



# **Sulfur Polymer Stabilization/Solidification of Elemental Hg and Hg Contaminated Soil, Sludge and Debris**

**P.D. Kalb**

**Environmental Research & Technology Division  
Brookhaven National Laboratory**

*Presented at*

***Breaking the Mercury Cycle: Long Term Management of  
Surplus & Recycled Mercury & Mercury-Bearing Waste***

*Boston, May 1 –3, 2002*



# Overview



- *Background*
- *Technology Description*
- *Technology Status*
- *Applications/Treatability Studies*
- *Summary/Conclusions*



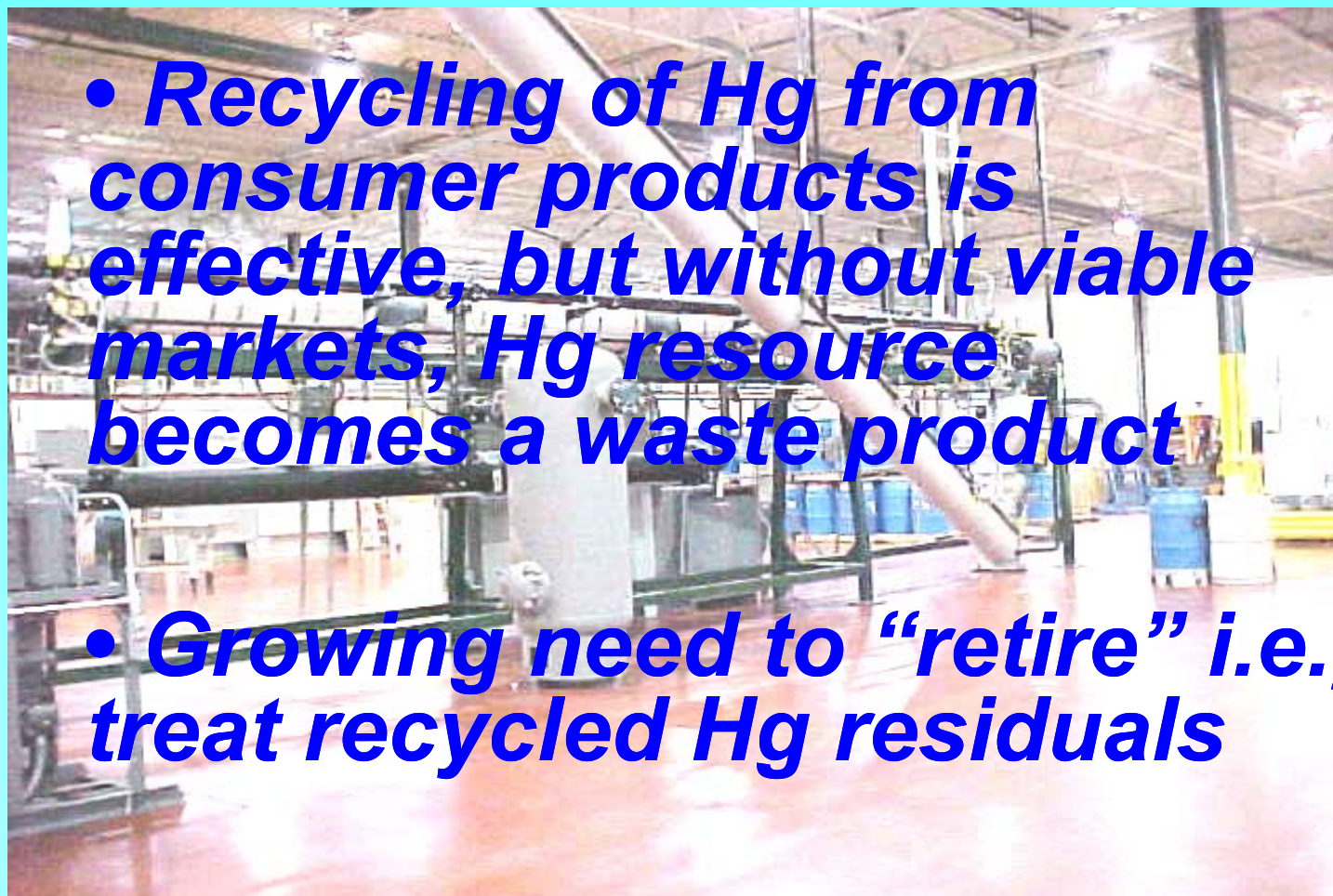
# Background

- *Elemental Hg and Hg contaminated wastes are found at most DOE facilities*
- *Hg is highly toxic, readily leachable and has high vapor pressure*
- *Conventional techniques (amalgamation):*
  - *Reduce Hg solubility but result in highly dispersible powders*
  - *Do not reduce mercury vapor pressure*
  - *Do not chemically or physically immobilize radionuclides*

# Understanding the Problem



- *Recycling of Hg from consumer products is effective, but without viable markets, Hg resource becomes a waste product*
- *Growing need to “retire” i.e., treat recycled Hg residuals*



