Treatment Technologies for Perchlorate

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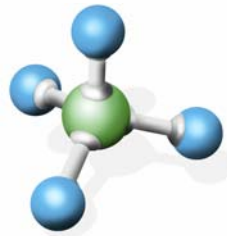
Global Demil Symposium



APPLIED RESEARCH ASSOCIATES, INC.
An Employee-Owned Company

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.

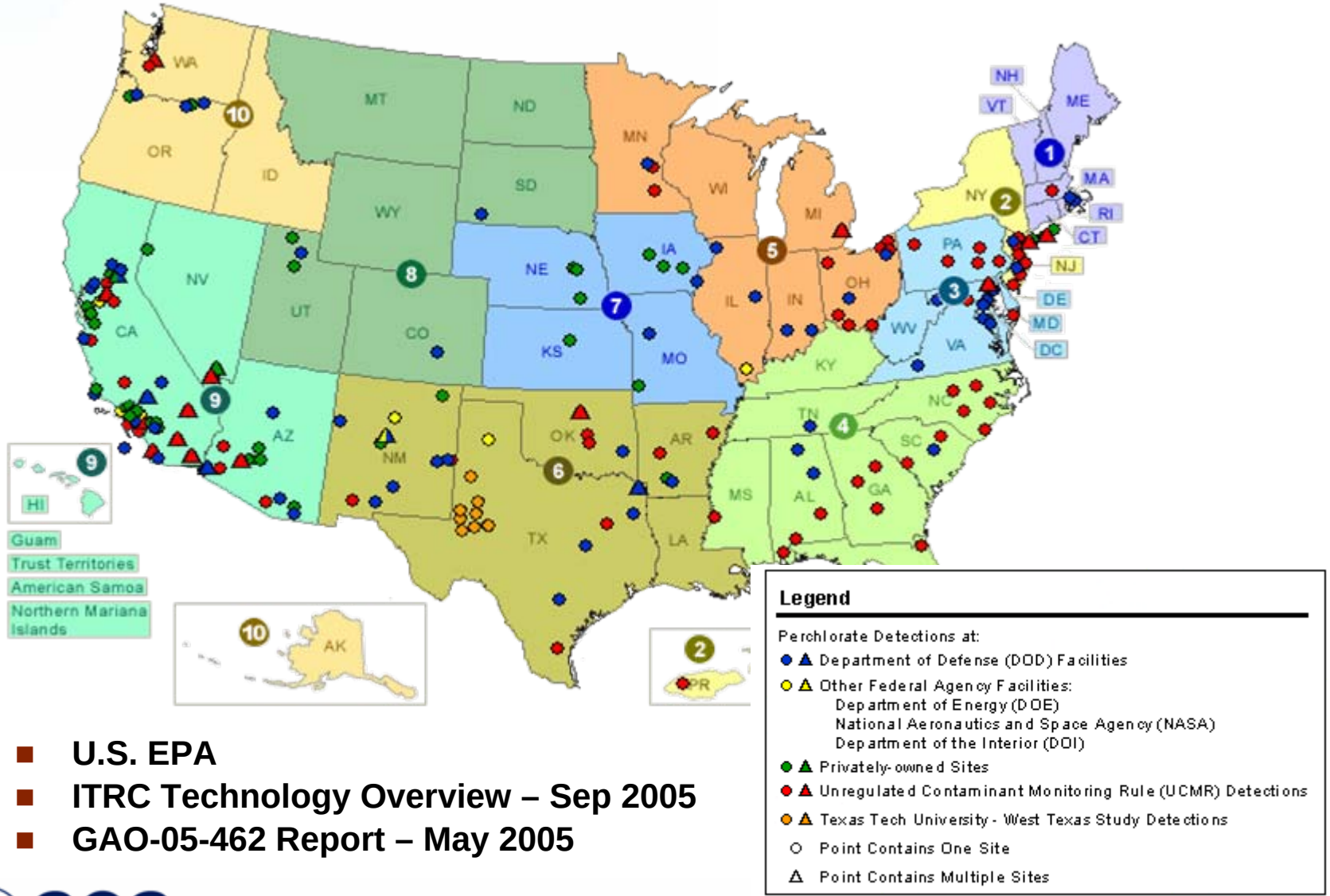
Insensitive Munitions

- 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



- 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 DoDI 4715.6**
  - **Military services issued corresponding guidance letters**
- **Current State Health-Based Goals – 1 to 14 ppb**
  - **California proposed MCL of 6 ppb**

