

THE EFFECT OF DILUTING GRANULAR IRON WITH A NON-REACTIVE POROUS MEDIUM ON CONTAMINANT TRANSFORMATION RATES

J.F. Devlin, Dept. of Geology, University of Kansas, Kansas, USA

J. Patchen, Terratech Inc., Overland Park, Kansas, USA

ABSTRACT

Granular iron is a constituent of permeable reactive barriers (PRBs), and is used to treat organic and inorganic contaminants in groundwater. To minimize the capital costs associated with installing an iron PRB, the iron is sometimes diluted with non-reactive porous media, such as sand. However, diluting the iron with sand introduces the possibility that mass transfer effects will begin to control the contaminant transformation rates, and little is known about the onset of this kinetic control mechanism. In this experiment, mini-columns of granular iron were prepared with the iron packed (1) as a plug of granular iron, (2) as a medium of evenly mixed beads and iron and (3) as intermediate mixtures. In addition, these packings were completed for various iron loadings, including 4% iron by weight, 25%, and 50%. Preliminary results suggest that only the most dilute iron columns exhibited noticeable mass transfer effects.

RÉSUMÉ

Le fer granulaire est un constituant des barrières réactives perméables (PRBs), et est employé pour traiter les contaminants organiques et inorganiques des eaux souterraines. Pour réduire au minimum les coûts associés à l'installation du fer PRB, le fer est parfois dilué avec des matériaux poreux non-réactifs, par exemple le sable. Cependant, la dilution du fer avec le sable présente la possibilité que les effets de transfert de masse commenceront à contrôler les vitesses de transformation de contaminant, et peu est connu au sujet du début de ce mécanisme cinétique. Dans cette expérience, les minicolonnes de fer granulaire ont été préparées avec le fer compacté (1) comme bouchon de fer granulaire, (2) comme milieu de grains et de fer également mélangés et (3) en tant que mélanges intermédiaires. Aussi, les colonnes ont été préparées avec différentes quantités de fer, y compris 4%, 25%, et 50% en poids de fer. Les résultats préliminaires suggèrent que seulement les colonnes de fer les plus diluées ont montré des effets apparents de transfert de masse.

1. INTRODUCTION

Granular iron is a well established porous medium used in permeable reactive barriers for groundwater remediation (Gavaskar et al., 1998). It is available commercially and has been found to be an effective agent for reducing many problematical contaminants, such as chlorinated solvents (Gillham and O'Hannesin, 1994), metals (Alowitz et al., 2002) and arsenic (Manning et al., 2002). The reductions occur quite rapidly, making it possible to complete the reactive barriers with thicknesses (in the direction of flow) of one metre or less. Where the contaminant concentrations are low, narrow barriers can, in principle, be effective, but trenching equipment may require a thick barrier be constructed. In cases like these, cost savings can be realized by diluting the granular iron with less expensive sandy fill. This practice has been successfully implemented at several sites (U.S. Environmental Protection Agency, 2002). A typical sand-iron mixture is 20% iron by weight, uniformly mixed (O'Hannesin and Gillham, 1998). Surprisingly, the literature contains very little basic information on sand-iron mixtures, so there is a need for systematic work to be done to establish the practical limits of granular iron dilution with non-reactive porous media.

This paper reports the results of a series of experiments in which granular iron was used to degrade a model contaminant (4-chloronitrobenzene, 4CLNB) in mini-columns containing undiluted iron and iron mixed with glass beads. It was hypothesized that sufficiently diluted iron would exhibit reaction kinetics controlled by mass

transfer effects rather than chemical reactivity, due to increased distances between reactive sites in the porous medium mix. The objective of the work was to determine the percent dilution of iron (by weight) at which this mass transfer control would express itself.

2. METHODS

2.1 Mini-Columns

Data were collected using mini-columns constructed from Pasteur pipettes (Figure 1). Water was pumped from a reservoir through the mini-columns at a flow that resulted in an average linear velocity within the columns of about 8.67×10^{-4} m/s. The reservoir initially contained an 8 mM solution of NaClO_4 , and this was successively spiked with 4CLNB to achieve concentrations of 4 μM , 20 μM , 70 μM , 150 μM and 250 μM . Samples of the effluent were collected at increasing intervals following each spike (time = 2, 3, 4, 5, 7, 10, 15 and 20 minutes for sample collection). Breakthrough curves were fitted with a solution to the advection-dispersion equation with first order decay and retardation (Devlin and Barker, 1996) to estimate the pseudo-first-order rate constant, k . With these data sets, k could be related to the rate constant for the reaction on the iron surface, λ , through (Devlin and March, 2003)

