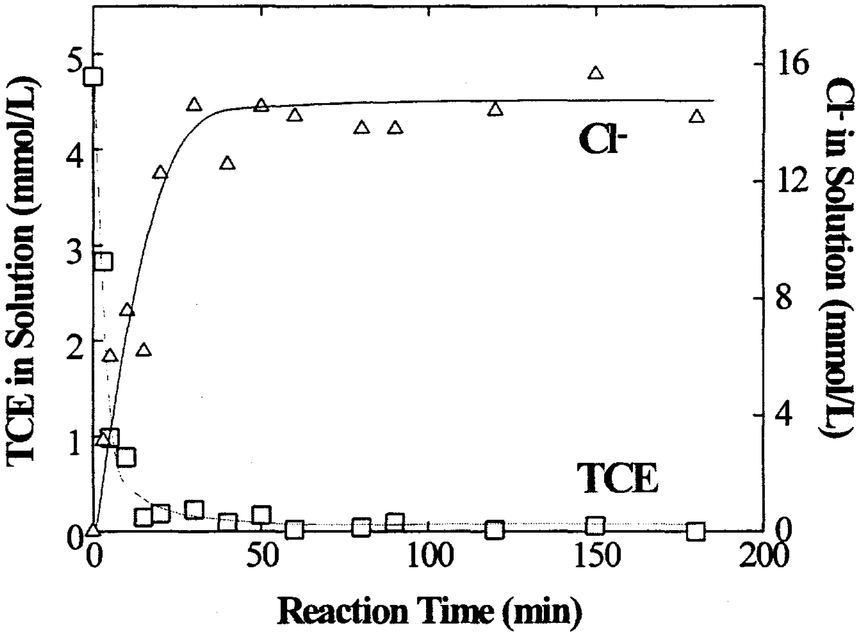


Fig. 4. Reaction kinetics between TCE and *2 M* NaOH at 80°C and by-product (Cl^-) formation.

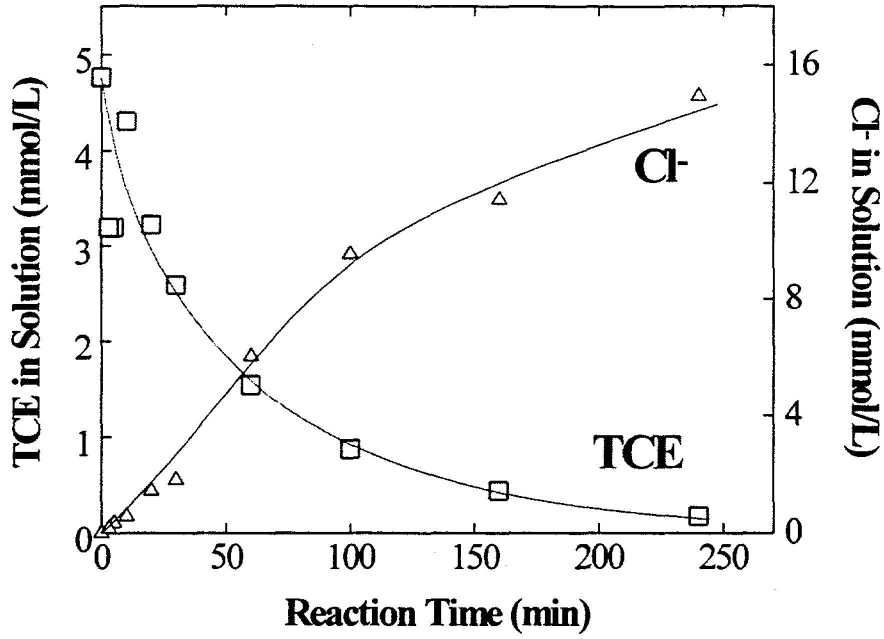


Fig. 5. Reaction kinetics between TCE and 2 *M* NaOH at 60°C and by-product (Cl⁻) formation.

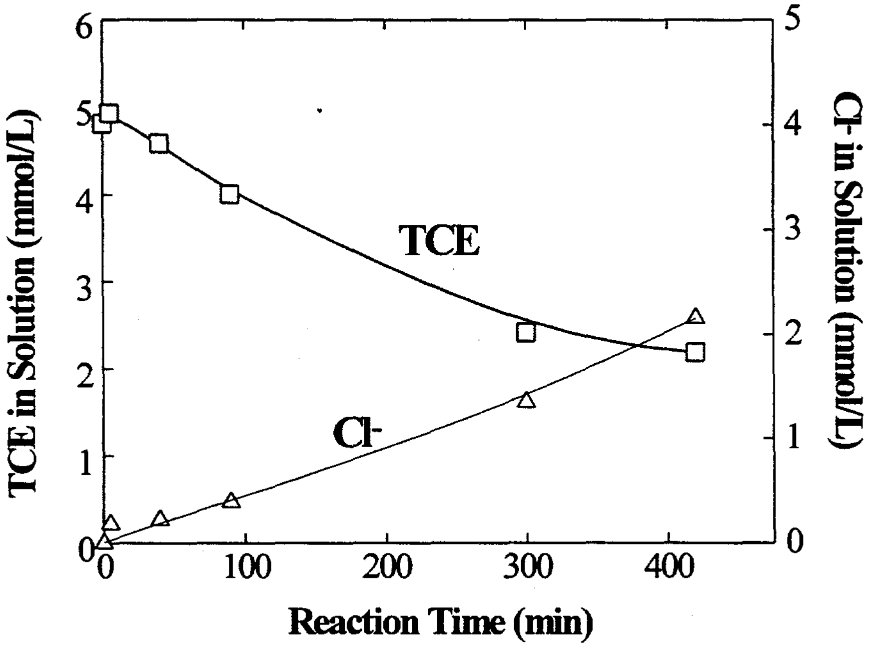


Fig. 6. Reaction kinetics between TCE and 2 *M* NaOH at 40°C and by-product (Cl⁻) formation.

$$\frac{d[TCE]}{dt} = -k[TCE], \tag{2}$$

where $k = k'(OH)^n$ is the observed rate constant of the reaction. The degradation of TCE is thus expected to follow a pseudo-first order rate law. A plot of natural logarithm of TCE concentration with time yielded straight lines as shown in Fig. 7. Note that data points beyond 20 min for reactions at 80 and 100°C were not plotted in Fig. 7 because no logarithm transformation can be made as TCE concentration in NaOH approached zero (or close to the detection limit). Table 1 lists the reaction rates between TCE and *2 M* NaOH at temperatures of 40, 60, 80, and 100°C, respectively. Based on these data, calculated half-lives of TCE in *2 M* NaOH were calculated to be about 347, 48.8, 3.96, and 2.38 min, respectively. Therefore, the degradation rate of TCE at 100°C was more than two orders of magnitude higher than that at 40°C.

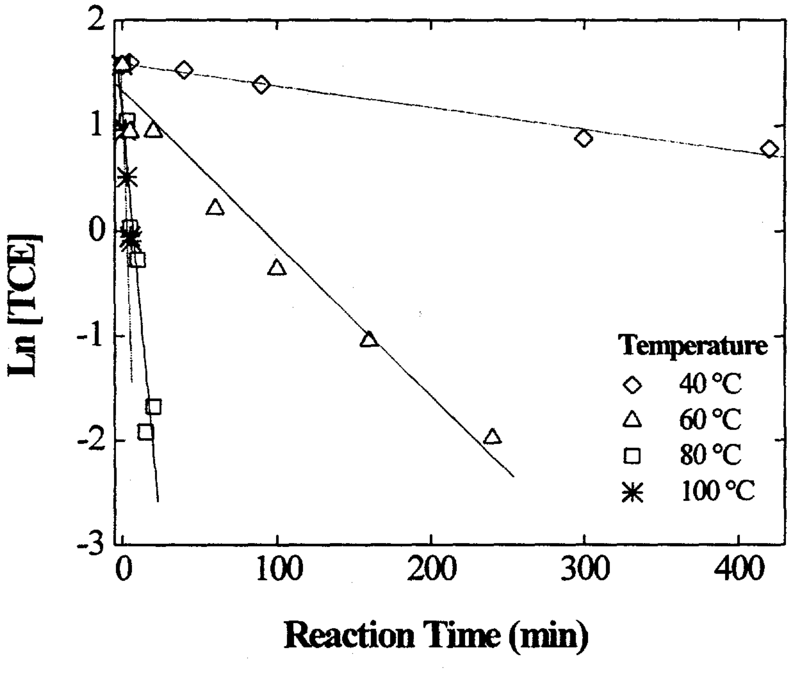


Fig. 7. Plots of natural logarithm of TCE concentration against reaction time between TCE and *2 M* NaOH at different temperatures.

