Case History:

Removal of Perchlorate from Groundwater
at the
Longhorn Army Ammunition Plant

Presented at the

Sixth In Situ and On-Site Bioremediation Conference

by
Bill Guarini
Envirogen, Inc.
609 - 936-9300

Acknowledgements

U.S. Army: Cyril Onewokae

David Tolbert

U.S. Army Corps of Engineers: Jonna Polk

Cliff Murray

Dawn Knight

Complete Environmental Systems

Deerinwater Environmental Systems

Aerojet

U.S. Filter/Envirex

Envirogen's Engineering Group

Presentation Overview

1. Sources of perchlorate
2. Biological degradation of perchlorate
3. Fluid Bed Reactor
4. Aerojet Full Scale System Success
5. Longhorn Army Ammunition Plant
   - History
   - Problem
   - Full Scale System Success
6. Summary

Sources of Perchlorate

- Fireworks and matches
- Airbag inflators
- Nuclear reactors and electronic tubes
- Lubricating oils
- Tanning and finishing leather
- Mordant for fabrics and dyes
- Electroplating aluminum refining
- Rubber manufacturing
- Paints and enamels
- Fertilizers

Sources of Perchlorate

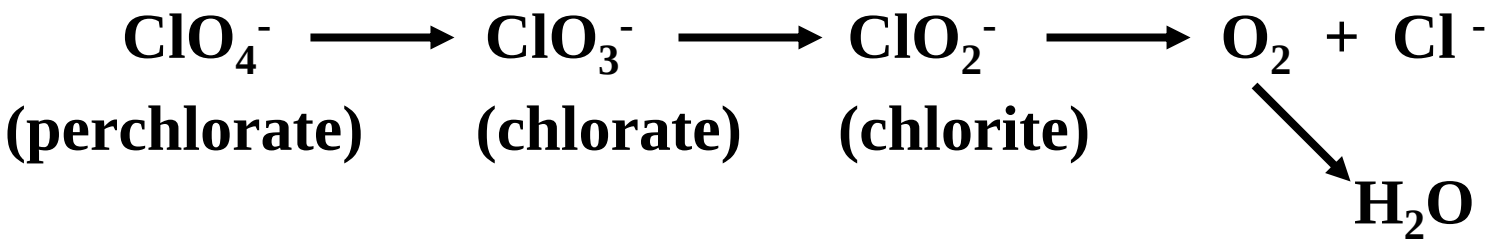
It has been estimated that **90%** of ammonium perchlorate released is as an oxidizer for **solid rocket propellant.**

Bacterial Metabolism

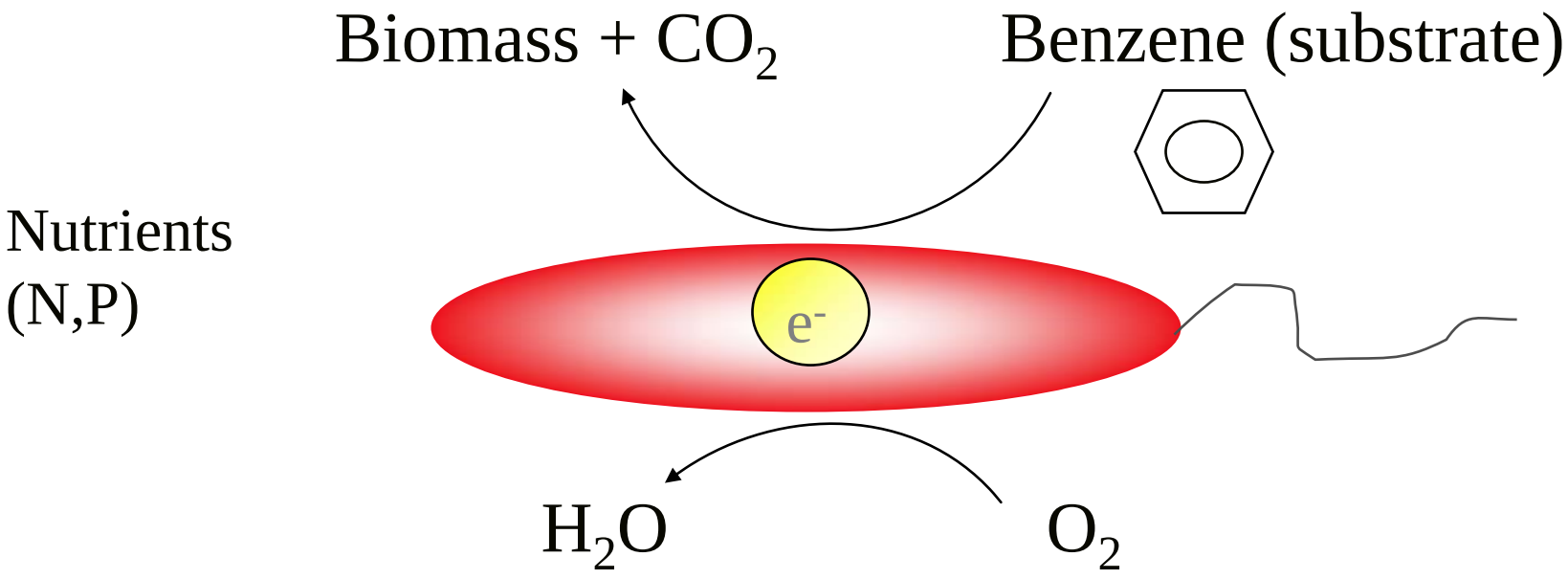
- **Requirements:**
  - Energy Source (organic or inorganic)
  - Electron Acceptor (O_2, NO_3, SO_4, CO_2)
  - Carbon Source (organic or CO_2)
  - Macronutrients (N,P,S)
  - Mineral Ions (Ca, K, Mg, Fe, Cu, Zn, Co, et al.)
  - Vitamins and/or Amino Acids

