ZVI AND ACTIVATED CARBON INTEGRATION LED TO THE EMERGENCE OF THE SYNERGY SOUGHT BUT NOT FOUND IN ZVI MIXTURES

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HISTORY OF ZVI

Zero valent iron (ZVI), in one form or another may be the most used technology for remediation of chlorinated solvent contamination (CVOCs) in soil and groundwater. It has been around since the early 1990's and its first commercial use was in construction of permeable reactive barriers (PRBs). So called, "Iron Walls" were disclosed in US Patent 5,266,213 by Robert Gillham and the University of Waterloo in Canada. Application of iron powder to plume wide treatment led to injection of powdered iron slurries into contaminated aquifers. Typical results are shown in Figure 1 **(Unit A C-9 Data)** which is data from a site in North Carolina. It was not uncommon for concentrations of parent compounds like trichloroethene (TCE) to increase due to mobilization of CVOCs from saturated soil before trending down through degradation by the iron. Over time, a few limitations became understood.

1. There is a considerable investment in time. Reductive dechlorination by the iron is a slow process and toxic byproducts (daughter products) are generated.
2. Iron is not able to degrade certain contaminants such as methylene chloride and vinyl chloride, or the rate of degradations is so slow as to render it ineffective.
3. The reaction of CVOCs with ZVI is a surface reaction and contact between the contaminant and ZVI must occur to be effective.
4. ZVI tends to passivate over time and becomes ineffective at degrading CVOCs.
5. Very often, successful degradation of parent contaminants like TCE occurred while accumulation of daughter products like cis-dichloroethene (cis-DCE) and vinyl chloride (VC) resulted.

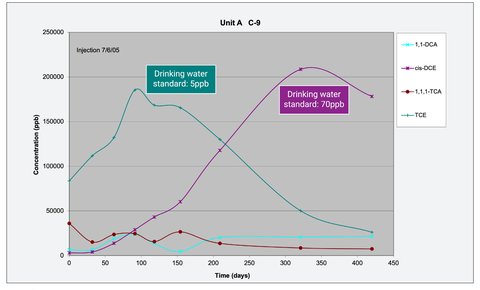


Figure 1

Over the years, many improvements to ZVI designed to address the previous limitations were introduced. The rate of reaction is tied to the metallic surface area and as particle size is reduced, the available surface area increases. Consequently, micro and nanoscale iron powders were developed to enhance reactivity. ZVI emulsified with vegetable oil was introduced by NASA targeting heavily impacted (DNAPL) sites. These products performed considerably better than previous coarse powders however they tended to be short lived in subsurface environments with life expectancy measured in months rather than years.

Another pathway was explored by Robert Gillham at Waterloo; a mixture of ZVI with absorbents and is described in US Patent 5,534,154 filed in July of 1996. The most significant limitation of the prior "Iron Wall" PRB installation was contact time. Contaminants like cis-DCE react slowly with ZVI and residence time becomes a critical parameter. The idea behind this patent is using a mixture of adsorbent (like activated carbon) and ZVI, the adsorbent will retard movement of contaminant and results in prolonging the contact time of contaminant with ZVI. Quoting from the patent, "it may be regarded that the adsorptive material acts as a retarder, to retard the passage of the contaminant and to keep the contaminant in close proximity to the metal for a very long period".

A few years later, one of Dr. Guillham's graduate students (Aiping Huo) conducted research in fulfillment of a Master of Science degree directed at mixtures of sorbents and ZVI. The thesis was published in 2001. Granular activated carbon (GAC) is a very effective sponge for absorption of organic compounds. Activation results in an extensive inner pore structure and the total surface area is very high, on the order of 900 to 1200 m2/gm carbon. Nearly all the absorption is confined to the micropore structure within the grains. Aiping evaluated several absorbents in addition to GAC in his research. In the abstract, it is mentioned that **"sorptive material with reversible and fast adsorption and desorption rates is a preferred material to be selected in this application"**.

This makes perfect sense as there must be contact between the contaminant and metal for reaction (degradation) to occur. Thus, a rapid dynamic of absorption and desorption is needed to retard movement of contaminant and maintain extended contact with the body of metal. Aiping noted that no desorption was observed for GAC. He concluded, **"the column tests confirmed that rapid desorption was important in order to achieve improved performance, thus eliminating GAC as an effective additive"**.

