# *Magnetic Separation SPI: Waste Water Treatment*


## Los Alamos National Laboratory

Joe Waynert, Coyne Prenger, Laura Worl,
Tony Ying, Bob Wingo, Jim Stewart, Dean Peterson

Jon Bernard, formerly ***DuPont***, presently ***LANL***
Chris Rey, formerly ***DuPont****, presently* ***ORNL***

Mike Johnson, ***New Mexico State University***



CRADA with DuPont established June 17, 2002

FY2004 Project Funding: $ 47.5 k (DOE)
$118.8 k (DuPont funds-in)
$ 79.2 k (DuPont in-kind)


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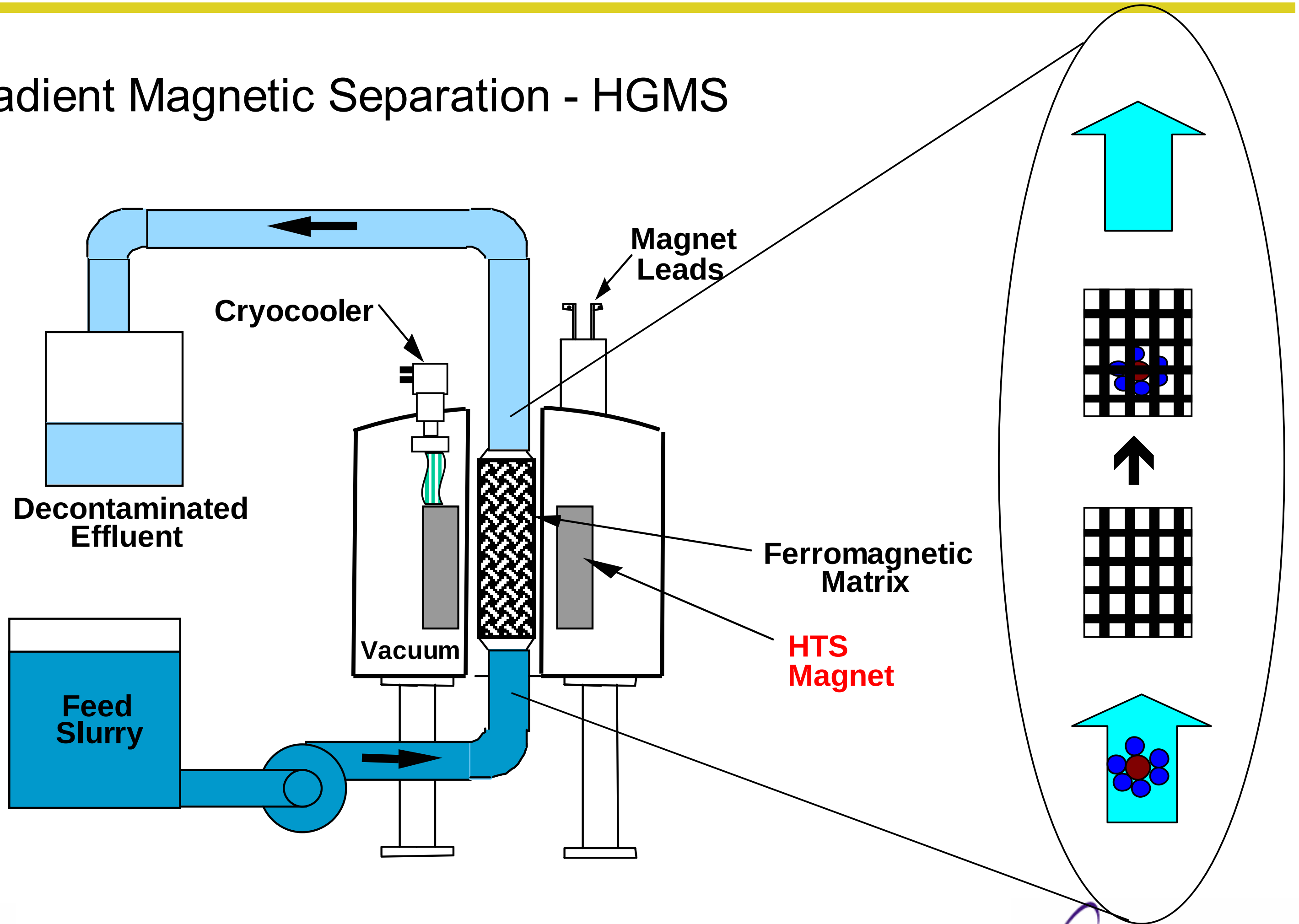
# Outline

