

Mercury Removal from Acidic, Alkaline, and Dilute Wastewaters

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ORNL Chem Tech's Mercury Work

- Assessment of technologies for treatment of mixed waste (hazardous and radioactive) containing mercury
- High-salt acidic and high-salt alkaline water waste
- Chemical leaching of mercury from mixed waste soils
- Mixed Waste Focus Area Mercury Working Group
 - › Demonstration of vendor technologies
 - › Verification of stored waste
- Removal of low levels of mercury from wastewaters and streams
- Removal of mercury from vacuum pump oils

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Selected Sorbents for Mercury Removal

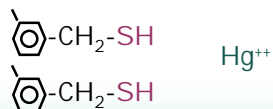
Sorbent name	Matrix Type	Active site	Particle size (mm)	pH range	Flow rate (BV/min)	Total capacity (eq/L)
Filtrisorb 300	Carbon	Activated Carbon	0.8-1.0	1-14		
Keyle:X	Polyacrylate	Thiol	0.6-0.8	1-14	0.54-1.07	3.4
IRC-718	Polystyrene	Iminodiacetic Acid	0.3-1.2	1.5-14	0.13-0.54	1.1
GT-73	Polystyrene	Thiol	0.3-1.2	1-13	0.27-1.07	1.4
SR-3	Polystyrene	Isothiourenium	0.3-1.0	0-6	0.08-0.33	1.7
SR-4	Polystyrene	Thiol	0.3-1.0	1-14	0.08-0.33	2.0
S-920	Polystyrene	Isothiourenium	0.9-1.5	1-13	0.27-0.80	1.5
SuperLig 618	Silica Gel	Organic Ligand	0.1-0.2	2-14	0.50-1.00	
SI R-200	Polystyrene	Thiol	0.3-1.0	2-10	0.13-0.40	1.2
SI R-400	Polystyrene	Isothiourenium	0.3-1.0	2-6	0.13-0.27	2.0
Forager Sponge	Polymer	Amine	12.7	1-14	0.10-0.50	0.1
ADA	Carbon	Noble Metal	0.5-4.0			
Mersorb 1.5 mm	Carbon	Sulfur	1.5-4.0	6-8	0.13	3.7

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Thiol-based Resins

- Sorbs heavy metals that form sulfur precipitate
 - › Mercury, Lead, Cadmium
- Binds positively charged ions (cations)
- Can be used at pH 1-14
 - › Ionac SR-4 by Sybron Chemicals, Inc.
 - › Duolite GT-73 by Rohm and Haas
 - › SI R-200 by ResinTech, Inc.
 - › Keyle:X by SolmeteX Corp.
 - › SAMMS by Pacific Northwest National Laboratory

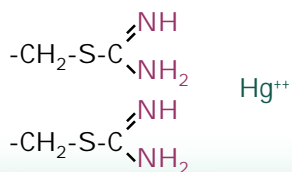


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Isothiouonium-based Resins

- Sorbs mercury, methyl mercury, and elemental mercury
- Can be used at pH 0-6 (also higher but then with thiol functionality)
 - › Ionac SR-3 by Sybron Chemicals, Inc.
 - › S-920 Purolite Company
 - › SIR-400 by ResinTech, Inc.



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Typical Test Protocol

- Batch screening tests for best sorbents
- Batch isotherm tests for best sorbents to find loading capacity
 - › Indication of column size
- Column studies to determine appropriate flow rate and length of column

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Sorbent Batch Tests for Mercury Removal

- Batch system

- > Screening

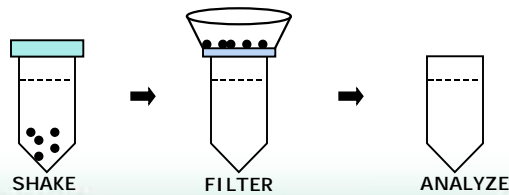
- equal amounts of different sorbents for same volume of liquid

- Performance criteria = best removal efficiency

- > Isotherm

- different amounts of same sorbent for same volume liquid, or equal amounts of sorbent, same volume of liquid, but different mercury concentrations

