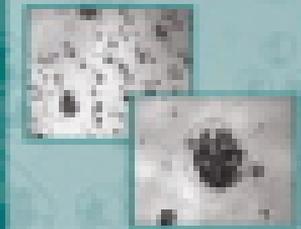


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## Environmental Applications of Nanoscale and Microscale Reactive Metal Particles



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# **Environmental Applications of Nanoscale and Microscale Reactive Metal Particles**



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# **Environmental Applications of Nanoscale and Microscale Reactive Metal Particles**

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# Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

## ACS Books Department

# Preface

In the past decade, research focusing on the use of nano- and micro- scale particles for environmental application has been at the forefront of environmental science and engineering. The enhanced reactivity of these materials has yielded a scientific renaissance leading to research on systems that had previously proven nearly impossible to degrade safely. Materials that may have lacked reactivity at the macro-size have become useful remediation tools as nanoscale particles. Nobel metals that would have never been used due to economics are now becoming feasible alternatives for field applications because of the low mass required when incorporated with nanoparticle base metals. In addition, the complexities of matrices that are innate to environmental remediation make these small particles of particular interest for improved emplacement technologies.

The book is divided into three sections that illustrate laboratory and mechanistic studies, field simulation studies, and technology demonstrations and field applications. Laboratory and mechanistic studies include research in degradation mechanisms of compounds ranging from polybrominated di-ethers and polychlorinated biphenyls to energetic compounds such as trinitrotoluene and triacetone triperoxide when exposed to reactive particles. Field simulation topics include bench-scale application to prove viability of technologies before progressing to deployment and finally studies done at the pilot-scale and field application level.

This book provides an international perspective of the current research efforts and recent results of leaders in the science of microscale and nanoscale environmental applications. Authors who have contributed to this book represent six countries from four different continents. The involvement of leading scientists from around the world is indicative of the importance placed on improving the quality of our most valuable natural resources.

This book is composed primarily of topics that were presented at sessions of the symposium organized by Cherie L. Geiger and Kathy Carvalho-Knighton (editors of this volume) under the support of the Division of Industrial and Engineering Chemistry. In addition, several bonus papers have been added to provide a complete overview of the current research.

As such, the book should appeal to chemists and engineers from academia, industry, and government who are involved in fundamental research, methods development and application. Our hope is that this book will provide a wealth of information and serve as an essential resource for a global perspective of the environmental application of nanoscale and microscale reactive particles.

## Acknowledgments

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And most of all, thanks to all of the authors whose exceptional contributions have made this volume so worthwhile.

## Chapter 1

# A Review of Environmental Applications of Nanoscale and Microscale Reactive Metal Particles

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The problem of environmental contamination has seen increased interest in recent years as the full impact of various contaminants on flora, fauna, and human beings is being uncovered. In light of this, a great deal of research has been conducted to develop remediation technologies capable of combating this problem. A large variety of pollutants are currently found in the environment, including organic halides, energetic materials, and heavy metals. One of the most promising avenues of research involves the use of microscale and nanoscale metal particles in the remediation process, due to the vast array of useful properties possessed by these particles. Different metals have been tested for activity against several different classes of environmental pollutants, and a synopsis of the results for many of these tests will be provided in this chapter.

## Introduction

### Traditional Remediation Options

The past century has introduced many technological and scientific advances which at the time appeared to be only beneficial to humanity. Time, along with further advances in instrumentation and analysis techniques, has shown that this has not always been the case. Many of these advances have turned out to have unanticipated and unpredictable consequences, some of which are now only beginning to be addressed. Many chemical compounds created in mankind's past fall into this category.

The scientific community has proposed a variety of methods for the remediation and/or containment of these environmental hazards, with varying degrees of success. Environmental contaminants such as those discussed in this chapter are often subject to stringent legislation which limits the detectable amount in the environment before action must be taken to reduce that level (or limit access). Therefore, a great deal of time has been invested in developing techniques to remediate such contaminated zones. Depending on the type of contamination present (halogenated organic compounds, heavy metals, energetic materials) and where that contamination is located (sediments/soil, groundwater, atmospheric, enclosed systems), different remediation options exist. Techniques currently in use or under investigation include incineration, dredging, landfilling, soil washing/extraction, microbial degradation, capping, monitored natural recovery (MNR), chemical reduction, chemical oxidation, photolytic/radiolytic degradation, and others. However, many of these techniques are hampered by specific limitations or drawbacks that make them impractical for large-scale field use. Some of the more commonly utilized options will now be discussed.

