

REINHOLD ENVIRONMENTAL Ltd.



2019 NO_x-Combustion-CCR Round Table Presentation

February 11 & 12, 2019, in Salt Lake City, Utah / Hosted by PacifiCorp

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Operational Benefits of Heavy Metals Capture with Hydrated Lime

February 12, 2019

**Reinhold NO_x-Combustion-CCR Round Table
Salt Lake City, UT**

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

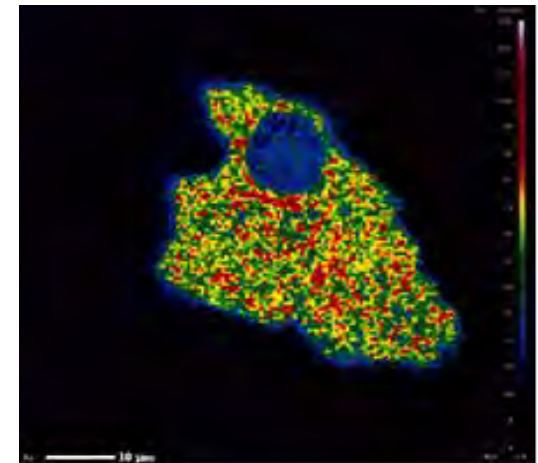
Fuel: Arsenic and Selenium Chemistry



- 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	<i>analyses in progress</i>
Chromium	CrOOH and clay minerals	mostly CrOOH, minor clay minerals	CrOOH, chromite, minor clays	organically associated

As concentrations on FeS₂ 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.

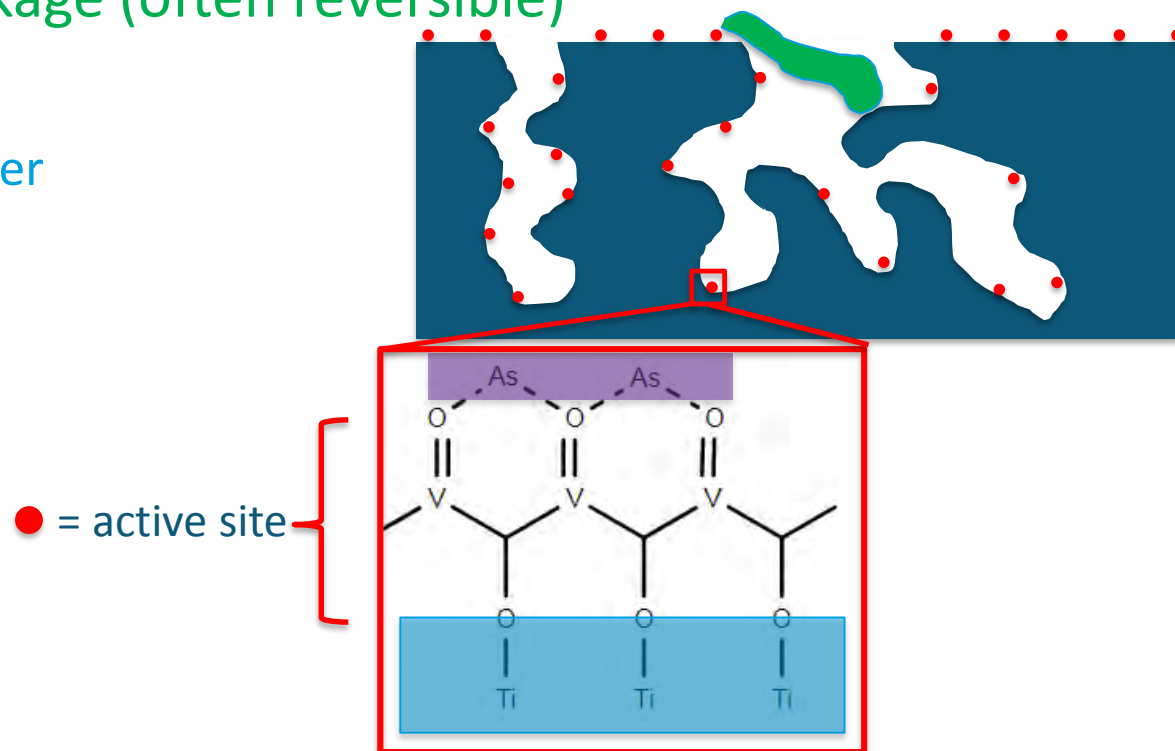
SCR Catalyst Poisoning Mechanisms

■ Chemical deactivation (irreversible)

- Na/K – react with V on catalyst surface to form inactive $\text{NaVO}_3/\text{KVO}_3$
- P – form inactive (vanado)phosphate surface layers
- As – poisoning of the active sites by AsO_4^{3-} ; formation of inactive vanadoarsenate $\text{V}^{+4}\text{O}(\text{As}^{+5}\text{O}_3)_2$.

■ Physical pore blockage (often reversible)

