A Novel Method for Remediation of PCBs in Weathered Coatings

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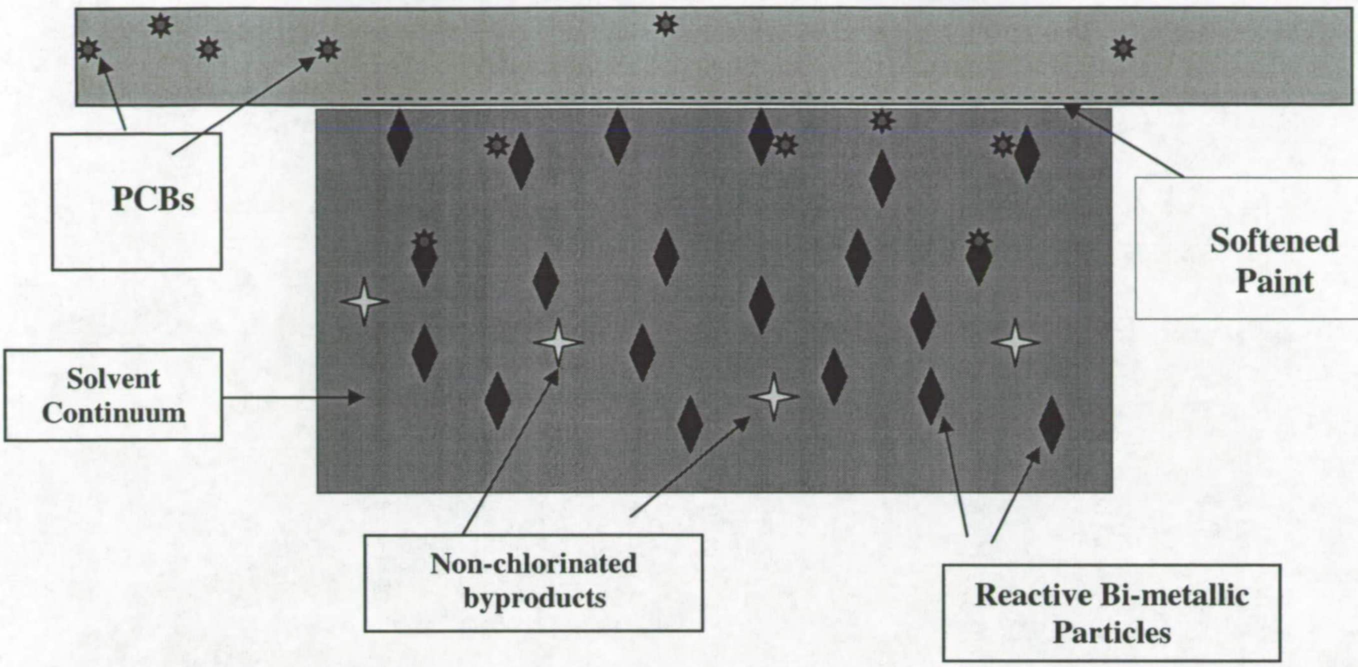
ABSTRACT: Polychlorinated biphenyls (PCBs) are a group of synthetic aromatic compounds with the general formula $C_{12}H_{10-x}Cl_x$ that were historically used in industrial paints, caulking material and adhesives, as their properties enhanced structural integrity, reduced flammability and boosted antifungal properties. Although the United States Environmental Protection Agency (USEPA) has banned the manufacture of PCBs since 1979, they have been found in at least 500 of the 1,598 National Priorities List (Superfund) sites identified by the USEPA. Prior to the USEPA's ban on PCB production, PCBs were commonly used as additives in paints and asphalt-based adhesives that were subsequently applied to a variety of structures. Government facilities constructed as early as 1930 utilized PCB-containing binders or PCB-containing paints, which are now leaching into the environment and posing ecological and worker health concerns. To date, no definitive *in situ*, non-destructive method is available for the removal of PCBs found in weathered coatings or on painted structures/equipment. The research described in this paper involves the laboratory development and field-scale deployment of a new and innovative solution for the removal and destruction of PCBs found in painted structures or within the binding or caulking material on structures. The technology incorporates a Bimetallic Treatment System (BTS) that extracts and degrades only the PCBs found on the facilities, leaving the structure virtually unaltered.

