REINHOLD ENVIRONMENTAL Ltd.

2016 NOx-Combustion-CCR Round Table Presentation

February 1 & 2, 2016, in Orlando, FL / Hosted by OUC

Reagents 101

A Background Primer on Utilization of Chemical Reagents in Coal-Fired Electrical Generating Stations

Reinhold Environmental – 2016 NOx Conference

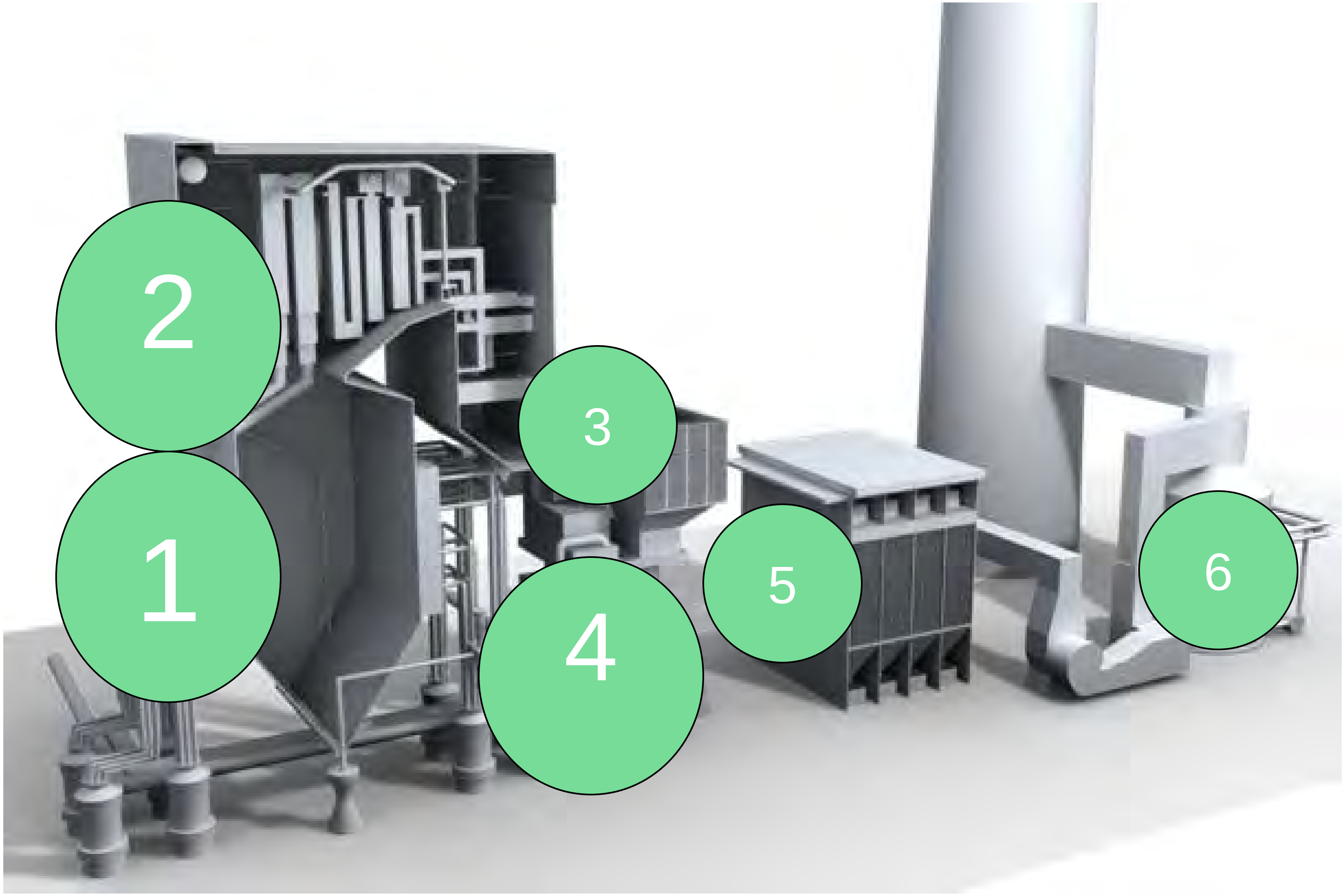
February 1, 2016

What do we mean by Reagent

- **For the purpose of the next 60 minutes:**

A Reagent is a chemical substance that is introduced into the power generation process for the purpose of controlling an unwanted consequence of Coal Combustion.

Where Do Reagents Get Used?



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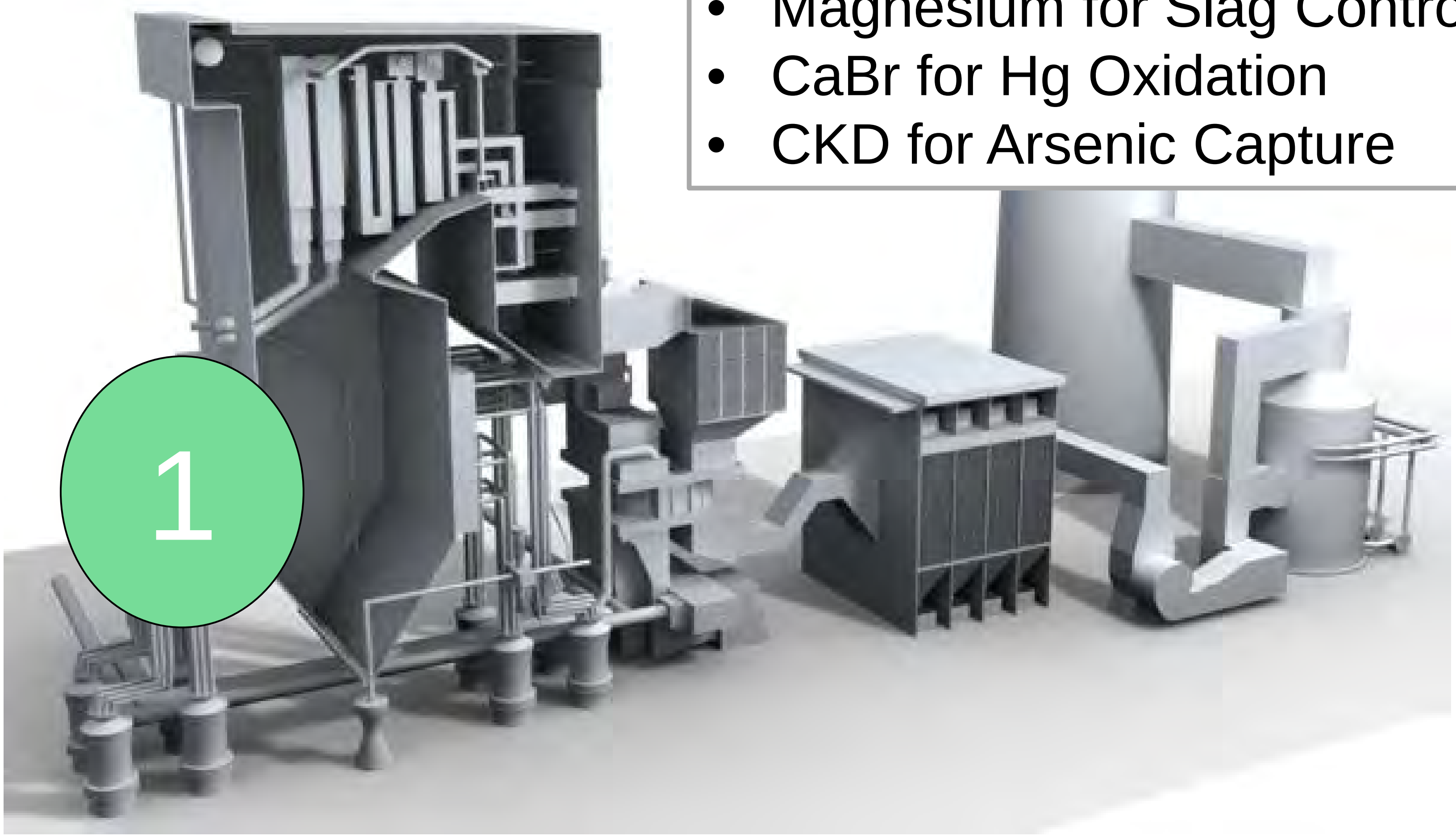
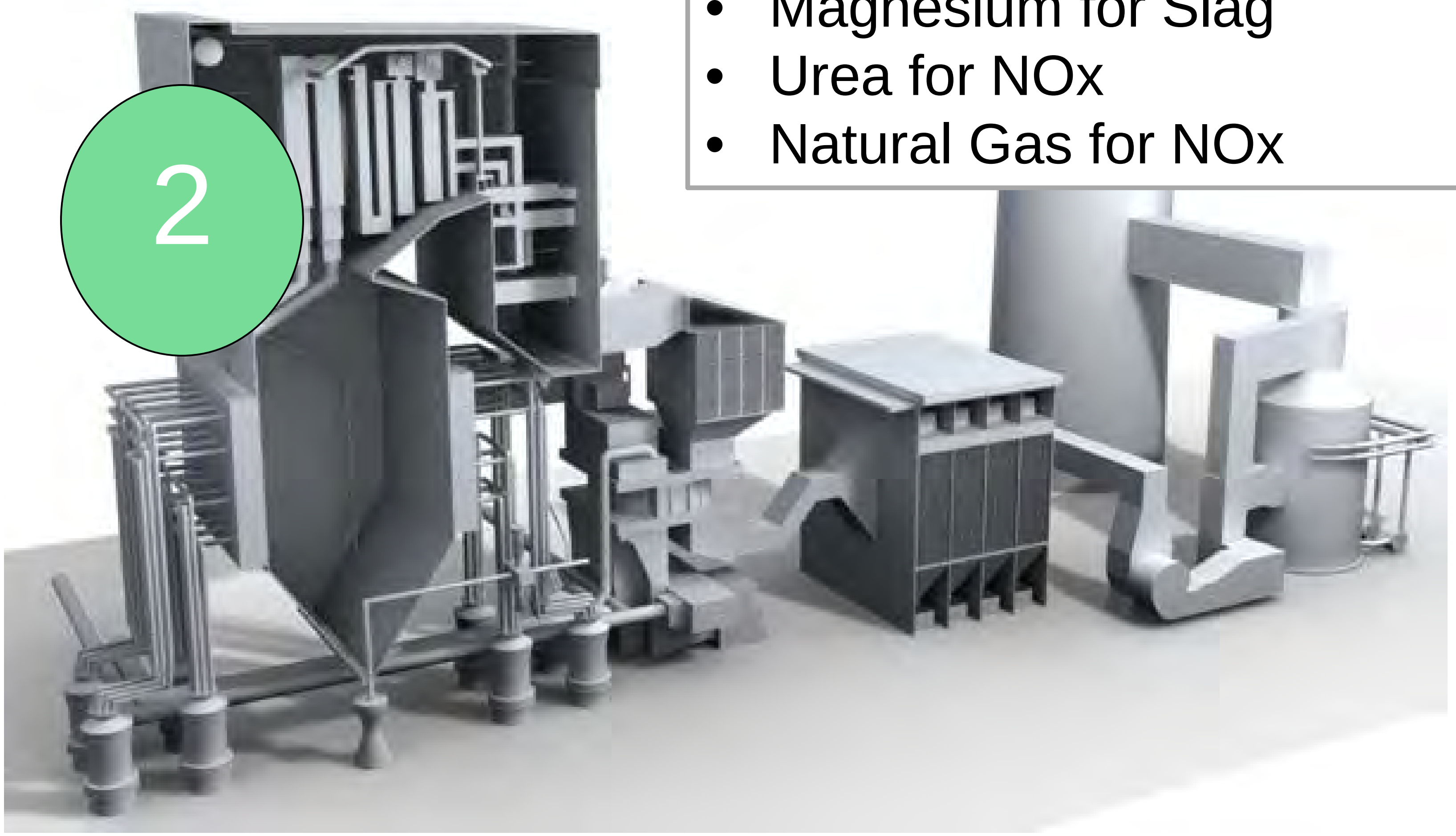


Furnace Injection:

- Magnesium for Slag Control
- CaBr for Hg Oxidation
- CKD for Arsenic Capture

Where Do Reagents Get Used?