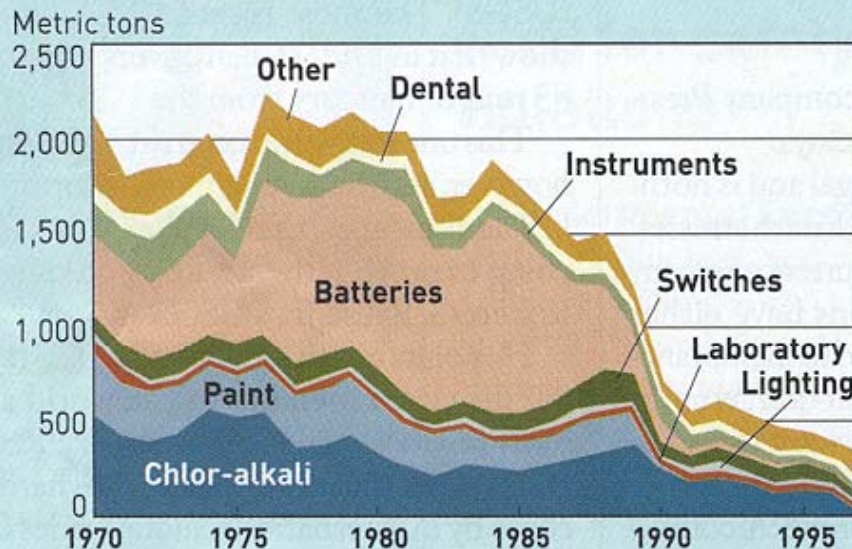


# Declining Hg Market



## MERCURY USE

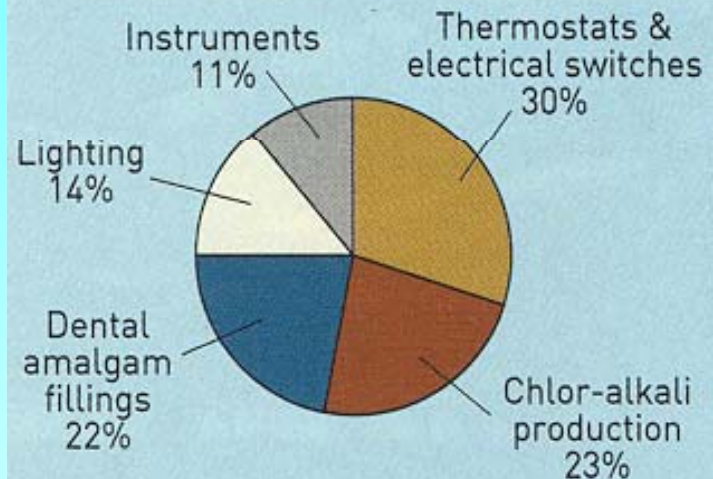
Sharp drop-off after 1985



SOURCE: U.S. Geological Survey Minerals Yearbook

## MERCURY USE

Chlor-alkali industry makes up 25%



Estimated 2001 U.S. demand = 220 tons

SOURCE: Bethlehem Apparatus Co.

***Industrial use has declined 250% in 20 years, sharply reducing the demand for recycle Hg***

# Understanding the Problem



***Even greater volumes of Hg have contaminated soil, air and water or are being stored pending treatment***

- 9 million lbs of Hg stockpiled by DOD***
- 5 million lbs from obsolete chlor-alkali plants***
- >50,000 yd<sup>3</sup> Hg contaminated soil at Oak Ridge National Laboratory***
- >7000 yd<sup>3</sup> soil at BNL Chemical Holes***

# Regulatory Requirements



Hg Category	Radioactive	Non-Radioactive	Leaching Std.
Elemental	AMALGM	NO TREATMENT STD (recycle only)	<b>Not required</b>
< 260 ppm	STABIL	STABIL	UTS limit 25 ppb
> 260 ppm	RMERC/ AMALG	RMERC	TCLP limit 200 ppb (soil)
> 260 ppm (w organics)	IMERC/ AMALG	IMERC	TCLP limit 200 ppb (ash)

# Technology Description



- *SPSS developed at BNL to provide improved, cost-effective treatment of Hg wastes*
- *Based on patented BNL Sulfur Polymer Microencapsulation technology for treatment of a variety of hazardous, radioactive, and mixed wastes*
- *Meets NRC criteria for long-term performance of low-level radioactive waste*
  - *Mechanical integrity*
  - *Long-term leachability*
  - *Biostability*
  - *Thermal stability*
  - *Radiation stability*

