

Reinhold Environmental Ltd.



2010 NO_x-Combustion Round Table & Expo Presentation

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MONTOUR POWER PLANT
Washingtonville, PA

Arsenic Mitigation at PPL Montour Lessons Learned

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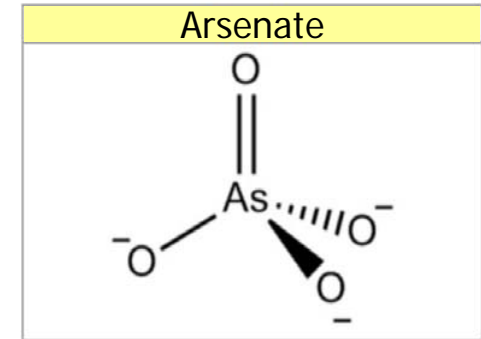
Martha Watson, E.ON Engineering

Agenda

- Background on Arsenic in Coals
- Removal & Capture of Arsenic - Poisoning Mechanism and Prevention
- Testing of Gaseous Arsenic
- PPL Montour Station Introduction
- PPL Montour Limestone Feed System
- Arsenic & CaO in Montour Coals
- Why add Limestone to Montour Coals?
- Economic Advantages of Arsenic Mitigation
- Reservations about Arsenic Mitigation
- Questions?

Arsenic (As) in Coals – Quick Facts

- Arsenic is a very coalphile element
- Coal contains organic and inorganic As, 3 dominant forms:
 - **Pyritic:** Arsenical pyrite, Arsenopyrite (FeAsS)
 - **Organic:** typically grouped with other sulphophile elements (Zn, Cd, Hg, etc.)
 - **Arsenate:** AsO_4^{-3}
- Arsenic distribution in coal is non-uniform – i.e. hard to get a representative sample
- During combustion most of As_{pyr} , As_{org} , and some “shielded” As-bearing micro mineral phases, volatilize as As_2O_3 into the gaseous phase and only a minor part like As_{clay} remains in bottom ash
- World average As content in bituminous coals is 9.0 and in lignites 7.4 ppm
- U.S. average As content in coal is 24 ppm
- Strong regional variations of As distribution due to geologic specificity of the individual coal basins



Arsenic in Coals – Summary of U.S Sources

Coal basin	Arsenic (ppm)			Calorific value (Btu/lb)			Arsenic input loadings (in 10 ³ lbs per 10 ¹² Btu)		
	Median	Mean	Number of samples	Median	Mean	Number of samples	Median	Mean	Number of samples
Appalachian, Northern	16	28	1,607	12,570	12,440	1,500	1.3	2.3	1,500
Appalachian, Central	7.8	22	1,742	13,360	13,210	1,643	0.6	1.7	1,643
Appalachian, Southern	29	71	974	12,850	12,760	968	2.2	5.8	968
Eastern Interior	10	19	289	11,510	11,450	255	0.92	1.7	255
Fort Union	4.2	8.5	280	6,340	6,410	257	0.7	1.4	257
Green River	1.2	4.8	391	9,950	9,560	264	0.13	0.44	264
Gulf Coast	2.2	3.2	141	6,440	6,470	110	0.34	0.54	110
Pennsylvania Anthracite	3.2	8.1	51	12,860	12,530	39	0.25	0.79	39
Powder River	1.6	4.2	602	8,050	8,080	486	0.2	0.5	486
Raton Mesa	0.99	1.4	40	12,500	12,300	34	0.073	0.1	34
San Juan River	0.92	2.5	185	9,380	9,640	169	0.095	0.26	169
Uinta	0.7	1.5	249	11,290	10,820	222	0.074	0.14	222
Western Interior	14	21	286	11,320	11,420	261	1.2	1.9	261
Wind River	2.4	7	41	9,630	9,570	41	0.25	0.75	41

[Data from Bragg and others, 1998 U.S., U.S. Geological Survey]

Removal & Capture of Arsenic (As) – Quick Facts

- Pre-combustion conventional coal cleaning:
 - May be efficient if As_{pyr} is the dominant form
 - Cannot remove organic bound or micro mineral arsenic (shielded grains of As-bearing sulphides)
- Arsenic is captured from flue gas on active cation sites of the fly ash surface (e.g. Ca^{2+} and Mg^{2+}) by means of chemisorption
- Arsenic can be readily leached from acid (SiO_2 -rich) bituminous coal ashes but can be very difficult from alkali (CaO -rich) lignite ashes
- $As_2O_3(g)$ condenses on the pore system of SCR catalyst



*** Gaseous arsenic is one of the predominant catalyst deactivation mechanisms in coal fired SCR applications in the US**

Capture of Arsenic (As) - Catalyst Poisoning Mechanism

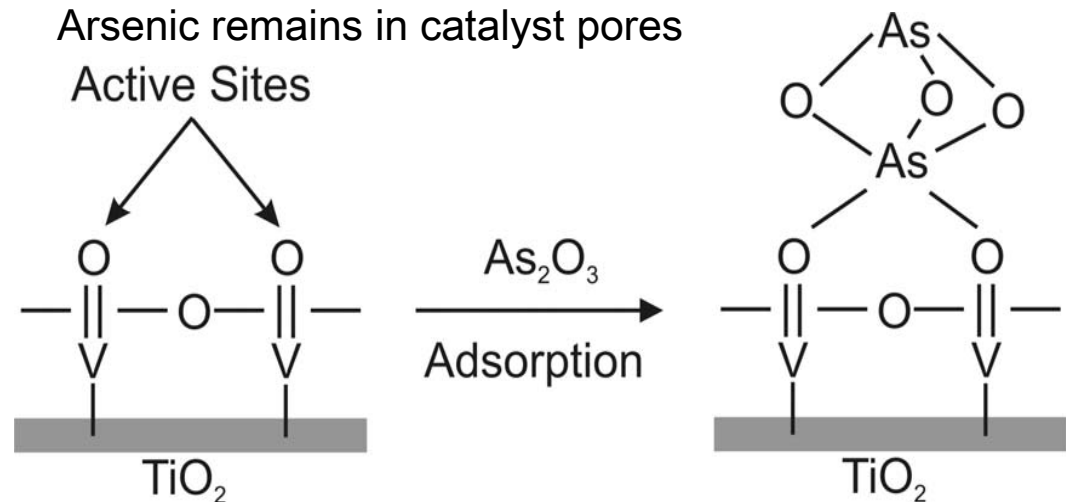
1. Physical Deactivation

- $\text{As}_2\text{O}_3(\text{g})$ molecules condense in the pore system of the catalyst thus reducing inner surface
- High inner surface area is key to high catalyst activity
- Pore condensation stops when equilibrium is reached between gaseous and condensed As.

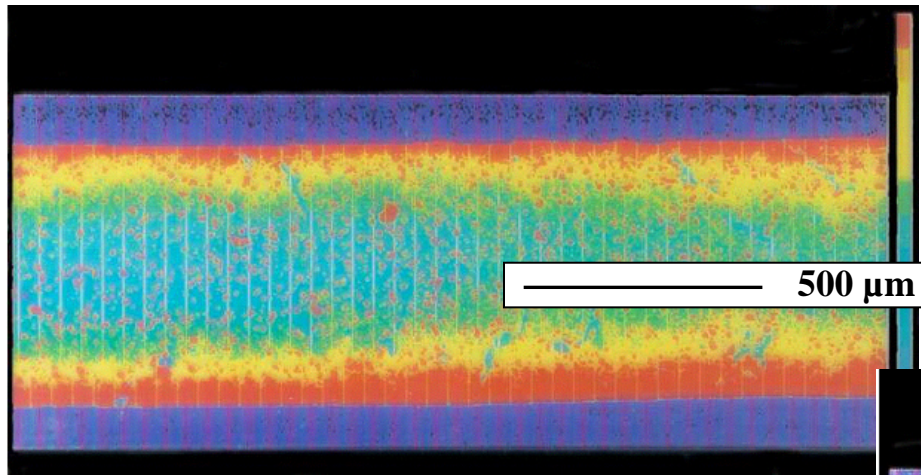
- If $\text{As}_2\text{O}_3(\text{g})$ \uparrow condensations starts again

- If $\text{As}_2\text{O}_3(\text{g})$ \downarrow Arsenic remains in catalyst pores

2. Chemical Deactivation

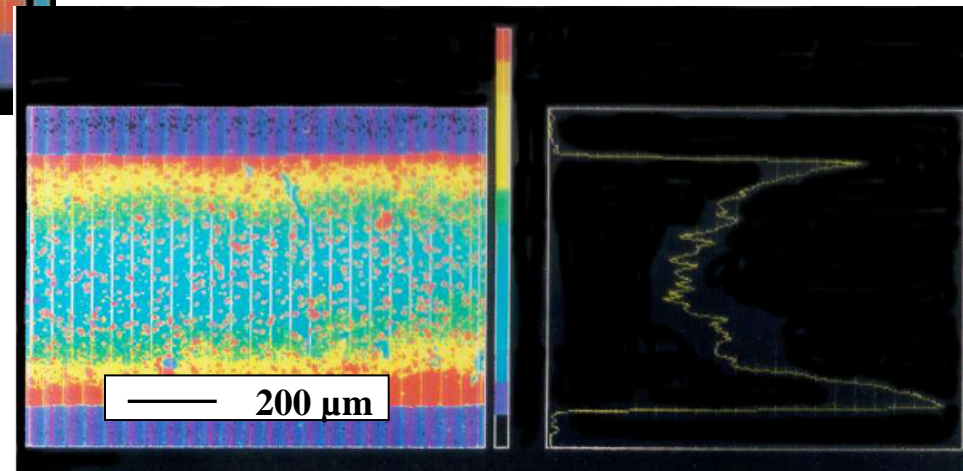


Capture of Arsenic - Poisoning on the Catalyst



Images of Poisoned Catalyst:

