2013 APC/PCUG Conference

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Mercury Overview

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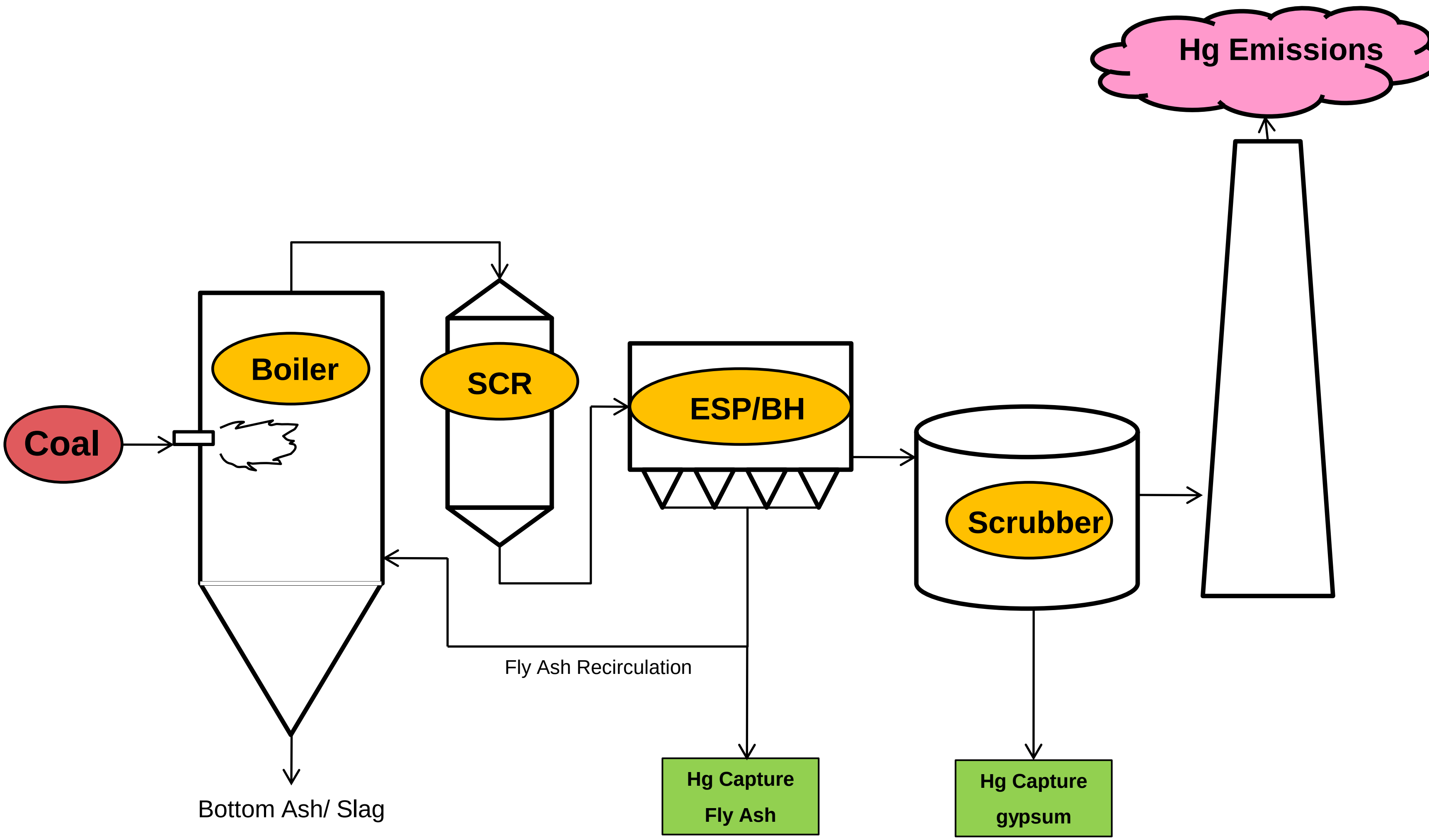
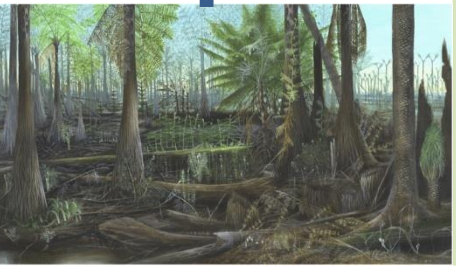
A Plant Tour – Mercury's Perspective

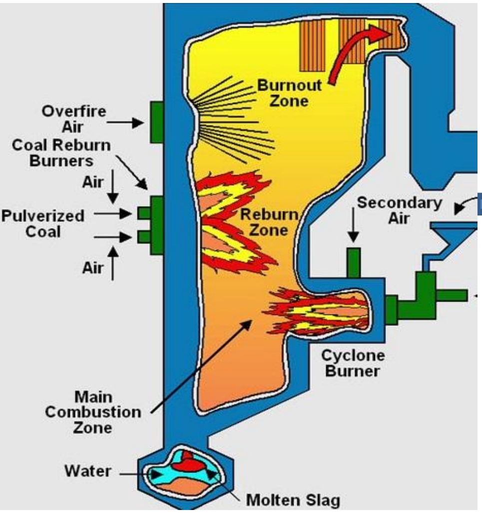


Coal: Mercury's home for 300 million years



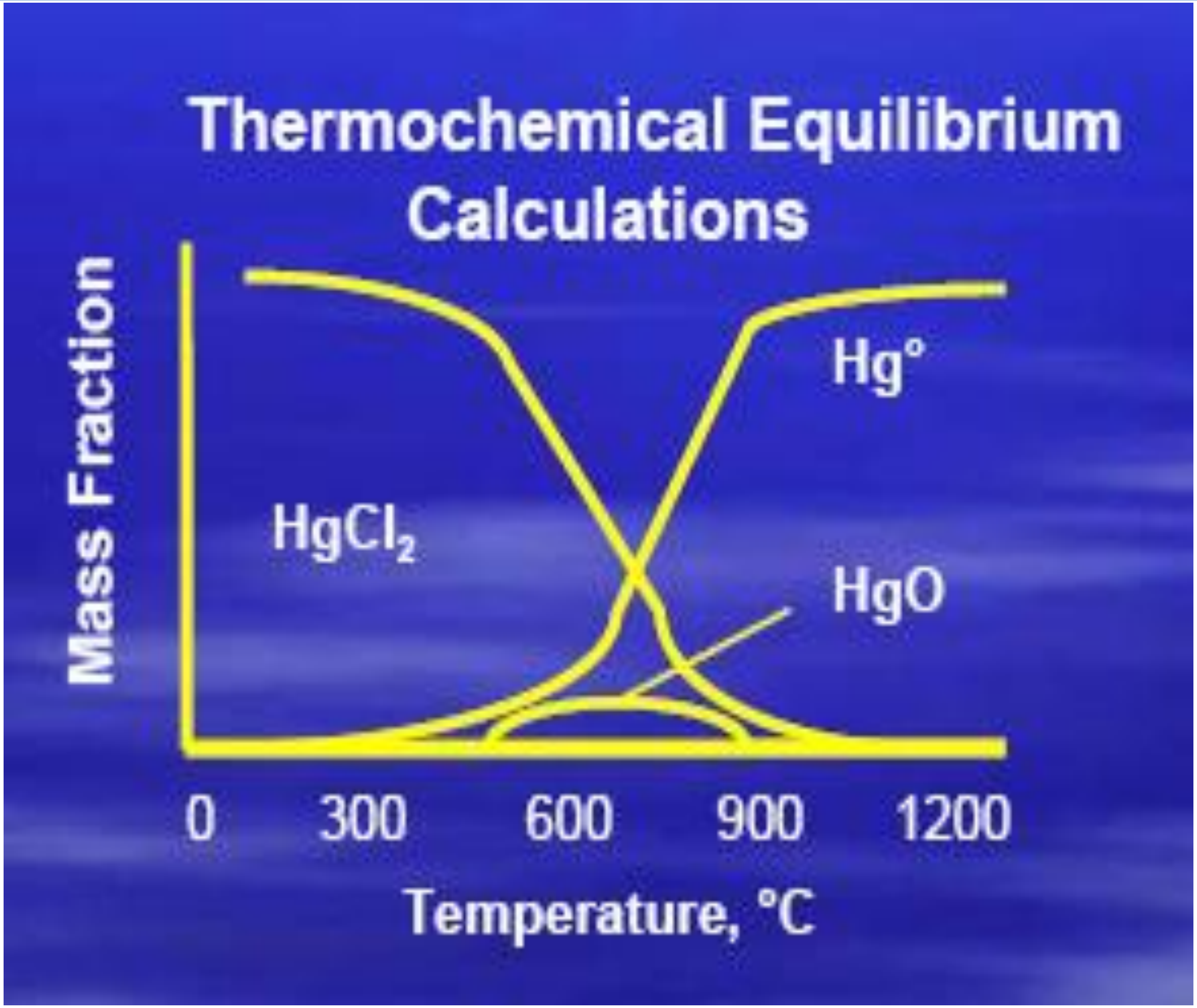
- Deposition and plant assimilation from the atmosphere is the source of coal mercury
- Many Possible Mercury Compounds: Hg^0, HgO,$HgCl_2$, $HgBr_2$, HgS, organic mercury, etc.
- Varies according to coal type, region, seam, mine, etc.

Boiler: High Temperature Converts Mercury



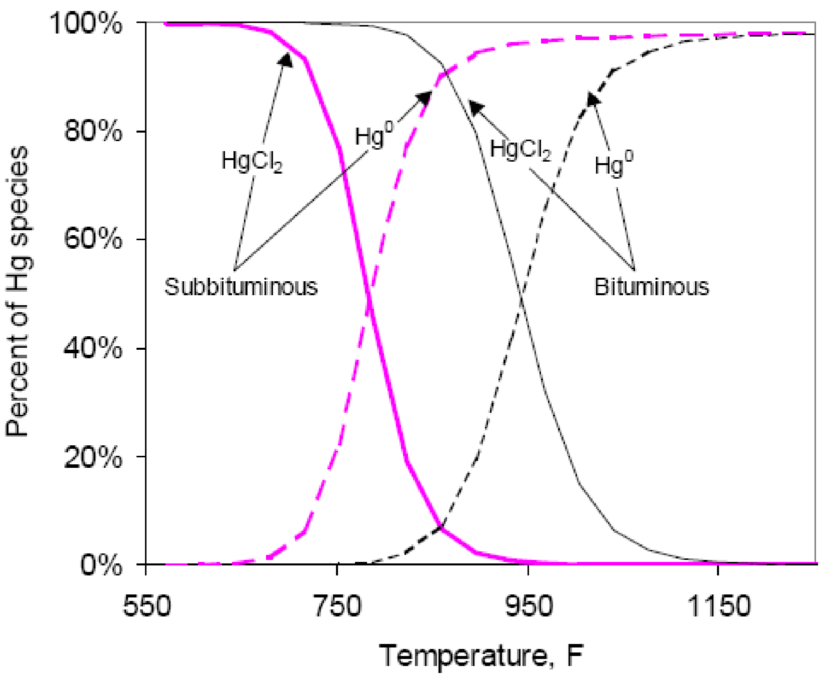
- **High Temperatures convert mercury compounds to elemental mercury**
- **Boiler creates additional species which influence mercury speciation and capture; HCl, HBr, SO_3, O_2, CO, H_2O, NOx, LOI**

