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Reductive Dechlorination in a Continuous Flow Electrolysis Cell

By

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A Thesis

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Abstract

Reductive Dechlorination in a Continuous Flow Electrolysis Cell

Halogenated organics constitute one of the largest single classes of hazardous chemicals and wastes. Electrochemical reduction may be a suitable method to treat wastewaters containing halogenated organics. This research addresses the principals of reductive dehalogenation with a focus on electrochemical processes.

Reductive dechlorination by electrolysis converts highly halogenated molecules into less halogenated species that are more susceptible to either chemical oxidation or biodegradation. The five target chemicals chosen for this study are (1) perchloroethylene, (2) trichloroethylene, (3) carbon tetrachloride, (4) chloroform and 1,1,1-trichloroethane. Two parallel pathways were observed for the degradation of these target chemicals: hydrogenolysis, and a pathway leading to the formation of completely dechlorinated products. Manipulation of the applied potential permitted control over the degradation rates of target chemicals as well as on the product distribution. At lower applied voltages, the pathway leading to complete dechlorination was dominant whereas at higher reference voltages, the hydrogenolysis was more important. The overall degradation rates of the target chemicals tested were increased by increasing the applied voltage. The operational costs were higher for alkenes as compared to those for alkanes.

Dedicated to

Dr. Craig S. Criddle

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Chapter 1

Introduction

Background

Chlorinated compounds derived from C_1 and C_2 hydrocarbons are manufactured industrially in quantities exceeding a total annual world production of 36 x 10^6 tons. More than 4 x 10^6 tons are used either as aerosol propellants or solvents in dry cleaning and metal degreasing (Giger & Moluar-Kubica, 1988). Owing to their wide spread usage and improper storage and disposal, these compounds have become ubiquitous environmental pollutants and have been identified in the atmosphere and aquatic environment. Of particular interest is the occurrence of these compounds in finished drinking waters, where chloroform and other trihalomethanes are found to occur due to the impact of water chlorination (Rook, 1974, Beller et.al., 1974, Glaze et.al., 1975, Trussell, 1978).

Halogenated aliphatic compounds are also prevalent groundwater contaminants and are a significant component of hazardous waste and landfill leachates. Approximately, 15-28 percent of all groundwater supplies in the United States contain synthetic organic chemicals (Gosset et. al., 1985). Among the most frequently detected contaminants are C_1 and C_2 chlorinated hydrocarbons such as perchloroethylene, trichloroethylene, 1,1,1 -trichloroethane, chloroform and methylene chloride (Westrick et. al., 1984, Roberts et.al., 1982). Although, in most instances extremely low concentrations of these contaminants are detected, there is a major concern that chronic exposure to chlorinated solvents proposes a carcinogenic or mutagenic hazard (Love & Eilers, 1982, Infante & Tsongas, 1982).

A wide spectrum of technologies are available for the treatment of halogenated wastes such as concentration techniques, chemical oxidation and reduction, and biological treatment. Chemical oxidation, although very effective, has the disadvantages of the cost of chemical addition or the generation of UV radiation or ozone. Highly halogenated compounds are also difficult to degrade using oxidation (Vogel et. al., 1987). Incineration recently has immerged as an effective method for the destruction of halogenated wastes, but it suffers from the disadvantages of costs and social acceptance and the need to meet rigorous air quality constraints (Theordore & Reynolds, 1987). Concentration techniques such as air stripping, activated carbon and membrane separation are widely used. These processes do not destroy the contaminants and generally generate concentrated side streams that require further treatment (Schmal et. al., 1987). Chemical reduction using hydrogen at high temperatures or other reducing agents have also been described in literature (Chang & Bozzelli, 1986, Mortland & Boyd, 1989).

Interest has been growing in the biological processes because they offer the prospect of converting the contaminants into harmless products rather than transferring them from one part of the environment to the other. The potential of degradation of trace contaminants when bacteria are attached as biofilms to solid surfaces in soils, natural water bodies, or engineered systems (Bouwer & McCarty, 1985). Aerobic degradation of polychlorinated aliphatics and ethanes have not shown promising results (Fogel et. al., 1986, Fathepure & Boyd, 1988). Thus a number of researchers(Criddle, 1989, Fathepure & Boyd, 1988, Feedman & Gossett, 1989 and many others) are currently studying the anaerobic degradation of halogenated contaminants in either in situ or above ground treatment systems.

Researchers in electrochemistry have compiled extensive information on the reductive dehalogenation, but most of this work has been conducted in non-aqueous environments. In this work, electrolysis experiments are conducted in water to demostrate that reductive dehalogenation of some halogenated aliphatics occurs via competing pathways. '

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Generally transformations of halogenated aliphatic compounds can be divided into two general classes (Vogel et. al., 1987) as shown in Table 1.1.

1. Reactions that require external electron transfer (oxidation and reduction).
2. Reactions that do not require electron transfer substitution and hydrohalogenation.

Electrochemical Reduction

Electrochemical deposition has been established as a widely used technology for the removal of medium or low concentration of metals from waste waters. By contrast, treatment of dilute process waste waters containing halogenated organics using electrolysis techniques has received much less attention (Schmal et al., 1986). Electrochemical processes have been commercially developed for the degradation of halogenated organic compounds (PCB's, aromatics) by Mazur et. al. (U.S. Patent No. 4,702,804) and Habeeb (U.S. Patent No. 4,585,533).

Electrochemical reduction of chloroform and 1,1,1- trichloroethane was studied (by Criddle et al., 1991) in a batch type electrochemical cell in the absence of many complicating factors found in biotic systems. Later, a detailed study was conducted by Rajayya (1992) to investigate the reductive dehalogenation of a number of halogenated aliphatics. These two studies have successfully demonstrated the transformations of these chemicals to less halogenated or completely dechlorinated species.

Dehalogenation Electrochemistry

The overall reaction of cathodic reduction for halogenated aliphatic can be written as

$$\mathrm{R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-}$$

Table .

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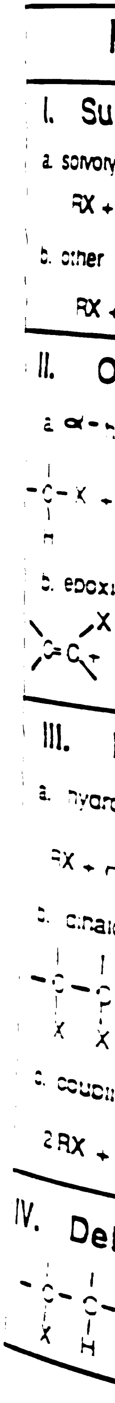

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RX +
II. O
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H
b. epoxi
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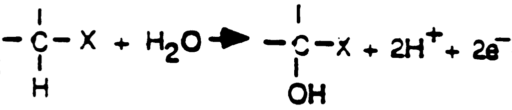
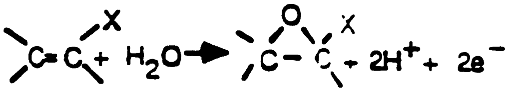
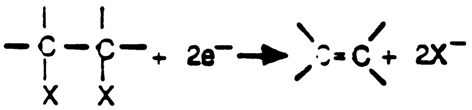
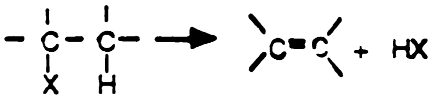
III.
a. hydro
RX +
b. dihal
−C−C−
X X
c. coupli
2RX +
IV. De
−C−C−
X H

Table 1.1 Transformations of halogenated aliphatic compounds (From Vogel et al.1987).

Reactions	Examples
I. Substitution	
a. solvolysis, hydrolysis $RX + H_2O \rightarrow ROH + HX$	$CH_3CH_2CH_2Br + H_2O \rightarrow CH_3CH_2CH_2OH + HBr$
b. other nucleophilic reactions $RX + N^- \rightarrow RN + X^-$	$CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$
II. Oxidation	
a. α-hydroxylation  $-\underset{H}{\overset{\vert}{C}}-X + H_2O \rightarrow -\underset{OH}{\overset{\vert}{C}}-X + 2H^+ + 2e^-$	$CH_3CHCl_2 + H_2O \rightarrow CH_3CCl_2OH + 2H^+ + 2e^-$
b. epoxidation  $\rangle C{=}C\langle^{X} + H_2O \rightarrow \rangle C\overset{O}{-}C\langle^{X} + 2H^+ + 2e^-$	$CHClCCl_2 + H_2O \rightarrow CHClOCCl_2 + 2H^+ + 2e^-$
III. Reduction	
a. hydrogenolysis $RX + H^+ + 2e^- \rightarrow RH + X^-$	$CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^-$
b. dihalo-elimination  $-\underset{X}{\overset{\vert}{C}}-\underset{X}{\overset{\vert}{C}}- + 2e^- \rightarrow \rangle C{=}C\langle + 2X^-$	$CCl_3CCl_3 + 2e^- \rightarrow CCl_2CCl_2 + 2Cl^-$
c. coupling $2RX + 2e^- \rightarrow R\text{-}R + 2X^-$	$2\,CCl_4 + 2e^- \rightarrow CCl_3CCl_3 + 2Cl^-$
IV. Dehydrohalogenation  $-\underset{X}{\overset{\vert}{C}}-\underset{H}{\overset{\vert}{C}}- \rightarrow \rangle C{=}C\langle + HX$	$CCl_3CH_3 \rightarrow CCl_2CH_2 + HCl$

The electrochemical cell offers a means of supplying electrons for this reaction as shown in Figure 1.1. (Criddle, 1989). In electrolysis, reduction and oxidation can be physically separated as electrons produced that are at the anode can be sent to the reducible target compound at the cathode. Electrolytic reduction can be achieved at high rates because a small voltage increase at the cathode can create powerful overpotentials for electron transfer. One of the major problems in this process is that the protons compete with the target chemicals in accepting electrons at the cathode and thus producing hydrogen gas. Also,

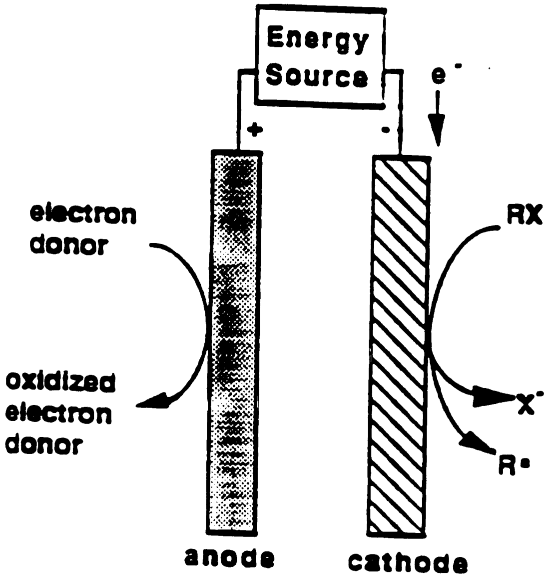


Figure 1.1 Reductive Dehalogenation by electrochemical cell.

the efficiency of electron transfer and the nature of products formed have great impact on cost effectiveness.

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Pathways of Reductive Transformation

Perchloroethylene (PCE) and Trichloroethylene (TCE)

A survey of U.S. EPA Office of Drinking water has revealed that PCE and TCE were two of the five most frequently found compounds in the groundwater (Westrick et. al.,1984). Numerous incidents of well contamination have been well documented (Giger et. al., 1977, Petura, 1981, Seraglitz et.al., 1978). Biological transformation of PCE and TCE in a contaminated site was reported by Parsons et. al. (1984). In this study, the appearance of cis and trans 1,2-dichloroethylene and the depletion of PCE and TCE were observed following incubation in microcosms containing muck from an aquifer recharge basin. Bouwer and McCarty (1985) studied the PCE and TCE transformations with biofilms grown under aerobic conditions but the results were not very encouraging. Less than 20 percent removal efficiency for these compounds were observed with a retention time of 2-3 months using acetate as the primary substrate.

The potential for biotransformation of halogenated organics has been investigated by a number of researchers recently. The use of continuous flow fixed film bioreactors for PCE and TCE transformation has been studied under anaerobic conditions (Bouwer et. al. 1983, Bouwer et. al., 1988). Further study has revealed that PCE is degraded under methanogenic conditions to form TCE, DCE, vinyl chloride (VC) and carbon dioxide (Vogel & McCarty, 1985). These studies clearly demonstrated that TCE and VC were the major intermediates in PCE transformation and suggested that the potential existed for complete mineralization of PCE to CO_2 in soil and aquifer systems.

Based on the above studies a general agreement exists that under anaerobic conditions PCE transformation proceeds by sequential reductive dechlorination to TCE, DCE and

VC. Each chlorine atom is replaced by hydrogen to give one of three possible DCE isomers. 1,1-DCE is the least significant intermediate; several studies have reported that cis-1,2-DCE predominated over trans-1,2-DCE (Parsons et. al., 1984, Parsons & Lage, 1985, Kleopfer et. al. 1985). Electrolytic reduction of PCE in a highly reducing environment has also indicated the production of TCE, t-DCE and products of complete dechlorination (Rajayya, 1992). Vinyl chloride was also observed as a daughter product of TCE in a microsm study involving biotransformation of methanogenic aquifer material (Wilson et. al.). Barrio-Lage et. al.(1986) have constructed the following pathway for the transformation of PCE to VC as shown in Figure 1.2. Other studies have indicated anaerobic dechlorination of PCE to produce carbon dioxide or chloroethanes as shown in figure 1.3 (Fathepure et al., 1988).

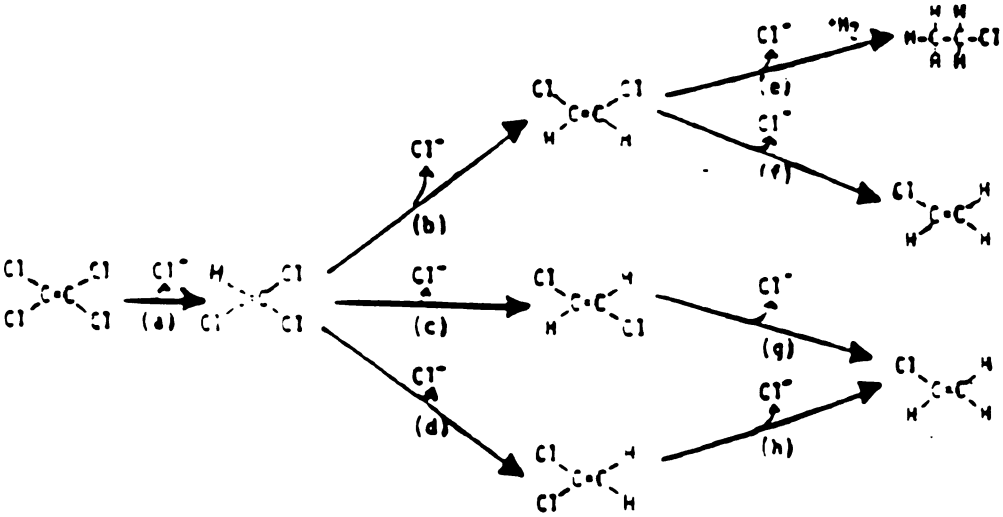

Figure 1.2 Pathways for transformation of PCE to VC.

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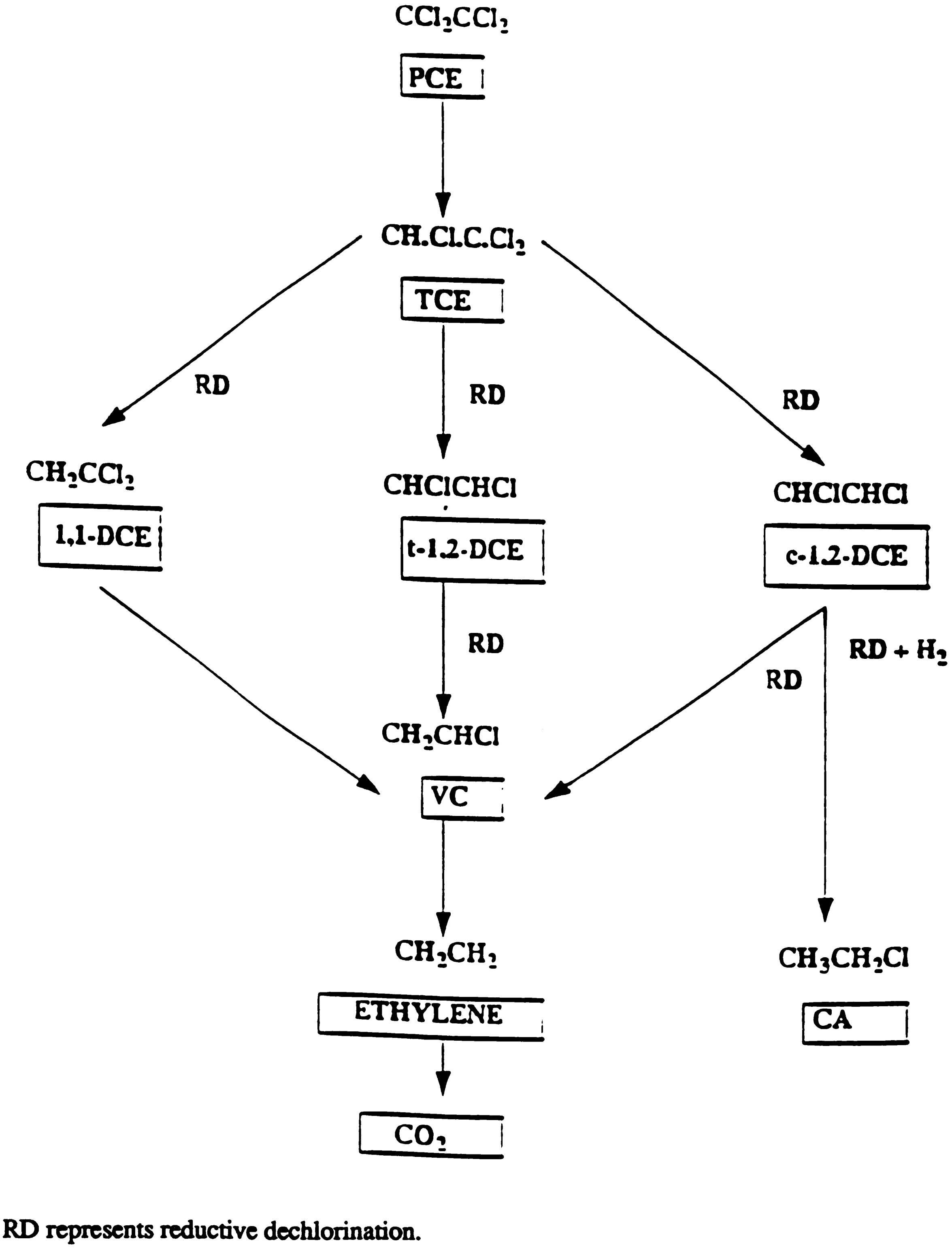
Figure 1.3 Suggested anaerobic dechlorination pathways for PCE and TCE Transformation (From Fathepure et al., 1988)



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Carbon Tetrachloride (CT)

Figure 1.4 provides a synthesis of various pathways for the transformation of CT (Criddle & McCarty, 1991). The various steps in this Figure are described below.

Reaction 1.

Although there is a possibility that CT may undergo direct hydrolysis to form CO_2, most researchers (Wade & Castro,1973, Koster & Asmus, 1971, Bakac &Espenson, 1986) agree that the first step in the CT reduction is the one electron reduction to form trichloromethyl radical and a chloride ion.

$$CCl_4 + e^- \rightarrow {}^{\bullet}CCl_3 + Cl^-$$

Reaction 2.

One of the suggested pathways(Fowler,1969) is the dimerization of trichloromethyl radical to produce hexachloroethane

$$2({}^{\bullet}CCl_3) \rightarrow C_2Cl_6$$

Reaction 3.

This pathway results from the sequential dechlorination of CT to chloroform and finally to dichloromethane. The hydrogenolysis reaction of CT to CF can be written as a two step process. First is the removal of chloride as given earlier in Step 1 and the second step is

$$\bullet CCl_3 + H^+ + e^- \rightarrow CHCl_3$$

Some researchers (Kubik and Anders,1981, Egil et al., 1988) have examined the possibility of above reaction as being a two step process such that

$$\bullet CCl_3 + e^- \rightarrow CCl_3^-$$

$$CCl_3^- + H^+ \rightarrow CHCl_3$$

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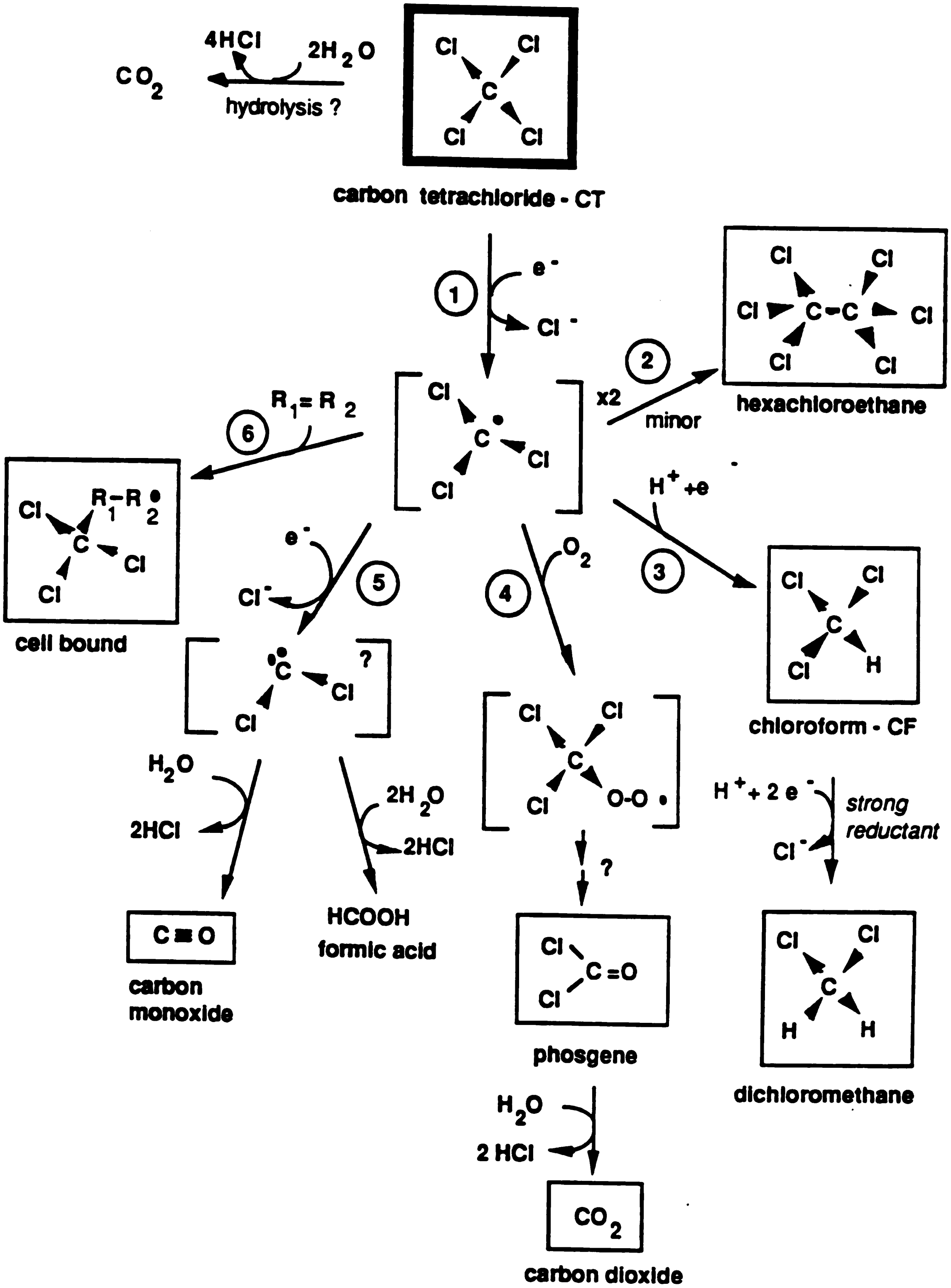
Figure 1.4 Known biotic and abiotic transformations of CT.(From Criddle & McCarty, 1991).*



*The products are shown in boxes.

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The other possible hydrogenation reaction (by Galli & McCarty, 1989, Vogel et al., 1987) is

$$\cdot CCl_3 + R\text{-}H \rightarrow CHCl_3 + R\cdot$$

Chloroform production can be avoided either by creating more reducing conditions resulting in the production of dichloromethane or by creating oxidizing conditions to produce CO_2.

Reaction 4.

Molecular oxygen rapidly adds to the trichloromethyl radical to give a peroxy radical (Sawyer & Roberts, 1983) by the reaction

$$\cdot CCl_3 + O_2 \rightarrow CCl_3OO\cdot$$

The peroxy radical can be converted to CO_2 by two pathways. In the first pathway takes hydrogen from an organic compound to produce trichlorohydroperoxide which hydrolyzes to produce H_2O_2 and phosgene (Asmus et al., 1985).

$$CCl3OO\cdot + R\text{-}H \rightarrow CCl_3OOH + R$$

$$CCl_3OOH + H_2O \rightarrow O{=}CCl_2 + H_2O_2 + HCl$$

In the second pathway, two peroxy radicals combine releasing molecular oxygen and alkoxy radicals (Monig et al., 1983).

$$2(CCl_3OO\cdot) \rightarrow 2CCl_3O\cdot + O_2$$

The alkoxy radical can degrade to form phosgene (Bahnemann et al., 1987)

$$CCl_3O\cdot \rightarrow O{=}CCl_2 + Cl\cdot$$

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$$CCl_3O^{\bullet} + H^+ + e^- \rightarrow CCl_3OH$$

$$CCl_3OH \rightarrow O{=}CCl_2 + HCl$$

Phosgene produced by all the above mentioned reactions can be further degraded to form CO_2 and hydrochloric acid.

$$O{=}CCl_2 + H_2O \rightarrow CO_2 + 2HCl$$

Reaction 5.

Dichlorocarbene (CCl_2) is formed from chloroform under basic conditions, (Hine, 1950;Andres, 1982;Krimse,1971; March 1985).

$$CHCl_3 + OH^- \rightarrow CCl_3^- + H_2O$$

$$CCl_3^- \rightarrow {:}CCl_2 + Cl^-$$

Dichlorocarbene is also formed by a two electron reduction of CT, as shown in the reaction (Anders,1982)

$$CCl_4 + 2e^- \rightarrow {:}CCl_2 + 2Cl^-$$

Dichlorocarbene hydrolyzes to give CO and /or formic acid(March, 1985).

$$:CCl_2 + H_2O \rightarrow CO + 2HCl$$

$$:CCl_2 + 2\,H_2O \rightarrow HCOOH + 2HCl$$

In the batch type electrolysis studies (Criddle, 1990, Rajayya, 1992) have observed two pathways: hydrogenolysis of CT, and an unknown pathway resulting in production of completely dechlorinated products.

Reaction 6.

CT can be incorporated into cell material by the addition to double bonds via pathway 6

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(March,1985).

Chloroform (CF)

The products of chloroform degradation differ from those of CT and high yields of formic acid are observed in one electron transfer of CF at a pH 7 (Amus et. al., 1985). The significant difference is a result of the existence of C-H bond in chloroform. In low oxygen system various steps of CF degradation can proceed as follows:

$$CHCl_3 + e^- \rightarrow CHCl_2 + Cl^-$$

$$CHCl_2 + O_2 \rightarrow CHCl_2OO$$

$$2CHCl_2OO \rightarrow 2CHCl_2O + O_2$$

$$CHCL_2O \rightarrow HCl + Cl\text{-}C{=}O$$

$$Cl\text{-}C{=}O \rightarrow Cl + CO$$

Addition of O_2 in last two reactions would ultimately lead to the production of carbon dioxide (Asmus et al., 1985).

1,1,1-Trichloroethane (TCA)

Figure 1.5 illustrates the different pathways possible for the transformation of TCA (Vogel et al., 1987), which can undergo two abiotic transformations as well as reductive dehalogenation by anaerobic microorganisms.

-Dehydrohalogenation is one possible abiotic process in which 1,1 dichloroethene is produced, which can further be transformed into to vinyl chloride by reductive dechlorination under methanogenic conditions.

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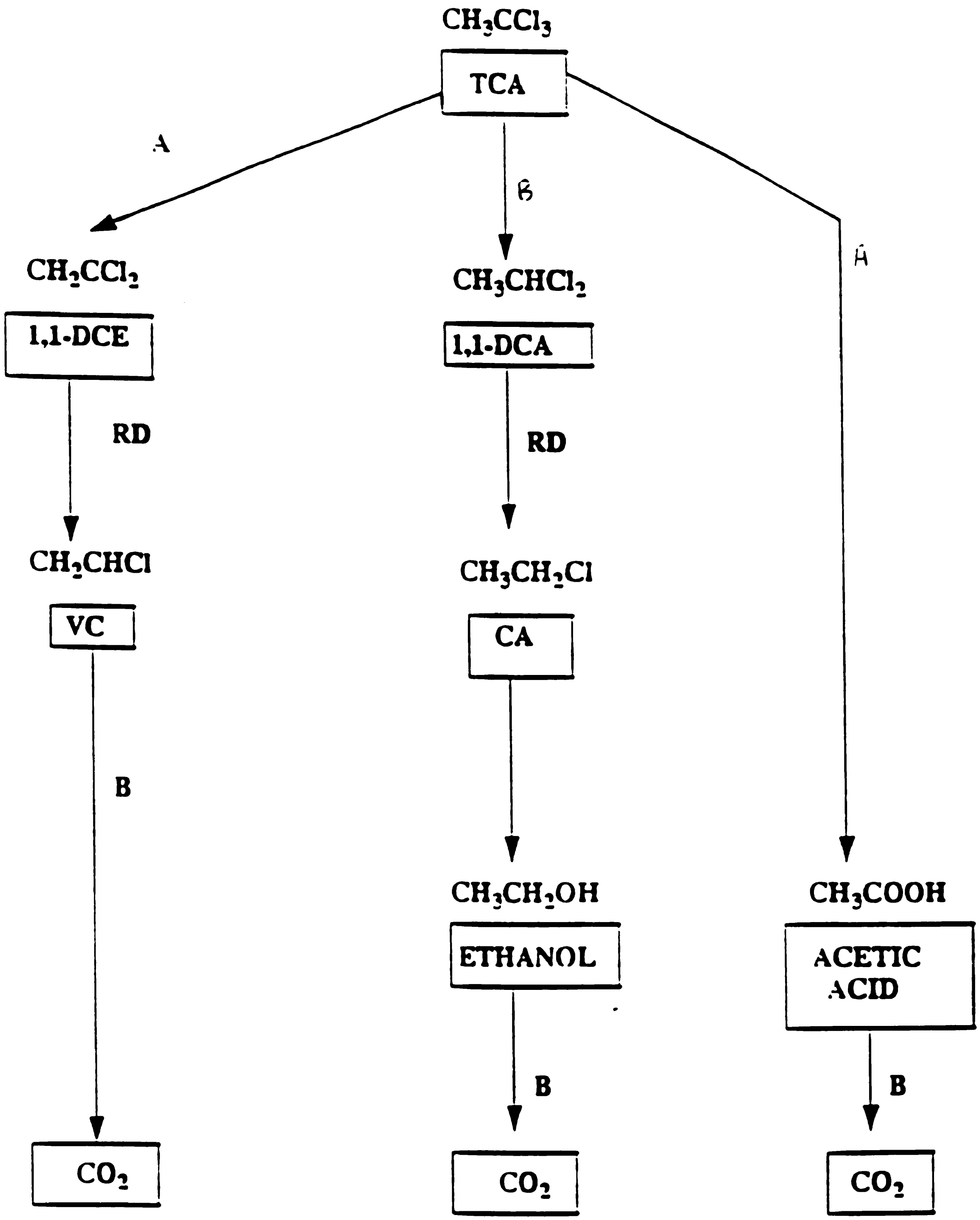

Figure 1.5 Pathways for the transformation of TCA under methanogenic conditions. A indicates abiotic conditions; B indicates biotic conditions; RD indicates reductive dechlorination. (From Vogel et al. 1987)

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-The other abiotic process is hydrolysis that produces acetic acid. Acetic acid is fairly inert chemically, but can be mineralized rapidly by microorganisms.

- Under the biological transformation route 1,1,1 trichloroethane is reduced to 1,1 dichloroethane and then transformed abiotically by hydrolysis to ethanol. which can be mineralized by microorganisms. The complex pathways shown in figure 1.5 are consistent with the field observations of products consistently found in groundwaters contaminated with TCA (Parson et al. 1984, Parson & Lage, 1985).

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Hypothesis

The underlying hypothesis of this work is that electrolysis can be used as an effective tool to transform halogenated aliphatics via competing pathways in a continuous flow system. This research adds to the current understanding of factors effecting these pathways and the rates of reductive dehalogenation of simple halogenated aliphatics. The rates of reductive dehalogenation, and the distribution of products can be by manipulated by varying the applied voltage. Five compounds chosen for this study are: perchloroethylene(PCE), trichloroethylene(TCE), carbon tetrachloride (CT), chloroform (CF) and 1,1,1-trichloroethane. The product distribution for each of these compounds is evaluated at four different applied voltages. Reactor configurations and factors effecting the cost and efficiency of the process are also investigated to explore electrolysis as a possible new treatment technology.

