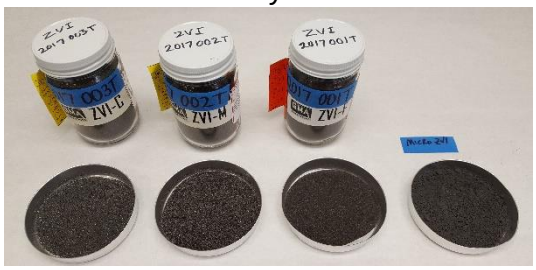
PREMIUM ZVI AMENDMENTS FOR THE REMEDIATION INDUSTRY

Provectus Environmental Products, Inc. (PEP) has teamed with GMA Industries, Inc. to offer our superior Zero Valent Iron (ZVI) amendments to the remediation industry.

- PEP ZVI - Micro
- GMA ZVI - Fine
- GMA ZVI - Medium
- GMA ZVI - Coarse
- Custom Formulations



The GMA production process for reclaiming cast steel abrasive is a controlled series of scalping, magnetic separation, cleaning via air wash separation and/or heat kiln decontamination followed by screening to size specification. Spiral separation can further separate round from non-round particles. All material recycled through our process meets or exceeds industry specifications for metallurgy, hardness and screening. Benefits of our product offerings include:

Technical
- Guaranteed Quality and Purity
- Demonstrated Reactivity
- Proven Effectiveness / Longevity
- Custom Formulations Available
- >35 Years Industry Experience

Economic
- >15% Lower Cost (on average)
- Recycled / Reuse Credits
- Made in the USA (FAR 52.225-11)

INTRODUCTION

The potential effectiveness of ZVI for remediation of groundwater impacted by chlorinated solvents has been documented since the early 1990s (Gillham, 1993). As described by Arnold and Roberts (2000), chemical transformation via ZVI occurs on particle surfaces and therefore involves at least three steps: (a) adsorption of the substrate to reactive sites on the ZVI particle surface, (b) reaction at the surface, and (c) desorption of the transformation product. In the absence of interspecies competition by catabolites, the kinetics of PCE transformation via α- and/or β-elimination reactions (and, to a lesser degree, hydrogenolysis and hydrogenation reactions) is therefore directly related to reactive surface area.

Intuitively, smaller particle sizes would promote more rapid degradation of target contaminants. However, when normalized for surface area, Liu *et al*. (2005) demonstrated that TCE degradation rates achieved with various nanoscale metals and bimetallic particles were similar to those measured with granular iron (Nurmi *et al*., 2005). Leaders in the field of ZVI technologies subsequently noted that sub-micron ZVI particles would have to remain at least 20 times as reactive as conventional sources over their lifetime to be cost-competitive (ETI, 2006).

GENERAL FEATURES

Knowing that reactive surface area is potentially associated with ZVI reactivity, scientists at Provectus have evaluated myriad ZVI particle sizes, shapes, forms and origins for their effectiveness during remedial actions. For over a decade, ZVI from GMA continuously demonstrated excellence in terms of quality, reactivity and performance. Some physical characteristics of our ZVI products are summarized below. For comparative analysis, available data (Hepure 1; Hepure 2) are presented for Ferox-Flow® and Ferox-PRB® (**Table 1**). Notable differences are particle size and shape, along with calculated surface area.

Table 1. Physical Parameters and General Characteristics for ZVI reagents.