- Overview of HTS Magnetic Separation
- Research Integration
- FY 2003 Review
- FY 2004 Results
- FY 2004 Performance
- FY 2005 Plans

# Overview - Magnetic Separation System

High Gradient Magnetic Separation - HGMS



# Magnetic Separation Equipment


# HTS Magnet Specifications

- 624 m of Bi-2223/Ag superconducting tape
- Overall coil dimensions of 18 cm OD, 15.5 cm height and 5 cm ID
- 2.5 cm warm bore
- Cooled by a two stage Gifford-McMahon cryocooler
- At 40 K the magnet can generate a central field of 2.0 T at a current of 120 A

# Features of Magnetic Separation

- Very efficient removal of magnetic particles *(kaolin clay, multi-billion dollar example)*
- New market applications - *waste water treatment, water purification, medical/biological separations, capture target compound*

  *(we are exploring NEW uses of this technology)*
- Clever chemistry to magnetically capture target molecules
- Potential near term success - *heavy metal removal from mine drainage*
  - 1000's of mines with heavy metal drainage issues
  - significant market opportunity if cost effective

# *HTS Magnetic Separation Benefits*

- Reduced electrical usage compared to resistive coil technology
- Can be portable with cryogen-free magnet *(important for temporary cleanup or remote site)*
- Smaller footprint than more conventional technologies- *potentially less expensive because less real estate*
- Fewer chemicals (safer) - *ferrite process vs conventional precipitation technique*
- Environmentally friendly - *ferrite process produces non-hazardous, non-leachable solid waste*

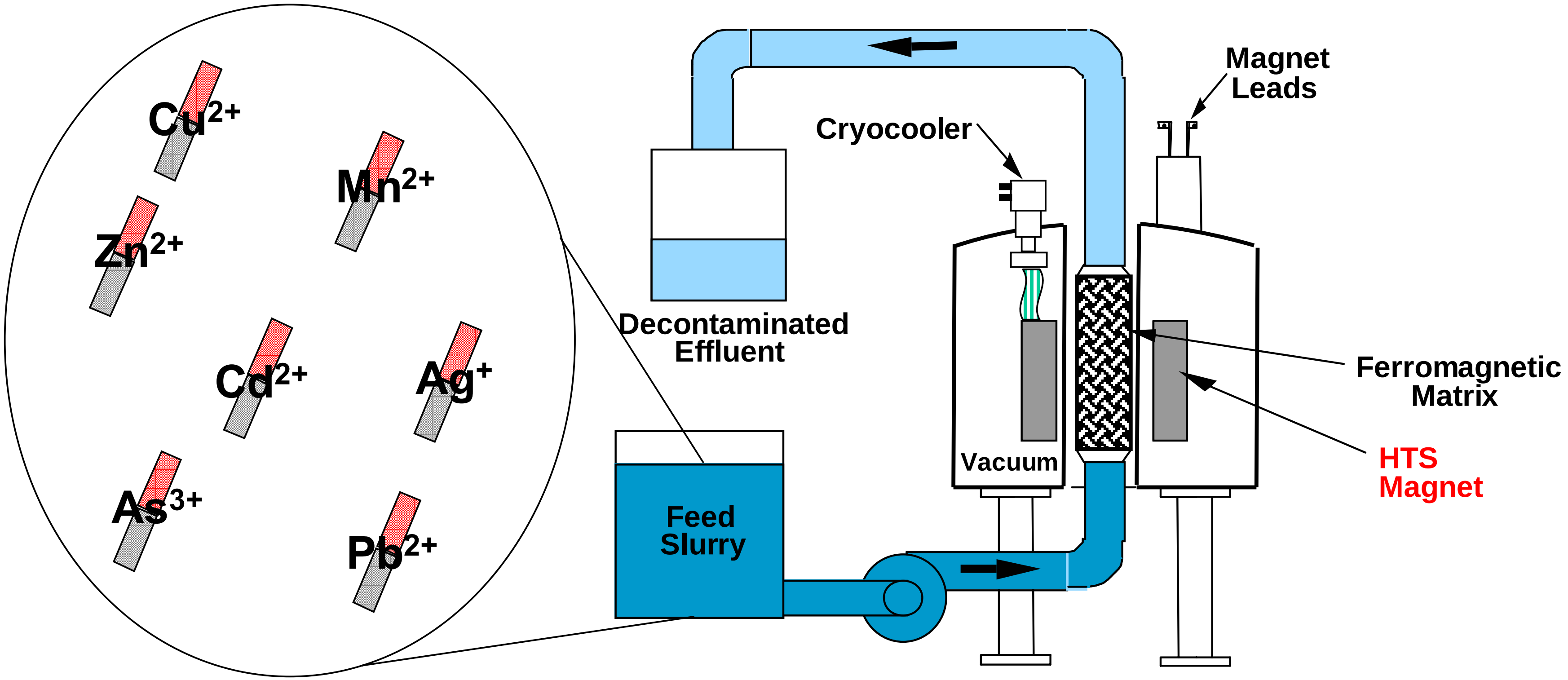
# Status: Magnetic Separation SPI Program

