A Study Of The Degradative Capabilities Of The Bimetallic System: Mg(pd/c) As Applied In The Destruction Of Decafluoropentane, An Environmental Contaminant

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A STUDY OF
THE DEGRADATIVE CAPABILITIES OF THE BIMETALLIC SYSTEM: Mg(Pd/C)
AS APPLIED IN THE DESTRUCTION OF DECAFLUOROPENTANE,
AN ENVIRONMENTAL CONTAMINANT

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Chemistry
in the College of Sciences
at the University of Central Florida
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2012

Major Professor: Christian A. Clausen III
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ABSTRACT

Pollution from hydrofluorocarbons (HFC) poses a serious challenge to the environmental community. Released from industrial operations, they have contaminated both the atmosphere and groundwater and are considered persistent in both media.\(^1\) For over the past 20 years, the practice of synthesizing hydrofluorocarbons as alternatives to chlorofluorocarbons (CFC) has been conducted in an effort to reverse the effects of stratospheric ozone layer depletion.\(^2,3\) However, in doing so these new fluorinated compounds exhibited an unexpected property as a potent global warming greenhouse gas (GHG) with radiative forcing potentials in the range of 100 to 10,000 equivalents greater than carbon dioxide.\(^4\) Conversely, HFCs exhibit desirable properties as precision cleaning solvents due to their low surface energy but that use has lead to releases contaminating groundwater resulting in recalcitrant pollution in the form of dense non-aqueous phase liquids (DNAPL).\(^5\) The Environmental Protection Agency (EPA) has recently requested studies on the environmental impact of HFCs with respect to a number of petitions received from various environmental action groups imploring the use of the Montreal Protocol as the vehicle by which to achieve elimination of the compounds from industrial operations.\(^6,7\) Additionally, results from studies requested by the international community have shown HFCs to exhibit developmental and neurological damage in animal life along with their impact to humans remaining not completely understood.\(^8,9,10\) Therefore, the potential hazards of HFCs to human health and the environment necessitates the development of an effective and environmentally responsible technology for their remediation from groundwater.

The National Aeronautics and Space Administration (NASA) has employed the use of various halogenated solvents in its spacecraft cleaning operations at its facilities for many years
and in that time experienced accidental releases which eventually resulted in environmental contamination. Many of the organic solvents employed in these operations consisted of halogenated compounds with most being partially chlorinated and fluorinated hydrocarbons. Through normal use and operation, releases of these materials found their way into the environs of atmosphere, soil and groundwater. Remediation of fluorinated compounds has not followed the successful path laid by clean-up technologies developed for their chlorinated counterparts. Fluorinated compounds are resistant however to those methods due to their unreactive nature stemming from the properties of the strong carbon-fluorine bond. This unique bonding property also ensures that their environmental persistence endures. One particular fluorinated groundwater contaminant, the HFC 1,1,1,2,2,3,4,5,5,5-decafluoropentane (DFP), which serves as an excellent cleaning agent and has been used by NASA since the late 1990’s and still remains in use today, was selected as the focus of this study.

For this study, various reductive metal systems were evaluated for their capability towards effective degradation of DFP. These included the metals: iron, magnesium, aluminum and zinc and several bimetallic alloys as well as attempts employing some on carbon support. Variations in protic solvent reaction media and acidic metal activation were also explored. The bimetallic reductive catalytic alloy, magnesium with palladium on carbon support Mg(Pd/C) in aqueous media, proved to be the successful candidate with 100% conversion to simple hydrocarbons. Mechanistic evaluation for degradation is proposed via a series of stepwise catalytic reduction reactions. Kinetic studies revealed degradation to obey second order reaction kinetics.

Further study should be conducted optimizing an in situ groundwater delivery method for field application. Additionally, the developed technology should be assessed against other
groundwater fluorocarbon pollutants; either as a method for remediating multiple fluorinated polluted sites or as a polishing agent where all other non-fluorinated halogen pollutants have been abated.
I dedicate this body of work to my Wife Elvira, my Daughter Abigail, my Son Andrew and my Mother Barbara; without whom I never would have been able to accomplish this goal.

Their love, support, encouragement and patience were essential to my success.
ACKNOWLEDGMENTS

I would like to thank the following: The NASA Graduate Fellowship Program for academic funding, of which without, achieving this goal would not have been possible. The NASA Kennedy Space Center Chemical Analysis Branch for their understanding and accommodating support, especially Kathy Loftin and Dionne Jackson for their kindness and free use of the laboratory facilities during this study. The NASA Kennedy Space Center Environmental Compliance Branch for their acceptance and support of the truly necessary leave of absence required to achieve this goal. My fellow UCF Environmental Chemistry Department Students; Phil Maloney, Simone Novaes-Card, Tamra Legron, and Marc Elie who provided wonderful support and were always willing to help out in any way, unquestioned. I would also like to thank Committee Members Seth Elsheimer and Michael Hampton for their guidance, insight, and engaging discussions during my studies, all integral to the success of my research objectives.

I also thank Committee Member Tim Griffin for his unparalleled generosity in use of the NASA Chemical Laboratories, and for his gracious and kind understanding and support of all my efforts during this project. I further thank Committee Member Cherie Yestrebsky for her inspiration, compassion, and generous nature towards ensuring my success. I could not have achieved this goal without her dedication to my efforts.

Finally, a lifetime of gratitude to my Advisor and Chair, Chris Clausen, whom other than my family, has been the greatest positive single driving force in my academics, my career and my life. I can never repay him for all that he has done for me, but I will certainly make every effort to do so through all my ambitions and goals for the future.
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<th>Description</th>
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<tr>
<td>CCNS</td>
<td>Cape Canaveral National Seashore</td>
</tr>
<tr>
<td>CCS</td>
<td>Center for Climate Strategies</td>
</tr>
<tr>
<td>C-F</td>
<td>Carbon-Fluorine Bond</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
</tr>
<tr>
<td>DCE</td>
<td>Dichloroethylene</td>
</tr>
<tr>
<td>DDT</td>
<td>Dichlorodiphenyltrichloroethane</td>
</tr>
<tr>
<td>DFP</td>
<td>Decafluoropentane</td>
</tr>
<tr>
<td>DNPAL</td>
<td>Dense Non-Aqueous Phase Liquid</td>
</tr>
<tr>
<td>DOT</td>
<td>Department of Transportation</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EPOC</td>
<td>Emerging Pollutant of Concern</td>
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<tr>
<td>EQC</td>
<td>Equilibrium Criterion model</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethyl Alcohol</td>
</tr>
<tr>
<td>FDEP</td>
<td>Florida Department of Environmental Protection</td>
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<tr>
<td>FIB</td>
<td>Focused Ion Beam microscopy</td>
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<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>GCTL</td>
<td>Groundwater Cleanup Target Level</td>
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<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
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<tr>
<td>GWP</td>
<td>Global Warming Potential</td>
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<tr>
<td>HFC</td>
<td>Hydrofluorocarbon</td>
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HOMO  Highest Occupied Molecular Orbital
i.d.  Inner diameter
IPA  Isopropanol/Isopropyl Alcohol
IPCC  Intergovernmental Panel on Climate Change
IUPAC  International Union of Pure and Applied Chemistry
KSC  Kennedy Space Center
LUMO  Lowest Unoccupied Molecular Orbital
MCP  Methylcyclopentane
MeOH  Methanol/Methyl Alcohol
mg/L  milligrams per liter
μg/mL  micrograms per milliliter
Mg(Pd/C)  Magnesium (zero-valent) alloyed with Palladium on Carbon support
MINWR  Merritt Island National Wildlife Refuge
mmt  million metric tons
MS  Mass Spectrometer
m/z  mass to charge ratio
NADC  Natural Attenuation Default Concentration
NASA  National Aeronautics and Space Administration
NIST  National Institute of Standards and Technology
ODC  Ozone layer Depleting Compounds
OSHA  Occupational Safety and Health Administration
PCE  Perchloroethylene
PFC  Perfluorocarbon
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>PFOA</td>
<td>Perfluorooctanoic acid</td>
</tr>
<tr>
<td>PFOS</td>
<td>Perfluorooctane sulfonate</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act</td>
</tr>
<tr>
<td>$\sigma^*$</td>
<td>Sigma antibonding orbital</td>
</tr>
<tr>
<td>TCE</td>
<td>Trichloroethylene</td>
</tr>
<tr>
<td>TIC</td>
<td>Total Ion Chromatogram</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environment Programme</td>
</tr>
<tr>
<td>VC</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>ZVI</td>
<td>Zero-Valent Iron</td>
</tr>
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<td>ZVM</td>
<td>Zero-Valent Metal</td>
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<tr>
<td>ZVZ</td>
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CHAPTER 1: INTRODUCTION

Motivation

The motivation to conduct this research stems from the desire to address a current environmental pollutant present in the groundwater at NASA Kennedy Space Center (KSC). The pollutant of concern is the fluorinated hydrocarbon 1,1,1,2,2,3,4,5,5,5-Decafluoropentane (DFP). At present, no currently applied technology has been successful in its remediation from groundwater.

For many years, NASA has engaged in aerospace hardware cleaning operations for all of its well-known spaceflight vehicle programs including Mercury, Gemini, Apollo, the Space Shuttle and International Space Station. These operations mainly employed the use of various classical organic cleaning solvents but as time progressed and safety and environmental regulations became more stringent, most were phased-out in favor of replacement by less flammable and less toxic halogenated solvents. By design, these new solvents improved flight vehicle cleaning and personnel safety as they did not exhibit the flammability and health hazards of their predecessors.\textsuperscript{21} Also, among the selection of hydrofluorocarbon cleaning solvents, DFP in particular stood out clearly as best choice for this application.\textsuperscript{10} However, over the years most halogenated solvent use has had to undergo percent compositional modification or total reformulation if not outright ban from use due to compliance with ever increasing environmental regulations.\textsuperscript{22,23} Driven by initiatives such as the Montreal Protocol, mostly known for its ozone protection initiatives, and the Kyoto Accords i.e., “Greenhouse Gas Emissions” (GHG) Program,
for addressing global warming and the impact of climate change; public focus and mindset began to change on these chemicals.\textsuperscript{24,25} Thus, halogenated pollutants have become of great concern to the environmental regulators and community alike, requiring increased responsible action by industry and proper environmental management in their use. To this point, NASA has successfully remediated many of its contaminated soils and groundwater of solvent contamination. Yet, success in remediation of these solvents has remained with chlorinated compounds and other non-halogenated materials.\textsuperscript{26,27} In the case of fluorinated organic solvents, both chlorinated and brominated hydrocarbons are more easily dehalogenated and reduced than their fluorinated counterparts.\textsuperscript{28} It is for this reason that the subject of this research became the challenge to develop a successful and environmentally responsible groundwater remediation technology for fluorinated hydrocarbons.

Concerns Regarding the Impact of Fluorinated Compounds

In recent years, there has been an ever increasing focus on the potential harm of fluorinated compounds to both the public and the environment. This comes as somewhat of a surprise since for quite a number of year’s fluorinated compounds have been utilized in applications ranging from refrigerants to agriculture to cookware coatings. Fluorine has found application as an additive to drinking water and in toothpaste formulations for the prevention of tooth decay, but only relatively recently come under scrutiny as the potential cause for fluorosis in humans; damage to dental enamel.\textsuperscript{29} Further concern regarding fluoridated drinking water was revealed in a study by Freni which linked the fluorination in livestock drinking water to
negative health impacts as exhibited through decreased bovine birth rates.\textsuperscript{30} Also, a study of sodium fluoride treated drinking water in rodent studies revealed adverse effect on male reproductive systems through oxidative stress.\textsuperscript{31} Additionally, direct links between fluoridated water and human osteosarcoma, i.e., bone cancer, were presented by Mahoney et al. in a study conducted in association with the New York State Cancer Registry which has registered 95\% of all cancer cases in the state since 1973.\textsuperscript{32} But, concern with fluorine does not stop with inorganic applications.\textsuperscript{33}

Two organic forms of fluorine that have recently been receiving both health and environmentally related attention are the fluorinated surfactants perfluorooctanoic acid (PFOA) and perfluoroctane sulfonate (PFOS). These compounds have been found in many forms that have direct exposure to humans such as food, air, water, dusts, and textiles. A study by Tittlemeir et al. provided human exposure data through these various environmental media for both PFOS and PFOA. The group also conducted additional studies providing evidence of negative impact to non-human primates via increased reduction in immunity by the thymus gland in females and reduced HDL cholesterol and thyroid hormones in males.\textsuperscript{34} Also the EPA recently issued Health Advisories for PFOA and PFOS citing epidemiological and toxicological studies of soils and surface waters at agricultural sites that were exposed to fluorinated surfactants from manufacturing facilities. Although levels of each compound were detected in the test media, the EPA advised that public water systems had not been negatively impacted.\textsuperscript{35} In another study by Lindstrom et al., fluorochemical contamination was found in waste solids from a wastewater treatment plant had been used as fill for agricultural fields in which the plant had originally received wastes from a fluorochemical manufacturing facility.\textsuperscript{36} This is another example which demonstrates the lack of control over fluorocarbon wastes and where they may
impact humans and the environment in unsuspecting ways. Further, studies conducted by Steenland et al. on data from workers at several PFOA manufacturing facilities showed correlations in mortalities and incidents of cardiovascular disease potentially linking the chemical to the cause of death.\textsuperscript{37}

In general, the concern over the role of fluorine and fluorinated compounds and their impact to human health and the environment has been increasing and no example is more evident of this trend than that exhibited by the growing concern over global warming and climate change through identification of the greenhouse gases most responsible for the effect, those being Hydrofluorocarbons (HFCs) and Perfluorocarbons (PFCs).

\section*{Hydrofluorocarbons and Perfluorocarbons}

\subsection*{Environmental Impact}

In the field of organic fluorine chemistry, these two main groups of compounds have become a concern to the environmental community. They are each recognized as the most potent contributing gases to the global warming phenomenon.\textsuperscript{4} It is ironic that these materials were manufactured to replace their chlorinated and brominated counterparts to mitigate ozone layer depletion and yet came to be the chemical compounds attributing greatest to the climate change crisis.\textsuperscript{38} The EPA has specifically addressed the magnitude of these two classes of greenhouse gases under what is known as “Global Warming Potential” (GWP). This method is
accomplished utilizing the carbon dioxide equivalency scale developed by the Intergovernmental Panel on Climate Change (IPCC) in which carbon dioxide is chosen as the base unit compound by which all other global warming compounds are measured thus yielding a GWP numerical value. Based upon this scale, HFCs have a GWP CO$_2$ equivalency between 120-12,000 and PFCs a value between 5,700-11,900, both depending upon molecular structure and halogen content.$^4$

The atmosphere however is not the only concern of environmental regulatory agencies regarding HFCs and PFCs. Impacts to soils, surface waters, and mostly groundwaters have also been of regulatory interest. Their release to the environment partitions to approximately a 50% split between the atmosphere and groundwater, slightly favoring groundwater.$^1$ Once present in groundwater, they become dense non-aqueous phase liquids or DNAPLs; organic compounds with densities greater than water and mostly insoluble.$^{39}$ This problem is twofold, since total removal has never been achievable due to pooling in various geologic strata within the aquifer system coupled with concerns over potential future migration and uncertain impact from any remaining DNAPL contaminant.$^{40}$ Over the years the EPA and state environmental regulatory agencies have issued abundant regulation regarding DNAPL contamination, especially once it has been established in groundwater. This action has come from serious concern over potential impact to the health of both communities and the environment.
Environmental and Health Concerns

A number of recent studies regarding fluorocarbon pollution have begun to heighten the level of awareness of both environmental and health organizations concerns regarding these pollutants. It has been known for some time that there exists a public exposure to fluorocarbon sand several recent studies reflect this circumstance. In 2008, Strynar established public health concerns in a study reflecting fluorocarbon contamination and exposure pathways for humans exist in the form of dusts in both homes and day care centers. This study conducted in the Carolina’s and Ohio showed that concentrations were present in over 95% of the samples taken. Also, the source most likely responsible for fluorocarbon presence was identified as textile degradation present in the homes. A separate study in Ottawa, Canada by Kubwabo et al. of fluorocarbon compounds present in house dusts confirmed that textiles were more than likely the cause of exposure to humans in the home. Of greater concern is the establishment of a potential link between exposure to fluorocarbons and the observed cases of autism in children. Specifically, a study by Johansson et al. demonstrated that PFCs may interfere with hormone function in humans and that higher concentrations have been found in newborns that later developed autism. A relationship between crawling behavior and textile exposure was indicated as a likely method of transference. In an additional study, a number of HFC compounds have been linked to reproductive system and developmental toxicity in rodents. Specific cases of low body weight and slight skeletal ossification of fetuses and maternal body weight and food consumption loss was observed. Among the list of fluorocarbons cited in the study were: pentafluoroethane (HFC-125), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane
(HFC-143a), 1,1-difluoroethane (HFC-152a), difluoromethane (HFC-32) and 1,1,1,3,3-pentafluoropropane (HFC-245fa).\(^9\)

Concerns regarding the potential effect of fluorocarbons on human health and the environment have not gone unnoticed by the regulatory agencies. Due to the increased use of fluorocarbons in the pharmaceutical and agrochemical industries, the EPA recently directed its own exposure research laboratories to develop a new analytical method for determination of trace amounts of these chemicals in soil and water.\(^44\) Additionally, EPA as recently as December 2011 approved the use of HFC refrigerant replacements such as propane, isobutane and blends of the same with ethane and n-butane.\(^45\) These are the very same refrigerants that were originally replaced by CFCs due to safety and flammability concerns regarding their application; their use has now come full circle. Finally, the pressure from the international community to halt production and use of HFCs became evident at the most recent convening in July 2012 of the United Nations’ Climate and Clean Air Coalition (CCAC) where the general consensus that continuing emissions of HFCs will offset goals already accomplished by past reductions of CFCs and HCFCs and that it is now time to focus on the phasing out of HFCs and finding replacements for their various industrial applications.\(^46\)

In the State of Florida, the Florida Department of Environmental Protection (FDEP) now considers fluorocarbons to be Emerging Pollutants of Concern (EPOC) which is essentially a list of anthropogenic source chemicals with potential for increasing the impact of pollution to state waterways, surface waters and groundwaters.\(^47\) In a report issued by FDEP and the Center for Climate Strategies (CCS), Florida has been identified as a major contributor to the United States’ worldwide contribution of GHGs. Specifically, coolant system demands in the residential, commercial and industrial sectors and transportation industry where HFCs serve as refrigerant
replacements to previous ozone depleting compounds (ODC) is increasing. The same report predicts increases in HFC emissions and releases to the environment in Florida at a 5% growth rate over the next twenty years, if left unaddressed.\textsuperscript{48} As the releases of HFCs continue to pose a threat to the environment on two fronts, air and water, and additional studies show growing concern for human health related issues along with unknown future impacts to Florida’s ecological environment, especially in limnological systems, regulatory oversight and future regulation can be expected to rise in the coming years for these compounds.

\textbf{Interest at NASA}

NASA’s Kennedy Space Center and its operations reside within and adjacent to two National Parks: Merritt Island National Wildlife Refuge (MINWR) and Cape Canaveral National Seashore (CCNS) respectively. NASA therefore is very sensitive to any matters of an environmental nature and maintains a very positive attitude towards future environmental regulation and openly works with the EPA to ensure all interests of both organizations are fully met.