### *Halogenated Organic Compounds (HOCs)*

One of the most commonly used remediation technologies at present is the incineration of contaminated wastes. This technology can be applied to most any type of contamination or hazardous waste, as long as the waste has been isolated (e.g. extracted from soils or sediments via solvent washing). This is an *ex situ* technique which thermally dechlorinates the contaminant into harmless products. However, incomplete combustion is a serious concern with this option. This can lead to the production of even more toxic byproducts, such as the production of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDFs), commonly referred to as dioxins, from the low-temperature

combustion of polychlorinated biphenyls (PCBs) (1-3). Incomplete combustion occurs when incineration is carried out at low temperatures, which is why the incineration of PCBs must be performed at temperatures of 1200°C or greater. This calls for a large increase in fuel consumption, which leads to increased costs for this remediation technique (3). An additional concern associated with incineration (and all other off-site *ex situ* processes) is the transport of the hazardous materials to the incineration site (4). Costs for this technique have been on the rise due to the limited facilities capable of performing high-temperature incineration (5).

A more recent development in the remediation of chlorinated wastes is degradation using microbial agents. Two distinct types of microbial degradation exist, utilizing either anaerobic or aerobic microbes to reductively dechlorinate or oxidize the halogenated compounds, respectively. Aerobic degradation causes the oxidation of waste through a series of intermediates, ultimately destroying the contaminant. Unfortunately, research has shown that aerobic microorganisms are not capable of degrading highly chlorinated compounds (6) and will preferentially degrade low-chlorinated congeners, which are not those primarily used in the mixtures found as environmental contaminants. In addition, aerobic micro-organisms are only found in the top few millimeters of soils and sediments, limiting their effectiveness as an *in situ* remediation option. Anaerobic microbes, on the other hand, degrade HOCs through reductive dechlorination, carried out via the removal of chlorine atoms as halogen ions. In the case of PCBs, a larger fraction of more highly chlorinated congeners can thus be degraded than when utilizing aerobic microbes, though this is normally limited to the dechlorination of *meta*- and *para*-substituted congeners. *Ortho*-substituted chlorines are much more resistant to this type of attack, which can lead to incomplete degradation of the contaminants (2, 7). Anaerobic treatment followed by aerobic treatment has been used successfully in the degradation of PCE and benzene, where neither treatment alone was capable of degrading both contaminants (6).

Sediment contamination, though prevalent in the United States, can be difficult to deal with because of the difficulty involved in accessing the sites of pollution. Several options exist, although the most commonly used is dredging of the contaminated sediments, followed by a second *ex situ* step such as landfilling. Dredging has a major drawback in that disturbing the contaminated sediments can lead to re-release of the contaminants into the surrounding water supply. This allows for the mobilization of the hazardous materials, and can spread the problem into surrounding areas that were previously free of contaminants. Some contaminants, such as PCBs, can also volatilize and enter the atmosphere while the dredged sediment is being de-watered (8). Even if the contaminants do not spread to new uncontaminated areas, release into the water system can cause increased contamination of local biota (9, 10). Another

serious limitation to dredging is that it does not eradicate the existing problem; it simply moves it from one location to another (in the case of landfilling) or requires an additional remediation technique (i.e. incineration) to complete the degradation.

Another common technique for remediation of sediments is called “capping”, and is often then followed by monitored natural recovery. Capping refers to the placement of an inert chemical substance above contaminated sediments in order to prevent the pollutants from interacting with or mobilizing into the surrounding water system. As in the case of dredging, this does not act to degrade the wastes themselves; it is a means to immobilize the immediate threat presented by the contaminant. Another problem associated with sediment capping is the possibility of breaches occurring in the “cap”, allowing release of the hazardous materials into the surrounding environment.

Monitored natural recovery (also called monitored natural attenuation, MNA) refers to allowing natural processes to reduce the magnitude and bioavailability of hazardous contamination over time. A variety of biological (biotransformation, biodegradation), chemical (sorption, oxidation, reduction) and physical (volatilization, dispersion, dilution) processes are considered pertinent to MNR. The time frame for MNR is much longer than that of other current remediation options, but it does have the advantage of being more cost-effective than other techniques, since an active *in situ* technology is not utilized. MNR is also less disruptive to the surrounding area, so in this way it is suitable for sensitive environments that might be destroyed by human activity (11). However, one risk is that nature can upset the recovery process in the form of sediment disturbances from phenomena like flooding, hurricanes, or earthquakes.