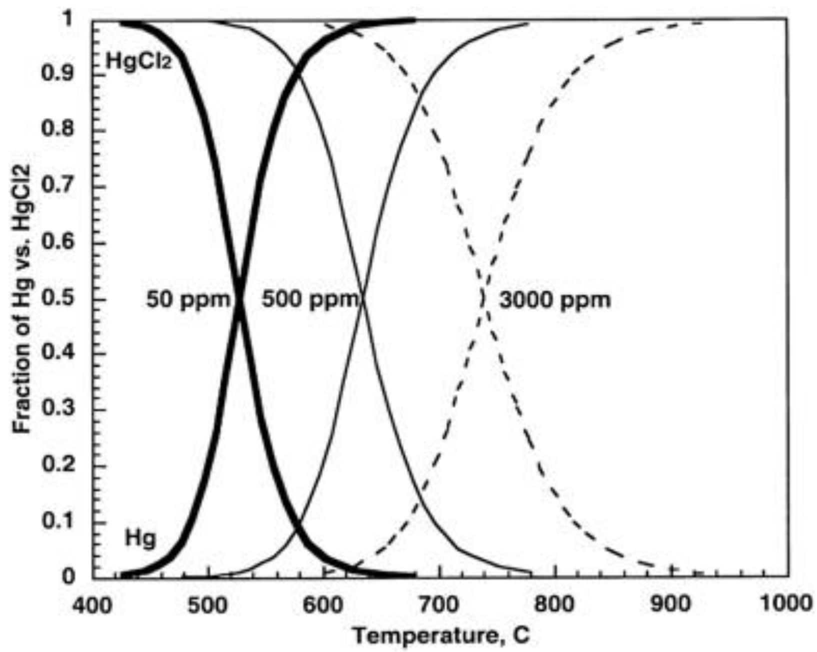
Boiler: Thermochemical equilibrium drives mercury speciation toward elemental mercury



Boiler: Many factors affect equilibrium, but at boiler temperatures, elemental mercury is always favored

QUALITATIVE EXAMPLES



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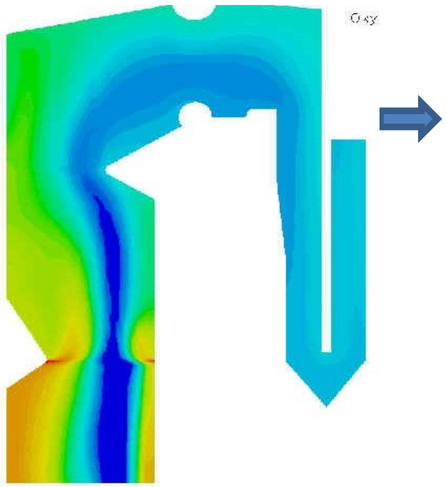
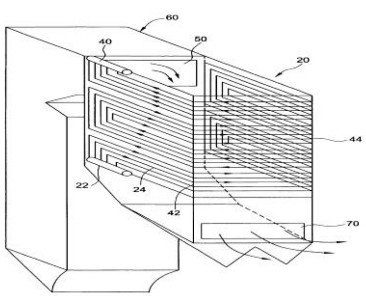
Review

Review of technologies for mercury removal from flue gas from cement production processes

Yuanjing Zheng[a, 1], Anker D. Jensen[a], Christian Windelin[b], Flemming Jensen[b]

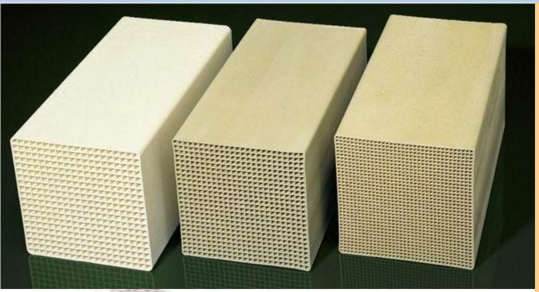
Convective Pass and Economizer:
Rapid cooling changes equilibrium temperature

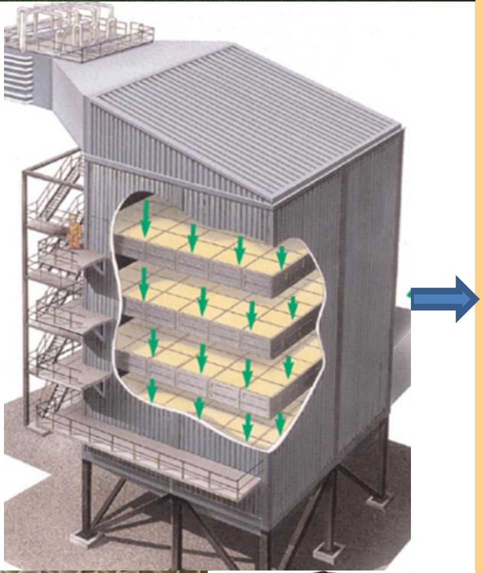


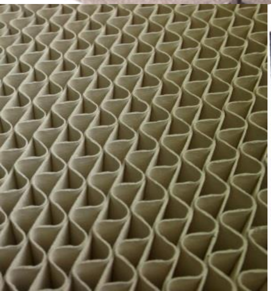


- **New lower temperature equilibrium conditions, very dynamic mercury conversion potential (residence time, flue gas species and chemical reactions, etc.)**
- **There is now at least the potential for oxidized mercury to exist**
- **Flue gas conditions now set for SCR or APH.**

SCR: Catalyst drives the potential reactions forward

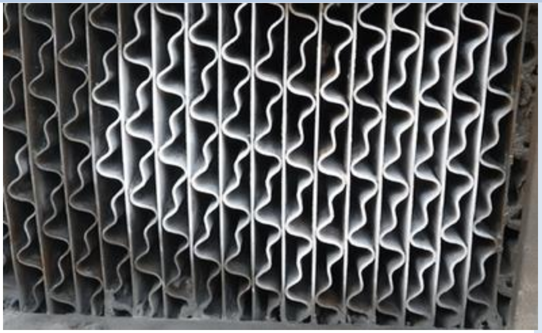


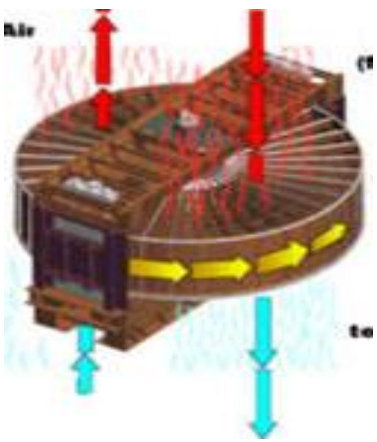




- Catalysts promote or "speed up" reactions. They are not consumed in the process – they are simply "expeditors".
- For SCR catalyst, mercury oxidation is a beneficial side-reaction.
- SCR generally produces the largest mercury speciation change of any single device - it also changes the concentrations of many other species via chemical reactions (SO_3, NO_x, possibly halogen form).

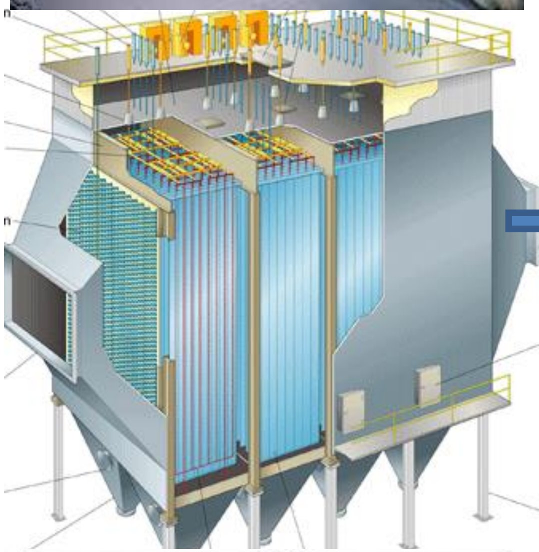
Air Preheater: The "forgotten" speciation driver





- Rapid cooling induces a new equilibrium potential – creates possibility of very different mercury speciation.
- Numerous flue gas reactions occur that have the potential to affect mercury speciation (H_2SO_4 formation, chemical adsorption, etc.).
- Temperature is now low enough for adsorption (capture) to occur.
- Very short residence time insures incomplete reactions toward new equilibrium conditions – very dynamic process.

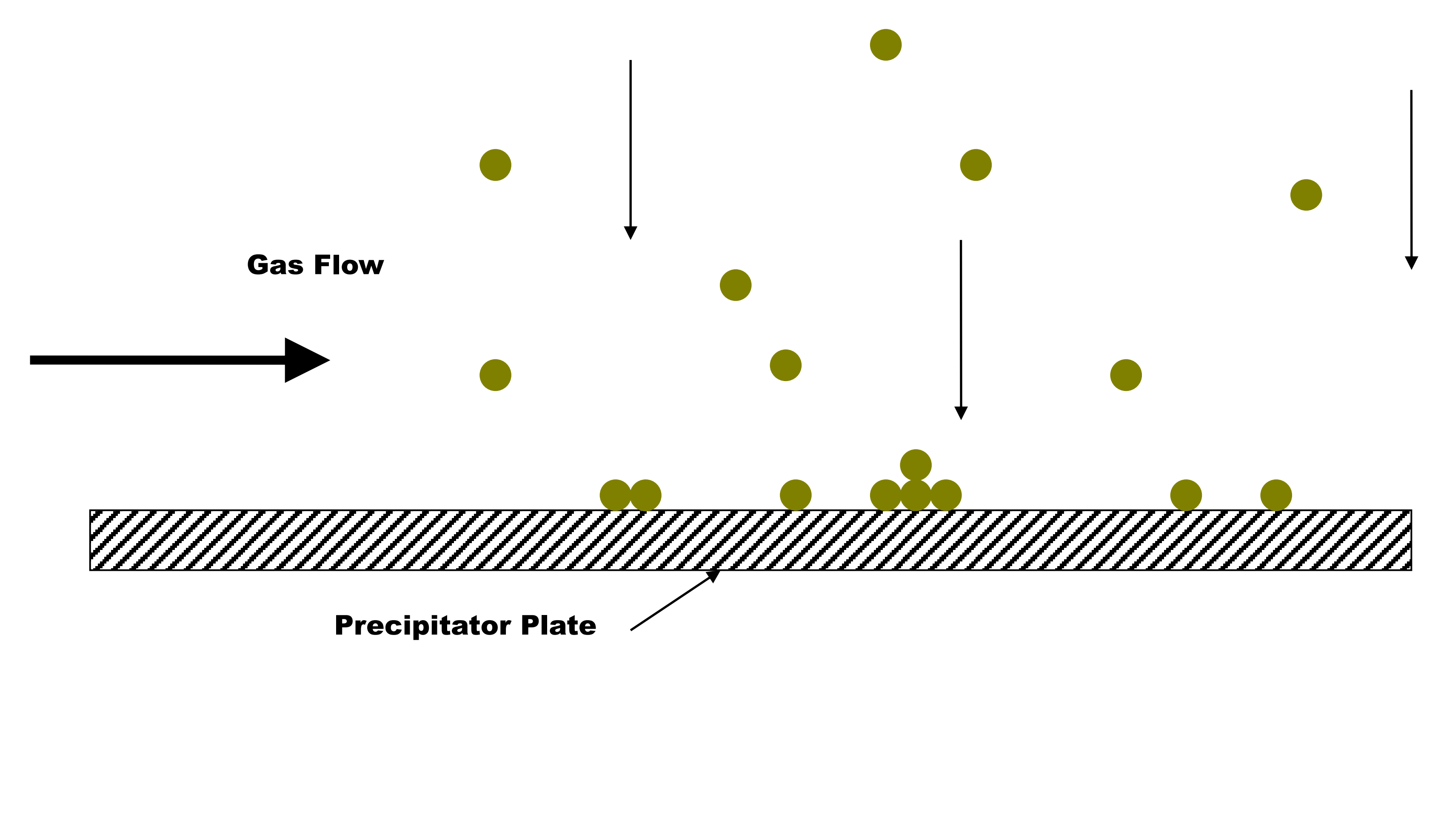
Particulate Collection: ESP



- Removes particulate and as a result removes any particle-bound mercury.
- First real mercury capture device in the flue gas train.
- Relatively long residence time (including ductwork) helps to drive mercury speciation and capture.
- Native unburned carbon (added activated carbon) promote strong adsorption potential.
- Chemical reactions continue as a function of equilibrium and residence time.
- Reaction and adsorption processes continue throughout the ESP – still very dynamic period for mercury speciation and capture.