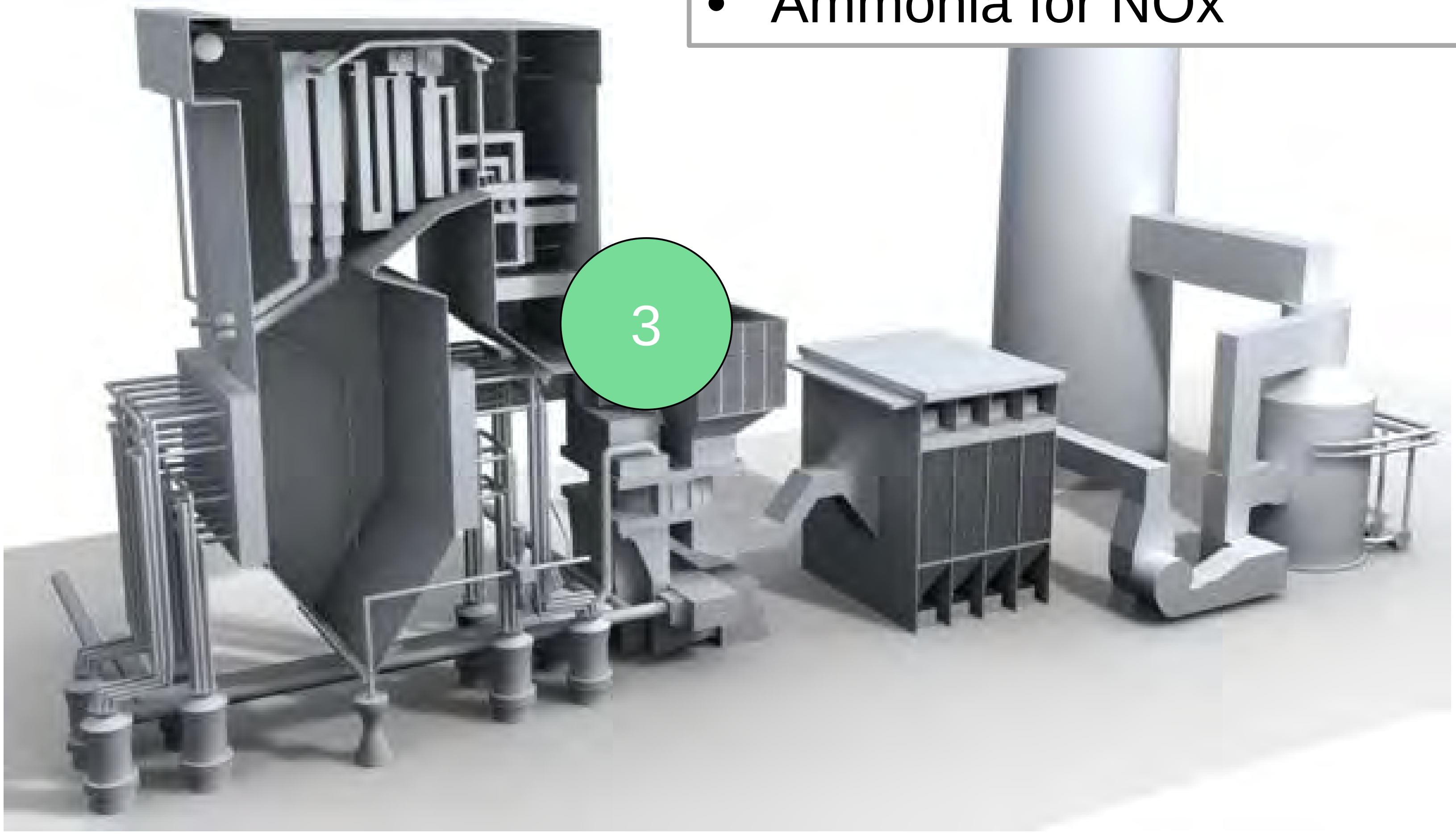
Upper-Furnace Injection:

- Magnesium for Slag
- Urea for NOx
- Natural Gas for NOx

Where Do Reagents Get Used?

Pre-SCR Injection:

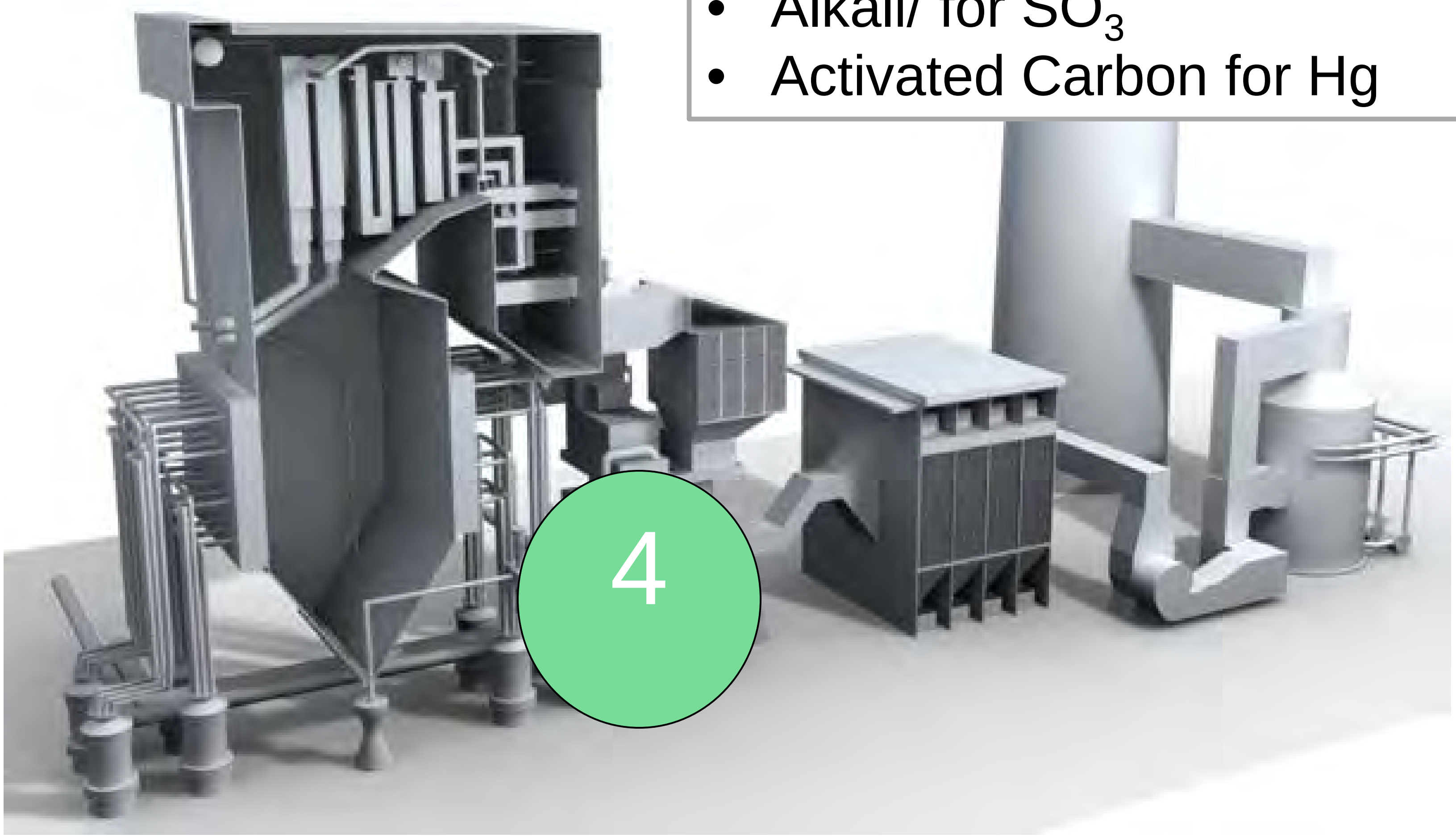
- Ammonia for NOx



Where Do Reagents Get Used?

Pre-AH Injection:

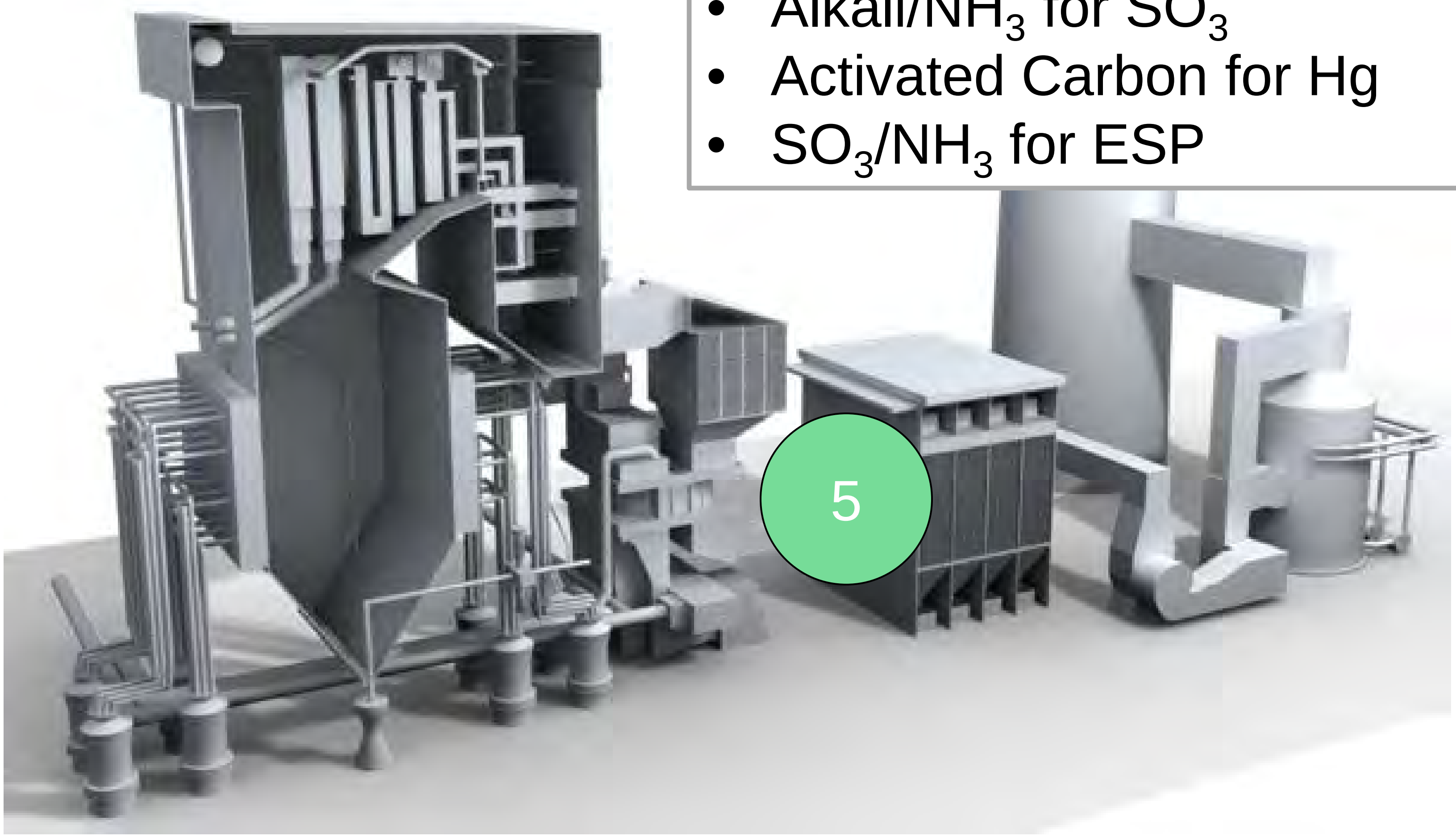
- Alkali/ for SO_3
- Activated Carbon for Hg



Where Do Reagents Get Used?