- DuPont appears to have realigned their R&D direction/portfolio; may discontinue support of SPI program
- LANL may have to identify new industrial partner: GE Water Technology; Bayer NA; Infilco Degremont; Calcon Carbon Corporation; …
- HTS magnetic separator offers significant operational energy savings
- LANL has over 10 years experience in magnetic separation:
  - process development
  - magnetic separation equipment
  - chemical analytical equipment/expertise
  - multi-disciplinary approach
    - Chemists; environmental engineers; specialists in magnetics, SC, modeling

# Research Integration

- Jon Bernard, DuPont employee thru 6/11/04
  - full-time stationed at LANL during CRADA
  - fully equipped laboratory in STC space at the LANL Research Park
  - integrated into LANL magnetic separation team
  - access to LANL analytical equipment & expertise
  - LANL employee as of 7/19/04
- Regular technical interchanges with DuPont, Wilmington
- Chemistry expertise of Dr. Johnson of New Mexico State University
- Bureau of Reclamation funding test bed at Leadville Mine Drainage Tunnel (LMDT) treatment facility
- Pilot plant partnership with Leadville Institute of Science and Technology (LIST)
- EPA participation: Leadville is superfund site
- Article to be published in Separation Science and Technology

# Chemical Preparation of the Feed and High Gradient Magnetic Separation (HGMS)



# FY03 Results
# Magnetite/Ferrite Synthesis

$$Fe^{2+} + Fe^{3+} + Fe^{3+} + 8\ OH^- \rightarrow GR_{(solid)} \rightarrow FeOFeFeO_{3\,(solid)} + 4\ H_2O$$

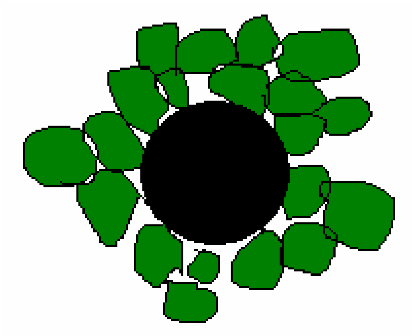
$$Fe^{2+} + M^{3+} + Fe^{3+} + 8\ OH^- \rightarrow GR_{(solid)} \rightarrow FeOMFeO_{3\,(solid)} + 4\ H_2O$$

$$M^{2+} + Fe^{3+} + Fe^{3+} + 8\ OH^- \rightarrow GR_{(solid)} \rightarrow MOFeFeO_{3\,(solid)} + 4\ H_2O$$

M = Metal (ie. $Cu^{2+}$, $Mn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Ag^{+}$, $As^{3+}$)

- $FeOFe_2O_3 = Fe_3O_4$ (magnetite)
- Substituted magnetite = **Ferrite**
- Synthesis gets “stuck” at an intermediate stage in LMDT at 9 °C

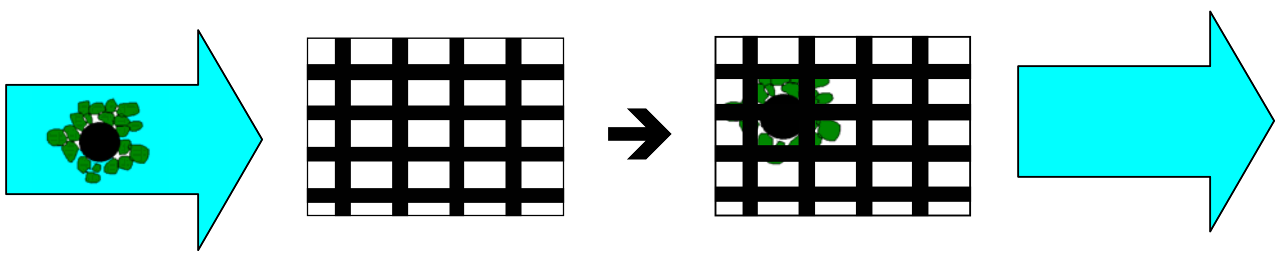
# FY03 Results
# Our Approach – Magnetic Seeding