Parameter	PEP Micro	GMA Fine	GMA Medium	GMA Coarse	Ferox® Flow*	Ferox® PRB*
1^{O} Application	EZVI	Injections	Variable	PRBs	--	--
Geometry	Spherical	Spheroidal / Angular	Spheroidal / Angular	Spheroidal / Angular	Sponge / Pseudo-flake	Sponge / Pseudo-flake
Origin	Synthesized	Cast Steel	Cast Steel	Cast Steel	Cast iron	Cast iron
Size (mesh)	>5000 to <2500	>1200 to <170	>200 to <50	>170 to <35	>1200 to <35	> 50 to <8
Size (micron)	>2.5 to <5	>12 to <90	>74 to <300	>90 to <500	>12 to <500	>297 to <2380
Ave. Size (µ)	3	45	100	297	125	297
Surface area (BET m2/g)**	(>0.9)	0.36 0.21	0.18 0.44	0.09 0.32	0.97	(0.7)
Surface area Geometric***	0.26	0.02	0.008	0.003	0.006	0.003
Iron (%)	>98	>98	>98	>98	>95	>95

Notes: *Ferox ZVI materials presented for comparative analysis (based on data available from references as noted, not reviewed by vendor). **BET analyses performed by MicroMetrics and Cathay Industries. ***Geometric mean calculated using spherical geometry, which yields values with recognized limitations.

Typical Particle Size Distribution / Sieve Analysis for GMA ZVI Product Lines

GMA ZVI - Coarse

Sieve Analysis				
Test Sieves			Test	
U.S. Mesh	Microns	Opening	%Ret	%Cum
35	495	0.0195	0.0	
50	295	0.0116	26.2	26.2
80	175	0.0069	36.1	62.3
120	124	0.0049	22.7	85.0
170	89	0.0035	11.3	96.3
pan	-	-	3.7	100.0

GMA ZVI - Medium

Sieve Analysis				
Test Sieves			Test	
U.S. Mesh	Microns	Opening	%Ret	%Cum
50	295	0.0116	0.0	
80	175	0.0069	21.6	21.6
120	124	0.0049	32.4	54.0
170	89	0.0035	31.8	85.8
200	74	0.0029	9.4	95.2
pan	-	-	4.8	100.0

GMA ZVI - Fine

Sieve Analysis				
Test Sieves			Test	
U.S. Mesh	Microns	Opening	%Ret	%Cum
170	89	0.0035	31.4	
200	74	0.0029	33.2	64.6
270	53	0.0021	28.1	92.7
325	43	0.0017	4.7	97.4
400	38	0.0015	1.4	98.8
pan	-	-	1.2	100.0

REACTIVITY TESTS

Laboratory tests were conducted by an independent, third-party (ReSolution Partners, LLC – Madison, WI) to assess ZVI reactivity with PCE under batch conditions, using procedures similar to those reported by Gillham and O'Hannesin (1994). In brief, all ZVI materials were acid-rinsed with 0.10 N HCl solution (2:1 L:S by volume) for 2 hours, rinsed with deionized water, and then vacuum filtered on 0.45 µm filter paper. A total of 10 g wet ZVI was immediately placed in 20 ml VOA vials with 3.45 ml DI water containing 0.3 ml of PCE-saturated DI water (1.5:1 L:S by volume) yielding an initial PCE concentration of 1,940 µg/L (based on data from control microcosms that contained no ZVI) and sealed with Teflon-lined caps. Moisture content measured on separate aliquots following drying in N_2-atmosphere desiccator determined ZVI dry weight. Replicate aliquots were obtained from each reaction vessel after 24 and 72 hours incubation and analyzed for chlorinated ethenes, ethene/ethane and acetylene using GC-PID (headspace). Change in pH and ORP were also measured. After 96 hours incubation the microcosms were re-spiked with an additional 1,780 µg/L of PCE and incubated for an additional 96 hours (174 hours total reaction time).

Results: Over the first 72 hr incubation period there was a clear correlation between ZVI surface area and PCE transformation rates, with the smallest ZVI particles (PEP Micro *ca*. 3 micron ZVI) exhibiting the fastest PCE removal rate of 10.58 µg/L per g ZVI/hr (**Table 2**). The relationship between reactive surface area and kinetics of PCE transformation has been previously established (Gillham and O'Hannesin, 1994), but other factors have been identified that may influence these responses (Horiba, 2016; Reinsch e*t al*., 2010; Tratnyek *et al.,* 2014). For example, ZVI degradation kinetics can reflect declining rate patterns over time resulting from interspecies competition from catabolites and occlusion of the reactive surfaces via ferrous iron and oxyhydroxide passivation. Indeed, during the short course of these studies, the smaller ZVI particles lost more of their reactivity than larger ones as measured in terms of PCE transformation kinetics. Notably, the sponge- or flake-type ZVI materials, with higher "internal" surface area, quickly lost up to >36% of their reactivity.

