

REINHOLD ENVIRONMENTAL Ltd.



2011 NO_x-Combustion Round Table & Expo Presentation

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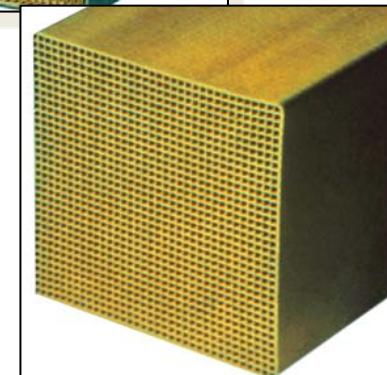
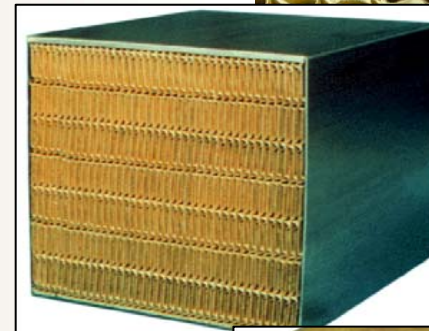
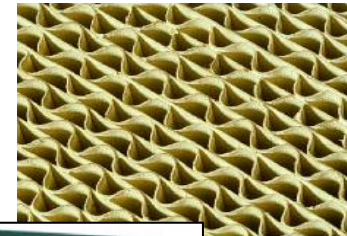
Combustion Additives for SCR Catalyst Deactivation Mitigation

*NO_x- Combustion Roundtable & Expo
Birmingham 2011*

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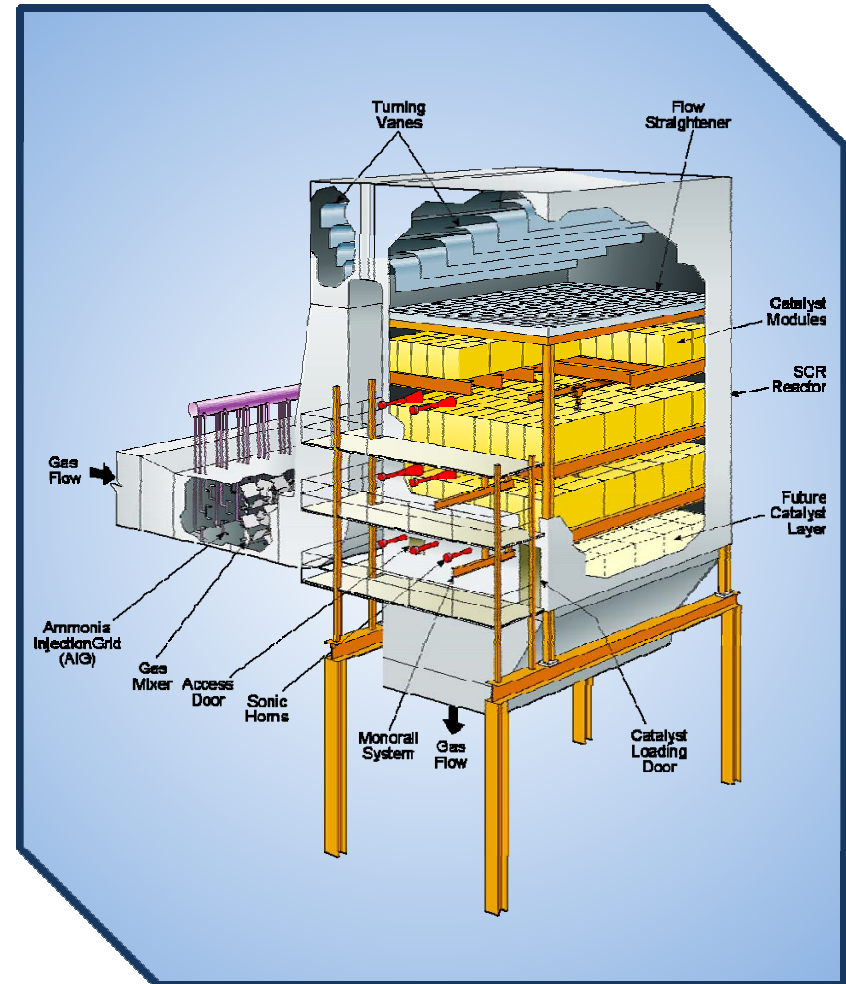
Presentation Overview