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Chapter 2
Electrochemical Reactor Theory

Fundamental Concepts

An electrochemical reaction is a heterogenous chemical process involving the transfer of the charge to or from an electrode, generally a metal, carbon or semiconductor. The charge transfer may be a cathodic process in which an otherwise stable species are reduced by transfer of electrons from an electrode, as shown in the reactions below:

$$2H_2O + 2e^- = H_2 + 2OH^-$$

$$Cu^{2+} + 2e^- = Cu$$

Conversely, the charge transfer may be an anodic process involving removal of electrons, from otherwise stable species, to the electrode. Example of such reaction would be:

$$CH_3OH + H_2O - 6e^- = CO_2 + 6H^+$$

$$2H_2O - 4e^- = O_2 + 4H^+$$

Electrolysis is only possible in a cell which contains both an anode and a cathode, and in order to avoid the accumulation of net positive or net negative charges, the amount of reduction at the cathode is equal to the amount of oxidation at the anode. Electric current flow between an anode and a cathode placed in an electrolyte is the combined result of electrode processes, charge transport and mass transport brought about by the imposition of an electric field across the electrodes. The relative strength of individual components in

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the total current flow depends essentially upon the strength of the electric field, if the nature and the composition of the electrolyte is known. In figure 2.1, a typical current-voltage drop relationship is shown. At the voltage drops below V_D (curve portion OA), extremely small current flows through the reactor due to a transient capacitive effect. This region is not of much interest in practical electrolysis. As the voltage is increased beyond V_D, there is a sharp increase in the current due to the electrolytic polarization. The current flow in this region is due to the kinetics of the electrode processes involved. The ohmic resistance of the electrolyte plays a much lesser role than the kinetic resistance. The portion BC represents the mixed control region where kinetic, convective and diffusive components are all significant contributors to the overall transport process. The last two become increasingly important as V is increased. The rising portion DE of the curve represents the on set of a new electrochemical process such as the electrolysis of water in aqueous solution.

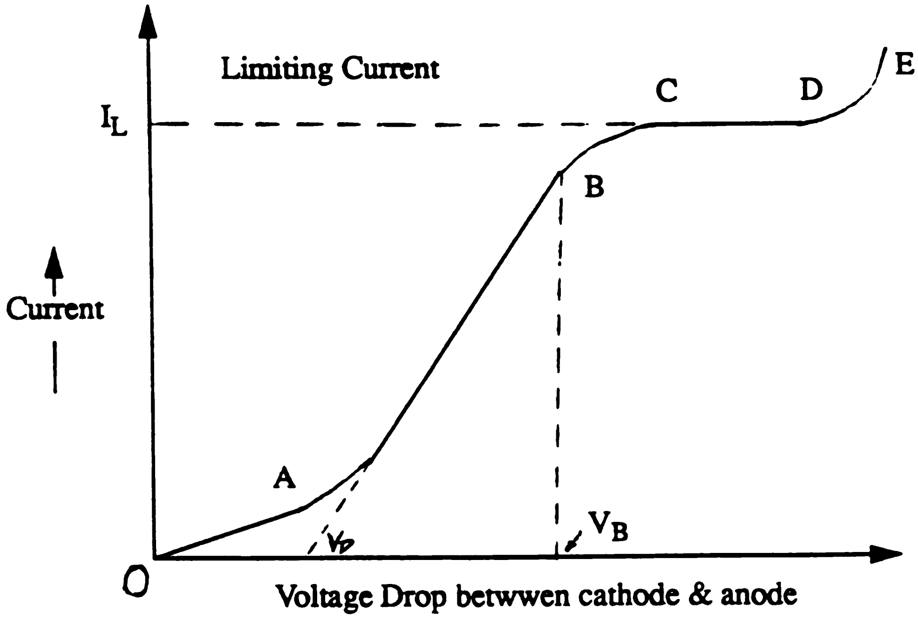

Figure 2.1 The variation of electric current in an electrochemical reactor with voltage drop across the anode and the cathode.

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In region CD, convective and diffusive components become fully predominant. This range is represented by the limiting current I_L, which is the largest current that can flow between the electrodes for a particular set of electrode reactions. In this region, the kinetic rates are so rapid that the concentration at the surface of the electrode approaches zero and the reaction rate is solely determine by the mass transfer. In most of the industrial electrochemical processes, the practitioner encounters only regions AC or AB of figure 2.1. In contrast, there are special situations where processes at one particular electrode will significantly determine the conditions for the reactor design. For example, in the deposition of Cu from aqueous $Cu(NO_3)_2$ solution, the cathode process is the discharge of cupric ions to Cu and anodic process results in the evolution of oxygen gas. The anode reaction will fall in region AB of the curve, but the cathode reaction can occur in region CD, if the voltage drop across electrodes is properly set. Then, the overall ionic transport process will be governed by the limiting current at the cathode. Hence cathodic process will be a significant factor in the process analysis and would determine the overall reactor behavior.

Simplified analysis of plug-flow model of electrochemical reactors

Consider two electrodes, an anode and a cathode separated by a certain distance, as shown in Figure 2.2. Electrolyte is flowing parallel to the electrodes at a constant volumetric flow rate Q and a current (of density i) is applied between the electrodes in a direction normal to the electrolyte flow. In the small section of the reactor shown in Figure 2.2, the mass balance equation at the steady state is written as

$$Qc_x - Qc_{x+\Delta x} = i_x \frac{\Delta A}{zF} \tag{2.1}$$

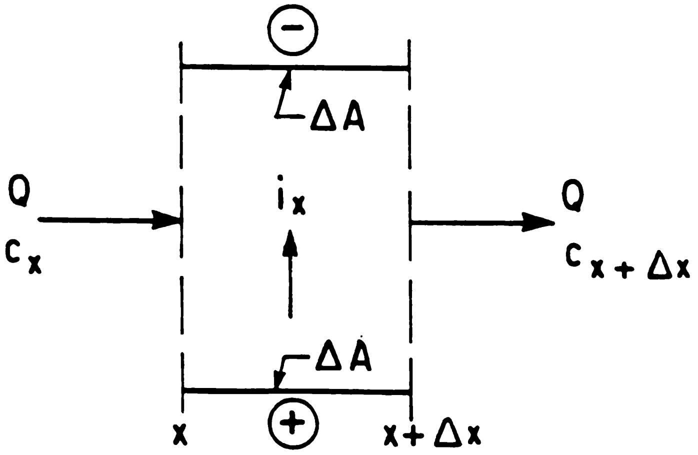


Figure 2.2 Illustration of plug-flow model.

In equation 2.2 c_x is the average concentration of an ionic species at an axial distance x. Considering Δ_x as a small increment in spatial position x, the Taylor expansion can be written for average exit concentration as

$$c_{x+\Delta x} = c_x + \frac{dc}{dx}\Delta x + \frac{d^2c}{dx^2}\frac{\Delta^2 x}{2} + ... \tag{2.2}$$

If Δ_x is very small, the squared and higher order terms can be neglected. Substituting equation 2.2 in 2.1 we get,

$$Qc_x - Q\left[c_x + \frac{dc}{dx}\Delta x\right] = i_x\frac{\Delta A}{zF} = i_x\frac{a\Delta x}{zF} \tag{2.3}$$

Where a is the electrode area per unit electrode length. Upon simplifying on the left hand side and dropping the multiplying factor Δ_x on both sides, we obtain the fundamental PFM equation,

$$\frac{dc}{dx} = -\frac{i_x a}{zFQ} \tag{2.4}$$

The overall material balance of the PFM is obtained by integrating equation (2.4).

$$\int_{c_1}^{c_2} dc = -\frac{a}{zFQ} \int_0^L i_x dx \tag{2.5}$$

where L is the electrode length, c_1 and c_2 are the average inlet and outlet concentrations of the reacting ion. Substituting the value of current given by the equation

$$I = a \int_0^L i_x dx \tag{2.6}$$

into equation (2.5), a very simple expression is obtained relating influent and effluent concentrations.

$$c_2 = c_1 - \frac{I}{zFQ} \tag{2.7}$$

Equation (2.7) does not require any information about the variation of the current density along the electrodes or the knowledge of the velocity profile between the electrodes. The importance of the PFM is that it will allow the estimation of the electrode length, hence electrode area, required for a specific conversion if variation of the current density with axial distance is known.

The current density can be expressed in terms of concentration driving force and apparent mass transfer coefficient as

$$i_x = zFk_x(c - c_e) \tag{2.8}$$

where c_e is the x axis dependent concentration of the reacting ionic species at the electrode. Combining equations 2.4 and 2.8, following expression is obtained.

$$\int_{c_1}^{c_2} \frac{dc}{c - c_e} = -\frac{a}{Q} \int_0^L k_x dx \tag{2.9}$$

The average mass transfer coefficient can be written as

$$k_m = \frac{1}{L} \int_0^L k_x dx \tag{2.10}$$

Substituting this in equation (2.9), the length of the electrode can be written as,

$$L = \frac{Q}{ak_m} \int_{c_1}^{c_2} \frac{dc}{c - c_e} \tag{2.11}$$

Under limiting conditions when $I = I_L$, we can assume $c_e = 0$, hence the above equation can be integrated to give a simpler form:

$$L_{min.} = \frac{Q}{ak_m} log_e \frac{c_1}{c_2} \tag{2.12}$$

where $L_{min.}$ is the minimum electrode length required for this reaction, according to the plug-flow model. Since the actual current flowing through the reactor will be smaller than I_L, the actual length of the reactor would be greater than L_{min}.

Estimation of Mass transfer Coefficient

The mass transfer coefficient k_m is a cornerstone of the rational design and analysis of electrochemical reactors. There are three methods for the computation of the mass transfer coefficient.

1. Determination of k_m via experimental boundary layer thickness and diffusivity data.
2. Approximation of k_m with either data obtained elsewhere by researchers or theoretical relationships in the literature related to a similar system.
3. Sometimes, mass transport data of acceptable accuracy does not even exist for a particular mass transport- geometric configuration. In such a case, heat transport data is employed assuming sufficient similarity between heat and mass transfer phenomena. (Fahidy, 1985).

These methods for estimation of mass transfer coefficient are discussed below.

1. Determination of k_m using diffusivity data

For a simple preliminary approach, the total current flowing through an electrolysis cell can be considered to be made up of two components: the first is due to the diffusion of the active ions as described by Fick's First Law; and the second is due to the migration of ions in an electric field. Let y be the distance normal to the electrode surface, d is the diffusivity of the electrode and t is the transference number of active ions. Then, ti is the portion of the current I carried by migration of the active ion, and the total current can be written as

$$I = zFD_lA_e\,(dc/dx)_{y=o} + tI$$

The current density i is given by

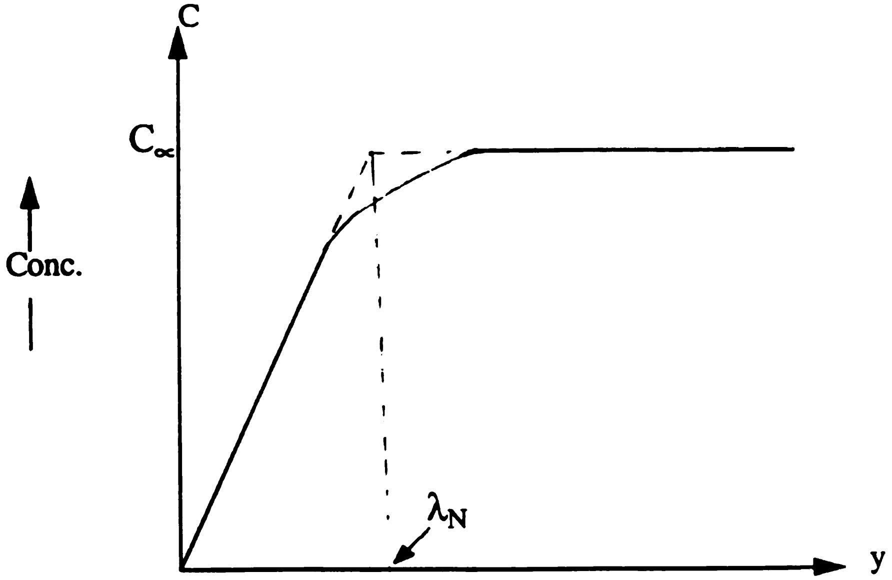
$$i = \frac{zFD_l}{1-t}\ (dc/dx)_{y=o}$$

Assuming $i_l \rightarrow 0$: $C_e \rightarrow 0$, the concentration derivative at the electrode surface may be replaced by the ratio C_∞ / λ_N, where λ_N is defined by the projection of the intersection in Figure 2.3. Consequently, expression

$$i_L = \frac{zFD_l}{1-t}\ \frac{C_\infty}{\lambda_N}$$

relates the limiting current density to the length of the Nernst boundary layer λ_N which is the average value of the boundary layer varying along the electrode. In the presence of other ions whose migration is faster than the migration of active ions, t approaches zero and the above expression is reduced to

$$i_L = zFD_l \frac{C_\infty}{\lambda_N}$$



Distance from electrode perpendicular to flow

Figure 2.3 Concentration profile along y-axis.

The final expression for λ_N is

$$\lambda_N = \frac{zFD_l\, C_\infty}{i_L}$$

The value of λ_N can be determined experimentally by observing the concentration from electrode surface perpendicular to the direction of flow. The mass transfer coefficient can then be defined as

$$K_m = D_l/\lambda_N$$

2. Estimation of mass transfer coefficient using empirical relationships

Although, the above mentioned method for the computation of k_m is most reliable yet the electrochemical engineer very often does not have the time and means necessary for such experimentation. Thus, there is a strong need to estimate the value of mass transfer coefficient using empirical relationships presented in the literature for systems that are similar to the system of interest. In this case, it is very important to exercise proper engineering judgement in estimating the values of mass transfer coefficients.

Most of the mass transfer data in the literature has conveniently been expressed in terms of dimensionless relationships relating to Sherwood number (Sh), Reynold's Number (Re), and Schmidt Number (Sc). These dimensionless numbers can be defined as

$$Sh = i_L L/zFDc\,, \qquad \text{where } k_m = (d/L)\ Sh$$

Where L = length of the reactor, D is the axial diffusivity.

$$Re = V_0\, L/\nu$$

and

$$Sc = \nu/D.$$

For a flat plate electrodes following relation holds good (Fahidy, 1985)

$$Sh = 0.0678\ Re^{1/2}\ Sc^{1/3}$$

For a porous packed bed electrodes the empirical relation (Fahidy, 1985) between these dimensionless variables is given by

$$Sh = \{(1-e)^{0.5}/(1-e)\}\ Re^{1/2}\ Sc^{1/3} \qquad \text{for } 0.25<e<0.5$$

$$40< (Re/1-e) <4000$$

A number of empirical relations have been given (Schmal at el., 1985) to represent the mass transport phenomenon for various electrode materials:

For a single platinum fibre (dia 10 μm), the following relation holds good

$$Sh = 6.1\ Re^{0.352} \qquad \text{for } 0.02<Re<0.15$$

Measurements on carbon felts (dia 25 μm), have been published by Kinoshita and Leach(1983) as

For 0.25 cm thick felt $\quad Sh = 1.29\ Re^{0.72} \quad$ for $0.01<Re<0.25$

For 0.175 cm thick felt $\quad Sh = 1.01\ Re^{0.61} \quad$ for $0.01<Re<0.25$

The mass transfer correlation for a single fiber electrode of 8 μm diameter is given by Schmal at el.(1985) as

$$Sh = 6.1\ Re^{0.352} \qquad \text{for } 0.02<Re<0.15$$

3. Estimation of k_m using heat transfer Data

As mentioned earlier, the process and equations in the heat transfer are compatible with those in mass transfer. Simmonsson (1984) has given an empirical relationship between Sh, Re, and Sc numbers for heat transfer for a single wire:

$$Sh = 0.9\ Re^{0.38}\ Sc^{0.31} \qquad \text{for } 0.1 < Re < 50$$

For dilute aqueous solutions, Sc=1400 resulting in

$$Sh = 5.1\ Re^{0.385} \qquad \text{For } 0.1 < Re < 50$$

Based upon several mass transfer studies, Schmal at el.(1985) have also concluded that carbon fibres have higher mass transfer coefficients and are very suitable for the treatment of aqueous waste. They also concluded that for scaling up purposes, the mass transfer properties of the fibres can be directly calculated from the relation for a single fibre and the total external surface area of the fibres in the felt.

Some of the modelling aspects of an electrochemical reactor are discussed in Appendix B.

Chapter 3
Materials & Methods

Experimental Setup

An electrochemical plug flow reactor was constructed to study the reductive dehalogination of contaminated waters as shown in Figure 3.1. The reactor consists of two plexiglass anode and cathode compartments that can be tightly held together by twelve screws provided along their circumference. Each compartment has an inlet and outlet port and a series of sampling ports along its length. A bell is provided at the top of each compartment to capture gases produced during electrolysis. The two compartments are separated by a proton permeable Nafion 117 membrane (Dupont Co., Wilmington, DE). The membrane is sandwiched between the two compartments, and the entire unit is screwed together. Each compartment has an O-ring along its cross section to prevent any leakage between the plexiglass and the membrane. Graphite fibers (Thornell VMA Material, Amco Performence Products, Greenville, SC) were used as cathode material for the following reasons, as given by Schmal et al. (1987).

-Electrodes with high specific surface area have higher volumetric removal efficiencies. Graphite fibers are well suited due to their high specific surface area.

-Graphite fibers are manufactured in large quantities for the production of strong, light weighted reinforced plastics and are readily available and cheap.

-Graphite fiber electrodes are less prone to clogging by small particles in the waste streams than many other possible electrode materials.

-Graphite fibers have a relatively high over potential for hydrogen evolution which is favorable for efficiency of the dehalogenation reaction.

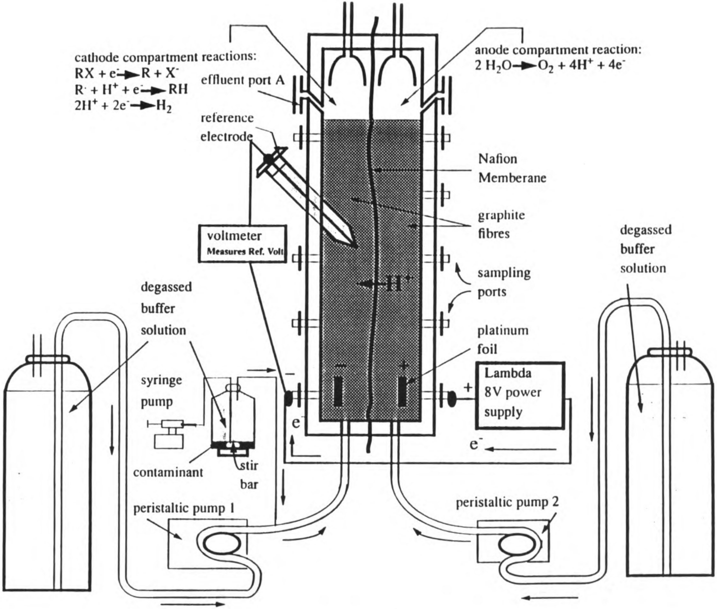


Figure 3.1 Electrochemical plug flow reactor for the electrolytic studies of reductive dehalogenation in water.

Graphite fibers were also used for the anode because the current required for reductive dehalogenation was found to be limited by the anode surface area when anode materials with less specific surface area were used. To prevent this limitation, anode surface area had to exceed that of the cathode. A regulated power supply source (Lambda Model LLS-6008) was used to apply a constant voltage between the anode and the cathode. The power supply source was programmed for a constant voltage, and this voltage was periodically adjusted by reprogramming the supply source to maintain a constant potential between the cathode and a reference electrode. A reference electrode (Orion Model 90-02 Double Junction Reference Electrode with Ag/AgCl with a 1M Na_2SO_4 filling solution) was placed in the cathode compartment, and the potential difference between the tip of the reference electrode and the point X on the cathode electrode were constantly monitored with a multimeter.

In order to achieve a constant concentration of the contaminant in the influent line, two separate flow lines were combined using a three way valve. One of these two lines delivered the degassed buffer solution (with pH of 7.0 using 0.1M NaH_2PO_4 + 0.06 M NaOH solutions) from a reservoir at a constant flow rate of 2.3 mL/min using a peristaltic pump. The second flow line provided a saturated solution of the contaminant at a flow rate varying from 0.05-0.1 mL/min depending upon the influent concentration desired after combining the two flow lines. Flushing of the anode compartment was accomplished by pumping at a constant rate of 2.7 mL/min.

General Experimental Procedure

The following sections describe the methodology followed in a typical experiment.

Assembly of the electrolysis cell

The pattern in which the fibers are packed in the two compartments had a significant effect on the dehalogenation and the voltage requirements. Under similar experimental conditions, a change in orientation of fibers resulted in significant variation in applied potentials (to maintain the same reference voltage) and also resulted in different degradation rates for the target chemicals. Thus, a standard pattern was adopted to pack both electrodes in all experiments. The graphite fibers are available in sheets of layered fibrous material. Pieces of standard size 6.0″ x 0.75″ were cut from these sheets stacked parallel to one another and weighed to obtain the required electrode weight. The weighed electrode material was soaked in water for 2 minutes and then squeezed by hand to remove most of the water. The graphite fibers were then packed in the cathode or anode compartment so that the flat surface of the layers was parallel to the membrane. Care was taken to ensure that the layered pattern of the fibers was not disturbed upon packing and sealing the electrode cell. To complete cell assembly, the membrane was placed between the two compartments, and the two compartments were tightly screwed together by the twelve screws that locked the membrane into position. The rest of the connections were made as shown in Figure 3.1.

Analytical Methods

After applying a voltage, effluent chloride concentration and volatile organics were constantly monitored. Volatile organics were also monitored before applying voltage in order to obtain the breakthrough curve. Chloride measurements were made with a chloride electrode (Orion Research, Inc. Cambridge, MA) connected to an Ion Analyzer (Orion Model 801, Cambridge, MA). For calibration, a 100 ppm standard NaCl solution and various dilutions were prepared to cover the range of expected effluent chloride concentrations. To monitor effluent chloride concentrations, 5mL samples were collected regularly and assayed. The chloride concentration in the effluent was also determined before applying a potential to determine the background chloride. This background chloride was subtracted from each observed chloride reading to obtain a corrected chloride concentration attributable to dechlorination reactions within the reactor. The effluent concentration of bromide (used in the tracer studies) was monitored using a bromide electrode (Orion Model 94-35). The calibration and measurement procedure was similar to the one adopted for chloride measurement.

A standard procedure was adopted to prepare the standards and secondary dilutions for the analysis of volatile organics. A 6-mL bottle weighed dry to the nearest milligram was filled with methanol and tightly capped with a Teflon Mininert valve (Alltech Associates, Inc., Deerfield, IL). After 15 minutes, the vial was reweighed to the nearest milligram. Care was taken that the weight remained constant and there was no evaporation of methanol from the vial. Using a 50–µL glass syringe, pure compound was injected into the methanol solution. The vial was weighed again and the pure compound was added to the methanol solution till the desired stock concentration of 20-30 mg/mL was achieved. Standards for all the compounds used for analysis in one experiment were prepared in the same serum bottle. Fresh standards were prepared for every experiment, and secondary dilutions were prepared immediately before GC analysis.

For secondary dilutions, a 20 mL vial containing 5 mL degassed buffer solution was spiked with 1-6 µL of methanol standard and quickly capped. A series of dilutions were prepared to cover the complete range of desired concentrations(0-30 mg/L). When the effluent concentrations were less than 4 ppm, a second set of standard solution was prepared in methanol using the same procedure indicated above, but over a lower concentration range. The ranges of standard stock solution concentrations and secondary dilution concentrations for

Table 3.1 Concentration ranges for the stock solutions and secondary dilutions.

Target Chemical	Volatile Products Analyzed	Stock Solutions (conc. in mg/mL)		Secondary Dilutions (conc. in mg/L)	
		low range	high range	low range	high range
PCE	PCE	0-5	0-30	0-4.8	0-36
	TCE	0-2	0-20	0-2.4	0-24
TCE	TCE		0-30		0-36
CT	CT	0-4	0-30	0-4.8	0-36
	CF	0-4	0-15	0-4.8	0-18
	MC		0-10		0-12
	CM		0-10		0-12
CF	CF	0-4	0-30	0-4.8	0-36
	MC	0-4	0-10		0-12
TCA	TCA	0-4	0-35	0-4.8	0-40
	DCA		0-30		0-36
	CA		0-10		0-12

Nomenclature:

PCE	Perchloroethylene or tetrachloroethylene
TCE	Trichloroethylene
CT	Carbon tetrachloride
CF	Chloroform
MC	Methylene chloride
CM	Chloro methane
TCA	Trichloroethane
DCA	Dichloroethane
CA	Chloroethane

various target chemicals and their products are given in table 3.1.

Samples were analyzed for volatile organics on a Perkin Elmer Auto System GC connected to a Auto Sampler (Hewlett Packard Model 19395A). The Flame Ionization Detector was used for the analysis. The samples were placed in the auto sampler and the standards were placed between them. The auto sampler was programmed for an equilibration time of 90 minutes, a bath temperature of 90°C, and a valve temperature of 95°C.

Electrolysis Experiments

A list of experiments and the typical conditions under which these experiments were conducted as given in Table 3.2. For all contaminant studies the following protocol was adopted.

Initially both compartments were filled with the degassed buffer solution. Peristaltic pump 1 was started, and the desired flow was established. Buffer was pumped through the cathode compartment for 15 minutes so that most of the air in the fibers was flushed out. The syringe pump was then started, marking the initiation of timing for each experiment.

The syringe pump was loaded with two 140-mL syringes containing 280 mL of degassed buffer solution, and was operated at a flow rate of 0.05-0.1 mL/min giving the desired influent concentrations of various target contaminants.

Samples were collected from the effluent port at regular intervals. In a typical sampling procedure, the bottom of port A was plugged by a glass stopper. The tip of a 5 ml glass syringe was lowered into the T joint and a 5 mL sample was collected as shown in Figure 3.2. This sample was transferred to a 20-mL vial and quickly capped. Samples were collected every 20-30 minutes until the influent concentration of the contaminant equaled the effluent concentration in the cathode compartment. This stage(breakthrough) was reached when all the

Table 3.2 List of experiments conducted

Expt. No.	Target Chemical	Reference Voltage*	Weight of Cathode (g)	Weight of Anode (g)	Cathode Pumping Rate (mL/min)	Anode Pumping Rate (mL/min)
1	PCE	-1.8	3.0	5.8	2.40	0.00
2	PCE	-1.9	3.0	5.8	2.42	2.68
3	PCE	-2.0	3.0	5.8	2.39	2.70
4	PCE	-2.1	3.0	5.8	2.45	2.70
5	PCE	-1.8	5.5	5.8	2.32	2.65
6	PCE	-1.8	5.5	5.8	2.35	2.67
7	PCE	-1.9	5.5	5.8	2.30	2.65
8	PCE	-2.0	5.5	5.8	2.33	2.73
9	PCE	-2.1	5.5	5.8	2.36	2.73
10	TCE	-1.8	5.5	5.8	2.32	2.70
11	TCE	-1.9	5.5	5.8	2.35	2.67
12	TCE	-1.9	5.5	5.8	2.29	2.68
13	TCE	-2.0	5.5	5.8	2.32	2.72
14	TCE	-2.1	5.5	5.8	2.34	2.69
15	CT	-1.0	5.5	5.8	2.33	2.68
16	CT	-1.0	5.5	5.8	2.36	2.65
17	CT	-1.4	5.5	5.8	2.32	2.74
18	CT	-1.5	5.5	5.8	2.30	2.74
19	CT	-1.8	5.5	5.8	2.29	2.71
20	CF	-1.0	5.5	5.8	2.33	2.75
21	CF	-1.4	5.5	5.8	2.30	2.74
22	CF	-1.5	5.5	5.8	2.30	2.75
23	CF	-1.8	5.5	5.8	2.32	2.72
24	CF	-1.8	5.5	5.8	2.34	2.73
25	TCA	-1.0	5.5	5.8	2.31	2.74
26	TCA	-1.4	5.5	5.8	2.30	2.73
27	TCA	-1.5	5.5	5.8	2.30	2.74
28	TCA	-1.5	5.5	5.8	2.32	2.74
29	TCA	-1. 8	5.5	5.8	2.34	2.75

* Versus Ag/AgCl reference electrode with $NaSO_4$ filling solution

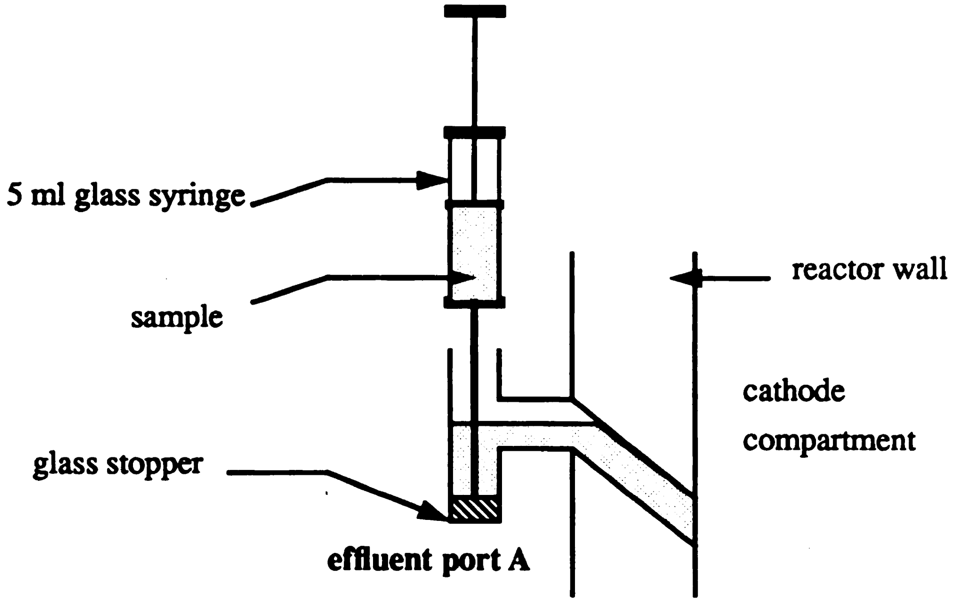


Figure 3.2. Effluent sampling.

degassed buffer solution in the cathode compartment was completely replaced by the contaminated water, and there was no more sorption of the contaminant either to the fibers or to the walls of the reactor. Generally it took 3-3.5 hours to achieve breakthrough.

Once breakthrough was achieved, peristaltic pump 2 was started, and a flow of 2.7 mL/min was maintained. Most of the air in the anode compartment was flushed out by pumping the compartment with degassed buffer solution for 15 min, and the power supply was switched on. The applied voltage was gradually increased until the reference voltage was equal to the desired set point. A constant reference voltage (between the cathode and the reference electrode) was maintained by manually adjusting the applied voltage. Samples were taken every 10-20 minutes. The electrolysis experiment was stopped when the chloride concentration remained constant for 40-60 minutes, indicating steady state conditions

Tracer Studies

Tracer studies are conducted to determine the diffusion characteristics of the reactor. After completing electrolysis of a test solution, the contaminated water in the cathode compartment was drained and filled with fresh degassed buffer solution. The cathode compartment was pumped with degassed buffer solution for 15 minutes to remove trapped air in the compartment. A standard solution of NaBr was then pumped at a flow rate of 2.3 mL/min. The effluent bromide concentrations were constantly monitored and the experiment was stopped when the effluent bromide concentration was constant for 20-30 minutes.

Efficiencies of electron transfer

The generic expression for hydrogenolysis of the target chemicals can be written as

$$C_aH_bCl_c + f\,e^- + f\,H^+ \rightarrow C_aH_{b+f-d}\,Cl_{c-d} + d\,HCl$$

The current (in Amps.) required for this hydrogenolysis reaction can be calculated by the equation

$$\dot{i}_{\text{hydrogenolysis}} = \frac{\text{moles of } C_aH_bCl_c \text{ degraded}}{\text{time (in sec)}} \times \frac{f \text{ moles of } e^-}{\text{mole of } C_aH_bCl_c \text{ degraded}} \times \frac{96.48\ 10^3 \text{coulomb}}{\text{mole of } e^-}$$

The efficiency of hydrogenolysis is calculated as

$$\eta_{\text{hydrogenolysis}} = \frac{\dot{i}_{\text{hydrogenolysis}}}{\dot{i}_{\text{total}}} \times 100$$

Let f_{max} and f_{min} represent the maximum and minimum number of electrons that can be transferred/ mole of target chemical degraded to achieve complete dechlorination. In addition to calculating the efficiency of hydrogenolysis, the maximum and minimum possible efficiencies $\eta_{total(m\ in)}$and $\eta_{total(max)}$ are also calculated by the above equations utilizing

f_{max} and f_{min} respectively instead of f. Here η_{min} and η_{max} represent the minimum and maximum efficiency of the pathway leading to complete dechlorination. To find the overall range of efficiency of the complete reaction, $\eta_{total(min)}$and $\eta_{total(max)}$ are calculated by using the following equations

$$\eta_{total(min)} = \eta_{hydrogenolysis} + \eta_{min}$$

$$\eta_{total(max)} = \eta_{hydrogenolysis} + \eta_{max}$$

Table 3.3 lists the values of f_{max} used for calculating $\eta_{(max)}$. The calculations for maximum efficiency are based upon the assumption that the maximum number of electrons used for dechlorination is equal to twice the number of chlorine atoms present in the target chemical (hydrogenolysis). In order to calculate $\eta_{(min)}$, it is assumed that at least 1.0 moles of electrons are used /mole of target chemical degraded to achieve complete degradation. This is not a correct assumption as complete dechlorination can be achieved via hydrolysis without any transference of electrons, but in such case no current will be

Table .3.3 assumed values of f_{max}

Chemical	f_{max}
PCE	8
TCE	6
CT	8
CF	6
MC	4
CM	2

required for the complete dechlorination pathway. Thus in order to chose a reasonable minimum value, f_{min} is assumed to be 1.