Biological Perchlorate Reduction

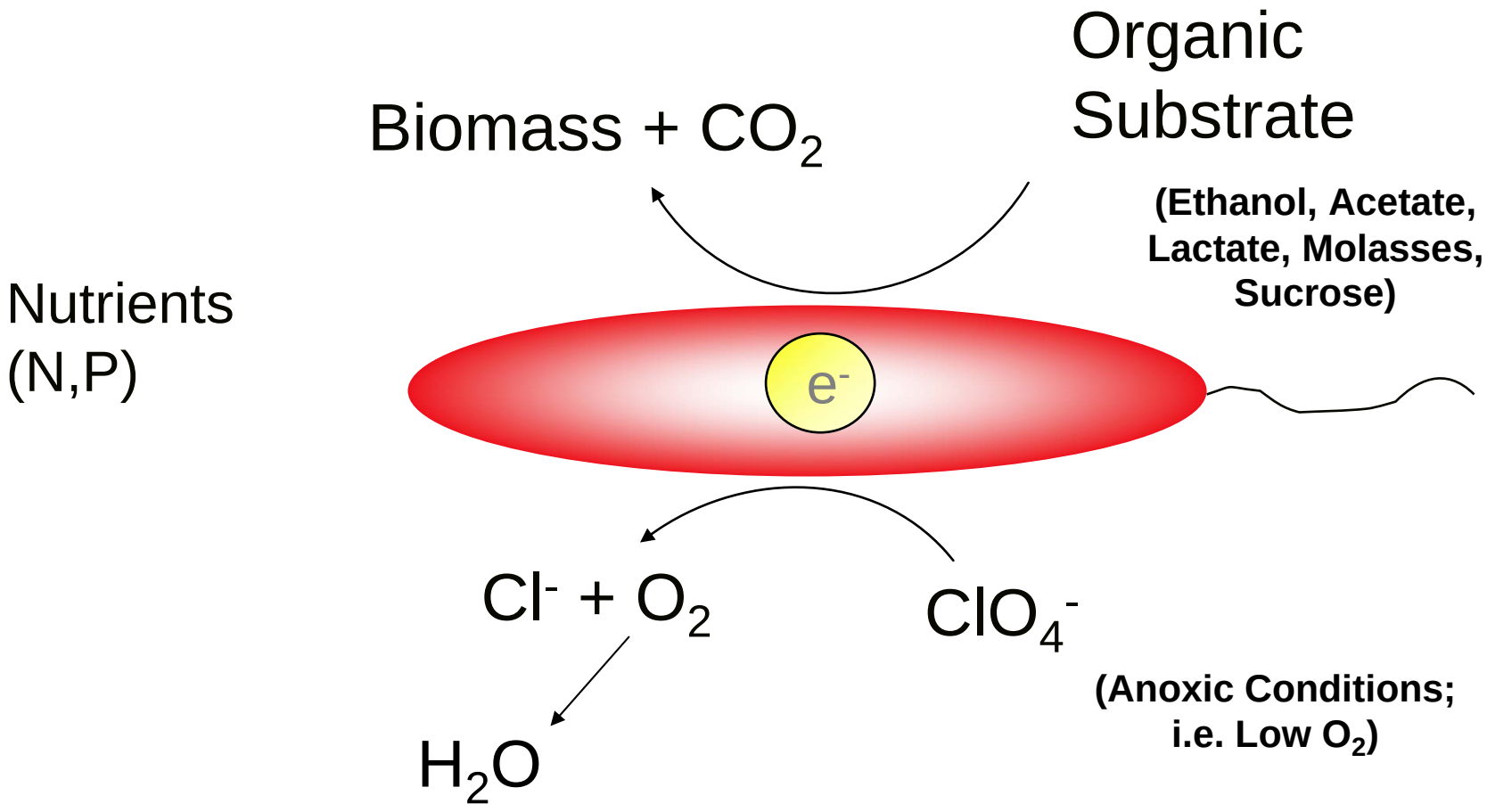
Terminal Electron Acceptor:



