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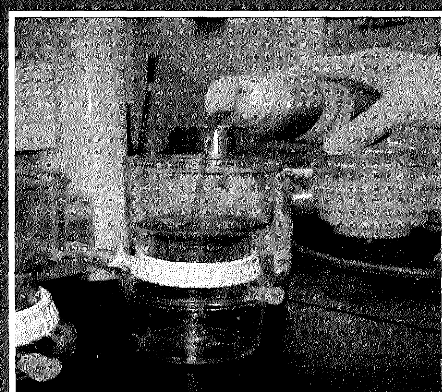
Improved Leach Testing to Evaluate Fate of Hg and other Metals from Management of Coal Combustion Residues

Susan Thorneloe[1], Gregory Helms[2], David Kosson[3], Florence Sanchez[3], Cathy Davis[2], Bernine Khan[1], and Peter Kariher[4]

[1]U.S. EPA/Office of Research and Development; [2]U.S. EPA/Office of Solid Waste, [3]Vanderbilt University, [4]ARCADIS

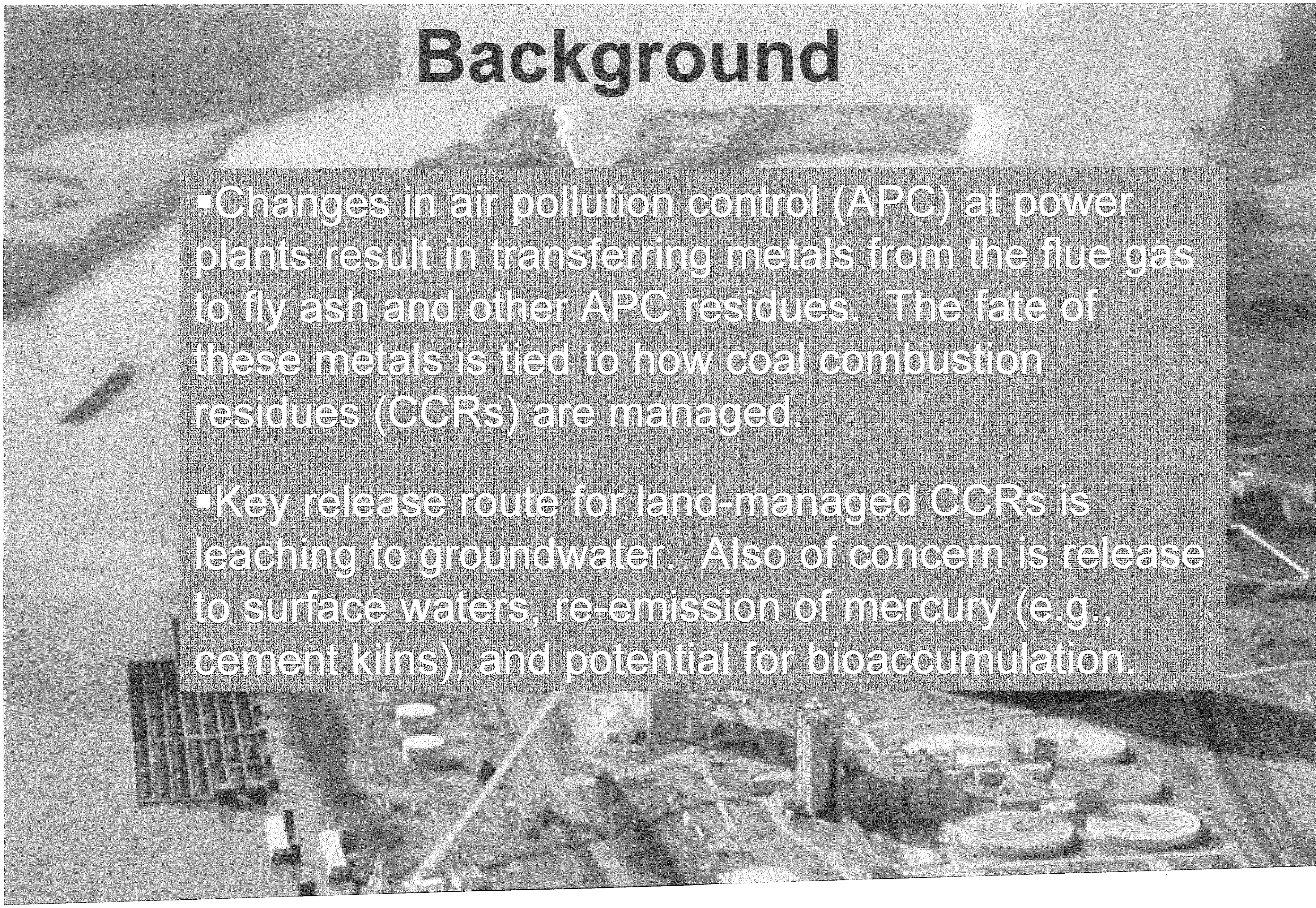
Presentation for Global Waste Management Symposium

Copper Mountain, Colorado



Office of Research and Development
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division

September 8, 2008



Background

- Changes in air pollution control (APC) at power plants result in transferring metals from the flue gas to fly ash and other APC residues. The fate of these metals is tied to how coal combustion residues (CCRs) are managed.

- Key release route for land-managed CCRs is leaching to groundwater. Also of concern is release to surface waters, re-emission of mercury (e.g., cement kilns), and potential for bioaccumulation.

Improved Leach Testing to Evaluate Fate

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Improved Leach Testing to Evaluate Fate of Hg and other Metals from Management of Coal Combustion Residues

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Historical and Projected Electricity Production by Fuel for 1980 – 2030 (billion kilowatt hours)

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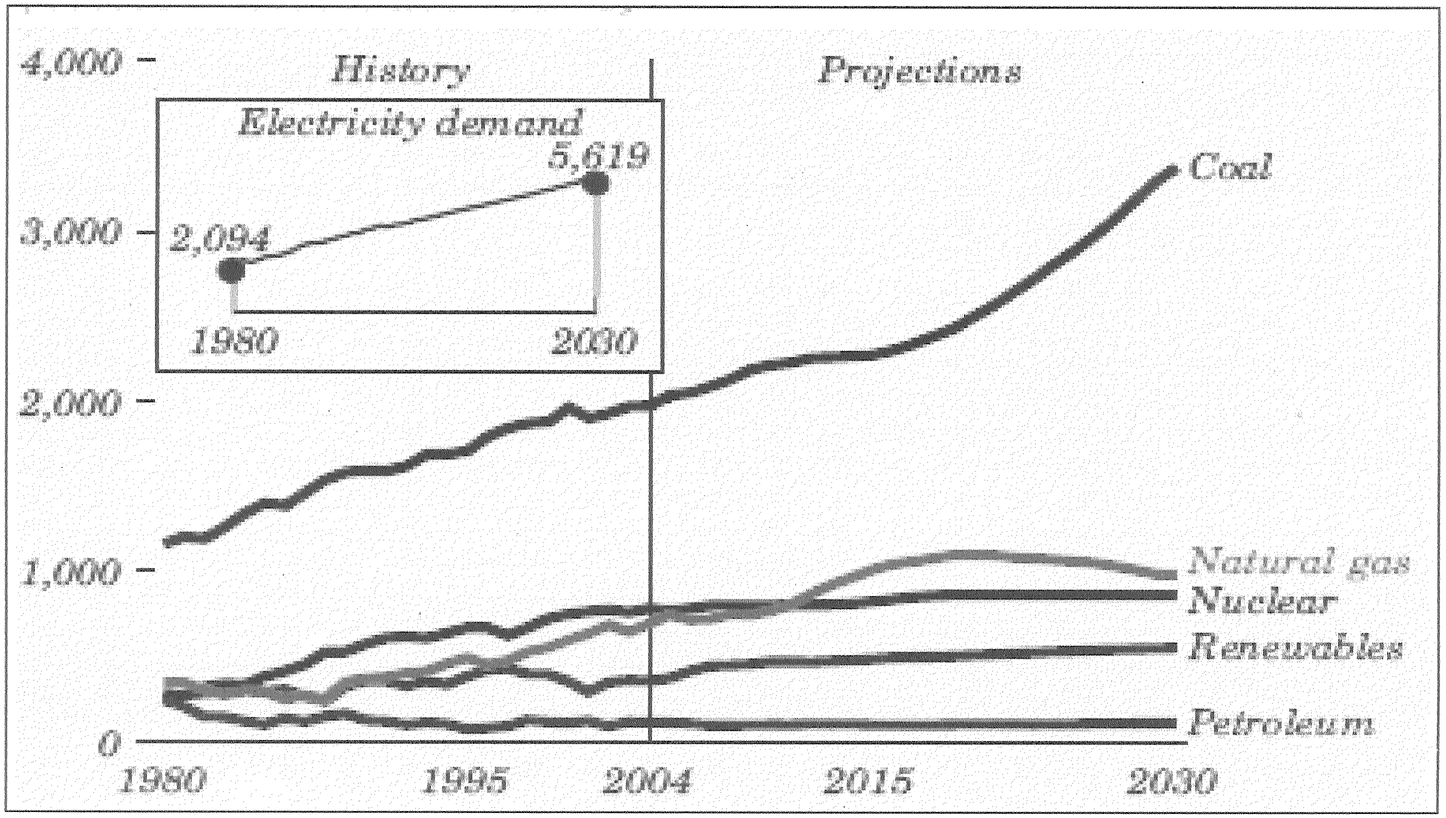
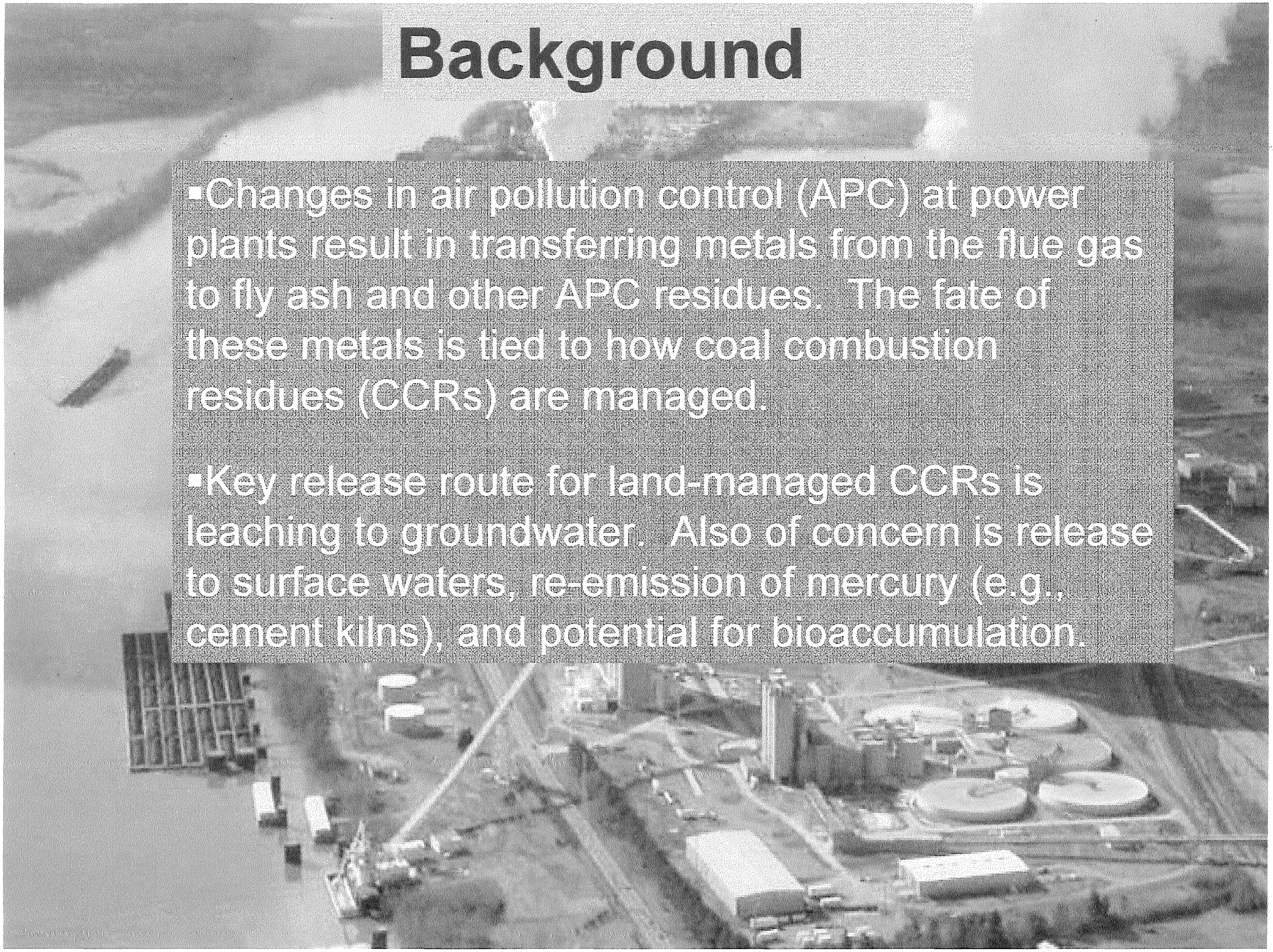


