

REINHOLD ENVIRONMENTAL Ltd.



**2018 NO_x-Combustion Round Table
& Expo Presentation**

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Dry Sorbent Injection : Past, Present, and Future ***Case Studies on Heavy Metals and Acid Gas Abatement***

Gerald (Jerry) Hunt

Ian Saratovsky, PhD

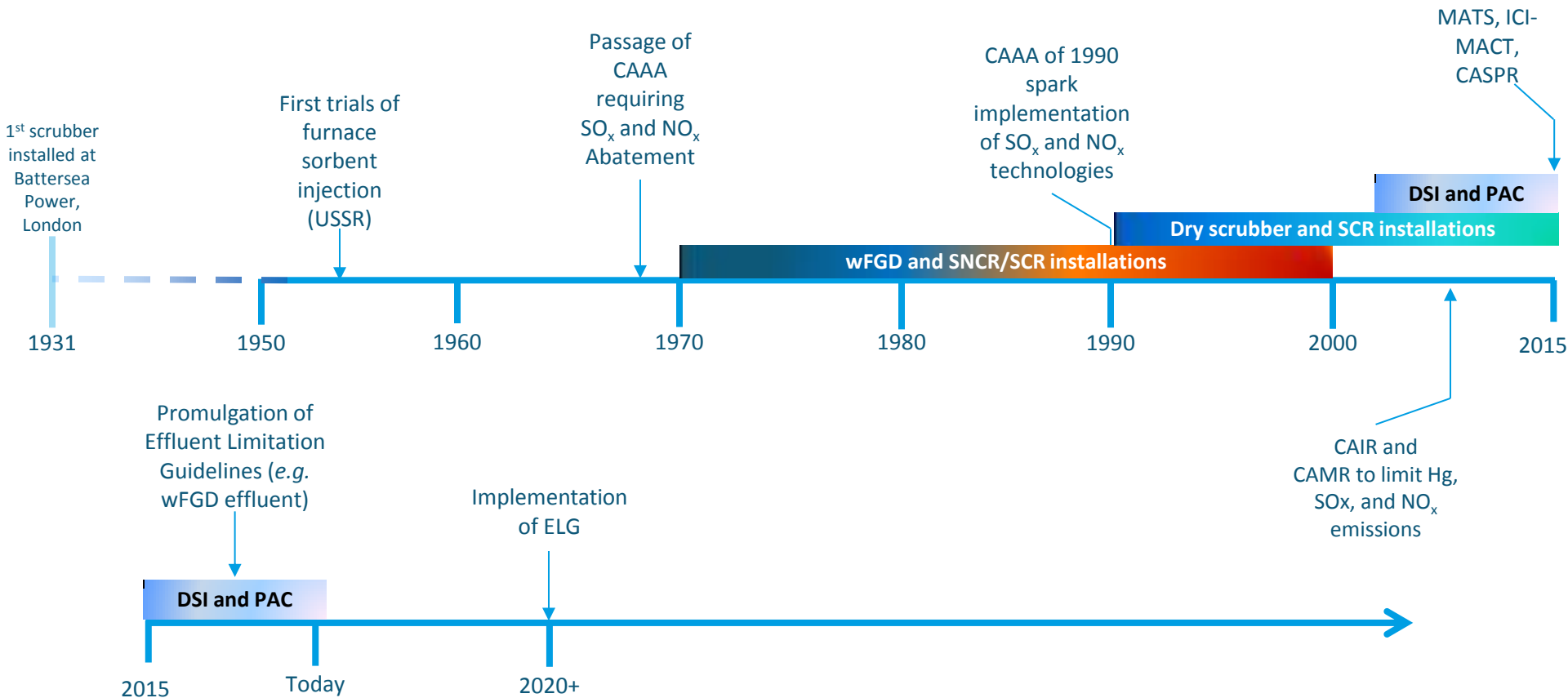
Martin (Marty) Dillon, PE

Greg Filippelli, PE

Topics

- *Past:* History of Acid Gas Abatement
 - Scrubbing
 - Dry sorbent injection (furnace and post-combustion)
- *Present:* Sorbents
 - Differences and critical factors
 - Case studies
- *Future:* Heavy Metals Abatement with DSI
 - Arsenic and selenium capture background
 - Case studies

Abridged History of Air Pollutant Abatement Technologies



Where It All Began

- Battersea Power Station (London) – 1931
 - Farmer in Manchester sued local utility for ruining crops
 - London Power mandated to implement pollution controls
 - designed first wet scrubbers
 - Water and iron oxide (catalyst) : $\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$
 - Once-through to/from Thames River
 - During drought periods, river dropped to $\text{pH} < 5$
 - “Gas washing” discontinued in 1960s



Where It All Began

- Battersea Power Station (London)
 - Plant decommissioned in 1986
 - 2017/2018



Modern Desulfurization: 2000 - 2025

- Wet FGD highly efficient – high capital
- Requirement to treat water effluent (2016 ELG Rule)
 - Unlikely that new wFGD will be built in U.S.
 - Many existing wFGD may become decommissioned
- Circulating Dry Scrubbers (CDSs) – medium capital
 - 92%-95% SO₂ reduction
- Dry sorbent injection (DSI) – low capital
 - Development since 1960s for SO₂, SO₃
 - Major driver for advancement in U.S. – HCl for MATS
 - HCl control up to 95%+
 - SO₃ control up to 95%+
 - SO₂ control: varies between 50% - 95%
 - depends on application

Dry Sorbent Injection (1950s – 2000)

- First attempts in 1930s
 - Limestone added to grate in grate-fired boiler
- 1950s – 1990s
 - Limestone injected into furnace
 - Utilization rates typically $\leq 10\%$; often $\leq 7\%$
 - Hydrated lime (*i.e.* Ca(OH)_2) injected into furnace
 - Utilization rates typically $\leq 18\%$
 - Performance often deemed “inadequate”
- 1990s – 2005
 - In-duct humidification (within 30 °C approach to adiabatic saturation)
 - B&W LIMB and Coolside processes
- 2005 and beyond
 - Dry sorbent injection system improvements
 - Engineering better sorbents
 - HCl regulations (*e.g.* MATS and ICI-MACT)
 - Widespread DSI system installation

Hydrated Lime Sorbents: Past and Present

Engineering Better Sorbents

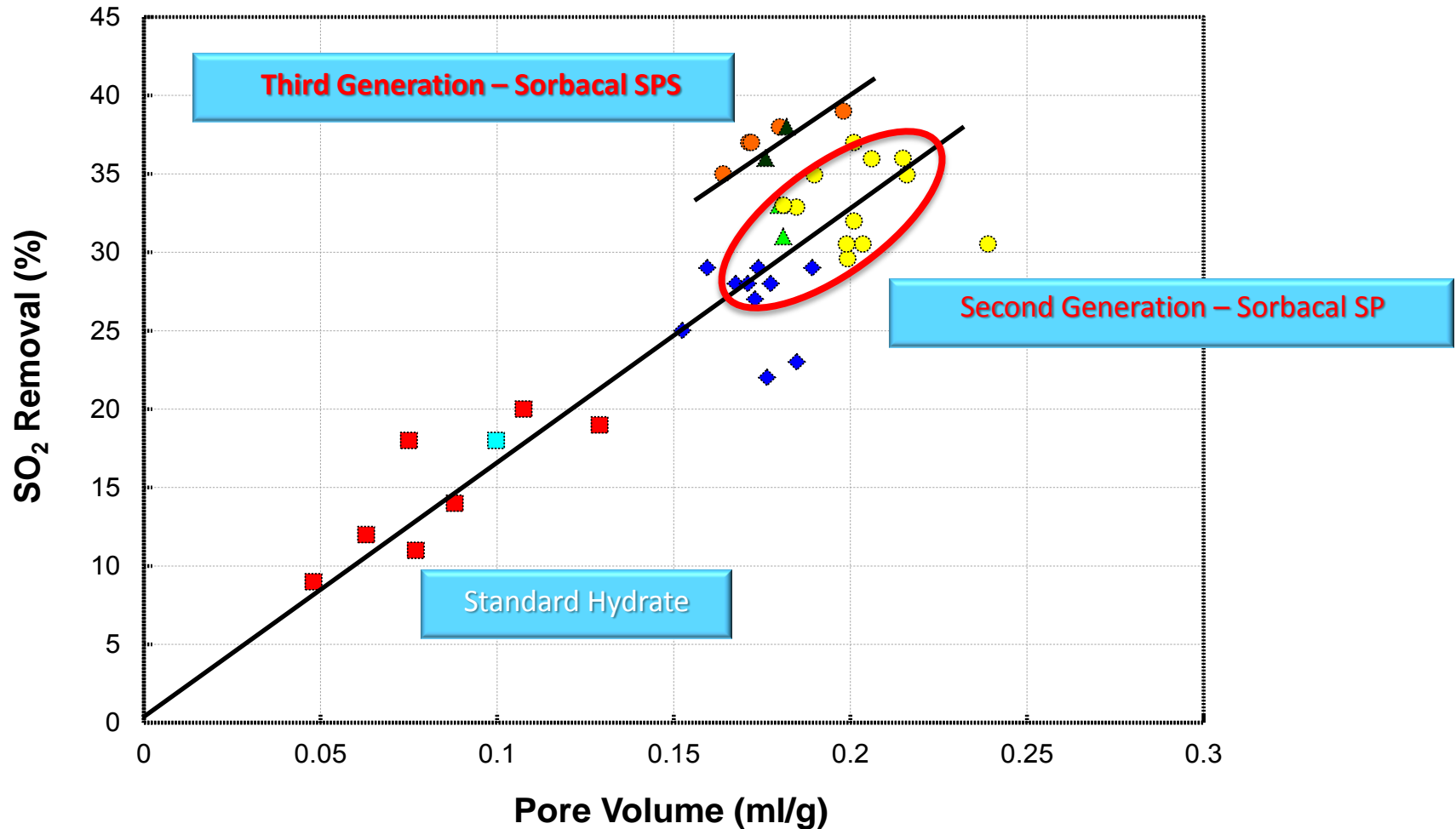


Sorbent	Standard Hydrated Limes	FGT Grade Sorbocal [®] H	Sorbocal [®] SP	Sorbocal [®] SPS
Figure				ACTIVATION 
Typical Available Ca(OH) ₂ - [%]	92 – 95	93	93	93
Typical Surface Area - [m ² /g]	14 – 18	20	40	40
Typical Pore Volume - [cm ³ /g]	~0.07	0.08	0.20	0.20
Typical D ₅₀ - [microns]	5 – 7	5 – 7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