- ▶ Deactivation by arsenic
- ▶ Deactivation by phosphorus
- ▶ Combustion additive development
- ▶ Field test results
- ▶ Economic considerations
- ▶ Blended additives



Selective Catalytic Reduction (SCR)

- ▶ Means of converting NO_x into N_2 and H_2O using ammonia in presence of catalyst
- ▶ Types of catalyst include honeycomb, plate and corrugated
- ▶ Ammonia source can be anhydrous ammonia, aqueous ammonia or urea
- ▶ Exposure to combustion flue gas results in SCR catalyst deactivation



Periodic Table of the Elements

1 H 1.01																	18 He 4.00														
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18														
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95														
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80														
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29														
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (208.98)	85 At (209.99)	86 Rn (222.02)														
87 Fr (223.02)	88 Ra (226.03)	89 Ac (227.03)	104 Rf (261.11)	105 Ha (262.11)	106 Sg (263.12)																										
																		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.91)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
																		90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237.05)	94 Pu (244.06)	95 Am (243.06)	96 Cm (247.07)	97 Bk (247.07)	98 Cf (251.08)	99 Es (252.08)	100 Fm (257.10)	101 Md (258.10)	102 No (259.10)	103 Lr (262.11)

Deactivation of SCR Catalyst by Arsenic

- ▶ Deactivation by arsenic experienced on Eastern bituminous and Illinois coal
- ▶ Independent of staged or un-staged combustion
- ▶ Calcium injection ties up gas phase arsenic, reducing concentration of gas phase arsenic reaching catalyst and thereby the rate of deactivation of catalyst
- ▶ Recommended calcium to arsenic ratio is set based on coal being fired
- ▶ Trusted mitigation technique uses injection of combustion additive



	Al 26.98	Si 28.09	P 30.97	S 32.07	Cl 35.45
30	31	32	33	34	35
7	Ga 69.72	Ge 72.61	As 74.92	Se 78.96	Br 79.90
48	49	50	51	52	53
d	In 75.00	Sn 118.71	Sb 121.76	Te 127.60	I 126.90

Deactivation of SCR Catalyst by Phosphorus

- ▶ Deactivation by phosphorus many times experienced on PRB coal
- ▶ Combustion conditions play major role in the deactivation process
- ▶ Commonly observed under staged combustion conditions as compared to unstaged combustion
- ▶ Form of phosphorus at SCR inlet is important contributor to deactivation
- ▶ The two forms of phosphorus at SCR inlet are particulate bound & gas phase

B	C	N	O	
10.81	12.01	14.01	16.00	19.00
13	14	15	16	
Al	Si	P	S	
26.98	28.09	30.97	32.07	35.45
31	32	33	34	
	Ge	As	Se	

