

Report for 2001MT261B: Enhanced Wet Air Oxidation of Sediment and Soil Contaminated with Recalcitrant Organic Compounds

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Enhanced Wet Air Oxidation of Sediment and Soil Contaminated with Recalcitrant Organic Compounds

James E. Duffy and Justin M. Ray

Department of Chemical Engineering, Montana State University, Bozeman, MT 59717

Abstract- Wet air oxidation (WAO) is investigated as a method of treating river sediments contaminated with polychlorinated biphenyls (PCBs). Aqueous slurries containing 2.5% (w/w) sediment were oxidized with oxygen in a one liter, high-pressure, batch reactor at temperatures up to 250°C. Concentrations of PCBs adsorbed on the sediment and reactor surfaces and dissolved in the water and gas phases after oxidation were determined by high-resolution gas chromatography. Results indicate that no significant wet oxidation of PCBs in sediment slurries occurs for temperatures at or below 250°C. However, during reactor heat-up, significant degradation of PCBs occurred at high temperature regions near the reactor wall even when bulk fluid temperature was quite low. The addition of a readily degraded organic compound did not result in enhanced degradation of PCBs through a kinetic coupling mechanism as has been observed for other recalcitrant organic compounds.

Introduction

Many coastal areas of the world have sediment that is contaminated with organochlorine compounds including polychlorinated biphenyls (PCBs). In the Great Lakes region alone, U.S. and Canadian environmental agencies have designated 43 areas of concern with heavy sediment contamination and just recently the U.S. EPA has ordered the dredging of 2.65 million cubic yards of sediment from the Hudson River that is contaminated with PCBs. Because of the hydrophobic nature of these compounds, they tend to bioaccumulate throughout the food web and, therefore, slow release of these contaminants to surface and groundwater provides a route for animal and human exposure. Many of these compounds (e.g. PCBs, DDT, pentachlorophenol, dioxins, and furans) are classified as hormonally active agents and significant prenatal exposure to these compounds from consumption of contaminated fish, meats, and dairy products can cause low birth weight, shorter gestation periods, IQ and memory deficits, and delayed neuromuscular development.¹

Currently, approved methods for treating these sediments involve dredging, de-watering, and either depositing the sediment in an approved chemical waste landfill or incinerating the sediment. There is widespread public opposition to both of these approaches. Moreover, incineration of sediments contaminated with PCBs can be very costly. Other treatment methods may be approved on a case-by-case basis.

Wet air oxidation (WAO) is a commercial process used to remediate aqueous waste streams containing organic solutes and to regenerate powdered activated carbon (US Filter/Zimpro PACT Process). Conventional wet air oxidation utilizes air or oxygen in conjunction with elevated temperatures and pressures to oxidize moderately contaminated waste streams. Fairly simple modifications to commercially available wet oxidation systems would

allow for the treatment of excavated sediment and soil following an initial screening to remove large debris and a separation step (e.g. hydrocyclone) to remove sand particles. These larger particles are not amenable to wet oxidation treatment but also are not expected to be contaminated with high concentrations of adsorbed organic compounds. The resulting fine silt and clay fractions, which are expected to contain the majority of contaminants, are amenable to wet air oxidation. However, as determined in several studies, many of these contaminants (including PCBs) are not effectively degraded by conventional wet oxidation except at temperatures in excess of 300°C and pressures in excess of 1500 psi.^{2,3} These high temperatures and pressures necessitate the use of very expensive materials, pumps, and air compressors.

Wet air oxidation of organic compounds proceeds via a free radical mechanism initiated by the thermal reaction of the organic substrate with oxygen.⁴



This step, which is believed to be rate limiting for most compounds, is extremely slow for chlorinated aromatics (e.g. PCBs and chlorinated benzenes) that do not contain other functional groups. The free radicals formed by this initiation step subsequently react with oxygen and other organic and inorganic compounds forming a variety of radical species including organic radicals and hydroxyl radicals.