- Cross Section
- Early stage
- Source: KWH



* NOx Round Table '09, Ed Healy et. al.:

“There is no such thing as an arsenic resistant SCR catalyst”

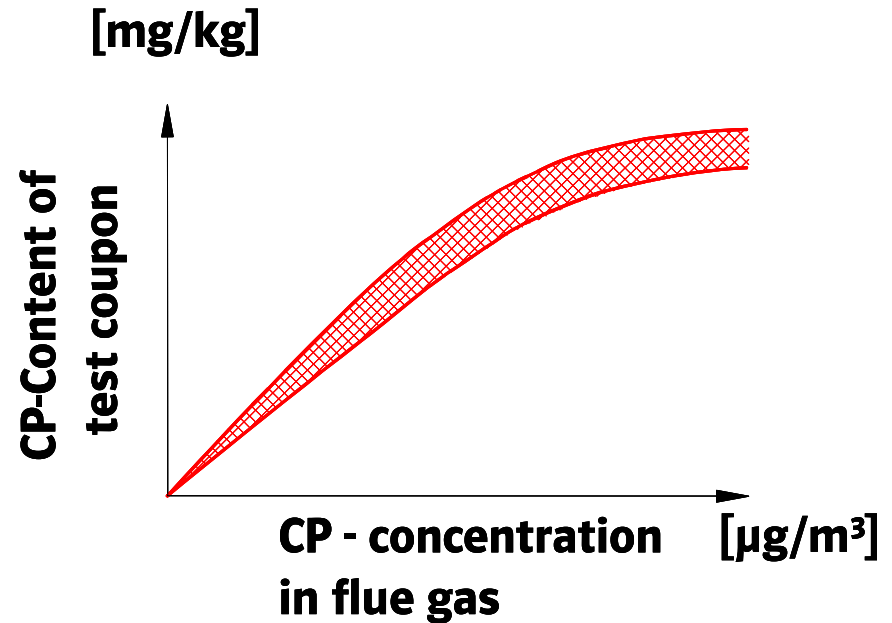
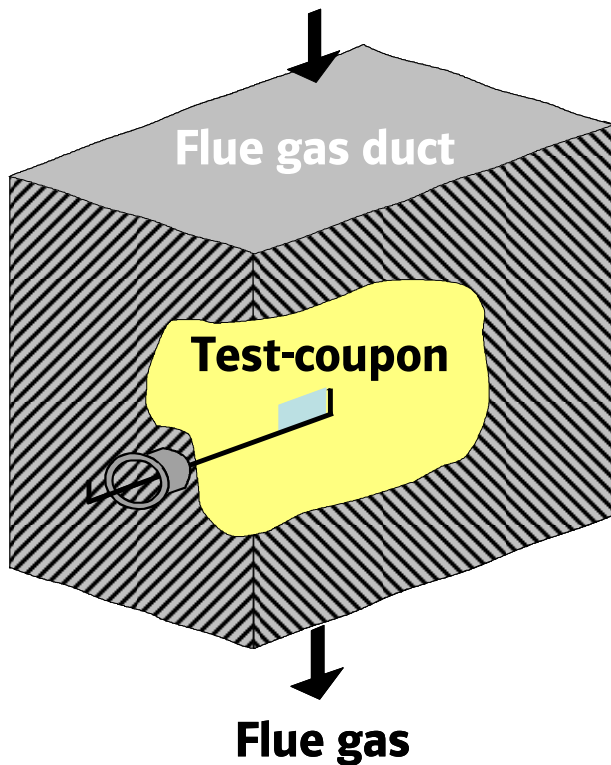
** Gaseous Arsenic has to be minimized in SCR

Capture of Arsenic (As) – How to Keep $\text{As}_2\text{O}_3(\text{g})$ out of the SCR?

- Only practical way: Ensure there is enough active cation sites on fly ash surface or in combustion zone to capture $\text{As}_2\text{O}_3(\text{g})$ and form solid arsenates, like
 - $\text{Ca}_3(\text{AsO}_4)_2$
 - $\text{Mg}_3(\text{AsO}_4)_2$
- Cations have to be freely available (CaO_{free})
 $\text{As}_2\text{O}_3(\text{g}) + 3 \text{CaO} + \text{O}_2 \rightarrow \text{Ca}_3(\text{AsO}_4)_2(\text{s})$
- Most common additive: Limestone (CaCO_3)
 $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- Dolomite ($\text{CaMg}(\text{CO}_3)_2$) would be even more effective
- Typical limestone specs for this application:
 $\text{CaCO}_3 > 60\%$ and $\text{MgCO}_3 > 3\%$

Capture of Arsenic (As) – Gaseous Arsenic Measurement

- Coupon testing is commonly used to predict arsenic poisoning of catalyst
- Coupon test is semi-quantitative method to detect gaseous catalyst poisons (CP) such as As_2O_3 , SiF_4 or submicron particulate matter like H_3PO_4

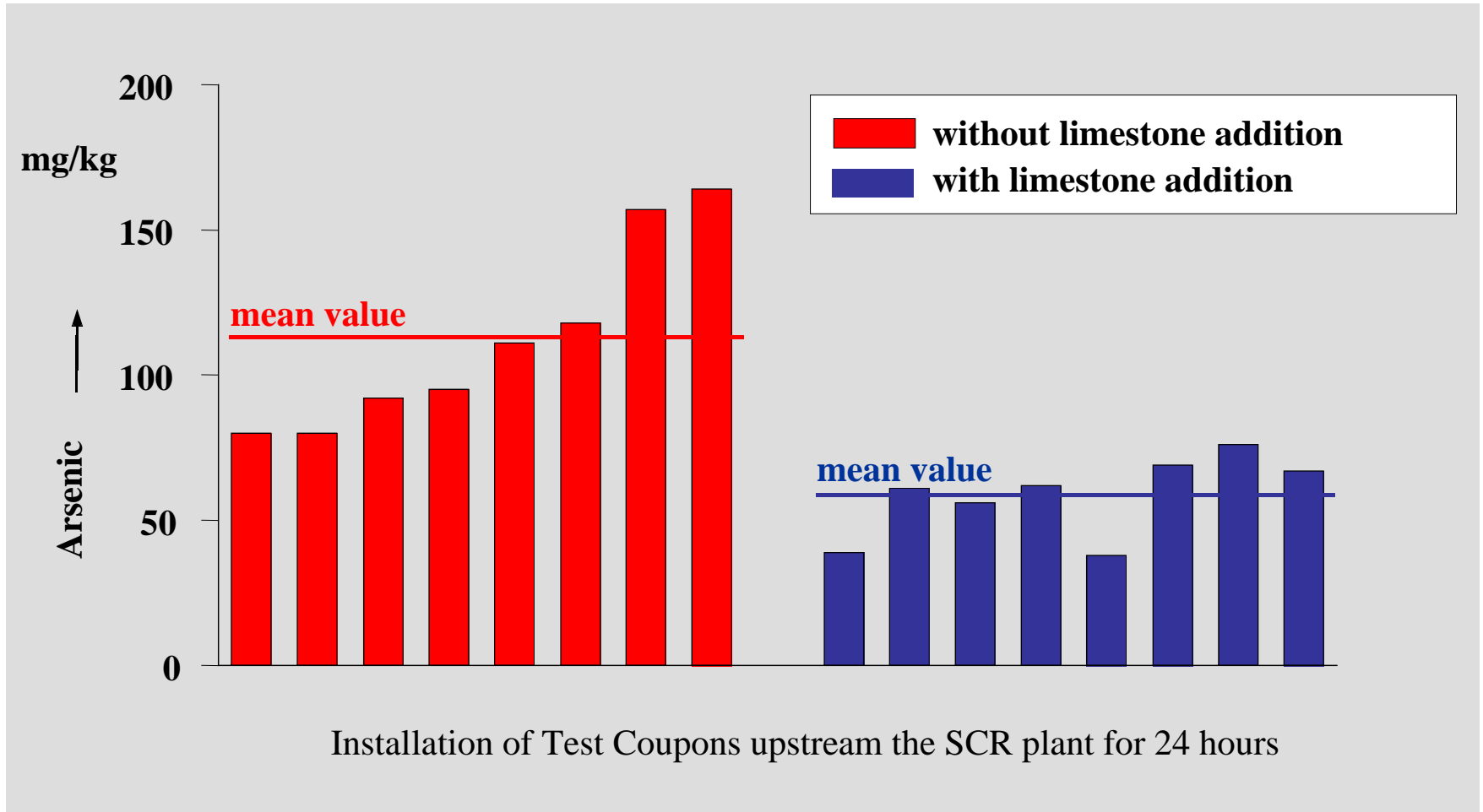


Capture of Arsenic (As) – Coupon Test Principle

- Test coupon is made using commercial plate type catalyst and has the size of a business card
- Temporarily installed in flue gas duct
- High gas velocity causes high turbulence at coupon surface resulting in a very fast mass transfer
- Thus test duration is only 24 h (for arsenic) up to max. one week
- Catalyst surface is analyzed by XRF (very sensitive because CP is enriched at surface)
- Method was calibrated for As by conventional gas sampling
- Method can easily be applied for optimization of CP mitigation strategies (e.g. limestone addition) and for the adjustment of co-combustion feed rates



