



Capture and storage of hydrogen gas by zero-valent iron

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ABSTRACT

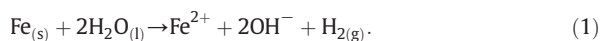
Granular Fe⁰, used to reductively degrade a variety of contaminants in groundwater, corrodes in water to produce H_{2(g)}. A portion enters the Fe⁰ lattice where it is stored in trapping sites such as lattice defects and microcracks. The balance is dissolved by the groundwater where it may exsolve as a gas if its solubility is exceeded. Gas exsolution can reduce the effectiveness of the Fe⁰ treatment zone by reducing contact of the contaminant with iron surfaces or by diverting groundwater flow. It also represents a lost electron resource that otherwise could be involved in reductive degradation of contaminants. It is advantageous to select an iron for remediation purposes that captures a large proportion of the H_{2(g)} it generates. This study examines various aspects of the H_{2(g)} uptake process and has found 1) H_{2(g)} does not have to be generated at the water/iron interface to enter the lattice. It can enter directly from the gas/water phases, 2) exposure of granular sponge iron to H_{2(g)} reduces the dormant period for the onset of iron corrosion, 3) the large quantities of H_{2(g)} generated by nano-Fe⁰ injected into a reactive barrier of an appropriate granular iron can be captured in the lattice of that iron, and 4) lattice-bound hydrogen represents an additional electron resource to Fe⁰ for remediation purposes and may be accessible using physical or chemical means.

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1. Introduction

Granular zero-valent iron (ZVI) has been used in the construction of permeable reactive barriers (PRBs) to remediate contaminated groundwaters since the applicability of the material to dehalogenate organic compounds was realized through laboratory experiments in the early 1990s (Gillham and O'Hannesin, 1994; Gottpagar et al., 1997; Matheson and Tratnyek, 1994; Reynolds et al., 1990; Schreiber and Reinhard, 1994). The ZVI not only serves as a ready source of electrons to carry out reductive dehalogenation reactions but also has been found useful in remediating other types of contaminants where reductive reactions can be beneficial, such as in the treatment of chromate, arsenate and nitrate in groundwaters (Bang et al., 2005; Fuller et al., 2013; Gould, 1982; Ritter et al., 2003). Most of these reduction reactions occur by sorption of the contaminant directly at the iron granules' surfaces, followed by electron exchange facilitated by the presence of magnetite or some

other semi-conductive iron metal surface alteration products (Odzimkowski and Simpraga, 2004; Roberts et al., 1996; Scherer et al., 1998). The surface material may develop by auto-reduction of a more oxidized passive layer upon contact of the iron granules with water under anaerobic conditions (Odzimkowski et al., 1998; Ritter et al., 2002; Zhang and Huang, 2006). Largely independent of these desired reductive remediation reactions, the electron resource of granular ZVI is gradually depleted due to the continuous production of hydrogen gas through the corrosion of ZVI by water under anaerobic conditions:



The produced H_{2(g)} constitutes a potential resource of electrons and may be: 1) transported from the PRB in the dissolved state 2) utilized in biodegradation reactions by H₂-utilizing bacteria or 3) exsolved from groundwater as a separate gas phase if the dissolved H₂ concentration exceeds its solubility. Whether a H₂ gas phase develops will depend

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on the corrosion rate of the iron, the groundwater flow rate, the PRB thickness, the maximum solubility of $H_{2(g)}$ at the temperature and pressure within the PRB, and PRB physical properties, such as pore sizes and distributions. The molal solubility of hydrogen ($mH_{2(aq)}$) is given by Henry's law expression:

$$mH_{2(aq)} = K_H P_{H_2} \quad (2)$$

where the P_{H_2} at which $H_{2(g)}$ would tend to exsolve is given by the total pressure within the PRB (atmospheric + hydrostatic pressure). The actual P_{H_2} required for the exsolution of a gas phase from groundwater could be lower if other dissolved gases are present, i.e. it is the sum of the partial pressures of all the dissolved gases (carbon dioxide, volatile organic compounds etc.) that determines the potential for the separation of a gas phase from a groundwater. At 25 °C, K_H , calculated from the solubility of $H_{2(g)}$ in water (Dean, 1992), is equal to $10^{-5.124}$ for P_{H_2} expressed in kPa. Fig. 1 shows example conditions where $H_{2(g)}$ saturation would occur during groundwater flow through a PRB for specific PRB thicknesses and granular iron corrosion rates. The diagram is constructed assuming a groundwater flow rate of 60 cm/day. It is noted that at this flow rate, unless the $H_{2(g)}$ generated is consumed by some other process(es), even a low corrosion rate of 0.3 mmol/kg/day could result in $H_{2(g)}$ exsolution and two-phase flow development for PRB thicknesses greater than 25 cm.