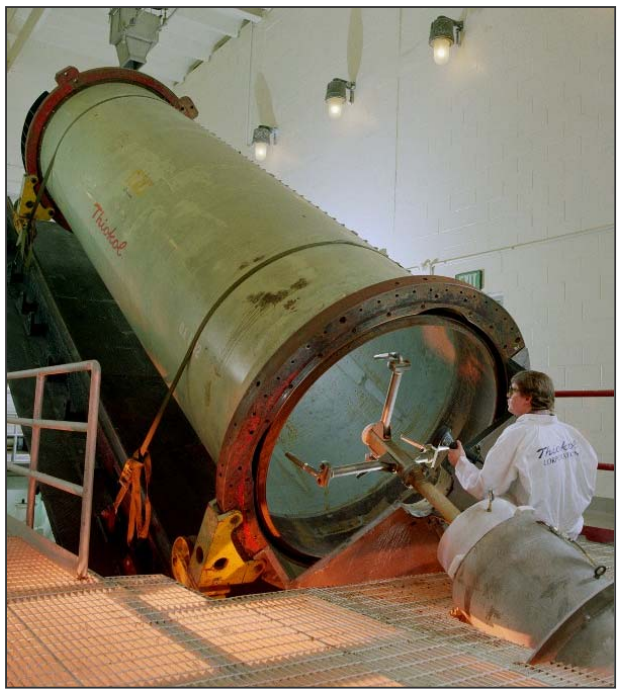
Perchlorate Demil via Water Washout

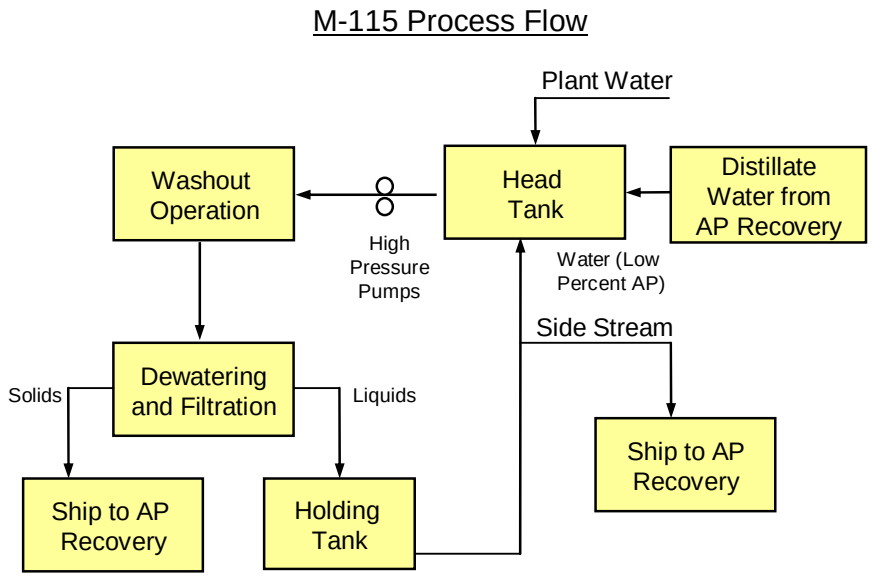
- **Water washout is an inherently safe process**
  - **Ammonium perchlorate exhibits high solubility (>10%)**
  - **Water completely desensitizes perchlorate**
- **Water washout is a very mature, proven process**
  - **Functional, simple, and robust**
  - **Successfully employed by ATK (Promontory, 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