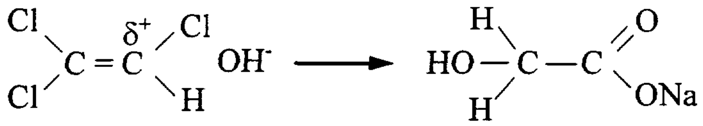
Table 1. Degradation rates and half-lives of TCE in 2 *M* NaOH at different temperatures

Temperature (°C)	Rate (min^{-1})	Half-life (min)
40	0.002	347
60	0.014	48.8
80	0.175	3.96
100	0.291	2.38

The Arrhenius equation, $k = A e^{-\frac{E_a}{RT}}$, was applied to estimate the activated energy of the reactions between TCE and NaOH, where A is the pre-exponential factor, E_a labels the activation energy, R is the gas constant ($8.314\ \text{J}\bullet\text{K}^{-1}\bullet\text{mol}^{-1}$), and T is the absolute temperature. A plot of $Ln(k)$ against the inverse of temperature yielded a linear relationship with an estimated activation energy of about 85 kJ mol^{-1} (Fig. 8). These results indicate that a high temperature would favor the reaction or dechlorination of TCE. For example, at room temperature (25°C), the estimated reaction rate is ~ 0.000439 min^{-1} with a half-life of about 26.3 h. On the other hand, at an elevated temperature (110°C), the reaction rate is ~0.891 min^{-1} with a half-life of ~0.8 min.

3.2 REACTION MECHANISMS AND BY-PRODUCTS

Figures. 3–5 have indicated that reaction between TCE and NaOH resulted in a stoichoimetric release of Cl^- (or dechlorination), that is, a complete degradation of 1 mole of TCE released 3 moles of Cl^-. However, these results give no indication of how TCE was degraded and what the reaction pathways or mechanisms are. A review of organic chemistry indicates that two major reaction pathways are possible for TCE dechlorination in NaOH: (1) nucleophilic substitution and (2) nucleophilic elimination when there are electron withdrawing substituents at the β-carbon. Because chlorine has a stronger electron negativity than hydrogen, it pulls electrons and results in a positive dipole moment at the α-carbon, as shown below.



Negatively charged hydroxyls (OH$^-$) attack the nucleophilic carbon center at an elevated temperature, resulting in a weakened C-Cl bond followed by an eventual release of all Cl$^-$ (or dechlorination of TCE).

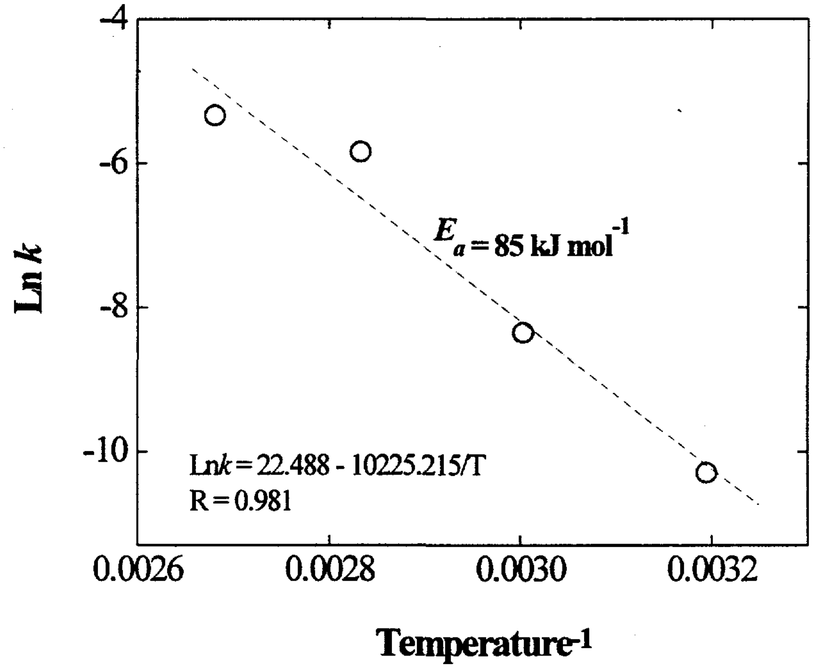


Fig. 8. Plot of natural logarithm of the observed rate constant against the inverse of the reaction temperature.

To elucidate the reaction mechanisms and pathways between TCE and NaOH, additional experiments were conducted to identify the possible intermediates and end products. A higher initial TCE concentration (~30.7 m*M*) was used because of a poor detection limit of some of the by-products, such as glycollate (>50 mg L^{-1}). Determination of the by-products (glycollate, monochloroacetate, and dichloroacetate) was accomplished by ion chromatographic analysis equipped with an UV/VIS detector at a wavelength of 210 nm. Figure 9 shows typical chromatograms of the reaction products between TCE and NaOH at 80°C at different reaction times. The retention times of glycollate, monochloroacetate, and dichloroacetate under the given experimental conditions were 17.7, 19.7, and 11.2 min, respectively (the peak at ~9.5 min was the solvent peak). Concentrations of these by-products as well as Cl^- were plotted against the reaction time (Fig. 10). These results demonstrate that the concentration of dichloroacetate deceased with reaction time whereas concentrations of glycollate and Cl^- increased consistently. On the other hand, concentrations of monochloroacetate increased initially but decreased further with reaction time. Clearly, the formation of these by-products and end products indicates a step-wise dechlorination of TCE from dichloroacetate, to monochloroacetate, and ultimately, to glycollate. However, a mass-balance analysis indicates that only about 60 % of TCE was converted to glycollate whereas ~100% of Cl^- was recovered from the degradation of TCE. Two possible explanations may apply to these observations. First, the degradation of TCE in NaOH followed a nucleophilic elimination or dehydrochlorination pathway. By eliminating HCl from TCE, an intermediate product, dichloroacetylene, may be formed. Dichloroacetylene is highly unstable and can auto-decompose into Cl^-, CO, or CO_2 in the presence of moisture. Cl^- was then trapped by NaOH, explaining a complete recovering of Cl^- but only a partial recovery of glycollate. Second, an analysis of glycollate is not very sensitive by the HPLC. The detection limit is ~50 mg L^{-1}. This could have attributed to a relatively large experimental error involved in these by-product measurements. Nevertheless, experimental results presented in Figs. 9–10 suggest that Cl^- and glycollate are the major reaction products and the nucleophilic substitution is the major reaction mechanism between TCE and NaOH.

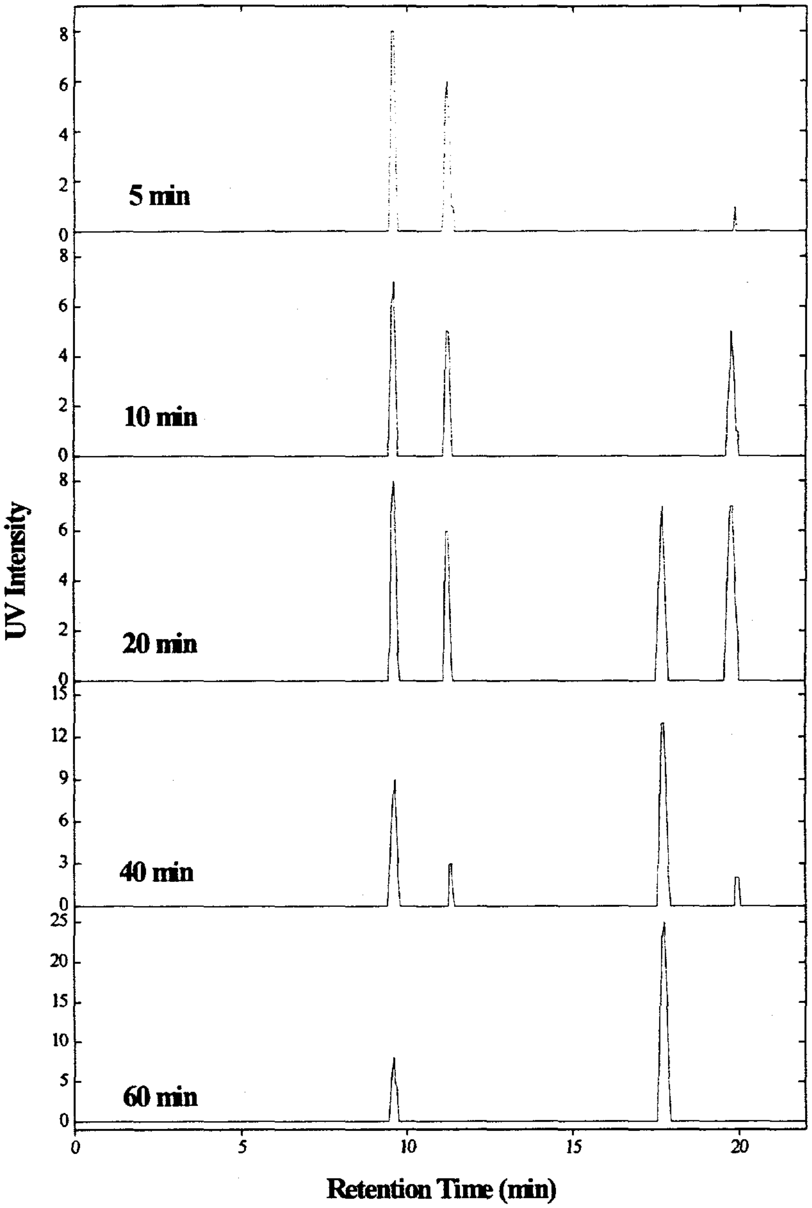


Fig. 9. Identification of the reaction by-products between TCE and 2 *M* NaOH at 80°C by ion chromatographic analysis. Elution peaks at 9.5, 11.2, 17.7, and 19.7 min are peaks of solvent, dichloroacetate, glycollate, and monochloroacetate, respectively

