REINHOLD ENVIRONMENTAL Ltd.

2019 REINHOLD Round Table Presentation

June 24 & 25, 2019, in Birmingham, Alabama / Hosted by Southern Company

Arsenic and Selenium Abatement with Hydrated Lime and Sorbent Trap Methods

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Reinhold Round Table
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Topics

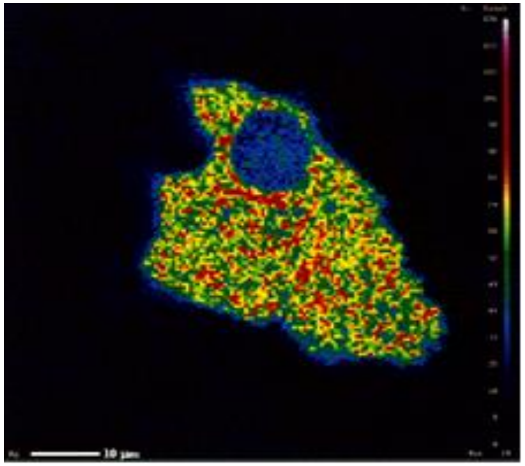
- Origin of heavy metals in coal
- Impacts on SCR operations
  - Catalyst poisoning, MOT
- Arsenic and selenium chemistry
- Impacts on ELG compliance
- Case studies and capture results
- As and Se measurement options

Fuel: Arsenic and Selenium Chemistry

- Present in coal in several forms:
  - Inorganic arsenic/selenium
    - Often associated with pyrites
  - Organic arsenic/selenium

	Pittsburgh	Illinois 6	Elkhorn/Hazard	Wyodak
Arsenic	mostly pyrite	mostly pyrite	pyrite and arsenate	organically associated and arsenate
Selenium	all pyrite	pyrite and organically associated	organically associated and pyrite	organically associated
Mercury	oxidized pyrite or soluble sulfides	mostly pyrite	oxidized pyrite or soluble sulfides	*analyses in progress*
Chromium	CrOOH and clay minerals	mostly CrOOH, minor clay minerals	CrOOH, chromite, minor clays	organically associated

As concentrations on FeS_2 particle



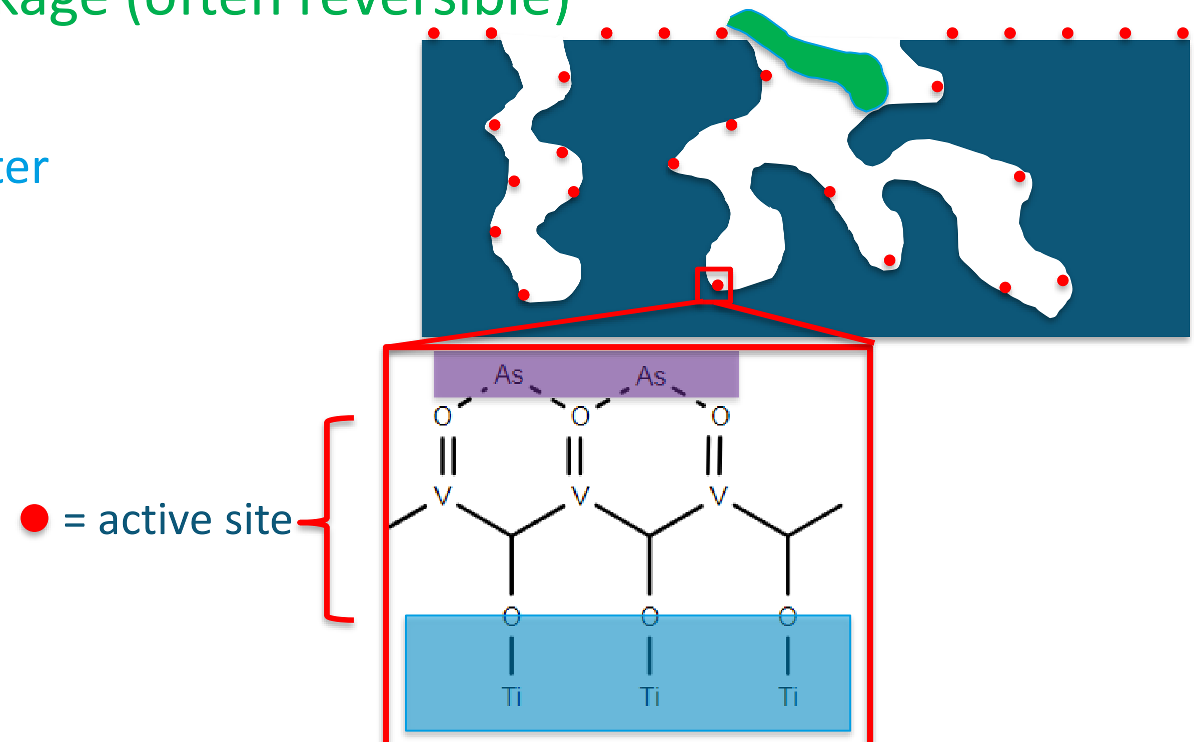
Elemental analysis (ICP-MS) of raw and treated bituminous coal

Trace element	*Concentration (lb/Tera Btu)*		*Reduction (%)*
	Raw Coal	After pyrite removal	
Arsenic (As)	4070	1330	67
Lead (Pb)	912	340	63
Mercury (Hg)	33	13	61
Selenium (Se)	191	96	50

(1) Senior, C.L.; Bool, L.E.; Helble, J.J. *et al.* Toxic Substances From Coal Combustion. DOE Report July 2001. https://www.osti.gov/servlets/purl/891188.
(2) Oder, R. R. "The Co-Benefits of Pre-Combustion Separation of Mercury at Coal-Fired Power Plants" Proceedings 98th Ann. Conf., AWMA, 2005, Minneapolis, MN.