Table 2. ZVI Reactivity as Change (Decrease) in PCE Removal (µg/L per g ZVI/hr)

Reaction Time	PEP Micro	GMA Fine	GMA Coarse	Ferox® Flow	Ferox® PRB
96 hours	10.58	7.00	2.87	9.68	8.27
174 hours*	8.21	6.53	2.90	6.73	5.26
Loss of Reactivity % reduction	22.4	6.7	0	30.5	36.4

***PCE removal rates measured 78 hours following re-spike after an initial 96 hr reaction period**

The PCE removal rates (*i.e*., slopes of lines for PCE removal) for both of the Ferox® sponge-type ZVI products were notably slower following re-spike after an initial 72 hours reaction time, with both the blue and green lines "flattening" over time (**Figures 1a/b**). However, reaction rates for the GMA ZVI materials (*i.e*., slopes of red, gray and black lines for PCE removal) were essentially the same for the first 72 hours and the second 96 hours following a PCE re-spike. Presumably, the more substantial loss of reactivity for the Ferox® ZVI is a result of deeply embedded internal surfaces of the "sponges" being rapidly occluded/obscured by surface encrustation *et cetera* thus rendering them physically unavailable hence, inert. Particles that are more spheroidal or angular geometries are less susceptible to such blockage (Horiba, 2016).