In accordance with the Montreal Protocol and EPA’s regulatory requirements for elimination of all ozone layer depleting substances, NASA was among the first US Government Agencies to take a more aggressive stance in permanently eliminating their use of these compounds.\textsuperscript{49} It should be noted that NASA satellites were the first to detect the thinning of Earth’s Ozone Layer in the mid 1980’s confirming the research of Farman et al.\textsuperscript{50} In the 1990’s, NASA’s focus was solely on the elimination of chlorinated and brominated refrigerants (CFCs),
fire suppressants (Halons) and chlorinated solvents since at the time, fluorinated compounds were not known for any adverse environmental affects.\textsuperscript{49} The EPA later approved the use of HCFCs and HFCs as refrigerant and solvent replacements to CFCs. For NASA, HFCs specifically found excellent application in solvent cleaning operations and were very well suited for the stringent requirements associated with the government specifications of aerospace flight hardware. One HFC in particular, 1,1,1,2,3,4,5,5,5-decafluoropentane (DFP), was developed especially for this type of application.\textsuperscript{51} The properties of DFP will be discussed in a subsequent section titled “Decafluoropentane”.

DFP has been used in solvent cleaning operations at Kennedy Space Center (KSC) since the 1990’s.\textsuperscript{20} At KSC, this solvent was utilized at two different locations, both under the same name of the “Component Refurbishment & Chemical Analysis” (CRCA) facility. Over the years, accidental releases of cleaning solvents at both locations had occurred resulting in contamination of the surrounding groundwater. NASA had used DFP in solvent formulations with chlorinated compounds as well, specifically trans-1,2-dichloroethene (t-DCE). The groundwaters at KSC that exhibit DFP contamination also show the presence of t-DCE. Figure 1.1 below shows a partial area map of Kennedy Space Center indicating the two currently known locations of DFP contamination coinciding with the previous and current sites of the aforementioned mentioned CRCA facility.\textsuperscript{52}
In cooperation with the Florida Department of Environmental Protection, NASA investigated the extent of contamination of some of the pollutants present at its sites. It should be noted that NASA used other cleaning solvents in their operations at the subject facilities also resulting in groundwater contamination with vinyl chloride (VC) and cis-1,2-dichloroethene (c-DCE). Table 1.1 shows results for groundwater sample analysis of the four main pollutants at one of the sites.

Table 1.1: NASA KSC Report on groundwater contamination concentrations of select halogenated pollutants (2007)\textsuperscript{52}

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>FDEP GCTL (µg/L)</th>
<th>FDEP NADC (µg/L)</th>
<th>2007 Maximum Groundwater concentration (µg/L)</th>
<th>Location of Pollutant</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1,2-DCE</td>
<td>70</td>
<td>700</td>
<td>3,300</td>
<td>CRCA</td>
</tr>
<tr>
<td>trans-1,2-DCE</td>
<td>100</td>
<td>1,000</td>
<td>9,200</td>
<td>CRCA</td>
</tr>
<tr>
<td>VC</td>
<td>1</td>
<td>100</td>
<td>17,000</td>
<td>CRCA</td>
</tr>
<tr>
<td>DFP</td>
<td>1,800</td>
<td>18,000</td>
<td>984</td>
<td>CRCA</td>
</tr>
</tbody>
</table>
In developing a clean-up strategy for the contaminated sites, NASA was provided with Groundwater Clean-up Target Levels (GCTL) and Natural Attenuation Default Concentrations (NADC) by the FDEP to comply with for the subject pollutants. GCTLs and NADCs are used by the regulatory agencies as limits for acceptable pollutant concentration values for both compliance and to ensure remediative action by the facility owners and operators. GCTLs are always more stringent than NADCs and allow for a facility to demonstrate suitable progress towards the remediation of a pollutant. The NADC is developed by multiplying the groundwater criteria by 10 for non-carcinogens and by 100 for carcinogens. If a pollutants concentration is below the GCTL then no action other than monitoring the concentration is required for that pollutant. However, if the concentration of the pollutant is above the NADC then a remediative plan must be put into place as soon as possible and the necessary corrective action taken to decrease the concentration of the pollutant below the NADC. Further, if the concentration is above the GCTL yet below the NADC, then some form of mitigating action must be taken to fully characterize and monitor the pollutant plume and determine if any changes in concentration levels are occurring. If found to be increasing in concentration, indicating a potential continuous source feed, similar action must be taken as in the case of being over the NADC value.\textsuperscript{53} NASA routinely provides confirmation sampling reports to the FDEP as a status detailing concentrations levels of various groundwater pollutants on KSC property.

In Table 1.1, for the location sampled, the concentration of DFP is reported as being 984 µg/L and t-DCE as 9,200 µg/L. The value for t-DCE falls above the NADC requiring action whereas the DFP value is below the GCTL requiring only monitoring. However, an additional KSC groundwater contamination report for another location showed detection levels of t-DCE to be greater than 50,000 µg/L. Knowing the relationship between t-DCE and DFP plumes
detected in groundwater at KSC, it can be posited that the DFP concentrations may be well over the GCTL with estimates of 5,000 µg/L or greater for this location. If determined to be the case, higher concentrations of DFP in the groundwater would necessitate immediate mitigating action including plume characterization and ultimately require an agreement as to the conditions constituting clean closure of the site. To date, NASA has not yet sampled for DFP at this location but remains in discussions regarding these pollutants with the FDEP.\textsuperscript{54}

**Decafluoropentane**

![Molecular model of 1,1,1,2,2,3,4,5,5,5-decafluoropentane](image)

*Figure 1.2: Molecular model of 1,1,1,2,2,3,4,5,5,5-decafluoropentane\textsuperscript{55}*

**Production**

1,1,1,2,2,3,4,5,5,5-Decafluoropentane, as seen in Figure 1.2, is strictly a synthetic compound and does not exist in nature. Initially manufactured by the E. I. du Pont de Nemours and Company, i.e., DuPont, the product has been in existence since 1990’s and at DuPont is produced under the trade name “Vertrel XF”. Applications of the product include: carrier
fluid/lubricant deposition, drying/rinsing agent, heat transfer fluid, high-voltage dielectrics, optics cleaning, particulate/ionic removal, and precision cleaning.\textsuperscript{51} Other products have been produced by DuPont which also includes DFP in their formulations. One of these, “Vertrel MCA”, is of interest to NASA and has been employed in aerospace hardware preparations at the Florida location. The product’s formulation consists of roughly 60\% t-DCE and 40\% DFP. DFP is currently manufactured around the world by a number of companies where its greatest demand is in industrial solvent cleaning and drying fluid applications.\textsuperscript{51} Some companies which still currently produce the chemical include BASF, 3M, Honeywell, Solvay, Arkema, StarChem, Mexichem, INEOS, Rhodia and of course DuPont.\textsuperscript{56}

According to reports by the United Nations, approximately 0.43 million metric tons (mmt) of DFP are produced per year in Europe alone, yet in the most recent years, this number seems to be decreasing due to awareness regarding it global warming properties.\textsuperscript{4} By contrast, in the United States, the National Energy Information Center has reported DFP production value of 7.1 mmt for 2008 and that number has been on the rise.\textsuperscript{57} This shows the sharp contrast between the policies of the US and the EU on greenhouse gas production and control.

Properties

DFP exhibits excellent properties as an industrial cleaning solvent. It has a low viscosity, high density and low surface tension. This provides the solvent with a shallow laminar flow over a varied surface morphology at a depth typically less than the diameter of any contaminant
particles thus allowing them to become easily dislodged from the metal surface. DFP is hydrolytically stable, relatively inert and volatizes quite easily. Volatilization is also further enhanced in fluorocarbons due to repulsive forces between molecules. It is also safe to use in the presence of ignition sources as it is nonflammable. The strength of the carbon-fluorine bond permits exposure to high temperatures without decomposition, a desirable trait for solvent application as heat is typically applied to assist contaminant removal. Also, due to low water solubility, DFP serves well in aqueous displacement and drying applications. Table 1.2 provides a selection of the more common physical and chemical properties of DFP, as provided by DuPont.

Unfortunately, the properties that make DFP attractive to use as an organic solvent are the same properties that make it persistent in the environment and therefore difficult to remediate. DFP does not breakdown easily, in either the atmosphere or water and when present in aqueous media, exists as a Dense Non-Aqueous Phase Liquid or DNAPL. Other than implied
by the name, a DNAPL is essentially any organic compound that is both hydrophobic and has a density greater than that of water. The environmental contamination related to DFP use and the associated aspects of its remediation will be discussed in the later sections of this chapter, “As Environmental Contaminant” and “Remediation Studies”.

Diastereomers

![Molecular structure of 1,1,1,2,3,4,5,5-decafluoropentane](image)

The DFP molecule, as seen in Figure 1.3, exhibits two chiral centers at the number 3 and 4 carbon. DFP has four possible diastereomer configurations and they are provided in Figure 1.4 below.

![The Four Diastereomers of DFP: A (3R,4R), B (3R,4S), C (3S,4R), D (3S,4S)](image)
The stereochemistry of DFP molecule may indeed provide the best insight into the likeliest degradation mechanism for initial defluorination. Specifically, the stereospecific positioning of the hydrogen atoms on the molecule may offer the right conditions for such an initial attack. Since each of the carbons at these locations has only one fluorine atom and one hydrogen atom present, they are provided with the longest carbon-fluorine bonds on the molecule and subsequently, the weakest bonded fluorine atoms as well. Additionally, in the proper conformation, the hydrogens would present themselves to be on the same side of the molecule for a given time period, this could present a reaction favorable electronic arrangement. These chiral locations are likely candidates for the initial reaction as opposed to the non-chiral carbons in the molecule with two or three fluorines bonded each in which rotational conformation is not as distinctive. Multiple fluorine bonded carbons have carbon-fluorine bonds that are shorter and stronger due to inductive effects and may be the most difficult to liberate.\textsuperscript{63} When considering the mechanism for degradation, the stereochemistry of the molecule should be thoroughly investigated.

Nomenclature

![DFP Structure](image)

Figure 1.5: Incorrect structure for DFP shown as: 1,1,2,3,4,5,5-decafluoropentane
A cautionary note is necessary for the subject research compound as its nomenclature has been misreported multiple times in the literature. In Figure 1.5, the DFP molecule described improperly reflects the compound as it should be named. The model in Figure 1.5 shows one of the hydrogens on the incorrect carbon. It shows the hydrogen on the second carbon when it should be on the fourth carbon. Even though this model could be flipped to reveal the correct structure, its naming convention is inaccurate. This name provided is in disagreement with the rules of nomenclature established by the International Union of Pure and Applied Chemistry (IUPAC). According to IUPAC, the name should be provided as: 1,1,1,2,2,3,4,5,5,5-decafluoropentane, not 1,1,1,2,3,4,4,5,5-decafluoropentane. This appears to be a common mistake found in both industry documentation and academic literature. Also, another common incorrect naming convention encountered that should be rejected is “2H,3H-decafluoropentane”, reflecting the compound name from the perspective of hydrogen placement on the molecule.

As Environmental Contaminant

Although technically an HFC greenhouse gas, DFP falls between a less fluorinated HFC and a PFC with respect to GWP. As it is almost the completely fluorinated analogue of pentane this is somewhat expected. Utilizing the IPCC global warming potential model for carbon dioxide equivalents under a 20 year time frame, DFP yields a value of 3,700 CO₂eq for GWP as a greenhouse gas and a half life in the atmosphere of 15 years. As shown in Table 1.3, DFP exhibits a GWP on the higher end of most of the HFCs contributing to global warming.
Table 1.3: Direct Global Warming Potentials (GWPs) of some Greenhouse gases Relative to Carbon dioxide

<table>
<thead>
<tr>
<th>Gas</th>
<th>Lifetime (years)</th>
<th>Global Warming Potential (Time Horizon in years)</th>
<th>20 yrs</th>
<th>100 yrs</th>
<th>500 yrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>CO$_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Methane$^6$</td>
<td>CH$_4$</td>
<td>12.0$^6$</td>
<td>62</td>
<td>23</td>
<td>7</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N$_2$O</td>
<td>114$^9$</td>
<td>275</td>
<td>296</td>
<td>156</td>
</tr>
<tr>
<td>Hydrofluorocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFC-23</td>
<td>CHF$_3$</td>
<td>260</td>
<td>9400</td>
<td>12000</td>
<td>10000</td>
</tr>
<tr>
<td>HFC-32</td>
<td>CHF$_2$</td>
<td>5.0</td>
<td>1800</td>
<td>550</td>
<td>170</td>
</tr>
<tr>
<td>HFC-41</td>
<td>CHF$_2$</td>
<td>2.6</td>
<td>330</td>
<td>97</td>
<td>30</td>
</tr>
<tr>
<td>HFC-125</td>
<td>CHF$_2$CF$_3$</td>
<td>29</td>
<td>5900</td>
<td>3400</td>
<td>1100</td>
</tr>
<tr>
<td>HFC-134</td>
<td>CHF$_2$CHF$_2$</td>
<td>9.6</td>
<td>3200</td>
<td>1100</td>
<td>330</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>CHF$_2$CF$_3$</td>
<td>13.8</td>
<td>3300</td>
<td>1300</td>
<td>400</td>
</tr>
<tr>
<td>HFC-143</td>
<td>CHF$_2$CH$_3$F</td>
<td>3.4</td>
<td>1100</td>
<td>330</td>
<td>100</td>
</tr>
<tr>
<td>HFC-143a</td>
<td>CF$_2$CH$_3$</td>
<td>52</td>
<td>5500</td>
<td>4300</td>
<td>1600</td>
</tr>
<tr>
<td>HFC-152</td>
<td>CHF$_2$CHF$_3$</td>
<td>0.5</td>
<td>140</td>
<td>43</td>
<td>13</td>
</tr>
<tr>
<td>HFC-152a</td>
<td>CH$_2$CHF$_2$</td>
<td>1.4</td>
<td>410</td>
<td>120</td>
<td>37</td>
</tr>
<tr>
<td>HFC-161</td>
<td>CHF$_2$CH$_3$F</td>
<td>0.3</td>
<td>40</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>HFC-227ea</td>
<td>CF$_3$CHFCF$_3$</td>
<td>33</td>
<td>5600</td>
<td>3500</td>
<td>1100</td>
</tr>
<tr>
<td>HFC-226eb</td>
<td>CF$_3$CHFCF$_3$</td>
<td>13.2</td>
<td>3300</td>
<td>1300</td>
<td>390</td>
</tr>
<tr>
<td>HFC-236ea</td>
<td>CHF$_2$CHF$_2$CF$_3$</td>
<td>10</td>
<td>3600</td>
<td>1200</td>
<td>390</td>
</tr>
<tr>
<td>HFC-236fa</td>
<td>CF$_3$CH$_3$CF$_3$</td>
<td>220</td>
<td>7500</td>
<td>9400</td>
<td>7100</td>
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<tr>
<td>HFC-245ea</td>
<td>CHF$_2$CHF$_2$CF$_3$</td>
<td>5.9</td>
<td>2100</td>
<td>640</td>
<td>200</td>
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<tr>
<td>HFC-245fa</td>
<td>CHF$_2$CHF$_2$CF$_3$</td>
<td>7.2</td>
<td>3000</td>
<td>950</td>
<td>300</td>
</tr>
<tr>
<td>HFC-365mfc</td>
<td>CF$_3$CH$_3$CF$_3$</td>
<td>9.9</td>
<td>2600</td>
<td>890</td>
<td>280</td>
</tr>
<tr>
<td>HFC-43-10mee</td>
<td>CF$_3$CHF$_2$CF$_3$</td>
<td>15</td>
<td>3700</td>
<td>1500</td>
<td>470</td>
</tr>
</tbody>
</table>

In Europe, DFP has been banned in Germany since its introduction to the market in the 1990’s and is not permitted for use in any of the country’s facilities. This is due solely to its GWP and concern over general emissions of the compound either directly or indirectly to the atmosphere. Additionally, it has been estimated by the National Energy Information Center that the emissions of HFCs in the United States alone were approximately 46 million metric tons (mmt) in 1995 and since then that level has risen to 143 mmt for 2008. For DFP, the same data trend is observed with values of 0.3 mmt in 1995 rising to 7.1 mmt in 2008, thus reflecting the ever increasing demand and use for HFCs in industry.

It has been determined that when DFP is released to the environment, per the Mackay Equilibrium Criterion (EQC) models, partitioning across environmental media depends upon the method of release. According to the Level I Model of the Mackay EQC, when release occurs on
surfaces where interaction with the atmosphere is direct, 99% DFP or greater is partitioned to the atmosphere. However, when release occurs from an underground piping delivery system or similar non-atmospheric contact containment or conveyance, Level III Model of the Mackay EQC describes partitioning across soil, sediment, water and air as yielding the following percentages 0.7%, 0.7%, 51.1% and 47.5% respectively. In a study by Tsai et al., partition coefficients of various hydrofluorocarbons were empirically determined to develop a model for the environmental fate of each compound. DFP was determined to be of the highest coefficient value among the HFCs tested. High partition coefficient values result in a greater likelihood of partitioning towards lipid-like phases that, in the environment, ultimately cause negative impact to aquatic species. Additionally, compounds with high partition coefficients tend to be stationary in the environment. However, this property is not necessarily entirely negative as it can also aid in the remediation effort at polluted sites.

A number of remediative techniques have been attempted, and some quite successfully, in the clean-up of various halogenated organic pollutants in both soils and groundwater. However, in addressing the pollution caused by HFCs and in particularly in groundwater, the task has been more challenging.

**Remediation Strategies**

Halogenated solvents had found application in numerous industrial cleaning operations due to their nonflammable properties thus increasing the safety of the worker. However, as awareness increased within industry regarding the improper use of halogenated solvents along
with a better understanding of their effect on the environment, a realization occurred with respect to their impact to groundwater. Specifically, their physical state within the groundwater media came to be known as DNAPLs or dense nonaqueous phase liquids. The term DNAPL is a direct reference to the high density and hydrophobic nature of these pollutants and their tendency to accumulate in deep pools within the aquifer strata. To this point, environmental remediation firms have found the cleanup of these pollutants to be quite challenging. To address this need, a number of remediation technologies have been developed.

The types of methods developed range from classic pump and treat technologies to in situ methods of flushing or oxidative treatments and bioremediation. Pump and treat technologies unfortunately require a great deal of equipment on site, high maintenance and costs and still remain mostly ineffective against DNAPLs. In more recent years, in-situ methods have become more desirable and among these methods, either solvent, surfactant or cosolvent flushing have been widely attempted as the approach to DNAPL contaminated sites. Both solvent and surfactant flushing requires the well injection of a liquid into the source zone, typically water or alcohol, and with surfactants if desired, followed by removal by well extraction along with any DNAPL made mobile by the process. However, problems arise when the DNAPL source is too deep or in difficult to reach locations within the strata or aquifer itself leading to poor permeability and failure to remove the DNAPL; this was the case in one Air Force Base study in Florida. Also, cosolvent flushing is sometimes employed as an alternate approach to DNAPL remediation where two solvents are used together, typically water and a miscible organic solvent like alcohol, in an attempt to recover the pollutant from both the vadose and saturated zones in the groundwater. Air sparging is another method where air is injected into the polluted groundwater source zone in an attempt to increase bioremediation of the pollutant. However, in
the case of HFCs, microbial degradation is not successful and even in the case of HCFCs, only the chlorinated component is successfully remediated. In some cases, a chlorine atom appears to be required in order for any type of breakdown to occur. In an article by Balsiger et al., it was determined that CFCs are biologically inert under aerobic conditions whereas under anaerobic conditions, dechlorination is possible. One example is the dechlorination of trichlorofluoromethane, CFC-11 to dichlorofluoromethane, HCFC-21 which was observed in samples of contaminated groundwater, but the non-chlorinated tetrafluoroethane, HFC-134a was not degraded, indicating the importance of the chlorine atom in the anaerobic biotransformation process. A further study conducted by Höhener et al. in which leading chloro and fluorocarbon groundwater contaminants were identified around the world; the group determined that biotransformation by methanotrophs, methane metabolizing bacteria, to be an effective method against partially chlorinated fluorocarbons but not fluorocarbons alone. It also appeared that even with chlorine atoms present, the more fluorinated the structure, the less susceptible the compound was to degradation.