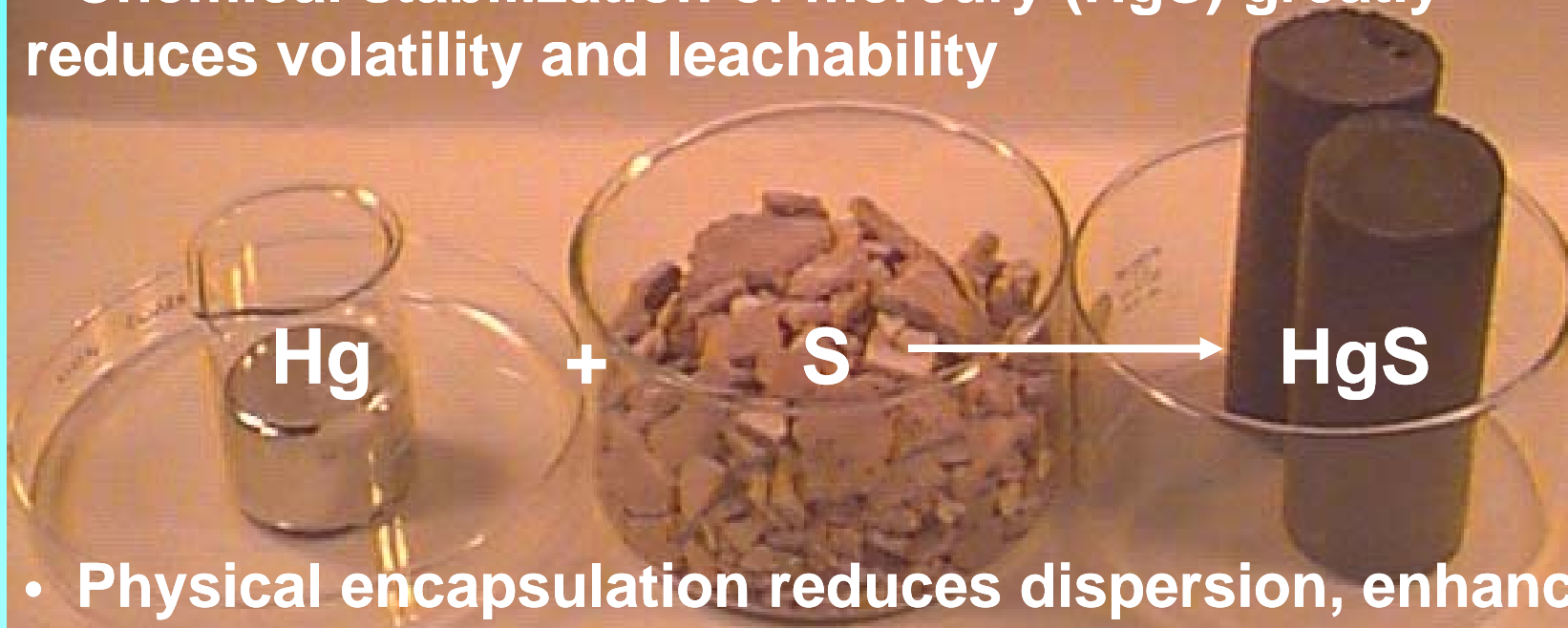


# Stabilization/Solidification of Mercury



## Two stage process:

- Chemical stabilization of mercury (HgS) greatly reduces volatility and leachability



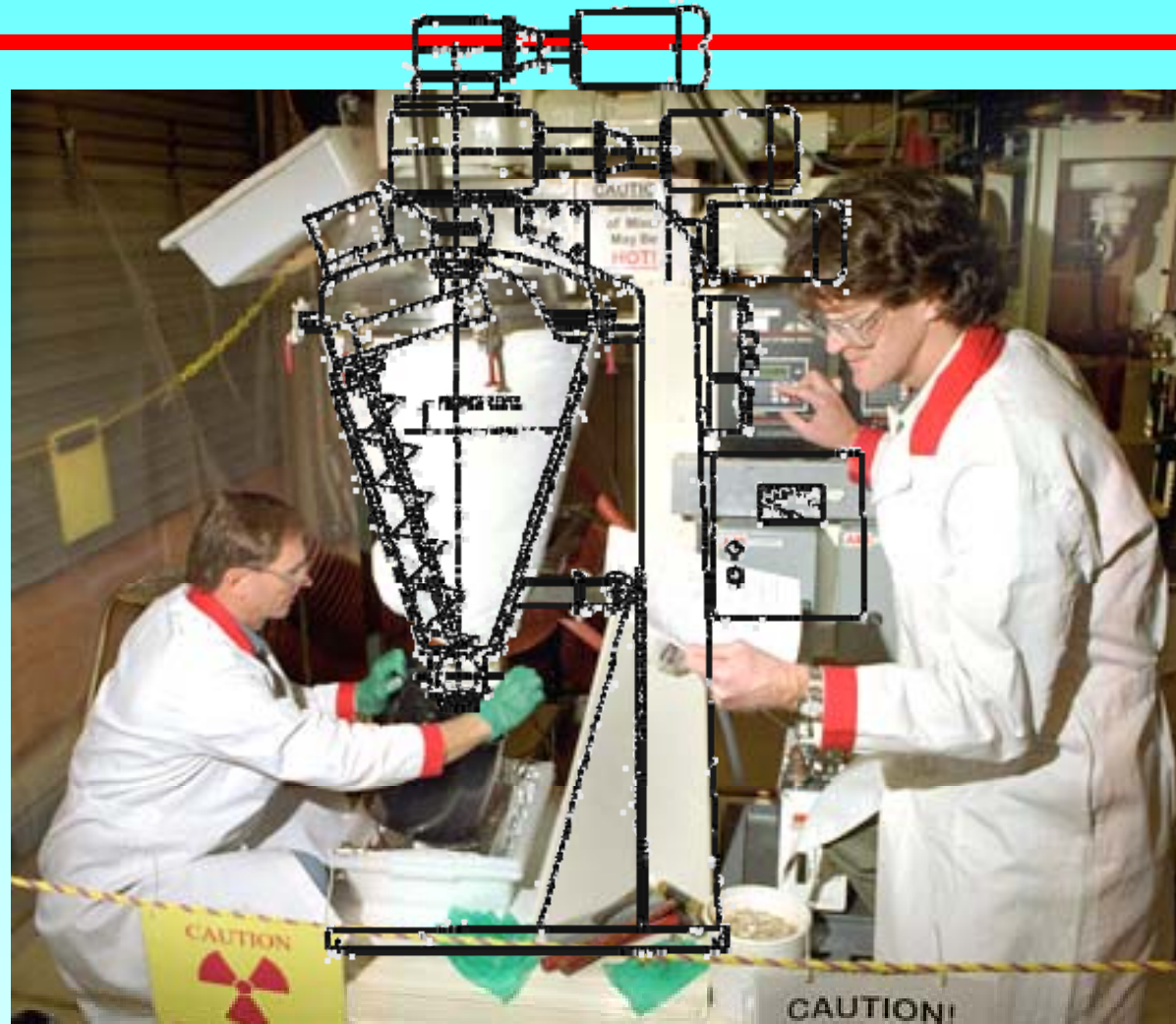
- Physical encapsulation reduces dispersion, enhances stability, further reduces leaching, and immobilizes radionuclides