SCR Catalyst Poisoning Mechanisms

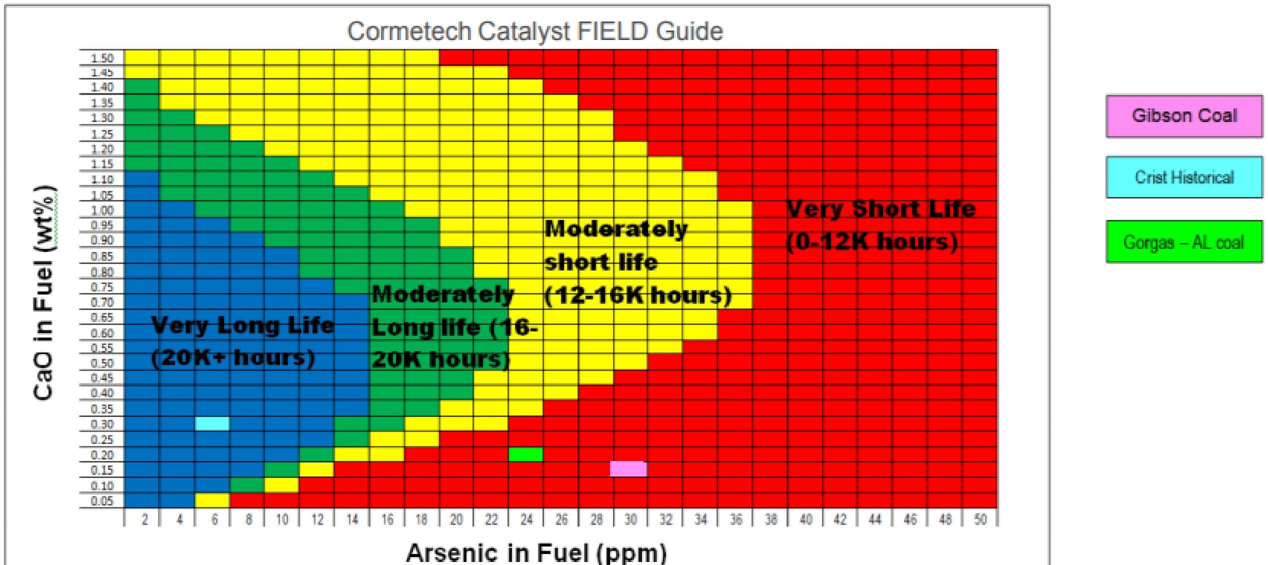
- Chemical deactivation (irreversible)
  - Na/K – react with V on catalyst surface to form inactive $NaVO_3$/KVO_3
  - P – form inactive (vanado)phosphate surface layers
  - As – poisoning of the active sites by AsO_4^{3-}; formation of inactive vanadoarsenate $V^{+4}O(As^{+5}O_3)_2$.
- Physical pore blockage (often reversible)
  - ABS (NH_4HSO_4)
  - Particulate matter



(1) Hein, K.R.G. *Catalogue of element related conditions that lead to increased deactivation.* EU Catalyst Deactivation Report 020315

Impact of Arsenic on SCR Catalyst Life

- Observation: Ca in ash can extend catalyst life

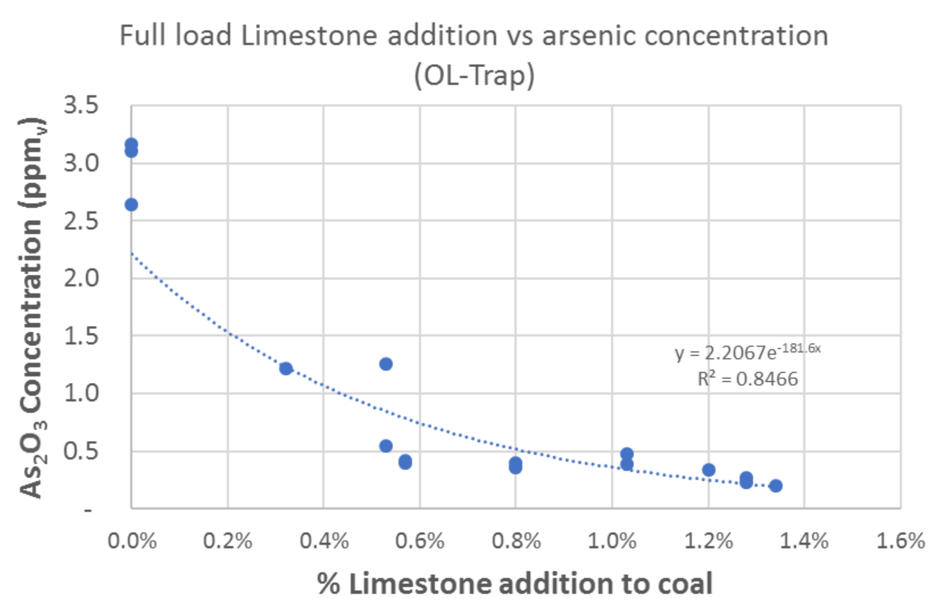


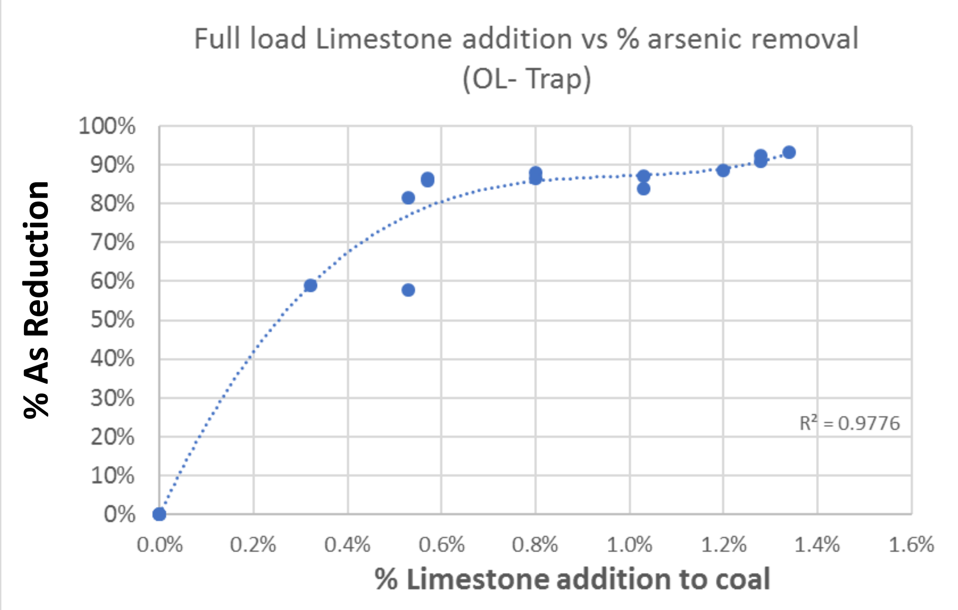
Fuel	Gibson Coal	Crist Historical	Gorgas (AL coal)
CaO in Ash (%, dry)	1.66%	3.13%	1.78%
Ash% (dry)	8.01%	9.79%	12.46%
Cao in Fuel (%,dry)	0.13%	0.31%	0.22%
As in fuel (ppmw, dry)	29.69	4.53	23.97
CaO/As Ratio (x 10^5)	4.5	67.6	9.3
Deactivation rate @ 16k hrs.	0.35	0.65	0.485

(1) Bookout, J. Mitigating Arsenic Poisoning of SCR Catalyst from Burning Gibson IB Coal. 2018 NO_x-Combustion Round Table, St. Louis MO. Workshop 08

Managing Catalyst Poisoning

- Calcium compounds can mitigate impacts of As and P poisoning
  - $3CaO_{(s)} + As_2O_{3(g)} + O_{2(g)} \Leftrightarrow Ca_3(AsO_4)_{2(s)}$
  - $3CaO_{(s)} + As_2O_{5(g)} \Leftrightarrow Ca_3(AsO_4)_{2(s)} + O_{2(g)}$
  - $3CaO_{(s)} + P_2O_{3(g)} + O_{2(g)} \Leftrightarrow Ca_3(PO_4)_{2(s)}$
  - $3CaO_{(s)} + P_2O_{5(g)} \Leftrightarrow Ca_3(PO_4)_{2(s)} + O_{2(g)}$