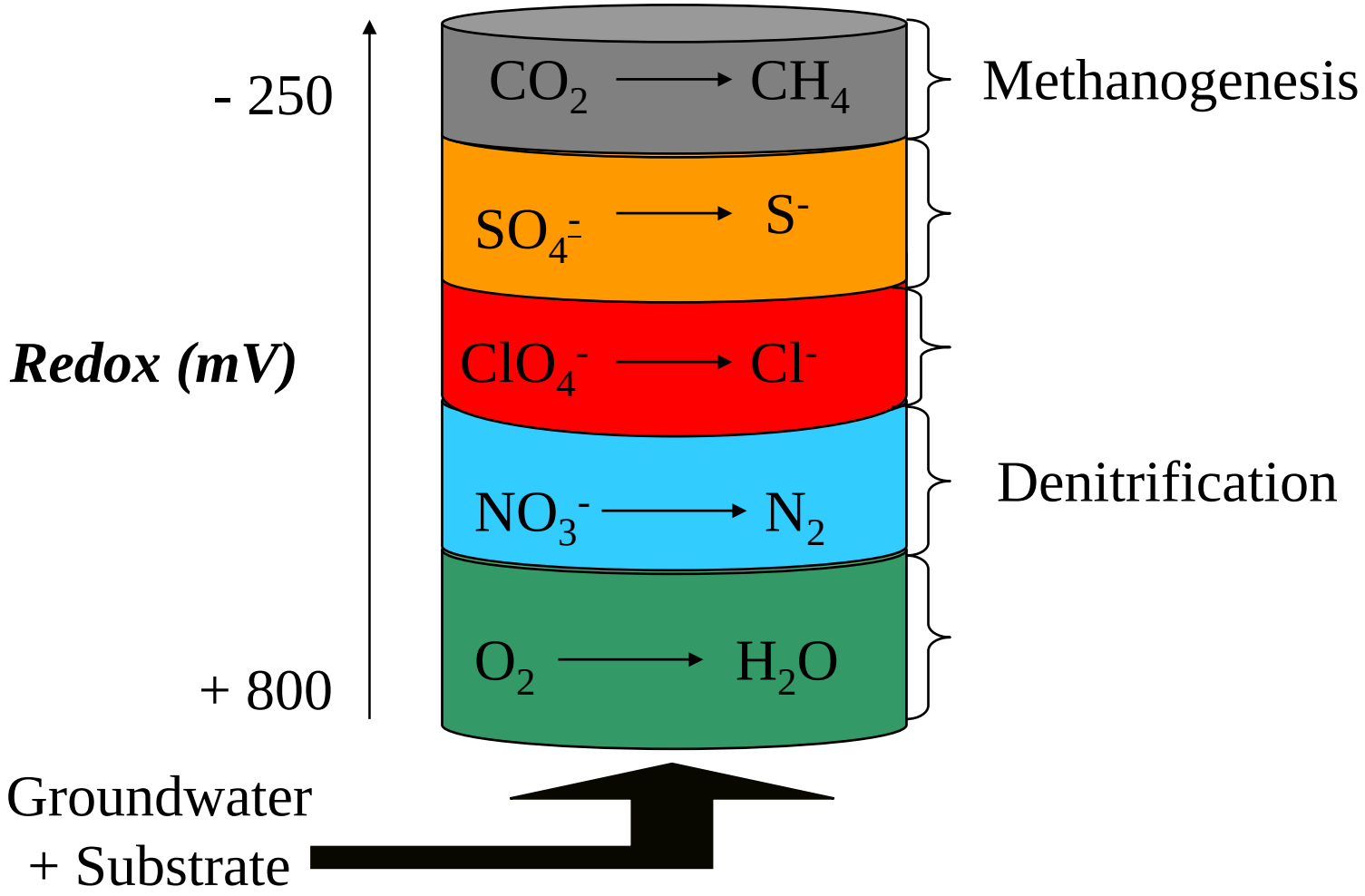
Organic Pollutants



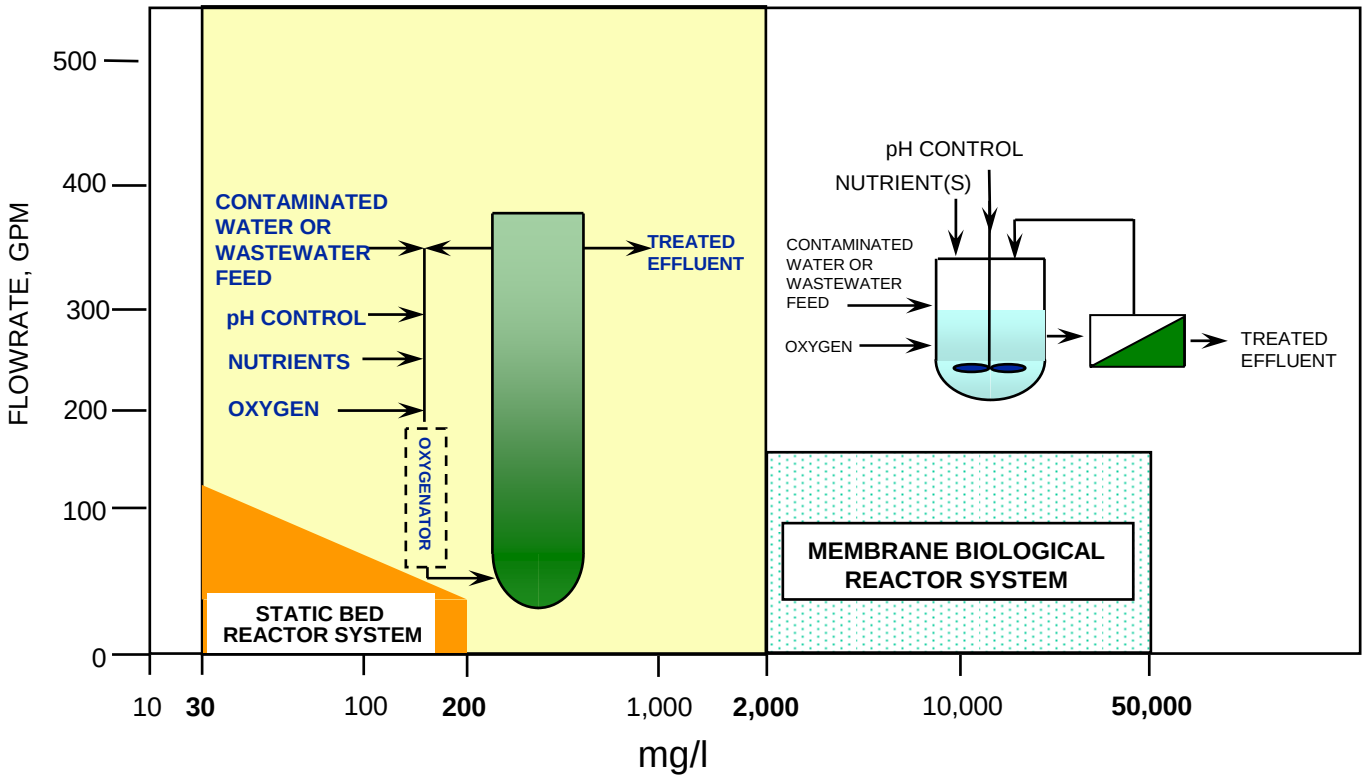
Perchlorate Reduction



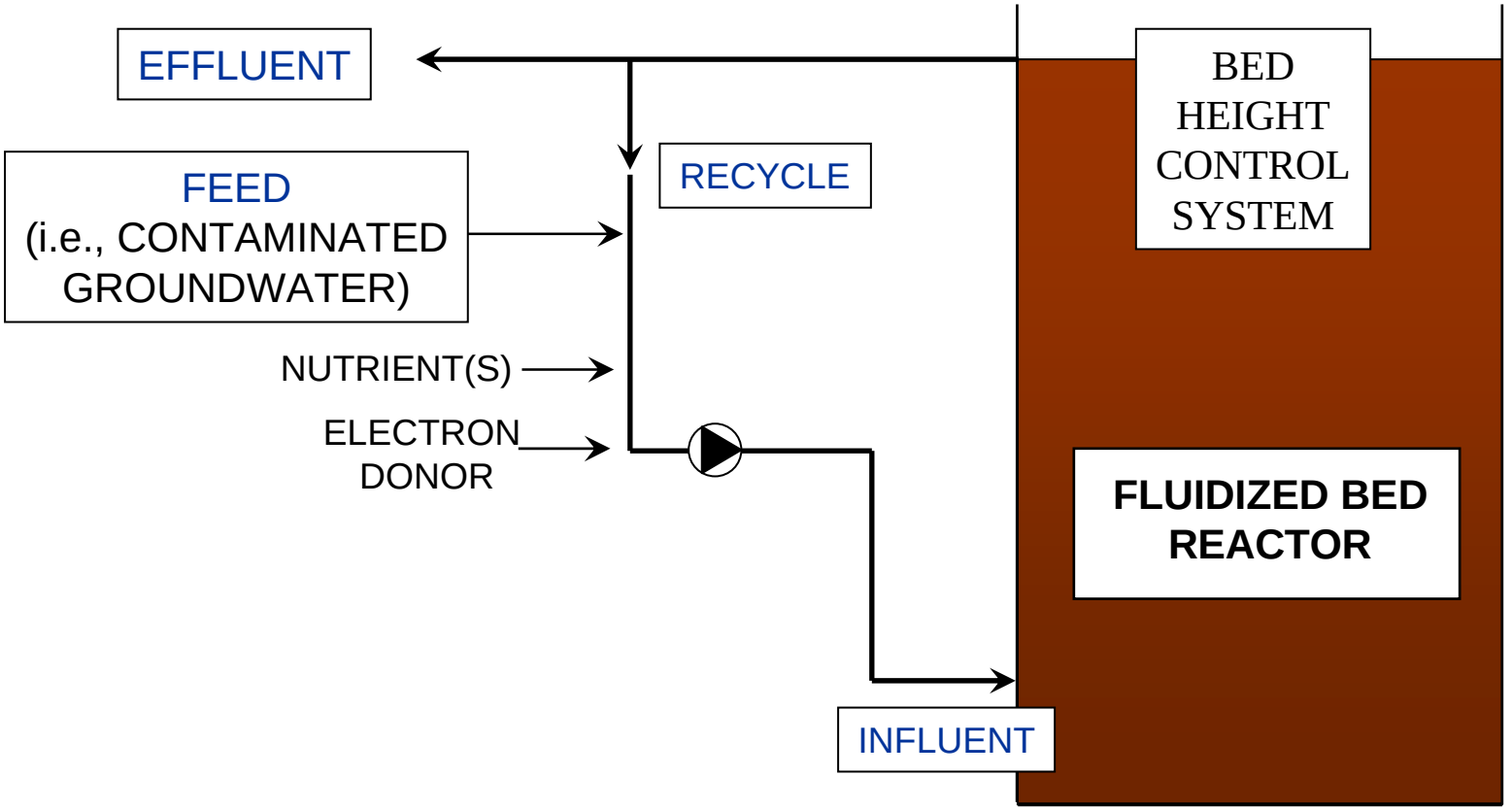
Utilization of Electron Acceptors



Bioreactor System Options for Treatment of Organic Chemicals



FBR Flow Schematic



FBR Advantages

- High biomass concentration means long SRT and short HRT
- High volumetric efficiency translates to compact system; installation in a building
- Simplicity of operation minimizes need for operator attention
- Small impact from changing feed conditions, as feed is combined with recycle before entering the reactor

