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Nanoscale zero valent iron and bimetallic particles for contaminated site remediation

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ABSTRACT

Since the late 1990s, the use of nano zero valent iron (nZVI) for groundwater remediation has been investigated for its potential to reduce subsurface contaminants such as PCBs, chlorinated solvents, and heavy metals. nZVI shows tremendous promise in the environmental sector due to its high reactivity and as such, numerous laboratory and field studies have been performed to assess its effectiveness. This paper reviews the current knowledge of nZVI/bimetallic technology as it pertains to subsurface remediation of chlorinated solvents and heavy metals. The manuscript provides background on the technology, summarizing nZVI reactions with chlorinated solvents and metals, and examines the factors affecting nZVI reactivity. Studies on subsurface transport of bare and coated nZVI particles are also reviewed and challenges with field implementation are discussed. This manuscript offers a comprehensive review of nZVI technology and highlights the work still needed to optimize it for subsurface remediation.

1. Introduction

In the past, liquid wastes were disposed through direct pumping into the ground, migrated into the ground from leaky storage ponds and through surface spills, with no recognition of the likelihood that these wastes could persist in the subsurface for decades, potentially contaminating drinking water sources. Effluent slurries with high heavy metal content and non-aqueous phase liquids (NAPLs) are two common waste liquids that have been frequently disposed of improperly following a variety of industrial processes. Both heavy metals and chlorinated solvents, a particularly persistent NAPL contaminant, can contaminate water sources for decades and are one of the more common contaminants at brownfield and industrialized sites. Although a number of innovative remediation technologies have been developed, such as steam and density modified displacement, stabilization/solidification and *in situ* redox manipulation e.g. [1–4], existing technologies are rarely able to achieve clean up goals in contaminated aquifers at the completion of remedial activities. The problem relates to the inability of existing remedial technologies to remove, sequester or convert sufficient contaminant mass in the subsurface to significantly reduce aqueous phase concentrations and contaminant flux. The decisions related to site remediation are therefore still subject to considerable debate despite over two decades of active research and development [5,6]. The development of new and innovative remediation technologies is, therefore, crucial to achieve clean up goals at contaminated sites and ensure an abundant source of safe water for future generations.

The use of nanometals for subsurface remediation of chlorinated compound and heavy metal contaminated sites has received significant attention in part due to the ability of nanometals to rapidly transform contaminants in controlled laboratory experiments. Nanometals used for these purposes include nano iron and zinc, however nanoscale zero valent iron (nZVI) is most commonly used. In addition, other metals such as palladium or nickel have been added to increase the reduction rate. This combination of nZVI with a noble metal is referred to as a bimetallic nanometal. The reactivity and the availability of existing technology to precisely design and synthesize nanometals make nanometals particularly attractive for the remediation of subsurface contaminants. This remediation technology involves a series of steps for nanometals:

(1) transport, in the aqueous phase (or other delivery fluid), to the contaminated zone;
(2) attachment to soils in the contaminated zone or partitioning to the NAPL/aqueous phase;
(3) reaction with the target contaminant to form less toxic or less mobile products.

Nanometals have potential for use in remediation of a wide range of priority pollutants as indicated by a number of controlled

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laboratory experiments e.g. [7–15]. However, further work is necessary to address the complexities associated with nanometal application at the field scale. For example, nanometals may react with various naturally occurring groundwater constituents decreasing the reducing equivalents available for reaction with the target contaminants. Another problem that has hampered the widespread implementation of nanometals is poor subsurface mobility. Due to strong attractive interparticle forces, primarily magnetic, nZVI, the typical nanometal used for remediation, tends to agglomerate to micron size particles, which have limited mobility in porous media. To overcome this problem, various polymers, and other coatings, have been used to stabilize nZVI particles, with varying degrees of success e.g. [16,17–24]. A number of field trials have been conducted to evaluate nZVI mobility and the impact of nZVI on chlorinated solvent contaminant mass and flux. However, several field scale applications have suffered from poor nZVI mobility [25,26]. Other studies have inferred good nZVI mobility but these mobility evaluations were based on measurements of contaminant reductions or total iron (i.e., including dissolved iron species) in wells downgradient of the injection well [27,28], rather than direct measurement of Fe^0 concentrations. Given these limited studies, additional work is required to assess field mobility and performance of nZVI/bimetallic nanometals at the field scale.

The goal of this review is to present the current state of knowledge related to the use of nZVI/bimetallic nanometals for the *in situ* remediation of chlorinated solvents and heavy metals. This work is divided into six main sections: nanometal reactivity with chlorinated compounds; reactivity with heavy metal target contaminants; factors affecting nZVI reactivity; nanometal mobility in controlled laboratory experiments; the current state of modeling nZVI subsurface transport; and outcomes of a series of nanometal field trials and lessons learned. Although nanometals have been used for the remediation of a variety of priority pollutants this work focuses on two classes (heavy metals and chlorinated solvents) that are of particular concern. Throughout this work, additional research needs and unresolved challenges are highlighted providing a comprehensive review as well as a look to the future of nZVI/bimetallic subsurface remediation.