Figure 1a. PCE, C_0 = 1,940 ug/L

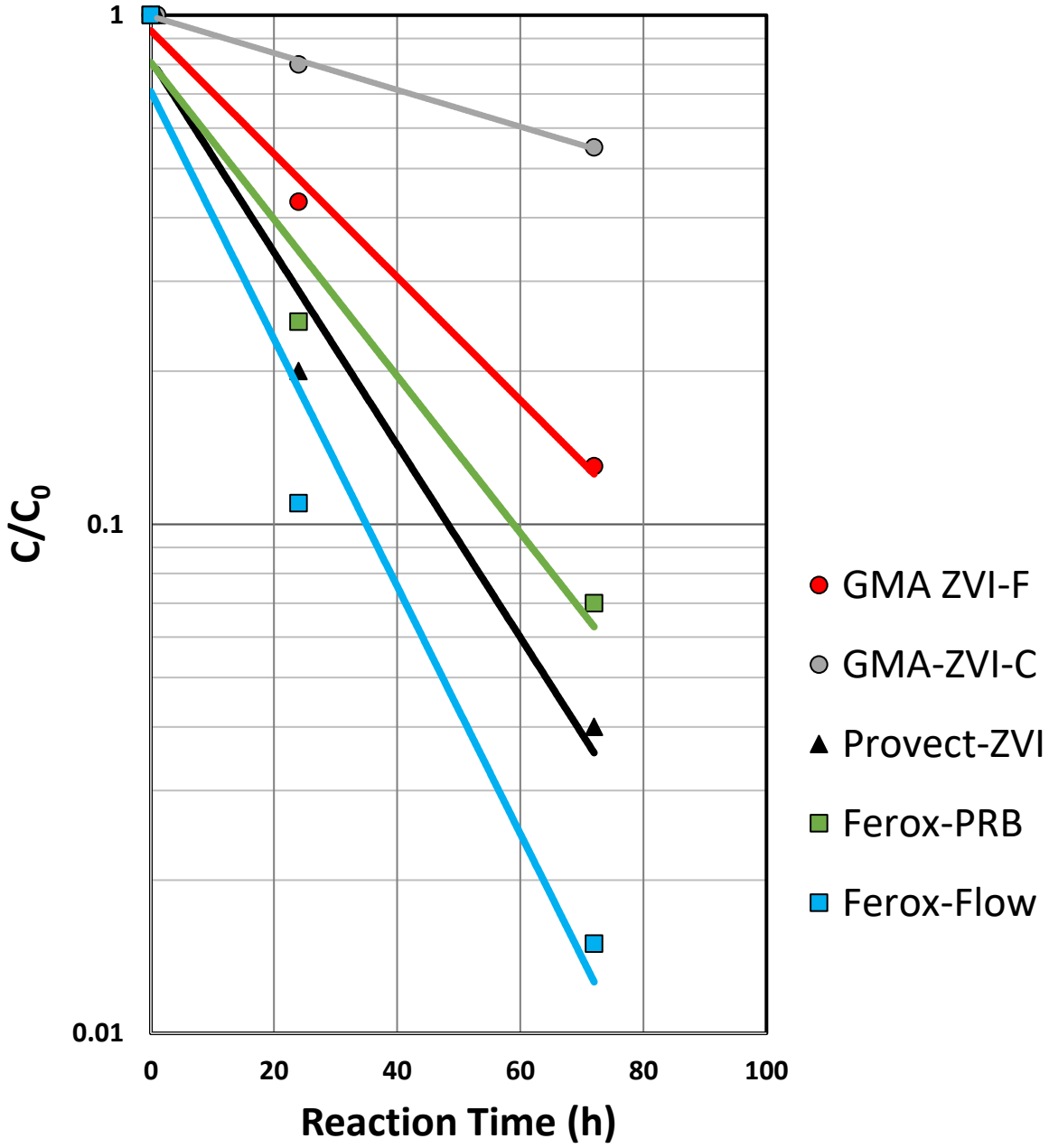
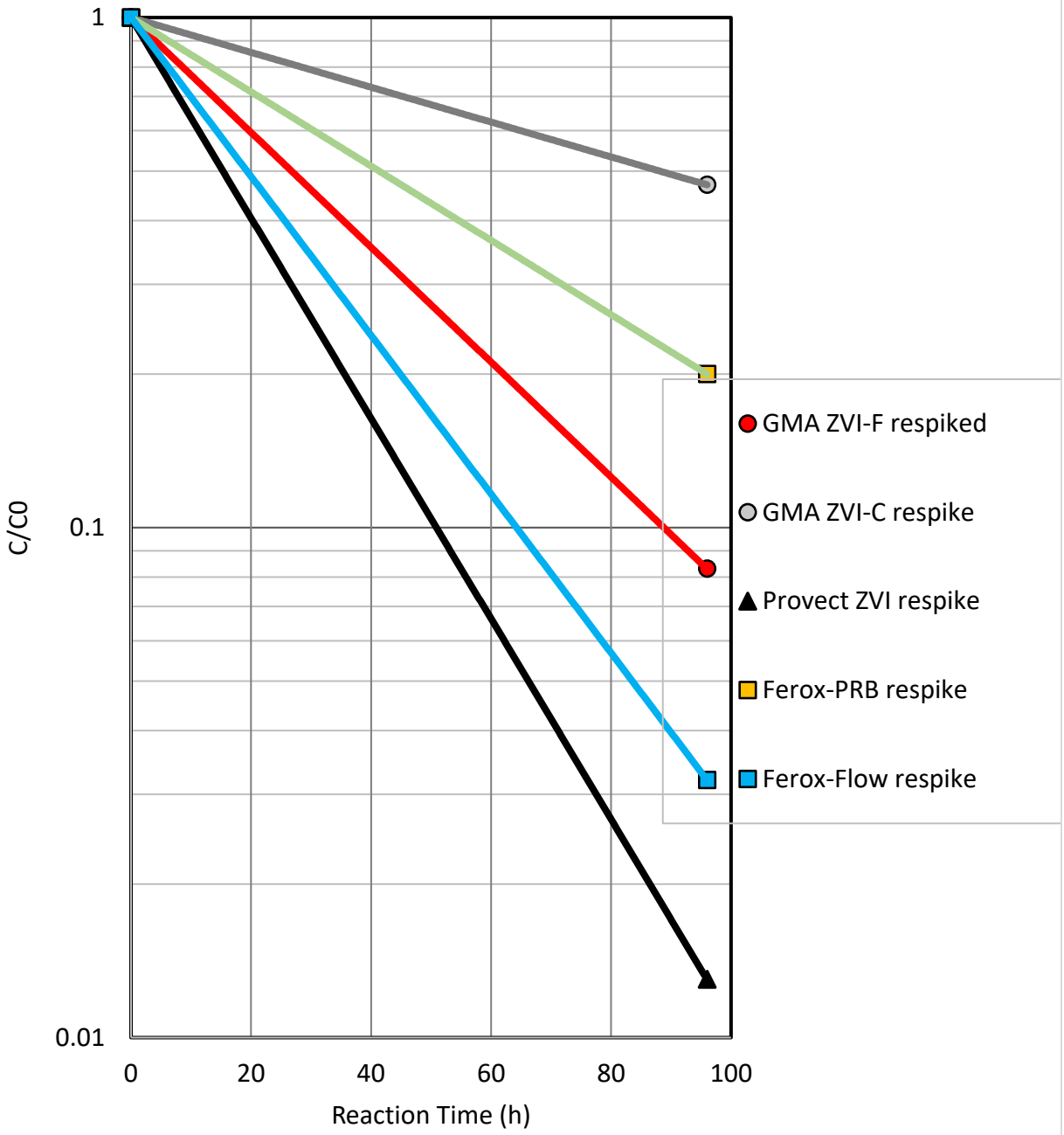


