An Examination of Zero-valent Iron Sources used in Permeable Reactive Barriers

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Abstract: The zero-valent iron (ZVI) used in permeable reactive barrier (PRB) installations comprises a kiln-fired, milled mixture of cast iron cuttings and borings arising from a variety of primary manufacturing processes. Confounding differences in commercial ZVI reactivity for VOC degradation has been documented by several research groups. This study examined in detail the chemical, metallurgic and surface properties of commonly used ZVI end products, as well as six individual feedstocks used in these mixtures, to determine if differences in reactivity can be traced to feedstock composition and/or milling procedures. Analyses included chemical leaching tests, reactivity column tests, surface area measurements, and examination of surface oxide coatings. In general, while there was no large differences in trichloroethene degradation rates, the end product and its corresponding feedstocks which exhibited a higher oxide content and rougher grain morphology degraded cis-1,2 dichloroethene (cDCE) and vinyl chloride (VC) faster than the second product. There was no readily apparent correlations arising between reactivity and chemical characteristics of these materials, although this portion of the study has not yet concluded. BET surface areas did not correlate well with observed VOC dechlorination rates.

Introduction: Over the past 10 years permeable reactive barriers (PRBs) have become an accepted means of *in situ* remediation of groundwater contaminated with chlorinated volatile organic compounds (VOCs). The granular iron used in these applications is available from a variety of commercial sources, and comprises a mixture of ductile and cast iron cuttings and borings that are obtained by these manufacturers from a number of primary industries that use iron in the production of automotive and related industrial parts. To create the end product used in PRB applications, a number of these "feedstocks" are mixed together, put through a rotary kiln at several hundred degrees Fahrenheit in proprietary gas mixtures, cooled by a variety of methods, milled and sorted to a specific grain size range.

While the VOC degradation reactions occurring in iron PRBs are generally accepted to be dependent on the surface area of the specific iron source, several studies have shown that different commercial iron sources with the same grain size range (and similar surface area) show differing reactivity to certain VOCs. For example, greater than a three-fold difference in cDCE and VC degradation rates was observed in column studies conducted in support of a large PRB application in New Hampshire (Krug and Berry-Spark, 1999). Similar trends have been noted in other comparative tests. Figure 1 summarizes column test results of two different iron sources with the same surface area (about 1.1 m^2/gm) that were tested initially with water containing only 10 mg/l VC, followed by water containing only 10 mg/l cDCE, then 10 mg/l TCE, and finally with water containing only 10 mg/l tetrachloroethene (PCE).

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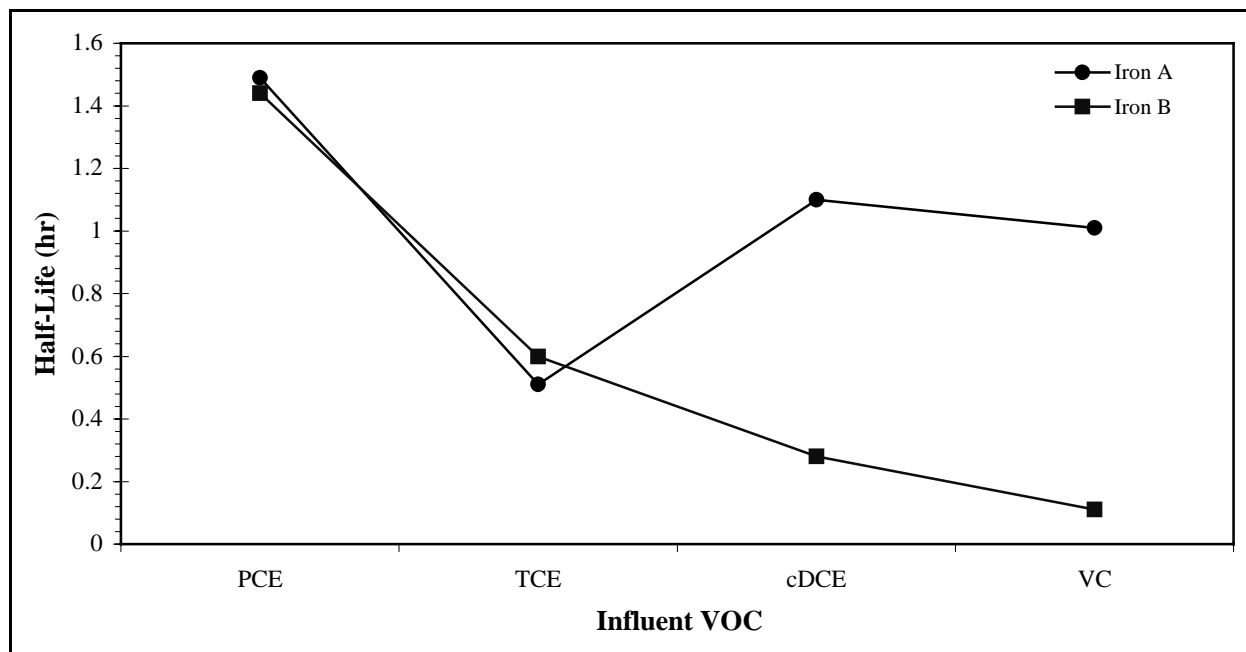
Figure 1

Although either iron source in Figure 1 might be suitable for use in some PRB applications (e.g., in groundwater dominated by PCE) the different reactivity for cDCE and VC would certainly influence the choice of iron to remediate plumes dominated by the latter VOCs. Given the similarities in surface area, it seems reasonable to question whether feedstock composition and/or iron processing causes these differences in reactivity. The remainder of the paper describes our progress to date in evaluating these influences.