ESP Physics

Inefficient gas-solid contacting

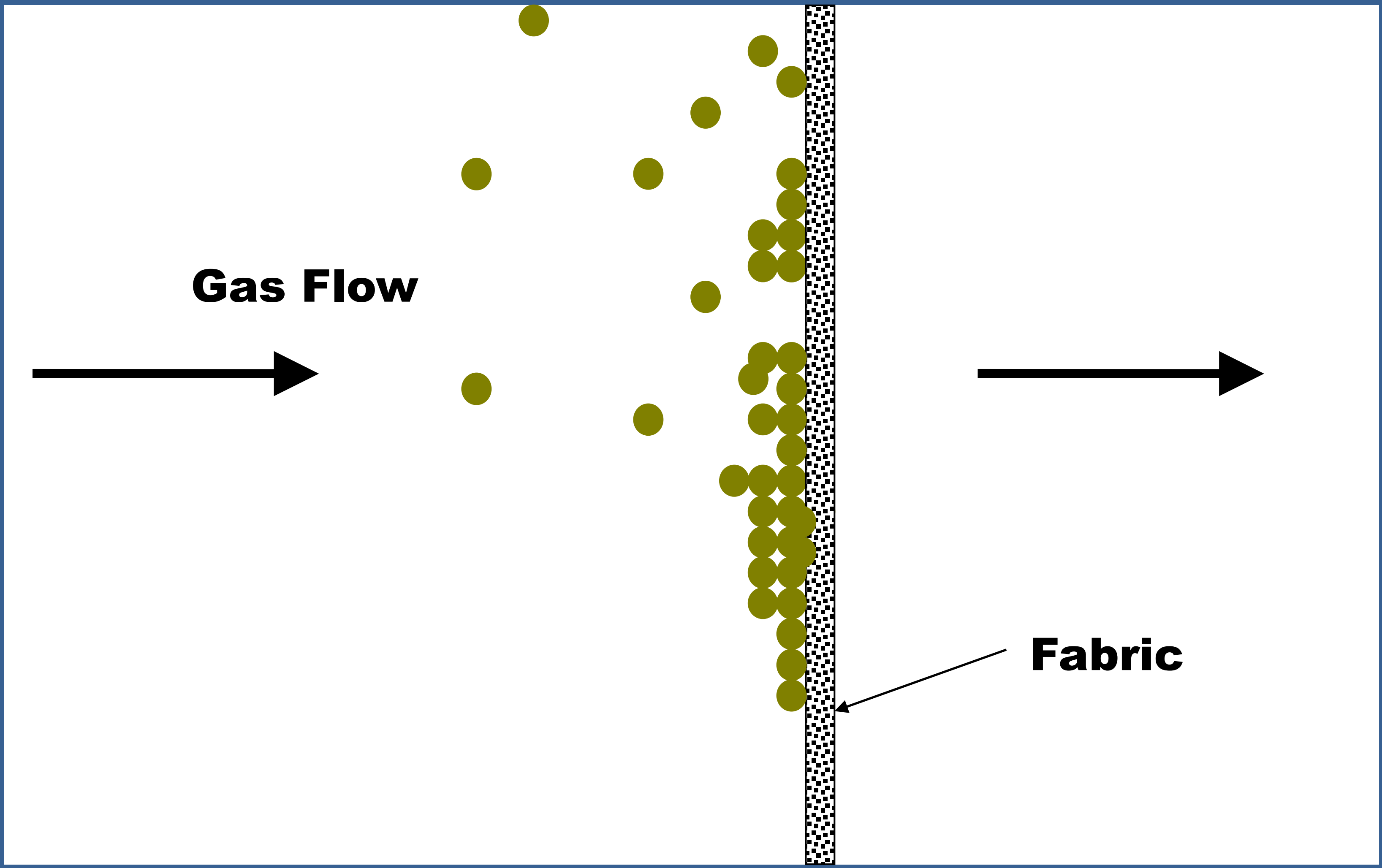


Particulate Collection: Baghouse

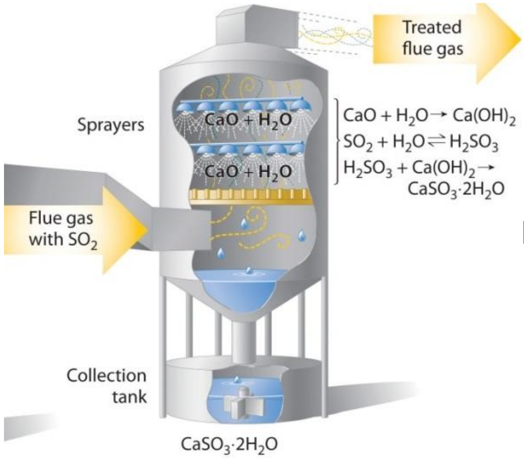
- Many factors similar to ESP
- Baghouse characterized by much better ash/gas contacting
- Improved overall (and especially fine) particulate removal
- Generally much improved native mercury capture or carbon utilization efficiency

Baghouse Physics

Efficient gas-solid contacting



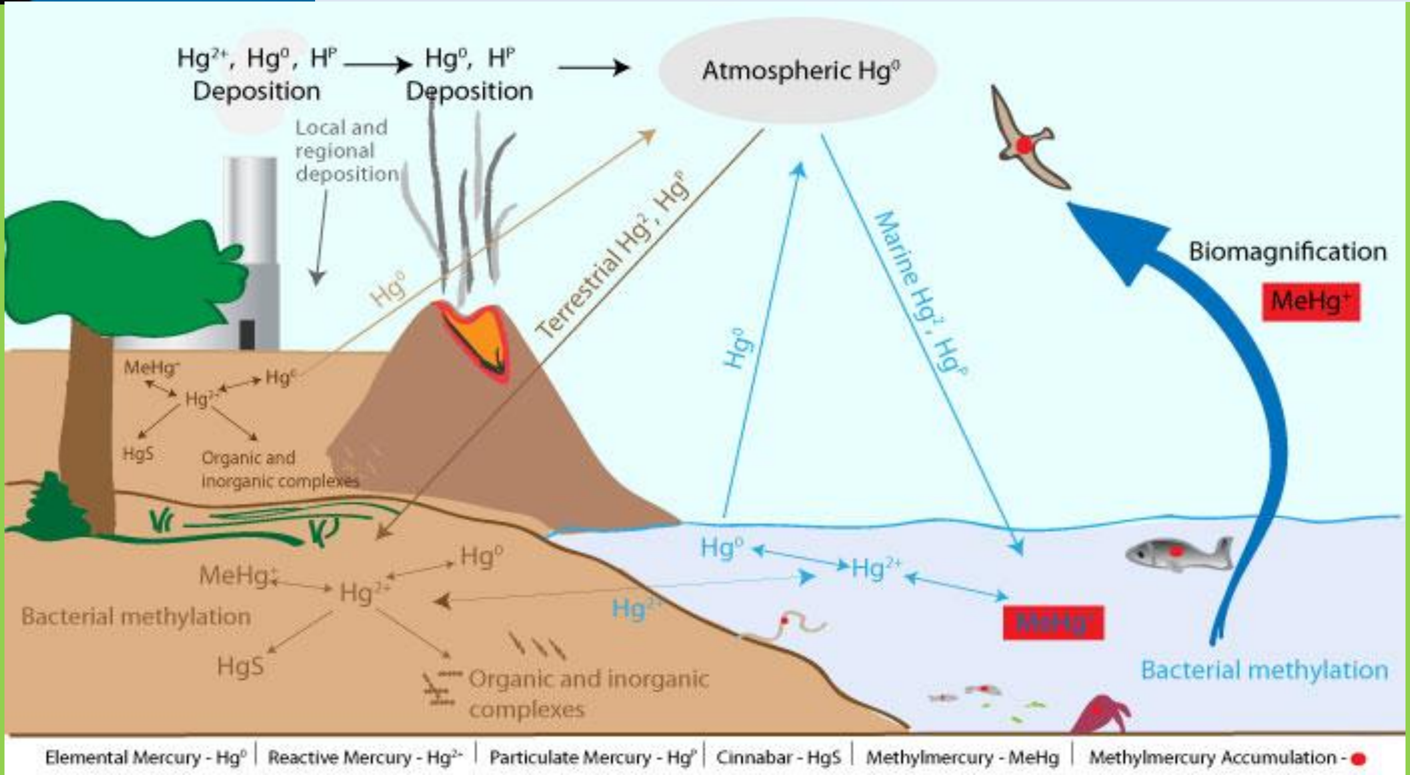
Scrubber: Major Mercury Removal Device



- **Additional cooling, perhaps promoting additional mercury reactions**
- **Generally very efficient at removing oxidized mercury**
- **Not good at removing elemental mercury**
- **Some speciation change might occur – i.e. "re-emissions"**
- **Transforms mercury from an air pollution constituent, to a potential water or solid waste constituent**

Stack: Release of flue gas to the environment

- **Total mercury the focus of regulations**
- **Mercury cycle begins again**
- **Mercury reactions continue in the atmosphere, water, and bio-systems**



Review: Drivers Affecting Mercury Speciation

Primary Theoretical Drivers (all are dynamic in a operating unit)

- **Chemistry**
- **Temperature**
- **Residence Time**
- **Adsorption Mechanisms**

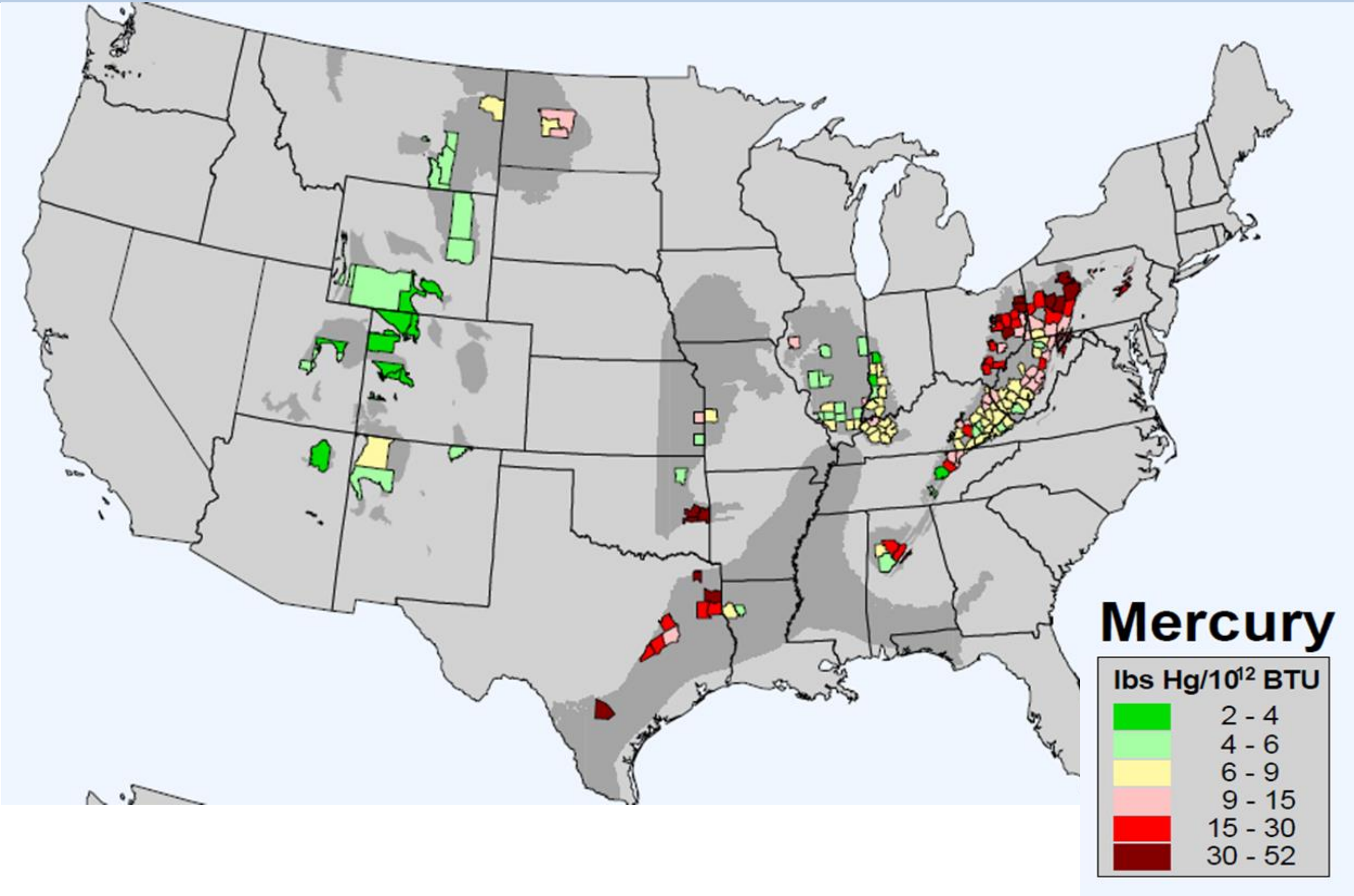
Practical Drivers for Coal-Fired Unit

- **Fuel Composition**
- **Boiler Design and Operation**
- **SCR Design, Operation and Catalyst Specifics**
- **APH Design and Operation**
- **ESP Design and Operation**
- **Baghouse Design and Operation**
- **Scrubber Design and Operation**