Key Mechanical Components

- Device and method used to distribute influent flow to the reactor
- Device and method used to control the expansion of the fluidized bed due to biofilm growth
- Method to control electron donor dosage rate

Aerojet's
Full Scale Perchlorate Treatment Plant

- 4 Fluidized Bed Reactors available
- Each reactor has a design capacity of
  - 1800 gpm Fluidization Rate
  - 900 gpm Feed Rate
- 4 reactors currently in use with combined feed rate of ~3500 gpm (~875 gpm each)
- Treating ~ five million gallons per day

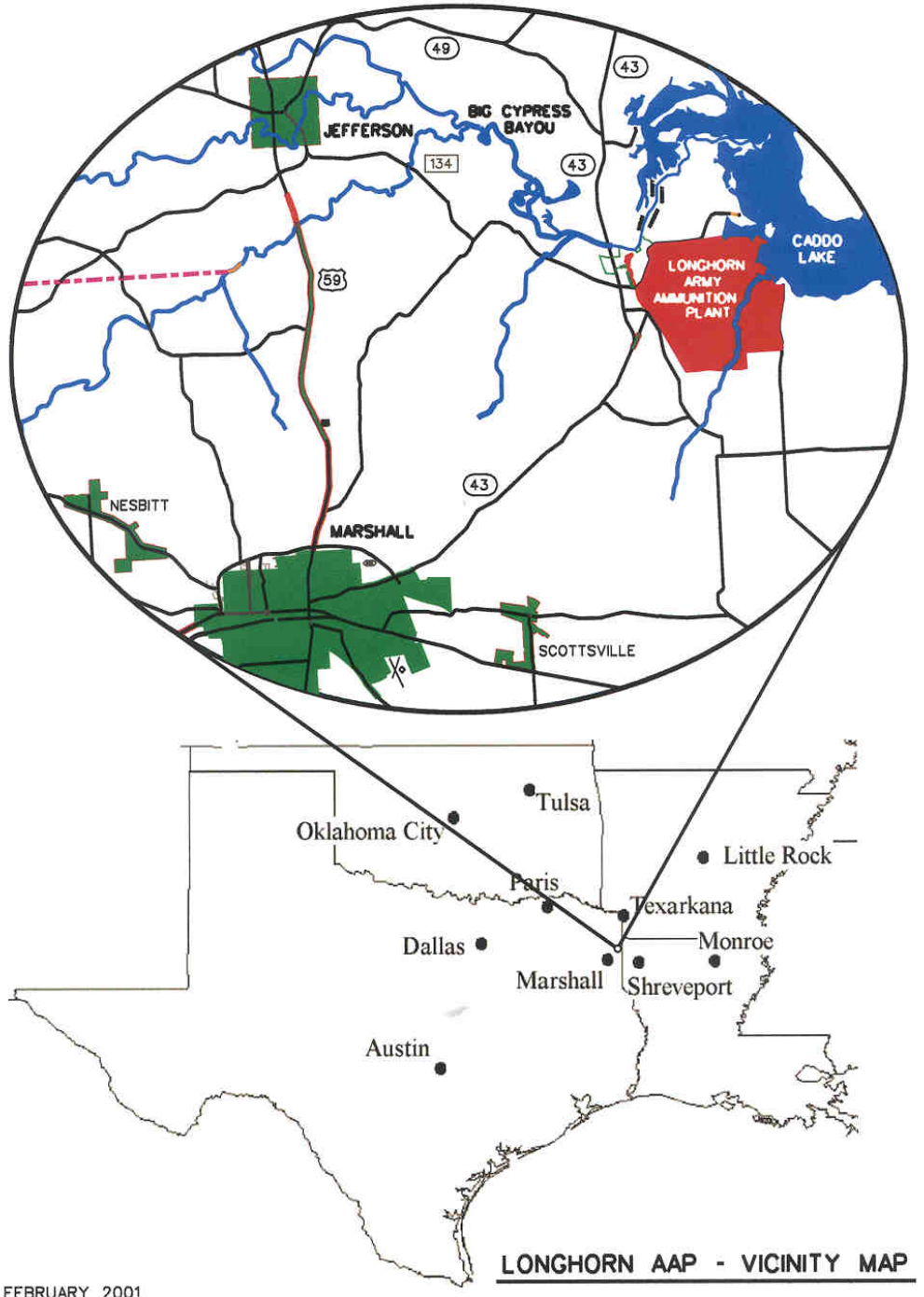
Aerojet's
Full Scale Perchlorate Treatment Plant

