Innovative Options for Ex-Situ Removal of Perchlorate and Explosives in Groundwater

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Katherine Weeks (AMEC)
Scott Veenstra (AMEC)
David Hill

Innovative Technology Evaluation (ITE) Team

- Army National Guard
- Army Environmental Center
- Army Corps of Engineers
- AMEC Earth and Environmental

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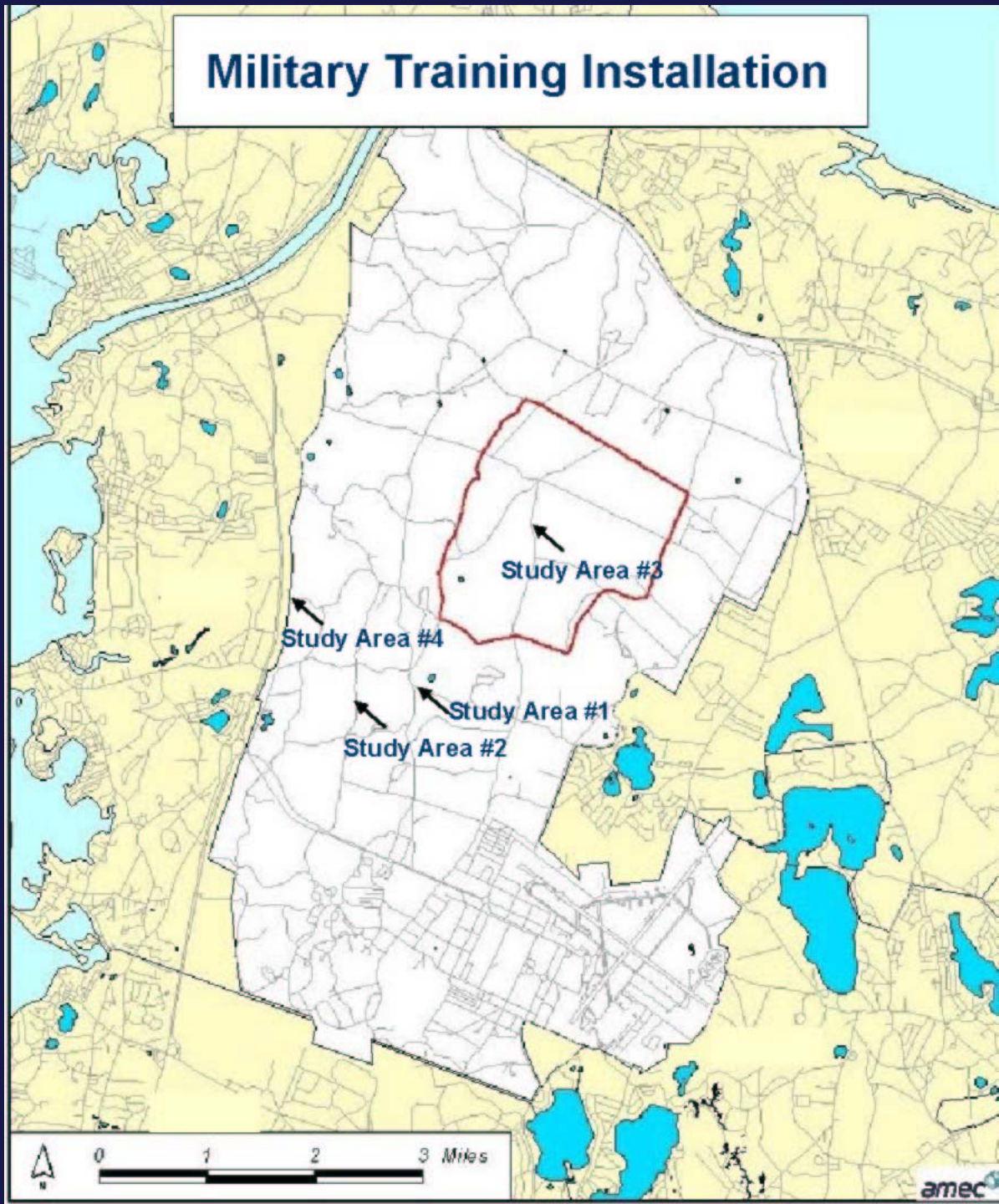
- US Filter Corporation
- Pennsylvania State University (PSU)
- The Purolite Company
- DL Maher (div. of Boart Longyear, Inc.)