Hydroxyl radicals are highly reactive with PCBs with measured rate constants being close to those corresponding to the diffusion-limited reaction.^{5,6}

Therefore, in wet oxidation processes, the degradation of recalcitrant compounds such as PCBs may be closely linked to the production of active radical species generated by the degradation of readily oxidized organic compounds or hydrogen peroxide. These “kinetic coupling” phenomena have been observed in the wet air oxidation of acetic acid and m-xylene in the presence of phenol and simple alcohols such as ethanol.⁷⁻⁹ For example, in experiments reported by Willms et al., the rate of degradation of m-xylene in the presence of an equimolar concentration of phenol was more than one order of magnitude greater than the rate for m-xylene alone.⁷ Birchmeier et. al. described a similar effect in studies of the oxidation of recalcitrant wet oxidation products (low molecular weight carboxylic acids) in the presence of phenol.⁸ Initially rapid oxidation rates became much slower as unreactive products were generated. The oxidation rates of the recalcitrant compounds increased again when more phenol was added.

In this paper, we report the effects of various operational parameters and additives on the wet oxidation of sediments contaminated with PCBs from the Hudson River (NIST SRM 1939a). The hypothesis that we are testing is that the destruction of PCBs during wet oxidation is dependant on the generation of radical species, specifically hydroxyl radicals, either in solution or at the sediment/water interface.

Experimental Methods

All experimental systems and procedures were the same as reported previously by Duffy et al.¹⁰ Briefly, a slurry of sediment in water (2.5 % w/w) was oxidized in a 1-L high-pressure reactor (Parr Scientific) using pure oxygen as the headspace gas as depicted in Figure 1. The

contaminated sediment (NIST SRM 1939a – PCBs in River Sediment) was originally obtained from the Hudson River and contains 11.4% (w/w) organic matter and approximately 75 mg/kg PCBs. Sulfuric acid was added to the slurry to achieve the desired initial pH of 2.6. Following acidification of the slurry, the reactor was sealed, pressurized with oxygen, and heated to the desired temperature (usually 250°C). The reactor was maintained at this temperature for the desired period of time (usually 1 hour) and then rapidly cooled to room temperature. The duration of a typical experiment including heat-up and cool-down was 110 minutes. Following cool-down, volatilized PCBs in the reactor headspace were captured by sparging the headspace gas through two bottles of acetone in series. An absence of PCBs collected in the second bottle indicated that all PCBs were collected in the first bottle. The effluent slurry was then filtered and PCBs in the water and sediment were extracted using liquid-liquid extraction with dichloromethane and sonication extraction with acetone/hexane, respectively. All internal reactor surfaces were rinsed twice with acetone. No PCBs were evident in the second rinsing indicating that all PCBs on the reactor surfaces were collected with one rinse. All samples were analyzed using high resolution gas chromatography. Details of the extraction and analysis procedures were reported previously.¹⁰

Results and Discussion

Validation of Experimental and Analytical Methods: The experimental protocols for extraction of the sediment were validated by comparing average recoveries from duplicate extractions to concentrations of PCBs certified by NIST. Results of these experiments have been previously reported and indicate that the methods utilized in these experiments resulted in quantitative extraction of the analytes of interest as compared to the certified values.¹⁰

Control Experiments: For wet air oxidation to occur, both elevated temperature and an oxidant (usually oxygen) are required. Control experiments were performed to verify that PCB losses were not occurring through avenues other than by oxidation. Results of these experiments have been previously reported and indicate that losses of PCBs by routes other than oxidation were negligible.¹⁰

Effect of Stir Rate: The possibility that the rate of oxygen transfer may limit the reaction rate in wet oxidation systems has been reported.^{11,12} The transfer of oxygen in a batch reactor system pressurized with oxygen is governed by the stir rate. Experiments were performed at different stir rates to determine any effects or limitations imposed by the mixing of the system. Multiple experiments were conducted at 1000 rpm to determine variability which is indicated by the error bars which represent one standard deviation. From these results (Figure 2), the system does not appear to be limited by mixing for stir rates of 500 rpm and above. All subsequent experiments were conducted at or above 700 rpm.