Gaseous Arsenic without/with Limestone Addition



PPL Montour Station Introduction

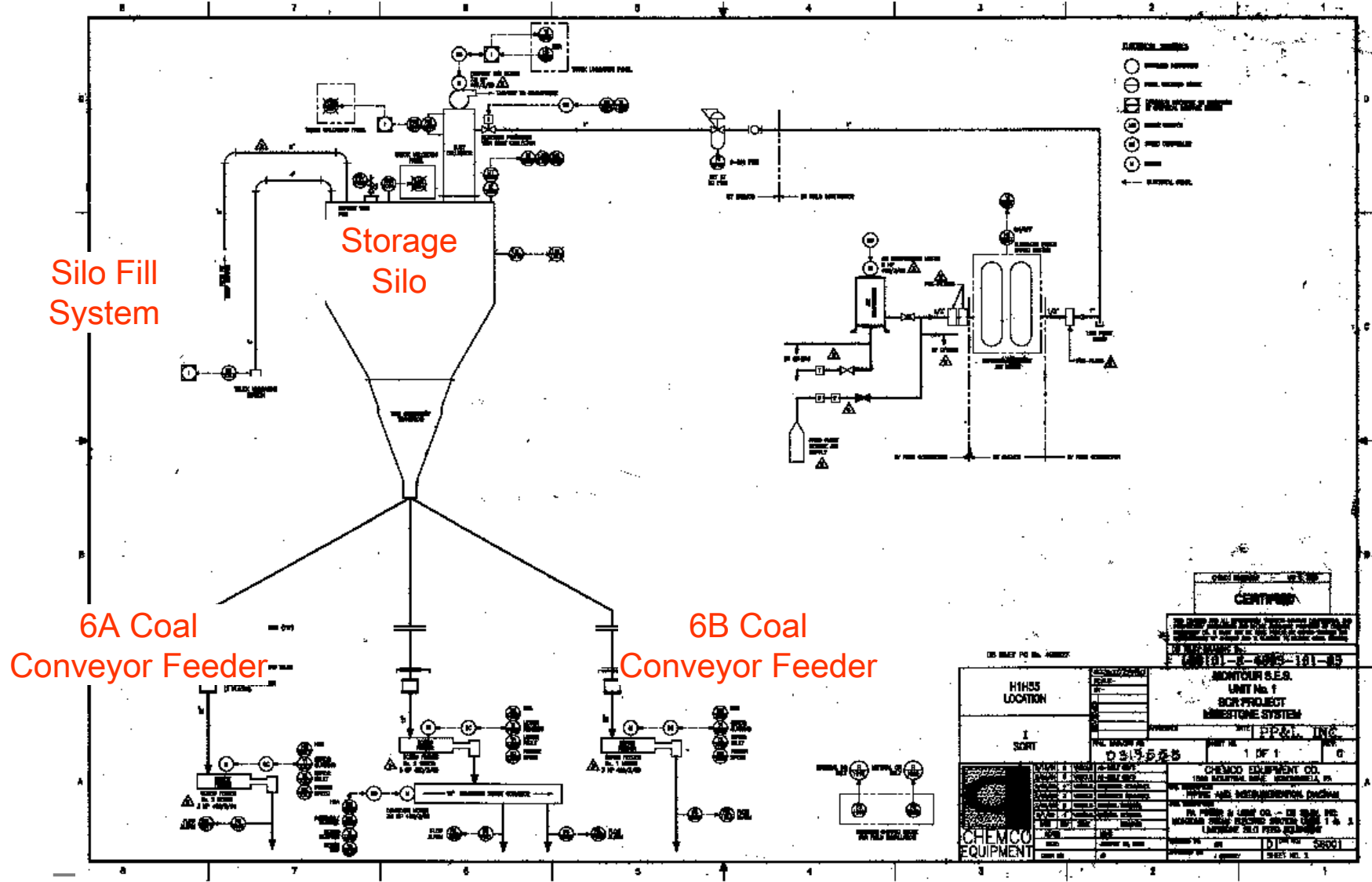
- Location: Washingtonville, PA
- Two 785MW T-fired, supercritical, CE Boilers from 1972 / 1973.
- Each Unit has six CE RPS Raymond Bowl type mills with dynamic classifiers and Alstom/ABB high efficiency exhauster wheels
- Liquid Anhydrous Ammonia Db Riley/Babcock Power SCR's commissioned in 2001 (Unit 1) and Unit 2 (2000). SCR's are equipped with Delta Wing Mixing Technology
- Two SCR reactors/unit, each reactor fits up to 4 layers of catalyst
- Current catalyst setup - 2.5 layers of KWH honeycomb and one layer of Cormetech honeycomb catalyst



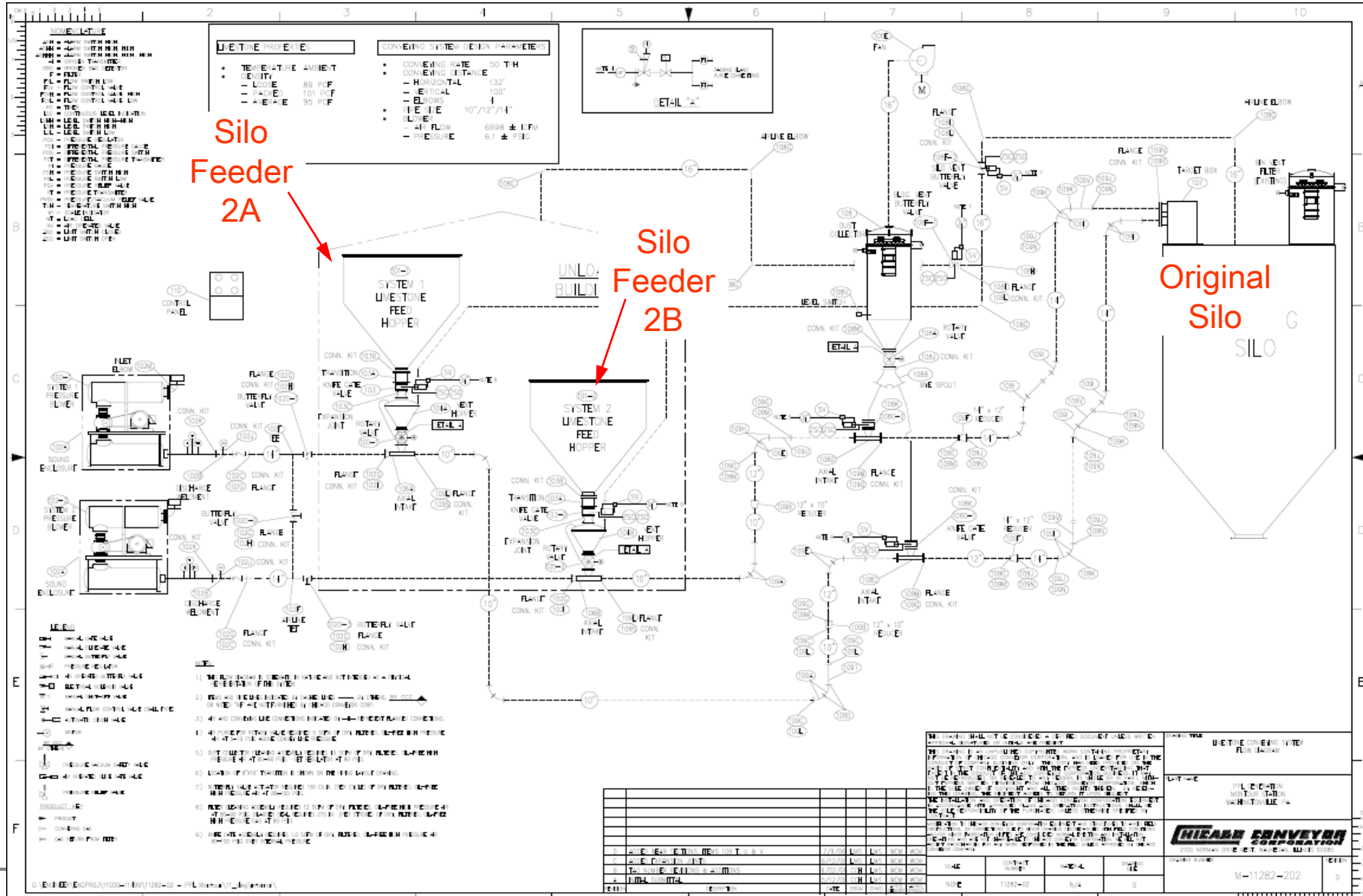
PPL Montour Station SCR Limestone Feed System

- Montour Limestone Feed System was installed in 2000, silo fill system was modified in 2008
- Required to meet SCR & Catalyst performance specifications
 - Coupon testing was used to verify
- Original system components:
 - 1,000T storage silo
 - 3 volumetric screw feeders supply limestone @ 20 tph to 2 coal conveyors
 - Truck or pit silo fill system
 - 2 silo feed settings (low and high)
- 2008 silo fill modifications:
 - Necessary for year-round operation
 - Silo is filled from two 25T hoppers
 - Storage silo feed settings were modified to create 4 set points

