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EXECUTIVE SUMMARY

This study was directed towards the development of a cost-effective technology for removing/degrading polychlorinated biphenyls (PCBs) from 001-Outfall surface water at the Paducah Gaseous Diffusion Plant (PGDP). Both batch and column experiments showed that palladized iron (Pd/Fe) can be used as a reactive material to treat PCB-contaminated aqueous solutions at room temperature. The reductive degradation rates with the bimetallic substrate are several orders of magnitude higher than those observed for biodegradation processes. Furthermore, in contrast to high-temperature processes where dioxins and furans are potentially produced, the major by-product of dechlorination by palladized iron is biphenyl, which is substantially less toxic than the parent compounds.

A PCB congener, 2,3,2',5'-tetrachlorobiphenyl (TeCB) dissolved in a 20% acetone/water solution was rapidly and completely dechlorinated by 100-mesh iron filings (Fisher Scientific) palladized at 0.25%. Half-lives measured in the batch dechlorination experiments were on the order of 0.10 to 0.17 h (6 to 10 min). The addition of iron oxide colloids to the acetone/water solution did not appear to significantly affect PCB dechlorination, while higher temperature (60°C) enhanced reaction rates. Rapid dechlorination of 2,3,2',5'-TeCB was also observed with iron foam aggregates (Cercona) palladized at 0.25%, with half-lives of 124 and 1.8 min measured from the batch and the column study, respectively. PCB dechlorination using palladized 40-mesh iron filings was found to be slow at 0.25% Pd, and appeared to be absent when the iron contained 0.05% Pd.

Arochlor 1260 congeners, which are present at PGDP 001-Outfall, were completely transformed to biphenyl by 100-mesh iron filings palladized at 0.25% when the congeners were dissolved in a 20% acetone/water solution.

Hydrogen gas formed by the oxidation/corrosion of zero-valence iron (Fe^0) appears to be a critical component in the dechlorination of PCBs by palladized iron. A significant gas generation was observed corresponding to the rapid dechlorination in the batch experiments with palladized 100-mesh iron filings (0.1%- and 0.25%-Pd) and palladized Cercona iron-aggregates (0.25%-Pd). Gas generation was not obvious with unpalladized 100-mesh filings, nor with 40-mesh palladized (0.05%, 0.25%) iron filings. The hydrogen

gas is generated by the oxidation/corrosion of Fe^0, a reaction that can be accelerated by Pd (i.e. galvanic corrosion). This reaction was suppressed in the 40-mesh iron because of the presence of a passivation (oxide) layer and a low surface Fe^0 content. High surface Pd and Fe^0 content appeared to be critical to the reactivity of iron filings towards PCBs.

Partitioning of PCB congeners onto iron from a 20% acetone/water solution is not significant. The measured partition coefficient for 2,3,2',5'-TeCB onto iron was on the order of 0.5 to 0.6 L/kg. Published sorption coefficients for 2,3,2',5'-TeCB on sediments from water are as high as $10^{5.6}$ L/kg. The binding of PCBs to soils and sediments is assumed to be from interactions with natural organic matter. On the other hand, PCB sorption on iron is most likely through PCB binding on mineral (iron and iron oxide) surfaces. In addition, the acetone present at a high concentration favors the dispersion of 2,3,2',5'-TeCB in solution.

Based on the PCB degradation rates measured in this study, flow-through reactors (filled with both Cercona foam-aggregates and 100-mesh iron palladized to 0.1 to 0.25%) can potentially be used to dechlorinate PCBs dissolved in PGDP 001-Outfall surface water. Cercona foam aggregates are more promising because of a higher conductivity compared to the 100-mesh iron filings.

The following are recommendations for future work prior to implementing PCB dechlorination by palladized iron at the PGDP 001-Outfall:

1. Column studies with varying reactor lengths, flow rates and PCB concentrations must be conducted to determine removal rate constants using palladized Cercona iron aggregates and 100-mesh iron filings. The reactive life of the bimetallic materials must be quantified, through long-term column experiments coupled with surface analysis of the spent materials.

2. If additional column studies confirm rapid dechlorination and the reagent capacities are reasonably high, a larger-scale pilot test of a plug-flow column should be designed and executed using field-contaminated water.

3. Detailed surface analyses of the reacted Pd/Fe should be conducted to elucidate reaction mechanisms as well as to investigate poisoning of bimetallic materials. Practical methods must be identified to regenerate spent bimetallic materials.

4. Other reactor configurations (e.g., fluidized bed) should be considered as alternatives to a column plug-flow reactor, particularly if clogging problems are encountered when using very fine iron particles in the column experiments.

5. Detailed batch and column experiments using single and multiple PCB congeners in surfactant/co-solvent solutions should be performed in order to extend this work to the remediation of PCB-contaminated soils.

1. INTRODUCTION

1.1 Existing Remediation Technologies for Polychlorinated Biphenyls

Contamination from polychlorinated biphenyls (PCBs) is a persistent problem within the Department of Energy complex, as well as in numerous industrial sites around the US. To date, commercially available technologies for destroying these highly stable compounds involve degradation at elevated temperatures either through incineration or base-catalyzed dehalogenation at 300°C [1,2]. Since the heating required with these processes substantially increases the costs for treatment of PCB-contaminated wastes, there is a need for finding an alternative approach where PCB can be degraded at ambient temperatures. In addition, degradation at high temperatures can lead to the production of more toxic compounds such as dioxins and furans. Aerobic and anaerobic biodegradation by indigenous organisms at contaminated sites has been explored [3,4]. However the kinetics of biological processes have been slow (half-lives on the order of weeks), and complete dechlorination of PCBs has been difficult to achieve [20].

The reductive dehalogenation of low-molecular weight chlorinated hydrocarbons [e.g., trichloroethylene (TCE)] by zero-valence iron and bimetallic substrate (e.g., iron/ palladium) is well documented in the literature [5-8]. The palladized iron (Pd/Fe) substrate caused more complete dechlorination of TCE at rates that were 1-2 orders of magnitude more rapid when compared with reduction by iron alone [6,7]. Based on the remarkable performance of Pd/Fe with TCE, the potential for dechlorinating the more recalcitrant PCBs was recently tested by researchers at the University of Arizona [9]. Previous work had already shown that PCB dechlorination with iron alone was possible only at high temperatures [10]. In the experiments conducted at University of Arizona, palladium (Pd) was deposited on iron particles that were <10 µm in diameter (Pd content was 0.05% of iron). Two grams of these palladized iron particles were then added to 5-mL of a 20-mg/L PCB (Arochlor 1260 or 1254) solution containing 20% methanol, 32% acetone and 48% water. Dechlorination at room temperature was inferred from the disappearance of PCB congeners, as well as the detection of biphenyl—the final dechlorination by-product. These early results demonstrated the potential for using Pd/Fe to dechlorinate PCBs; the work described here further develops this potential through more extensive experiments.

1.2 Objectives and Scope

This study was directed towards the development of a cost-effective technology for removing/degrading PCBs from 001-Outfall surface water at the Paducah Gaseous Diffusion Plant (PGDP). In addition, the results from this study can also be applied to other sites having effluent streams containing PCBs. The objectives of this work are: (1) to investigate the feasibility/effectiveness of Pd/Fe to remove/degrade PCBs from 001-Outfall surface water, and (2) to determine PCB degradation rates and dechlorination by-products using various combinations of iron-filing sizes and Pd contents.

Aside from the treatment of PCB-contaminated aqueous media, Pd/Fe can potentially degrade PCBs in fluids (gaseous or liquid) generated by solid-phase extraction processes such as surfactant/co-solvent soil washing, low temperature thermal desorption (LTTD), or liquified gaseous extraction (LGE). Among the three extraction processes, the extract generated by surfactant/co-solvent soil washing is most similar to the aqueous solutions used in this study. As such, the results of this study can be used to develop a surfactant washing-based remediation technology for PCB-contaminated soil at PGDP switchyards.

This report is organized as follows: Section 2 contains a description of the experimental methods used at Oak Ridge National Laboratory (ORNL) for dechlorination tests, partition coefficient measurements, and for a column study. The results of these experiments are described in Section 3, and a discussion of these results are presented in Section 4. Section 5 summarizes PCB dechlorination experiments that were conducted in surfactant and co-solvent solutions at the University of Arizona. Surface analyses were also performed at the University of Arizona, and the results are presented in Section 6. Finally, conclusions of this study and recommendations for further work are given in Section 7.

2. EXPERIMENTAL METHODS

A majority of the experiments in this study consisted of batch tests to characterize PCB dechlorination by various combinations of iron filing types and Pd content. A single PCB congener, 2,3,2',5'-tetrachlorobiphenyl (TeCB) was used in the study to quantify degradation rates and identify dechlorination by-products. Arochlor 1260 was also used in the investigation to demonstrate the ability of Pd/Fe to completely dechlorinate all the congeners present in a PCB mixture.

PCBs are extremely hydrophobic, having very low aqueous solubility and a high affinity for solid surfaces [11]. To evaluate degradation of PCBs in aqueous solutions, acetone was used to disperse the organic compounds in water. The use of 20% acetone/water solutions also reduced errors introduced by the adsorption of TeCB on the glass reactor vessels.

2.1 Dechlorination Experiments

Subsampling procedure-- Initial dechlorination experiments were conducted following the subsampling protocol developed for TCE [6]. In these initial experiments, a known volume (140 mL) of 2,3,2',5'-TeCB/acetone/water solution was combined with iron filings (10 g) in 150-mL Teflon bottles. Samples were collected by withdrawing 1-mL aliquots of the aqueous solution with a syringe for determining dissolved 2,3,2',5'-TeCB. These aliquots were then extracted with 1 mL of hexane, and the extracts were analyzed for PCBs on a gas chromatograph equipped with an electron capture detector (GC/ECD).

Sacrificial Sampling-- In this procedure, multiple small-volume vials were prepared, and were sacrificially extracted and analyzed at specified reaction time intervals. Each reactor consisted of a 12-mL glass vial with a Teflon-lined silicone septum cap. Prior to an experiment, a number of glass vials were filled with either 2-g of palladized or unpalladized iron filings. Stock solutions were made by dissolving TeCB in methanol. The stock solutions were then used for preparing 1 to 2 mg/L (3.5-7 μM) TeCB in 20% acetone/water. These solutions were prepared in 150-mL Teflon bottles and stirred with a Teflon-coated stir bar for at least 30 minutes. Five-mL of this TeCB solution were then added to each of the 12-mL vials pre-filled with Pd/Fe or iron filings (iron control). A number of 12-mL vials were filled with solution alone to serve as blank controls. The vials were then placed on a reciprocal shaker until they were extracted.

To monitor the degradation of TeCB with time, duplicate Pd/Fe vials were sacrificially-analyzed at pre-determined time intervals using the following extraction procedure: (1) 2-mL of methanol were added to the vials being extracted, (2) the vials were then vortexed for 5-min, (3) 4-mL of hexane were added to each vial, and (4) the vials were placed back on the reciprocal shaker. Twenty-four hours after the hexane was added to the vials, 1-mL aliquots of the hexane extracts were removed from the vials and were placed in 1.5-mL autosampler vials.

Analysis of the hexane extracts were then performed on a gas chromatograph (GC, HP5890, Series II, Hewlett-Packard, Wilmington, DE) with an electron capture detector (ECD). The initial oven temperature was set at 150°C for 1-min. It ramped to 175°C at 10°C/min, to 220°C at 1.3°C/min, and to 240°C at 10°C/min. The injector temperature was set at 275°C, detector at 300°C. The carrier gas was helium; make-up gas was nitrogen; flow rates were 2 mL/min through the column, make-up gas at 64 mL/min, anode purge at 9 mL/min. The GC was equipped with a 0.32 mm column (HP-5, Hewlett-Packard, Wilmington, DE). For biphenyl analysis, a flame ionization detector (FID) was used on the same GC and using the same type of column (HP-5). The oven temperature was initially set at 100°C for 0.5-min, ramped to 219°C at 10°C/min, to 225°C at 1°C/min, and to 280°C at 30°C/min. The carrier gas was helium (1 mL/min), and make-up gas was nitrogen (22 mL/min). The GC was calibrated for retention times and concentrations using single-congener standard solutions obtained from Ultra Scientific.

Blank (no iron) controls and iron (unpalladized) controls were also extracted following the same procedure during each of the batch tests. Since the entire contents of the vials/reactors were extracted with hexane, both the dissolved and adsorbed TeCB were quantified, and reductions in TeCB levels relative to the controls can be attributed to dechlorination.

2.2 Measurement of the Partitioning Coefficient for 2,3,2',5'-TeCB on Iron Filings

In this study, the partitioning coefficient of 2,3,2',5'-TeCB on iron surface was measured using the following procedure: (1) Teflon bottles were pre-filled with 50 mL of a 23% solvent/water solution that contained a fixed mass of 2,3,2',5'-TeCB, (2) varying amounts of iron (0, 5, 10 and 20 g) were added to these bottles, and (3) after a 24-h equilibration time, 1-mL aliquots were taken for aqueous 2,3,2',5'-TeCB determination. The sample was extracted with 1-mL of hexane and was subsequently analyzed on the GC. For a given mass of sorbent, the sorbed concentration (C_S, mg TeCB per kg of iron) was calculated as follows:

$$C_s = \frac{(C_0 - C_a)V}{m}$$

where m is the mass of sorbent, V is the volume of solution, C_0 is the initial concentration and C_a is the aqueous concentration at equilibrium. The partitioning coefficient, K_d, was then calculated as follows:

$$K_d = \frac{C_s}{C_a}.$$

2.3 Dechlorination of 2,3,2',5'-TeCB in a Packed Column

The column experiment set-up, schematically shown in Fig. 1, consisted of a 2.5-cm diameter glass chromatographic column, an HPLC pump, and sampling ports at the inlet and outlet ends of the chromatographic column. The column was wet-packed (using an unspiked 20% acetone/water solution) with 0.25% Pd, -1/8+1/16 Cercona foam aggregates to a depth of 2 cm. After flushing the packed column with several pore volumes of an unspiked 20% acetone/water solution, TeCB was introduced from a reservoir containing 0.5 mg/L of 2,3,2',5'-TeCB in a 20% acetone/water solution. One-mL aqueous samples were collected from the influent and effluent sampling ports at various times. All 1-mL aqueous samples were extracted with 1 mL of hexane for 24 hours, and the extracts were subsequently analyzed on the GC/ECD and GC/FID.

After the column test, residual PCBs were extracted from the column material (~15 grams) using 10 mL of methanol and 20 mL of hexane. The column hexane extract was analyzed on both the GC/ECD and GC/FID.

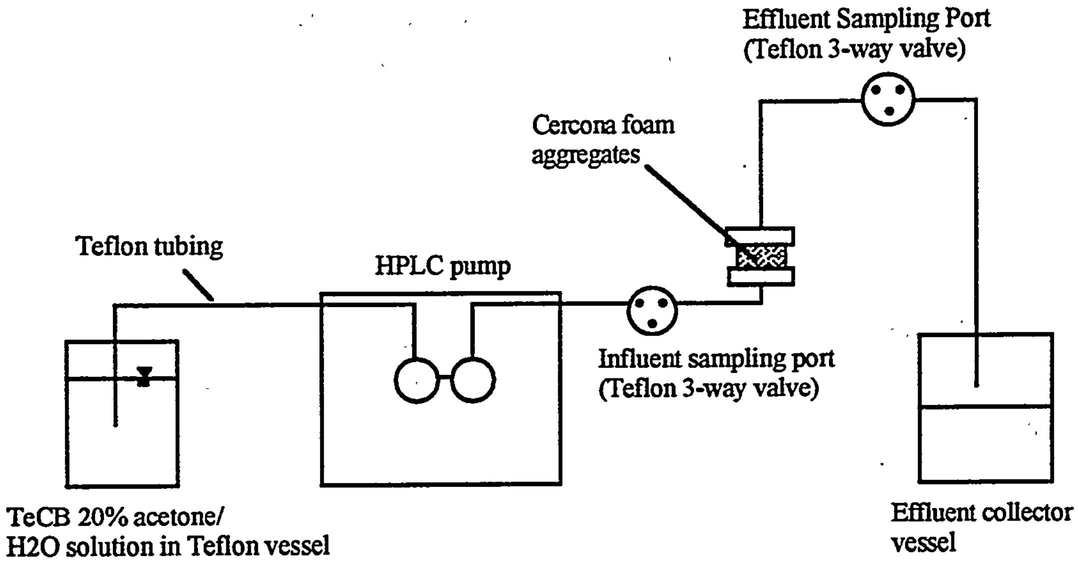


Figure 1. Schematic of set-up for column study.