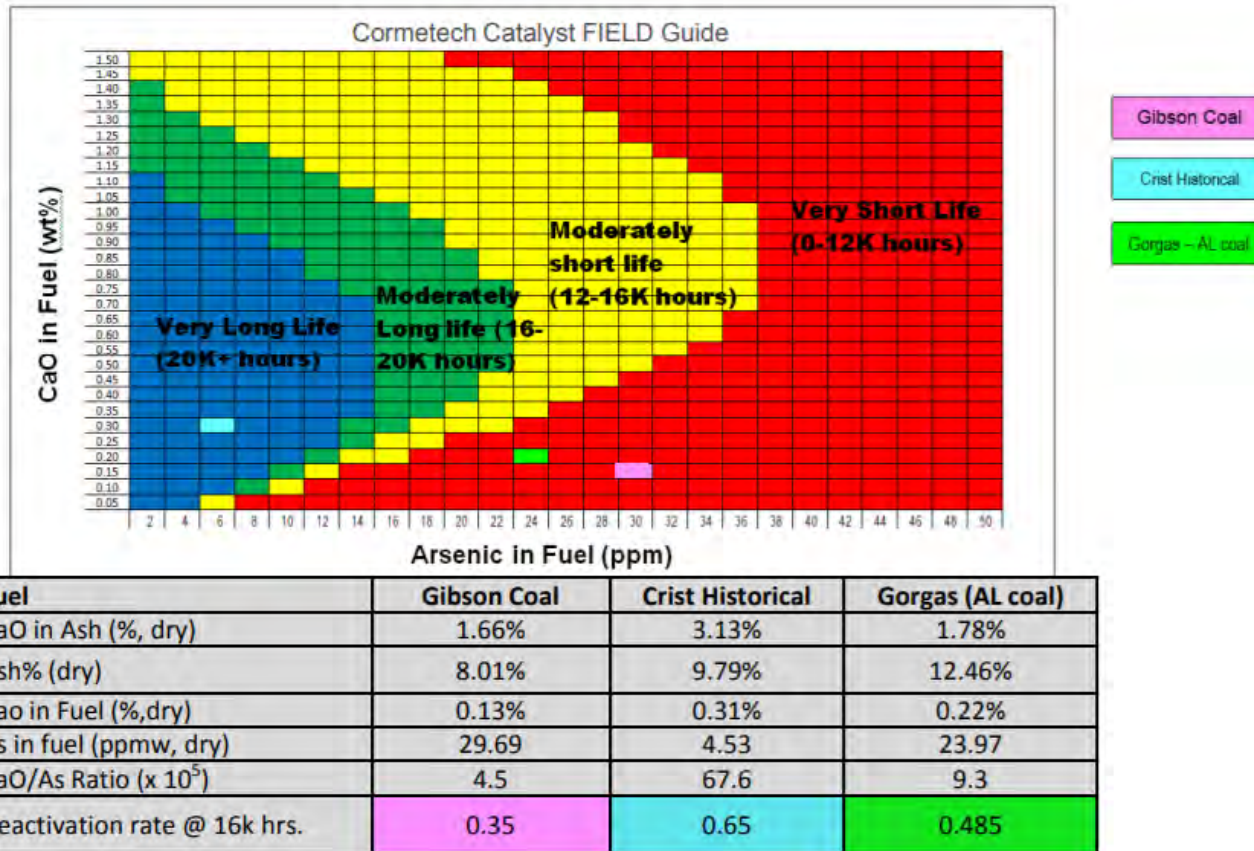
- ABS (NH_4HSO_4)
- Particulate matter



Impact of Arsenic on SCR Catalyst Life



- Observation: Ca in ash can extend catalyst life



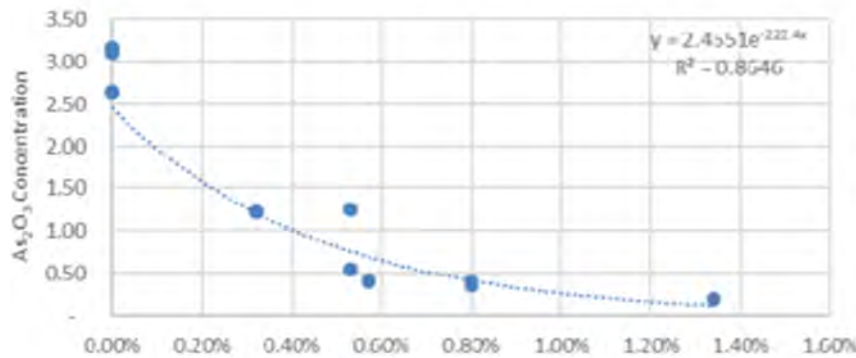
Managing Catalyst Poisoning



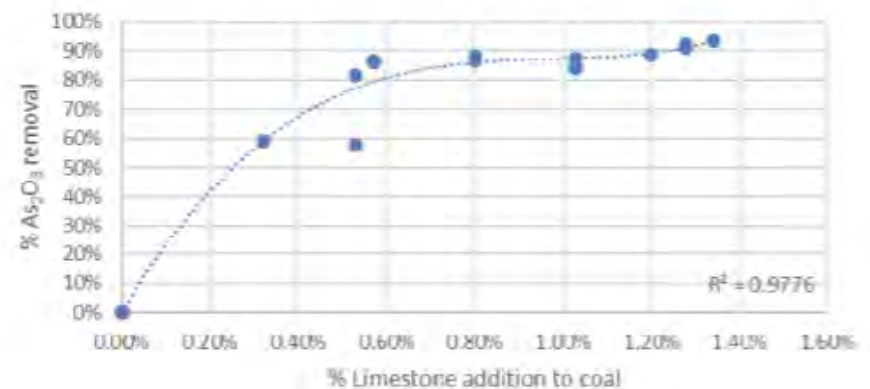
■ Calcium compounds can mitigate impacts of As and P poisoning

- $3\text{CaO}_{(s)} + \text{As}_2\text{O}_{3(g)} + \text{O}_{2(g)} \rightleftharpoons \text{Ca}_3(\text{AsO}_4)_2(s)$
- $3\text{CaO}_{(s)} + \text{As}_2\text{O}_{5(g)} \rightleftharpoons \text{Ca}_3(\text{AsO}_4)_2(s) + \text{O}_{2(g)}$
- $3\text{CaO}_{(s)} + \text{P}_2\text{O}_{3(g)} + \text{O}_{2(g)} \rightleftharpoons \text{Ca}_3(\text{PO}_4)_2(s)$
- $3\text{CaO}_{(s)} + \text{P}_2\text{O}_{5(g)} \rightleftharpoons \text{Ca}_3(\text{PO}_4)_2(s) + \text{O}_{2(g)}$

Full load Limestone addition vs arsenic concentration (Trap)