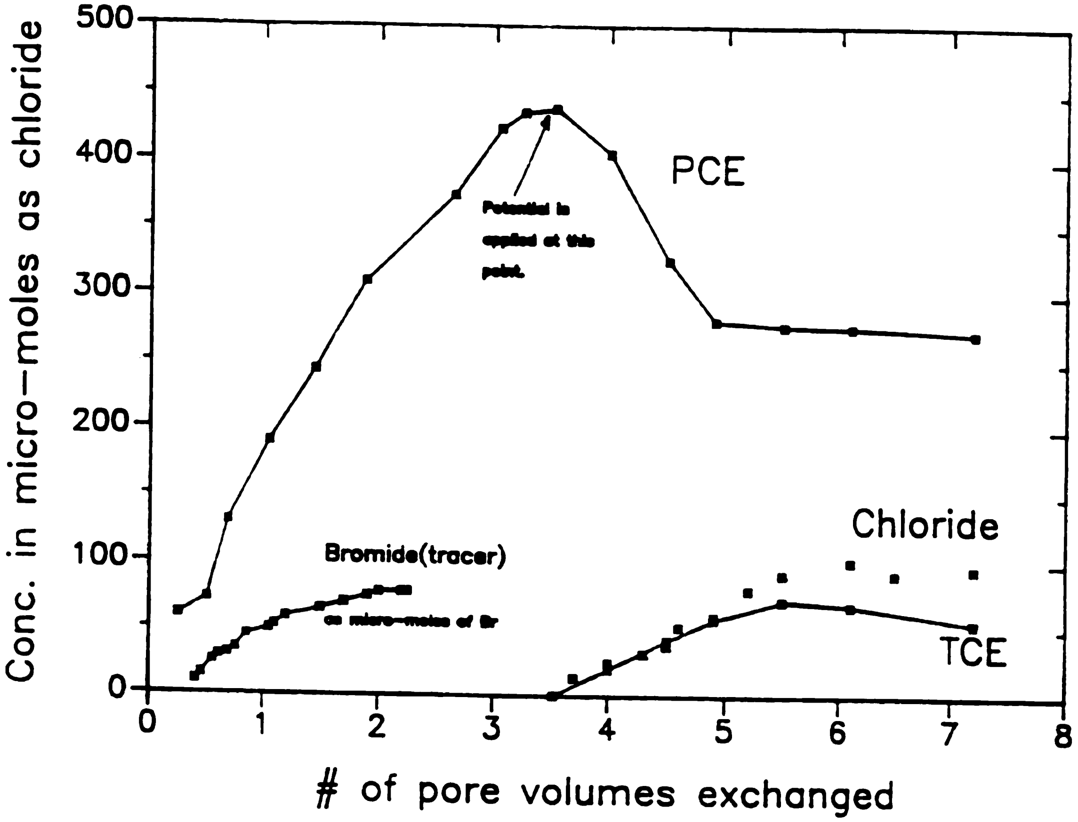
The results of each experiment were reported as the compounds degraded or produced (represented in micro moles as chloride) plotted against the number of pore volumes exchanged. The number of pore volumes exchanged were obtained by dividing the time elapsed since the beginning of the experiment for each sample by the effective reactor retention time as observed by the tracer studies.

Chapter 4.
Results & Discussion

The results of electrolytic degradation of the target chemicals (PCE, TCE, CT, CF and TCA) are represented in this chapter. Each degradation curve is accompanied by mass balance curves for the chlorine and carbon. All chloride measurements were corrected for background chloride present in the influent. Chlorine mass balances were obtained from the concentrations of volatile reactants, volatile products and aqueous free chloride in the effluent. Carbon balance curves were constructed using the concentrations of volatile reactants and products. Due to hydrogen evolution in the reactor, stripping of volatile organics was also observed. A good carbon balance could not be obtained because the effluent was not analyzed for the dissolved organic carbon in the aqueous phase. This resulted in an unidentified sink term in the carbon balance curves. Degradation rates of various target chemicals and the production rates of the volatile products and free chlorides are also calculated. As described in Chapter 3, efficiency calculations and cost analyses were tabulated for each experiment conducted. Patterns of degradation are compared with those of Rajayya (1992) as summarized in Table 4.13. Calculations were preformed to estimate the amount of PCE sorbed to the fibres. The amounts of other sorbed chemicals can be calculated using the same approach as the one used for PCE.

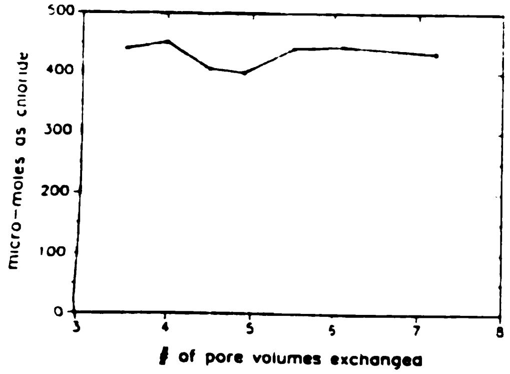
Tetrachloroethylene

The results of PCE degradation, including the mass balance curves for all nine experiments conducted, are shown in figures 4.1-4.12 and figures 4.14-4.28. In all these experiments, two parallel pathways were observed for the PCE degradation: hydrogenolysis of PCE to TCE, and degradation of PCE to completely dechlorinated products. The degradation rates of PCE, and the production rates of TCE and free chloride are shown in Tables 4.1 and 4.2. Figures 4.13 and 4.29 show the percentages of PCE degradation contributing

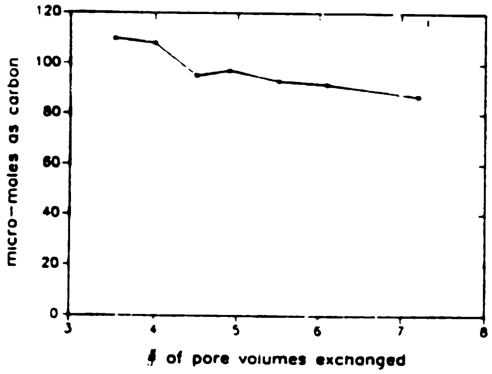


PCE DEGRADATION AT REF. VOLTAGE OF −1.8V

FIGURE 4.1



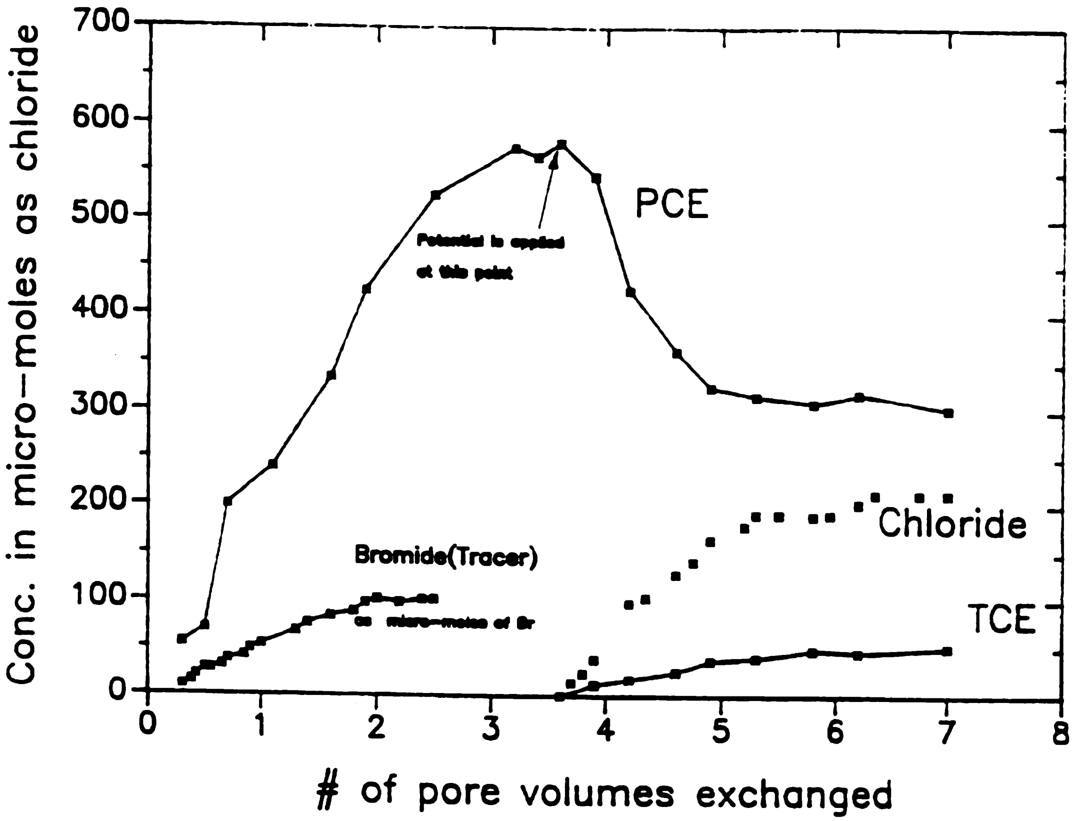
CHLORINE BALANCE FOR PCE DEGRADATION AT −1.8V



CARBON BALANCE FOR PCE DEGRADATION AT −1.8V

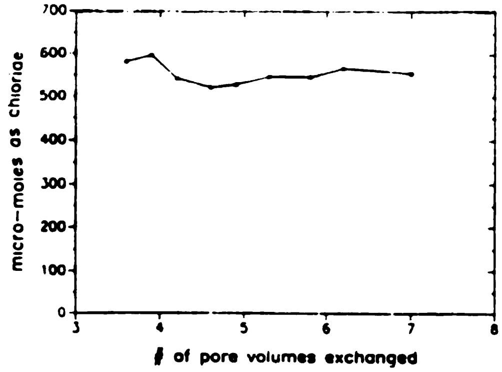
FIGURE 4.2

FIGURE 4.3



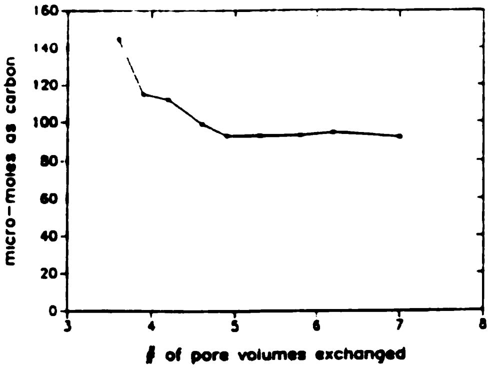
PCE DEGRADATION AT REF. VOLTAGE OF −1.9V

FIGURE 4.4



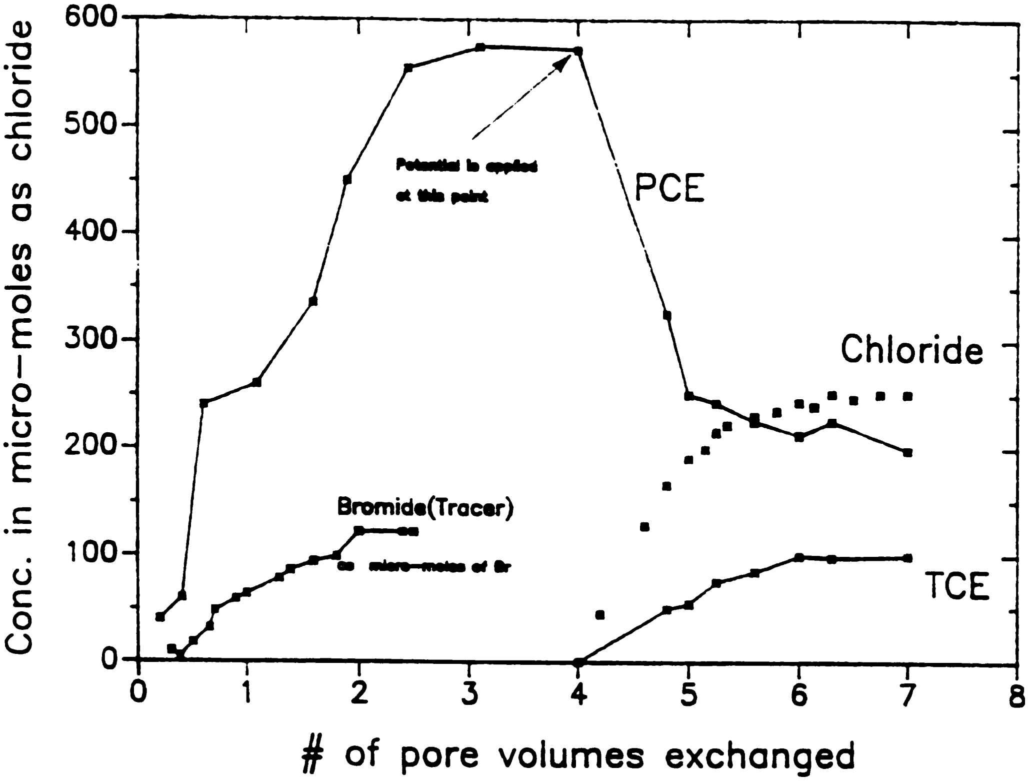
CHLORINE BALANCE FOR PCE DEGRADATION AT −1.9V

FIGURE 4.5



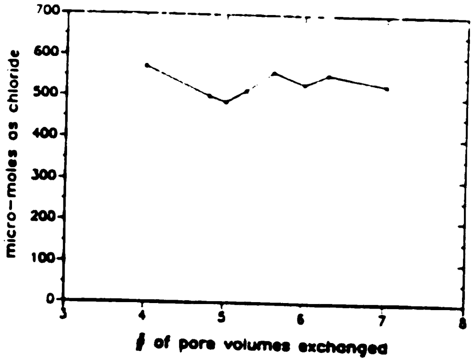
CARBON BALANCE FOR PCE DEGRADATION AT −1.9V

FIGURE 4.6



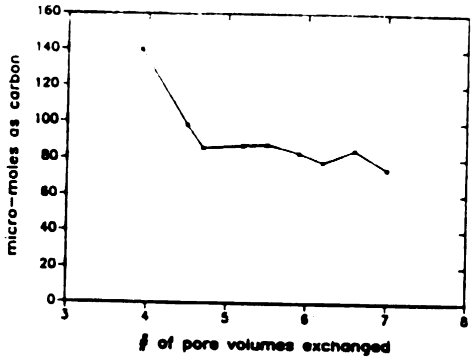
PCE DEGRADATION AT REF. VOLTAGE OF −2.0V

FIGURE 4.7



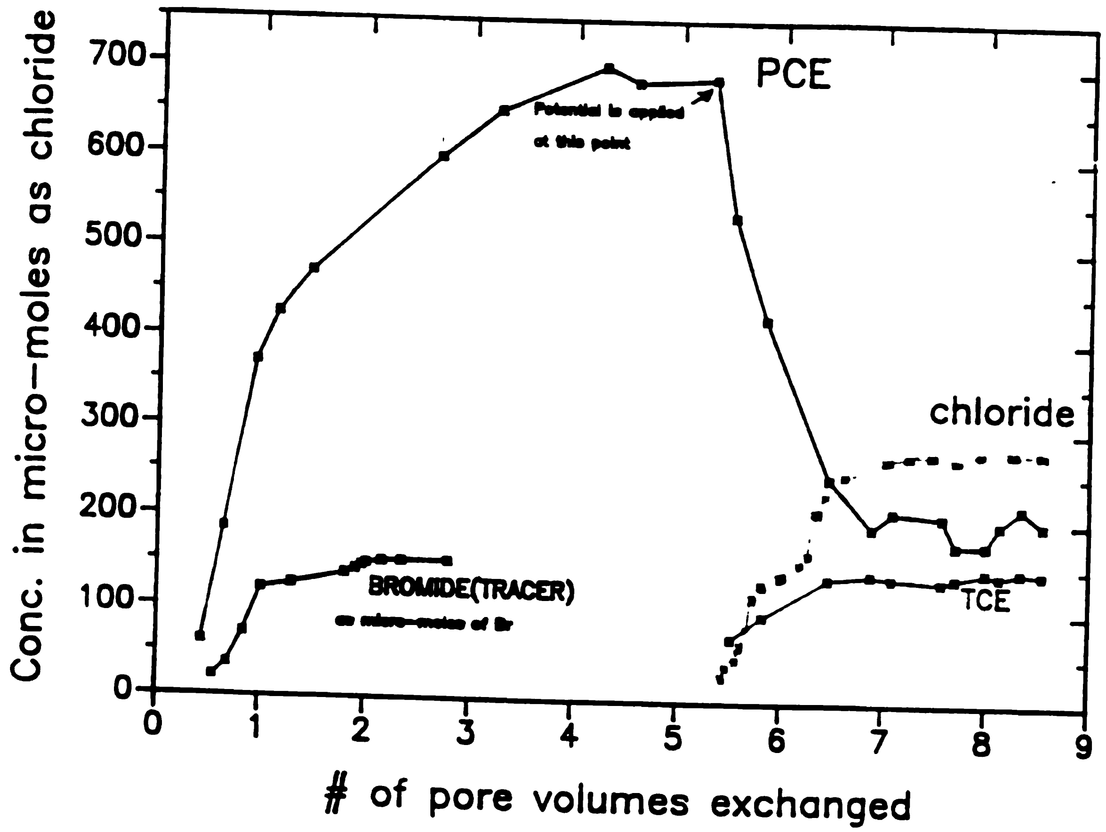
CHLORINE BALANCE FOR PCE DEGRADATION AT −2.0V

FIGURE 4.8



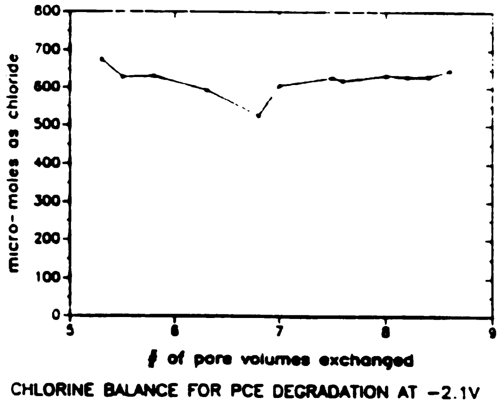
CARBON BALANCE FOR PCE DEGRADATION AT −2.0V

FIGURE 4.9



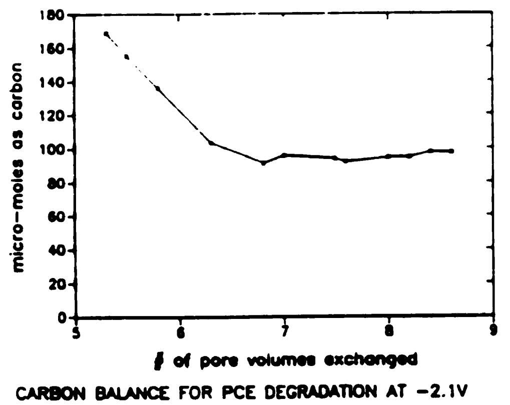
PCE DEGRADATION AT REF. VOLTAGE OF −2.1V

FIGURE 4.10



CHLORINE BALANCE FOR PCE DEGRADATION AT −2.1V

FIGURE 4.11



CARBON BALANCE FOR PCE DEGRADATION AT −2.1V

FIGURE 4.12

Table 4.1 PCE degradation using 3.2 g cathode fibres and 5.8 g anode fibres.

Expt. No.	Ref. Voltage	PCE Degradation Rate(µ moles/min as chloride)	TCE Production Rate(µ moles/min as chloride)	Chloride production Rate (µ moles/min as chloride)
1	-1.8	1.65	0.73	0.91
2	-1.9	2.51	0.48	2.03
3	-2.0	3.54	1.01	2.51
4	-2.1	4.72	1.51	2.83

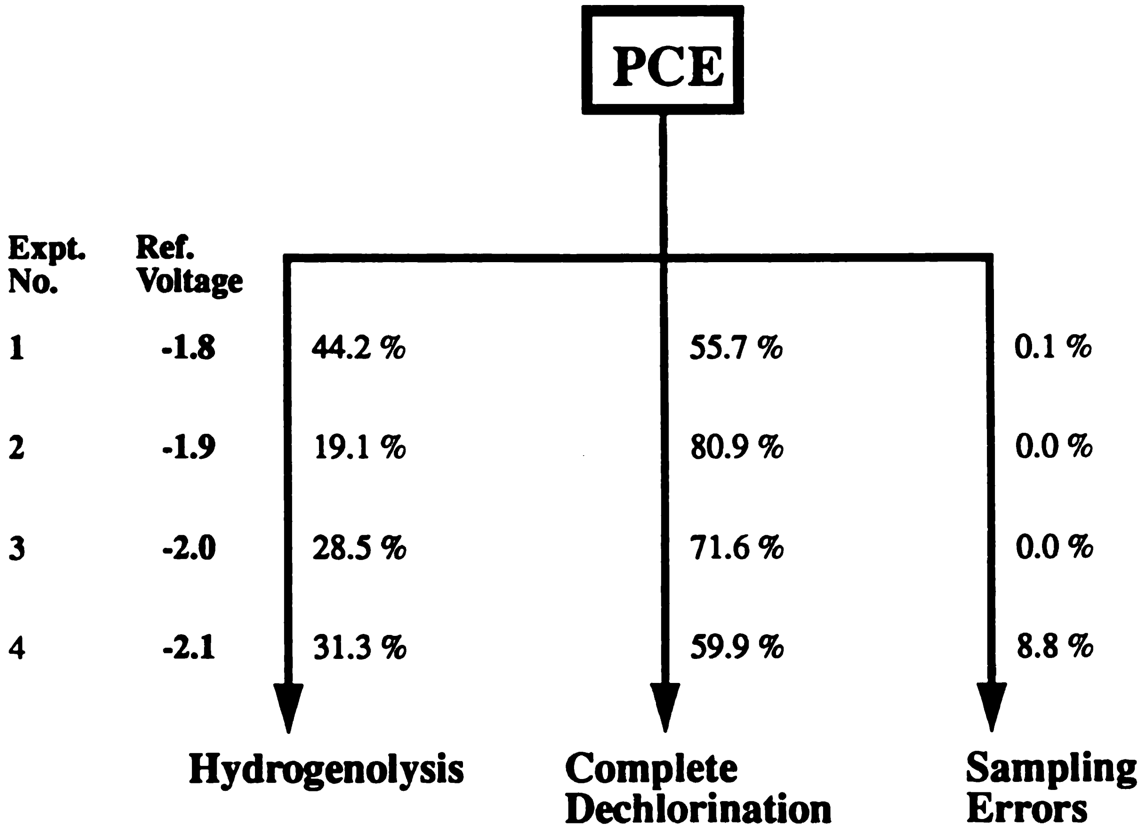
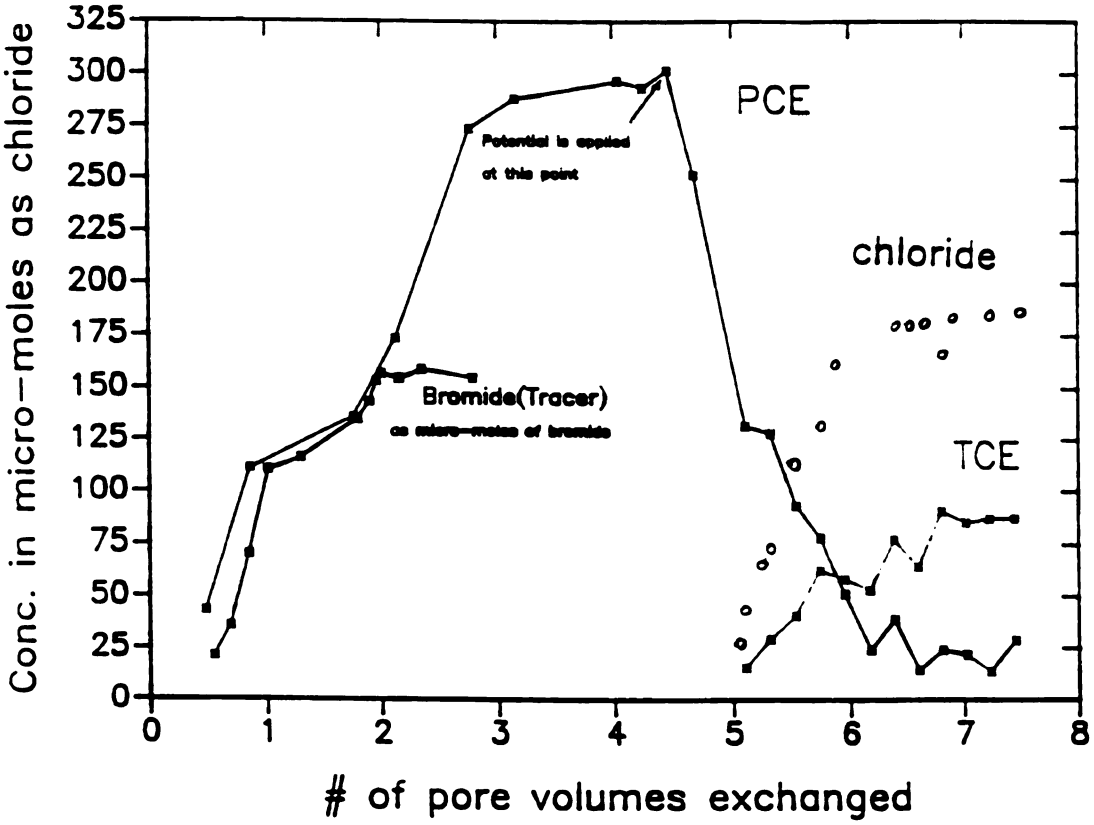
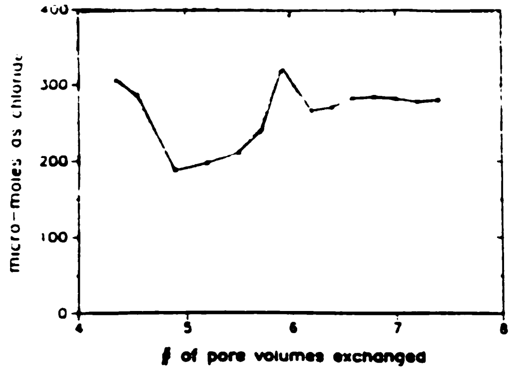


Figure 4. 13 Parallel Pathways for the PCE degradation using 3.2 g cathode and 5.8 g anode fibres.



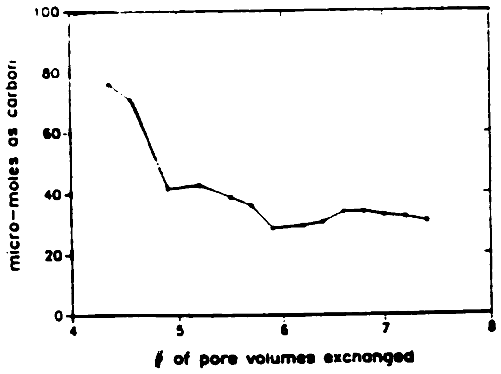
PCE DEGRADATION AT THE REF. VOLTAGE OF −1.8V

FIGURE 4.14



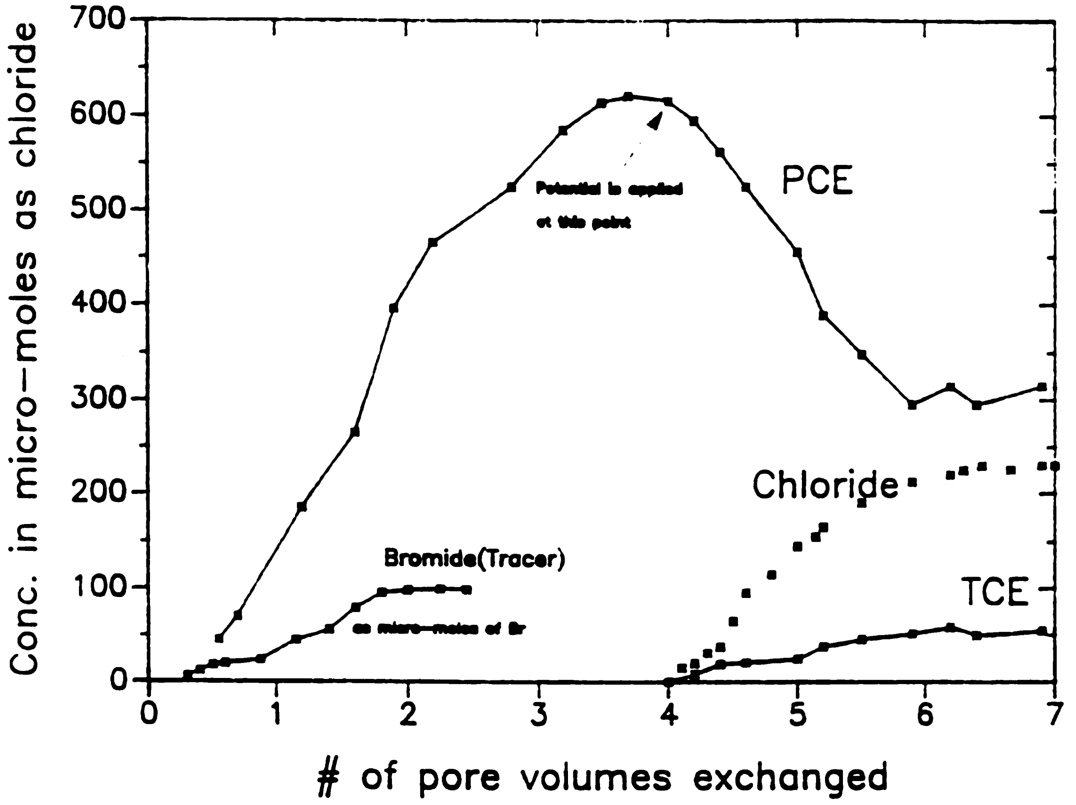
CHLORINE BALANCE FOR PCE DEGRADATION AT −1.8V

FIGURE 4.15



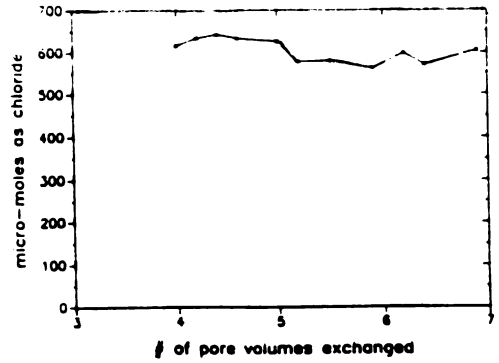
CARBON BALANCE FOR PCE DEGRADATION AT −1.8V

FIGURE 4.16



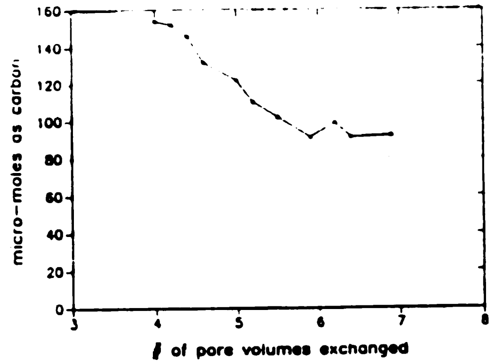
PCE DEGRADATION AT REF. VOLTAGE OF −1.8V

FIGURE 4.17



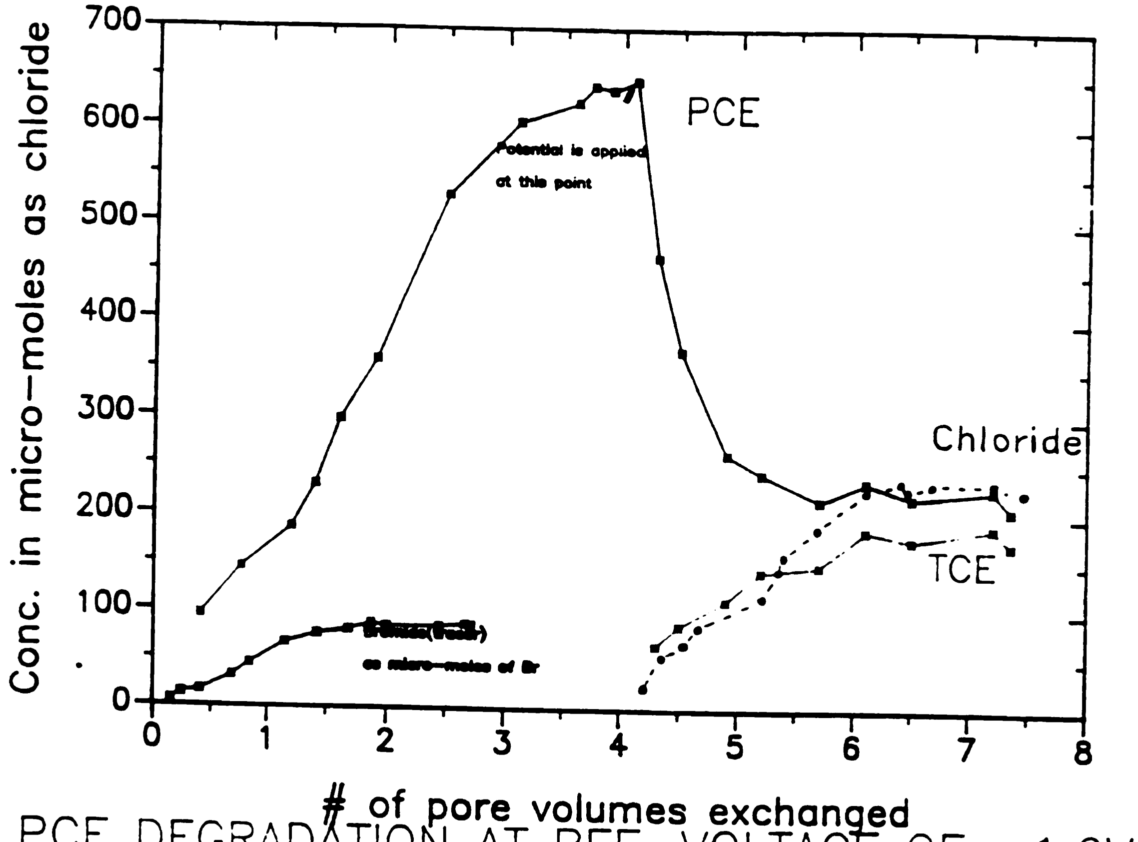
CHLORINE BALANCE FOR PCE DEGRADATION AT −1.8V