Source: DOE/EIA, 2006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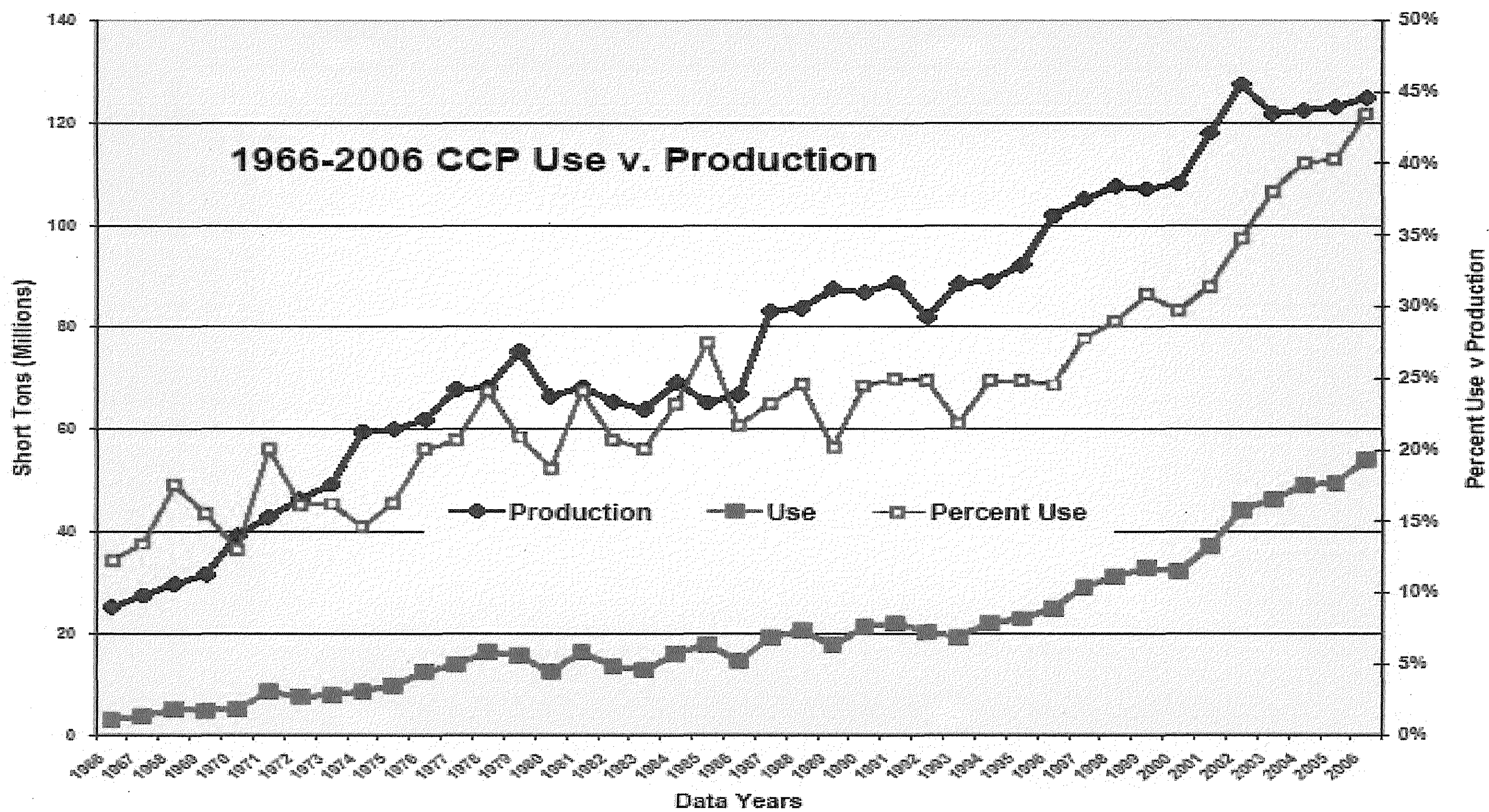
▪Key release route for land-managed CCRs is leaching to groundwater. Also of concern is release to surface waters, re-emission of mercury (e.g., cement kilns), and potential for bioaccumulation.

Production vs Use Statistics from the American Coal Ash Association (http://www.acaa-usa.org/)



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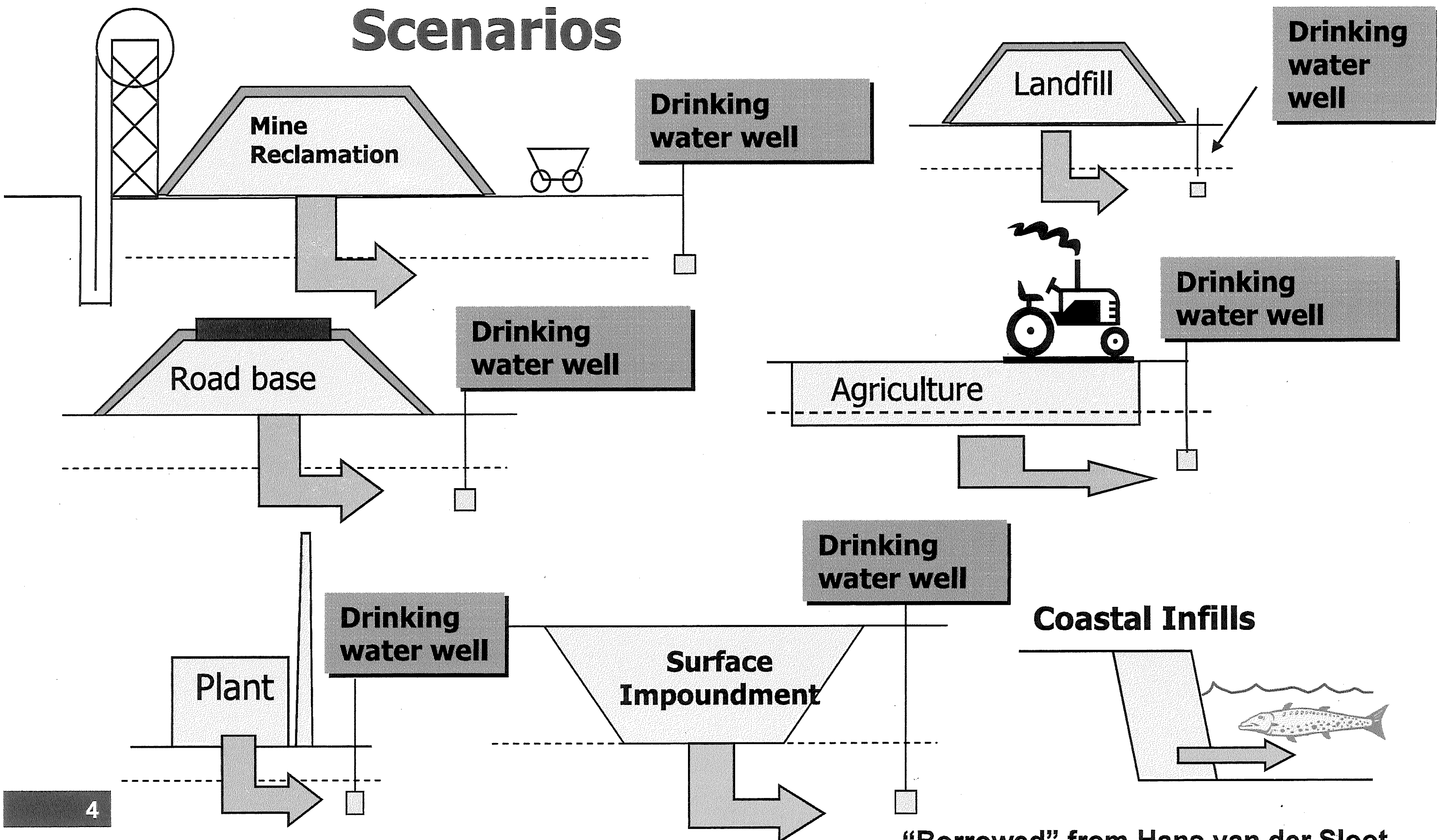
Wide Range of Potential CCR Management Practices & Release Scenarios