INTRODUCTION

In 2003, researchers at the Kennedy Space Center and the University of Central Florida began investigating the potential of using a solvent-based treatment system to remove PCBs found in paints located on a number of structures at three NASA Centers. This research led to the development of a Bimetallic Treatment System (BTS) comprised of elemental magnesium (Mg) particles enriched with a small number of catalytic palladium (Pd) sites that is utilized in conjunction with a solvent system that is capable of reacting with Mg to produce the hydrogen atoms that are required to complete the hydrodehalogenation reaction cycle. BTS technology has two functions: first, to extract the PCBs from weathered, decades-old coating material, such as paint; and second, to degrade the extracted PCBs to nonhalogenated by-products. Figure 1 represents the pictorial architecture of BTS.

This paper introduces BTS formulations that are capable of extracting PCBs *in situ* from painted structures and effectively degrading them via a dehalogenation process. The dechlorination process is discussed along with potential mechanistic pathways. Factors involved in the selection of the individual components including the bi-metallic particles and the solvent continuum will be presented along with kinetic studies demonstrating degradation rates.

FIGURE 1 Pictorial Diagram of a Bimetallic Treatment System.



MATERIALS AND METHODS

BTS' removal and degradation of PCBs occurs via two independent processes; the chemical extraction of the PCBsfrom the structure and the PCB's subsequent destruction in the presence of the catalyst system. BTS' goal is to extract PCBs without destroying the paint and partition them into an environmentally friendly solvent. Our research indicates this can usually be accomplished within 24-72 hours of BTS contact. PCBs are extremely hydrophobic and prefer to be in the BTS instead of hardened paint or binder material. The solvent is used to open, but not destroy the paint's polymeric lattice structure, allowing pathways for PCB movement out of the paint and into the solvent. The solvent and reactive system containing the metal and proton donor are blended together along with thickening agents to create a paste-like product that can be applied to the PCB-laden surface. A number of solvent systems have been tested and are compatible with the BTS. After the BTS is removed from the paint surface, the lattice structure returns to its original configuration, with minimal change in surface appearance, texture, or hardness.

The catalyst system developed by the team is manufactured using a mechanical alloying method. It has been optimized for use in BTS and typically consists of 0.1% Pd on Mg. Several experiments were run using the dry metal in aqueous PCB solutions to determine the catalyst to metal ratio. The Mg/Pd bimetal is a potent hydrodechlorination reagent capable of removing the chlorine from a high concentration solution of chlorocarbons in minutes (Engelmann, 2003). Literature suggests the degradation end-product for the dehalogenation of all Aroclor mixtures is the biphenyl ring, which is a benign end-product (Doyle, 1998). Magnesium metal, a powerful reducing agent, reacts with water to form hydrogen gas (H_2) and magnesium hydroxide (Brown et al., 2005). Palladium is a well-documented hydrogenation catalyst that chemisorbs molecular hydrogen, weakening the bond between the hydrogen atoms, forming atomic hydrogen bound to the palladium surface (McMurray, 2000) and (Tsuji, 2004). It is hypothesized that the interaction of the bimetallic Mg/Pd system with a solvent containing available hydrogen moieties (i.e. alcohols or water) results in the generation of atomic hydrogen at particular sites on the metal surface. The unbound, atomic hydrogen is available for reaction with PCB molecules that come into contact with the catalytic surface resulting in a reductive dehalogenation reaction. The proposed reaction mechanism is shown below:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

$$H_2 \text{ (Pd catalyst)} + RCl \rightarrow RH + HCl$$

Rapid and complete dechlorination of PCBs in aqueous/solvent systems in the presence of the catalyst system described above has been documented (Doyle, et al.,1998). Table 1 illustrates the typical degradation results achieved in an aqueous system comprised of water, 10% methanol, and the bimetal. Methanol was added to the water to increase the solubility of PCBs in the stock solution. The samples were run via GC/MS using a modified version of EPA method 8270. Addition of the Mg/Pd particles to an aqueous system immediately begins to produce large amounts of hydrogen gas.

Due to safety concerns associated with the large production of hydrogen when the Mg/Pd was added to water, other potential solvents such as pure methanol and ethanol solutions were tested resulting in similar rates of PCB dehalogenation as shown in Tables 2 and 3. The oxidation of the magnesium metal is not as exothermic when alcohols are substituted for water thus decreasing the likelihood of potential ignition of hydrogen gas. The solvents themselves carry flammability cautions that must be addressed in the field during BTS application using best management practices.