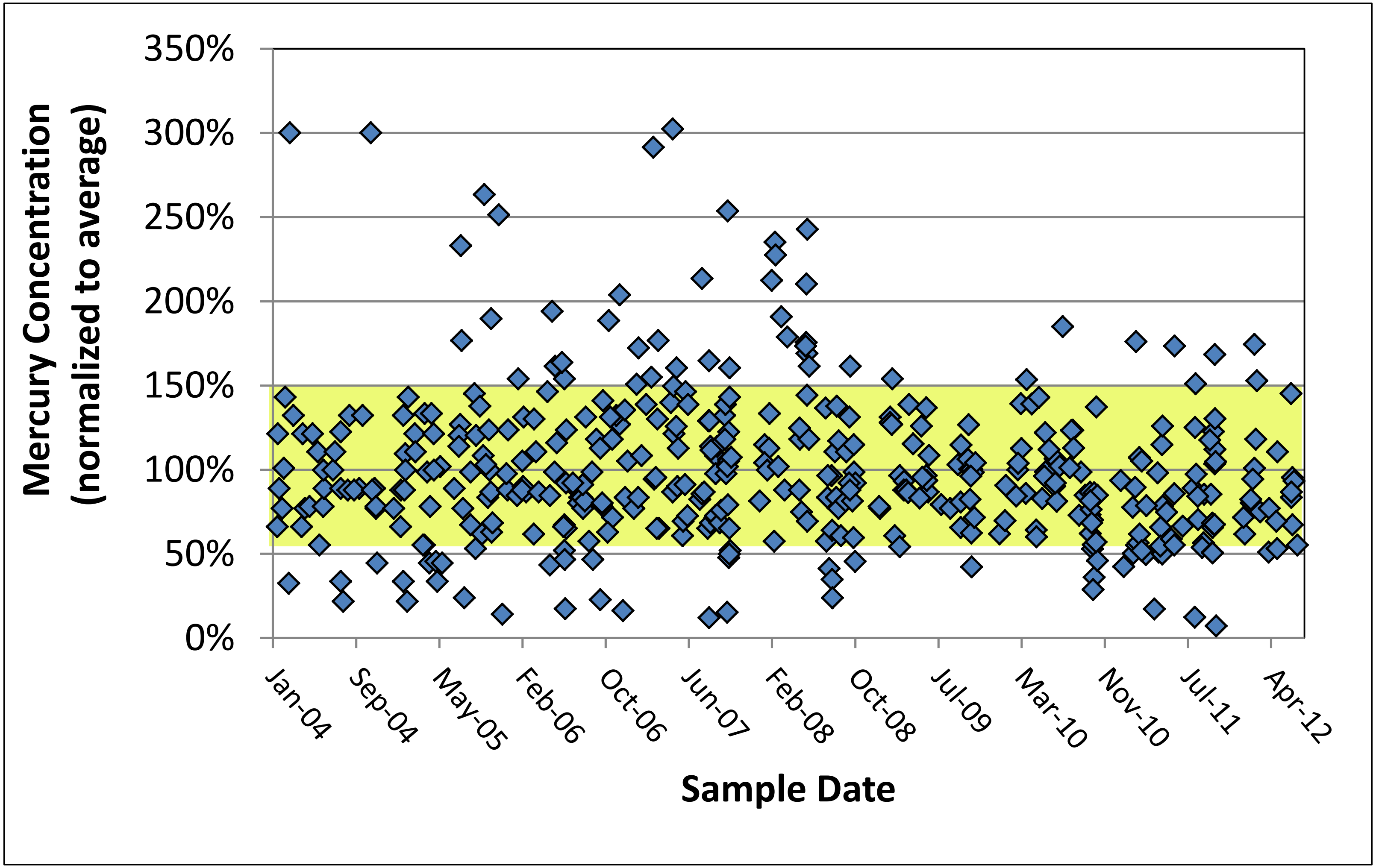
Detailed Analysis: FUELS

single most important global driver of mercury behavior

Fuel Composition – Distribution of Mercury



Example Mercury Variability large eastern bituminous plant 80% of data in 50% to 150% range



Uncontrolled Mercury Emissions as a Function of Btu and Mercury Concentration

Coal Btu/lb (dry basis)	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24	0.26	0.28	0.30
14,000	1.4	2.9	4.3	5.7	7.1	8.6	10.0	11.4	12.9	14.3	15.7	17.1	18.6	20.0	21.4
13,500	1.5	3.0	4.4	5.9	7.4	8.9	10.4	11.9	13.3	14.8	16.3	17.8	19.3	20.7	22.2
13,000	1.5	3.1	4.6	6.2	7.7	9.2	10.8	12.3	13.8	15.4	16.9	18.5	20.0	21.5	23.1
12,500	1.6	3.2	4.8	6.4	8.0	9.6	11.2	12.8	14.4	16.0	17.6	19.2	20.8	22.4	24.0
12,000	1.7	3.3	5.0	6.7	8.3	10.0	11.7	13.3	15.0	16.7	18.3	20.0	21.7	23.3	25.0
11,500	1.7	3.5	5.2	7.0	8.7	10.4	12.2	13.9	15.7	17.4	19.1	20.9	22.6	24.3	26.1
11,000	1.8	3.6	5.5	7.3	9.1	10.9	12.7	14.5	16.4	18.2	20.0	21.8	23.6	25.5	27.3
10,500	1.9	3.8	5.7	7.6	9.5	11.4	13.3	15.2	17.1	19.0	21.0	22.9	24.8	26.7	28.6
10,000	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0	22.0	24.0	26.0	28.0	30.0
9,500	2.1	4.2	6.3	8.4	10.5	12.6	14.7	16.8	18.9	21.1	23.2	25.3	27.4	29.5	31.6
9,000	2.2	4.4	6.7	8.9	11.1	13.3	15.6	17.8	20.0	22.2	24.4	26.7	28.9	31.1	33.3
8,500	2.4	4.7	7.1	9.4	11.8	14.1	16.5	18.8	21.2	23.5	25.9	28.2	30.6	32.9	35.3
8,000	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5

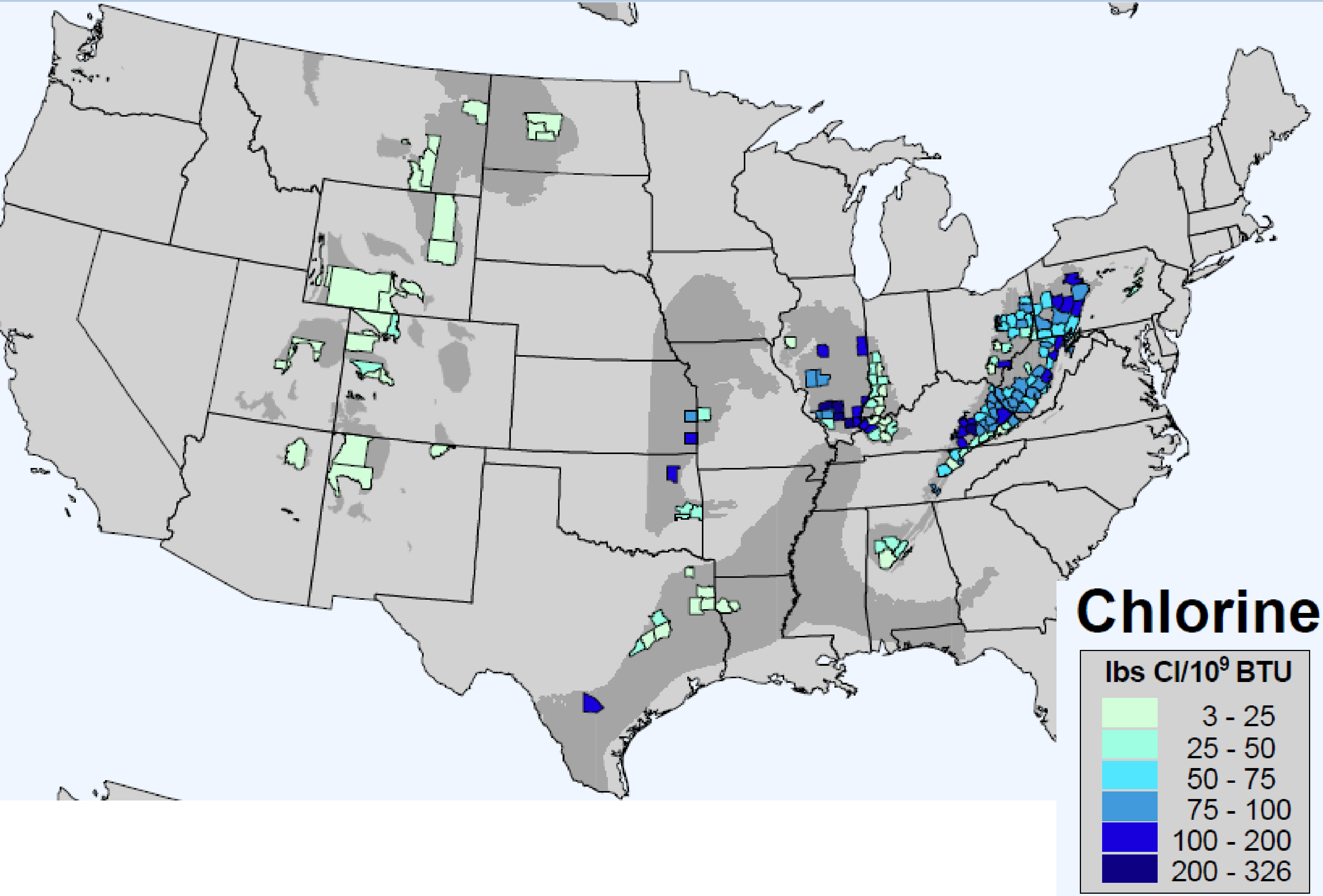
Coal Mercury Content (ppmw, dry)

Required Mercury Removal (%)