- Bed Reactor

	Influent	Effluent
– Dissolved O_2	5.3 ppm	<0.5 ppm
– CLO4	~3500 ppb	<4.0 ppb
– TCE	1500 ppb	1500 ppb
– NDMA	110 ppt	110 ppt
– Nitrate-N	1.5 ppm	<0.11 ppm
– Nitrite-N	<0.076 ppm	<0.076 ppm
– Sulfate-S	6.0 ppm	6.0 ppm
– Ethanol	NA	<1.0 ppm
– pH	~7.5	~7.5


ENVIROGEN

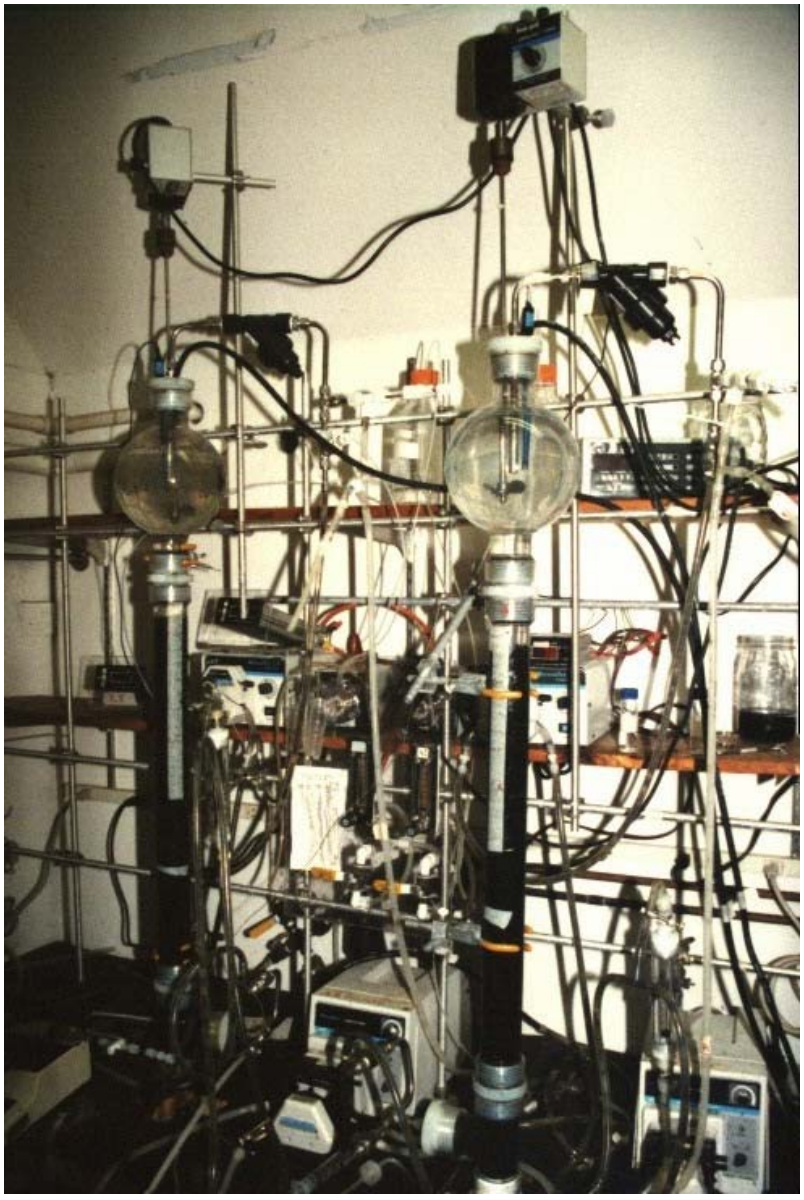
Longhorn Army Ammunition Plant



LHAAP History

1942-1945	LHAAP opened; Monsanto Chemical Company - TNT
1952-1956	Universal Match Corporation - pyrotechnic ammunition
1955-1965	Thiokol Corporation - rocket motor facility
1965	Pyrotechnic and illuminating ammunition re-established
1965-1997	Multi-functional; INF
1990	NPL
1991	Federal Facilities Agreement
1997	Caretaker Status
2000	Fish and Wildlife Service Memorandum of Agreement