$$kC_{\text{water}} = \frac{-\lambda \frac{\text{Fe}}{V_{\text{water}}} C_{\text{max}} C_{\text{water}}}{\frac{1}{J} + \frac{C_{\text{max}}}{1 + JC_{\text{water}}} + C_{\text{water}}} \quad [1]$$

where C_{water} = concentration of 4CLNB in water (M/L^3), Fe = mass of granular iron in a column (M), V_{water} = volume of water in a column (L^3), C_{max} = Langmuir constant indicating the sorption capacity of the granular iron surface for 4CLNB (M/M) and J = a Langmuir constant related to the affinity of 4CLNB for the granular iron

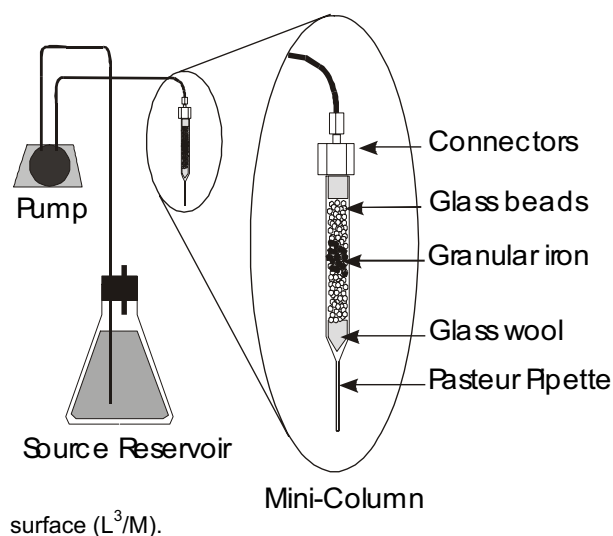


Figure 1: Schematic of the mini-column set-up. In this depiction, the iron is packed as a plug (see text).

Mini-columns with 4 iron loadings, 4%, 15%, 25% and 50% by weight, were prepared for testing. For each loading, the iron was mixed with the glass beads in 4 different ways, in separate columns: (1) the iron was emplaced as a plug (P), as depicted in Figure 1; (2) the iron was mixed with approximated one third of the beads (M1); (3) the iron was mixed with approximately two thirds of the beads (M2); (4) the iron was uniformly mixed with the beads (M). With this array of columns, it was possible to assess the onset of mass transfer kinetics as a function of the degree of iron dilution under various iron loading scenarios.

2.2 Chemical Analysis

All samples were collected in 2 mL sampling vials and crimp sealed immediately. The vials were centrifuged for 5 minutes at 10-12K rpm and then loaded on an autosampler tray for analysis by HPLC. All samples were analysed within 48 hours of collection, and the large majority were analysed with 24 hours of collection. In the former case, samples were stored in a refrigerator at 4 °C until centrifugation and loading on the autosampler.

Analysis was performed with an Agilent 1100 HPLC equipped with a diode array detector and a Zorbax Reverse Phase SB-C18 column (dimensions 4.6x150 mm and 5 micron packing). Samples were analyzed isochratically with a mobile phase of 40% water, 30% acetonitrile, 30% methanol and a flow rate of 1 mL/min.

3.0 Results and Discussion

The testing showed that estimates of k diminished with reduced iron loadings (Figure 2). This follows from the expected positive correlation between amount of reactive surface (Fe) and reaction rate. High reaction rates led to high estimates of k .

The testing also revealed overall decreases in k as function of increasing 4CLNB concentrations. This is also an expected result, based on previous work by Devlin et al. (1998), and Morkin et al., (2000) and is evident in Figure 2 as a general decline in the elevations of the surfaces as 4CLNB concentration increases. In this case, k decreases because the finite number of reactive sites on the granular iron surface limit the reaction rate.

Columns packed with 15% and 4% iron both exhibited decreasing values of k as the degree of mixing with beads was increased. The trend is most easily made out in Figure 2 in the 4 μM and 20 μM surfaces, and the 15% iron loading. There was no consistent indication of a rate constant decline in the 50% and 25% iron loading data sets. In fact, in the latter case, there appeared to be an increase in the estimated k . A possible explanation for this phenomenon is discussed in section 3.2, below.