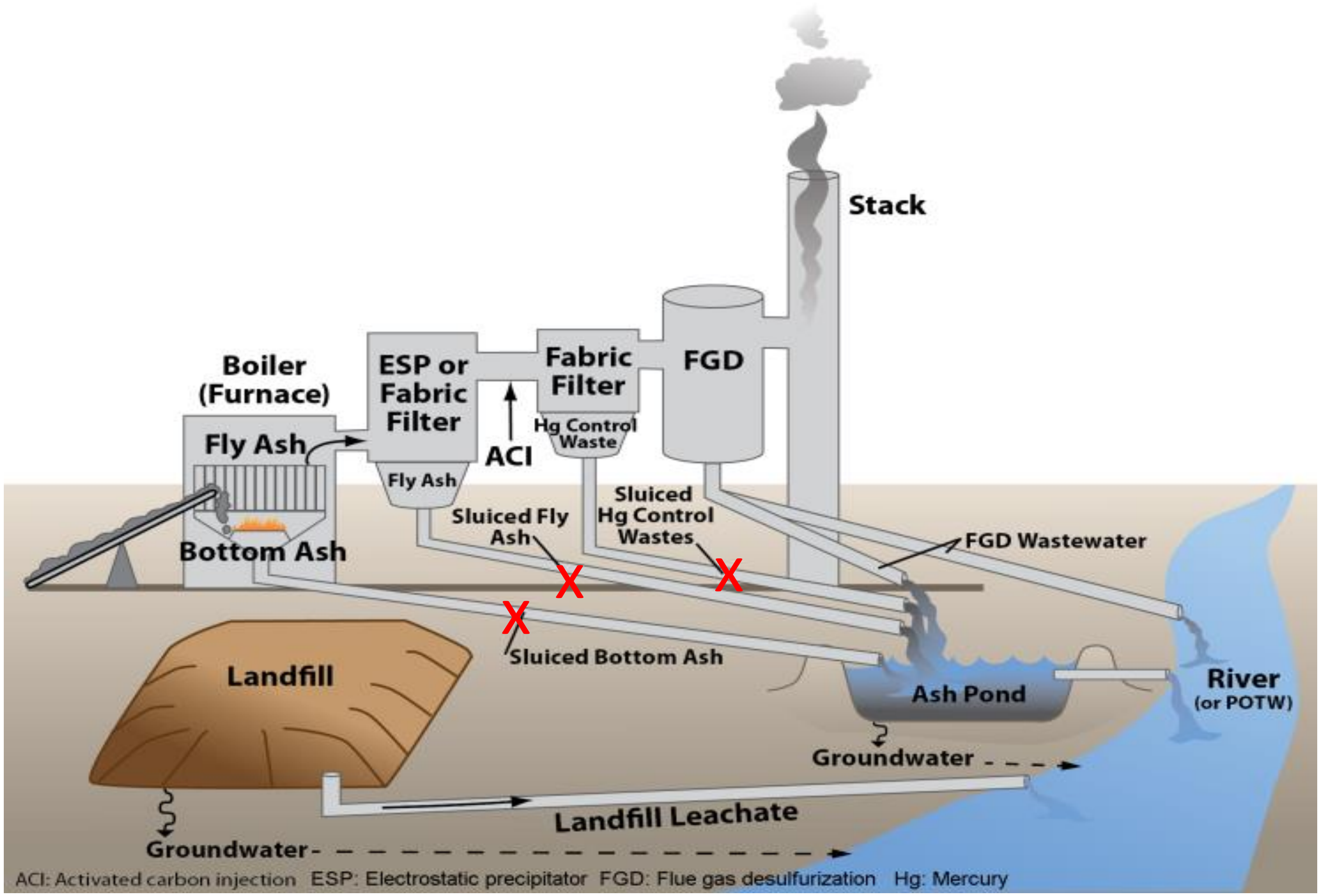
(1) Bookout, J. Mitigating Arsenic Poisoning of SCR Catalyst from Burning Gibson IB Coal. 2018 NO_x-Combustion Round Table, St. Louis MO. Workshop 08

Impact of SO_3 Capture on SCR Catalysts

- For combined As capture and SO_3 reduction, hydrated lime is likely a better Ca source
  - Higher reactivity = less material
  - Need DSI system; more complex than feeding with fuel
- Capture of SO_3 ahead of SCR reduces potential to form ABS
  - Reduce NH_3 slip: ensure that AIG is optimized
- Ability to turndown unit below the specified minimum operating temperature (MOT)
- Driven by cost savings

Impacts of Heavy Metals on ELG Compliance

Power Plant Water Effluent Sources

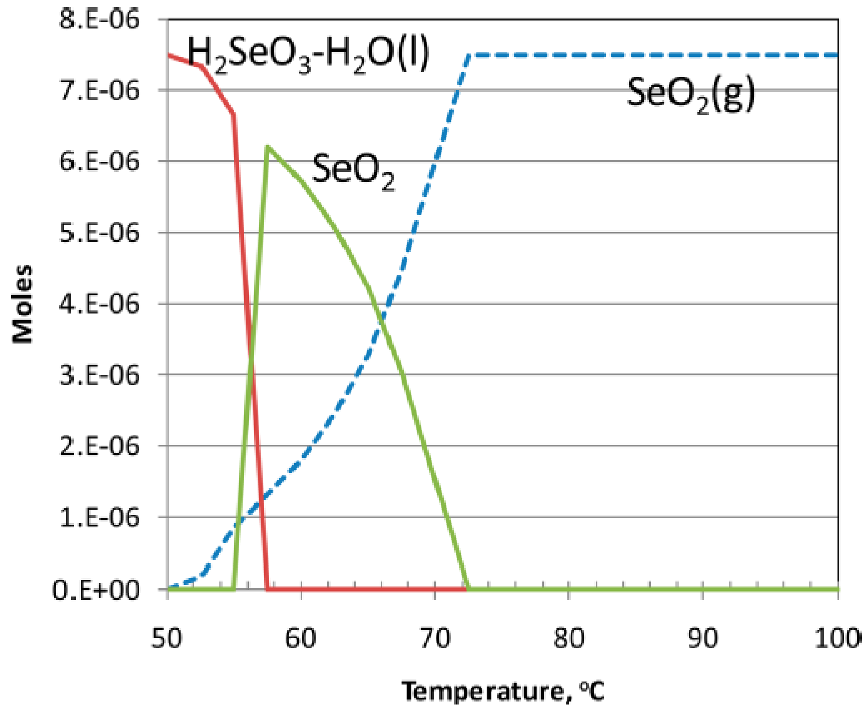


- Conversions to dry ash handling systems
- Treatment of wFGD, ash pond, and landfill effluents
  - Numerical limits on As, Se, Hg, nitrate/nitrite as N

Role of Hydrated Lime in ELG Compliance

- As and Se reduction in flue gas
  - Dry sorbent injection (DSI)
  - Convert gaseous pollutants into particulate matter
  - Do no harm: no/minimal impact on leaching
- As and Se capture/stabilization in WWTP
  - Adsorption/reaction to form less soluble species
- Capture of HCl ahead of PCD, wFGD
  - Reduce blowdown rate by capturing HCl
  - Reduced blowdown rate = reduced water treatment volumes
  - Need longer term testing to evaluate

What Form is Se in?
Se Speciation vs. Temperature



<u>T > 70 ºC</u> (*e.g.* > 158 ºF - furnace through wFGD inlet)

- **$SeO_{2(g)}$ predominates**

<u>T < 70 ºC</u> (*e.g.* < 158 ºF - wFGD inlet through stack)