Post-AH Injection:

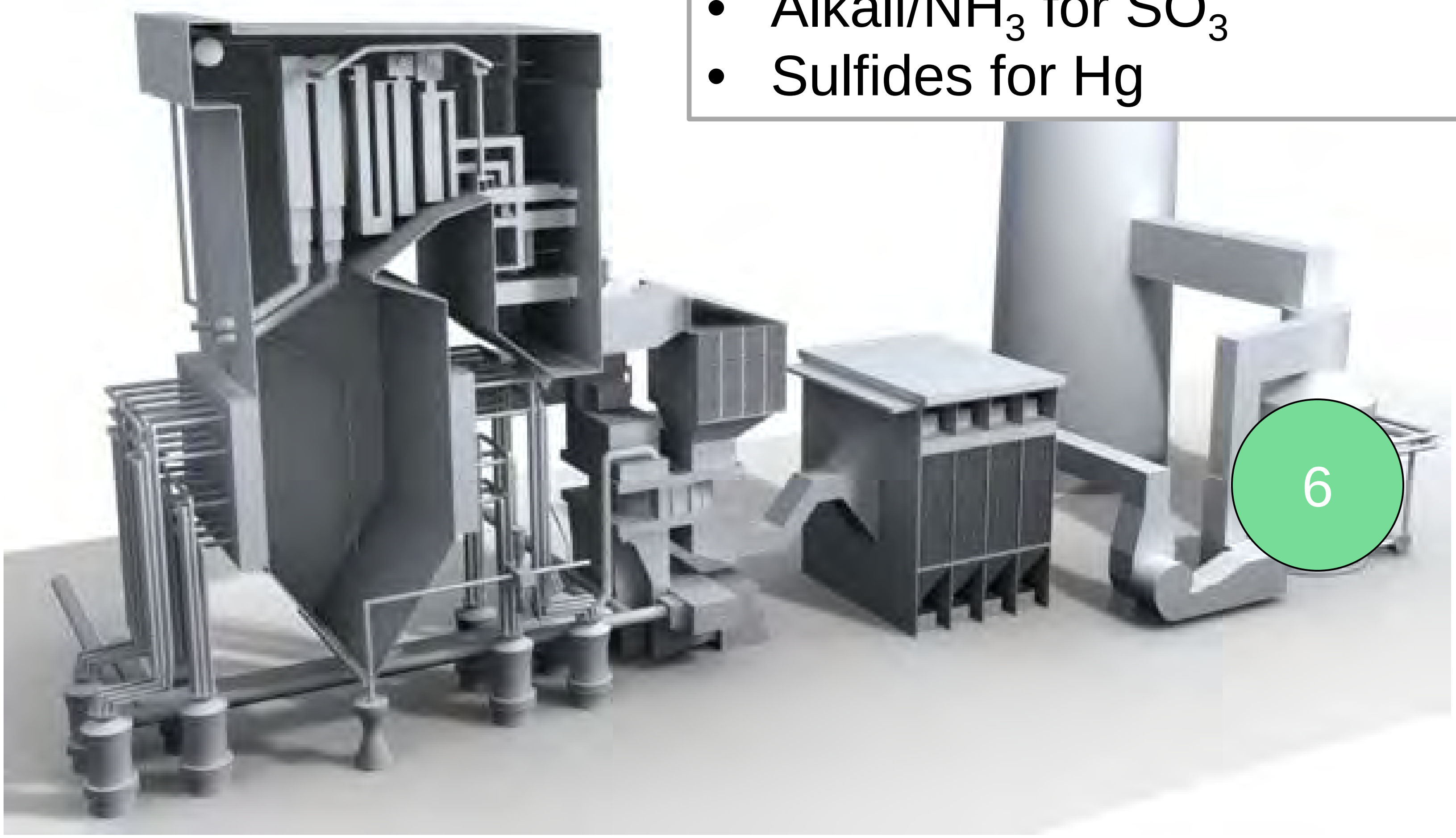
- Alkali/NH_3 for SO_3
- Activated Carbon for Hg
- SO_3/NH_3 for ESP



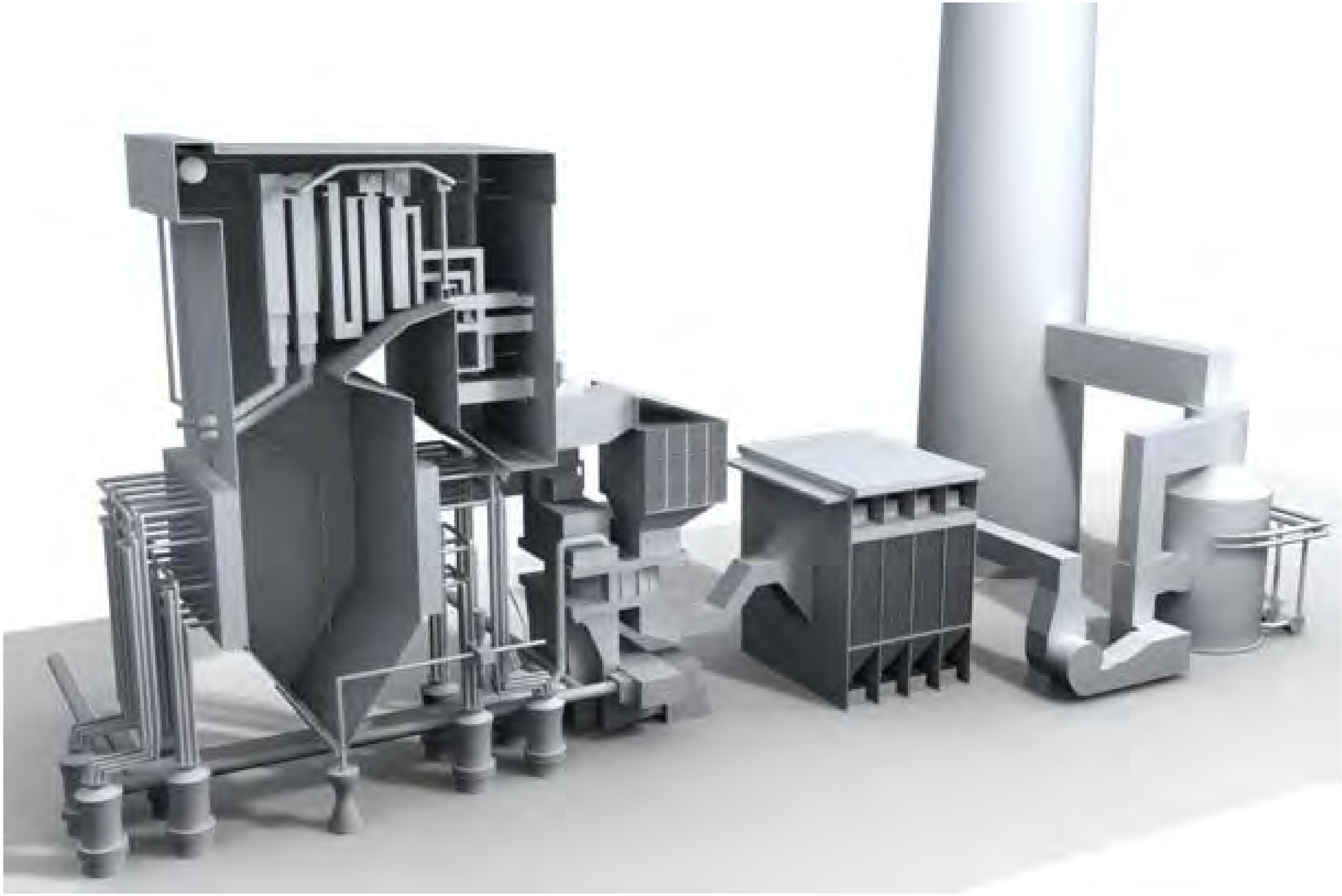
Where Do Reagents Get Used?

Pre-FGD Injection:

- Alkali/NH_3 for SO_3
- Sulfides for Hg



Where is your plant in this cocktail?



Reagent Cocktails - PRB

- **PRB Burning Plants:**
  - Low Halogen in the coal requires halogen addition for Hg oxidation
  - Natural Gas, Urea or Ammonia will be required for NOx
  - Activated Carbon will be required for Hg
  - SO_3 Conditioning for ESP Performance
  - Sulfides will be required for Re-entrainment
  - MgO or Mg(OH)2 may be useful for runny or vitrified deposits
  - CKD is Not required for Arsenic
  - Alkali is Not required for SO_3
- **Section 45 Additive is a Cocktail of its own.**

