

REINHOLD ENVIRONMENTAL Ltd.



2010 APC Round Table & Expo Presentation

July 18-20, 2010, in Concord, NC / Hosted by Duke Energy

All presentations posted on this website are copyrighted by Reinhold Environmental, Ltd (RE). Any unauthorized downloading, attempts to modify or to incorporate into other presentations, link to other websites, or obtain copies for any other uses than the training of attendees to RE's Conferences is expressly prohibited, unless approved in writing by RE or the original presenter. RE does not assume any liability for the accuracy or contents of any materials contained in this library which were presented and/or created by persons who were not employees of RE.

Metals Beyond Mercury: Measurement and Control of Other HAPs

Connie Senior
Reaction Engineering International

Reinhold APC Conference
July 19-20, 2010

Outline

- Upcoming utility MACT rule and Hazardous Air Pollutants (HAPs)
- Utility Information Collection Request (ICR)
 - Acid Gases
 - Organics
 - Dioxins & Furans
 - Non-Hg Metals
- Prospects for measurement and control

Mercury and Beyond

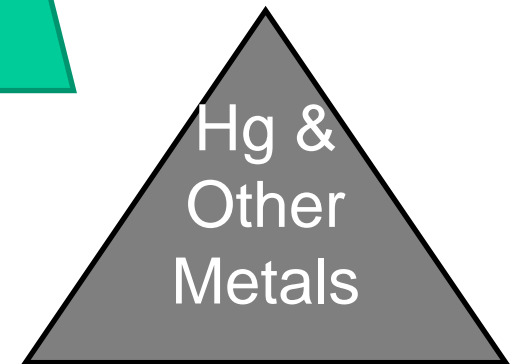
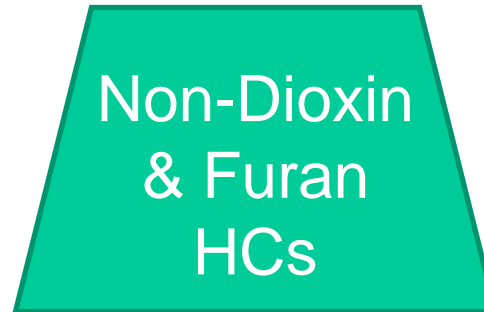
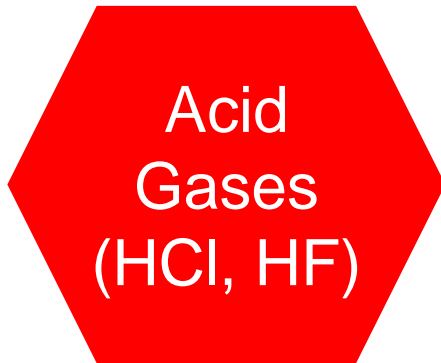
- Clean Air Mercury Rule (CAMR) vacated by DC Circuit Court (February 2008)
- EPA announced intent to control Hg through Section 112 of CAA (February 2008)
 - Maximum Achievable Control Technology (MACT)
 - Applies to ALL hazardous air pollutants (HAPs)
- Schedule from Consent Decree:
 - Utility MACT proposed by March 2011
 - Rule promulgated by November 2011
 - Implementation expected by November 2014

Hazardous Air Pollutants

- CAA Section 112 specifies Hazardous Air Pollutants (HAPs), including metals
- What do we know about emissions of other HAPs? Impact of Hg control processes?
- What is the outlook for control of emissions?
- EPA decided to collect information on HAP emissions from utility boilers using an Information Collection Request (ICR)

The HAP Roll Call

- EPA considered these groups of HAPs in requesting information from utilities for the MACT:



EPA's ICR Strategy

- EPA selected sources that should be “best performing” sources for a HAP group
- Each facility required to test after the last control device or at the stack
- EPA required testing for approximately 15% of all coal-fired EGUs for 3 of the HAP groups
 - metal HAP and PM; non-dioxin/furan organic HAP, total hydrocarbon, CO, and VOC; and acid gas HAP and SO₂
- 50 boilers chosen randomly for dioxins/furans

Acid Gas HAPs

- Acid-gas HAPs (HCl and HF) are more soluble in water than SO_2
 - HCN, representing the “cyanide compounds,” also water-soluble and will be considered an “acid-gas HAP”
- Both HCl and HF will be more rapidly and readily removed from a flue gas stream than SO_2 in scrubbers and FBCs

Acid Gas HAPs

- EPA is considering emissions of SO_2 as a potential surrogate for emissions of the acid HCl and HF

“Should emissions of SO_2 be deemed inappropriate as a potential surrogate for emissions of the acid-gas HAP, we are also gathering sufficient data on HCl, HF, and HCN to be able to establish individual emission limits.”

- U.S. EPA



Acid Gas HAPs ICR Testing

- EPA selected 170 units with the newest FGDs
- Testing includes
 - HCl, HF, HCN, SO₂, O₂, CO₂, and moisture from the stack gases
 - Chlorine, fluorine, and sulfur content, HHV, and proximate/ultimate analyses of the coal

Sources/Conditions for Organic HAPs

- From unburned fuel
 - Benzene, toluene, ethylbenzene and xylene (BTEX), hexane, naphthalene, etc.
- From quenching
 - Acetaldehydes, formaldehydes, acrolein, CO
- From by-product chemistry in rich pockets
 - Benzene and toluene, polyaromatic hydrocarbons

Surrogates for Organic HAPs

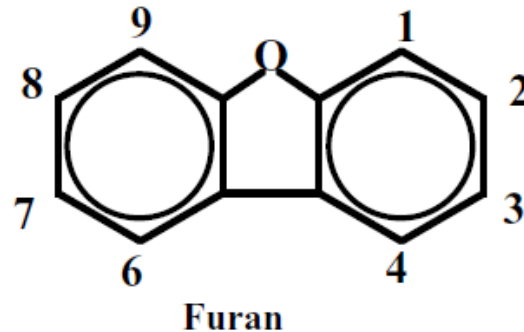
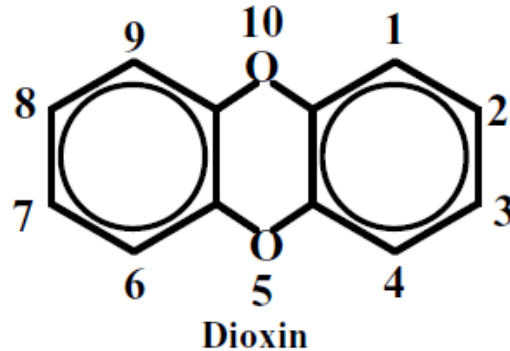
- In the past, emissions of CO, volatile organic compounds (VOC), and/or total hydrocarbons (THC) used as surrogates for the non-dioxin/furan organic HAPs
 - Based on the theory that efficient combustion leads to lower overall organic emissions.
- EPA wants to test possible surrogates and obtain more measurements of non-dioxin/furan organic HAPs

Organic HAP Testing in ICR

- EPA identified the 170 newest units as being representative of the most modern, and, thus, presumed most efficient, units
 - Required to test for CO, VOC, THC
 - All tested units would be required to test for moisture from the stack gases and HHV and proximate, ultimate analyses of the coal
- From these 170 units, subset of 50 units chosen
 - Required to test for polycyclic organic matter (POM), NO_x, formaldehyde, methane, O₂, and CO₂, in addition to CO, VOC, and THC

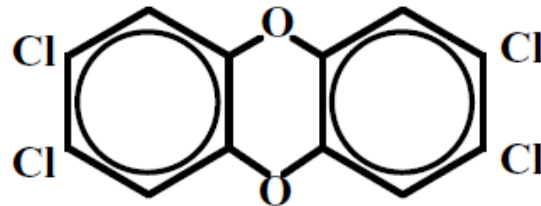
Dioxins and Furans: A Brief Review

- Chlorinated organic compounds
- Persistent organic pollutants in environment

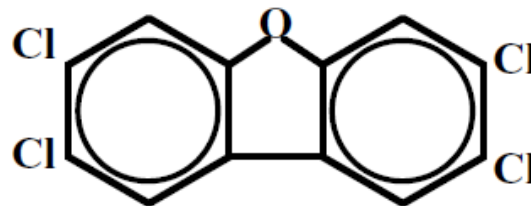


Dioxins and Furans: A Brief Review

- Chlorinated organic compounds
- Persistent organic pollutants
- Examples:



2,3,7,8 — Tetrachlorodibenzo(p)dioxin



2,3,7,8 — Tetrachlorodibenzofuran

- There are 210 different congener configurations!