- Chemical activation of pores enhances acid gas reactivity

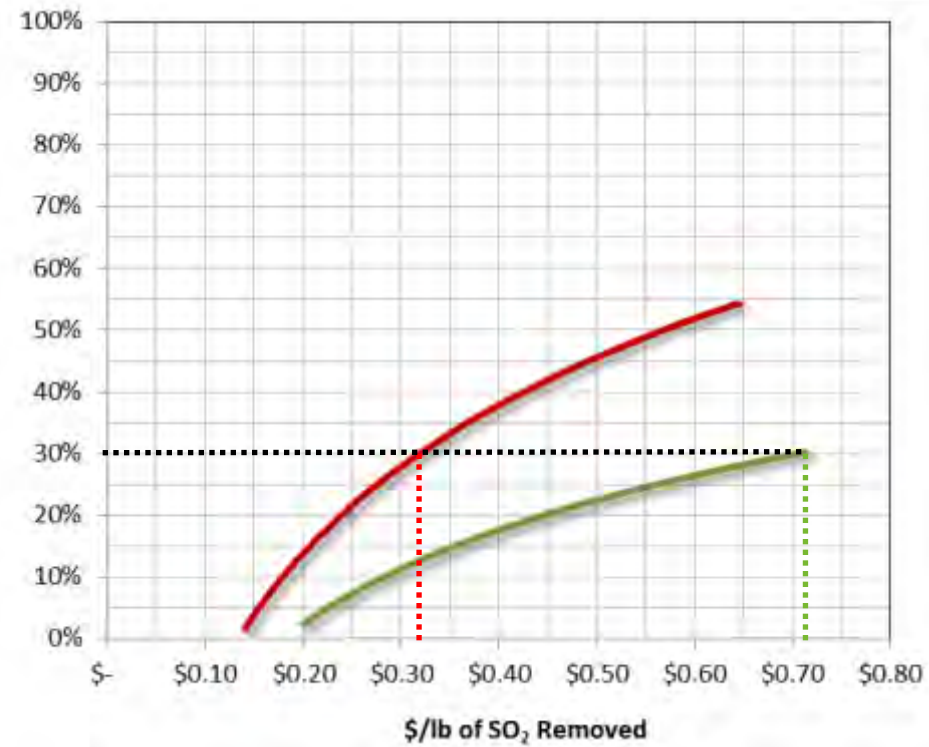
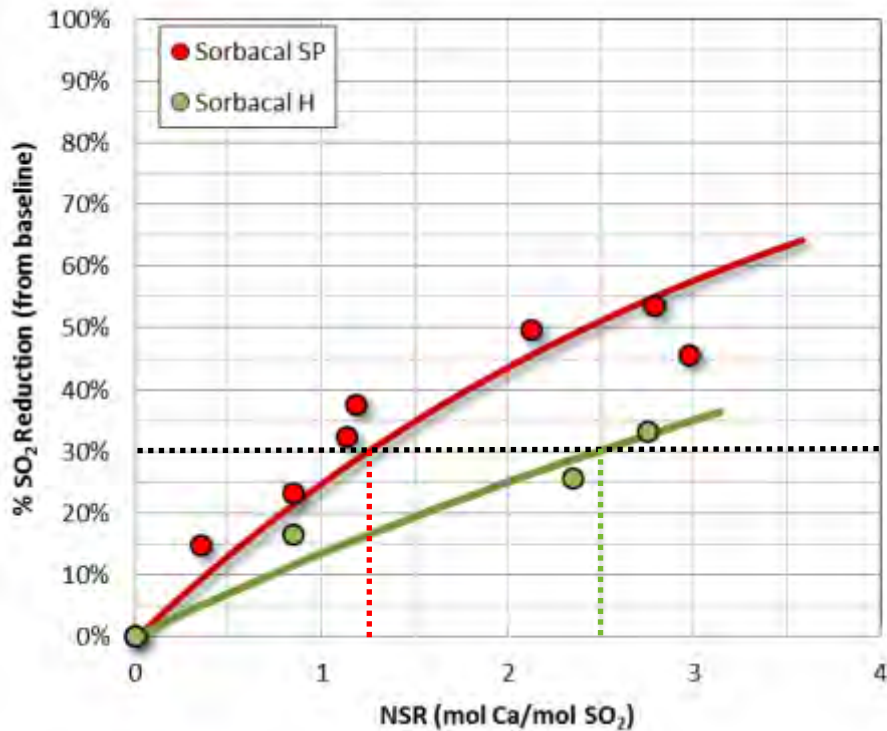
Reactivity Property Relationships

- Linear relationship between reactivity and pore volume



Why Enhanced Sorbents like Sorbacal[®] SP?

- Efficiency savings result in cost savings



Benefits of Enhanced Sorbents

- Reduced sorbent consumption (typically 30%-50% less)
 - Cost savings on annual sorbent spend
- Less fly ash generated
 - Cost savings on reduced fly ash disposal
- Increased DSI silo storage capacity
- Fewer trucks delivered to site
- Less mass loading on ESP/FF and ash handling systems
- Fuel flexibility to utilize higher Cl/sulfur fuels

Critical Properties of Hydrated Lime

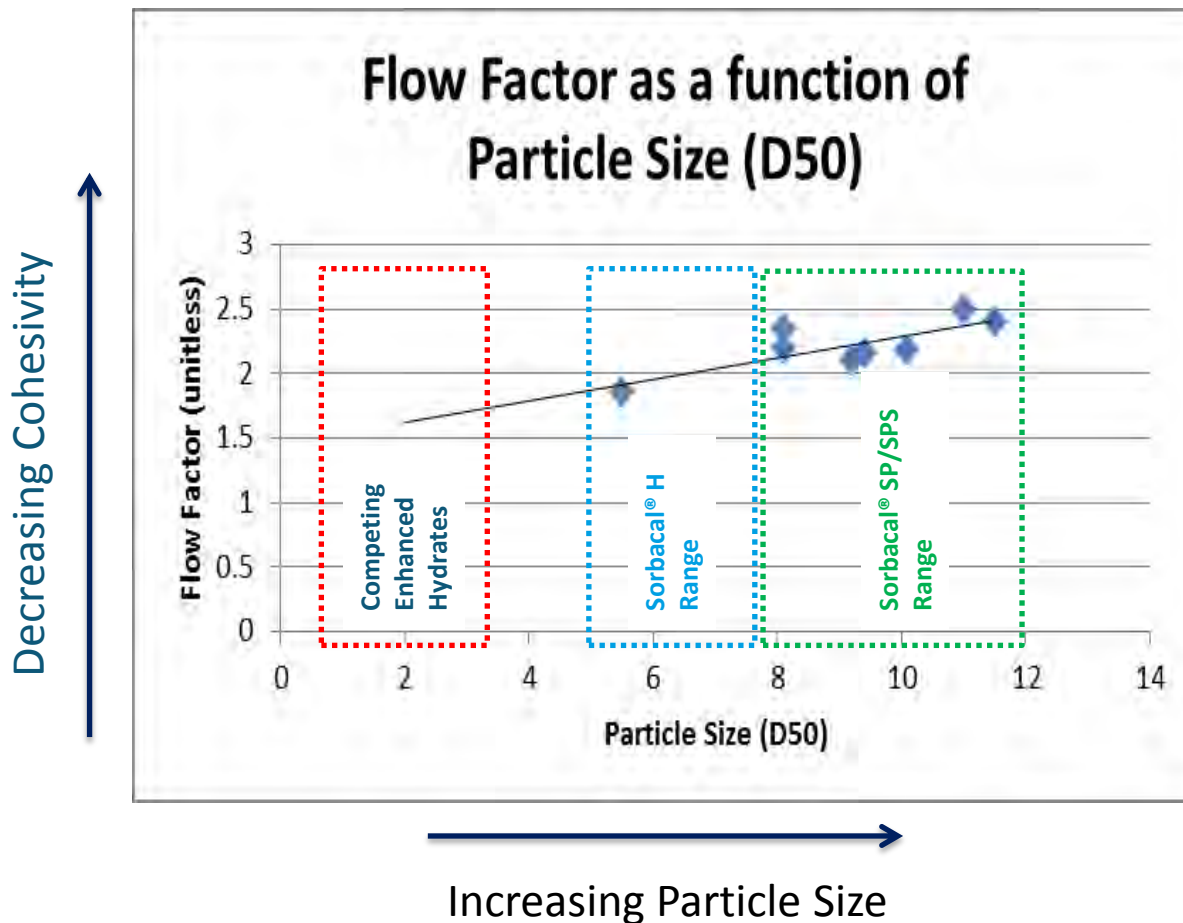
- Hydrate lime suppliers have pursued numerous product enhancements to improve performance
 - Improved reactivity
 - Increased chemical utilization
 - Physical modification
 - Surface additives