- **$SeO_{2(g)} + H_2O_{(l,g)} \Leftrightarrow H_2SeO_{3(l,aq,aerosol)}$**

Ref: Senior, C.L.; Tyree, C.A.; Meeks, N.D.; Archarya, C.; McCain, J.D.; Cushing, K.M. *Environ. Sci. Technol.*, **2015**, *49*, pp. 14376-14382

Does Calcium React with Se?
Results of Theoretical Studies

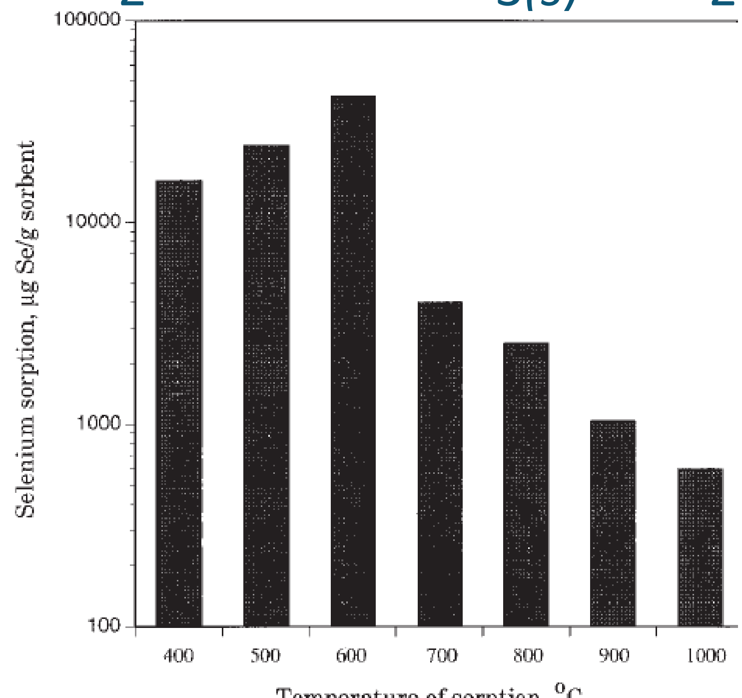
Binding Energies (kcal/mol)	Sorbent	
Adsorbate	**CaO**	**$Ca(OH)_2$**
$SO_{2(g)}$	-26.34	-24.07
$Hg^0_{(g)}$	-2.89	-3.59
$HgCl_{2(g)}$	-8.5	-5.32
$SeO_{2(g)}$	-39.23	-38.4

- Hg^0 *does not* significantly adsorb onto CaO or $Ca(OH)_2$
- $HgCl_{2(g)}$ physically adsorbs onto CaO and $Ca(OH)_2$
- $SO_{2(g)}$ chemically adsorbs onto CaO and $Ca(OH)_2$
- $SeO_{2(g)}$ chemically adsorbs onto CaO and $Ca(OH)_2$
- **Binding energy of $SeO_{2(g)}$ + CaO/$Ca(OH)_2$ > $SO_{2(g)}$ + CaO/$Ca(OH)_2$**

Ref: Sasmaz, E.; Wilcox, J. *Master's Thesis;* Worcester Polytechnic Institute, 2015

Capture Temperatures

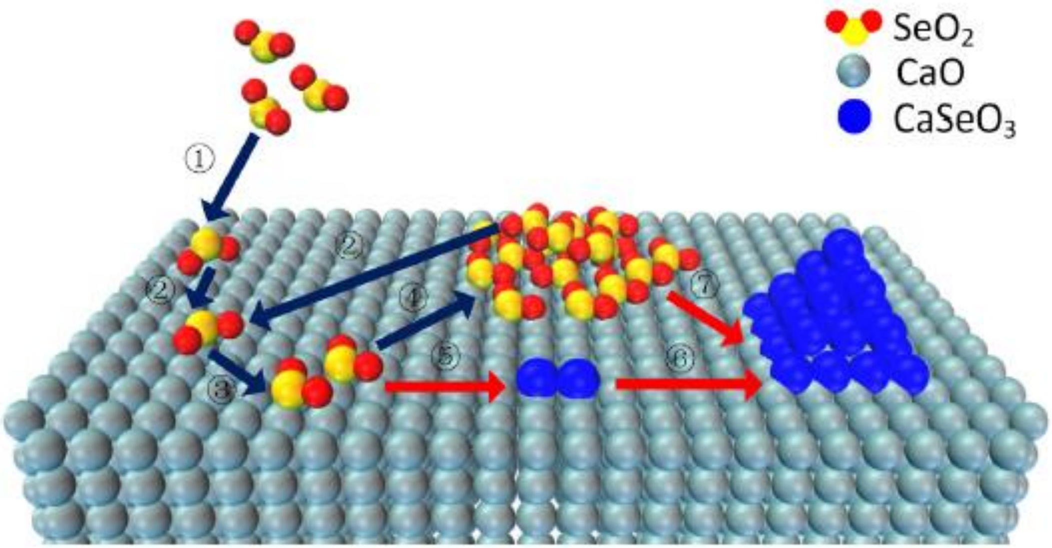
$SeO_{2(g)} + Ca(OH)_2 \Leftrightarrow CaSeO_{3(s)} + H_2O_{(g)}$



- "Calcium hydroxide is an effective sorbent in capturing selenium…"
- Optimal capture zone: 400 °C (752 °F) – 600 °C (1112 °F)
  - Economizer outlet injection
- Competition exists between $SeO_{2(g)}$ and $CO_{2(g)}$
  - Under these conditions, reaction with $CO_{2(g)}$ is kinetically slower than with $SeO_{2(g)}$
- $CaSeO_3$ is predominant product (not $CaSeO_4$)

Ref: Ghosh-Dastidar, A.; Mahuli, R.; Agnihotri, R.; Fan, L.-S. *Environ. Sci. Technol.* 1996, 30, p. 447-452

$SeO_{2(g)}$ Adsorption Mechanism



1) Physisorption
2) Chemical reaction
3) Surface diffusion
4) SeO_2 aggregation
5) Nucleation
6) Growth
7) Nucleation and Growth

- $SeO_{2(g)}$ is captured on the $CaO/Ca(OH)_2$ surface
- A surface film of $CaSeO_3$ forms
- Further diffusion into pores
- Removal by the PCD

Reference: Fan, Y.; Zhuo, Y.; Li, L. *App. Surf. Sci.* **2017**, *420,* p. 465-471

Hydrated Lime Injection on Se Removal

- **High $SeO_{2(g)}$ removals achievable with DSI**
  - $CaSeO_{3(s)}$ particles captured by fabric filter/ESP

- **$H_2SeO_{3(l,aq,aerosol)}$ removal ahead/across wFGD**
  - "$Ca(OH)_2$ promotes capture through condensation on larger, higher surface area particles, which are efficiently removed across the wFGD"

Ref: Senior, C.L.; Tyree, C.A.; Meeks, N.D.; Archarya, C.; McCain, J.D.; Cushing, K.M. *Environ. Sci. Technol.*, **2015**, *49*, pp. 14376-14382