- Performance criteria = highest loading at same concentration



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Acidic Waste Streams

- Idaho National Engineering and Environmental Laboratory (INEEL) has about 2 million gal of a high-salt acidic waste that contains about 400 ppm Hg

- > Na 41 g/L
 - > HNO₃ 100 g/L
 - > Al 15 g/L

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Screening Test Results (I NEEL waste)

Sorbent (functionality)	Final Hg Concentration (ppm)	% Removal
SR-4 (thiol)	205	25.6
SuperLig 618	213	25.2
Durasil 70	265	3.6
SR-3 (thiuronium)	267	3.0
Mersorb	273	0.5
Filtersorb 300	274	0.4
IRC-718 (iminodiacetate)	278	0.0

24-hr batch test
0.1 g sorbent in 50 mL I NEEL simulant
Initial mercury concentration of 278 ppm

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Alkaline Waste Streams

- The Savannah River Site (SRS) has about 100 million gal of a high-salt alkaline waste that contains about 440 ppm Hg
 - > NaOH 30 g/L
 - > Na (other) 80 g/L
- The Oak Ridge Y-12 Plant has about 21,000 gal of dilute lithium hydroxide (LiOH) solution containing 30 to 60 ppm Hg
 - > Li 3 g/L
 - > Na 0.14 g/L
 - > Si 0.14 g/L

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Screening Test Results (SRS waste)

Sorbent (functionality)	Final Hg Concentration (ppm)	% Removal
Mersorb (sulfur)	0.8	99.3
Durasil 70	21.9	79.7
SR-3 (thiuronium)	22.4	79.2
SuperLig 608	24.1	75.1
Filtersorb 300	60.2	44.1
SR-4 (thiol)	66.6	38.2
IRC-718 (iminodiacetate)	68.4	36.5

24-hr batch test
 0.1 g sorbent in 50 mL SRS simulant
 Initial mercury concentration of 108 ppm

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Screening Test Results (LiOH waste)

Sorbent (functionality)	Final Hg Concentration (ppm)	% Removal
Durasil 70	6	74.2
SR-3 (thiuronium)	7.2	69.1
IRC-718 (iminodiacetate)	7.5	67.8
Mersorb (sulfur)	8	65.7
SR-4 (thiol)	9.6	58.8
Filtersorb 300	13.8	40.8
SuperLig 608	17.2	26.2

24-hr batch test
 0.2 g sorbent in 50 mL LiOH
 Initial mercury concentration of 23.3 ppm

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Dilute Waste Streams

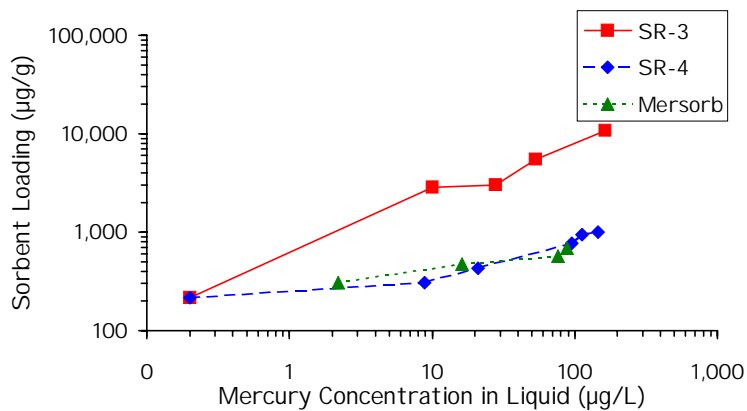
- The Oak Ridge Y-12 Plant has contaminated groundwater collecting in building sumps. The water has a neutral pH and mercury levels of a few hundreds ppb.
 - > Ca 0.06 g/L
 - > Na 0.01 g/L
 - > Si 0.01 g/L

Screening Test Results (Y-12 sumpwater)

Sorbent (functionality)	Final Hg Concentration (ppb)	% Removal
SR-3 (thiourenium)	<0.5	>99.8
SR-4 (thiol)	<0.5	>99.8
Mersorb (sulfur)	2.5	99
Durasil 70	25	90
IRC-718 (iminodiacetate)	31	86.7
Filtersorb 300	112	60.3

