

REINHOLD ENVIRONMENTAL Ltd.



**2013 APC Round Table
& Expo Presentation**

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Multi Pollution Control using Mitagent™ Combustion Additive

***2013 Reinhold APC Conference
St. Louis, Missouri – July 8-9, 2013***

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Mandar Gadgil
Air Quality Control System, Engineer

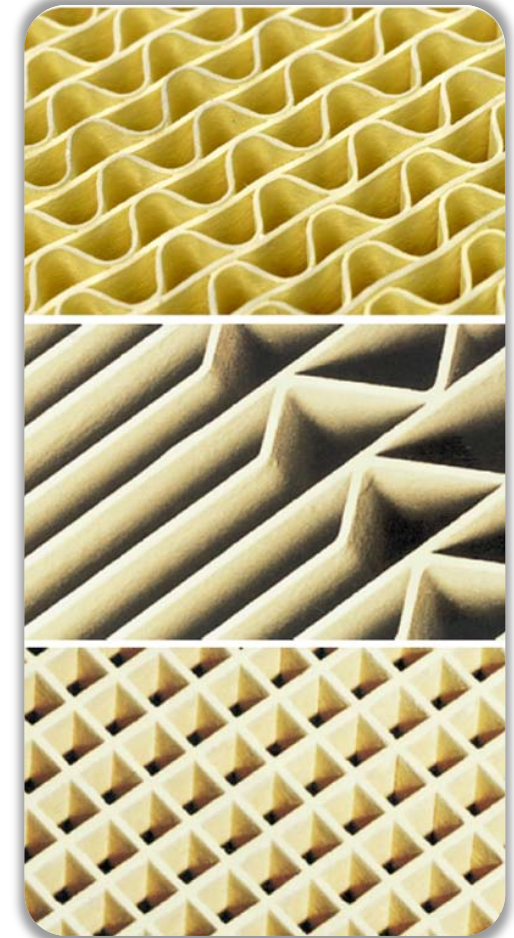
Presentation Agenda

Mitagent™ Combustion Additive Development

Selenium Speciation in Coal Combustion

Bromine Effects on Selenium Speciation

Selenium Mitigation



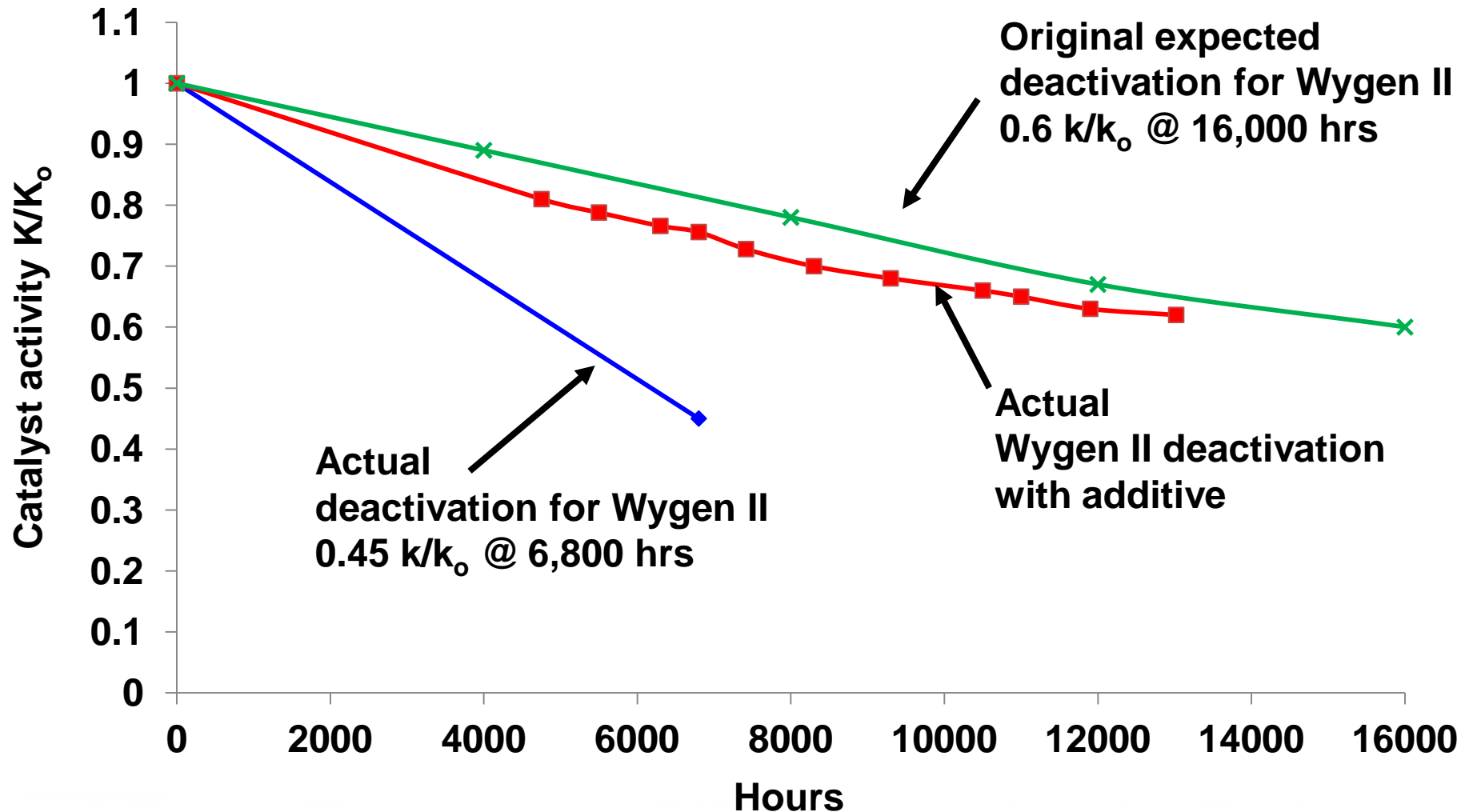
Periodic Table of the Elements

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)

Mitagent™ Additive Development

- **Mitagent 15 was developed to reduce rate of SCR catalyst deactivation on staged PRB units due to phosphorus poisoning and hence improve the performance**
- **Performance of Mitagent™ 15 demonstrated at Wygen II, 100 MW unit with SCR, SDA and fabric filter air quality control system**
- **Mitagent™ 95 was developed to control gas phase phosphorus entering the SCR and has since been discovered to facilitate Hg oxidation**
- **Improved Hg oxidation will reduce the cost of Hg emissions compliance by reducing ACI rates**
- **Performance of Mitagent 95 was demonstrated at 300 MW PRB unit with SCR, CDS and fabric filter air quality control system**

Wygen II – Catalyst Performance



Observations from Mitagent 15 Testing

- **With additive injection, the rate of deactivation slowed significantly on a staged combustion unit**
- **No negative impacts were observed on the furnace or any back-end equipment**
- **Applicability is independent of SCR catalyst type and pitch**