“Borrowed” from Hans van der Sloot

Illustration of Multi-Pollutant Control at a Coal-Fired Power Plant

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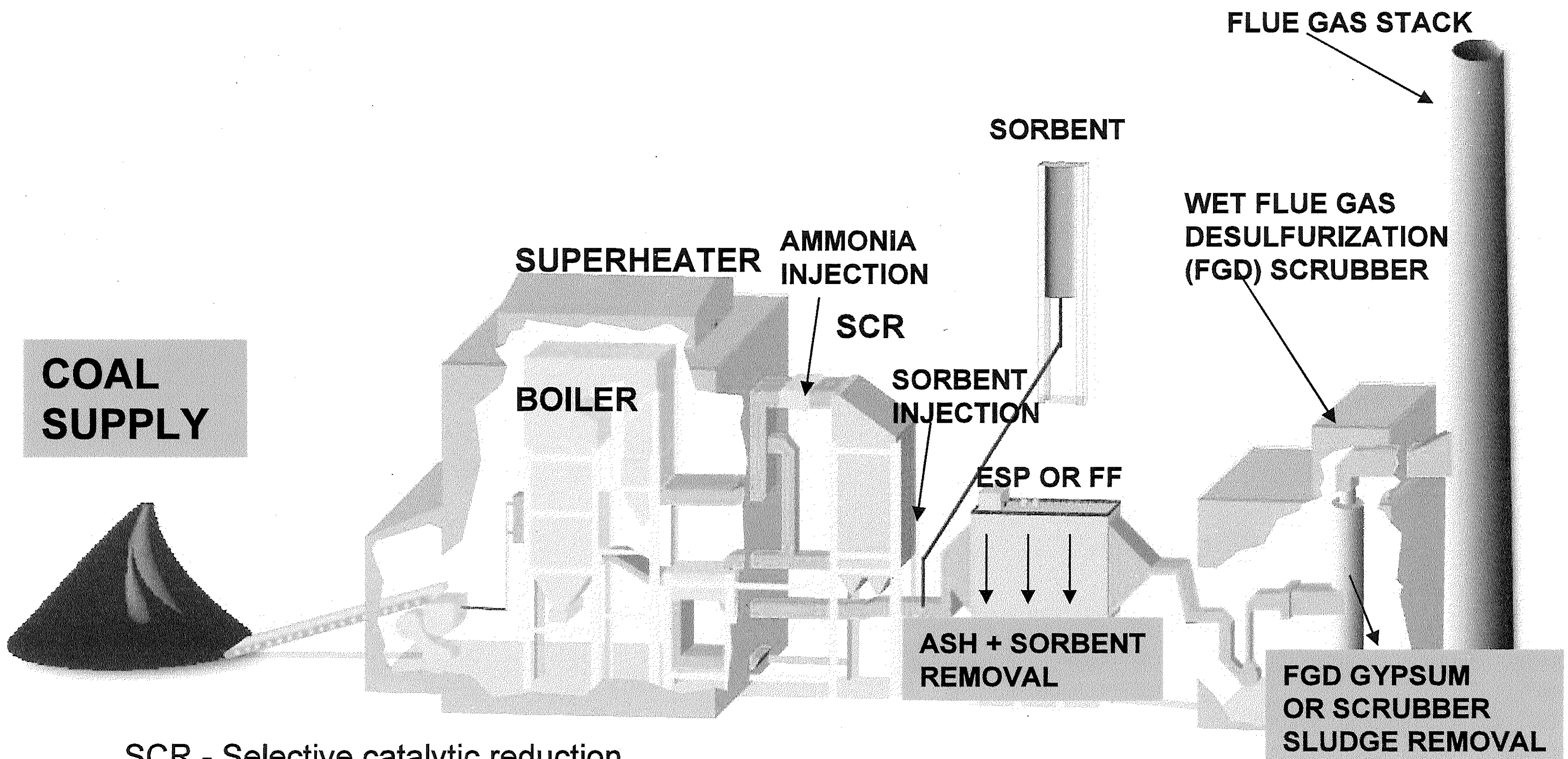

SCR - Selective catalytic reduction
ESP – electrostatic precipitator
FF – fabric filter

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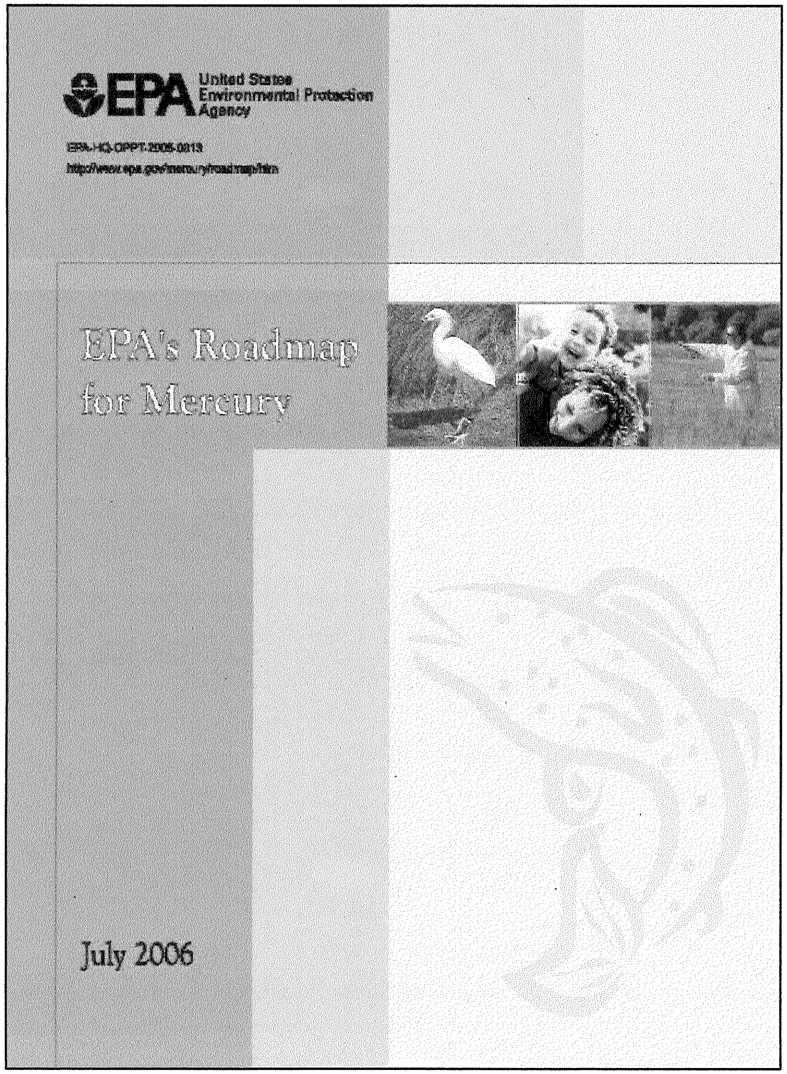
EPA's Mercury Roadmap



EPA has committed to developing a report on fate of mercury and other metals from land disposal and commercial use of CCRs from plants equipped with multi-pollutant control technologies (p.67, http://www.epa.gov/mercury/roadmap.htm

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Leach Testing Protocol

- After conducting review of available data (EPA-600/R-02-083, Dec 2002) it was determined that
  - Range of leach tests were in use (no comparability in available data);
  - Leach tests being used did not incorporate field conditions known to affect leaching (i.e., pH, infiltration rate, Redox conditions)
    - assessed leaching potential at a single set of conditions
    - focused on initial conditions; final leaching conditions often unknown.
  - Final test conditions represent conditions under which leaching actually occurs, and so better represent field leaching.
- EPA's Office of Research and Development (ORD) sought input from EPA's Office of Solid Waste (OSW) on recommended leach testing approach for fate of Hg and other metals from management of CCRs

Leach Testing Protocol

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- After conducting review of available options, OSW recommended the use of the leach testing framework and probabilistic assessment published at:
  - Kosson, D.S., van der Sloot, H.A., Sanchez, F. and Garrabrants, A.C., 2002. ***An Integrated Framework for Evaluating Leaching in Waste management and Utilization of Secondary Materials***. *Environmental Engineering Science* 19(3):159-204.
  - Sanchez, F., Kosson, D.S., 2005. ***Probabilistic approach for estimating the release of contaminants under field management scenarios*.** Waste Management, 25(5), 643-472.
- Effort underway to adopt what is considered a more reliable leach testing into EPA's "SW846"
- Will include development of
  - technical background document providing field vs lab leach data comparisons and
  - guidance on how leach data can be used in decision making

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Leach Testing Protocol

- Kosson et al. have integrated the research into a testing framework focused on supporting environmental decision-making
  - Use of equilibrium and diffusion-limited testing provides the tools needed to produce results that are more representative of actual field conditions than a single-point leach test.
- Four test methods addressing parameters know to influence leaching
  - Equilibrium-based tests
    - pH dependent leach test method
    - L/S ratio dependent leach test method
  - Column test method
    - Results to be used in conjunction with equilibrium test results
  - Diffusion-limited leach test method
    - Tank test of solid/compacted granular material
    - Results to be used in conjunction with equilibrium test results
- Outputs can be used with data on site conditions to generated probabilistic leaching estimate for more realistic inputs to groundwater transport modeling

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Outputs From Leach Testing of CCRs

- Report 1 – Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control (EPA-600/R-06/008, Feb 2006)
  - Samples obtained from six utilities with and without use of sorbents for Hg control
- Report 2 – Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers (EPA/600/R-08/077)
  - Samples obtained from eight facilities with wet scrubbers
  - For five utilities, samples obtained with and without post-combustion NOx control
- Report 3 –Anticipate draft by Spring 2009
  - Will include data from ~fourteen additional sites to attempt to span range of coal types and air pollution control configurations
- Report 4 – Anticipate draft by Spring 2010
  - Contains probabilistic assessment of potential leaching of metals based on plausible management practices through disposal or use in engineering, commercial or agricultural applications
  - Will evaluate fate of Hg and other metals from management of CCRs resulting from use of multi-pollutant control technologies as identified in EPA's Mercury Roadmap