3.1 The Onset of Mass Transfer Kinetic Control

In order to assess the role of mass transfer kinetics in the various column experiments, ratios (r_{ij}) were calculated for each iron loading according to the relation below (Figure 3),

$$r_{ij} = \frac{k_{ij}}{k_{\text{plug } j}} \quad [2]$$

where k_{ij} = the rate constant for mixing condition i (M1, M2 or M) and loading j (4% to 50%) and $k_{\text{plug } j}$ is the rate constant from the iron plug column (P) associated with loading j . It was inherently assumed in this analysis that mass transfer limitations did not exist in the iron plug columns. Because the method used to estimate k treated all reactive zones as if they were equal in length, the values of k for a given loading series (e.g., 4%, 15%, 25% or 50%) should all have been identical unless mass transfer effects were important in some of them. Absence of mass transfer limitations would have led to ratios from equation [2] with values of 1 in all cases ($r_{ij} = 1$). On the other hand, where mass transfer limitations were important, then $k_{\text{plug } j} > k_{ij}$ and $r_{ij} < 1$. From the ratios plotted in Figure 3, it is immediately apparent that mass

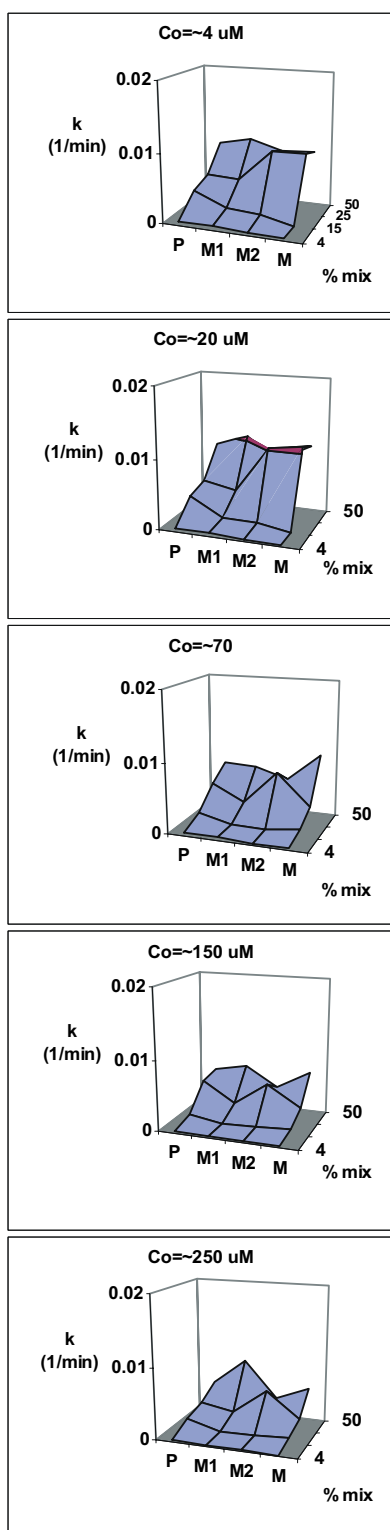


Figure 2: Surfaces depicting the relationship between pseudo-first-order rate constants, mixing scenario and iron loading.