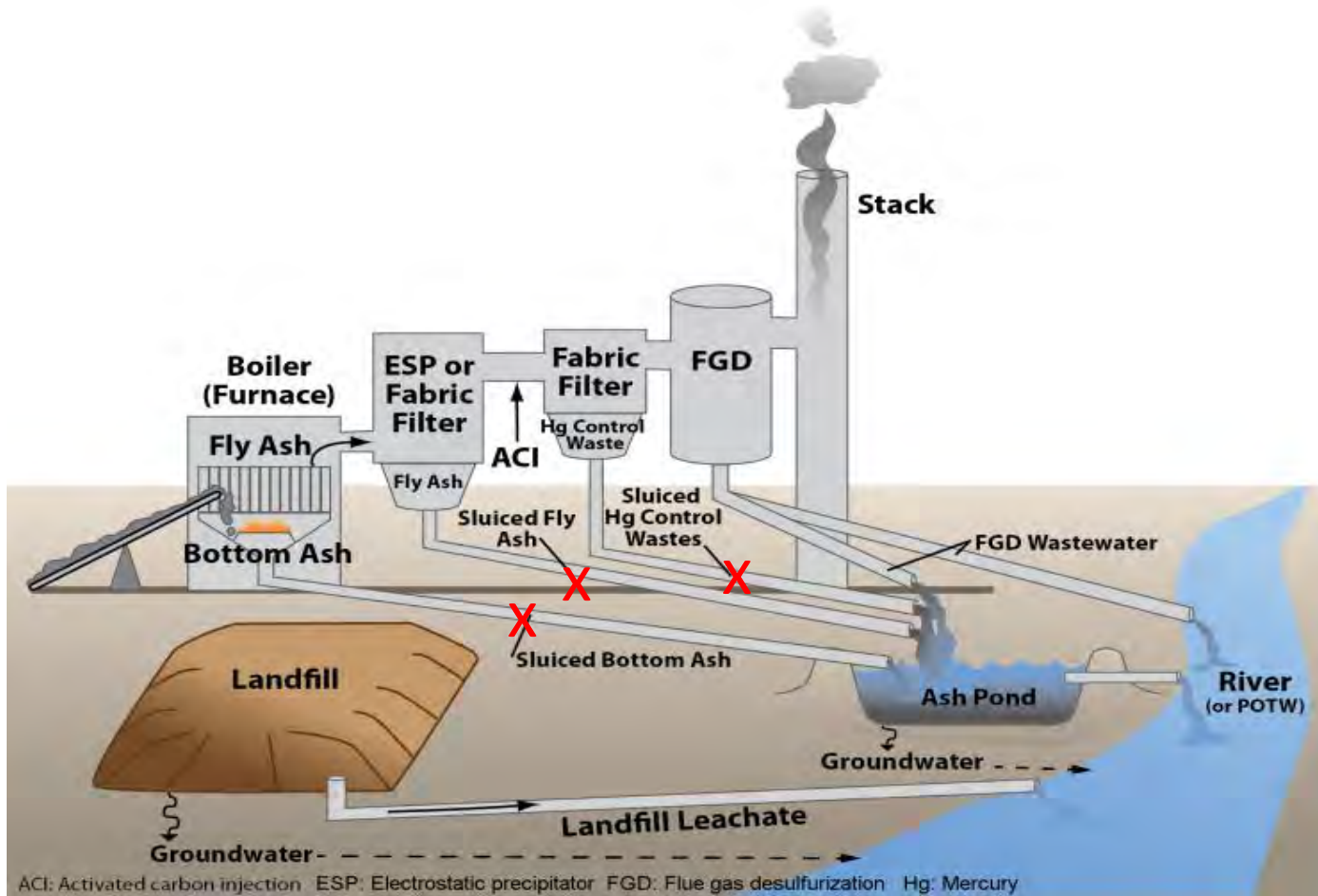
Full load Limestone addition vs % arsenic removal (OL-Trap)



- Capture of SO₃ ahead of SCR reduces potential to form ABS
 - Reduce NH₃ 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



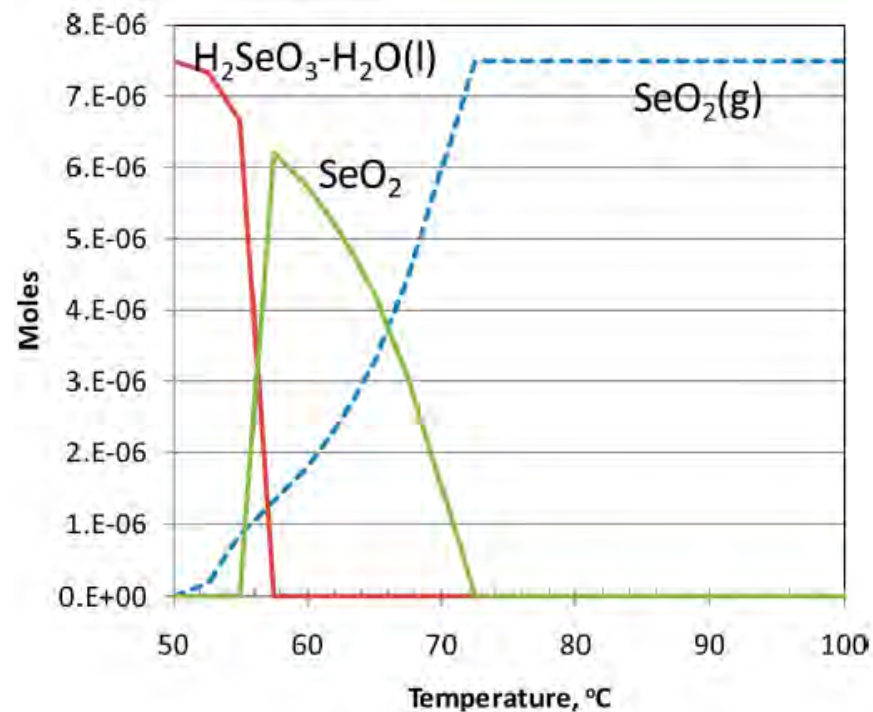
- Conversions to dry ash handling systems
- Treatment of wFGD, ash pond, and landfill effluents
 - Numerical limits on As, Se, Hg, nitrate/nitrite as N

- 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

- 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



T > 70 °C (e.g. furnace through wFGD inlet)

- SeO_{2(g)} predominates

T < 70 °C (e.g. wFGD inlet through stack)

- $\text{SeO}_{2(g)} + \text{H}_2\text{O}_{(l,g)} \rightleftharpoons \text{H}_2\text{SeO}_{3(l,aq,aerosol)}$