PPL Montour Station SCR Limestone Feed System (Original)



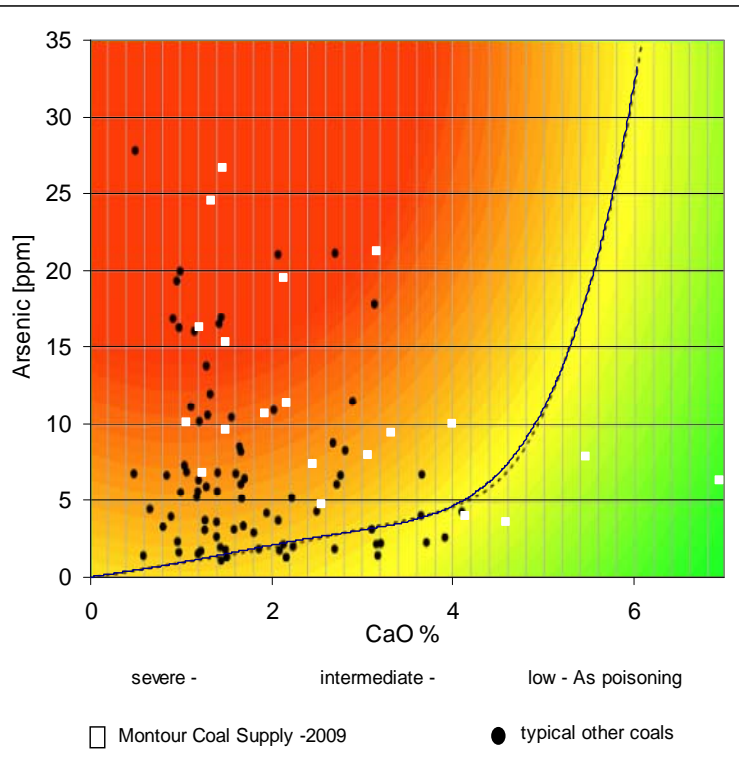
PPL Montour Station SCR Limestone Feed System (Modified Silo Fill)



Arsenic in Montour Coals – Summary of 2009 Deliveries

Coal Source	Arsenic (ppm)			Calorific value (Btu/lb)			CaO (ppm)
	Median	Mean	Number of samples	Median	Mean	Number of samples	Mean
Source #1	10.0	10.6	37	12,994	12,995	156	1.92
Source #2	8.23	7.90	5	13,025	13,016	18	5.48
Source #3	4.41	4.73	8	12,664	12,639	9	2.55
Source #4	4.58	3.94	52	13,069	13,065	93	4.15
Source #5	25.3	24.5	20	12,445	12,436	21	1.34
Source #6	4.65	3.57	49	13,231	13,176	60	4.59
Source #7	19.2	21.1	5	12,428	12,456	6	3.17
Source #8	11.5	11.3	29	12,745	12,731	44	2.18
Source #9	18.6	19.4	21	12,428	12,391	23	2.13
Source #10	4.90	6.29	26	13,056	13,061	41	6.95
Source #11	17.8	16.3	9	12,276	12,312	9	1.20
Source #12	7.52	9.62	3	12,710	12,686	3	1.50
Source #13	15.8	15.3	3	12,311	12,157	4	1.50
Source #14	8.79	7.92	13	12,621	12,617	23	3.07
Source #15	27.9	26.6	15	12,686	12,672	22	1.46

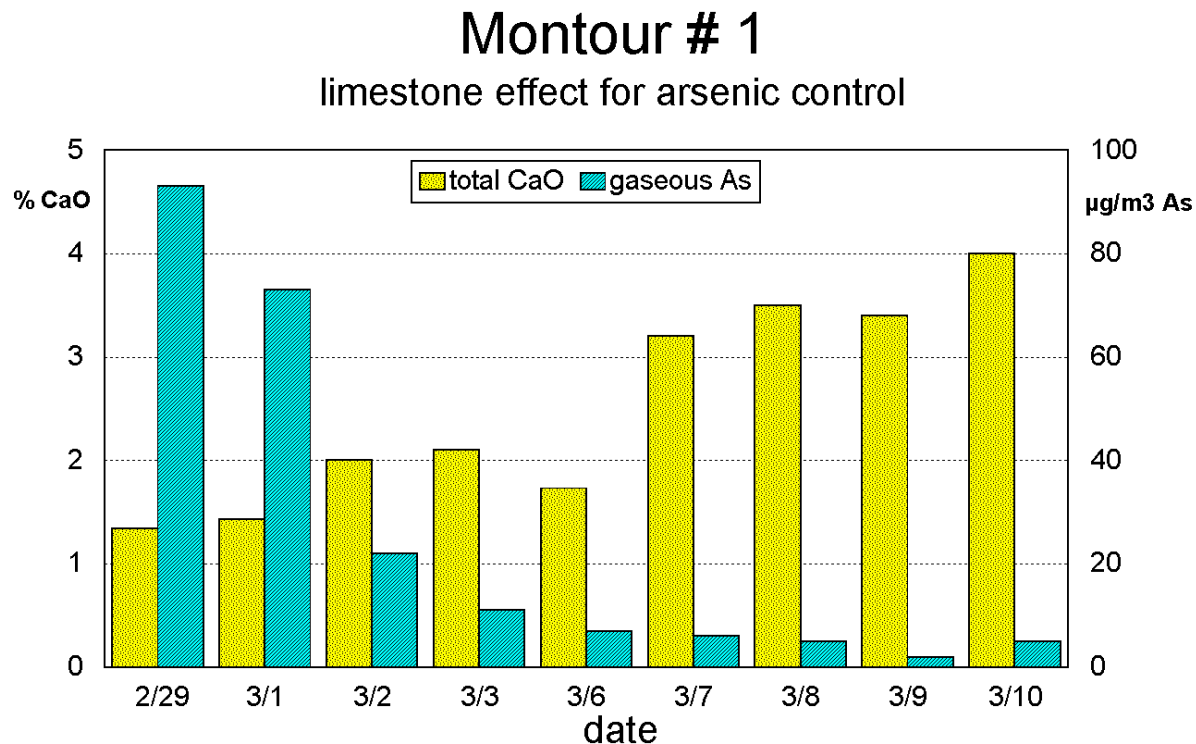
Arsenic % CaO in Montour Coals



No.	SOURCENAME	Arsenic in Coal [ppm]	CaO in Coal [%]	Ash dry	Ash FT Fluid [°F]	Ash FT Fluid [°C]	CaO needed [%]	Limestone Injection [%]
Average Fuel Parameters - 2009								
1	Spencer	15.32	1.50	14.14	2,615	1,435	5.31	1.0
2	Valier Coal Yard	26.66	1.46	12.63	2,405	1,318	5.82	1.0
3	Fallen Timber	24.53	1.34	13.49	2,588	1,420	5.75	1.1
4	Hoffman (Belford)	21.19	3.17	14.17	2,473	1,356	5.61	0.6
5	Huskin Run	19.46	2.13	14.72	2,508	1,376	5.53	0.9
6	Owens #2	16.33	1.20	14.65	2,564	1,407	5.37	1.1
7	Bailey	10.64	1.92	7.52	2,478	1,359	4.97	0.4
8	Birch River	10.12	1.06	12.85	2,800	1,538	4.92	0.9
9	Hopedale Mine	11.33	2.18	9.79	2,490	1,366	5.03	0.5
10	Shade Creek	9.62	1.50	12.06	2,647	1,453	4.87	0.7
11	Brooks Run	7.34	2.45	11.78	2,800	1,538	4.59	0.5
12	Dodge Hill Mine (Dekovan)	4.73	2.55	9.74	2,340	1,282	4.03	0.3
13	Fola	6.80	1.24	12.96	2,800	1,538	4.51	0.8
14	Pontiki	9.36	3.32	8.46	2,698	1,481	4.84	0.2
15	Tuskie	7.92	3.07	7.15	2,491	1,366	4.67	0.2
16	Mine 84	10.00	4.00	7.30	2,564	1,407	4.91	0.1
17	Emerald	3.94	4.15	8.89	2,332	1,278	3.69	0.0
18	Federal #2	3.57	4.59	7.93	2,253	1,234	3.45	0.0
19	Loveridge	6.29	6.95	8.54	2,331	1,277	4.41	0.0
20	Blacksville #2	7.90	5.48	8.36	2,398	1,314	4.67	0.0