Bench Scale FBR Glass Reactor

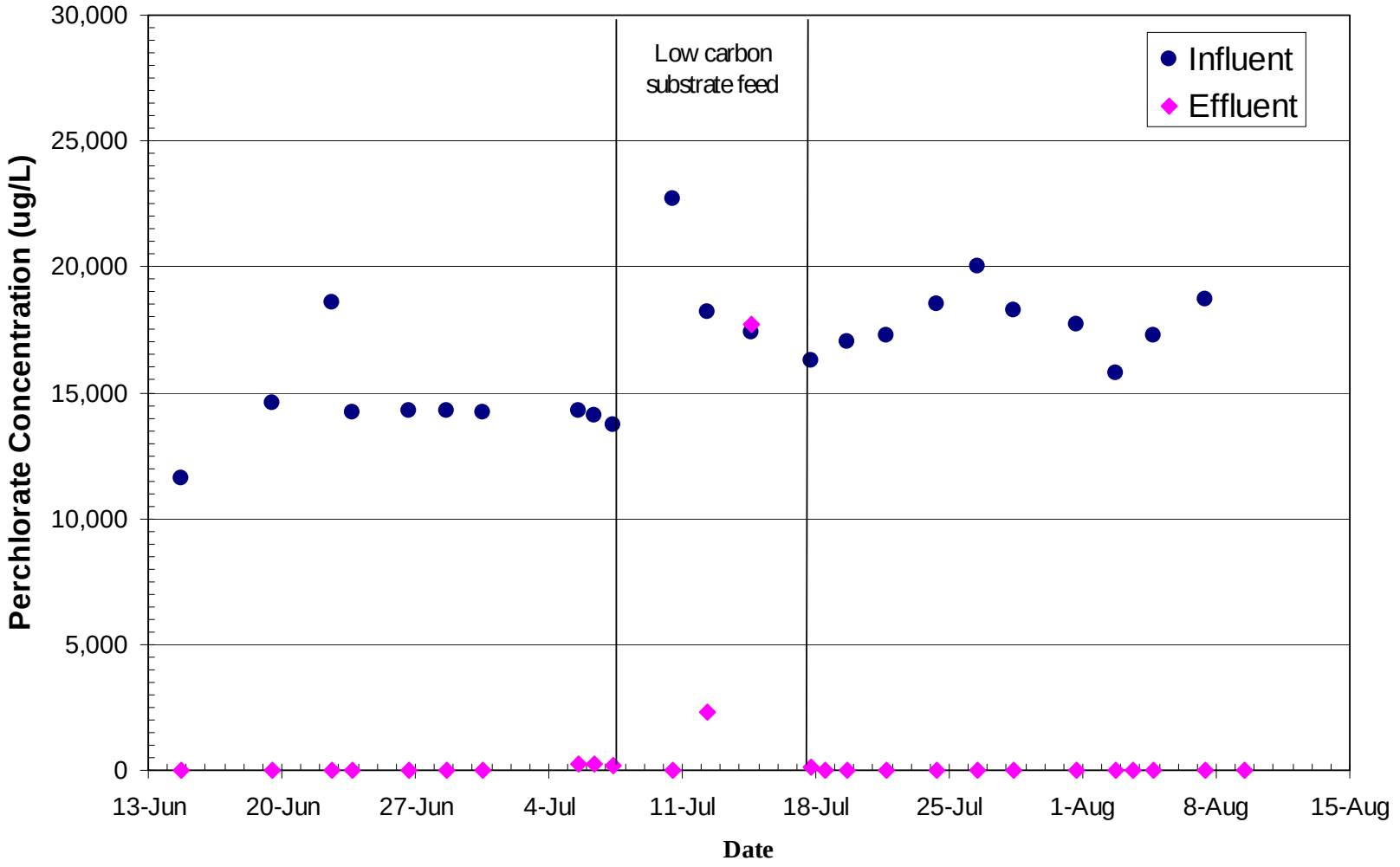


Results of Phase 1 - Sample Characterization

Parameter	Method	Units	Drum #1	Drum #2	Drum #3	Average	Std. Dev.
Oxygen (O_2)	D.O. Probe	mg/L	4.0	3.5	Not Analyzed	**3.8**	0.4
Perchlorate (ClO_4^-)	EPA 300.0	mg/L	15.1	14.7	14.4	**14.7**	0.4
Chlorate (ClO_3^-)	EPA 300.0	mg/L	0.5	0.5	0.5	**0.5**	0.0
Nitrate-N (NO_3^--N)	EPA 300.0	mg/L	1.9	1.9	1.8	**1.9**	0.1
Nitrite-N (NO_2^--N) [1]	HACH Method 8507	mg/L	0.016	0.013	0.011	**0.013**	0.003
Ortho-phosphate-P (PO_4^--P)	EPA 300.0	mg/L	<0.2	<0.2	<0.2	**<0.2**	N/A
Ammonia-N (NH_3-N)	EPA 350.2	mg/L	<0.5	<0.5	<0.5	**<0.5**	N/A
Sulfate (SO_4^{-2})	EPA 300.0	mg/L	290	310	310	**303**	11.5
Chemical Oxygen Demand (COD)	EPA 410.4	mg/L	56	21	12	**30**	23.2
Total Organic Carbon (TOC)	EPA 415.1	mg/L	<1	1	<1	**<1**	N/A
Oil & Grease (O&G)	EPA 413.1	mg/L	Less than 10 mg/L for a composite sample			**N/A**	N/A
Total Suspended Solids (TSS)	EPA 160.2	mg/L	12	14	4	**10**	5.3
Volatile Organic Contaminants (VOCs)	SW-846 8260	mg/L	Not Analyzed	Less than 0.10 to 0.05 mg/L for all on 8260 list except for acetone @ 0.18 mg/L	Less than 0.10 to 0.05 mg/L for all on 8260 list		N/A
Priority Pollutant Metals	EPA 200.7 and EPA 245.1 (Hg)	ug/L	Less than PQL for all on 200.7 list (and Hg) except for Ni @ 1.7 ug/L and Zn @ 198 ug/L	Less than PQL for all on 200.7 list (and Hg) except for Ni @ 1.8 ug/L and Zn @ 131 ug/L	Not Analyzed	**1.8 for Ni and 165 for Zn**	0.1 for Ni and 47.4 for Zn
Broth Tube Toxicity/Inhibition Test	Internal SOP	N/A	Not Toxic or Inhibitory	Not Toxic or Inhibitory	Not Toxic or Inhibitory	**N/A**	N/A