FIGURE 4.18



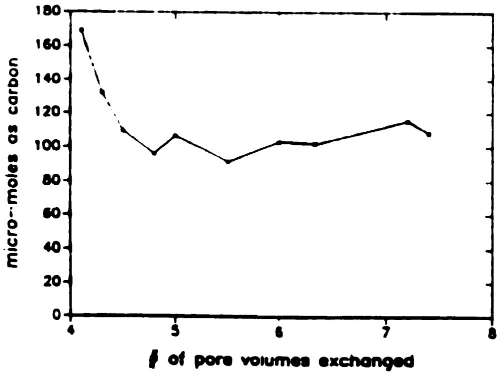
CARBON BALANCE FOR PCE DEGRADATION AT −1.8V

FIGURE 4.19



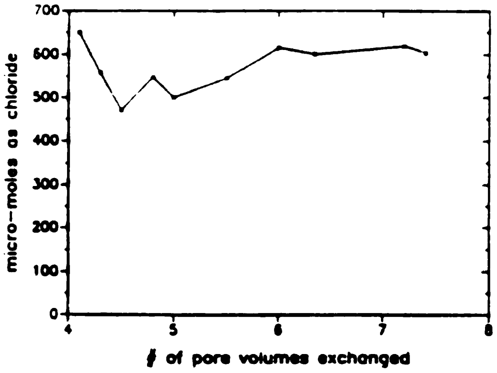
PCE DEGRADATION AT REF. VOLTAGE OF −1.9V

FIGURE 4.20



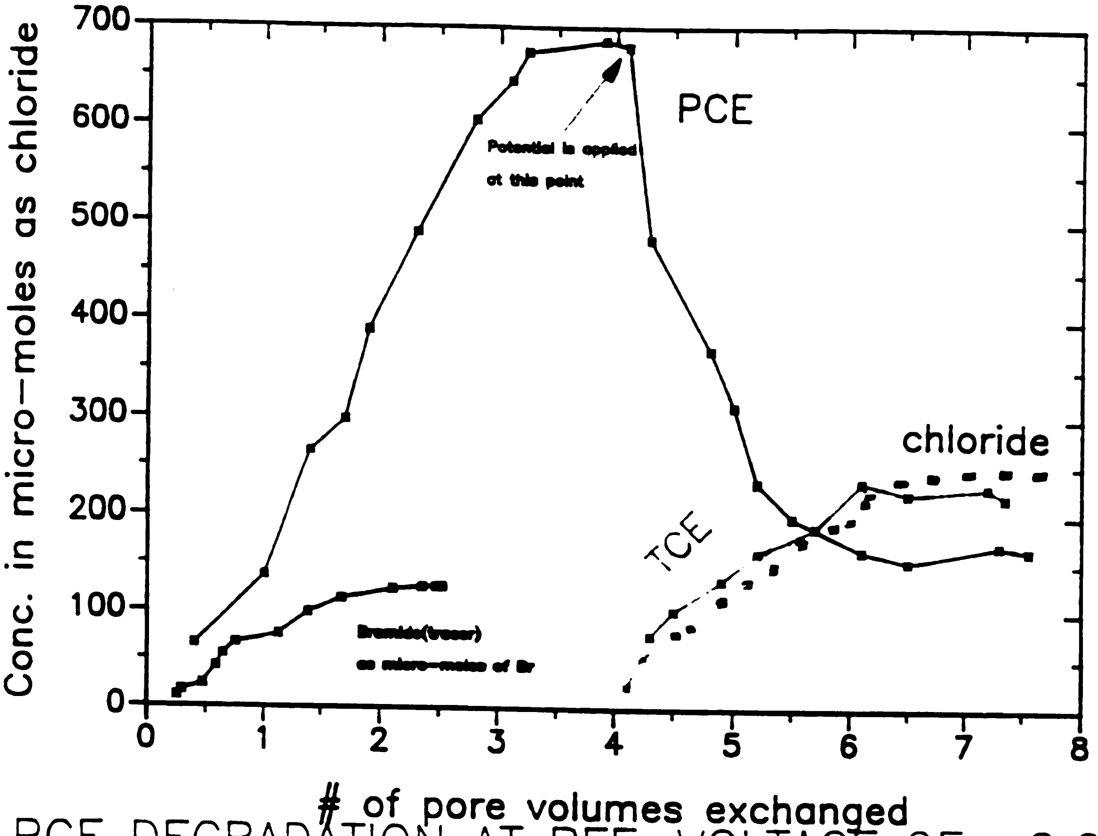
CARBON BALANCE FOR PCE DEGRADATION AT −1.9V

FIGURE 4.21



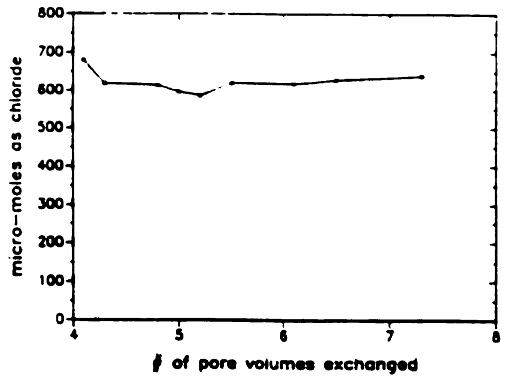
CHLORINE BALANCE FOR PCE DEGRADATION AT −1.9V

FIGURE 4.22

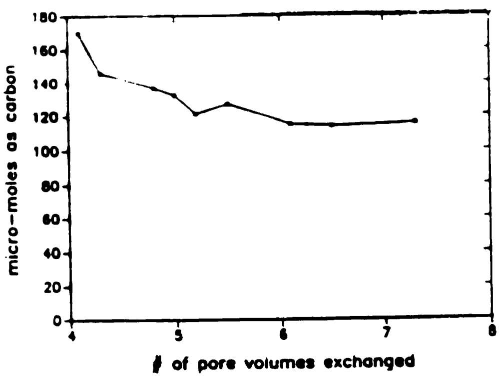


PCE DEGRADATION AT REF. VOLTAGE OF −2.0V

FIGURE 4.23



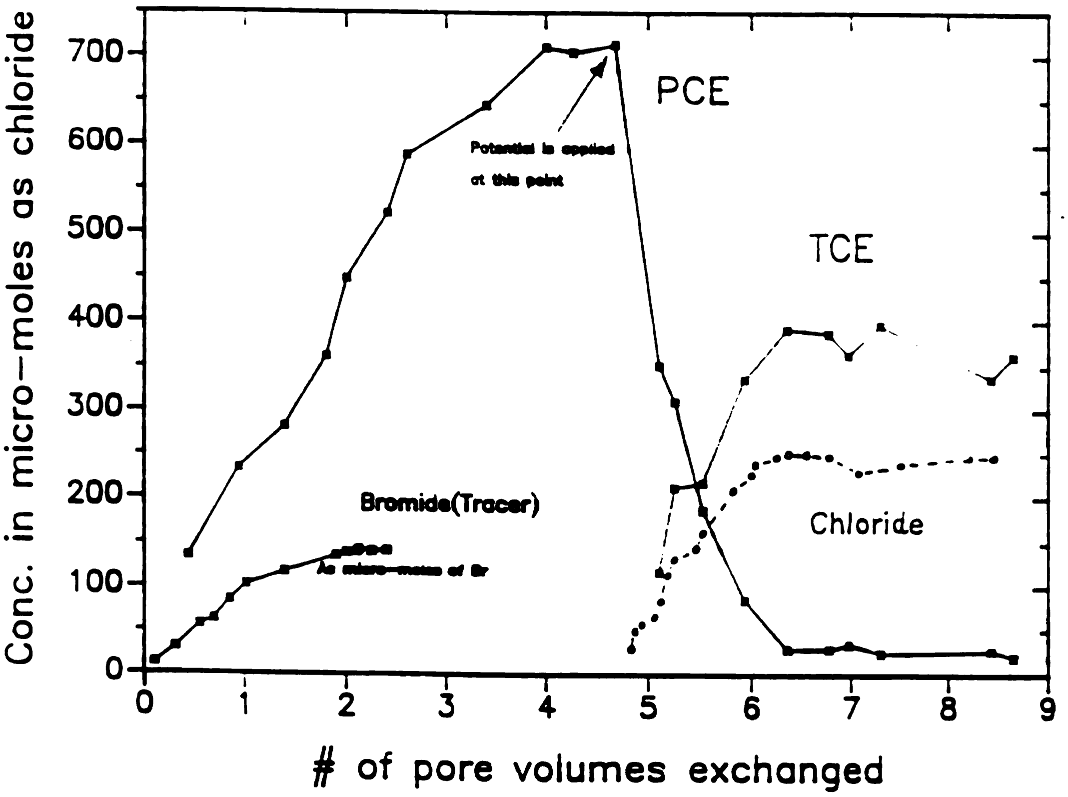
CHLORINE BALANCE FOR PCE DEGRADATION AT −2.0V



CARBON BALANCE FOR PCE DEGRADATION AT −2.0V

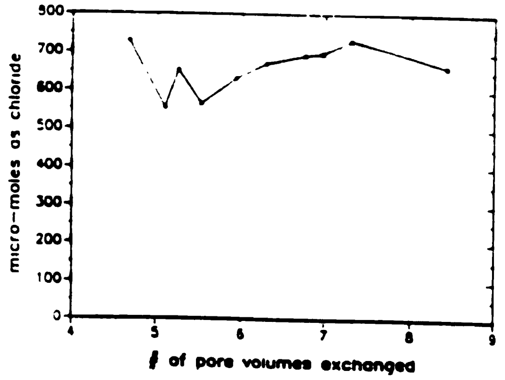
FIGURE 4.24

FIGURE 4.25



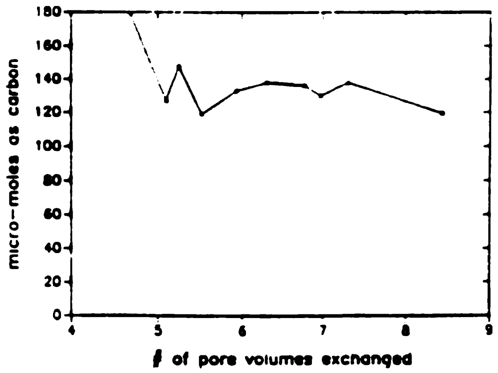
PCE DEGRADATION AT REF.VOLTAGE OF -2.1V

FIGURE 4.26



CHLORINE BALANCE FOR PCE DEGRADATION AT -2.1V

FIGURE 4.27



CARBON BALANCE FOR PCE DEGRADATION AT -2.1V

FIGURE 4.28

Table 4.2 PCE degradation using 5.5 g cathode fibres and 5.8 g anode fibres.

Expt. No.	Ref. Voltage	PCE Degradation Rate (μ moles/min as chloride)	TCE Production Rate (μ moles/mi as chloride)	Chloride production Rate(μ moles/min as chloride)
5	-1.8	2.85	0.82	1.80
6	-1.8	3.03	0.56	2.32
7	-1.9	4.68	1.97	2.44
8	-2.0	5.47	2.59	2.65
9	-2.1	7.44	4.28	2.65

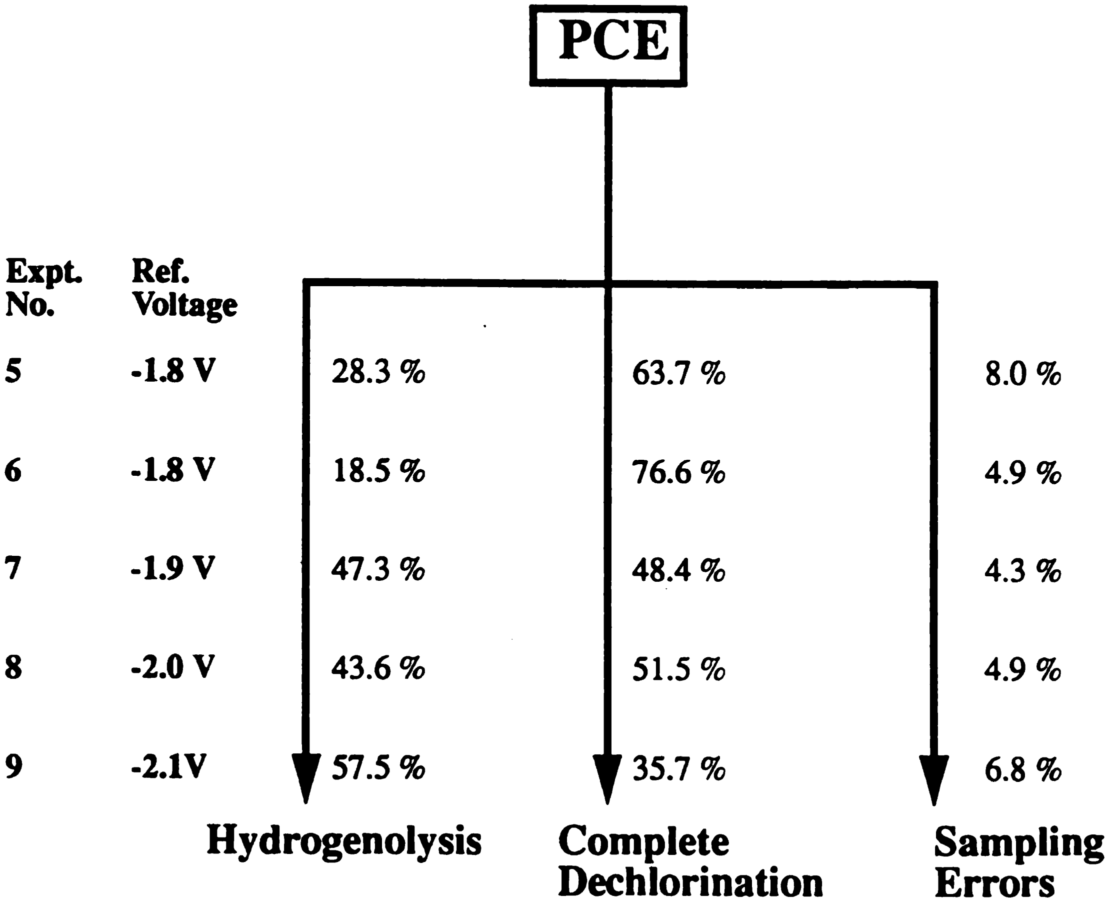


Figure 4. 29 Parallel Pathways for the PCE degradation using5.5 g cathode and 5.8 g anode fibres.

to various pathways at different reference voltages. Table 4.3 tabulates the complete range of efficiencies of electron transfer for all nine experiments. This table also gives the energy consumed in degrading one mole of PCE and provides a preliminary cost analysis. Based upon the above results, following observations are made:

1. An increase in reference voltage resulted in an increase in the degradation rate of PCE. Also, an increase in the cathode surface area from 3.2 g to 5.5 g not only resulted in an increase in PCE degradation rate, but also reduced the energy consumption considerably.

2. At lower voltages, the pathway leading to complete dechlorination was dominant. At higher reference voltages, the hydrogenolysis of PCE began to dominate and resulted in higher production of TCE. These results are consistent with those obtained by Rajayya (Table 4.13). An increase in hydrogenolysis rates at higher voltages was consistently observed in all experiments except for Expt. 1. This may be because Expt. 1 was not conducted under the same anode pumping conditions as Expts. 2-9.

3. Experiments 5-9 (with 5.5 g cathode fibres) provided evidence that energy requirements/ mole of PCE degraded are significantly less at reference voltage of -1.8 V using 5.5 g cathode fibres. Thus in order to reduce operating costs, a reference voltage of -1.8 V is recommended for the experimental conditions indicated. An additional advantage of operation at this voltages is the fact that the pathway resulting in complete dechlorination was predominant. On the other hand, these advantages should be weighed against the higher capital cost of a large reactor because PCE degradation rates increase nearly three fold at a reference voltage of -2.1 V thus reducing the size of the reactor required. At least two possibilities exist for the additional treatment of the effluent from this reactor: (1)biological treatment or (2) additional electrolytic treatment. Electrolysis of TCE to produce completely dechlorinated products is discussed in the following section. Economics will be the major factor

Table 4.3 Efficiency and energy requirement calculations for PCE degradation.

Expt. No.	Ref. Voltage	Applied Voltage (V)	Applied Current (amp)	η_{hydro} %	η_{min} %	η_{max} %	$\eta_{total(min)}$ %	$\eta_{total(max)}$ %	Energy consumed/ mole of PCE degraded (KWh)	Cost* $/1000 gallons
1	-1.8	4.81	0.32	0.24	0.47	3.76	0.71	4.00	62.19	5.66
1	-1.9	5.42	0.45	0.13	0.70	5.57	0.83	5.70	64.78	5.90
3	-2.0	7.10	0.55	0.21	0.65	5.39	0.86	5.60	73.54	6.70
4	-2.1	9.20	0.68	0.25	0.57	4.53	0.92	4.78	88.36	8.04
5	-1.8	2.42	0.36	0.28	0.72	5.74	1.00	6.02	20.37	1.85
6	-1.8	2.61	0.34	0.22	0.90	7.24	1.12	7.46	19.52	1.78
7	-1.9	3.15	0.50	0.41	0.55	4.40	0.96	4.81	22.43	2.04
8	-2.0	3.41	0.58	0.44	0.48	3.85	0.92	4.29	24.10	2.19
9	-2.1	3.85	0.65	0.47	0.42	3.36	0.89	3.83	22.42	2.04

* Cost is calculated with the current rate of $0.04/KWh charged (for the commercial use of electricity) by Board of Water & Electricity, Lansing, MI to treat the PCE contaminated solution with an influent concentration of 100 ppm.Cost does not include capital expenditure. Energy calculations are made assuming zero order degradation for PCE.

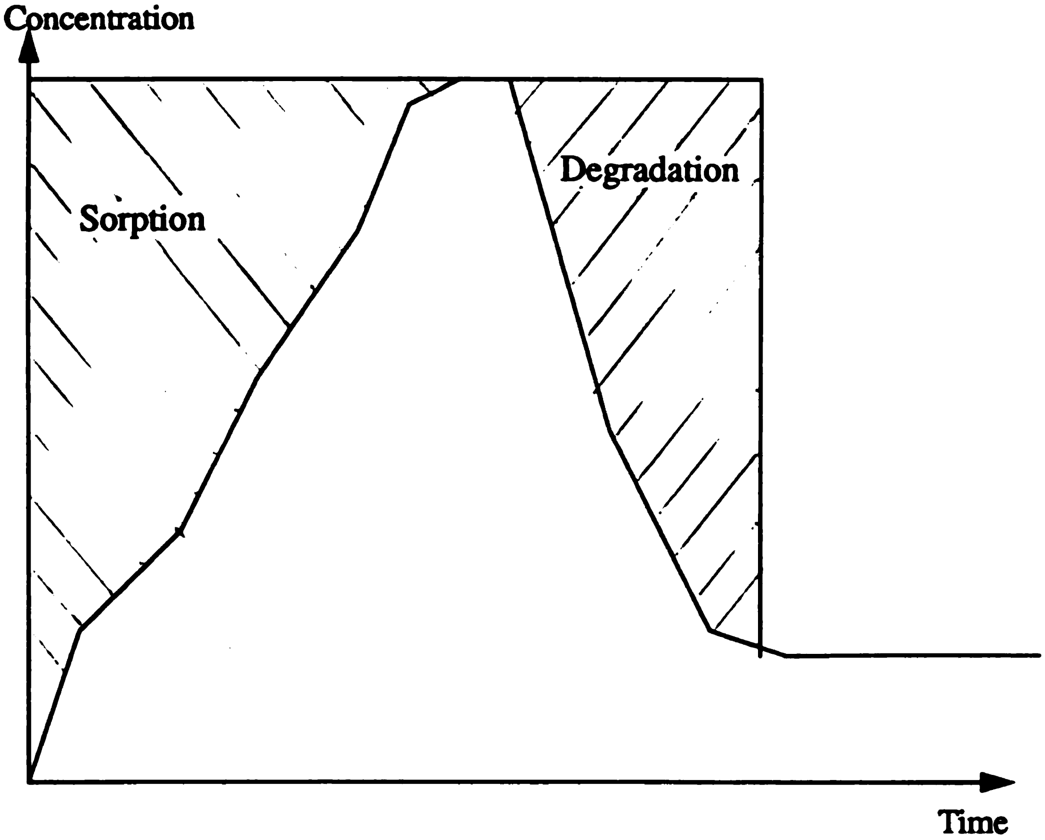


Figure 4.29a Sorption and degradation area. in a generalized curve.

Table 4.4 Sorption study for PCE using 5.5 g fibers in the cathode chamber.

Expt. No.	Ref. Voltage	Calculated sorption (mg)	Calculated degradation (mg)
6	-1.8V	23.3	8.42
7	-1.9V	25.7	7.16
8	-2.0V	26.7	11.7
9	-2.1V	24.1	14.0

in selecting one option over another.

4. Amount of PCE sorbed to the fibres can be calculated by the left hand side hached area representing the sorption as shown in Figure 4.29a. Similarly the the amount of PCE degraded can be estimated utilizing the right hand side hached area. There is a possibility that PCE might be desorbed after applying the potential. In that case, the amount of degradation shown in Table 4.4 truely represents the total degraded plus desorbed PCE. The phenomenon of sorption and desorption (after applying the voltage) is further complicated by the fact that TCE produced might also be undergoing sorption-desorption.

5. From Table 4.1 , it is indicated that the TCE production rates were higher at a reference voltage of -1.8 V than at the reference voltage of -1.9V. This seems to be in contradiction to the observation made by the remaining eight experiments that hydrogenolysis path is predominant at higher voltages. This is perhaphs due to the reason that Experiment 1(at Ref. Voltage of -1.8V) was conducted without any pumping of the anode chamber and thus the experimental conditions for Experiment 1. were not the same as those for the other experiments.

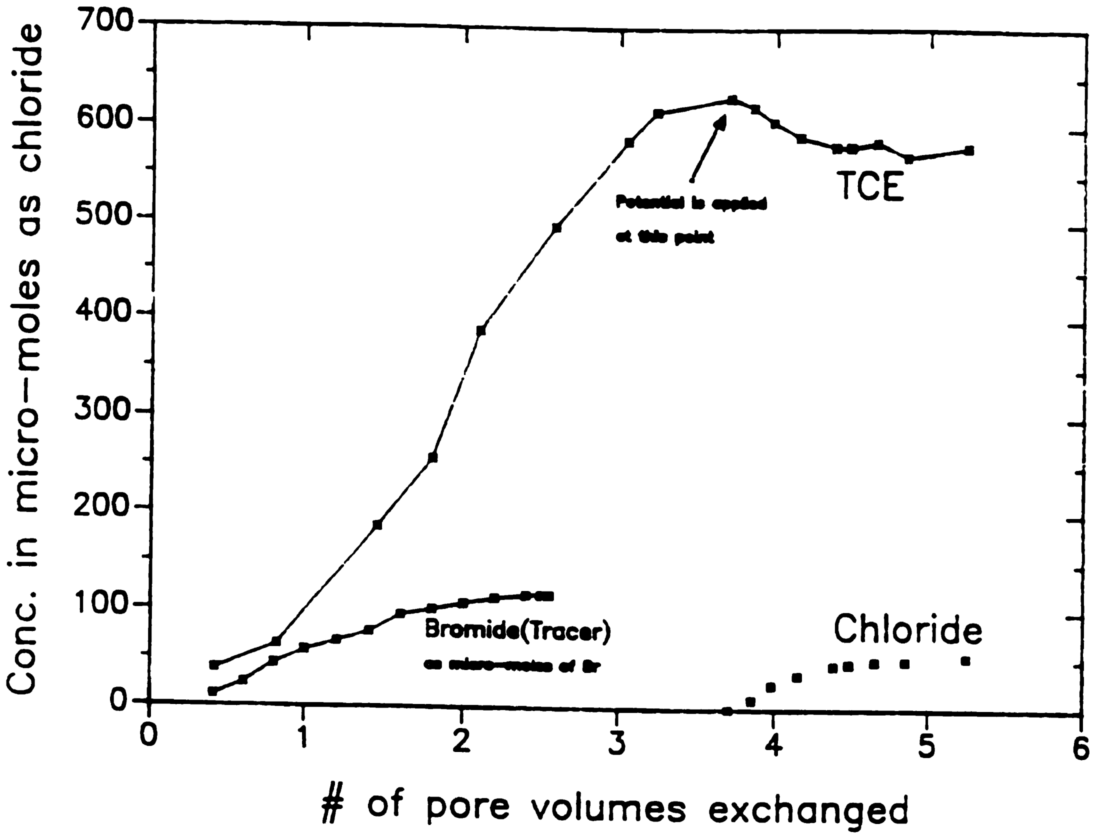
Trichloroethylene

Of all the chemicals studied, TCE was the most resistant to reduction. As indicated in figures 4.30 -4.44, degradation of TCE resulted in the production of completely dechlorinated products. As shown in Table 4.5 and Figure 4.45, the effluent chloride accounted for 90-95% of the initial chloride present in TCE. Hydrogenolysis was not observed, even at higher reference voltages. This contrasts with the results of Rajayya (Table 4.13) in which production of t-DCE, ethylene and trace amounts of VC were observed. A possible explanation for this discrepancy is that the batch type experiments of Rajayya were conducted in more reducing environment (Ref. voltage of -1.2 and -1.4 V instead of Ref. Voltage of -0.8V to -1.0V used for other chemicals) thus making the hydrogenolysis pathway was more significant. Another possible explanation is that TCE might have been transformed to ethylene and was not detected in the effluent samples as FID was used to analyze the volatile organics.

As shown in Table 4.6, the efficiencies of electron transfer were also low as compared with those of PCE (Table 4.3). The energy requirements/ mole of TCE degraded were lowest at reference voltage of -2.1 V. This is due to the increased TCE degradation rate with increased reference potential. Very little degradation was observed at a reference voltage of -1.8 V. The operating costs for TCE treatment were nearly twice as much as that of PCE at corresponding voltages. In spite of the high operating costs, there is a distinct advantages of electrolytic reduction of TCE over other target chemicals degraded:

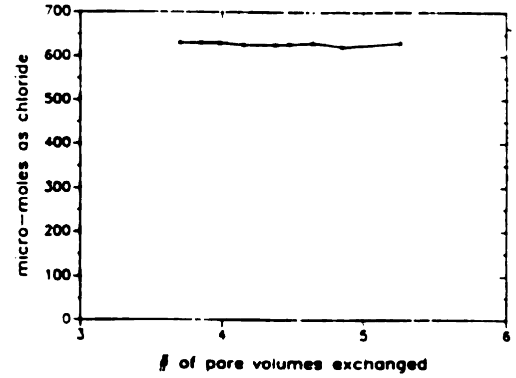
-TCE degradation resulted in the formation of completely dechlorinated products. No further treatment would be necessary if the dechlorinated products are shown to be non toxic.

- Operation of reactor at higher reference voltage of -2.1 resulted in higher TCE degradation rates and lower operating costs when compared with the reactor operation at lower reference voltages.



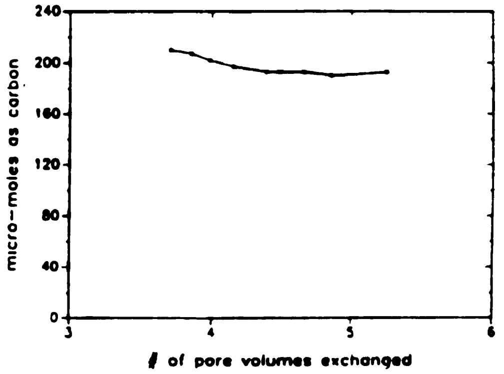
TCE DEGRADATION AT REF. VOLTAGE OF −1.8V

FIGURE 4.30



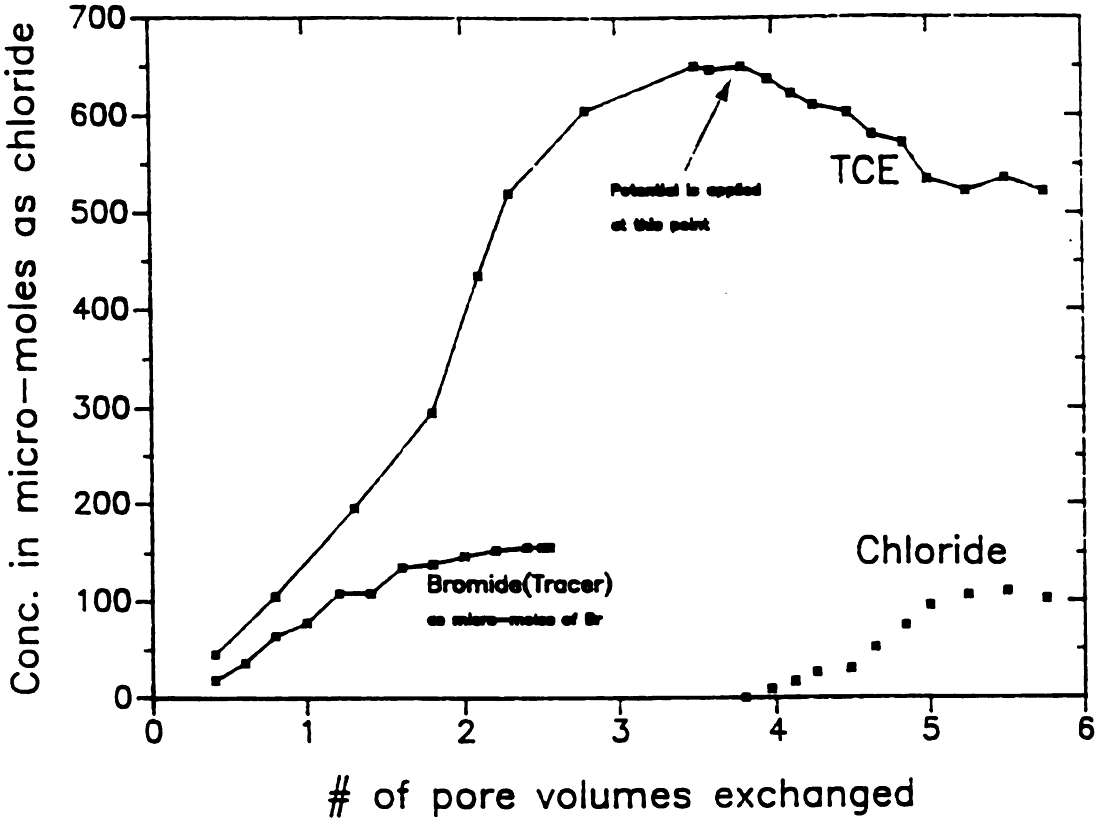
CHLORINE BALANCE FOR TCE DEGRADATION AT −1.8V

FIGURE 4.31



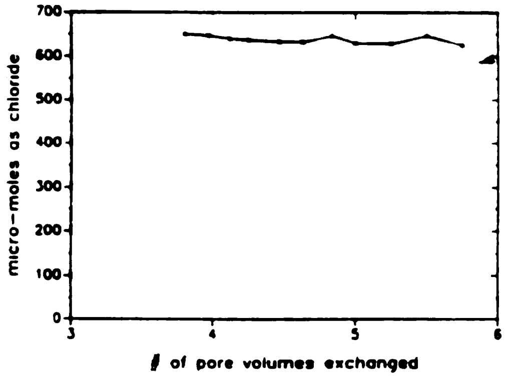
CARBON BALANCE FOR TCE DEGRADATION AT −1.8V

FIGURE 4.32



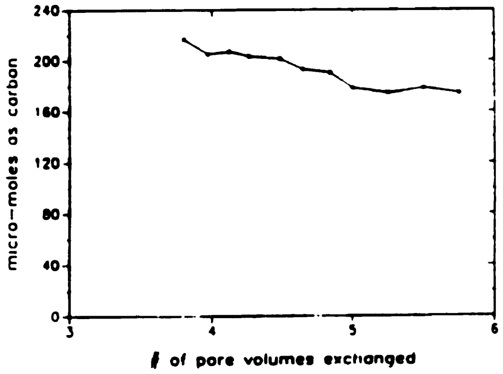
TCE DEGRADATION AT REF. VOLTAGE OF −1.9V