Green Rust

## Magnetic seeding – A template effect:

- Produces a suitably magnetic particle
- Allows for magnetic separation



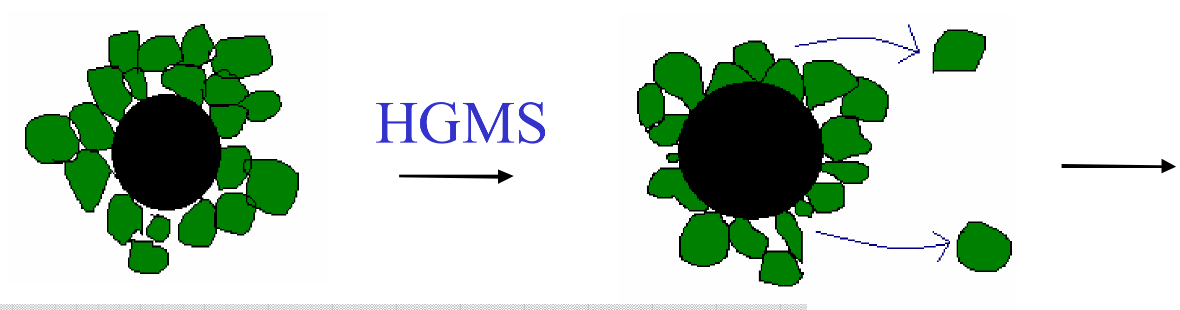
# FY04 Goals

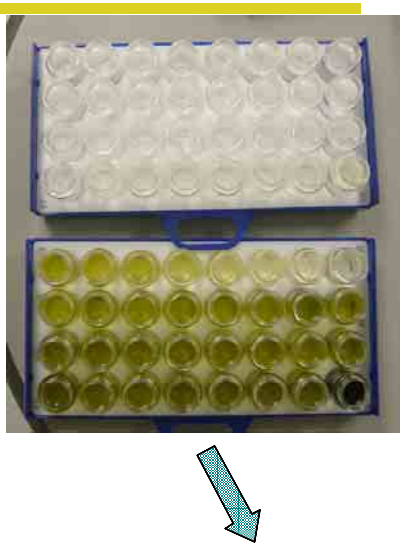
- Optimize ferrite & HGMS processes
- Determine controlling parameters and ranges
  - Particle concentrations (magnetite seed, $Fe^{2+}$)
  - Type of stainless steel wool (extra-fine to coarse)
  - Applied magnetic field strength
  - Flow velocity in the separator
  - Residence time in the separator
- Determine scaling issues from laboratory to pilot plant

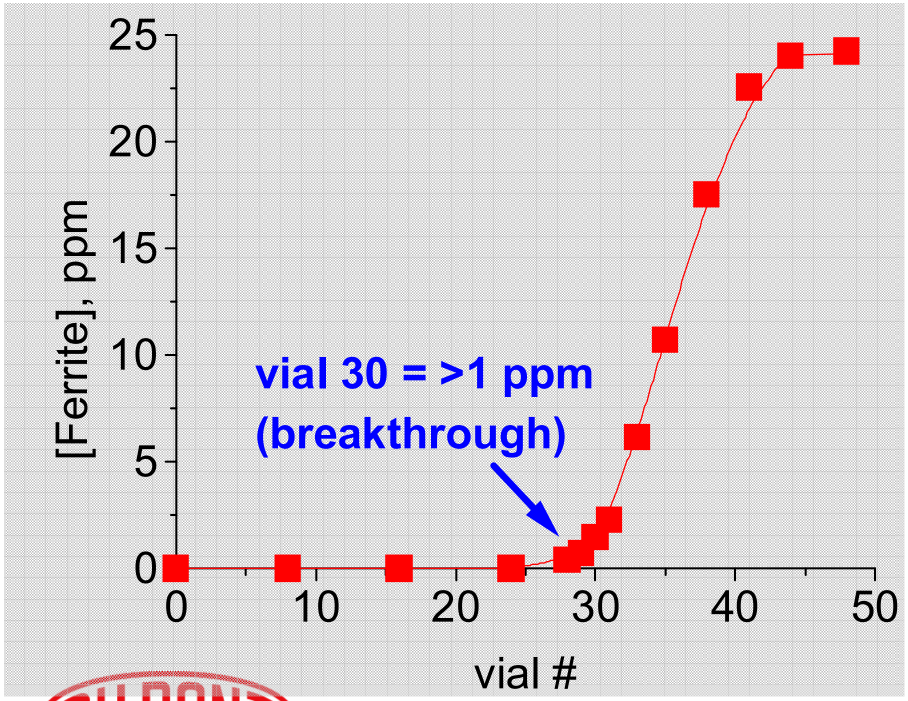
# *Heavy Metal Contaminants at the LMDT*