Dioxins and Furans: A Brief Review

- Not all Dioxins and Furans are created equal

CONGENER	TOXIC EQUIVALENCY FACTOR (TEF)		
	HUMANS/ MAMMALS	FISH ^a	BIRDS ^a
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1 f
1,2,3,4,7,8-HxCDDD	0.1 a	0.5	0.05 f
1,2,3,6,7,8-HxCDD	0.1 a	0.01	0.01 f
1,2,3,7,8,9-HxCDD	0.1 a	0.01	0.1 f
1,2,3,4,6,7,8-HpCDD	0.01 a	0.001	0.1 f
OCDD	0.0001 a	-	-
2,3,7,8-TCDF	0.1	0.05	1 f
1,2,3,7,8-PeCDF	0.05	0.05	0.1 f
2,3,4,7,8-PeCDF	0.5	0.5	1 f
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1 c,f
1,2,3,6,7,9-HxCDF	0.1	0.1 c	0.1 c,f
1,2,3,7,8,9-HxCDF	0.1 a	0.1 c,e	0.1 c
2,3,4,6,7,8-HxCDF	0.1 a	0.1 c	0.1 c
1,2,3,4,6,7,8-HpCDF	0.01 a	0.01 b	0.01 b
1,2,3,4,7,8,9-HpCDF	0.01 a	0.01 b,e	0.01 b
OCDF	0.0001 a	0.0001 b,e	0.0001 b
3,4,4',5-TCB (81)	0.0001 a,b,c,e	0.0005	0.1
3,3',4,4'-TCB (77)	0.0001	0.0001	0.05
3,3',4,4',5-PeCB(126)	0.1	0.005	0.1
3,3',4,4',5,5'-I xCB (169)	0.01	0.00005	0.001
2,3,3',4,4'-PeCB(105)	0.0001	<0.000005	0.0001
2,3,4,4',5-PeCB(114)	0.0005 a,b,c,d	<0.000005 b	0.0001 g
2,3',4,4',5-PeCB(118)	0.0001	<0.000005	0.00001
2',3,4,4',5-PeCB(123)	0.0001 a,c,d	<0.000005 b	0.00001 g
2,3,3',4,4',5-HxCB (156)	0.0005 b,c	<0.000005	0.0001
2,3,3',4,4',5'-HxCB (157)	0.0005 b,c,d	<0.000005 b,c	0.0001
2,3',4,4',5,5'-HxCB (167)	0.00001 a,d	<0.000005 b	0.00001 g
2,3,3',4,4',5,5'-HpCB (189)	0.0001 a,c	<0.000005	0.00001 g

"-" indicates no TEF because of lack of data

a) limited data set

b) structural similarity

c) QSAR modelling prediction from CYP1A induction (monkey, pig, chicken, or fish)

d) no new data from 1993 review

e) in vitro CYP1A induction

f) in vivo CYP1A induction after in ovo exposure

g) QSAR modelling prediction from class specific TEFs

Dioxins and Furans: A Brief Review

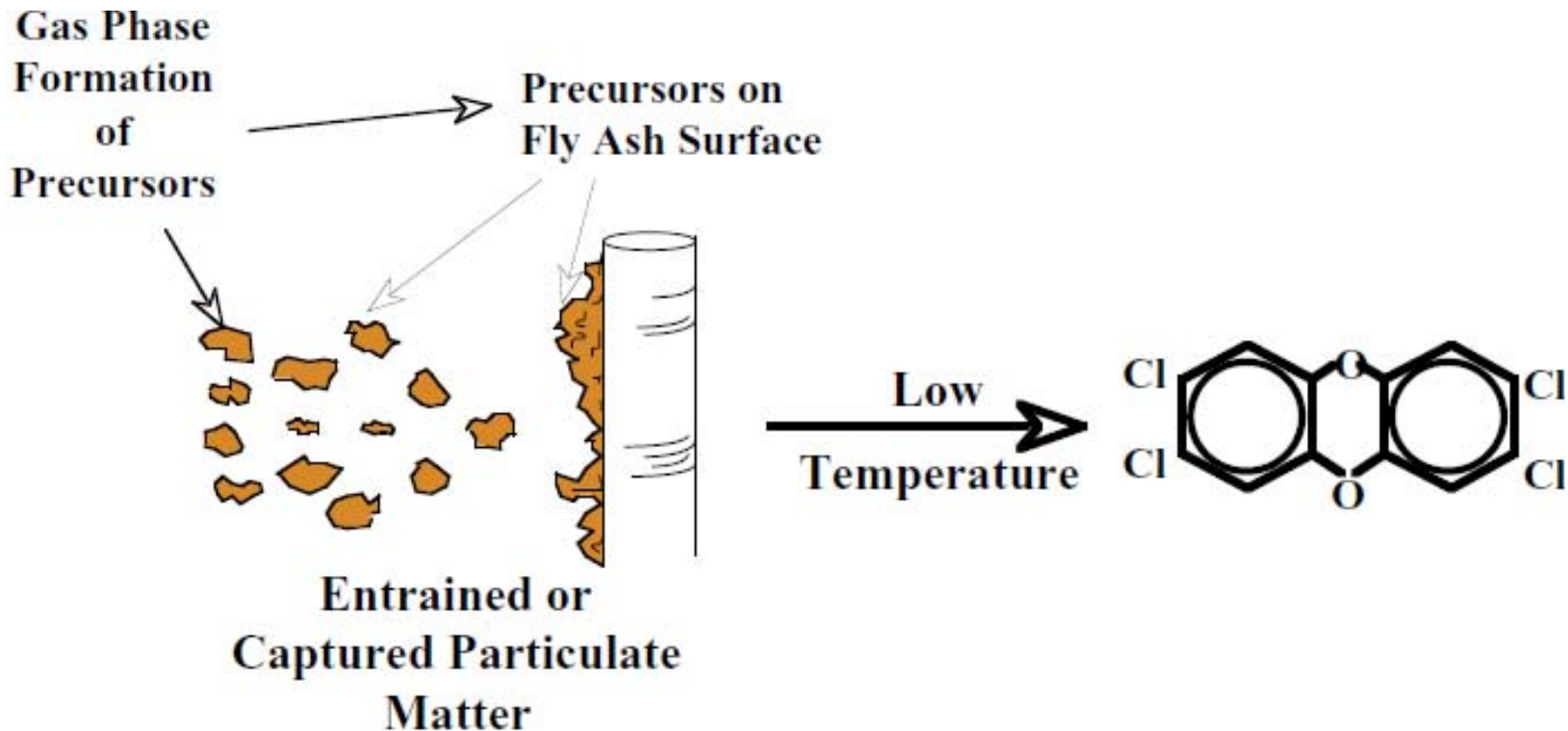
- Dioxin formation takes place both at high temperatures (combustion zone) and post-combustion when chlorine combines with unburned hydrocarbons
- Formation results from poor mixing, quenching, cool temperature pathways, gas-particle interactions, lack of particle burnout, sooting