### *Heavy Metals*

Remediation of heavy metals is generally classified into three categories: containment or capping, *ex situ treatment*, and *in situ* treatment. Containment involves isolating the contaminant and preventing its migration via the application of physical barriers made of steel, cement, bentonite or grout. This method can be employed either *ex situ* or *in situ*; however, commercial availability presently favors *ex situ* usage. Containment following isolation (often dredging) can be performed by means of solidification, which enables the contaminant itself to be trapped within a solid matrix or stabilized; this containment strategy requires chemical reactions to reduce contaminant mobility. Vitrification is another stabilizing method in which electrodes are inserted into the contaminated material, allowing the application of electrical current. Physical and chemical changes that take place during vitrification are

driven by the applied current, although this requires large amounts of energy. As the material cools, the contaminant will be solidified in a glasslike matrix (12).

The *ex situ* methods involve the removal of soil or sediments from the environment and then the use of various treatment options such as soil washing, physical separation, or hydrometallurgical recovery (for highly contaminated soils). *Ex situ* methods for sediments are performed after dredging. Each year, three hundred million cubic yards of sediments are dredged to maintain the navigability of US waterways. Of those, three to twelve million cubic yards are so heavily contaminated that they require special handling and remediation (12). Re-suspension of the offending contaminant into the surrounding water environment during sediment removal is of particular concern with the dredging of sediments for *ex situ* treatment, as it can exacerbate the problem (13). Another complication inherent to sediment remediation is the high level of silt, clay and organic matter present, which can impede effective remediation. Sometimes the problems engendered by remediation can be worse than the initial presence of the contaminant. In these cases, the best option may be leaving the sediment as is and implementing continuous monitoring (14).

Common *in situ* methods for heavy metal remediation include soil flushing, electrokinetic techniques, and phytoremediation. Soil flushing consists of infiltrating the affected soils with extracting solutions. These solutions may contain chemical additives such as organic or inorganic acids, and complexing agents such as ethylenediaminetetraacetic acid, EDTA (15). While not as disruptive as *ex situ* methods like dredging, soil flushing can prove problematic because strict control must be kept over the mobilized contaminants to prevent their migration to other areas. Electrokinetic techniques require the insertion of electrodes and the passage of a low current which promotes the migration of metals and anions to the appropriate electrodes, where they can be removed by electroplating or precipitation (16). Phytoremediation involves certain plant species and their propensity to accumulate metals such as cadmium, copper, lead, nickel and zinc. When cultivated in a contaminated area, these plants can help to extract metals from the surrounding soil and sequester them in their tissues (12, 14).

### *Energetic Materials*

Both *ex situ* and *in situ* techniques have been employed for the remediation of highly energetic materials such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT), to varying degrees of success. *Ex situ* techniques include the use of granulated carbon, anaerobic bioreactors, UV-oxidation reactors, and electrochemical cells. All of these techniques suffer

from high implementation costs stemming from re-injection and pumping, which limits the overall usefulness and applicability of these techniques (17).

## Support for Remediation by Microscale and Nanoscale Metallic Particles

A variety of metals have been investigated for possible use as part of an environmental remediation technology. Some of the earliest research in this vein concentrated on the use of zero-valent metals for the reductive dehalogenation of commonly used industrial solvents and wastes. Early success was seen in the use of granular iron turnings for the remediation of contaminants including chlorinated ethylenes (18), carbon tetrachloride (19, 20), and halogenated aromatics (20). Early applications of this technology included the installation of permeable reactive barriers (PRBs) to reduce contaminants found in groundwater flow (21-23). While PRBs did prove capable of remediating the contaminants found in underground plumes, they were unable to treat the source zone of the contamination (23). This was due to the difference in the inherent natures of the zero-valent iron being used and the contaminant itself. Many of these halogenated groundwater contaminants fell under the classification of dense non-aqueous phase liquids (DNAPLs) (24-26). As such, they had a hydrophobic nature, while the zero-valent iron surface was more hydrophilic. The metal was thus only capable of treating the dissolved phase contaminant, not the liquid DNAPL zone itself, due to the lack of interaction between the metal and the contaminant (25, 27).

In spite of this, metal particles have proven to be effective in the remediation of several important halogenated organics (18-20, 28-33). Additional research has shown that granular zero-valent iron also is capable of reducing and precipitating heavy metals such as hexavalent chromium (34, 35), and degrading nitroaromatics such as nitrobenzene (36), pentaerythritol tetranitrate (37), and nitroglycerin (38).