Summary of Results from Report 1

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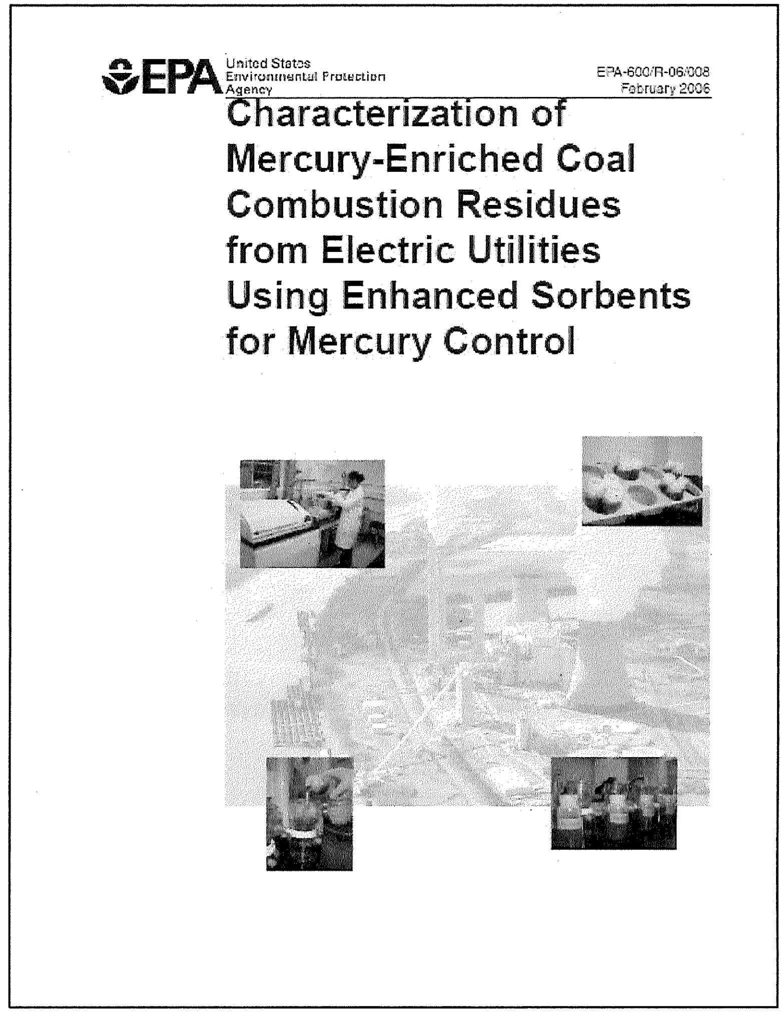
- Report "1" (EPA-600/R-06/008, Feb 2006) available online - http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf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EPA-600/R-06/008
February 2006

Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control

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Major Findings from Report 1 on Sorbents for Enhanced Mercury Capture

- Mercury is strongly retained by the resulting CCR and unlikely to be leached at levels of environmental concern.

- Arsenic and selenium may be leached at levels of potential concern both with and without enhanced mercury control technology -
  - Highest As leach values at 20% of toxicity characteristic (TC)
  - Highest Se leach value is 10 times the TC
- Leachate concentrations and the potential release of mercury, arsenic, and selenium do not correlate with total content.
- Laboratory leach data compares very well to field leach data.

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Results for Leach Testing Analysis for Coal Fly Ash From Six Facilities Using Sorbents for Enhanced Hg Capture

(Published in EPA/600/R-06/008, Feb 2006)

	Hg	As	Se
Total in Material (mg/kg)	0.1 -1	20 - 500	3 - 200
Leach results (ug/L)	Generally 0.1 or lower	<1 - 1000	5 – 10,000
MCL (ug/L)	2	10	50
TC (ug/L)	200	5,000	1,000
Variability relative to pH*	Low	Moderate to High	Moderate

MCL - Maximum concentration limit (for drinking water)

TC - Toxicity Characteristic – Threshold for hazardous waste determinations

*Variability defined as-
low - <1 order of magnitude difference
med - 1 to 2 orders of magnitude difference
high - >2 orders of magnitude difference

Report 2 – Focus on Facilities with Wet Scrubbers

- 23 samples were collected from eight facilities using wet scrubbers:
  - Fly ash - 5 samples
  - FGD gypsum - 6 samples
  - Scrubber sludge (natural or inhibited oxidation; mix of $CaSO_3$ and $CaSO_4$) – 5 samples
  - Fixated Scrubber Sludge (SS mixed with fly ash and often lime) – 7 samples

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Highlights from Report 2

- For FGD gypsum (four facilities):
  - Total metals concentration in FGD gypsum appears lower than fly ash and scrubber sludge.
  - Leach results appear to suggest that Hg leaching is of minimal concern but there may be a concern for leaching of other metals from some facilities (e.g., Cd, Mo, Se, Tl).
- For fly ash (three facilities), scrubber sludge (three facilities), and fixated scrubber sludge (four facilities), there are potential environmental concerns for some metals from some facilities if managed in an unlined unit (e.g., Sb, As, Ba, Cd, Cr, Mo, Se, Tl).
- For scrubber sludge and fixated scrubber sludge (scrubber sludge blended with fly ash and sometimes lime), there are potential environmental concerns for some metals from some facilities if managed in an unlined unit (e.g., Hg, Sb, As, Ba, Cd, Cr, Pb, Mo, Se, Tl).
- Post-combustion NOx control may be a factor in release of Cr and other metals from fly ash, scrubber sludge and fixated scrubber sludge. Collecting additional data to clarify what factors may influence this (i.e., type of catalyst, coal chloride content).

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Results from Report 2 for FGD Gypsum from Four Facilities

	Hg	Sb	As	Ba	B	Cd	Cr	Co	Pb	Mo	Se	Tl
Total in Material (mg/kg)	0.01 – 0.5	2 - 6	2 - 4	3 - 60	NA	0.3 – 0.5	6 – 20	1 - 4	1 - 12	2 - 12	2 - 30	0.6 - 2
Leach results (ug/L)	<0.01-0.6	<0.3 - 10	0.5 - 10	40 - 400	40 – 70,000	<0.2 - 50	<0.3 – 50	<0.2 - 10	<0.2 - 10	1 - 600	4 – 3,000	<0.3 - 20
MCL (ug/L)	2	6	10	2,000	7,000 DWEL	5	100	15	15	200 DWEL	50	2
TC (ug/L)	200	-	5,000	10^5	6,500	10^3	5,000	5,000	5,000	-	1,000	-
Variability relative to pH	Low to Med.	Low	Low to Med.	Low	Low to Med	High	Med. to High	Low	Low	Low	Low to Med	Low

MCL - Maximum concentration limit (for drinking water)

DWEL - Drinking water equivalent level

TC - Toxicity Characteristic – Threshold for hazardous waste determinations

***Variability defined as-**
- **low - <1 order of magnitude difference**
- **med - 1 to 2 orders of magnitude difference**
- **high - >2 orders of magnitude difference**

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Results from Report 2 for Fly Ash from Three Facilities

	Hg	Sb	As	Ba	B	Cd	Cr	Co	Pb	Mo	Se	Tl
Total in Material (mg/kg)	0.04 – 0.6	3 - 15	70 - 90	600 – 1,500	NA	0.7 – 1.5	100 - 200	20 - 50	40 - 90	10 - 20	2 - 30	3 - 13
Leach results (ug/L)	<0.01-0.4	<0.3 - 200	7 - 300	90 – 4,000	200 – 300,000	<0.2 - 30	1 – 4,000	<0.3-200	<0.2 - 2	100 – 40,000	7 - 400	<0.3 - 300
MCL (ug/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2
TC (ug/L)	200	-	5,000	10^5	6,500	1,000	5,000	-	5,000	-	1,000	200
Variability relative to pH	Low to High	Med. to High	Low to Med.	Low	Med. to High	High	Low to Med.	High	Med.	Low to Med.	Low to Med.	Med.

MCL - Maximum concentration limit (for drinking water)

DWEL - Drinking water equivalent level

TC - Toxicity Characteristic – Threshold for hazardous waste determinations

***Variability defined as-**
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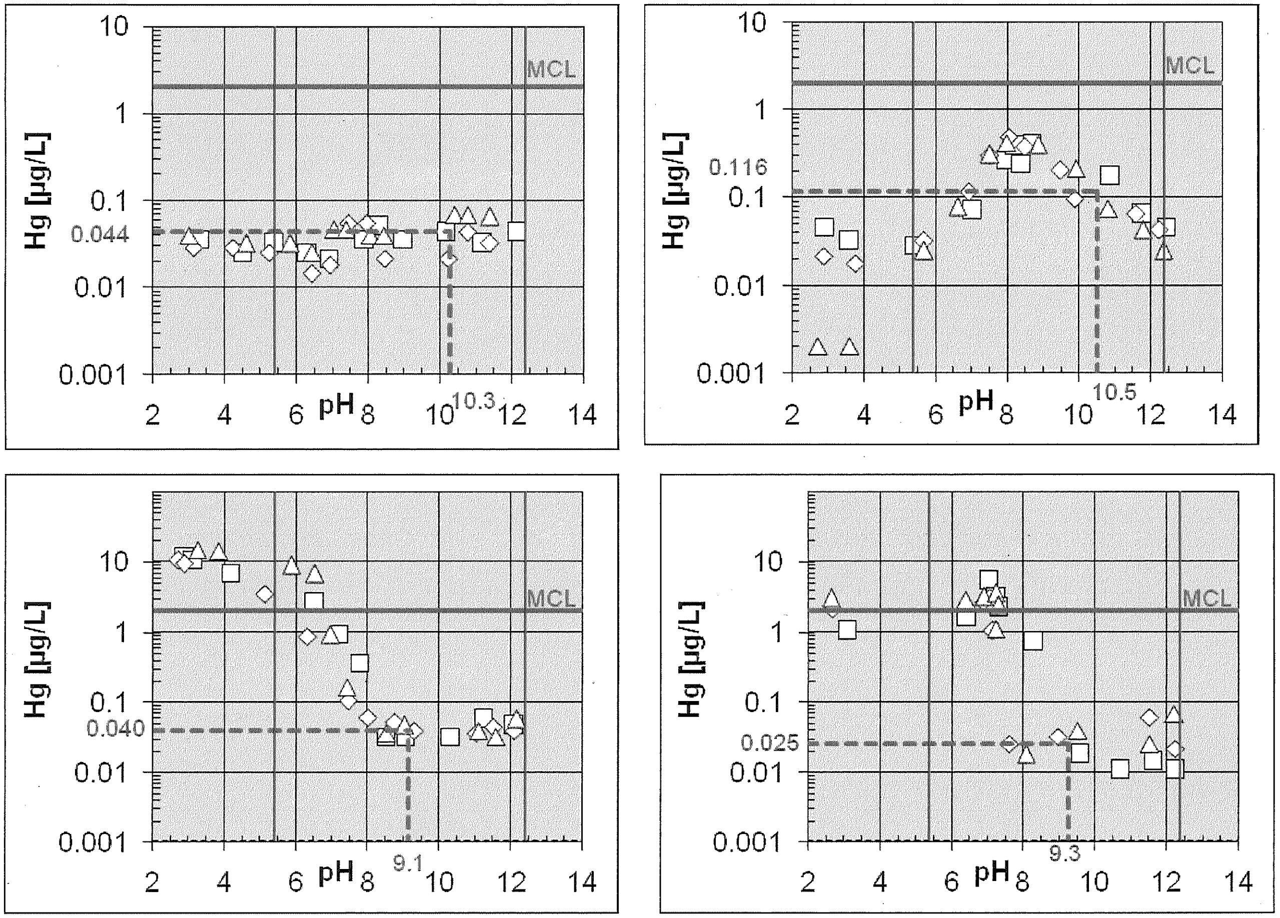