Dioxin and Furan Formation Pathways

- ~~Destroyed PCDD/PCDF originating with waste~~
- ~~Gas-phase formation (Furnace to 900°F)~~
 - ~~From chlorinated precursors and from simple organics and chlorine donors (~1300°F)~~
 - ~~– From complex organics and chlorine donors~~
- Fly ash formation pathway (< 900°F)
 - Need chlorine and organic precursors
 - Condensation of precursors and surface chlorination

Dioxin and Furans Formation Pathway in Coal-Fired Boilers

- Fly ash formation pathway (< 900°F)



Dioxin and Furan Emissions

- Dioxin/furan emissions from coal-fired utility boilers are generally considered to be low, because
 - Insufficient amounts of available chlorine and/or dioxins or precursors in fuel
 - Inhibition of fly ash formation pathway by the presence of sulfur
- EPA wants some additional data either to base a surrogate standard or to establish an emission limit for dioxin/furan

Dioxin and Furan Sampling in ICR

- 50 units selected at random to conduct emission testing for dioxins/furans
- Activated carbon a potential control technology for dioxin/furan emissions (MWC experience)
 - ICR request includes some units with activated carbon injection (ACI) systems installed
- Each unit required to test for
 - Dioxins/furans, O₂, CO₂, and moisture from the stack gases
 - Chlorine and sulfur content, HHV, and proximate, ultimate analyses of the coal



Dioxin and Furan Sampling in ICR

- 50 units selected at random to conduct emission testing for dioxins/furans
- Activated carbon a potential control technology for dioxin/furan emissions (MWC experience)
 - ICR request includes some units with activated carbon injection (ACI) systems installed
- Each unit required to test for
 - Dioxins/furans, O₂, CO₂, and moisture from the stack gases
 - Chlorine and sulfur content, HHV, and proximate, ultimate analyses of the coal



Hazardous Air Pollutant Metals

- CAA Section 112 specifies Hazardous Air Pollutants (HAPs), including metals:
 - Antimony Compounds
 - Arsenic Compounds (inorganic including arsine)
 - Beryllium Compounds
 - Cadmium Compounds
 - Chromium Compounds
 - Cobalt Compounds
 - Lead Compounds
 - Manganese Compounds
 - Mercury Compounds
 - Nickel Compounds
 - Radionuclides (including radon)
 - Selenium Compounds

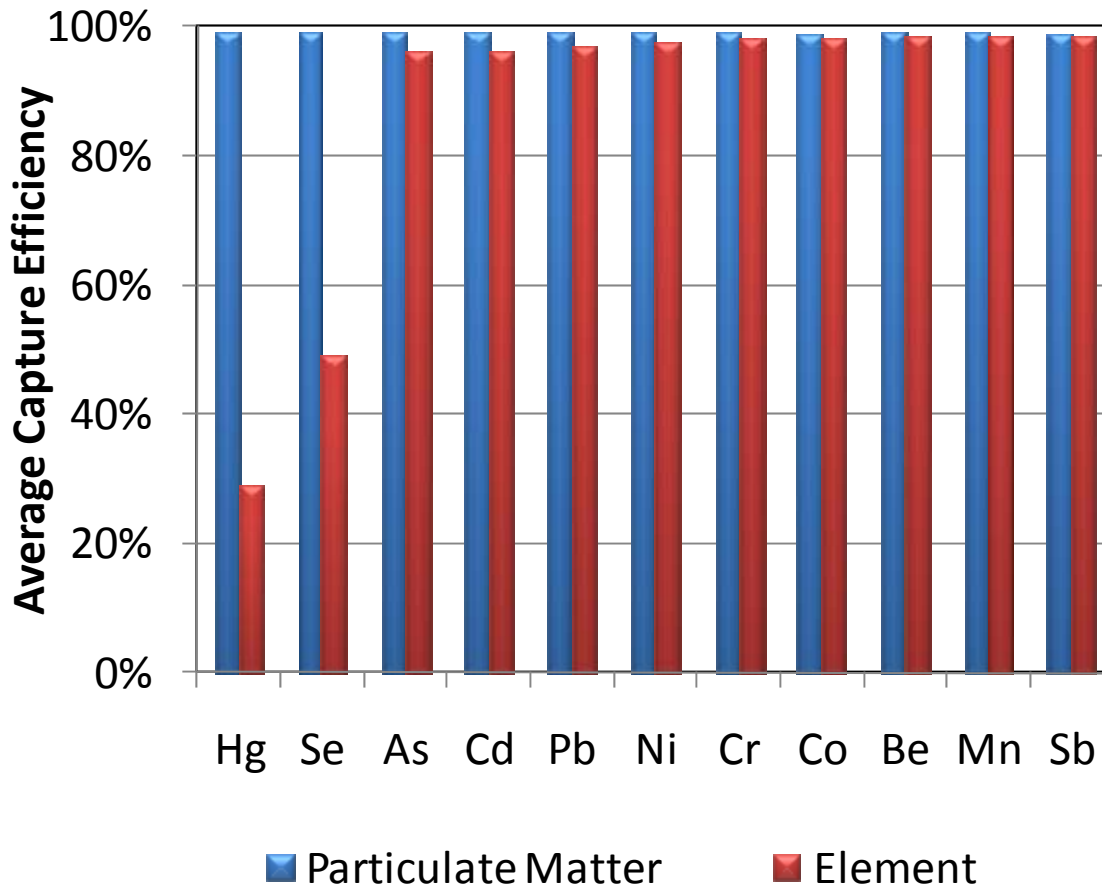
HAPs Metals in ICR

- EPA selected 170 units with the newest PM controls installed
- Required to test after that specific PM control (or at the stack if the PM control device is not shared with one or more other units)
 - Required to test for Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, Ni, Se, PM (total filterable, fine [dry], fine [wet]), O₂, CO₂, and moisture
 - Also required to analyze coal for the metals above (including Hg), Cl, HHV and proximate, ultimate analyses

Prospects for Measurement & Control

Hg &
Other
Metals

Capture Efficiency in ESPs



- PISCES/DOE field data
- Most HAP metals have the same capture efficiency as PM
- Capture of these metals in ESP \geq 97%