to meet 1 lb/Tbtu - based on coal Btu and Hg content

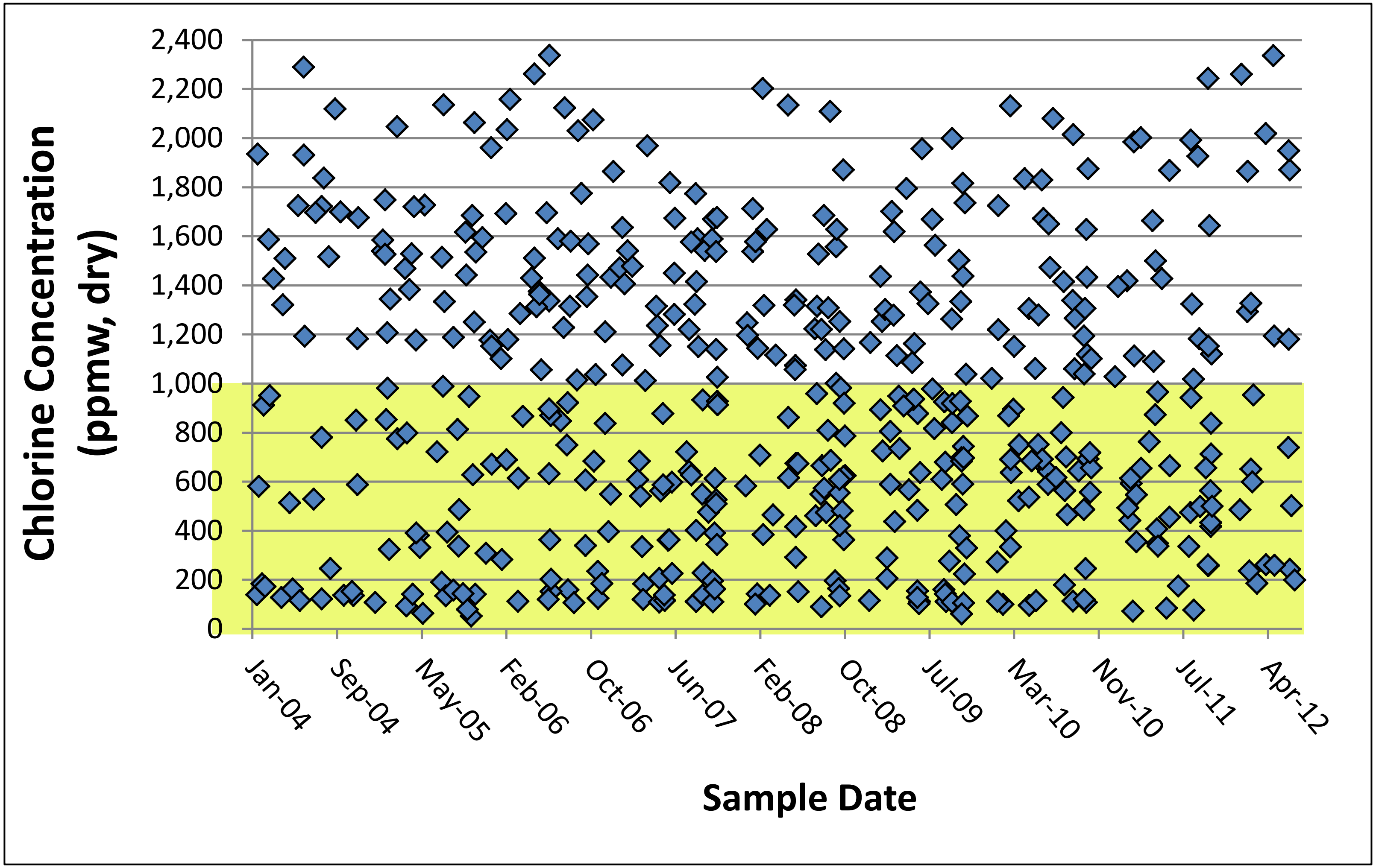
Coal Btu/lb (dry basis) \ Coal Mercury Content (ppmw, dry)	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24	0.26	0.28	0.30
14,000	30	65	77	83	86	88	90	91	92	93	94	94	95	95	95
13,500	33	66	78	83	87	89	90	92	93	93	94	94	95	95	96
13,000	35	68	78	84	87	89	91	92	93	94	94	95	95	95	96
12,500	38	69	79	84	88	90	91	92	93	94	94	95	95	96	96
12,000	40	70	80	85	88	90	91	93	93	94	95	95	95	96	96
11,500	43	71	81	86	89	90	92	93	94	94	95	95	96	96	96
11,000	45	73	82	86	89	91	92	93	94	95	95	95	96	96	96
10,500	48	74	83	87	90	91	93	93	94	95	95	96	96	96	97
10,000	50	75	83	88	90	92	93	94	94	95	95	96	96	96	97
9,500	53	76	84	88	91	92	93	94	95	95	96	96	96	97	97
9,000	55	78	85	89	91	93	94	94	95	96	96	96	97	97	97
8,500	58	79	86	89	92	93	94	95	95	96	96	96	97	97	97
8,000	60	80	87	90	92	93	94	95	96	96	96	97	97	97	97

Fuel Composition – Distribution of Chlorine

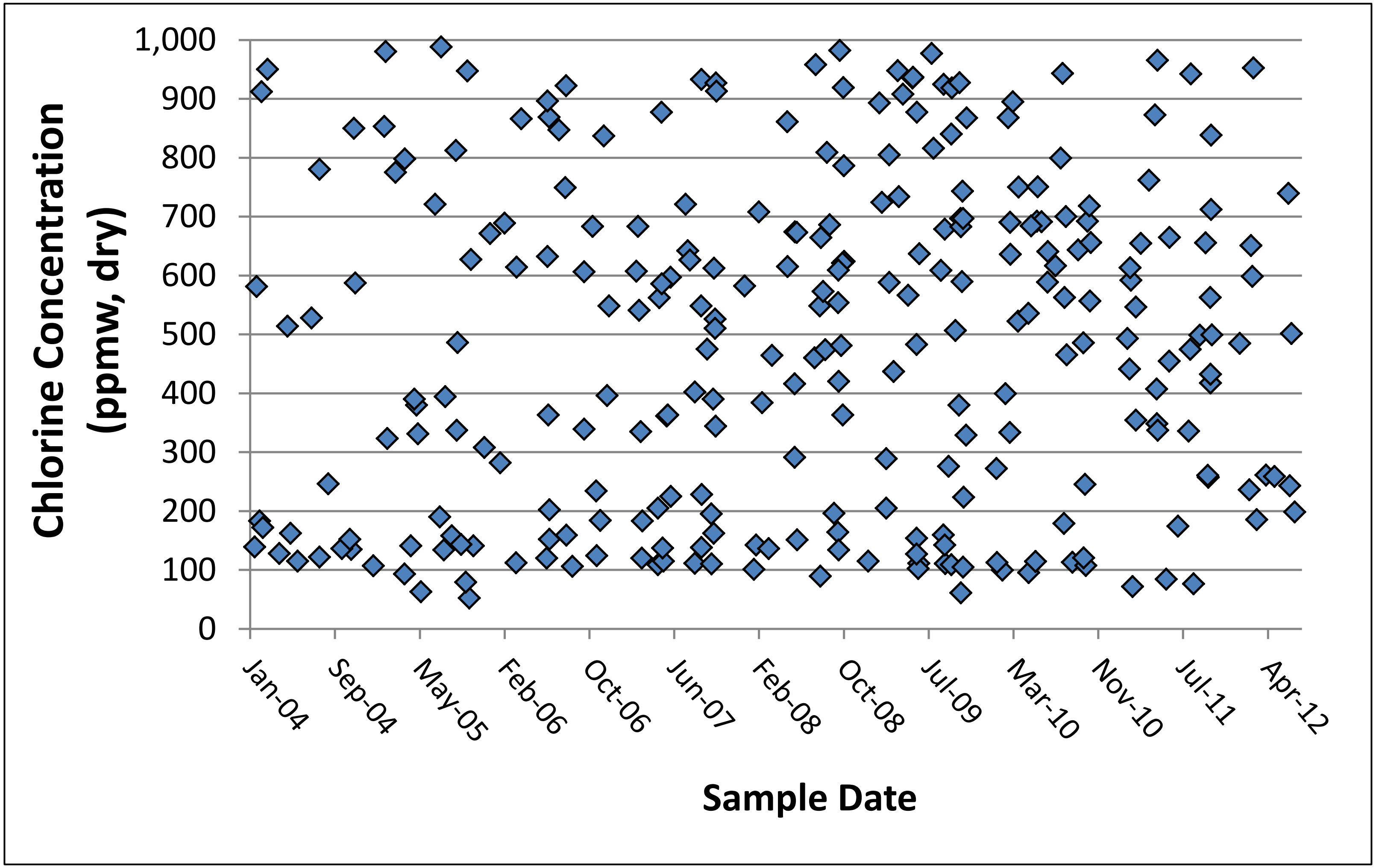


Example Chlorine Variability large eastern bituminous plant

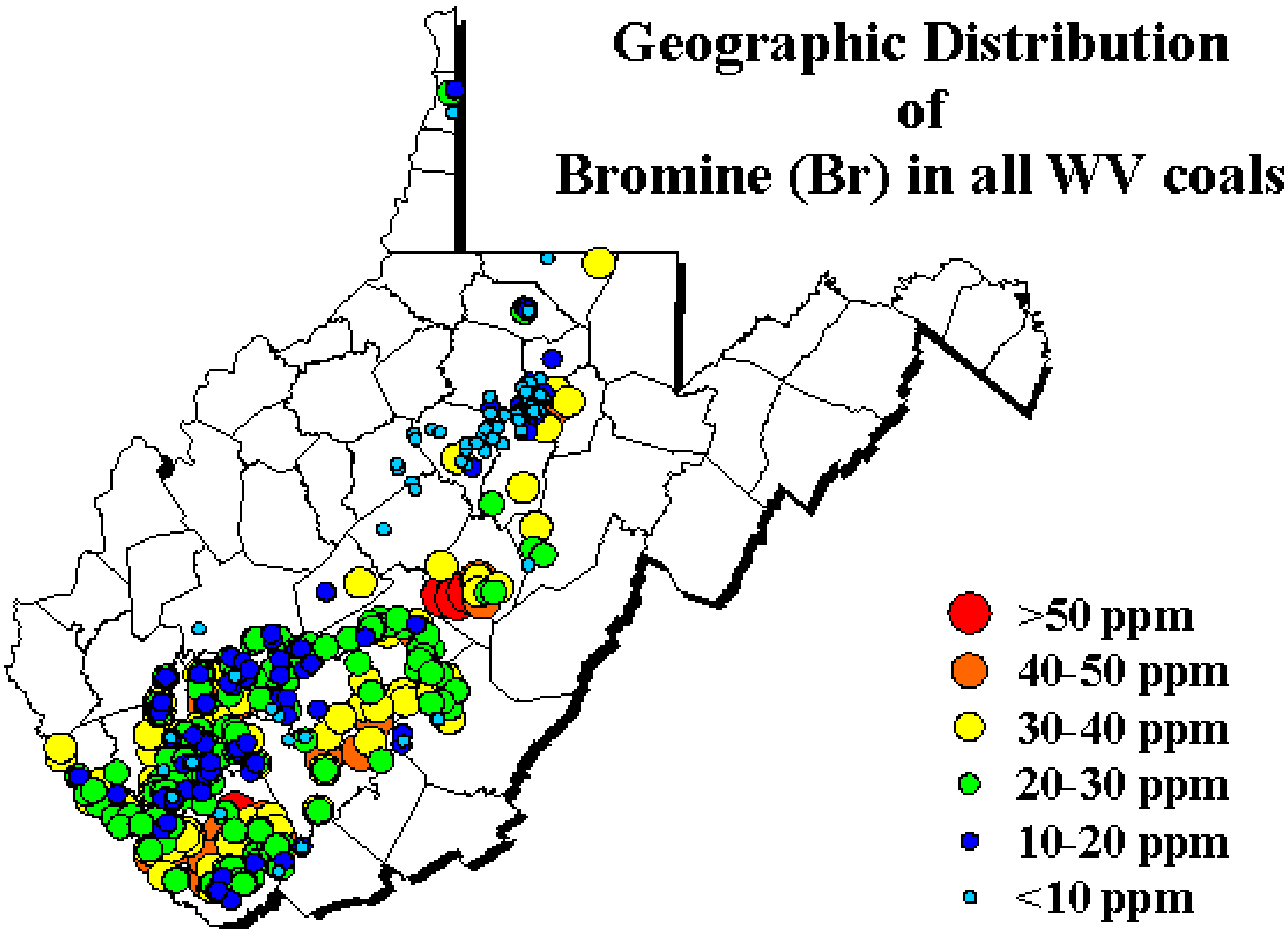
(1,000 ppmw on coal ≈ 70 ppmv in flue gas)