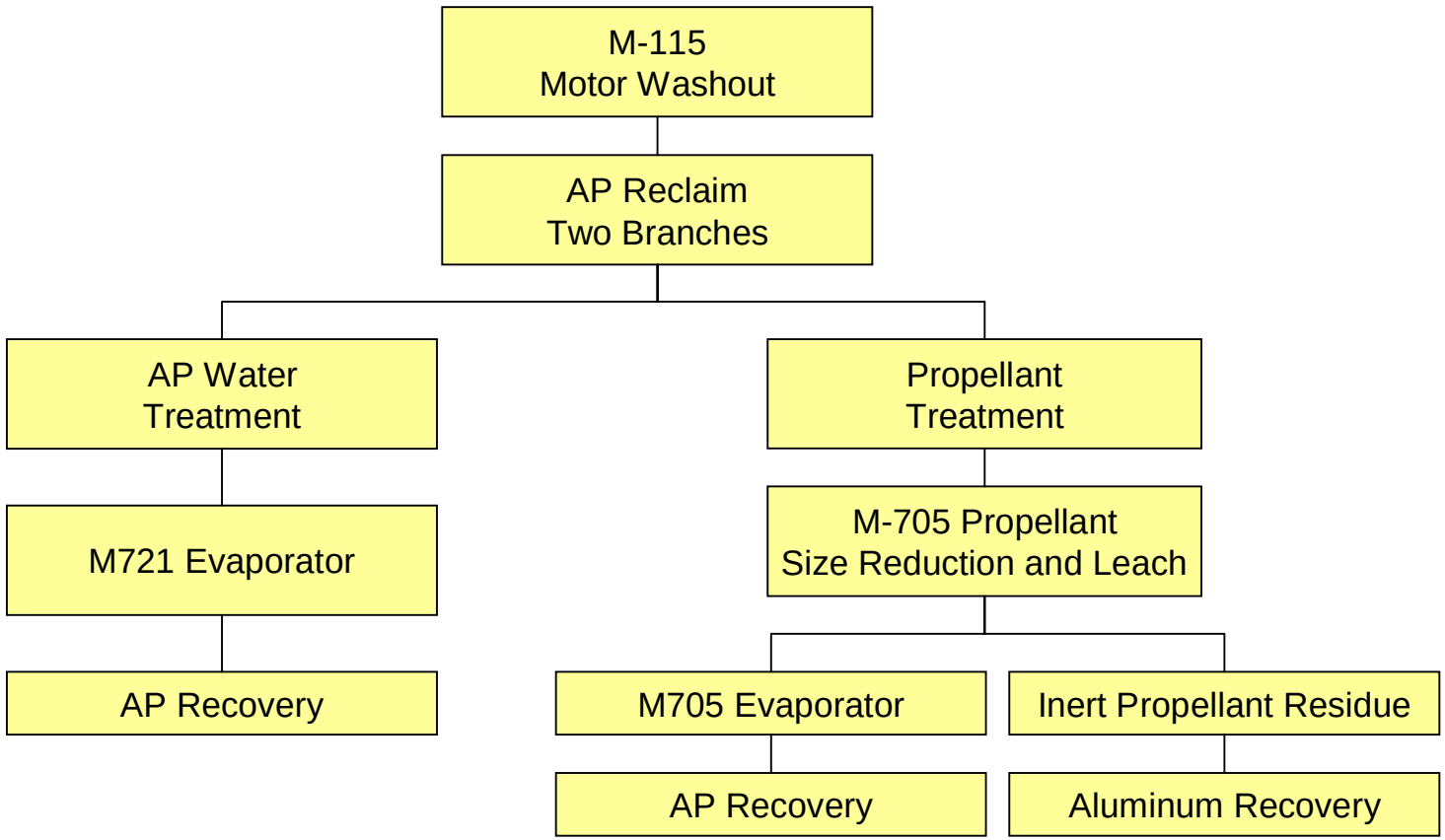
Tactical Motor Washout

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

Black Brant

Composite

AP Reclamation Process



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

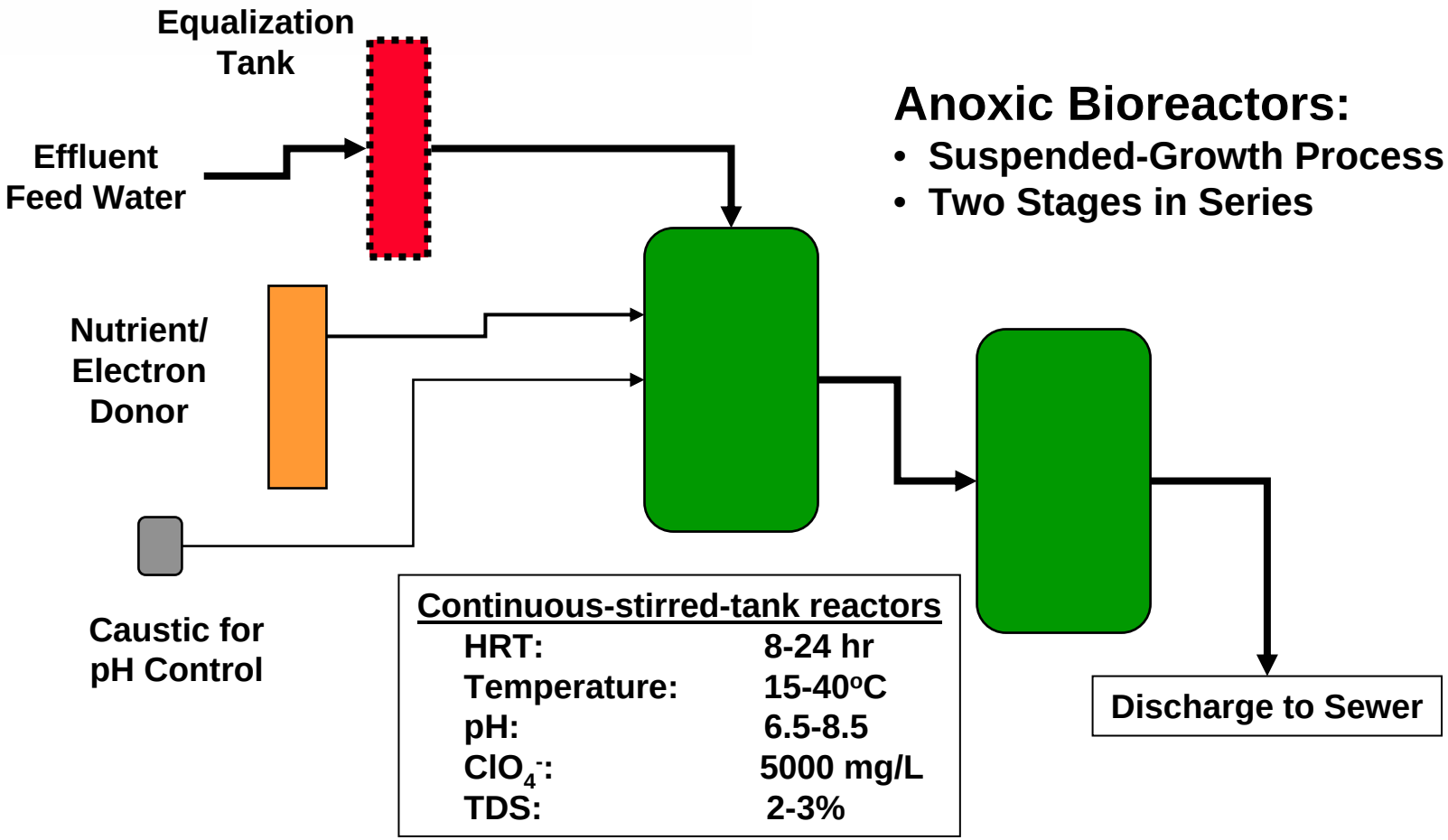
Perchlorate Effluent Treatment

- Demil & Propellant Production Generate Effluents
- Biodegradation Processes
  - Continuous-stirred-tank-reactor (CSTR)
  - Fluidized bed reactor (FBR)
  - Result in Perchlorate Destruction: $ClO_4^- \rightarrow Cl^- + 2O_2$
- 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

