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The specific reactive surface area of granular zero-valent iron in metal contaminant removal: Column experiments and modelling

Tom M. Statham, Lachlan R. Mason, Kathryn A. Mumford*,
Geoffrey W. Stevens

Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

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ABSTRACT

A series of dynamic-flow kinetic experiments were conducted to assess the removal rates of aqueous Cu^{2+} and Zn^{2+} ions by zero-valent iron (ZVI), a promising material for inclusion in cold-climate remediation applications. The influence of experimental parameters on contaminant removal rates, including aqueous flow rate, operating temperature, and the concentrations of ZVI, salt and dissolved oxygen, was investigated.

A mass transport model has been developed that accounts (i) aqueous-phase dispersion processes, (ii) film diffusion of contaminant ions to the reactive ZVI surface and (iii) the reactive removal mechanism itself. Regression to the experimental data indicated that when oxygen is present in the solution feed Cu^{2+} and Zn^{2+} removal processes were limited by film diffusion. In de-aerated solutions film diffusion still controls Cu^{2+} removal but a first-order surface reaction provides a better model for Zn^{2+} kinetics.

Using air as the equilibrium feed gas, the reactive proportion of the total surface area for contaminant removal was calculated to be 97% and 64% of the active spherically-assumed geometric area associated with ZVI media for Cu^{2+} and Zn^{2+} , respectively.

Relative to a gas absorption area, determined in previous studies, the reactive proportion is less than 0.41% of the unreacted ZVI total surface area. These findings suggest that only part of the iron oxyhydroxide surface is reacting during ZVI based metal contaminant removal.

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1. Introduction

Zero-valent iron (ZVI) is a widely used reactive material for contaminant removal in remediation and water treatment technologies (Gillham, 2010). Despite its successful commercial application, the relative importance of different removal mechanisms is known to vary with type and concentration of ZVI, contaminants, and other medium components (Alowitz and Scherer, 2002; Wilkin and McNiel, 2003; Rangsvik and

Jekel, 2005; Noubactep, 2008). A detailed understanding of removal mechanisms is required in order to optimise the design of in situ permeable reactive barriers (PRBs) and other low-cost water treatment systems (Gillham, 2010; Rangsvik and Jekel, 2011; Hussam and Munir, 2007). Whether contaminant removal is (i) dominated by reactions at localised defects in a developing iron oxyhydroxide layer or (ii) distributed across the entire iron oxyhydroxide film has broad implications for technology development (Gaspar et al., 2002).

* Corresponding author.

E-mail address: mumfordk@unimelb.edu.au (K.A. Mumford).

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To date, experimental investigation of contaminant removal mechanisms has focused on qualitative understanding of the reaction site and quantitative characterisation of kinetic rate constants. Surface analysis techniques, such as auger electron microscopy, have identified localised regions of reactive sites and removal products on the iron oxyhydroxide surface (Gaspar et al., 2002; Rangsivek and Jekel, 2005). Results suggest that contaminant removal may occur at defects in an iron oxyhydroxide layer surrounding an elemental iron core (Gaspar et al., 2002). Multi-site models have been proposed to conceptualise the iron surface area as a collection of different reactive sites (Bandstra and Tratnyek, 2004; Burris et al., 1998; Bi et al., 2010). Bi et al. (2010) investigated reactive and non-reactive sorption sites for the treatment of trichloroethene by ZVI using the transient and steady-state sections of column breakthrough curves. The modelling results indicated that only 2% of sorption sites controlled reactivity (Bi et al., 2010); which could further emphasise the importance of variations in the iron oxyhydroxide layer. Contaminant treatment kinetic rate constants have also been determined using rotating-disc cementation (Lee et al., 1978; Ku and Chen, 1992) and column experiments with varying solution velocities and/or multiple sampling points (Komnitsas et al., 2007; Wüst et al., 1999). These observations have aided in the qualitative understanding of reactive surfaces, however quantification of ZVI reactive proportion of the total surface area from experimental data has not yet been undertaken.