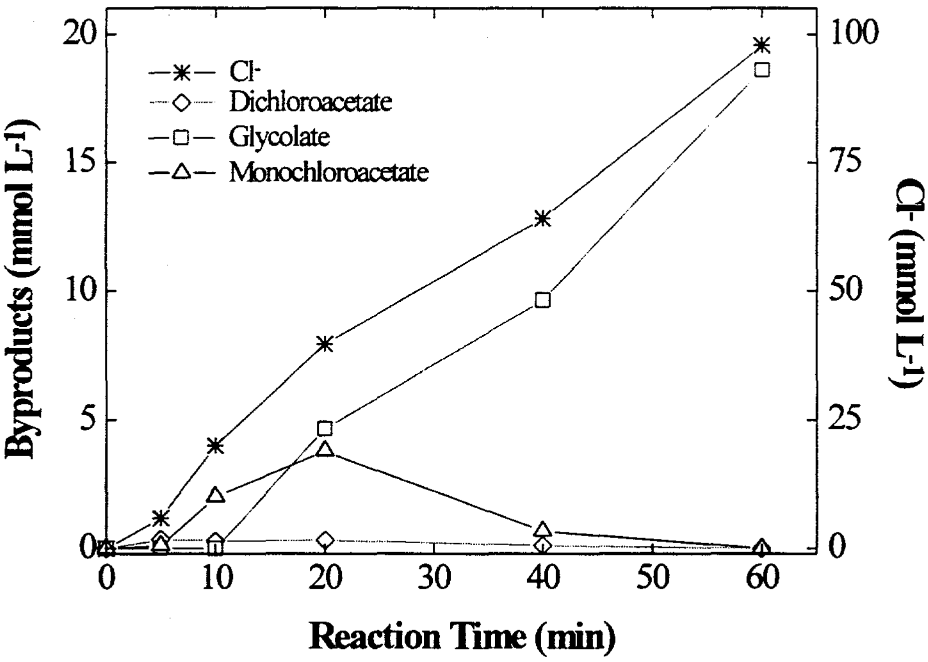


Fig. 10. By-products formation between TCE and 2 *M* NaOH at 80°C.

Similarly, we studied the by-product formation for reactions between TCE and NaOH at a lower temperature (60°C) (Figs. 11–12) The rates of TCE dechlorination and by-product formation were much slower at 60°C than that at 80°C, as discussed earlier. Even after ~450 min, TCE was only partially dechlorinated (i.e., ~50% of Cl^- and 30% of glycollate were recovered). In addition, monochloroacetate and dichloroacetate persisted in the system. Both of these by-products are highly toxic.

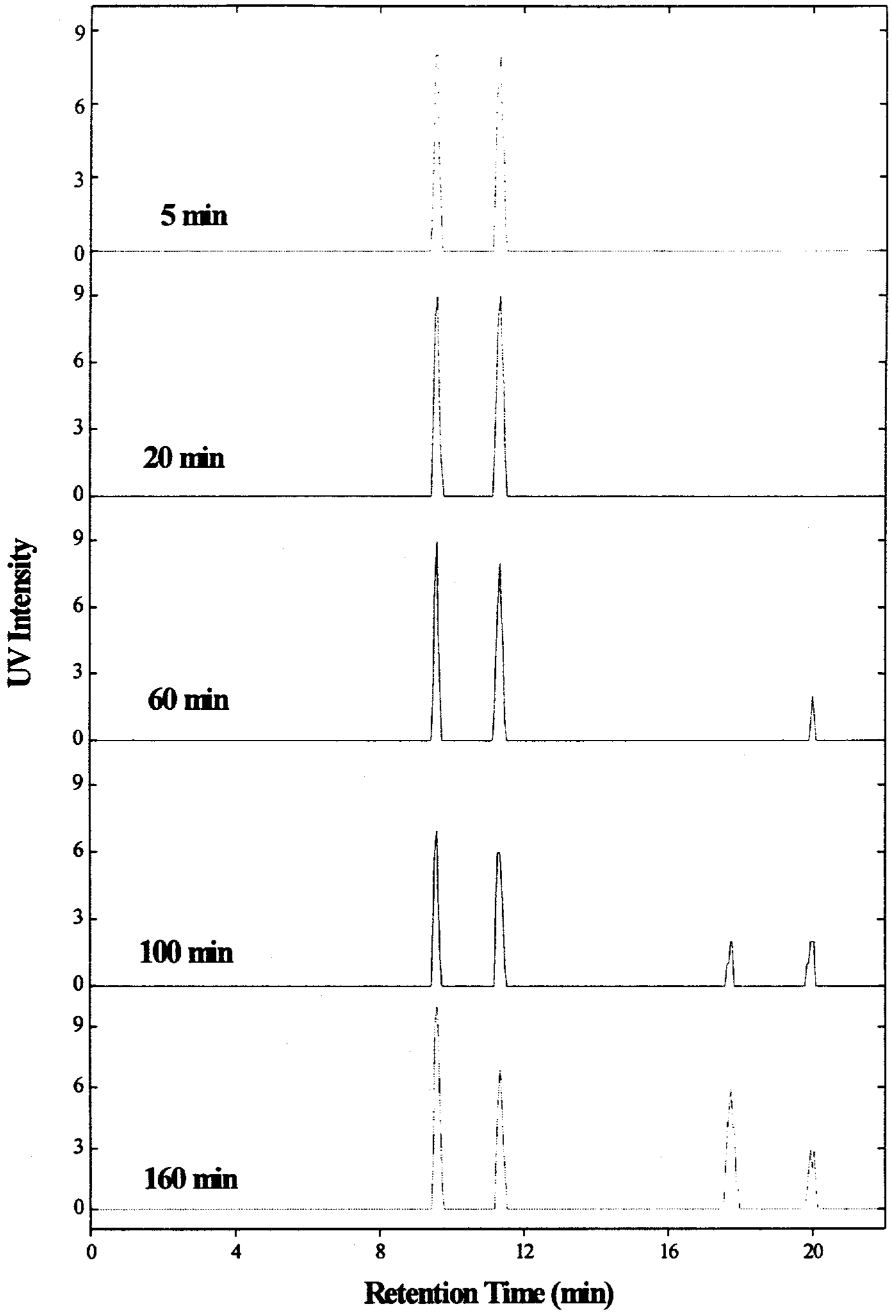


Fig. 11. Identification of the reaction by-products between TCE and 2 M NaOH at 60°C by ion chromatographic analysis. Elution peaks at 9.5, 11.2, 17.7, and 19.7 min are peaksof solvent, dichloroacetate, glycollate, and monochloroacetate, respectively

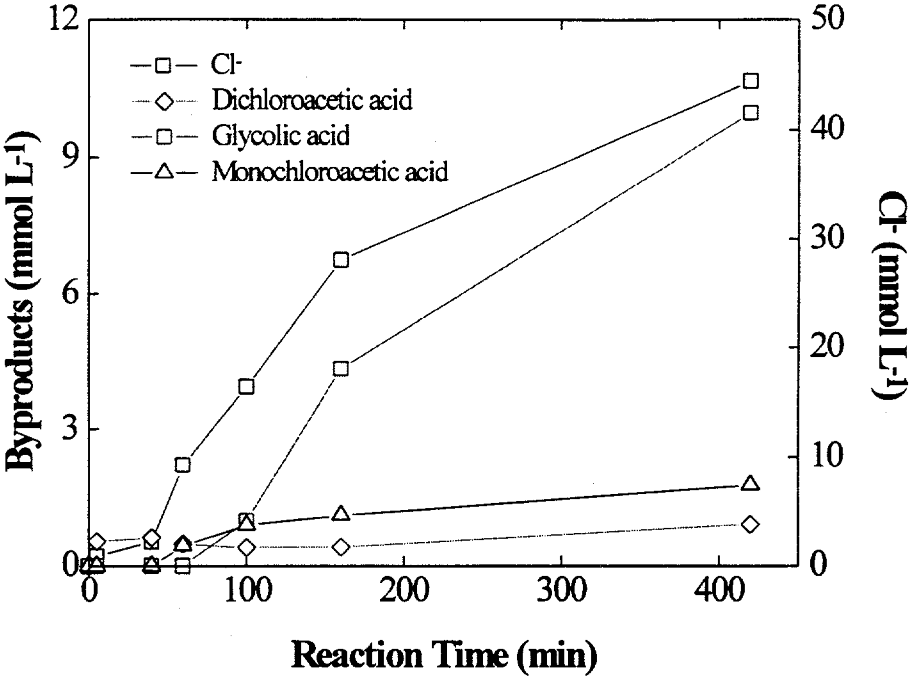


Fig. 12. By-products formation between TCE and *2 M* NaOH at 60°C

3.3 DEGRADATION OF CHLOROFORM IN NaOH

Similar experiments were performed between chloroform and NaOH with the Mininert micro-reaction vessels (Figs. 13–14). Results indicated that the reaction rate between chloroform and NaOH was extremely fast. Within about 30 s, no detectable amounts of chloroform were left in the solution phase, as determined by GC analysis. In fact, the reaction was so fast at 80°C, only one data point was collected practically because of the time required for initial mixing and sampling (~30 s). Analysis of by-products indicated that Cl^- and formate were released stoichiometrically after 3 min. In other words, degradation of 1 mole of chloroform formed ~ 1 mole of formate and 3 moles of Cl^-. Note that although no detectable amounts of chloroform can be measured after 30 s of reaction, concentrations of Cl^- and formate increased gradually. These results suggest that, upon interaction between NaOH and chloroform, chloroform was dechlorinated and formed some intermediate products, which ultimately degraded to formate and Cl$^-$. However, these intermediate products was not identified given the experimental conditions for the HPLC analysis. No further attempts were made to identify these intermediate products.