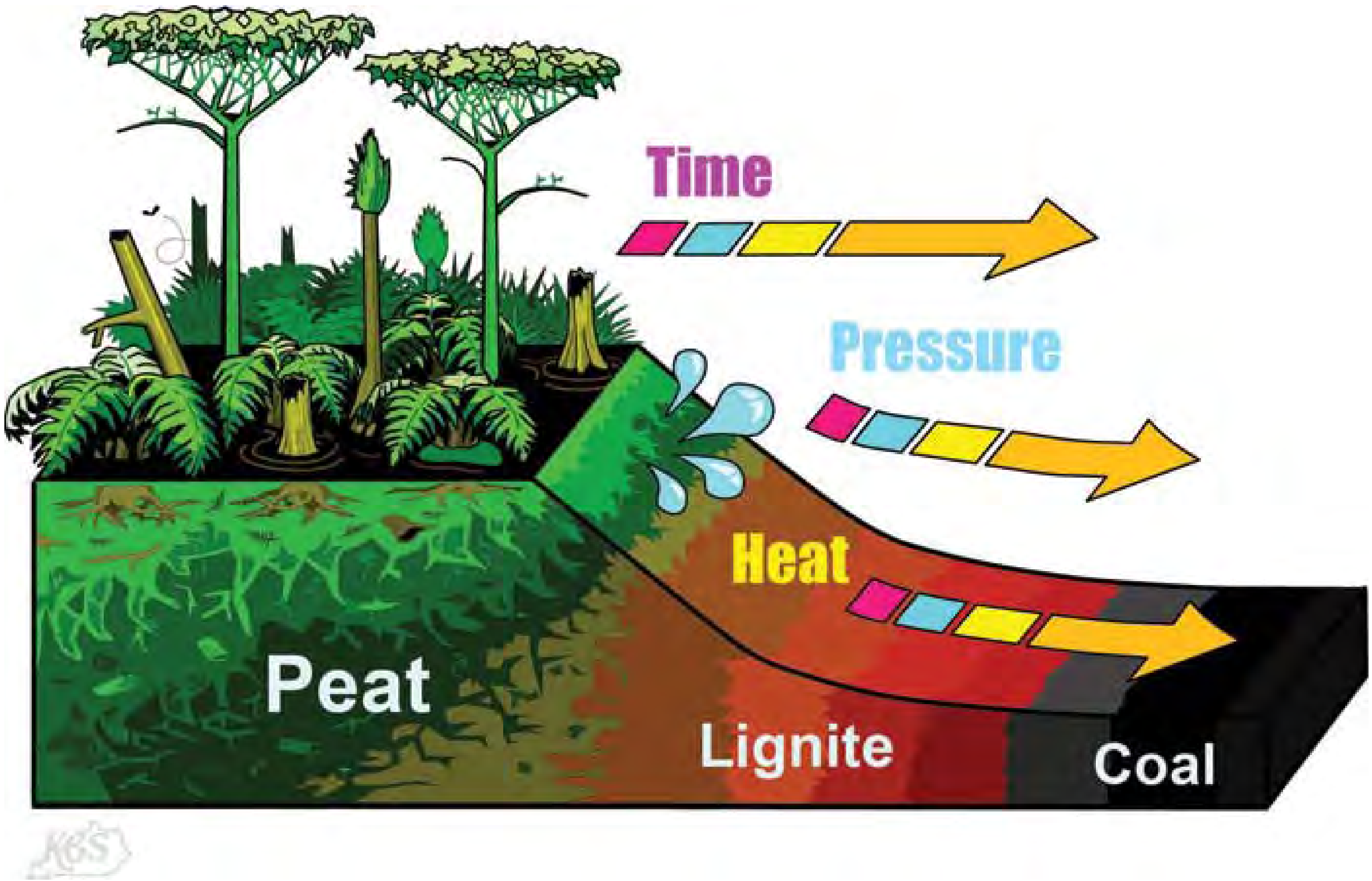
Reagent Cocktails – ILB/NAPP

- **High Sulfur Burning Plants:**
  - MgO or $Mg(OH)_2$ should be considered for upper furnace and superheat slagging
  - Natural Gas, Urea or Ammonia will be required for NOx
  - Alakali Injection is Mandatory for SO_3
  - Activated Carbon may be required for Hg
  - Halogen treatment may not be required, or required occasionally
  - Sulfides may be required for Re-entrainment
  - CKD or Pulverized Limestone may help arsenic
  - SO_3 Conditioning in Not Required for ESP Performance

But if the Mix is Wrong:

Reagent Usage in High Sulfur Coal Applications

Coal is Complex Material



Coal Composition

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SGS Minerals Sample ID: 511-1281701-001

		Method	As Received	Dry	DAF
Moisture, Total %		ASTM D3302	12.76		
Ash %		ASTM D7582	11.31	12.96	
Sulfur %		ASTM D4239	3.44	3.94	
Gross Calorific Value	BTU/LB	ASTM D5865	10883	12474	14332
Carbon %		ASTM D5373	60.95	69.86	
Hydrogen %		ASTM D5373	4.27	4.89	
Nitrogen %		ASTM D5373	1.35	1.55	
Oxygen %		ASTM D3176 (by diff)	5.92	6.80	

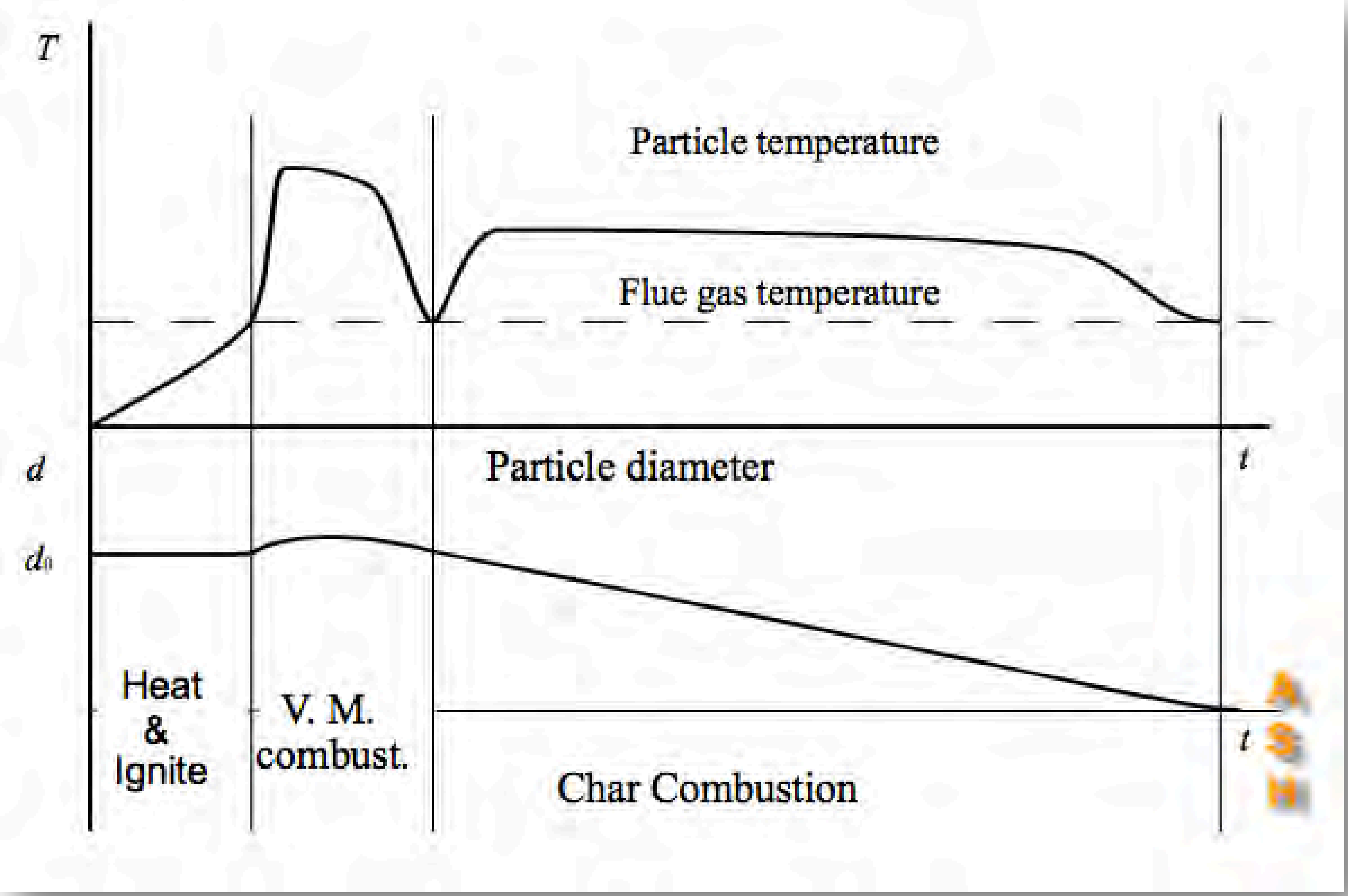
Tests	Result	Unit	Method
Sample Weight	11.5	---	
UOM, Sample Weight	lb	---	
FUSION TEMPERATURE OF ASH, REDUCING			
Initial Deformation	2050	øF	ASTM D1857
Softening	2120	øF	ASTM D1857
Hemispherical	2270	øF	ASTM D1857
Fluid	2370	øF	ASTM D1857
FUSION TEMPERATURE OF ASH, OXIDIZING			
Initial Deformation	2480	øF	ASTM D1857
Softening	2520	øF	ASTM D1857
Hemispherical	2530	øF	ASTM D1857
Fluid	2540	øF	ASTM D1857

Sulfur in Coal

- **Sulfur Generally Occurs in Four Forms**
  - Pyritic Sulfur (Included and Excluded)
  - Sulfate Sulfur
  - Organic Sulfur
  - Free Sulfur

- **Pyritic Sulfur (FeS_2) is Often the Most Important:**
  - Influences Slagging
    - E.g., ***Multiplicative*** in Duzy Ash Chemistry Index
  - Influences Acid Gas Formation

Coal Combustion



Slagging, Fouling & Scaling

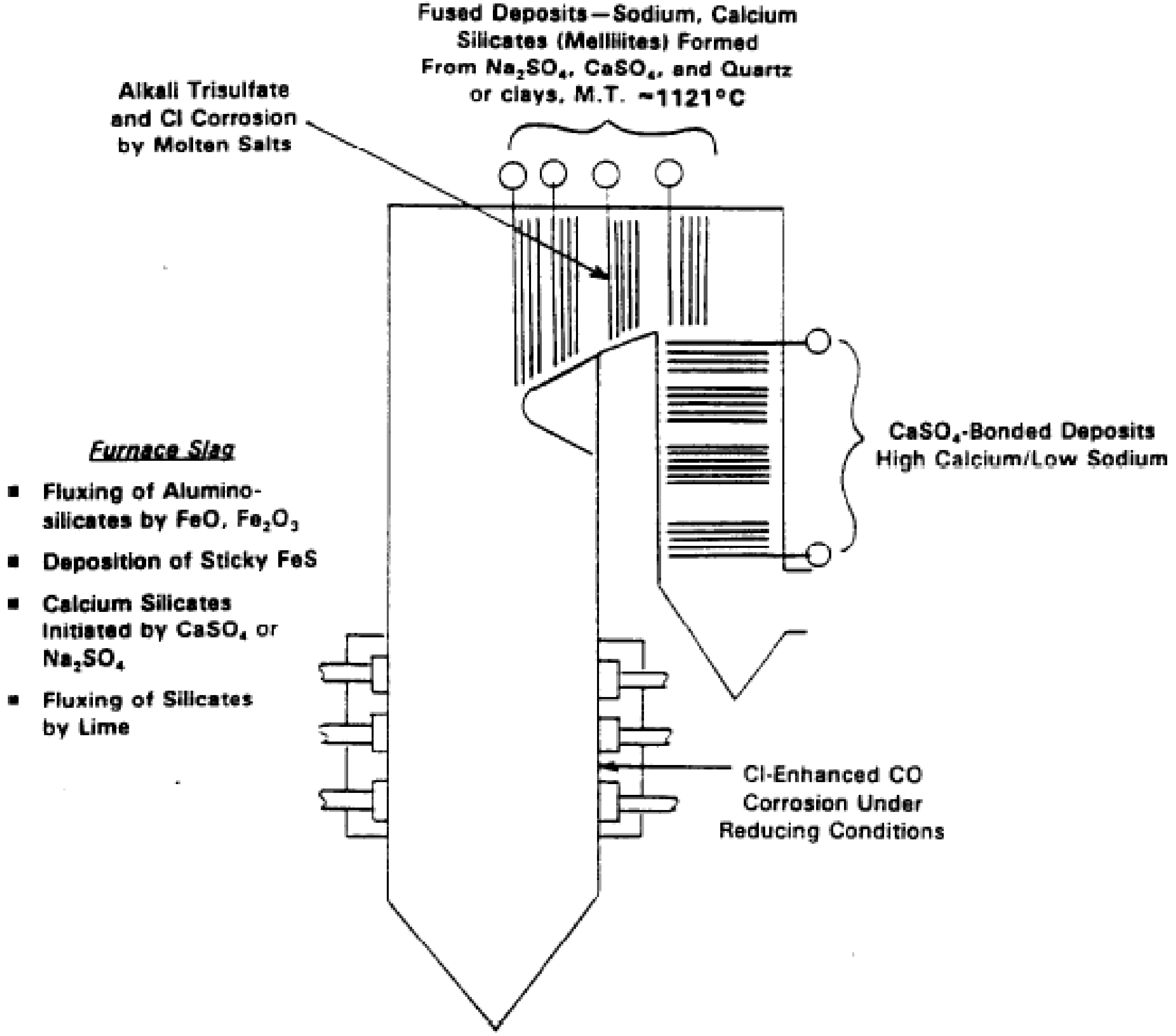


Fig. 1. Typical slagging, fouling, and corrosion found at various locations in the steam generators.