FIGURE 4.33



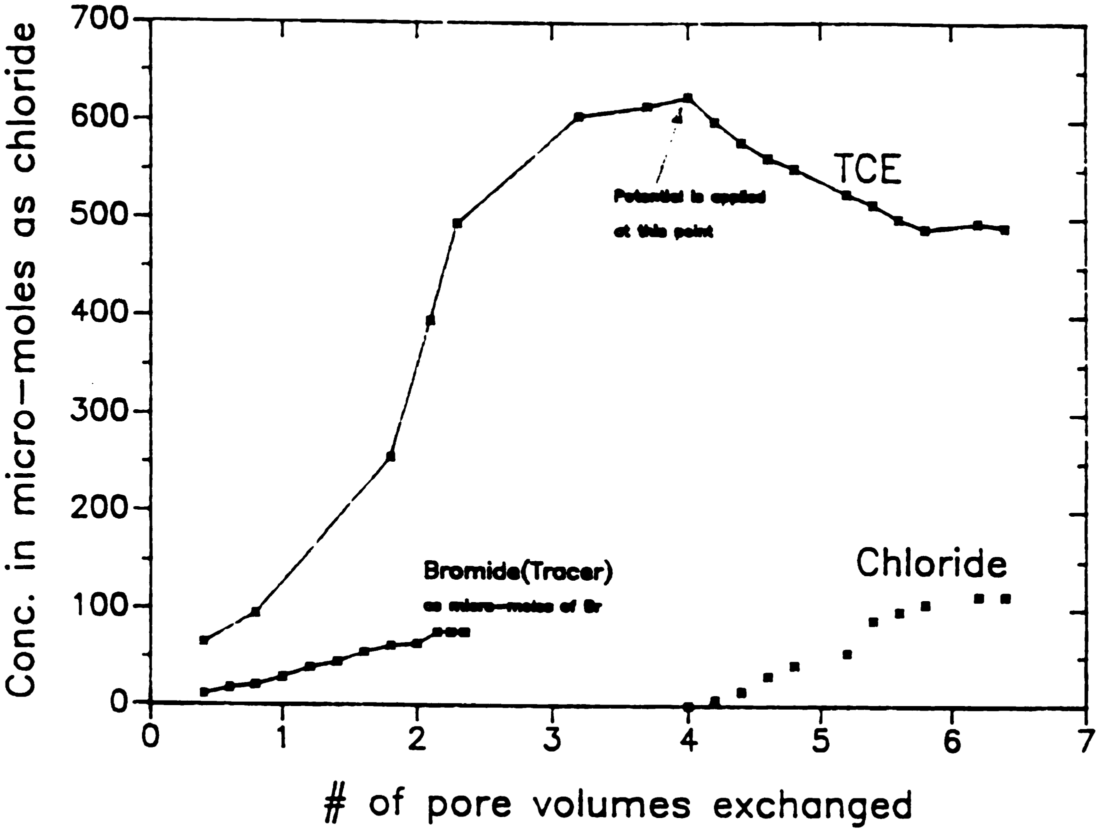
CHLORINE BALANCE FOR TCE DEGRADATION AT −1.9V

FIGURE 4.34



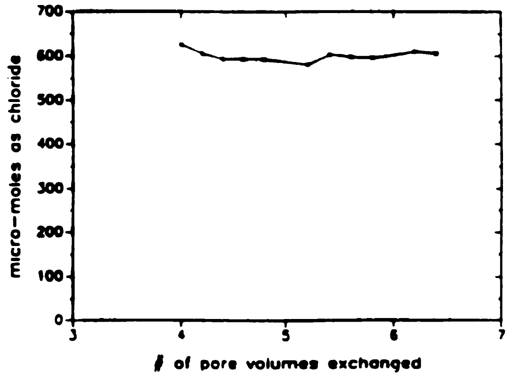
CARBON BALANCE FOR TCE DEGRADATION AT −1.9V

FIGURE 4.35



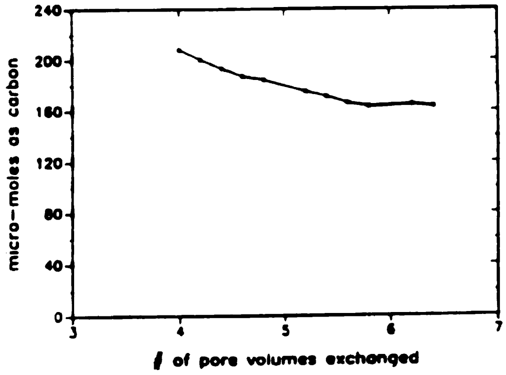
TCE DEGRADATION AT REF. VOLTAGE OF −1.9V

FIGURE 4.36



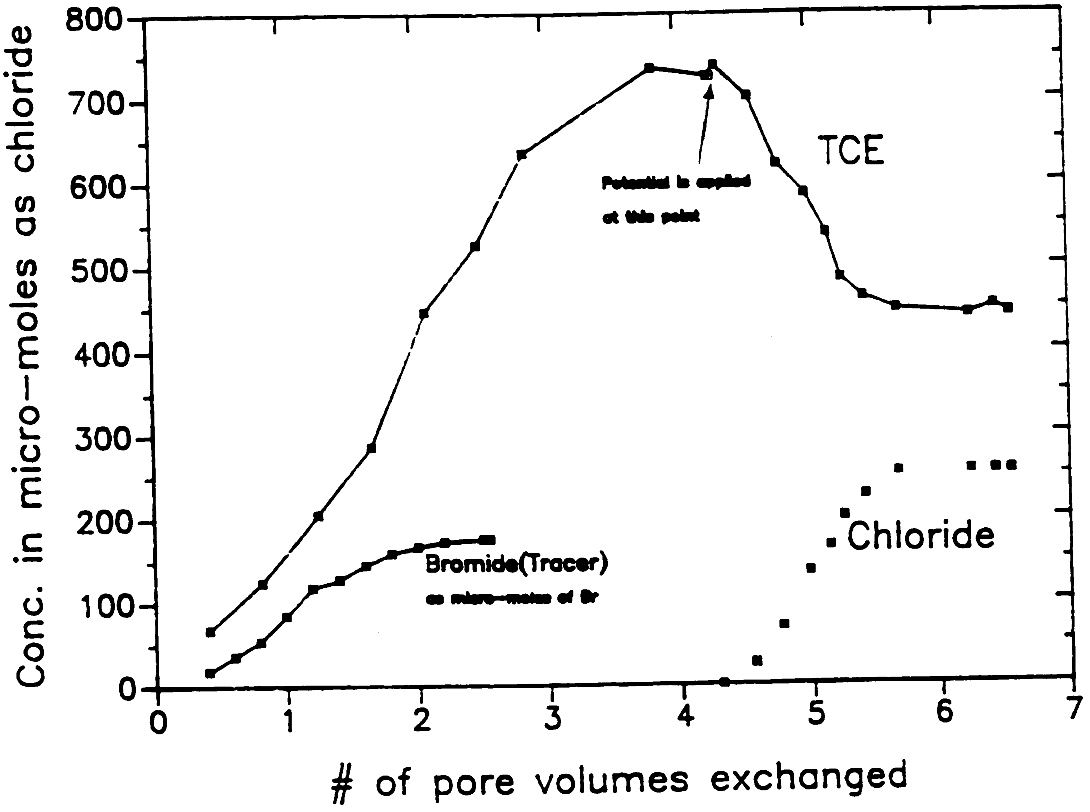
CHLORINE BALANCE FOR TCE DEGRADATION AT −1 9V

FIGURE 4.37



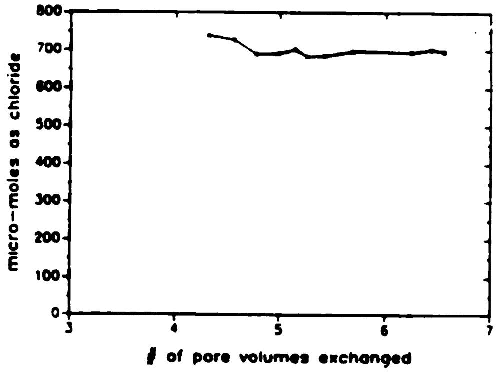
CARBON BALANCE FOR TCE DEGRADATION AT −1.9V

FIGURE 4.38



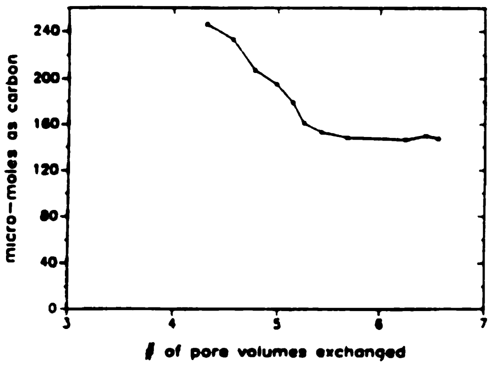
TCE DEGRADATION AT REF. VOLTAGE OF −2.0V

FIGURE 4.39



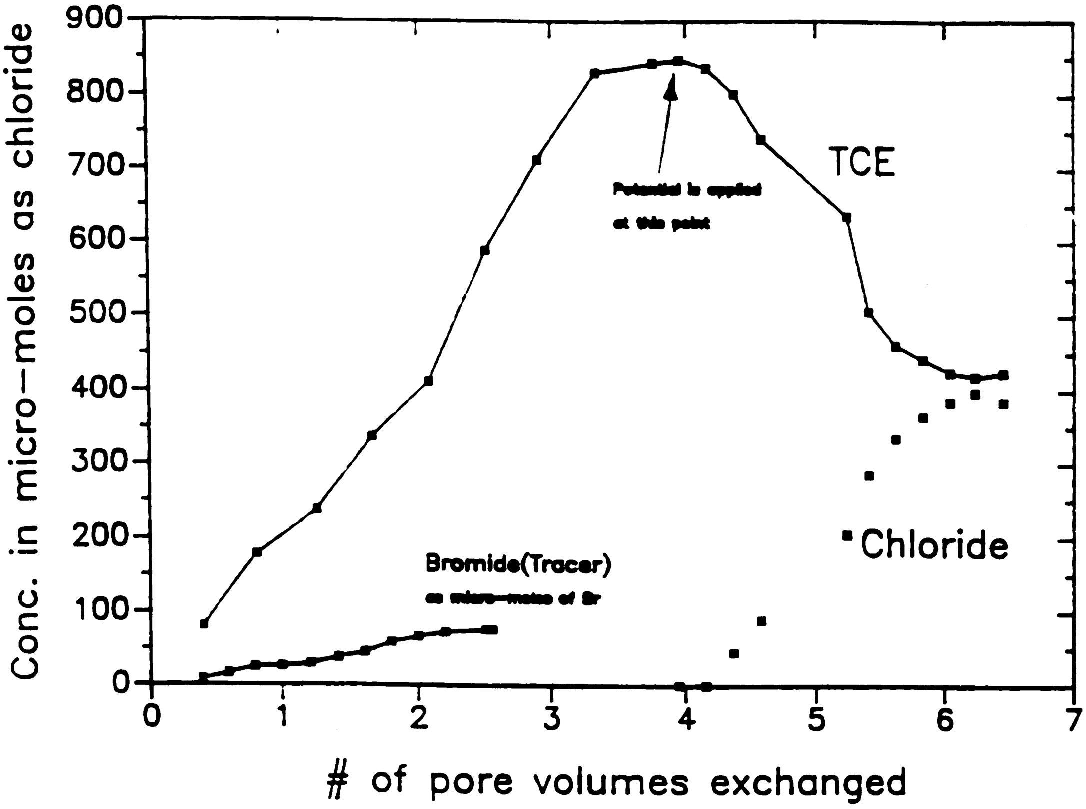
CHLORINE BALANCE FOR TCE DEGRADATION AT −2.0V

FIGURE 4.40



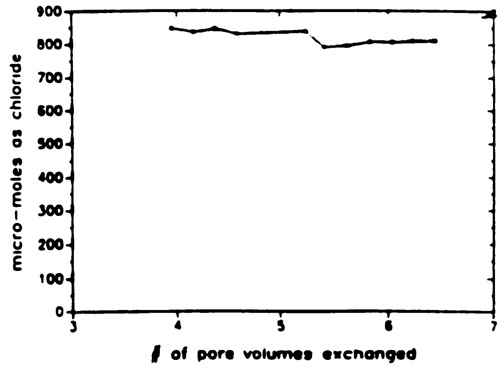
CARBON BALANCE FOR TCE DEGRADATION AT −2.0V

FIGURE 4.41



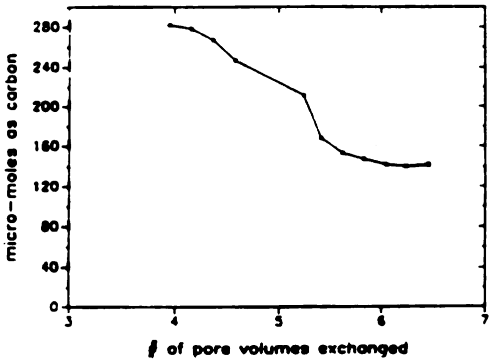
TCE DEGRADATION AT REF. VOLTAGE OF −2.1V

FIGURE 4.42



CHLORINE BALANCE FOR TCE DEGRADATION AT −2.1V

FIGURE 4.43



CARBON BALANCE FOR TCE DEGRADATION AT −2.1V

FIGURE 4.44

Table 4.5 TCE degradation using 5.5 g cathode and 5.8 g anode fibres.

Expt. No.	Ref. Voltage	TCE Degradation Rate Rate(μ moles/min as chloride)	Chloride Production Rate Rate(μ moles/min as chloride)
10	-1.8	0.56	0.53
11	-1.9	1.33	1.22
12	-1.9	1.41	1.30
13	-2.0	2.92	2.68
14	-2.1	4.25	4.09

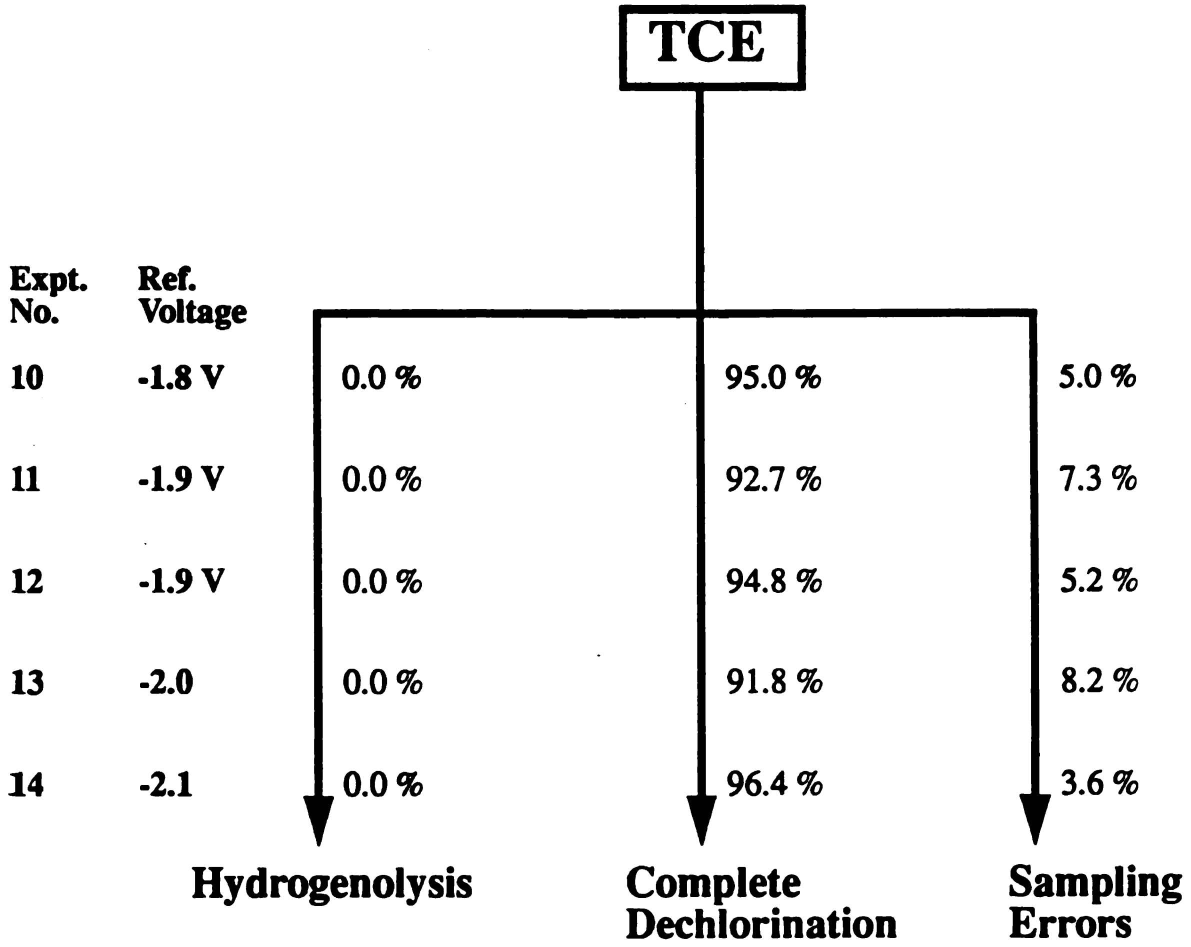


Figure 4.45 Parallel Pathways for the TCE degradation using5.5 g cathode and 5.8 g anode fibres.

Table 4.6 Efficiency and energy requirement calculations for TCE degradation.

Expt. No.	Ref. Voltage	Applied Voltage (V)	Applied Current (amp)	η_{hydro}	η_{min}	η_{max}	$\eta_{total(min)}$	$\eta_{total(max)}$	Energy consumed/ mole of TCE Degraded (KWh)	Cost* $/1000 gallons
10	-1.8	2.60	0.30	0.00	0.29	1.71	0.29	1.71	39.00	4.48
11	-1.9	3.20	0.43	0.00	0.43	2.56	0.43	2.56	51.71	5.95
12	-1.9	3.35	0.45	0.00	0.42	2.51	0.42	2.51	53.46	5.22
13	-2.0	3.52	0.59	0.00	0.72	4.35	0.59	4.35	35.56	4.08
14	-2.1	4.00	0.65	0.00	0.95	5.68	0.65	5.68	30.60	3.50

* Cost is calculated with the current rate of $ 0.04/KWh charged (for the commercial use of electricity) by Board of Water & Electricity, Lansing, MI to treat the TCE contaminated solution with an influent concentration of 100 ppm. Cost does not include capital cost. Energy calculations are made assuming zero order degradation for TCE.

Carbon Tetrachloride

The results of CT degradation were very interesting and encouraging. Both hydrogenolysis and the pathway leading to completely dechlorinated products were observed as shown in Figures 4.46 -4.60. Figure 4.46a represents the observed hydrogenolysis pathway for the five experiments conducted to study CT degradation.

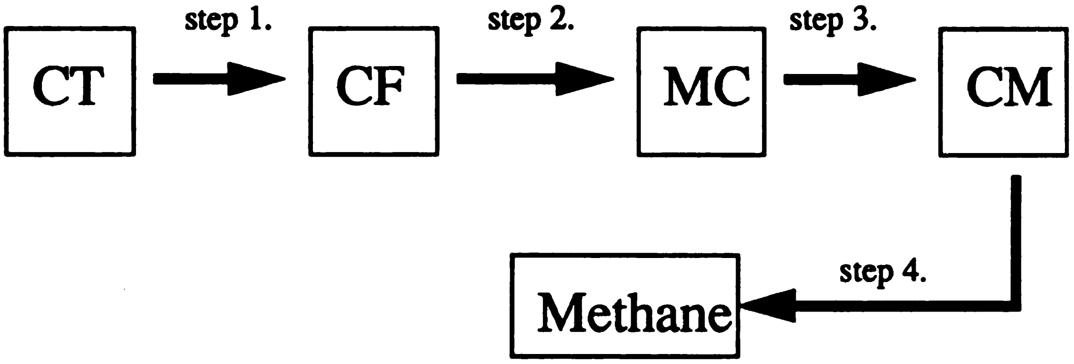
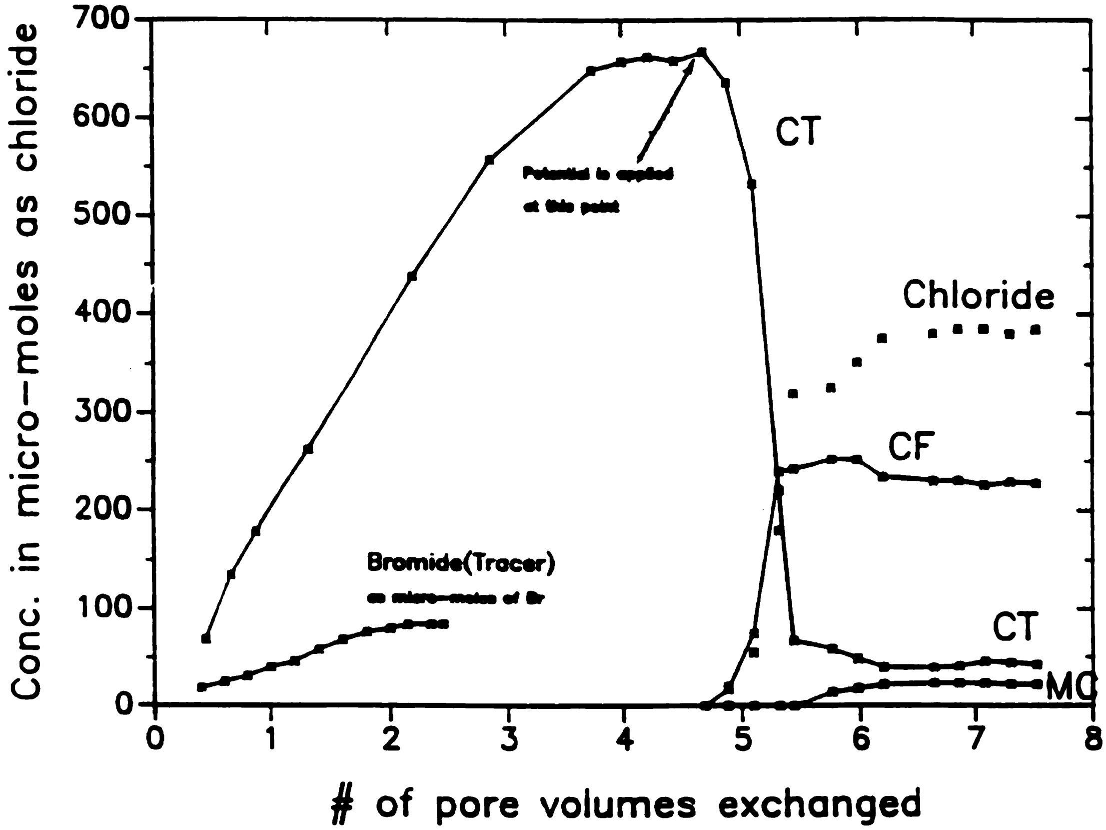


Figure 4.46a

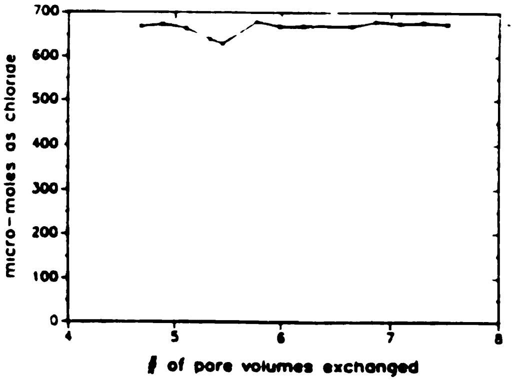
At reference voltage of -1.0 V, only steps 1&2 were observed, but at reference voltage of -1.4 & -1.5 V, the hydrogenolysis pathway was pushed to step 3 resulting in the formation of CM. At reference voltage of -1.8 V, there is a strong indication of methane production although the methane was not quantified in the effluent. The idea of methane production is reinforced by the fact that there is a sudden increase in chloride production at reference voltage of -1.8V as shown in Figure 4.61a and Table 4.7. Another interesting observation is the fact that no CM detected in the effluent at the reference voltage of -1.8. A possible explanation is that Step 4 occurs faster than Step 3 such that all chloromethane produced is quickly transformed to methane which was not detected on the GC using FID detector. The results are consistant with those obtained by Rajayya(1992). As shown in Table 4.13 large dechlorination is observed at the higher refrence voltage of -1.1V.

Due to high CT degradation rates even at low reference voltages, energy requirements are very low compared with those of PCE and TCE. As shown in Table 4.8, the operation of



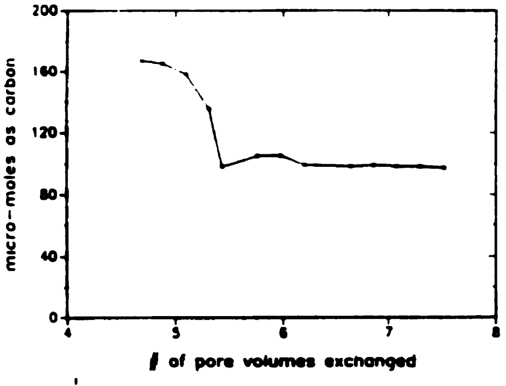
CT DEGRADATION AT REF. VOLTAGE OF -1.0V

FIGURE 4.46



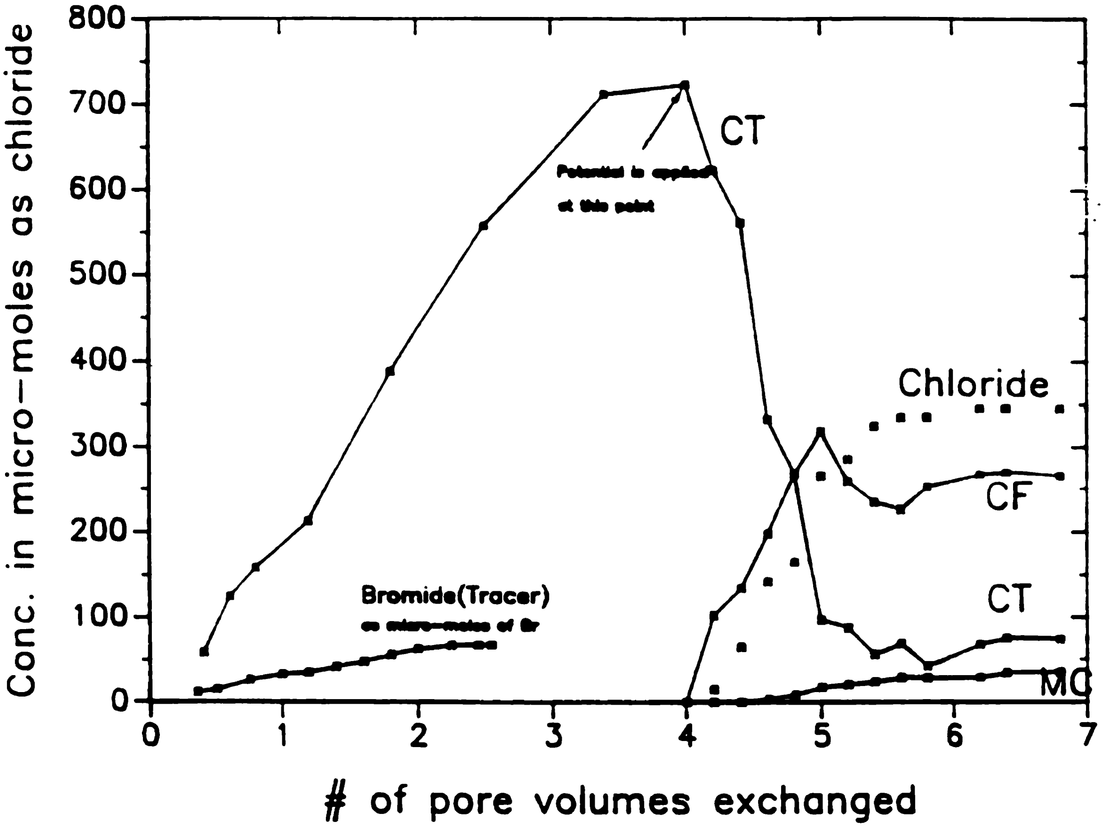
CHLORINE BALANCE FOR CT DEGRADATION AT -1 0V

FIGURE 4.47



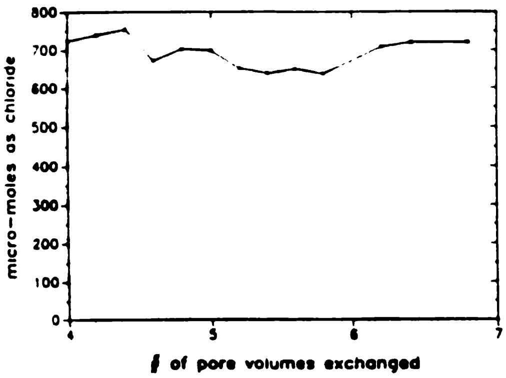
CARBON BALANCE FOR CT DEGRADATION AT -1.0V

FIGURE 4.48



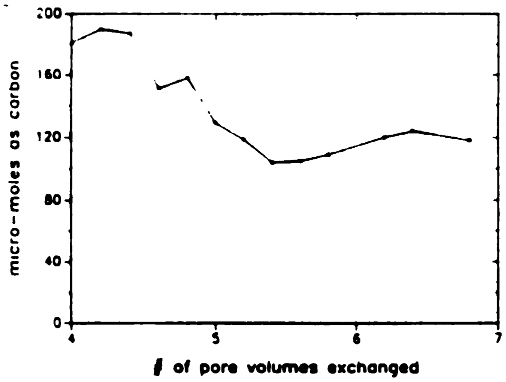
CT DEGRADATION AT REF. VOLTAGE OF −1.0V

FIGURE 4.49



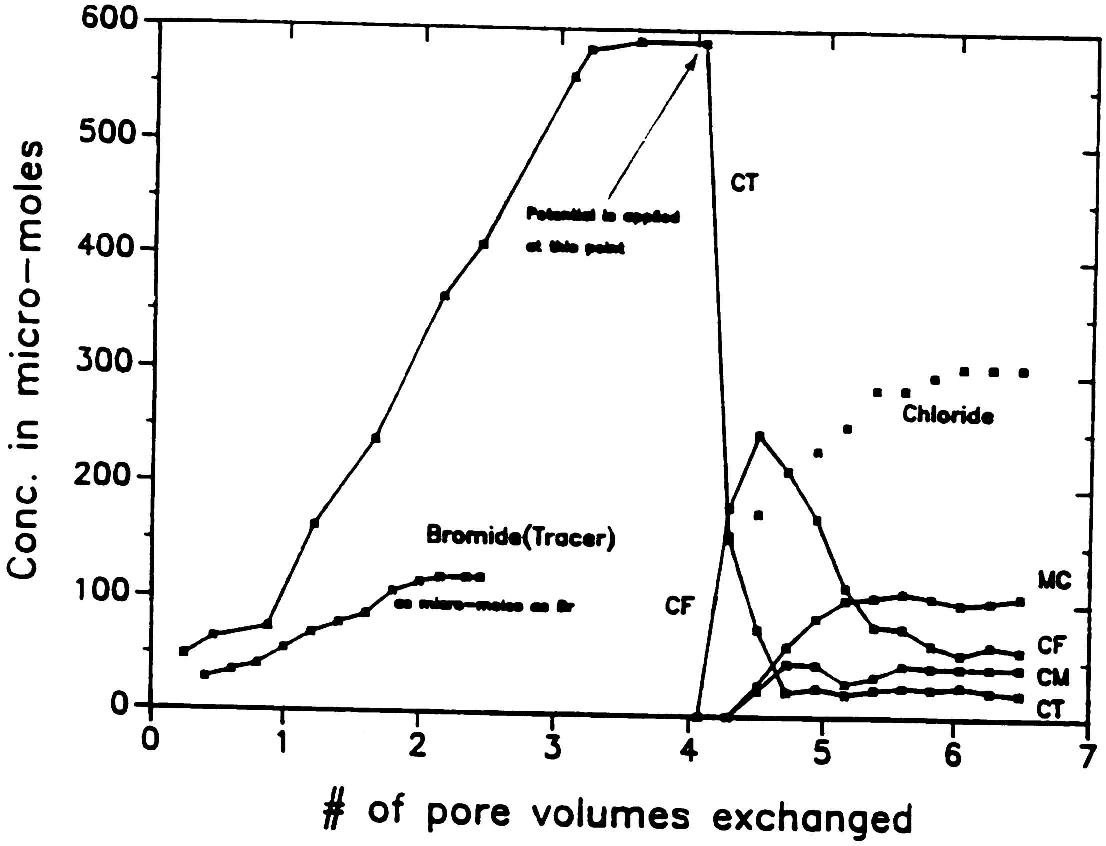
CHLORINE BALANCE FOR CT DEGRADATION AT −1.0V

FIGURE 4.50



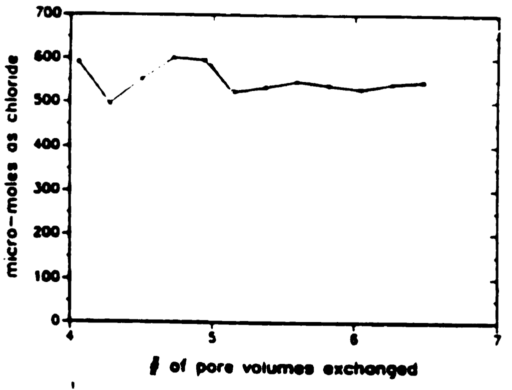
CARBON BALANCE FOR CT DEGRADATION AT −1 0V