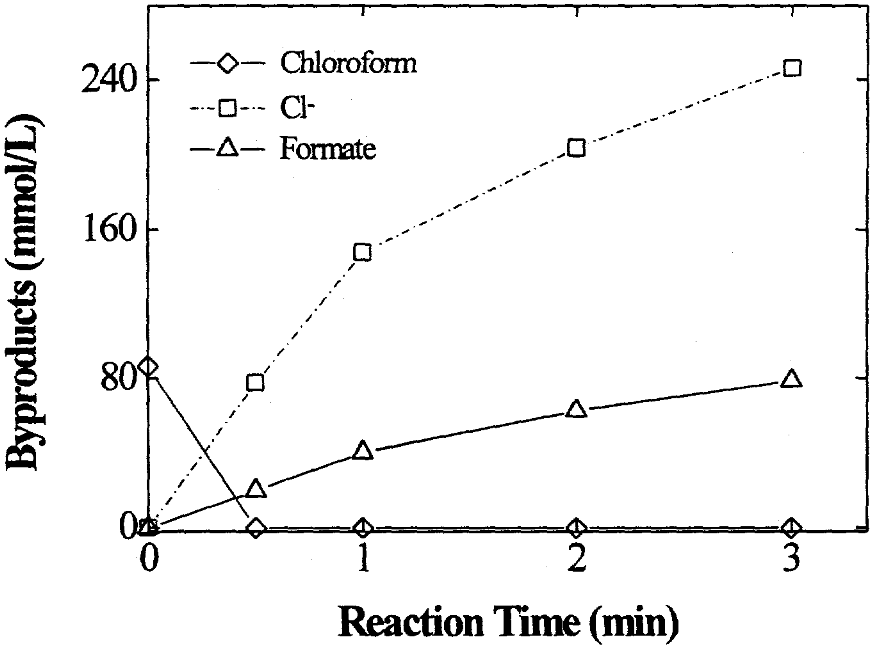


Fig. 13. Degradation and by-product formation of chloroform in 2 *M* NaOH at 80°C.

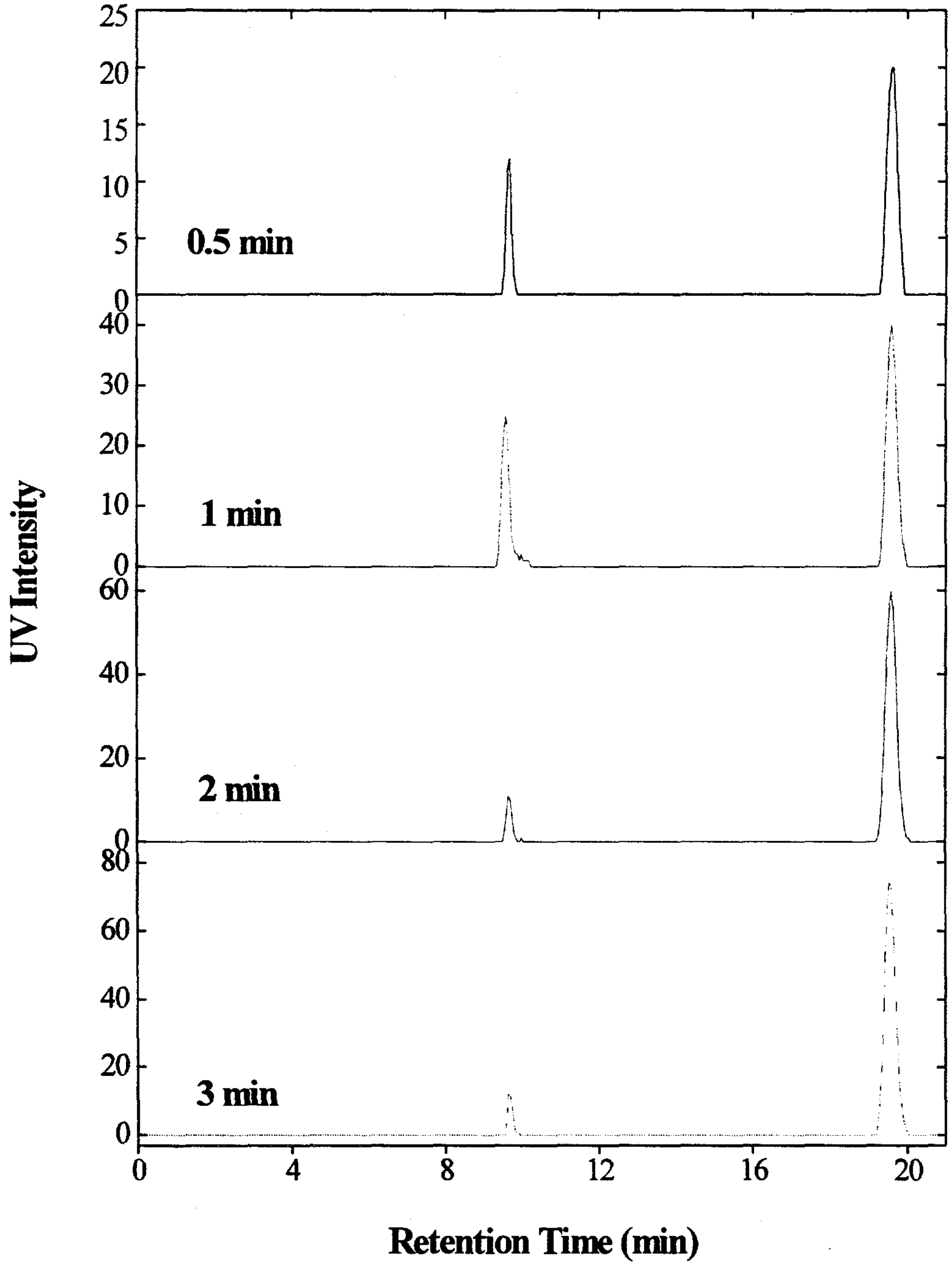


Fig. 14. Identification of the reaction by-products between chloroform and 2 *M* NaOH at 80°C by ion chromatographic analysis. Elution peaks at 9.5 and 19.5 min are peaks of solvent and formate, respectively.

Reactions between chloroform and NaOH were also studied at 40°C (Fig. 15). Even at such a reduced temperature, the degradation rate of chloroform was faster than that of TCE at temperatures above 80°C. At 1 min, ~80% of chloroform was transformed, and an increased Cl^- concentration was observed with time. These results demonstrate that chloroform can be dechlorinated or degraded more readily than TCE.

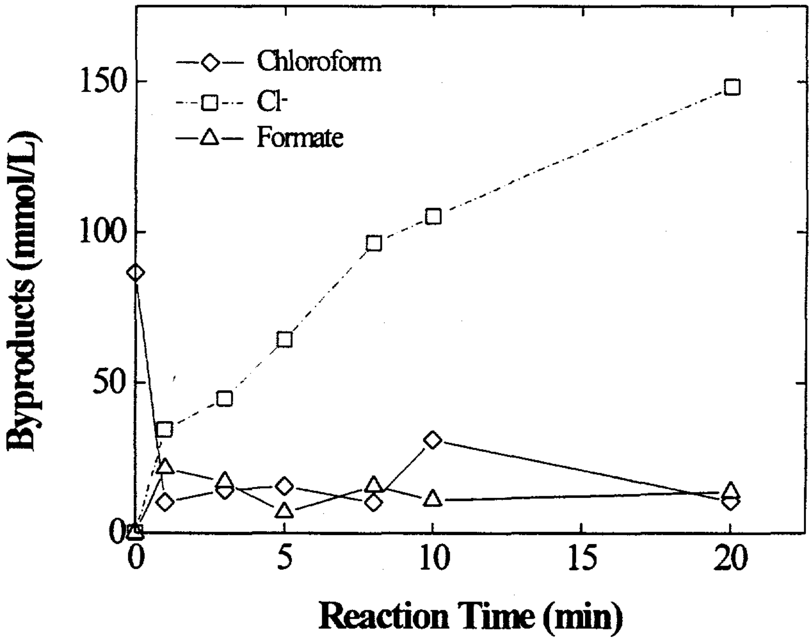


Fig. 15. Degradation of chloroform and by-product formation in 2 M NaOH at 40°C.