Example Chlorine Variability large eastern bituminous plant

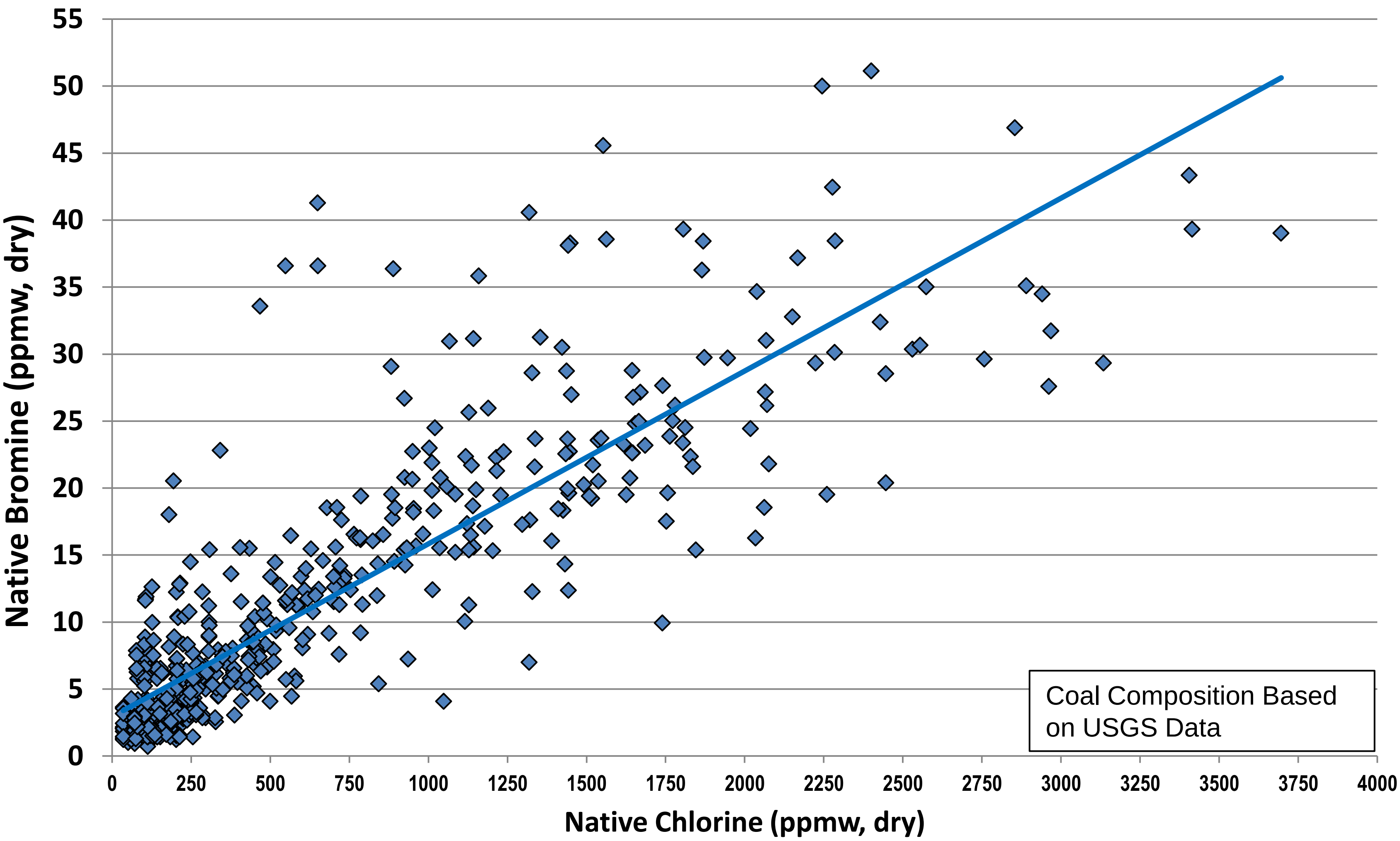


Fuel Composition – Distribution of Bromine



Bromine and Chlorine Inter-Relationship

Coals low in Chlorine will also generally be low in Bromine



Primary Coal Types for Mercury Considerations

1. Eastern Bituminous (mid to high chlorine)
2. Southern Appalachian (low chlorine)
3. South American (very low chlorine)
4. Powder River Basin (very low chlorine)

Comparative Representative Coal Analyses
Ultimate Properties

Ultimate Properties	High Chlorine Eastern Bituminous	Low Chlorine Southern Appalachian & S.A.	Power River Basin
Total Moisture (%)	6.54	6.95	27.03
Ash Dry (%)	11.48	13.67	6.88
HOC Dry (Btu/lb)	13,009	13,019	12,040
Total Sulfur Dry (%)	1.17	1.39	0.37
Carbon Dry (%)	73.78	73.67	70.37
Hydrogen Dry (%)	4.79	4.52	4.67
Nitrogen Dry (%)	1.50	1.56	1.00
Oxygen Dry (%)	6.26	5.19	16.71
Volatiles Dry (%)	34.06	29.88	42.92
Fixed Carbon Dry (%)	53.43	56.57	50.20
Ash Fusion IT (%)	2,530	2,396	2,143
Ash Fusion ST (%)	2,612	2,530	2,171
Ash Fusion HT (%)	2,654	2,397	2,186
Ash Fusion FT (%)	2,709	2,741	2,254
Grindability Index (HGI)	43.66	59.81	49.82

Comparative Representative Coal Analyses
Ash Mineral Properties

Ash Mineral (%)	High Chlorine Eastern Bituminous	Low Chlorine Southern Appalachian & S.A.	Power River Basin
Al_2O_3	26.64	27.03	16.46
Fe_2O_3	9.15	11.22	5.60
CaO	1.64	1.47	20.47
MgO	1.05	1.21	4.54
MnO_2	5.15	3.11	0.03
P_2O_5	0.33	0.45	1.04
K_2O	2.51	2.70	0.42
SiO_2	52.57	52.36	34.37
Na_2O	0.42	0.39	1.42
SO_3	1.29	1.48	12.62
TiO_2	1.41	1.35	1.16

Comparative Representative Coal Analyses
Trace Element Properties

Trace Element (ppm, dry, whole coal)	High Chlorine Eastern Bituminous	Low Chlorine Southern Appalachian & S.A.	Power River Basin
As	11.67	37.55	0.70
Ba	150.81	305.78	345.24
B	2.40	1.92	0.31
B	0	0	0
Cd	0.080	0.100	0.056
Cl	1,000-3,500	50-350	~50
Co	8.18	10.26	2.73
Cr	16.73	20.97	3.90
Cu	21.12	25.76	11.92
F	97.93	91.87	58.00
Hg	0.084	0.171	0.081
Li	0	0	0
Mg	0.073	0.101	0.191
Mn	29.56	34.93	12.10
Mo	0	0	0
Na	0.032	0.037	0.074
Ni	14.07	17.56	3.90
Pb	8.17	8.40	2.70
Sb	1.15	2.40	0.05
Se	3.25	1.97	0.66
Sr	0.0049	0.0116	0.0075
V	35.64	46.87	14.83
Zn	17.31	19.14	10.60

Fuel Effects on Mercury Speciation in the Boiler, Convective Pass, and Economizer

Location	High Chlorine EB	Low Chlorine EB & South American	PRB
Boiler	Complete conversion to elemental mercury	Complete conversion to elemental mercury	Complete conversion to elemental mercury
Convective Pass	Little driving force for mercury oxidation	Little driving force for mercury oxidation	Little driving force for mercury oxidation
Economizer to SCR or APH inlet (w/o SCR)	Some mercury oxidation (20-40%)	Possible mercury oxidation, but limited (10-20 %)	Very little mercury oxidation (<10%)

Fuel Effects on SCR Mercury Oxidation

Location	High Chlorine EB	Low Chlorine EB & South American	PRB
SCR	Strong potential for mercury oxidation, SCR less sensitive to catalyst, ammonia, temperature, etc. (Hg^{2+} = 80%+)	Moderate potential for oxidation, usually highly sensitive to operating parameters, especially actual halogen levels, ammonia, NOx, temperature, etc. (Hg^{2+} = 40-80%)	Mercury oxidation severely limited by low halogens, alkali nature of ash seems to further suppress Hg-halogen reactions, advanced catalyst may help, and halogen supplementation will have dramatic effect (Hg^{2+} < 40%)

Fuel Effects on Air Preheater Mercury Speciation and Capture

Location	High Chlorine EB	Low Chlorine EB & South American	PRB
APH	Driving force for mercury oxidation continues as a function of halogens and temperature, some deposition may occur, sulfuric acid formation (Hg^{2+} = 90%+) Some capture possible	Moderate driving force for oxidation to continue, lower temperature helps (Hg^{2+} = 60%+) Some capture possible	Very little driving force for oxidation (Hg^{2+} = 30%+) Some capture possible, but usually very limited

Fuel Effects on ESP/Baghouse Mercury Speciation and Capture

Location	High Chlorine EB	Low Chlorine EB & South American	PRB
ESP	Oxidation of mercury may continue simultaneously with capture (> 50% Hg^T capture) possible), speciation at outlet will be variable due to the capture of Hg^{2+}	Oxidation of mercury may continue simultaneously with capture (> 30% Hg^T capture possible), speciation at outlet will be variable due to the capture of Hg^{2+}	Limited potential for continued oxidation, some capture still possible (> 20% Hg^T capture possible), speciation at outlet will be variable due to the capture of Hg^{2+}
Baghouse	Similar to APH but with improved capture	Similar to APH but with improved capture	Similar to APH but with improved capture

Fuel Effects on Scrubber Capture

Location	High Chlorine EB	Low Chlorine EB & South American	PRB
Scrubber	Scrubber will generally exhibit high rate of Hg^{2+} capture, halogens appear to have a synergistic effect* on improved capture efficiency, good overall capture (~90%+) High proportion of Hg^0 in emissions	High rate of Hg^{2+} capture still occurs, but synergistic effect may not be as apparent, overall capture marginal (50-80%) High proportion of Hg^0 in emissions	High rate of Hg^{2+} capture still occurs, overall capture limited, though (30-70%) High proportion of Hg^0 in emissions

*High halogens may improve the efficiency with which oxidized mercury is captured, in addition to increasing the overall proportion of oxidized mercury present.