Partitioning of PCBs following Oxidation: The distribution of PCBs between the gaseous phase, aqueous phase, and sediment and reactor surfaces following cool-down is depicted in Figure 3. The individual congeners were chosen so as to provide one representative from each of the homologue groups in the range from two to seven chlorine atoms. For congeners containing only a few chlorine atoms, a substantial fraction partitioned to the aqueous and gaseous phases. This fraction decreased significantly for the more highly chlorinated congeners. In fact, congeners containing five or more chlorine atoms were not detectable in the gas phase. The distribution of congeners between the solid surfaces (sediment and reactor) and aqueous phase is consistent with published solid/water distribution ratio trends for individual congeners. In

subsequent experiments, PCBs collected from the gas and water phases, the sediment, and the reactor rinse were combined into one sample for analysis.

Effect of Temperature on the Rates of Destruction of PCBs: Temperature is an extremely important variable in the wet oxidation process. System pressure, reaction rates, the solubilities of organic compounds and oxygen, and the rates of desorption of organic compounds from particulate matter are all appreciably affected by temperature.^{2-4,13-16}

The present studies of wet air oxidation of sediment contaminated with PCBs were conducted at temperatures ranging from ambient to 250°C. The percentages of selected individual congeners remaining after each experiment are depicted in Figure 4. For reaction temperatures above ambient, a significant fraction of the PCBs were destroyed. Since PCBs are recalcitrant to wet air oxidation at temperatures up to 300°C,² this result was initially very surprising. However, a study of PCB degradation as a function of reaction time at 250°C (Figure 5) indicates that all of the degradation occurs during reactor heat-up. Subsequent measurement of reactor wall temperature during heat-up (Figure 6) indicates localized wall temperatures well in excess of 400°C near the heating elements. After heat-up, wall temperatures stabilized at levels near that of the bulk fluid and no further degradation was observed. Therefore, we conclude that PCB degradation in all experiments was occurring only in very high temperature regions at or near the reactor wall and that oxidation of PCBs in regions with temperatures at or below 250°C is insignificant. The extensive degradation of PCBs during reactor heat-up does however indicate that the potential exists for significantly accelerating the wet oxidation of recalcitrant compounds at low bulk fluid temperatures and pressures by passing the solution or slurry over very hot surfaces.

Figure 4 also shows that di and tri-chlorinated congeners were much more effectively degraded as compared to their more highly chlorinated homologues. This behavior is likely the result of faster desorption and/or faster reaction of the less chlorinated congeners. Yang et al. investigated the extraction of PCBs from a heavily contaminated industrial soil. Analysis of their kinetic data indicates that in subcritical water at 250°C and 50 atm, congeners containing only a few chlorine atoms are rapidly extracted in less than 10 minutes whereas the more highly chlorinated congeners require up to 1 hour for complete extraction.¹⁷ The PCB congeners containing only a few chlorine atoms also react more readily with hydroxyl radicals via a hydrogen abstraction mechanism. Sedlak et al. investigated the aqueous phase oxidation of PCBs using Fenton's reagent.⁶ In these studies, relative reaction rates for the oxidation of individual congeners in an Aroclor 1242 solution were determined by competition experiments. These researchers demonstrated the existence of a linear relationship between the number of non-halogenated sites and the average reaction rate. For each chlorine atom added to the biphenyl structure, there is a 10% reduction in the reaction rate.

