

Factors in the Long-Term Performance of Granular Iron PRBs

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Abstract: The primary cost advantage of granular iron permeable reactive barriers (PRBs) over conventional groundwater treatment systems is derived from anticipated low operating and maintenance costs. Thus long-term performance of granular iron is a topic of great practical importance, as well as scientific interest. This paper summarizes two studies relevant to this topic. In the first, column studies were conducted such that solution chemistry, open circuit potential and mineral composition on the surface of the iron grains could be measured simultaneously. The results demonstrated rapid autoreduction of the passive oxide film present initially on commercial granular iron materials, and further demonstrated the persistence of these films, and thus slow reduction of TCE in the presence of competing oxidants (nitrate in this case). The second study demonstrated the formation of a precipitate front at the influent surface of granular iron. As a consequence of declining reactivity, the precipitates did not form in quantities that significantly reduced the hydraulic conductivity. However, as a result of reduced activity behind the front, calcium carbonate would continue to precipitate at the front, causing the front to migrate progressively into the iron. The practical consequences are highly dependent on the inorganic chemical characteristics at a site, as well as the required service life of the PRB.

The use of granular iron, implemented as an in situ permeable reactive barrier (PRB) for treatment of groundwater containing halocarbons, is promoted as a cost-effective alternative to conventional treatment methods. Capital costs for construction of a PRB containing granular iron are comparable to those of pump-and-treat, and thus the proposed cost advantage is gained primarily through reductions in operating and maintenance costs. The extent to which these savings will be realized depends upon the long-term treatment integrity of the PRB. As a new technology in the early 1990s, there was no data base of performance and very limited experimental or theoretical evidence upon which to forecast performance life time and integrity. The topic has therefore attracted considerable research attention.

The initial field demonstration of the technology showed no decline in performance over the five year duration of the study (O'Hannesin and Gillham, 1998), and the evidence suggests that the initial installation at an industrial site (January, 1995) continues to perform effectively. Though the evidence is encouraging, and is becoming more convincing as the period of record lengthens, there continues to be an uncertain basis for predicting performance well into the future. The primary issues concern the longevity of the iron are the activity of the iron surfaces and the effects that precipitates may have on the permeability of the PRB.

Summaries of two studies conducted at the University of Waterloo will be presented, the first concerns the surface condition and activity of commercial-grade granular iron in contact with aqueous solution and the second concerns the formation and consequences of precipitates.

Mineral Transformations On The Iron Surface: The early studies of the use of granular iron for degrading chlorinated organic compounds (Gillham and O'Hannesin, 1994; Matheson and

Tratnyek, 1994, for example) used pure forms of electrolytic iron and frequently the surfaces were cleaned by acid washing prior to experimentation. Though surface films would form immediately upon exposure to an oxidizing environment, these materials are substantially different from the granular iron used in commercial applications. Commercial iron is generally collected as a byproduct of machining operations, it is passed through a rotary kiln to remove cutting oils and other foreign materials and is ground and sieved. The results are iron grains with a metallic core and thick high-temperature oxidation film. The film consists of an inner electron-conducting magnetite layer (Fe_3O_4) and an outer hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) layer. Because Fe_2O_3 is non-conducting with respect to electrons, the presence of hematite and maghemite are expected to be passivating, and thus commercial granular iron would be expected to be non-reactive.

In this study (Ritter, 2000) a flow-through glass column was designed that permitted the simultaneous measurement of solution chemistry, open circuit potential of the iron grains, and monitoring, by *in situ* Raman spectroscopy, of changes in the mineral composition on the surface of the iron grains. The column was packed dry with granular iron obtained from Connelly GPM Inc. (Chicago, IL). The influent solutions included Millipore water, 1.5 mg/L trichlorethylene (TCE) in water, 100 mg/L nitrate in water and 1.5 mg/L TCE plus 100 mg/L nitrate in water.

Raman spectra showed that the hematite and maghemite peaks on the dry iron surfaces disappeared to below detection within minutes upon contact with water, while the magnetite peak continued to grow over time. Furthermore, the solution pH and open circuit potential of the iron, when plotted on a modified Pourbaix diagram indicated the conditions to move rapidly from the region of Fe_2O_3 stability and to be maintained within the region of Fe_3O_4 stability over the duration of the test (35 days). The Raman spectra and the open circuit potential measurements obtained for the column with 1.5 mg/L TCE in the influent solution were very similar to those reported for water. Thus, the evidence suggests that the autoreduction of the passive Fe_2O_3 film to electron conducting Fe_3O_4 and maintenance of Fe_3O_4 as the dominant surface film may be a critical first step in the applicability and long-term performance of the technology.