FIGURE 4.51



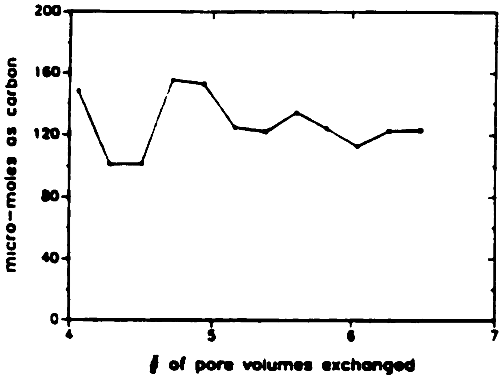
CT DEGRADATION AT REF. VOLTAGE OF −1.4V

FIGURE 4.52



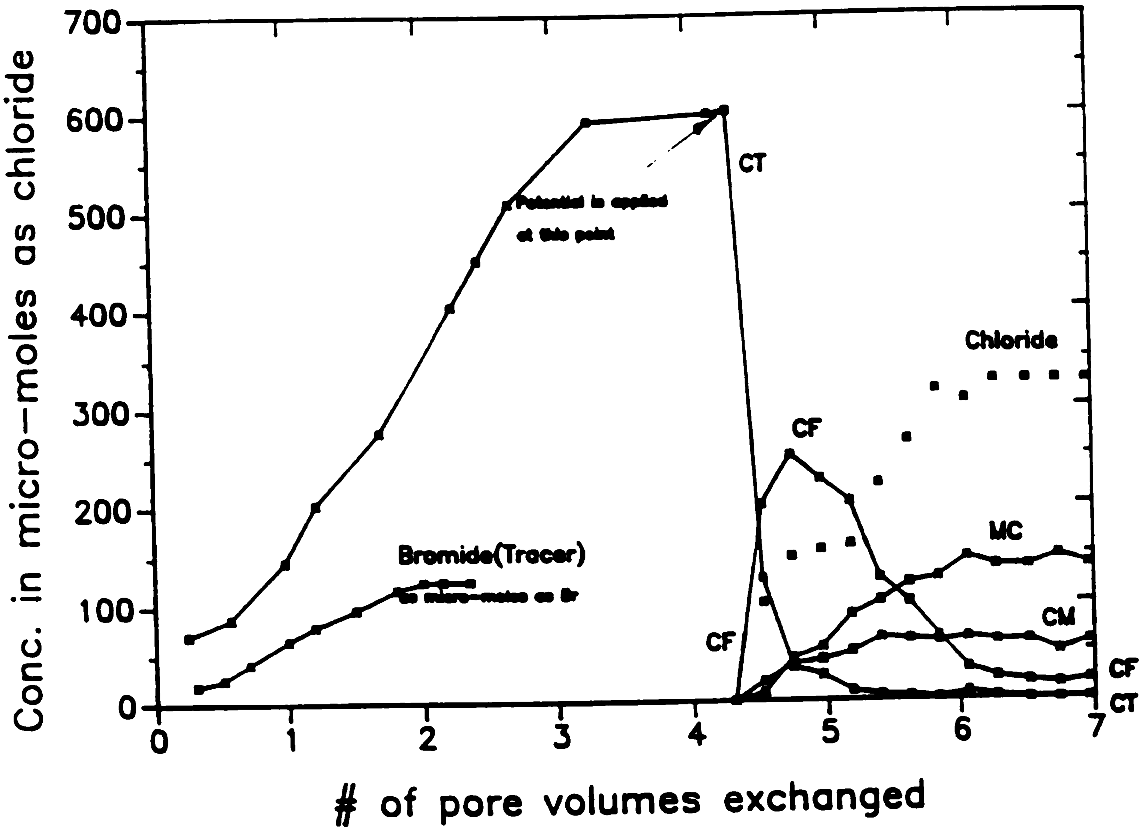
CHLORINE BALANCE FOR CT DEGRADATION AT −1.4V

FIGURE 4.53



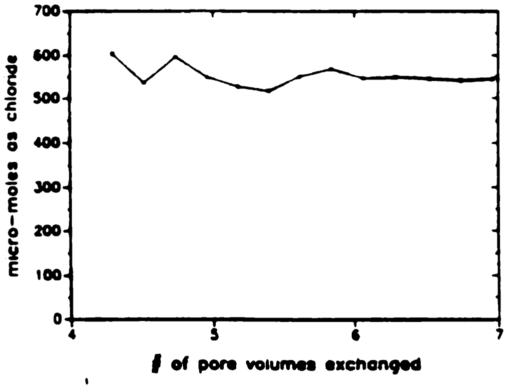
CARBON BALANCE FOR CT DEGRADATION AT −1.4V

FIGURE 4.54



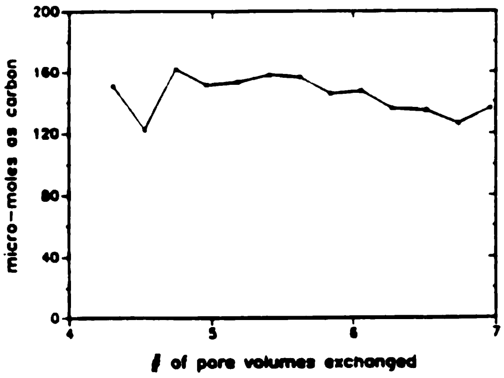
CT DEGRADATION AT REF. VOLTAGE OF −1.5V

FIGURE 4.55



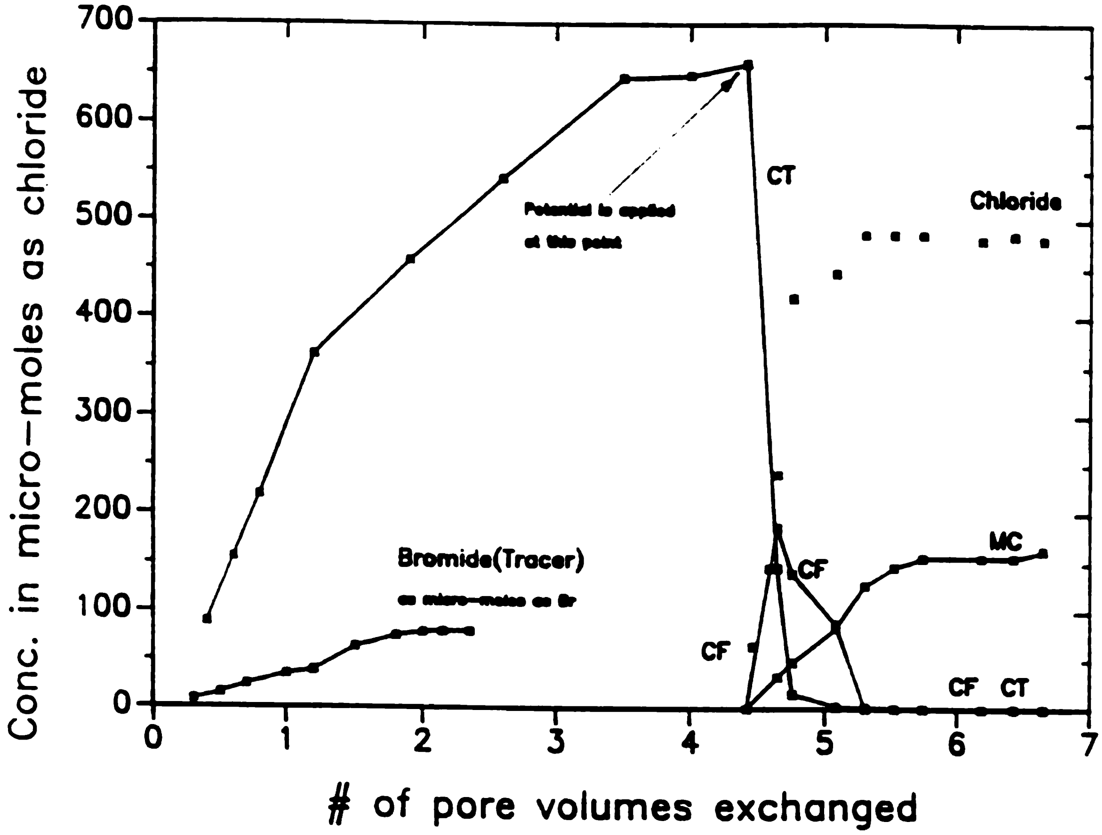
CHLORINE BALANCE FOR CT DEGRADATION AT −1.5V

FIGURE 4.56



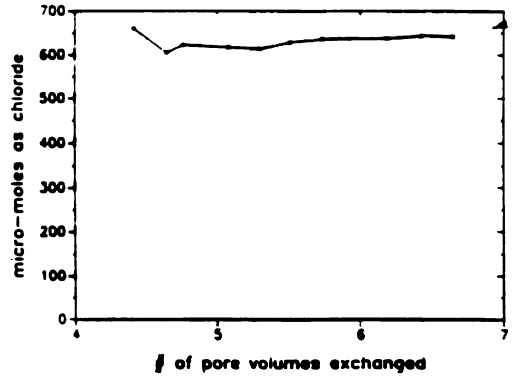
CARBON BALANCE FOR CT DEGRADATION AT −1.5V

FIGURE 4.57



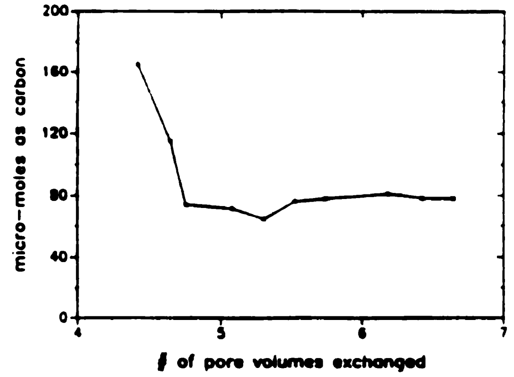
CT DEGRADATION AT REF. VOLTAGE OF −1.8V

FIGURE 4.58



CHLORINE BALANCE FOR CT DEGRADATION AT −1.8V

FIGURE 4.59



CARBON BALANCE FOR CT DEGRADATION AT −1.8V

FIGURE 4.60

Table 4.7 CT degradation using 5.5 g cathode and 5.8 g anode fibres.

Expt.	Ref. Voltage	CT Degradation Rate (μ moles/min as chloride)	CF Production Rate (μ moles/min as chloride)	MC Production Rate (μmoles/min as chloride)	CM Production Rate (μ moles/min as chloride)	Chloride Production Rate (μ moles/min as chloride)
15	-1.0	6.49	2.39	0.29	0.00	3.98
16	-1.0	6.91	2.81	0.37	0.00	3.72
17	-1.4	7.44	0.86	1.32	0.47	4.12
18	-1.5	9.11	0.37	2.12	0.83	4.93
19	-1.8	14.14	0.00	3.19	0.00	10.10

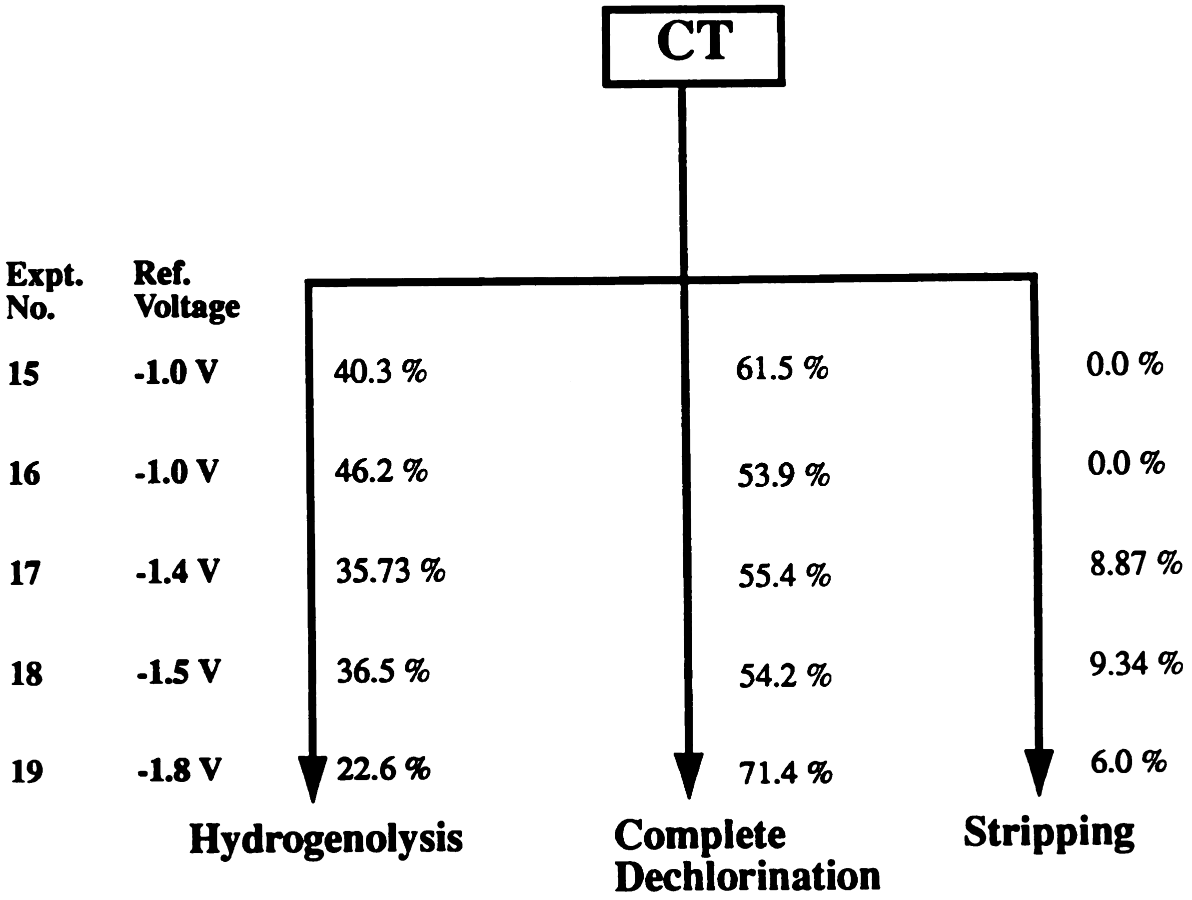


Figure 4.61 Parallel Pathways for the CT degradation using5.5 g cathode and 5.8 g anode fibres.

Table 4.8 Efficiency and energy requirement calculations for CT degradation.

Expt. No.	Ref. Voltage	Applied Voltage (V)	Applied Current (amp)	η_{hydro} %	η_{min} %	η_{max} %	$\eta_{total(m\ in)}$ %	$\eta_{total(max)}$ %	Energy consumed/ mole of CT degraded (KWh)	Cost* $/1000 gallons
15	-1.0	2.00	0.04	4.27	11.76	94.08	16.03	98.35	0.82	0.08
16	-1.0	2.10	0.04	5.46	9.70	77.56	15.16	83.02	0.73	0.08
17	-1.4	2.30	0.07	1.75	2.69	21.50	4.44	23.25	1.45	0.14
18	-1.5	2.45	0.16	1.51	0.36	2.99	1.88	4.50	2.86	0.27
19	-1.8	2.71	0.26	0.98	2.04	16.32	3.02	17.30	3.33	0.33

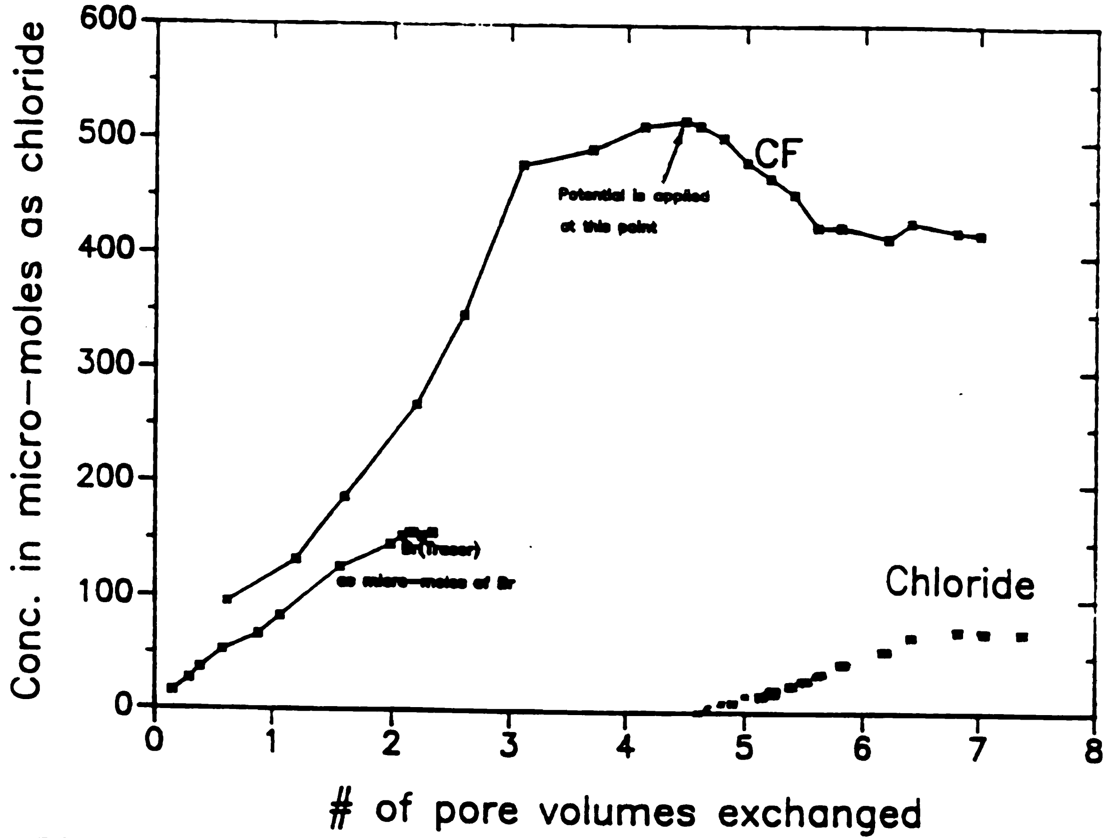
* Cost is calculated with the current rate of $ 0.04/KWh charged (for the commercial use of electricity) by Board of Water & Electricity, Lansing, MI to treat the CT contaminated solution with an influent concentration of 100 ppm. Cost does not include capitol expenditure. Energy calculations are made assuming zero order degradation for CT.

reactor at -1.0 V will result in low operating costs but this factor should be weighed against the advantages of higher dechlorination rates and higher degradation rates for reactor operation at a reference voltage of -1.8V.

Chloroform

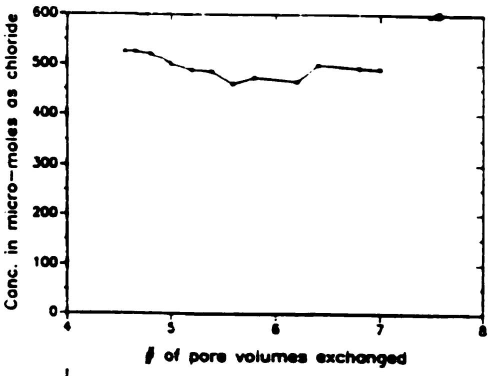
Figures 4. 4.62 to 4.76 represent the results of CF degradation at various reference voltages. The products obtained are very consistent with those indicated by the CT degradation in the previous section as well as those obtained by Rajayya (Table 4.13). With an increase in reference potential, the hydrogenolysis path becomes more important over the dechlorination pathway, as indicated by Table 4.9.

Operation of reactor at lower operating voltages between -1.0 and -1.4 V is strongly recommended due to low operating costs and higher dechlorination rates as shown in Table 4.10.

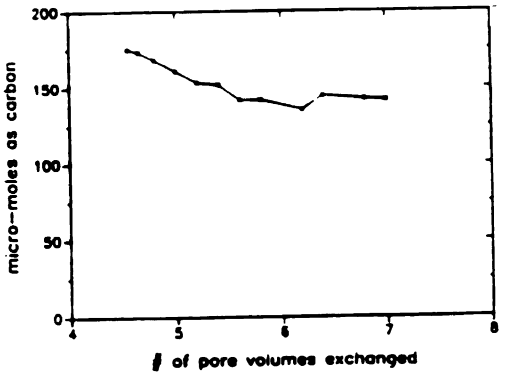


CF DEGRADATION AT REF. VOLTAGE OF −1.0V

FIGURE 4.62



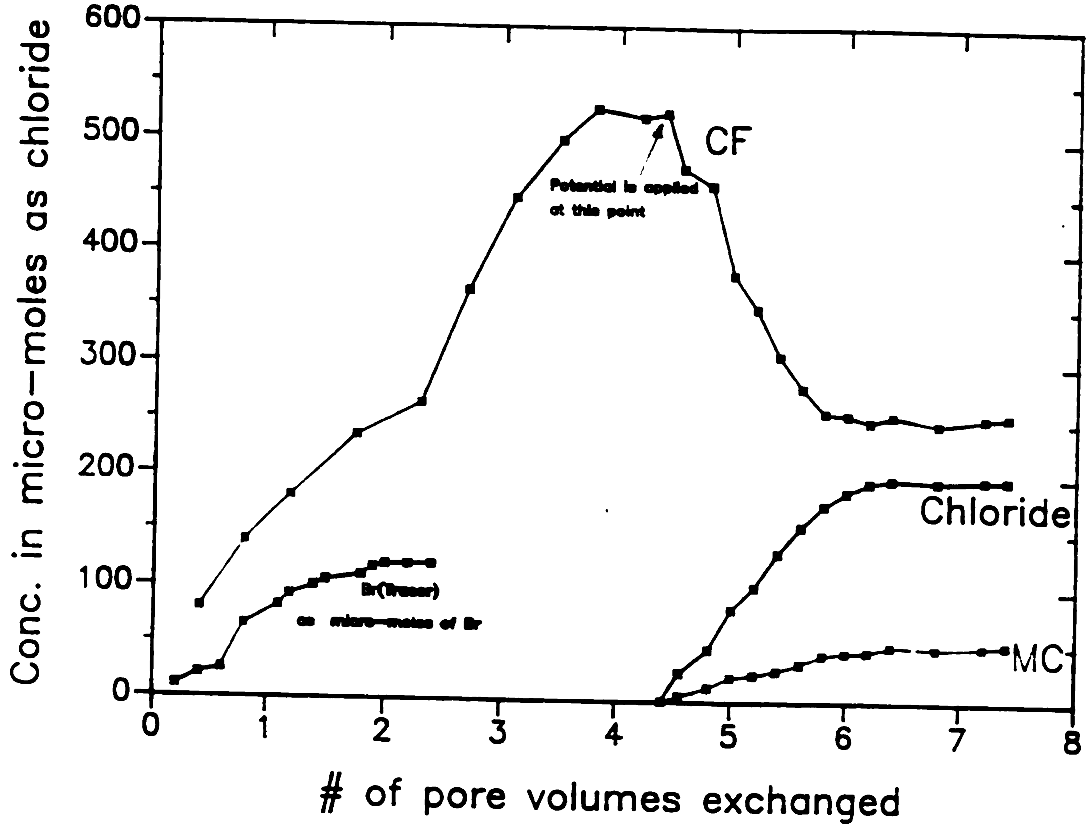
CHLORINE BALANCE FOR CF DEGRADATION AT −1.0V



CARBON BALANCE AT REF. voltage of −1.0V

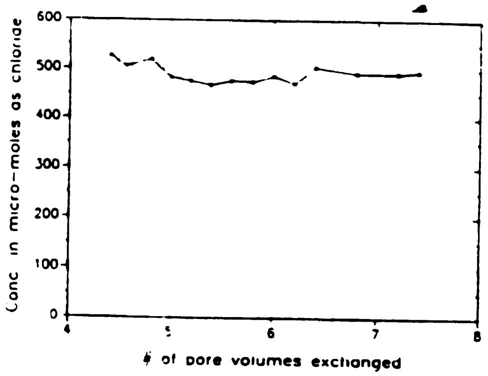
FIGURE 4.63

FIGURE 4.64



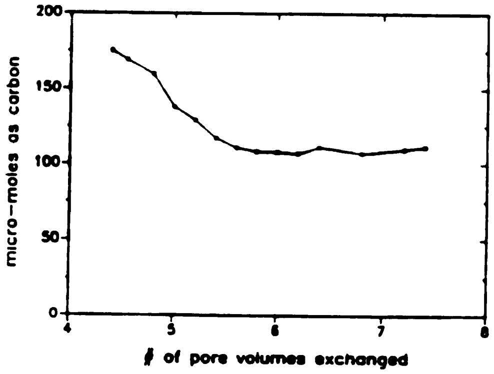
CF DEGRADATION AT REF. VOLTAGE OF −1.4V

FIGURE 4.65



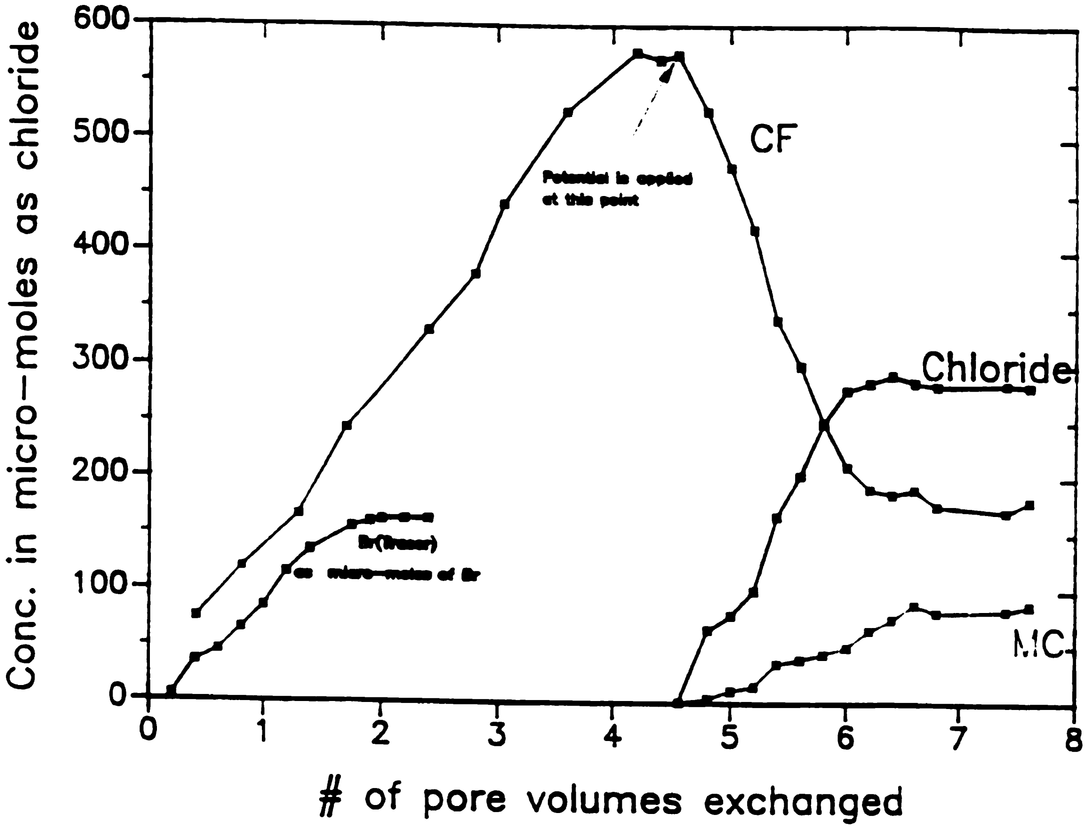
CHLORINE BALANCE FOR CF DEGRADATION AT −1.4V

FIGURE 4.66



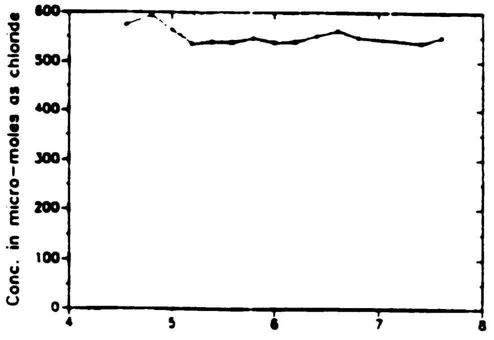
CARBON BALANCE AT REF. voltage of −1.4V

FIGURE 4.67



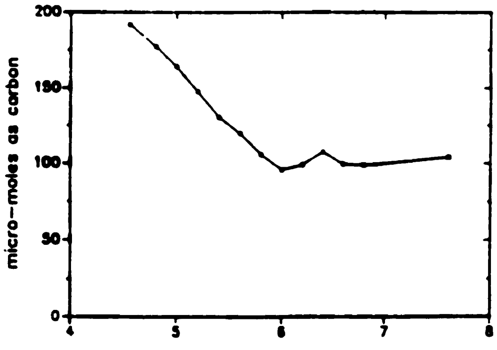
CF DEGRADATION AT REF. VOLTAGE OF −1.5V

FIGURE 4.68



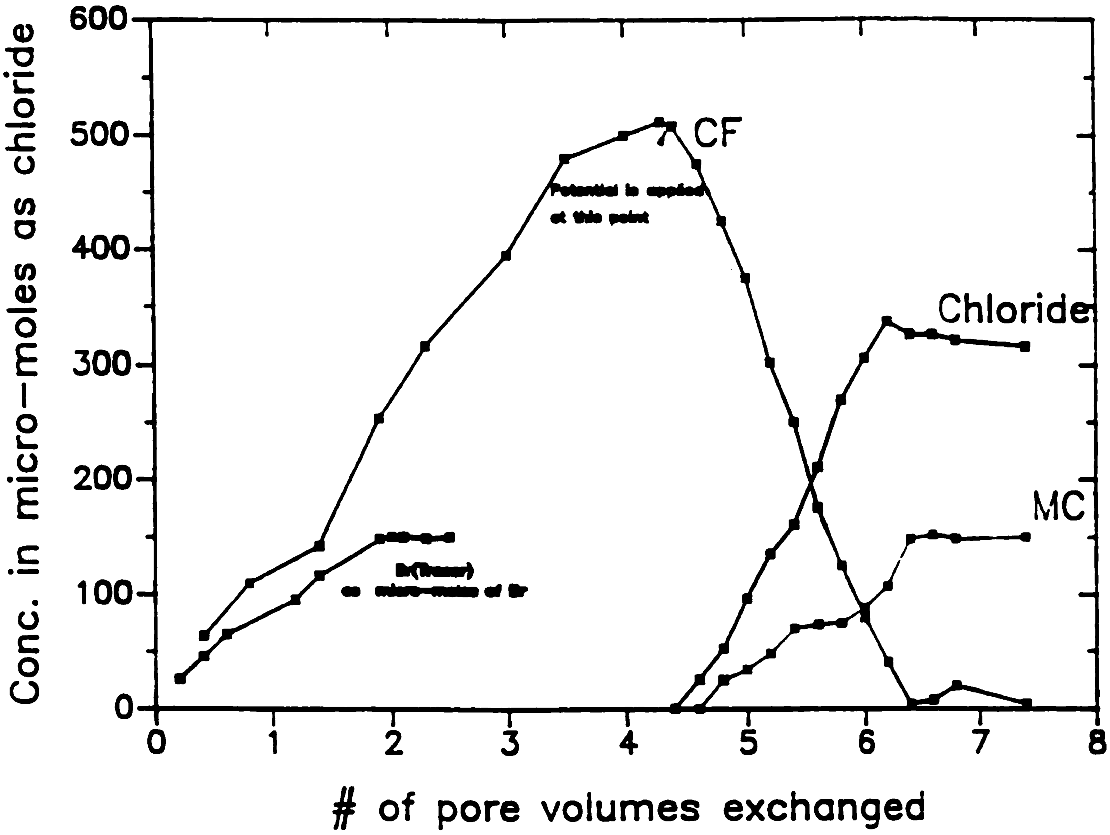
CHLORINE BALANCE FOR CF DEGRADATION AT −1.5V

FIGURE 4.69



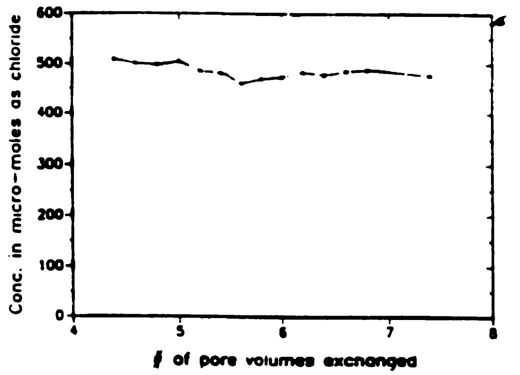
CARBON BALANCE AT REF. voltage of −1.5V

FIGURE 4.70



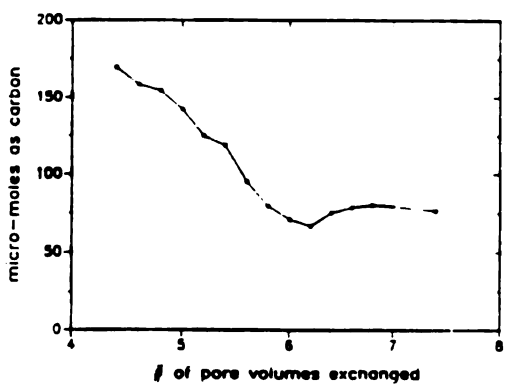
CF DEGRADATION AT REF. VOLTAGE OF −1.8V

FIGURE 4.71



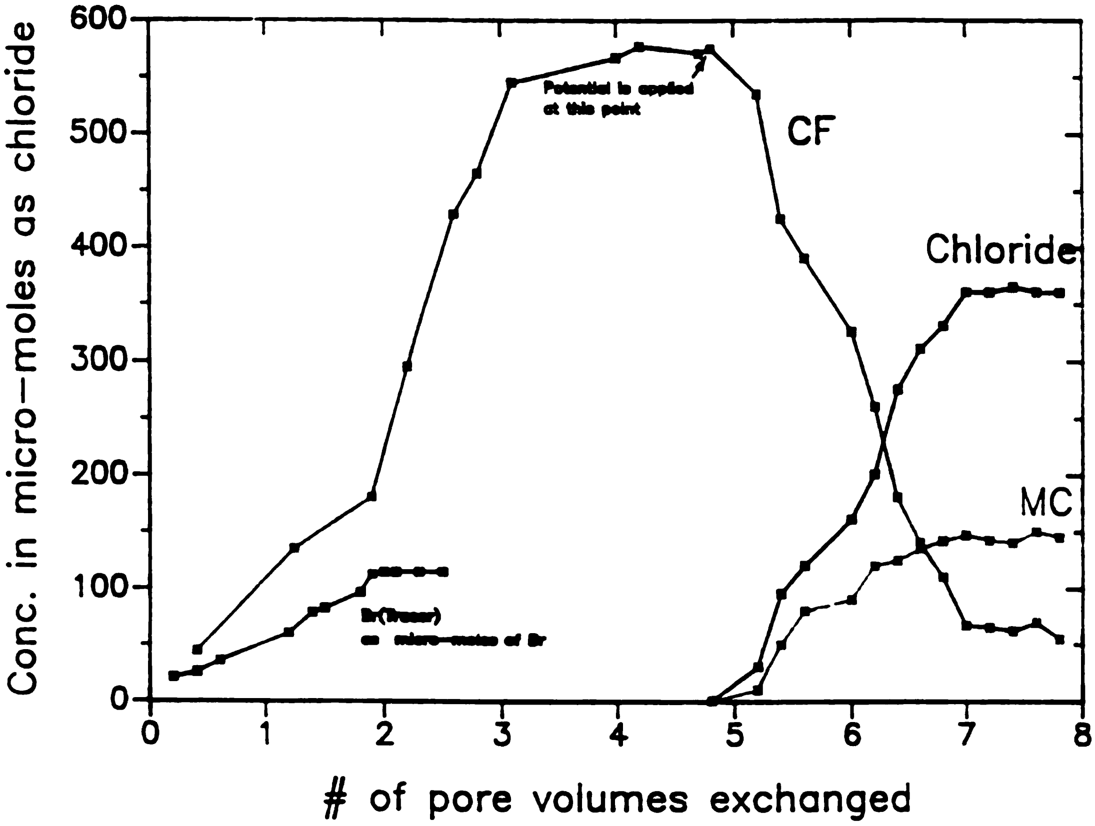
CHLORINE BALANCE FOR CF DEGRADATION AT −1.8V

FIGURE 4.72



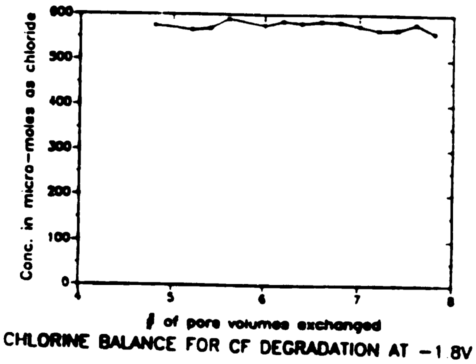
CARBON BALANCE AT REF. voltage of −1.8V

FIGURE 4.73



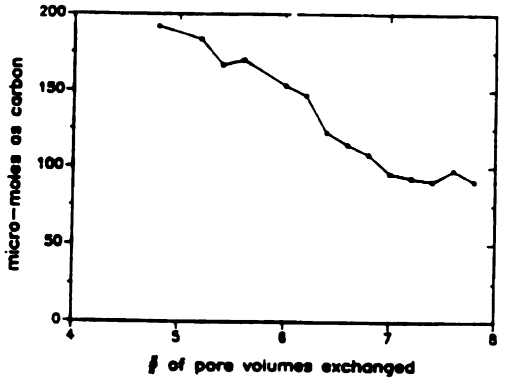
CF DEGRADATION AT REF. VOLTAGE OF −1.8V

FIGURE 4.74



CHLORINE BALANCE FOR CF DEGRADATION AT −1.8V

FIGURE 4.75



CARBON BALANCE AT REF. voltage of −1.8V

FIGURE 4.76

Table 4.9 CF degradation using 5.5 g cathode and 5.8 g anode fibres.