ITE History and Mission

- History - Impact Area and Ranges at Site used for training since 1911
- Mission - Evaluate innovative remediation technologies to treat low levels of perchlorate and explosives in soil and groundwater



Ex Situ Groundwater Treatment Technology Evaluation

Technologies evaluated

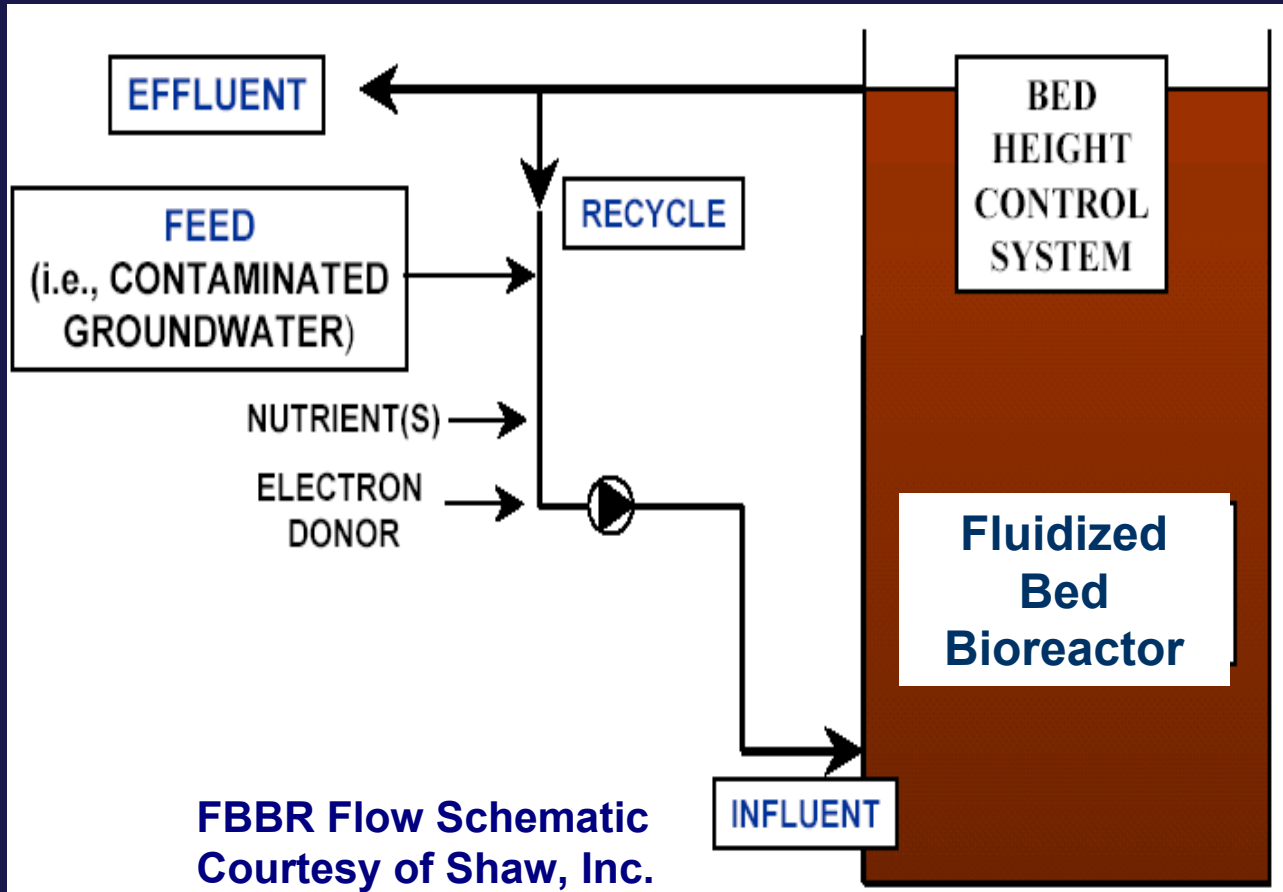
- Fluidized Bed Bioreactor (FBBR)
- Granular Activated Carbon (Standard GAC)
- Granular Activated Carbon tailored by the addition of a proprietary cationic monomer (Tailored GAC)
- Ion Exchange Resin (IX Resin)