Additional BTS formulation properties that must be addressed for each site-specific application include viscosity and stability. The BTS must be viscous enough to remain where it is applied and several thickening agents have been tested. Adding a stabilizing agent ensures the BTS will not evaporate and leave the unprotected Mg/Pd exposed. Due to the extreme reactivity of BTS, the choice of thickening and stabilizing agents is complex. During BTS formulation testing, a number of reagents were evaluated to ensure the rate of dehalogenation was not inhibited by its addition to the system. Table 3 presents data obtained with the addition of glycerin as a stabilizing agent and thickener, showing no interferences of this additive on the PCB dehalogenation.

Combining the optimal solvent catalyst system, thickeners and stabilizing agents forms a paste-like BTS system. As stated earlier, each structure requires specific formulation optimization to ensure success. For example the launch umbilical tower (LUT) for the retired Apollo program required the use of toluene or limonene as a solvent to soften the paint to allow PCB migration. For experiments with this structure, we applied specific paste formulations to sample structures and compared analytical results prior and post application of BTS. Analyses of these samples is quite complex. We have found that most structure have varying levels of PCBs by weight percent on the same structure. This may be due to weathering of the paints or variations in the paint thickness. Table four represents the results of a study on the LUT structures.

A field deployment of several BTS formulations and application strategies were tested on the inside of a retired engine test stand at Marshal Space Flight Center (MSFC) in Huntsville, Alabama. The objective of this field deployment was to transition laboratory generated results to a real-world setting to determine the effectiveness of the BTS, and to optimize application procedures. Using lessons learned from this transitional study, it was anticipated that the NASA/UCF team would be better able to make further recommendations on application strategies for BTS deployment. The plan was to try several BTS formulations, application procedures and exposure durations. Five gallon drums were made of inactive toluene-based BTS and inactive limonene-based BTS. One gallon of active limonene-based BTS, toluene-based BTS and no-metal BTS were also made. At the time of publication of this paper, the data was still being acquired for this field deployment. Preliminary results are listed in Table 6.

RESULTS AND DISCUSSION

The data in Tables 1 and 2 show that the degradation of PCBs can be achieved rapidly and completely in the presence of the catalyst system developed by the project team. The data in Table 2 demonstrates that the dechlorination process can take place without the presence of water. The suspected reaction in non-aqueous conditions involves utilizing the slightly acidic proton on the alcohols as the hydrogen that is replacing the chlorines in the dechlorination reaction. Future experiments testing this hypothesis will include the use of deuterated alcohols to track the potential movement of the hydrogen from the alcohols.

By-products formed with the reduction reaction are similar for both reactions including water and without water. The data obtained from snapshots of the reaction show that the dechlorination process does occur somewhat stepwise. This is evident by the formation of lower molecular weight chlorinated biphenyls, signified by the earlier retention times that were not present in the same ratio in the untreated 100 mg/l PCB 1254 sample. Note the changing ratios of later eluting peaks in Figure 2. Additional by-products that may also be produced are lower molecular weight hydrocarbons. These compounds would be masked within the solvent peak if analyzed under typical PCB methods such as EPA method 8270. Future experiments will be conducted using headspace extraction to better characterize the presence of more volatile by-products. The by-products formed and the potential mechanisms of the dehalogenation reaction will be discussed in future publications.