Continuous-stirred-tank reactors

HRT:	8-24 hr
Temperature:	15-40°C
pH:	6.5-8.5
ClO_4^-:	5000 mg/L
TDS:	2-3%

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 Promomtory

- 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 ≥ 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/ft^3
- Regeneration & Residuals Treatment Conducted Off Site

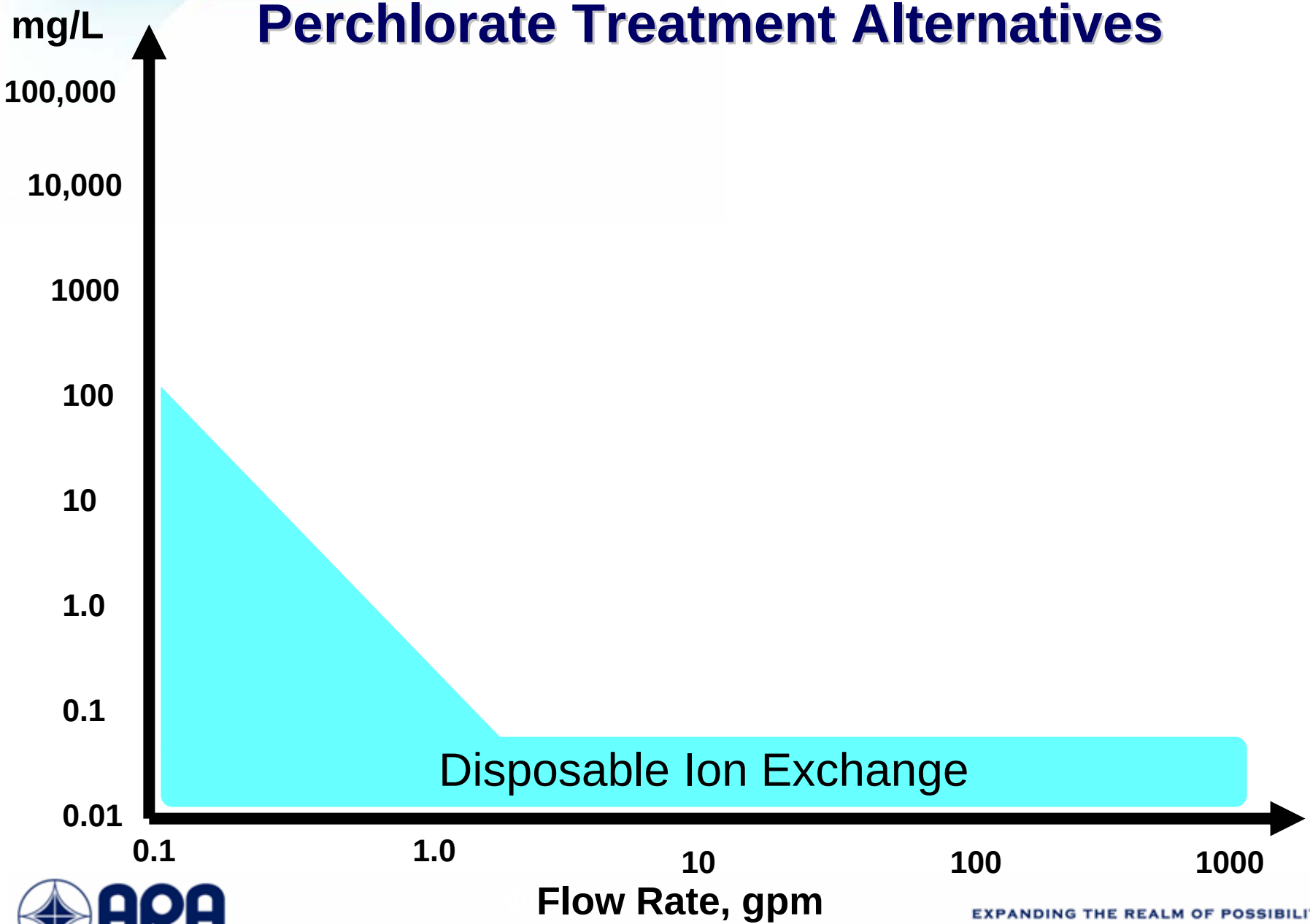
Benefits of WBA Resin Process

- **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 that a single unit operation
  - May reduce the footprint of the treatment system
  - May permit perchlorate recovery