3.4 REACTIONS OF TCE WITH NaOH IN ZHE

As indicated previously, our initial experiments were performed in ZHEs. A major problem with this experimental setup is that the degradation rate of TCE can not be accurately determined because of an initial heating period (~25–30 min). Commonly, within the first 25 min of reaction, we observed an "increased" TCE concentration in NaOH solution. This observation was attributed to poor mixing and a low solubility of TCE in aqueous solution at a relatively low temperature. After an initial injection of TCE, large quantities of TCE probably sit at the bottom of the ZHE (because TCE is heavier than water) while a sample was taken at the top by raising the piston upward. As heating progressed, mixing is no longer a concern because TCE becomes more soluble in NaOH solution and because of increased thermal mixing. As shown in Figure 16 for TCE reactions in 2 *M* NaOH, we observed an "increase" TCE concentration within the first 25 min, and then the TCE concentration decreased rapidly. These results nevertheless confirmed our studies performed in Mininert micro-reaction vessels (Sect. 3.1–3.3), that is, TCE reaction kinetics with NaOH was very fast and the half-life is on the order of minutes at an elevated temperature.

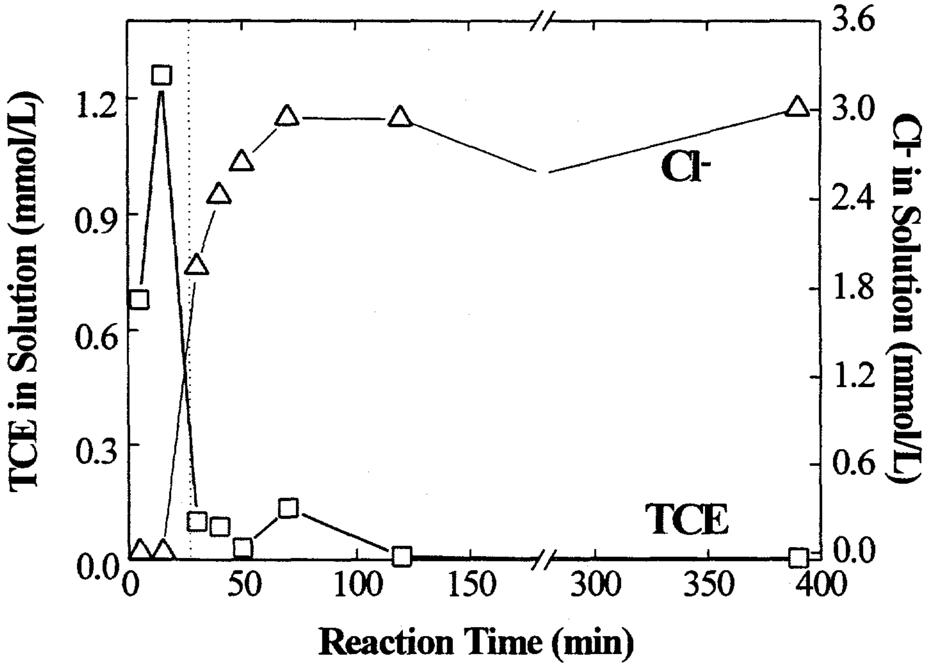


Fig. 16. Reaction kinetics between TCE and 2 *M* NaOH at 100°C and by-product (Cl⁻) formation in ZHE. Note: the first two data points (0-25 min indicated by a dotted vertical line) are a result of initial heating and mixing problems after injection of TCE into NaOH.

Similarly, we performed these experiments at different temperatures (Figs. 17–18). At lower temperatures, TCE degraded at a reduced rate as indicated by a relatively slow decrease in TCE concentration and slow increase in Cl^- concentration. At 25°C, no significant dechlorination of TCE was observed within the reaction time studied.

To verify if a significant TCE loss occured during the batch experiment, one set of the experiment was performed with ^{14}C-labeled TCE as a tracer. In other words, when TCE is dechlorinated or transformed to other nonvolatile organic compounds (such as Na-glycollate), we would expect a constant ^{14}C-radioactivity in the solution although TCE concentration decreases over time by GC analysis. On the other hand, ^{14}C-radioacitivity decreases if there is a TCE volatilization loss during the experiment (Gu et al. 1995). Results (Fig. 19) indicated that >95% of ^{14}C-radoactivity was recovered during the reaction and remained relatively constant over the reaction time (after ~30 min). The first two data points were low and again attributed to a poor mixing and low solubility of TCE at a relatively low temperature during the initial heating period.

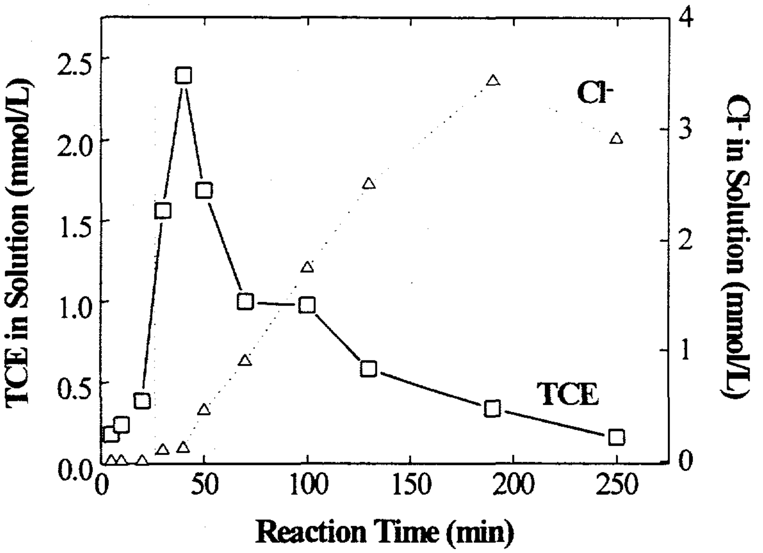


Fig. 17. Reaction kinetics between TCE and 2 *M* NaOH at 60°C and by-product (Cl⁻) formation in ZHE. Note: the first few data points are a result of initial heating and mixing problems after injection of TCE into NaOH.

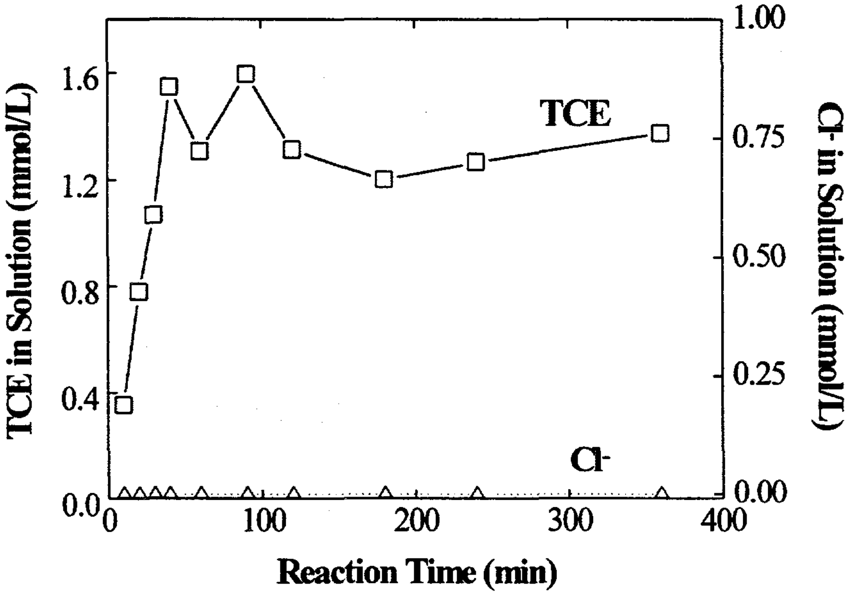


Fig. 18. Reaction kinetics between TCE and 2 *M* NaOH at 25°C and by-product (Cl⁻) formation in ZHE. Note: the first few data points are a result of initial mixing problems after injection of TCE into NaOH.