Results of Mercury Leaching Concentration (5.4<pH<12.4)

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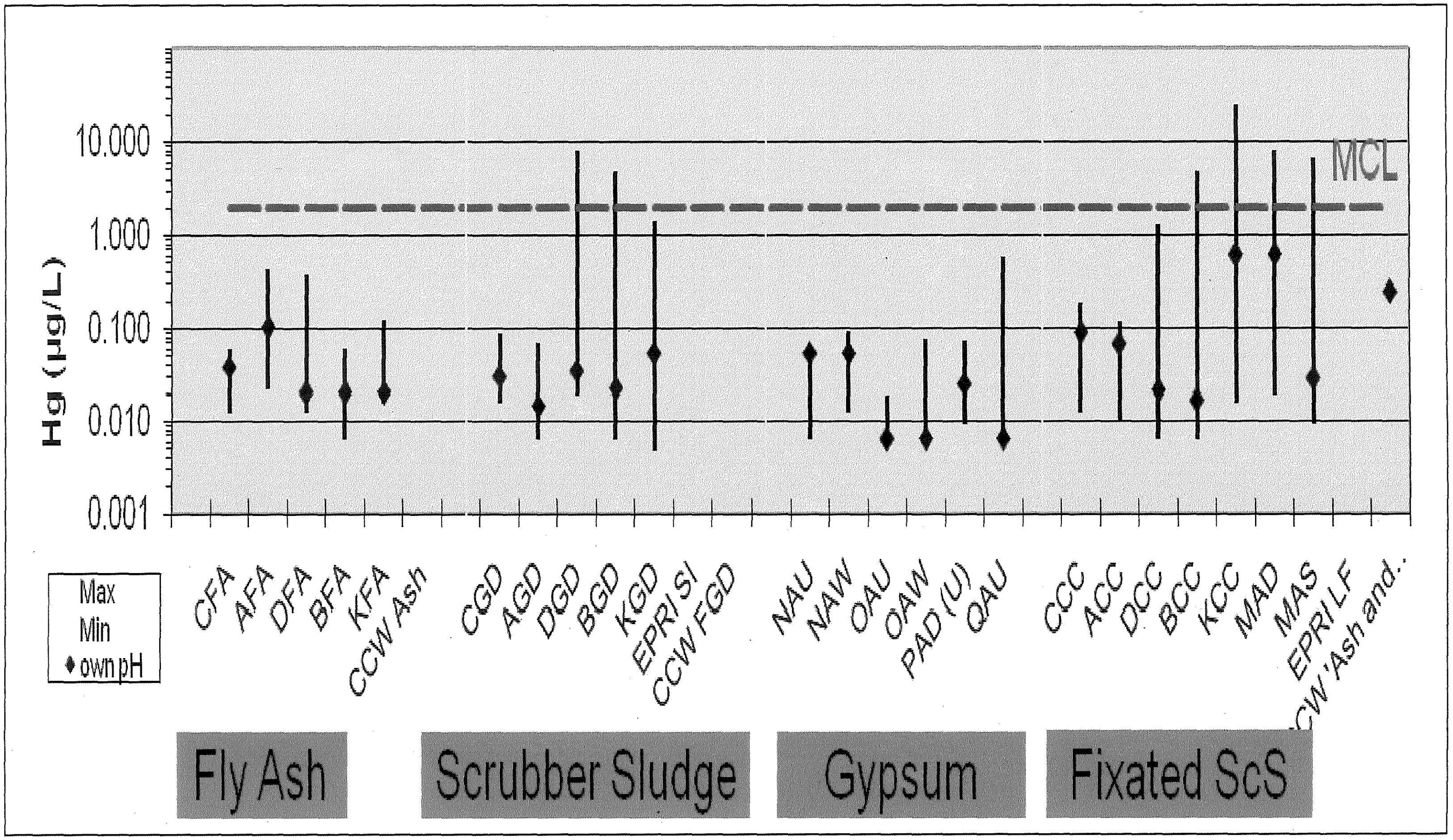

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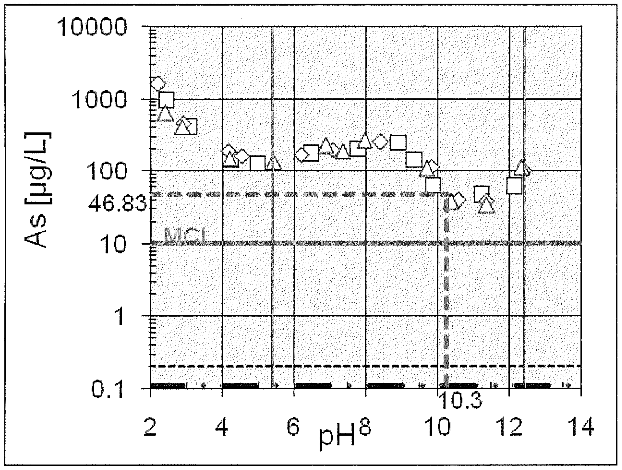
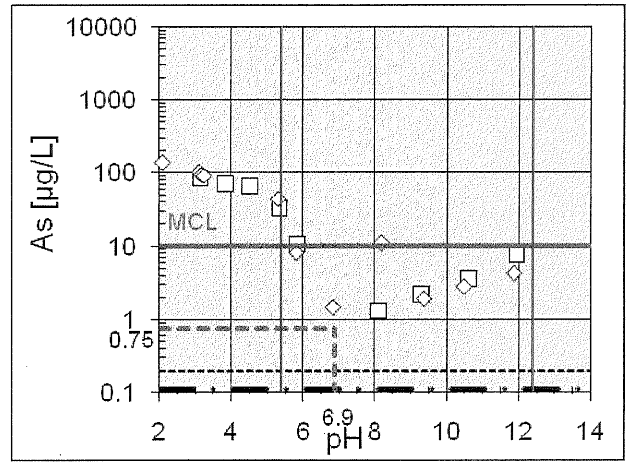
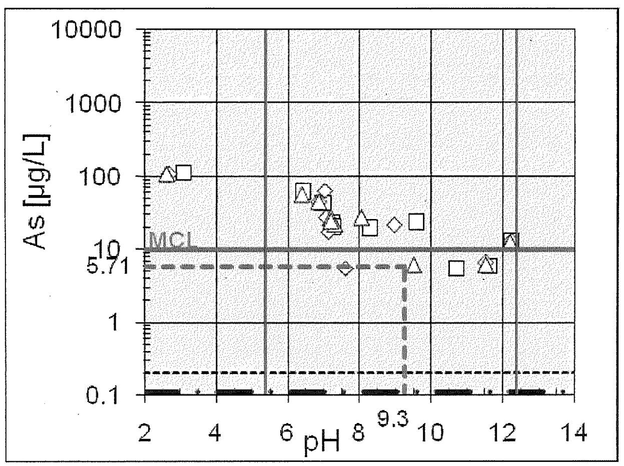
Results of Arsenic Leaching Across pH Range Comparing Different CCR types



