Treatment Technologies for Perchlorate

Edward N. Coppola
430 West 5th Street, Suite 700
Panama City, FL 32401
(850) 914-3188
ecoppola@ara.com

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Overview

- Perchlorate Background
- Water Washout
  - Ammonium Perchlorate (AP) Recovery
- Treatment of AP-Contaminated Effluents
  - Biodegradation of High-Strength Effluents
  - Ion Exchange of High-Strength Effluents
Perchlorate Use

- Oxidizer in Solid Fuel Rockets
  - 12 strategic & 40 tactical motors
- Oxidizer in Explosives and Fireworks
- Ordnance & Insensitive Munitions
  - Over 250 items
- Gunpowder, Flares, Air Bags
- Found as a Contaminant in:
  - Sodium chlorate-based herbicides
  - Fertilizers and nitrates (imported from Chile)
- Naturally Occurring in U.S.
Insensitive Munitions

- Contain Perchlorate Oxidizers to Reduce Shock Sensitivity
- Wastewater Generated during Production and Loading Ops
- PAX-21
  - Melt Pour Explosive
  - Composition B Replacement
  - RDX, DNAN (2, 4-dinitroanisole), AP (ammonium perchlorate)
  - Mortar explosive
- AFX-757
  - Composite explosive
  - Joint Air-to-Surface Stand-Off Missile (JASSM)
Pathways to the Environment

- Manufacture of Propellant & Explosive Ingredients
- Production of Propellant & Explosive Formulations
- Manufacture of Ordnance Items
- Operational Test & Evaluation - Training
- Ageing and Surveillance Testing
- Destruction or Disposal of Unserviceable Items
- Reclamation, Reuse, or Conversion
- Demilitarization and Disposal
Perchlorate Occurrence

Legend

Perchlorate Detections at:
- △ Department of Defense (DOD) Facilities
- ▲ Other Federal Agency Facilities:
  - Department of Energy (DOE)
  - National Aeronautics and Space Agency (NASA)
  - Department of the Interior (DOI)
- ● Privately-owned Sites
- ● Unregulated Contaminant Monitoring Rule (UCMR) Detections
- □ Texas Tech University - West Texas Study Detections
  - Point Contains One Site
  - ▼ Point Contains Multiple Sites

U.S. EPA
ITRC Technology Overview – Sep 2005
GAO-05-462 Report – May 2005
Perchlorate Guidance

- Reference Dose (RfD) Established by EPA
  - January 26, 2006 U.S. EPA Memorandum to Regional Administrators
  - 0.0007 milligram/kilogram-day (mg/kg-day)
  - Drinking Water Equivalent Level: 24.5 parts-per-billion

- DoD Guidance Letter Issued January 26, 2006
  - Established 24 ppb as the “Level of Concern”
  - “DoD will comply with applicable state or federal standards whichever is more stringent”
  - Environmental Quality Status Class I under DoD 4715.6
  - Military services issued corresponding guidance letters

- Current State Health-Based Goals – 1 to 14 ppb
  - California proposed MCL of 6 ppb
Perchlorate Demil via Water Washout

- Water washout is an inherently safe process
  - Ammonium perchlorate exhibits high solubility (>10%)
  - Water completely desensitizes perchlorate
- Water washout is a very mature, proven process
  - Functional, simple, and robust
  - Successfully employed by ATK (Promontory, UT) since 1962
- Water washout allows reuse of cases and hardware
  - Metal or filament wound cases
- Environmentally Sound Process
  - Permits recovery of high purity perchlorate
  - Aqueous residual streams can be efficiently treated
ATK Thiokol Washout Experience

- Over 39 million pounds propellant removed
- Propellant removed from over 4,700 motors and warheads
- Propellant removed from 28 different types of motors and warheads
  - ICBM solid rocket motors
  - Tactical solid rocket motors
  - Space booster solid rocket motors
  - Tactical missile warheads
- Continually upgrading system for safety, environmental, and efficiency improvements
- Presently designing systems for tactical-size production applications
- ATK Thiokol evaluation and recommendations based on:
  - Over 40 years of continuing experience
  - Using mature technologies
ATK Thiokol Water Washout Operation

M-115 Process Flow

- Washout Operation
- Head Tank
- Distillate Water from AP Recovery
- Plant Water
- Side Stream
- Solids
- Liquids
- Ship to AP Recovery
- Holding Tank
- Ship to AP Recovery
- High Pressure Pumps
- Water (Low Percent AP)

ATK THIOKOL PROPULSION

ATK Alliant Techsystems

ARA

EXPANDING THE REALM OF POSSIBILITY
Tactical Motor Washout

- Typically save the case
- HARM, STANDARD Missile, Sidewinder, others
- Close-loop water
- AP recovery or direct reuse
- PBX warheads
- Internal and external customers
AP Reclamation Process