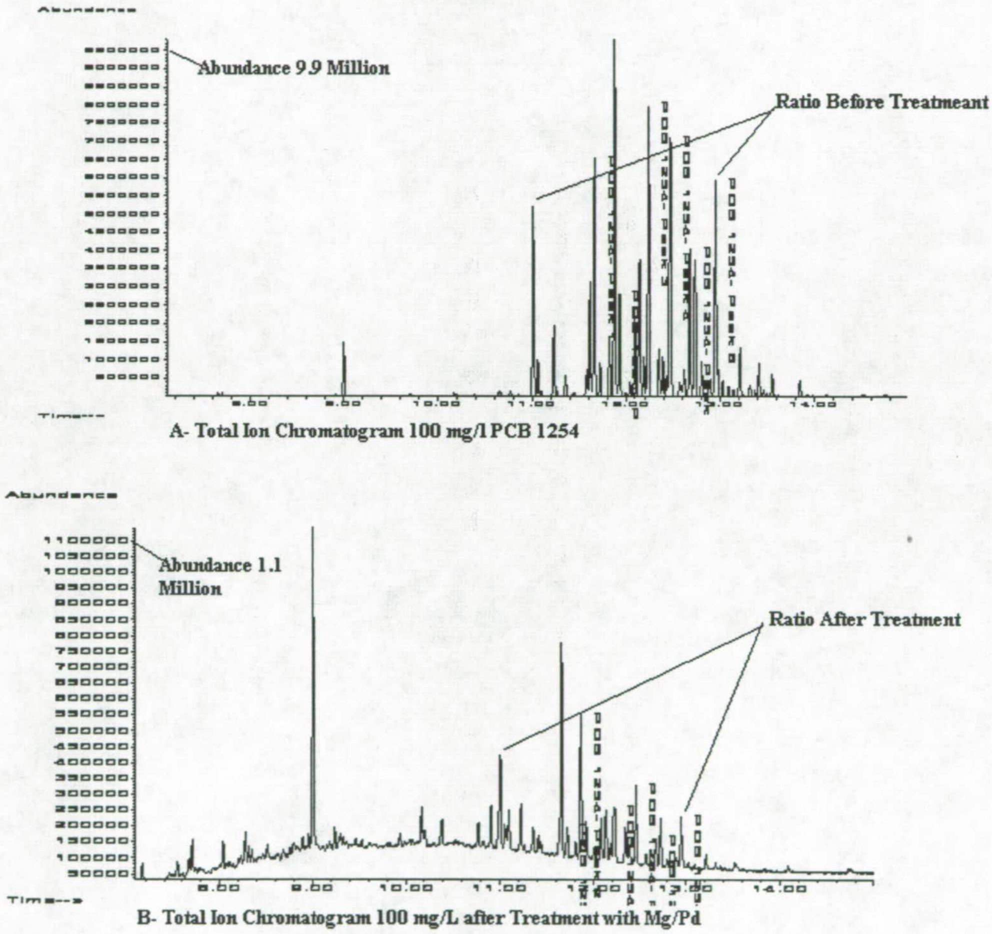
TABLE 1 Exposure of standard aroclor 1260 in 10% methanol in water solution to 1.0 g Mg/Pd

Sample Identification	Aroclor 1260 (mg/l)	% PCB Degradation
Extracted Standard (no Mg/Pd) 5.9 mg/L Initial Concentration	5.9	0
Standard exposed to Mg/Pd 1.0 hr	0.4	92 %
Standard exposed to Mg/Pd 4.0 hr	<0.1	>98 %
Standard exposed to Mg/Pd 4.0 hr (dup)	<0.1	>98 %

TABLE 2 Exposure of standard aroclor 1254 in methanol only to 0.5 g Mg/Pd

Sample Identification	Aroclor 1254 (mg/l)	% PCB Degradation
Extracted Standard (no Mg/Pd) 5.5 mg/L Initial Concentration	5.5	0
Standard exposed to Mg/Pd 0.5 hr	0.3	95 %
Standard exposed to Mg/Pd 1.0 hr	<0.1	>98 %
Standard exposed to Mg/Pd 2.0 hr	<0.1	>98 %
Standard exposed to Mg/Pd l 4.0 hr	<0.1	>98 %

FIGURE 2 Total ion chromatograms showing differing peak ratios of a 100mg/l Solution before and after treatment with Mg/Pd.



The data represented in Table 3 demonstrates that the addition of glycerin as a thickening and stabilizing agent does not alter the efficacy of the catalyst to degrade PCBS. Other thickening agents such as starch and calcium stearate were also tested and produced similar results.

TABLE 3 Exposure of standard aroclor 1260 in ethanol with and without the addition of glycerin.

Sample Identification	Aroclor 1260 (mg/l)	% PCB Degradation
Extracted Standard (no Mg/Pd) 10.6 mg/L Initial Concentration	10.6	0
Standard exposed to Mg/Pd 24 hr	<0.1	>99 %
Standard exposed to Mg/Pd with glycerin 24 hr	<0.1	>99 %

Once the BTS formulations were optimized, the system was tested on real world samples. Table 4 represents typical data obtained from applying the BTS to structures at Kennedy Space Center. Note the final concentrations of PCBs were well below the action level of 50 mg/Kg.

Table 4 Launch umbilical tower (LUT) paint treated with BTS paste consisting of Mg/Pd, glycerin and methanol. Exposure time 24 hrs.