Methodology: Two commercial iron suppliers (sources noted as source A and source B, herein) were contacted to obtain current samples of the commercial end product, and also samples of the six major feedstocks comprising this end product. The suppliers graciously fired and milled each feedstock in as close a manner as possible to the process used for the mixed commercial product (i.e., to a grain size of between – 8 and +50 mesh). Upon receipt, the samples were subjected to the following analyses:

(i)   column reductive dechlorination rate tests with simulated groundwater containing 10 mg/L TCE and 1 mg/L VC;
(ii)   surface area measurements by the BET method;
(iii)   metallographic examination of epoxy impregneted cross-sections of mineral grains;
(iv)   XRD analyses of the ground bulk phase and oxide coatings;
(v)   scanning election microscopic (SEM) surface examination; and
(vi)   1:1 HCl digestion of bulk phases and oxide coatings, followed by Inductively coupled Plasma (ICP) analyses of the leachate.

For brevity, detailed descriptions of test methodologies are omitted here.

Results: The composition of the influent simulated groundwater in the columns allowed us to determine half-lives for TCE and apparent half-lives for the predominant DCE intermediates (cDCE and 11DCE) and VC produced due to TCE degradation. These results are summarized in Figure 2. Note that these results must be viewed with some caution as the molar conversion of some of the influent TCE to these products will influence their apparent half-lives. However, the data supports the trend seen in the end products. TCE half-lives fall within a narrower range for all materials. In general, end product B and its feedstocks show lower apparent half-lives (higher degradation rates) than end product A and its feedstocks for the DCE isomers and VC. As one might expect, the half-lives for the commercial end products appear near the mid-point of the individual feedstocks. The specific surface area of the feedstocks were quite variable, from 0.15 m^2/g (A-0091) to 2.2 m^2/g (B-1139). There was no clear correlation of surface area to observed VOC degradation rate, within or between the source groups (Figure 3). All the B source feedstocks were above 1.0 m^2/g, while source A feedstocks were between 0.5 and 1 m^2/g, with one exception. A-0091 which had a reported surface area of only 0.15 m^2/g, yet appeared as reactive as some other A group feedstocks with much higher surface areas (Figure 3).
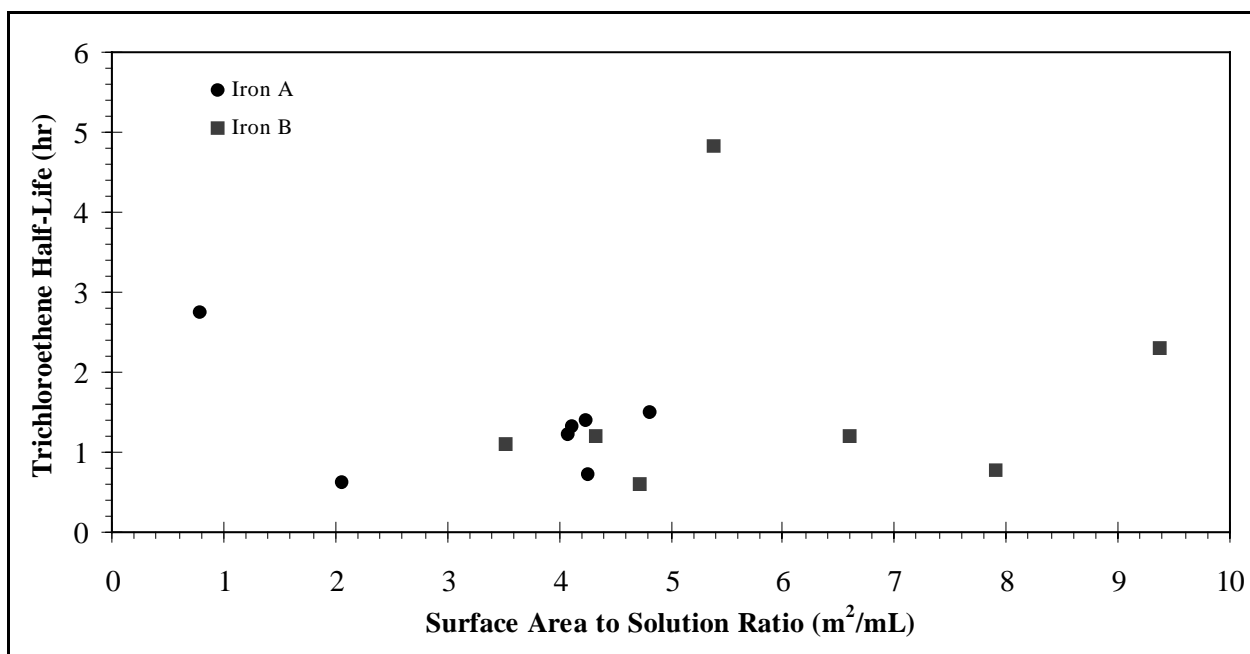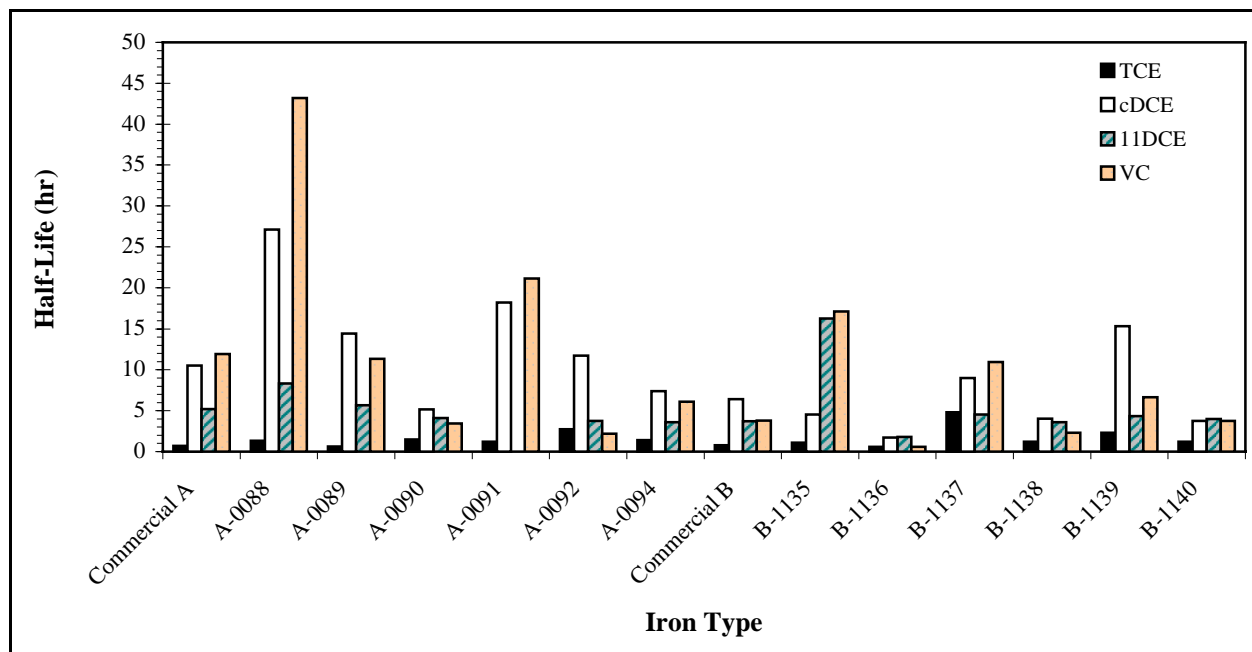