Arsenic Capture - Thermodynamics

Reactions	Equilibrium Constant
$6CaO + As_4O_{10(g)} \Leftrightarrow 2Ca_3(AsO_4)_2$	1.14×10^{150}
$6CaCO_3 + As_4O_{10(g)} \Leftrightarrow 2Ca_3(AsO_4)_2 + 6CO_{2(g)}$	1.07×10^{58}
$2CaO + As_{4(g)} + 6H_2O_{(g)} \Leftrightarrow 2Ca(AsO_2)_2 + 6H_{2(g)}$	2.80×10^{40}
$2CaCO_3 + As_{4(g)} + 6H_2O_{(g)} \Leftrightarrow 2Ca(AsO_2)_2 + 6H_{2(g)} + 2CO_{2(g)}$	2.50×10^{8}

All possible gas phase reactions are thermodynamically favorable

Ref: HSC Chemistry Thermodynamics Package

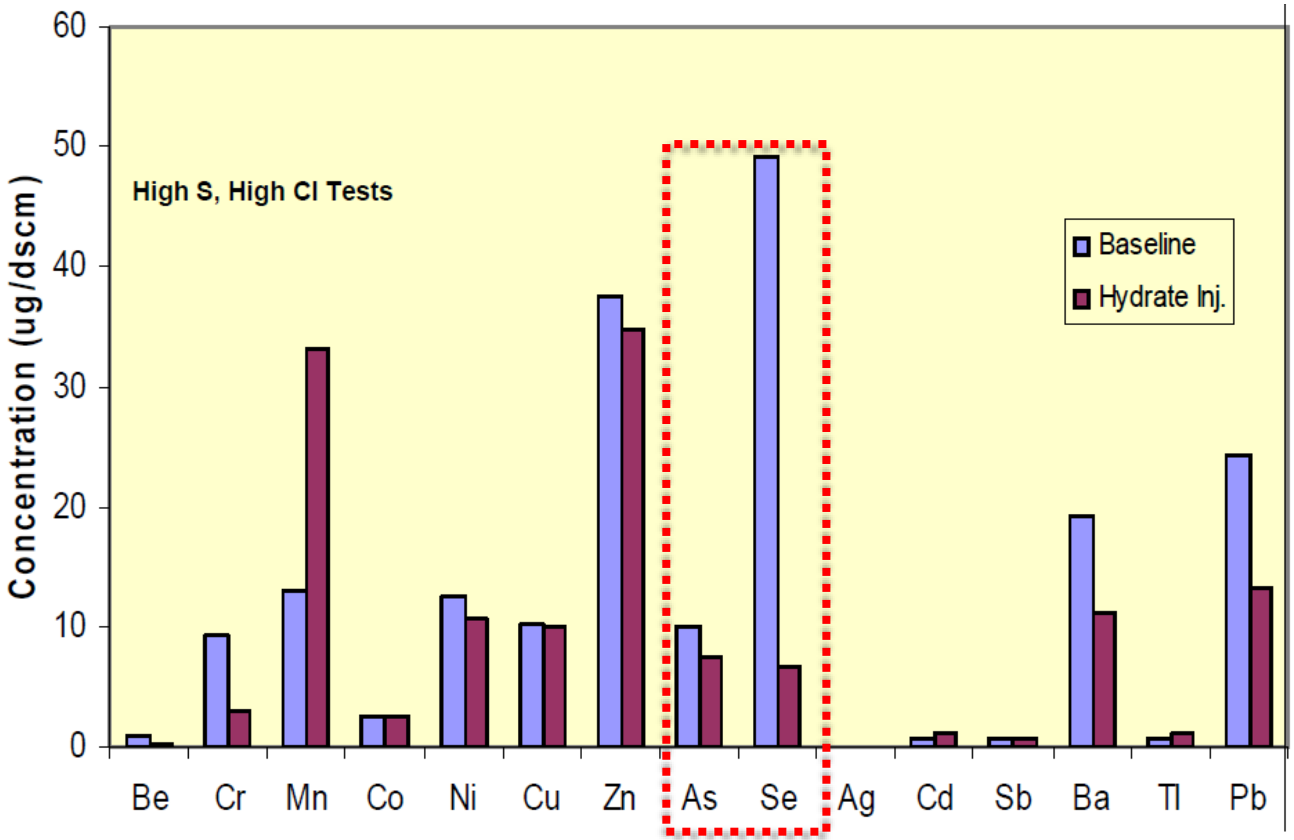
Fate of Se and As Compounds

Compound	Solubility (25 °C)	Compound	Solubility (25 °C)
$Na_3(As^{V}O_4)_{(aq)}$	Soluble	$Ca_3(As^{V}O_4)_2 \cdot nH_2O_{(aq)}$	0.013 g/100 mL
$NaAs^{III}O_{2\,(aq)}$	156 g/100 mL	$Ca_5(As^{V}O_4)_3OH_{(aq)}$	insoluble
$Na_2(Se^{VI}O_4)_{(aq)}$	Soluble	$CaSe^{VI}O_{4(aq)}$	8.3 g/100 mL
$NaSe^{IV}O_{2(aq)}$	85 g/100 mL	$CaSe^{IV}O_{3(aq)}$	0.35 g/100 mL

- **Calcium compounds less soluble than sodium counterparts**
  - Reduced leaching potential after incorporation with fly ash
- **Use of hydrated lime in the WWTP**
  - pH adjustment
  - Stabilization of As and Se species