24-hr batch test
0.1 g sorbent in 200 mL ground water
Initial mercury concentration of 300 ppb

Batch Isotherm Results (Y-12 sump water)



$$K_d (L / g) = \frac{\text{Loading} (\mu\text{g} / \text{g})}{\text{Concentration} (\mu\text{g} / \text{L})}$$

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Trace-Level Streams

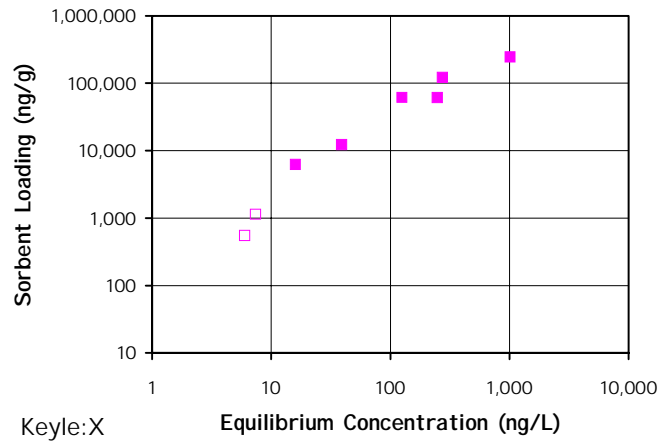


- Creek carrying process- and groundwater (Oak Ridge Y-12 Plant, Upper East Fork Poplar Creek)
- 1500 gallons/min
- 600-1000 ppt
- 12 ng/L NPDES goal or 51 ng/L CERCLA goal
- Current operation targets side streams for treatment with GAC

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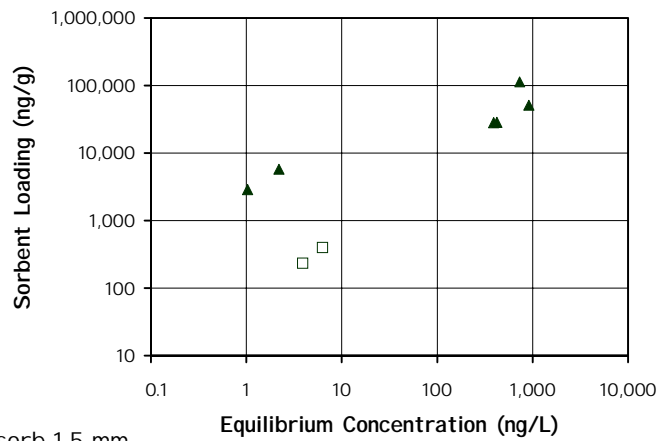
Batch I isotherm Results (Y-12 creek water)



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Batch I isotherm Results (Y-12 creek water)



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Summary of Batch Testing (1000 ng/L)

Sorbent	K_d (dry basis) (gal/lb)	K_d (bed basis) (L/LBV)
SR-4 (thiol)	60,000 est	235,000 est
Keyle:X (thiol)	30,000	67,700
SIR-200 (thiol)	9,500	48,800
Mersorb 1.5 mm	8,400	39,500
SR-3 (thiuronium)	6,000	26,700
Forager Sponge (amine)	360	270

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Typical Test Protocol

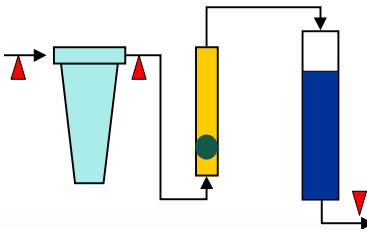
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Sorbent Column Tests for Mercury Removal

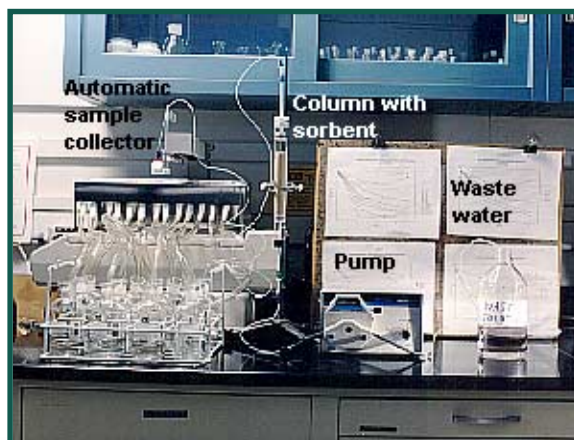
- Column packed with sorbent
 - › Short-term studies to scope out appropriate flow rates if they are not known
 - Run short times at different flow rates
 - › Long-term studies to obtain data suitable for scale-up
 - Run long times at same flow rate