Sorbent	Standard Hydrated Lime	Sorbacal® H	Sorbacal® SP	Sorbacal® SPS	Units
Figure					-
Typical Available Ca(OH) ₂	92 – 95	93	93	93	%
Typical Surface Area	14 – 18	> 20	~40	~40	m ² /g
Typical Pore Volume	~0.07	0.08	~0.20	~0.20	cm ³ /g

Sorbacal® SP/SPS
 Specific Surface Area: ≥40 m²/g
 Porosity: ~0.20 cm³/g
 D₅₀: 8-12 μm

Typical Hydrated Lime
 Specific Surface Area: 20 m²/g
 Porosity: ~0.07 cm³/g
 D₅₀: 2-5 μm

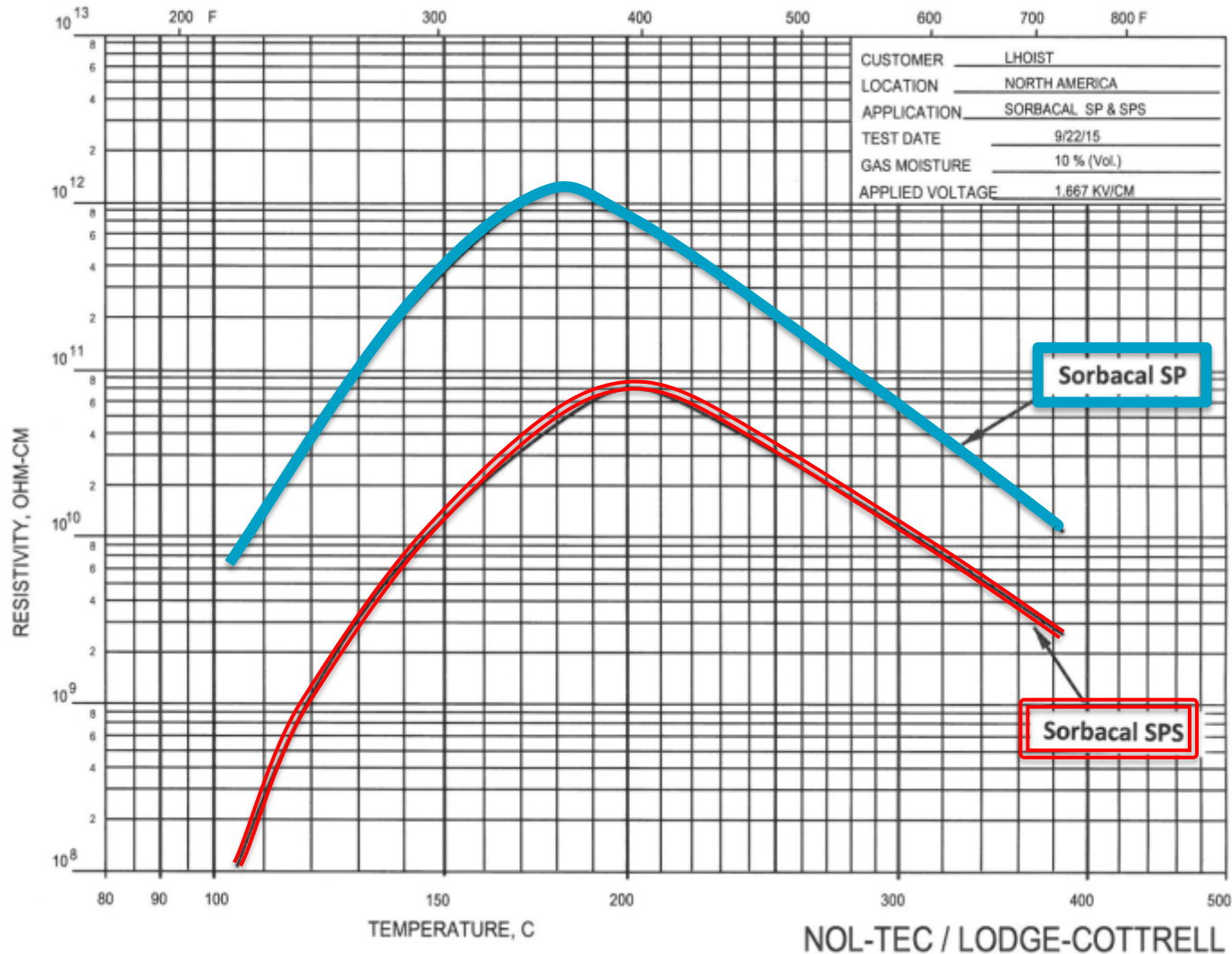
Effect of Particle Size on Flowability



- Flow Factor improves with increasing D_{50} PSD
- Approximately a 22% improvement in flow properties associated with an increase in particle size from a $D_{50} = 5 \mu\text{m}$ and a $D_{50} = 10.5 \mu\text{m}$

Particle size directly impacts the flow/handling characteristics of the material

ESP Performance : Sorbacal[®] Products

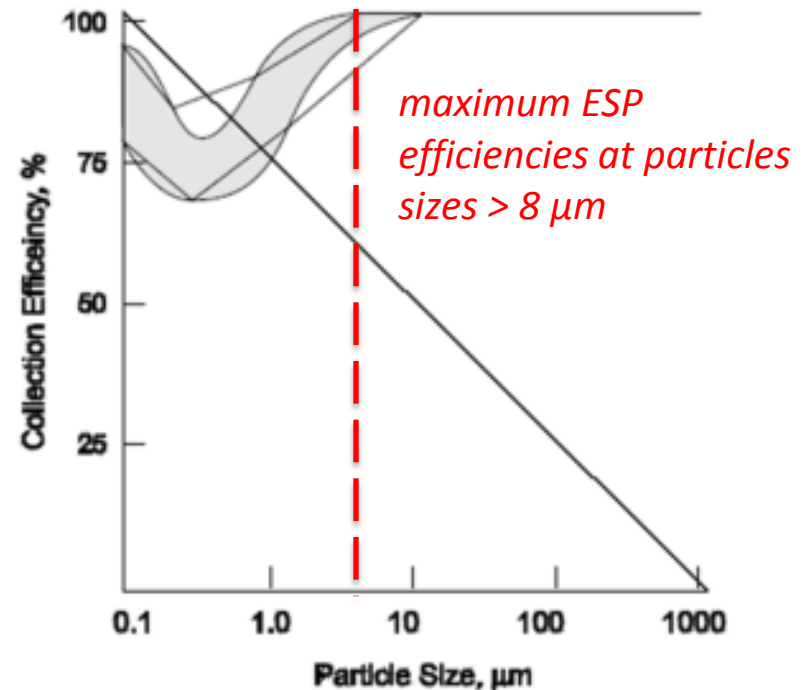


Impact of Particle Size on ESP Performance

ESP Performance Parameters:

- Particle size distribution
 - Ask for D_{10} , D_{50} , and D_{90}
- Ash Loading
- Ash Resistivity

Effect of particle size on ESP collection efficiency



Richards, J. R. Control of Particulate Matter Emissions Student Manual Control of Particulate Matter Emissions Student Manual. APTI Course 413, Third Ed. 2000, 1–358

Present: What Are We Doing Today?