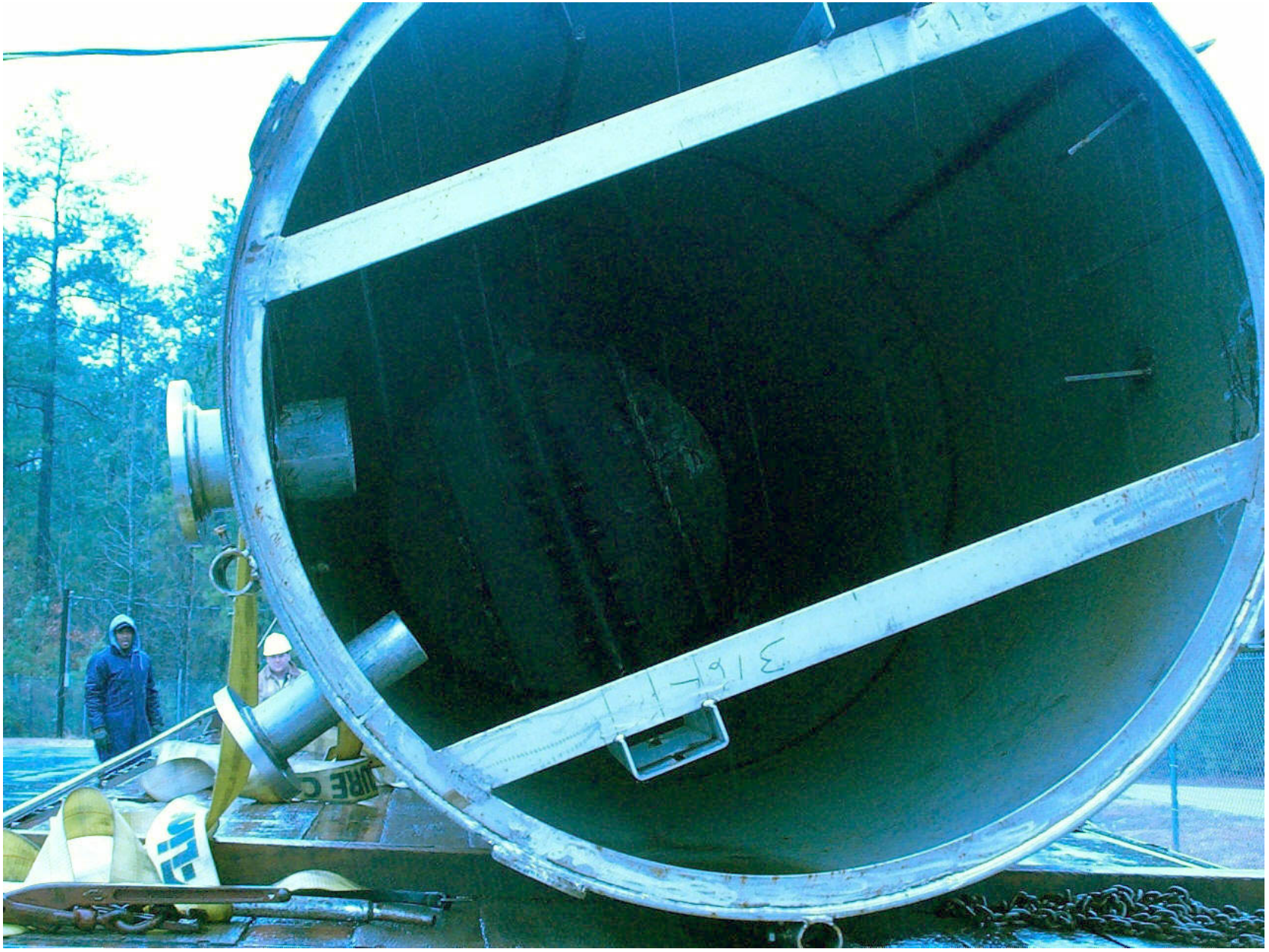
[1] EPA Method 300.0 (Ion Chromatography) gave initial results of 330, 340, and 320 mg/L for nitrite-N. The samples were re-run, and the peak was determined to be chloride (Cl^-) at an average concentration of 710 mg/L. The nitrite-N results were confirmed by an independent laboratory using Method EPA 353.2.