Perchlorate Treatment Alternatives



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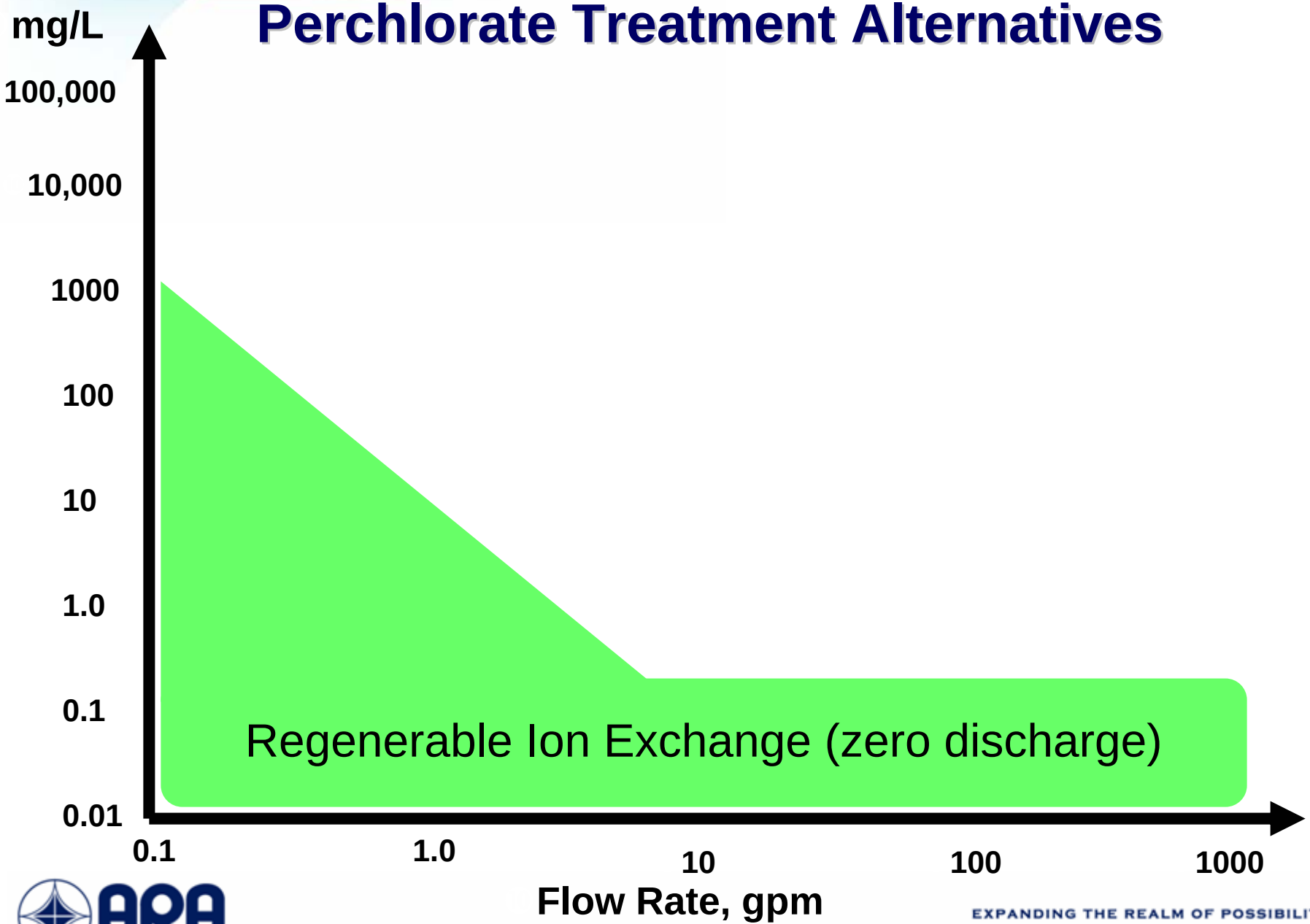