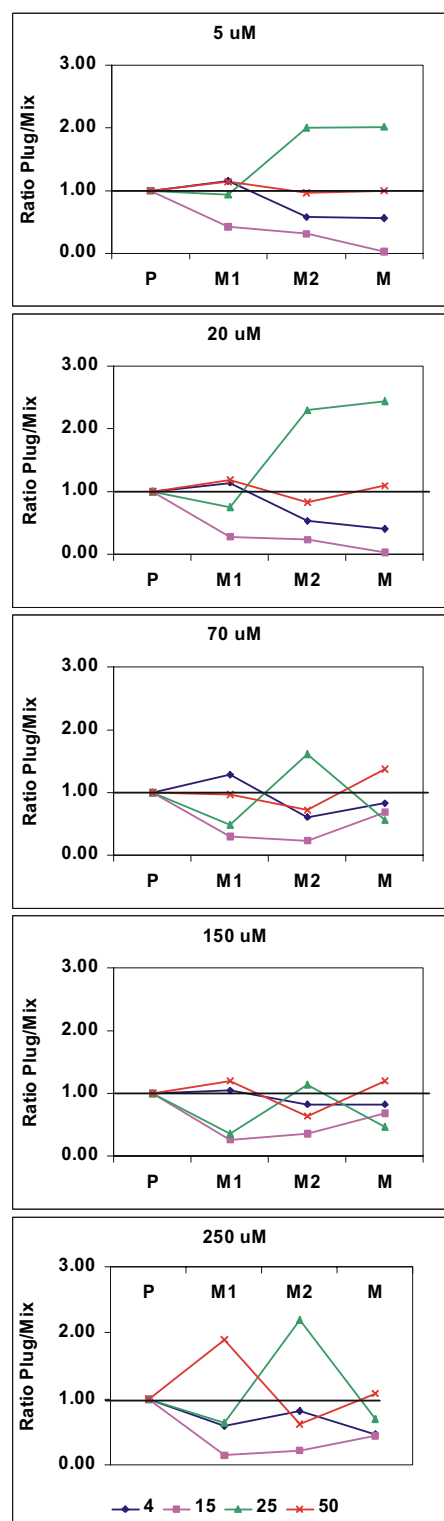


Figure 3: Ratios of rate constants. Ratios below unity indicate a likelihood that mass transfer is influencing the kinetics.

transfer had no noticeable effect on the 50% iron loading columns, and had at most a marginal effect on the 25% iron loading columns. However, both the 15% and 4% columns consistently returned ratios less than unity for mixing conditions M2 and M, corresponding to iron to water ratios of less than 2 g/mL. This degree of iron dilution is therefore indicated as the tipping point, beyond which treatability testing must take into account mass transfer effects in the performance of a PRB containing granular iron mixed with glass beads. Further work is needed to extend this finding to other filler materials.

3.2 Apparent Reactivity Enhancements ($r_{ij} > 1$)

If the columns containing plugs of iron represent the most concentrated iron packings, they should also correspond to the highest rates of contaminant degradation and the highest estimated values of k . However, several cases in Figure 3 were found to yield ratios considerably larger than unity (25% loading, 4 μ M, 20 μ M, M2 and M, for example). A possible explanation for this counter-intuitive result is given below.

When the iron is packed without dilution (plug), mass transfer effects are minimal or absent and $Fe/V \approx 3$ -5 g/mL. As seen in Figure 3, limited dilution of iron does not introduce mass transfer effects. However, the iron-bead mixes do result in increased path-lengths through the reactive zones. Increased path-lengths translate to increased residence times and a greater degree of contaminant degradation. In fitting the breakthrough curves to the transport-reaction equation, increased degradation resulted in higher estimates of k . The effect was not noticeable in the 50% columns because the path-length was not increased sufficiently for the apparent enhancement to be observed (Fe/V declined from about 5 to 2.5 g/mL in P50 to M50, respectively, suggesting that mass transfer limitations were also minimal throughout the 50% series). It was also absent in the 15% and 4% columns because the mass transfer effects became important before the path-lengths could compensate ($Fe/V = 2$ g/mL in 4% M1 $Fe/V = 1.8$ g/mL in 15% M2). The conditions necessary for the apparent enhancement were met in the 25% iron loading columns, where for 25% M2 $Fe/V > 2$ and the path-length was about 4 times longer than P25%. This is a potentially useful insight, since it suggests that barrier performance might be optimised by dilution of the granular iron medium in some cases.

In order to test if the increase in path-length was responsible for the relatively large k ratios in the 25% iron loading columns, the k estimates were corrected for path-length and re-plotted (Figure 4). As predicted, the apparent enhancement disappeared with the correction, supporting the notion that increased path-length was related to the apparent increase in reactivity.

The practical benefit of this finding is that for a given iron loading, a PRB might be designed to take advantage of increases in residence time without reaction rate declines due to mass transfer effects. This could be achieved by diluting the iron with a non-reactive porous medium,

maintaining $Fe/V > 2$ (note that this Fe/V criterion has only been demonstrated to apply to glass beads; further work is required to determine the equivalent criterion for sand or other non-reactive filler materials). This could lead to cost savings and performance enhancements in some cases. The data in this study suggest this strategy is safest when contaminant concentrations are low (less than 70 μ M in this study) and surface saturation effects are minimal.