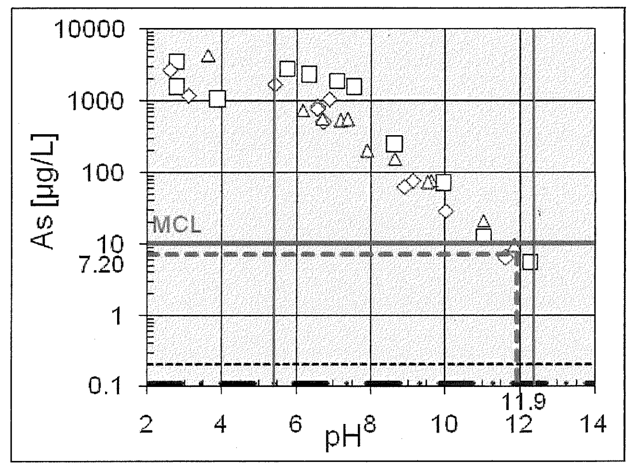
Fly Ash, Facility B – SCR off



Gypsum (U), Facility Q

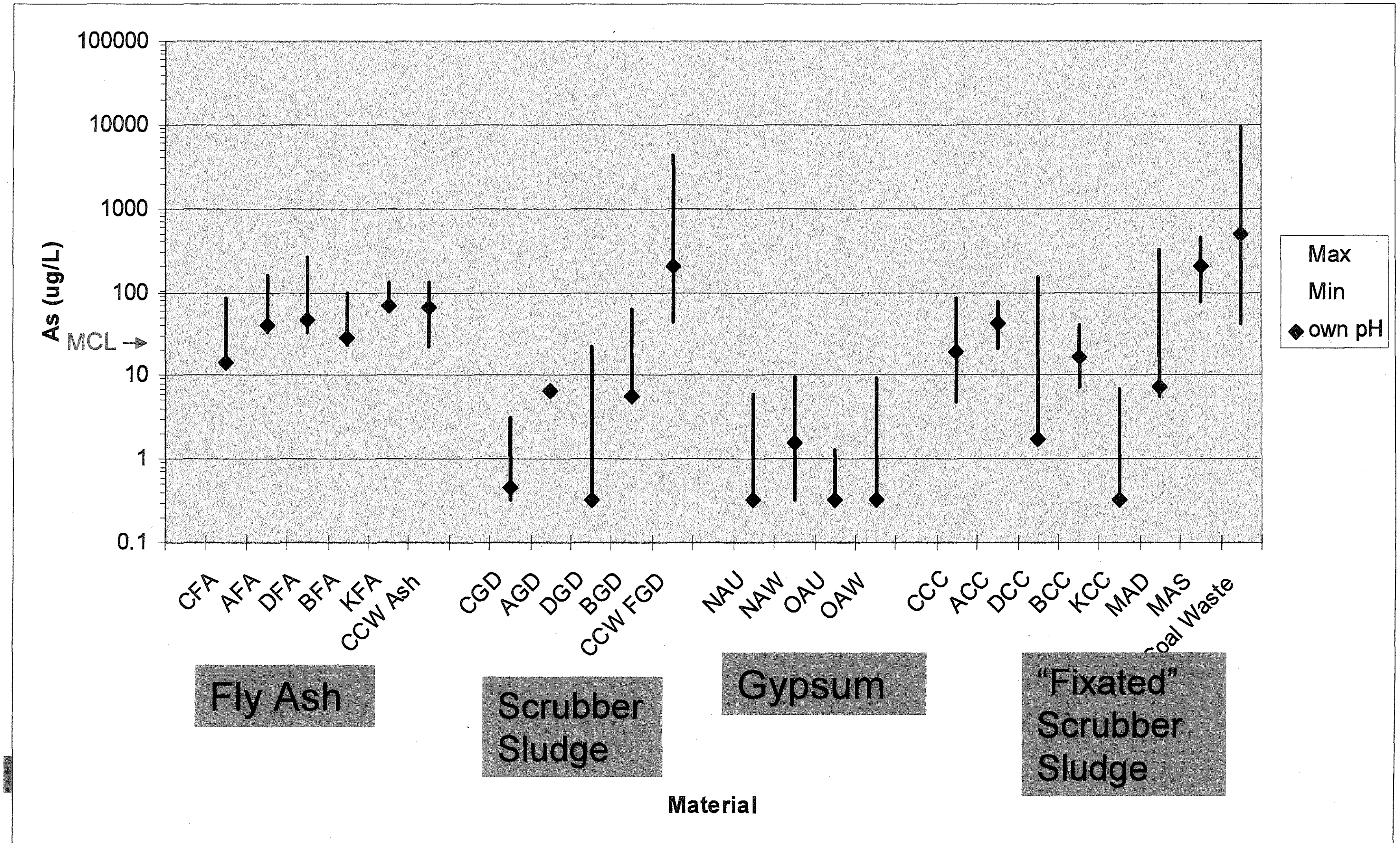


Scrubber Sludge, Fac. B – SCR in use



Fixated ScS, Fac. M – SCR not in use

Results of Arsenic Leaching Concentration for pH Range of 5.8<pH<12



Results of Chromium Leaching Across pH Range Comparing Any Potential Differences with Post-Combustion NOx Control In Use

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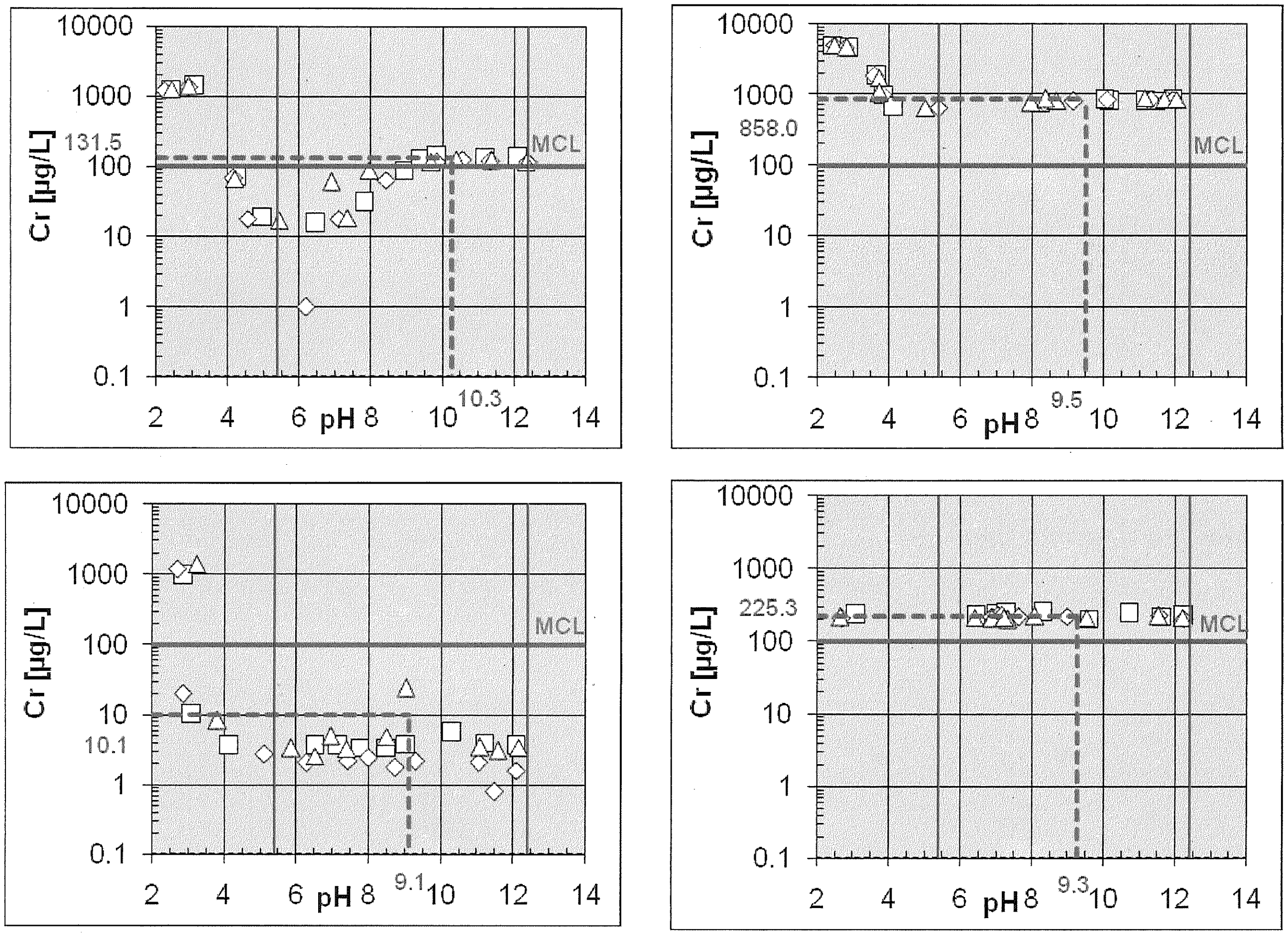

Fly Ash (Facility B, SCR)

Scrubber Sludge (Facility B, SCR)

No Post-Combustion NOx Control in use

Post-Combustion NOx Control in use

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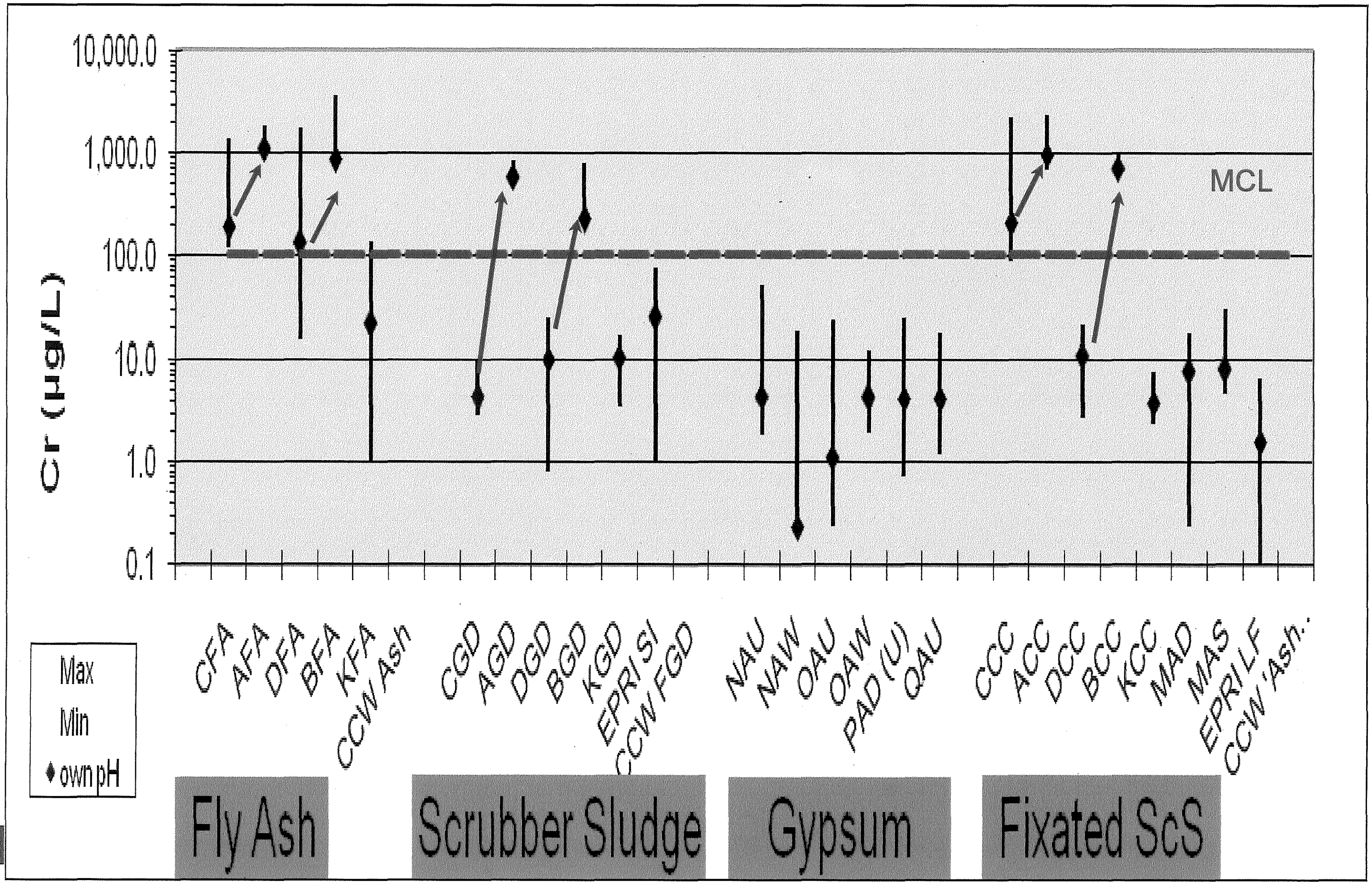
Results of Chromium Leaching Concentration (5.4<pH<12.4)