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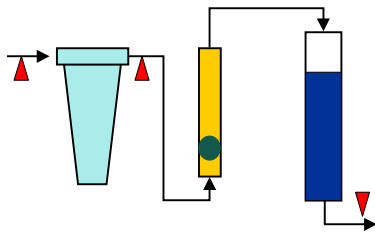
Equipment in Column Studies (lab scale)



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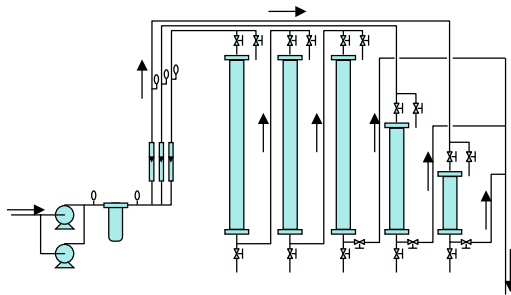
Equipment in Column Studies (bench-/field-scale)



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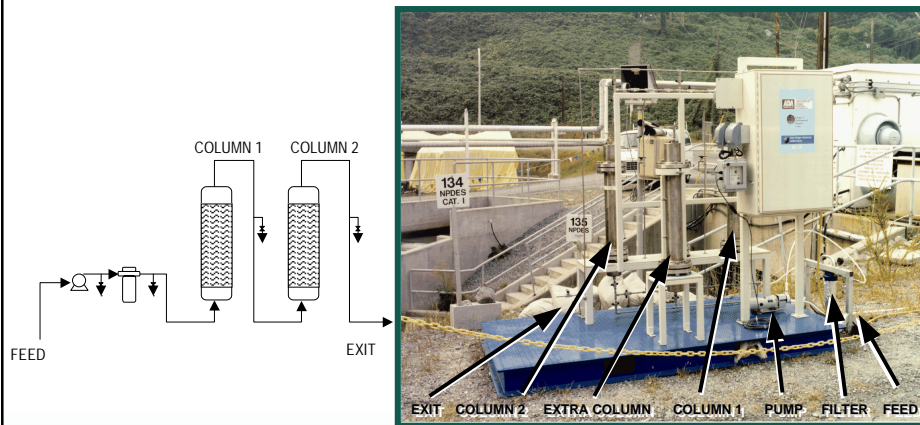
Equipment in Column Studies (bench-/field-scale)



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Equipment in Column Studies (pilot-scale)



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Screening Test Results (I NEEL waste)

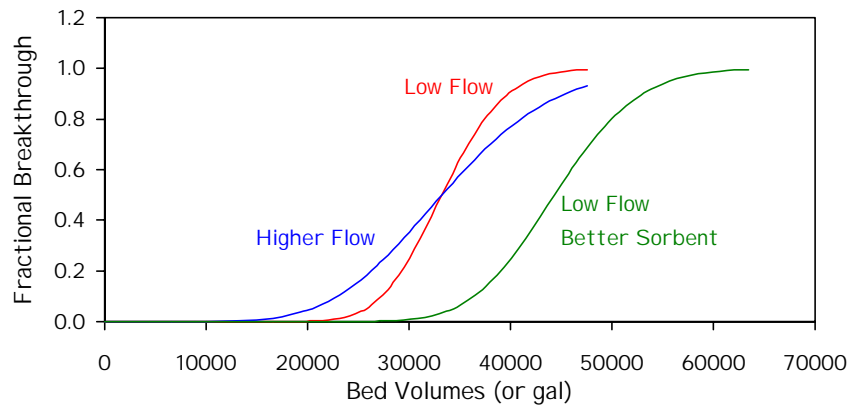
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24-hr batch test
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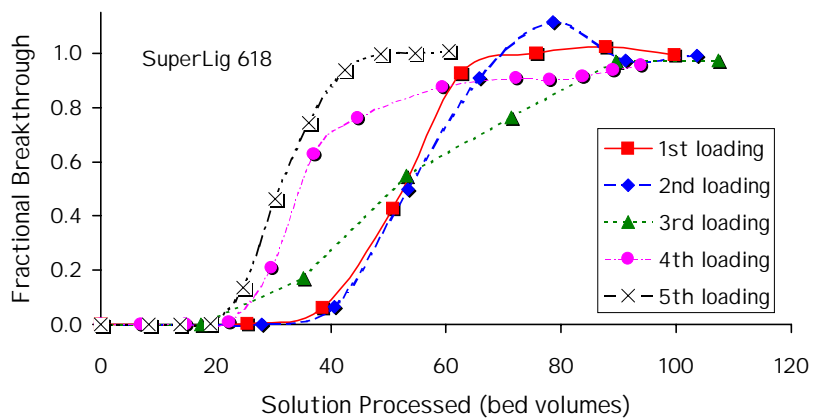
Expected Performance in Long-term Column Studies