Longhorn Army Ammunition Plant Bench-Sale Results

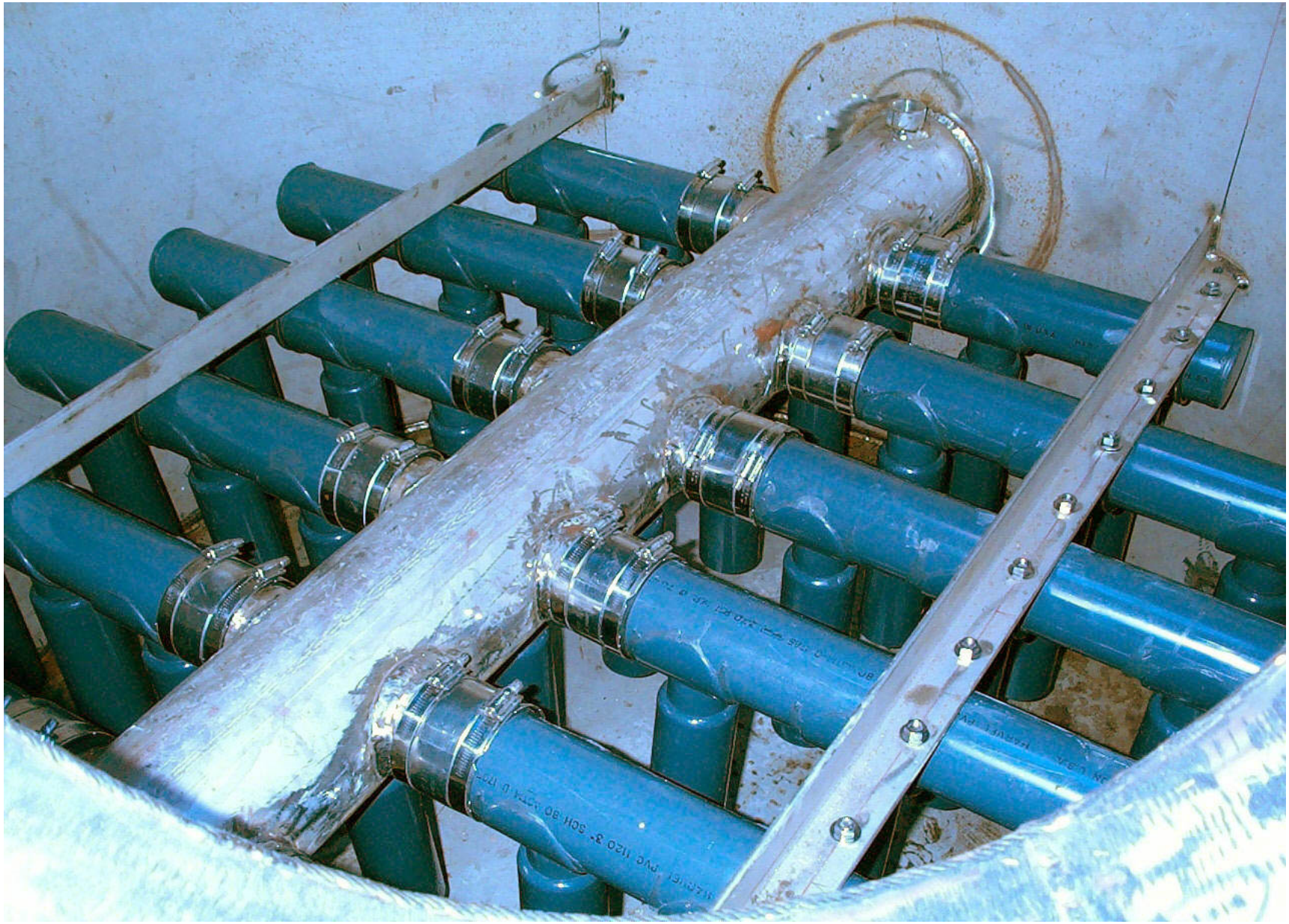


Longhorn Army Ammunition Plant
Full Scale FBR Installation
(Perchlorate Reduction)

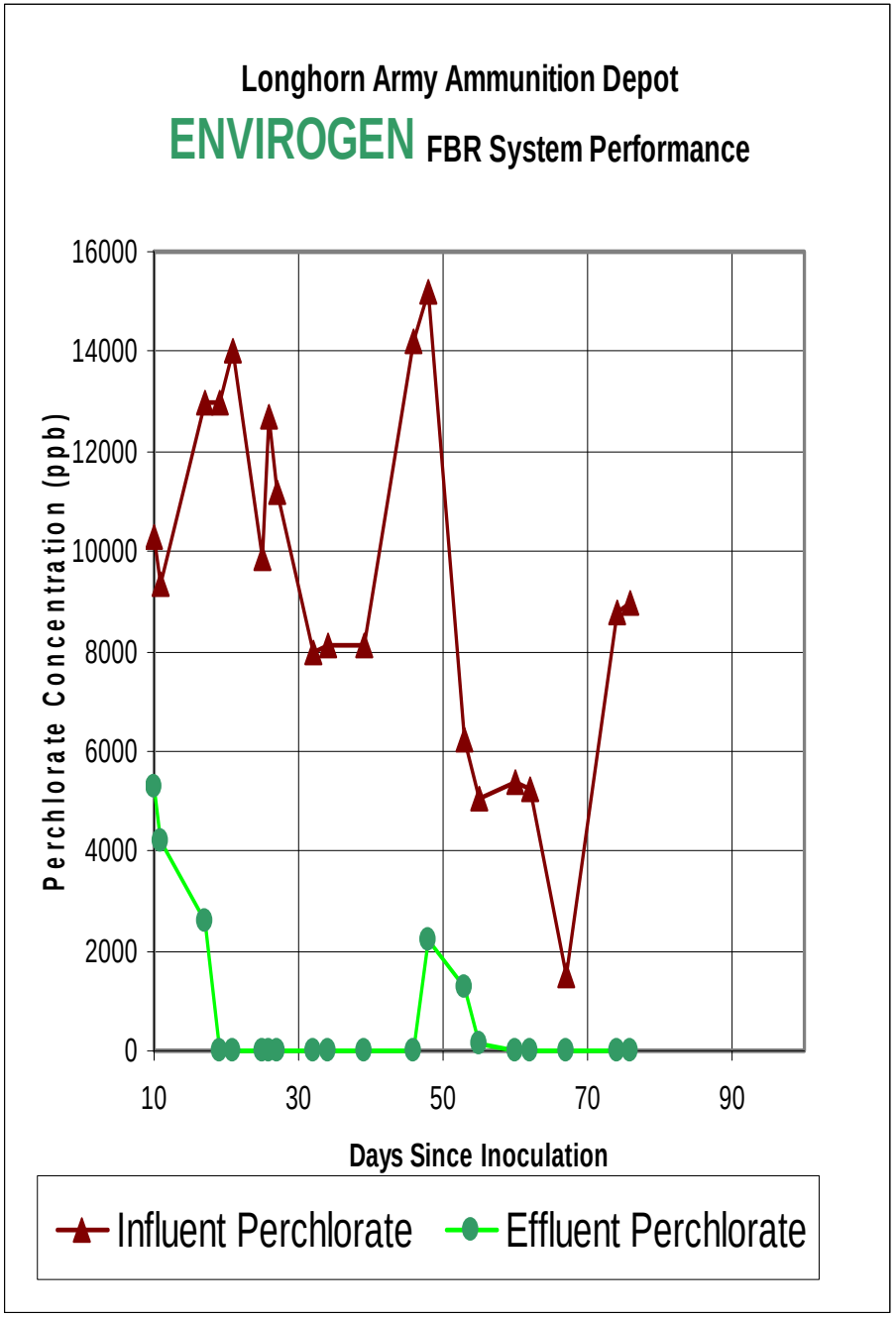
- Design Basis
  - 50 gpm
  - One 5 ft. dia. unit
  - Acetic acid as electron donor
  - GAC media
  - Perchlorate up to 22,000 ppb




WELD/BURN OR



UPDATE


Longhorn Army Ammunition Depot
ENVIROGEN FBR System Performance
Perchlorate Concentration (ppb)
16000
14000
12000
10000
8000
6000
4000
2000
0
10
30
50
70
90
Days Since Inoculation
Influent Perchlorate
Effluent Perchlorate

Summary

- Biological Fluid Bed Reactor successfully treating more than 7.0 million gallon per day of groundwater containing perchlorate
- Consistent effluent perchlorate levels below practical quantitation limits (4 ppb)
- Single FBR treats from 50 to 1,000 gpm
- No flow rate limits with multiple units
- Thank you - Bill Guarini, Envirogen, Inc.
  609 - 936-9300 x 135