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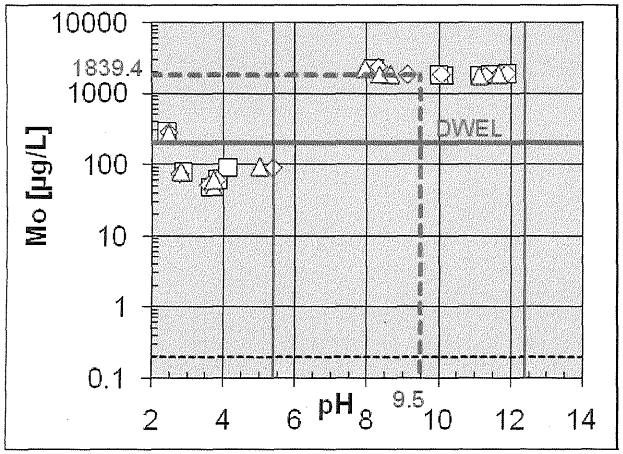
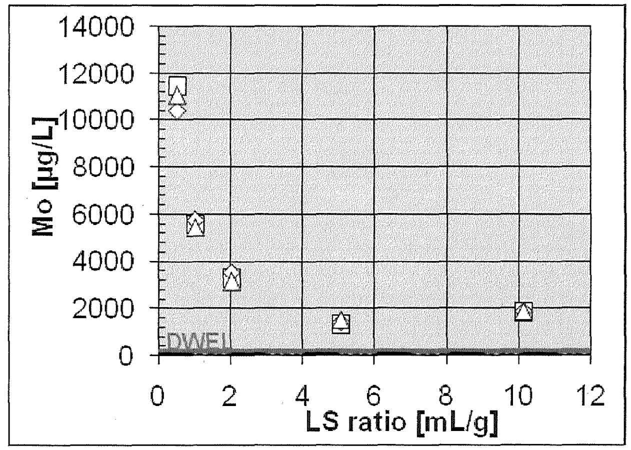
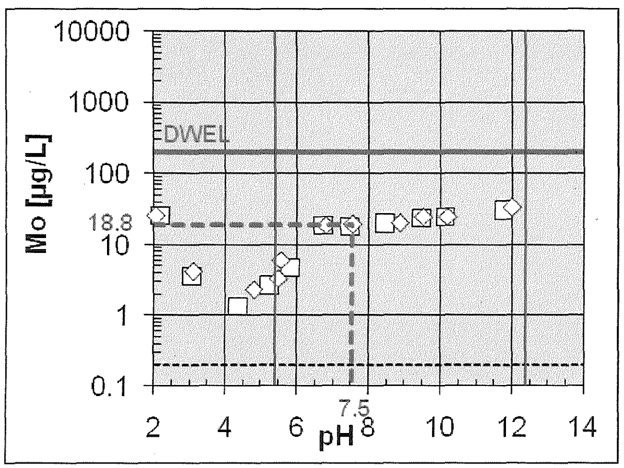
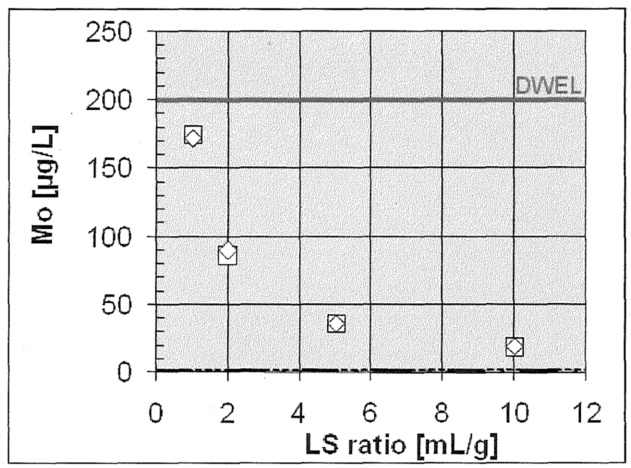
Example Results of Molybdenum Leaching Across pH Range and Liquid to Solid Ratio





Fly Ash (Facility B, SCR In Use)





Gypsum (Facility O, Gyp-U)

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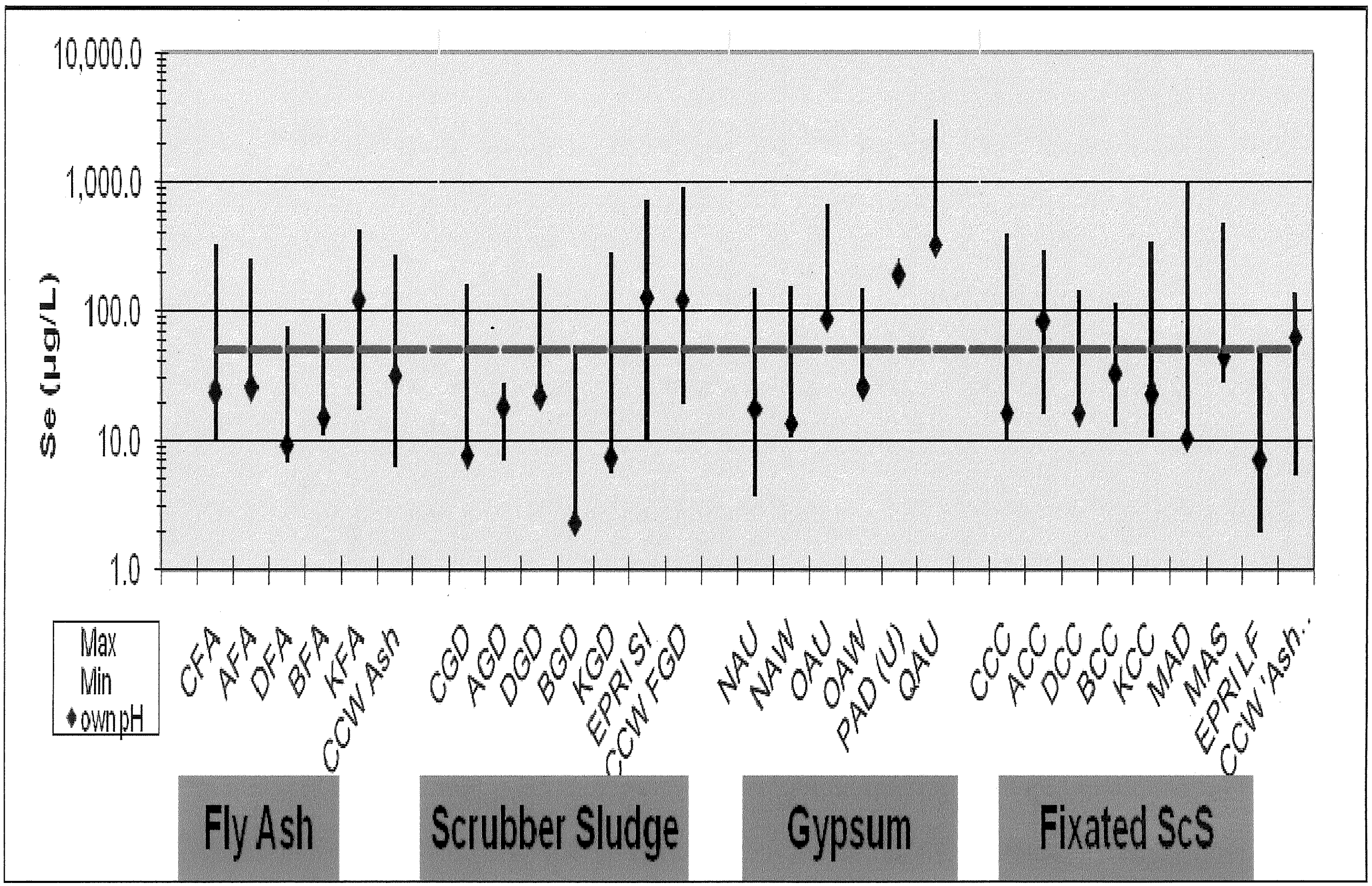
Results of Selenium Leaching Concentration (5.4<pH<12.4)



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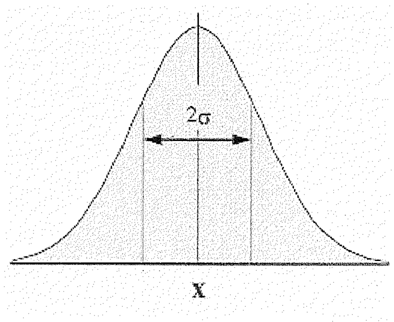
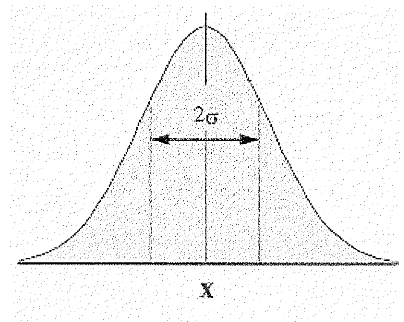
"Report 4" Will Include Probabilistic Analysis of Potential Release Rates Based on Plausible Management Practices

Inputs → **Outputs**



Percolation/Equilibrium Model

$$M_{mass}^{t_{year}} = LS_{site} \times S_{field\ pH}$$



Monte Carlo technique

- Distribution of inputs
  - LS ratio
  - Field pH
- Use of experimental solubility curves

- Distribution of outputs
  - 100 yr cumulative release estimates [µg/kg CCR]
    - 5th percentile
    - Median
    - 95th percentile
    - Compare with total content

Illustration of Results Being Developed to Predict 100-Year Release Rates for Hg and As