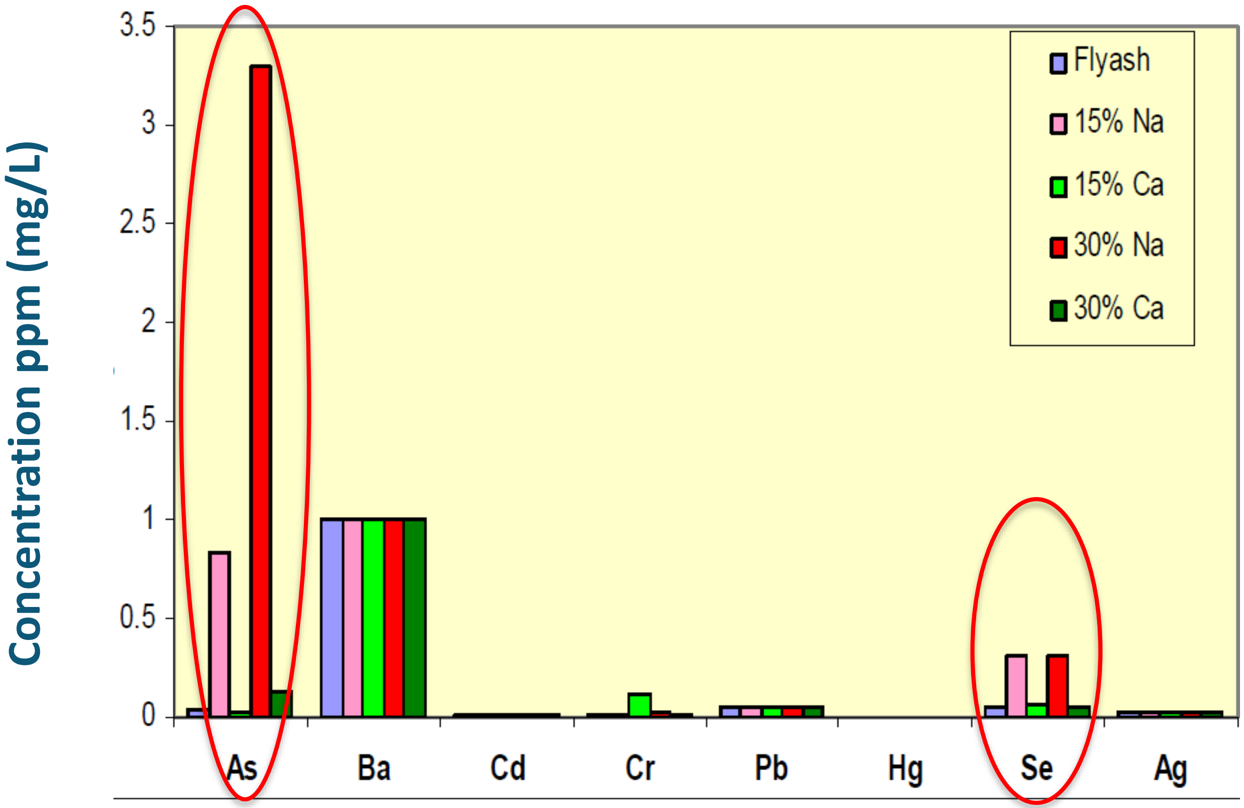
Se Abatement Trial Results

Pilot-Scale Boiler Data– *Proof of Concept*



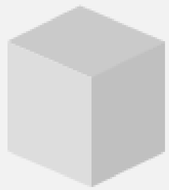
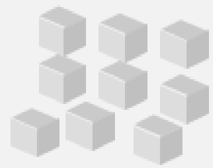
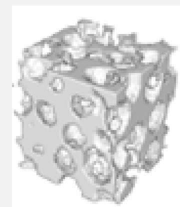
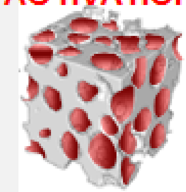
- **ILB coal fired to produce high SO_2, high HCl concentrations in the flue gas**
  - Provide competition for heavy metals on hydrated lime adsorption sites
  - EPA M29 used to quantify metals concentrations

Pilot-Scale Boiler Data – Ash Leaching

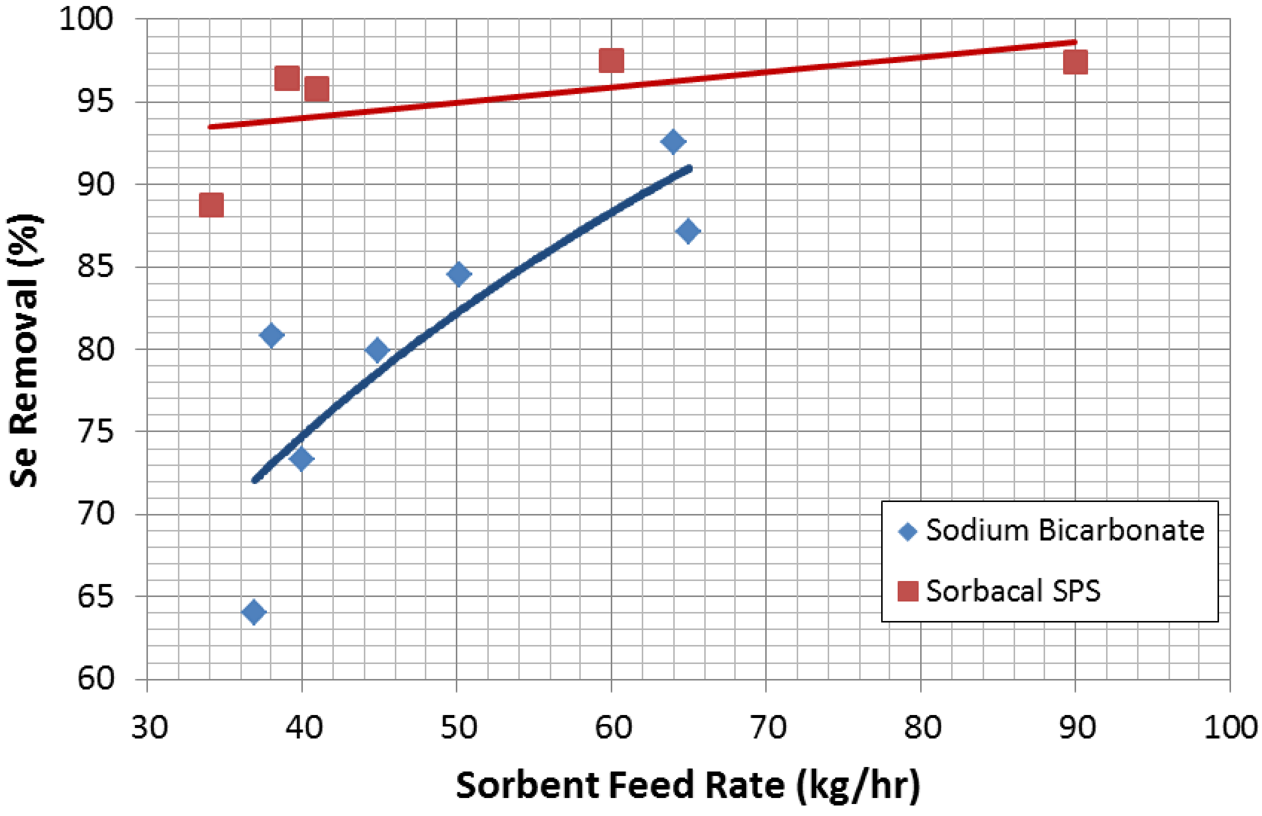


- **HL decreased leaching of As and Se, SBC injection increased leaching**
- **TCLP and SPLP results were similar**
  - Discussion of correct leaching protocol to use is critical for ELG compliance

Hydrated Lime Physical Properties

Sorbent	Standard Hydrated Limes	FGT Grade Sorbacal® H	Sorbacal® SP	Sorbacal® SPS
Figure				ACTIVATION 
Typical Available $Ca(OH)_2$ - [%]	92 – 95	93	93	93
Typical Surface Area - [m^2/g]	14 – 18	20	40	40
Typical Pore Volume - [cm^3/g]	~0.07	0.08	0.20	0.20
Typical D_{50} - [microns]	5 – 7	5 – 7	8 – 12	8 – 12