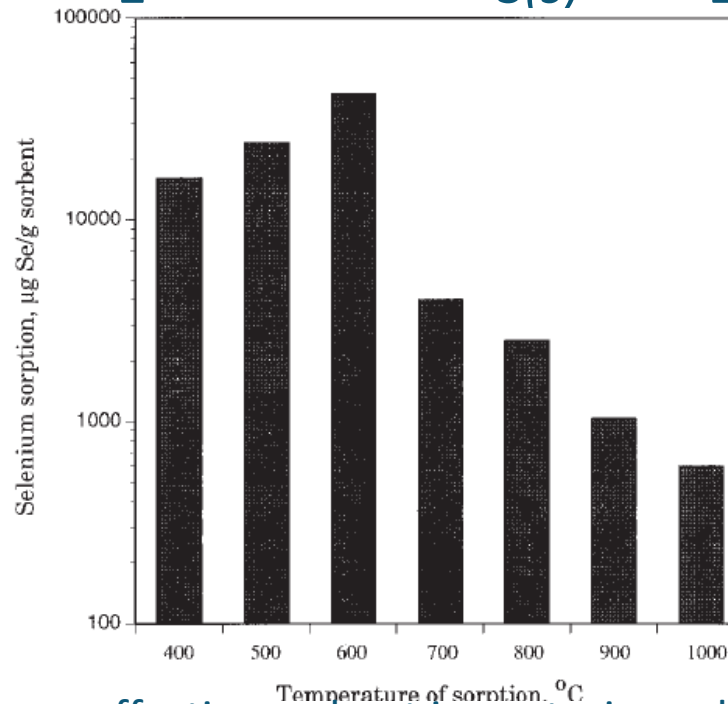
Does Calcium React with Se?

Results of Theoretical Studies

Binding Energies (kcal/mol)	Sorbent	
Adsorbate	CaO	“hydrated CaO”
$\text{SO}_{2(g)}$	-26.34	-24.07
$\text{Hg}^0_{(g)}$	-2.89	-3.59
$\text{HgCl}_{2(g)}$	-8.5	-5.32
$\text{SeO}_{2(g)}$	-39.23	-38.4

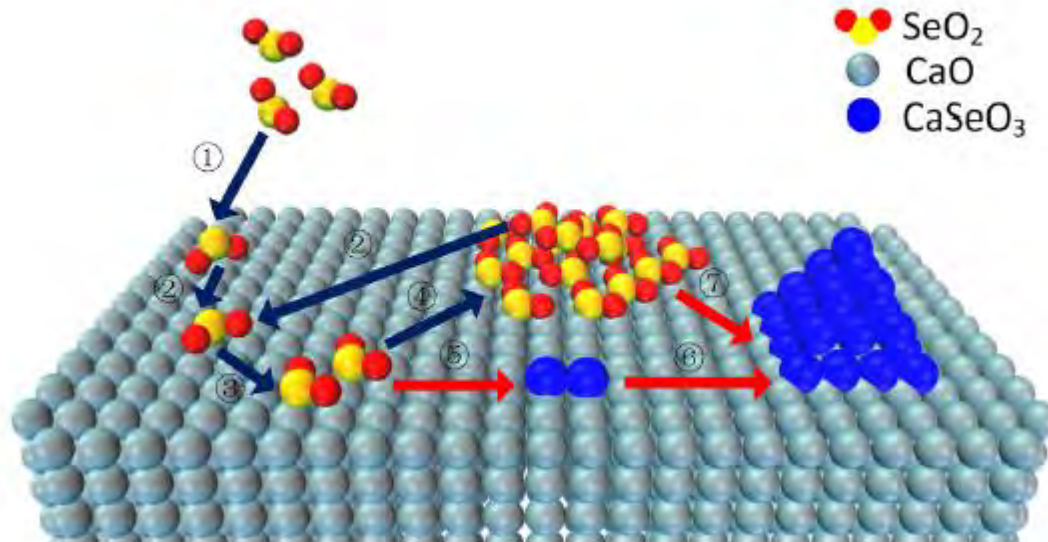
- Hg^0 *does not* significantly adsorb onto CaO or $\text{Ca}(\text{OH})_2$
- $\text{HgCl}_{2(g)}$ physically adsorbs onto CaO and $\text{Ca}(\text{OH})_2$
- $\text{SO}_{2(g)}$ chemically adsorbs onto CaO and $\text{Ca}(\text{OH})_2$
- $\text{SeO}_{2(g)}$ chemically adsorbs onto CaO and $\text{Ca}(\text{OH})_2$
- **Binding energy of $\text{SeO}_{2(g)} + \text{CaO}/\text{Ca}(\text{OH})_2 > \text{SO}_{2(g)} + \text{CaO}/\text{Ca}(\text{OH})_2$**

Capture Temperatures



- “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 $\text{SeO}_{2(g)}$ and $\text{CO}_{2(g)}$
 - Under these conditions, reaction with $\text{CO}_{2(g)}$ is kinetically slower than with $\text{SeO}_{2(g)}$
- **CaSeO_3 is predominant product** (not CaSeO_4)

SeO_{2(g)} Adsorption Mechanism



- 1) Physisorption
- 2) Chemical reaction
- 3) Surface diffusion
- 4) SeO₂ 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 CaSeO₃ forms
- Further diffusion into pores
- Removal by the PCD

- **High $\text{SeO}_{2(g)}$ removals achievable with DSI**
 - $\text{CaSeO}_{3(s)}$ particles captured by fabric filter/ESP

- **$\text{H}_2\text{SeO}_{3(l,aq,aerosol)}$ removal ahead/across wFGD**
 - “ Ca(OH)_2 promotes capture through condensation on larger, higher surface area particles, which are efficiently removed across the wFGD”

Arsenic Capture - Thermodynamics



Reactions	Equilibrium Constant
$6\text{CaO} + \text{As}_4\text{O}_{10(g)} \rightleftharpoons 2\text{Ca}_3(\text{AsO}_4)_2$	1.14×10^{150}
$6\text{CaCO}_3 + \text{As}_4\text{O}_{10(g)} \rightleftharpoons 2\text{Ca}_3(\text{AsO}_4)_2 + 6\text{CO}_{2(g)}$	1.07×10^{58}
$2\text{CaO} + \text{As}_{4(g)} + 6\text{H}_2\text{O}_{(g)} \rightleftharpoons 2\text{Ca}(\text{AsO}_2)_2 + 6\text{H}_{2(g)}$	2.80×10^{40}
$2\text{CaCO}_3 + \text{As}_{4(g)} + 6\text{H}_2\text{O}_{(g)} \rightleftharpoons 2\text{Ca}(\text{AsO}_2)_2 + 6\text{H}_{2(g)} + 2\text{CO}_{2(g)}$	2.50×10^8