Site Contaminant and Aquifer Characteristics

Parameter	Area #1	Area #2	Area #3	Area #4
Perchlorate (µg/L)	100	5	1	1
RDX & HMX (µg/L)	200	0	6	0
Nitrate as N (mg/L)	2.2	<0.12	0.05	0.1
Sulfate (mg/L)	4.6	6.1	4.4	5.0
Chloride (mg/L)	7.6	7.9	7.2	8.7
Total Organic Carbon (mg/L)	<1.0	<1.0	0.59	0.68
Orthophosphate as P (mg/L)	<0.2	<0.2	<0.2	<0.2
Iron (mg/L)	<0.5	<0.5	<0.5	<0.5
pH (S.U.)	5.8	6.3	5.4	5.7
Dissolved Oxygen (mg/L)	9.8	9.4	10.6	9.2

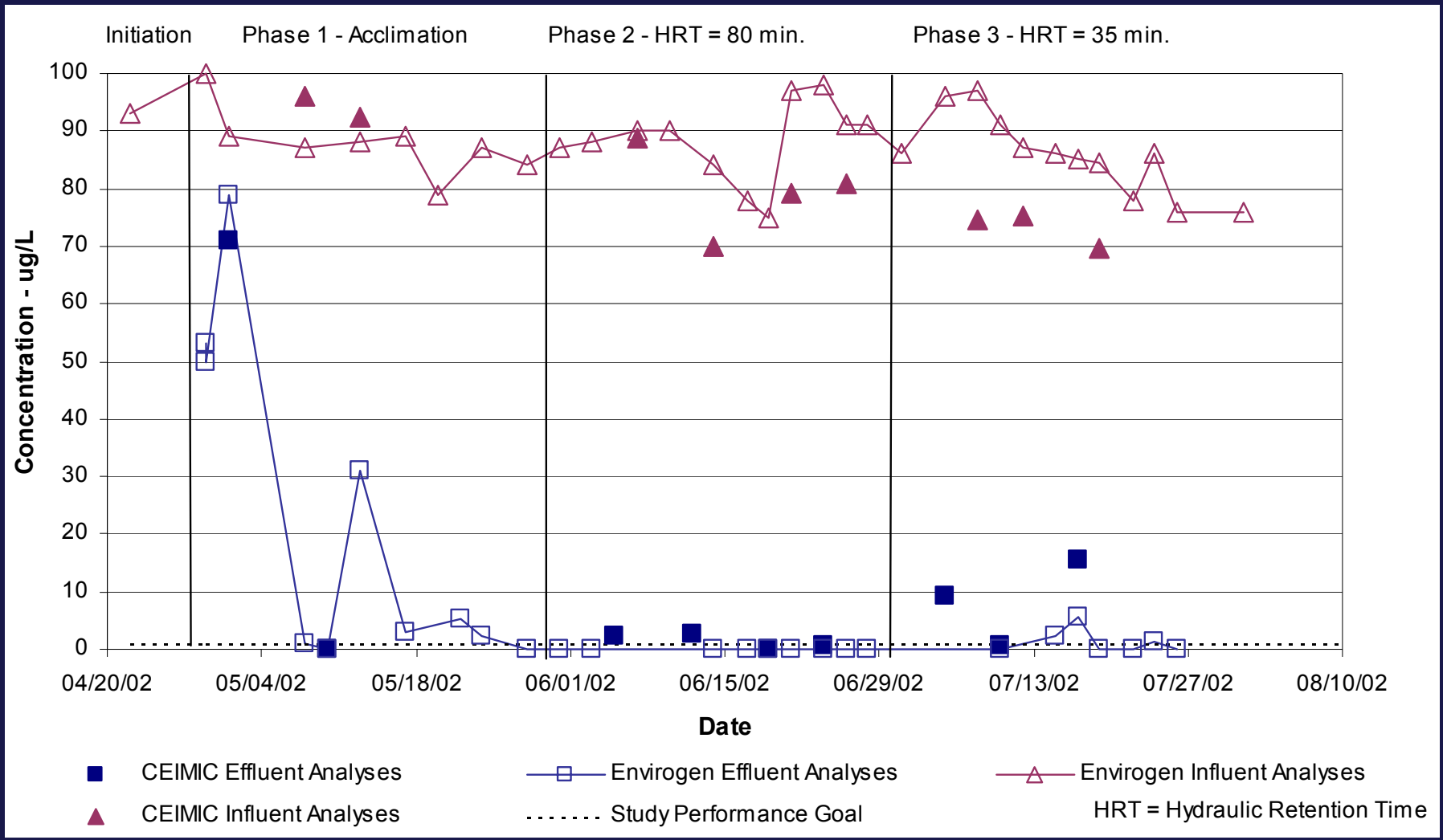