In reviewing the remediative methods discussed to this point, general concerns associated with the applications of each of these methods are several fold with the major issue being cost. These methods are not easily predictable with respect to economic return on investment and the initial capital costs are typically high. Additionally, some of these methods can be very aggressive and will sometimes cause a wider distribution of the source plume and even relocate the highest concentrated zones of the DNAPL. Figure 1.6 shows the degree of equipment required for a remediative operation of this magnitude.
What has been successful in remediating halogenated solvent DNAPLs from groundwater is the application of various reductive metal dehalogenation treatment systems. These methods achieve degradation of the halogenated solvent to a simple hydrocarbon by the process of reductive dehalogenation.

**Reductive Metal Systems**

There have been a number of successful reductive metal technologies applied in the cleanup of halogenated solvent pollutants in the environment. Typically enlisted in the reductive approach to halogenated compounds are the transition metals and none more than iron have been used as much in this regard. Iron was first used in the initial dechlorination efforts of most of the chlorofluorocarbon solvent releases to the environment. The dechlorination of trichloroethylene in an aqueous solution was first achieved using iron metal. In more recent years, studies
involving Zero-Valent Iron (ZVI), the metal has found use in chlorinated solvent remediation in groundwater. Specific examples include the hydrodechlorination of TCE to ethane via a stepwise reductive dehalogenation through the intermediates of DCE and VC. More recently, nano-scale ZVI has been applied to dechlorination efforts in the reductive dehalogenation of chlorinated methane. There are many other examples but in each of these cases, iron was simply successful due to its ability to overcome the carbon-chlorine bonding energy and effectively dehalogenated the molecule. However, oxidation of the metal surface becomes a problem as this deactivates the metal and hinders any further dehalogenation. One method used to overcome this is the mechanical alloying of the metals by the ball-milling process prior to reaction with the halogenated compound. Additionally, metal activation through use of a minute amount of acid, inorganic or organic depending upon the metal, seems to also enhance the metals reductive capabilities.

As might be expected, other transition metals have found use in the dehalogenation of chlorinated solvents. In a study by Schrick et al., hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel–iron nanoparticles has been achieved. In the past 10 years, there has been a trend towards the use of bimetallic systems in dehalogenation reactions, mostly due to efforts attempted where monometallic methods failed. Another trend in recent years is to employ a catalyst in conjunction with a reductive metal or metals to achieve the desired dehalogenation. The literature reflects successful efforts with the reductive metal dehalogenation of polychlorinatedbiphenyls (PCBs) as their hazards to the environment has been identified for some time and is well understood. Several studies employed the successful use of the bimetal system of magnesium and palladium in methanol for the reductive dehalogenation of PCBs at ambient temperatures. Also, in a study by Kwon, involving cobalt and nickel as the
effective reductive metal system for dehalogenating PCBs, although metal complexes that enhanced bioactivity were also studied. Further, zero-valent magnesium has also been successfully used in the dechlorination of PCBs but on solid substrates and not in aqueous media.

The success in the dehalogenation of organic halides by reductive metal systems appears to reside in the ability of the metals to overcome the carbon-halogen bond energy and the employ of a catalyst may be used as well to achieve this outcome. The only other apparent criterion required is in maintaining a clean metal surface area for the dehalogenation reaction to take place and this is achieved through either mechanical alloying or acid activation prior to reaction. Table 1.4 shows a list of select metals which provides a number of candidates to be explored in the application of dehalogenation of halogenated organic pollutants.
Table 1.4: Standard Reduction Potentials of Select Metals at 25 °C

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}^+<em>{(aq)} + e^- -----\rightarrow \text{Li}</em>{(s)}$</td>
<td>-3.05</td>
</tr>
<tr>
<td>$\text{K}^+<em>{(aq)} + e^- -----\rightarrow \text{K}</em>{(s)}$</td>
<td>-2.93</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Ba}</em>{(s)}$</td>
<td>-2.90</td>
</tr>
<tr>
<td>$\text{Sr}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Sr}</em>{(s)}$</td>
<td>-2.89</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Ca}</em>{(s)}$</td>
<td>-2.87</td>
</tr>
<tr>
<td>$\text{Na}^+<em>{(aq)} + e^- -----\rightarrow \text{Na}</em>{(s)}$</td>
<td>-2.71</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Mg}</em>{(s)}$</td>
<td>-2.37</td>
</tr>
<tr>
<td>$\text{Be}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Be}</em>{(s)}$</td>
<td>-1.85</td>
</tr>
<tr>
<td>$\text{Al}^{3+}<em>{(aq)} + 3 e^- -----\rightarrow \text{Al}</em>{(s)}$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$\text{Mn}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Mn}</em>{(s)}$</td>
<td>-1.18</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Zn}</em>{(s)}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$\text{Cr}^{3+}<em>{(aq)} + 3 e^- -----\rightarrow \text{Cr}</em>{(s)}$</td>
<td>-0.74</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Fe}</em>{(s)}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$\text{Cd}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Cd}</em>{(s)}$</td>
<td>-0.40</td>
</tr>
<tr>
<td>$\text{Co}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Co}</em>{(s)}$</td>
<td>-0.28</td>
</tr>
<tr>
<td>$\text{Ni}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Ni}</em>{(s)}$</td>
<td>-0.25</td>
</tr>
<tr>
<td>$\text{Sn}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Sn}</em>{(s)}$</td>
<td>-0.14</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Pb}</em>{(s)}$</td>
<td>-0.13</td>
</tr>
<tr>
<td>$2 \text{H}^+_{(aq)} + 2 e^- -----\rightarrow \text{H}_2(g)$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{Sn}^{4+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Sn}^{2+}</em>{(aq)}$</td>
<td>+0.13</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}<em>{(aq)} + e^- -----\rightarrow \text{Cu}^{+}</em>{(aq)}$</td>
<td>+0.13</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}<em>{(aq)} + 2 e^- -----\rightarrow \text{Cu}</em>{(s)}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}<em>{(aq)} + e^- -----\rightarrow \text{Fe}^{2+}</em>{(aq)}$</td>
<td>+0.77</td>
</tr>
<tr>
<td>$\text{Ag}^+<em>{(aq)} + e^- -----\rightarrow \text{Ag}</em>{(s)}$</td>
<td>+0.80</td>
</tr>
</tbody>
</table>

In regards to the dehalogenation of hydrofluorocarbons, especially those as DNAPLs in groundwater, the available literature does not hold much promise. Reductive metal systems would appear to be a potentially successful candidate method to employ against HFCs. Also, the
higher the reduction potential of the metal or bimetals, the more likely they are to be effective in cleaving the carbon fluorine bond.

One successful study in the partial hydrodefluorination of an HFC has been performed previously. In the early 1980’s, Witt et al. was successful in the hydrogenolysis of 1,2,3-trifluoroethane over Pd/C to 2,2-difluoroethene and 2,2-difluoroethane and with 100% conversion, as seen in Figure 1.7. However, the reaction required temperatures much higher than ambient conditions which would not be suited for direct applications in the environment.\textsuperscript{84}

\[
\begin{align*}
\text{H} & \quad \text{F} \\
\text{F} & \quad \text{C} \\
\text{H} & \quad \text{F} \\
\end{align*}
\xrightarrow{\text{Pd} \, \text{C}}
\begin{align*}
\text{H}_2\text{C} & \quad \text{=C} \\
\text{F} & \quad \text{F} \\
\end{align*}
+ \begin{align*}
\text{H}_2\text{C} & \quad \text{=C} \\
\text{F} & \quad \text{H} \\
\end{align*}
\]

Figure 1.7: Hydrodefluorination of 1,2,3-trifluoroethane, Witt et al.\textsuperscript{84}

Additionally, the same group study noticed that it became increasingly more difficult to remove fluorine atoms from carbons where other fluorine atoms were bonded to the same carbon. This was attributable to the induction effect of a greater dipole moment across the C-F bonds in the molecule.\textsuperscript{84}

It can be concluded that any attempt to reductively dehalogenate the HFC molecule must include the key capability of being able to overcome the energy of the strong carbon-fluorine bond. Additionally, a pathway for removal of the fluorine atoms from the molecule must also be possible and in the case of DFP, it is probable.\textsuperscript{85} Further, if any catalyst were to be employed in the metal reductive system to assist in the effort, it must be able to resist deactivation by fluorine itself.\textsuperscript{86}
Research Objectives

The main goals of this research are to first, successfully attain complete degradation of DFP to what is ultimately recognized as environmentally harmless reaction products. Secondly, to not contribute any further to environmental pollution, not only from a reaction products standpoint but any remaining starting materials, reaction byproducts or other components of the system. Lastly, the process must be cost effective including both the implementation and operational phases and any sustaining measures.

Proposed Technology

In order to meet the research objectives and achieve complete degradation of the subject halogenated organic pollutant, the proposed technology will initially consist of a reductive metal system employing either a solitary reductant metal, bimetallic alloy, or solitary metal in conjunction with a heterogeneous metal catalyst. Additionally, reductive dehalogenation of the pollutant will be tested in varying protic solvents in combinations with the different metal systems to determine the best combination of metal and media. Metal activation will be achieved through either subjection to mechanical alloying or acid activation or both to provide a clean reactive surface area free of as much oxidation as possible. No toxic byproducts or remaining starting materials should exist upon reaction completion. The final resulting reaction products should be simple hydrocarbons that easily undergo biodegradation to wastes of non-environmental concern.
CHAPTER 2: SELECTION, PREPARATION, AND EVALUATION OF METAL SYSTEMS

Metals Selection for Potential DFP Degradation

Introduction

In evaluating the various potential metals for use in this study, a review of the literature provided an understanding of the most probable candidates for pursuing reductive metal dehalogenation of organohalides, especially in the desired target environment of groundwater. In the past, quite a bit of reductive metal research has been conducted with the hopeful goal of complete degradation of these pollutant compounds. The literature also reveals that the more successful metal morphologies are often those of micro and nano scale zero-valent metals. The main advantage in using micro and nano scale metals, especially for organic pollutant plumes in groundwater, is the increased surface area for greater likelihood of metal and organic interaction. Applications of zero-valent metals are favored over charged valency metal compounds as zero-valent metals simply permit electron donation to either the protic solvent or organic pollutant itself to initiate reduction depending upon the mechanism associated with the particular reaction.

A partial list of some of the more successful metals for reductive dehalogenation includes: copper, nickel, zinc, aluminum, magnesium, tin, and iron. Among this list, iron has enjoyed remedial application the most over the years primarily due to its relative abundance, low
Iron has been applied mostly and quite successfully towards the reductive dehalogenation of chlorinated solvents found in groundwater. One of the earliest environmental pollutants which was of great concern to the public and subsequently EPA was dichlorodiphenyltrichloroethane or DDT, which due to tremendous public protest was banned by the EPA in 1972. Previously, DDT was remediated through incineration which caused additional environmental problems, but Sayles et al. were able to completely dechlorinate DDT at 20°C in aqueous solution using powdered zero-valent iron. Further study with ZVI lead to the understanding of the dehalogenation mechanism being a surface phenomenon and methods to increase this effect would come later, i.e., further micro and nano applications. One such study in the mid 1990’s determined the importance of the metal surface parameter. This lead to an understanding of the need for water soluble materials providing the bridge for the required reductive electron transfer to halocarbon and further understanding of the potential for reductive metals to act on these hydrophobic pollutants. This of course led to further study permitting an understanding of the limits of ZVI in groundwater applications. An additional evaluation tested the endurance of zero-valent iron in long duration reactions for the reduction of trichloroethylene where data showed effectual reduction in groundwater continuing for a period of time slightly over two months. Moreover, the use of Permeable Reactive Barriers (PRB) imbedded with iron have been employed incorporating the reductant metal and inert material as a wall placed in such a manner that halogenated organic contaminants in groundwater flow are subjected to reductive forces dehalogenating any pollutants present in the stream. One of the earliest studies providing evidence of success by this method was by O'Hannesin et al., where trichloroethene and tetrachloroethene were reductively dehalogenated by a iron-silicon PRB.
Other metals have been investigated to determine reductive dehalogenative properties and if they could improve on what had been established with iron. Some of these attempts initially include the use of the new metal in conjunction with iron, or the use of a “bimetal”. For example, in a study by Roberts et al., they were able to demonstrate that chloroethylenes can be effectively reduced under normal environmental conditions by either iron or zinc, both of zero valency.\(^9^6\) It was established in the study that reduction of perchloroethylene (PCE) completely to acetylene was a stepwise reaction through the intermediates of TCE, DCE, and VC. Iron showed more equivalent concentrations of intermediates through the reductive process while zinc initially provided greater amounts of TCE from PCE then continued like iron. This observation was not completely understood yet stereospecificity was suspected as the mechanism. This brings up a cautionary note of employing reductive metals and the implications of reaction products or intermediates that may arise and the environmental considerations that follow. The desired resulting reaction products may not always be in greatest concentration and an undesired intermediate may achieve higher levels. This was always a concern during the subject example application in which VC is known to be less likely to undergo anaerobic reduction than other chlorocarbons and could be the majority reaction product which is of greater toxicity than the original pollutant starting materials.\(^9^7\) Another example of producing more toxic byproducts than the starting material was by Grittini et al., where attempted degradation of PCBs using ZVI lead to formation of partially dechlorinated compounds with reported increased toxic effects.\(^9^8\) Conversely, one study by Boronina et al., demonstrated destruction of carbon tetrachloride in water with both zinc and tin separately with the unique difference of zinc driving reduction to methane while tin oxidized the chlorocarbon to carbon dioxide, both acceptable products from an ecological standpoint.\(^9^9\)
Iron was not always the main consideration as reductive metal choice in addressing polluted waterways, although it was almost always included among the list of candidates. One of the earliest studies with alternative metals demonstrated the use of a successful method using a fluidized reductant bed for dechlorination of hexachlorocyclo-pentadiene. At the time, this new process by Sweeny et al. included not only iron powders, but zinc and aluminum as well.\textsuperscript{100}

Zinc has emerged in the literature as being notable as an effective reductant metal for groundwater pollution. It has been known to be more effective than iron in the reduction of carbon tetrachloride even with varying particle size but is adversely affected with respect to media composition with the presence of interfering species.\textsuperscript{101} Zero-valent zinc has been described for the rapid dechlorination of pentachlorophenol in aqueous solution.\textsuperscript{102} ZVZ has actually been compared with ZVI in one study and shown to be more effective in the degradative dechlorination of a number of chlorinate phenol compounds. Specifically, zinc showed a much greater reactivity towards pentachlorophenol than iron and was believed to be attributable to the greater chlorination of the base molecule.\textsuperscript{103}

Aluminum has experienced some application in reductive dehalogenation of aqueous organic pollutants as well. It was one of the first metals recognized along with iron and zinc for its potential in this use.\textsuperscript{100} In a study by Bokare et al., the group demonstrated that zero-valent aluminum was more effective than zero-valent iron in the reduction of carbon tetrachloride due to its greater thermodynamic driving force.\textsuperscript{104} Aluminum has also been shown to be effective under alkaline conditions where the formation of hydroxide ion would inhibit oxide formation on the aluminum surface, an ideal condition for remediation in groundwater.\textsuperscript{105}

Another reductive metal which must be considered as candidate for this study is magnesium, simply due to its very high reduction potential alone.\textsuperscript{106} Magnesium also undergoes
passivation in water, forming a protective hydroxide layer preventing complete degradation of
the metal and if protected by other means, a supported catalyst layer for example, permits
expectations of continued reduction. One study by Morales et al., provided a comparison
between zero-valent magnesium and the same with palladium catalyst for the dechlorination of
various chlorinated phenols under ambient temperatures and pressures. Chlorophenols are
known for their difficulty in degradation under ambient conditions yet palladium assisted
magnesium showing enough increase in reduction over zero-valent magnesium alone to warrant
further investigation into the bimetal for this study. It was noted during this review that both
aluminum and magnesium are promising as reductive metal candidates for this study since both
are naturally abundant in the environment and considered non detrimental as well.

Conversely, two other metals mentioned previously in the section require that a notation
on their employ in environmental remediative applications be reviewed. Mention is made in the
literature of the success of both copper and nickel in various reductive dehalogenation
reactions. However, the environmental regulatory agencies do not look favorably upon the use
of these metals for environmental restorative applications. Over the years, the EPA has
suspected the toxicity of many metals released to the environment and issued numerous toxicity
studies of their impact. The EPA’s nickel toxicity studies proved the metal to be toxic to aquatic
organisms. Also, the same was found for copper toxicity in the aquatic environment. These data essentially rendered neither of these candidate metals qualifiable for this study. It
should also be noted that the EPA considers eight additional metals completely unsuitable for
application towards environmental remedial action. These metals are listed in the EPA
hazardous waste regulations and defined as “toxic” under the Resource Conservation and
Recovery Act (RCRA) of 1976. Table 2.1 provides a list of these hazardous waste metals and their regulatory threshold limits for hazardous waste determination.\textsuperscript{113}

Table 2.1: The EPA’s Hazardous Waste Metals per the “Toxicity Characteristic”\textsuperscript{113}

<table>
<thead>
<tr>
<th>Hazardous Waste Code*</th>
<th>Contaminant</th>
<th>CAS Number</th>
<th>Regulatory Level (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D004</td>
<td>Arsenic</td>
<td>7440-38-2</td>
<td>5.0</td>
</tr>
<tr>
<td>D005</td>
<td>Barium</td>
<td>7440-39-3</td>
<td>100.0</td>
</tr>
<tr>
<td>D006</td>
<td>Cadmium</td>
<td>7440-43-9</td>
<td>1.0</td>
</tr>
<tr>
<td>D007</td>
<td>Chromium</td>
<td>7440-47-3</td>
<td>5.0</td>
</tr>
<tr>
<td>D008</td>
<td>Lead</td>
<td>7439-92-1</td>
<td>5.0</td>
</tr>
<tr>
<td>D009</td>
<td>Mercury</td>
<td>7439-97-6</td>
<td>0.2</td>
</tr>
<tr>
<td>D010</td>
<td>Selenium</td>
<td>7782-49-2</td>
<td>1.0</td>
</tr>
<tr>
<td>D011</td>
<td>Silver</td>
<td>7440-22-4</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*Title 40 Code of Federal Regulations, Part 261.24(b)

As has previously been mentioned, the use of certain bimetals has proven effective in addressing halogenated organic pollutants. Two systems in particular emerge as obvious choices in this application; bimetallic catalytic systems and reduction-oxidation bimetals. Several examples of each exist in the literature with potential application towards reduction of halogenated contaminants in groundwater. The bimetallic system nickel-iron was proven to be very successful in the reductive dechlorination of chlorophenols under aqueous conditions.\textsuperscript{114} This study provided an example of a catalytic reductive metal system where it was noted that dechlorination increased linearly with increased nickel coating on iron. Nickel served as the acting catalyst while oxidation of iron provided the necessary electron transfer for reduction of the chlorophenols. Unfortunately, nickel is not one of the environmentally favorable metals nor condoned by EPA so even though promising, this particular bimetal selection was not considered for this study. Another bimetallic review involved the application of galvanized steel in
groundwater and was found to be effective in reducing a number of halogenated solvents, namely trichloroethane, tetrachloroethane, tetrachloroethene, hexachloroethane, and tribromomethane. This is an example of the redox system where zinc protects iron from complete oxidation by serving as the sacrificial anode due to their potential difference, allowing iron to continue the reduction process.