3. RESULTS

3.1 Dechlorination Using the Subsampling Procedure

In the initial experiments where a subsampling procedure was used, TeCB levels decreased rapidly within an hour in both solutions with iron and Pd/Fe filings (see Fig. 2). Because dechlorination by-products were only detected in the solution combined with Pd/Fe, decreases in TeCB concentration measured in the solution with iron alone were mainly from adsorption. Although dechlorination can be inferred from the detection of less chlorinated biphenyls in the solution with Pd/Fe, adsorption complicates the derivation of dechlorination rates from data obtained from subsampling experiments. Consequently, sacrificial sampling was used in subsequent batch studies.

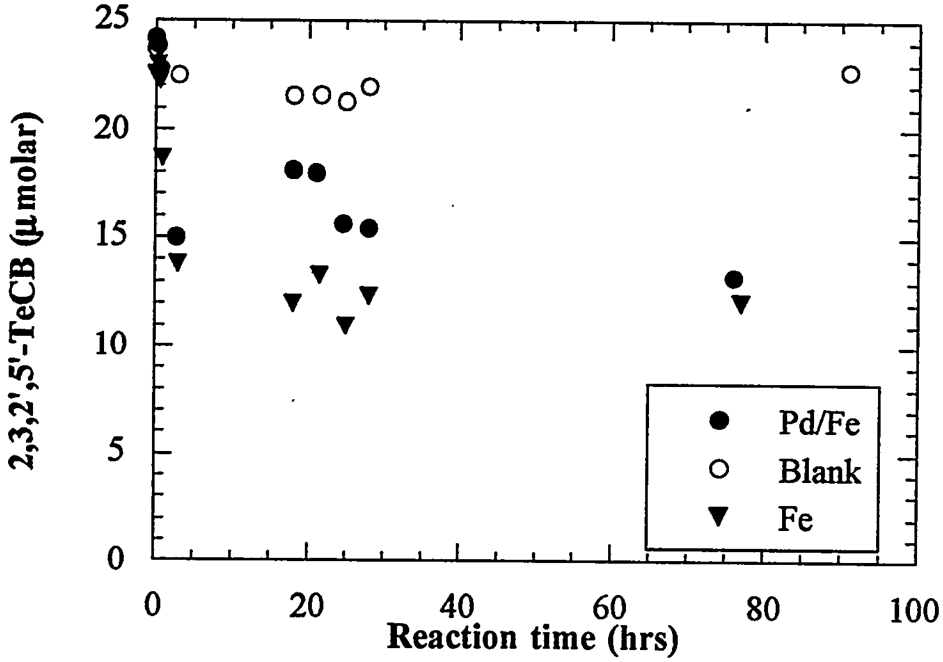


Figure 2. 2,3,2',5'-tetrachlorobiphenyl removal rates using palladized iron filings from subsampling procedure. Aqueous concentration of 2,3,2',5'-tetrachlorobiphenyl in 140 mL of 50% acetone/water solution. Pd/Fe: 10 g palladized iron filings. Fe-10 g unpalladized iron filings. Blank-no solids present.

3.2 Dechlorination Using the Sacrificial Sampling Procedure

PCB dechlorination using various combinations of Pd content and type of iron were characterized through a series of batch experiments using the sacrificial sampling procedure described in Section 2.1 (Table 1). Two types of tests were conducted: screening tests and comprehensive experiments with less frequent and more frequent sampling intervals, respectively. In general, screening tests were performed first to verify whether dechlorination will occur for untested combinations of iron type and Pd content. The comprehensive tests were conducted whenever dechlorination rates were desired. Only the results of the comprehensive tests are reported here.

Initial tests were also carried out to obtain an extraction procedure by using different proportions of solvents to extract 2,3,2',5'-TeCB from a solution. The best extraction efficiency was obtained when 2 mL of methanol and 4 mL of hexane were used to extract 4 mL of a 20% acetone/water solution (see Fig. 3). The methanol is believed to facilitate the desorption of the PCBs from iron surface into the aqueous solution, from which the PCBs transfer into the hexane. This extraction method was used for the rest of the experiments in this study.

Table 1. Summary of batch dechlorination experiments with zero valence iron

Iron Mesh Size[a]	Palladium Content	Initial PCB Concentration (mg/L)	Other Conditions[b]
40 (JM-2966)	0.05%	1.0	
40	0.25%	1.5	
100	0.25%	1.5	
100	0.25%	1.5	with colloids
100	0.25%	1.5	60°C
100	0.25%	1.0	Arochlor 1260
-100+200	0.10%	1.0	
-100+200	0.25%	1.0	
-1/8+1/16-in[c]	0.25%	1.0	

[a] "-100+200" indicates that filings pass through a 100-mesh size sieve but are retained on a 200-mesh size sieve.

[b] Unless otherwise noted, all experiments were conducted at room temperature using 2,3,2',5'-tetrachlorobiphenyl in 20% acetone/water solutions.

[c] Crushed Cercona iron foam.

3.2.1 Dechlorination by 40-mesh Iron Filings

PCB dechlorination using palladized 40-mesh iron filings was found to be very slow, and appears to be absent when the iron contain <0.05% Pd. Fig. 3 shows the rate of removal of 2,3,2',5'-TeCB in a 20% acetone/water solution in the presence of 40-mesh palladized (0.05%) iron filings. Concentrations of 2,3,2',5'-TeCB in solutions after the treatment with Pd/Fe were essentially identical to the aqueous concentrations measured in the presence of iron alone. Changes in measured concentration in the Pd/Fe and iron solutions were primarily a result of changes in extraction methods (see Fig. 3).

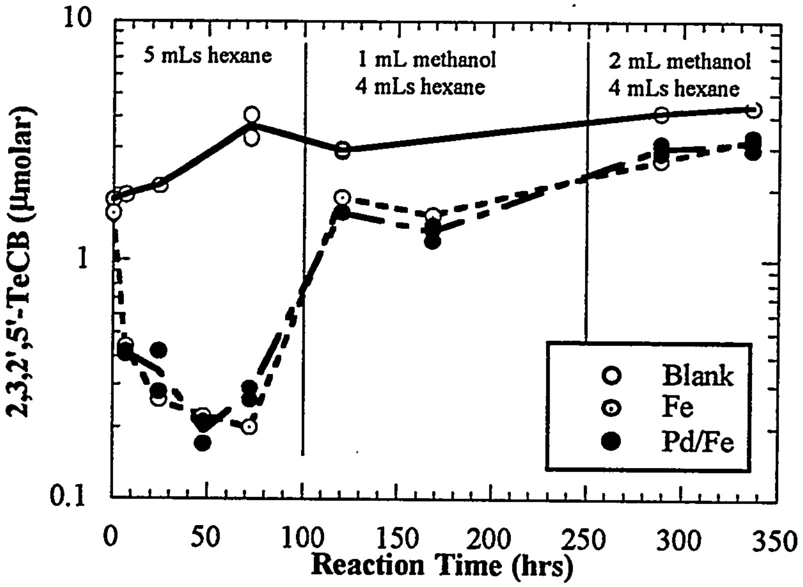


Figure 3. Reaction rate for 2,3,2',5'-tetrachlorobiphenyl with 40-mesh Pd/Fe (0.05%-Pd, JM2966). Initial concentration of TeCB was 1.0 mg/L (3.4 μM), dissolved in 20% acetone/water. Solution to solid ratio (w/w) was 2.5. Annotation along top of graph indicates extraction solvents used.

At increased palladium levels, a slow reaction was observed. Fig. 4 shows the decrease of 2,3,2',5'-TeCB in a 30-day batch study with 40-mesh Fisher iron filings which were palladized to a level of 0.25%. The dechlorination by-products were detected starting on the fifth day, with 2,3,2'-trichlorobiphenyl (TCB) predominating (Fig. 5). Changes in concentrations of the parent TeCB and its by-products were gradual, indicating a slow reaction rate. Near 100% carbon mass balances were achieved for this experiment.

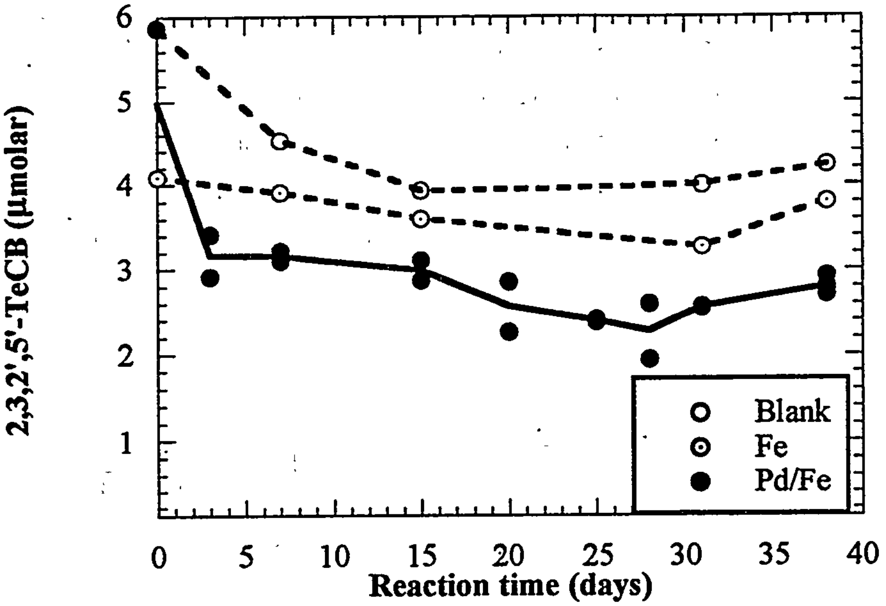


Figure 4. Effect of higher palladium content (0.25%-Pd) on the reaction rate of 2,3,2',5'-tetrachlorobiphenyl (40-mesh palladized Fisher iron). Initial concentration of TeCB was 1.5 mg/L (5.4 µM) in 20% acetone/water. Solution to solid ratio (w/w) was 2.5.

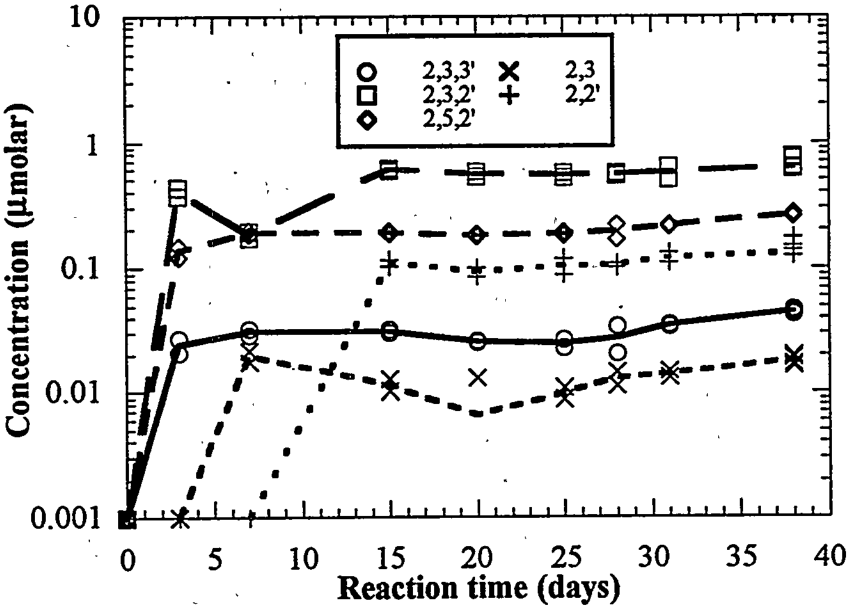


Figure 5. Dechlorination by-products of 2,3,2',5'-tetrachlorobiphenyl detected in 20% acetone/water solution with Pd/Fe filings (see Figure 4).

3.2.2 Dechlorination by 100-mesh Iron Filings

Fast dechlorination at 0.25%-Pd--After a screening test of 0.25% Pd -100-mesh Fisher iron filings showed complete dechlorination of 2,3,2',5'-TeCB from 20% acetone/water solution in 24 hours, a more comprehensive study with more frequent sampling intervals was conducted to better quantify the dechlorination rate. As shown in Fig. 6, 2,3,2',5'-TeCB was no longer detected after 2 h, and was completely transformed to biphenyl in 10 h. Chlorinated by-products included 2,5,2'-TCB, 2,3,2'-TCB, 2,2'-dichlorobiphenyl (DCB), 2,3-DCB, and 2-chlorobiphenyl (MCB); these were all removed from solution down to non-detect levels (approximately 0.001 μM) at 10 h.

Effect of colloids present in PCB solution--The effect of ferric oxyhydroxide colloids on PCB dechlorination was investigated in this study. PGDP 001-Outfall surface water has a high total solids content probably originating from rusted pipes along the drainage system. The sorption of PCBs onto these suspended solids may hinder dechlorination by Pd/Fe since the latter is a surface reaction. In this experiment, the 2,3,2',5'-TeCB 20% acetone/water solution was amended with hematite (Fe_2O_3) to a level of 20.3 mg/L. Dechlorination of 2,3,2',5'-TeCB in this solution was rapid, with TeCB levels decreasing almost two orders of magnitude in a half hour (Fig. 7). TeCB concentrations then reached plateau between 1/2 and 4 h, then dropped to non-detect levels at 5 h. The parent TeCB was completely transformed to biphenyl within 10 h. Dechlorination by-products shown in Fig. 7 are very similar to those detected earlier (Fig. 6). Degradation of the less chlorinated biphenyls appears to be slightly slower in the presence of the colloids when compared to the experiment without colloids, although these compounds still dropped down to non-detect levels after 10 h.

Effect of temperature--The effect of temperature on PCB dechlorination was conducted by heating the solutions to 60°C prior to the addition of Pd/Fe filings. The reaction vessels were kept at 60°C during the reactions. A 99% conversion to biphenyl occurred within 10 minutes (Fig. 8). Less than 1% of TeCB was present up to 2 h, but was no longer detected after 5 h. The peak concentrations of dechlorination by-products were lower than what was observed at room temperature (Figs. 6 and 7). This is attributed to the more rapid degradation of the lower chlorinated by-products at a higher (60°C) temperature. The decrease in biphenyl concentration over time (see Fig. 8) is possibly a result of volatilization and leakage through the vials' permeable silicone septum caps.

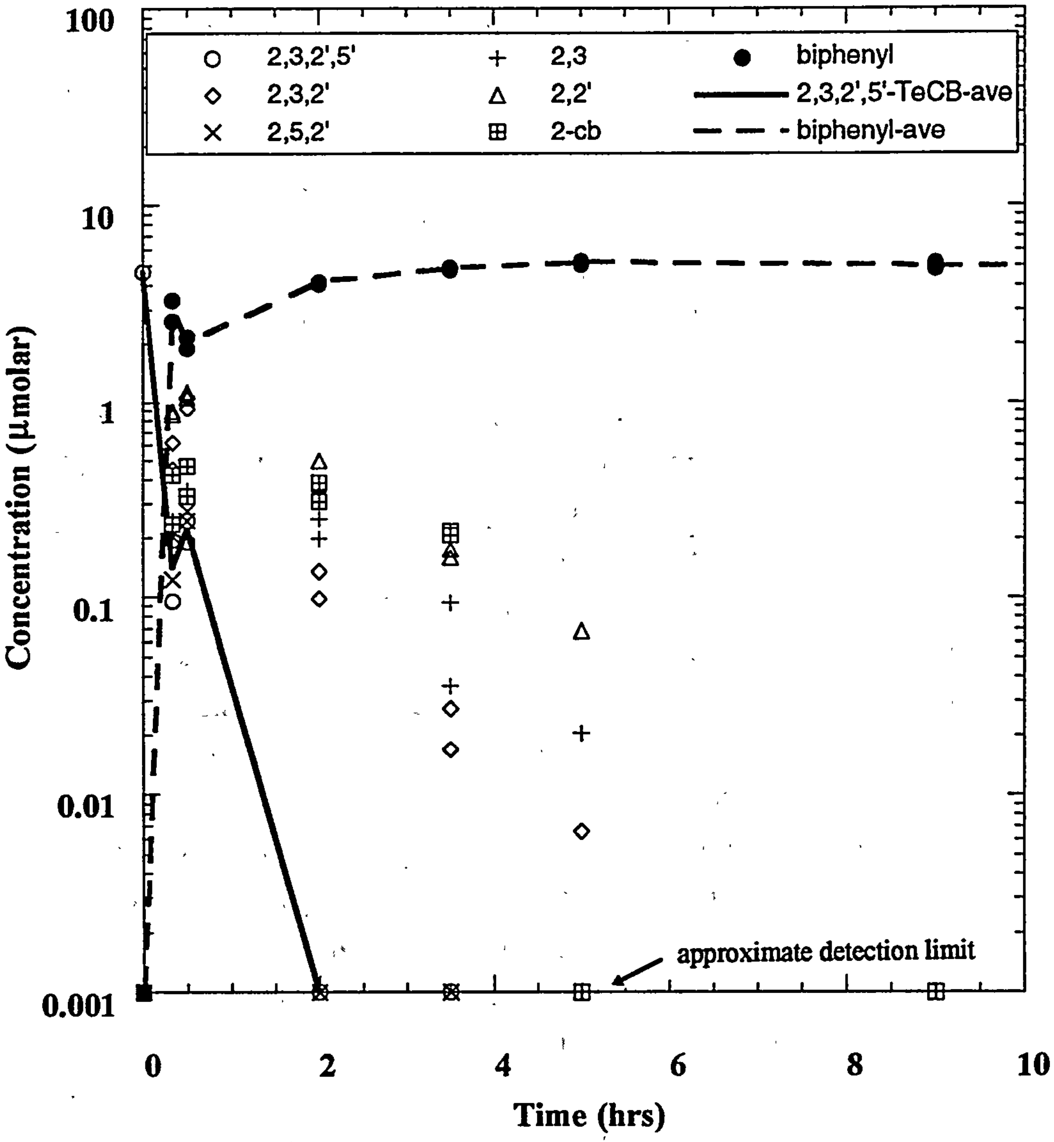


Figure 6. Effect of smaller iron particle size (100-mesh) on dechlorination by-products of 2,3,2',5'-tetrachlorobiphenyl. Initial TeCB was 1.5 mg/L (5.1 μM) in 20% acetone/water. Iron was palladized to 0.25% with 100-mesh Fisher iron. Solution to solid ratio (w/w) was 2.5. The dominant by-product was biphenyl.

