The Evolution of a Field Application of nano Scale Zero Valent Iron (nZVI) in a Deep Low Permeability Aquifer
Site Description

- Site is approximately 72 acres located in Goodyear, Arizona
- located in the western part of the Salt River Valley in the Sonoran Desert of central Arizona
- semi-arid climate, average rainfall 7.1 inches per year
Site Location Map
Site History

- operated by Unidynamcis Phoenix Inc. from 1963 to 1993
- used for research, design, development, testing and manufacturing of ordnance components and related electromechanical devices used in defense and aerospace applications
- site utilized approx. 180 different chemicals during its operation
- site consisted of 25 buildings, 10 – 750 gallon sedimentation tanks, 12 drywells, and 2 shallow oxidation ponds
- disposal of non explosive waste chemicals was done exclusively onsite through drywells, sedimentation tanks, and oxidation ponds
- Placed on NPL in late 1980s
Regional Geology and Hydrogeology

- site is located within the basin and range physiographic province, West Salt River Valley
- soils are primarily sandy loams, loams, and clay loams on alluvial fans and valley plains
- three hydrogeologic alluvial sub units:
  1. Upper Alluvial Unit (UAU) – gravel, sand and silt, mostly unconsolidated
  2. Middle Alluvial Unit (MAU) – silt, siltstone, silty sand and gravel, weakly consolidated, moderately well cemented
  3. Lower Alluvial Unit (LAU) – clays, silts, mudstone, evaporites, sandstone, gravel, conglomerate and andesitic basalt, moderately to well cemented, upper part of unit is weakly to well cemented and contains inter-bedded sand, gravel and conglomerate
Site Geology and Hydrogeology

- site overlies the UAU
- 350 ft thick
- local stratigraphic sequence of UAU:
  1. Subunit A – silty sands with thin lenses of gravel and fine-grained soil, from surface to 160 ft bgs, 1/3 to 1/2 of lower portion saturated and considered an aquifer, depth to water 70 to 80 ft bgs, regional groundwater flow, north-northwest
  2. Subunit B – sandy silts and/or clay, 50 to 70 feet thick, fully saturated, possibly discontinuous in north areas of the site
  3. Subunit C – silty sands, sandy silts, gravely sands, 130 ft thick, fully saturated and considered an aquifer, local gradient west north-west
Contaminants of Concern

- Primary COCs identified at the site include:
  - TCE
  - perchlorate
  - found in all subunits
  - highest soil concentrations to date found in the main dry wells area (5,585 ppm TCE, 41.5 ft bgs)
  - highest GW concentrations to date located upgradient of the main drywells area (41,500 ug/L TCE, 110 ft bgs)
Main Drywells Area
nZVI Chemistry

Zero-Valent Iron Reactions

(1) Direct reduction on metal surface:
\[ \text{Fe}^0 + \text{H}_2\text{O} + \text{XCl} = \text{Fe}^{2+} + \text{OH}^- + \text{XH} + \text{Cl}^- \]

(2) Anaerobic iron corrosion:
\[ \text{Fe}^0 + 3\text{H}_2\text{O} = \text{Fe}^{2+} + 3\text{OH}^- + \text{H}_2 + \text{H}^+ \]

(3) Reductive dehalogenation by hydrogen gas:
\[ \text{H}_2 + \text{XCl} + \text{catalyst} = \text{XH} + \text{H}^+ + \text{Cl}^- \]

(4) Aerobic iron corrosion:
\[ 2\text{Fe}^0 + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{Fe}^{2+} + 4\text{OH}^- \]
Bench Test Column

- 4 columns were tested
  - 3 with 2%, 1%, 0.5% nZVI,
  - one with 0.5% palladium coated nZVI

Column packed with a mixture of site soil and various percentages of PolyMetallics™ nZVI

Flow Direction

Influent – site groundwater spiked with known concentration of TCE, flow rate based on site groundwater flow velocity

Effluent sampled for TCE
Results of Column Test

ZVI Column Study - TCE Trends

Concentration (µg/L) vs. Pore Volumes

- 2.0% ZVI
- 1.0% ZVI
- 0.5% ZVI
- 0.5% PZVI

90% Reduction of TCE
Lessons Learned from Column Test

- column test proved concept, nZVI will reduce TCE
- column test must approximate site conditions as closely as possible, no ZVI was injected through the site material in the column
- kinetics testing was not completed, should be completed for all technologies with reaction rates
Field Pilot Test

- nZVI was shipped in 50 gallon drums in a water slurry
- drums were onsite several weeks prior to injection
- slurry was measured and mixed with potable water to produce a 20% nZVI injectate mixture
- mixing was done in a 500 gallon polytank through recirculation
- recirculation hose clogged, so material was mixed with a mechanical mixer prior to addition to the polytank
- mixing was completed for 30 to 45 minutes prior to injection
Field Pilot Test

- nZVI slurry was injected under pressure (50 psi) into well IW-01
- immediate back pressure resulted in reduction of injection pressures
- refusal of nZVI slurry occurred, moved to injection well IW-02
- same injection refusal occurred
- 50 lbs of nZVI were injected
- projected volume was to be 1000 lbs
Lessons Learned from Pilot Test Phase I

- Material properties are very critical to delivery (i.e. particle size and age)
- Chemical properties including pH, ionic strength and surface chemistry (coatings) have the potential to influence mobility
- Agglomeration is a persistent problem with nZVI and can be caused by material age, shipping conditions and groundwater chemistry
- Agglomeration is irreversible, additional mixing will not sufficiently reduce agglomerated particle size
- Site specific chemistry must be considered
- Mixing and injection techniques should be tested at the bench scale to the extent practicable
- Information on kinetics of material are required
Post Injection Testing

• Falling Head Tests
  – Performed on both Injection Wells
  – Pre-Injection Recovery ~ 15 minutes
  – Post-Injection Recovery ~ 4 – 5 hours
Phase II Pilot Test

• bench testing for batch kinetics on raw nZVI and nZVI amended with dispersant solution were completed prior to Phase II test
• 2 additional injection wells were installed in June 2007
• Phase II field injections were completed summer 2007
Injection System Layout
Injection System Layout

- Injection Well
- Monitoring Well

Apparent Groundwater Flow Direction

Note: Not to Scale
Phase II Injection Results

IRZ IW-01 (5 Feet Downgradient)

IRZ IW-03 (20 Feet Downgradient)

IRZ IW-08 (14 Feet Downgradient)
Summary of Field Pilot Testing Phase II

- Injected 2,700 gallons of nZVI solution (~50 lbs) over three days
- nZVI distribution was likely limited to the immediate screen area
- Preliminary data indicate rapid decline in TCE concentrations in wells near the injection location, but rebound was prevalent
- Injection wells are not re-usable
Phase III - Pilot Test

- injection under pressure
- nZVI solution increased to 21 g/L
- nZVI preparation remained the same
- goal to inject 8000 gallons over 4 fractures
- 350 lbs nZVI per fracture
- Completed February 2010
Injection Technique

-
TCE Results
Hydrogen Results
Conclusions

• Pressure injection method was successful in delivering the calculated volumes of nZVI
• Radius of influence was estimated at 20 feet from injection point
• Future applications are under discussion
• Method may be cost prohibitive based on use of nZVI, injection method with more cost effective injectate will be necessary to ensure delivery of amendment
Acknowledgements

CRANE POLYFLON
A Crane Co. Company
Questions?