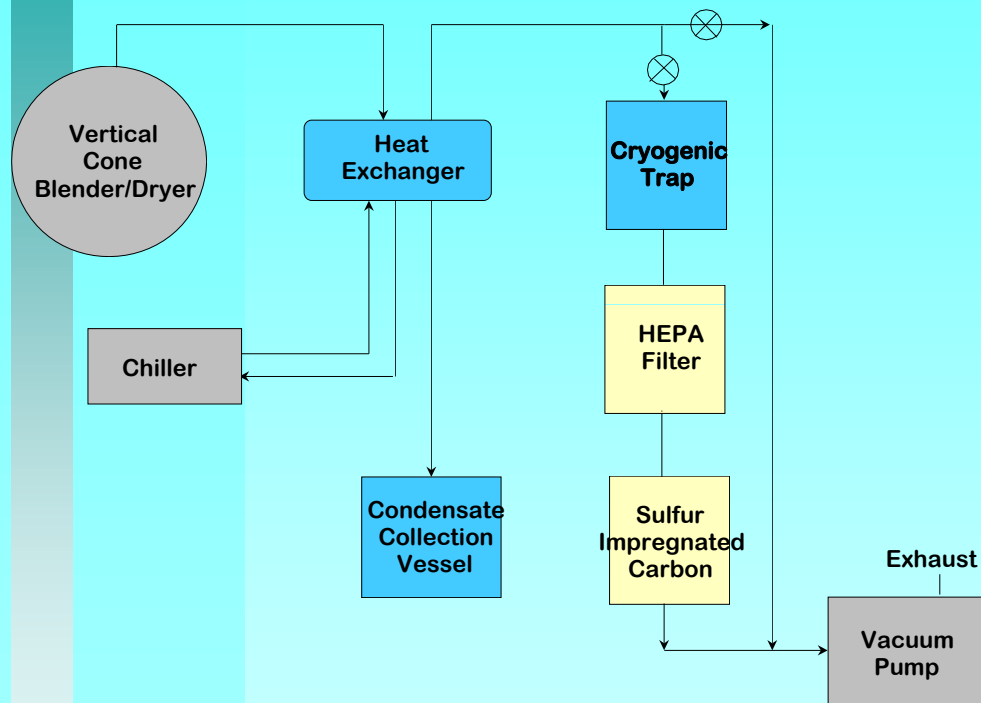
# Sulfur Polymer

- *Sulfur Polymer Cement (SPC) was developed by the USBM as a low-cost alternative construction material (approx. \$0.12/lb)*
- *Produced from by-product, waste sulfur*
- *Contains 95% elemental sulfur, 5% organic modifiers to enhance stability*
- *Low-temperature, low viscosity thermoplastic process results in high waste loadings*
- *BNL adapted SPC for radioactive and mixed waste microencapsulation. U.S. Patent issued in 11/97*

# BNL Pilot-Scale SPSS Process



# Pilot-Scale Off Gas System





# Mass Balance: Hg Capture Efficiency

Off Gas Component	Hg, g Drum E-1	Hg, g Drum A-4	Total Hg, g
Chiller Trap	1.442	2.791	4.233
Cryogenic Trap	0.504	0.229	0.733
Total Condensate	1.943	3.02	4.966
Carbon Trap			0.089
Total Hg in Off Gas			5.055
% Hg Trapped			<b>0.33</b>
Capture Efficiency			<b>99.67 %</b>



# Technology Status

- ***Bench- and Pilot-scale testing have been completed at BNL:***
  - ***BNL Hg contaminated soil***
  - ***BNL elemental Hg***
  - ***Los Alamos National Laboratory elemental Hg***
  - ***Los Alamos National Laboratory Hg contaminated debris***
  - ***DOE/EPA simulated Hg sludge***
  - ***Hg residuals from gold mining operations***