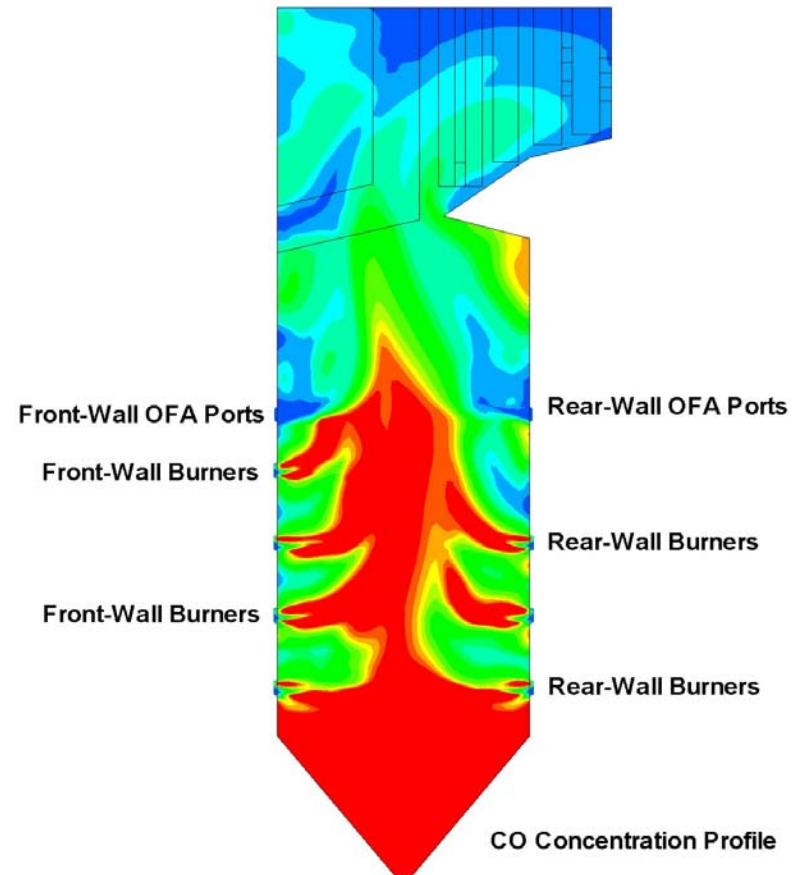
Particulate Bound Phosphorus

- ▶ Phosphorus distribution by particle size
- ▶ Acid dew point effects
- ▶ Leaching studies @pH 5, 7 and 9
- ▶ Minimal phosphorus leachability from fly ash
- ▶ Particulate bound phosphorus poisoning ruled out
- ▶ Role of SO₃?
- ▶ Role of gas phase phosphorus ?