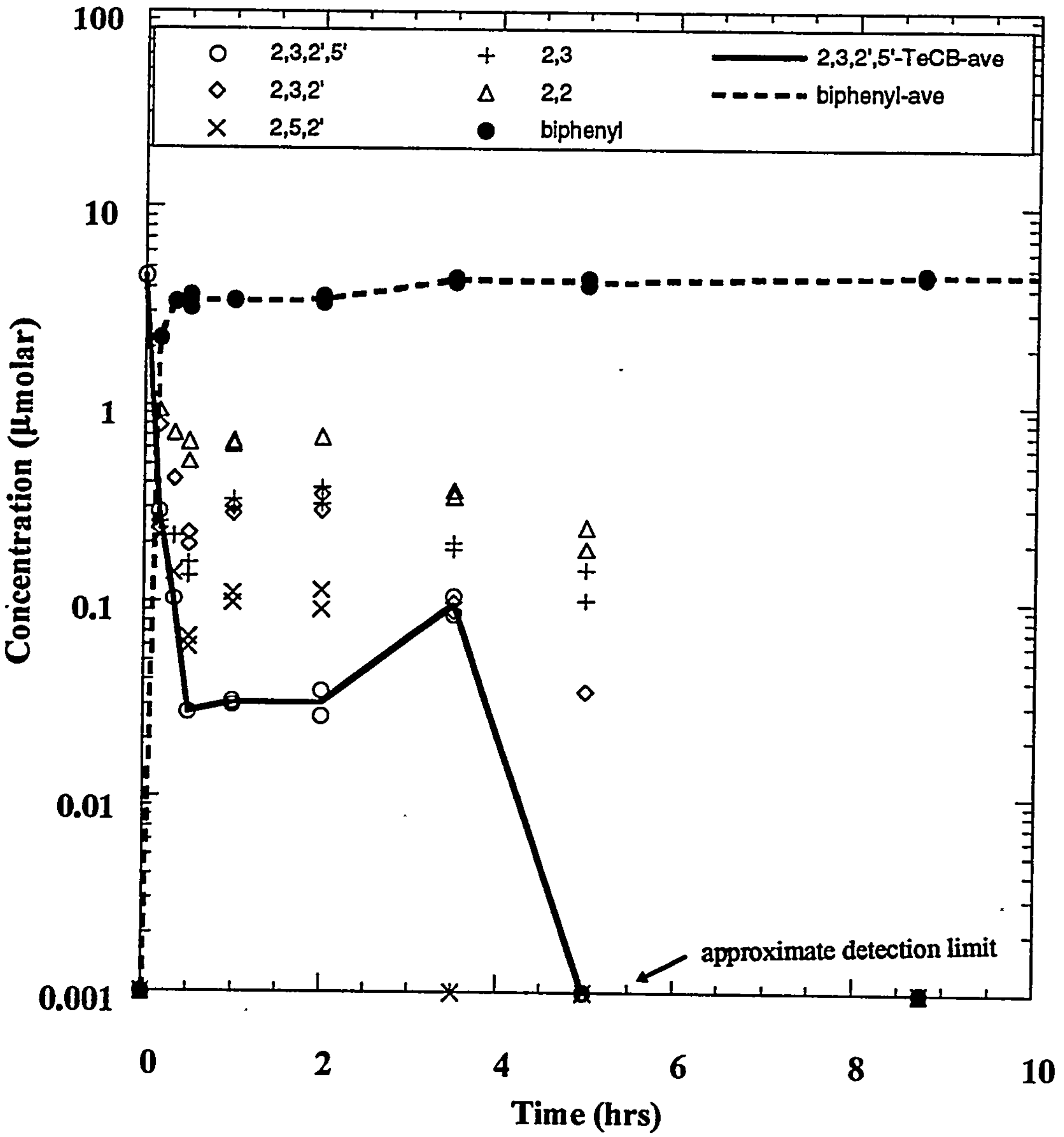


Figure 7. Effect of colloids on the by-product distribution in 20% acetone/water solutions during dechlorination of 2,3,2',5'-tetrachlorobiphenyl with Pd/Fe filings (0.25%-Pd, 100-mesh Fisher Fe). Solution to solid ratio (w/w) was 2.5. Initial TeCB was 1.5 mg/L (5.1 μM). Initial concentration of Fe_2O_3 colloid was 20 mg/L.

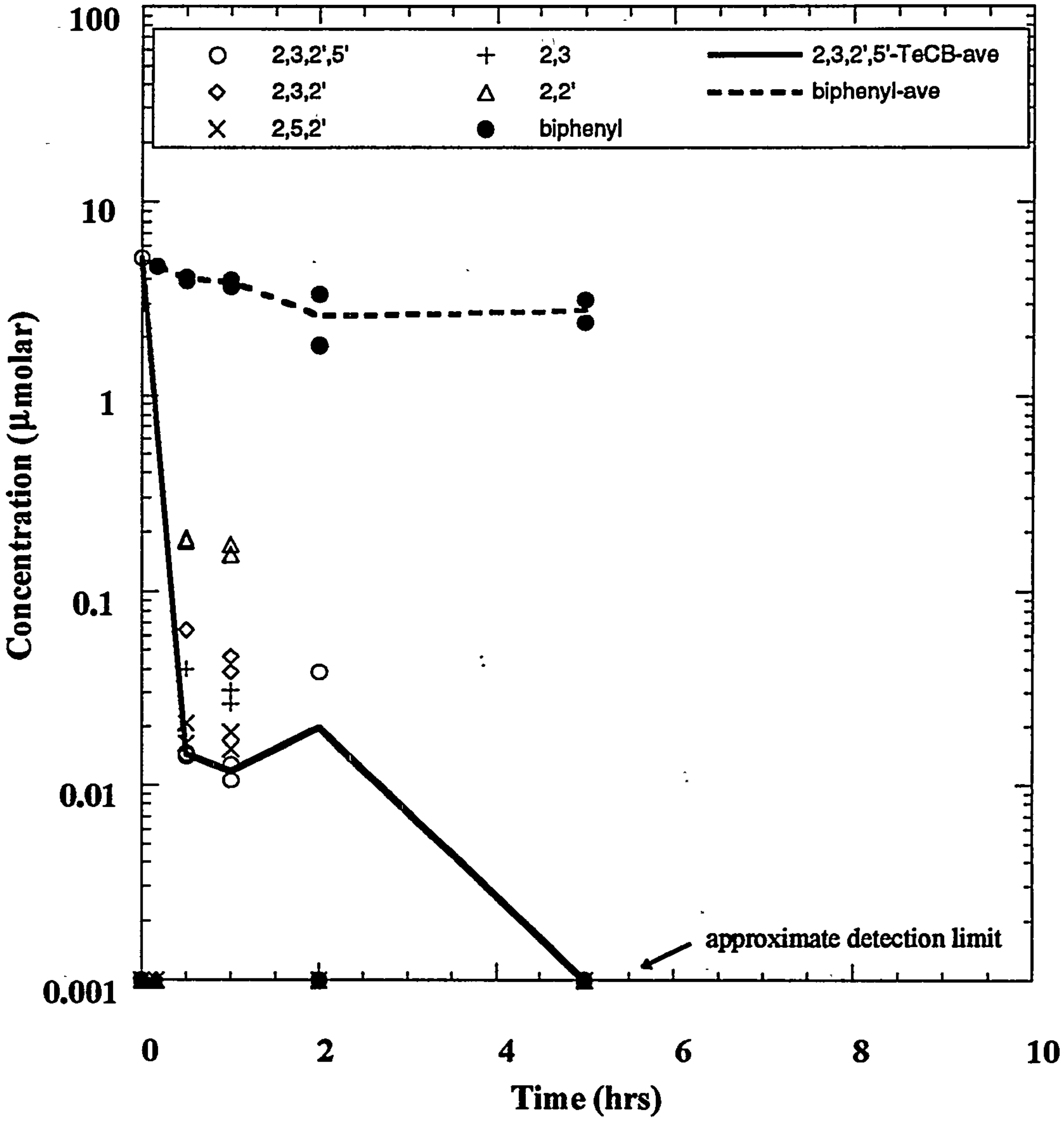


Figure 8. Temperature effect on the by-product distribution in 20% acetone/water solutions for 2,3,2',5'-tetrachlorobiphenyl dechlorination with Pd/Fe filings (0.25%-Pd, 100-mesh Fisher Fe). Solution to solid ratio (w/w) was 2.5. Initial TeCB was 1.5 mg/L (5.1 μM). Temperature was 60°C.

Effect of iron particle size--The batch studies described above showed that PCB dechlorination at room temperature was possible using an appropriate form of Pd/Fe filings. Such rapid PCB degradation at room temperature has never been observed before. For use at the PGDP Outfall, however, 100-mesh filings may not be a suitable material for a passive plug-flow reactor. Aside from large head losses and clogging which may be encountered using this fine-grained iron material, the 100-mesh filings also contained a significant amount of very fine iron particles that can be suspended by water flowing through a reactor.

A sieve analysis of 100-mesh Fisher filings showed that ~30% was retained on a 200-mesh sieve. Dechlorination of 2,3,2',5'-TeCB by palladized iron filings (0.25%) was investigated with the size fraction passing a 100-mesh and retained on a 200-mesh (-100+200-mesh). The reduction rates for 2,3,2',5'-TeCB (Fig. 9) were very similar to the unsieved filings (Fig. 6). A rapid degradation of TeCB within the first 30-minutes was observed, and after 8 h, the TeCB was undetectable. The by-product distribution (see Fig. 9) is also similar to the unsieved filings (see Fig. 6).

Since previously palladized 100-mesh filings were used for the experiment shown in Fig. 9, it was important to verify the actual Pd content of the -100+200-mesh size fraction. Pd/Fe samples were digested with nitric acid (EPA Method 3050A), and were analyzed for Pd content using an inductively coupled plasma mass spectrometer (ICP-MS). The Pd content of the -100+200-mesh iron filings was almost three times that of the Pd content of the -200-mesh iron filings (Table 2). Pd appeared to have preferentially deposited on the larger filings, even though a larger proportion of the -100 mesh filings were finer than 200-mesh. Accordingly, the dechlorination is expected to occur faster with the fraction of -100+200 filings.

Table 2. Palladium content in size fractions of 0.25% Pd -100-mesh Fisher iron filings retained and passing a 200-mesh screen.

Sample No.	Size Fraction	Pd content (mg/kg)
1	-200	10.2
2a	-100+200	28.9
2b	-100+200	31.5

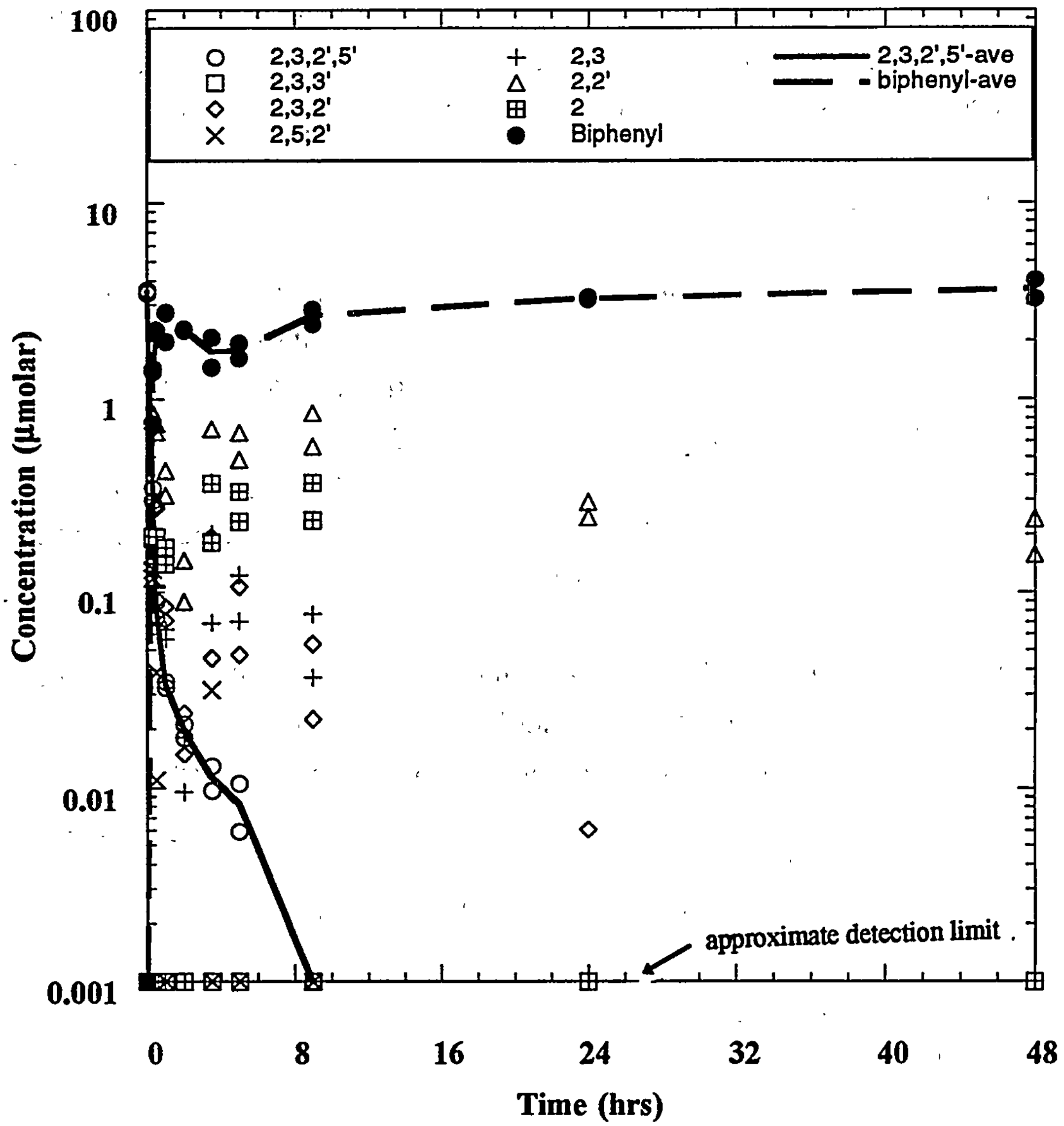


Figure 9. Effect of fine particle size (-100+200-mesh) on dechlorination by-products of 2,3,2',5'-tetrachlorobiphenyl with Pd/Fe filings (0.25%-Pd). Solution to solid ratio (w/w) was 2.5. Initial TeCB was 1 mg/L (3.4 µM) in 20% acetone/water solutions.