# Technology Status



- *Second patent pending*
- *Commercial license issued for treating elemental Hg resulting from gold mining operations*
- *BNL negotiating additional commercial license agreements for treatment of other Hg wastes*
- *Full-scale deployment for treatment of elemental Hg planned*

# Treatment of BNL Elemental Hg And Hg Contaminated Soil



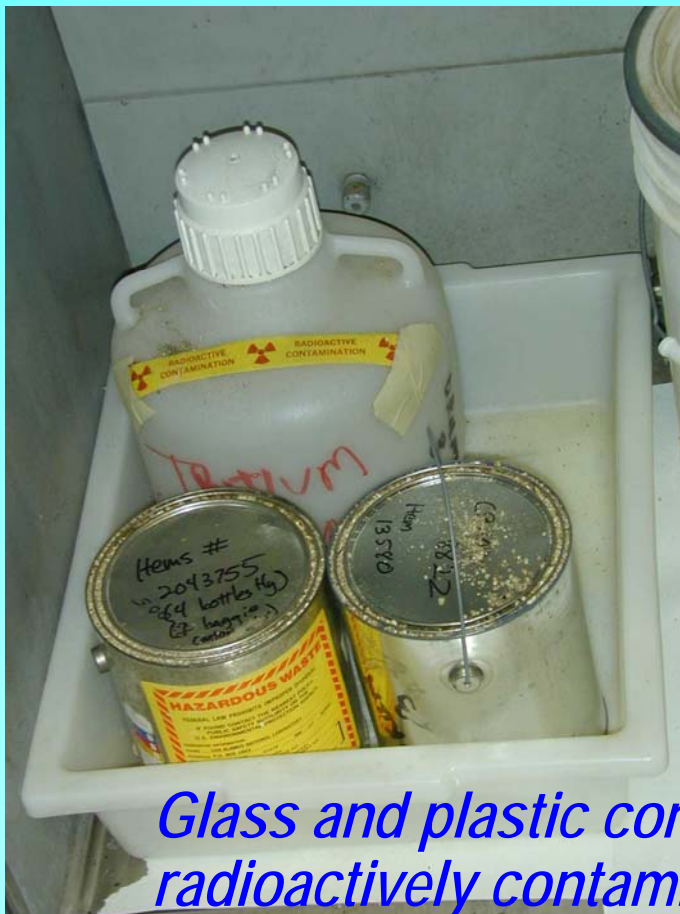
- *SPSS successfully treated > 400 lbs elemental Hg*

- *SPSS successfully treated BNL Chemical and Animal Holes high Hg soils containing ~5000 ppm Hg:*

- *>1000 lbs of mixed waste Hg soil*
- *60 dry wt % soil formulation*
- *No volume increase*
- *TCLP below UTS limits achieved*



# LANL Mixed Waste Mercury for SPSS Treatability



*Glass and plastic containers containing radioactively contaminated elemental Hg*