Fluidized Bed Bioreactor Overview

- FBBR experience
  - In use at DoD and commercial sites - Longhorn AAP (TX), Aerojet (CA)
  - Vendor – Shaw Environmental & Infrastructure, Inc.
  - Prior demonstration at lab scale on TNT but not RDX
- FBBR study
  - Bed medium (GAC)
  - Biomass
  - Nutrient substrate
  - Nutrients (N, P)
  - pH control
  - Fluidization control



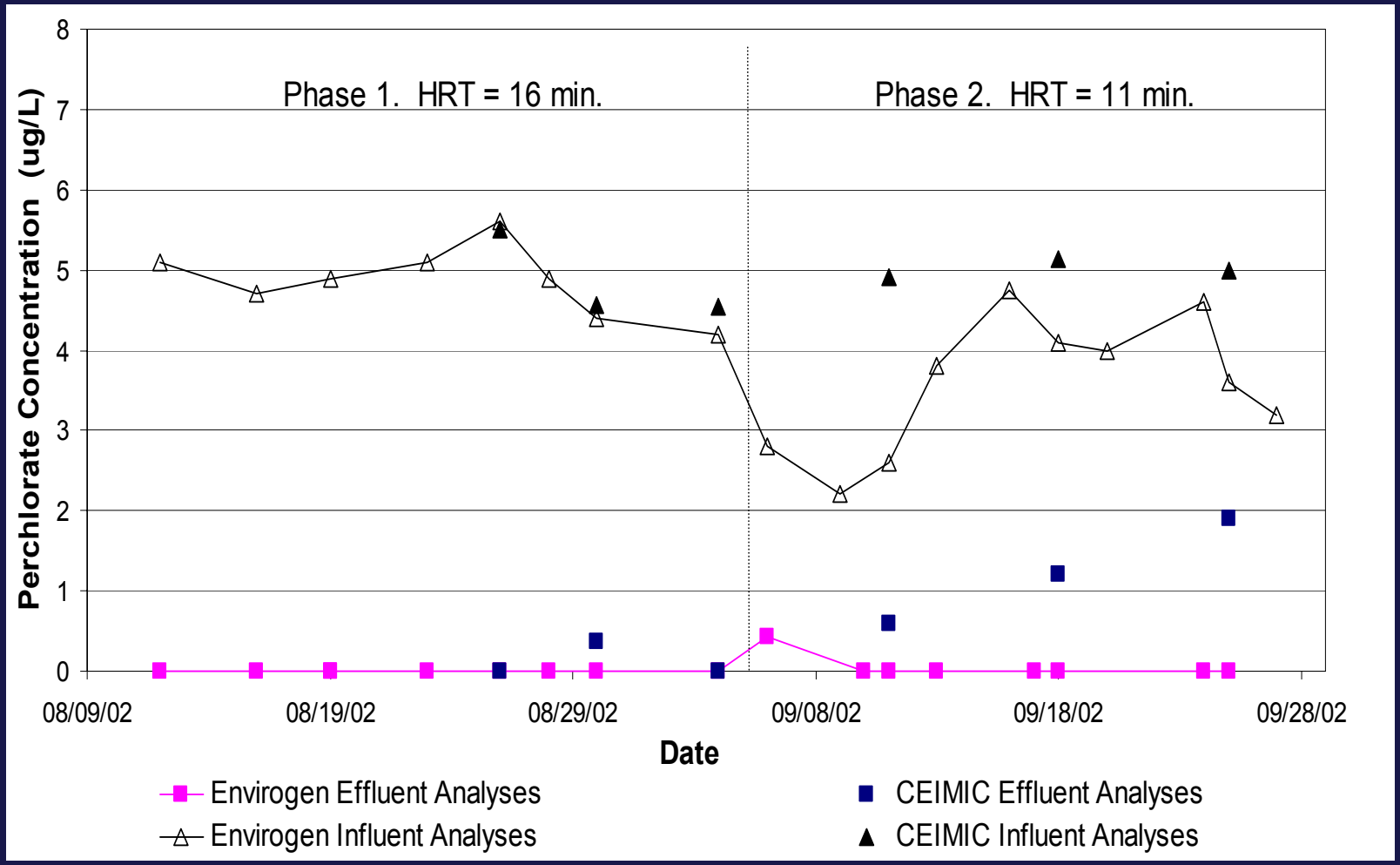
FBBR Flow Schematic
Courtesy of Shaw, Inc.