Efforts to Enhance Wet Oxidation Rates through Generation of Active Radical Species: As stated earlier, several authors have demonstrated that kinetic coupling can result in the accelerated degradation of a recalcitrant species when it is oxidized in the presence of a readily degraded species. An example of this kinetic coupling is the enhanced wet oxidation of organic species in the presence of hydrogen peroxide. Hydrogen peroxide readily decomposes at elevated temperature to form two hydroxyl radicals which can subsequently react with organic species present in solution or at solid/solution interfaces. The effect of hydrogen peroxide addition during wet oxidation of sediments contaminated with PCBs has been reported previously.¹⁰ These experiments indicate that oxidation of PCBs is significantly accelerated in

the presence of hydrogen peroxide (Figure 7). In these experiments, hydrogen peroxide was added following heat-up to the designated temperature. For experiments without peroxide addition, all PCB degradation occurred during reactor heat-up as previously described. We believe that the increased oxidation is primarily the result of hydroxyl radical attack initiated by thermal decomposition of hydrogen peroxide.

Active radical species are also generated by wet oxidation of organic species. To test the hypothesis that readily degraded organic matter may generate the active radical species necessary for PCB destruction, aqueous solutions of phenol were added to the sediment/water slurry with a high-pressure pump following heat-up to 250°C. Phenol was chosen because it readily degrades at 250°C and has been shown to accelerate oxidation of other recalcitrant compounds.⁷⁻⁹ Twenty milliliters of phenol solution with a concentration of 50 gm/L was pumped in at 10 mL/min for 2 minutes (total added phenol = 1 gm). No additional degradation of PCBs (beyond that occurring during heat-up) was observed in these experiments. Therefore, we infer that wet oxidation of phenol at 250°C does not produce highly active radical species (hydroxyl radicals) in concentrations sufficient to result in measurable co-oxidation of PCBs.

Transition metal catalysts (iron and copper salts) have also been shown in a number of studies to accelerate the oxidation of recalcitrant organic species. In a single experiment, copper sulfate was added to the sediment slurry at a concentration of 5 mM prior to wet oxidation at 250°C. A copper salt was chosen to test the effect of a homogenous catalyst because it has been shown to be catalytically active in a variety of situations.^{3,13,18,19} No significant degradation of PCBs (beyond that occurring without catalyst during heat-up) was observed.

Conclusions

1. No significant degradation of PCBs occurs during wet air oxidation of contaminated sediments at temperatures at or below 250°C.
2. Significant degradation of PCBs was observed during heat-up periods in which the reactor wall reached temperatures well above 300°C in regions near the heating elements. This degradation is believed to occur on or near the wall surface.
3. Addition of hydrogen peroxide during wet oxidation of sediments results in significant degradation of PCBs even at the relatively low temperature of 125°C. This enhanced degradation is believed to occur via hydroxyl radical attack initiated by thermal decomposition of hydrogen peroxide.
4. Addition of phenol during wet oxidation of sediments at 250°C does not result in degradation of PCBs through kinetic coupling as has been observed for other recalcitrant organic species.
5. Addition of homogeneous copper catalyst does not accelerate the wet oxidation of PCBs at 250°C.

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Publications and Presentations: This work has not yet been published; however a similar version of this report will soon be submitted. The journal has yet to be determined. This work was presented at the 2002 Montana AWRA conference.

Other Notable Achievements: None.

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Figure 1. Schematic diagram of the reactor system.

Figure 2. Effect of reactor stir rate on PCB destruction. Conditions: temperature = 250°C; partial pressure of oxygen = 300 psi; initial pH = 2.6.

Figure 3. Distribution of PCBs between gas, liquid, and solid phases following WAO.

Conditions: temperature = 225°C; initial pH = 2.6; partial pressure of oxygen = 300 psi; stirring rate = 720 rpm.

Figure 4. WAO of sediment slurries at temperatures of 25, 125, and 250°C. Conditions: stirring rate = 720 rpm; partial pressure of oxygen = 300 psi; initial pH = 2.6.

Figure 5. Effect of reaction time on PCB destruction. Conditions: temperature = 250°C; stirring rate = 1000 rpm; partial pressure of oxygen = 300 psi; initial pH = 2.6.

Figure 6. Bulk fluid and heating band temperatures during WAO experiments.

Figure 7. PCB destruction during WAO with and without hydrogen peroxide addition.