# LANL Mixed Waste Mercury for SPSS Treatability



*Flasks of mixed waste elemental Hg  
for processing*



*TCLP pellets of SPSS treated  
elemental Hg*

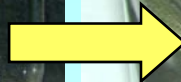
# SPSS Macroencapsulation



*Crushed glass debris*



*Modified  
Processing System*



*Treated glass debris*



# SPSS Macroencapsulation





# Mercury Sludge Treatability Study



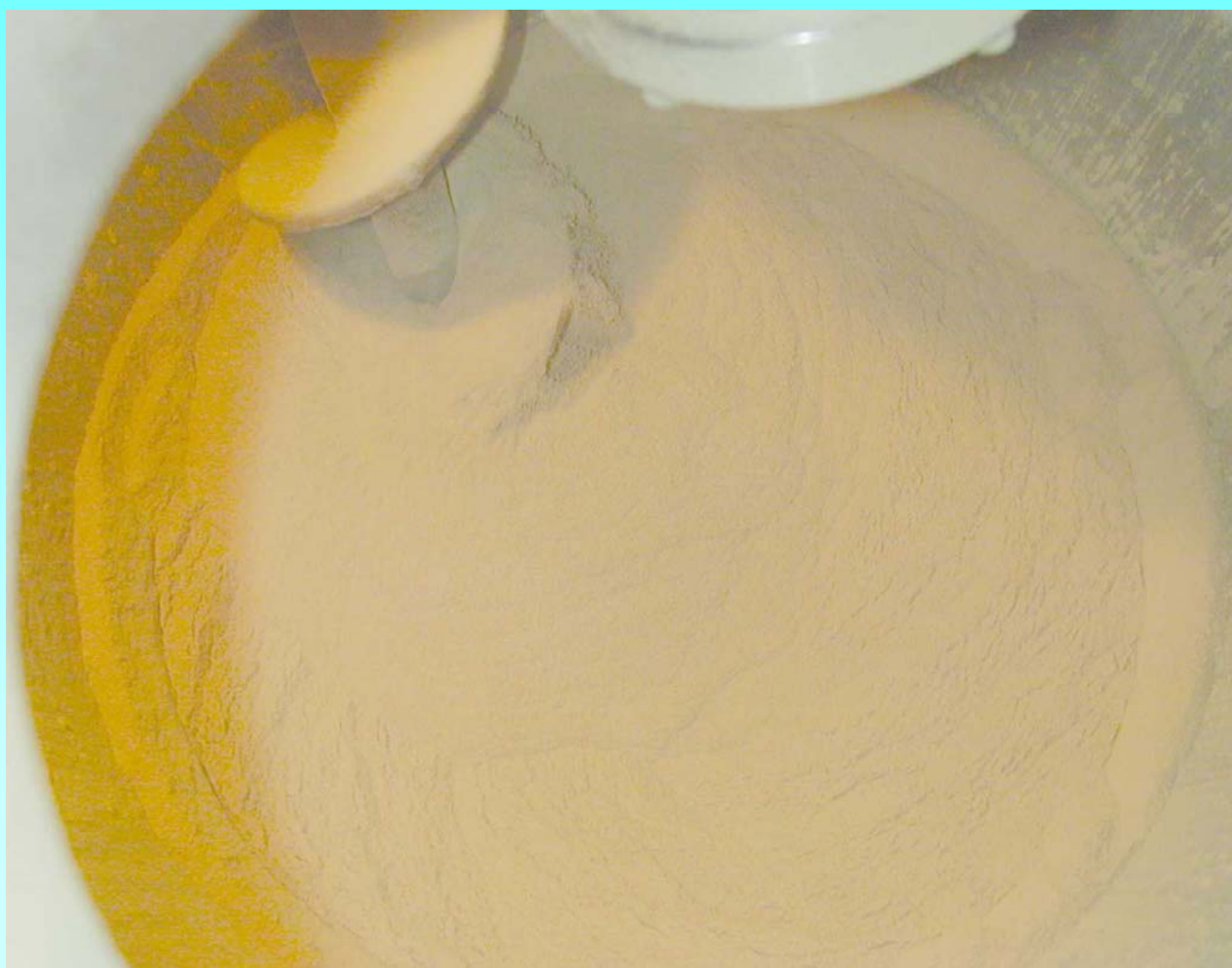
- *Direct stabilization of high Hg (>260 ppm) contaminated sludges (MER 04)*
- *Sponsored by DOE TMFA*
- *Collaboration with EPA OSW*
  - *Data to support ANPR for Hg treatment*

# Simulated Hg Sludge Description



- **5000 ppm Hg (0.5 wt%)**
  - **Elemental**
  - **Nitrate**
  - **Chloride**
  - **Oxide**
  - **Organo-chloride**
- **50 wt% inorganic solids (DE,  $Al(OH)_3$ ,  $FeCl_3$ , NaCl)**
- **49.5 wt%  $H_2O$**