The use of catalytic systems seems to be the more abundant example of success in the literature. Among the catalytic reductive metal combinations that appear in citation over the past 10 to 15 years, palladized iron seems to top the list. One of the earliest studies employing both these metals as a catalytic reductant system was by Muftikian et al., in the rapid dechlorination of TCE, DCE and PCE to ethane in aqueous solution. This initial study demonstrated that the combination of consumable metal, iron, and unconsumable metal, palladium provided an advantage for reduction over previous methods. As recently as 2009, this bimetallic combination was still finding successful applications in contaminated aqueous media. For example, Shih et al., described the rapid dechlorination of aromatic chlorocarbons like hexachlorobenzene and its reductive intermediates as being achieved using the Pd/Fe. Still in other studies, further evidence of catalytic reductive bimetals have proven effective against chlorinated solvents in groundwater, namely palladized iron and palladized zinc.

Furthermore, investigations into other multiple combinations in metal systems have been explored. In one such study, magnesium and aluminum were prepared as an alloy along with iron and silicon by mechanical milling to provide a treatment for dechlorination of trihalomethanes. In this reaction, the determined mechanism was suggested as metal surface adsorption by the catalyst surface (Fe-Si), followed by direct electron transfer with oxidation of the reductive metals (Mg-Al) achieving subsequent hydrodehalogenation of the chlorinated
contaminants. The alloy proved effective for dechlorination of chloroform, carbon tetrachloride, and trichloroacetic acid in drinking water systems.\textsuperscript{108} Observations in the literature support the service of palladized magnesium as it seems to be growing in use replacing palladized iron as the catalytic reductive option of choice. The catalytic bimetal Mg-Pd was also found to be effective in the total dechlorination of DDT by use of bimetallic particles under standard pressure and room temperatures.\textsuperscript{106} Palladized magnesium has also been used effectively in the dechlorination of PCBs and under ambient temperature and pressure; however, methanol as opposed to aqueous solution was used as the protic solvent.\textsuperscript{119} Other catalysts as well have been used effectively in dehalogenation reactions. Some were discovered over 25 years ago for their effective capabilities in this regard. One such catalyst from that time allowed for rapid dehalogenation of aromatic halides with palladium on activated carbon (Pd/C).\textsuperscript{120} In this particular study, Pd/C dechlorinated both monochlorinated and polychlorinated aromatics applying catalytic transfer hydrogenolysis under room temperatures and pressures.

However, it should be noted that all of the aforementioned studies and their successes are at least partially attributed to the fact that they involved the dehalogenation of chlorinated and not fluorinated organic compounds. In order to address a potentially successful approach to the reductive dehalogenation of fluorocarbons, we must review the primary barrier to that goal and that is the carbon-fluorine bond.
The Carbon-Fluorine Bond

The carbon-fluorine bond is among the strongest bonds known in the field of organic chemistry.\textsuperscript{121,122} A review of bond energies between carbon and the various halogens quickly provides confirmation that the carbon-fluorine bond would require the greatest amount of energy to overcome, see Table 2.2.\textsuperscript{123}

Table 2.2: Comparison of Bond Energies for the Carbon-Halogen Bonds, Carbon-Hydrogen bond provided as additional reference.\textsuperscript{123}

<table>
<thead>
<tr>
<th></th>
<th>C-H</th>
<th>C-F</th>
<th>C-Cl</th>
<th>C-Br</th>
<th>C-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>412kJ mol(^{-1})</td>
<td>484kJ mol(^{-1})</td>
<td>338kJ mol(^{-1})</td>
<td>276kJ mol(^{-1})</td>
<td>238kJ mol(^{-1})</td>
</tr>
</tbody>
</table>

In order for the subject pollutant, decafluoropentane to undergo the desired complete dehalogenation some electronic interaction must take place in order to achieve C-F bond activation and subsequent liberation of all fluorines as ions in solution. Additional hydrogenation of DFP to the hydrocarbon analogue should be favorable with respect to steric substitution of hydrogen for fluorine. As fluorine and hydrogen atoms both share Van der Waals radii closer than with any other halogen atom (Fluorine: 1.47 Å and Hydrogen: 1.20 Å), their substitutions should offer minor change in steric stress along the molecule.\textsuperscript{124}

However, there is quite a difference in polarity between hydrogen and fluorine atoms when bonded to carbon. Fluorine, being the most electronegative element on the periodic table, pulls all electron density towards itself in the formation of the covalent bond with carbon. Yet, in doing so induces such a strong dipole that the produced inductive effect forms a polar covalent bond.
bond with the fluorine exhibiting the strong partial negative charge and the carbon as partial positive, see Figure 2.1.125

![Carbon-Fluorine Polar Covalent Bond](image)

Figure 2.1: Two Different Representations of the Carbon-Fluorine Polar Covalent Bond

Further, the C-F bond strength is also increased by the exceptional electronegativity of the fluorine atom. The fluorine atoms lone pairs of electrons are held closely due to the pull of the inner orbital unshielded nine protons in its nucleus both further strengthening and shortening these bonds making the fluorines on the molecule very unreactive.124 However, the C-F bond does have at least one weakness and that is in its sigma antibonding orbital (σ*) or what can also be referred to as it lowest unoccupied molecular orbital (LUMO).58,126 In a study of multiple approaches to C-F bond activation, metal electron donation to the LUMO of fluorocarbons was proposed as the successful mechanism of defluorination.19

The selection of metals for this study would have to be able to donate electrons to the C-F bond for liberation of the fluorines for dehalogenation and complete reduction if any attempt is going to be successful; this is discussed in the next section.
Metals Selection

During the selection process for the candidate metals for this study, it became apparent that at least three main criteria must be met for application in groundwater. First, the metal or metals must have both a high enough reduction potential, i.e., electron donation character, alone or combined, to activate the carbon-fluorine bond for dehalogenation. Secondly, the metal must not be of a toxic nature to any target aquatic species as defined by EPA toxicity criteria and further, it would be best that the metal exhibit no adverse effects to the environment at large. Thirdly, and to a somewhat lesser extent, the metal must also not be adversely affected in reductive capability by the presence of potentially interfering species that would render it ineffectual in its purpose.

Based upon the reduction potential requirement alone, several metals seem to be obvious choices for the study. Namely iron, due to its reported history in reductive dehalogenation applications in aqueous media. Also, the current study group has achieved remarkable progress with emulsified ZVI which may be an opportunity for investigation in DFP degradation as a future delivery method to its DNAPL zones in groundwater.\(^{16}\) Zinc has also been mentioned as an effective dehalogenation metal for halocarbons, especially for rapid dechlorination as well as being more effective than iron in this regard. Aluminum is clearly in the same category as zinc and iron with an even greater reduction potential and aluminum has been noted in the literature to catalytically reduce fluorocarbons albeit with organometallic complexes.\(^{127}\) Aluminum is also noted as functioning successfully under alkaline conditions which is known to be the case in Florida limestone aquifers. But, magnesium is recognized for being both the most thermodynamically driven reducing agent of the group and seems to be frequently paired with
both other metals and catalysts in pursuing environmental clean-up of halogenated groundwater pollutants. It exhibits favorable properties in establishing its own oxidized protective layer in protic solvents and continues to provide reductive capability. Additionally, combinations of each of these metals and in conjunction with catalytic supports are worthy of investigation in the attempted hydrodefluorination (HDF) of DFP. Table 2.3 provided the reduction potentials of the metals chosen for the study, with hydrogen as reference.

Table 2.3: Reduction Potentials of Candidate Metals chosen for DFP Degradation Study

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^0 ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}^{2+}<em>{\text{aq}} + 2 \text{e}^- \rightarrow \text{Mg}</em>{\text{s}} )</td>
<td>-2.37</td>
</tr>
<tr>
<td>( \text{Al}^{3+}<em>{\text{aq}} + 3 \text{e}^- \rightarrow \text{Al}</em>{\text{s}} )</td>
<td>-1.66</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}<em>{\text{aq}} + 2 \text{e}^- \rightarrow \text{Zn}</em>{\text{s}} )</td>
<td>-0.76</td>
</tr>
<tr>
<td>( \text{Fe}^{2+}<em>{\text{aq}} + 2 \text{e}^- \rightarrow \text{Fe}</em>{\text{s}} )</td>
<td>-0.44</td>
</tr>
<tr>
<td>( 2 \text{H}^+_{\text{aq}} + 2 \text{e}^- \rightarrow \text{H}<em>2</em>{(g)} )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{Fe}^{3+}<em>{\text{aq}} + \text{e}^- \rightarrow \text{Fe}^{2+}</em>{\text{aq}} )</td>
<td>0.77</td>
</tr>
</tbody>
</table>

\(^{1}\text{For all half-reactions the concentration is 1M for dissolved species and the pressure is 1 atm for gases. These are standard state values.}\)}
Preparation of Metals

Mechanical Alloying

The mechanical alloying of metals has been a common practice for some time in achieving bimetallic catalytic reductive systems.\textsuperscript{78} It was decided for this study that in order to achieve a favorable morphology, mechanical alloying would be performed for all bimetals and catalytically enhanced metal systems to be investigated. Monometals assessed against the fluorocarbon would be performed with their existing commercially available morphologies. Mechanical alloying was accomplished by the use of a ball mill shaker apparatus for each of the different metal systems. The apparatus for the ball milling process consisted of a dual one gallon can holder and shaker manufactured by Red Devil, model number 5400 employing special wooden holding discs constructed to contain three stainless steel milling canisters (15.24 cm length, 5.08 cm i.d.) with stainless steel screw caps, three canisters per side, with 1.27 cm diameter stainless steel ball bearings. Note the three “pipe-like” canisters between the shaker plates shown in Figure 2.2.
Ball Milling Procedure

The use of 16 stainless steel ball-bearings of 1.27 cm diameter each was placed into each of the three stainless steel canisters. The “canister” consisted of a pipe, of dimensions 15.24 cm in length and an internal diameter of 5.08 cm, with stainless steel screw-on end caps. This step was repeated for the remaining two canisters. To the ball bearings, ethanol from Acros (anhydrous 99.5+%) was poured into each canister to just cover the bearings. A slow stream of inert helium gas (99.99%) from Airgas was used to fill the remaining space inside the canister to prevent sparks or ignition, the cap was then screwed on tightly. The three canisters were placed between the wooden holders for secure mount in the shaker apparatus. An additional canister set-up was placed into the holder on the other side as a counterweight. The canisters were then shaken for a period of 10 minutes in order to free any previously milled metal materials from the inside walls of the canisters and the bearings themselves. The canisters were then removed from the shaker apparatus and opened. The ethanol was discarded and the canister and bearings were
then washed thoroughly with soapy water to remove any freed previously milled material, and then rinsed with distilled water followed by acetone and allowed to dry thoroughly. Once dry, the bearings were returned to the canisters ready for the addition of the desired mechanically alloyed metal powders. After the determination has been made as to which metals to add in what percentages, the metal powders are weighed and placed into the canisters and on the bearings. Inert gas is once again used to fill the space inside the canister, and the caps screwed on tightly. The canisters and counterweight canisters are returned to the holders on the shaker apparatus and shaken for the desired time period. Once the desired allotted time has passed, the canisters are allowed to rest for a cooling off period to allow heat from the ball-milling process to dissipate. The canisters are then removed from the apparatus and opened, the bearings separated out in an appropriate mesh sifter apart from the resulting mechanically alloyed bimetal powder.

Benefits of Mechanical Alloying

There are several benefits to mechanical alloying where reductive metal particles are concerned. Essentially, the physical removal of any oxidized layer that has formed on the metal surface is optimized. This of course increases reactivity when the metal is subjected to any reducing substrate. Additionally, the metal’s surface area is increased with the formation of an alternate metal morphology due to folding, overlapping and forming convolutions inside and on the surface of the metal thus increasing reactivity. Further, since the basic morphology of the metal has changed along with it are the formation of distinctive features within the alloy
structure, not merely surficial, but internal structures such as cavities and crevices that are generated during the alloying process. It is believed these structures form during the alloying process with the physical folding and overlapping of metal surfaces under heat and pressure as these constructs evolve and are captured in the cooling phase of formation. It should be noted that when these structures form, a degree of catalyst and support material is lost into the internal construct and thereby decreases the amount of available surficial mass over what was originally predicted from measurements upon composition.

Materials and Methods

Experimental Procedure for Metal Systems Evaluation

Each individual metal system study, monometallic or bimetallic with or without catalyst, was prepared, conducted, and evaluated in the same manner and as follows. The reaction vessel for all studies made use of a 22 mL quartz glass vial with 20 mm diameter opening (#14-4440-324) from Teledyne Tekmar, and were sealed with the accompanying aluminum crimp caps (#14-4436-000) fitted with Teflon-lined rubber septa (#14-5818-043) obtained from same. Each vial was weighed empty to tare weight then was added the desired mass of each powdered metal using an Ohaus Discovery model# DV314C analytical balance. All metals throughout the entire series of studies were weighed as closely as possible to a mass of 200 mg and a minimum of three vials were established for each set of experimental conditions. Metals were obtained from
various manufacturers: iron, aluminum and zinc from Sigma Aldrich, magnesium from Hart Metals, Inc., and palladium on activated carbon and carbon black from Acros. To each vial of metal powder was then added a 5 mL volume of the desired protic solvent media, typically a low molecular weight alcohol, aqueous solution or combination; various reaction media are discussed in detail in Chapter 3. Methanol and isopropanol were obtained from Fisher Scientific while ethanol from Acros. Water for aqueous media was obtained from a Thermo Scientific Barnstead nanopure water system model #D11791 equipped with D375 0.2μm pore size hollow fiber filter operating at 18.1 MΩ-cm resistivity. Upon combining the metal system and reaction media, a 20-30 second period of gentle stirring of the vial was performed to facilitate complete mixing. This action also promoted the generation of hydrogen gas from reduction of the protic solvent by the metal. Qualitative analysis for the confirmation of hydrogen gas was determined by a simple flame ignition test validating that at least 4% by volume in the reaction vial atmosphere was hydrogen. All vials were allowed to stand in ventilation hood for a period of 15-30 minutes depending upon degree of gas evolution. Some studies also required the use of acid activation for a particular metal system and if so performed, additional gas evolution standing time of 20 minutes was added. In the case of iron containing systems, 2 drops of 6M HCl were added to the 5 mL media solution. The 6M HCl was obtained from Fisher and subsequent stock dilution with nanopure water. To specific magnesium containing systems, 1% glacial acetic acid in alcohol solution was added. Glacial acetic acid was obtained from Fisher Scientific.

After the reaction vials were allowed to stand until gas evolution had almost ceased, a precise volume of DFP was then added to obtain the desired concentration. Upon DFP addition, the vial was immediately crimp-capped to capture any potentially evolving reaction products. Decafluoropentane, in neat form, was obtained from E. I. du Pont de Nemours and Company.
under the trade name Vertrel XF, product #4310. Figure 2.3 shows the typical study set-up with triplicate vials all of identical composition for DFP degradation evaluation. In this example the metal system is Mg(Pd/C) with DFP in aqueous solution.

Vials were then placed on an orbital shaker table unit from Barnstead Lab-line “Lab Rotator” Model # 2314. The orbital shaker provided the motion required to simulate groundwater flow for all reaction vial samples in all studies. Rotational velocity was set to a constant 80 rpm for the desired duration for each set of vials. Typical shaker exposure times ranged from a few days up to one to three weeks depending upon the desired reaction duration. Additionally the shaker table top was modified with an external cardboard structure to accommodate a range of sample vials from one to approximately forty at any given time. Also, the modification met safety precautions associated with vial rupturing due to pressure increases and potential cap failure. Further, vials were placed into the structure and secured using plastic
bubble wrap to minimize vibrational contact and thus potential breakage during shaker duration. Figure 2.4 shows the modification made to the shaker table top for these purposes.

![Image](image_url)

Figure 2.4: Orbital Shaker Apparatus Modification (front view) and Reaction Vial Sample Placement (top view)

For each set of metal system-DFP sample vials, a set of both reaction blanks and control vials were also established. A blank consisted of a vial containing only the protic solvent to be used in the study. Control vials contained both the protic solvent or solvents, and the initial concentration of DFP. Typically an alcohol carried over into the aqueous solution from the original DFP stock dilution. In the case of an alcohol as protic solvent, the DFP dilution was always made in the same alcohol so as to minimize the solvents present in solution. The term reaction media, for the purposes of this study, refers to the solution containing all compositional elements for an experiment with the exception of the presence of the metal system. Depending upon the study, the reaction media could also include the aforementioned acid activation reagent and whenever acid activation was employed, this component was also included in the control
vials. Reaction vials were maintained on the orbital shaker during the desired reaction duration for each study. Orbital shaker monitoring was performed to ensure no interruption in shaker performance or ancillary power or equipment failures impacted the duration of the study. During rest periods between sample runs, routine maintenance on the orbital shaker was performed to ensure the drive belt system was operating properly. Any worn belts were replaced, even ahead of likely breakage times to ensure no malfunction would impact reaction time duration for samples. Upon completion of the reaction time duration, the samples were removed from the shaker for analysis.

Analytical Instrumentation

Analysis of samples was performed on one of two analytical instruments, either a Gas Chromatograph coupled with Mass Spectrometer (GC-MS) or a Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID). Initial treatment of samples analyzed on the GC-MS was by use of an auto sampling headspace analyzer. In the analyzer, sample vials are transferred to a platen where the sample was heated to a set point while inert gas flow, helium, sweeps the headspace from a dual functioning needle that also collects sample and accumulates onto a sorbent trap. The trap, consisting of a carbosieve packing material, is purged after a set time period and after all possible volatile material concentration has been removed from the vial and collected on the trap. Upon purging to the transfer line; the sample is delivered to the gas chromatograph injector and placed onto the column. The parameters for the HT3 headspace analyzer utilized throughout the study are provided in Table 2.4. The combined gas
chromatograph and mass spectrometer instrumentation used for this study was a Thermo Electron Corporation Trace GC Ultra coupled with a DSQ II MS. The headspace analyzer was a Teledyne Tekmar HT3 autosampler capable of both static and dynamic sample analysis. The GC column applied to all studies for this instrument was a Restek Rtx-502.2 Catalog #10916 with length of 60 m and 0.25 mm i.d. and stationary phase column packing consisting of 5% diphenylpolysiloxane and 95% dimethylpolysiloxane with film thickness of 0.25 μm. The DSQ II mass spectrometer consists of an ion source or volume, quadrupole assembly/mass analyzer and ion detector for capturing signal output. All samples were scanned from a starting mass of 35 m/z to avoid interference from all typical mass compounds below that range, i.e., oxygen, nitrogen, water, etc. Figure 2.5 shows the gas chromatograph with mass spectrometer and headspace autosampler instrumentation used in this study.

![Figure 2.5: The Gas Chromatograph (middle) Mass Spectrometer (left) and Headspace Analyzer (right) instrumentation used throughout the study](image)

Additional sample analysis was performed on an Agilent Technologies model 7890A gas chromatograph equipped with flame ionization detector (GC-FID). The GC column utilized with this instrument was a Restek Rt Q-PLOT Catalog #19718 with length of 30 m and 0.32 mm i.d.
and stationary phase column packing consisting of 100% divinyl benzene with a film thickness of 10 µm. Sample injections for the Agilent GC were performed manually by direct inject method with Hamilton Company gastight syringes of various volumes. This instrument was used primarily for analysis of hydrocarbon reaction products from the degradation of DFP, especially those below the set detection limit of the mass spectrometer. Figure 2.6 shows the GC-FID instrument utilized for hydrocarbon detection and confirmational analysis. A summary of the instrumental method parameters for both gas chromatographs and their respective detectors is provided in Table 2.5.