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Column Studies with INEEL Waste



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Field Testing at the Oak Ridge Y-12 Plant Site (trace levels of mercury)

- Traditional sorbents and sorbent developed by ADA Technologies and PNNL/ORNL
- Independent contractor and university oversight
- Independent analysis performed by Frontier Geosciences
- Sorbent selection
- Batch testing for isotherms
- Small-scale column testing
 - > short term
 - > long term
- Pilot-scale testing with ADA

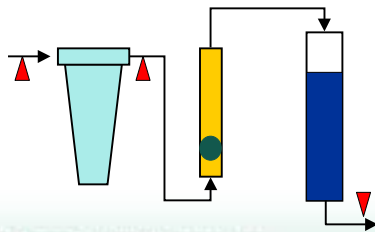


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Short-term Column Studies

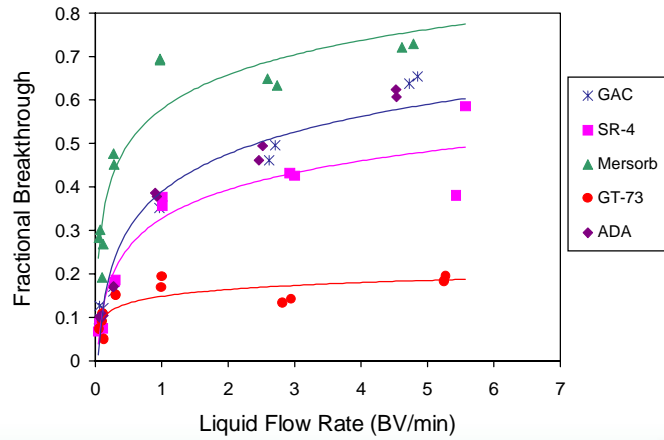
- Constant supply of pressurized water by sump pump
- 1- μm prefiltration unit
- Five or six columns in parallel
- Individual flow control
- Sorbent beds were 1" in diameter and 4" to 5" tall



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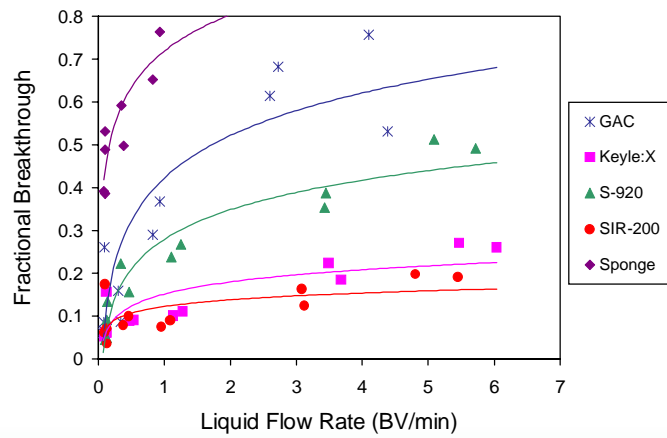
Short-term Column Studies (Y-12)