Detailed Analysis: SCR

single most important speciation driver

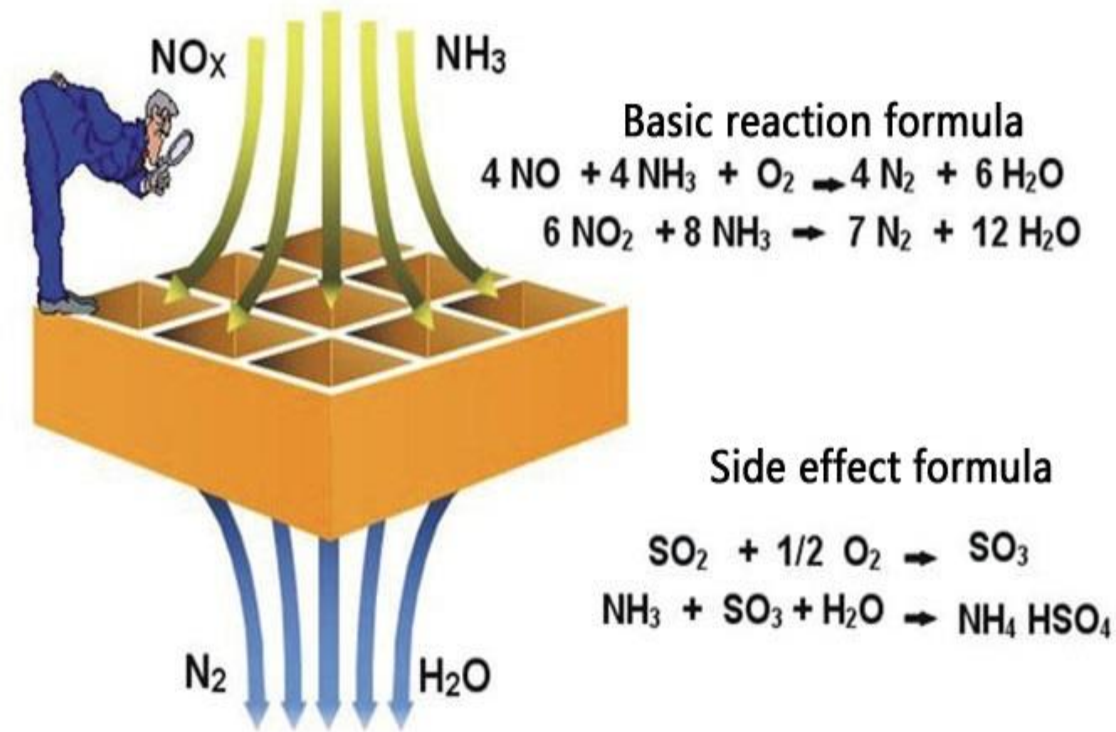
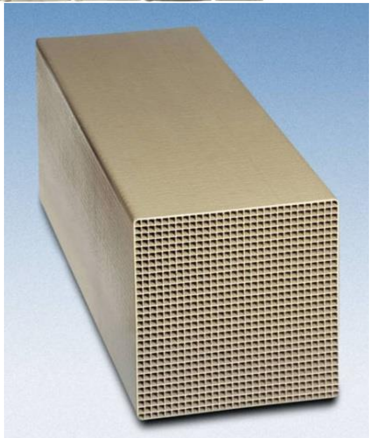
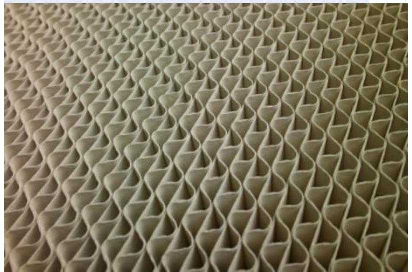
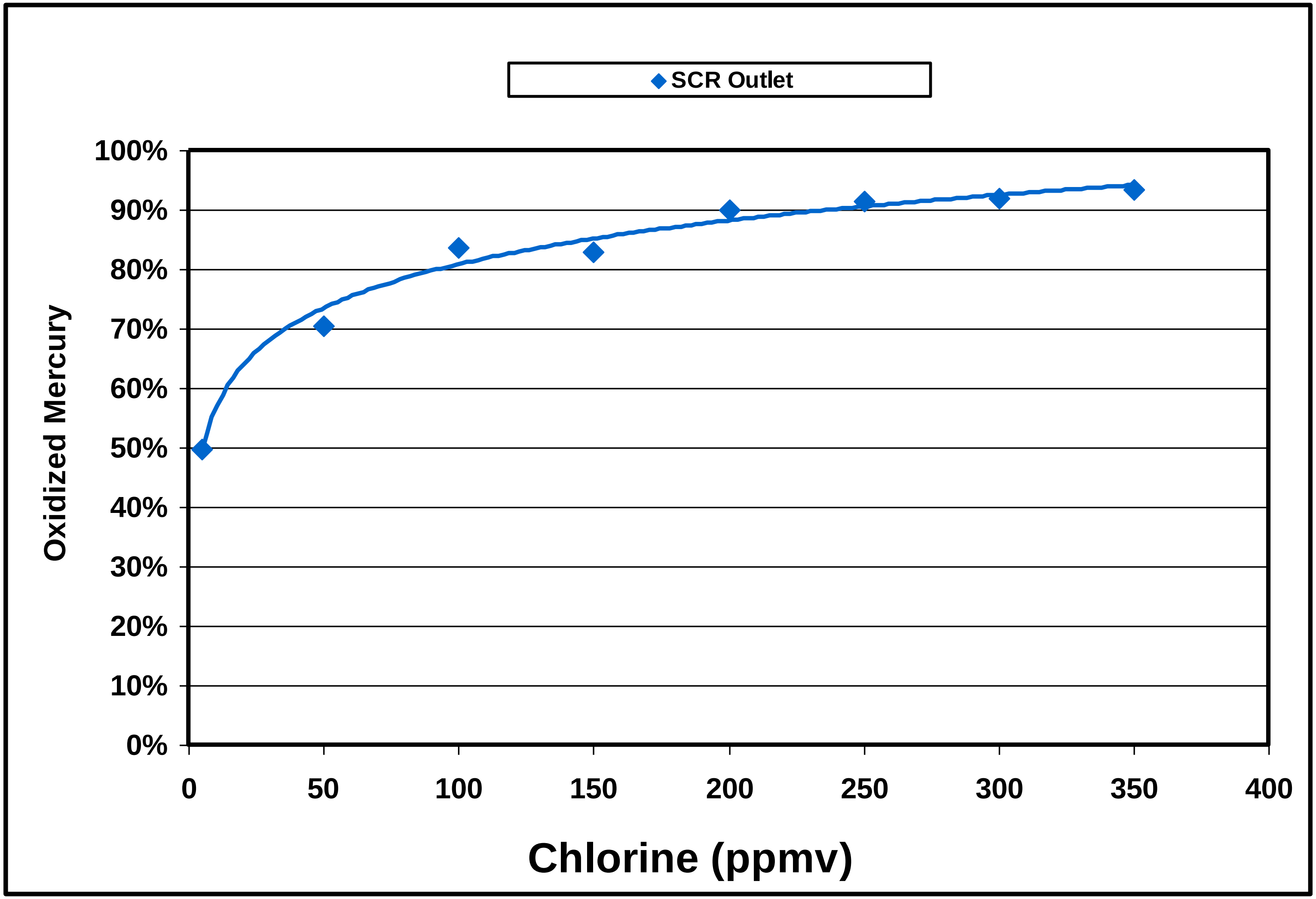


Image Courtesy: Xiangtan Weida electrical and machinery manufacture Co.,LTD
Address: No.71, Hehua Middle Raod,Xiangtan City, Hunan Province,CHINA
Website: http://www.tilemachinery.com



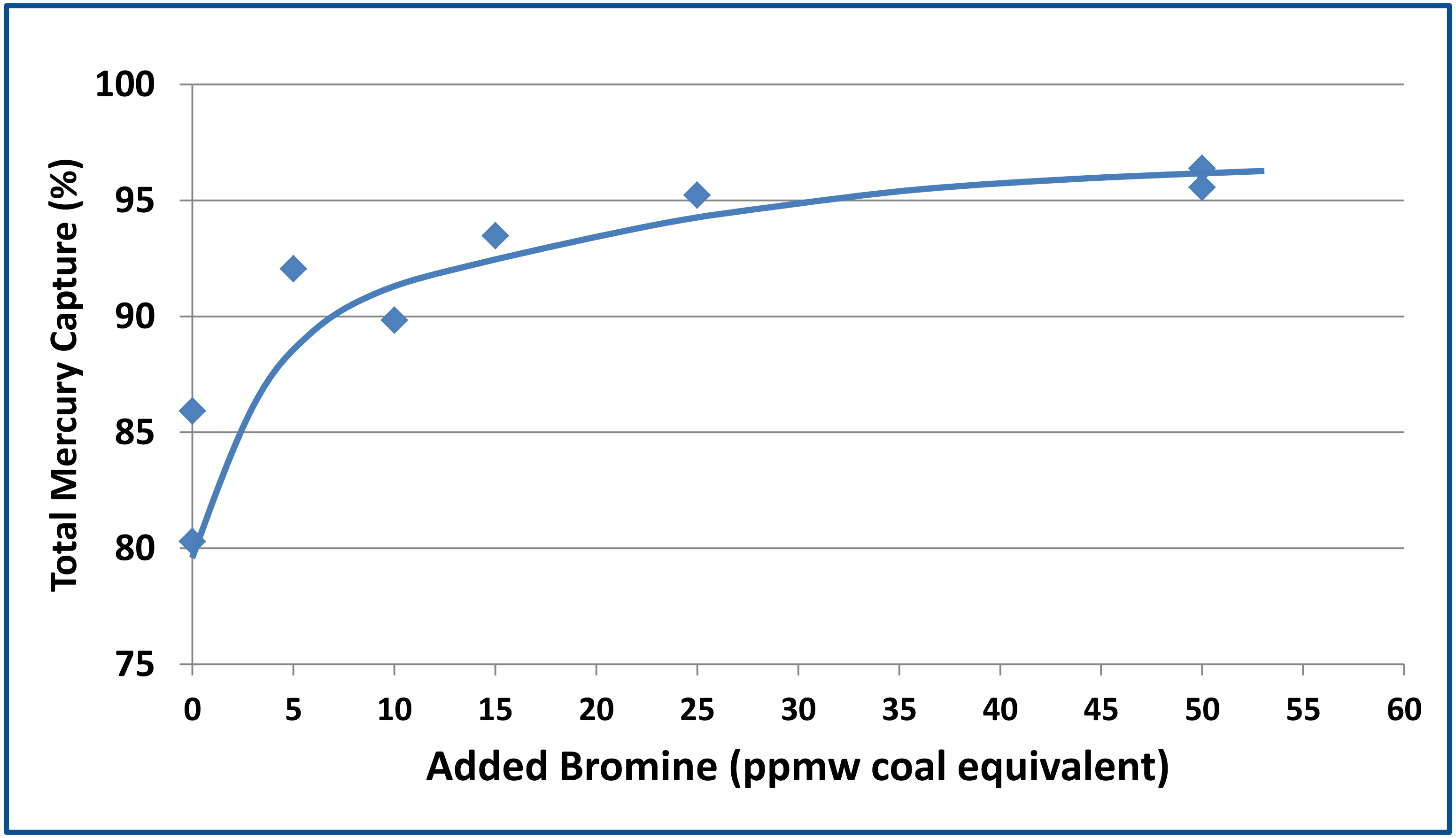


Example Effect of Chlorine on SCR Hg Oxidation



Example: Bromine Addition with SCR-Wet Scrubber

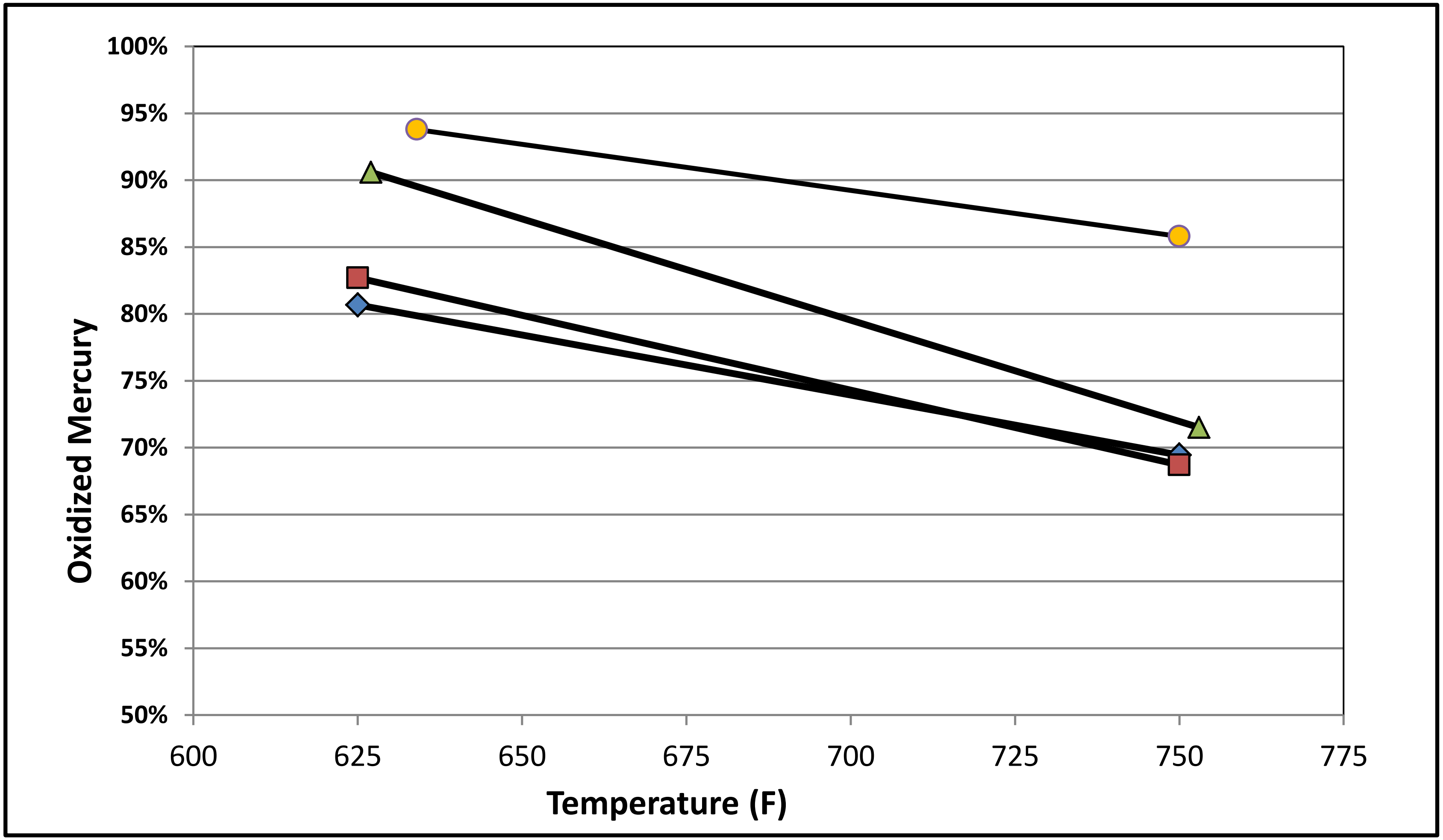
MRC Data - low chlorine eastern bituminous coal



Caution ! Example only –effects may be significantly shifted in the field.