| Contaminant | Influent water (mg/L) | Target (mg/L) |
|---|---|---|
| Zn | 3.6 | 0.084 |
| Cu | < 0.009 | 0.009 |
| Pb | 0.0031 | 0.003 |
| Cd | 0.02 | 0.0009 |
| Ag | < 0.001 | 0.00005 |
| Fe | 1.4 | 1.00 |
| Mn | 1.8 | ~~0.295~~ 0.05 |

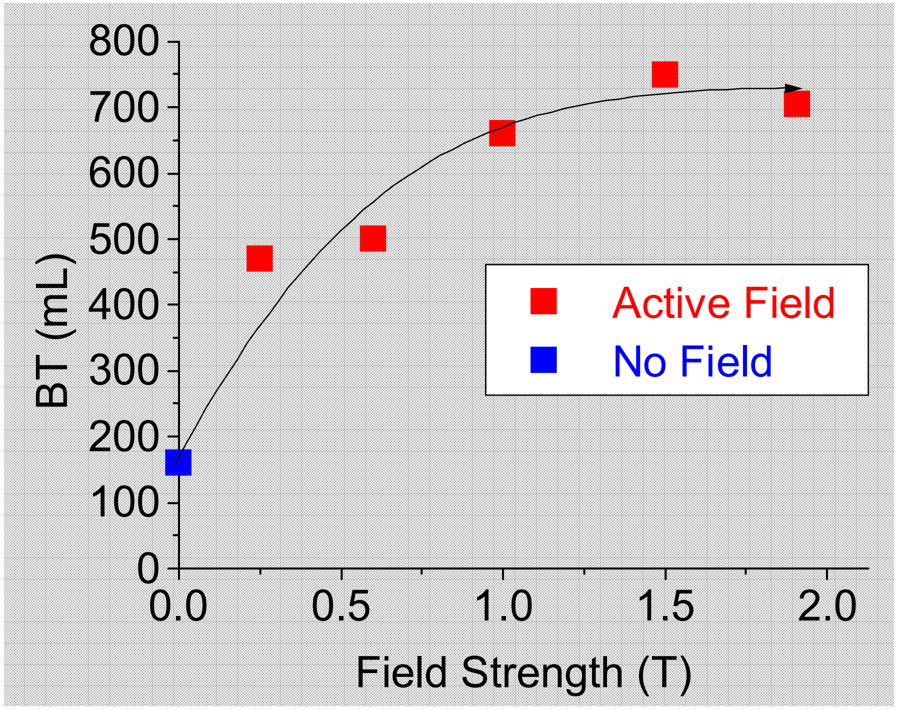