Pyrite Oxidation

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- $FeS_2 \rightarrow (1\text{-}x)\ Fe_{(1\text{-}x)}S + (1\text{-}x)\ S$
- $Fe_{(1\text{-}x)}S + (1+x/2)\ O_2 \rightarrow (1\text{-}x)\ FeO + SO$
- $Fe_{(1\text{-}x)}S + (1\text{-}x)\ SO \rightarrow (1\text{-}x)\ FeO + (1\text{-}x/2)S_2$
- $Fe_{(1\text{-}x)}S + (1\text{-}x)\ O \rightarrow (1\text{-}x)\ FeO + S$
- $FeS_2 + O_2 \rightarrow FeS + SO_2$
- $FeS_2 + SO \rightarrow FeS + S_2 + O$
- $FeS + O_2 \rightarrow FeO + SO$
- $FeS + SO \rightarrow FeO + S_2$
- $FeS + O \rightarrow FeO + S$
- $2FeO + O2 \rightarrow Fe_2O_3 + O$
- $FeO + Fe_2O_3 \rightarrow Fe_3O_4$

Fouling Mechanisms

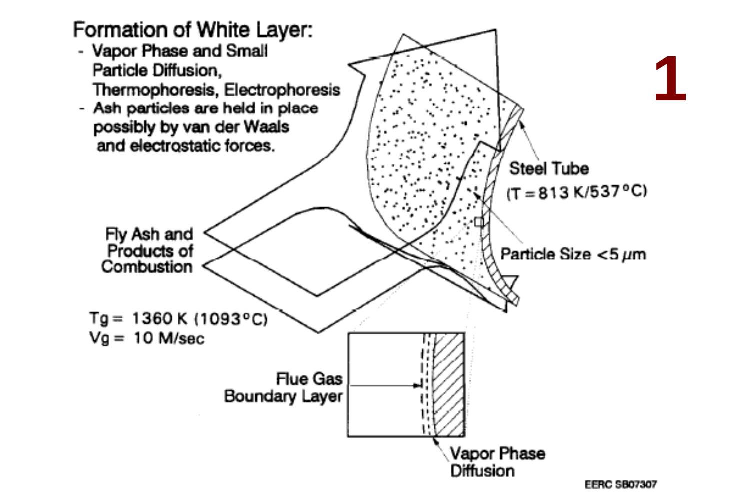


Fig. 21. Formation of initial deposit in fouling deposits[79] (courtesy of Dr. S. Benson, University of North Dakota).

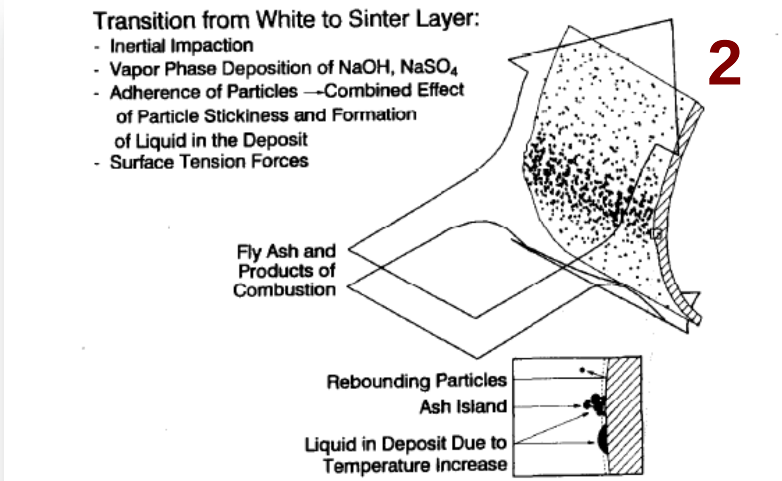


Fig. 22. Formation of transitional deposit layers in fouling deposits[79] (courtesy of Dr. S. Benson, University of North Dakota).

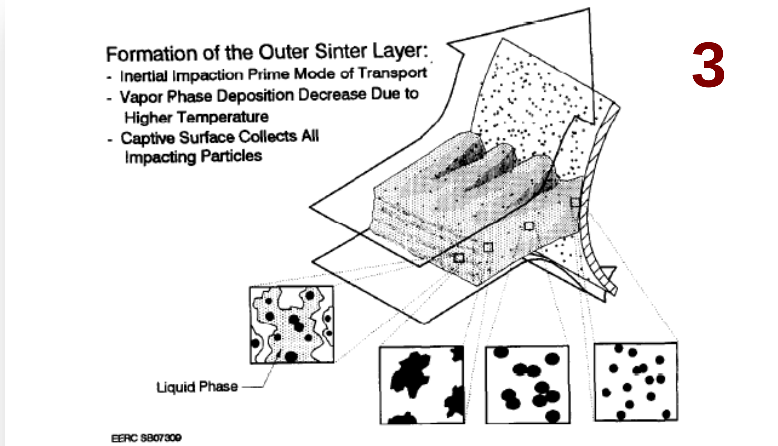
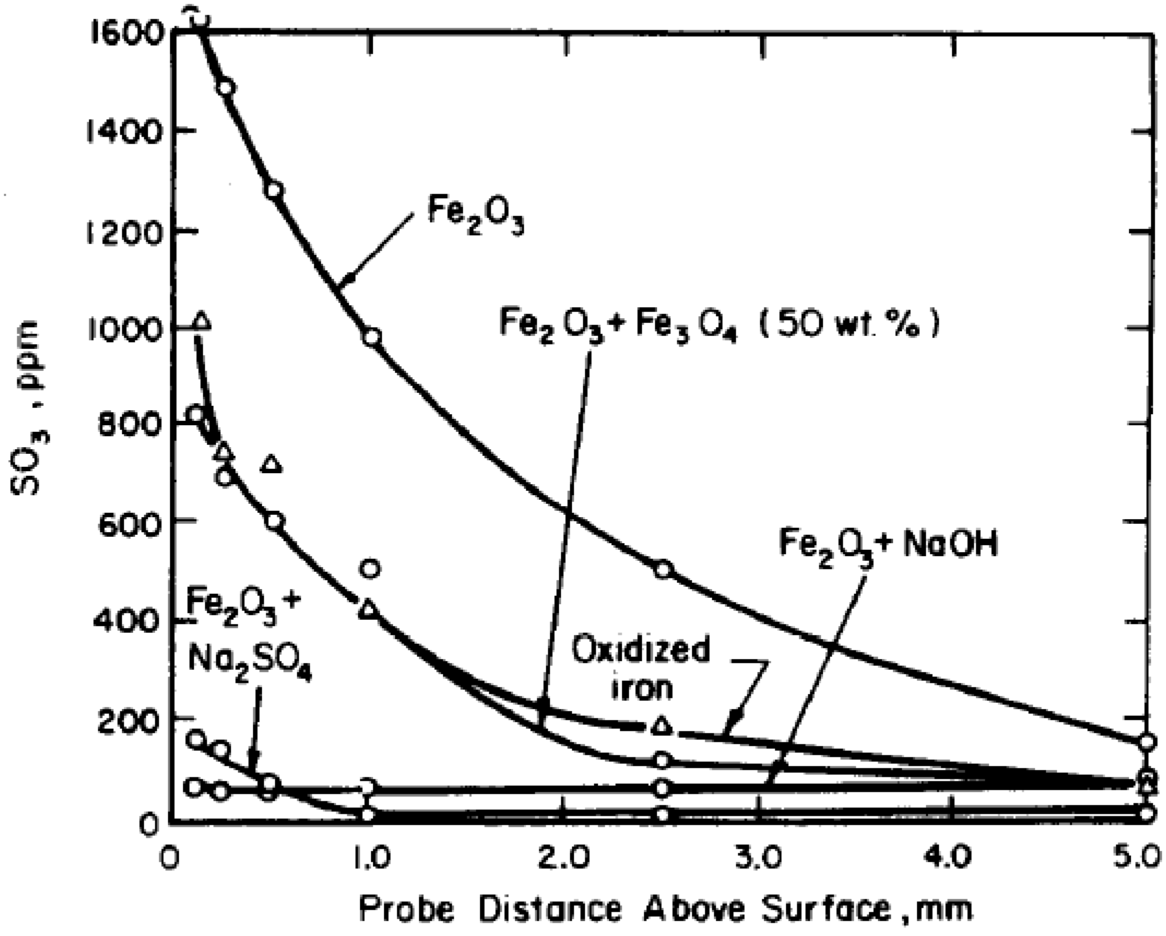


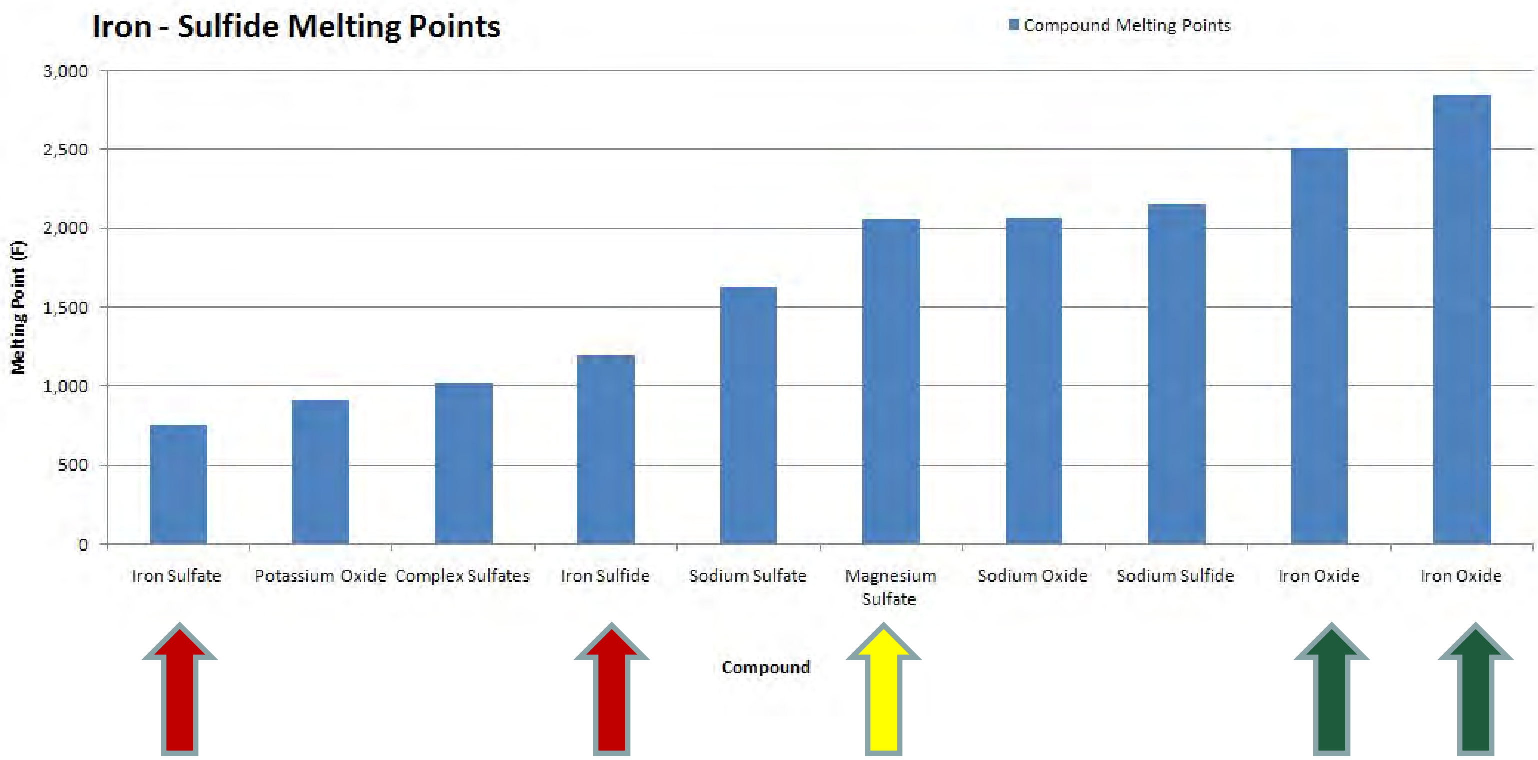
Fig. 23. Formation of outer layers in a fouling deposit[79] (courtesy of Dr. S. Benson, University of North Dakota).