The initial work using metal particles such as zero-valent iron focused on the macroscale, using easily obtainable and less-costly iron turnings as a basis for the chemical remediation. Since then, work has focused on using smaller particles (from several microns to submicron in diameter) which provide increased reactivity. These small metallic particles possess many inherent advantages in terms of environmental remediation. One of the most obvious is the enhanced reactivity of the particles due to the increase in surface area available for reaction (39-42).

There are three common effects that are known to occur when using microscale and nanoscale particles.

1. Reaction rates are increased when compared to larger particles with smaller surface areas (39, 41).
2. Contaminants that do not react readily with larger particles (such as PCBs and hexachlorobenzene) show enhanced degradation with microscale/nanoscale particles (39, 41).
3. More completely reacted byproducts are formed from contaminants (such as the production of methane rather than chloroform from carbon tetrachloride) than when larger bulk particles are used (40).

While some of these advantages are primarily due to the increased surface area of the smaller micro/nanoscale particles, this is not the only effect that decreased size has on their properties. It is well documented that micro- and nanoscale particles have different properties than those exhibited by bulk media comprised of the same elements. In the range of 1 to 100 nanometers, particles are in an intermediate phase between atomic and bulk states. In this size range, their electronic properties can be quite different than those of bulk metal turnings. This is primarily due to the fact that in the microscale and nanoscale range, both physical and chemical properties mainly rely upon the atoms located at the surface of the particles rather than those deeper in the bulk material. This often leads to a more active metal particle (43).

### **Contaminants of Interest**

Micro/nanoscale particles have been proven to be effective in the remediation of a large number of environmental contaminants. These different compounds can vary widely in physical and chemical characteristics, demonstrating the versatility of these particles for use in remediation efforts. There are three main categories into which these compounds of interest can be broken down: halogenated organics, heavy metals, and energetic materials. Each category of contaminants has its own unique challenges and obstacles to overcome, yet microscale and nanoscale metal particles have been shown to successfully degrade or sequester analytes from each category.

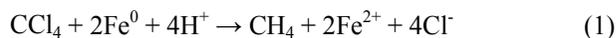
#### *Halogenated Organic Compounds*

The most prevalent types of contaminants discussed in the literature are halogenated organic compounds. Aliphatic chlorinated compounds have been used for a variety of purposes over the years, such as trichloroethylene (TCE) which was used as an industrial solvent with a wide variety of applications including as an extraction solvent, a dry cleaning solvent, and a metal degreaser. Chemicals of these types have been implicated in a variety of health effects such

as liver or kidney damage and spontaneous abortions, and many are considered carcinogenic (44). Aliphatic HOCs which have proven susceptible to remediation using metal particles include carbon tetrachloride (45, 46), chloroform, dichloromethane, chloromethane, bromoform (47), dibromochloromethane, dichlorobromomethane, tetrachloroethene (48), trichloroethene (49-52), *cis*-dichloroethene, *trans*-dichloroethene, 1,1-dichloroethene, vinyl chloride (48), and others (53). Aromatic halogenated compounds pose a more significant challenge, due to the inherent stability afforded by the aromatic nature of these molecules. These include halogenated benzenes (41, 54), halogenated phenols (55), polychlorinated biphenyls (39), polybrominated diphenylethers, and polychlorinated dibenzo-*p*-dioxins (33, 56). Limited success has been reported using single-metal micro and nanoscale particles alone; remediation for these compounds often requires the addition of a catalyst to create a bimetallic particle which is capable of dehalogenating aromatics (57).

The resistance of these compounds to degradation is both logical and ironic. PCBs, for example, were chosen for industrial applications due to the fact they are resistant to both chemical and thermal degradation. Now that their toxicity has been discovered, this recalcitrance has become a serious environmental concern.

The mechanism for degradation of HOCs using zero-valent metal particles is thought to occur primarily through reductive dechlorination. Aliphatic compounds such as carbon tetrachloride are readily capable of accepting electrons which are supplied by the oxidation of the zero-valent metal particles. The commonly accepted stoichiometric equation for the degradation of carbon tetrachloride with zero-valent iron is shown in Equation 1.



There are three proposed mechanisms for how this degradation takes place (58).

1. Reduction of the contaminant at the surface of the zero-valent metal particle.
2. Generation of oxidized form of the metal particle (e.g. ferrous ion) and subsequent reduction of contaminant by the oxidized form.
3. Generation of hydrogen at the surface of the metal particle, followed by reduction of the contaminant by hydrogen.