All possible gas phase reactions are thermodynamically favorable

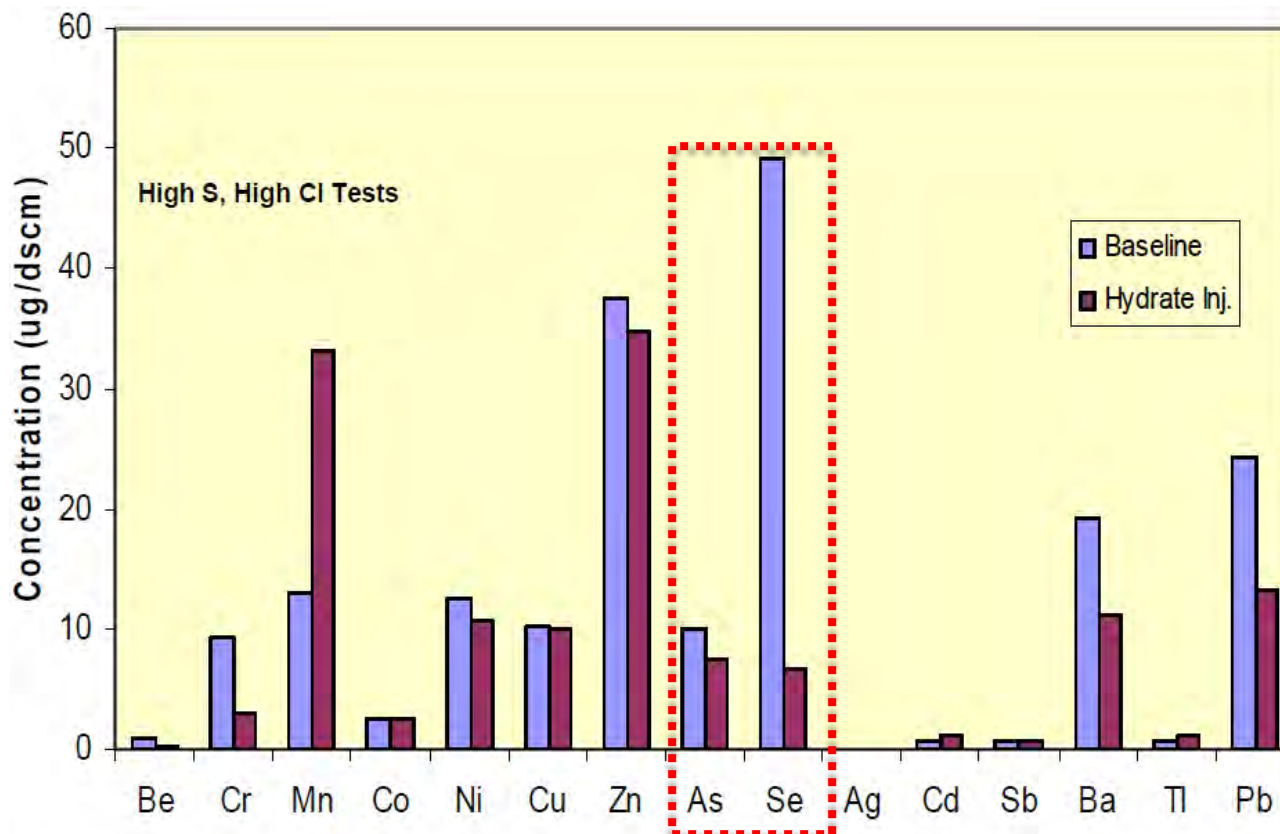
Fate of Se and As Compounds

Compound	Solubility (25 °C)	Compound	Solubility (25 °C)
$\text{Na}_3(\text{As}^{\text{V}}\text{O}_4)_{(\text{aq})}$	Soluble	$\text{Ca}_3(\text{As}^{\text{V}}\text{O}_4)_2 \cdot n\text{H}_2\text{O}_{(\text{aq})}$	0.013 g/100 mL
$\text{NaAs}^{\text{III}}\text{O}_2_{(\text{aq})}$	156 g/100 mL	$\text{Ca}_5(\text{As}^{\text{V}}\text{O}_4)_3\text{OH}_{(\text{aq})}$	insoluble
$\text{Na}_2(\text{Se}^{\text{VI}}\text{O}_4)_{(\text{aq})}$	Soluble	$\text{CaSe}^{\text{VI}}\text{O}_4_{(\text{aq})}$	8.3 g/100 mL
$\text{NaSe}^{\text{IV}}\text{O}_2_{(\text{aq})}$	85 g/100 mL	$\text{CaSe}^{\text{IV}}\text{O}_3_{(\text{aq})}$	0.35 g/100 mL

- **Calcium compounds less soluble than sodium counterparts**
 - Reduced leaching potential following incorporation with fly ash
 - At neutral pH