Transport models have also been applied to predict contaminant removal by ZVI (Mayer et al., 2002; Yabusaki et al., 2001; Li et al., 2006; Jeen et al., 2007; O et al., 2009; Carniato et al., 2012). These models use laboratory-defined rate constants scaled to reactive media surface areas (Mayer et al., 2002). Currently, due to varying solution parameters and ZVI source, calibration of some rate constants (based on gas generation and other reaction parameters) is required to model different systems (Jeen et al., 2007; Carniato et al., 2012). Developing new methods of determining reactive surface areas may help in the further understanding of contaminant removal and development of these predictive models.

This study forms part of a broader research program investigating the application of ZVI-based PRBs at contaminated coastal Antarctic sites (Statham et al., 2015a, b), where design of remediation technologies is limited by environmental and logistical considerations. Antarctic PRB systems have been implemented previously (Mumford et al., 2013), using media other than ZVI, in the context of hydrocarbon remediation. These previous studies have elucidated unique design challenges, for example diurnal and seasonal variation in water flow rates and associated variations in the degree of contaminant loading (Mumford et al., 2014). Hence, this study emulates site-specific parameters, including operating temperature, soil salinity, and dissolved oxygen concentration, and quantifies their influence on contaminant removal performance. This process will aid placement, media selection and sizing of future ZVI remediation technologies. While the current research focuses on melt water management, general insights into ZVI behaviour can potentially aid in the development of nano-ZVI based remediation techniques (Zhang, 2003; Tratnyek and Johnson, 2006). The model contaminants Cu^{2+} and Zn^{2+} have been selected as these represent potential metals of concern at

coastal Antarctic sites (Snape et al., 2001; Northcott et al., 2003); the selection also enables a comparison of contaminants that are, respectively, reducible and non-reducible by metallic iron. A combination of experimental and numerical modelling techniques is used to evaluate the contributions of species diffusion and reaction mechanisms to net contaminant removal rates. Comparison of model-determined reactive surface areas with the total column ZVI surface area can provide further insight into contaminant interaction with iron oxyhydroxide surfaces. While the current findings are readily applicable to cold-climate PRB design, the fundamental results also outline the quantification of ZVI reactive surface areas, which will aid in the general development of ZVI-based water treatment systems.

2. Experimental and modelling methods

2.1. Experimental method

Experiments were conducted using a vertical glass column of length $L = 12.8$ cm and diameter $d_c = 2.8$ cm. Columns were dry-filled with a homogeneous mixture of 0–8 wt% Peerless iron (Peerless Metal Powders & Abrasive, cast iron aggregate –8/50 mesh, average diameter 0.50 mm; for other iron properties refer to Statham et al. (2015b)) and an inert packing of ballotini glass spheres (sieve-determined average diameter of 0.58 mm). Dry media was homogenised by combining enough ZVI and ballotini for one column in a bag and shaking and turning this mixture end over end for 1 min. An average porosity of 0.40 was subsequently determined gravimetrically using Milli-Q water. Liquid was pumped through Masterflex FDA viton tubing from one of two feed reservoirs upwards through the column by a calibrated peristaltic pump (see Fig. S1); the vertical up-flow direction was selected to reduce the occurrence of channelling (Inglezakis et al., 2001) and ensure that the media were saturated. Unless stated otherwise, the column, piping and ballotini were acid washed and rinsed with Milli-Q at the start of each experiment, and all experimental uncertainties shown use the standard error from triplicate results.

The temperature dependent column longitudinal dispersion coefficient, D_l , was determined using a salt tracer method (Woinarski et al., 2006). The conductivity response for a series of 0.1 M sodium chloride step-concentration-change tracers in a ballotini-only column were fitted using CXTFIT (Toride et al., 1995); a representative tracer breakthrough curve is shown in Fig. S3.

The removal rates of two contaminant metals were studied, Cu^{2+} and Zn^{2+} , both prepared from chloride salts. This was achieved using two different procedures: (i) fixed inlet concentration and (ii) step-change inlet contaminant concentration.

2.1.1. Fixed inlet contaminant concentration

Changes in Cu^{2+} and Zn^{2+} concentration across the column length were determined at set flow rates. Solution was pumped into the column for 4 PV (where PV denotes the column pore volume) to establish a steady state; this time was deemed sufficient based on the results of conservative and reactive tracer tests. After this time, 20 mL of sample was collected and

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