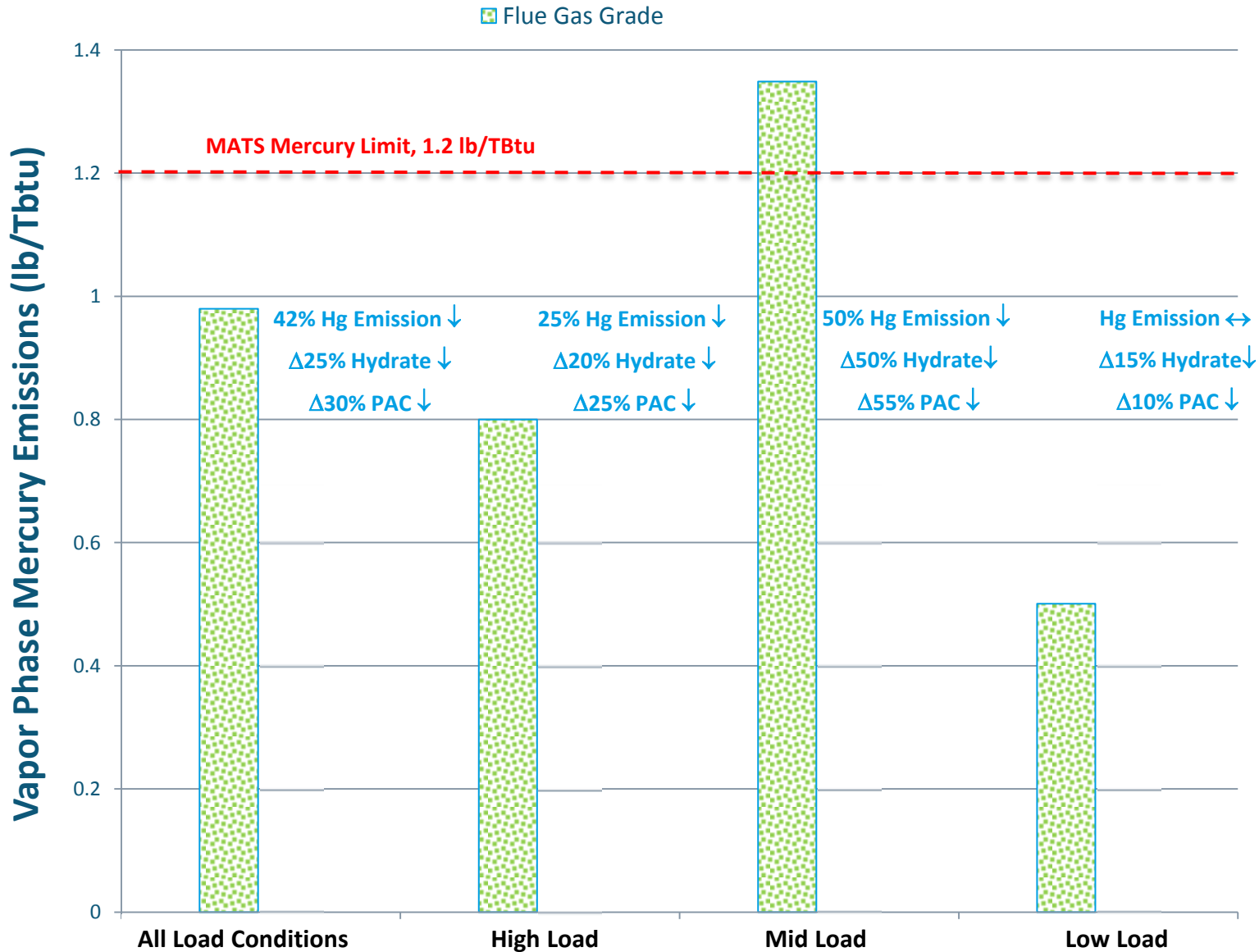
DSI: 2012 - Present

- Acid gas regulatory compliance
 - SO₂ and HCl are primary targets
 - MATS, ICI-MACT, NESHAP, NAAQS, etc.
- System optimization
 - Upgrades to enhanced sorbents
 - Modification of injection location
 - Smarter DSI systems for improved sorbent distribution
 - Parametric testing and tuning
- SO₃ control
 - Blue plume abatement
 - Corrosion protection (APH and ESP/baghouse)
 - SCR minimum operating temperature (MOT)
 - Ammonium bisulfite (ABS) condenses at relatively high temperatures
 - Removal of SO₃ ahead of SCR = lower loads can be attained
- Facilitate Hg abatement - PAC protection
 - SO₃ competes with Hg for binding sites
 - Capture of SO₃ prior to PAC injection

PAC Protection – Utility Unit (2017)

- Boiler → Econ → **DSI** → AH → **ACI** → ESP → ID Fan → Stack
- Process conditions
 - Flue gas flow rate: ~1 M ACFM
 - Flue gas moisture: ~6% by volume
 - Baseline concentrations: ~30 ppm_v SO₃
 - Flue gas temperature at DSI location 325°F
- DSI → Array with multiple lances
- Sorbents Tested → Flue Gas Grade vs. Sorbacal[®] SPS
- Challenges → Vapor Phase Hg due to SO₃ interference



Utility PAC Protection – Test Data

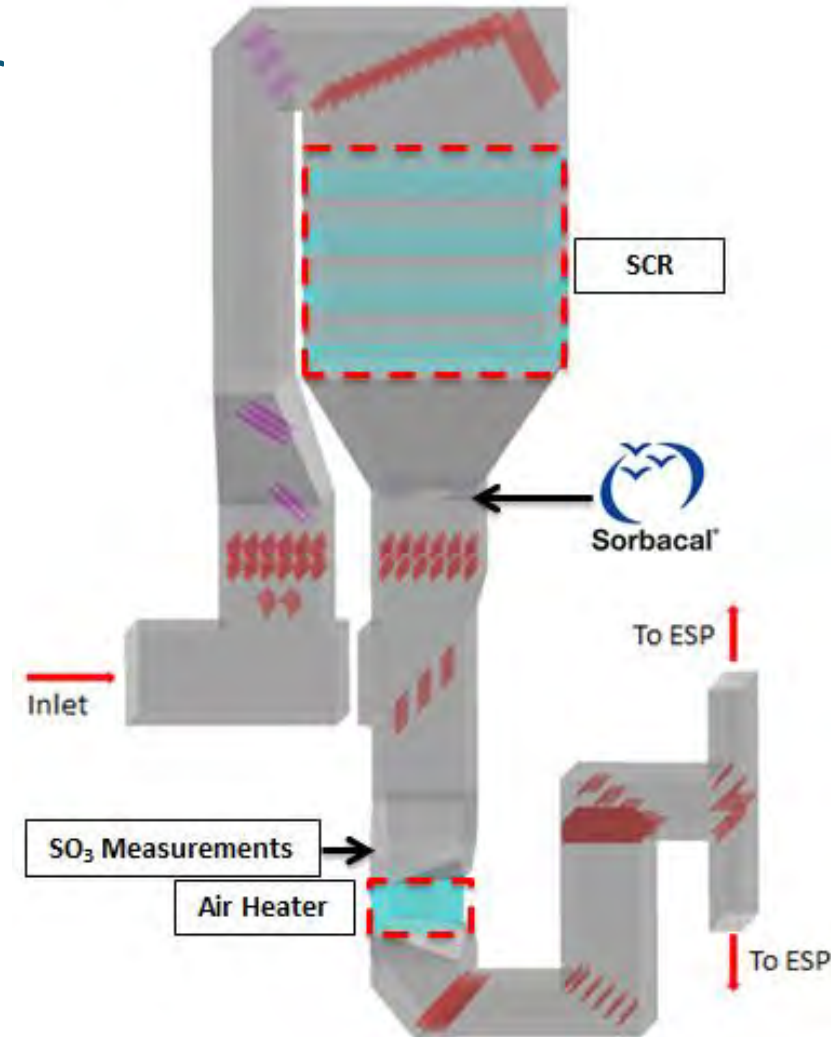


Operational Benefits Associated with Upstream SO₃ Control

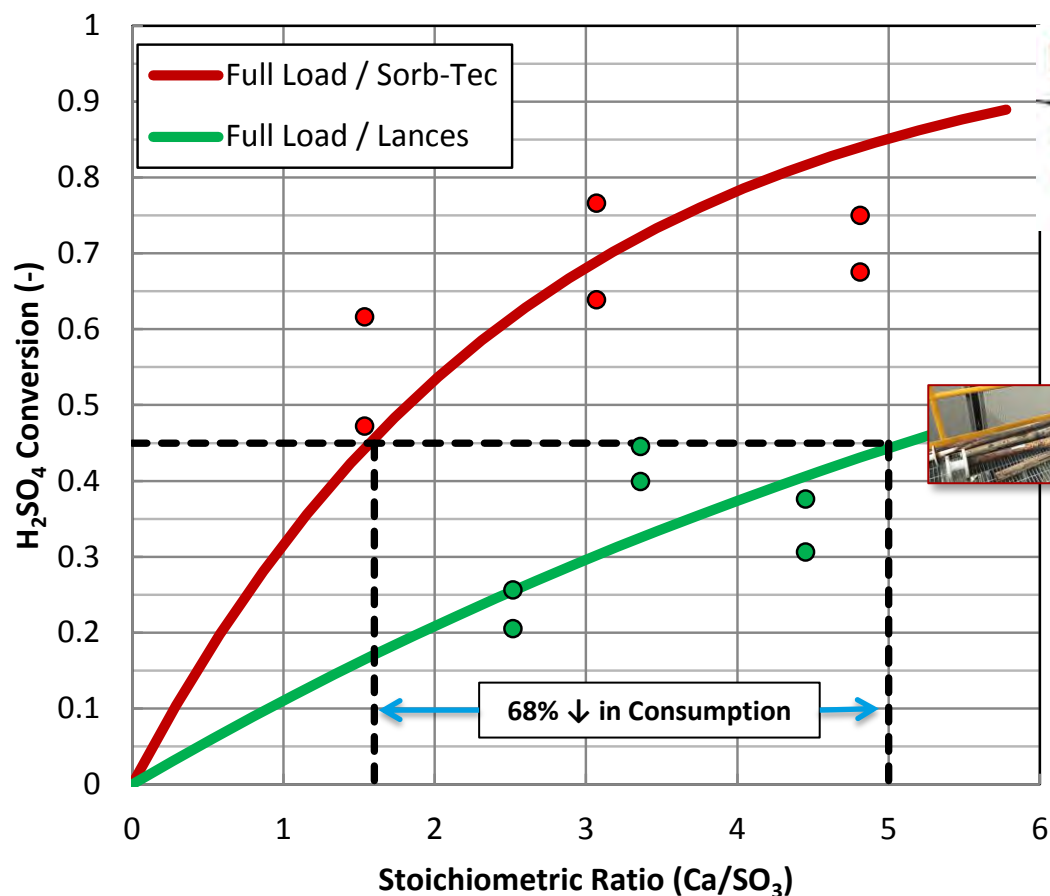
- Reduced air heater fouling
 - Eliminate resulting unplanned outages
 - Reduce outage duration
- Avoid SCR minimum operating temperature (MOT) constraints
 - Achieve desired boiler minimum operating load
 - Allows for economics-driven, rather than ABS-driven
 - Avoid having to bypass SCR
 - Avoid purchasing NO_x credits
- Back-end Corrosion Protection
- Heat Rate Improvement
 - Full benefits may not be achievable w/o modification to air heater and/or baskets
- Avoid trona and need for quench air