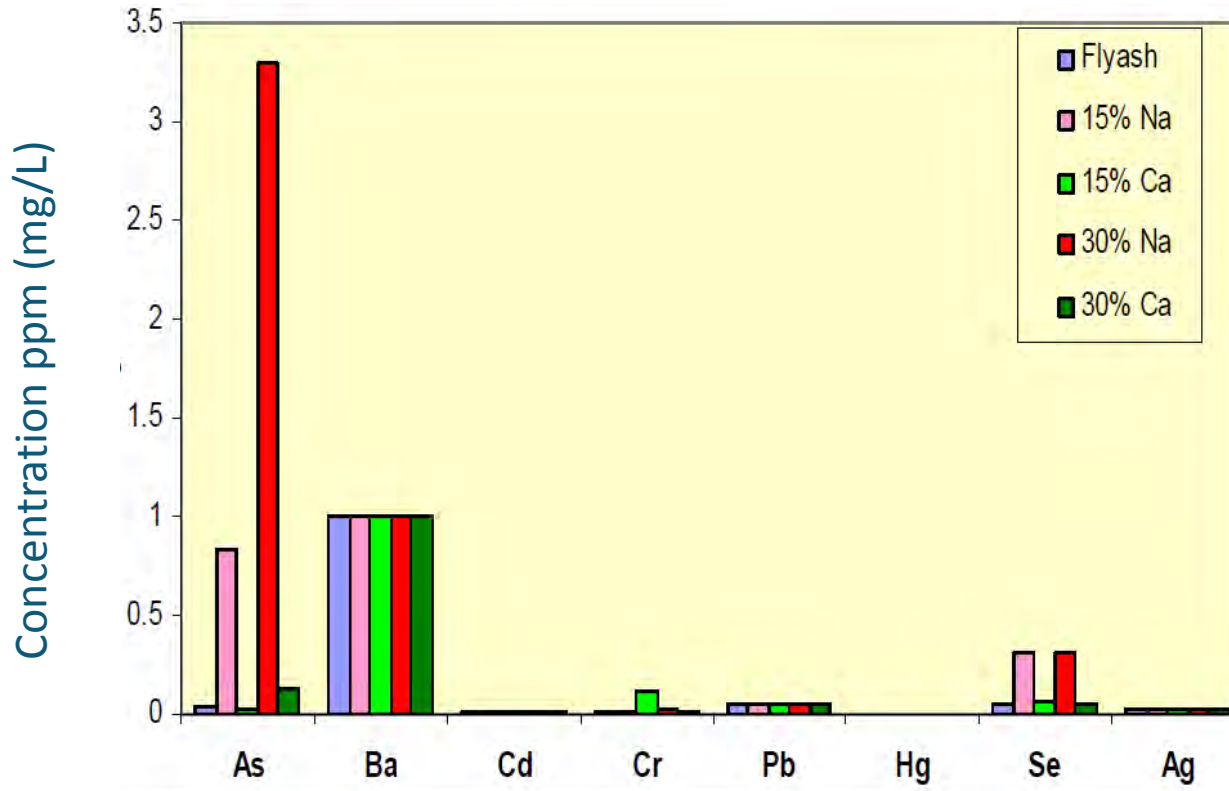
Se Abatement Trial Results

Pilot-Scale Boiler Data– Gas Phase



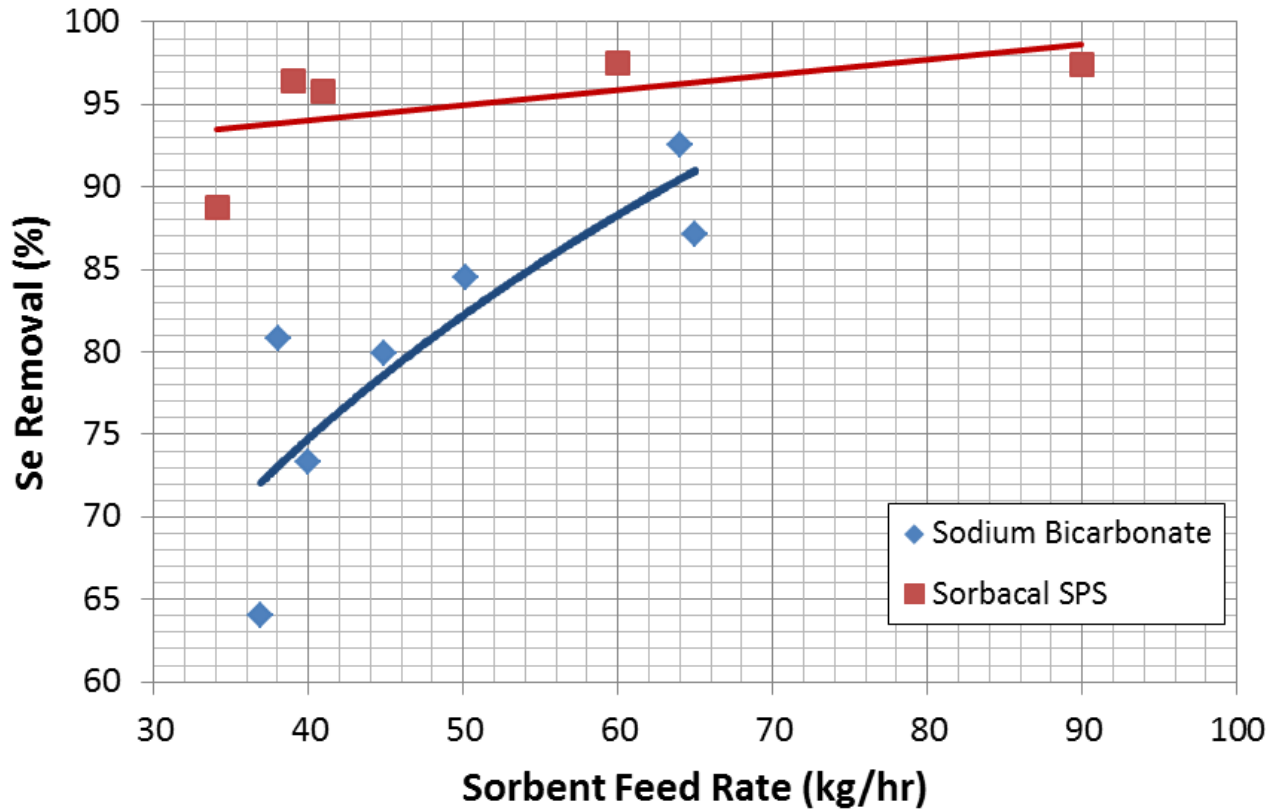
- **ILB coal fired to produce high SO₂, high HCl concentrations in the flue gas**
 - Provide competition for heavy metals on hydrated lime adsorption sites
 - EPA M29 used to quantify metals concentrations