2. Background

2.1. Development of zero valent metals for remediation

Although environmental nanotechnology for remediation applications was mainly developed in the last decade following the seminal work of Wang and Zhang [29], larger micron and millimeter size metals for contaminant destruction have been employed for some time. The first use of zero valent metals for degradation of chlorinated compounds in the environment was studied by Sweeney and Fischer [30] who used metallic zinc for the degradation of halogenated organic compounds. Subsequently, iron powder was used for the removal of chlorinated compounds from wastewater [31,32] as well as contaminated groundwater [33–35].

Gillham and O'Hannesin [34] were the first to show the effectiveness of zero valent iron (ZVI) for chlorinated ethane, ethene and methane degradation with normalized (to 1 m^2/ml) contaminant half-lives ranging from 0.013 to 20 h based on a series batch tests with ZVI. Matheson and Tratnyek [36] also reported rapid dehalogenation of carbon tetrachloride (CT) and chloroform using iron particles. In addition, ZVI was found to be effective for the remediation of a variety of priority pollutants, including metals [37–43], polychlorinated biphenyls (PCBs) [44,45], chlorinated pesticides [46–48], nitro aromatic compounds [49–51] and nitrates [52,53].

These studies, along with others [54–56], have resulted in application of ZVI, mostly in the form of permeable reactive barriers (PRBs) [33,38,57–61]. Although PRBs are effective at limiting off site migration of contaminants, they do not specifically target contaminant source zone remediation and have limited applications due to construction restrictions (i.e. depth of wall). Wang and Zhang [29] reported a method of synthesizing nanoscale ZVI (nZVI). This breakthrough was important for two reasons: the nZVI particles have a very high surface area to weight ratio, resulting in higher reactivity rates than micron scale ZVI when normalized to mass [12,29,35,62–64] and nZVI particles are smaller than most porous media pore throats. As a result, nZVI particles could theoretically be transported through the subsurface to a contaminant source zone. Since 1997, many studies have shown that nanometals are able to rapidly degrade a wide variety of priority pollutants e.g. [8,10,12–15,65]. Bimetallic nanoparticles and stabilizers have also been investigated and have been shown to enhance the reactivity and mobility of nanoparticles, respectively [11,16,21,27,66,67].

2.2. nZVI particle structure

Bare nZVI particles are typically less than 100 nm in diameter. In aqueous solutions, all nZVI particles react with water and oxygen to form an outer iron (hydr)oxide layer. As a result, nZVI particles have a core-shell structure [63,65,68] (Fig. 1). The thin and distorted oxide layer allows electron transfer from the metal (1) directly through defects such as pits or pinholes, (2) indirectly via the oxide conduction band, impurity or localized band, and (3) from sorbed or structural Fe^{2+}, thus sustaining the capacity of the particles for reduction of contaminants [62]. The outer (hydr)oxide layer may also act as an efficient adsorbent for various contaminants, including metals, as will be discussed in Section 4.

nZVI can be synthesized by a number of methods, including the sonochemical method, the electrochemical method, the gas phase reduction method, and the liquid phase reduction method [29,69–72]. Among these, gas phase reduction and liquid phase reduction are the most common methods for synthesizing nZVI for remediation purposes. nZVI particles synthesized by these methods rapidly develop a core-shell structure due to reaction with air or water, but may differ in particle size, surface area, degree of crystallinity, and thickness and composition of oxide shell [12,63,73]. Reactive nanoscale iron particles (RNIP), commercially

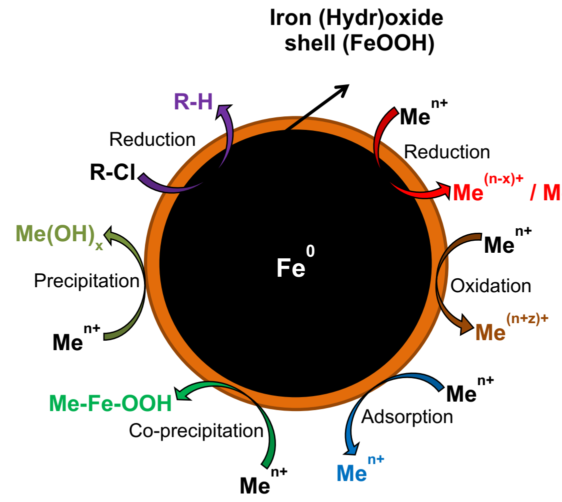

Fig. 1. Core–shell structure of nZVI depicting various mechanisms for the removal of metals and chlorinated compounds. Adapted from Li et al. [62].