Figure 2.6: Gas Chromatograph equipped with a Flame Ionization Detector for hydrocarbon detection
Table 2.4: Operating Parameters for the HT3 Headspace Analyzer throughout the Study

<table>
<thead>
<tr>
<th>VARIABLE</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valve Oven Temp (°C)</td>
<td>110</td>
</tr>
<tr>
<td>Transfer Line Temp (°C)</td>
<td>110</td>
</tr>
<tr>
<td>Trap Sweep Temp (°C)</td>
<td>35</td>
</tr>
<tr>
<td>Platen/Sample Temp (°C)</td>
<td>40</td>
</tr>
<tr>
<td>Sample Preheat Time (min)</td>
<td>1.00</td>
</tr>
<tr>
<td>Sweep Flow Rate [ml/min]</td>
<td>35</td>
</tr>
<tr>
<td>Sweep Flow Time (min)</td>
<td>10.00</td>
</tr>
<tr>
<td>Dry Purge Time (min)</td>
<td>5.00</td>
</tr>
<tr>
<td>Dry Purge Flow [ml/min]</td>
<td>50</td>
</tr>
<tr>
<td>Dry Purge Temp (°C)</td>
<td>30</td>
</tr>
<tr>
<td>Desorb Preheat (°C)</td>
<td>245</td>
</tr>
<tr>
<td>Desorb Temp (°C)</td>
<td>260</td>
</tr>
<tr>
<td>Desorb Time (min)</td>
<td>2.00</td>
</tr>
<tr>
<td>Trap Bake Temp (°C)</td>
<td>300</td>
</tr>
<tr>
<td>Trap Bake Time (min)</td>
<td>12.00</td>
</tr>
<tr>
<td>Trap Bake Flow [ml/min]</td>
<td>225</td>
</tr>
</tbody>
</table>

Table 2.5: Gas Chromatograph and Detector Parameters for Analysis of the Study

<table>
<thead>
<tr>
<th>Instr.</th>
<th>Parameter</th>
<th>Thermo Electron GC-MS</th>
<th>Agilent Tech GC-FID</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>Injector Temp (°C)</td>
<td>150</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>Injector Mode</td>
<td>Splitless</td>
<td>Splitless</td>
</tr>
<tr>
<td></td>
<td>Carrier Flow [ml/min]</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Oven</td>
<td>Initial Temp (°C)</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Initial Time (min)</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Rate (deg/min)</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Final Temp (°C)</td>
<td>220</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Hold Time (min)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Detector Temp (°C)</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>Transfer Line Temp (°C)</td>
<td>250</td>
<td>N/A</td>
</tr>
<tr>
<td>MS</td>
<td>MS Scan Mode</td>
<td>Full</td>
<td></td>
</tr>
<tr>
<td></td>
<td>First Mass (m/z)</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Last Mass (m/z)</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>FID</td>
<td>H2 Flow [ml/min]</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Air Flow [ml/min]</td>
<td></td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>Makeup Flow [ml/min]</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>
Evaluation of Metal Systems

During the course of the study, multiple monometallic and bimetallic alloys were explored to find a suitable metal system capable of the required reductive dehalogenation. Metals were both used in their existing purchased commercial states and altered morphologies brought about by the mechanical alloying process. Additionally, each of these metals was evaluated in different protic solvents and depending upon the metal composition, iron vs. magnesium for example, an accompanying acid activator of either strong mineral acid or weak organic acid was present in the reaction media as well. Acidic treatment was conducted in an attempt to remove oxidized layers and reveal a degree of clean metal surface for potential reaction with the fluorocarbon. Table 2.6 provides a detailed description of each of the various metal systems including morphology, composition, and the various reaction media solutions sought in the reductive dehalogenation of DFP.

Table 2.6: Metal Systems Evaluated for DFP Degradation

<table>
<thead>
<tr>
<th>Metal/Bimetal</th>
<th>Fe</th>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
<th>Mg/Mg</th>
<th>Mg/Fe</th>
<th>Mg/Al</th>
<th>Fe/C</th>
<th>Mg/C</th>
<th>Pd/C</th>
<th>Mg-Pd/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morphology</td>
<td>Mesh - 325</td>
<td>Powder (1-3μm)</td>
<td>Mesh - 200</td>
<td>Dust (&gt;10μm)</td>
<td>Milled Powder (1-3μm)</td>
<td>Milled Powder (1-3μm)</td>
<td>Milled Powder (1-3μm)</td>
<td>Powder 10% Pd (&lt;4μm)</td>
<td>Milled Powder (1-3μm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>50%</td>
<td>50%</td>
<td>Mg 60% Al 40%</td>
<td>Fe 95% C 5%</td>
<td>Mg 90% C 10%</td>
<td>Mg 92% Pd 1% C 7%</td>
</tr>
<tr>
<td>DFP (ppm)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>1, 10, 20</td>
</tr>
<tr>
<td>Protic Solvent</td>
<td>Aq MeOH ETOH</td>
<td>Aq MeOH ETOH</td>
<td>Aq MeOH</td>
<td>Aq MeOH</td>
<td>MeOH ETOH</td>
<td>ETOH</td>
<td>ETOH</td>
<td>Aq MeOH ETOH</td>
<td>Aq</td>
<td>Aq ETOH</td>
<td></td>
</tr>
<tr>
<td>Activator</td>
<td>6M HCl</td>
<td>1% HOAc</td>
<td>1% HOAc</td>
<td>1% HOAc</td>
<td>1% HOAc</td>
<td>1% HOAc</td>
<td>1% HOAc</td>
<td>6M HCl</td>
<td>1% HOAc</td>
<td>None</td>
<td>1% HOAc None</td>
</tr>
<tr>
<td>Reaction Products</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>C2, C3, C5, C6 HC’s</td>
</tr>
</tbody>
</table>

From the table, it can be seen that only one metal system was successful in the reductive dehalogenation of DFP. The successful reaction and the products formed will be discussed in
Chapter 4. A discussion of the other metal systems and the various reaction media attempted will be addressed first. A review of the monometals in contrast to the bimetals provides insight into either the success or failure of each system.

The Solitary Metals (Monometals)

Each metal system that involved only a solitary metal or monometal was attempted with three different protic solvents and with and without respective acid activation in each media. For example, magnesium metal was tested in the protic solvent ethanol with 1% glacial HOAc in ethanol (v/v) for activation. In another instance, magnesium was attempted in aqueous solution only with no acid activation and so on with each metal being attempted in at least two of the three protic solvents with or without activation. It should be noted that only iron and magnesium were attempted in all three protic solvents, while zinc and aluminum were attempted in only aqueous and methanol. It should be further noted that iron was the only metal which received hydrochloric acid activation treatment due to the required presence of a stronger acid for removal of the oxidized layer. Each of the other metals, zinc, aluminum and magnesium, being much more reactive were activated more gently with glacial acetic acid to remove their oxidized layers.

The four monometals: iron, zinc, aluminum and magnesium were each attempted first in the reduction of DFP. These metals were purchased in morphological states commercially available and not mechanically altered prior to any application. Each metal was attempted in methanol solution initially to minimize the oxidation associated with aqueous solutions.
Additionally, metals in alcohol media had shown promise with other studies within the group regarding dehalogenation reactions.\textsuperscript{130,131,132} When these efforts produced no results for this study, acid activation was employed to remove any atmospheric oxidized layer that may have been present. This however also revealed no additional progress in dehalogenation. An additional use of ethanol solvent was attempted with iron and magnesium as that media had also shown promise within the work group.\textsuperscript{80} Aqueous solution was attempted as well being the ultimate target media in which the pollutant was being dealt with. None of these monometals or their various combinations with protic solvents and acid activation was successful in any way. The formation of a white cloudy precipitate was noticed in each vial employing only alcohol media. This was believed to be the formation of various metal methoxides and ethoxides from the reaction of the two. Also, whenever acetic acid was used, additional white precipitate formation occurred in the form of various metal acetates. It is believed that the combination of not being able to remove the entire oxidized layer and generating additional interfering precipitates lead to the inability to activate the carbon-fluorine bond. Figure 2.7 shows the reaction vials of the four monometals after attempted reaction revealing their metal oxidized compounds.

![Reaction vials](image)

Figure 2.7: Comparison of Fe, Al, Mg, Zn; one week reaction time with oxidative formation present
It was determined that use of two different zero-valent metals together as a binary system or bimetallic approach might be successful. Once again the metals iron, magnesium and aluminum would be used but this time in various percent alloyed combinations. The mechanical alloying process described previously which utilized the ball milling equipment was employed again for this purpose. This bimetallic approach relied upon the reduction-oxidation principle. With a greater reductive metal providing sacrificial protection to a lesser reductive metal, donation of electrons from the greater to the lesser occurs while in turn, electrons are then provided to the halogenated organic compound. The three bimetals alloyed for this purpose were magnesium-iron, magnesium-aluminum and the unique alloyed approach of mechanically alloying magnesium with itself to increase activity. This is obviously not a true bimetal but is included in this discussion for simplification as it received the same morphological manipulation as the two distinct bimetallic alloys. Mechanically alloying metals together provides the two-fold benefit of removing any oxidized layers exposing unreacted metal surface and increasing metal surface area for enhanced reaction opportunity. Both the alloys of magnesium-iron, and magnesium-aluminum were attempted for fluorocarbon degradation in ethanol, both with and without 1% glacial acetic acid activation. The magnesium-magnesium alloy was attempted in both methanol and ethanol and with and without 1% glacial acetic acid. Both alcohols were evaluated with magnesium due to previous observations of the successful dehalogenation of chlorocarbons within the study group. As was observed with the monometals, whenever acetic acid was present the formation of the white precipitate, the metal acetate, was observed and when alone in alcohol media, the corresponding alcohol oxide was also noted. Both observations
were seen as well with the magnesium self alloyed example. Yet, none of these alloys were successful in dehalogenation of the fluorocarbon. It was believed that the inability to activate the carbon-fluoride bond once again resided with the absence of a clean metal surface for adsorption of the fluorocarbon from the precipitates formed. However, it was speculated that if the fluorocarbon had been able to be adsorbed onto the metal surface, the necessary electron transfer from one of the metals might have possibly occurred. It was then believed that the introduction of carbon, as an adsorbent, to bring the fluorocarbon into close approximation if not direct contact with the metal surface would possibly facilitate the necessary electron transfer.

The additional metal systems of iron and magnesium individually on activated carbon were attempted next. Some precedence had been set for this in the literature as well since metal on activated carbon had been one of the earliest successful hydrodefluorination attempts. Witt et al. had successfully hydrodefluorinated the alpha carbon of a low molecular weight fluorocarbon compound but at elevated temperatures greater than any allowable in situ method for groundwater. Iron on carbon was attempted in ethanol with hydrochloric acid activation and magnesium on carbon was attempted in methanol, ethanol and aqueous solution with and without 1\% glacial acetic acid. Magnesium was treated to a greater range of variables in solvent media for reductive attempts due to other successful dehalogenation work. Each of these various combinations of metal system and reaction media unfortunately produced no results towards defluorination of the pollutant compound. It was believed that interference from precipitate formation was once again a hindrance towards the desired result. Further, that even if the carbon layer had adsorbed some measure of the fluorocarbon material and even brought it into direct contact with the metal surface, the necessary electron transfer may not have been able to occur due to the lack of a partner metal for bonding with or holding the fluorocarbon to allow
transference in the first place. Even though carbon adsorption would seem to aid in retention for the desired outcome, fluorocarbons are known to undergo desorption if either the hydrogen bonding or van der Waals effects are insufficient in maintaining their retention.\textsuperscript{133} At this point, it was decided to attempt a bimetal which also incorporated the activated carbon moiety.

In review of successful dehalogenation reactions in the literature and previous work inside the research group, the alloyed bimetal of magnesium-palladium on activated carbon Mg(Pd/C) had been successful where others were not.\textsuperscript{128,134,135} The bimetal was generated using the same mechanical alloying process, the ball mill, applied to the other bimetals in the study. Defluorination of the pollutant was attempted in the protic solvents of ethanol and aqueous solution both with and without 1\% glacial acetic acid activation. The magnesium-palladium on carbon metal system was found to be successful in all four attempted configurations of protic solvent and acid activator for the reductive dehalogenation of DFP.

\textbf{Mg(Pd/C): The Successful Candidate!}

Mg(Pd/C) was determined to be the successful candidate for the hydrodefluorination of DFP. It appeared that the bimetallic alloy provided the appropriate model of reductive metal and supported catalyst to conduct the degradation of the fluorocarbon. The bimetal was developed using the aforementioned ball milling process, discussed previously in this chapter under “Metals Preparation”. The specific procedure for producing the bimetal was as follows: 78 g of powdered zero-valent magnesium metal, (1-3 \( \mu \)m) from Hart Metals, Inc., was weighed out and
placed into the ball milling canisters, to this was added 7 g of 10% palladium, unreduced on activated carbon, from Acros #19503-0100, for a total alloy mixture mass of 85 g. Once placed in the ball mill shaker, the canisters were operated for 45 minutes duration followed by a 15 minute cooling period. This provided a mechanically milled alloy of composition: 91.77% Mg, 7.41% C, and 0.823% Pd. It should be noted that the mass values selected for the bimetal composition had previously been established by research conducted within the group for most dehalogenation reactions; the choice was made to start with this compositional ratio.\textsuperscript{119,136} Further, as mentioned previously, loss of some catalyst mass is inevitable in the mechanical alloying process. This is certainly true of the internal morphological features brought about by ball milling with folds, overlapping and convolutions occurring during metal alloying. Magnesium is a particularly soft metal and a loss of catalyst material within the reductive metal will occur as palladium is a metal of greater hardness. On the Mohs hardness scale, magnesium exhibits a relative hardness value of 2.5 compared with palladium’s value of 5.0.\textsuperscript{137}

The loss of additional catalyst material occurs during milling in a different manner as well. Upon completion of milling, there is always a portion of metal powder remaining adhered to the surfaces of the canister walls and the ball bearings. The exact recovery and composition of the bimetal must be annotated to be some value less than what is reported as ideal, from initial mass values. In the case of this study, the final percentage of palladium present in the bimetal alloy is something less than 0.823%. This is also true for the carbon and magnesium mass as well and all should be taken into consideration when reporting compositional mass values for the bimetal when drawing conclusions about its success. A word of caution must always be exercised in this regard.
The bimetal system provides a dual functionality in order to accomplish reductive dehalogenation. The magnesium provides the necessary electron donation to the carbon-fluorine bond for activation and the palladium-carbon support provides the active bonding site for the halogenated molecule. Additionally, catalyst adsorption also provides the conditions required for the electron transfer to occur. While bonded to the catalyst surface, electron transfer from magnesium can traverse the carbon layer support to the palladium adsorbed DFP molecule and activate the carbon-fluorine bond, thereby permitting liberation of fluorine in the ionic state. The role of carbon layer itself is not completely determined. It is unclear if the carbon layer also attributes to the degradation of DFP other than as a conduit for electron transfer from the transition metal. It is believed that the increased porosity of activated carbon adds to the adsorption of DFP and its association with the metal surface. This may also permit activation of the C-F bond, but desorption probably does not occur, even after defluorination is complete; this hypothesis will be discussed in Chapter 5. The formation of some precipitate was also observed for each of the four different reaction media. Again, precipitate formation was observed to be greater in those with the presence of alcohol, the acid activator or both. Although, in this example the interference of the precipitates did not prevent the reaction from occurring, yet a greater yield in production of reaction products was noted when these compounds were not as prevalent; this will be reviewed in detail in the next chapter regarding reaction media.

A view of the metal system components in the reaction vial after one week’s reaction duration with DFP are provided in Figure 2.8. Also, in the same figure are two Focused Ion Beam (FIB) images, one of the bimetal system surface and another exposing the inner morphology of convolutions and overlapped layers within the alloy construct.
Figure 2.8: Mg(Pd/C) vials at one week reaction time with DFP in aqueous media, followed by two Focused Ion Beam (FIB) Images of Mg(Pd/C) surface area (100 μm) and sliced section to reveal internal morphology (5 μm).\textsuperscript{128}

In Figure 2.8, the center image of the bimetallic surface was used for surficial catalyst percentage calculation. It was determined by surface area analysis that the percentage of palladium on activated carbon present is approximately <1% of the total surface area. However, a precise analysis would be required for more accurate data.

One concern with the successfully developed system was the degree of contribution of the carbon supported palladium catalyst or in other words, how important was the magnesium to the reaction or could the supported catalyst reductively defluorinate the DFP alone? An experiment was conducted involving only the supported catalyst and fluorocarbon to ensure the presence of the reductive transition metal was truly required.
Reaction with Pd/C only

It has been reported in the literature that Pd/C alone has proven to be a successful catalyst in the hydrodechlorination of aromatic halides and in aqueous environment under normal temperatures and pressures. Therefore, it was necessary to determine if the presence of magnesium was required at all for the degradation reaction to take place. In order to ascertain the role of the magnesium in the reaction and if the catalyst alone would generate the same or different reaction products, the reaction was carried out under identical conditions but with only palladium on carbon as the metal system. Additionally, the palladium study was performed in aqueous media only, desiring to avoid any of the precipitate formation observed previously with alcohol and acetic acid.

It was revealed that no reaction took place with the fluorocarbon by Pd/C alone. It is concluded that the transition metal and the catalyst are both required for the reaction to occur; without the presence of each there is no reaction. It is assumed magnesium provides the necessary electron transfer and serves as the producer of the reductive hydrogen from the protic solvent while the catalyst provides the active site for adsorption and permits the necessary duration required for electron transfer from the zero-valent magnesium to the fluorocarbon.

It was observed that the reaction products produced are all hydrocarbons. This was fortuitous since hydrocarbon end products can be broken down in the environment by natural biodegradative processes, one of the goals of the study. The hydrocarbons produced were not completely unpredictable as evidence by the formation of n-pentane. However, also observed
were three hexane isomers: n-hexane, 2-methylpentane (2MP) and 3-methylpentane (3MP), and the cyclohexane isomer, methylcyclopentane (MCP). Later, it would become apparent that both methane and propane are produced as well but their discovery was elusive. A discussion regarding the reaction products generated from the degradation of DFP and their specific organic reactions will be discussed in Chapter 5, “Discussion”. Focus now turns to the various reaction media and their degree of success in conjunction with the bimetal Mg(Pd/C).
CHAPTER 3: DETERMINATION OF THE OPTIMAL REACTION MEDIA

Evaluation of the Various Reaction Media

Introduction

The selection of reaction media was based upon three criteria. First, that which best resembles the intended application environment, groundwater. Second, if possible would promote the solubility of the fluorocarbon to maximize interaction with the metal system; and third, a protic solvent must be used in order to provide the necessary reduction of the pollutant to the highly desired hydrocarbon end products.

However, there was concern with respect to media selection in regards to two aspects. Selection of any organic solvent could potentially interfere with the reaction by competing with the fluorocarbon for catalytic binding sites or reacting with it to produce potentially undesirable byproducts. Additionally, regarding sample analysis, consideration should be given to media selection to preclude any retention time interference, i.e., peak overlap with potential reaction products. Although it is true that this problem can be compensated for, numerous trials might be necessary with alternate solvents to ensure undetected peak elution did not occur. Therefore, care was taken in selection of solvents with elution retention times that would not interfere with the expected reaction product pentane or any probable partially fluorinated byproducts.
A quick review of a list of common protic solvents in Table 3.1 immediately reveals several valid choices as potential candidates for meeting the required criteria of aqueous-like, polar, and protic. The protic organic solvents most like water in properties are methanol and ethanol, excluding acetic acid as it was to be used for metal activation and not the solvent itself. Solvents with the highest dipole moments are desirable because they are more likely to successfully interact through hydrogen bonding with the hydrofluorocarbons only hydrogen atoms and aid in its solubility. The two alcohols will easily react in the presence of a strong reductive metal, like magnesium, forming their respective oxide group ions. Aqueous solution would also provide the necessary reducing environment for the reaction. Therefore, the two alcohols and aqueous solvents were chosen for the reaction media studies.
Comparison of Different Reaction Media

To determine the optimal reaction media, a series of studies were conducted that utilized each of the three selected protic solvents in both the presence and absence of the metal activating acid. The criteria evaluated were effectiveness of acid activation and solvent success in regards to product evolution. Moreover, which solvent was better for reduction and whether or not acid activation enhanced metal activity, and ultimately, which combinations of the two revealed the most effective overall reaction media.