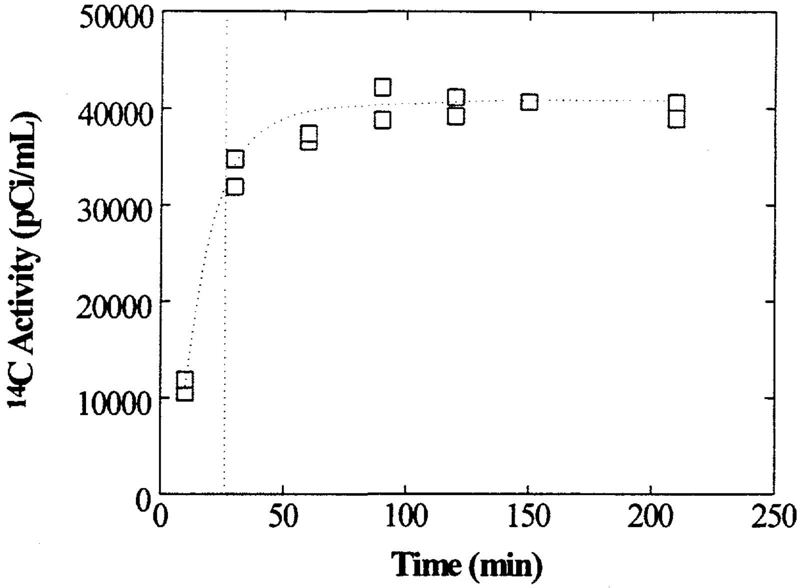


Fig. 19. Mass balance analysis of ^{14}C-radioactivity after ^{14}C-labeled TCE interaction with 2 *M* NaOH at 100°C in ZHE.

Additional experiments were performed to optimize the reaction conditions so that TCE or other chlorinated VOCs could be rapidly dechlorinated. This would allow for engineering applications of this technique for environmental cleanup purposes such as to remove/destroy TCE in the off-gas stream during soil vapor extraction and groundwater pump-and-treat processes. First, we determined the TCE reaction kinetics under varying NaOH concentrations (Figs. 20–21). As expected, the reaction rate in 0.1 *M* NaOH at 100°C was much slower than that in 2 *M* NaOH (Fig. 16). These results were attributed to a reduced reactant (OH^-) concentration. However, an increase in NaOH concentration to 4 *M* did not appear to increase the reaction rate between NaOH and TCE at 80°C (Fig. 21). No satisfactory explanation can be given at this point although a poor control of the reaction temperature of the ZHE may be a contributing factor.

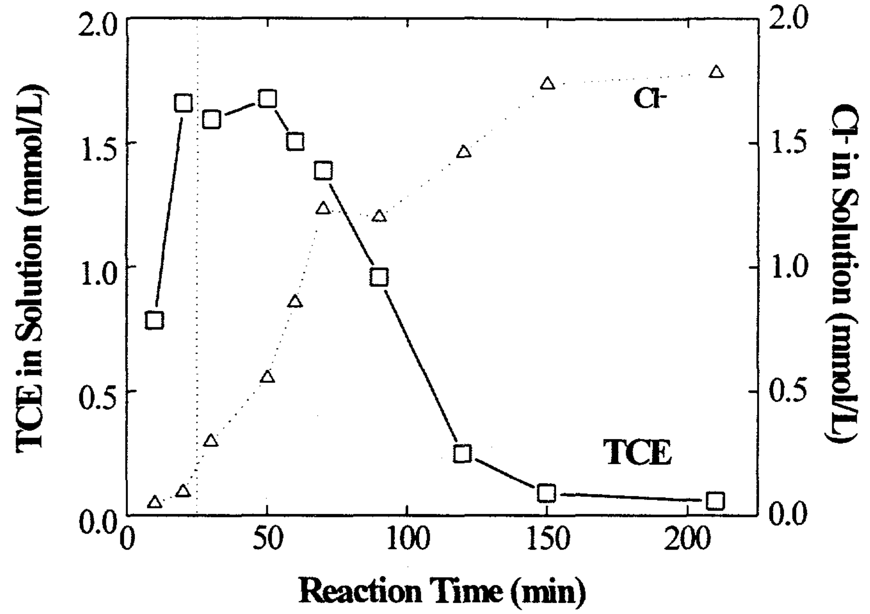


Fig. 20. Reaction kinetics between TCE and 0.1 M NaOH at 100°C and by-product (Cl⁻) formation in ZHE. Note: the first few data points are a result of initial heating and mixing problems after injection of TCE into NaOH.

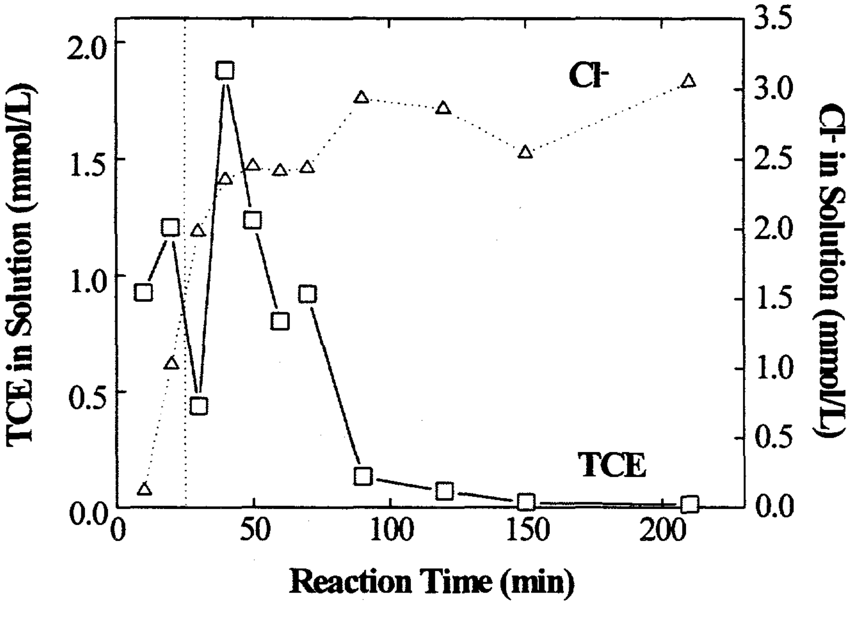


Fig. 21. Reaction kinetics between TCE and 4 *M* NaOH at 100°C and by-product (Cl⁻) formation in ZHE. Note: the first few data points are a result of initial heating and mixing problems after injection of TCE into NaOH.

Two different alkalis (i.e., 1 *M* KOH or 1 *M* Na_2CO_3) were also tested for their effectiveness in degrading TCE (Figs. 22–23). KOH performed similarly as NaOH in degrading TCE (Fig. 22). Note: 1 *M* KOH at 80°C was used in this experiment. Compared with Figs. 16–17 (TCE in 2 *M* NaOH), KOH did not appear to perform much better than NaOH in chemical destruction of TCE. Na_2CO_3 appeared to cause degradation of TCE as shown in Fig. 23. TCE concentration in ZHE decreased with the reaction time. However, no dechlorination (or Cl^- release) was observed during the reaction. These results suggest that Na_2CO_3 is ineffective compared with NaOH or KOH in causing the complete dechlorination of TCE. No further studies were conducted with these two bases.

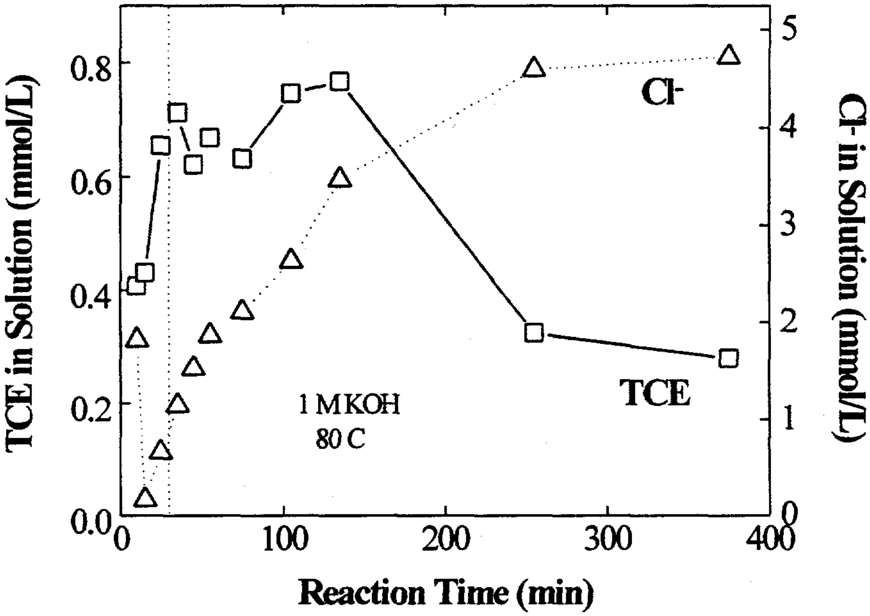


Fig. 22. Reaction kinetics between TCE and 1 M KOH at 80°C and by-product (Cl^-) formation in ZHE. Note: the first few data points are a result of initial heating and mixing problems after injection of TCE into KOH.