# *Particulate Breakthrough*



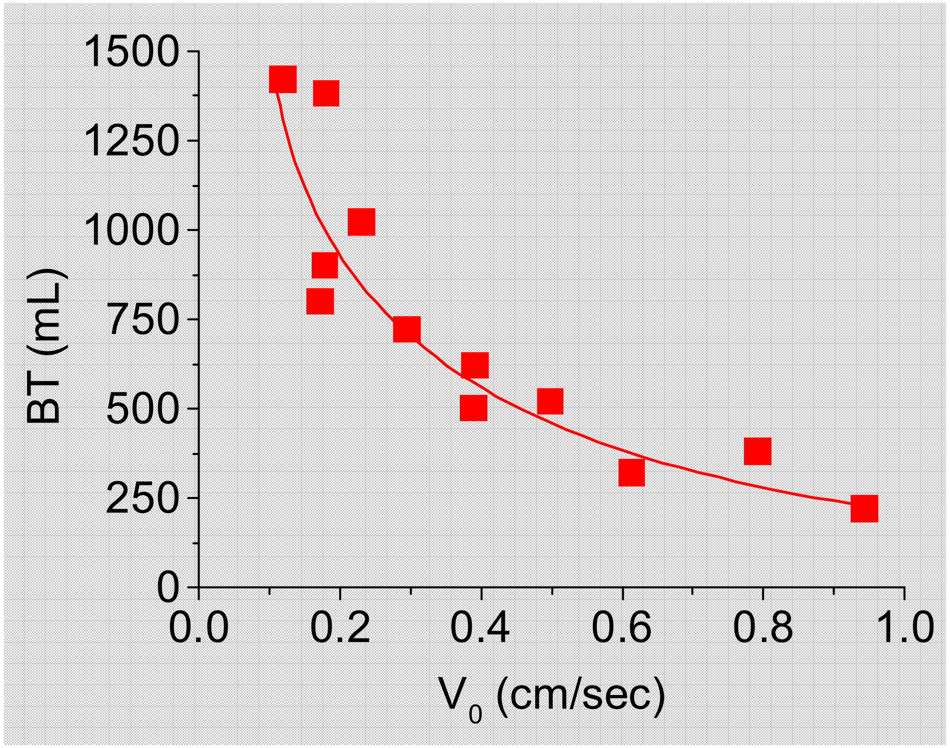



# FY04 Results
# Effect of Field Strength



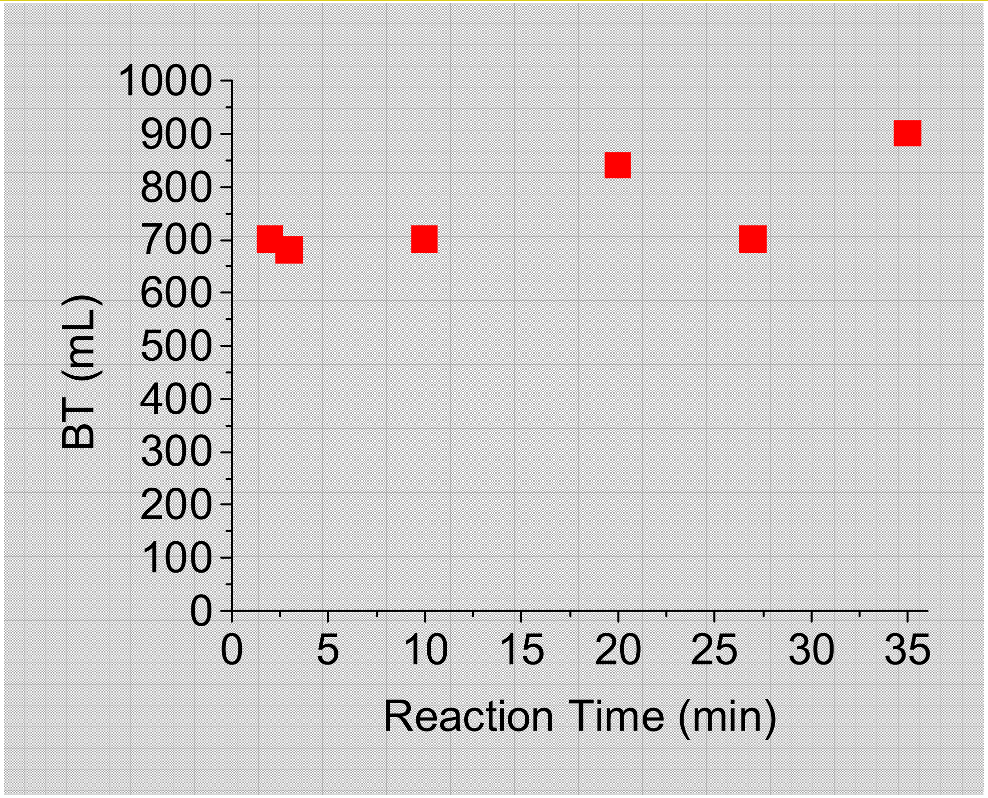

- Increasing separator capacity with increasing field
- Minimal increase above 1.0 T
  - Consistent with saturation magnetization of steel wool