1. Inner layer formed by ultra-fine particles held by impact or electrostatic forces
2. Transition layer is bound by sticky particles and liquid formed in the deposit
3. Outer layer is higher temperature with buildup formed by impaction and held by inner layer liquid

Surface Effects Strong



Why Does MgO Work?



Magnesium Effective Zone

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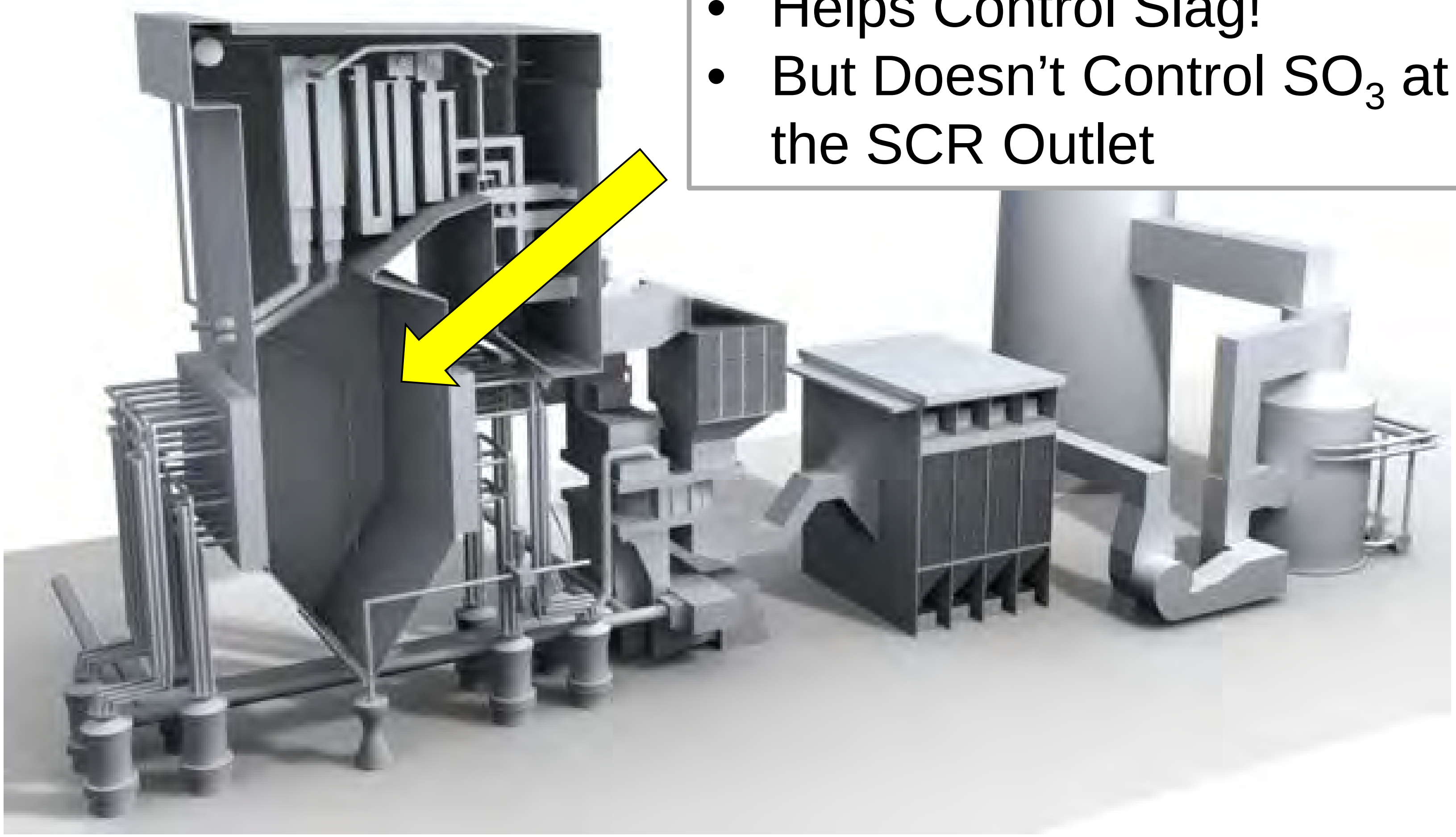

Magnesium Injected Here:

- Helps Control Slag!
- But Doesn't Control SO_3 at the SCR Outlet

Application on the Coal Belt

- **Single point rake application**
- **Low cost, low maintenance**
- **Applied on coal belt prior to bunkering**
- **Difficult to optimize**

Injection System

- Concentric, dual fluid injectors
- 200-3000 gm/Min/Injector
- Air Carrier provides variable penetration depth control and protection of addition from premature devolatilization
- Self purging for variable use applications
- Low cost, low maintenance

SO_3 Mitigation

Where is SO_3 Created

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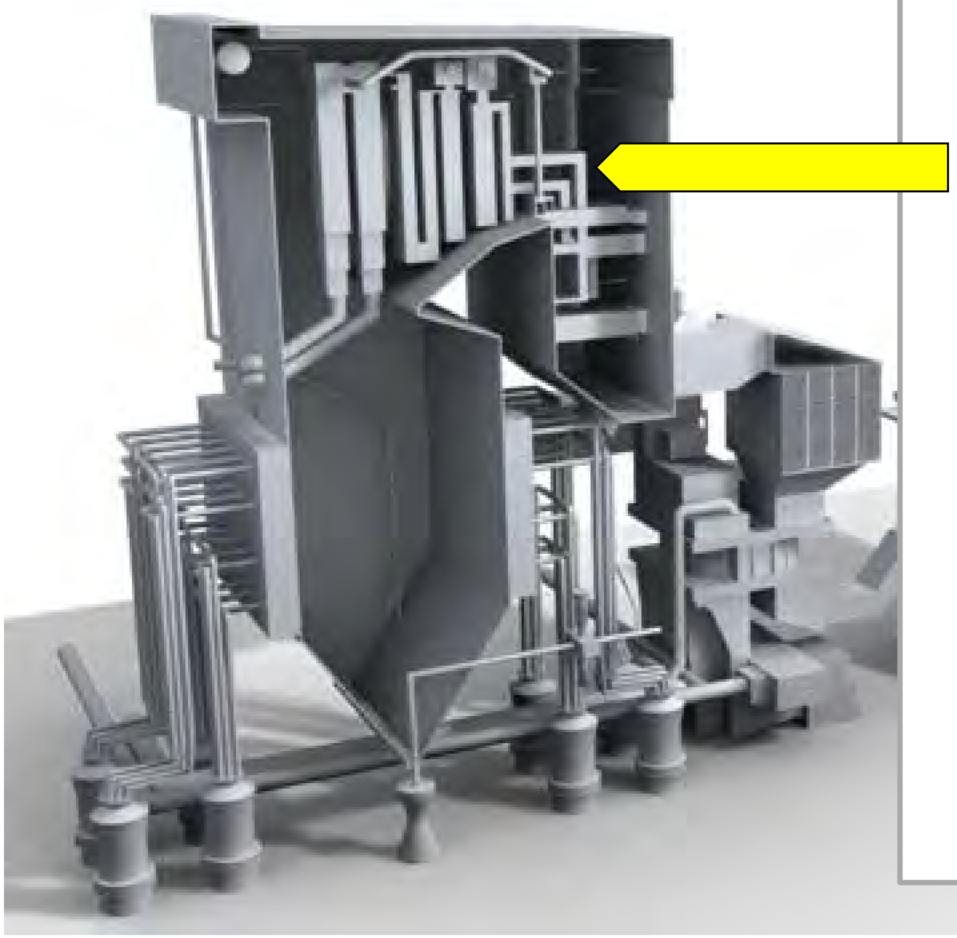
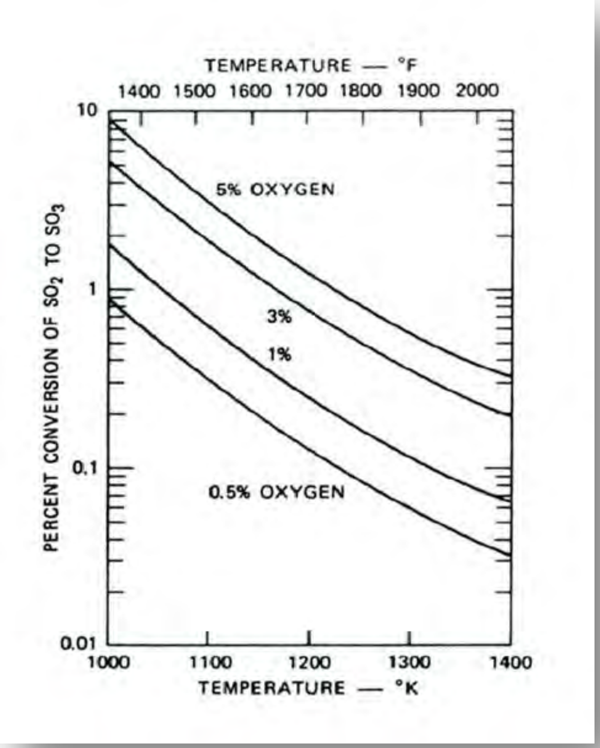
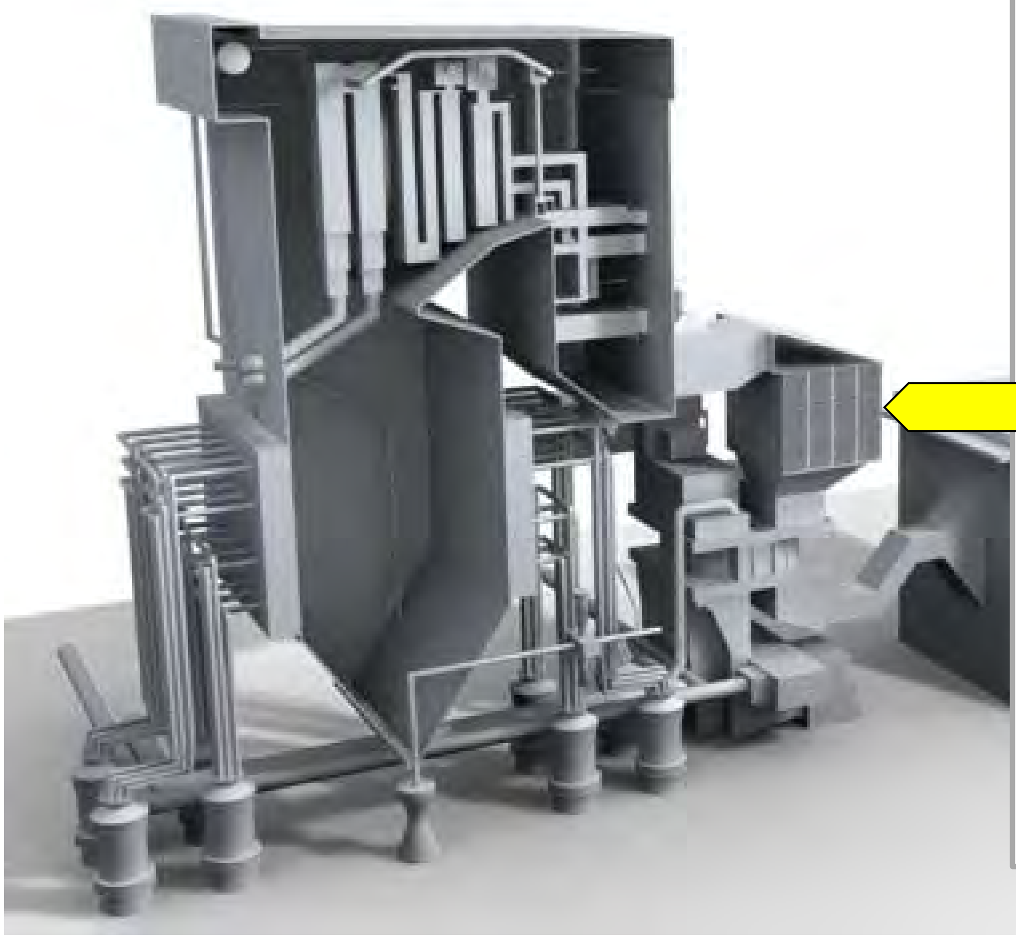