Exp. No.	Ref. Voltage (Volts)	CF Degradation Rate(μmoles/min)	MC Production Rate(μmoles/min)	Chloride Production Rate(μmoles/min)
20	-1.0	1.13	0.0	0.94
21	-1.4	2.88	0.53	2.11
22	-1.5	3.84	0.82	2.69
23	-1.8	4.93	1.37	3.48
24	-1.8	5.07	1.45	3.19

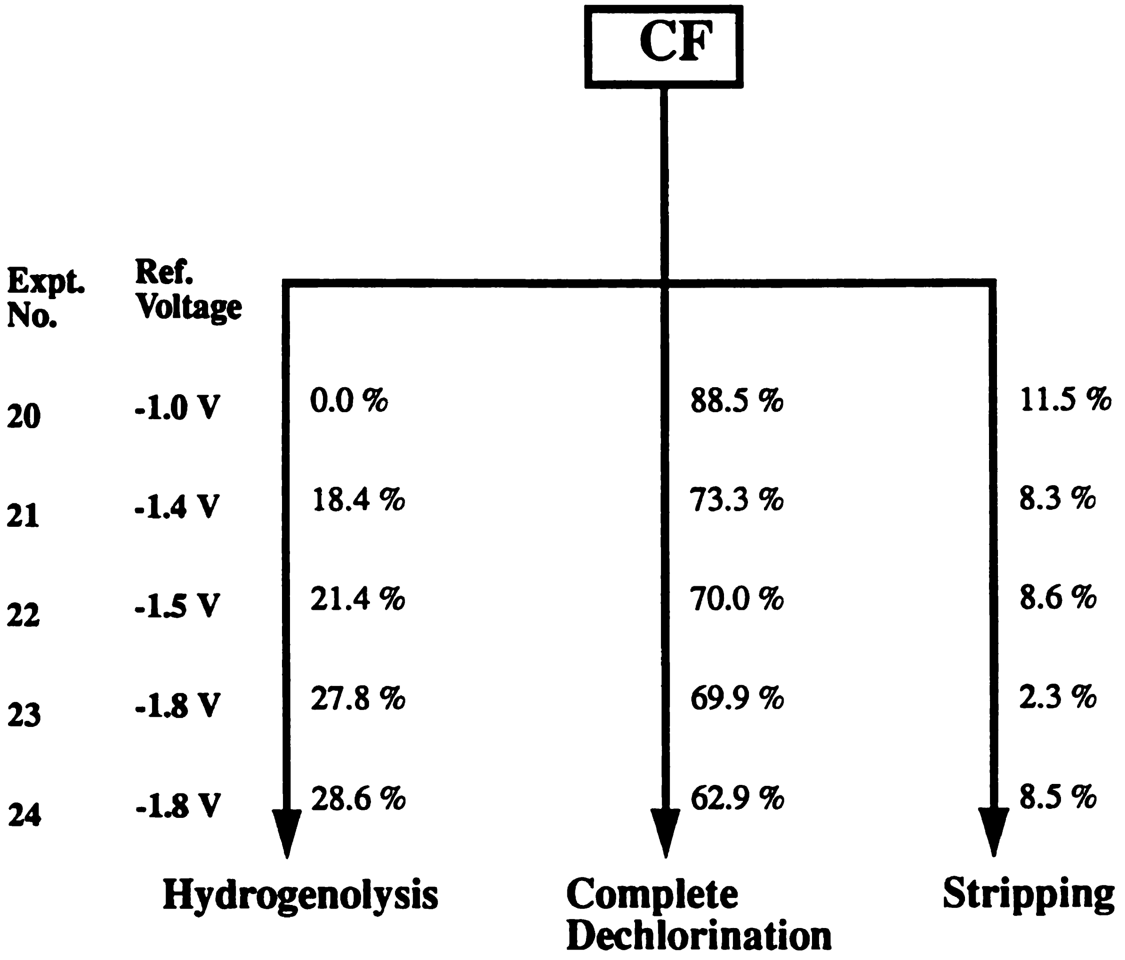


Figure 4.77 Parallel Pathways for the CF degradation using5 5 g cathode and 5.8 g anode fibres.

Table 4.10 Efficiency and energy requirement calculations for CF degradation.

Expt. No.	Ref. Voltage	Applied Voltage (V)	Applied Current (amp)	η_{hydro}	η_{min}	η_{max}	$\eta_{total(m\ in)}$	$\eta_{total(max)}$	Energy consumed/ mole of CF Degraded (KWh)	Cost* $/1000 gallons
20	-1.0	2.03	0.04	0.00	2.22	13.34	2.22	13.34	3.59	0.45
21	-1.4	2.24	0.05	1.08	5.13	30.79	6.21	31.87	1.94	0.26
22	-1.5	2.33	0.10	0.77	2.61	15.66	3.38	16.43	4.03	0.50
23	-1.8	2.52	0.32	0.69	0.92	5.49	1.61	6.18	5.91	0.74
24	-1.8	2.44	0.30	0.56	0.66	3.98	1.15	4.54	3.28	0.40

* Cost is calculated with the current rate of $ 0.04/KWh charged (for the commercial use of electricity) by Board of Water & Electricity, Lansing, MI to treat the CF contaminated solution with an influent concentration of 100 ppm. Cost does not include Capital cost. Energy calculations are made assuming zero order degradation for CF.

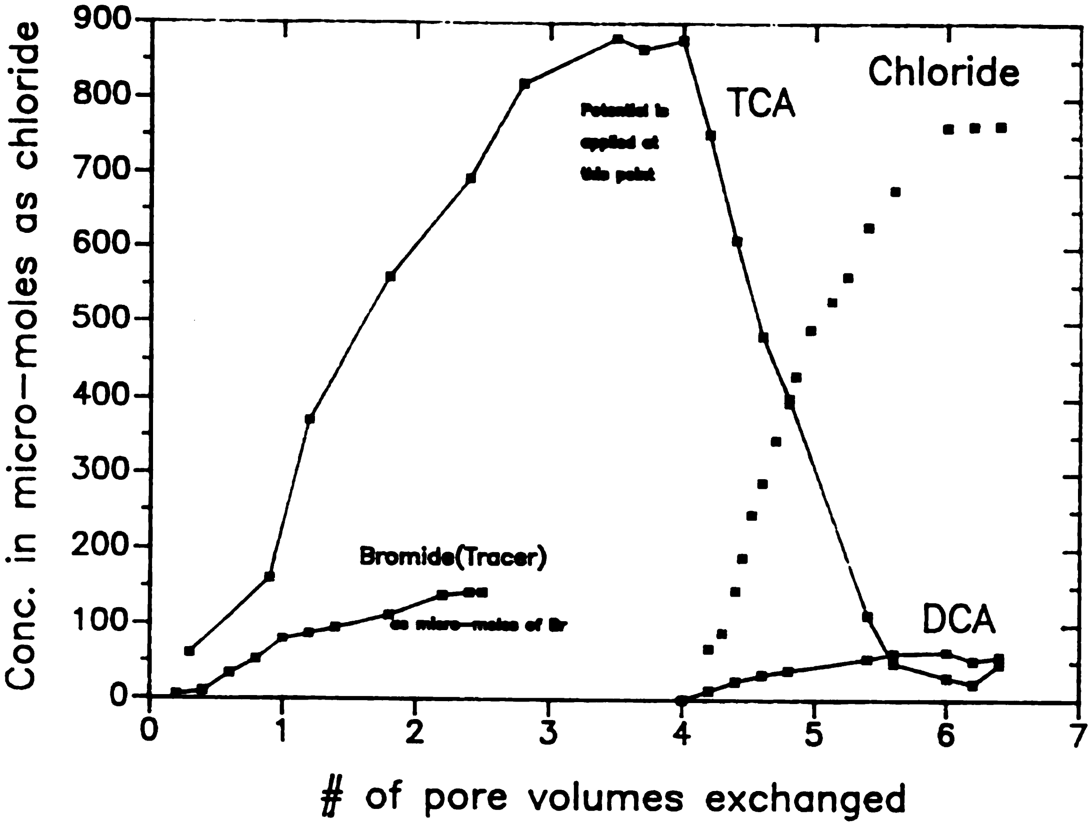
TCA

The results of TCA degradation are shown in Figures 4.78-4.93. It is clear from Table 4.11 and Figure 4.94 that the effluent chloride accounted for 90-95% of the initial chloride present in TCA. Pathway leading to complete dechlorination is predominant at lower voltages. As the reference voltage was increased, hydrogenolysis started dominating resulting in the production of DCA and CA. These results are consistent with those obtained in previous electrolysis studies(Rajayya1992, Criddle & McCarty 1991).

Efficiencies of electron transfer were high at lower voltages and there was a gradual drop in efficiencies as the reference voltage was increased. Similar trend was observed for the energy requirements and the cost. There are two distinct advantages of operating at lower voltages:

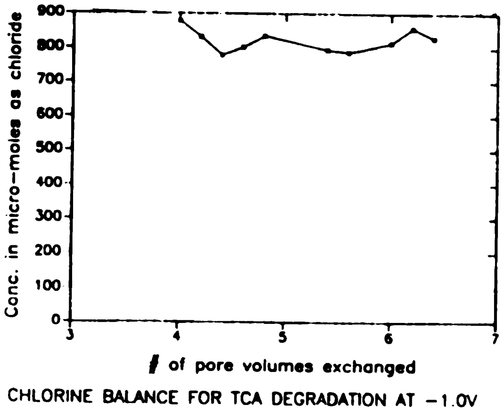
-Production of completely dechlorinated products.

- Lower operational costs.



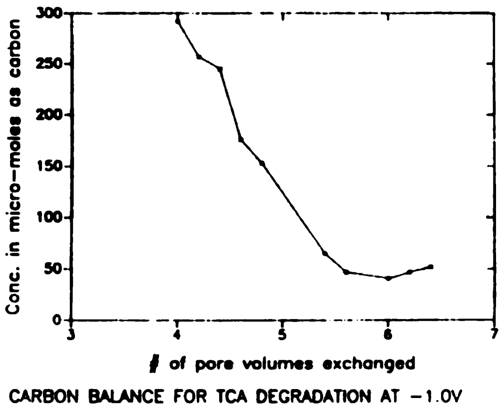
TCA DEGRADATION AT REF. VOLTAGE OF −1.0V

FIGURE 4.78



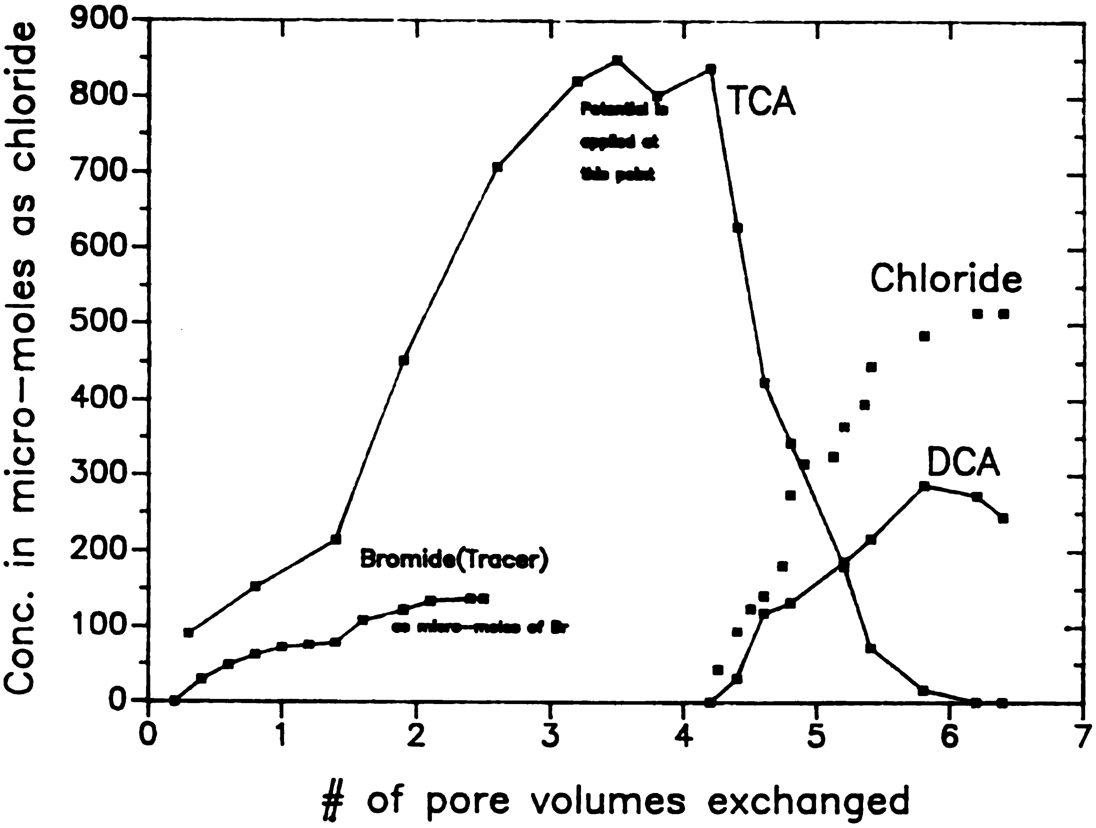
CHLORINE BALANCE FOR TCA DEGRADATION AT −1.0V

FIGURE 4.79



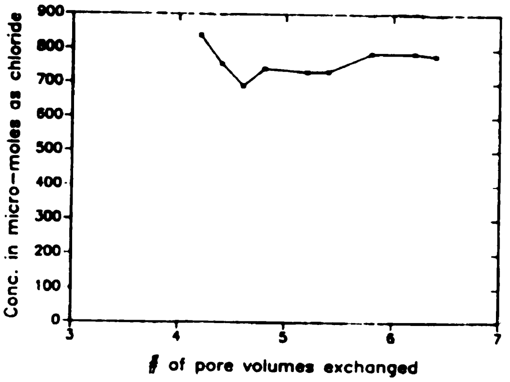
CARBON BALANCE FOR TCA DEGRADATION AT −1.0V

FIGURE 4.80



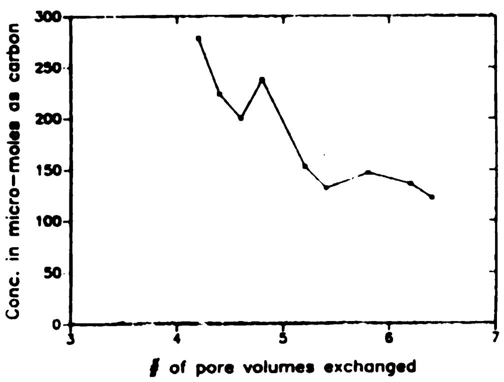
TCA DEGRADATION AT REF. VOLTAGE OF −1.4V

FIGURE 4.81



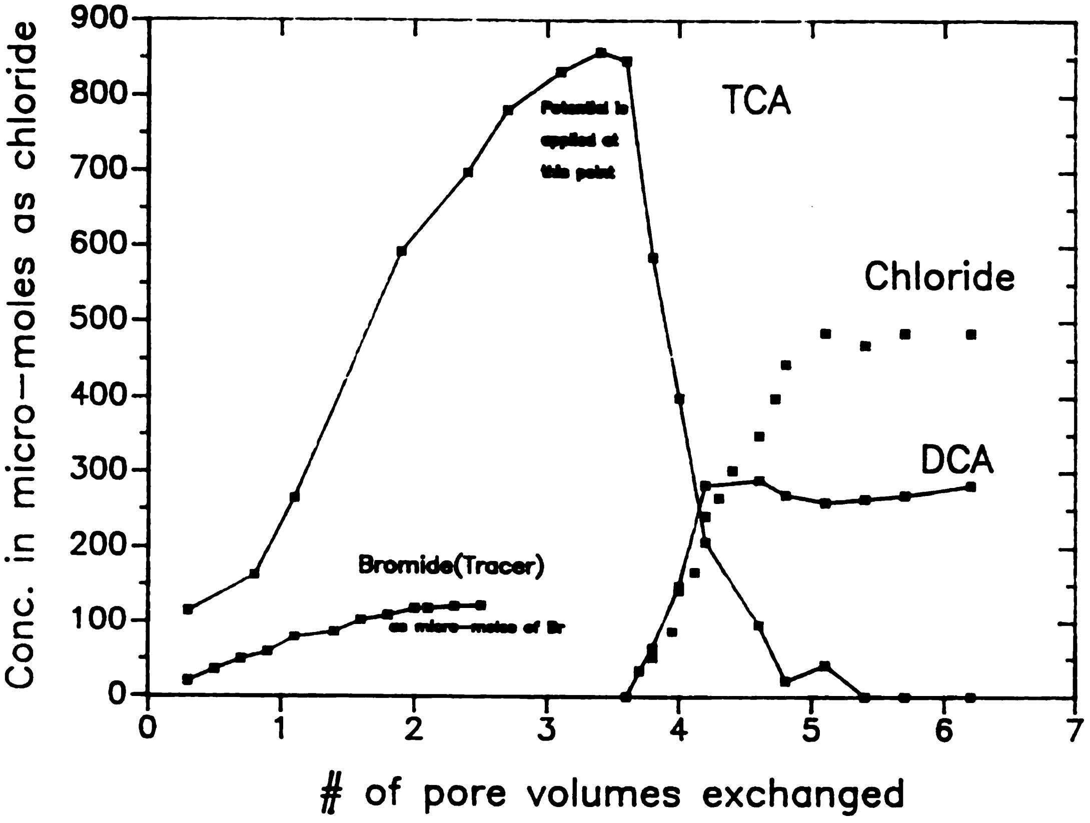
CHLORINE BALANCE FOR TCA DEGRADATION AT −1.4V

FIGURE 4.82



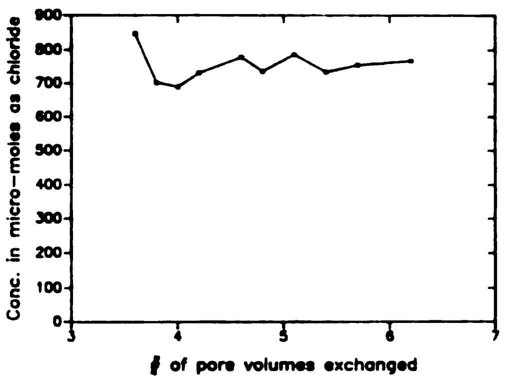
CARBON BALANCE FOR TCA DEGRADATION AT −1.4V

FIGURE 4.83



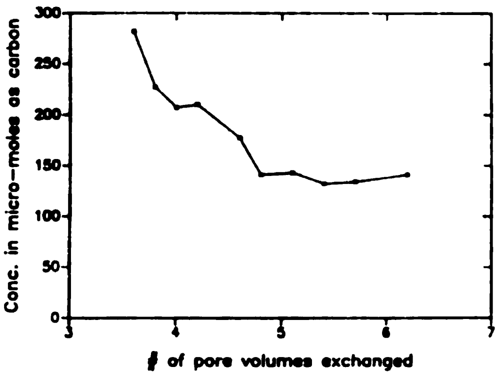
TCA DEGRADATION AT REF. VOLTAGE OF −1.5V

FIGURE 4.84



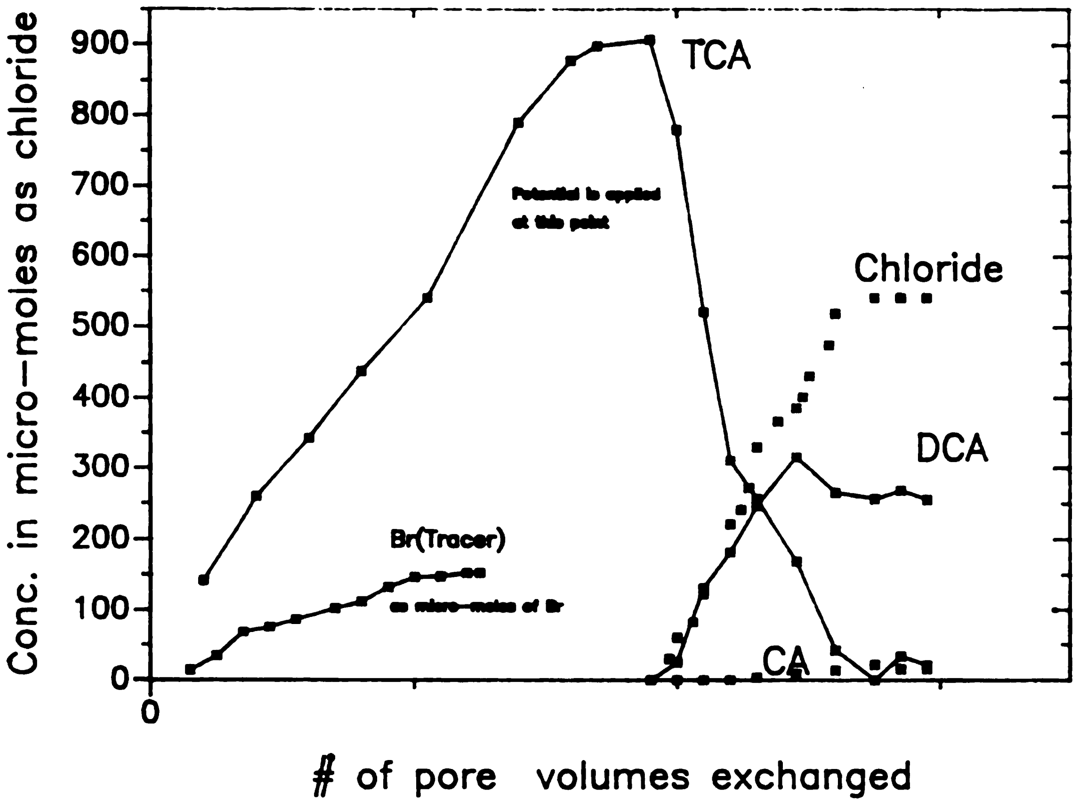
CHLORINE BALANCE FOR TCA DEGRADATION AT −1.5V

FIGURE 4.85



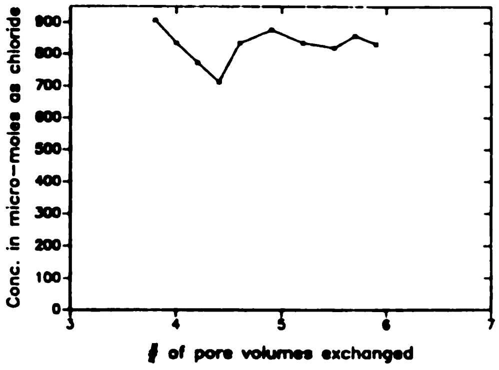
CARBON BALANCE FOR TCA DEGRADATION AT −1.5V

FIGURE 4.86



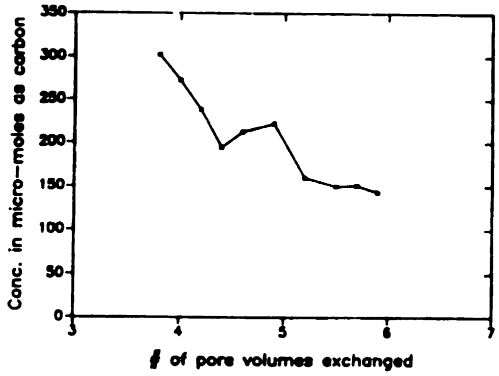
TCA DEGRADATION AT REF. VOLTAGE OF −1.5V

FIGURE 4.87



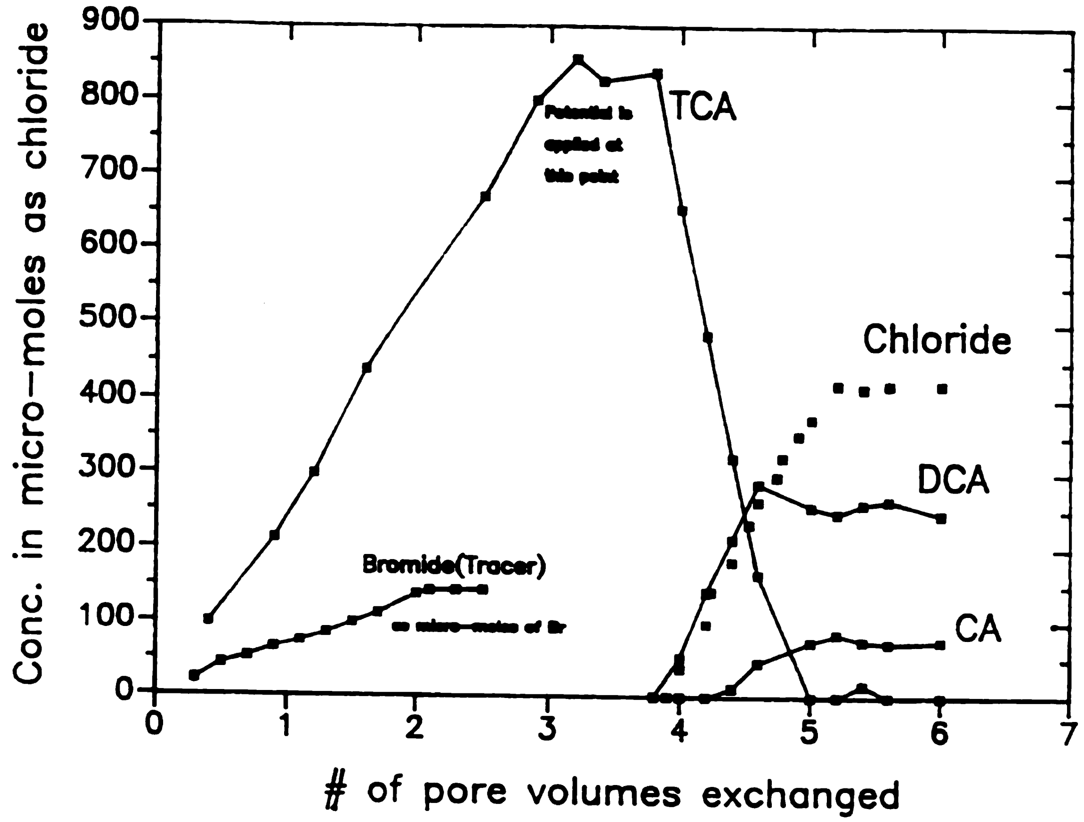
CHLORINE BALANCE FOR TCA DEGRADATION AT −1.5V

FIGURE 4.88



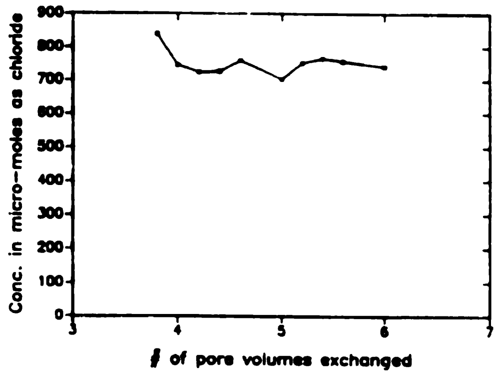
CARBON BALANCE FOR TCA DEGRADATION AT −1.5V

FIGURE 4.89



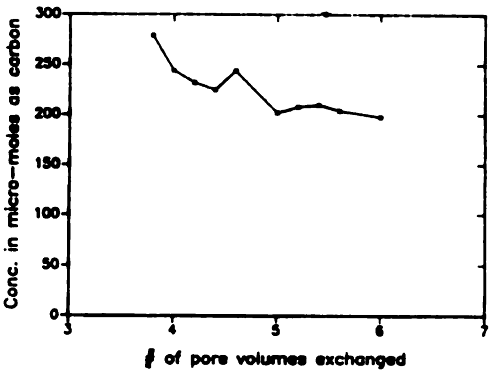
TCA DEGRADATION AT REF. VOLTAGE OF −1.8V

FIGURE 4.90



CHLORINE BALANCE FOR TCA DEGRADATION AT −1.8V

FIGURE 4.91



CARBON BALANCE FOR TCA DEGRADATION AT −1.8V

FIGURE 4.92

Table 4.11 TCA degradation using 5.5 g cathode and 5.8 g anode fibres.

Expt.	Ref. Voltage	TCA Degradation Rate μ moles/min as chloride	DCA Production Rate μ moles/min as chloride	CA Production Rate μmoles/min as chloride	Chloride Production Rate μ moles/min as chloride
25	-1.0	9.12	0.31	0.00	8.12
26	-1.0	9.90	2.88	0.00	6.07
27	-1.4	10.6	3.52	0.00	6.09
28	-1.5	11.1	3.10	0.26	6.57
29	-1.8	12.8	3.72	1.13	6.30

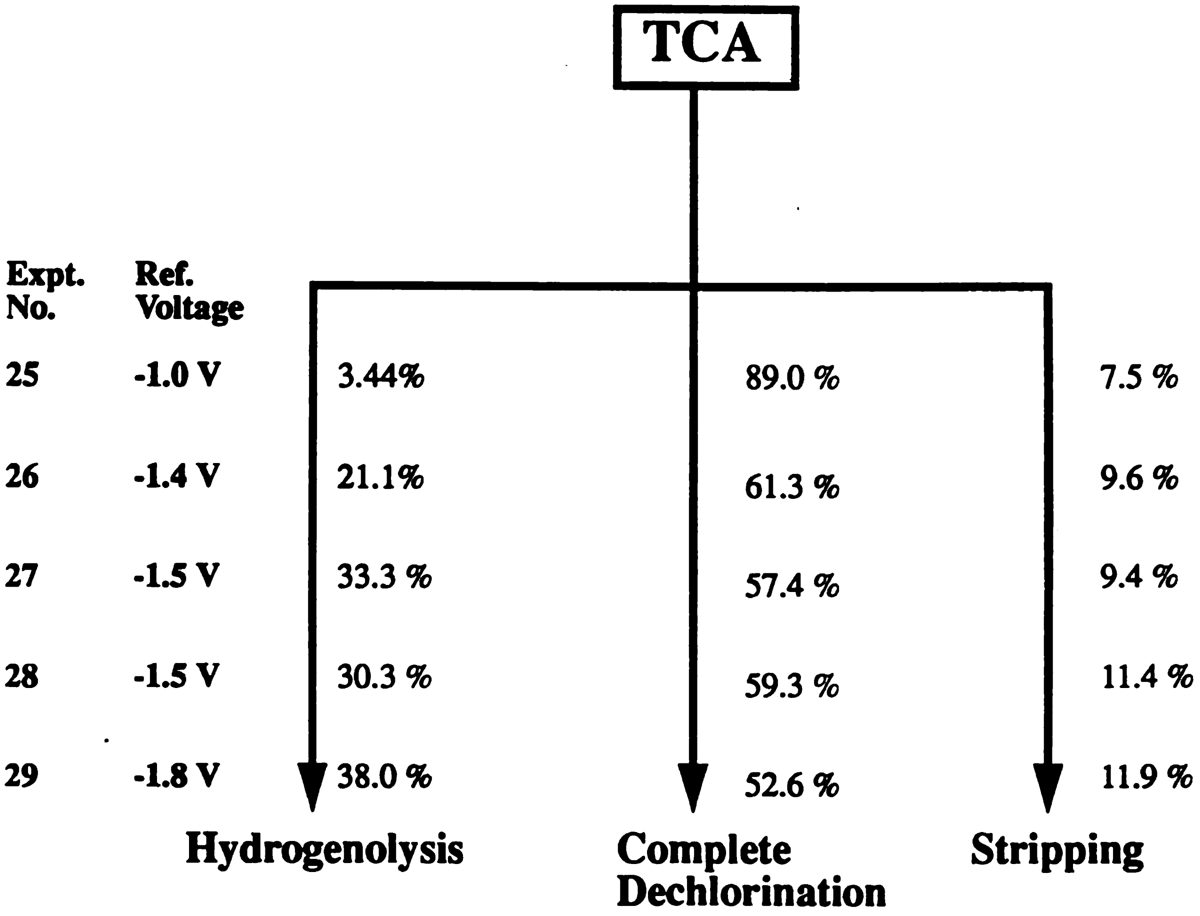


Figure 4.93 Parallel Pathways for the TCA degradation using5.5 g cathode and 5.8 g anode fibres.