Vial studies were run in triplicate and samples were analyzed as one each per vial. The standard volume used in each sample vial was 5 mL of alcohol or water and 1% glacial acetic acid in either methanol or ethanol solution. When acetic acid was added to aqueous media, the stock solution of 1% acetic acid in ethanol was used. A separate acetic acid solution involving only methanol was used for the methanol solvent studies. For each run, blanks and controls were established as baselines. Blanks consisted of the reaction media composition, alcohol or water with or without the acid; and controls were the same as a blank but included the desired concentration of DFP. Each sample consisted of the same composition as the control, with the addition of the bimetal reductive catalyst. Each reaction vial was established by weighing approximately 200 mg of bimetal into an empty vial. The protic solvent was added to this and vials were allowed to stand in the hood for 15 minutes to vent hydrogen gas. Sample vials were hand stirred gently upon addition of the acetic acid and allowed to stand for an additional five minutes for further hydrogen gas evolution. An aliquot of DFP stock solution diluted in ethanol, at the desired concentration typically between 10 to 20 ppm, was added to the vial and quickly capped and crimped to capture and seal in any potential reaction products. An additional gentle
stirring step was conducted to ensure thorough mixing of all contents. All control and sample vials were then placed on the orbital shaker at a rotational velocity of 80 rpm for one week’s reaction duration. At the end of this time period, vials were removed from the shaker and placed in the auto sampling carousel of the headspace analyzer. Sample vials were always preceded in the carrousel by both blank solution vials and control solution vials and an additional blank vial was placed at the end of a run. Multiple sample vials from different runs were always separated by blanks in between vials. Additionally, standards of previously determined reaction products, pentane and hexane isomers, were established in a range from 0.1 ppm to 10.0 ppm with intervals at 1.0, 3.0, 5.0 and 7.0 ppm, for determination of product concentrations. Standards were always place on the auto sampler carrousel before the first blank of any sample analysis and preceded by a blank vial. Blank vials were also placed in between different standard concentration vials as well. All reagent grade methanol, isopropanol, pentane and hexane isomer solutions were obtained from Fisher Scientific, ethanol was from Acros. All aqueous media was generated by the aforementioned water purifier from Barnstead. Samples were analyzed by GC-MS under the parameters established in Chapter 2: Analytical Instrumentation.

Following analysis of the methanol solvent vials, the protic solvent was eliminated from further study. It was determined that methanol was eluting at a retention time that caused peak overlap with that of pentane. Adjustment to the GC method did not improve separation adequately. Since pentane was expected to be the main reaction product, the alcohol solvent studies were permanently changed to employ only ethanol as representative. Ethanol retention time occurred later than pentane under the current method and the two peaks could be distinguished from one another.
The four different reaction media scenarios now consisted of the following: ethanol alone, ethanol with acetic acid, aqueous alone and aqueous with acetic acid. Each set of reaction vials were all subjected to the same set of reaction conditions, i.e., volume of reaction media, mass of bimetal, concentration of DFP, concentration of acid activator (where applicable), ambient temperature, orbital shaker revolution speed and reaction duration. Figure 3.1 provides a comparison of the effectiveness of the four different reaction media by way of the formation of three of the major reaction products from the degradation of DFP.

![Figure 3.1: Comparison of the production of selected reaction products contrasting the four different media solutions](image)

It was apparent that the best reaction media was aqueous solution and absent the acetic acid metal activator. This was curious since in previous degradation studies, the employ of acetic acid always enhanced metal activation and thus reductive capability. Additionally,
since the hydrofluorocarbon is known to be soluble in alcohols, it would seem that ethanol solution would provide adequate dissolution and thus enhance degradation through more frequent molecular contact with the metal’s surface.\textsuperscript{139} However, the formation of a white milky precipitate was observed in all vials that contained either ethanol, acetic acid or both. This was reminiscent of the prior metal selection studies in which the same occurrence was observed. It can be concluded that both the precipitates formed from the ethoxide and acetate of magnesium are passivating the metal surface and inhibiting reaction with the fluorocarbon. This would identify both ethanol solutions and the aqueous acetic acid solution as less than optimal leaving only the aqueous as significantly effective in the reaction. Figure 3.2 provides visual of the cloudy precipitate formation visible in the liquid column in all but the aqueous (water) reaction media.

Figure 3.2: Visual comparison of final reaction phase for different mixtures of reaction media and metal activation (1E ethanol only, 1EAA ethanol with acetic acid, 1W water only and 1WAA water with acetic acid)
Aqueous: The Optimal Media

Aqueous media without the presence of any acid activator proved to be the most effective choice in reaction media for the degradation of DFP. Precipitate formation interferes with successful reductive dehalogenation of the fluorocarbon due to catalyst deactivation. The aqueous solution allows for the best interaction between metal and fluorocarbon as no interfering precipitates in solution are present. However, unlike the precipitates of ethoxide and acetate formed in those solutions, aqueous media still allows for the formation of magnesium hydroxide from water but not to the degree of catalytic deactivation of the aforementioned precipitates. The difference for this observation lies in the solubility of the precipitates formed. Magnesium acetate is soluble in water and therefore constant dissolution and reformation is occurring and obscuring the active sites on the catalyst surface. Magnesium hydroxide formation however occurs on the magnesium surface and once produced, this process ceases and the protective layer is formed on the reductive metals surface. In Figure 3.3, a comparison between the two reaction media and this observed effect is evidenced by the greater amount of reaction products produced in the absence of the acetate precipitate formation.
Additionally, it should be mentioned that even in the aqueous solution, some ethanol is present as it was carried over in the aliquot from the DFP stock dilution to generate the necessary concentration in the vial. This relatively minute amount of ethanol is apparently not enough to generate any appreciable amount of interfering precipitate for the reaction. Aqueous media proved superior to the aqueous and acetic acid solution by almost double the production of reaction products and more than 10 times that observed in the two ethanol solutions; thus making it the media of choice for all further studies.
Additional Reaction Media Studies

A Study of Tap Water

Once it had been determined that the reaction was most successful in aqueous media and that only nanopure water had been provided as the protic solvent, an evaluation of an alternate but equivalent media was necessary to demonstrate the metal systems effectiveness in the presence of potentially interfering ions. Since the ultimate target solution for the technology was groundwater, it was determined that tap water would serve as a suitable surrogate solvent with an even greater potential for a negative effect on the reaction.

The State of Florida’s groundwater is relatively pure and free of other ionic species when compared to tap water. The Floridan aquifer is known to contain sulfate, bicarbonate, chloride, calcium, and sodium ions. However, tap water is also know to contain sulfate, chloride and sodium ions but in addition lists fluoride, nitrate, nitrite, copper and lead as well; along with solids and silts from degrading water pipes and a number of other contaminants from wastewater treatment facilities.\textsuperscript{140,141} It was determined that the success of the technology in tap water would provide greater assurances of future field application in groundwater, with respect to the presence of other ionic species.
It can be seen from the chart in the Figure 3.4 that the degradation reaction products are relatively equal in either nanopure or tap water solution. Therefore it can be concluded that the metal system should perform adequately in groundwater even with other ions present. The noted slight increase in reaction products, with the exception of 2-MP which is more dramatic, in tap water over nanopure media may be due a synergistic effect in either enhancing catalytic activity or promoting defluorination, but is speculation and would require additional study to investigate what is occurring.

The Role of Alcohol in the Reaction

Since alcohols were typically carried over into the reaction media when making dilutions from stock solutions for various DFP concentrations, a determination of any potential effect attributed to the reaction by the presence of the alcohol became necessary. Various alcohols were used as diluents to attain various DFP concentrations throughout the study and were
believed to possibly be contributing to the various reaction products observed. Specifically, the formation of hexane from the fluorocarbon analogue of pentane was suspicious, especially with the apparent addition of an extra carbon to the chain; this made the alcohols potential contributors.

In order to determine this, two sets of vial studies were established and each with a different alcohol being minorly present in aqueous solution. Ethanol and Isopropanol were employed as test subjects for the reactions. It was expected that by utilizing the two different alcohols separately, and if they were indeed contributing to the reaction products formed, the uniquely different molecular structures would alter the contribution to the reaction and be expressed in the form of different reaction products. To ensure these conditions, the stock dilutions of DFP were prepared in their respective alcohol solutions to obtain aliquots of DFP for the desired concentration in the study.

The study revealed that using different alcohols with different molecular structures made no difference in the reaction products observed, nor were any appreciable differences in quantities produced either. It was concluded that the alcohol does not participate in the reaction and that some other mechanism must be responsible for the observed reaction products, specifically those that exhibit an increase in carbon number along the backbone chain of the molecule.
Changes in pH

A study was conducted to determine if the reaction causes any notable change in the pH of the reaction media. The concern was two-fold; if the degradation of DFP would change the pH due to hydrofluoric acid formation and if the reaction would produce a change great enough to possibly be of environmental concern. Four different reaction media scenarios were developed for the study. All four would contain 200 mg of the metal system, Mg(Pd/C) and 5 mL of aqueous reaction media. In order to establish a baseline effect with the presence of acetic acid, two groups of vials were established; one with only the bimetal and water and the other with same and addition of 1% acetic acid solution. These vials would serve as the control for behavior of acetic acid in solution without any presence of DFP. The second two groups of vials were established the same as the first set with the exception of DFP being added to both. These vials would provide evidence for any change in pH due to the reaction as compared to the vials in which DFP was absent. If there were an observed change in pH that deviated from the controls, this would demonstrate that the bimetal reaction with DFP causes a pH variation in the media and would potentially impact the environment.

The pH of each set of reaction vials was measured at time intervals during the course of the reaction, and same in the case of the control vials to establish a comparison. Time intervals initially consisted of minutes and then hours of reaction time with a final reading taken at 24 hrs duration, well beyond the previous 90min reading of any observed incremental change. The pH measurements were taken with an Ecotestr-pH2 from Synotronics, and standard buffer solutions of 4.0, 7.0 and 10.0 were obtained from Fisher Scientific to calibrate the probe. Calibration
procedure was conducted per manufacturer’s instructions and the probe was rinsed well with nanopure water between uses.

A review of the data demonstrated that the samples where acetic acid was present, a slightly more acidic pH reading was observed and the presence or absence of DFP made no difference in those observations. This observation is exhibited in Figures 3.5 and 3.6 comparing pH changes both with and without the presence of DFP in solution with and without acetic acid. This study confirms that the slight increase in pH occurs due to the reaction of magnesium with water forming magnesium hydroxide. Further, that the change in pH is neither affected nor caused by the degradation of DFP in solution. Also, pH change is not significant enough to cause any undesirable environmental impact, especially in the Florida aquifer where groundwater pH is typically alkaline due to the presence of limestone.

![Figure 3.5: Comparison of Reaction Change in pH, both with and without Acetic Acid (DFP Absent)](image_url)
A study to determine if DFP degradation brings about any changes in temperature was conducted in parallel with the aforementioned pH study. The same four reaction media solutions were produced and evaluated for any notable temperature change. Again, the concern was of a dual nature in regards to any variations in temperature brought about by the reductive defluorination of DFP or any observed temperature increase high enough to warrant concern as thermal pollution. As can be seen in Figures 3.7 and 3.8, a greater increase in temperature was observed for reaction vials containing acetic acid than those without it. Magnesium’s reaction with acetic acid in the formation of magnesium acetate is greater exothermically than for the formation of magnesium hydroxide in aqueous solution. However, as observed in the study the presence of DFP and its degradation does not cause any deviations in reaction temperature. Also, changes in temperature are minor and not enough to cause any environmental concern.
Figure 3.7: Comparison of Change in Temperature both with and without Acetic Acid (DFP Absent)

Figure 3.8: Comparison of Change in Temperature both with and without Acetic Acid (DFP Present)

Optimization of the Reaction Media

Aqueous solution alone was determined to be the optimal reaction media for the degradation of DFP by Mg(Pd/C). It is the solvent of choice in application intended for groundwater and being a polar protic solvent, provides the necessary reductive capabilities for
the metal system to act upon the fluorocarbon. However, in so far as promoting the solubility of DFP to increase interaction with the bimetal, this condition relies solely upon van der Waals forces with the molecules only two hydrogen atoms which is not the optimal condition. However, aqueous media was still the most effective choice. It did not produce the catalyst interfering precipitates associated with acetic acid or alcohol solutions. It was still very effective even with the presence of potentially interfering ions as observed with tap water. Further, the slight rise in pH and reaction temperature experienced with the metal hydroxide formation was not significant enough to neither cause any environmental concerns nor hinder the degradation of the pollutant hydrofluorocarbon. Therefore, aqueous solution was employed throughout the rest of the study as the sole reaction media.
CHAPTER 4: EVALUATION OF THE REACTION

Degradation of DFP

Decafluoropentane undergoes total catalytic hydrodefluorination in aqueous solution in the presence of Mg(Pd/C) to the reaction products: methane, propane, n-pentane, 2-methylpentane, 3-methylpentane, n-hexane, and methylcyclopentane. Of these products, n-pentane was fully expected in relation to the initial fluorinated analogue molecule, as were any partially fluorinated five member carbon chain compounds; although, the six carbon member compounds were not anticipated and no partially fluorinated analogues were evident. The proposed mechanism for their occurrence, as well as methane and propane evolution will be discussed fully in the next chapter.

The chromatogram shown in Figure 4.1 clearly illustrates retention time peaks for the reaction products in order of their elution off the column. They are as follows: propane, n-pentane, 2-methylpentane (2MP), 3-methylpentane (3MP), n-hexane, and methylcyclopentane (MCP). Elution of the isomers of DFP are shown in the top chromatogram i.e., the DFP Control, at retention times of 4.32 to 4.79 minutes. The three subsequent chromatograms are of different reaction vial samples, each of 10ppm DFP concentration at one week’s reaction time. These chromatograms clearly show the degradation of DFP and formation of the reaction products. The retention time peak for n-pentane occurs at 7.57 minutes and the hexane isomers of 2MP, 3MP, n-hexane, MCP follow at 11.13, 12.04, 12.90, and 14.94 minutes respectively; propane occurs at 3.68 minutes, preceding the position of DFP.
Figure 4.1: Chromatogram of Reaction Products from the degradation of DFP by Mg(Pd/C) in Aqueous Solution

Doublet peaks are not completely understood but believed to be related to degradation of the headspace analyzer trap packing material. Doublet peaks began to appear after the headspace analyzer trap had been exposed to excessive amounts of alcohol and acetic acid from previous samples. It should be noted that budgetary constraints did not permit for replacement of the trap.

Confirmation of observed reaction product formation was verified by analysis on GC-MS with a series of standards including n-pentane and the various hexane isomers. Product sample mass spectra were compared to the National Institute of Standards and Technology (NIST) Library of compounds. Spectral library matching confirmation was always observed to be between 63% and 90% probability for all compounds. In Figure 4.2, the series of charts provide mass spectral peak comparisons of standard library data with those observed for each of the sample reaction products. Note that mass spectral scan initiated at 35 m/z for all samples.
Figure 4.2: Mass Spectral Peak Comparisons of the various Reaction Products (in red), to the NIST Library Spectra (in blue), from left to right in rows beginning at the top are: propane, n-pentane, 2-methylpentane, 3-methylpentane, n-hexane, and methylcyclopentane

The percentages of reaction products relative to one another were typically of a recurring nature. Of the hexane isomers, n-hexane is the highest concentration, followed in order by 2-methylpentane, 3-methylpentane and methylcyclopentane. The concentration of n-pentane varied, depending upon the initial concentration of DFP, but typically appeared in value between 2-methylpentane and 3-methylpentane; this relationship will be discussed in detail later in this section. Propane concentration was always found to be the least of the reaction products. This was even true with respect to methane evolution, although methane concentration was always
less than n-pentane or lower than the least concentration hexane isomer. Figure 4.3 provides the relative comparisons of reaction products to one another as they form over the course of a six hour reaction time period, with n-hexane being the greatest concentration and propane the least.

![Graph showing reaction product formation over time](image)

Figure 4.3: Comparison of Reaction Product Formation (DFP 1ppm in Aqueous at 0, 2, 4, and 6 hour intervals)

Degradation of DFP in contrast to reaction product formation was determined by running standards of both DFP and each of the reaction products in concert with various samples from a particular study. Standards were established over the linear range in concentrations of 0.1 ppm to 10.0 ppm with intervals of 1.0, 3.0, 5.0, and 7.0 ppm in between. Concentration values were determined using the linear regression method from relative abundances for each compound’s peak area observed on the chromatogram. Figure 4.4 provides the typical relationship noted between the degradation of DFP and the reaction products formed throughout the study.
Figure 4.4: DFP Degradation and Reaction Product formation (DFP 20 ppm in aqueous)

The chart also confirms that the reaction halts at around 24 hours reaction time with some minor deviations under longer durations as some products experience slight increases or decreases in concentration. This data would appear to reflect either a deactivation of the catalyst surface or a change in relationship between the reductive metal and fluorocarbon or the metal’s availability to interact entirely. These relationships will be discussed further in Chapter 5.

As mentioned previously, there exists a relationship between the initial DFP concentration and amount of n-pentane produced from the reaction. It was observed that whenever there was a higher concentration of DFP starting material, more n-pentane was produced and when lesser amounts of initial DFP were present, less n-pentane was formed; a direct relationship. It is proposed that initial hydrodefluorination must favor pentane formation over production of the hexane isomers. This observation can most likely be explained by a different reaction mechanism being responsible for the formation of the major reaction products. However, it was also observed that when more n-pentane formed, less of the three minor hexane isomers were detected, namely 2MP, 3MP, MCP. The cause for these observations is proposed
to be an effect of the stereochemistry of the DFP molecule. Specifically, DFP exists in two sets of diastereomers when manufactured resulting in one set of diastereomers being in greater percentage than the other. This condition along with the interaction and adsorption on the catalyst surface creates a set of conditions to cause reaction product formation in these observed percentages. The specifics of this mechanism will be discussed in Chapter 5. However, Figure 4.5 supports this observation with a comparison of the percentage of products produced with different initial DFP concentrations.

Figure 4.5: Comparison of the Relative Percentage of Reaction Products with Different Initial Concentrations of DFP, (Top 1 ppm at 6 hrs GC-MS, Bottom 10 ppm at 24 hrs GC-FID)
In Figure 4.5, note that the relative percentages of 2MP, 3MP, and MCP are less with initial concentration of 10 ppm DFP than with 1 ppm DFP, whereas n-Pentane’s percentage is greater under the reverse. Additionally, the lower chart in Figure 4.5 shows the typical relative methane production compared to the other products. Analysis performed on GC-FID permitted observation of methane, unlike the 35 m/z scanning limitation of GC-MS.

**Confirmation of Reaction Products**

In order to confirm the initially observed reaction products and potentially detect the presence of additional compounds, specifically those of lower molecular weight, the use of flame ionization detection (FID) was applied to further sample analysis. This method would also provide for detection of any compounds that may exist below that of the detection limit previously set for the mass spectrometer, 35 m/z. In particular, the formation of methane, ethane, and propane were sought out first to possibly explain the observance of hexane and its isomers. If indeed some sort of carbon chain rearrangement were taking place, either by methyl addition to pentane or chain breaking into two and three member chains possibly followed by alkyl addition, the six member carbon chains were being formed in some manner.