- **Stack sampling for metals showed a decrease in selenium emission in conjunction with Mitagent 15 injection**



Observations from Mitagent 95 Additive Testing

- **Demonstrated ability to control stack Hg to a level below 1.2 lb/Tbtu (MATS compliance limit)**
- **Demonstrated ability to achieve a 45% reduction in gas phase phosphorus at the SCR inlet**
- **Can achieve Hg emissions reduction using SCR, CDS and fabric filter for majority of operating period**
- **ACI may be necessary as trim control but not as primary driver**
- **No increase in undesirable hydrogen halide stack emissions observed with injection**
- **Reduction in gas phase selenium emission observed at stack even with bromine injection**



Effect of Bromine Injection on Selenium

- **Bromine or bromine compound injection is a very effective method for Hg oxidation**
- **It has been observed that bromine or bromine compound injection results in a change in selenium speciation**
- **On units with wet scrubbers this results in an undesirable level of selenium in the wet scrubber slurry**
- **Selenium in a Se(VI) oxidation state is difficult to remove effectively from a wet scrubber's waste water discharge using the standard precipitation and filtration technique**



Effect of Bromine Injection on Selenium

- **It was postulated that bromine compound injection was negatively affecting the Se partitioning between gas and particulate phase**
- **Gas phase sampling was performed on flue gas entering FGDs to understand the effects of bromine compounds on Se speciation**
- **In the case of Hg, the effect of bromine or a bromine compounds is predominantly observed after the air heater**