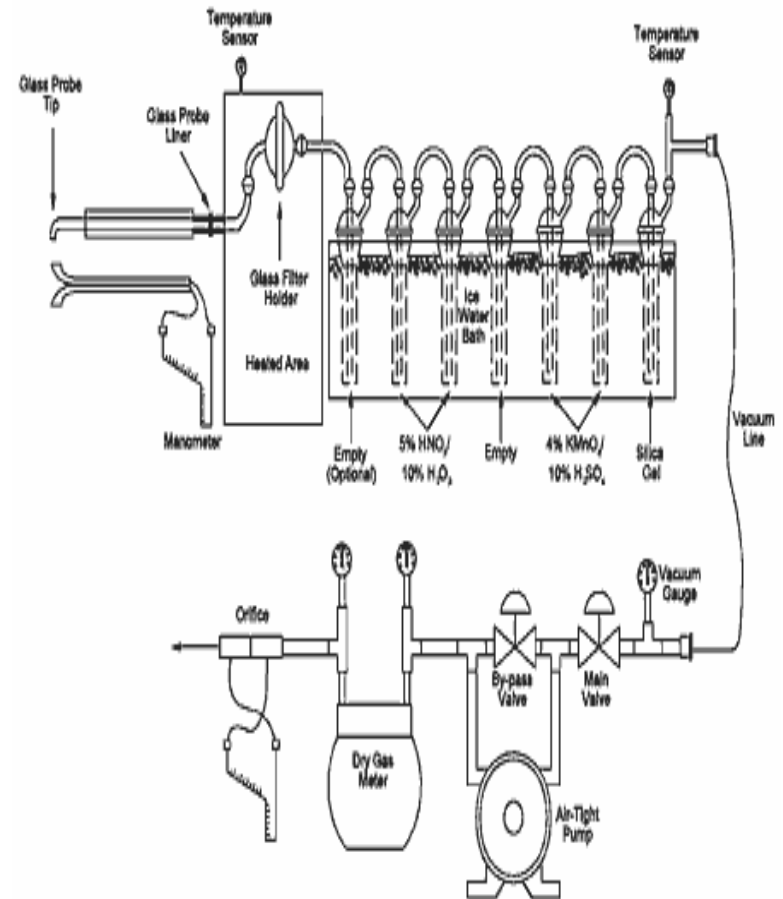
Staged Combustion Effects

- ▶ More CO in furnace due to staging
- ▶ Carbothermic reduction of phosphorus-bearing minerals
- ▶ Phosphorus bearing inorganic minerals are reduced by CO, thus releasing gas phase phosphorus
- ▶ Even unstaged, if poor combustion exists in furnace the same effect is observed