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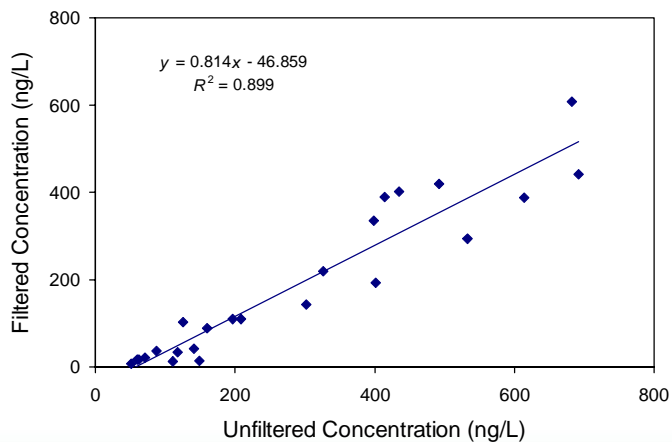
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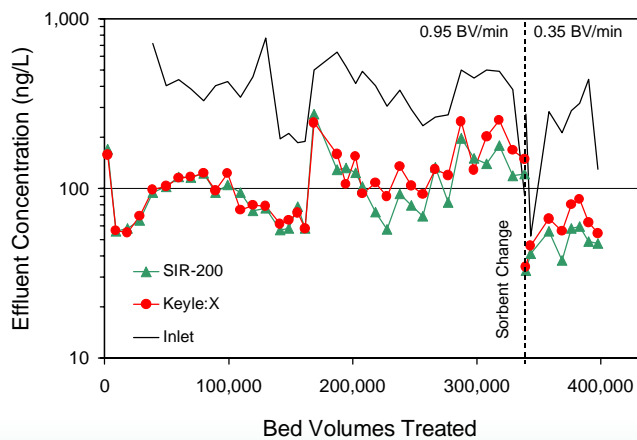
Mercury-Associated Particulates (Y-12)



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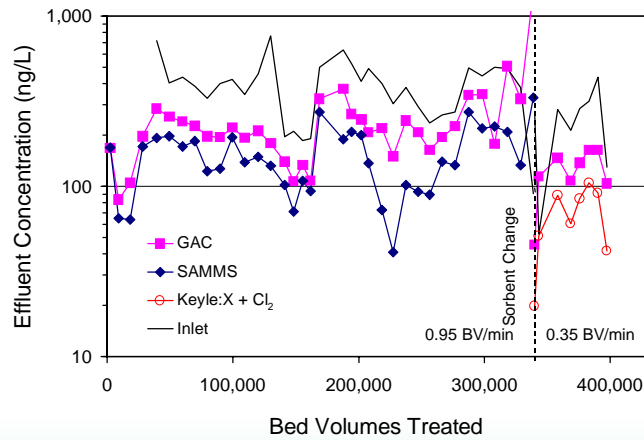
Long-term Column Studies (Y-12)



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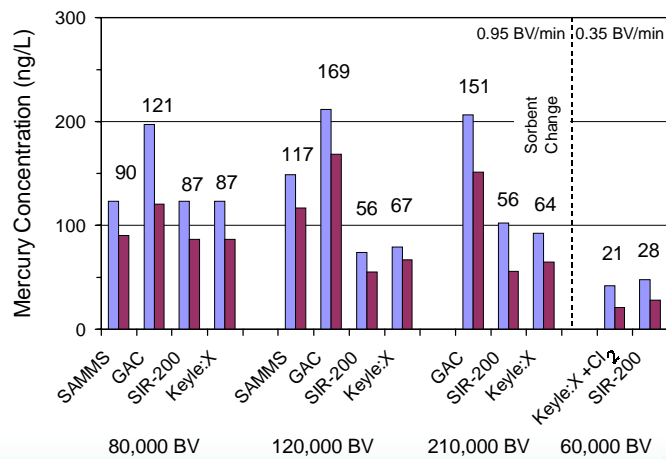
Long-term Column Studies (Y-12)