Figure 2

Figure 3

The trace metal contents in both the bulk iron and oxide phases by ICP were remarkably similar throughout the 16 samples tested. All samples contained about 2 to 3% silicon, 2 to 3% carbon, 0.3 to 0.5% manganese, 0.1 to 0.2% copper, and varying amounts of other metals in the <0.1% (100s of ppm) range. These values are typical of gray cast iron. No clear correlation between degradation rate and total trace metal content were apparent, although the potential for any correlation between specific trace metals and degradation rates are still being evaluated. We note that sample B-1136 had trace metal contents at the high end of the ranges given above.

There were no clear contrasts between source A and source B feedstocks observed during metallographic examinations, which revealed both flake and rosette-type graphite carbon structures in most samples. Ferrite and iron carbide were relatively common in all samples. The bulk source B commercial end product examined with XRD had slightly higher FeO content, consistent with its more oxidized appearance. Both end products also showed XRD peaks for iron carbide and silicon. XRD examination of surface coatings of the source B materials revealed slightly higher magnetite/maghemite material than source A, but no distinct mineralogic differences were revealed. SEM photomicrographs of the 16 samples showed the source B materials to possess generally rougher grain surfaces and more oxide coatings than the source A materials.

Conclusions and Future Work: While we have not explored all correlations among parameters in this large data set, the results to date indicate processing of these iron feedstocks, as well as their chemical composition may have significant influences on the resulting reactivity of commercial iron end products used in PRBs. The kiln firing atmosphere, cooling history, and

milling procedure appear to cause differences in surface morphology and the type and amount of oxide coatings in source B relative to source A. However, this rationale does not explain the reactivity differences within a feedstock group which were supposedly processed the same way. Clearly, there is a need to explore these relationships further in future research. One significant aspect of results to date is the apparent limited use of BET surface areas in predicting degradation behaviour. This finding has led us to investigate other means of defining the "reactive" surface area of these materials.

References:

Krug, T.A. and Berry-Spark, K. "Case Study of a Permeable Reactive Barrier at the Somersworth Landfill Superfund Site". Presentation at the US EPA – RTDF Short Course, Boston, MA, June 1999.

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