Effect of Pd content--Dechlorination of TeCB at a palladization of 0.25% on -100-mesh iron was observed to be very fast, thus offering a treatment solution at room temperature. Earlier results showed that the dechlorination was nonexistent and very slow at Pd loadings of 0.05% and 0.25%, respectively, using 40-mesh filings. Clearly both the iron particle size and the Pd loading affect the dechlorination rate. To investigate dechlorination at a lower Pd loading, a batch study was conducted using the -100+200-mesh size fraction of 100-mesh filings palladized at 0.1%. The dechlorination rates and by-product distribution with this material are illustrated in Fig. 10. Compared with higher Pd-loaded iron (Fig. 9), the initial disappearance of the parent TeCB is about the same. However, the residual TeCB (about 0.1% remaining) did not go below the detection limit after 48 hours.

Dechlorination by-products were similar in the solutions with iron palladized to 0.1% and 0.25%, except for 2,3,3'-TCB which was only detected at 10 minutes in the solutions with 0.25% Pd/Fe. However, the by-product distributions as a function of reaction time were quite different (Figs. 9 and 10). The less chlorinated biphenyls were disappearing at a slower rate in the 0.25% Pd/Fe, particularly 2,2'-dichlorobiphenyl which was not reduced to non-detect levels even after 48 h. Slower degradation in the 0.25% Pd/Fe was not expected because a higher Pd content should increase the reactivity of the iron filings. In fact, more rapid degradation in 0.25% Pd/Fe was noted in a preliminary study (data not shown). However, this 0.25% Pd/Fe that was used in the experiment shown in Fig. 9 had been palladized 2 months before the experiment was conducted, whereas the 0.1% Pd/Fe were palladized only 20 days before. The presence of an iron oxide/passivation layer on "aged" 0.25% Pd/Fe filings may have contributed to its reduced dechlorination power when compared to the more recently palladized 0.1% Pd/Fe filings. This is further discussed in Section 4.1.

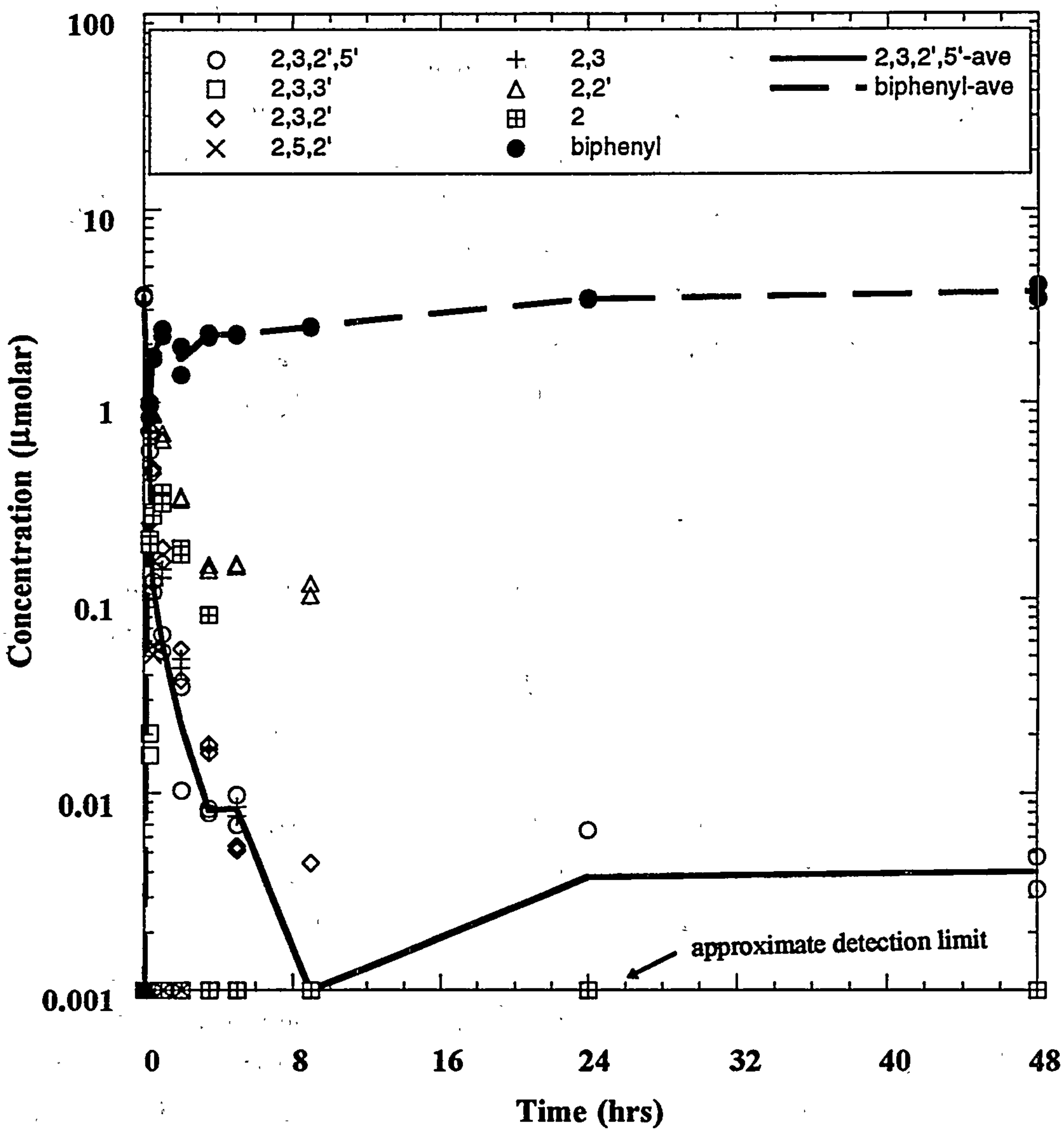


Figure 10. Same conditions as in Fig. 9, with reduced palladium content (0.1%-Pd). By-product distribution for 2,3,2',5'-tetrachlorobiphenyl dechlorination with -100+200 size fraction of 100-mesh Pd/Fe filings. Solution to solid ratio (w/w) was 2.5. Initial TeCB was 1 mg/L (3.4 µM) in 20% acetone/water solutions

Dechlorination of Arochlor--The experiments described above have demonstrated that 100-mesh Fisher iron filings with 0.25% Pd can completely dechlorinate 2,3,2',5'-TeCB in a 20% acetone/water solution. The dechlorination of a PCB mixture was investigated using a 1 mg/L of Arochlor in 20% acetone/water. This solution was prepared from a standard of 100-mg/L Arochlor 1260 dissolved in methanol (UltraScientific). Five-mL solutions were delivered into vials with 2-g of Pd/Fe filings (0.25% Pd -100 mesh Fisher), 2 g of 40-mesh iron filings (Fe control), and vials without solids (blank controls). After 5 and 24 h, Pd/Fe, iron and blank control vials were sacrificially analyzed as described in Section 2.1. These extracts were then analyzed on a GC/ECD and GC/FID. The temperature program used on the GC/ECD was revised to detect and separate the congeners in the Arochlor 1260 mixture.

Fig. 11 compares GC chromatograms for blank and iron control vials after 5 h, with the chromatograms for the Pd/Fe vials at 5 and 24 h. This figure shows that the congeners in an Arochlor 1260 mixture can be dechlorinated by 0.25% Pd, -100 mesh Fisher iron filings within 5 h. Dechlorination was also demonstrated by the presence of biphenyl in the Pd/Fe vial extracts, as detected by the GC/FID (see Fig. 12).

Gas evolution -- In all the batch studies with 100-mesh iron filings, significant gas generation was observed in the vials with palladized Fe. This was inferred from the observed bulging of these vials' septum caps as well as a distinct fizzing sound when these vials were opened. This was not true for the blank and iron control vials, nor was it observed in the vials with 40-mesh iron filings palladized at 0.05% and 0.25%. The 100-mesh filings were electrolytic grade, which contain higher Fe^0 than the 40-mesh iron. A higher rate of hydrogen production is expected as Pd enhances the oxidation of iron. In addition, a higher Fe^0 content will produce more H_2 gas as the by-product of iron oxidation.

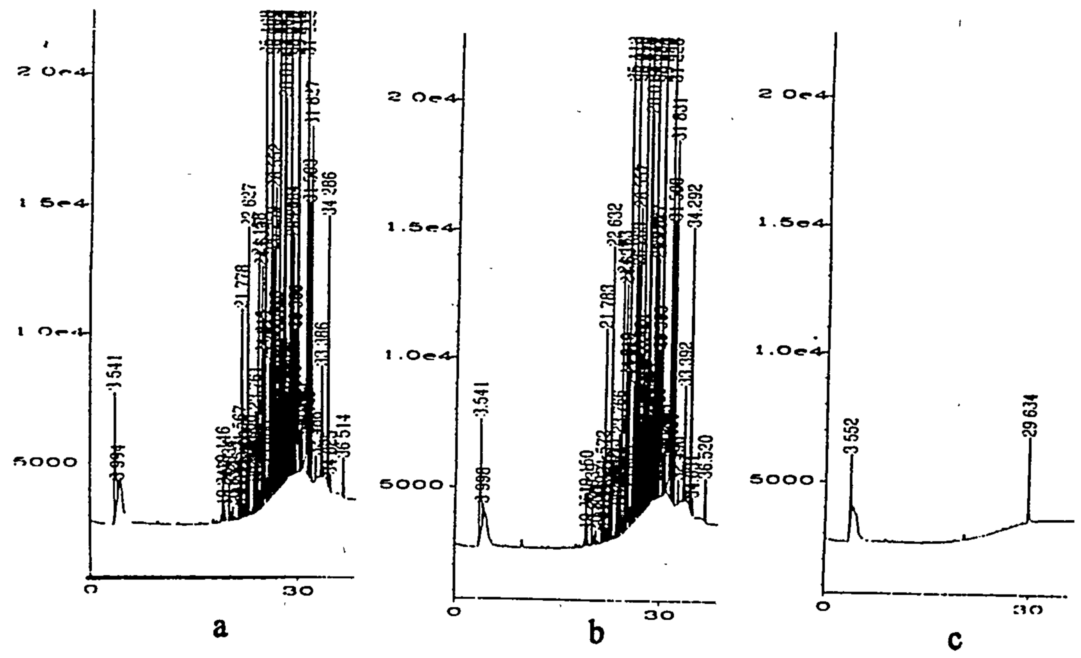


Figure 11. Chromatograms from GC/ECD analyses after Arochlor 1260 was equilibrated with solids for 24 h. Solutions spiked with 1 mg/L of Arochlor 1260 in 20% acetone/water. Solution to solid ratio (w/w) was 2.5. (a) Blank control, (b) iron filings, and (c) Pd/Fe filings (0.25%-Pd, -100-mesh).

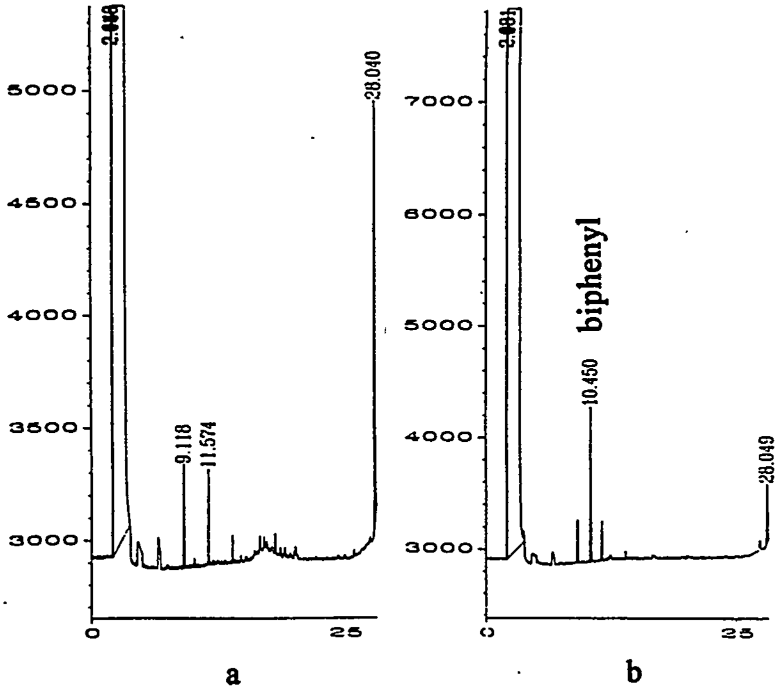


Figure 12. Biphenyl analyses with GC/FID after equilibrating Arochlor 1260 for 24 h. Solutions spiked with 1 mg/L of Arochlor 1260 in 20% acetone/water solution. Solution to solid ratio (w/w) was 2.5. (a) iron (b) Pd/Fe (0.25%-Pd, -100-mesh).

3.2.3 Dechlorination Using Cercona Iron Foam Aggregates

The experiments described in the previous subsection have shown that -100+200-mesh filings palladized at either 0.25% or 0.1% can rapidly dechlorinate 2,3,2',5'-TeCB (and other PCB congeners). Because of the fine sizes of these filings, potential problems, such as clogging and large pressure drops are anticipated when used in a plug-flow reactor. The use of iron foam was explored in this work. The advantage of using Cercona iron foam aggregates is that these aggregates can be loosely packed into a column, providing a large hydraulic conductivity. Preliminary experiments indicated that it is feasible to use such aggregates in dechlorination and a detailed study is reported here.

The Cercona aggregates used in the TeCB degradation study had a nominal size between 1.6-3.2 mm (-1/8 +1/16-mesh) and Pd content was 0.25%. The dechlorination rate of 2,3,2',5'-TeCB and the production of biphenyl (Fig. 13) were slower than that with -100-mesh filings (Fig. 6). Furthermore, the reaction rate appeared to decrease after 2 h as observed for -100-mesh filings (Figs. 11 and 12). Near complete transformation to biphenyl occurred at 48 h, with residual 2,3,2',5'-TeCB and its dechlorination by-products present. As with the parent compound, the lower chlorinated by-products were undergoing dechlorination but at a slower rate than what was observed with the 100-mesh filings.

3.3 Partition Coefficient of 2,3,2',5'-TeCB on -100+200-mesh Iron Filings

One of the concepts for using Pd/Fe to dechlorinate PCBs at the PGDP 001-Outfall is to divert contaminated surface water through an appropriately-sized plug-flow reactor packed with Pd/Fe media. Because of the known affinity of PCBs for solid surfaces, the iron media can potentially act as a sorbent that would quickly remove PCBs from the surface water, as well as provide reactive surfaces on which adsorbed PCBs are degraded. If the sorptive capacity of the iron surface is high, dechlorination rates do not have to be very rapid in order to achieve fast removal of PCBs from the flowing surface water.