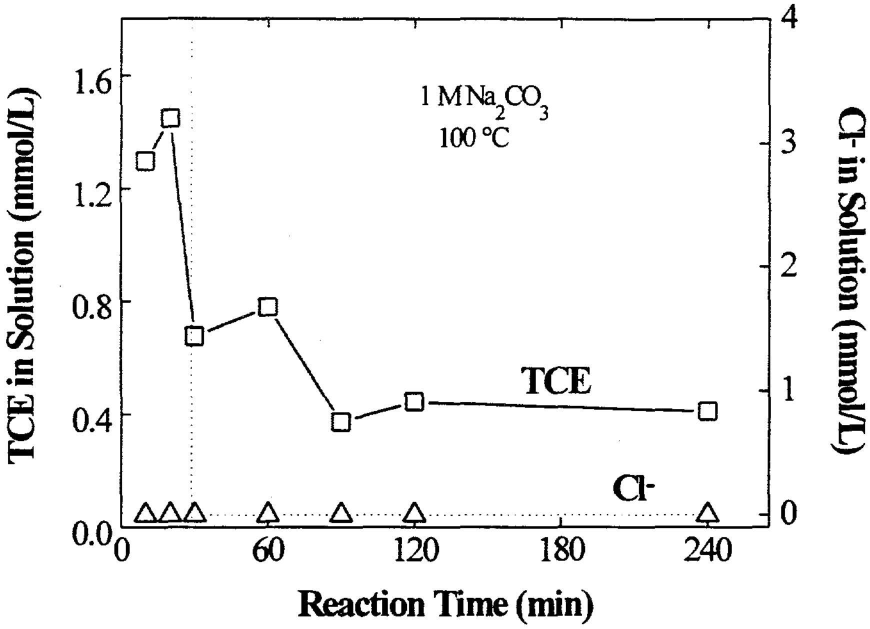


Fig. 23. Reaction kinetics between TCE and 1 *M* Na_2CO_3 at 100°C and by-product (Cl^-) formation in ZHE

Finally, different chemical reagents such as PEG, (0.5%) and TiO_2 (0.5%) were studied for their effects on the reaction rate between TCE and 1 *M* NaOH at 80°C (Figs. 24–25). Reactions between TCE and NaOH and 0.5% PEG were also performed at an elevated pressure (2 atm). PEG was selected because it has been used as a phase transfer catalyst for the dechlorination of PCBs in strong bases (Brunelle and Singleton 1983). Results indicated that, under these experimental conditions, TCE was dechlorinated relatively fast. However, the degradation rate was not substantially improved in comparison with those experiments performed in 2 *M* NaOH without any additives. Because of limited time, no further studies were carried out.

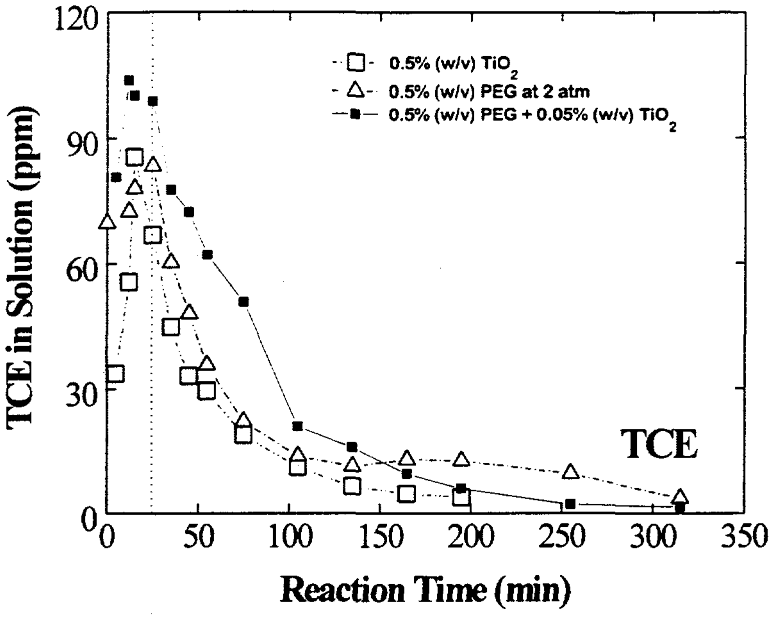


Fig. 24. Reaction kinetics between TCE and 1 *M* NaOH in the presence of PEG or TiO_2 at 80°C in ZHEs. Note: the first few data points are a result of initial heating and mixing problems after injection of TCE into NaOH

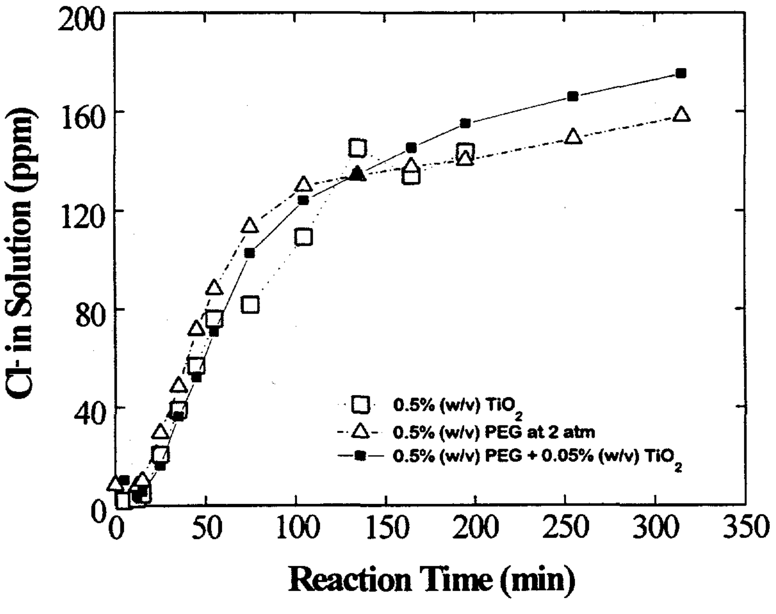


Fig. 25. By-product (Cl^-) formation for reactions between TCE and 1 M NaOH in the presence of PEG or TiO_2 at 80°C in ZHEs.

3.5 REACTIONS OF OTHER CHLORINATED VOLATILE ORGANIC COMPOUNDS WITH NaOH IN ZHE

Other chlorinated VOCs such as trichloroethane and chloroform were also evaluated for their reactions with NaOH in ZHE. Figure 26 shows that TCA reacted rapidly with 2 *M* NaOH at 100°C and caused a rapid dechlorination of TCA. If the first two data points were ignored as a result of the initial heating, the degradation rate of TCA appeared to be only slightly slower than that of TCE under similar experimental conditions. On the other hand, the degradation rate of chloroform was much faster than that of TCE under similar experimental conditions (Fig. 27). In fact, no detectable amounts of chloroform were in the solution after the initial heating period (~25 min). These results are consistent with those experiments performed in Mininert micro-reaction vessels as discussed in Sect. 3.3.

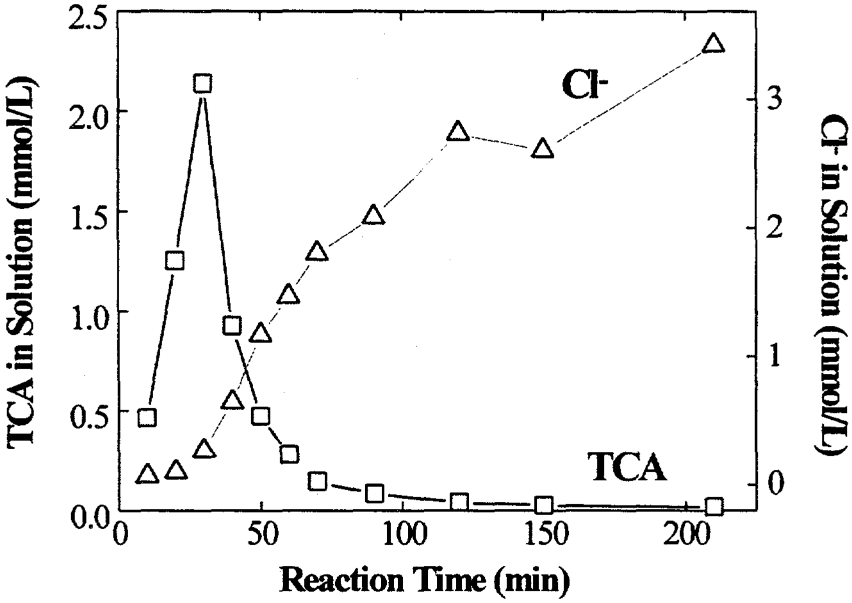


Fig. 26. Reaction kinetics between TCA and 2 *M* NaOH at 100°C and by-product Cl⁻) formation in ZHE. Note: the first two data points (0-25 min) are a result of initial heating and mixing problems after injection of TCA into NaOH.