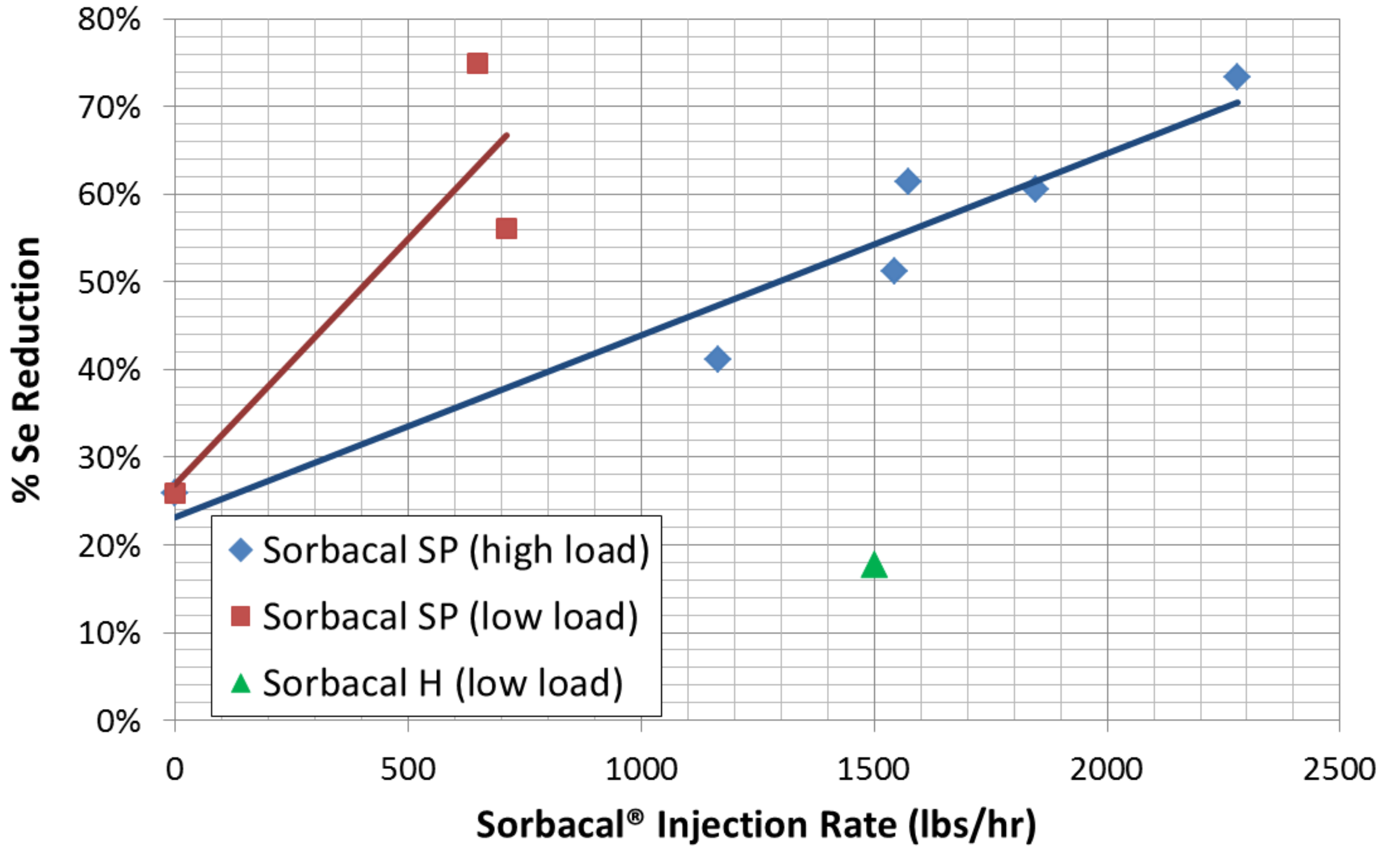
Se Reduction – Glass Plant



- Feeding Sorbacal® SPS continuously since 2008
- Continuously achieve >90% Se reduction

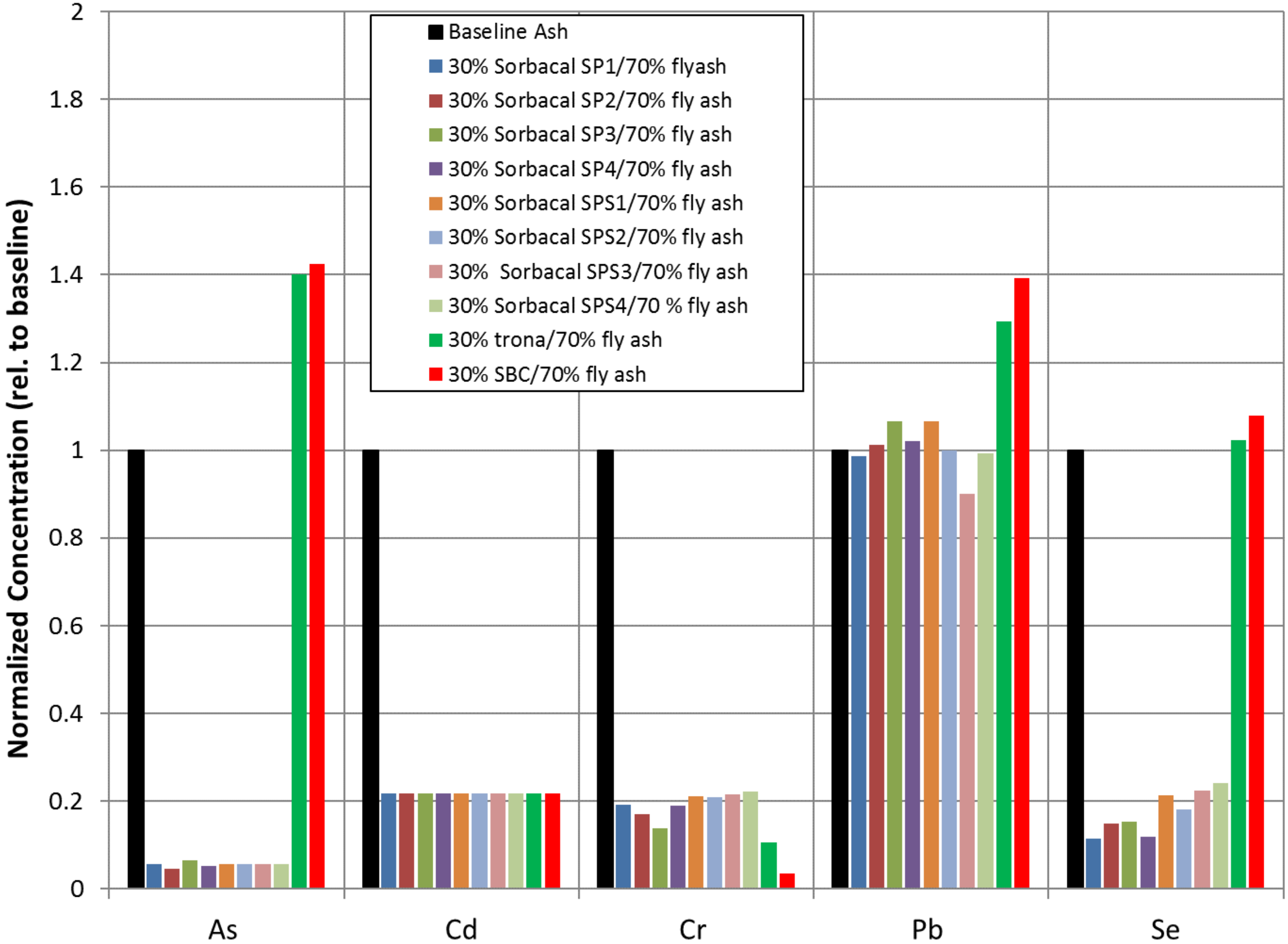
Do Physical Properties Impact Capture?