The partition coefficient measured for 2,3,2',5'-TeCB on -100+200-mesh iron filings (Table 3) was substantially lower than reported values in the literature for the sorption of PCBs on soils and sediments. For example, a K_d value of $10^{5.6}$ L/kg was measured for

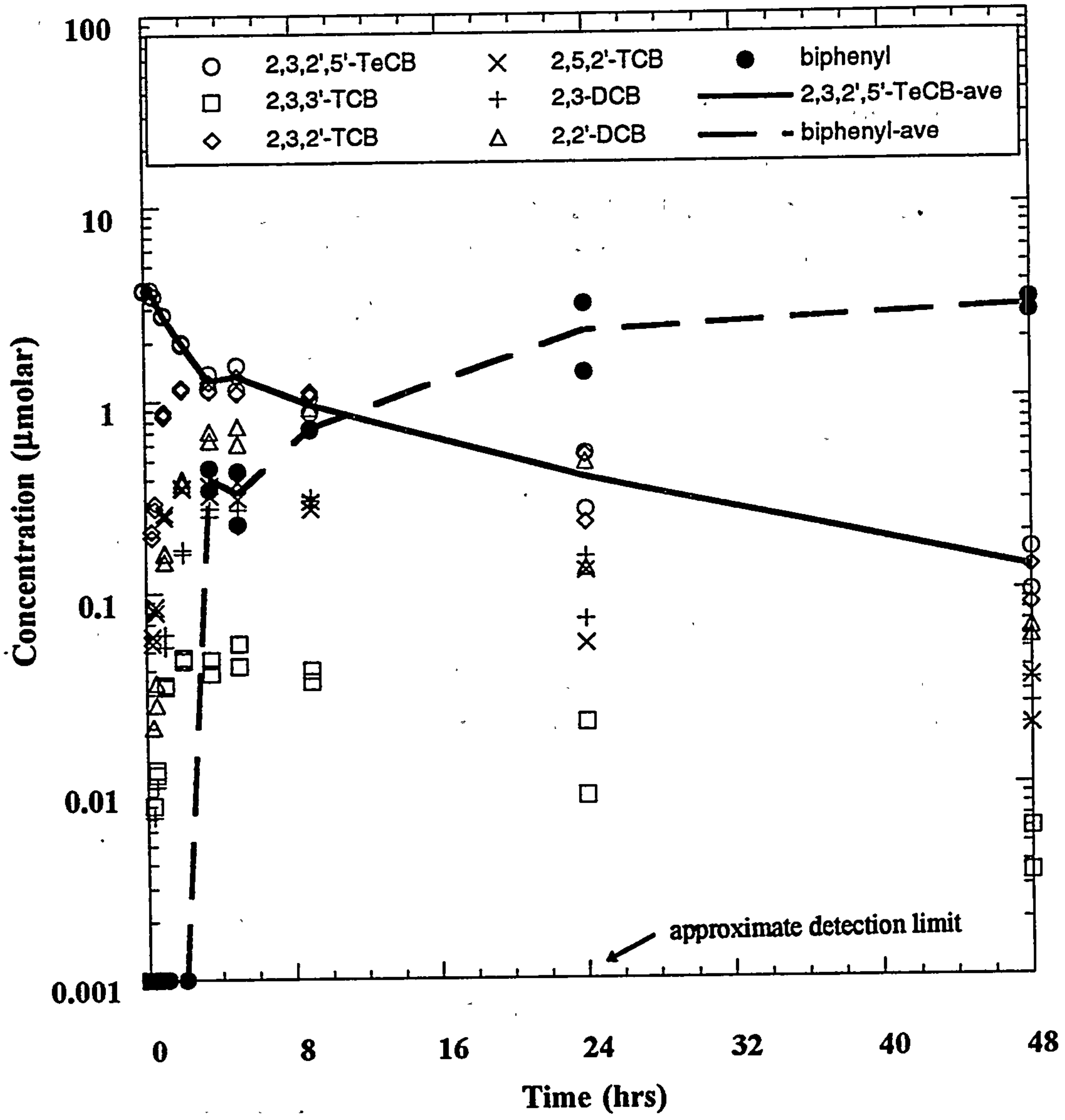


Figure 13. Dechlorination kinetics and by-product distribution from reaction of 2,3,2',5'-tetrachlorobiphenyl with palladized Cercona aggregates (-1/8 +1/16-mesh, Pd-0.25%). Solution to solid ratio (w/w) was 2.5. Initial TeCB was 1 mg/L (3.4 µM) in 20% acetone/water solutions.

2,3,2',5'-TeCB sorption on Lake Superior sediments [12]. The binding of PCBs to soils and sediments is assumed to consist mostly of interactions with natural organic matter [13]. On the other hand, PCB sorption on iron is most likely through PCB binding on mineral (iron and iron oxide) surfaces. In addition, the high solvent content (23%) of the aqueous solution should contribute greatly to the reduced K_d. This co-solvent effect on the partitioning behavior of organics is well documented in the literature [14].

Table 3. Partitioning of 2,3,2',5'-tetrachlorobiphenyl (K_d) on -100+200-mesh Fisher iron filings in a 4.6% methanol/ 19.1% acetone/76.3% water solution at room temperature (22°C).

Mass of Solid (g)	Average Aqueous Concentration (mg/L)	Estimated Sorbed Concentration (mg/kg)	Calculated K_d (L/kg)
0.00	0.79		
5.00	0.75	0.42	0.56
10.00	0.72	0.36	0.50
20.00	0.63	0.41	0.64

3.4 Dechlorination in a Flow-through Column Packed with Palladized Cercona Iron Aggregates

Previous studies on TCE degradation by zero-valence iron has shown that dechlorination rates obtained from column studies tend to be faster when compared with those obtained from batch tests, because of higher iron mass to solution ratios in the former systems. A column study was conducted on 0.25% Pd Cercona iron foam aggregates. The open and more porous structure of the aggregates is more suitable for use in a flow-through reactor than -100-mesh iron filings.

Because of the high sorption coefficient published for PCBs [12], it was not known whether any by-products would be detected in the aqueous effluent. However, based on the preliminary sorption work conducted in this study (Section 3.2), the partitioning of 2,3,2',5'-TeCB from 20% acetone/water onto iron was not as high as originally expected, and breakthrough of this PCB congener as well as its by-products occurred in the column study (Fig. 14). The initial breakthrough of TeCB was steep, followed by a gradual increase in the TeCB concentration. At 50 pore volumes, the system was approaching a pseudo steady state with the effluent concentration of TeCB at 59% of the influent concentration. A true steady state condition was not established within the duration of the experiment. The slow increase of TeCB concentration in the effluent after 150 pore volumes in the column study may be an indication of decreased reactivity of the Cercona aggregates. This is consistent with the observation in the batch study where the dechlorination rate after 5 h was slower than the initial rate (Fig. 13). Surprisingly, biphenyl was not present in the effluent extract, even though the batch study showed the production of biphenyl (see Fig. 13).

An attempt was made to perform a mass balance for the column study by quantifying the amount of 2,3,2',5'-TeCB and its dechlorination by-products sorbed onto the Cercona foam aggregates. After the column study, the reactor material (~15 g) was extracted with 10 mL of methanol and 20 mL of hexane. Samples of the hexane extract were then analyzed in duplicate on the GC/ECD and GC/FID (Table 4). The total mass of PCBs extracted from the column material was 0.051 μmoles, which is <2% of the total 2,3,2',5'-TeCB introduced into the column over the 5-h period (2.95 μmoles). The total mass of PCBs accumulated in the effluent was 1.63 μmoles, obtained by integrating the breakthrough curves. Hence, about 57% of the total mass was recovered from column extract and effluent. Losses might have occurred through sorption on the column tubing, the column itself (which was made of glass), or inefficient extraction of the PCBs from the column material.

Table 4. Total mass of 2,3,2',5'-TeCB and dechlorination by-products (in μmoles) as determined with a GC. Samples are extracted from palladized Cercona foam aggregates (0.25%-Pd) used for a column study.

Sample	2,3,2',5'	2,3,3'	2,3,2'	2,5,2'	2,3	2,2'	biphenyl	SUM
Extract 1 (ECD)	0.0248	0.0003	0.0036	0.0010	0.0009	0.0042		0.0348
Extract 2 (ECD)	0.0246	0.0003	0.0035	0.0010	0.0009	0.0041		0.0343
Extract 1 (FID)							0.0160	0.0160
Extract 2 (FID)							0.0170	0.0170

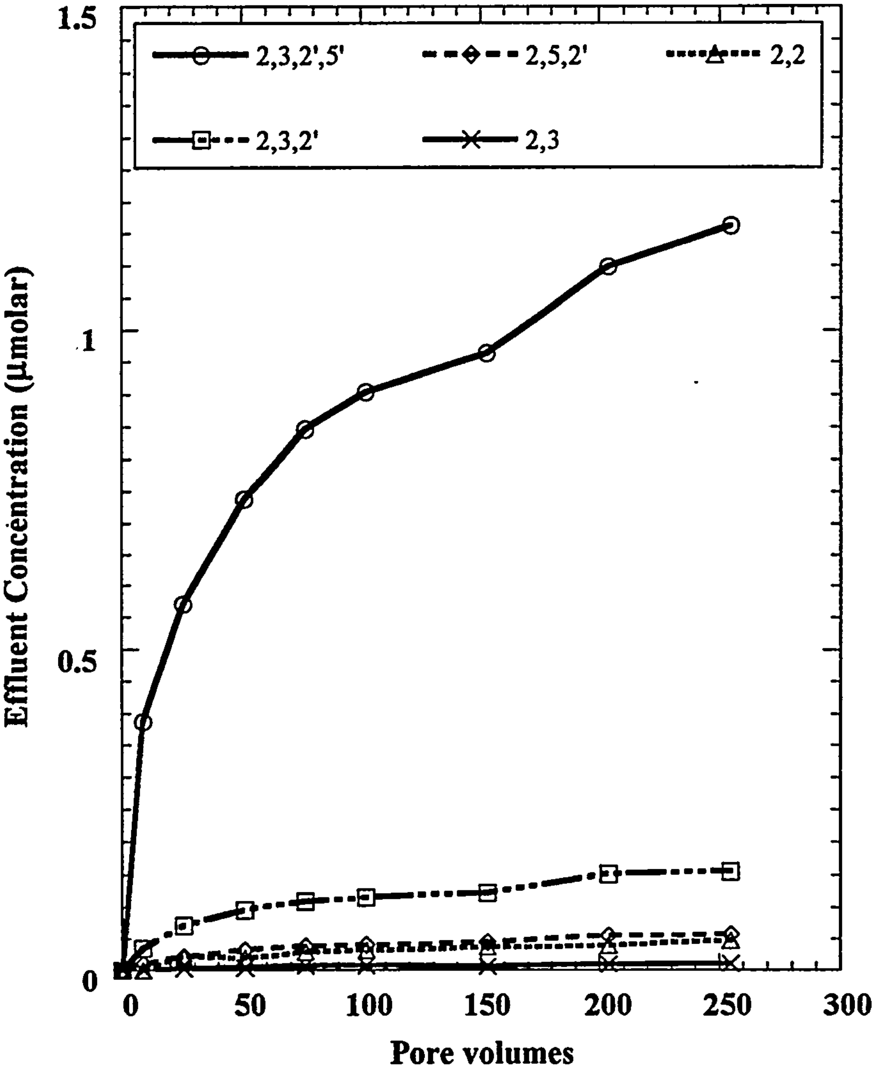


Figure 14. Effluent 2,3,2',5'-tetrachlorobiphenyl concentration and dechlorination by-products vs. total pore volumes. Column media: palladized Cercona iron aggregates (0.25% Pd). Flow rate: 5 mL/min. Aqueous influent contains 0.5 mg/L (1.97 µM) 2,3,2',5'-tetrachlorobiphenyl, and 20% acetone.

4. DISCUSSION OF DECHLORINATION EXPERIMENTS

4.1 Dechlorination Pathways and Degradation Rates

Dechlorination pathways-- The degradation of 2,3,2',5'-TeCB by Pd/Fe appears to occur in a step-wise fashion, as indicated by the detection and persistence of less chlorinated by-products in the batch studies. The hypothesized dechlorination pathways, illustrated in Fig. 15, were developed from the by-products detected in the batch studies and the column work. The dominant trichlorobiphenyl in this study was 2,3,2'-TCB, followed by 2,5,2'-TCB. The 2,3,3'-TCB was only detected persistently over a finite time with the Cercona aggregates in the batch experiment. The other possible dechlorination by-product, 2,5,3'-TCB was never detected in any of the experiments. The predominance of 2,3,2'-TCB and 2,5,2'-TCE over the other trichlorobiphenyl by-products is consistent with the observation made by others that the meta-chlorines are more reactive than the ortho-chlorines [15], although removal of ortho-chlorines was observed in anaerobic biodegradation [21] and reductive dechlorination with palladized iron.

Degradation rates-- Similar to TCE degradation by zero-valence iron [6], the initial dechlorination of 2,3,2',5'-TeCB follows a first-order reaction. However, a reduced dechlorination rate was observed for extended reactions. This was particularly evident in the experiment with colloids added, at a higher temperature (60°C), and with Cercona aggregates (Figs. 7, 8, 13). Possible reasons for decreasing degradation rates could be surface precipitation of oxides (i.e., reduction of Fe^0 surface content, see discussion below under "Gas Evolution"), sorption of PCBs covering active sites, and catalyst poisoning. Further investigation is needed since the reactive life of Pd/Fe will significantly impact the use of the material for degrading dissolved PCBs.

For purposes of comparing the different types of iron and Pd content, the first-order initial rate constants were derived from the kinetic experiments (Table 5).

Table 5. Summary of degradation constants (*k*) from batch dechlorination tests at room temperature (22EC)

Fe size (mesh)	Pd (%)	k (min^{-1})	Half-life (hr)	Test conditions
100	0.25	0.1131	0.10	
100	0.25	0.1665	0.07	with colloids
100	0.25	> 0.12	< 0.10	60°C
40	0.25	8x10-6	1444	
-1/8+1/16	0.25	0.0056	2.1	Cercona aggregates
-100+200	0.10	0.0686	0.17	
-100+200	0.25	0.0761	0.15	

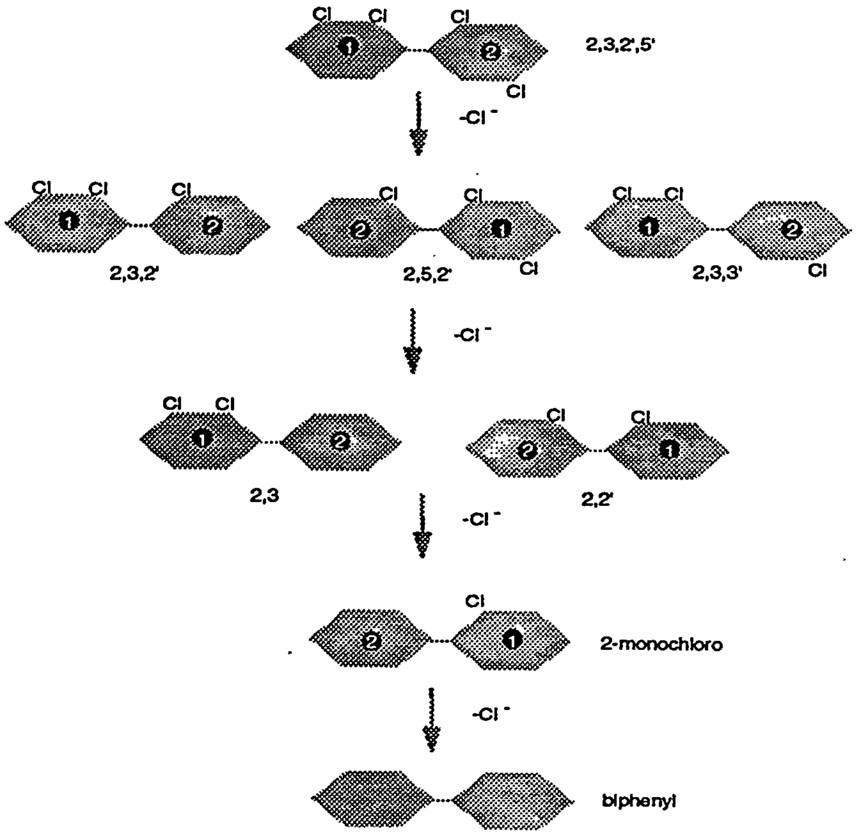


Figure 15. Proposed dechlorination pathway for 2,3,2',5'-tetrachlorobiphenyl by palladized iron.

Degradation Rate from the Column Study– The results of the column study can be used to estimate the removal rate for 2,3,2',5'-TeCB with palladized Cercona foam aggregates. By assuming a pseudo steady state had been reached at the last sampling interval of the column study (~250 pore volumes, Fig. 14), the relative effluent concentration (C/C_o) is a function of the degradation coefficient and other physical properties of the reactive material:

$$\frac{C}{C_0} = \exp\left[-\frac{L}{v}\lambda\left(\frac{K_d\rho_{Fe}}{\theta}\right)\right] = \exp\left[-\frac{L}{v}\lambda_{eff}\right] \qquad [1]$$

where L = length of the column, v = pore velocity, λ is the degradation rate for the adsorbed phase, K_d is the partition coefficient of 2,3,2',5'-TeCB on the Cercona foam, ρ_{Fe} is the packed density of the Cercona foam aggregates and θ is the porosity of the column. λ_{eff} is an effective degradation rate that accounts for adsorption. Eq. [1] was obtained by solving the following equation governing the transport of a single reactive solute [16] under steady state conditions and assuming a linear adsorption isotherm:

$$\frac{\rho}{\theta}\frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = 0 = -v\frac{\partial C}{\partial x} - \lambda\frac{\rho}{\theta}S = -v\frac{\partial C}{\partial x} - \lambda\frac{\rho}{\theta}K_d C. \qquad [2]$$

Based on the effluent C/C_o from the column study (0.59), column length (2 cm), column diameter of 2.5 cm, a flow rate of 5 mL/min and an assumed porosity of 0.7, the effective removal coefficient, λ_{eff}, was calculated to be 0.38 min^{-1}. This is two orders of magnitude higher than the degradation coefficient measured in the corresponding batch study (see Table 4), although it should be noted that this removal coefficient is a combination of dechlorination and adsorption. The fact that a large fraction of the TeCB and by-products were recovered from the solution indicated that the sorption contribution to the removal is minimal.