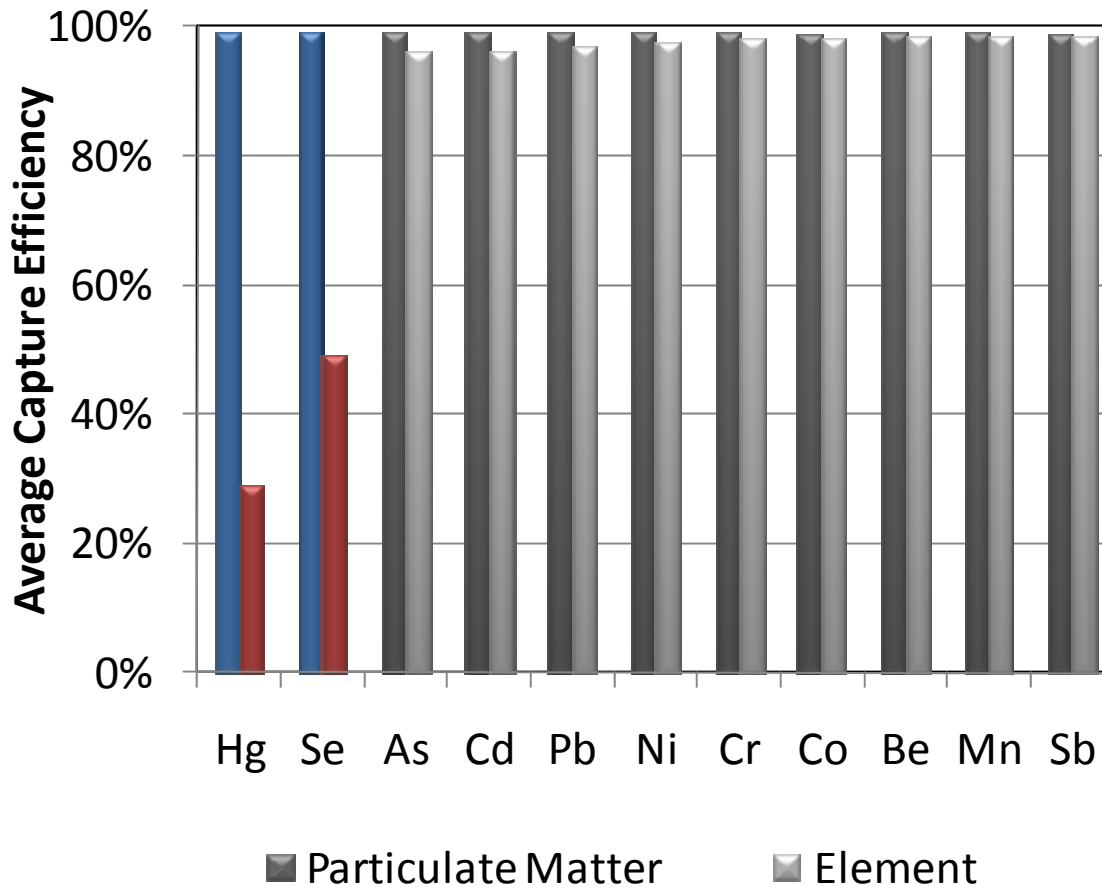
Source: Helble, 2000

Reinhold APC Conference ~ July 19-20, 2010



Hg &
Other
Metals

Capture Efficiency in ESPs



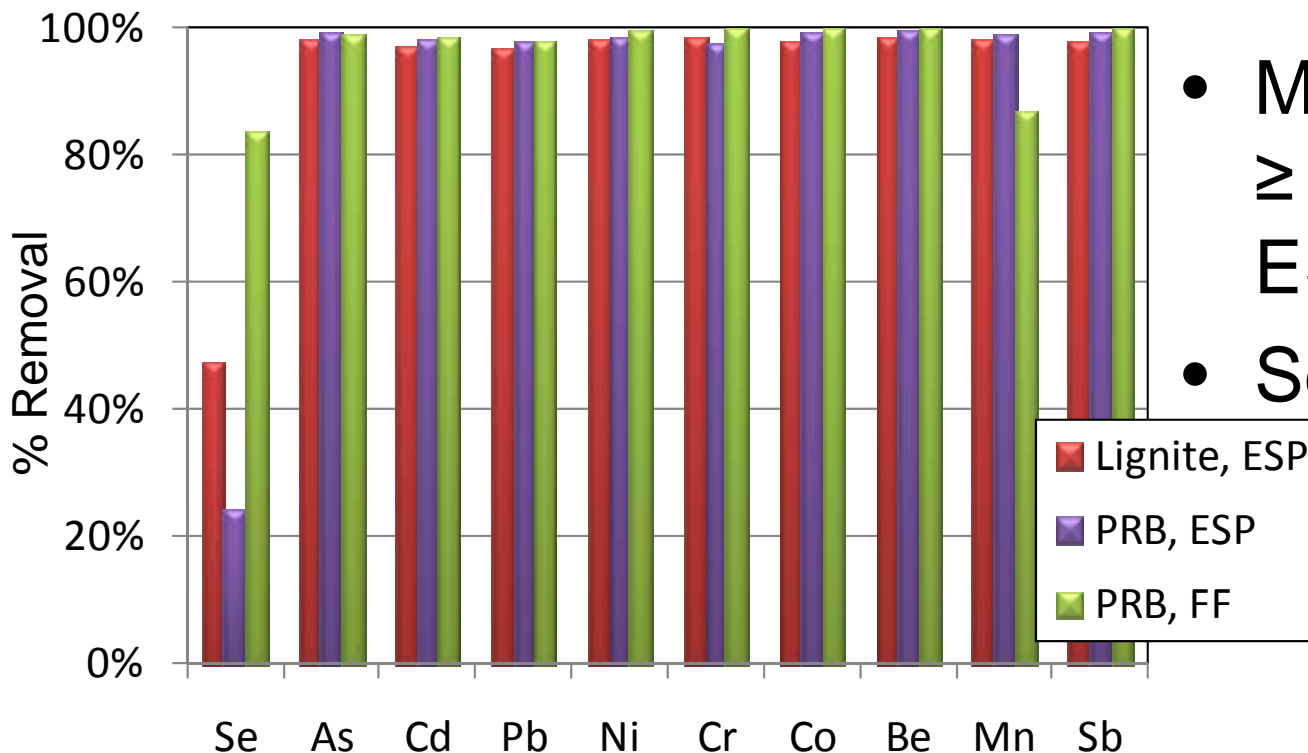
- The exceptions:
 - Mercury
 - Selenium
- These HAPs cannot be controlled effectively with an ESP alone