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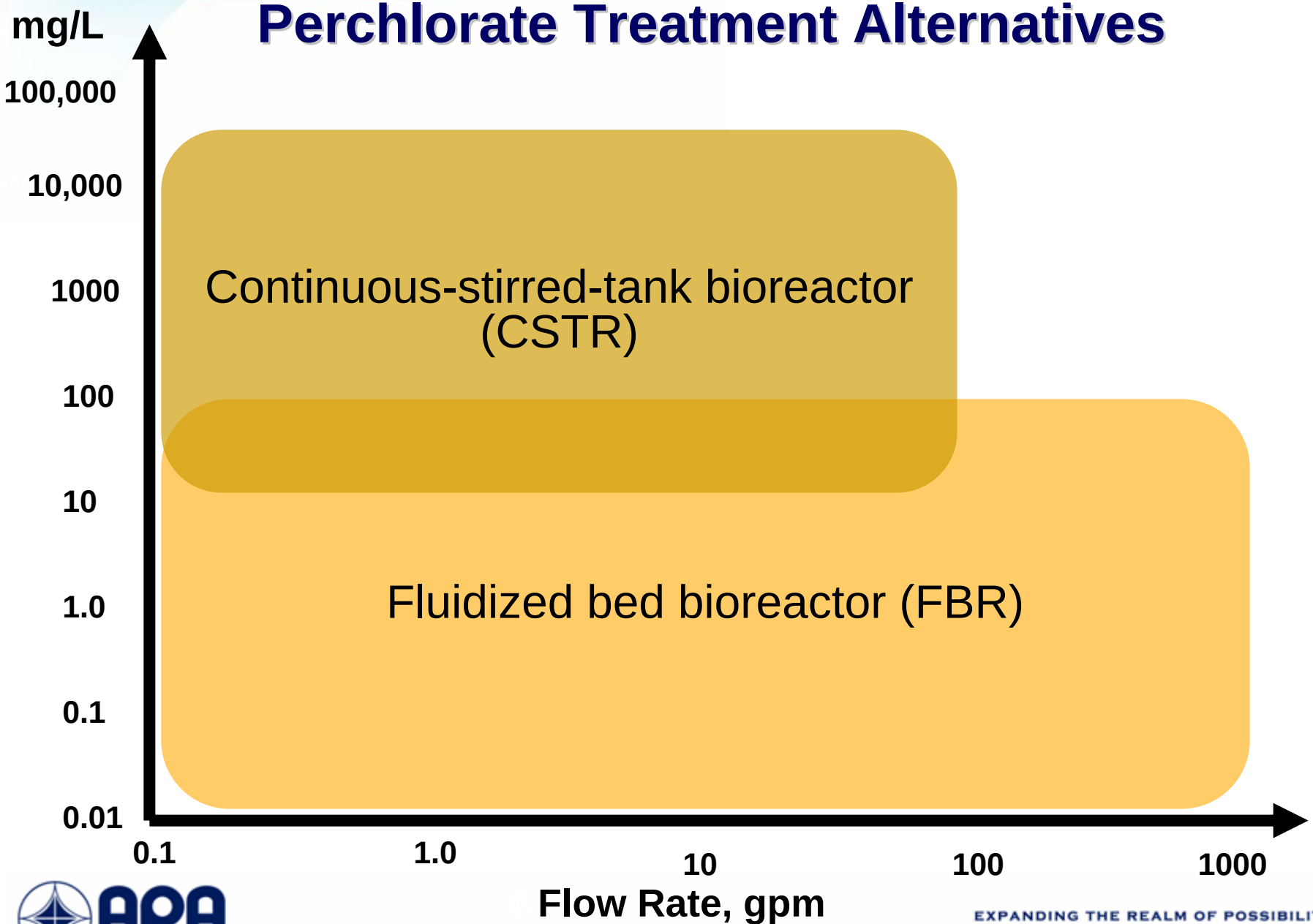