It must be noted that the validity of the degradation coefficient from the column study depends on the assumption that equilibrium had been achieved at the end of the column experiment. The column effluent appeared to be increasing, albeit gradually towards the end of the column test. Therefore, 0.38 min^{-1} may be an overestimate of the actual removal coefficient. To further evaluate Cercona foam aggregate at 0.25% palladization as a reactive material for degrading PCBs in PGDP 001-Outfall, additional column experiments with longer run times and at varying flow rates and column lengths must be performed. Such experiments would better elucidate the long-term performance of a flow-through reactor.

Effect of Surface Fe^0 Content and Specific Surface Area-- Both surface Fe^0 content and specific surface area of the base material are important for dechlorination as observed by Horney, et al. [17] in TCE degradation. Electrolytically-prepared 100-mesh filings have a higher Fe^0 to iron oxide ratio when compared to heat-treated 40-mesh filings (the latter appears more oxidized than the former). Specific surface areas for 100-mesh, 40-mesh and Cercona aggregates were 0.08, 2.42, and 1.76 m^2/g, respectively, as measured by the BET technique with N_2. The slow degradation with 40-mesh filings even with 0.25% Pd indicates that a high surface Fe^0 content may be more critical than specific surface area for effective dechlorination of PCBs. The Cercona foam aggregates have a slightly lower specific surface area relative to 40-mesh filings. It is possible that the Fe^0 to Fe-oxide ratio in Cercona foam is higher when compared to 40-mesh filings, since the former were fired under a reducing H_2 atmosphere during production.

Gas Evolution-- The hydrogen gas generated during the dechlorination of PCBs with palladized iron can be described by the following:

$$Fe^0 + 2\,H_2O \rightleftarrows Fe^{2+} + H_2 + 2OH^-.$$

Since extensive gas evolution was only observed in the palladized 100-mesh iron filings, it appears that the formation of H_2 was accelerated by the presence of Pd on the iron filings. This may be a result of a galvanic (bimetallic) effect. Since the oxidation potential of Pd is higher than that of iron, Pd will always be at the zero oxidation state at the expense of Fe^0 (Fe^0 is oxidized to Fe^{2+}). In addition, H_2 generation was minimal in 40-mesh filings even at a high Pd content, because this type of iron contained an oxide (passivation) layer with low surface Fe^0 content. The slow dechlorination observed in 40-mesh filings with 0.25% Pd coupled with the lack of gas evolution with this iron type suggests that H_2 generation may be a critical component in the dechlorination of PCBs by palladized iron filings. The dechlorination would then occur through the following reaction with Pd as a catalyst [18]:

$$H_2 + RX \longrightarrow RH + H^+ + X^-.$$

The catalytic effect of Pd on the dehalogenation of organics by H_2 is a well-known phenomenon in organic synthesis [19]. The "aging" or reduction of reactivity of palladized iron may be a result of a reduction in the Fe^0 surface content that decreased the H_2 generation. The Pd catalyst-poisoning is another possible reason for the rate reduction.

The amount of hydrogen generation was not determined in this study. A separate investigation (not published) indicated that the initial rate of hydrogen production is about 2 mmol/kg-Fe/day, with an average of 0.6 mmol/kg-Fe/day. A system can be designed to deal with the safety concerns related to hydrogen production.

Additional experiments must be conducted to better understand the dechlorination of PCBs by palladized iron filings. Knowing the underlying reaction mechanisms would benefit any efforts towards the design and optimization of this treatment process.

4.2 Using Palladized Iron to Degrade PCBs in PGDP 001-Outfall Surface Water

The experiments reported above have demonstrated that PCBs can be rapidly transformed to biphenyl using certain forms of palladized iron. Using the experimental data from this work, estimates were made for the volume and length of a palladized iron plug-flow reactor required to remove 95% of PCBs from surface water flowing at 0.5 gpm (see Table 6). This table shows that if reaction rates are on the order of 0.01 min^{-1}, plug-flow reactors with reasonable sizes can be used to treat surface water discharging from the PGDP 001-Outfall. Of the iron types tested, Cercona foam aggregates with 0.25% Pd are the most promising to use because these can be loosely packed, reducing pressure drops which can be problematic if the plug-flow reactor is to be operated passively. The high degradation constant measured in the column study must be confirmed with additional, longer-duration column experiments which would also show this material's long-term reactivity. The -100+200-mesh fraction of 100-mesh Fisher iron filings palladized either at 0.1% or 0.25% also appears promising. Further considerations of using this material at the PGDP Outfall should also include column tests to measure degradation rates and reactor life.

Table 6. Estimated volume of palladized iron required to remove 95% of PCBs from surface water flowing at 0.5 gpm.

Iron type (Type of test)	Degradation rate (min^{-1})	Half-life (min)	Retention time for 95% removal (min)	Volume of Pd/Fe required[a] (m^3)	Length of plug-flow reactor[b] (m)
-100 mesh, 0.25% Pd	1.48[c]	0.5[c]	2.0	0.01	0.09
Cercona aggregates, 0.25% Pd	0.02[c]	33.1[c]	142.9	0.32	4.56
Cercona aggregates, 0.25% Pd	0.38[d]	1.8[d]	7.8	0.02	0.25
-100+200 mesh 0.1% Pd	0.99[c]	0.7[c]	3.0	0.01	0.13

[a] Assuming a porosity of 0.6 and 0.84 for 100-mesh iron and Cercona aggregates, respectively.

[b] Length calculated from required volume assuming a 0.3 m-diameter reactor.

[c] Estimated from batch reaction rate using the following equation:

$$k_c = k_b \frac{r_b}{r_c},$$

where k_c is the estimated column reaction rate constant, k_b is the measured batch reaction rate constant, r_b and r_c are the batch and column solution to solid ratios, respectively.

[d] Reaction rate constant measured from the column study.

5. PCB DECHLORINATION IN CO-SOLVENT AND SURFACTANT SOLUTIONS

This section summarizes experiments conducted at the University of Arizona. The focus was on the dechlorination of PCB mixtures in solvent and surfactant solutions. This work is significant for extending the applicability of palladized iron to the treatment of PCB-contaminated soils. The presence of surfactants or co-solvents can potentially inhibit the reaction, based on the observation that compounds more soluble in an aqueous solution are typically less susceptible to degradation by iron filings. This is attributed to the lower rate of mass transfer from the aqueous solution to the solid surface. Hence, any addition to the solution that increases the solubility of the compound to be degraded is expected to slow the dechlorination reaction. Data obtained with methanol showed that TCE was not dechlorinated in a solution of the pure solvent. However, dechlorination was still quite rapid even with 50% methanol. Likewise, subsequent experiments showed that pentachlorophenol was easily degraded in the presence of ethanol.

The success of the experiments with alcohols led to the decision to briefly test some surfactant solutions. The two surfactants that have been studied to data are Triton X-405 and dodecylbenzene sodium sulfonate. Experiments were performed with Arochlor 1260 at 20 mg/L or 40 mg/L in a solution of methanol and acetone. (The methanol/acetone solution was used to maintain the high concentrations of PCBs in solution.) The surfactants were then added at a loading of 0.25%. Batch dechlorination reactions were then performed with a solution to solid ratio of 5:2, using 10 µm-sized electrolytic iron powder palladized at 0.05%. In a packed column, the solution to solid ratio is substantially higher than in a batch reactor.

Fig. 16 shows chromatograms from the analyses of a 20 mg/L PCB methanol/acetone/ water solution before and after treatment with palladized iron. Within 10 minutes, no chlorinated species were evident in solution. Fig. 17 shows the effect of increasing the PCB concentration. At 40 mg/L, there were still some chlorinated compounds after nearly two hours. However, when the amount of Pd was increased from 0.05% to 0.5%, the 40 mg/L of PCBs was dechlorinated rapidly.

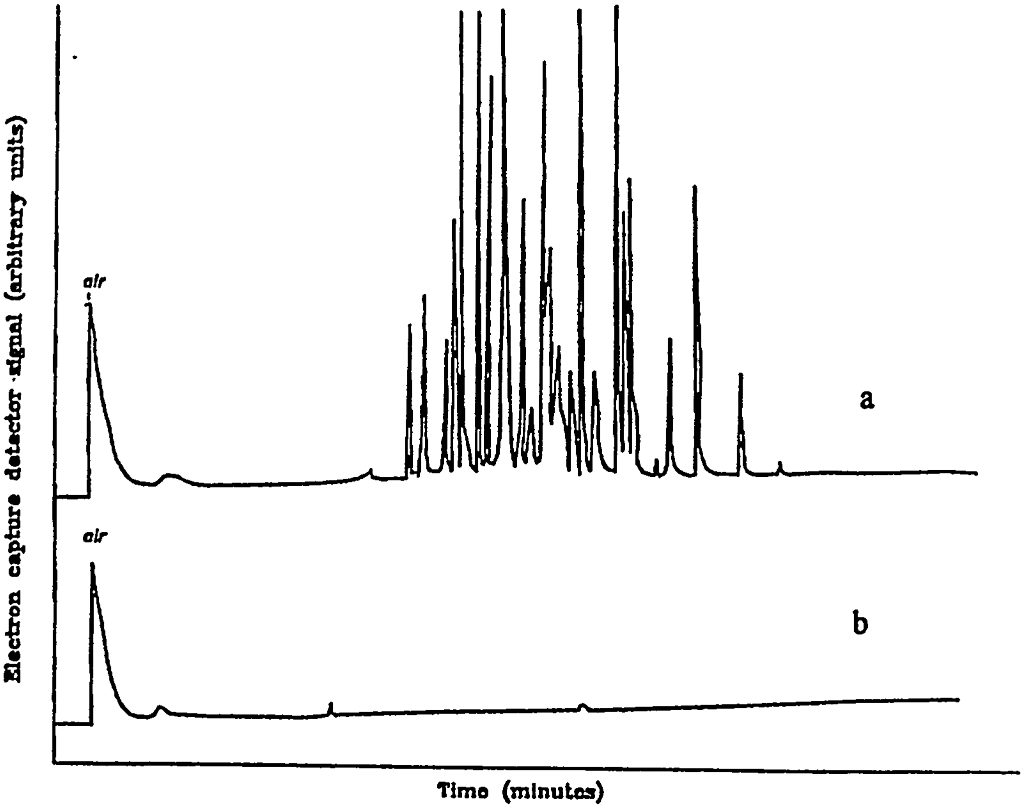


Figure 16. Arochlor 1260 methanol/acetone/water solution (20 mg/L): (a) before and (b) after mixing it with 10-µm iron filings with 0.05% Pd for 10 minutes.

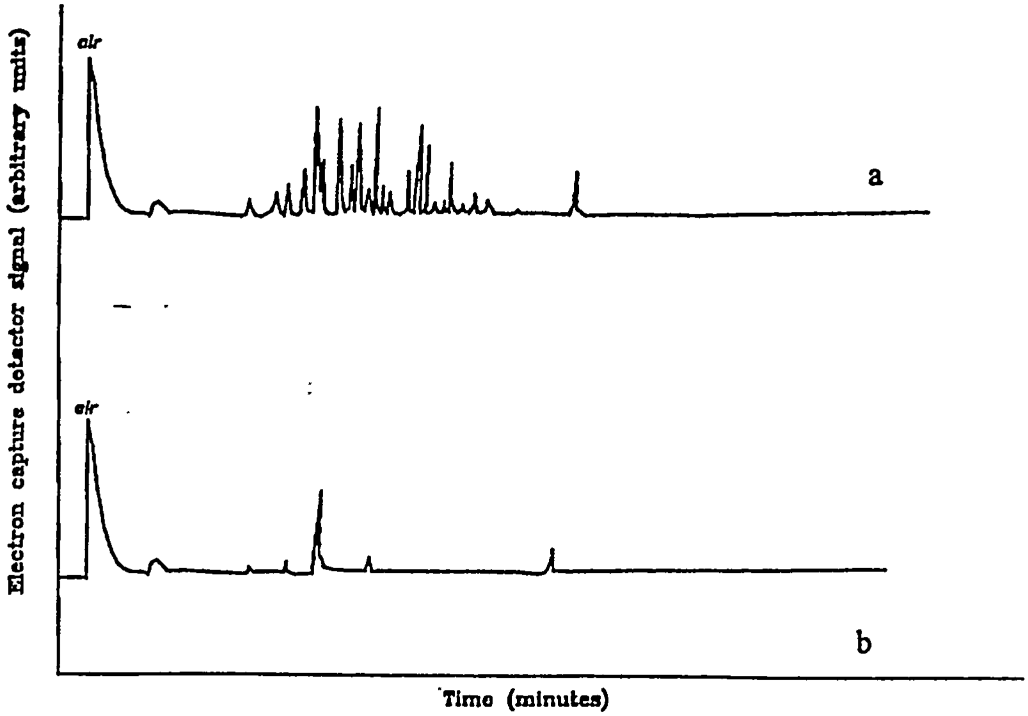


Figure 17. Arochlor 1260 methanol/acetone/water solution (40 mg/L): (a) after reacting with 10-µm iron filings (0.05% Pd) for 1 hour and 46 minutes, (b) after reacting with 10-µm iron filings (0.5% Pd) for 5 min.

For the experiments with the surfactants, 20 mg/L of PCBs were used with 0.05% palladized 10-µm iron filings. Fig. 18a shows the chromatogram after 7 minutes for the solution containing Triton X-405. Dechlorination was essentially complete. Fig. 18b shows the extent of dechlorination after six minutes for the solution containing dodecylbenzene sulfonate. The reaction was substantial, but somewhat less than for Triton X-405. Since the surfactant experiments were conducted at very high solvent concentrations (25% methanol and 25% acetone), additional tests must be performed to confirm PCB dechlorination in surfactant solutions with substantially lower solvent concentrations. Under the latter conditions, PCBs are more likely to dissolve within surfactant micelles, thereby hindering its mass transfer to Pd/Fe surfaces and potentially reducing dechlorination rates.

Finally, repetitive use of the Pd/Fe with PCB surfactant solutions was examined. The results (Fig. 19) demonstrate that reactivity declines with time but is easily restored with a simple HCl rinse.

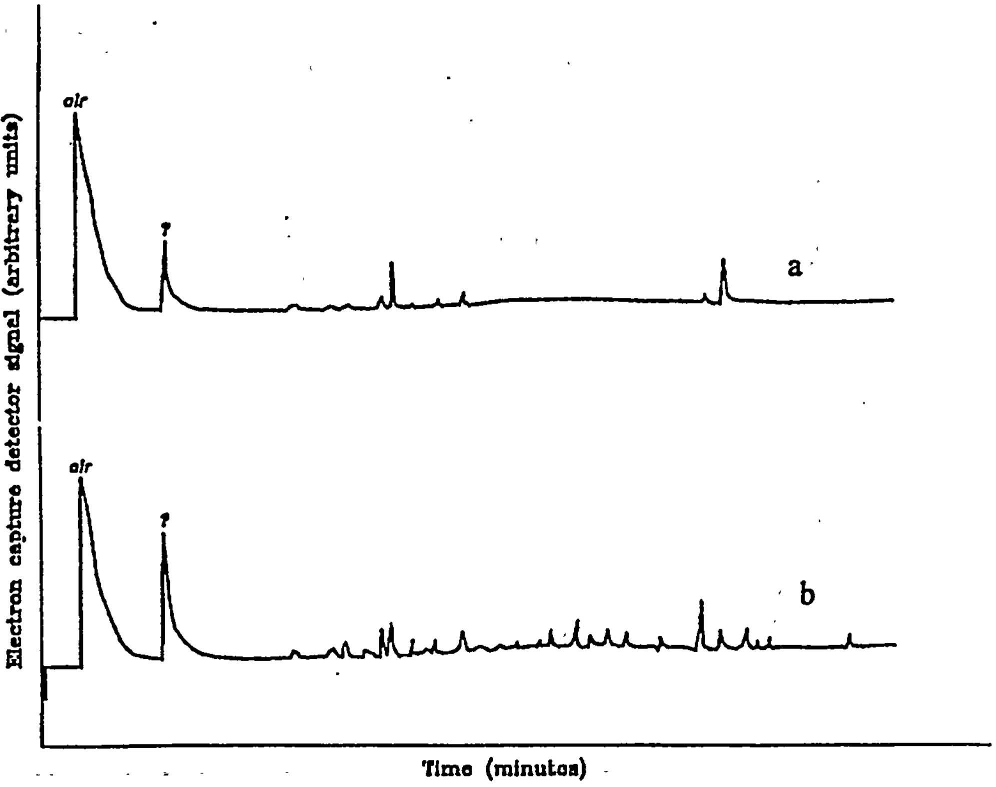


Figure 18. Arochlor 1260 (20 mg/L) aqueous solutions with 25% methanol, 25% acetone, 0.24% v/v surfactant mixed with 10-µm iron filings with 0.05% Pd, (a) solution containing Triton X-405 after 7 minutes, (b) solution containing dodecylbenzene sodium sulfonate after 6 minutes.