Source: Helble, 2000

Reinhold APC Conference ~ July 19-20, 2010



Capture in ESPs and FFs

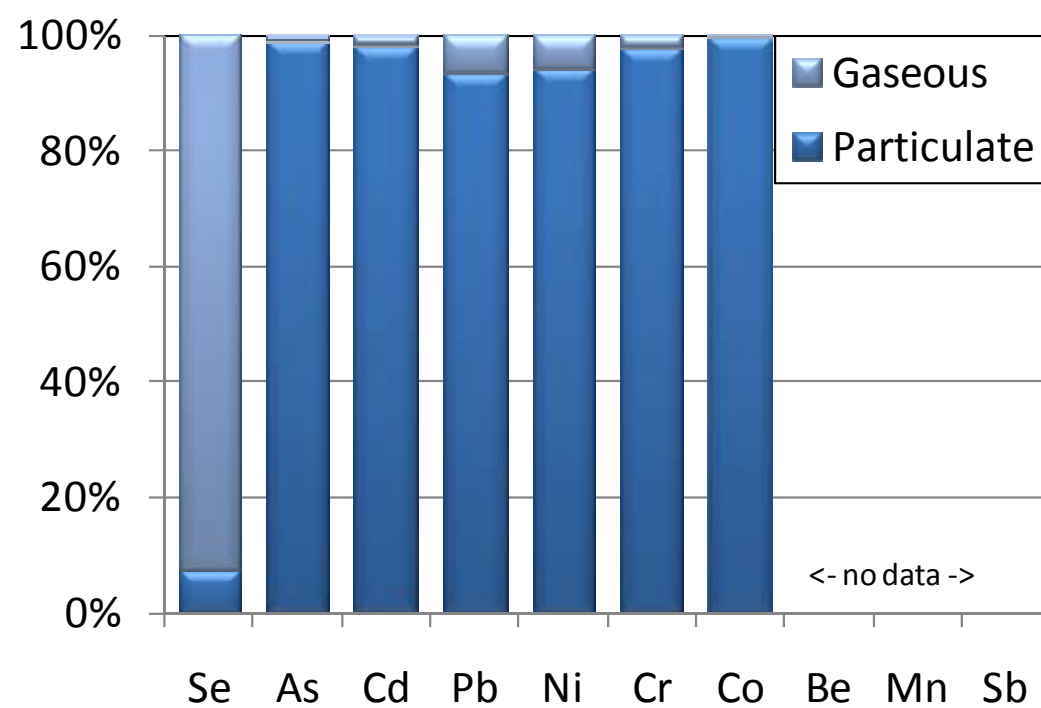


- Most metals have $\geq 97\%$ removal in ESP or FF
- Se is exception

Source: Pavlish, 2009

Hg &
Other
Metals

Selenium Volatility

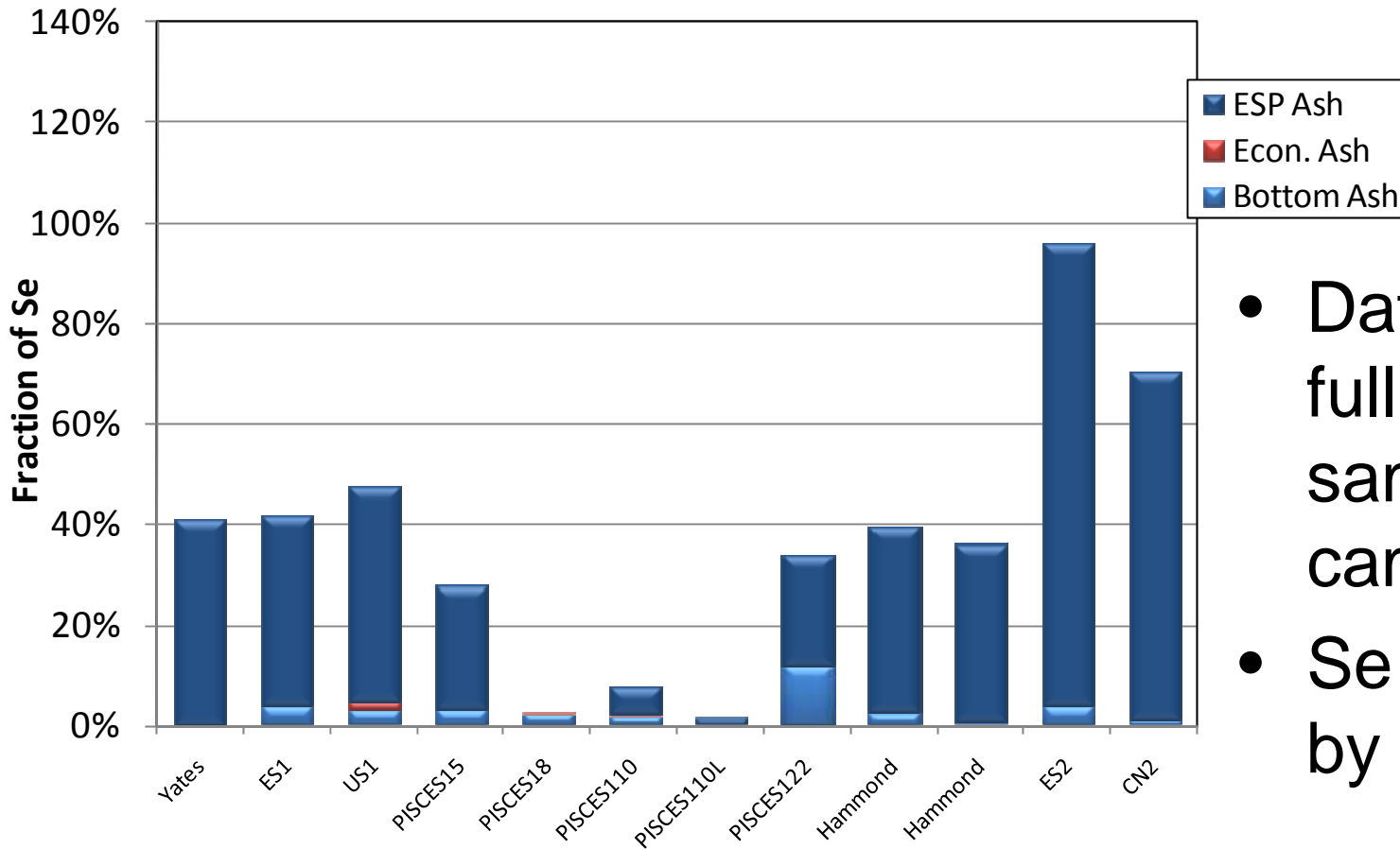


- Se can escape ESPs and FFs because it is in the gas-phase
- Method 29 stack data from boiler with ESP+FF burning Lignite-PRB blend