SO₃ Case Study – Operational Benefits

- LNA teamed up with  for DSI trial at Large EGU to control SO₃
- Objective: Achieve 15-20 ppmv H₂SO₄ at AHI
- Standard lances tested vs. 
- Four (4) gas sampling trains simultaneously sampling at air heater inlet (AHI)

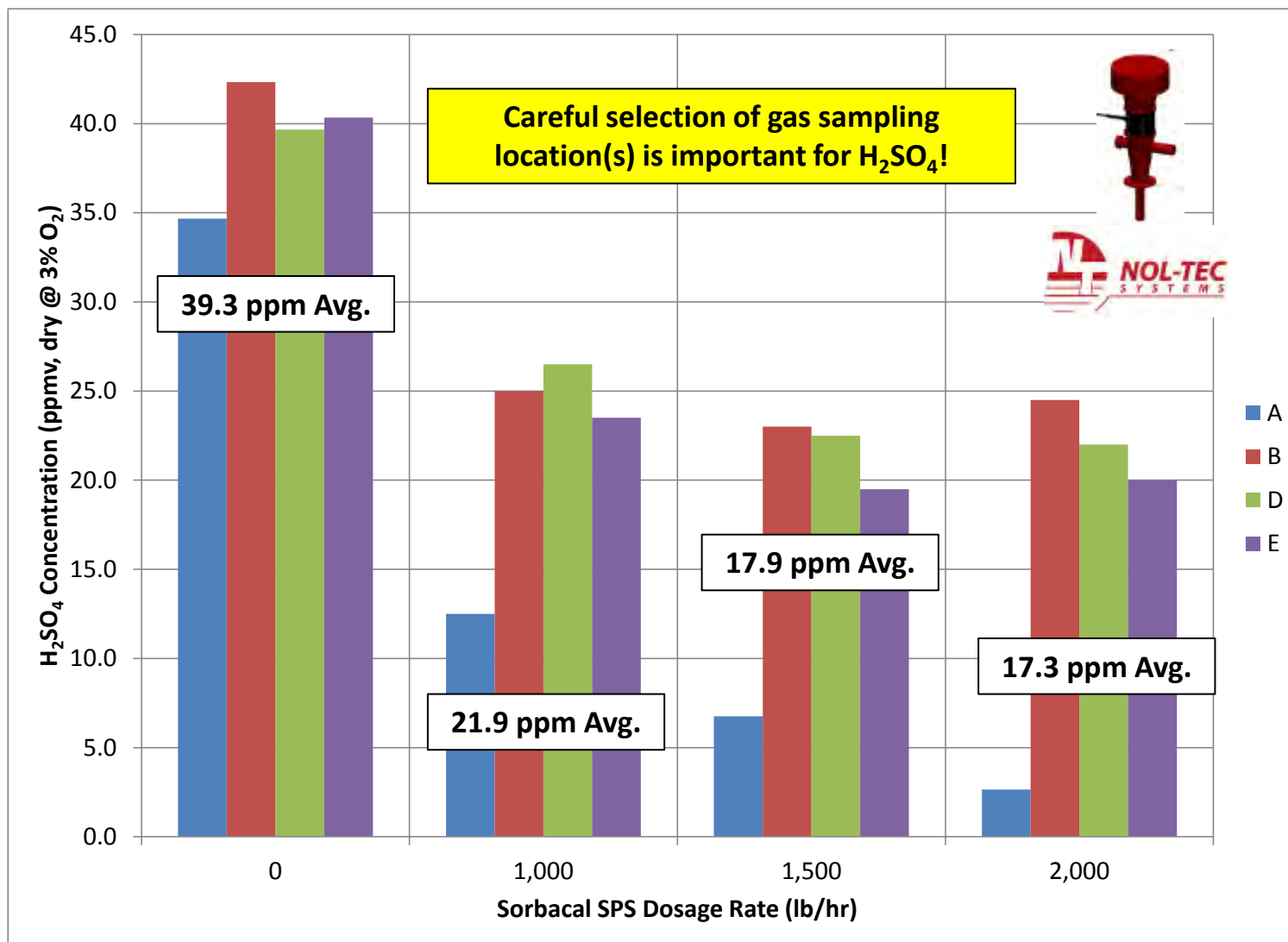


SO₃ Case Study – Operational Benefits

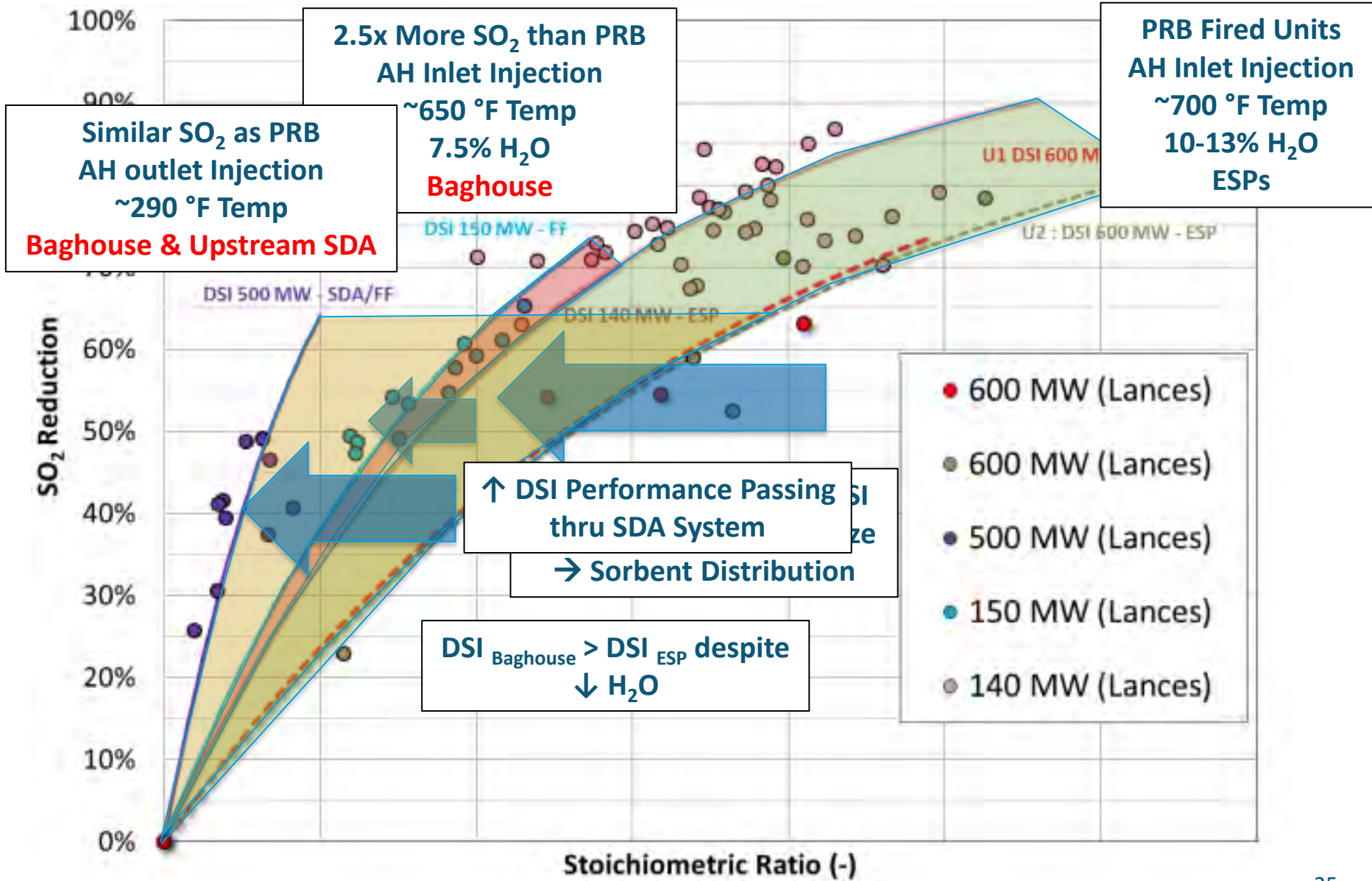


- Sorb-Tec ↓ dosage by 68% over standard lances
- “Good” mixing in-flight is challenging
 - < 2 seconds in-flight
- Desired H₂SO₄ concentration unattainable with lances alone