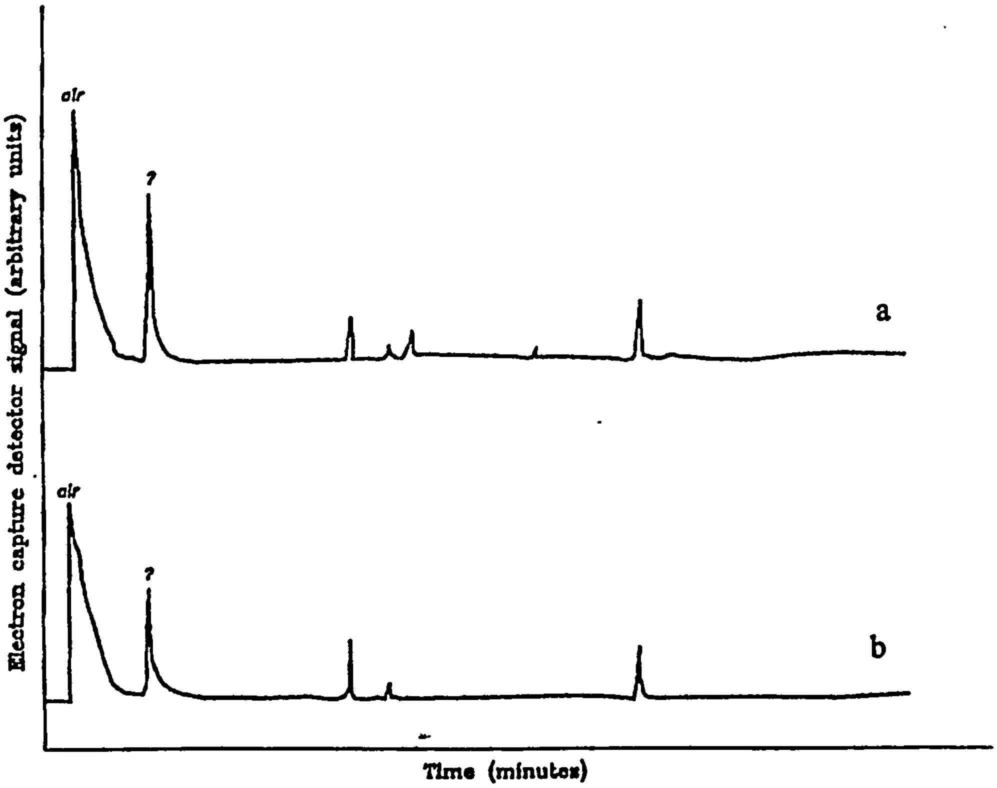


Figure 19. Arochlor 1260 (20 mg/L) aqueous methanol/acetone solutions that were added to 10-µm iron filings with 0.05% Pd: (a) fifth repetition with same Pd/Fe, mixed for 7 minutes, (b) after Pd/Fe had been washed with dilute HCl, mixed for 7 minutes.

6. SURFACE ANALYSIS

The dechlorination of PCBs with palladized iron is believed to be a heterogeneous reaction that initially requires adsorption on the metallic surface. Consequently, a study of the metallic surface is essential to fully understand and optimize the reaction. This section summarizes the surface analytical measurements that have been performed at the University of Arizona. The purpose of the measurements was to examine the longevity of the palladized iron surface and to obtain additional information regarding the reaction mechanism.

The Pd/Fe surface has been investigated with the following techniques: Raman Spectroscopy, Surface Enhanced Raman Spectroscopy (SERS), Rutherford Backscattering Spectrometry (RBS), Proton Induced X-Ray Emission (PIXE), PIXE with a highly focused ion beam (Micro-PIXE) and X-ray Photoelectron Spectroscopy (XPS). Raman and SERS were found to be of limited use because these techniques lacked sufficient sensitivity. The other techniques have all provided useful data to some extent.

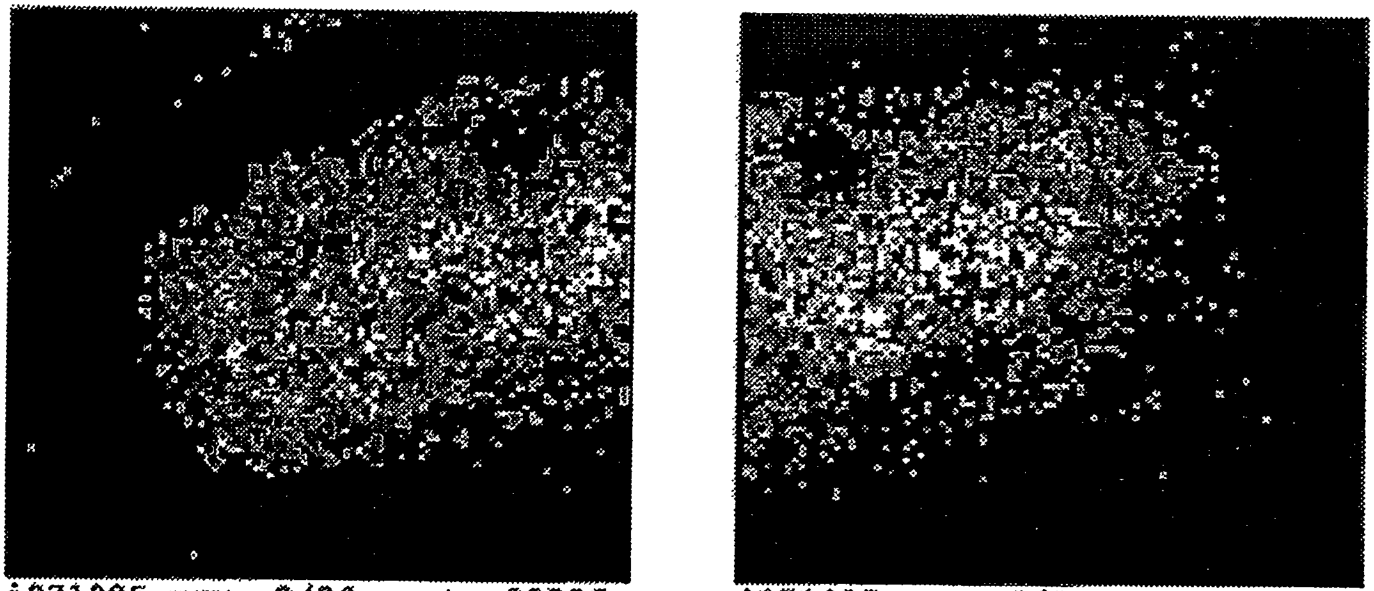
Rutherford Backscattering Spectrometry (RBS)-Limited use of RBS has demonstrated that the Pd has not penetrated into the iron but is resident on the surface. Under highly-controlled conditions, it should be possible to determine the thickness of the Pd layer using RBS.

Proton Induced X-ray Emission (PIXE)-PIXE was used to confirm the RBS results regarding the location of the Pd on the iron surface. No unique information was obtained. PIXE can be used to calculate the concentration of Pd on the iron surface.

X-ray Photoelectron Spectroscopy (XPS)-XPS (sometimes known as Electron Spectroscopy for Chemical Analysis or ESCA) is commonly used to examine the chemical state of elements on a surface. In this technique, the surface of the sample is sputtered with an argon ion beam and a characteristic photoelectron is ejected. The energy of the photoelectron is related to the binding energy of electrons in the substance under study. For example, Fig. 20 presents results obtained from a thin film of palladized iron prior to exposure to organic compounds.

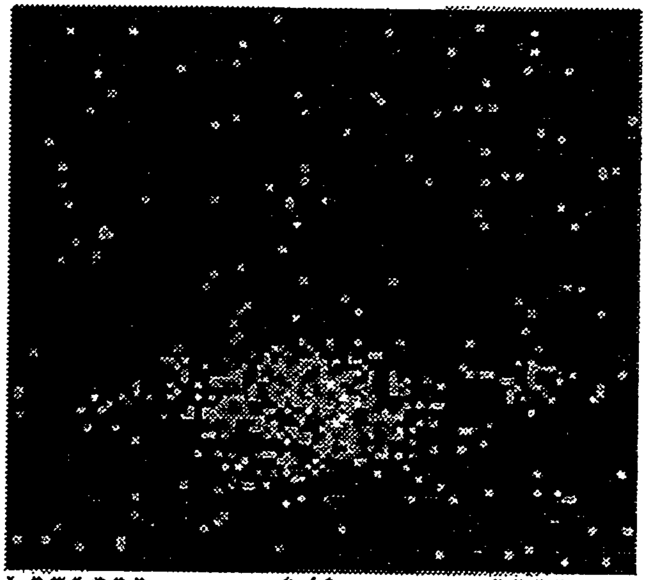
Figure 20. Micro-PIXE surface analysis of palladized iron filings.

Date: July 10, 1995



i071095.xry 2/20 cnts 22296
Pd K-alpha, beta 2300 sec
Sample #1 125 um x 125 um

j071095.xry 2/22 cnts 22839
Pd K-alpha, beta 2500 sec
Sample #1 125 um x 125 um



k071095.xry 1/9 cnts 2737
Pd K-alpha, beta 1750 sec
Sample #2 125 um x 125 um

Micro-PIXE-The use of a highly focused proton beam permits much greater resolution regarding the characteristics of the metallic surface. Micro-PIXE results proved that the Pd was not uniformly distributed but formed "islands" on the iron surface (Fig. 20). Additional studies, to determine the features of the iron surface that cause the palladium clusters, can be performed in the future.

When the Pd/Fe surface is exposed to TCE (Fig. 21, compare with Fig. 20), a larger carbon peak is observed and Cl is visible on the surface. In contrast, when PCBs are exposed to the surface (Fig. 22, compare with Fig. 20), only C is visible. It is not known whether there is no Cl present or whether the resolution is inadequate to observe it. The presence or absence of chlorine at this step could have significant bearing on determining the reaction mechanism. Additional analyses of this type should be performed in the future. After exposure to TCE, the complexity of the Cl peak on the Pd/Fe surface (Fig. 21, inset B) indicates that Cl is present in two or more distinct states. Indeed, the data demonstrate the presence of several fragmented C-Cl bonds on the Pd/Fe surface.

The Pd peak is shifted after reaction with TCE (Fig. 22) indicating that it is a probable binding site for the hydrocarbon. The Pd peak is not shifted after reaction with PCBs (Fig. 23). The significance of this finding is unknown and will require additional experiments to explain.

The shape (size and complexity) of the carbon peak after exposure to PCBs (Fig. 23, inset) indicates the presence of a number of carbon species that are bound to the Pd/Fe surface. The original carbon peak, prior to reaction with TCE or PCBs is shown in Fig. 20 (inset). The carbon peak after reaction with TCE is shown in Fig. 22 (inset A). As noted above, in the PCB reaction, unlike the TCE experiment, there is no detectable shift of the Pd peak. There are also no discernible shifts in the iron or O peaks meaning that it is not possible to determine to what atoms the carbon-containing species are bound.

With both TCE and PCB reactions, the surface bound carbon-containing compounds are not volatile and are not readily desorbed under high vacuum conditions. However, a water rinse of the Pd/Fe film after reaction with TCE or PCBs removes the carbon-containing species. An XPS spectra following the aqueous rinse closely resembles that from an unused film (Fig. 24, compare with Fig. 20). Furthermore, palladium remains bound to the iron even after reduction of the hydrocarbon and subsequent rinsing.

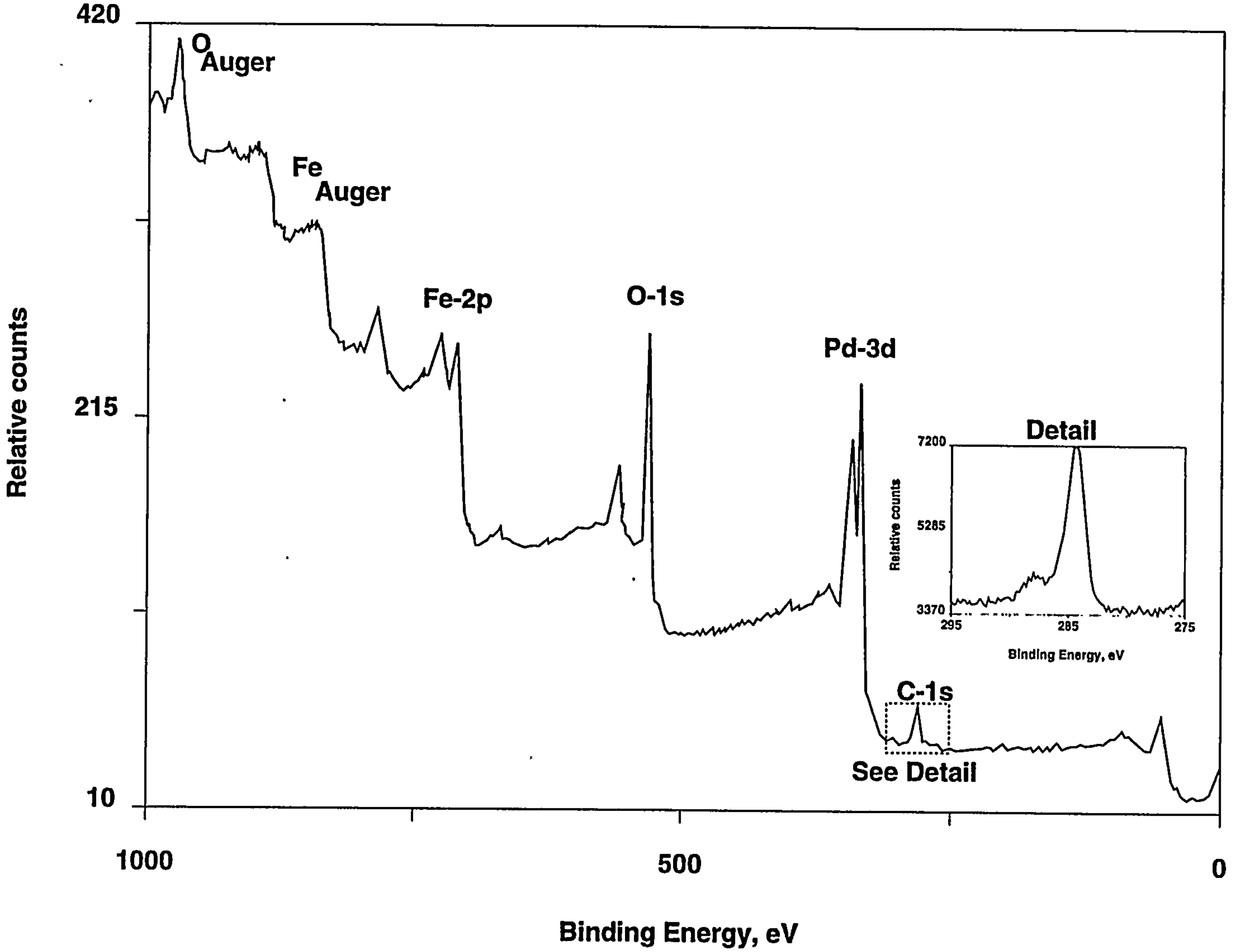


Figure 21. XPS results for a clean, unreacted palladized, iron film.