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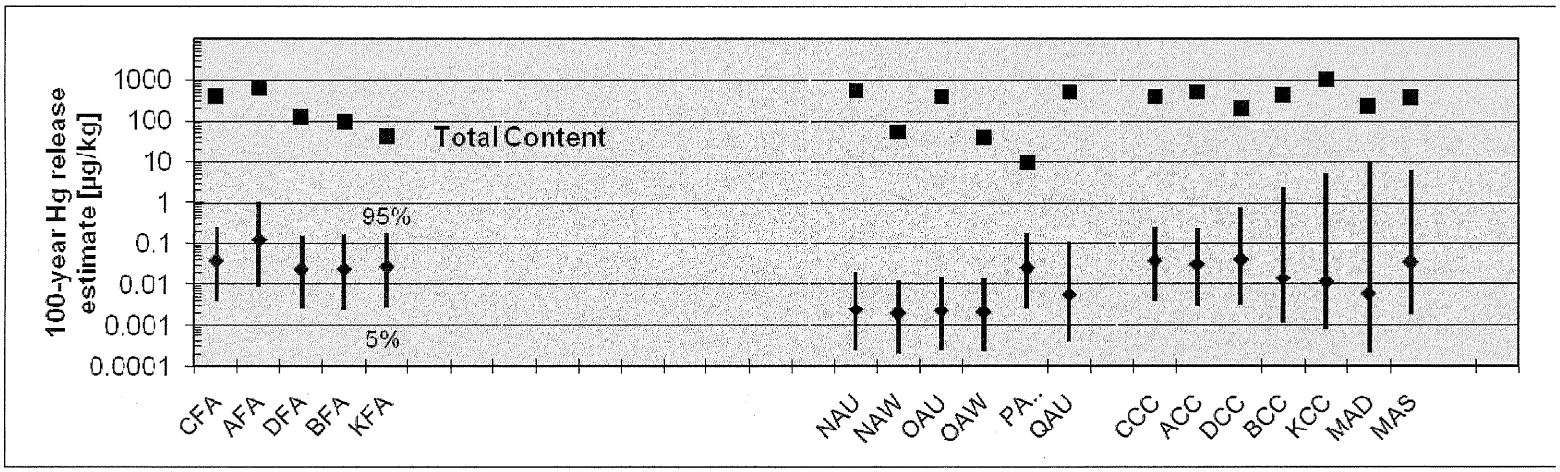

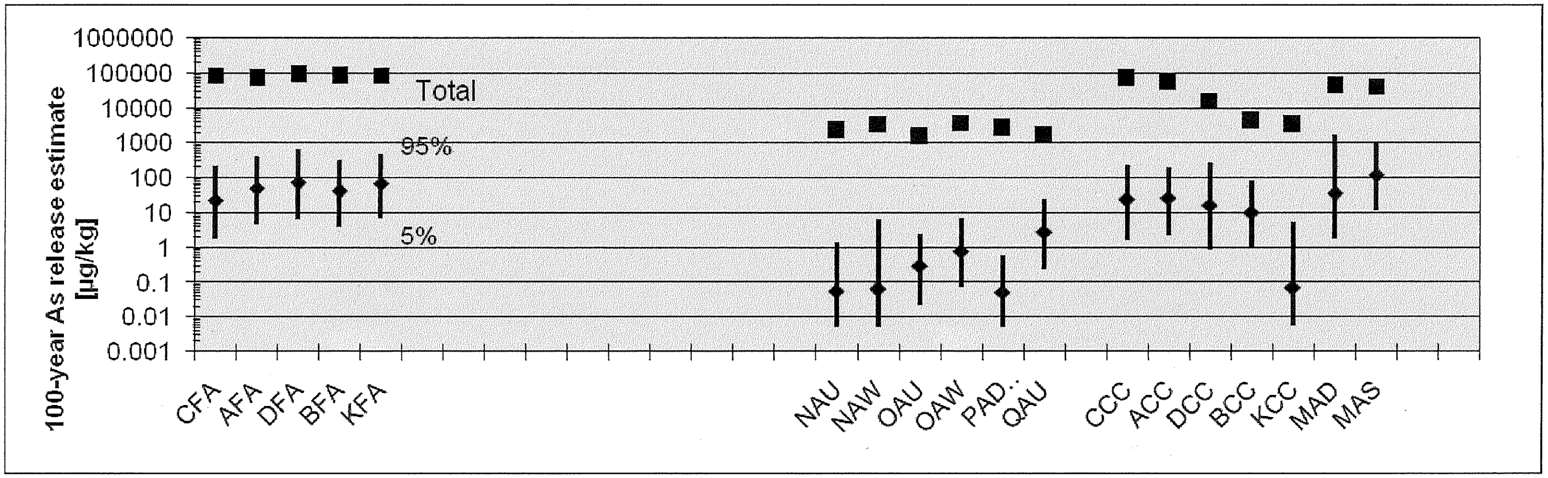

Illustration of Results Being Developed to Predict 100-Year Release Rates for Cr and Se

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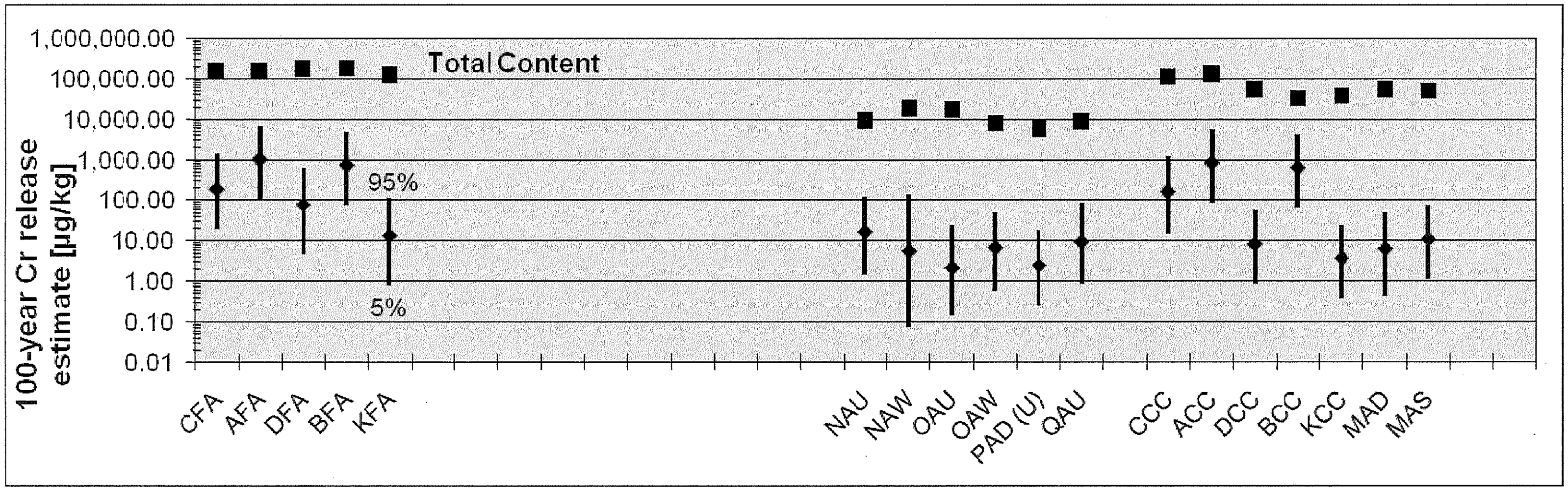

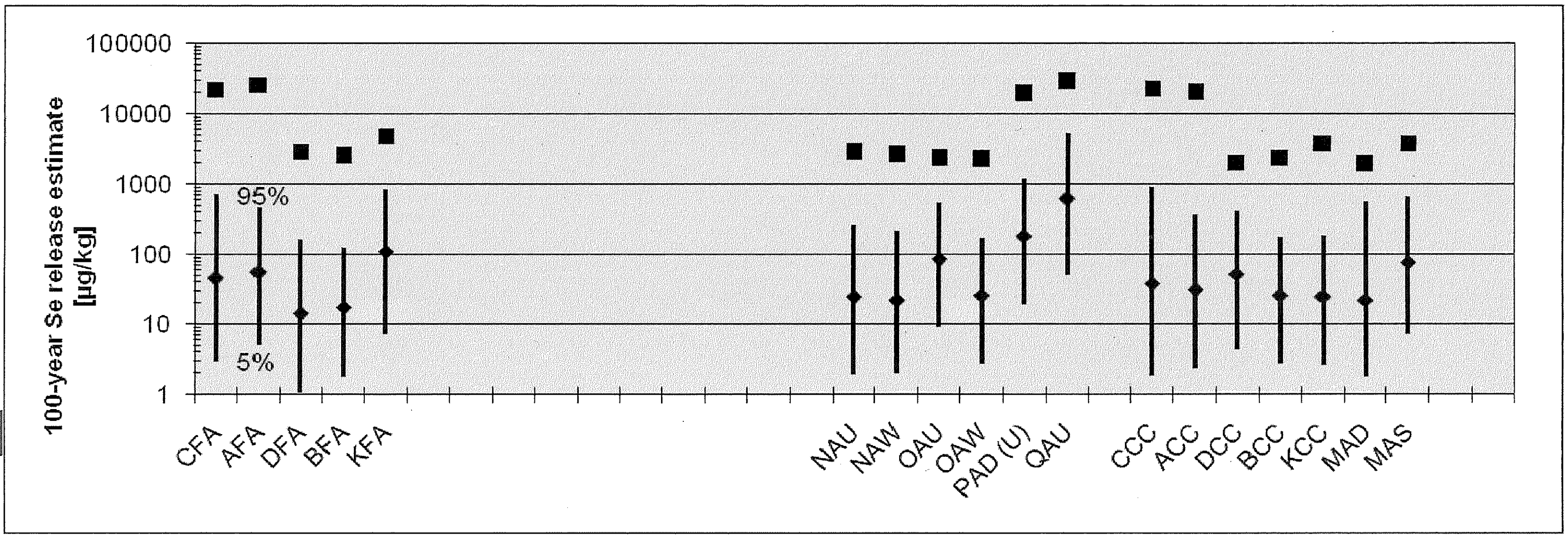

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Decision Support Tool for CCR Management

- Using results from Reports 1 – 4, we are developing a Decision Support Tool (DST) for environmental assessment of CCRs.
- The DST would be used by:
  - –Power plants to assess CCR management options
  - –Regulatory authorities to evaluate proposed CCR management methods
- The DST would facilitate:
  - –Management and assessment of leaching data
  - –Consistent assessment of data across the industry
  - –Use of leaching data as a source term for groundwater fate and transport models.

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Decision Support Tool for CCR Beneficial Use Decisions

- DST inputs would include:
  - Waste type
  - Leach testing results (metals concentrations, pH)
  - Facility data (management unit type, size, pH and other conditions)
  - Waste characterization data collected and evaluated in the course of developing EPA/ORD Reports 1-4 (pre-loaded)
- DST outputs would include:
  - Probabilistic assessment of metals leaching that matches specific materials to specific management practices. Will evaluate leaching potential over 100 years or other specified time horizon.
  - A leaching source term that can be used with a groundwater fate and transport model to estimate likelihood of groundwater contamination
    - Focus is on beneficial use decisions
    - Also can be used as input for permitting land disposal units.