Figure 1b. Re-Spike PCE, C0 = 1,780 ug/L



CONCLUSIONS

- In general, ZVI particles that lose reactivity over a short period of time in the subsurface are usually not strong candidates for remedial applications.
- High ZVI surface area alone does not always equate to high reactivity, especially not over a period of time that is required for remedial applications (need for reactivity can range from months to many years).
- Independent, third-party tests demonstrated that all Provectus/GMA ZVI products had high reactivity that was better sustained over time.
  - PEP Micro ZVI demonstrated the fastest, sustained rate of PCE removal
  - Ferox® ZVI lost >36% of its reactivity over a short period of time (*ca*. 200 hours).
  - GMA-ZVI materials maintained their performance over the same period of time.
- GMA offers multiple types of highly reactive ZVI that can be specially selected for your project needs:
  - **PEP ZVI –** Micro (average 3 microns, or 4,800 mesh)
  - **GMA ZVI** – Fine (average 45 microns, or 400 mesh
  - **GMA ZVI** – Medium (average 100 microns, or 150 mesh)
  - **GMA ZVI** – Coarse (average 297 microns, or 50 mesh)
  - **Custom Formulations**

ORDERING

GMA ZVI products are available in a variety of packaging sizes and can be shipped internationally. PEP ZVI - Micro is specially package in 25 kg metal drums under a nitrogen blanket.

Please contact Customer Service at 800 869-9946 or email (Sales@gmaind.com) for pricing and logistics support.

38127 Ecorse Rd, Romulus MI 48174-0037

Phone: (800) 869-9946 Fax: (734) 595-1310

Website: http://www.gmaind.com/zero-valent-iron/

PROVECTUS ENVIRONMENTAL PRODUCTS, INC.
2871 West Forest Road, Suite 2 | Freeport, IL 61032
Tel: (815) 650-2230 | Fax: (815) 650-2232 | Email: info@ProvectusEnv.com

Turn-Key, Risk-Reward, Pay-for Performance, Remedial Guarantees/Warranties

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