# FY04 Results
# Effect of Superficial Velocity



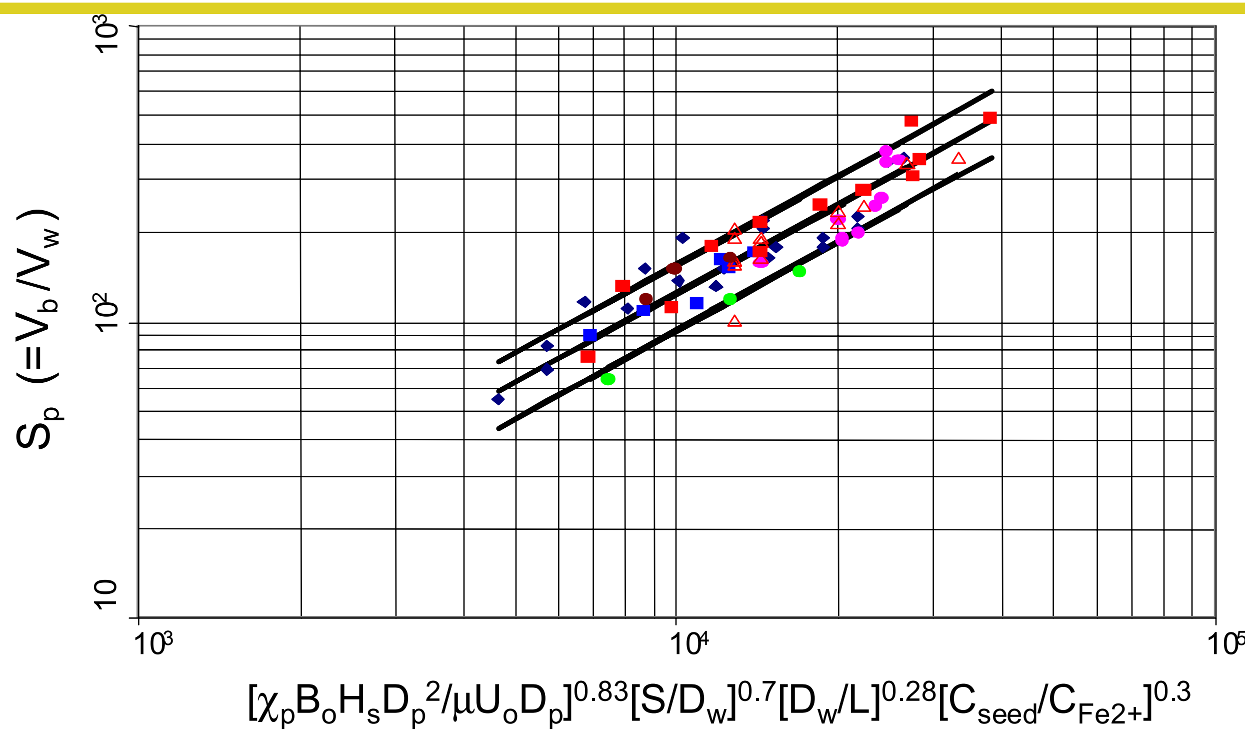

• There will be a trade-off between separator capacity, process time

# *FY04 Results*
# *Effect of Reaction Time*




- Short reaction times adequate
- ~ 3 minutes necessary to stabilize the pH

# FY04 Results
# Separator Performance Correlation




$$S_p = \frac{V_b}{V_w} = A_o \left[\frac{\chi_p B_o H_s D_p^2}{\mu U_o D_p}\right]^{0.83}\left[\frac{S}{D_w}\right]^{0.7}\left[\frac{D_w}{L}\right]^{0.28}\left[\frac{C_{seed}}{C_{Fe^{+2}}}\right]^{0.3}$$

# FY04 Results

## Optimized Laboratory-Scale Procedure for LMDT Water

- Metal removal from LMDT is a feasible process at the laboratory-scale using HGMS