All GC-FID samples were analyzed on a Restek Q-PLOT column under the GC method previously described in Chapter 2: “Analytical Instrumentation”. Standards for the gases methane and propane were obtained from Scott Specialty gases and commercially provided as 10% of the standard gas with helium as balance. Sample identification of each gas was determined with calibration gas standards using 1.0 μl syringe injections of known gases to
identify retention times. Sample injections were compared to the standards for sample peak elution identification. At a minimum, standards were run a series of five times to ensure correct identification of sample peak retention times. Background room air samples were also run to ensure no ambient gases present were interfering with analysis. Additionally, the previous practice of developing DFP stock dilutions with ethanol was replaced with isopropanol as the diluent provided better peak separation from the reaction product pentane. Analysis with FID confirmed the presence of all previously identified reaction products by GC-MS with the addition of methane. The chromatogram in Figure 4.6 shows all seven hydrocarbon reaction products over 24 hours and provides a sense of the relative concentration in comparison to each other. Also present in the chromatogram is the isopropanol peak from the original stock dilution of DFP.

Figure 4.6: Chromatogram of the Reaction Products of DFP (10 ppm) Degradation in Aqueous w/IPA, Analysis by GC-FID (Q-PLOT Column)
To better elucidate the relative percentages between reaction products, a comparison of reaction time and peak area are provided in Figure 4.7. This graph illustrates reaction product data for a set of 12 hour time period trials versus three different sets of 24 hour reaction times trials with all other variables being held constant. This contrast provides insight into potential reaction mechanisms and reaction product associations that may not have been previously evident.

It can be observed from the chart that in the three different sets of 24 hour reaction trials, propane production was only significant enough to be evidenced in one of them. Also, in that set of trials, the hexane isomers of 2MP, 3MP and n-hexane appear to decrease in production as propane is produced in greater amounts. The reaction products of n-pentane and MCP appear to not be affected by relationship with propane. The association between these products is speculated to be a matter of carbon balance, or where one reaction product is forming in greater amounts, others must compensate by production decreases.

![Figure 4.7: Comparison of Reaction Product Formation for Different Reaction Times, Analyzed by GC-FID](image-url)
Another observation provided in Figure 4.7 relates to the production of methane. Since production of methane was not observed previously, it can now be seen in relation to the other reaction products and a curious trend emerges. It was noted that methane production stays rather constant over time while all other reaction compounds tended to increase. It can be speculated again that a balance must be maintained across reaction product formation. Also, the methane production may indeed increase over time but additional formation is being consumed in the production of other reaction products. The explanation for these observed trends is not completely understood, but further elucidation on reaction mechanisms and molecular relationships are discussed in Chapter 5.

**Balanced Equations for the Reaction**

The overall reaction for the reductive de fluorination of decafluoropentane to its various hydrocarbon reaction products and lone byproduct is offered in Figure 4.8. In attempt to provide

\[
\text{C}_5\text{H}_2\text{F}_{10} + \text{H}_2 \xrightarrow{\text{Mg(Pd/C) aq}} \text{C}_x\text{H}_y + \text{HF}
\]

Figure 4.8: Overall Reaction Equation for the Reductive Defluorination of DFP
an overall balanced equation for the reaction, difficulty is encountered in producing a clearly balanced hydrocarbon product since more than one reaction is occurring and the reactions themselves are complex. In order to provide some sense of what is essentially occurring within the reaction media, the following balanced equations for each individual reaction product are provided in Figure 4.9. Note that the “hexane(s)” refer to the three isomers of: n-hexane, 2-methylpentane and 3-methylpentane. These reactions will be discussed in detail in Chapter 5 to reveal the mechanism responsible for the observed reaction product distributions mentioned previously.

<table>
<thead>
<tr>
<th>Reaction Product</th>
<th>Balanced Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane:</td>
<td>( \text{C}_5\text{H}<em>2\text{F}</em>{10} + 14\text{H}_2 \rightarrow 5\text{CH}_4 + 10\text{HF} )</td>
</tr>
<tr>
<td>Propane:</td>
<td>( 3\text{C}_5\text{H}<em>2\text{F}</em>{10} + 32\text{H}_2 \rightarrow 5\text{C}_3\text{H}_8 + 30\text{HF} )</td>
</tr>
<tr>
<td>Pentane:</td>
<td>( \text{C}_5\text{H}<em>2\text{F}</em>{10} + 10\text{H}_2 \rightarrow \text{C}<em>6\text{H}</em>{12} + 10\text{HF} )</td>
</tr>
<tr>
<td>Hexane(s):</td>
<td>( 6\text{C}_5\text{H}<em>2\text{F}</em>{10} + 59\text{H}_2 \rightarrow 5\text{C}<em>6\text{H}</em>{14} + 60\text{HF} )</td>
</tr>
<tr>
<td>Methylcylopentane</td>
<td>( 6\text{C}_5\text{H}<em>2\text{F}</em>{10} + 54\text{H}_2 \rightarrow 5\text{C}<em>6\text{H}</em>{12} + 60\text{HF} )</td>
</tr>
</tbody>
</table>

Figure 4.9: Series of Balanced Equations for the Final Reaction Products, Mg(Pd/C) in aqueous should be understood over each reaction arrow.

Carbon Balance

Attempt was made to determine the fate of all atoms in the reaction. As previously mentioned, the reaction is complex and multiple reactions are occurring simultaneously. However, from the reaction data a carbon balance was attempted for the fate of all carbons
throughout the conversion of the fluorocarbon to the various hydrocarbon products. Figure 4.10 provides the relationship between the initial total carbon at the beginning of the reaction and the carbon present as reaction products at the conclusion of a 20 hour reaction time period.

![Figure 4.10: Carbon Balance for the Mg(Pd/C) degradation of DFP, 20 hours reaction time](chart)

The chart in Figure 4.10 provides the remaining “unreacted” DFP, the carbon that was converted to products as “reacted”, and the remaining “unrecovered” carbon from the initial DFP starting material. Almost 80% of the total carbon in the reaction is accounted for. It is possible that some of the unrecovered DFP material may reside within the carbon layer of the bimetal system as adsorbed and unreacted.
Varying the Conditions of the Reaction

Reactant Addition Sequence

The standard sequence employed in all reaction studies for this project was the following: addition of the reaction media volume to the reaction vial containing the weighed metal system followed by addition of DFP to achieve the desired concentration in solution. If any acid activator were also employed, this reagent was added prior to the DFP allowing activation of the metal surface. For this study, the standard method was compared to an alternative procedure to determine if reactant addition sequence provided any notable difference in reaction product formation. The alternative procedure consisted of initially combining the DFP solution and reaction media followed by addition of the metal system to that solution. For this comparison, one set of reaction vials was developed using the standard method and another equal set developed using the alternative method.

Figure 4.11: Reaction Product Formation comparison of the Typical Reactant Addition Sequence vs. an Alternate Addition Sequence
As can be seen from the reaction product formation provided in Figure 4.11, there is only a slight difference in reaction product formation for the selected reaction products. This is believed to be attributable to the condition that no aspect of the reaction can take place until the necessary reactants have been brought together. In other words, the initial hydrodefluorination of DFP cannot begin to occur until adsorption of the hydrofluorocarbon on the catalyst surface provides a pathway for electron donation from the magnesium to the C-F bonds present on the DFP molecule, thus the product yield is almost identical.

Glycerin Effect as a Safety Precaution

Due to the nature of magnesium and its tendency to flash over in an oxidizing atmosphere, there existed a desire to ensure safe operation with use of any “greater than laboratory quantities” in field applications. The use of glycerin has been employed in the past to protect highly reductive metal powders from undesired rapid oxidation and potential injury of personnel. However, a loss of reductive capability was a concern with the application of this safety measure. A study was conducted to determine if the presence of glycerin would negatively impact the bimetals reductive ability on DFP.

A series of vials containing only the Mg(Pd/C) were weighed and set aside before adding any reaction media solvents. A few drops of glycerin were added to the metal powder accompanied by gentle rolling of the vial until the glycerin had completely coated the metal surface. To this mixture was added the typical volume of aqueous solution followed by the
aliquot of DFP to achieve desired concentration. Vials were allowed to stand for 15 minutes following aqueous media addition and a marked decrease in gas evolution was noted. After the addition of DFP, the vials were capped tightly and sealed and placed in the orbital shaker for one week’s time period. As a control, the same reaction mixtures were established in parallel omitting the glycerin addition step and place alongside in the orbital shaker for identical reaction time duration.

In reviewing the results provided of the study provided in Figure 4.12, it can be established that the bimetal samples which received the glycerin coating actually performed better than the bimetal samples that did not receive the glycerin treatment. This is most probably due to the protective layer on the metal provided by the glycerin. As glycerin washed away from the metal surface and allowed the reaction to occur, other metal surface area was protected from reaction with water and hydroxide layer formation. Due to the effect of the glycerin coating, the metal was able to perform more efficiently. It can be concluded that the use of glycerin on the bimetal for safety precaution during field application would only assist in the degradation of the pollutant in groundwater.

Figure 4.12: Comparison of Glycerin Coated Bimetal to Non-coated Bimetal in Reaction Product Formation of the Degradation of DFP by Mg(Pd/C) in Aqueous Solution
Kinetics Study

The degradation of DFP in aqueous solution with Mg(Pd/C) was determined to follow second order reaction rate kinetics. This was somewhat unexpected as all other group studies involving dechlorination reactions employing zero-valent metals and bimetal systems had followed pseudo first order reaction rate equations.\textsuperscript{119,136} Although, this is not completely unexpected as fluorocarbons and chlorocarbons exhibit different properties with respect to their dehalogenation reactions.\textsuperscript{144} Specifically, with respect to their bonding with carbon, fluorine being much more electron dense due to its high electronegativity will not be dehalogenated as easily as chlorine, which has less electron density and requires less energy to activate any chlorine-carbon bonds. A previous discussion in Chapter 2 on the carbon-fluorine bond addressed these concepts in detail.

In order to determine the order for the reaction with respect to DFP degradation a series of reaction vials were established in which reaction time between the bimetal and the fluorocarbon were maintained carefully. Employing the direct inject method of sample introduction to the GC-MS due to the reaction occurring primarily within the first 18-20 hours, this technique was necessary to ensure analysis within the reaction time window. To carry out injections, 1.0 µl samples were pulled from reactions vials by gastight syringe at intervals of 2, 4 and 6 hours time and injected onto the column. It was not desirable to pull samples too close to the reactions end time, as samples pulled during the peak of the reaction would provide the best results for reaction order determination. Additionally, control vials were established with known DFP concentrations in aqueous media and DFP standards were developed at concentration intervals of: 0.1, 1.0, 3.0, 5.0, 7.0, and 10.0 ppm for calibration curve determination. Data
obtained from the analysis were calculated for zeroth, first, and second order reaction degradation plots with respect to DFP. These plots can be seen in Figures: 4.13, 4.14, and 4.15. The best reaction order fit for the degradation data was determined to be second order reaction kinetics.

Figure 4.13: Zeroth Order Degradation Plot of DFP with Mg(Pd/C)

Figure 4.14: First Order Degradation Plot of DFP with Mg(Pd/C)
Figure 4.15: Second Order Degradation Plot of DFP with Mg(Pd/C)

The reaction obeys second order rate kinetics as the degradation of DFP progresses throughout the reaction. However, the rate also decreases as the reaction proceeds and DFP degradation begins to stabilize until no further reaction is occurring. This occurs because of the major steps of the reaction that are associated with the degradation of DFP. Initially DFP must adsorb onto the catalyst surface. Once adsorbed, defluorination can begin to occur followed by hydrogenation of the molecule. Once this step is complete, desorption occurs in the form of a hydrocarbon product and another DFP molecule can then adsorb to the same catalyst site and the cycle repeats. Therefore, the two major steps in the reaction obeying second order kinetics are either adsorption onto the catalyst surface followed by hydrodefluorination or the defluorination step itself then followed by the action of hydrogenation. In either case, the defluorination phase is most probably the rate determining step in the reaction and this has been supported in the literature for various dehalogenation reactions of haloalkanes. The study determined that the rate limiting step in dehalogenation reactions was the actual liberation of the halogen ion from the
parent molecule.\textsuperscript{145} This concept is further supported by work achieved by Curtis et al., where catalyst surface adsorption and electron transfer to the halogen atom were necessary before ionic conversion producing the halo leaving group was even possible.\textsuperscript{146}

In addition to the defluorination step, one other possible rate effect influencing the reaction could be the carbon adsorption of the fluorocarbon. In other bimetallic systems containing the moiety carbon, adsorption of the organohalide seemed to produce an increased rate effect by getting or gathering the pollutant.\textsuperscript{147} This may not hold true with the subject bimetal system of this study. The initial interaction between DFP and the catalytic reductive system would suggest favoring adsorption to the catalyst surface over adsorption by the carbon layer. The electronic attraction between the catalytic palladium sites and the fluorines of DFP would be stronger than the adsorptive capabilities of carbon for the organic compound. However, it should be mentioned that it is possible that the carbon layer may be contributing to the dehalogenation process by enhancing the interface between the metal system and fluorocarbon molecule. Since DFP is a DNAPL and its solvency in aqueous solutions is almost non-existent, primarily due to the hydrogen bonding property of water, carbon adsorption should enhance the interaction between the bimetal and the fluorocarbon, and thus can only be a benefit in DFP’s degradation.
CHAPTER 5: DISCUSSION

The Reaction Mechanism

The reaction mechanism for the reductive dehalogenation of DFP by Mg(Pd/C) in aqueous solution proceeds through multiple reaction pathways and is complex with respect to several molecular interactions that occur during the course of the reaction. The complexity of hydrodehalogenation reactions has been noted previously. Hagh and Allen, consider the pioneers of hydrodehalogenation reactions, encountered this in the early 1990’s. They proposed reaction pathways typical of the hydrodechlorination reactions of vinyl chloride and epichlorohydrin employing fuel hydroprocessing catalysts such as cobalt-molybdenum, nickel-molybdenum, and platinum and palladium in addressing wastes produced from manufacturing. They noticed that these reaction pathways were complicated even for the dechlorination of simple molecules.

Degradation of the organohalide DFP progresses through several complex stages ultimately yielding the seven hydrocarbon reaction products. These stages are as follows: hydrodefluorination to olefin formation, metathesis to further olefins, and lastly hydrogenation of olefins to alkanes. Each one of these mechanisms will be taken in-turn and discussed.
Hydrodefluorination of DFP

As molecular movement of the decafluoropentane molecule occurs within the aqueous media of the reaction vessel, association begins to occur with the reductive bimetallic catalyst surface ultimately leading to adsorption. Witt et al. noted that adsorption of fluorocarbons on metals is by direct attraction between the fluorine atoms and the metal surface.\textsuperscript{84} Once adsorbed to the active palladium site, the carbon-fluorine bonds of the DFP molecule become susceptible to the aforementioned bond weakness, electron donation to their lowest unoccupied molecular orbital’s (LUMO).\textsuperscript{58} Direct dehalogenation of DFP at the bimetallic surface begins with electron donation by highly reductive zero-valent magnesium through the Pd/C construct directly to the C-F bond sigma antibonding orbital.\textsuperscript{126} At that point, the fluorine atom accepts the electron into its outer shell and initial defluorination begins to occur in the form a liberated fluoride ion into the aqueous solution. Concurrently, diatomic hydrogen generated from the reduction of water by zero-valent magnesium, adsorbs to the catalyst surface whereby homolytic cleavage occurs forming the necessary hydrogen radicals for hydrogenation of the defluorinated parent molecule. Once activation of the carbon-fluorine bond is complete and fluoride ion liberation has occurred, the remaining carbon atom with its lone electron is able to accept a hydrogen radical forming the carbon-hydrogen bond thereby completing the hydrogenation step to the alkane. It is unclear if defluorination takes place sequentially along the DFP carbon backbone or at random along the chain, but is suspected that the reaction initiates with the only two carbon-hydrogen bonds present on the molecule. These two chiral sites exhibit the weakest carbon-fluorine bonds present and likeliest points of initial attack, remembering that the greater the number of fluorine atoms bonded to the carbon the shorter and stronger the carbon-fluorine bonds. It could even be
suggested that the central carbon is favored over the adjacent partially hydrogenated carbon since it is known that the inductive effects of fluorines attached to neighboring carbons influence the bond distance and thus bond strength of neighboring atoms. The central DFP carbon shares bonds only with neighbors CF$_2$ and CHF, whereas the adjacent carbon shares bonds with CFH and CF$_3$ making the central carbon the likelier candidate for initial defluorination. Therefore, it is proposed that hydrodefluorination initiates with the central CFH carbon atom and continues along the DFP molecule with each carbon-fluorine bond becoming weaker with subsequent hydrogenation on adjacent carbons until finally the corresponding saturated hydrocarbon analogue of DFP is formed, i.e., pentane. However, it is conversely proposed that while adsorption of the parent compound remains, an alternate step occurs instead resulting in the formation of the olefin pentene. Although this was never directly observed, olefin formation from dehalogenation reactions has been noted in the literature. In one case, bromide ions were liberated from the starting material from electron donation to their carbon-bromine bonds in their lowest sigma antibonding orbital’s and olefin formation always followed. Additionally, in the use of zero-valent zinc in the reductive dehalogenation of trichloropropane conversion resulted in the formation of propene. Further, in the synthesis of the DFP molecule, the final step in the process is the cis hydrogenation across the double bond of decafluoro-2-pentene. It is understood that the reverse reaction of defluorination would result in double bond formation in the same location on the molecule. So, it is assumed that following defluorination, and subsequent hydrogenation, these reactions shall lead to formation of the olefin and not the saturated analogue. Further, the formation of olefins on the catalyst surface establishes the criteria required for the aforementioned mechanistic reaction known as metathesis.
In Figure 5.1 below, the various stages of the reaction are depicted. At the top of the diagram, Step 1 we see hydrodefluorination at the catalyst surface of DFP to the alkane generating free fluoride ion in to the aqueous solution. Step 2 shows the evolution of hydrogen gas from water on the zero-valent magnesium surface and subsequent hydrogen gas adsorption and generation of the H* radical. In Step 3, we notice adsorption of DFP to the catalyst surface again but this time the olefin is produced and stays adsorbed, however, fluoride ions are still liberated. Step 4 shows the set-up for the metathesis reaction with two pentene molecules still adsorbed to the catalyst surface. It should be noted that these reactions are occurring simultaneously and the steps do not necessarily reflect a reaction sequence.

Figure 5.1: Diagram of the Overall Reaction Mechanisms (Note: Numbered Steps are not sequential.)
Figure 5.2 provides the hydrodefluorination reaction for DFP to the five carbon olefin and fluoride ion to aqueous solution. This is shown for overall clarification of the initial reaction as well as establishes the first step in the next set of reaction mechanisms to be discussed.

![Figure 5.2: Hydrodefluorination Reaction (Olefin Formation)](image)

The Metathesis Reaction

The “olefin metathesis” reaction, originally conducted at the Goodyear Tire and Rubber Company in the late 1960’s, provides the most likely mechanism responsible for the observed formation of the hexane isomer reaction products from a starting material with one less carbon in the chain, pentane.\textsuperscript{153} Essentially, two pentene molecules align on the catalyst surface to allow electron interaction and delocalization across the double bonds giving rise to the formation of the “quasicyclobutane” intermediate; this step is known as disproportionation. Once rearrangement has occurred, the resulting redistribution step allows for the formation of both butene and hexene. In this study, the completely saturated alkane hexane was observed, however formation
of butane was not but instead propane and methane were the resulting reaction products. It is assumed that the corresponding olefins are indeed forming during metathesis, not truly “observed” but upon complete hydrogenation and catalytic desorption, the alkane analogues emerge. The reactions provided below should be understood as occurring during catalyst adsorption, see Figures 5.3 and 5.4.