FBBR Area #1 Study Results



FBBR A (Acetic Acid) Effluent Perchlorate vs. Time

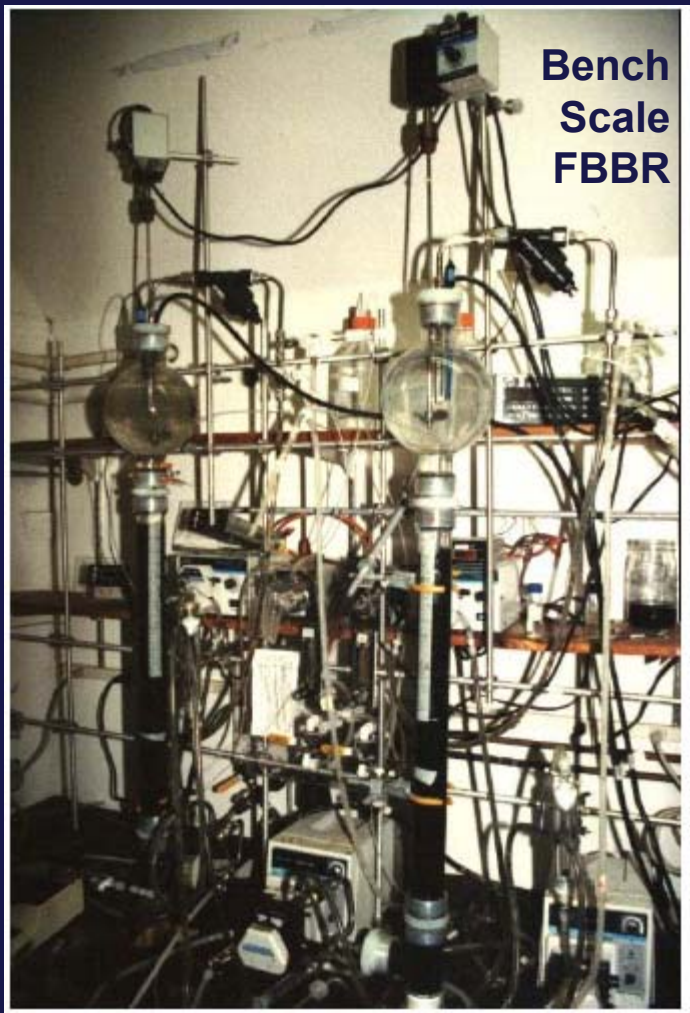
FBBR Area #2 Study Results



FBBR A (Acetic Acid) Effluent Perchlorate vs. Time

FBBR Study Conclusions

- Area #1 Study (Perchlorate and RDX)
  - Perchlorate degraded to <1.0 µg/L at Hydraulic Retention Time (HRT) of 35 min.
  - RDX degraded to <2 µg/L at HRT of 80 min.
- Area #2 Study (Perchlorate alone)
  - Perchlorate degraded to <1.0 µg/L at HRT of 16 min.
  - Addition of nitrate is required when perchlorate and other electron acceptors are low.



Granular Activated Carbon (Standard GAC)

- GAC - an old friend to water treatment, used on explosives
- Theory
  - Contaminants held onto carbon surface via adsorption
  - Contaminants removed but not destroyed
  - Initial Breakthrough - after carbon's capacity is exhausted, levels in effluent are above detection limits
  - Rapid Small Scale Column Tests (RSSCTs) predict performance of a full-scale system
- Goal - Can Standard GAC remove perchlorate from groundwater at very low concentrations?
- Test - RSSCTs to find how much groundwater can be processed before breakthrough
  - Carbon provided by US Filter
  - Tests performed by PSU (Dr. Fred Cannon, Bob Parette)

Standard GAC RSSCTs

Parameter	Test #1	Test #2	Test #3	Test #4	Test #5
Source Study Area	#4	#1	#1	#1	#3
Perchlorate (µg/L)	1	5	5	5	1
Influent RDX (µg/L)	0	0	0	0	5.5