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




Se Reduction – Glass Plant



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

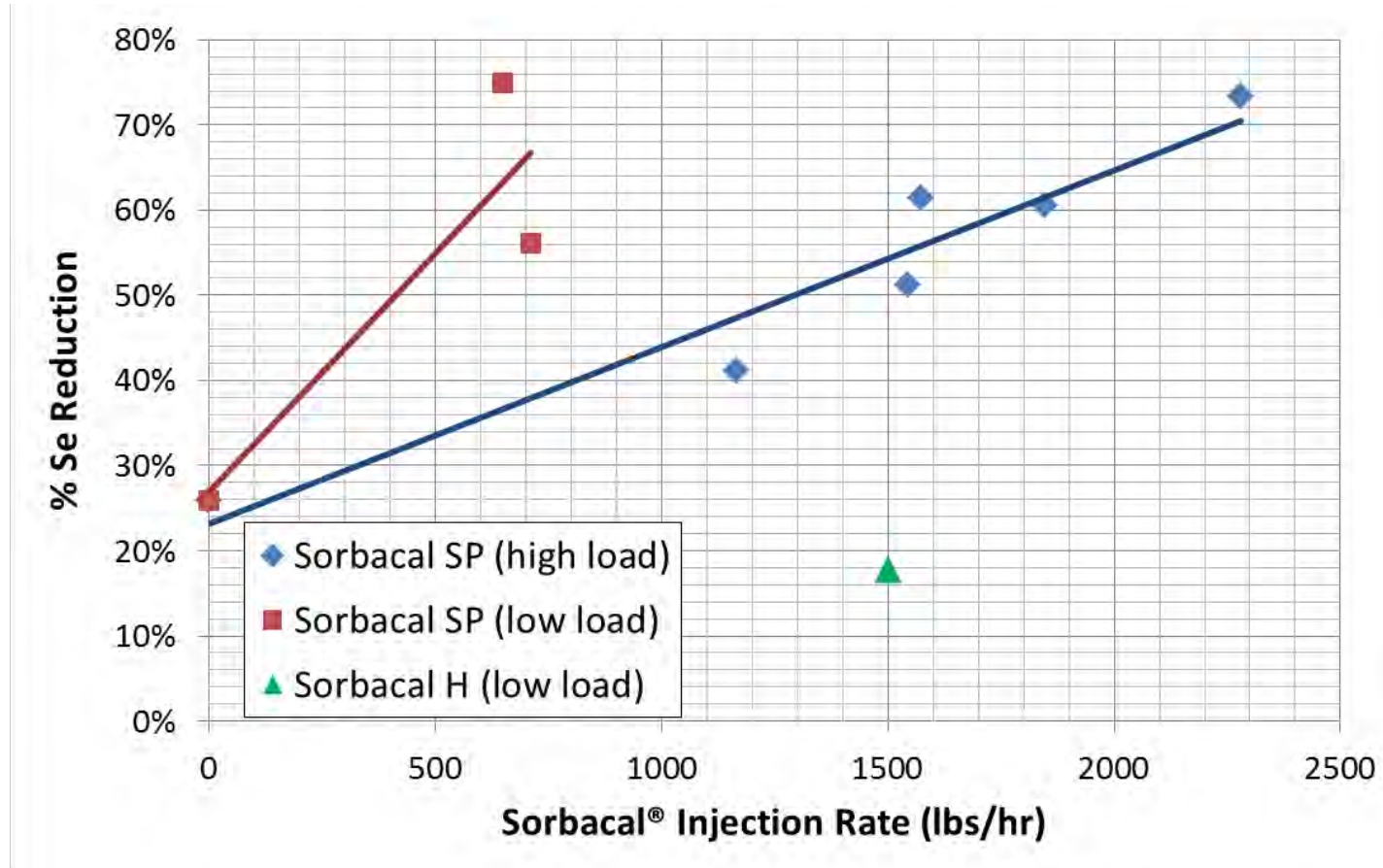
Hydrated Lime Physical Properties



Sorbent	Standard Hydrated Limes	FGT Grade Sorbocal [®] H	Sorbocal [®] SP	Sorbocal [®] 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

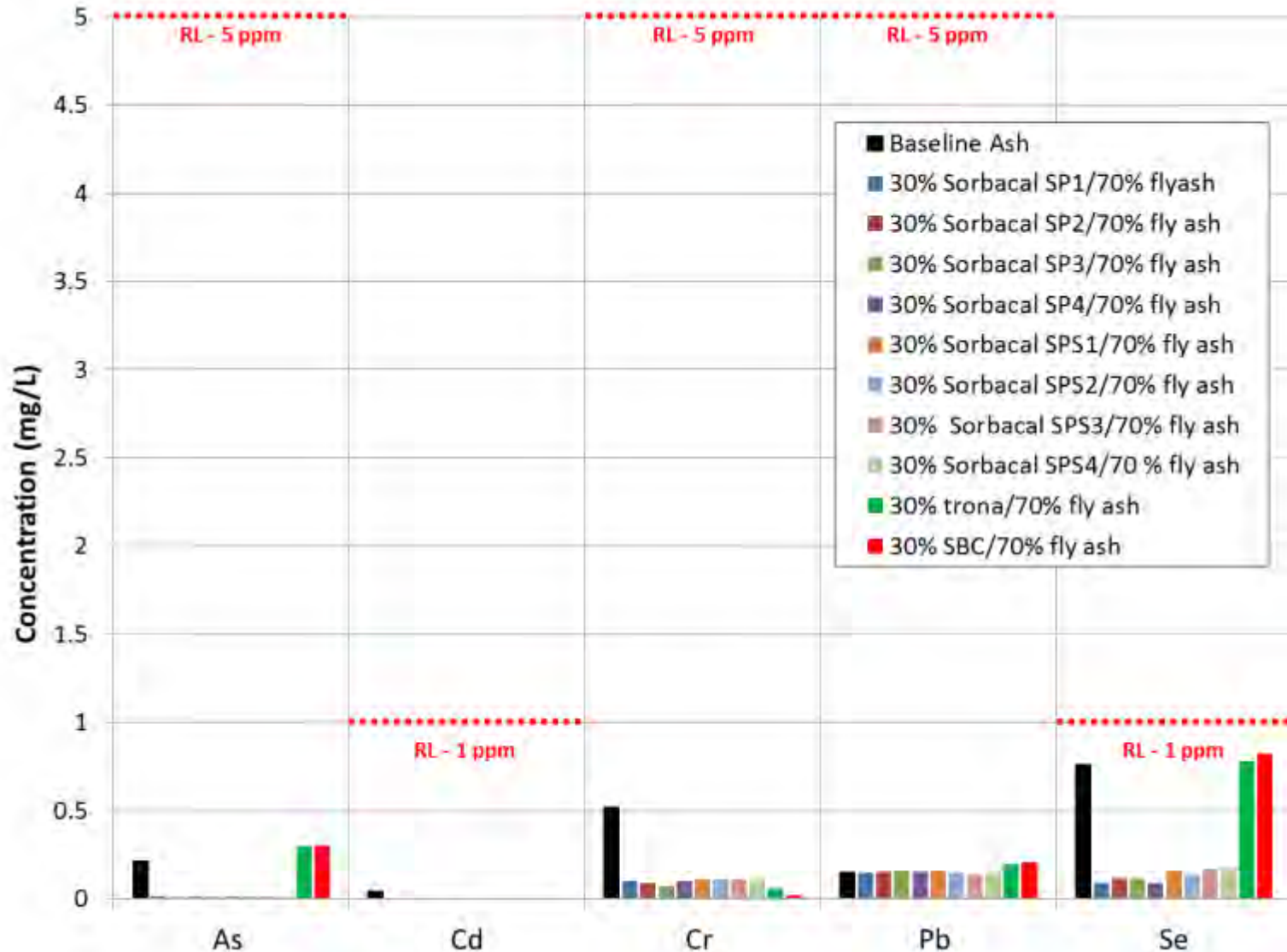
Do Physical Properties Impact Capture?