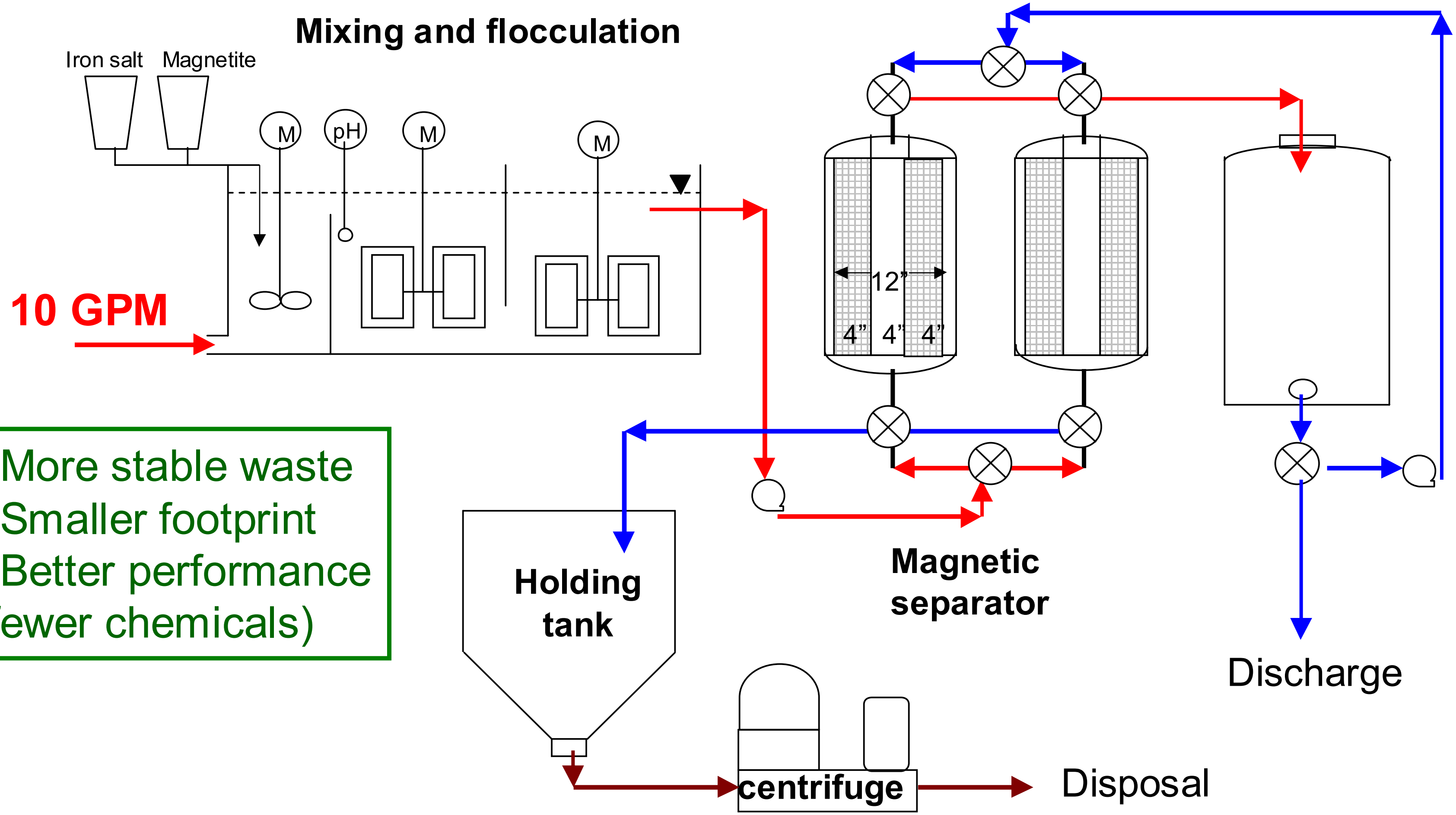
Optimized procedure might involve:

1. 100 ppm magnetite seed and 100 ppm Fe(II)
2. 3-4 minute reaction time
3. High matrix packing density
4. Superficial velocity ~ 0.2 cm/sec
5. Maximum field strength < 1.0 T
6. No excess oxygen required
7. Extra fine or finer stainless steel wool matrix
8. Column cleaning best with high velocity backflush, air sparge and column agitation

# Scale-Up Considerations - Leadville

1. Automation
   - Computerized monitoring
   - Chemicals, pH, mixing, flow rate, flow path
2. Chemicals expected to scale directly
3. Column considerations (size, quantity of matrix)
   - Affects processing cycles
   - Dependant on water volume and composition
   - Monitor possible column capacity degradation
4. Ferrite synthesis
   - Method of solid/liquid separation (ie. filter press, centrifuge)
   - Control exposure to oxygen ($N_2$ generator?)
5. Cost
   - Selection of capital equipment

# Pilot Plant: A Continuous Process That Fits on 2 Pallets




- More stable waste
- Smaller footprint
- Better performance (fewer chemicals)

# *FY04 Performance*

All CRADA deliverables have been met

- ✓ Determined controlling parameters and ranges for ferrite process
  - *Parameter sensitivity evaluation and optimization*
- ✓ Optimized ferrite & HGMS processes
  - *optimized process for specific application/site*
  - *determined how process variables might change for different conditions/application*
- ✓ Determined scaling issues from laboratory to pilot plant
  - *quantities of chemicals, processing times*
- ✓ Established a pilot plant partner with LIST
  - Achieved initial penetration of a new market

# *FY05 Plans*

- Extend CRADA with DuPont or find another industrial partner
  - Extend technology to other sites/applications
  - Refine HGMS procedure
- Establish a larger HTS magnet system at LANL
- Design, fabricate, assemble, test, verify operational capability of pilot plant

# *Los Alamos Research Park*