Se Reduction - Utility Unit (2017)



- Se capture more efficient at lower loads
- Enhanced sorbents more efficient than standard hydrated lime
  - Surface area and pore volume drive performance

Reduced Impact on Leaching



- **Sorbacal® SP and SPS injection reduce leaching of RCRA metals in bituminous fly ash**

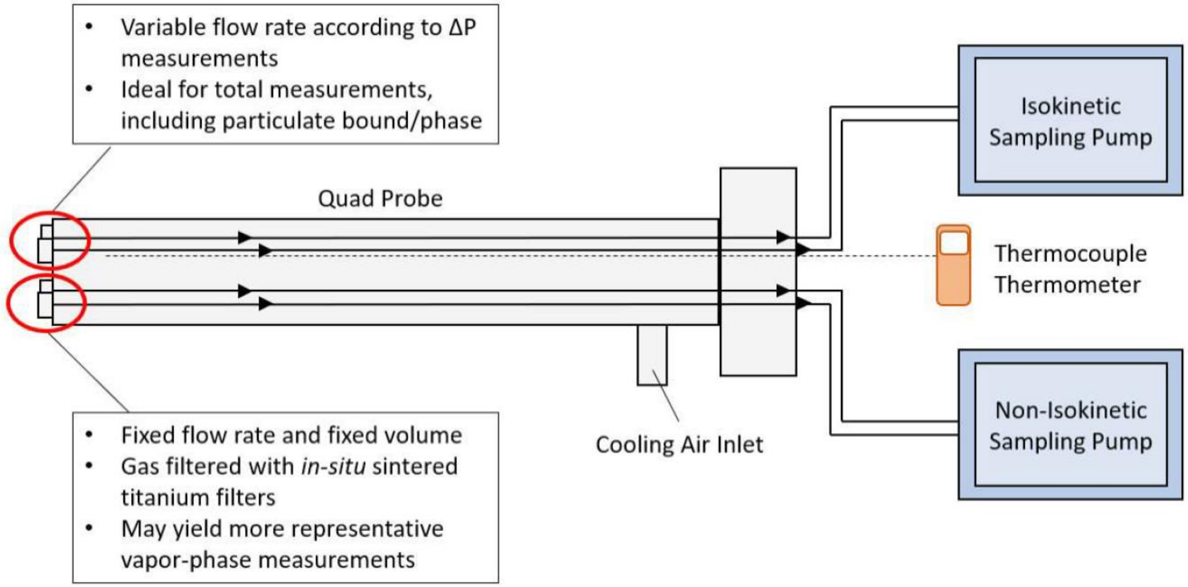
Arsenic and Selenium Measurement Methods

Se/As Sorbent Traps: Sampling

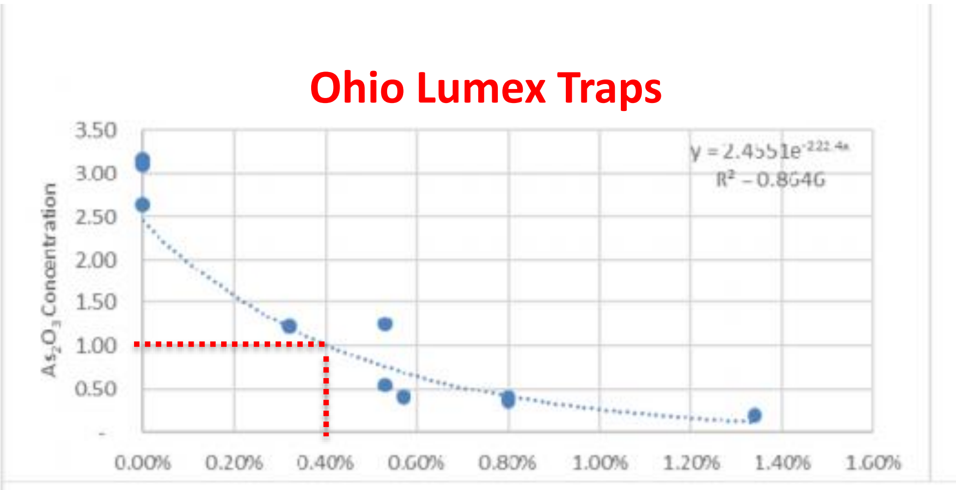
- Sampling equipment is nearly identical to that required for Hg traps.
- Probe must be cooled if sample gas is >170°C
- In high-particulate environments, filter tips should be attached to traps.

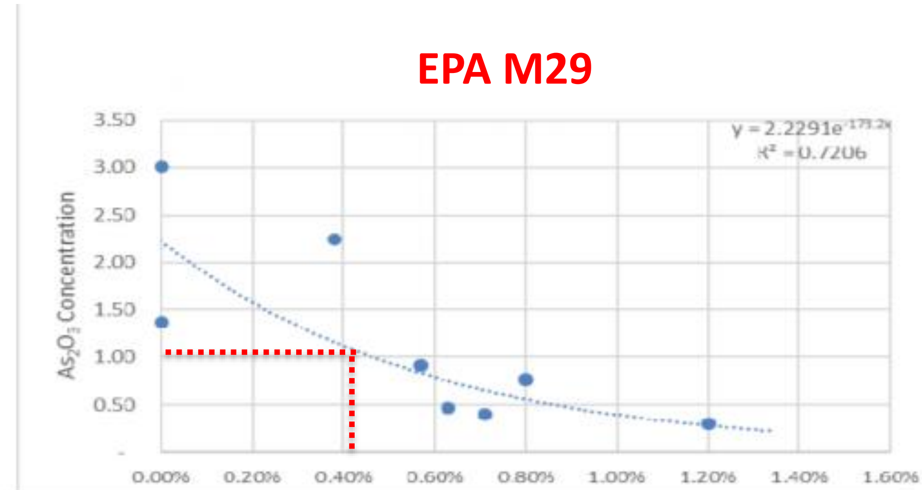
Partitioning

- Growing interest in ability to differentiate vapor-phase Se/As from filterable Se/As.
- Filterable Se/As can be removed at ESP, vapor-phase As_2O_3 poisons catalysts and vapor-phase SeO_2 easily makes it to the FGD (thereafter entering the effluent stream).
- Some experiments have been done with sorbent traps to partition Se/As, by comparing isokinetically sampled traps with filtered traps.



Comparisons between EPA M29 and OL Traps





- Traps and M29 results correlate fairly well
- M29 measurement results significantly more scattered
- Traps are relatively cost effective and simple to collect multiple replicates, in multiple locations (*i.e*. self consistency)

(1) Bookout, J. Mitigating Arsenic Poisoning of SCR Catalyst from Burning Gibson IB Coal. 2018 NO_x-Combustion Round Table, St. Louis MO. Workshop 08

Conclusions

- Limestone effectively mitigates SCR poisoning by As and P
- Hydrated lime ahead of SCR to mitigate SO_3 and As
  - Prevent/minimize formation of ammonium bisulfate to allow operation at lower loads
  - Minimize arsenic poisoning
- DSI with hydrated lime can effectively reduce arsenic and selenium concentrations prior to wFGD
- HCl reduction ahead of wFGD can reduce blowdown rates and volume of effluent to be treated
  - Longer term trials are needed
- New measurement methods make testing significantly easier and less costly
  - Ohio Lumex traps have demonstrated statistical correlation with M29