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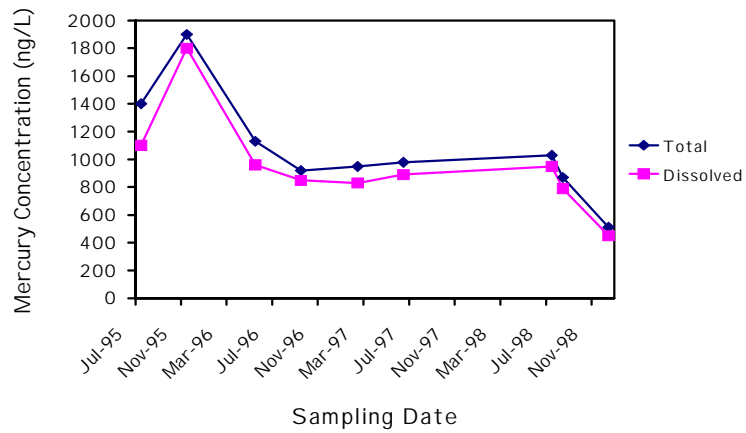
Mercury-Associated Particulates (Y-12)



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Historic Data (Y-12)



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Trace-Level Streams

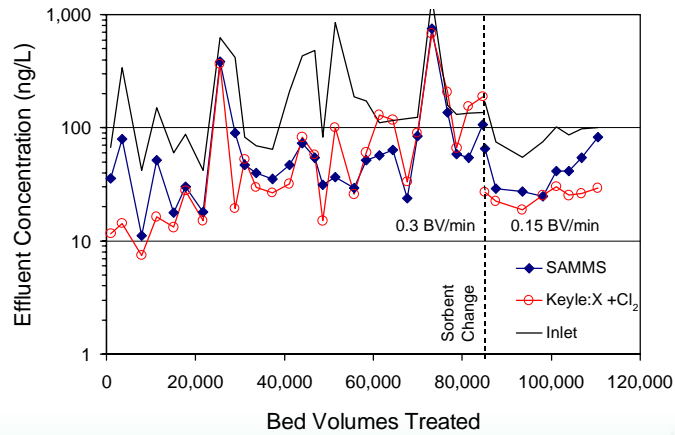
- Wastewater treatment plant at Oak Ridge National Laboratory
- 350 gallons/min
- 200 ppt (ng/L)
- 19 ppt NPDES goal
- Current operation includes GAC



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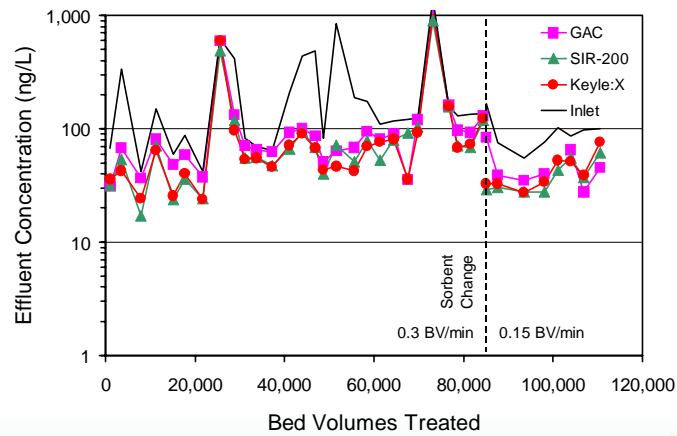
Long-term Column Studies (WWTP)