- M-115 Motor Washout
  - AP Reclaim Two Branches
    - AP Water Treatment
      - M721 Evaporator
        - AP Recovery
    - Propellant Treatment
      - M-705 Propellant Size Reduction and Leach
        - M705 Evaporator
          - Inert Propellant Residue
            - AP Recovery
            - Aluminum Recovery
Products

- AP wet cake
  - Purity - 99.8% pure AP
  - Water content 2-3% moisture

- Reclaimed AP products
  - Perchloric acid production
  - Fireworks
  - Commercial explosives
  - Commercial rocket motor production

- Residue
  - Aluminum recovery
  - Landfill
  - Currently exploring fuel alternatives
Perchlorate Effluent Treatment

- Demil & Propellant Production Generate Effluents
- Biodegradation Processes
  - Continuous-stirred-tank-reactor (CSTR)
  - Fluidized bed reactor (FBR)
  - Result in Perchlorate Destruction: \( \text{ClO}_4^- \rightarrow \text{Cl}^- + 2\text{O}_2 \)
- Ion Exchange Processes
  - Non-regenerable, single-use resin
  - Brine-regenerable, strong base anion resin
  - Caustic regenerable, weak base anion resin
  - Result in Perchlorate Concentration
    - In resin or regenerating solution
Biodegradation of Perchlorate-Contaminated Wastewater

- Effective for High Concentrations
  - Up to 5000 mg/L or saturated solutions (with dilution)
- Effective for High TDS Effluents
  - From 2-3% salt to over 7% for membrane systems
- Simultaneous Reduction of Co-Contaminants
  - Nitrate, nitrate esters, nitroaromatics, nitramines
  - Heavy metals
- Treated Water can be Discharged to Sewer
- Mature, Robust, Inexpensive Technology
- Demonstrated Track Record
The ARA Biodegradation Process for Effluents Containing Perchlorate

Anoxic Bioreactors:
- Suspended-Growth Process
- Two Stages in Series

Equalization Tank
Effluent Feed Water

Nutrient/Electron Donor

Caustic for pH Control

Continuous-stirred-tank reactors
- HRT: 8-24 hr
- Temperature: 15-40°C
- pH: 6.5-8.5
- ClO₄⁻: 5000 mg/L
- TDS: 2-3%

Discharge to Sewer
ARA System at ATK, Promontory, UT

- 1996-97 - Production Prototype
  - AF Research Lab, Tyndall AFB
  - Sponsored by ESTCP & JOCG
- Dec 1997 - Inoculation and Start-up
  - First operational ClO$_4^-$ system
  - Continuous operation thru present
- March 1999 Optimization Project
  - Reduced nutrient costs >90%
  - Desugared molasses
- 2001-2002 – Modification Project
  - Simultaneously treats 3 effluents
  - Up to 8000 lb/month perchlorate
Performance of System at Promontory

- Treats ~1M Gallons of Wastewater per Year
- Destruction Rates During 2006
  - Perchlorate: average 1500 lb/mo – maximum 4000 lb/mo
  - Nitrate: average 1500 lb/mo – maximum 6000 lb/mo
- Cost Savings ~$2M per Year
- Effluent Biodegradation is an Enabling Technology for Perchlorate and Rocket Motor Case Recovery and Reuse
  - Minuteman remanufacture – 700, 1st and 2nd stage motors
    - Reused cases valued at ~$2M per set
    - Credit for recovered ammonium perchlorate ~$15K/mo.
  - Space Shuttle RSRM production and case reclamation
  - Delta Strap-on Solid Rocket motor (SSRM) production
- Supports Energetic Material Development and Production
  - CL20, TTB, PAX, decoy flares, nitration processes
2nd Generation Biodegradation System for Effluents Containing Perchlorate

- Hodgdon Powder Company – Pyrodex Plant
  - Near Herington, Kansas
- Effluent from Gunpowder Manufacturing
  - Perchlorate >3000 mg/L
  - Nitrate >2000 mg/L
- ~3 gpm Treatment Rate
- Inoculated 27 April 03
- Discharge to POTW
  - KDHE Permit <100 ppb
- Land Application
  - Soil Remediation
  - 2006 & 2007
Wastewater Holding Ponds
Two-Stage Bioreactor
Performance of the Pyrodex Plant

- Over 150 Effluent Tanks Filled, Tested, and Discharged
  - All below discharge limit (100 ppb) and EPA-314 MDL (~20 ppb)
  - Over 3 million gallons of wastewater treated