Contaminant absorbed within GAC is prevented from any contact with ZVI, no matter how homogeneous the mixture is because the ZVI is outside, physically separated from the GAC. The GAC effectively insulates the contaminant, preventing any physical contact with ZVI. Contaminant absorbed is not available to react with ZVI. This patent was never commercialized.

A LONG-AWAITED SOLUTION

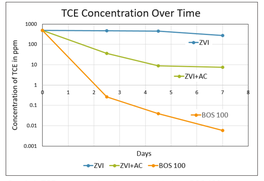
RPI introduced its BOS 100® product in 2006. Granular activated carbon is impregnated with a solution of an iron salt. This impregnated carbon is processed in a rotary furnace at a temperature of 850 degrees centigrade under a reducing atmosphere. At this temperature, the iron salt decomposes and liberates metallic iron. As the iron is forming, it partially dissolves into the carbon forming iron carbide and cast-iron grading to nanoscale deposits of crystalline metallic iron. The fact that it is partially dissolved into the carbon creates a chemical bond between the carbon and metallic iron. **BOS 100® is not simply carbon or ZVI, it is a unique material with abilities exceeding that of ZVI and absorbent.**

Most of us throughout the environmental industry model reaction/degradation using first order kinetics. In this model, the rate of reaction is a function of concentration. Think about an absorbent. It rapidly strips the contaminant from groundwater, significantly reducing the residual concentration. Most of the contaminant now resides in the microporous structure of the carbon. The concentration inside the carbon is easily two orders of magnitude higher than what originally existed in the groundwater. In BOS 100®, the metallic iron also resides within the microporous structure of the carbon. **Finally, we have the metallic iron exactly where we want it, in direct contact with the contaminant.** Not only is there contact, but the concentration within the carbon is 100 times higher than what was originally present in groundwater, so the rate of degradation will be 100 times faster. This effect is further enhanced because the surface area of metallic iron is also very large. After all, it is nanoscale deposits of metallic iron. In fact, the metallic surface area within BOS 100® is larger than commercial n-ZVI products.

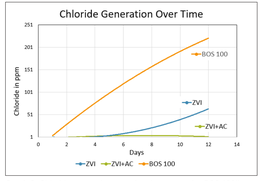
BOS 100® is the perfect marriage between activated carbon and metallic iron. Far removed from the physical mixtures of AC and ZVI described in the Waterloo 154' patent.

THE BENCH TEST

Three sets of test vials were set up to evaluate performance of sulfided microscale ZVI, BOS 100®, and a mixture of sulfided-ZVI and activated carbon. 3.25 g of a brand-name Sulfided microscale ZVI, 3.25 g of the same ZVI mixed with 325 mg of AC, or 5 g of BOS 100®, which has 325 mg of iron integrated into its AC structure, were dosed with 500 ppm of TCE in tests that were otherwise identical. The ZVI has 10x more iron by dose than the BOS 100®.



Graph 1. TCE concentration decreases with time. BOS 100® demonstrates the largest decrease, while ZVI alone indicates the least decrease.



Graph 2. Chloride generation over time is greatest for BOS 100®. ZVI generates more chloride than does ZVI and AC mixed.

In the first graph, TCE concentration versus time for the ZVI-only test shows that the TCE concentration minimally decreases (Blue line). The ZVI and AC combination fares better (Green line). The BOS 100® performs the best (Orange line). Most vendor presentations stop at this first graph, the results of which are absorption-driven. **But degradation is quintessential to environmental restoration. Solid proof of TCE degradation is chloride generation.**

In the second graph, the chloride generation over time does not mirror the TCE decrease observed in the first graph. BOS 100® leads the pack in chloride generation. In contrast, ZVI generates 8.5x less chloride than BOS 100® but still outperforms **the ZVI and AC mixture which is the least effective of the three**.

The contrast between the ZVI and the ZVI and AC mixture is telling. In the first graph, the ZVI and AC mixture absorbs the TCE, lowering its concentration in the solution. This same absorption protects the TCE from the ZVI, so less chloride is produced than by ZVI alone. The BOS 100® is different. It generates 16x more chloride than the ZVI and AC mixture because the iron is integral to the AC. When TCE is absorbed, it collocates with the iron.

THE IMPOSSIBLE DNAPL REMEDIATION

Not long ago, the extensive apartment complex pictured to the right was not there. Instead, there was an open field with soil and groundwater heavily impacted by TCE. DNAPL existed at multiple locations with TCE at 25,000 to 54,000 ppm in soil. Groundwater TCE was in the hundreds of ppm. Site remediation could have been considered technically impractical. RPI's BOS 100® was used at the site, and years later, the complex above was built on DNAPL-ground zero!