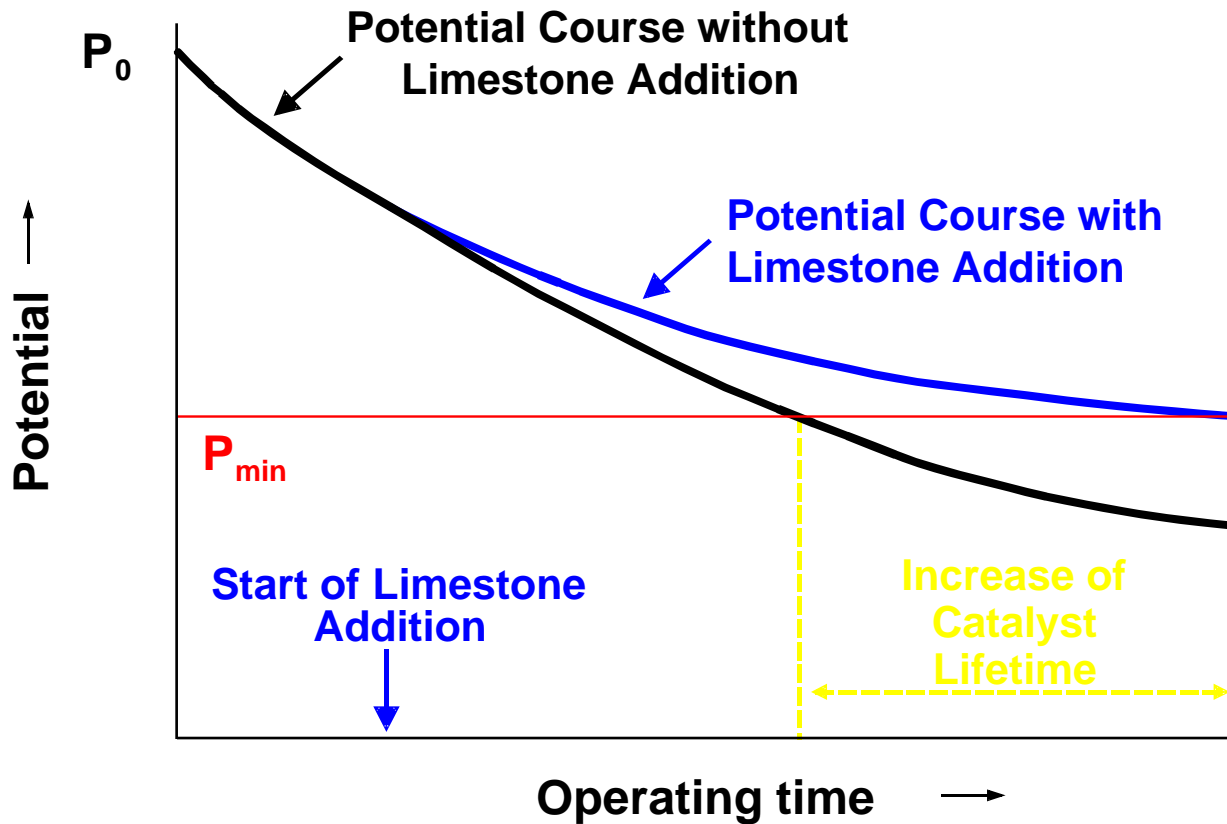
Why Add Limestone at Montour?

- Adding limestone to coal reduces the amount of $As_2O_3(g)$ available to poison the catalyst.



Why Add Limestone at Montour?

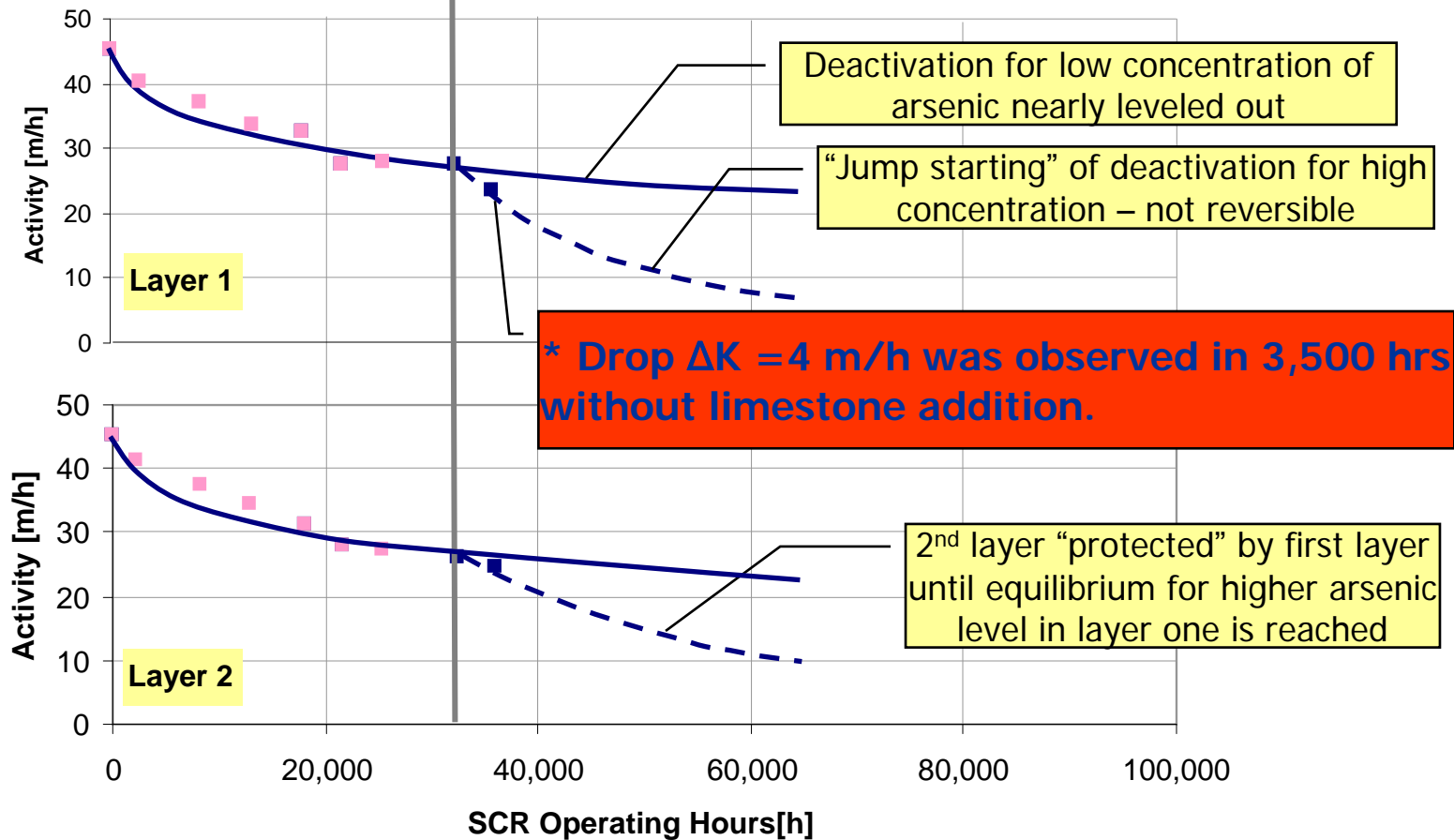
* Limestone addition increases the Catalyst lifetime.



Why Add Limestone at Montour?

Operation with adding limestone

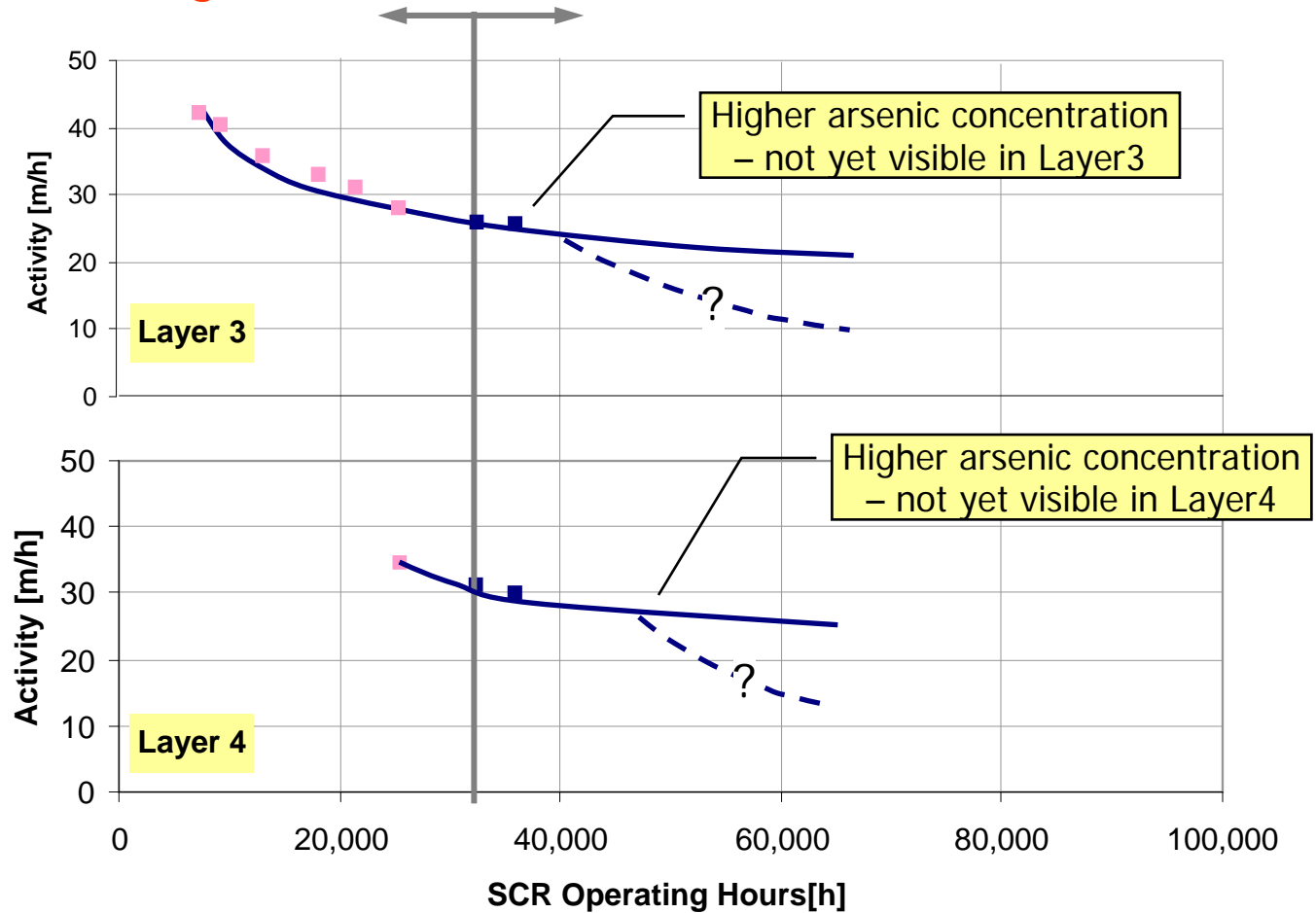
Operation without adding limestone



Why Add Limestone at Montour?