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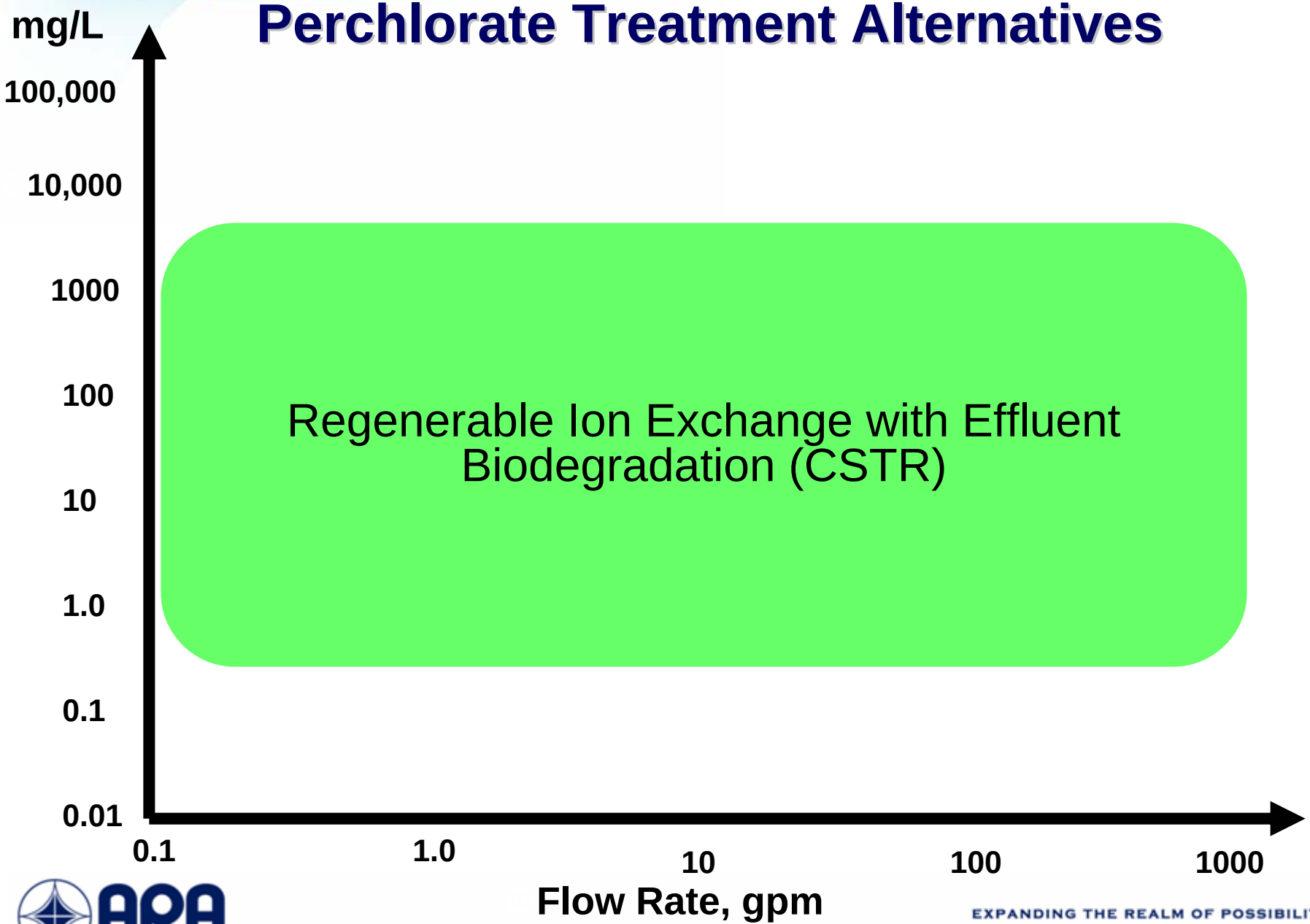

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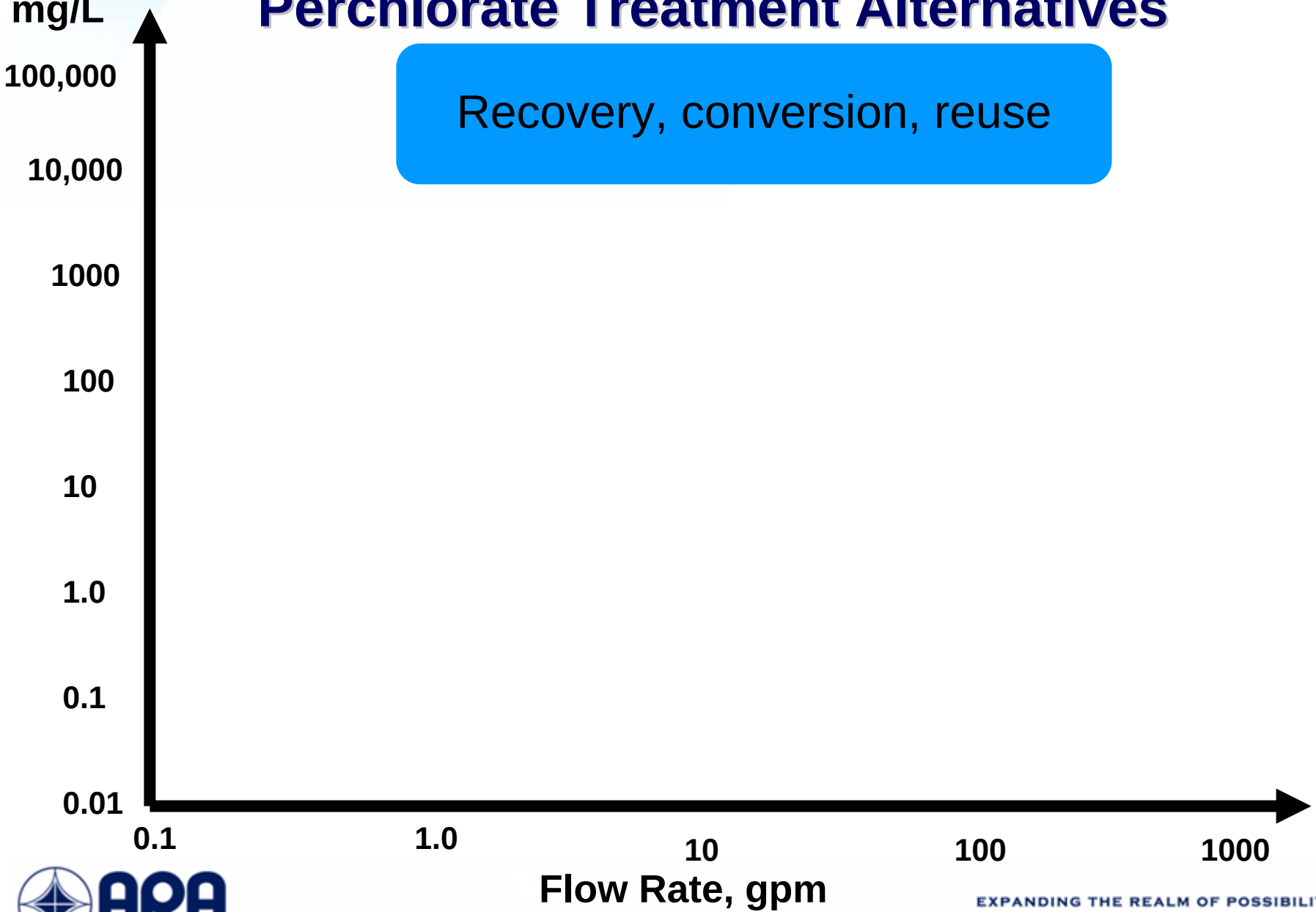