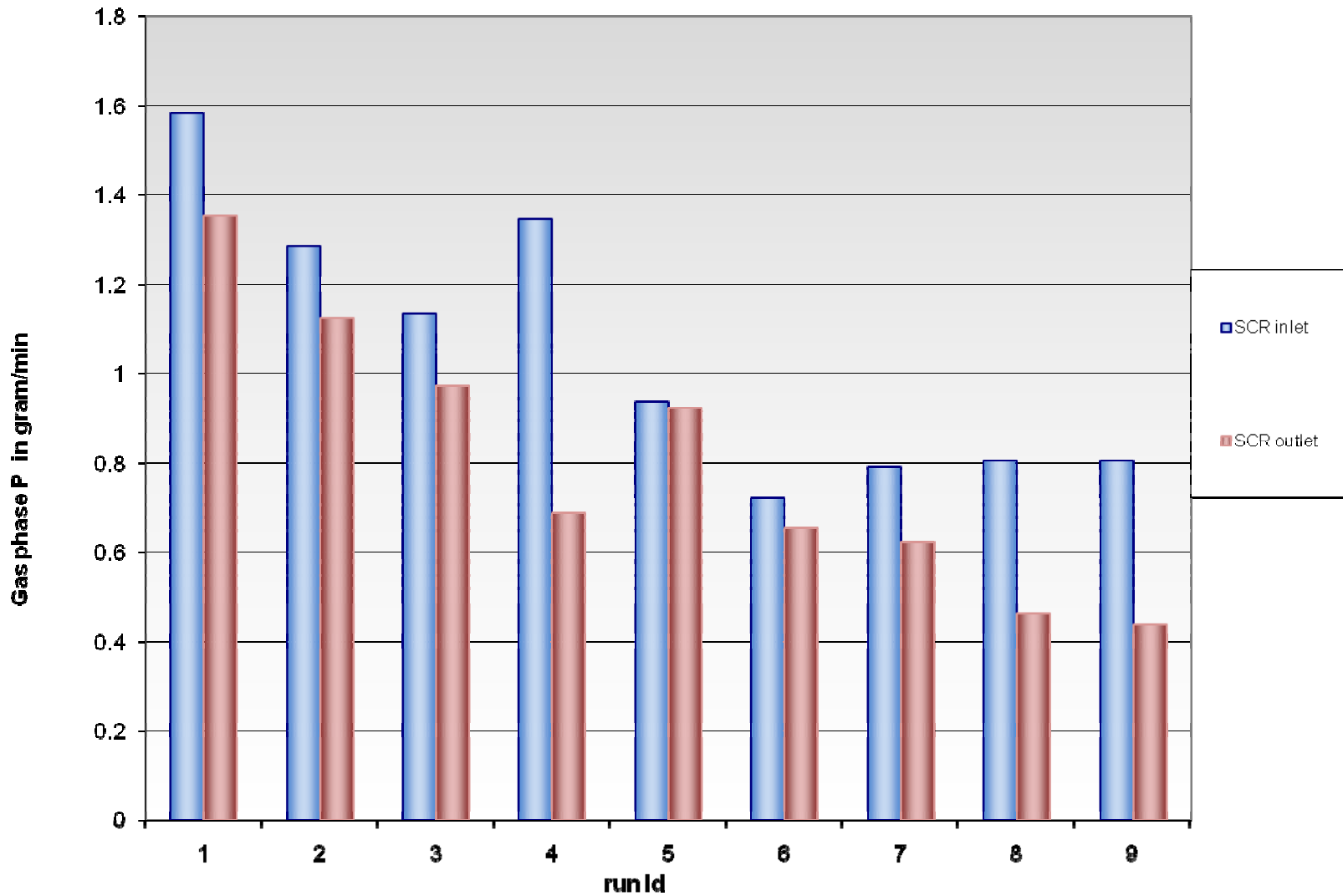


Gas Phase Phosphorus Sampling

- ▶ Initially high measurement variability due to particulate break through
- ▶ Developed a modified sampling method based on EPA M29
- ▶ Modifications to impinger solutions
- ▶ Extensive flue traverse to obtain representative gas sample
- ▶ 2 hour sampling time for each run

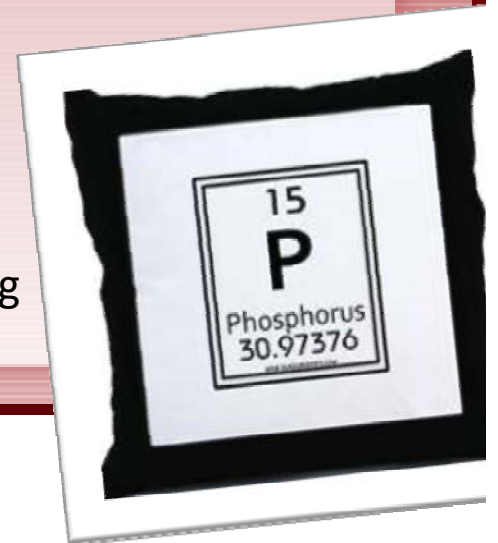


Simultaneous Gas Phase Sampling



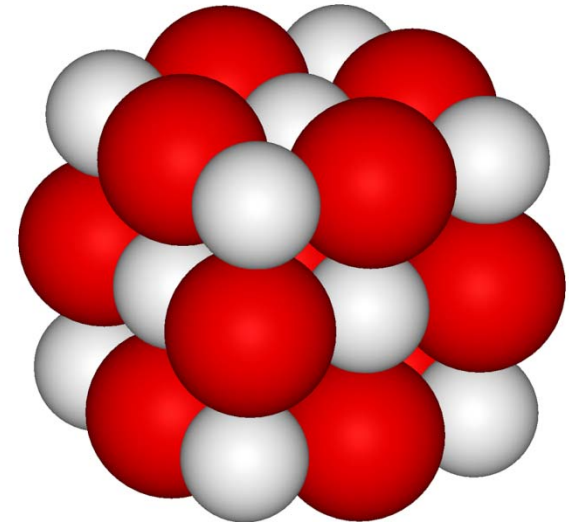
Deactivation by Gas Phase Phosphorus

- ▶ Explains why rapid deactivation observed only on staged units
- ▶ Raman spectroscopy indicated formation of V-P bonds
- ▶ Chemical deactivation by gas phase phosphorus
- ▶ V-P bond formation indicated gas phase phosphorus adsorbs on active sites just like ammonia does
- ▶ Phosphorus adsorption more prominent on lower layers, causing more deactivation than first layer
 - In presence of ammonia, phosphorus adsorption may be suppressed
 - Second and third layers see less ammonia than first layer
 - More P accumulation at outlet section than inlet within a log