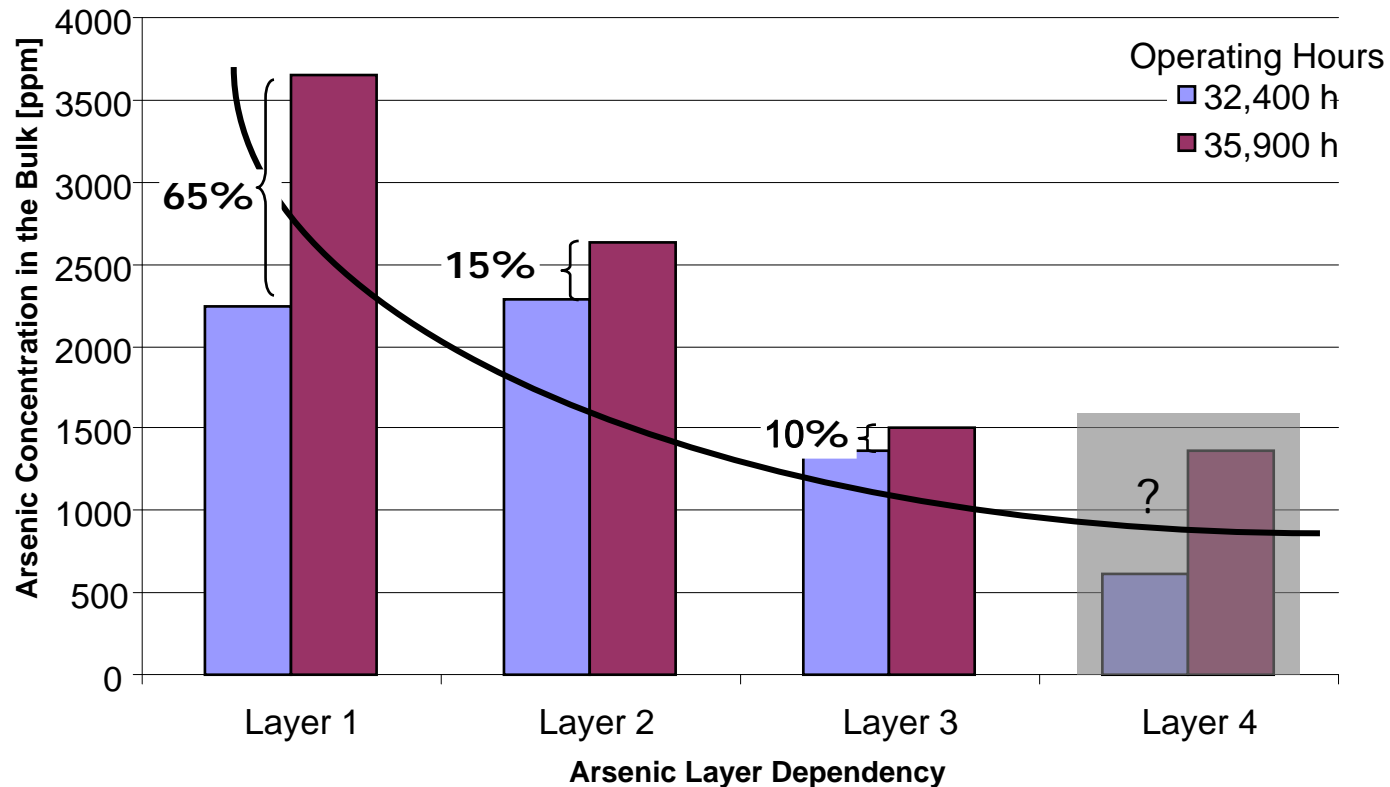
Operation with adding limestone

Operation without adding limestone



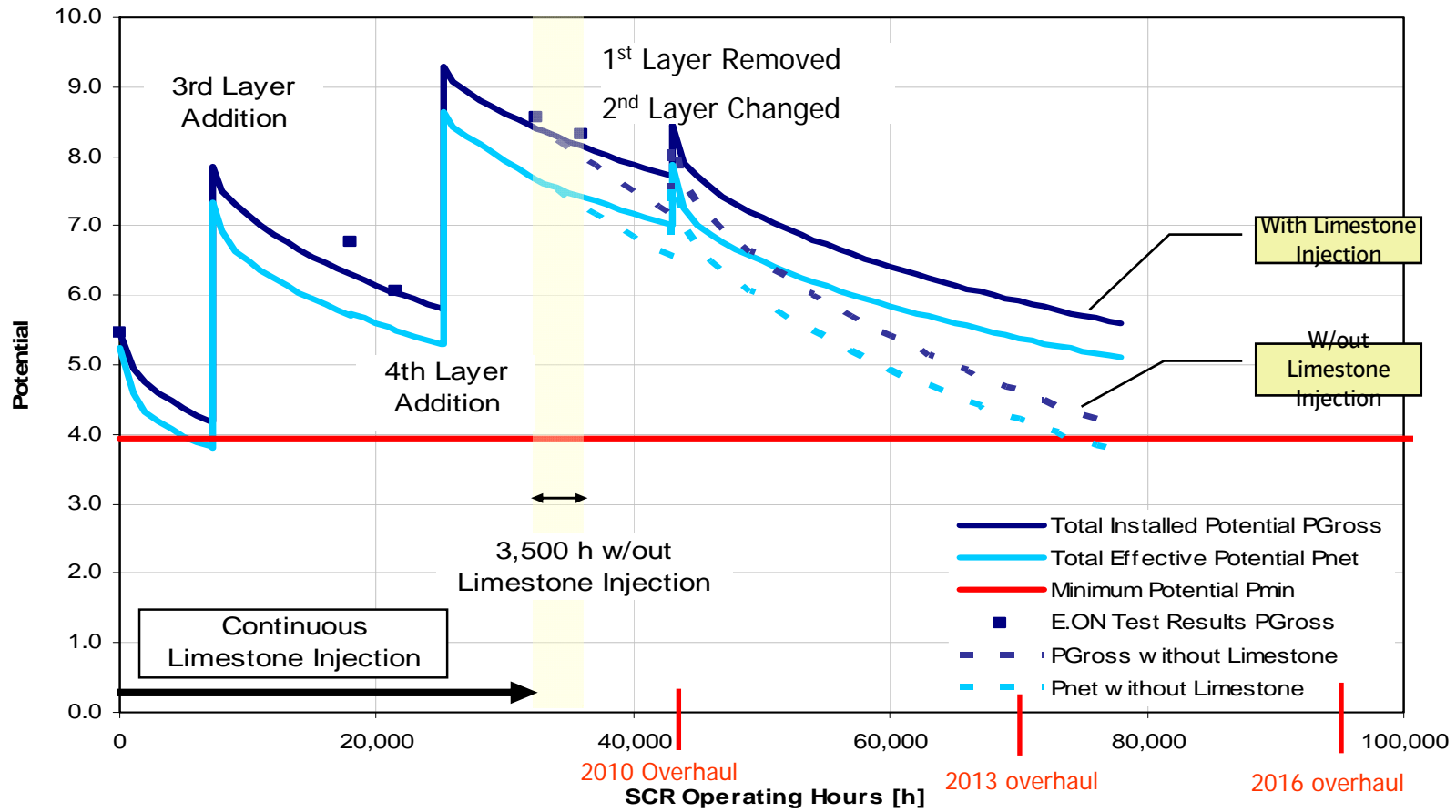
Why Add Limestone at Montour?

* In 3,500 hours without limestone, As concentrations increased in all layers. Top layer saw biggest increase of 65%.