The finished site with full apartment construction

SITE BACKGROUND

The site was underlain by river deposits and sedimentary bedrock. Impacted alluvium included approximately 5 meters (m) of interbedded granular and fine-grained deposits. Beneath the source area was approximately 15 m of well-graded sands and gravels underlain by an aquitard of silt and silty clay where DNAPL pooled at the interface. Impacts did not extend into the underlying claystone bedrock.

Subtle facies changes resulted in solute concentrations that varied by orders of magnitude in distances of only centimeters (cm). This inherent complexity was the impetus for quantitative, high-resolution data to characterize site conditions and design, implement, and demonstrate the performance of the BOS 100® remedial program.

This is the site prior to the apartment complex being built

The DNAPL portion of the plume was reduced from percent-level concentration to closure levels. The dissolved-phase plume was also mitigated and site-closure monitoring began in 2011. A Request for No Action Determination was submitted and closure of the site was granted.

LONGEVITY

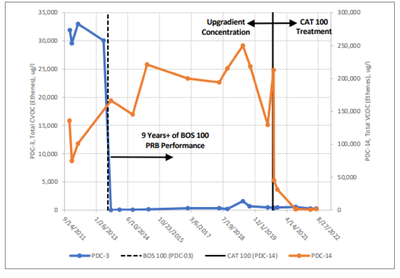
BOS 100® and CAT 100 persist in degrading halogenated compounds long after vegetable oils, ZVI (sulfonated and otherwise), and various other products have been consumed, passivated, or polished off. For in situ remediation products, longevity is inseparable from quality.

BOS 100® attains its quality through time in the furnace. A ZVI base is not mixed or soaked into the activated carbon. The ZVI is not somehow rattling around in the carbon or merely deposited on its surface. Metallic iron is fired at 850°C into the activated carbon under a reducing atmosphere. Iron and carbon become an inseparable molecular structure in the furnace with characteristics beyond that of activated carbon or ZVI. One of these characteristics is – longevity.

Having BOS 100® as its base, CAT 100 builds on the stability of BOS 100® by adding a microbial population that degrades the contaminants and preserves the metallic iron. This combination is a figurative double shot of endurance.

Longevity is a quality characteristic that saves your client money. The need for multiple installations of an in situ product due to poor durability is a quality problem that raises costs. Regarding in situ remediation, longevity is quality.

Total CVOCs (Ethenes only) Versus Time – BOS 100® & CAT 100 shows longevity. The graph, moving from left to right, shows the activity of BOS 100® in a PRB application (Blue line) against an untreated area (Orange line). Total CVOCs have been contained and, thus, remediated for nine (9) years. At approximately six years post-PRB installation, the area around the previous control (Orange line) was treated with CAT 100 by in situ injection. Total CVOCs have been restrained for about 3 years. The regulatory authority has placed the site in managed closure.



BOS 100® OUTPERFORMS EVERY TYPE OF nZVI

- **Risk Reduction** – unlike ZVI which has no ability to rapidly reduce concentrations of contaminants in groundwater or soil, BOS 100® can reduce concentrations in groundwater by 90% to 98% overnight.
- **Rate of degradation** – because metallic iron resides deep within the microporous structure of activated carbon, the rates of degradation by BOS 100® is roughly 100 times faster than that of sulfided nZVI.
- **Longevity** – metallic iron in BOS 100® has been shown to outlive/outperform sulfided nZVI by years.
- **Ability to degrade "recalcitrant" contaminants** – BOS 100® can readily degrade difficult contaminants like vinyl chloride.

TIMELINE OF INNOVATION

- **NOVEMBER 1993** – Iron Wall patent 5,266,213 Robert Gillham/Waterloo
- **1996** – Mixtures adsorbents and ZVI – 5,534,154 Robert Gillham/Waterloo
- **OCTOBER 2001** – Emulsified ZVI – 6,664,298 B2 NASA
- **JULY 2004** – nanoscale ZVI and Bimetallic Compositions David Vance
- **AUGUST 2004** – Activated Carbon Impregnated with Metallic Iron – 8,097,559 RPI BOS 100®
- **AROUND 2011** – nZVI – introduced around 2011 with significant research over the last five years on Sulfided nZVI
- **MAY 2016** – Marriage of BOS 100® and Bio – 10,583,472 B2 RPI CAT 100