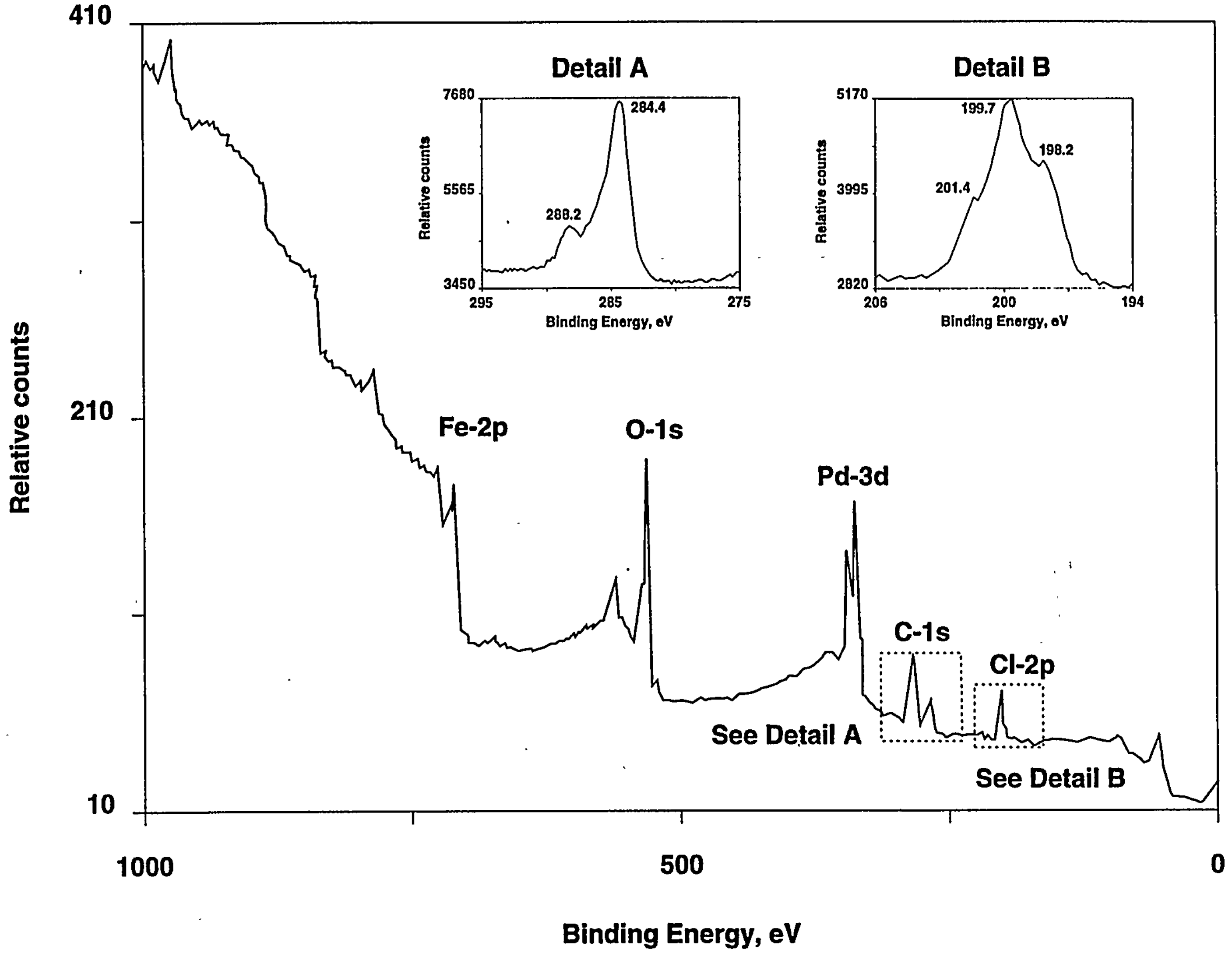


Figure 22. XPS results for a palladized iron film following reaction with TCE.

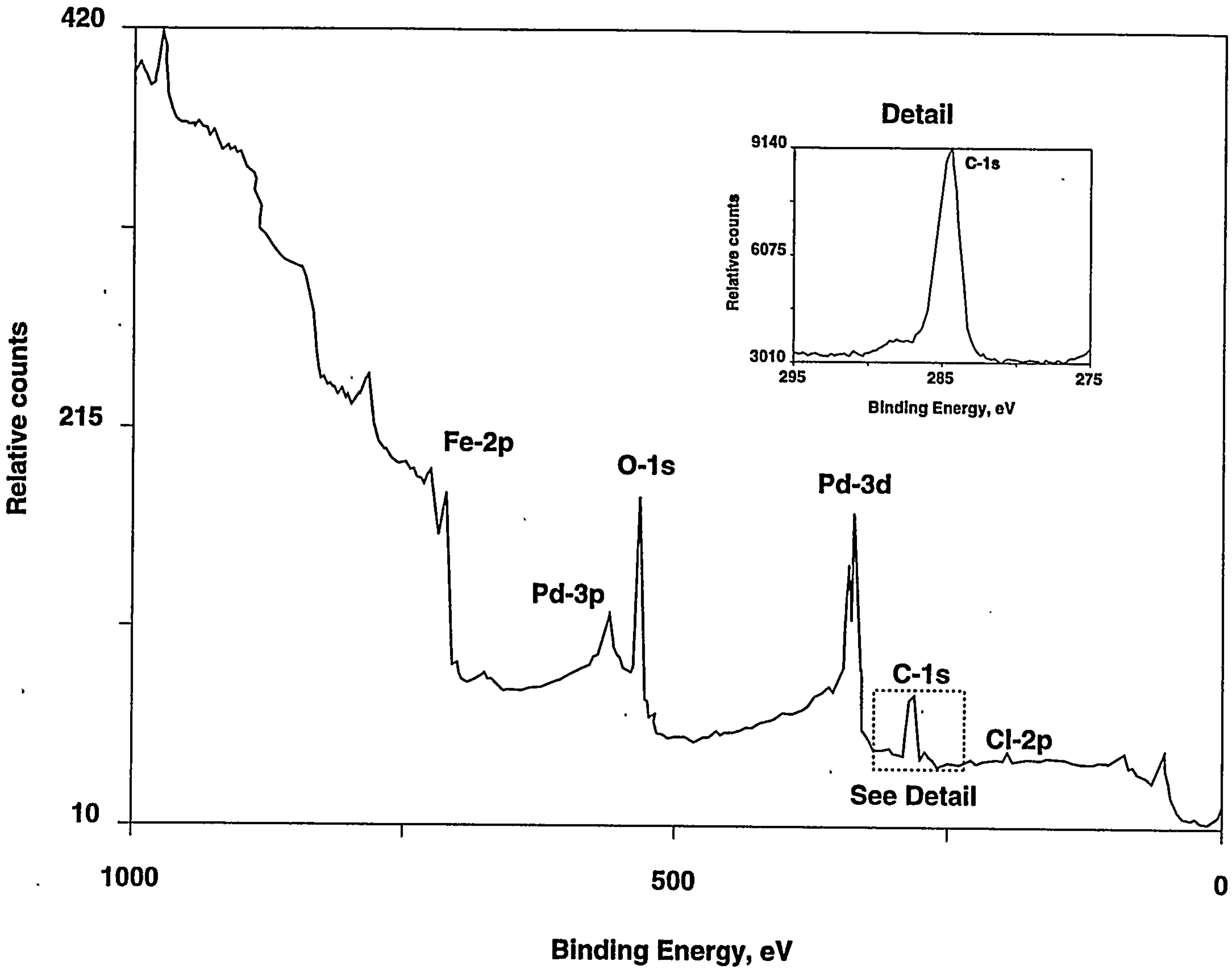


Figure 23. XPS results for a palladized iron film following reaction with a PCB congener.

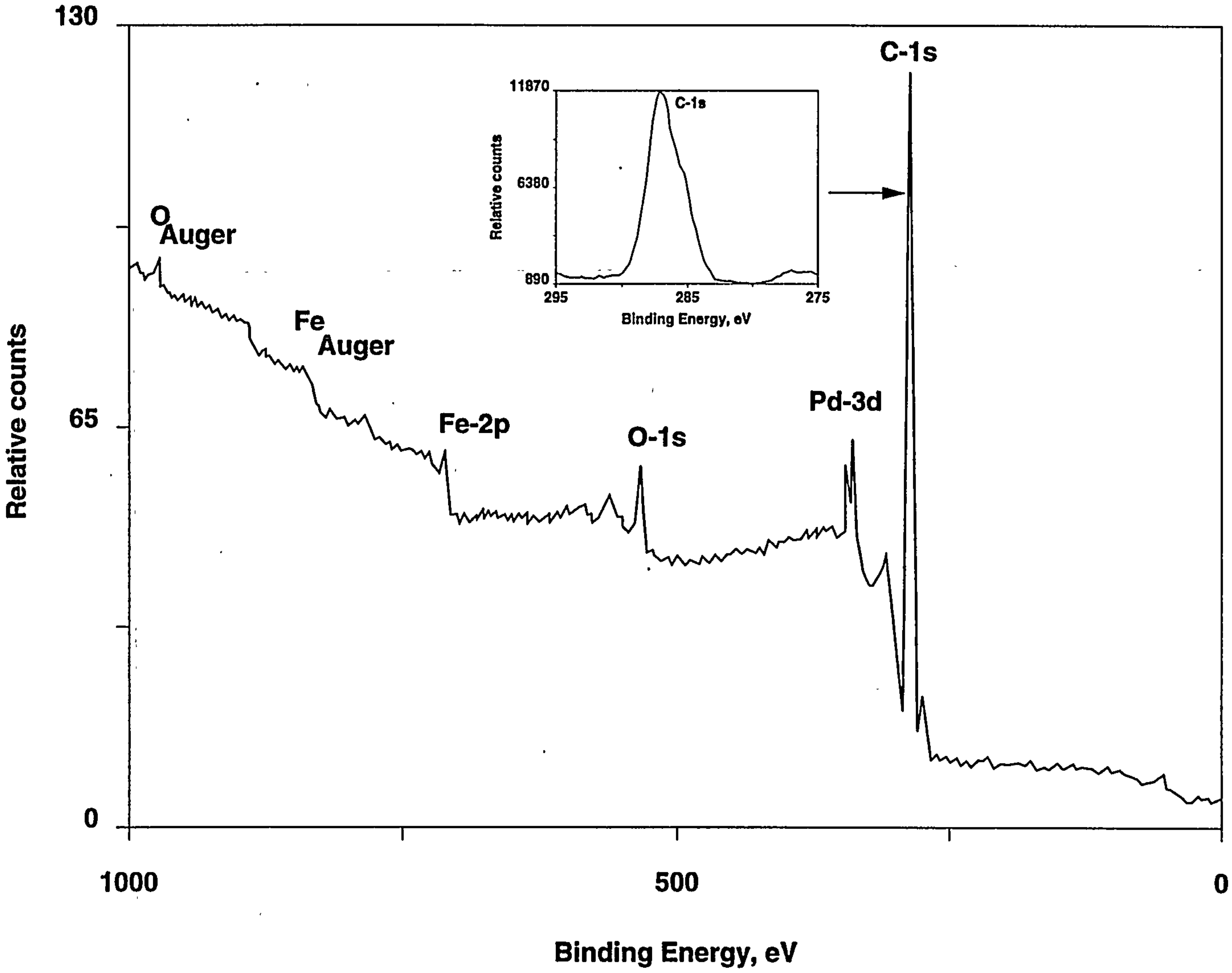


Figure 24. XPS results for a palladized iron film after reaction with TCE and an aqueous rinse.

7. CONCLUSIONS AND RECOMMENDATIONS

This study shows that palladized iron can be used as a reactive material to treat PCB-contaminated aqueous/acetone solutions at room temperature. Reductive degradation rates with the metals are several orders of magnitude higher than those observed for biodegradation processes. Furthermore, in contrast to high-temperature processes where dioxins and furans are potentially produced, the major by-product of dechlorination by palladized iron is biphenyl which is substantially less toxic than the parent compounds. Specific findings of this study include:

1. A PCB congener, 2,3,2',5'-TeCB dissolved in a 20% acetone/water solution was rapidly and completely dechlorinated by 100-mesh iron filings palladized at 0.25%. Complete dechlorination was confirmed through the quantitative recovery of biphenyl. Comparable degradation rates were observed with -100+200-mesh iron filings palladized at 0.1% and 0.25%. Half-lives measured in the batch dechlorination experiments were on the order of 0.10 to 0.17 h (6 to 10 min). Addition of iron oxide colloids to the acetone/water solution did not appear to significantly affect the rates and the by-product distribution of PCB dechlorination. Reaction rates were more rapid at 60EC than at room temperature. Arochlor 1260 congeners dissolved in a 20% acetone/water solution were completely transformed to biphenyl by 100-mesh, 0.25% Pd iron filings.

2. Rapid dechlorination of 2,3,2',5'-TeCB was also observed with Cercona iron foam aggregates palladized at 0.25%. Half-lives from the batch tests and the column study were 124 and 1.8 min, respectively. The significantly higher degradation rate in the column study are a result of a lower solution to solid ratio when compared to the batch experiments. The degradation rate calculated from the column study was based on the reduced 2,3,2',5'-TeCB concentration in the effluent at 50 pore volumes (a pseudo steady state condition). The true steady state condition was not established within the duration of the experiment. Additional column experiments must be conducted to better quantify degradation rates and reactive life of palladized iron under flow-through conditions.

3. PCB dechlorination using palladized 40-mesh iron filings was found to be slow even at 0.25% Pd, and appeared to be absent when the iron contained 0.05% Pd. The slow reaction is primarily from the lack of zero valence iron on the surface because of the presence of a passivation (oxide) layer on the 40-mesh iron. The dependence of reaction rates on surface areas was not observed. The specific surface area for the 40-mesh filings

($2.42\ m^2/g$) was the highest among the 3 types of iron tested, yet the reaction rate was the slowest.

4. Significant gas evolution in the batch experiments was observed with palladized (0.1%, 0.25%) 100-mesh filings. Some gas evolution was also observed with the palladized (0.25%) Cercona iron aggregates. This was not observed with unpalladized 100-mesh filings or with palladized (0.05%, 0.25%) 40-mesh filings. The hydrogen gas generated was the result of oxidation/corrosion of Fe^0. This Fe^0 corrosion reaction could be accelerated by palladium, because palladium has a higher oxidation potential than Fe^0. This reaction was suppressed in the 40-mesh iron because of the presence of a passivation layer, with low surface Fe^0 content. Since gas generation was always accompanied by rapid dechlorination, H_2 formation may be a critical component of PCB dechlorination by Pd/Fe filings. High Pd and Fe^0 surface content appear to be critical to the reactivity of iron filings.

5. Partitioning onto iron from acetone/water solution is not significant. The measured partition coefficient for 2,3,2',5'-TeCB onto iron was on the order of 0.5 to 0.6 L/kg. Published sorption coefficients for 2,3,2',5'-TeCB on sediments are as high as $10^{5.6}$ L/kg. The binding of PCBs to soils and sediments is assumed to be from interactions with natural organic matter. On the other hand, PCB sorption on iron is most likely through PCB binding on mineral (iron and iron oxide) surfaces. In addition, the acetone at a high concentration favors the dispersion of PCBs in solution.

6. Plug-flow reactors packed with Cercona foam or 100-mesh iron filings palladized to 0.1% to 0.25% can potentially be used to dechlorinate PCBs dissolved in PGDP 001-Outfall surface water. Cercona iron foam aggregates are more promising because of their higher conductivity compared to the 100-mesh filings.

7. Rapid PCB dechlorination by 0.05% palladized 10-micron iron particles was observed in aqueous solutions containing 0.24% surfactant (Triton X-405 or dodecylbenzene sodium sulfonate), 25% acetone and 25% methanol. This demonstrates the potential for extending this process to remediating the PCB-contaminated soils that are believed to be the source of contamination in the PGDP 001-Outfall.

8. Surface analysis by X-ray photoelectron spectroscopy (XPS) is a useful tool for understanding the dehalogenation of PCBs and TCE by palladized iron filings.

Preliminary findings show differences between chemical surface characteristics of Pd/Fe surfaceexposed to TCE and PCBs, which also indicate differences in underlying reaction mechanisms.

The following are recommendations for future work that need to be performed prior to implementing PCB dechlorination by palladized iron at the PGDP 001- Outfall:

1. Column studies with varying reactor lengths, flow rates and PCB concentrations must be conducted to determine removal rate constants using palladized Cercona iron aggregates and 100-mesh iron filings. The reactive life of palladized Cercona iron aggregates and 100-mesh iron filings must be quantified, through long-term column experiments coupled with surface analysis of the spent material.

2. If additional column studies confirm rapid dechlorination and the reagent capacities are reasonably high, a larger-scale pilot test of a plug-flow column should be designed and executed using field-contaminated water.

3. Detailed surface analyses of the reacted Pd/Fe should be conducted to elucidate reaction mechanisms as well as to investigate poisoning of bimetallic materials. Practical methods must be identified to regenerate spent bimetallic materials.

4. Other reactor configurations (such as fluidized bed) should be considered as alternatives to a column plug-flow reactor, particularly if clogging problems are encountered when using very fine iron particles in the column experiments.

5. Detailed batch and column experiments using single and multiple PCB congeners in surfactant/co-solvent solutions should be performed in order to extend this work to the remediation of PCB-contaminated soils.

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