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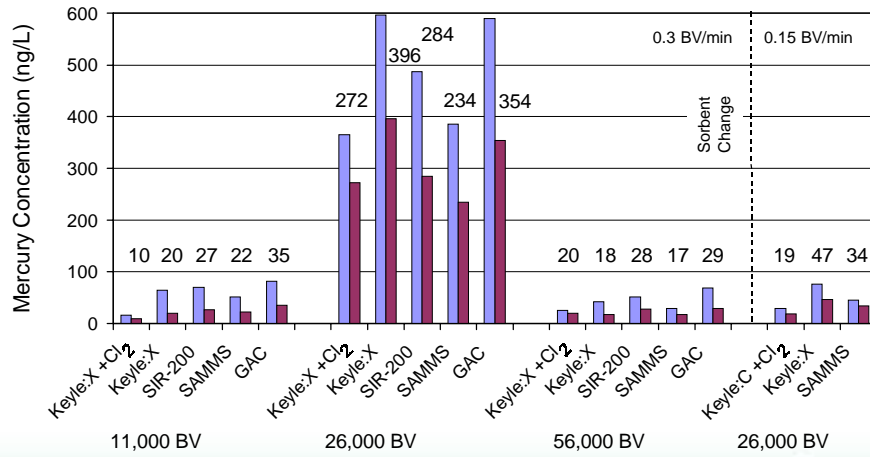
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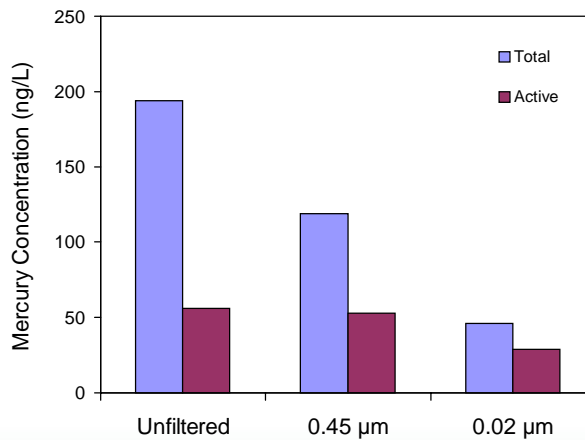
Mercury-Associated Particulates (WWTP)



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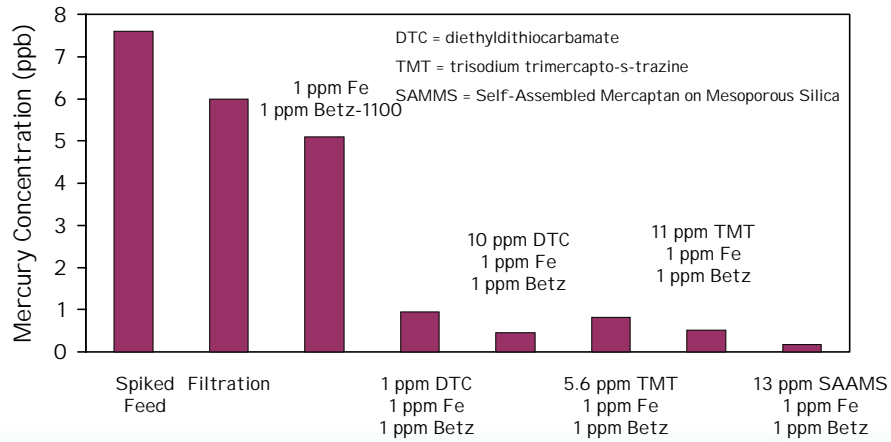
Mercury Speciation (WWTP)



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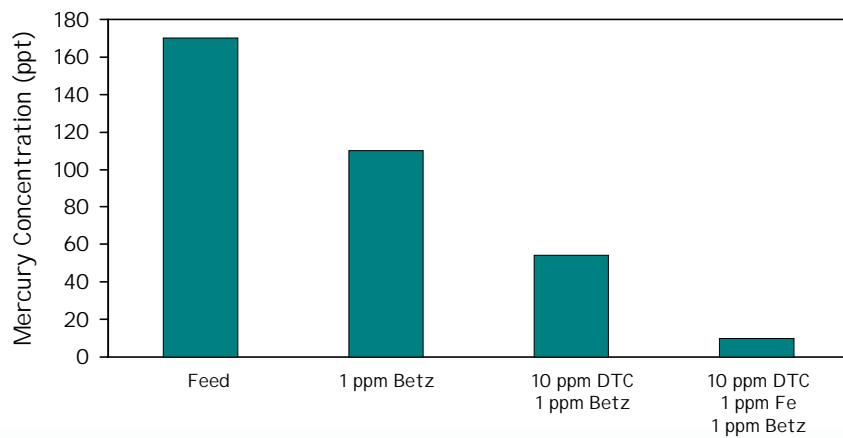
Precipitation Studies (WWTP)



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Precipitation Studies (WWTP)



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Thank You! Questions?

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 - > klassonkt@ornl.gov

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