# Pilot-Scale SPSS Processing



# SPSS Processing of Hg Sludge

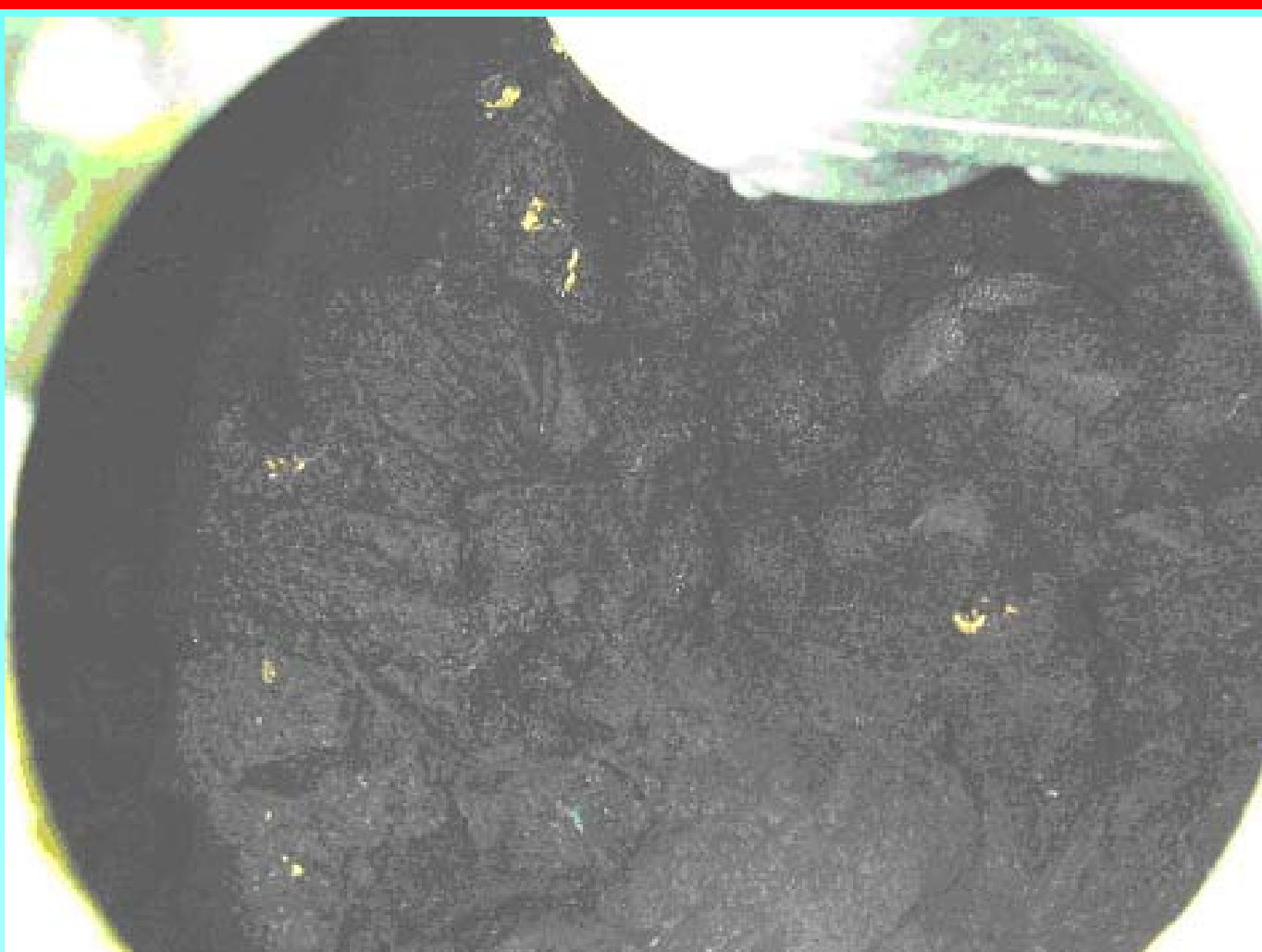




# SPSS Processing of Hg Sludge



# SPSS Processing of Hg Sludge





# SPSS Processing of Hg Sludge



# Processing and Performance Results



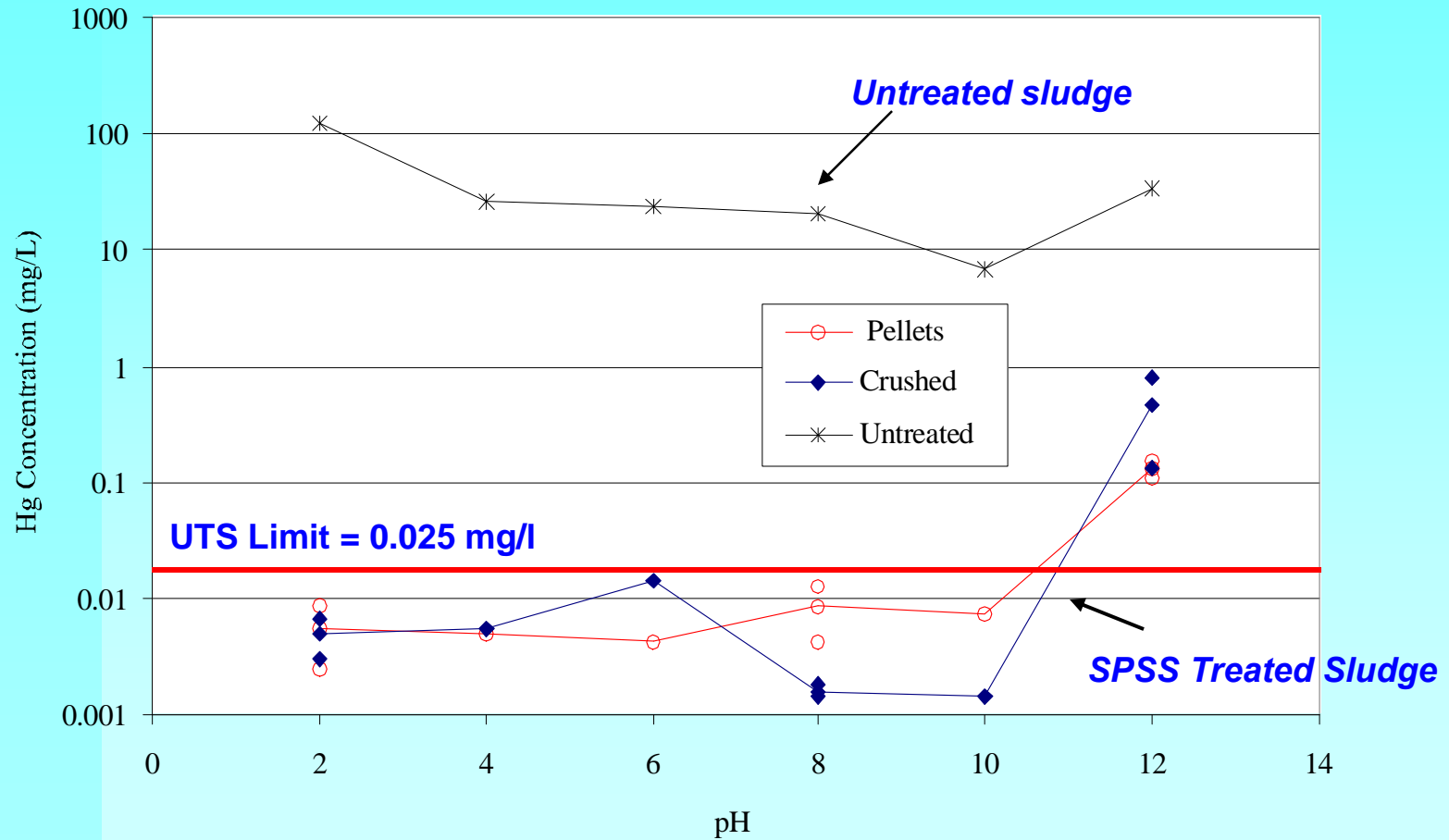
- *Limited bench-scale process optimization of formulas and parameters*
- *Maximum waste loadings:*
  - *60 wt % wet sludge*
  - *30 wt % dry sludge*
- *Lower loading efficiency compared with soil due to particle size/viscosity effects*
- *Waste form volume increase of 36%*