Recovery, conversion, reuse

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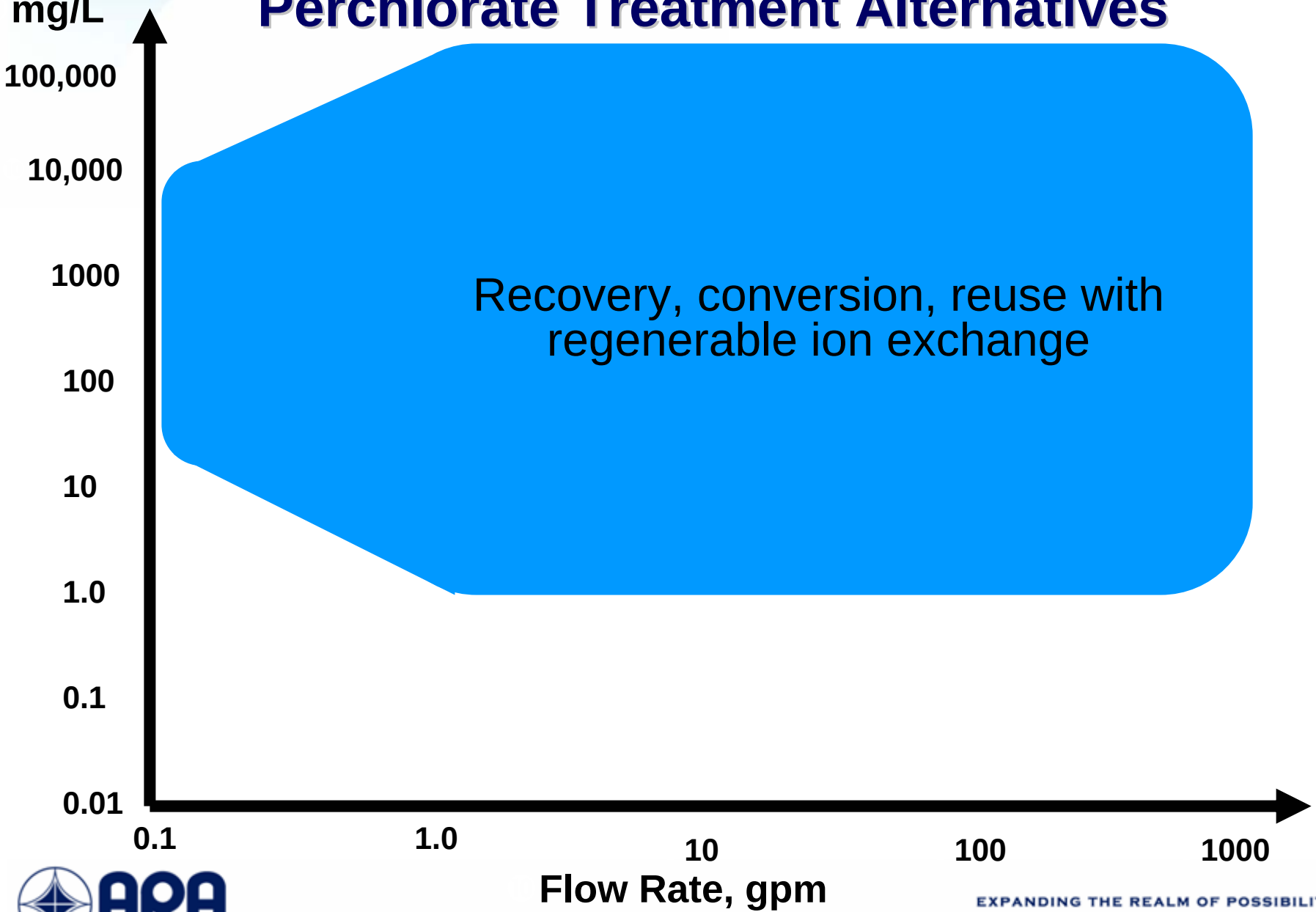

Summary

- **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