SO₃ Case Study – Operational Benefits



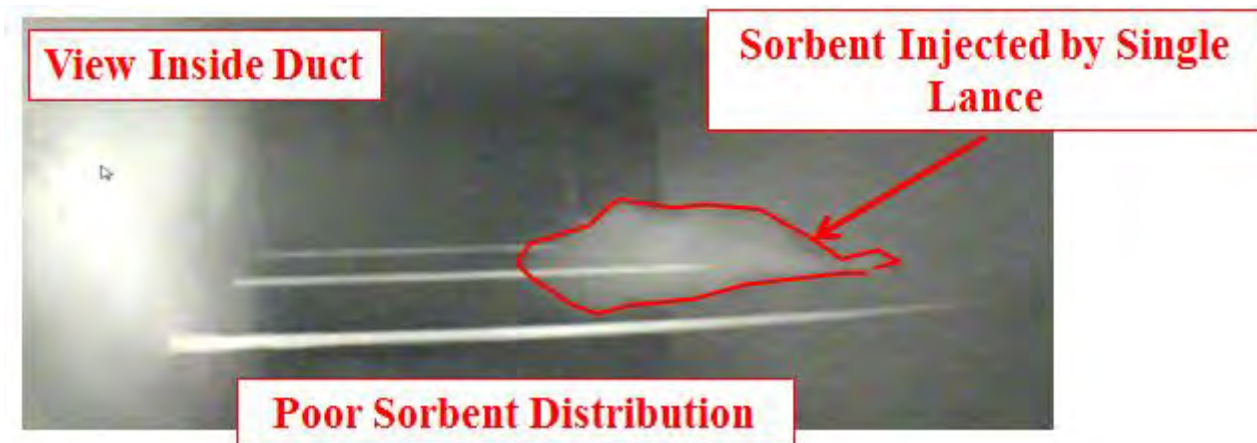
SO₂ – Unit Size Impacts



System Optimization for Cost Improvement

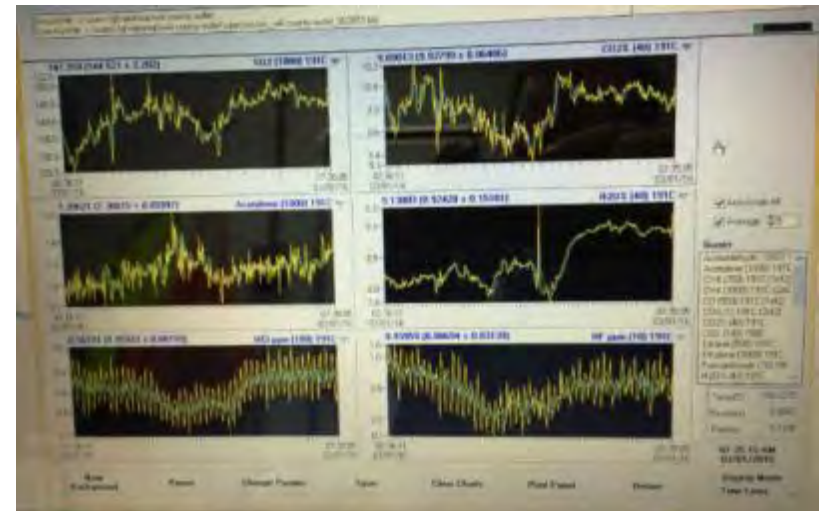
Continuous Improvement

- Identify potential performance improvements
 - Parametric tests
 - Sorbent distribution optimization
 - Duct camera
 - Better lances/more lances
 - Analytical tools (*e.g.* pre- and post-injection measurements)
- More efficient sorbents
 - Enhanced sorbents often provide reduced total cost



Analytical Tools

- Two FTIRs to measure pre- and post-injection
 - Simultaneous HCl, SO₂, CO₂, H₂O
- Monitor impact of process variable on performance
- Evaluate improvements from enhanced sorbents, improved lances/lance configurations

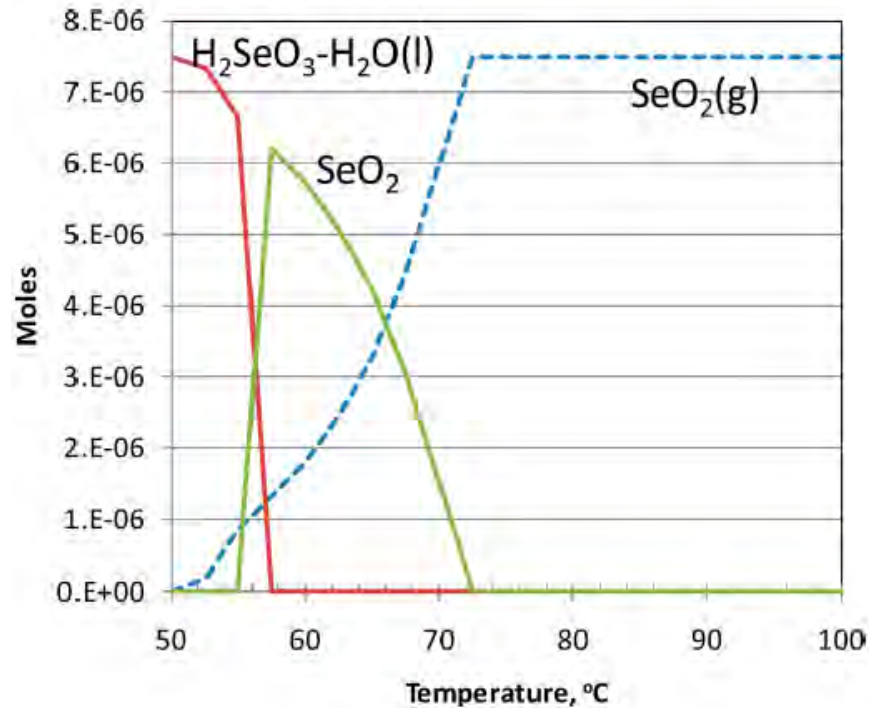


Future: Hydrated Lime Capture of Arsenic and Selenium

Role of DSI in ELG Compliance

- Does hydrated lime capture As and Se?
 - Under what conditions?
 - Does chemistry support field trials?
- Fate of reaction products?
 - What happens after hydrated lime reacts with As and Se?
 - Stable in landfills with respect to leaching?

Gas Phase 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 Hydrate Capture Se?

Results of Theoretical Studies

Binding Energies (kcal/mol)	Sorbent	
	CaO	“hydrated CaO”
Adsorbate		
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

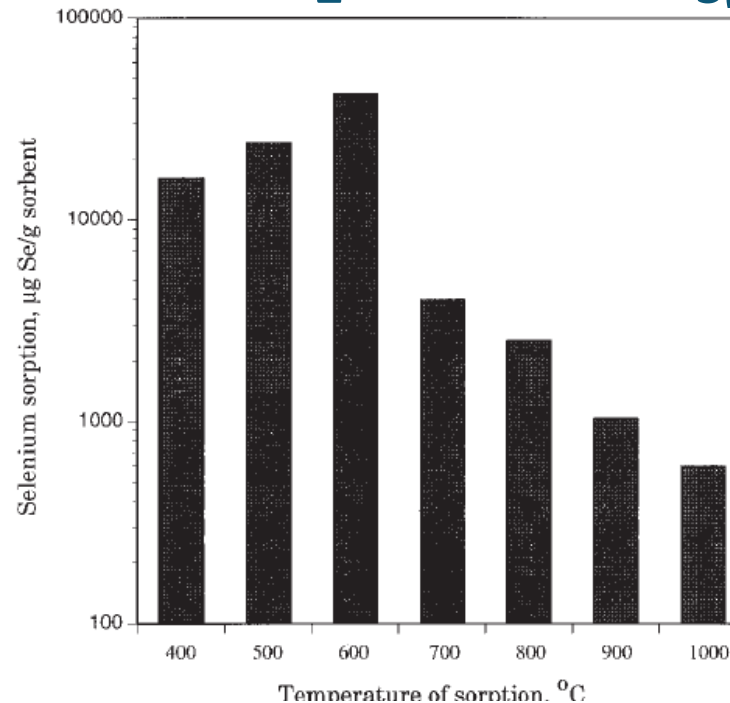
- Hg⁰ *does not* significantly adsorb onto CaO or Ca(OH)₂
- HgCl_{2(g)} physically adsorbs onto CaO and Ca(OH)₂
- SO_{2(g)} chemically adsorbs onto CaO and Ca(OH)₂
- SeO_{2(g)} chemically adsorbs onto CaO and Ca(OH)₂
- **More favorable : SeO_{2(g)} + CaO/Ca(OH)₂ > SO_{2(g)} + CaO/Ca(OH)₂**

Hydrated Lime Injection for Se Removal

- 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”

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 $\text{CO}_{2(g)}$
 - Reaction with $\text{CO}_{2(g)}$ is kinetically slower than with $\text{SeO}_{2(g)}$
- CaSeO_3 is predominant product (not CaSeO_4)