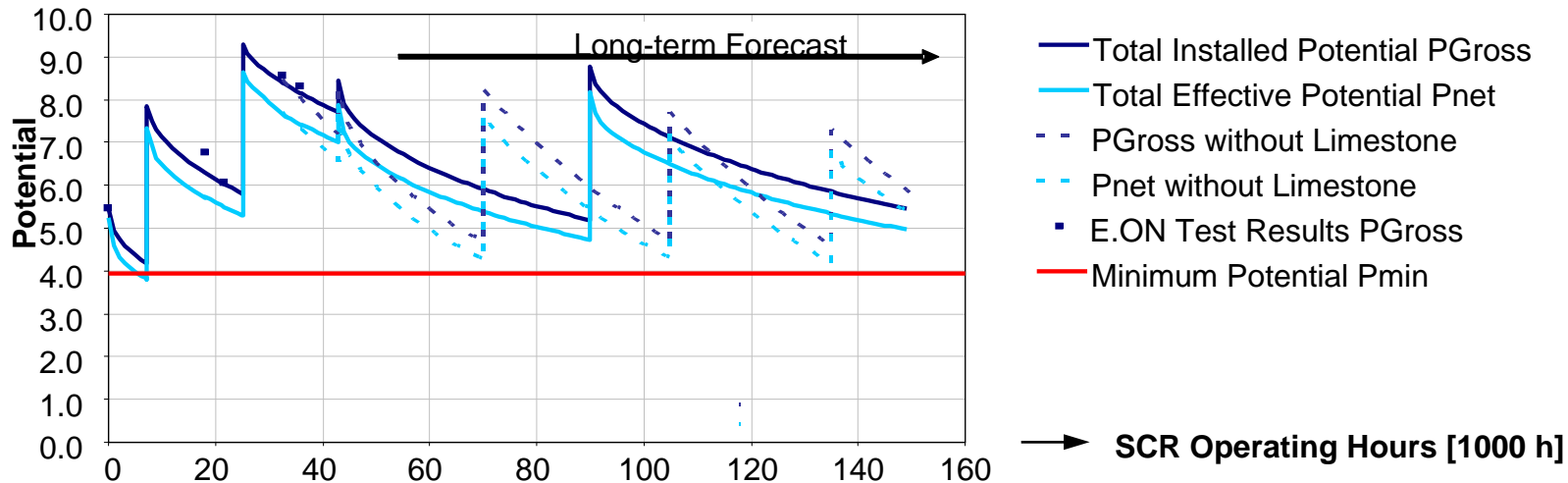


Why Add Limestone at Montour?

- * Potential for more frequent replacements.
- * May not have enough potential to make 3-yr outage opportunities.



Economic Advantage of As Mitigation



Forecast between now and 100,000 hours:

- With Limestone injection:
 - 1 replacement project (2010): \$4-5M
 - \$3M (Limestone)
 - \$.70M (Maintenance; materials & labor)
- Without Limestone injection:
 - 3 replacement projects (2010, 2013, 2016) = \$12-15M

*** Economic Advantage = \$3-6M over 6 years**

Reservations about Arsenic Mitigation

- Limestone feeding system is an easy retrofit
- Operation and maintenance are manageable & economical
- * Arsenic is one of the predominant deactivation mechanism in the US, but only a few limestone feeding systems are installed.

Montour reservations:

- Limestone sinters and is not effective!
 - Catalyst data w/ and w/o limestone tells different story
 - University research supports claim that limestone is NOT sintered during combustion
- Most of the limestone is rejected in mills!
 - Catalyst data w/ and w/o limestone tells different story
 - Mill dump data evaluated at Montour
- Operation of the limestone feed system causes increased wear on mills! (grindability)
 - Difficult to evaluate, many variables
- Limestone addition increases boiler slagging / fouling!
 - Montour losses due to slagging were less than or equal during OTAG and non-OTAG months



Reservations about Arsenic Mitigation - Grindability

* Same mills in cement plants and power plants

- Pure limestone has an HGI of 90

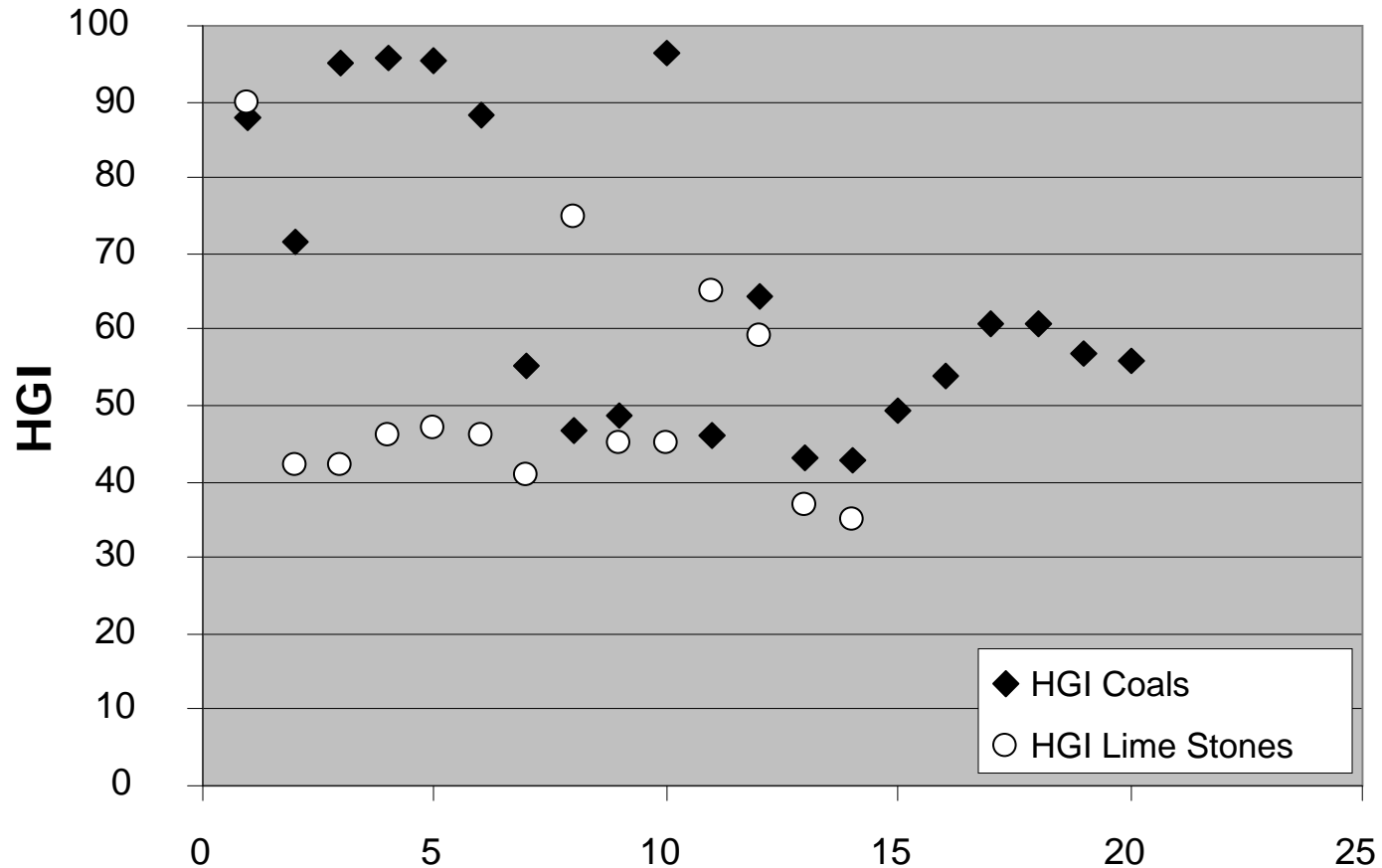
Sample No.	Work index	HGI	CaCO ₃	MgCO ₃	SiO ₂	Na ₂ O	K ₂ O	Petrography	Location
601	11.08	42	91.43	2.90	4.0	0.23	0.10	Bryozoan-crinoid grainstone	Gilbertsville, KY
602	12.14	42	93.03	2.90	2.9	0.22	0.11	Ooid-skeletal grainstone	Cave in Rock, IL
603	8.88	46	89.46	6.85	2.6	0.04	0.19	Ooid grainstone	Princeton, KY
604	10.60	47	83.93	10.53	4.1	0.32	0.25	Skeletal packstone wackestone	Clarksville, TN
605	9.13	46	88.04	1.67	8.5	0.45	0.09	Bryozoan-crinoid grainstone packstone	Gilbertsville, KY
606	11.20	41	93.43	3.11	1.2	0.02	0.19	Mudstone (micrite)	Carntown, KY
607	6.87	75	96.96	1.88	0.04	0.02	0.08	Crinoid grainstone	Valmeyer, IL
608	9.74	45	87.49	5.79	5.3	0.03	0.14	*	Smithland, KY
609	10.74	45	94.11	2.28	2.3	0.14	0.09	Ooid-crinoid grainstone	Cave in Rock, IL
610	7.63	65	97.68	2.01	0.1	0.06	0.08	Ooid-skeletal grainstone	Fredonia, KY
611	10.59	59	91.61	4.20	3.2	0.18	0.09	Ooid-crinoid grainstone	Rosiclare, IL
612	11.18	37	59.11	35.72	3.5	0.27	0.53	Medium- and fine-crystalline dolomite	Cumberland City, TN
613	9.58	35	93.03	3.84	1.9	0.16	0.16	*	Pembroke, KY

*Combination: Ooid grainstone, crinoid-bryozoan wackestone-mudstone. fine-crystalline dolomite, quartz-pellet grainstone, shale.

•Combination: Ooid-pellet grainstone, skeletal packstone, skeletal mudstone, dolomitic skeletal wackestone-packstone.