Table 4.12 Efficiency and energy requirement calculations for TCA degradation.

Expt. No.	Ref. Voltage	Applied Voltage (V)	Applied Current (amp)	η_{hydro} %	η_{min} %	η_{max} %	$\eta_{total(min)}$ %	$\eta_{total(max)}$ %	Energy consumed/ mole of CT degraded (KWh)	Cost* $/ 1000 gallons
25	-1.0	1.92	0.06	0.83	21.7	130	22.5	131	0.63	0.07
26	-1.4	2.21	0.12	3.85	4.27	25.6	8.12	29.5	1.34	0.15
27	-1.5	2.49	0.15	3.77	2.73	16.4	6.50	20.2	1.77	0.20
28	-1.5	2.39	0.17	3.91	2.49	14.9	6.40	18.8	1.83	0.21
29	-1.8	2.61	0.32	4.13	1.45	8.71	5.58	12.3	3.27	0.37

* Cost is calculated with the current rate of $ 0.04/KWh charged (for the commercial use of electricity) by Board of Water & Electricity, Lansing, MI to treat the TCA contaminated solution with an influent concentration of 100 ppm. Cost does not include capitol expenditure. Energy calculations are made assuming zero order degradation for TCA.

Table 4.13 Degradation and production rate information (From Rajayya, 1992)

CT Degradation

Ref. Voltage	CT degradation rate (μ moles/min)	CF production rate (μ moles/min)	MC production rate (μ moles/min)	CM production rate (μ moles/min)	chloride prod. rate (μ moles /min)
-0.9V	1.26	0.28	0.03	0.00	0.57
-1.1V	3.47	0.59	0.31	0.05	2.36

CF Degradation

Ref. Voltage	CF degradation rate (μ moles/min)	MC production rate (μ moles/min)	CM production rate (μ moles/min)	chloride production rate (μ moles/min)
-0.9V	1.64	0.14	0.06	1.14
-1.1V	3.06	0.26	0.14	2.36

TCA degradation

Ref. Voltage	TCA degradation rate (μ moles/min)	DCA production rate (μ moles/min)	CA production rate (μ moles/min)	chloride production rate (μ moles/min)
-0.9V	2.19	0.05	0.03	1.58
-1.1V	2.44	0.16	0.03	1.96

PCE degradation

Ref. Voltage	PCE degradation rate (μ moles/min)	TCE production rate (μ moles/min)	t-DCE production rate (μ moles/min)	chloride production rate (μ moles/min)
-1.2V	1.25	0.42	0.02	0.73
-1.4V	2.78	0.92	0.06	1.53

TCE degradation

Ref. Voltage	TCE degradation rate (μ moles/min)	t-DCE production rate (μ moles/min)	chloride production rate (μ moles/min)
-1.2V	0.42	0.00	0.26
-1.4V	1.39	0.06	0.48

Chapter 5
Conclusions

Parallel pathways exist for the degradation of halogenated aliphatics undergoing electrolysis: hydrogenolysis, which becomes predominant by increasing reduction potentials and another pathway resulting in the formation of completely dechlorinated products. The second pathway was predominant at lower applied voltages. The overall degradation rates of the target chemicals tested were increased by increasing the applied voltage. The operational costs were higher for alkenes as compared to those for alkanes.

The choice of operating reference potential is very crucial from economic point of view and hence the following factors should be carefully considered in selecting the optimum applied voltage: By controlling the applied voltage, the desired products of electrolytic reduction can be obtained while minimizing unwanted products. The operation of reactor at lower reference voltages has the distinct advantages of lower operating cost and the formation of highly dechlorinated products. The main disadvantage of operating the reactor at lower voltages is the higher capital costs. An increase in voltage results in a significant increase in degradation rates. Operation of reactor at higher voltages will reduce the size of the reactor resulting in lower capital costs.

Last but not the least important design consideration is the possible need for additional treatment of the effluent from the electrochemical reactor is to meet desired effluent standards. Biological treatment and additional electrolysis are two of the many possible alternatives.

Chapter 6

Recommendations for Future Work

In considering the future research needs, first and foremost step should be the identification of the products of complete dehalogenation. Some of these products have been identified by Rajayya(1992), yet additional experiments are recommended to characterize the dissolved organic products. As mentioned in Chapter 3, the degradation rates of target chemicals at a fixed reference voltage should be cathode surface area limited and hence the anode surface area has to exceed the anode surface area in the reactor. Further research is needed to determine the optimum ratio of the weights of cathode and anode fibres to achieve maximum degradation. Another factor that will influence the degradation cosiderably is the anode compartment pumping rate and its correlation with cathode pumping rate. Experiments are recommended to optimize the anode pumping rate. A mixture of aliphatics should also be studied to evaluate the performance of the reactor for such conditions.

Further research is needed to identify the most economical technology for the treatment of effluent from the electrochemical reactor. As the products of electrolysis can be controlled by changing applied voltage, a number of technologies can be considered to treat this effluent. Optimum reference and applied voltages should be obtained by combining the effects of secondary treatment on electrolysis.

Experiments should also be performed to study the effects of pH, temperature, dissolved oxygen and the nature of the electrolyte on the electrolytic reduction process.
Dissolved oxygen can result in altering the products of electrolysis and hence may result in production of CO_2(Criddle & McCarty, 1991). Modification of cathode materials to improve mass transfer properties should also be investigated. Use of certain cathode materials which are highly conductive and sorb the target chemicals should also be explored.

Instead of using water as the proton donor in the anode chamber, a fluidized powdered iron bed may result in a decrease in applied voltage because iron requires less energy (eV) than water to produce protons.

One of the major contributor to the capital cost of the reactor the Nafion Membrane. In the absence of a membrane, the reduced products at the cathode can get oxidized at the anode to form the reactants again. A different configuration of reactor as shown in figure 6.1 is recommended. In this new design chloride exchange resins can be used to eliminate the possibility of the reverse reaction at the anode. Experiments should be conducted to explore the possibility of elimination of membrane by this new process.

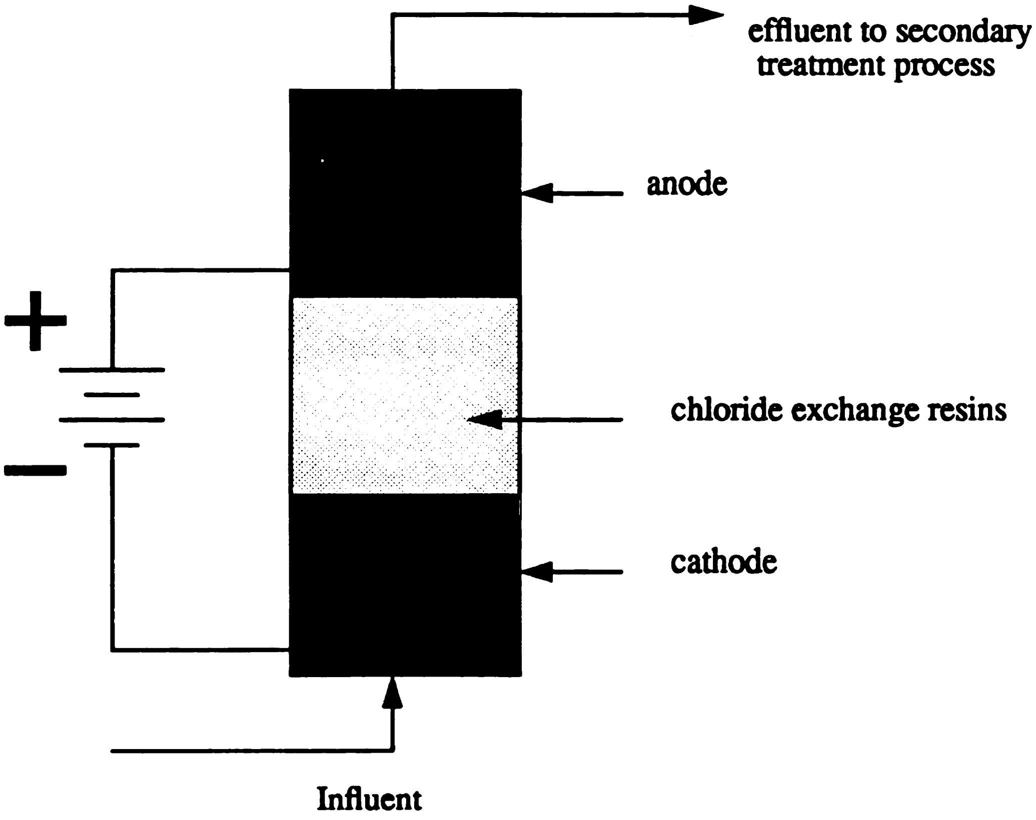


Figure 6.1 Recommended reactor configuration using chloride exchange beeds.

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Appendix A
QA/QC Protocol

Calibration and Standardization

* A six point calibration curve was generated for the analysis of volatile organics. The concentrations of the standards always bracketed the concentrations quantified.

*A different set of standards were prepared for the analysis of volatile organics when the effluent concentrations were less than 4 ppm.

* Fresh standards were prepared for each experiment and secondary dilutions were prepared immediately before GC analysis.

* Standards were placed between the samples in the Auto-Sampler in the GC analysis.

* A six point calibration curve was prepared for the chloride and bromide measurements. Although calibration measurements were done in the beginning of each the experiment, the standards were saved and the MV readings were again taken and compared with the earlier measurements to ensure consistency of chloride probe with time.

* The same buffer solution was pumped through the cathode and anode chamber.

* Duplicate experiments were performed for at least one of the four reference voltages at which experiments were performed for each target chemical.

* Same buffer solution was prepared in the preparation of standards for the volatile organics, chloride and bromide measurements.

* Rigorous sorption studies were conducted separately for each target chemical to establish the time in which the breakthrough was achieved in absence of electrolysis.

* Care was taken to ensure that the orientation of the fibres in both the chambers was the same for every experiment. For all experiments related to one target chemical, pieces of size 6.0″ x 0.75″ were cut from the same sheet of the carbon fibres (fibres are available in

large sheets of different thicknesses).

* Reference voltage was constantly monitored and applied voltage was adjusted after regular intervals (not exceeding 5 minutes) to keep reference voltage constant.

Membrane was soaked in 1% HNO_3 solution after finishing experiments for each target chemicals to remove any deposits that might reduce its proton permeability.

* Statistical analysis was done to estimate 95% confidence intervals of the applied voltage and applied current w.r.t. reference voltage as shown in appdendix D.

Sampling

* Initial sampling intervals before electrolysis were 25-30 min but sampling interval was reduced to 15-25 minutes after electrolysis was started. Sampling continued untill the effluent chloride concentration was constant for 30-45 minutes.

* In taking samples for volatile analysis, care was taken to ensure that samples were not taken close to the time when hydrogen bubbles escaped from the reactor outlet.

Record Keeping

* All chromatograms were saved.

* All results were entered in a bound note book in pen.

* Statistical analysis to estimate the regression coefficients was done by using PLOTIT software package (Scientific Programming Enterprises, Haslett, MI).

Appendix B

Modelling of Electrochemical Plug Flow Reactor

Although detailed modelling of experimental system used was beyond the scope of this thesis, some preliminary mathematical analysis was conducted. The results of this analysis are presented in this appendix. Hopefully the approach adopted here for the mathematical modelling of a plug flow electrochemical reactor will prove useful for the development of appropriate expressions for the design and simulation of reactors for dehalogenation. A solution technique is developed to determine the relationship between the influent and effluent concentrations. Emphasis is also given to methods determining the mass transfer coefficient at the cathode. The following assumptions were made in the model development of the model

1. Reaction is assumed to be mass transfer-limited rather than reaction-limited.
2.The aqueous solution used is assumed to be of high ionic strength.
3. The diffusion equation is developed for steady state condition so that sorption of contaminant to the electrode can be neglected.
4. All target chemicals are assumed to undergo first order degradation reaction. This assumption is probably incorrect as the potential varies along the length of reactor, but is adopted as a reasonable first approximation.

Determination of Diffusivity Constant

Estimation of the diffusivity constant D_l is closely related to the residence time of the reactor. An experimental study can be performed to determine the diffusivity by measuring the residence time of tracer. Assuming that the tracer is injected at time t=0, the concentrations of the tracer are determined at regular intervals at the outlet port. Let (t_i, C_i) be a set of tracer concentrations vs. time at the outlet. The sample variance is given by

$$S_c = \frac{1}{\tau^2_A}\left[\sum_{i=1}^{N}\frac{t_i^2\ C_i}{C_T} - \sum_{i=1}^{N}\frac{(t_i\ C_i)^2}{C_T^2}\right]$$

Where

$$\tau_A = \sum_{i=1}^{N}\frac{t_i\ C_i}{C_T}$$

$$C_T = \sum_{i=1}^{N} C_i$$

For a closed plug flow system,

$$S^2_C = 2\left[\frac{D_L}{\bar{v}\ L_R}\right] - 2\left[\frac{D_L}{\bar{v}\ L_R}\right]\left[1 - \exp\left\{\frac{\bar{v}L_R}{D_L}\right\}\right]$$

From this equation D_L can be determined by trial & error analysis.

Mass Balance

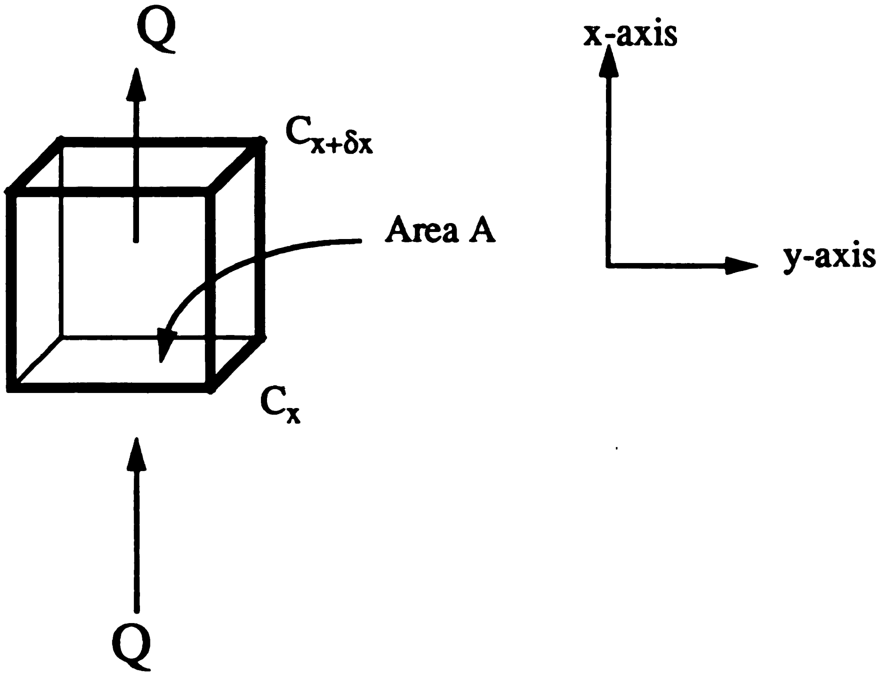


Figure B.3 Mass balance on a small element of electrochemical plug flow reactor.

In any small element of the reactor, the accumulation of the contaminant is a net result of mass coming in, mass going out, and degradation.

[Accumulation] = [Mass In] - [Mass Out] - [Reaction]

[Accumulation] = $(A\ \delta x\ \varepsilon)\ \delta C$

[Mass In] = $Q\ C_x\ \delta t - A\ D_H\ (\delta C/\delta x)_x\ \delta t$

[Mass Out] = $Q\ C_{x+\delta x} - A\ D_H\ (\delta C/\delta x)_{x+\delta x}\ \delta t$

[Reaction] = $(r_c\ A\ \delta x)\ \delta t$

The total shell balance equation can be written as

$$(A\ \delta x\ \varepsilon)\ \delta C = [Q\ C_x\ \delta t - A\ D_H\ (\delta C/\delta x)_x - Q\ C_{x+\delta x} + A\ D_H\ (\delta C/\delta x)_{x+\delta x} - (r_c\ A\ \delta x)]\ \delta t$$

Dividing both sides of the equation by A $\delta x \delta t$

$$\varepsilon\, \delta C/\delta t = (Q/A)\,(C_x - C_{x+\delta x})/\delta x - D_H\,[(\delta C/\delta x)_{x+\delta x} - (\delta C/\delta x)_x]\,/\delta x - r_c$$

Clearly if $\delta x \rightarrow 0$, then $\delta t \rightarrow 0$ and thus

$$\delta C/\delta t = dC./dt$$

$$(C_x - C_{x+\delta x})/\delta x = dC/dx$$

$$[(\delta C/\delta x)_{x+\delta x} - (\delta C/\delta x)_x]\,/\delta x = -d^2C/dx^2$$

Hence the expression

$$dC/dt = (D_H/\varepsilon)\, d^2C/dx^2 - (v/\varepsilon)\, dC/dx - r_c/\varepsilon$$

Where

$$(D_H/\varepsilon) = D_L$$

$$(v/\varepsilon) = \bar{v}$$

The final equation is

$$dC/dt = D_L\, d^2C/dx^2 - \bar{v}\, dC/dx - r_c/\varepsilon$$

Assuming steady state, the equation reduces to

$$\boxed{D_L\, d^2C/dx^2 - \bar{v}\, dC/dx - r_c/\varepsilon = 0}$$

Boundary Conditions

In order to solve this differential equation, two boundary conditions are needed. These boundary conditions can be obtained as follows

Assuming C_0 is the concentration of the contaminant entering the reactor at x=0. The concentration at the entrance is reduced by diffusion and is given by

$$\boxed{\bar{v}\, C_{entrance} = \bar{v}\, C_0 + D_L\, dC/dx \qquad \text{at } x=0}$$

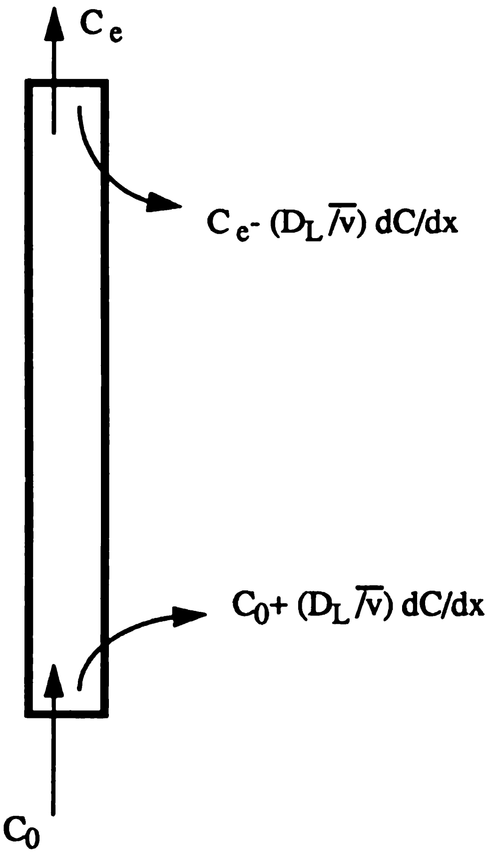
is the first B.C.

Similarly at the outlet x=L

$$\bar{v}\, C_{outlet} = \bar{v}\, C_e - D_L\, dC/dx \qquad \text{at } x=l$$

in this case two possibilities exit

1. $dC/dx < 0$, which implies that the concentration at the exit is greater than the concen tration at end point in the reactor.
2. $dC/dx > 0$, in this case concentration has to pass through a minimum value somewhere in the reactor before rising at the d/s end.



It if quite obvious that none of the above possibilities is feasible and hence it is correct to assume that

$$\boxed{dC/dx = 0, \text{ at } x\text{-}L}$$

which is the second B.C.

Using these two boundary conditions the differential equation can be solved.

Appendix C.

Calibration constants for volatile products and chloride analysis

b_0= is the intercept of the linear calibration curve
b_1= is the slope of the linear calibration curve
r^2= is the coefficient of correlation of the linear calibration curve

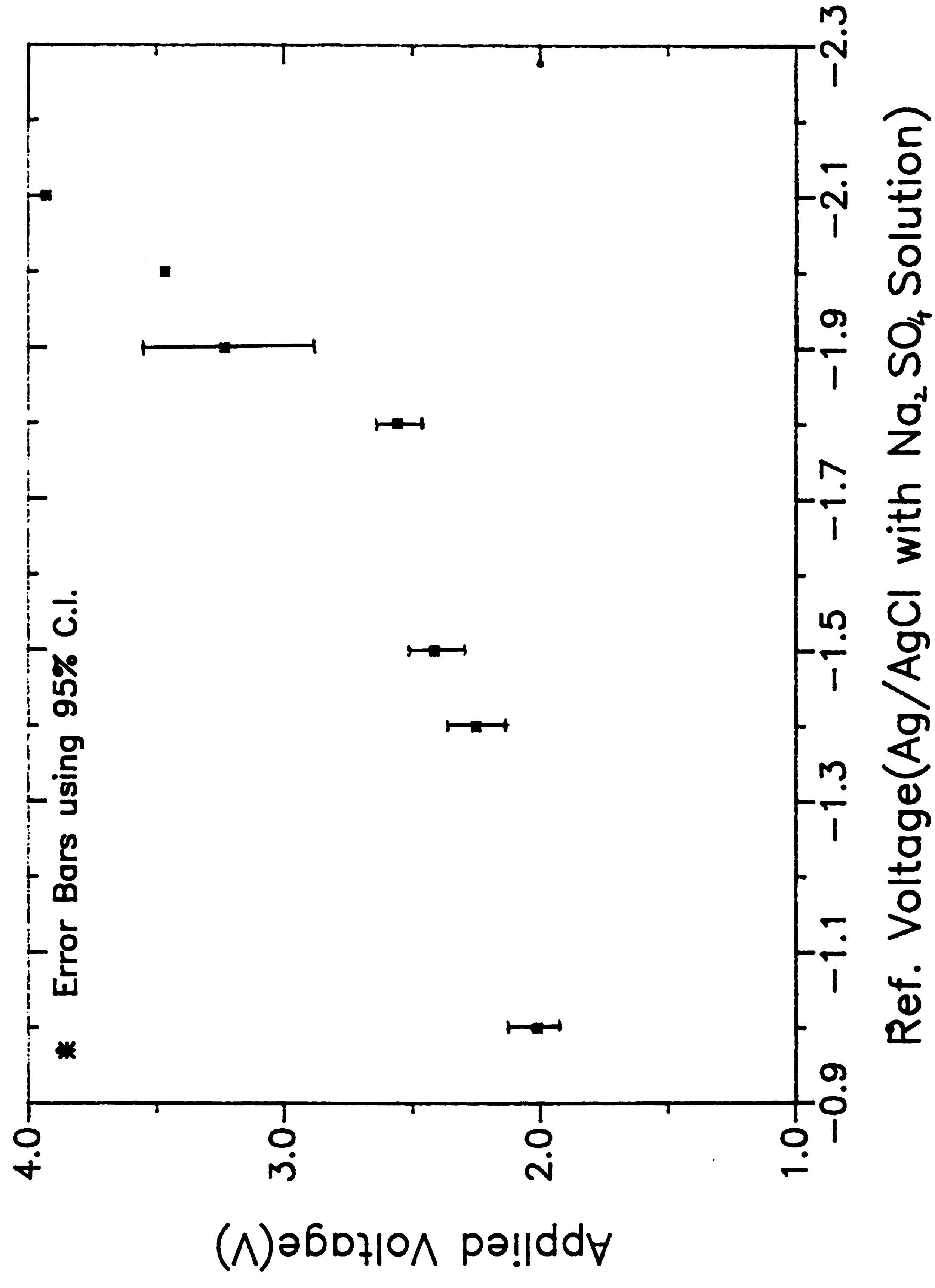
Expt. No.	Target Chemical	Analytes	Calibration Constants					
			Low Range			High range		
			b_0	b_1	r^2	b_0	b_1	r^2
1	PCE	PCE				-0.984	0.472	0.997
		TCE				-0.421	0.358	0.995
		Chloride				241.7	-57.71	0.998
2	PCE	PCE				0.831	0.564	0.994
		TCE				0.240	0.421	0.996
		Chloride				235.8	-56.34	0.998
3	PCE	PCE				-0.236	0.459	0.992
		TCE				0.132	0.439	0.995
		Chloride				240.9	-55.33	0.998
4	PCE	PCE				0.352	0.882	0.994
		TCE				0.048	0.687	0.997
		Chloride				225.5	-56.75	1.000
5	PCE	PCE				-0.780	1.235	0.997
		TCE				-0.231	0.632	0.996
		Chloride				254.9	-55.95	0.999
6	PCE	PCE				2.151	0.776	0.992
		TCE				0.800	0.564	0.994
		Chloride				234.5	-58.28	1.000
7	PCE	PCE				1.278	1.464	0.993
		TCE				-0.456	0.983	0.994
		Chloride				243.9	-58.98	0.997
8	PCE	PCE	0.23	0.25	0.997	0.874	0.678	0.995
		TCE	0.12	0.29	0.992	0.954	0.547	0.993
		Chloride				242.2	-57.63	0.998
9	PCE	PCE	0.32	0.46	0.998	1.437	0.897	0.991
		TCE	0.09	0.32	0.996	-0.125	0.792	0.995
		Chloride				231.3	-55.73	0.997

Expt. No.	Target Chemical	Analytes	Calibration Constants					
			Low Range			High Range		
			b_0	b_1	r^2	b_0	b_1	r^2
10	TCE	TCE				0.892	1.223	0.994
		Chloride				187.6	-58.53	0.998
11	TCE	TCE				1.259	0.889	0.992
		Chloride				182.3	-55.44	0.997
12	TCE	TCE				-1.473	0.759	0.995
		Chloride				177.6	-62.15	0.996
13	TCE	TCE				-1.629	0.658	0.991
		Chloride				193.2	-60.22	0.998
14	TCE	TCE				1.438	0.626	0.992
		Chloride				211.0	-54.32	0.999
15	CT	CT	-0.279	0.435	0.995	2.102	1.127	0.990
		CF	-0.173	0.218	0.996	1.148	0.874	0.993
		MC				-1.293	0.795	0.994
		CM				-1.434	1.674	0.991
		Chloride				198.7	-56.73	0.999
16	CT	CT	0.375	0.227	0.995	1.133	0.674	0.994
		CF	0.673	0.216	0.995	1.189	0.885	0.985
		MC				0.455	0.628	0.990
		CM				-1.936	1.199	0.989
		Chloride				205.3	-55.91	0.996
17	CT	CT	-0.011	0.476	0.992	1.876	0.983	0.994
		CF	0.453	0.589	0.995	1.342	1.167	0.994
		MC				-1.248	0.467	0.993
		CM				-2.865	2.934	0.991
		Chloride				189.2	-56.49	0.999
18	CT	CT	0.468	0.593	).996	-0.452	1.797	0.992
		CF	-0.349	0.461	0.992	1.456	1.820	0.995
		MC				2.348	0.893	0.991
		CM				3.484	2.010	0.991
		Chloride				215.9	-57.26	1.000
19	CT	CT	0.226	0.401	0.992	0.923	0.648	0.996
		CF	-0.986	0.276	0.990	-0.673	0.597	0.992
		MC				-2.174	3.245	0.991
		CM				-1.639	3.469	0.989
		Chloride				186.5	-55.18	0.995

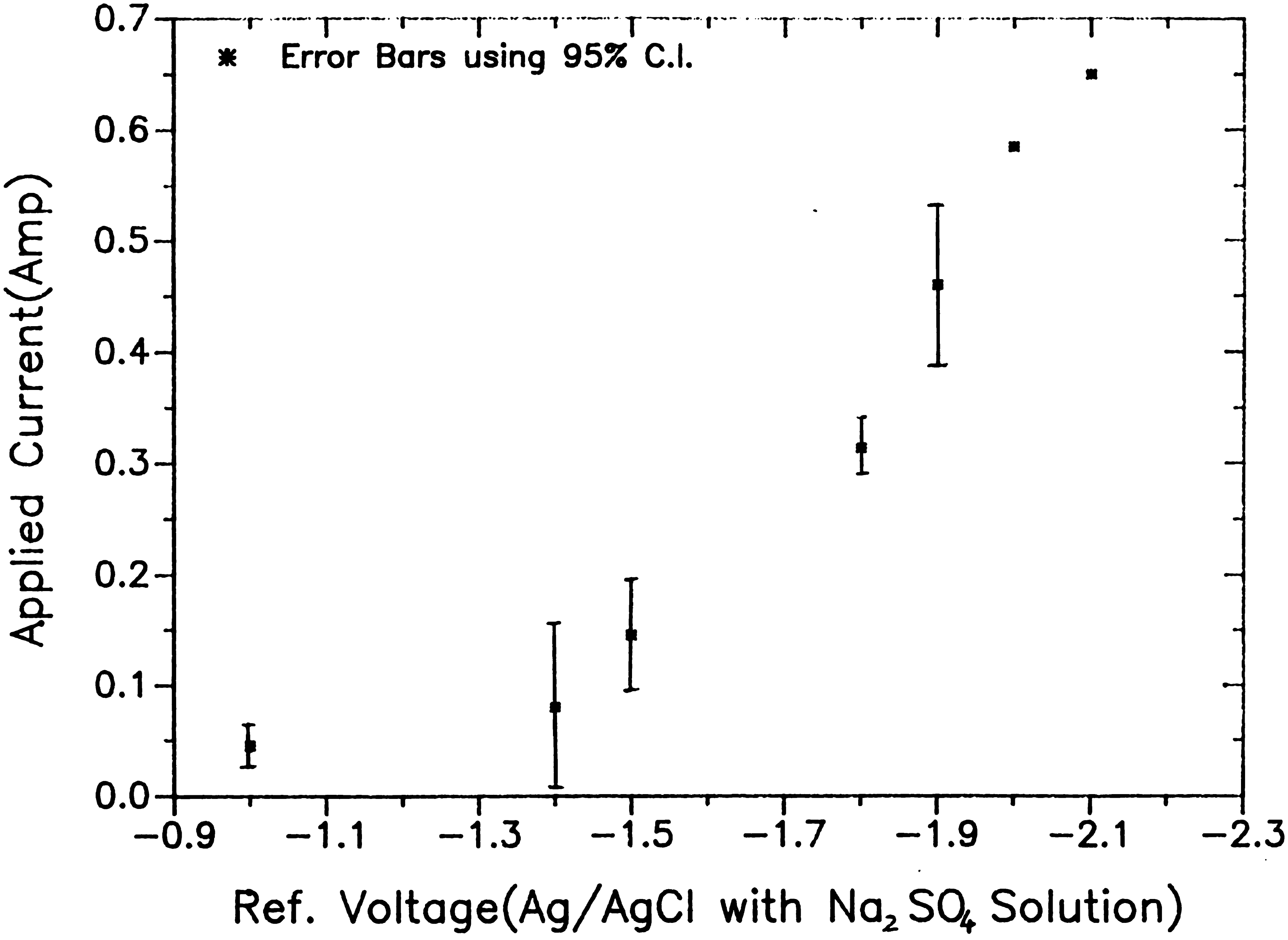
Expt. No.	Target Chemical	Analytes	Calibration Constants					
			Low Range			High Range		
			b_0	b_1	r^2	b_0	b_1	r^2
19	CF	CF				-1.453	2.45	0.990
		MC				0.284	3.76	0.984
		Chloride				213.8	-54.9	0.995
20	CF	CF				-2.45	2.629	0.993
		MC				-1.659	3.429	0.994
		Chloride				223.9	-60.1	0.998
21	CF	CF	-0.267	0.887	0.993	-1.342	1.491	0.991
		MC				-4.350	2.243	0.994
		Chloride				213.9	-59.0	0.998
22	CF	CF	1.134	1.274	0.991	0.259	2.450	0.986
		MC				-2.041	3.331	0.996
		Chloride				205.9	-57.4	0.999
23	CF	CF	-0.532	1.956	0.994	2.225	1.848	0.992
		MC				4.672	2.529	0.995
		Chloride				245.0	-59.4	1.000
24	CF	CF	-1.126	1.786	0.996	1.593	2.560	0.991
		MC				2.864	2.652	0.990
		Chloride				234.0	-58.2	0.995

Appendix D

STATISTICAL ANALYSIS



Applied Voltage(V)
4.0
3.0
2.0
1.0
−0.9
−1.1
−1.3
−1.5
−1.7
−1.9
−2.1
−2.3
Ref. Voltage(Ag/AgCl with Na₂SO₄ Solution)
✱ Error Bars using 95% C.I.


Error Bars using 95% C.I.
Applied Current(Amp)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
−0.9
−1.1
−1.3
−1.5
−1.7
−1.9
−2.1
−2.3
Ref. Voltage(Ag/AgCl with Na_2SO_4 Solution)