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

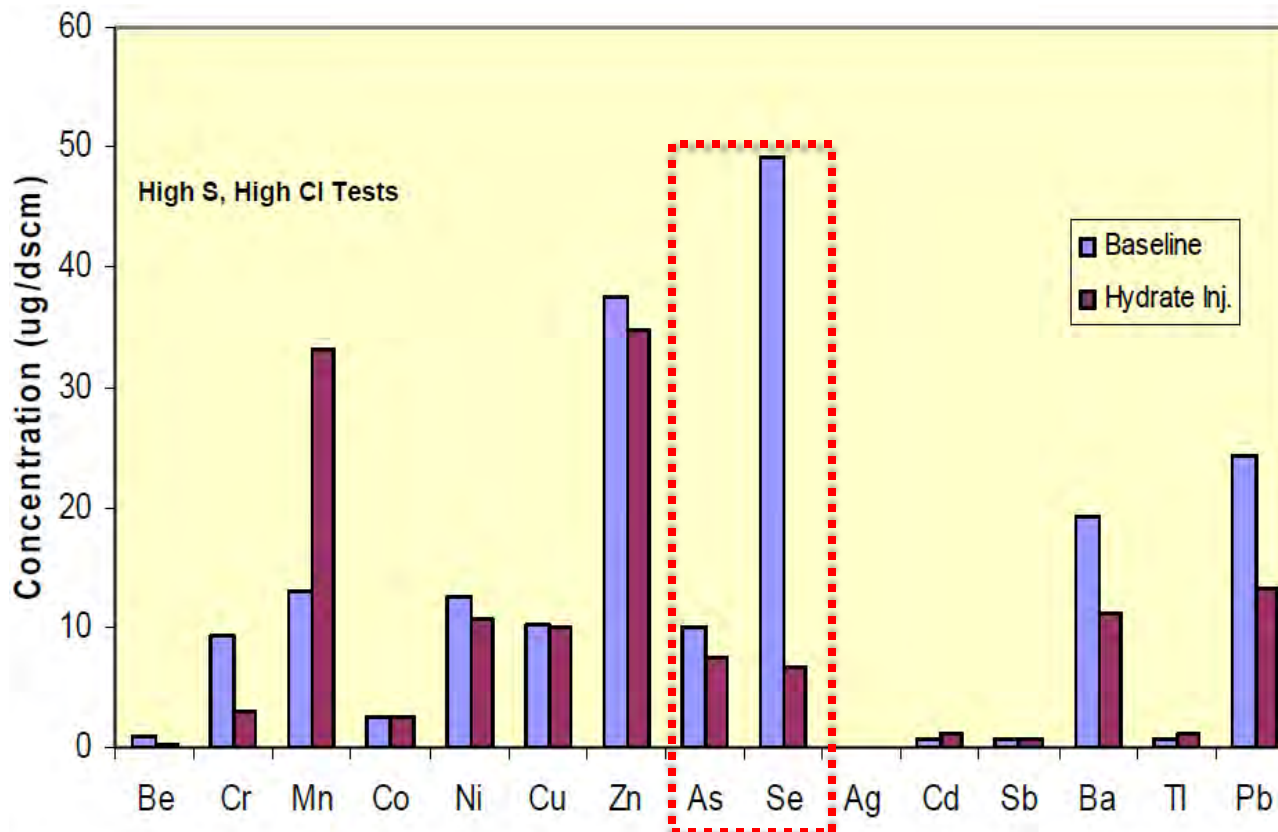
Fate of Se and As Compounds

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 products less soluble than sodium counterparts**
 - Reduced leaching potential following incorporation with fly ash
 - Under neutral pH, at room temperature

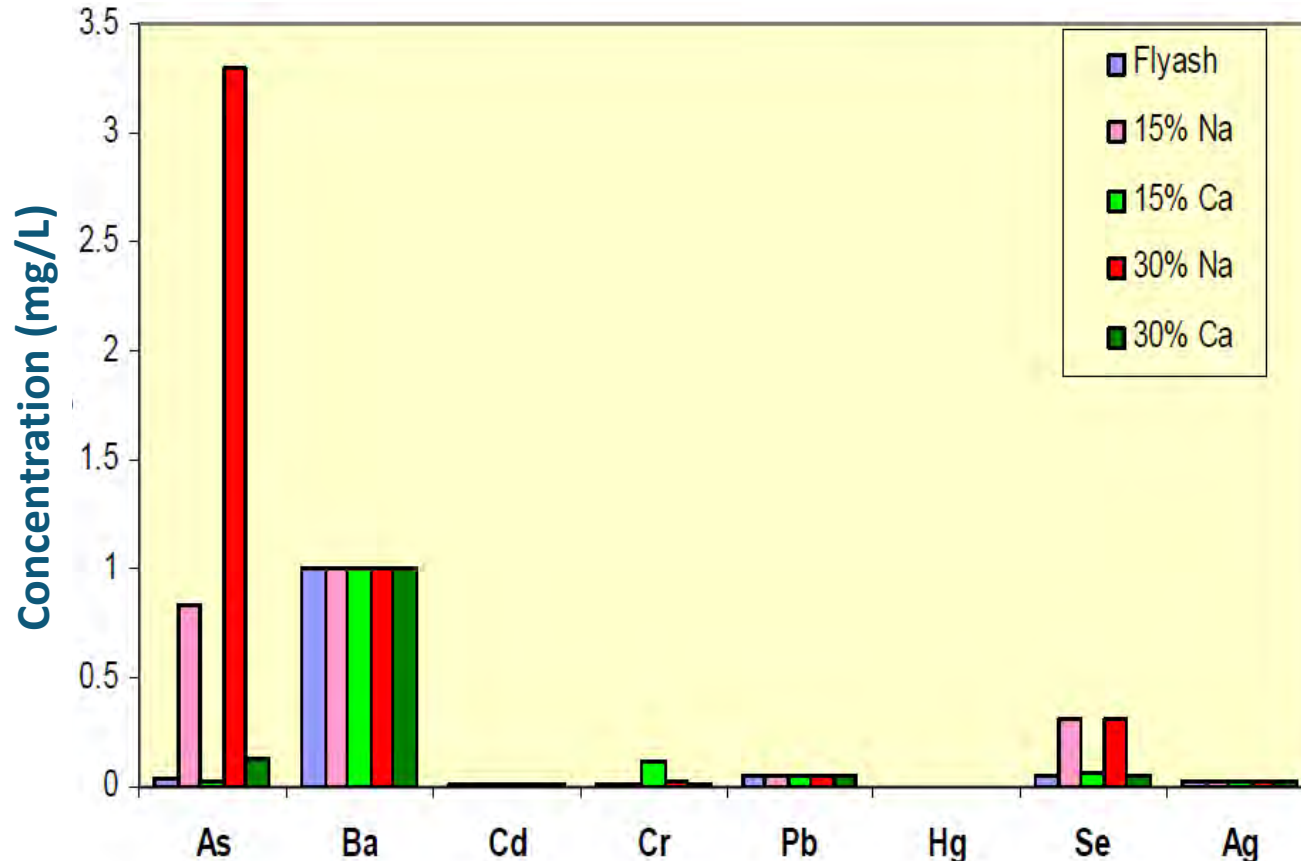
Se Abatement Trial Results

Pilot-Scale Boiler Data – Gas Phase



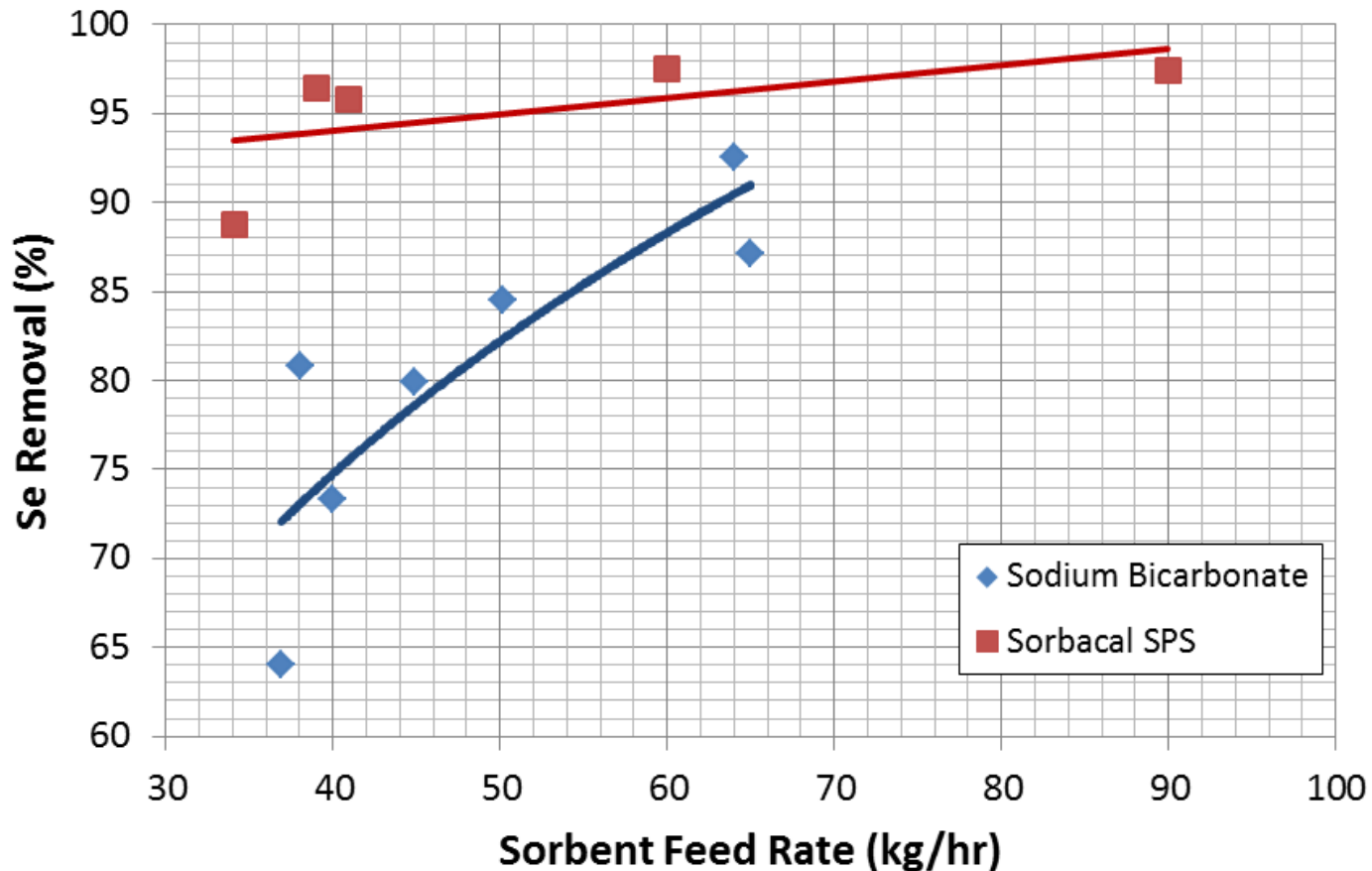
- ILB coal fired to produce high SO₂, high HCl concentrations in the flue gas
 - Provide competition for heavy metals on hydrated lime adsorption sites