In the column that received TCE and nitrate solution, a relatively minor amount of nitrate reduction was observed. The Fe_2O_3 passive layer persisted on the surface. Furthermore, based on the pH and potential measurements, the Fe_2O_3 layer was stable in the presence of the nitrate solution. Thus nitrate, a strong oxidant and known corrosion inhibitor, resulted in maintenance of the passive Fe_2O_3 film, thus reducing the reactivity of the iron. Very low rates of TCE reduction were observed in the presence of nitrate. In this column the pH and potential were within the range of Fe_2O_3 stability, and the range of FeOOH , also a protective species. Hence it appears that nitrate maintains the stability of the passive films, thus limiting further reduction of both nitrate and TCE.

This study demonstrated clearly that the rapid autoreduction of the surface oxides to non-passive forms is a fortunate and essential step in the applicability of the technology. Furthermore, from the results reported here, the gradual accumulation of the non-passivating oxides (magnetite in particular), did not appear to have a negative effect on performance. However, in the presence of competing oxidants (nitrate in this case) the passive films could persist, severely reducing the

rates of dechlorination of TCE. Thus the presence of competing oxidants needs to be considered in applying the technology at a particular site.

Effects Of Mineral Precipitation On Reactivity And Permeability: As a consequence of iron corrosion by water, OH^- is released to solution causing an increase in pH, often to values as high as 10 or greater. The increase in pH causes a shift in the $\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibrium, resulting in the precipitation of carbonate minerals. While iron carbonates, calcium carbonates and magnesium carbonates have all been identified, in most groundwater environments, calcium carbonate would be expected as the dominant precipitated phase. While the rate of precipitation will be strongly influenced by the inorganic chemistry of the influent solution, based on the results of laboratory tests, Sivavec, as quoted in Wilson (1995), estimated that 10% of a barrier's porosity could be lost over a period of 10 years. In addition, from core samples collected 18 months after installation of a field test facility, Vogan *et al.* (1999) reported calcium carbonate precipitates equivalent to about 10% of the initial porosity, but limited to a region approximately 10 cm thick in the up-gradient face of the installation. While it is clear that precipitates form, several important questions remain concerning their effect on permeability, reactivity and overall performance.

This study was undertaken in an attempt to quantify the relationship between porosity loss and decline in permeability, to monitor the progression of precipitate formation and to examine the effect of precipitate formation on reactivity.

Four laboratory columns, each 3.8 cm ID and 10 cm long, and with three sampling parts located at different distances from the influent end, were packed with a commercial iron material (Master Builders). Each column received a different solution: 1) distilled water (control); 2) 10 mg/L TCE; 3) 300 mg/L CaCO_3 ; and 4) 10 mg/L TCE + 300 mg/L CaCO_3 . The columns were operated generally in excess of 18 months and at a flow velocity of about 85 cm/day (approximately 10 pore volumes per day). Loss of porosity due to both gas and precipitate formation were determined by periodically weighing the columns and permeability was determined from flow rates and manometer readings.

The results indicated that at early time and for all columns, approximately 5 to 15% of the initial water-filled porosity was lost due to entrapment of hydrogen gas. In the columns receiving CaCO_3 , there was a further reduction of about 17 to 22% of the initial porosity due to precipitation. Gas formation resulted in a decline in hydraulic conductivity of about a factor of ten; however, although the volume of precipitate formation appeared to be comparable, the precipitates did not result in a further measurable decline in hydraulic conductivity. Though further analysis of the data is required, it appears that the hydrogen gas, as a non-wetting fluid, occupies the largest pores and therefore has a major influence on hydraulic conductivity. The precipitates would occur as a uniform coating over the iron grains, and this configuration appears to have much less influence on hydraulic conductivity.

Of particular importance, results obtained from the two columns receiving CaCO_3 in solution indicated that after about three to five months, there is little further accumulation of precipitates and thus there is no reason to anticipate a further decline in permeability. The results therefore suggest that under the conditions of this experiment, loss of permeability due to precipitate

formation is not likely to be a significant problem. Results obtained from the column receiving TCE + CaCO₃ clearly showed a declining rate of TCE degradation. Combining this observation with the trends in pH and E_h indicates declining reactivity of the granular iron surfaces. It is unclear however, if this is a direct consequence of the presence of the precipitates or if it is an indirect consequence of the precipitates influencing the presence or absence of passive films on the iron surface.

In this case, significant precipitate formation and loss of reactivity occurred within the first three months of operation. Though the results cannot be readily transferred to field conditions, considering the high flow rate used in the tests and the relatively high bicarbonate concentration in the influent solution, the results are at least qualitatively comparable to those reported by Vogan *et al.* (1999).

The evidence suggests that a calcium carbonate precipitation front will move through the PRB. Behind the front, in the zone of precipitate accumulations, the hydraulic conductivity will remain relatively high, though the reactivity of the iron will be low. Ahead of the front, the iron should be close to its original reactivity. The design of a PRB should consider the occurrence of a precipitate front and could accommodate the front by making the barrier thicker than would otherwise be the case or by anticipating that some form of maintenance would be required. The degree to which the precipitate front would influence the design would depend on numerous factors including the inorganic geochemistry of the water at the site and the required service life of the PRB.

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