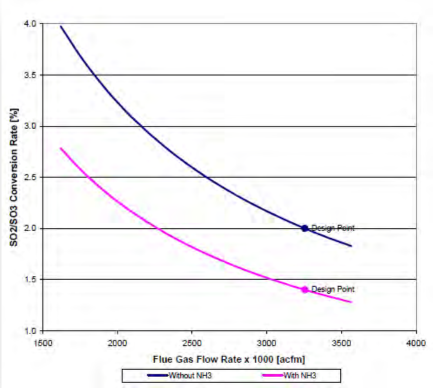
Backpass Generation:

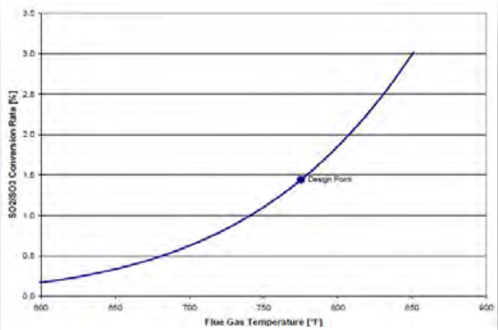


Where is SO_3 Created



SCR Generation:





Reagent Requirements

- **Once you understand the Sources of SO_3, then you can understand the reagent required to manage it.**

- **Basically:**
  - Determine the mass weight of the acid
  - Determine the reagent to be used
  - Determine the molar ratio based on the sorbent/acid reaction
  - Determine the desired SO3 residual level at the selected location
  - Do the math !

Determine the Amount of Acid Present

Quantify the Conditions

Dry Sorbent Injection Calculation Spreadsheet
Rev. 17 - 11/23/2015
By: Chothani/Branning/Lockert

STEP 1: Enter Coal Properties

FUEL PROPERTIES			
Coal-Btu/Lb	12,000	Btu/Lb	HHV basis
Coal-S	2.76	%	
Coal-Cl	0.080	%	
Coal-F	0.0067	%	

STEP 2: Enter Other Unit Conditions

OTHER UNIT CONDITIONS			
Gross MW Rating	670	GMW	If unknown, set to Net MW x 1.06
Excess Oxygen	3.5	%	
Net Heat Rate	9,800	BTU/KWH	
SO2 to SO3 Conversion Rate	2	%	
Fuel Factor, Fd	9,780	dscf/MMbtu	Select Fuel Factor from Table at right ------->
Fuel Factor, Fw	10,640	wscf/MMbtu	Select Fuel Factor from Table at right ------->

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Determine the Pre-Treatment Gas

PRE-TREATMENT CONDITIONS AT AIR HEATER INLET DUCT				
Parameter	Wet Basis		Dry Basis	
Heat Input	6,194	MMBTU/hr	6,194	MMBTU/hr
Flue Gas Flow, 0% O2	65,907,774	wscf/hr	60,580,642	dscf/hr
Flue Gas Flow, 0% O2	5,144,878	Lb/hr	4,892,215	Lb/hr
Flue Gas Flow, Actual O2	68,397,282	wscf/hr	62,931,959	dscf/hr
Flue Gas Flow, Actual O2	5,339,213	Lb/hr	5,086,550	Lb/hr
H2O	252,663	Lb/hr	0	Lb/hr
H2O, Actual O2	8.1	%	0	%
O2	194,335	Lb/hr	194,335	Lb/hr
O2	3.50	%	3.81	%
SO2	4.60	Lb/MMBTU	4.60	Lb/MMBTU
SO2	28,464	Lb/hr	28,464	Lb/hr
SO2, Actual O2	2560	ppm	2786	ppm
SO3	0.1192	Lb/MMBTU	0.1192	Lb/MMBTU
SO3	738	Lb/hr	738	Lb/hr
SO3, Actual O2	51	ppm	56	ppm
HCl	0.069	Lb/MMBTU	0.069	Lb/MMBTU
HCl	425	Lb/hr	425	Lb/hr
HF	0.006	Lb/MMBTU	0.006	Lb/MMBTU
HF	36.4	Lb/hr	36.4	Lb/hr

Select the Reagent to be Used

Sorbent Considerations

- **Magnesium Oxide – Magnesium Hydroxide**
  - Simply put, this is too expensive for post-SCR SO_3 management.
- **Ammonia**
  - Ammonia injection ahead of the Air Heater will lead to high levels of ABS formation and AH fouling. This is not a good location for ammonia injection.
  - Ammonia injection at the AH Outlet to create Ammonium Sulfate fume works and is cost effective from a capital and O&M perspective. However, the ammonia-in-ash residual makes the flyash non-salable and there are risks of ammonium bisulfate fouling of the ESP if SO3 levels jump without closed loop control. Very few utilities use this method directly (some use it indirectly, but more on that later)

Sorbent Considerations

- **Trona – Sodium Bicarbonate – Soda Ash**
  - Pre-Hot Side ESP – This material is effective here since the sodium can enhance the performance of the Hot-side ESP and residual sodium will be capture. Problems may occur if sodium is over-injected leading to high levels of sodium bisulfate formation in the SCR passage
  - Pre-AH - These Sodium-based reagents are highly effective in capturing SO_3. However, when used ahead of the Air Heater there is a high risk of air heater fouling due to sodium bisulfate formation. AECOMM (formerly URS) utilizes a very fine sodium particle delivered in a water carrier ahead of the SCR. This has proven to be effective and generally safe for the AH as long as closed loop control is maintained.
  - Post-AH – Several installations use trona as a reagent at this location. It is effective at SO_3 capture but, again, is sensitive to Sodium Bisulfate formation if Na/SO_3 ratio gets too far below 2.0 and can lead to ESP and internal fouling when gas temperature exceed 320F (approximately)

Sorbent Considerations

- **Hydrated Lime**
  - Hydrate Lime is becoming the material of choice for Acid Gas Treatment.
  - It produces no secondary salts when over, or under, injected.
  - When distribution is managed and closed loop control is employed it can be injected pre-Air Heater, pre-ESP or even post-ESP.

Unless there are compelling reasons to the contrary, we generally recommend hydrated lime for flue gas treatment use!

Select your Sorbent Reaction

Sodium Reactions		
2 $(Na_2CO_3.NaHCO_3.2H_2O)$ ->	$3Na_2CO_3 + CO_2 + 5\ H_2O$	(Trona first calcines to Sodium Carbonate)
$Na_2CO_3 + SO_3$ ->	$Na_2SO_4 + CO_2$	
$Na_2CO_3 + 2\ HCl$ ->	$2\ NaCl + H_2O + CO_2$	
$Na_2CO_3 + 2\ HF$ ->	$2\ NaF + H_2O + CO_2$	

Calcium Reaction	
$Ca(OH)_2 + SO_3 + H_2O$ ->	$CaSO_4 + 2\ H_2O$
$Ca(OH)_2 + 2HCl$ ->	$CaCl_2 + 2\ H_2O$
$Ca(OH)_2 + 2HF$ ->	$CaF_2 + 2\ H_2O$

Magnesium Reactions	
$Mg(OH)_2 + SO_3 + H_2O$ ->	$MgSO_4 + 2\ H_2O$
$Mg(OH)_2 + 2HCl$ ->	$MgCl_2 + 2\ H_2O$
$Mg(OH)_2 + 2HF$ ->	$MgF_2 + 2\ H_2O$

Determine the Molar Ratios

		Mole Factor-SO2	Mole Factor-SO3*	Mole Factor-HCl*	Mole Factor-HF*
MW of H2SO4	98				
MW of SO3	80				
MW of SO2	64				
MW of Trona	226	0.6666667	0.666666667	0.333333333	0.333333333
MW ofNa2CO3	106	1	1.00	0.5	0.5
MW of NaHCO3	84	2	1	1	0.5
MW of Ca(OH)2	74		1	0.5	0.5
MW of Mg(OH)2	58.3		1	0.5	0.5
MW of MgO	40.3		1	0.5	0.5
MW of HCL	36.5				
MW of HF	20				

*Mole Factor = # of Moles of Sorbent per Mole of Acid. For E.G. you need 2 Moles of Trona for every 3 Moles of SO3

For Hydrated Lime the Mole Factor is 1.0 meaning it takes one mole of HL to react with one mole of H_2SO_4.