Influent HMX (µg/L)	0	0	0	0	0.5
EBCT (min)	20	5	7	20	10
BV to Perchlorate BT	30,000	15,000 to 25,000	20,000	20,000 to 24,000	40,000 to 46,000
BV to RDX BT	N/A	N/A	N/A	N/A	308,000
Effective Bed Life (mo)[1]	13	2	3-4	9-11	9-10

EBCT = Empty Bed Contact Time BV = Bed Volumes BT = Breakthrough

[1] Effective Bed Life = time between media change-outs (months)

Modified Granular Activated Carbon (Tailored GAC)

- Theory - Increasing number of positive charges on GAC surface improves perchlorate adsorption
- Goal - Can modified GAC offer an economical alternative to conventional GAC?
- Test - Preload the GAC with organic monomer with a strong positive charge (Tailored GAC)
  - Tests performed by PSU (Dr. Fred Cannon, Bob Parette)
- Materials - Proprietary cationic monomer - NSF approval is pending

Tailored GAC RSSCTs

Parameter Source Study Area	Test #6 #2	Test #7 #3	Test #8 [3] #3
Perchlorate (µg/L)	5	1	1
Influent explosives (µg/L)	0	6	6
EBCT (min)	5	9	9
BV to Perchlorate BT	77,000 to 170,000	270,000	270,000
BV to RDX BT	N/A	8,000	308,000
Effective Bed Life (mo) [1]	9 - 19	56 [2]	56

EBCT = Empty Bed Contact Time BV = Bed Volumes BT = Breakthrough

[1] Effective Bed Life = time between media change-outs (months)

[2] Bed Life applies only to perchlorate treatment, not RDX treatment

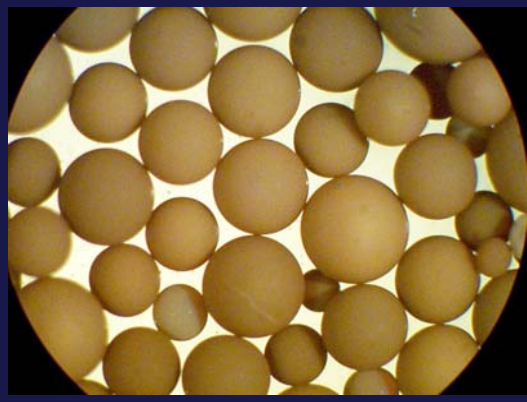
[3] Test #8 combines results from Tests #5 & #7 (2 columns: 1 Tailored GAC, followed by 1 Standard GAC)