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

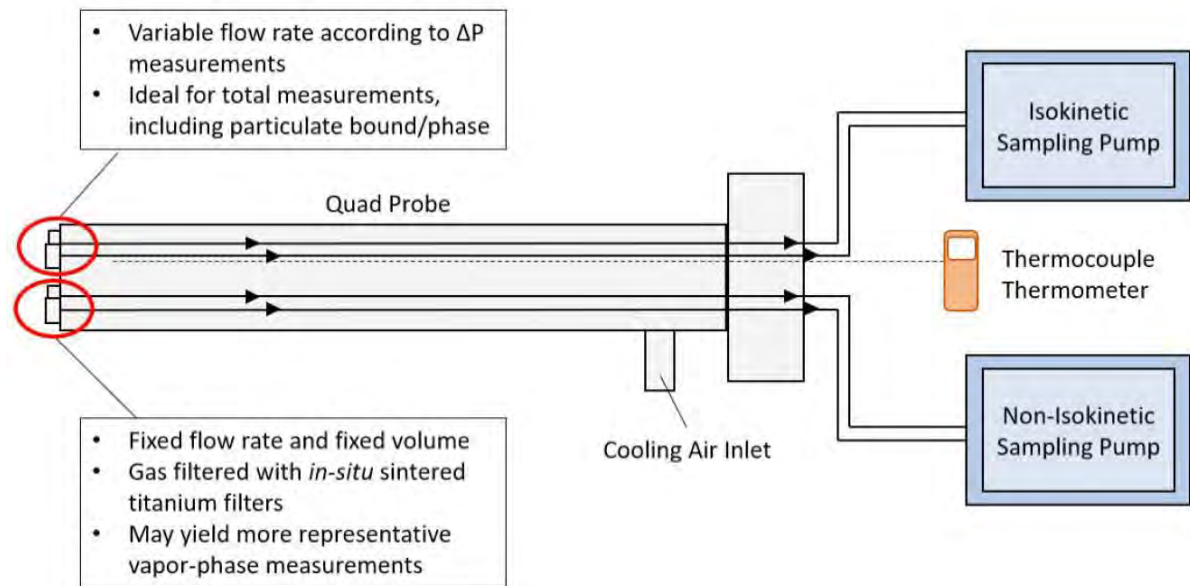
Se/As Sorbent Traps: Sampling

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



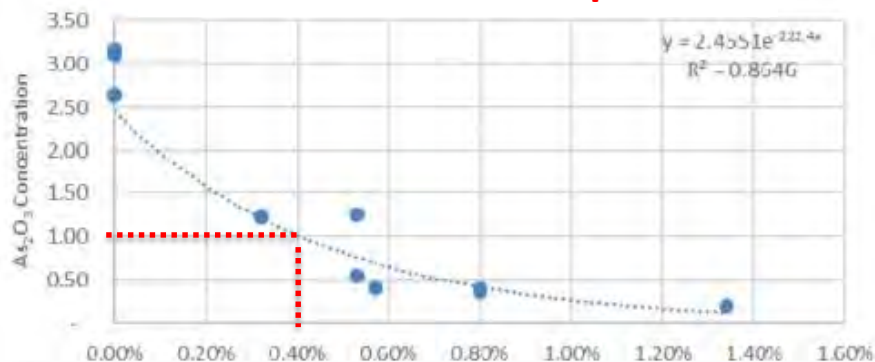
Partitioning

- 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.

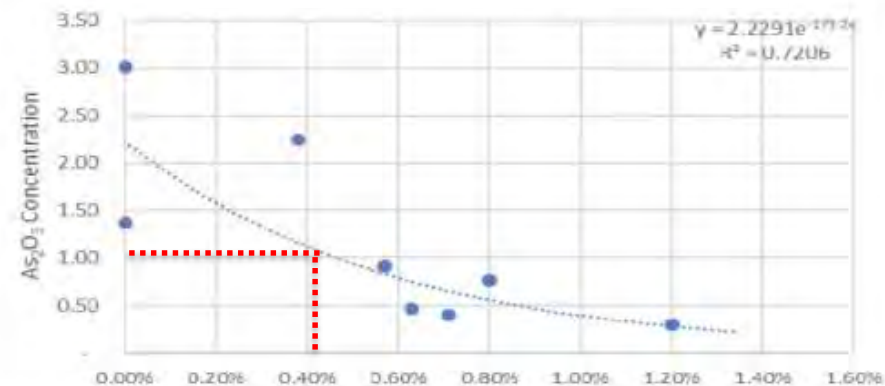


Comparisons between EPA M29 and OL Traps

Ohio Lumex Traps



EPA M29



- 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)

Conclusions



- Limestone effectively mitigates SCR poisoning by As and P
- Hydrated lime ahead of SCR to mitigate SO₃ 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