Aside from potential use in microbial and non-biogenic hydrogenation reactions, which may be beneficial, hydrogen production carries mostly negative effects—depleting the electron resource of the PRB and if a gas phase develops potentially reducing effective contact of the contaminant with iron surfaces (Johnson et al., 1996; Zhang and Gillham, 2005). Another possible negative effect of gas phase development would be reduction or diversion of the contaminant flow through the PRB (Johnson et al., 2008; Kamolpornwijit et al., 2003). Fortunately, not all the $H_{2(g)}$ produced by anaerobic corrosion ends up in the water (and gas) phase(s). A portion enters the crystal lattice of the iron granules

themselves (Zakroczymski, 1985). Individual H atoms produced by corrosion of ZVI develop at the iron/water interface and either assemble into H_2 molecules and dissolve in the groundwater or diffuse into the lattice as individual atoms and subsequently accumulate as H_2 molecules in traps, such as voids, defects, grain boundaries, and microcracks. (Iyer and Pickering, 1990). Some hydrogen permeates the lattice and can exit iron particles. Most are trapped with high binding energies (Zakroczymski, 1985), allowing $H_{2(g)}$ to build up in the lattice. High pressures can develop in these traps and contribute to a number of failure mechanisms of iron and steel materials, such as stress corrosion cracking and blistering (Shewmon, 1976).

The proportion of hydrogen that enters the lattice versus that which dissolves in the water phase depends on the physicochemical characteristics of the ZVI, such as method of production, milling history, number of lattice defects and properties of the surface oxide film.

The objective of this study is to examine the hydrogen capture and storage properties of two commercial granular irons used in the construction of PRBs and to delineate the implications and applications of this phenomenon in developing groundwater remediation technologies for PRBs.

2. Materials and methods

2.1. Materials

Three ZVI materials were used in this study:

- 1) Toda—A nano-sized iron obtained from the Toda Kogyo Corp. (Japan). The material is produced by the reduction of ferric oxides with $H_{2(g)}$ at high temperature. An analysis of this iron shows an elemental Fe^0 content of 65%, the balance being magnetite (Fe_3O_4)—the only other XRD-identifiable compound in this material. The BET surface area is 24 m^2/g and the particle size ranges from 200 to 400 nm.
- 2) QMP-58—A micro-sized granular iron produced by Quebec Metal Powders Ltd., Sorel Tracy, PQ, now a subsidiary of Rio Tinto, in a process where jets of high-pressure water are directed at molten iron metal derived as a byproduct of the

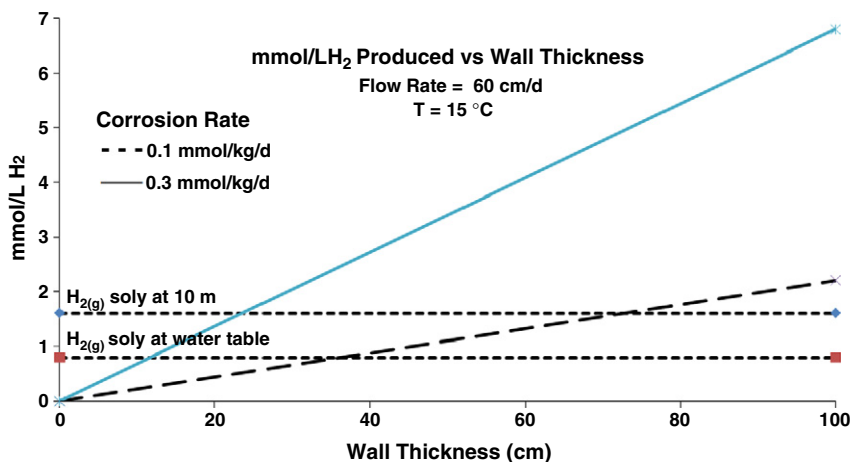


Fig. 1. PRB wall thickness that could result in $H_{2(g)}$ exsolution from groundwater from groundwater flowing at 60 cm/day for two apparent corrosion rates; at water table condition (100 kPa) and at 10 m below the water table (200 kPa).

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