# Processing and Performance Results



- ***TCLP = Toxicity Characteristic Leaching Procedure***
  - ***Target performance:  $\leq 25$  ppb, Universal Treatment Standard***
  - ***Results from certified lab:  $<10$  ppb***
- ***EPA seeking additional info beyond TCLP for proposed rulemaking***
- ***Constant pH leach test at broad range of pH (2 –12) conducted at U of Cincinnati***

# Performance Testing: Constant pH\*



\* Conducted by the Univ of Cincinnati

# SPSS Commercialization



- *BNL issued license to Newmont Mining for application to treat Hg wastes in mining industry*
- *Working with Bethlehem Apparatus for commercial application to treat elemental Hg*
  - *DoD Hg stockpile*
  - *Formerly recycled Hg*
- *Commercialization for treatment of radioactively contaminated Hg (mixed waste Hg)*

# Mercury Use in the Third World

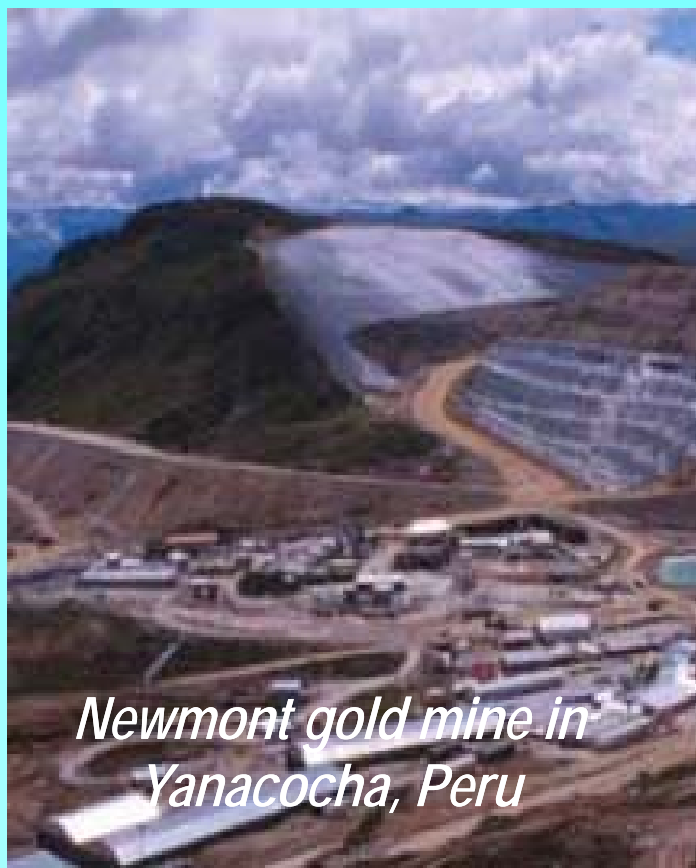


The impact of mercury emissions not only can be felt by local people and their environment, but can also adversely increase the global atmospheric mercury burden. For instance, back-country, low-tech gold mining is notorious for its mercury air emissions, . . . and is one of the leading sources of mercury emissions on a global scale.

*C&E News 2/5/01*



# Newmont Mining SPSS License



*Newmont gold mine in  
Yanacocha, Peru*

- *Largest gold producer in Latin America (1.8 mil oz. produced in 2000)*
- *5 tons of Hg/month*
- *Currently recycling Hg, but concern over potential mis-use of recycled Hg*
- *BNL conducted treatability study*
- *Exclusive license for SPSS applications to mining*

# Summary/Conclusions

- *SPSS is a cost effective, simple process to treat broad range of Hg wastes*
- *SPSS Micro effectively treats:*
  - *Elemental Hg*
  - *High Hg contaminated soils (~5,000 ppm Hg)*
  - *High Hg contaminated sludge with a broad range of inorganic and organic Hg salts (~5,000 ppm Hg)*
- *SPSS Macro effectively treats Hg contaminated debris*



# Summary/Conclusions

- *Hg is chemically stabilized and solidified - Solidification reduces leachability and eliminates dispersibility of radionuclides and Hg*
- *Exceeds regulatory performance requirements*
- *Licensed to treat Hg residuals from mining operations*
- *Negotiating with commercial partners for treatment of elemental Hg (e.g., DoD stockpile) and mixed waste Hg*