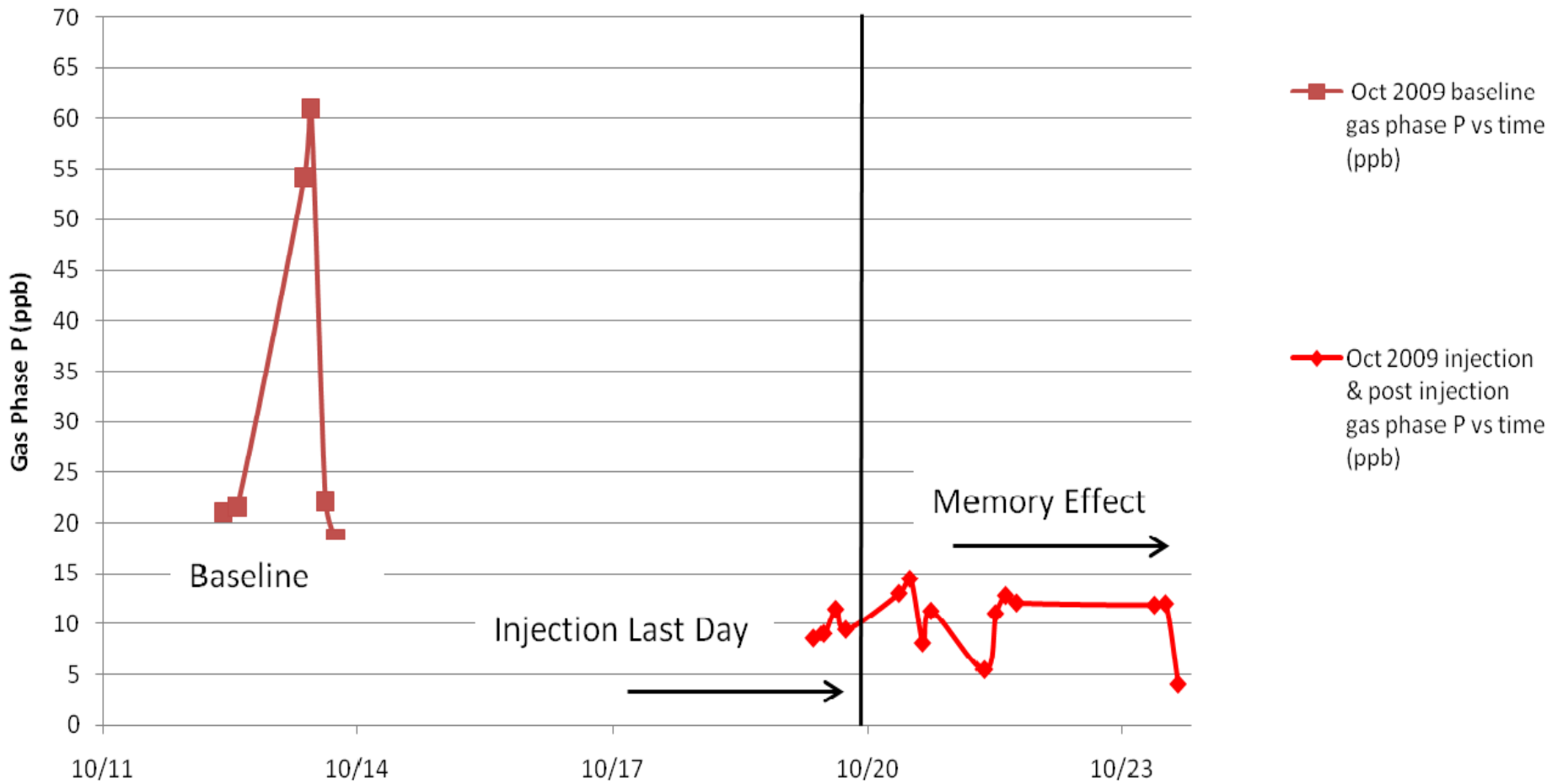
Combustion Additive Development

- ▶ Injection of calcium oxide to tie up gas phase arsenic
- ▶ B&W investigations for tying up gas phase phosphorus
- ▶ Impact on boiler performance
- ▶ Technical feasibility of injection
- ▶ Short term testing
- ▶ Long term testing
- ▶ US & International patent pending