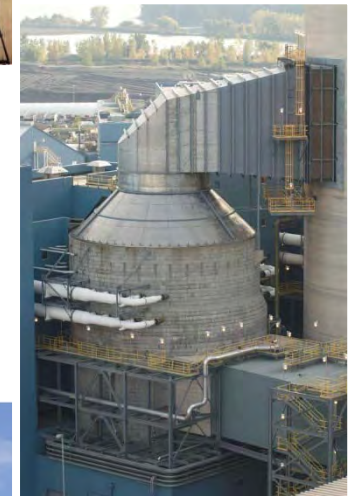
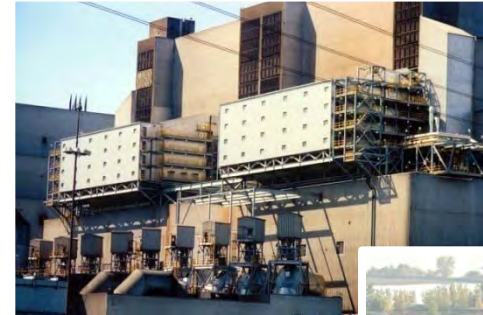
Selenium Speciation in Coal Combustion

- **Se is a trace element found in coal**
- **Se vaporizes during the combustion process regardless of whether such combustion is staged or un-staged**
- **As the combustion gases cool down in the convection pass and across air heater the Se speciation changes**
- **Depending upon the oxidation state, Se can exist in either one or both of a gas phase and/or a particulate-bound phase**
- **Gas phase Se can be removed by FGDs**



Effect of Bromine Injection on Selenium Speciation

- **Testing performed on PRB coal-burning unit with SCR, ESP and WFGD emissions control devices**
- **Testing performed at SCR and WFGD inlet using B&W PGG's modified M29 gas phase sampling technique**
- **Modifications include stack thimble and filter to reduce particulate breakthrough and modifications to impinger solutions to capture gas phase samples**
- **Impinger solutions analyzed by ICPMS to determine gas phase selenium concentration**



Effect of Bromine Injection on Selenium

<i>Sampling Location</i>	<i>Br Injection Rate in ppm</i>	<i>Gas phase Se Emission Rate (lb/hr)</i>	<i>% Increase</i>
SCR inlet	0	0.18	NA
SCR inlet	30	0.20	11%
WFGD inlet *	0	0.05	NA
WFGD inlet *	30	0.11	110%

Effect of Bromine Injection on Selenium

- **Testing at SCR inlet and WFGD inlet not performed simultaneously**
- **A small increase was observed in the gas phase selenium emission rate at SCR inlet when adding Br for Hg oxidation**
- **Gas phase Se emission rate more than doubled at WFGD inlet location when adding Br for Hg oxidation**
- **Se-Br compound formation may be taking place after the air heater during Br injection resulting in the formation of less particulate bound selenium thereby resulting in an increase in gas phase selenium**



Selenium Mitigation

- **An increase in particulate bound selenium was observed during long-term testing of Mitagent™ 15 at Wygen II**
- **It has been unexpectedly discovered that iron can control gas-phase selenium speciation**
- **Certain iron-selenium compounds (e.g., iron selenite) are less water soluble and thus less leachable than other selenium compounds**
- **As a result, in combination with the injection of one or more iron-containing compounds, it is possible to use bromine or a bromine compound for Hg oxidation while mitigating the negative impact of bromine injection on selenium speciation**

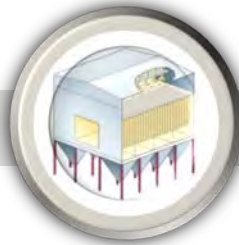


Effect of Mitagent 95 Injection on Gas Phase Emissions

Stack Sampling Date	Test ID	Gas phase Hg Emission Rate (lb/ Tbtu)	Gas Phase Se Emission (lb/ Tbtu)	Gas Phase P Emission (lb/ Tbtu)
1/10	With BPAC injection	0.7	0.41	8.1
1/11	Baseline	3.6	0.27	7.9
1/12	With 300 ppm Cl addition	1.4	0.49	7.6
1/13	30 ppm Br addition	1.0	0.57	8.2
1/14	30 ppm of bromine in form of Mitagent™ 95 additive	1.1	0.14	4.5

Observations from Mitagent 95 Injection

- **It was observed that gas phase phosphorus, selenium and mercury were reduced**
- **ACI does not remove gas phase selenium**
- **Bromine injection alone resulted in Hg emissions below MATS limit but resulted in an increase in the level of gas phase selenium**
- **As a result of Mitagent 95 additive injection it is possible to simultaneously reduce Hg and Se gas phase levels**





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THANK YOU. QUESTIONS?

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