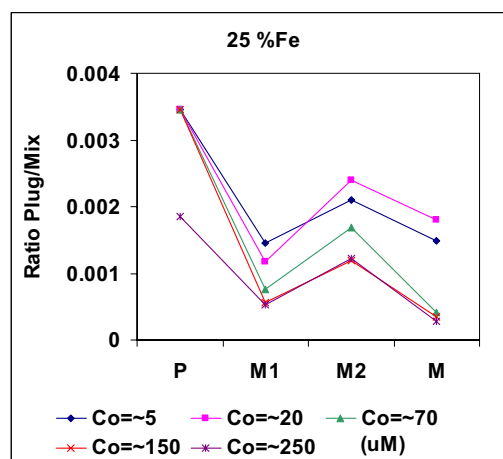


Figure 4: Correcting the 25% iron loading column k values for path-length. The correction more than accounts for the apparent reactivity enhancements visible in Figure 3.

3.3 Reaction Kinetics

Equation [1] expresses the rate of disappearance of 4CLNB ($kC_{water} = dC/dt$) as a function of 4CLNB sorption to the iron surface (in terms of C_{max} and J) and the concentration of iron surface (Fe/V). Equation [1] assumes instantaneous equilibrium sorption; it does not account for mass transfer effects. Therefore, if concentration series data from the plug columns (minimal or no mass transfer) are used to estimate the parameters in [1] (C_{max} , J , λ), the model should be capable of predicting the iron-bead mixtures' trends in k in all columns where mass transfer is not influencing the kinetics. These calculations were completed for the 50% and 4% columns, representing the end-members of the experiment. Equation [1] was found to describe the data from all these experiments except those from the mixed 4% column (Figure 5). This result supports the previous findings that mass transfer was not important for the plug columns or the high iron loading (50%) column, but was an important factor in the reaction rates in the highly diluted column (4% mixed).

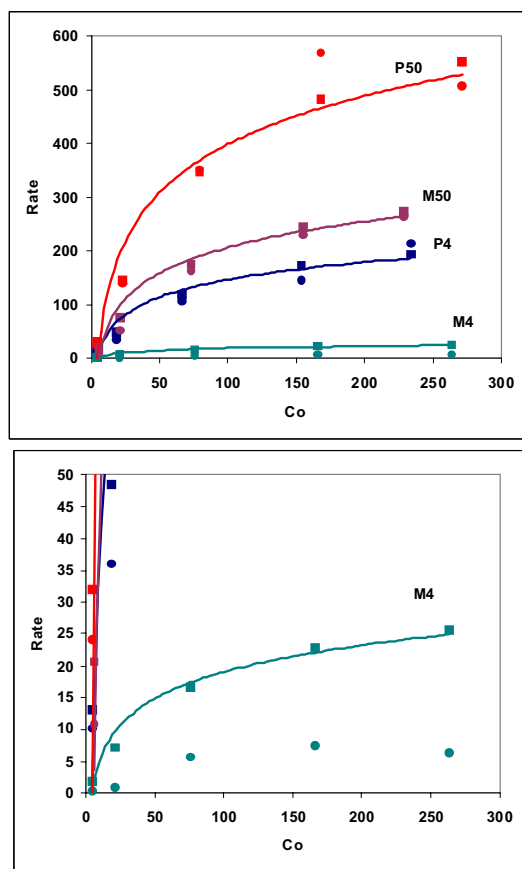


Figure 5: Equation [1] describes the data from P50%, P4% and M50% very well but overpredicts the degradation rate of 4CLNB in M4%. This result is consistent with mass transfer effects influencing the kinetics in M4%.

4.0 CONCLUSIONS

The dilution of granular iron in PRBs with glass beads was found to compromise PRB performance due to mass transfer effects only if the Fe/V ratio was permitted to drop below 2 g/mL. This corresponds to a uniform mix of glass beads and iron less than 25% by weight iron. It was shown that under some conditions, dilution of the iron medium with beads is beneficial, since it resulted in an increased residence time of contaminants in the PRB, with no mass transfer limitations to limit the degradation rates. As alluded to in the introduction, practitioners have already taken advantage of this phenomenon, but further work is needed to determine more precisely the conditions under which this advantage can be exploited to greatest advantage, and to extend the work to other filler material, such as sand.

A general kinetic model that explicitly accounts for iron surface concentration (as Fe/V) and surface sorption was found to accurately predict rates of 4CLNB degradation with granular iron in cases where mass transfer effects

were minimal, but over predict reaction rates in other cases. This result is a second, independent analysis validating the conclusions of this work.

This study is one of very few that have examined the effects and limitations of diluting granular iron with a non-reactive porous medium. While additional experiments are needed to confirm the results presented here, this study provides preliminary guidelines for PRB designers who wish to optimise PRB performance and minimize costs.

5.0 ACKNOWLEDGEMENTS

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