Source: Pavlish, 2009

Hg &
Other
Metals

Selenium Emissions from ESP Plants

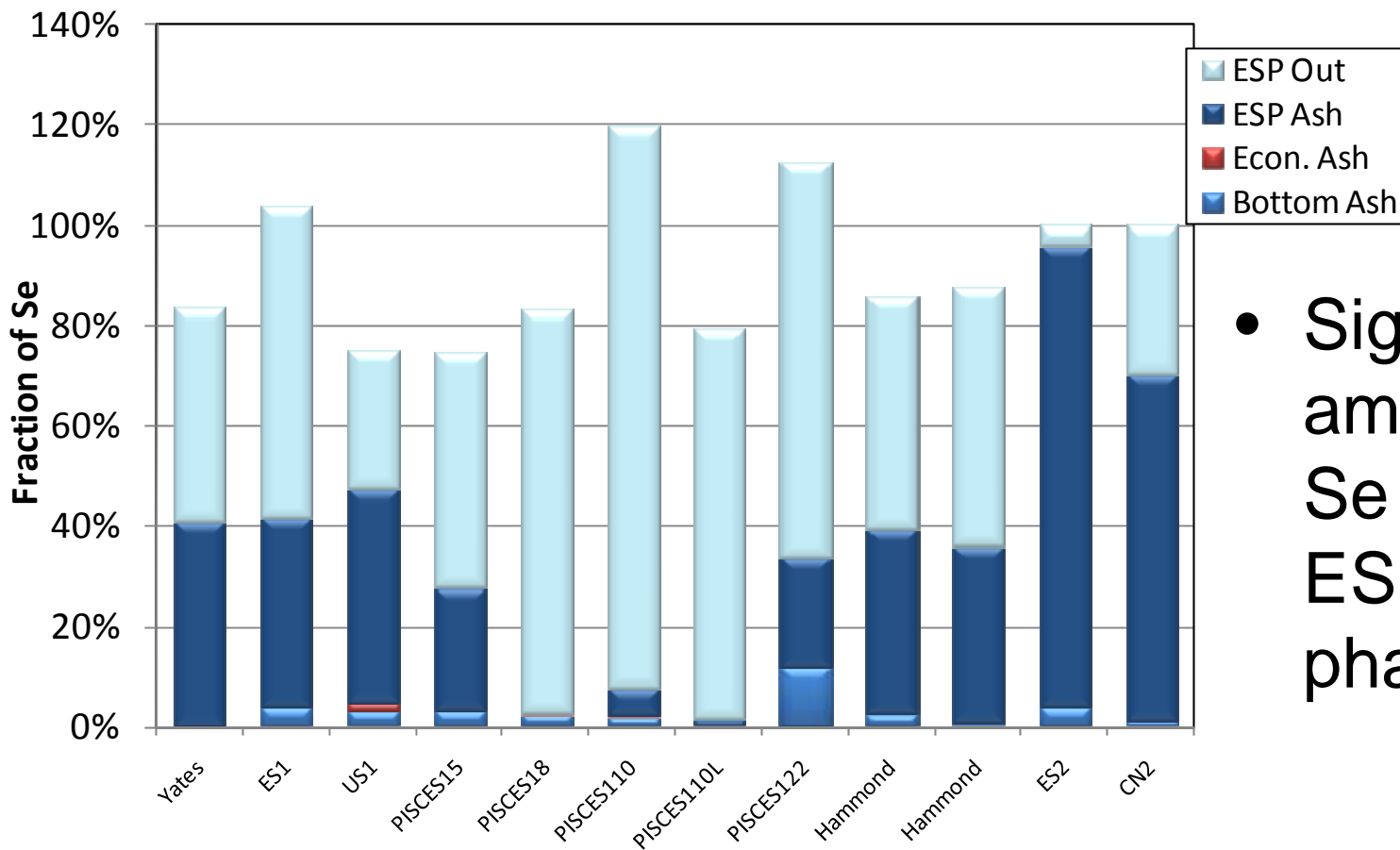


- Data from full-scale sampling campaigns
- Se removed by ash

Source: Senior, 2009
Reinhold APC Conference ~ July 19-20, 2010

Hg &
Other
Metals

Selenium Emissions from ESP Plants

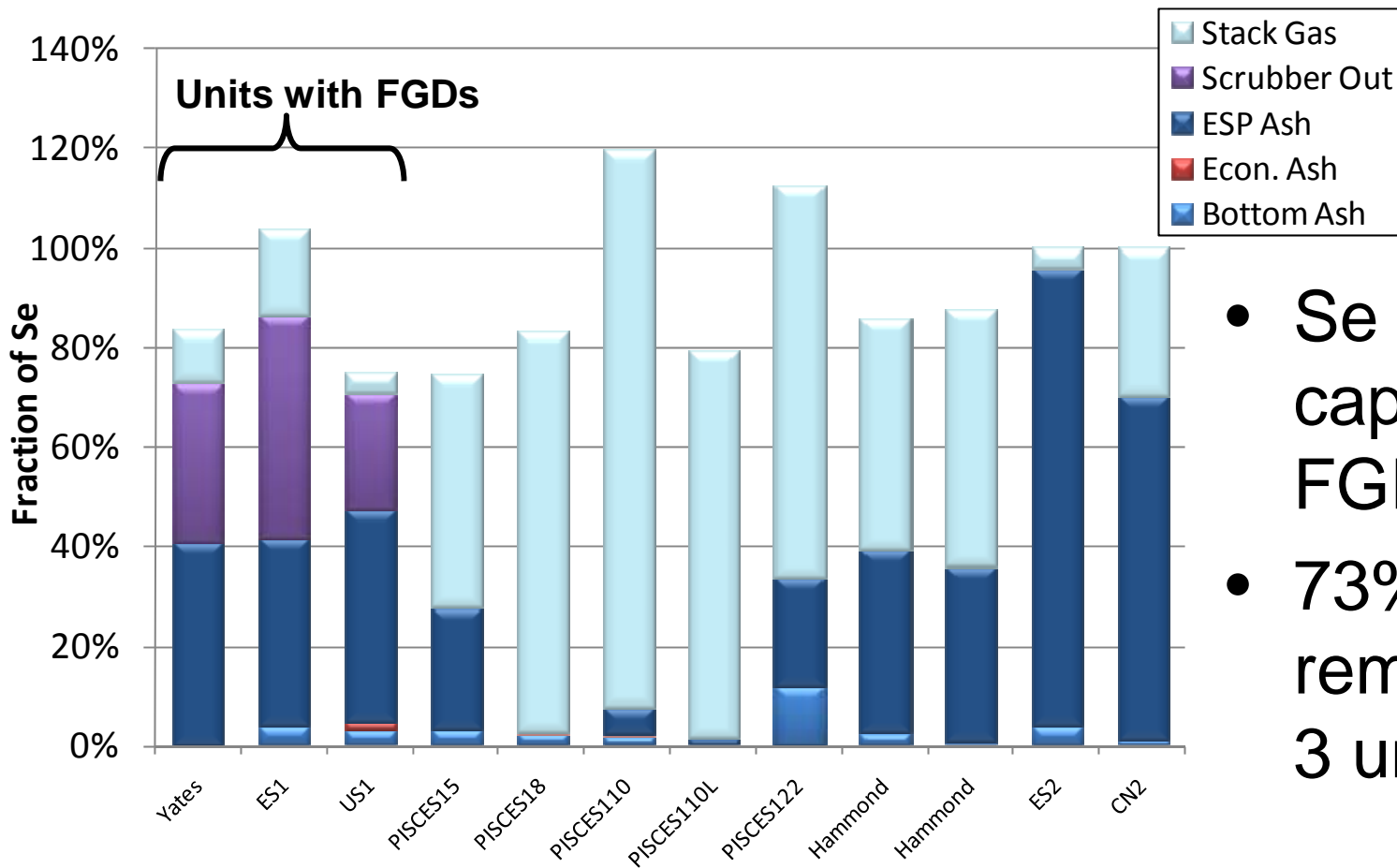


- Significant amount of Se exits ESP in gas phase

Source: Senior, 2009
Reinhold APC Conference ~ July 19-20, 2010

Hg &
Other
Metals

Selenium Emissions from ESP Plants



- Se can be captured in FGDs
- 73% removal avg. 3 units

Source: Senior, 2009
Reinhold APC Conference ~ July 19-20, 2010

Fate of Se within Scrubbers

- Data from Meij from coal-fired boiler in Netherlands
 - Average of 16 datasets from burning bituminous coal
 - Se distributed among gypsum product, wastewater, and scrubber sludge
- Average Se removal across FGD: ~60%

	Inputs		Outputs
Suspended fly ash	2%	Suspended fly ash	2.5%
Gas-phase	90%	Gas-phase	53.5%
Limestone	9.2%	Gypsum	16%
Process water	0.8%	Wastewater	17%
Lime	---	Sludge	11%

Se Interaction with Carbon

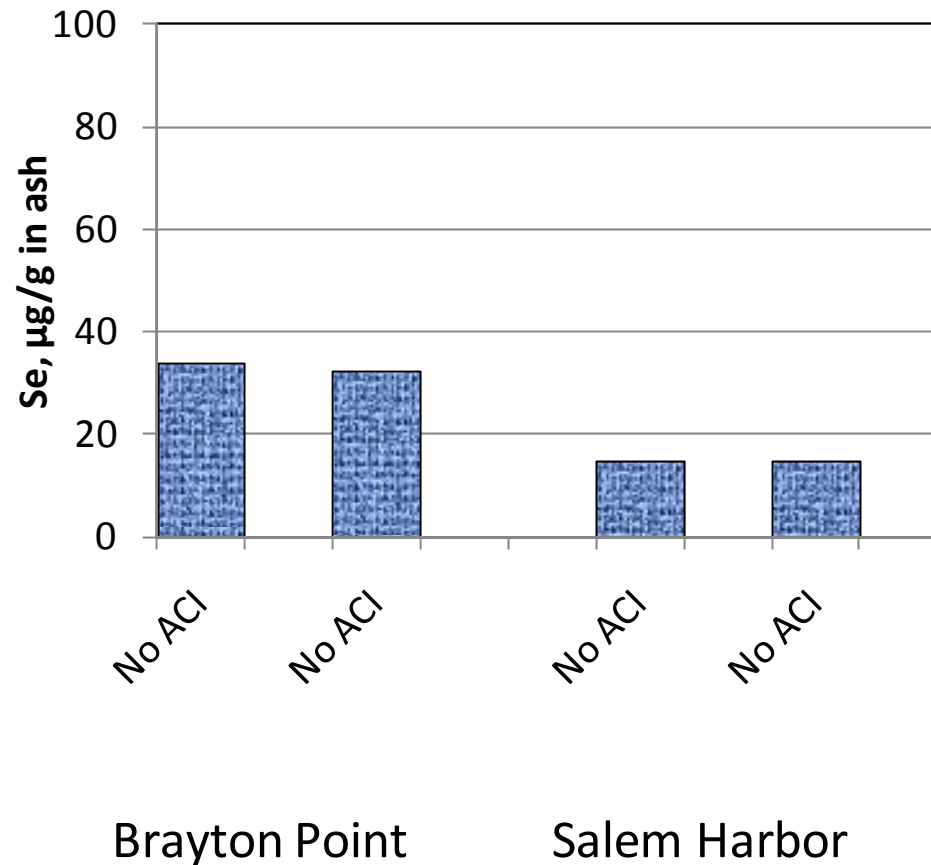
- Laboratory fixed-bed experiments show that activated carbon can adsorb $\text{SeO}_{2(g)}$ at post-air heater temperatures
- Breakthrough capacities have been reported as 2,000-3,000 $\mu\text{g/g}$
 - Comparable to capacities for Hg
- What happens in the “real” world?