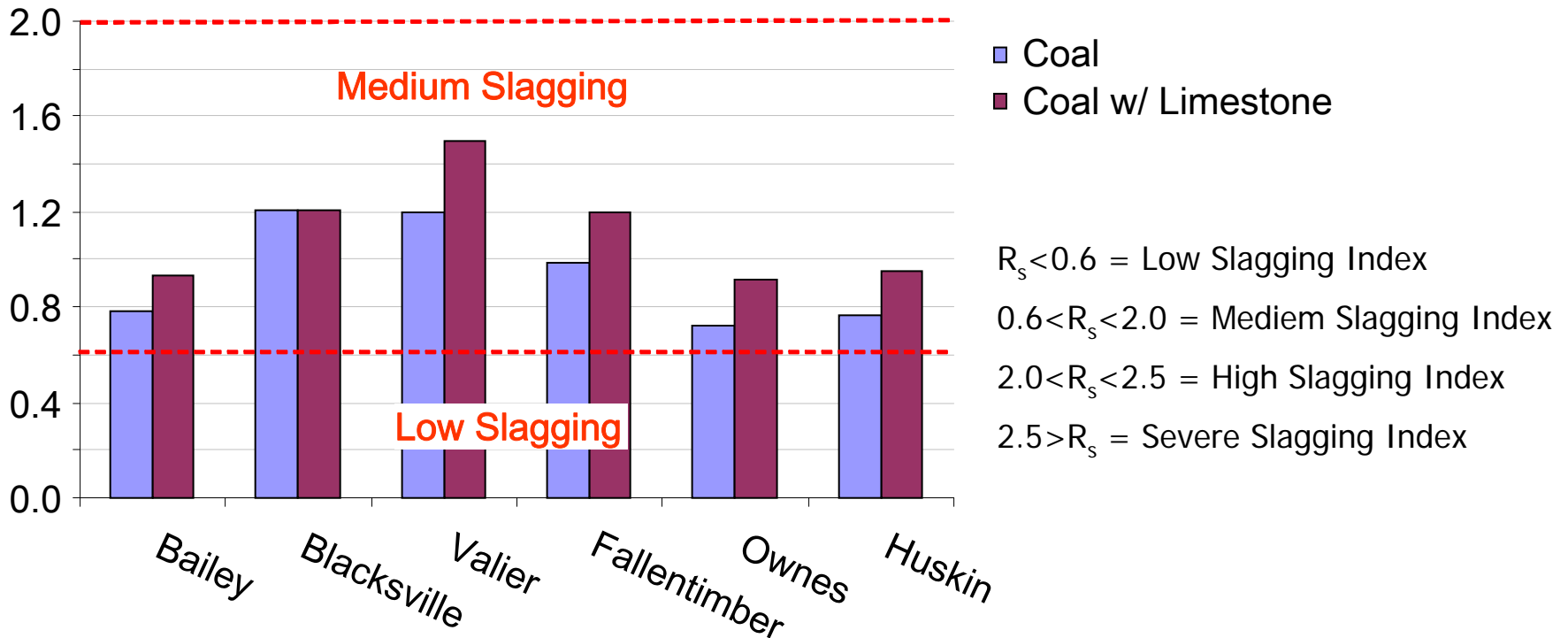
Source: Application of the Hardgrove grindability index in carbonate characterization, J.C. Hower et.al.

Reservations about Arsenic Mitigation - Grindability



Reservations about Arsenic Mitigation - Slagging

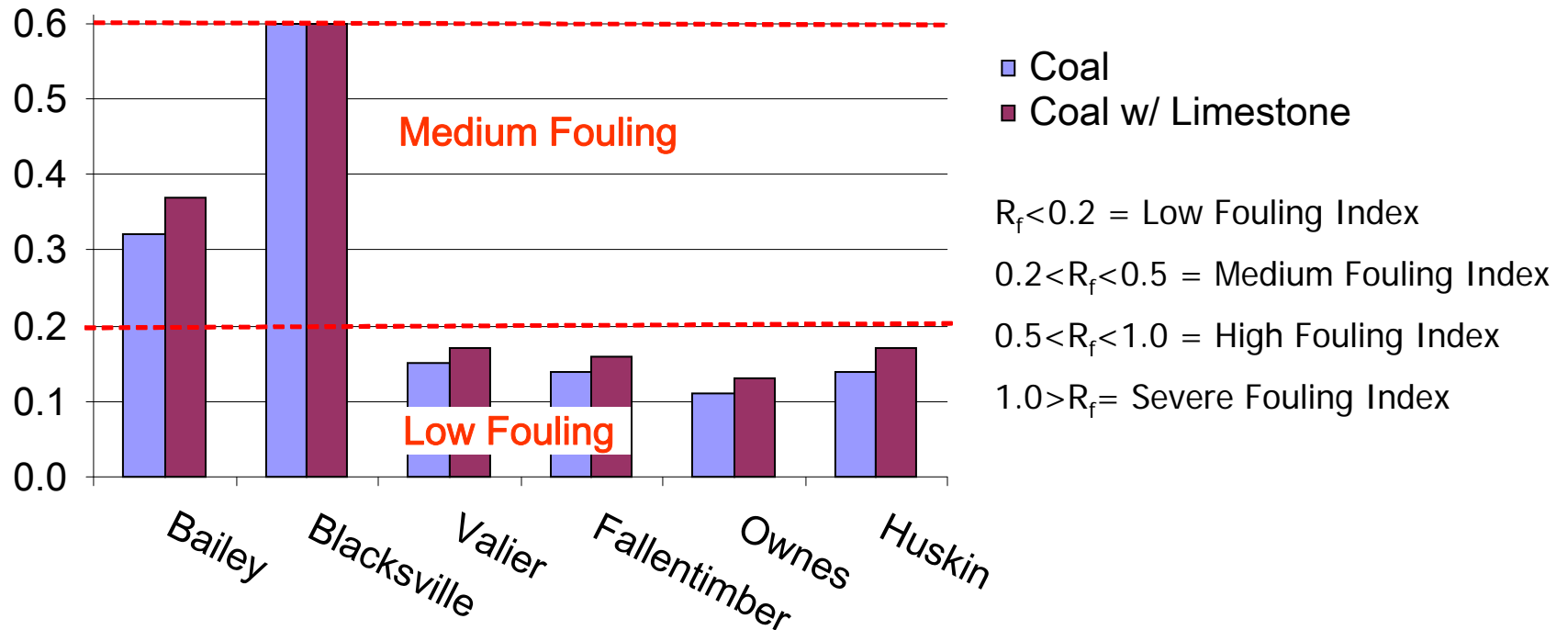
Slagging Index of Coal and Coal w/ Limestone Mixtures from PP&L Montour Station



* Adding Limestone to the coal does not significantly change the Slagging Index

Reservations about Arsenic Mitigation - Fouling

Fouling Index of Coal and Coal w/ Limestone Mixtures from PP&L Montour Station



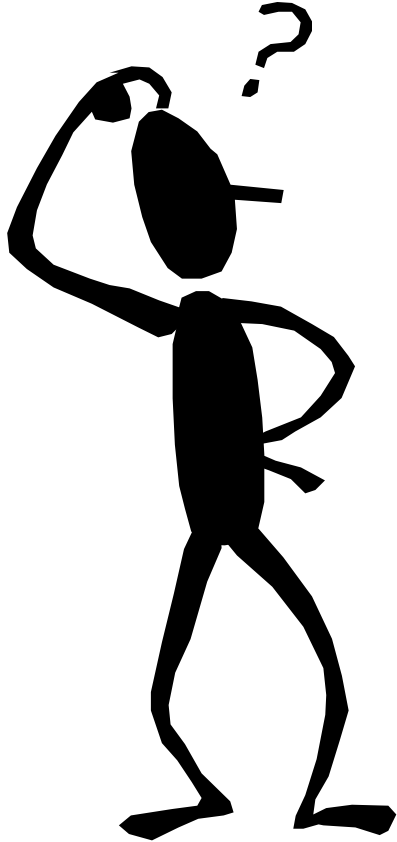
* Adding Limestone to the coal does not significantly change the Fouling Index

Summary

- $\text{As}_2\text{O}_3(\text{g})$ is one of the predominant catalyst deactivation mechanisms in coal fired SCR applications in the US
- There is no such thing as an arsenic resistant SCR catalyst. Gaseous Arsenic has to be minimized to prevent poisoning.
- Cations (such as CaO) have to be freely available to keep $\text{As}_2\text{O}_3(\text{g})$ out of SCR. Limestone is most common additive.
- Montour experiences:
 - Adding limestone to coal reduces the amount of $\text{As}_2\text{O}_3(\text{g})$ available to poison the catalyst.
 - Limestone addition increases the Catalyst lifetime.
 - Activity of Layer 1 dropped 4 m/h in 3,500 hrs without limestone addition.
 - In 3,500 hours without limestone, As concentrations increased in all layers. Top layer saw biggest increase of 65%.

Summary

- Montour experiences (cont.):
 - Potential for more frequent replacements.
 - May not have enough potential to make 3-yr outage opportunities.
 - Economic Advantage = \$3-6M over 6 years (catalyst replacement projects versus limestone & system maintenance)
- Reservations should be carefully reviewed:
 - Limestone addition will lead to increased mill wear:
 - **Same mills in cement plants and power plants.
 - **Coal and Limestone have similar HGI
 - Limestone addition will lead to boiler slagging:
 - ** Adding Limestone does not significantly change the Slagging Index
 - Limestone addition will lead to boiler fouling:
 - ** Adding Limestone does not significantly change the Fouling Index.



Questions?