SCR Outlet Oxidized Mercury vs. Temperature

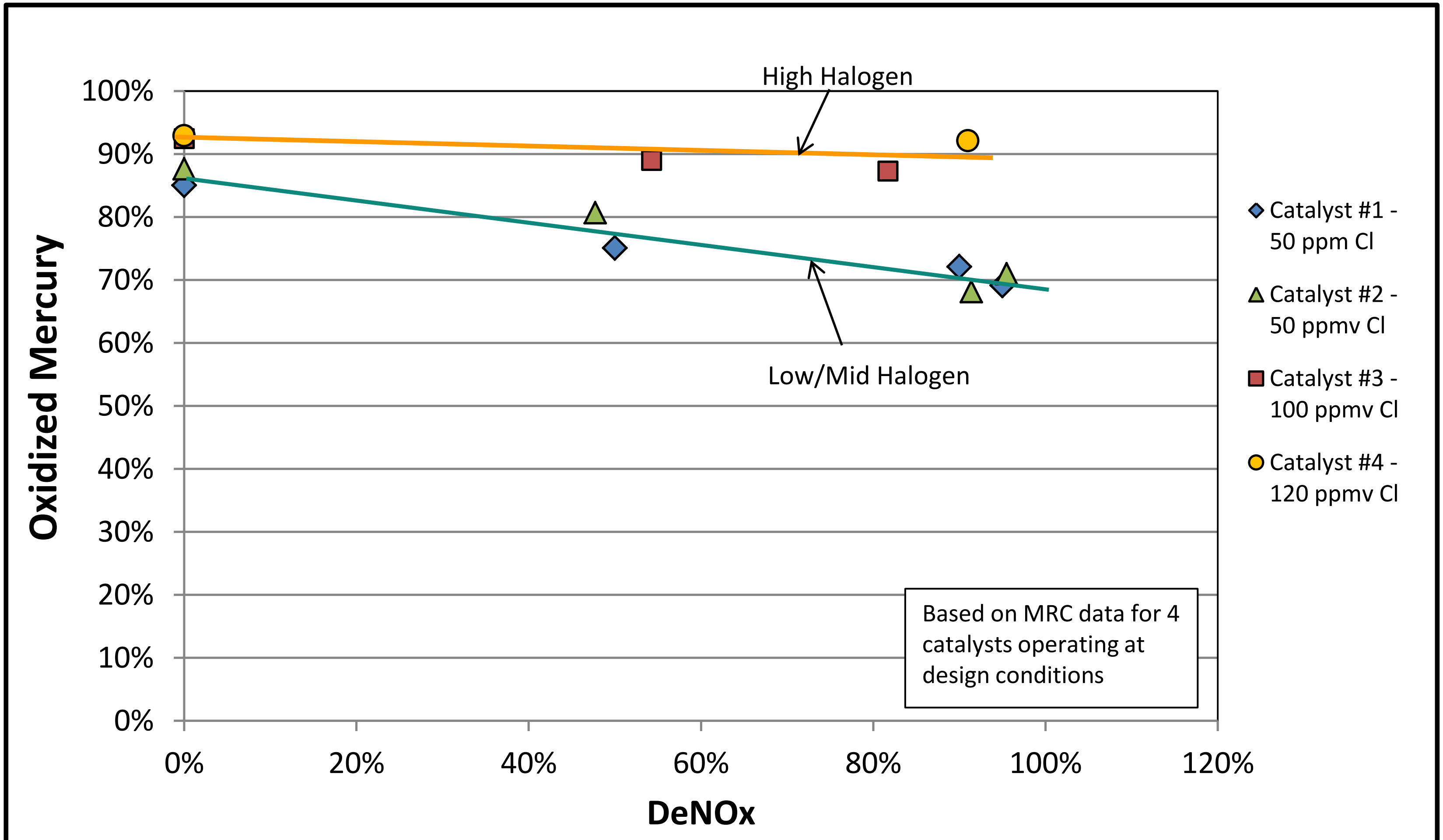
lower temperatures favor oxidized mercury



Based on MRC data
4 catalysts

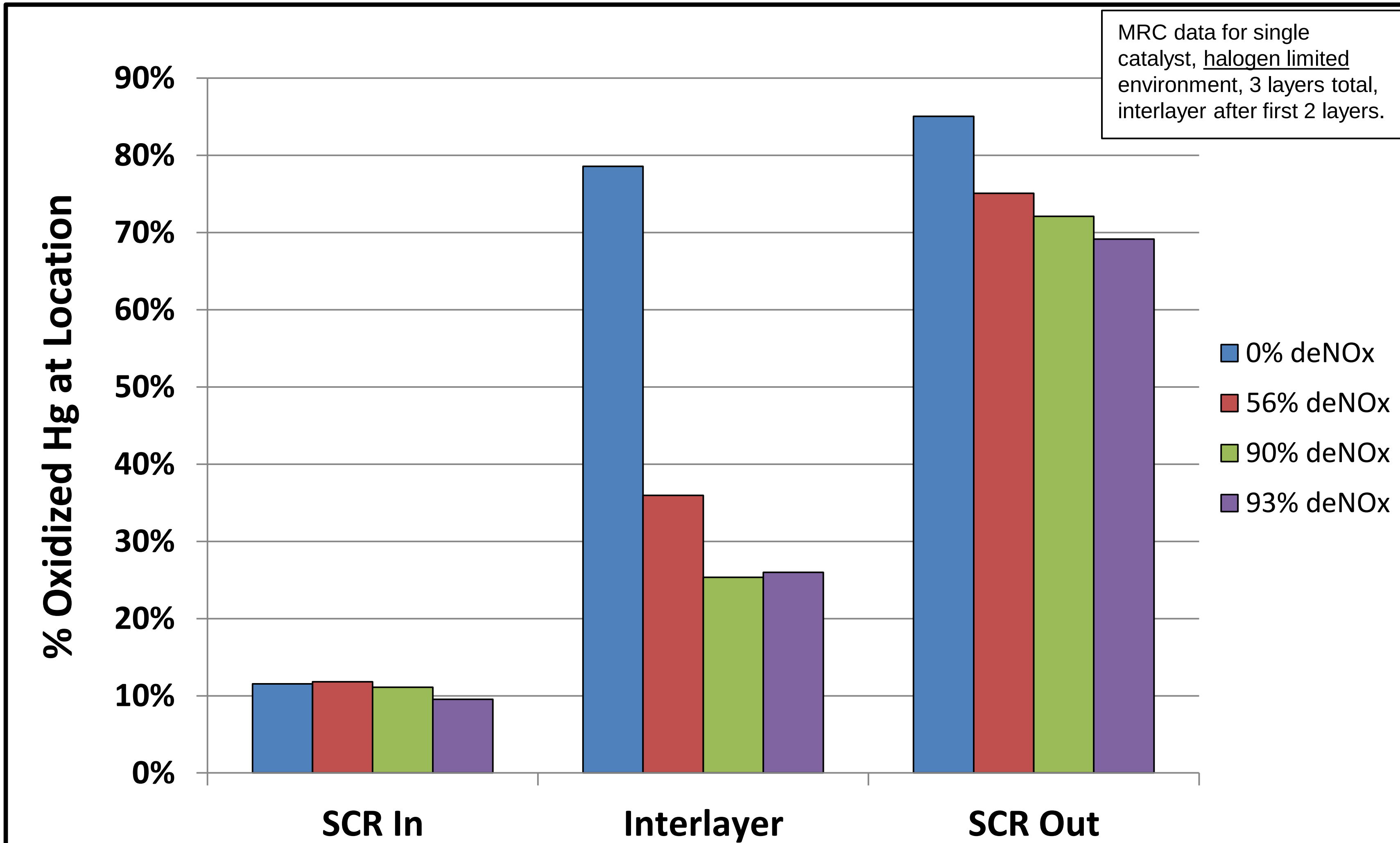
Effect of Ammonia: Suppression of Hg Oxidation

halogens can help to mitigate the effect

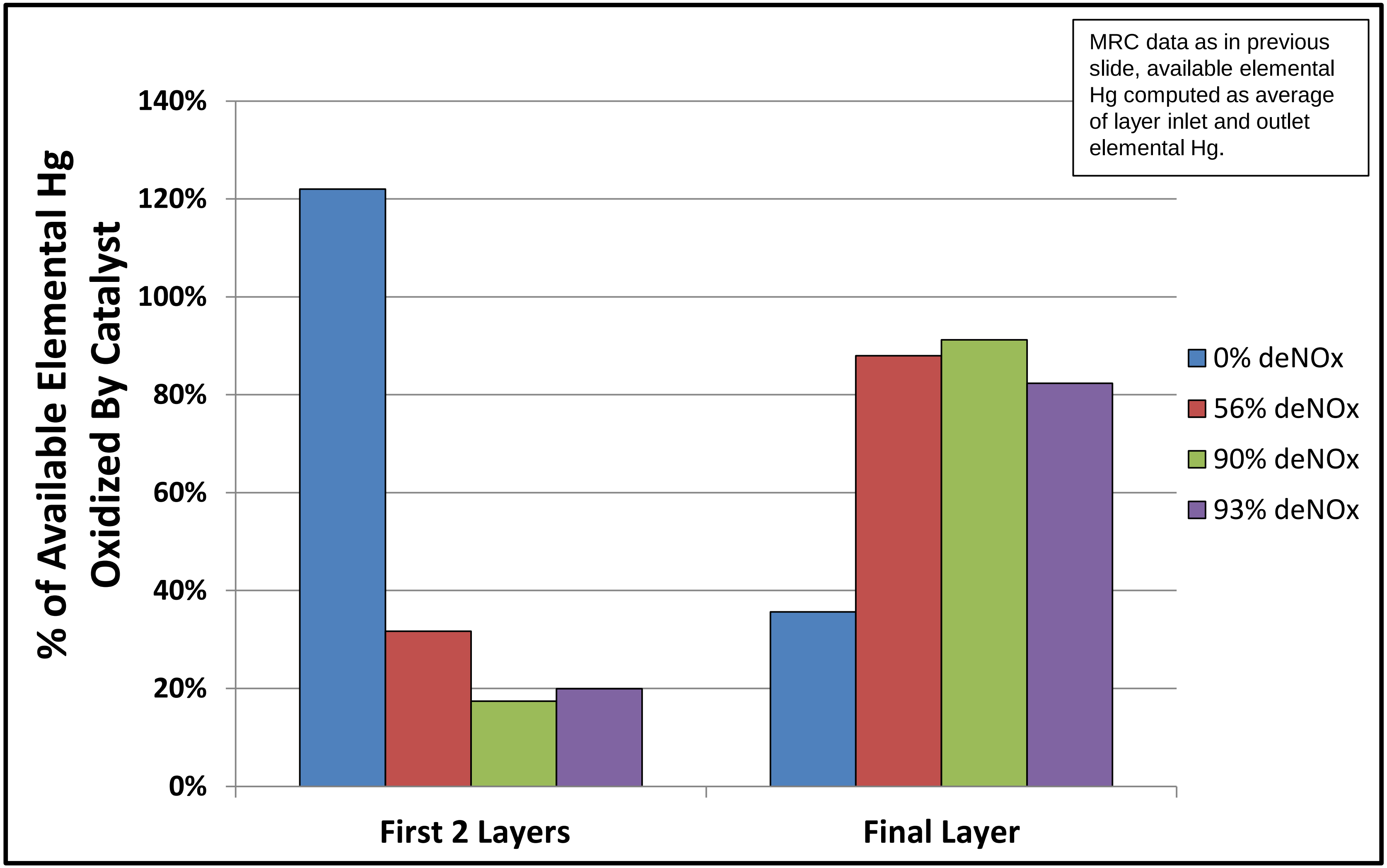


Caution ! Example only – halogen effects may be significantly shifted in the field.

Effect of Ammonia: Absolute Speciation as a Function of Catalyst Layer



Effect of Ammonia: Dynamic Speciation as a Function of Catalyst Layers



SUMMARY

1. Almost everything affects mercury speciation or capture!

2. Fuel composition is probably the most important single parameter governing a unit's ability to control mercury emissions.

3. Be cautious about making mercury behavior assumptions – behavior does not translate well from one facility to another – too many factors affect mercury behavior.

4. Be wary of analysis approaches that do not take into consideration the "big picture" – isolated analyses do not adequately capture the integrated effect on mercury behavior.

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