Pilot-Scale Boiler Data – Ash Leaching



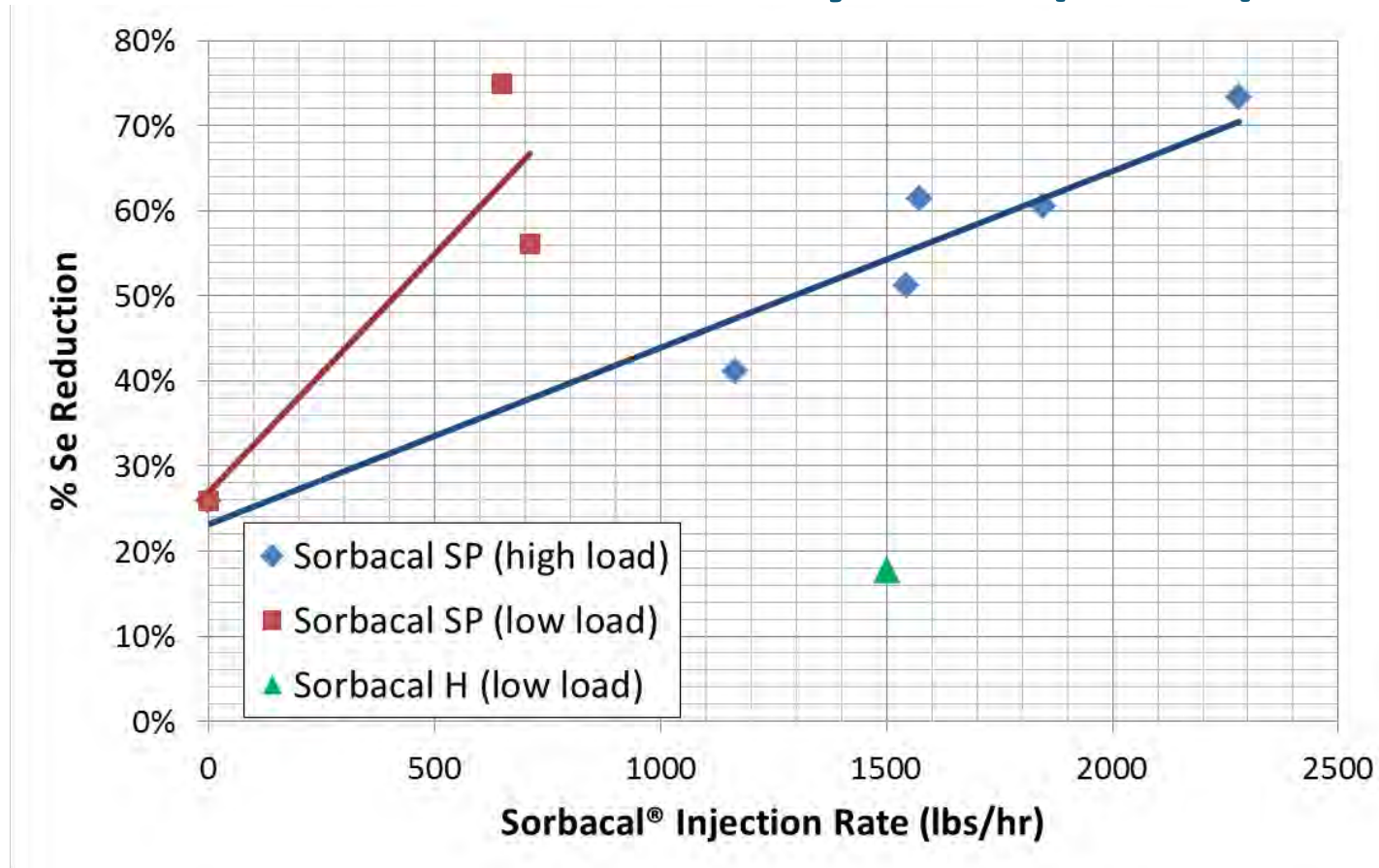
- Hydrated lime decreased leaching of As and Se
 - SBC injection increased leaching
- TCLP and SPLP results were similar

Se Reduction – Glass Plant



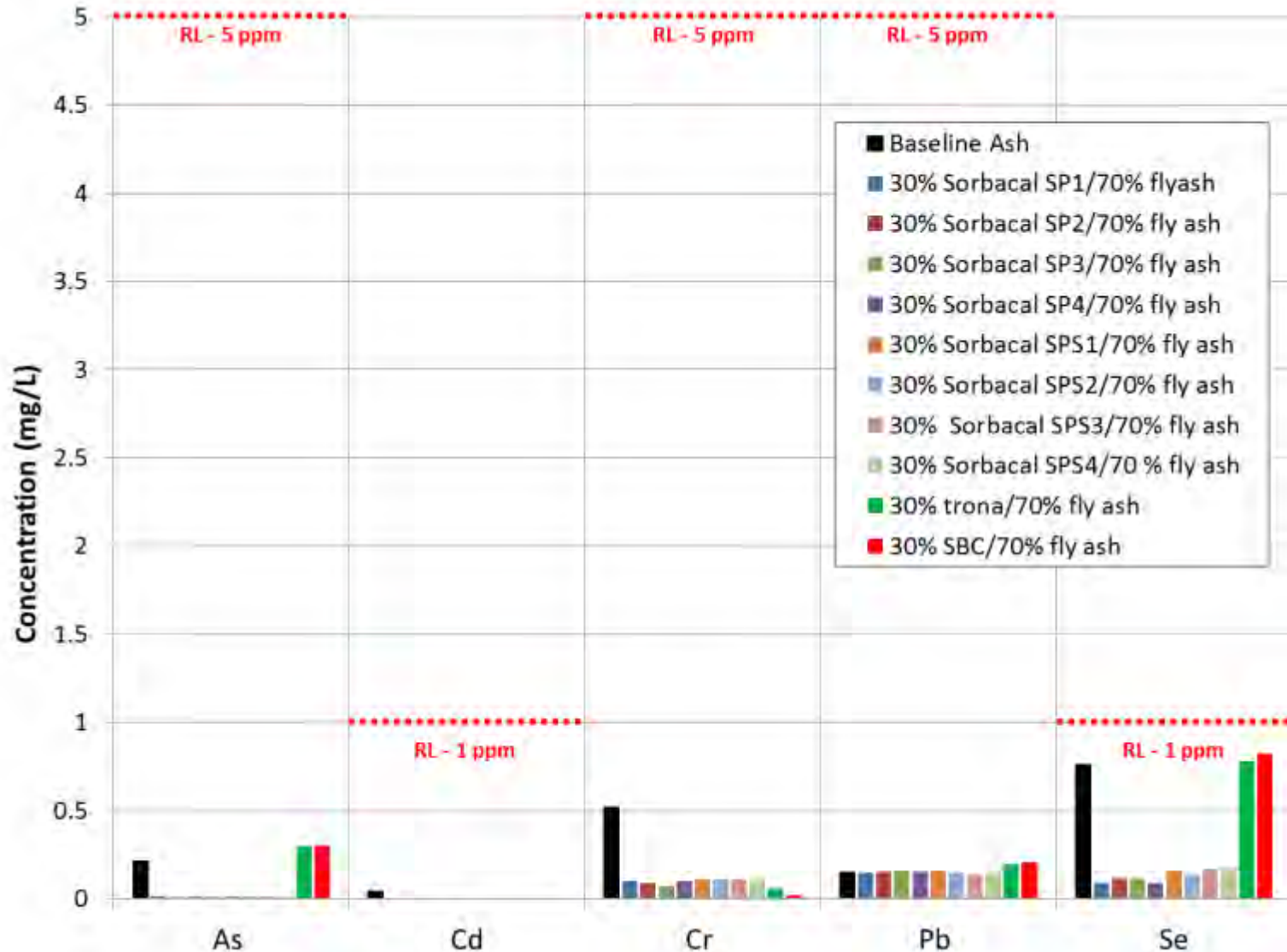
- Feeding Sorbacal[®] SPS continuously since 2008
- Primarily driven by Se, HF, and SO₂ capture

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



■ Sorbocal® SP and SPS injection reduce leaching of RCRA metals in bituminous fly ash

Thank you for your time!



Lhoist North America Flue Gas Treatment Solutions Team

Marty Dillon, PE

Melissa Sewell Marty.Dillon@lhoist.com

Lhoist North America

Director, Flue Gas Treatment [Gerald \(Jerry\) Hunt](mailto:Gerald.Hunt@lhoist.com)

Office 720.536.5294

Cell 817.255.6257

melissa.sewell@lhoist.com

www.lhoist.us

Greg Filippelli, PE

Greg.Filippelli@lhoist.com

Dr. Ian Saratovsky

Ian.Saratovsky@lhoist.com

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