Se Interaction with Carbon: Example 1

- Data from demonstrations of activated carbon injection (DOE/NETL program) using Norit FGD (Darco Hg)
 - **Brayton Point Unit 1**
 - 240 MW tangential-fired boiler
 - Eastern low-sulfur bituminous coal
 - Two ESPs in series => carbon injection between ESPs
 - **Salem Harbor Unit 1**
 - 80 MW front-wall-fired boiler
 - South American low-sulfur bituminous coal
 - Cold-side ESP

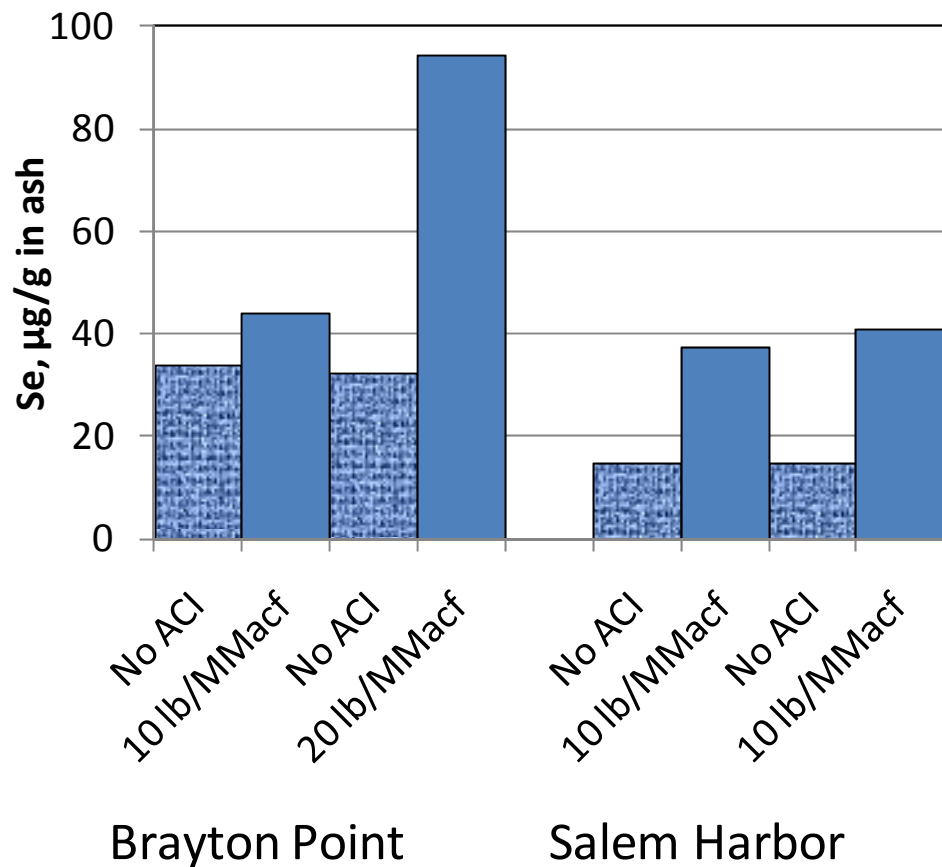
Se Interaction with Carbon: Example 1

- Baseline (No ACI) calculated from
 - baseline fly ash Se content
 - activated carbon Se content



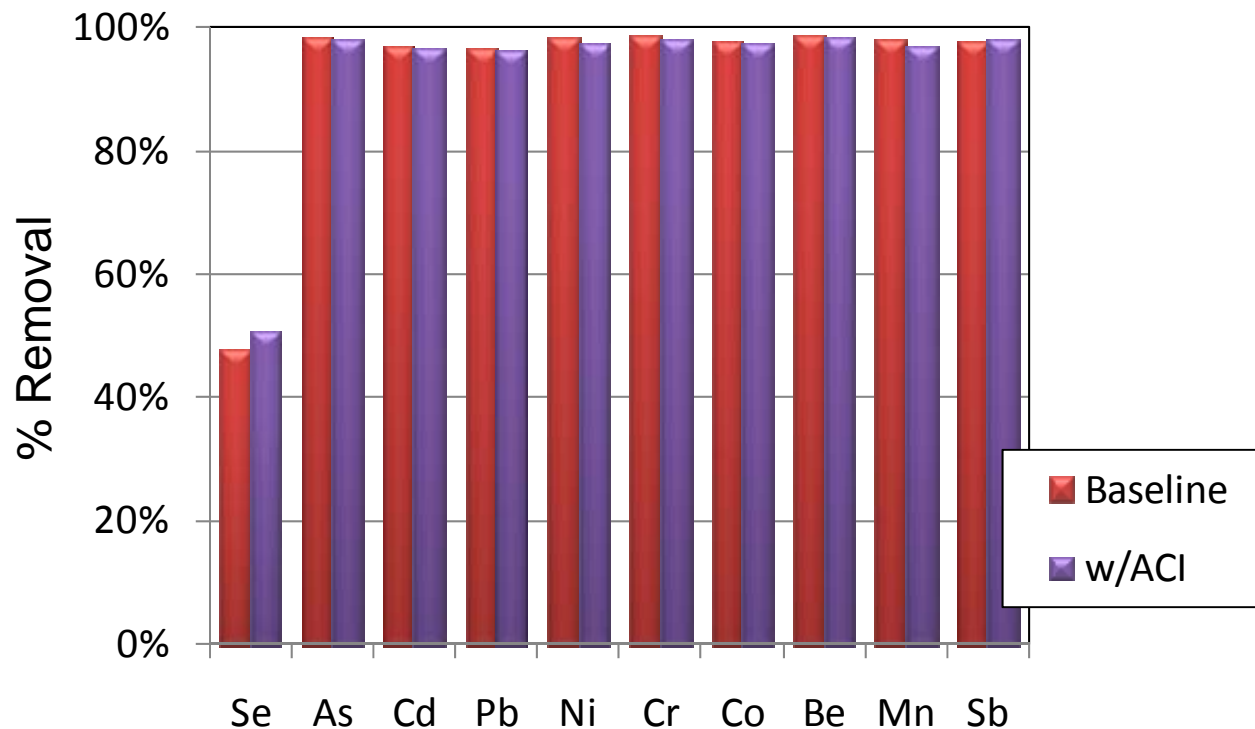
Se Interaction with Carbon: Example 1

- Increase in Se not due to Se content of activated carbon
- Net removal of Se from flue gas due to activated carbon injection
- Baseline (No ACI) calculated from
 - baseline fly ash Se content
 - activated carbon Se content



Se Interaction with Carbon: Example 2

- Method 29 data from Texas lignite-fired boiler with ESP
- ACI had no impact on Se removal