Sample Identification	Initial Concentration Aroclor 1260 (mg/Kg)	After BTS Aroclor 1260 (mg/Kg)	% PCB Removal
LUT A Green 05/11/05	110	0.8	>99 %
LUT A Green 05/18/05	260	9.7	96 %
LUT Red 05/18/05	7.7	0.2	97 %

For the MSFC field projects, structure samples were not available to be tested in the laboratory prior to outdoor application. The laboratory experiments required the use of limited samples (weathered paint chips only) to determine approximate concentrations before and after application of the BTS. Tables 5 and 6 exhibit the lab and field data obtained from using BTS at MSFC. The initial concentrations of PCBs within the paint are over an order of magnitude lower than the 50 mg/kg action level established by the EPA, making this site far from an ideal location to test the applicability of BTS for the remediation of PCB in painted structures. However, this data does show the wide range of applicability of BTS systems on paints with relatively high levels of PCBs to paints with levels below conventional action level.

TABLE 5 Initial laboratory testing of Marshall Space Flight Center paint chips treated with BTS paste consisting of Mg/Pd, glycerin and ethanol. Exposure time of 24 hrs.

Sample Identification	Initial Concentration Aroclor 1260 (mg/Kg)	After BTS Aroclor 1260 (mg/Kg)	% PCB Removal
4696 F1 Stand	4.6	0.8	83 %
4553 F1 Stand	6.3	<0.3	95 %

TABLE 6 Field results using a limonene-based BTS paste at MSFC building 4696 F1 stand.

Time of Exposure (hr)	Initial Concentration Aroclor 1254 (mg/Kg)	After BTS Aroclor 1254 (mg/Kg)	% PCB Removal
8	3.46	2.65	23.4%
8 dup	3.24	2.87	10.7%
24	3.28	2.39	27.2%
24 dup	3.11	2.23	28.3%
72	4.18	1.79	57.2%

Due to the wide variety of structural properties associated with each particular PCB-laden paint, the choice of solvent(s) incorporated into BTS is specific to the paint being treated. Treatability tests run by the team have shown that solvent systems that work very well at softening and removing the PCBs found in one variety of paint can be ineffective when applied to another. Therefore, the final formulation of BTS must be determined in the laboratory, in treatability tests using paint samples from the proposed area prior to determining the final formulation of BTS to apply. A number of "standard formulations" have been developed to address paints that have weathered under different conditions and which contain varying percentages of PCBs. It is important to note that "softening " of the paint simply refers to opening the polymeric lattice structure of the paint and is not intended to imply that the paint softens to a degree that it can be wiped off the structure or that any other action must be taken because the paint is "softer". It can in fact remain on the structure after BTS application. The catalyst system may be reclaimed to recover the noble metal, Pd. The non-toxic BTS formulation may be applied using a "paint-on and wipe-off" process, that in the end leaves the structure PCB-free and virtually unaltered in physical form.

The application of BTS to binder materials containing PCBs does have the potential to alter the adhesive qualities of the material while removing and degrading the PCBs. Therefore, for caulking materials or binders containing PCBs, the structure would in most instances require reapplication of a new binder after the application of BTS. Site-specific evaluation of the pull-strength of the material would be necessary in order to make this determination. A good example is the potential application of BTS to binder materials that contain as high as 20% by weight Aroclor 1268. If BTS removes 20% of the binder's weight, the material cannot be expected to have the same adhesive properties as before and therefore the structure would be altered, and a new binder would be required to replace the old. This is in contrast to the application of BTS to paints where there is virtually no impact to the surface of the paint. BTS has been applied to LUT pieces and no visual impact to the paint is noticeable. Reapplications of a new coat of paint, or simply leaving the structure "as is" are alternatives

CONCLUSIONS

In summary, BTS is comprised of a bimetallic catalyst system incorporated into a solvent that is not only capable of efficiently extracting PCBs from multiple, thick layers of extremely weathered, decades-old paint within days, but also functions as a hydrogen donation source for the degradation of PCBs. BTS does not remove or destroy the painted structure upon which it is applied. New paint may be applied once the old has been treated, or the existing paint may be left in place as no visual difference is notable. Once the BTS has been allowed to react until complete PCB degradation has occurred, the solvent may be disposed of as a non-TSCA regulated waste. BTS may also be applied utilizing dip tanks where pieces of caulking or adhesives are treated in batches of BTS prior to disposal. BTS has far reaching implications to older facilities across the world; allowing them to be remediated and reused by implementing a PCB cleanup technology that removes and degrades the PCBs while on the structure. BTS has the capability of removing PCB's from paints that range in concentrations from extremely high (> 700 mg/Kg) to very low (<5 mg/Kg). BTS has been field-tested with statistically significant reduction rates achieved.

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