## Heavy Metals

Heavy metals are a prevalent source of contamination found in the environment, and present several risks to the local biota. Contaminants of these types are capable of bioaccumulation, and therefore present a risk to organisms found higher up the aquatic food chain, including human beings (59). Certain heavy metals have priority status on the Environmental Protection Agency's National Priority (Superfund) List, including cadmium, copper, lead, mercury, nickel and zinc. Exposure to heavy metals (such as lead) can lead to a variety of ill-effects, including but not limited to neurological impairment, organ damage and immune system depression. Contamination of this type is caused by domestic and industrial effluents, storm water runoff, and leaching from minerals. Anthropogenic sources of lead include lead-zinc smelters and the production of ammunition, solder, glass, piping, insecticides, paints, and lead storage batteries (60, 61).

The use of zero-valent metal technologies for the remediation of heavy metals has been explored for several years. Studies have shown that nano-scale and microscale zero-valent metals can reduce or remove heavy metals more efficiently than larger-scale metallic particles or conventional absorptive media. Nanoscale and microscale iron particles have shown success in remediating heavy metal contaminants such as cadmium, lead, silver, nickel, arsenic, and zinc (53, 62). Two primary mechanisms have been documented for the remediation of these contaminants: reduction of the contaminants to a more inoffensive form, or the surface-mediated sorption of the contaminant (53).

An example of a heavy metal which undergoes the first remediation mechanism (reduction) is chromium in the presence of zero-valent iron. Chromium exists in two primary forms in the environment, hexavalent and trivalent. The adverse affects of chromium in the environment primarily depend upon its valence state, due to the difference in solubility that this creates.  $\text{Cr}^{6+}$  is considered the more toxic and immediately dangerous species, as it is water-soluble and capable of transport throughout an ecosystem once it has been released. Conversely,  $\text{Cr}^{3+}$  is considered to be a much less toxic species than  $\text{Cr}^{6+}$  because it so much less soluble and more immobile within the environment. Remediation of chromium contamination is considered successful once reduction from  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  has been achieved. The reaction pathway involves the reduction of dissolved chromate ( $\text{CrO}_4^{2-}$ ) to insoluble  $\text{Cr}^{3+}$  (63). Precipitation then occurs with iron oxide and iron hydroxides, incorporating the contaminant within the surface oxide layer (34). Research has shown this reaction to be pseudo-first-order with respect to the normalized surface area of the zero-valent iron used. Use of nanoscale iron has shown rate constant increases of up to 30 times when compared to degradation utilizing conventional iron filings (64). Similar but less impressive increases have been seen with

microscale iron. Uranium is also removed from water by zero-valent iron via reduction. Uranium(VI) in the form of uranyl ions ( $\text{UO}_2^{2+}$ ) is directly reduced to uranium(IV) in the form of  $\text{UO}_2$ , which is a solid and will precipitate or adsorb to the iron oxides and hydroxides as in the case of chromium (65). Other heavy metal contaminants that are primarily reduced by zero-valent metals include copper, silver, and mercury (53).

Remediation of  $\text{Ni}^{2+}$  has been shown to be controlled by both reduction and surface complexation. Initially, the contaminant is adsorbed to the surface of zero-valent iron primarily as a nickel hydroxide, followed by reduction to a zero-valent form (53). The concentration of the zero-valent form increases until equilibrium is achieved, at which point XPS analysis demonstrates that 50% of the nickel has been reduced to the zero-valent form and remaining 50% exists as surface adsorbed hydroxide. Other metals with a standard reduction potential slightly above that of the zero-valent metal being used, such as lead(II), are also remediated by a combination of reduction and sorption to the surface of the metal particle (53).

### *Energetic Materials*

Nanoscale/microscale metallic particles have recently been used as a remediation technique for the cleanup of energetic materials. Residual energetic materials are often found in sites where the production and use of munitions has occurred over the years, such as military installations. Testing has shown that partial detonation of munitions at these sites has caused the dispersal of these contaminants onto the soil surface, where transport to ground water may then occur (66). Research has demonstrated that several of the more commonly used energetic materials (TNT, RDX, TATP) are susceptible to reductive degradation upon exposure to zero-valent metals such as magnesium and iron (67-69). Other nitrated materials such as nitroglycerin, nitrobenzene, and PETN have also been successfully denitrated by metallic particles (36-38).