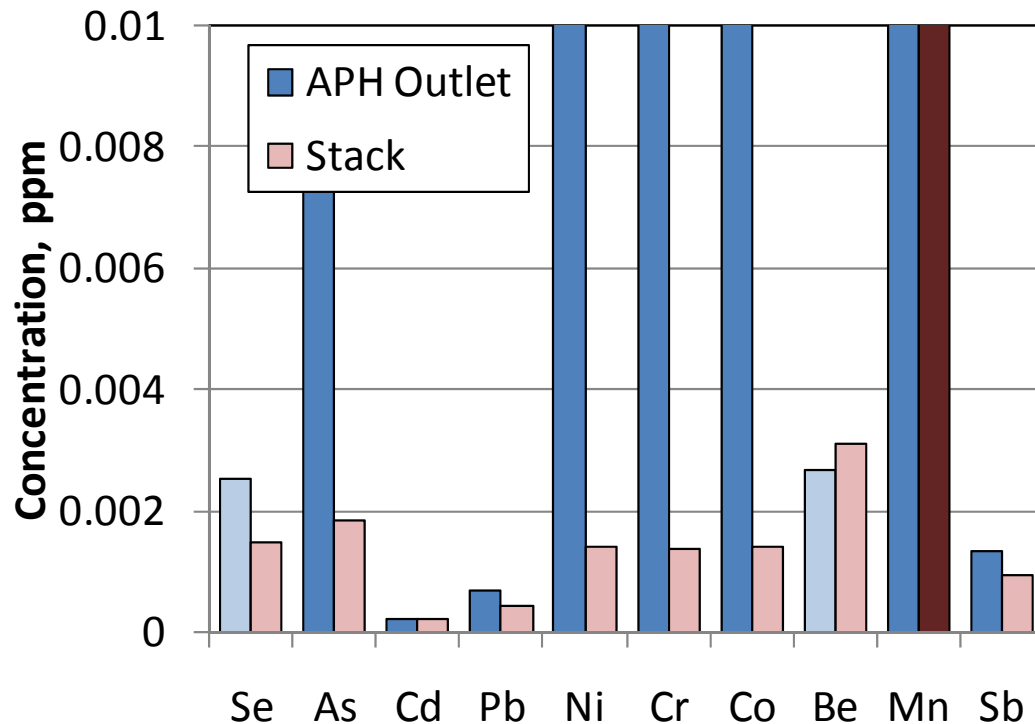


Behavior of HAP Metals in Coal-Fired Boilers: Current Understanding

- Most HAP metals removed with >97% efficiency using particulate control (ESP or FF)
- Significant amounts of Se can be found in gas phase at low temperatures ($\text{SeO}_{2(g)}$) at ESP or scrubber inlet
 - $\text{SeO}_{2(g)}$ can be captured by ACl, capture efficiencies not known
 - $\text{SeO}_{2(g)}$ can be captured in wet scrubbers: 60-70% efficiency??
- PM good surrogate for most HAP metals, but what about Se?
- More well-characterized full-scale data needed

Measurement issues

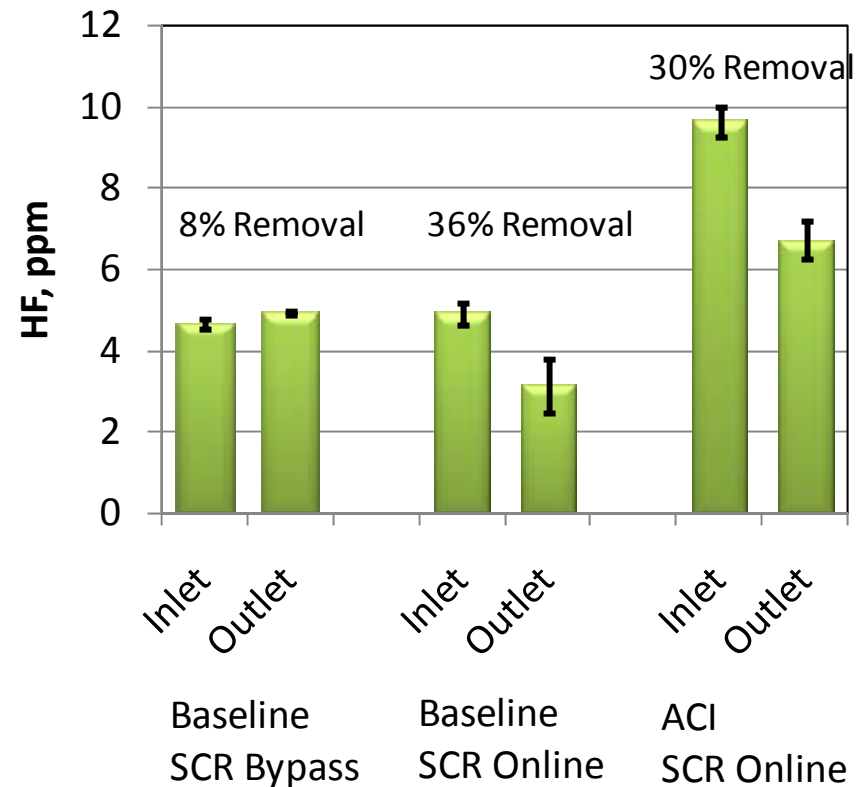
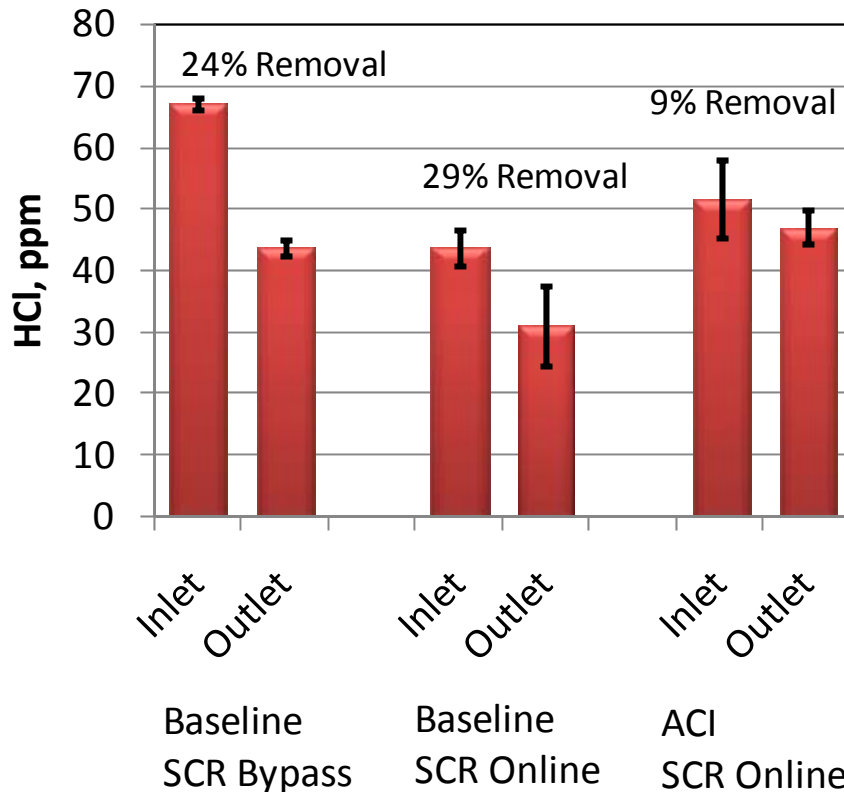
- Low concentrations of HAP metals make measurements in flue gas challenging
- Example: Holcomb (SDA/FF, PRB Coal)



- Dark bars indicate ABOVE detection limit
- Light bars indicated BELOW detection limit
- In stack, most HAP metals BELOW M29 detection limit
- Not enough data for mass balance

Halogens and ACI: Removal across ESP

- Halogens (HCl, HF) also on the HAPs list



Data from Plant Monroe

Halogens and ACI

- Halogens (HCl, HF) also on the HAPs list
- So far, ACI has not had a significant impact on emissions of HCl, HF
 - Review of M26A data for Holcomb, Meramec, Monroe
 - All three used halogenated AC

Prospects for Measurement and Control

- Measurement issues
 - Low concentrations of HAP metals make measurements in flue gas challenging
- Better measurements needed
 - Stack measurements are not enough!
 - Mass balance and data quality -> MACT process uses top 12% of units, so measurements must be accurate!
- Effect of ACI, scrubbers on emissions of organics, metals and halogens must be better understood with more field data

Questions?

senior@reaction-eng.com