RSSCT Results & Conclusions

- For 5 µg/L perchlorate in groundwater
  - Standard GAC - operational life is 3 - 4 months (10-minute EBCT)
  - Tailored GAC - operational life is ~ 20 months (5- minute EBCT)
- For 1 µg/L perchlorate and 6 µg/L explosives in groundwater
  - Standard GAC - operational life is ~ 9 months (10-minute EBCT)
  - Tailored GAC followed by Standard GAC - operational life is ~ 56 months (8.5-minute EBCT)
- Sorption differences
  - Standard GAC very effective for explosives, slightly effective for perchlorate
  - Tailored GAC very effective for perchlorate, ineffective for explosives

Ion Exchange Resins (IX Resins)

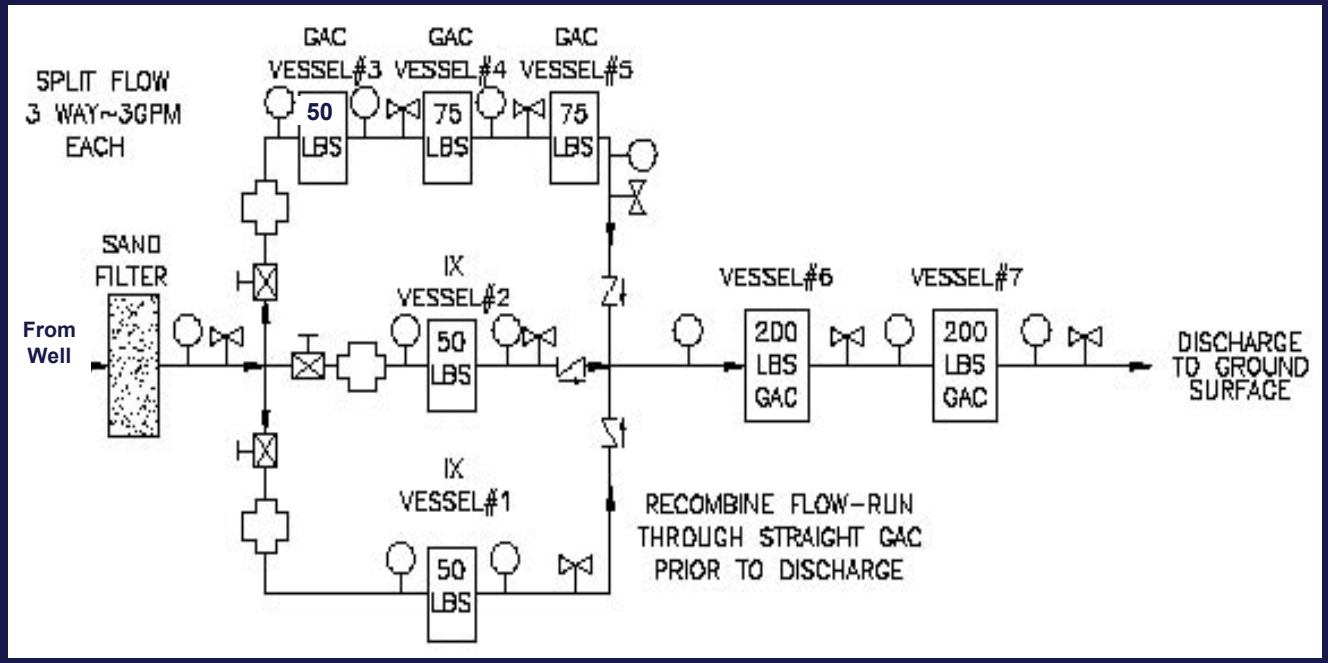
- Theory - Anions held to a +charged surface are exchanged for other anions. These IX resins do not remove explosives/other neutral species
- Test - Field studies using Type I Styrenic Resins & Nitrate-Selective Resins
- Perchlorate Selective Resins evaluated, but appear to have similar effective bed life to Nitrate-Selective Resins for treating perchlorate at the site, at higher expense
- Materials - Purolite A520E, Purolite A600E are NSF approved for use in water supply