![Chemical reaction diagram](image)

**Figure 5.3:** Classical Metathesis Reaction (Showing Carbon addition)

![Chemical reaction diagram](image)

**Figure 5.4:** Net Metathesis Reaction for this Study (“Observed”, as saturated forms)

Propane and Methane

One possible explanation for the observed formation of propane and methane from pentene metathesis may lie with the reaction known as “olefin dismutation”. It has been reported
in the literature that during butene metathesis reactions, the formation of the “quasicylobutane” intermediate is once again suggested as the reaction route in which butene undergoes olefin dismutation to both lower and higher carbon number reaction products.\textsuperscript{154} The formation of both propene and ethene has been observed employing either cobalt or molybdenum catalysts on Al\textsubscript{2}O\textsubscript{3} support, yet methane formation was not confirmed. These reactions require the formation of mixed butene isomers as reactants for the various observed end products. In the metathesis reaction studies by Bradshaw et al., it was noted that the quasicylobutane intermediate formed from 1-butene metathesis would yield hydrocarbons of higher and lower molecular weight. It is not known if the formation of butene isomers proceeds entirely from the pentene metathesis reaction in this study. However, due to the nature of adsorption onto the catalyst surface of the olefins it is possible that electron migration might occur during adsorption thereby forming the mixed isomers. This type of migration has been previously observed on catalytic palladium.\textsuperscript{155} Note that this reaction also results in the formation of the five and six carbon member chain olefins as well, further support for formation of the observed reaction products. The reactions for the study are provided in Figure 5.5.

Figure 5.5: Olefin Dismutation Reactions, as reported by Bradshaw et al.
In Figure 5.5, it is noted that ethene formation is also observed in the reaction. However this may provide explanation for the observed formation of methane in the subject reaction of this study. Methane formation from ethene, with hydrogen in abundance, is quite possible under similar conditions and has been reported by Kemball et al., in the literature, see Figure 5.6. Their study on ethene decomposition in the presence of hydrogen employing nickel catalysts resulted in high conversion rates to methane. It was also noted that any carbon formed during the reaction was further converted to methane by the presence of excess hydrogen, which would support observations in this study as well as hydrogen is in abundance due to magnesium’s reaction with water.\textsuperscript{156}

\begin{center}
\begin{tabular}{c c c}
1. & CH\textsubscript{2}=CH\textsubscript{2} & Ni (Kieslguhr) \\
& & CH\textsubscript{4} + C \\
2. & C + 2H\textsubscript{2} & Ni (Kieslguhr) \\
& & CH\textsubscript{4} \\
\end{tabular}
\end{center}

Figure 5.6: Methane Formation Reactions, as reported by Kemball et al.

**Hydrogenation of Olefins**

Each of the initial olefin reaction products: propene, pentene, and hexene undergo hydrogenation to their corresponding alkanes. Transition metal catalyst on supports are well-known as a common hydrogenation catalyst of alkenes to alkanes.\textsuperscript{85} Figure 5.7 provides the proposed reactions to observed end products for the study.
Isomers of Hexane and Methylcyclopentane

The remaining reaction products: 2-methylpentane, 3-methylpentane and methylcyclopentane, it is proposed are formed by alkyl addition and ring closure reactions respectively, the former two from pentene and the latter from hexene. While these reactions are not completely unexpected, the observed formation of the branched isomers of hexane may lie with the effect of dual adsorption of both methane and the olefin onto the catalyst surface. In a study by Koerts et al., silica supported ruthenium and cobalt catalysts were employed to conduct homologization of low molecular weight compounds, including olefins to generate branched chain hydrocarbons; methyl addition to a greater carbon chain was demonstrated. Adsorption of methane on the metal catalyst surface to yield the methyl radical has been observed.
previously. In Figure 5.8, we see the proposed alkyl addition across the olefin double bond to yield the two reaction products.

![Figure 5.8: Alkyl Group Addition](image)

In regards to the formation of methylcyclopentane, this too has been reported and is a common rearrangement. As reported by Burch et al., n-hexene over platinum-tin and platinum-alumina was easily converted to methylcyclopentane. Applying this synthesis to the DFP study, it is proposed that ring closure reaction occurs by the same method, the mechanism is essentially identical, Figure 5.9.

![Figure 5.9: Ring Closure to Cycloalkane](image)
Reaction Pathway Summary

In an attempt to provide an overall summarization of the various reaction mechanism and their corresponding end products, the following is offered. Essentially, once the olefin pentene is formed, three reaction routes proceed, they are the following: hydrogenation to the alkane, methyl group addition to both 2- and 3-methylpentane and metathesis to initially hexene, propene and methane with ultimate hydrogenation to hexane and propane; Figure 5.10. Additionally, as seen in Figure 5.11, once hexene forms, two outcomes occur; direct hydrogenation to hexane and ring closure of the olefin to methylcyclopentane. A simplification of the synthesis of methane and propane is provided in Figure 5.12. In the figure, it can be seen that methane is generated from both the decomposition of ethene and hydrogenation of carbon in the presence of a catalyst and propane is an end product of the butene metathesis reaction.

Figure 5.10: Simplification of the reaction pathways of Pentene.
Figure 5.11: Simplification of the reaction pathways of Hexene.

Figure 5.12: Simplification of Methane and Propane formation.
Observations on Pentane and Hexane Production

As was stated previously, pentane production has been observed to vary with the initial concentration of DFP. Specifically, higher introductory concentrations of DFP lead to more pentane production than with lesser amounts. Also, as more pentane occurs less of the hexane isomers of 2MP, 3MP, MCP are detected. Hexane production itself stays relatively constant during these changes but then hexane is produced by more than one reaction pathway, i.e., both pentene and butene metathesis. One possible explanation of this is that pentane formation takes only one DFP molecule to accomplish its formation, not so in the case of the metathesis driven hexane isomers where two molecules in proximity must occur. However, with increased amounts of DFP, both scenarios may be temporarily favored. The greater amount of DFP possibly provides for both an increase in lone molecules for pentane formation and paired molecules for hexane formation.

However, the mechanism more than likely responsible for less of the hexane isomers, 2MP, 3MP, MCP and greater formation of both pentane and hexane themselves may lie in an equilibrium that occurs at some point during the reaction in favor of pentane and hexane as end products as opposed to their products from alkyl addition and ring closure reactions. In the case of the alkyl addition reaction, it was previously described as requiring methane for completion. Since multiple reactions are occurring throughout the process, it is possible that methane formation decreases at some point preventing the branched isomers. The decrease in methylcyclopentane is not understood but could be related to conditions favoring the continued formation of the straight chain molecule and not the ring compound. Further study would be required to determine these conditions.
Stereochemistry and Mechanism

The stereochemistry of the DFP molecule may provide the driving force for the formation of the reaction products observed from its catalytic reductive dehalogenation. Before providing evidence of this, a brief review of the molecule’s stereochemistry is in order. The DFP molecule exhibits two chiral centers located at its third and fourth carbon where one hydrogen atom and one fluorine atom each is attached. Figure 5.13 provides identification of the chiral centers, per the red arrows, and only fluorine atom attachment is depicted.

These chiral centers provide the molecule with the stereoisomeric property of four different diastereomers. DFP’s four diastereomers can be understood as occurring in two different conformational sets or forms, one set where the hydrogens are located on the same side of the molecule in a syn configuration or “Threo” and another set where the hydrogens are located on opposite sides of the molecule in anti configuration or “Erythro”. Also, each conformation within a set can be further distinguished from one another by the right and left rotational properties of diastereomers. Therefore, DFP exhibits the following four sets of
diastereomers and is elucidated in Figure 5.14. Note in the figure that for grouping, diastereomers A and D exhibit the threo form and B and C exhibit the erythro form.

![Figure 5.14: The Four Diastereomers of DFP: A (3R,4R), B (3R,4S), C (3S,4R), D (3S,4S)](image)

It is proposed that one of two possibilities is responsible for the observation that more hexane is formed than pentane during the reaction. One is that stereoselectivity occurs during catalyst adsorption as a driving force for olefin formation over that of the completely saturated molecule. Put another way, there exists a diastereoselectivity for the precise stereomolecular adsorption and resultant product formation. For example, a threo diastereomer adsorbs to the catalyst surface and undergoes defluorination of the fluorines opposite their respective hydrogens. Proceeding at either simultaneous or near simultaneous moments, the respective carbon atoms they both shared experience electron delocalization around their centers providing the suitable electronic environment for double bond formation resulting in the olefin, “pentene”, see Figure 5.15. Conversely, adsorption of a erythro diastereomer with opposing hydrogens on the molecule experiencing defluorination would be sterically unfavorable as the remaining bonded hydrogen atoms accompanying delocalization about their carbon centers drive formation of the single bond and subsequent desorption from the catalyst’s surface in the formation of the alkane “pentane”, see Figure 5.16.
In the literature, a study by Bingham et al., revealed electron destabilization occurs in fluorine substituted low molecular weight straight chain hydrocarbons based upon their stereochemistry and related this to both saturated and unsaturated examples. Therefore, any formation of pentane would undergo catalyst desorption and be released into the reaction media while any pentene is retained on the catalyst surface thereby establishing the necessary parameters for the metathesis reaction. This establishes how alkane and alkene formation occur but still not why greater amounts of hexane than pentane are produced. This observation is related to the manufacturer’s formulation of the DFP product.
By examining the compositional formulation for DFP from DuPont, the DFP isomers are reported to be in the ratio of 89% (R’R’/S’S’) to 11% (R’S’/S’R’). This yields the product formulary set of three diastereomers as being greater than the erythro diastereomers. Returning to the previous discussion on stereoisomeric adsorption to the catalyst surface and the resultant product formation, it can be seen that the percentage of stereoisomers leading to the olefin formation, i.e., threo, is greater than that of the alkane producing isomers, erythro. This correlates with the observed reaction product formation of less pentane as compared to hexane and its isomers.

Further evidence of this stereomolecular influenced degradation is provided in the compounds manufacturing process. Although the process used by DuPont was proprietary, others have accomplished the goal and described a process which reflects the same percent composition as that described by DuPont. The manufacturing process of DFP provides insight and an explanation for the reaction product percentages observed by its degradation. Specifically, the final step in the synthesis of the product is described as the “hydrogenation of the fluorinated olefin decafluoro-2-pentene on carbon supported palladium catalyst”. This is critical since it is known that carbon adsorbed olefins undergoing hydrogenation typically do so yielding a product that has undergone cis addition and that the greater percentage isomeric product will be observed with the two hydrogens on both sides of the molecule. This will not always be the case of course and thus the minor percentage isomer is also observed.

However, the other possible explanation for observing more hexane than pentane in the reaction is based upon the proximity of catalytically adsorbed olefins during hydrodefluorination. In this scenario, it is believed that all DFP molecules undergo the same hydrodefluorination process always yielding the olefin as reaction product. The difference between hexane or
pentane formation lies in the proximity of olefin molecules to one other on the catalyst’s surface. If the olefins are proximal to one another, metathesis may then occur until final desorption to provide the hexane isomers. If adsorbed olefins are lone or not proximal, then hydrogenation proceeds to complete saturation followed by surface desorption providing the product pentane. Figure 5.17 elucidates these two proposed “proximity mechanisms” for olefin metathesis and olefin hydrogenation.

![Diagram of Proximity Mechanism](image)

Figure 5.17: Illustration of the “Proximity Mechanism” for Olefin Metathesis and Olefin Hydrogenation

Additionally, the reason for the observation of greater amounts of hexane than pentane under this scenario is speculated to be, that the overall presence of olefins on the catalyst surface is always prevalent enough to typically favor the occurrence of metathesis. This is not in direct contradiction to the previous statements about the effects observed for hexane and pentane production trends with respect to increases or decreases in initial DFP concentration. Those scenarios were based upon more or less DFP being present for establishing likely reaction pathways. In this case, it is merely being stated that on the catalyst surface, regardless of DFP concentration, enough olefins are present to favor the metathesis reaction than not. Also of note,
is that the olefin product is never observed. The most likely reason for this observation is that the olefin stays adsorbed to the catalyst surface until the process of hydrogenation is complete only then allowing desorption of the totally saturated molecule.

**Biodegradation of Reaction Products**

The reaction products formed from the hydrodefluorination of DFP are all hydrocarbons. It is understood that naturally occurring bacteriological action in soils and groundwater will degrade hydrocarbon compounds to their ultimate environmental fate of glycolipids which are in-turn eaten by other organisms.\(^{161}\) In particularly, microbial action is well-known in the destruction of hydrocarbons with n-alkanes being the most susceptible to biodegradative action, stated in a review of biodegradation by Leahy et al.\(^ {162}\) Also, as stated in a study by McCarty et al., that established hydrocarbon end products formed following the successful dehalogenation reaction are of no harm to the environment.\(^ {163}\) Thus, the described methods in this study will leave the environment clean and free from the subject halogenated pollutant concern.

**Proposed Methods of Field Deployment**

This section is considered future work for the study and would need to be evaluated under field conditions. In order to achieve a successful interaction between the bimetal system technology and the groundwater pollutant one of two approaches is most likely, either an ex situ or in situ method.
Pump and Treat Technology

Although not the optimal choice, due to the costs associated with the degree of on-site equipment and maintenance required for this method, it is still a viable option for DNAPL removal and degradation. This could be achieved through the physical pumping of DNAPL contaminated groundwater to a catalytic reductive reactor containing the bimetal-catalyst system for dehalogenation treatment and ultimate hydrogenation of DFP to hydrocarbons. The resultant reaction products could then either be managed through product recovery and possible reuse or disposed of as hydrocarbons at a much lesser cost than the original fluorocarbon.

Aquifer Direct Injection

This method could be achieved by delivery of the catalytic reductant metal system via an oil-water-surfactant emulsion transport injected directly into the pollutant source zone plume within the aquifer. As is performed with other direct delivery methods, the use of injection wells and sampling well monitoring system would be employed to determine progress towards DFP degradation. In this method, the metal system is contained within the emulsion itself, an oil emulsion present within an aqueous volume in which the organic pollutant is attracted inside the emulsion micelles providing the required interaction between pollutant and catalytic bimetallic system necessary for degradation. The resultant hydrocarbon reaction products, along with the oil emulsion itself, would then undergo biological breakdown by microbial action already present within the aquifer system.
Future Work

The Bimetallic System

The successful bimetallic system of this research, Mg/(Pd/C) consisting of both a reductant metal component and a supported transition metal catalyst may provide the foundation for combinations of other successful bimetallic systems as applied to DFP or other alkyl fluoride pollutant remediation. Further investigation should be conducted into other metals serving in the reductant and catalyst roles with the goal of attaining a more economical system than with that of palladium. Additionally, an investigation should be conducted into the precise amount of palladium that is required for the reaction to occur. The mechanical alloying process causes a certain amount of palladium to be lost during milling. Therefore the reaction actually requires less than originally provided for the formation of the bimetal. Any reductions in cost of the technology would result in the benefit to potential users in future applications.

Additional Pollutants

Application of the developed technology system should be investigated on other halogenated organic pollutants such as other recalcitrant hydrofluorocarbons and potentially fully fluorinated analogues such as perfluorocarbons. Additionally, other fluorinated organic compounds known to be of pollutant concern such as the newly emerged fluoroethers would serve as potential future candidates as well.
Pollutant Polishing System

The invention also may yield a more efficient and environmentally responsible approach to pollutant polishing than current applications. The combination of this technique with existing methods that only achieve clean-up to a certain point could be enhanced by this technology as a polishing step and final removal of pollutants from either soils or groundwater. This technology would be of particular interest to multiple halogenated compound pollutant sites where all other halogenated materials have been successfully remediated and only the fluorinated compounds remain.
A new technology has been developed in the field of Environmental Chemistry for addressing recalcitrant fluorinated organic compounds as pollutants in groundwater. Specifically, this study has shown that the compound decafluoropentane successfully undergoes hydrodefluorination in aqueous solution via catalytic reductive dehalogenation by Mg(Pd/C) to the hydrocarbon reaction products of methane, propane, n-pentane, n-hexane, 2-methylpentane, 3-methylpentane and methylcyclopentane. This reaction occurs at temperatures which are reflective of those encountered in Floridian aquifer systems, typically 22 °C. The reaction does not generate any partially fluorinated byproducts nor produce any other toxic materials. This new development permits a method of safely degrading fluorinated compounds in groundwater in a manner consistent with environmental sustainability.

In respect to the destruction of DFP, 100% conversion was found to occur with 1 ppm initial DFP starting material in about 20-24 hours using the described amounts of the bimetal. Higher concentrations such as 20 ppm DFP only achieve about 73% conversion in the same time period thus completing the reaction. However, the concentration levels of the pollutant in groundwater at NASA facilities was at its worst case estimated to be about 5 ppm and typically found to be less than 1 ppm, thus the intended treatment should be adequate to achieve complete destruction of the pollutant. Locations with higher concentrations of DFP in groundwater systems would require additional study to optimize the technology for application in those areas. Since the bimetallic system developed for this technology incorporates palladium into its matrix, potential cost reductions could be realized through alternate catalyst studies. Although, the amount of palladium required for successful degradation during this study was determined to be
less than 1%, it could very well be far less. Additional determinations for the optimal palladium requirement should be explored further.

It was also determined that the mechanical alloying process of ball milling provided the necessary morphology required for the pollutant to bimetal interaction to ensure successful degradation. This is an essential requirement for the metals to be alloyed together so as to be in constant contact and be able to provide the combinative effect of electron donation from magnesium and catalytic bonding from palladium for reductive dehalogenation to occur; the reaction would not be successful if the metals were simply a heterogeneous mixture. Aqueous solution was determined to be the optimal reaction media for the reaction. Minimal precipitate formation was noted when compared with others, particularly alcohols. Also, it was noted that degradation occurs to the same extent even in the presence of potentially interfering ionic species. The presence of alcohols was determined to not play any role in the reaction, in particularly with respect to compositional elements in product formation. Alteration of the reaction media in both pH and temperature were determined to neither contribute nor impede the reaction and neither condition provided concern for any undesirable environmental conditions. The employ of glycerin as a bimetal protective coating and safety precaution for field applications did not hinder the bimetals degradative capability yet actually enhanced it. The order of reactant addition was determined to not adversely impact the degradative process demonstrating that the reaction occurs by either route ensuring success for random encounters of the bimetal and pollutant in groundwaters.

It was proposed that the organic reaction mechanisms by which all saturated hydrocarbon products were generated was the hydrodefluorination of DFP by reductive dehalogenation to the five carbon chain olefin followed by both olefin metathesis and olefin hydrogenation to the seven
distinct reaction products. Further, reaction product concentrations were proposed to be reflective of the specific stereochemistry of the DFP molecule reflecting the adsorptive bonding character of diastereomers to the catalyst surface as the driving mechanism. Additionally, molecular proximity of adsorbed olefins was also proposed for the observed differences in concentrations between the major reaction products.

In regards to the bimetallic system, future studies should be conducted to optimize the catalyst metal in either amount employed or in alternative choice with respect to reducing associated costs of precious metals.

The hydrofluorocarbon degradative technology should be successful in the intended application environment if a suitable form of bimetal containment and delivery method accompanies deployment to the groundwater system. Further study involving proven methods of delivery from other bimetal systems or entirely new methods should be examined. The technology should also be considered for application towards other fluorinated organic pollutants in aqueous media.

At the present time, hydrofluorocarbons are quite possibly at their outset of becoming one of the next major noteworthy pollutants. This could potentially bring high regulatory focus in their regard on issues regarding public safety and health and potential impact to the environment. Much like the pollutants of the past: mercury, lead, asbestos, DDT, PCBs, dioxins, CFCs and others, which were all considered to be harmless at one point in time, now famous for either environmental toxicity or public health concerns; the time for hydrofluorocarbons may now be upon us. Recent studies with possible links to autism and reproductive disorders accompanied by the already proven threat to climate change through global warming make them a high priority for the world health and environmental communities to address. Difficult to remediate
due to their molecular stability lending to their recalcitrance in the environment, makes them arduous to deal with in any media. Yet, they remain legal compounds for manufacture in the United States and around the world and therefore accidental releases and exposures will continue to occur.

The technological developments of this study provide one small step in the direction of opportunity in beginning to address these pollutants and negate their effects in both potential impact to public health and increasing environmental consequences.
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