- Kansas Dept. of Health and Environment (KDHE) Reduced Sampling and Analysis Requirement to Every Fourth Tank

- Won Kansas Water Environment Association (KWEA) Award
  - Industrial Wastewater Pretreatment Category

- Remediation Progress
  - 16,000 yd$^3$ of soil remediated
  - Perchlorate reduced >95%
    - From 45 mg/kg
  - >500 kg of perchlorate destroyed
  - Kleinfelder – Topeka, KS
Wastewater Ion Exchange Treatment

- Effective for Dilute or Concentrated Effluents
  - Dilute (ppb to ppm) – high flow rates (>100 to 1000 gpm)
  - Concentrated (10s to 1000s ppm) – low flow rates

- Treatment Capacity is a Function of Concentration
  - Performance affected by other anions

- Single-Use Approach
  - Demonstrated technology
  - Resin and perchlorate destroyed by incineration
  - Expensive – resin replacement and disposal
    - $50 to >$150/kg of perchlorate removed
  - Little or no capital expenditure may be required
Regenerable Ion Exchange Technology

- Brine Regenerable Strong Base Anion (SBA) Resin
  - Generates $\geq 1\%$ perchlorate-contaminated salt brine

- Ferric Chloride Regenerable SBA Process (ORNL)
  - Concentrated HCl and ferric chloride solutions

- ARA & The Purolite Company Developed a Weak Base Anion (WBA) Resin Process (Patent Pending)
  - Ion exchange & regeneration pH dependent
  - Reduces spent regenerating solution to as little as 0.02%
  - Effluent is safely handled and easily treated
    - Scavenger process for low concentration applications
    - Biodegradation for high concentration applications
Pilot Demonstration - Redstone Arsenal

- ESTCP Sponsored
- 6-inch Groundwater Extraction Well
- Perchlorate: 1500–2200 ppb
- Bicarbonate: 150 ppm
- Nitrate: 4 ppm
- Sulfate: 3 ppm
- Chloride: 4 ppm
- TCE: 3100 ppb
Pilot System Design & Operation

- Conventional Lead-Lag Configuration
- Integrated Pre- and Post-Treatment
- 24 hr/day – 7 Day/Week Operation
- 2-inch Diameter Ion Exchange Columns
- Macroporous Polystyrene Divinylbenzene WBA Resin (Purolite D-4170)
  - 36-inch bed depth
- 12 to 24 BV/hr Treatment Rate
  - 1.5 – 3 gpm/ft³
- Regeneration & Residuals
  Treatment Conducted Off Site
Benefits of WBA Resin Process

- More Efficient than Brine Regeneration
  - Low volume of effluent
  - “Zero discharge” potential

- Perchlorate-Selective
  - Perchlorate removal to less than method detection limit
  - High capacity compared to brine-regenerable processes

- Effective Wastewater Treatment Process
  - Feasibility tests conducted on several wastewaters
  - Effective from ppb to 1000s of ppm perchlorate
  - Effective in presence of high anion concentration
    - 100s to 1000s of ppm NO$_3^-$, SO$_4^{2-}$, and Cl$^-$

- Low O&M Cost
Which Treatment Process do I Need?

- Depends on:
  - Perchlorate concentration
  - Effluent flow rate
  - Co-contaminants present
  - Disposition of treated water
  - Desire to recover perchlorate

- A Combination of Processes:
  - May be less expensive than a single unit operation
  - May reduce the footprint of the treatment system
  - May permit perchlorate recovery
Perchlorate Treatment Alternatives

mg/L

Flow Rate, gpm

Disposable Ion Exchange
Perchlorate Treatment Alternatives

Regenerable Ion Exchange (zero discharge)

Flow Rate, gpm

mg/L
Perchlorate Treatment Alternatives

- Continuous-stirred-tank bioreactor (CSTR)
- Fluidized bed bioreactor (FBR)
Regenerable Ion Exchange with Effluent Biodegradation (CSTR)
Perchlorate Treatment Alternatives

Recovery, conversion, reuse
Perchlorate Treatment Alternatives

Recovery, conversion, reuse with regenerable ion exchange
Summary

- **Water Washout is Proven, Safe, Reliable Process**
  - Permits component, AP, and aluminum recovery
  - Permits perchlorate reuse or conversion
  - Can be performed without perchlorate discharge

- **Biodegradation of Perchlorate-Containing Effluents**
  - Robust, mature, low cost (~$2/kg of perchlorate)
  - Commercial operation since 1997

- **Ion Exchange for Perchlorate-Containing Effluents**
  - Single-use processes in commercial operation

- **Regenerable WBA Resin Technology**
  - Improves economics for high-concentration effluents