Ion Exchange Resin Beads
Courtesy of The Purolite Company

Field Study - Tailored GAC, IX Resins

- Goal #1 - Is Tailored GAC effective at field scale?
- Goal #2 - How much will monomer leach from Tailored GAC?
- Goal #3 - Will a “polishing” GAC vessel capture leached monomer?
- Goal #4 - Can IX resins treat low concentrations of perchlorate?



Field Study - Tailored GAC, IX Resins

Media	Tailored GAC	N – S Resin	T1 - S Resin
Source Study Area	#2	#2	#2
Perchlorate (µg/L)	3	3	3
Explosives (µg/L)	0	0	0
EBCT (min)	5	5	5
Bed Volumes to date	21,000	21,000	21,000
Predicted Bed Volumes	>150,000	72,000	15,000
Predicted Bed Life (mo)[1]	> 16	> 8	> 1.5

N-S = Nitrate Selective ion exchange resin
T1-S = Type I Styrenic ion exchange resin
EBCT = Empty Bed Contact Time
BV = Bed Volumes
[1] Predicted Bed Life = time between change-outs (months)

Field Study: Tailored GAC and Ion Exchange Treatment

ITE Field Study Results & Conclusions

- Initial effluent from a Tailored GAC unit contains < 1 mg/L monomer; after one month < 0.1 mg/L.
- Preliminary: The Nitrate Selective Resin will likely remove perchlorate using an EBCT of 5 minutes, for an operation bed life of ~ 8 months.
- Preliminary: The Type I Styrenic Resin will likely remove perchlorate using an EBCT of 5 minutes, for an operation bed life of ~ 2 months.

Implementation Cost Comparison

Treatment Scenario	Comparative Cost
5 µg/L perchlorate	
° Standard GAC	2x
° Tailored GAC	1.5X
° Nitrate Selective IX Resin	4x
1 µg/L perchlorate, 6 µg/L explosives	
° Standard GAC	1X
° Tailored GAC[1]	2X
° Nitrate Selective IX Resin	4X

Assumptions:
- Costs are for media only, except for Tailored GAC, where extra analytical costs are added. If monomer is NSF approved, costs are reduced by 0.5X
- [1] Tailored GAC system requires extra Standard GAC vessel to treat explosives

ITE Study Recommendations

- Standard GAC can treat very low concentrations of perchlorate
- Standard GAC can be especially effective when explosives are present in addition to perchlorate
- Ion Exchange Resins can treat low concentrations of perchlorate to very low treatment goals.
- Tailored GAC may be an economical alternative to ion exchange resins. Further work to obtain NSF approval should be pursued.
- Applicability of ITE results to other sites is dependent on site characteristics -- RSSCTs, field studies recommended

References and Resources

- AMEC Earth & Environmental, Inc.
  - Katy Weeks – katherine.weeks@amec.com
  - Scott Veenstra – scott.veenstra@amec.com
- Shaw Environmental and Infrastructure, Inc.
  - Paul Togna - paul.togna@shawgrp.com
  - Bill Guarini - william.guarini@shawgrp.com
- Pennsylvania State University
  - Dr. Fred Cannon - fcannon@psu.edu
  - Bob Parette - rbp122@psu.edu
- US Filter
  - Dr. James Graham - GrahamJ@USFilter.com
  - Tim Peschman - PeschmanT@USFilter.com
- The Purolite Company
  - Tedd Begg - tbegg@puroliteUSA.com
  - Francis Boodoo - fboodoo@puroliteUSA.com