Repeatability Test Results at Wygen 2

Injection Test

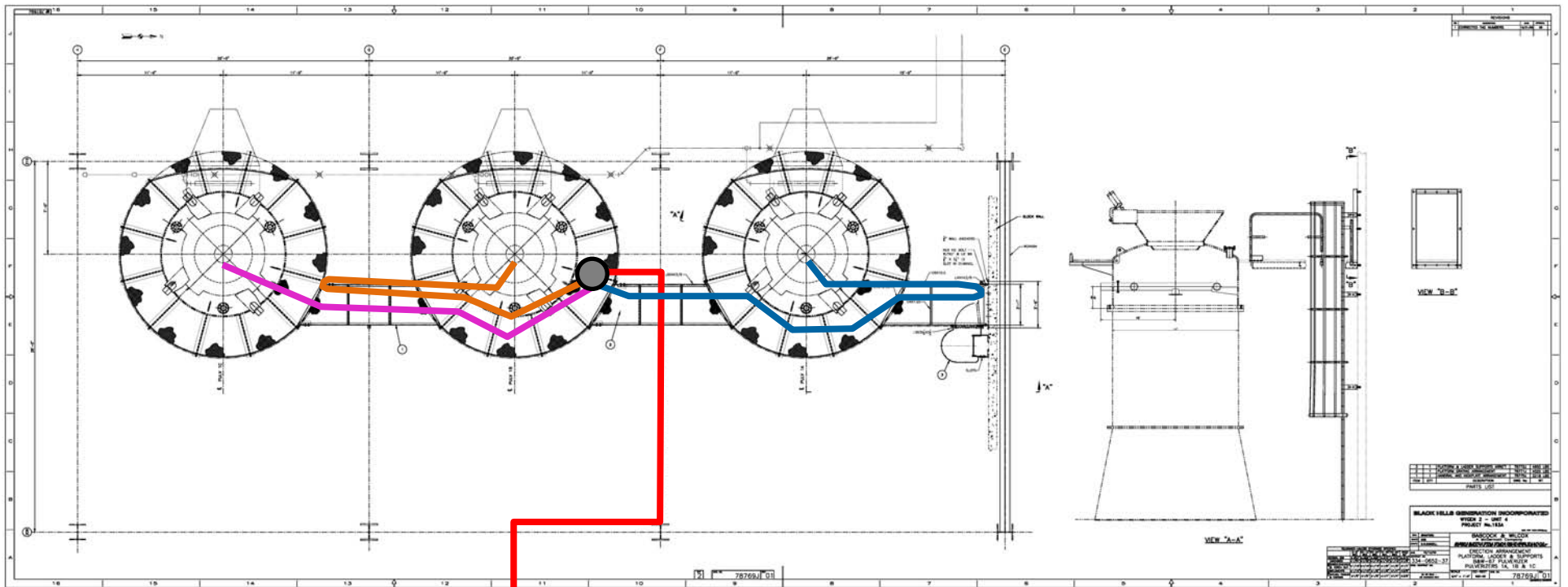


Long Term Injection

- ▶ To demonstrate a reduction in the rate of catalyst deactivation
- ▶ Wygen 2 a 100 MWe unit
- ▶ Wyodak mine PRB coal
- ▶ Deep Staged combustion
- ▶ Experienced rapid catalyst deactivation due to phosphorus in the past with new catalyst
- ▶ Present catalyst is 6.9 mm pitch single layer
- ▶ Regenerated with 5% plugging at time of installation



babcock & wilcox power generation group







Long Term Injection

- ▶ Completed 7950 hours of continuous injection of additive to date
- ▶ Plant coal flow is around 135,000 lbs per hour
- ▶ Test injection rate was less than 100 lb/hr
- ▶ Simple Pneumatic additive injection system