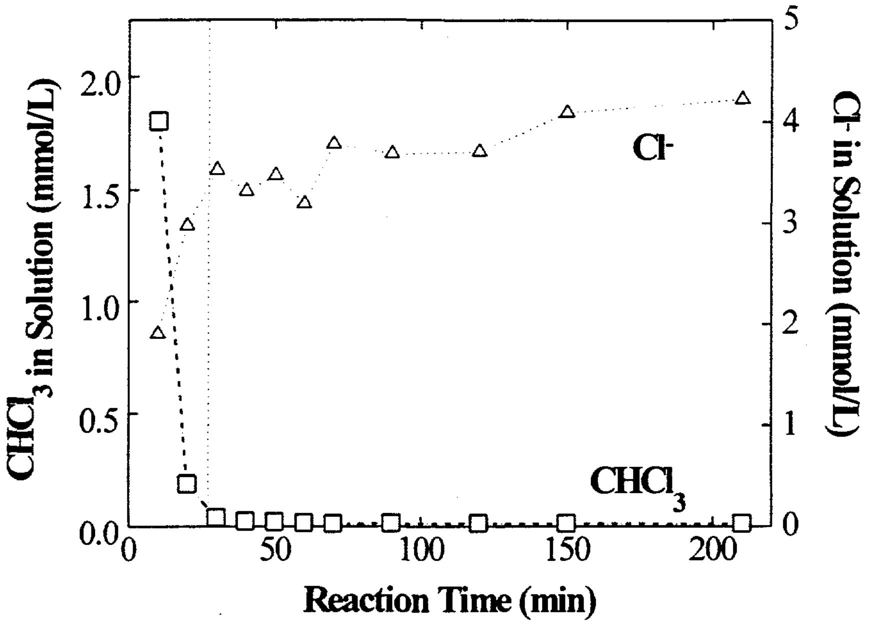


Fig. 27. Reaction kinetics between chloroform and 2 *M* NaOH at 100°C and by-product (Cl^-) formation in ZHE.

It is generally concluded, therefore, that chlorinated VOCs can be effectively and rapidly dechlorinated by strong alkalis such as NaOH at an elevated temperature. A potential application of this technique is to use strong alkali to degrade or destroy chlorinated VOCs in the off-gas stream during the soil vapor extraction or groundwater pump-and-treat processes. Currently, VOCs in the off-gas are commonly treated by adsorption on activated carbon, which is relatively expensive and often generates large quantities of secondary wastes. On the basis of this exploratory research, we designed a new chemical treatment system that can potentially replace the activated carbon treatment module to remove/destroy chlorinated VOCs in the off-gas.

3.6 VAPOR-PHASE DESTRUCTION OF TCE

A prototype vapor-phase destruction system (Fig. 2) was constructed to evaluate TCE degradation under continuous, flow-through conditions. TCE-contaminated gas (10 mg/L mixed with N_2, Scotty Specialty Gases, Inc.) was used for the experiment. The destruction efficiency was evaluated at three different flow rates, 3, 5, and 10 cfhv (or 1.4, 2.4, and 4.7 L/min) (Fig. 28 and Table 2). Note: the blank was run at 2.4 L/min through the alkaline destruction column at room temperature with interlock packing materials completely immersed in NaOH solution. This may slightly underestimate the initial TCE concentration in the "off-gas" because of the reaction and absorption of TCE by the alkaline solution. At room temperature, we expected that only a very small percentage of TCE vapor may be degraded when it passed through the column (with an average residence time of ~2 min). Nevertheless, results indicated that > 70% of vapor-phase TCE was removed/destroyed at a flow rate of 1.4 L/min when temperature of the alkaline solution was raised to 95°C; more than 85% of TCE was removed at a flow rate of 2.4 L/min. Interestingly, at the highest flow rate (4.7 L/min) with an average residence time of ~ 1 min, we observed the highest TCE removal efficiency (~90%) although batch experiments (Sect. 3.1 indicated a half-life of ~ 2.5 min. These observations may be partially attributed to a channeling effect because, at a low flow rate, TCE/N_2 bubbles may not be effectively interacting with the packing materials in the column. This may result in the formation of large air-bubbles and preferential flows, which limit the mass transfer between vapor-phase TCE and NaOH solution. On the other hand, at a high flow rate, TCE/N_2 vapor effectively interact with the interlock packing materials and leads to a turbulent flow that creates smaller TCE/N_2 bubbles for TCE to contact/interact with NaOH. These experiments were continuously run and monitored until the supply of TCE/N_2 was exhausted. The capacity of the column to absorb/degrade TCE was not evaluated because it was impractical or too costly to run these experiments. However, in theory, 1 mole of TCE (~136 g) shall require 3 moles (120 g) of NaOH to be completely dechlorinated.

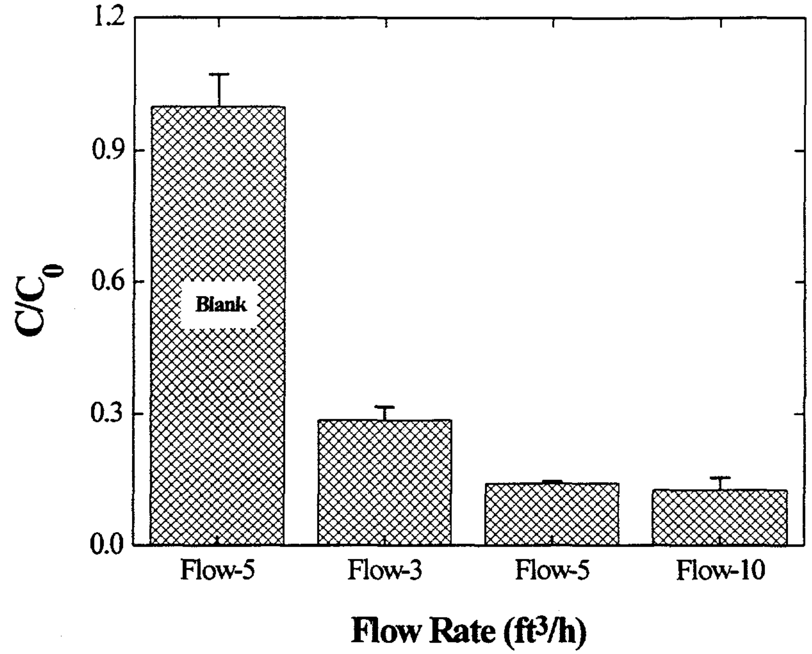


Fig. 28. Vapor-phase TCE degradation through the alkaline destruction column (2 *M* NaOH at 95°C) at different flow rates. Note: the column interlock packing materials are immersed in ~5 L 2 *M* NaOH. Error bar equals 1 σ.

Table 2. Vapor-phase TCE degradation in 2 *M* NaOH at 95°C in a flow-through destruction column

Flow Rate (ft^3/h)	RT* (min)	GC Peak Area	Std Deviation	C/C_0
Blank (25°C)	2	3801870	275098	1
3	3.5	1085100	117235	0.285
5	2	542856	14279	0.143
10	1	486051	101464	0.128

* RT = estimated average residence time.

4.0 SUMMARY AND RECOMMENDATIONS

A number of batch experiments were performed for reactions between chlorinated VOCs and NaOH under varying experimental conditions. Results indicated that TCE can be rapidly and completely degraded in NaOH at an elevated temperature. The half-life for TCE degradation is < 4 min. at ~80 °C; the end products were identified to be Cl^- and Na-glycollate, both of which are non hazardous. Degradation of chloroform was even faster (on the order of seconds) under the same experimental conditions. A bench-scale destruction unit was constructed and verified for its effectiveness in degrading vapor-phase TCE under continuous, flow-through conditions. Results indicated that the degradation rate of TCE can be even faster in a flow-through column than that observed in batch reactors.

The above bench-scale test of the prototype TCE-destruction column demonstrates that this technology can be applicable for off-gas treatment of chlorinated VOCs during soil vapor extraction and groundwater air-stripping operations. The new treatment system is expected to be cost-effective and to have a high capacity to absorb/degrade TCE in comparison with carbon adsorption approach. For example, treatment of 1000 m^3 of soil containing 100 mg/kg TCE (~165 kg) by soil vapor extraction requires ~8200 kg activated carbon but requires < 150 kg NaOH (the calculation was based on a TCE adsorption capacity of 2% on activated carbon). More importantly, perhaps, treatment with carbon adsorption will generate large quantities of secondary hazardous wastes that must be treated or disposed of. On the other hand, the alkaline destruction system will only generate small quantities of residual NaOH and non hazardous salts that can be solidified by evaporation and easily disposed of. Additionally, the alkaline destruction system will not be subjected to fouling as commonly observed when carbon adsorption is used. Hot air or steam used for soil vapor extraction is also expected to enhance the performance of the alkaline destruction system. A field-scale demonstration of this technology is thus recommended and is expected to have a great impact on the environmental restoration and management of VOC contaminated soils and groundwater.

Because of limited time, batch and column experiments were focused primarily on the degradation of TCE in this study with limited batch experiments performed with chloroform and TCA. Further studies are also recommended to determine the reaction rate, mechanisms, and by-product formation between different alkalis and other chlorinated VOCs (or in general, halogenated organic compounds) in both batch and column experiments. These studies are essential for selection of an optimum condition and a successful implementation of this technology for treatment of VOC off-gas streams.

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