## **Specific Metal Particle Applications**

A variety of different metallic particles and compounds have been investigated for use in the remediation of environmental contaminants over the past twenty years. These have included microscale/nanoscale zero-valent metal particles, enhancement via metal catalysts; bimetallic reductive compounds, transition metals, and others. It is difficult to create a completely comprehensive list of all metals used in remediation technologies; however the following is a list of selected metals that have undergone testing for use in environmental

technologies. It is by no means a complete list, nor does it attempt to delineate every documented use of metals in remediation processes.

## Alkaline and Alkali Earth Metals

Alkaline and alkali earth metals have been studied extensively in the scientific community and have been identified as viable electron sources in reductive methods of remediation.

### *Alkaline Metals*

Alkaline metals such as sodium have been documented as capable of acting as electron sources for the reductive dehalogenation of contaminants. A specific example of remediation using sodium metal has been demonstrated in the reductive dehalogenation of brominated flame retardants and solvolysis oils. A Na/NH<sub>3</sub> mixture is capable of complete debromination of printed circuit board material, and an optimum debromination temperature of 100°C-120°C was eventually determined. In this case, the sodium acts as a source of solvated electrons capable of reducing the contaminants (70).

Similarly, potassium has been used as an electron donor source in the remediation of halogenated organic contaminants. Certain studies have shown an enhanced capability for dehalogenation when potassium is alloyed with sodium, as in the work done by Miyoshi *et al* (71). Complete dechlorination of 2,2',4,4',5,5'-hexachlorobiphenyl was demonstrated, and this technique also did not produce any toxic byproducts as are often seen during degradation of polychlorinated biphenyls.

### *Magnesium*

Magnesium has a high reduction potential of -2.2V vs. standard hydrogen electrode (SHE), compared to -0.44V vs. SHE for iron (72). Combined with the fact that magnesium forms a self-limiting oxide layer rather than being completely consumed when exposed to an oxic environment, this makes it a good candidate for field environmental applications (73).

Magnesium zero-valent metal has been employed for the degradation of halogenated organic molecules under a variety of conditions. In a flash vacuum pyrolysis process, it was found to completely dehalogenate a variety of benzylic halides into the corresponding dibenzyls and toluenes (74). Elemental magnesium has also been used to debrominate cyclopropyl bromide in the presence of diethyl ether and gentle heat under an argon atmosphere. This

reaction was found to yield 25-30% cyclopropane and 25% cyclopropyl magnesium bromide, a Grignard reagent. Cyclopropyl radical disproportionation on the surface of the magnesium was found to be responsible for 85% of cyclopropane production, providing an insight towards the mechanism (75). While this is true in the ground state, the reaction of triplet state magnesium with benzyl halides was found to proceed via the abstraction of the halogen by the magnesium, which is present as a biradical (76).

Zero-valent magnesium has also been used to reduce chromium(VI), as an alternative to iron which is often used for this purpose. Free magnesium metal is less toxic than free iron, and its oxides are more soluble than iron oxides, which could help to forestall the clogging of permeable reactive barriers. While chromium(VI) was successfully reduced by magnesium, the free metal was found to solubilize in water to the extent that the pH could not be mediated over time (77).

### *Calcium*

Metallic calcium has been used to degrade polychlorinated dibenzo-p-dioxins, coplanar polychlorinated biphenyls, and dibenzofurans by stirring in ethanol under mild conditions (56). Calcium is similar to magnesium in that particles are stable in air due to the presence of an oxidized outer layer that prevents further reaction with the environment, making it safer to handle than sodium.

## **Transition Metals**

### *Iron*

Zero-valent iron has met with great success in the dehalogenation of chlorinated organic molecules. Matheson and Tratnyek (19) have demonstrated the ability of fine iron powder (43 $\mu$ m to 149 $\mu$ m) to reduce carbon tetrachloride to methylene chloride under anaerobic conditions. Studies conducted by Gillham and O'Hannesin (Gillham 1994) showed that 149 $\mu$ m iron powder was able to dechlorinate (though not always completely) 13 of the 14 chlorinated compounds tested with half-lives several orders of magnitude lower than those reported for natural abiotic processes. Further work by Orth and Gillham (78) focused on identifying the products of the TCE and iron reaction. Their work indicated that only a small percentage of chlorinated byproducts were produced, and the majority of products consisted of various small hydrocarbons. While chlorinated aromatic compounds are more difficult to degrade than chlorinated