Molar Ratio of HL to Acid = 74/98

Actual Sorbent Needed

- **738 Pounds/Hr. in our example**
  - Mole Ratio of $H_2SO_4:SO_3 = 98/80$
  - 738 x (98/80) = 904 Lb/Hr. of sulfuric acid vapor
- **904 Pounds/Hr. of acid requires:**
  - 904 x (74/98) = 682 Lb./Hr. of Hydrated Lime
- **Stoichiometric Ratio Selection:**
  - We use a 3.0 SR for starting purposes
  - 682 Lb./Hr. x 3 = 2,048 Lb./Hr. of Hydrated Lime

	Sorbent for SO3		Sorbent for HCl	Sorbent for HF	Total-All Acids
Sorbent-Trona	4171	Lbs/Hr	877	137	5185
Sorbent-Na2CO3	2935	Lbs/Hr	617	97	3648
Sorbent - NaHCO3	2326	Lbs/Hr	977	76	3379
Sorbent-Ca(OH)2	2049	Lbs/Hr	431	67	2547
Sorbent-Mg(OH)2	1614	Lbs/Hr	339	53	2006
Sorbent-MgO	1116	Lbs/Hr	234	37	1387

*Mole Factor = # of Moles of Sorbent per Mole of Acid. For E.G. you need 2 Moles of Trona for every 3 Moles of SO3

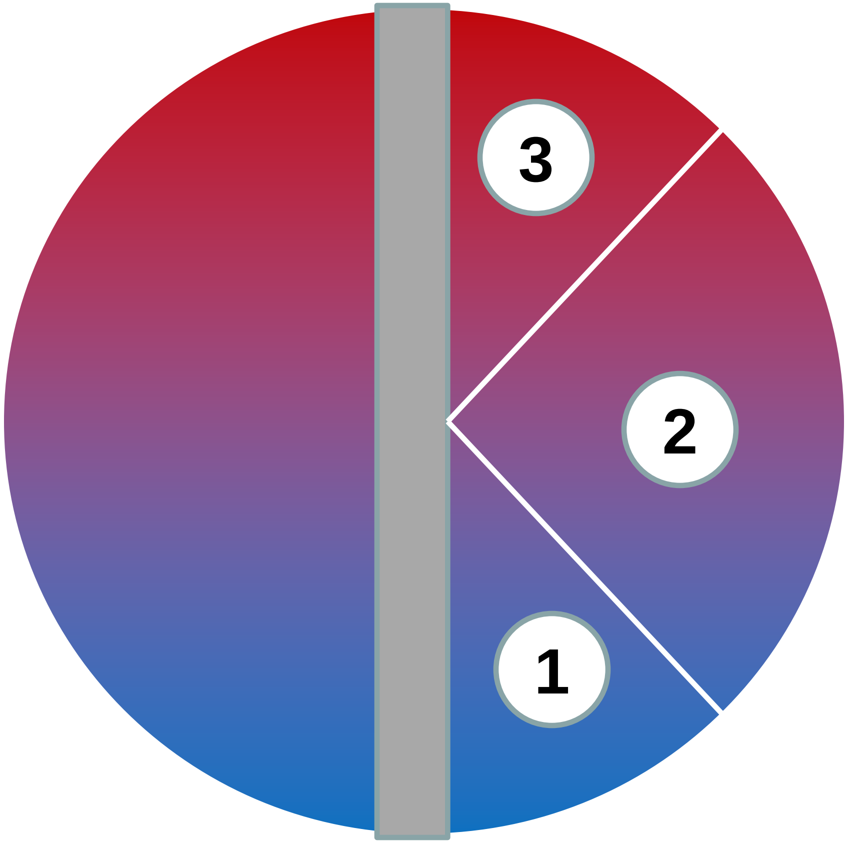
Why a 3.0 Stoichiometric Ratio?

Particle Size

- **For starters, while the average particle size of hydrated lime can be in the 10 micron range, it size is huge compared to the size of a sulfuric acid vapor molecule.**
- **Hydrated Lime comes in various performance categories. Some are more effective than others based on their ability to capture more acid with less hydrate.**
- **Even with the highest performance products, though, not every molecule of calcium hydroxide reacts with every molecule of sulfuric acid vapor.**

Beyond that there are distribution and mixing issues

Stratification

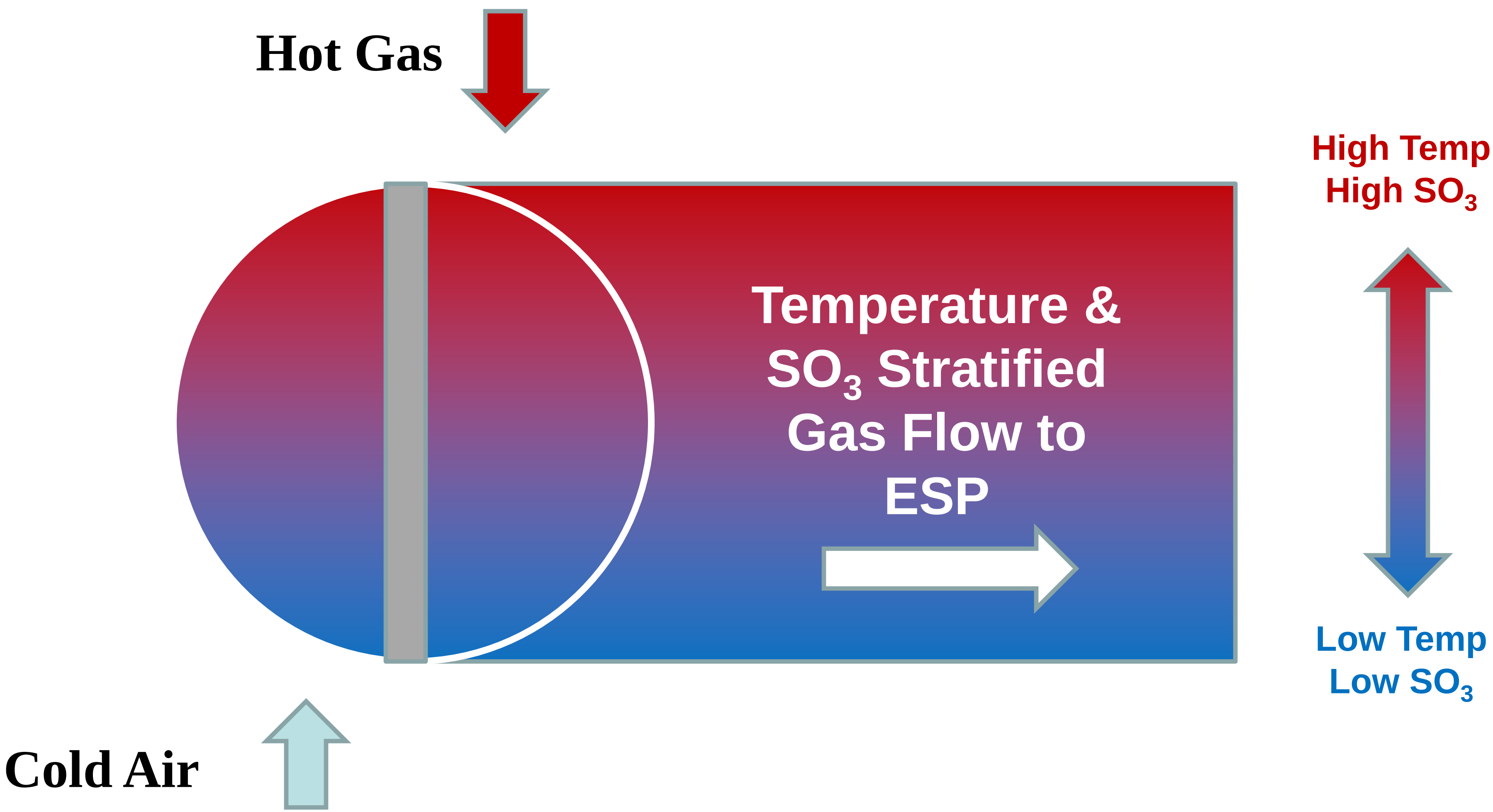


1: Acid Vapor preferentially condenses on the AH plates creating an acid lean flue gas

2: AH plates warm to a point where acid vapor no longer condenses leaving an acid neutral flue gas

3: AH plates heat up to a point where condensed acid is re-vaporized creating an acid rich flue gas

Stratification



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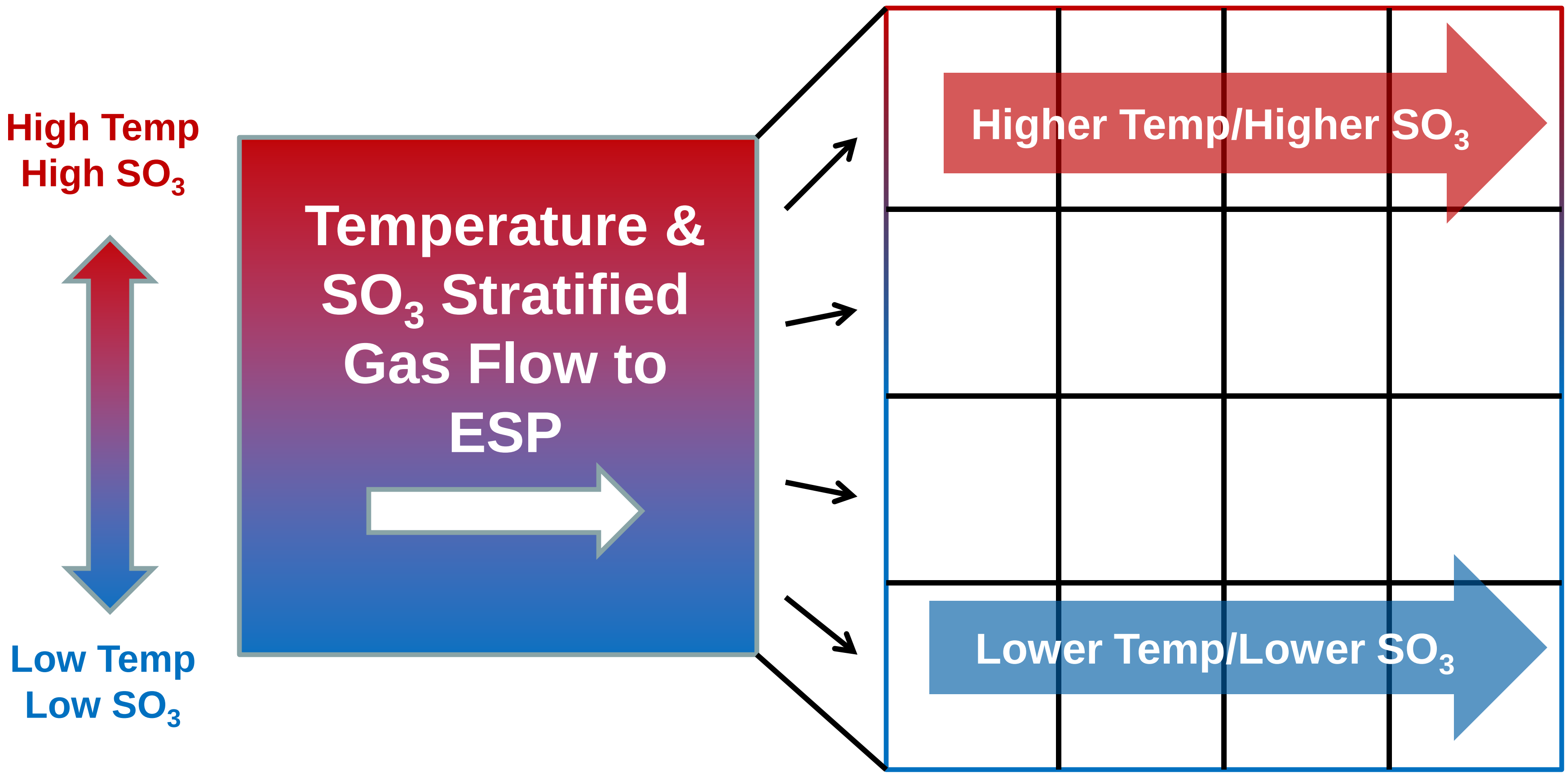
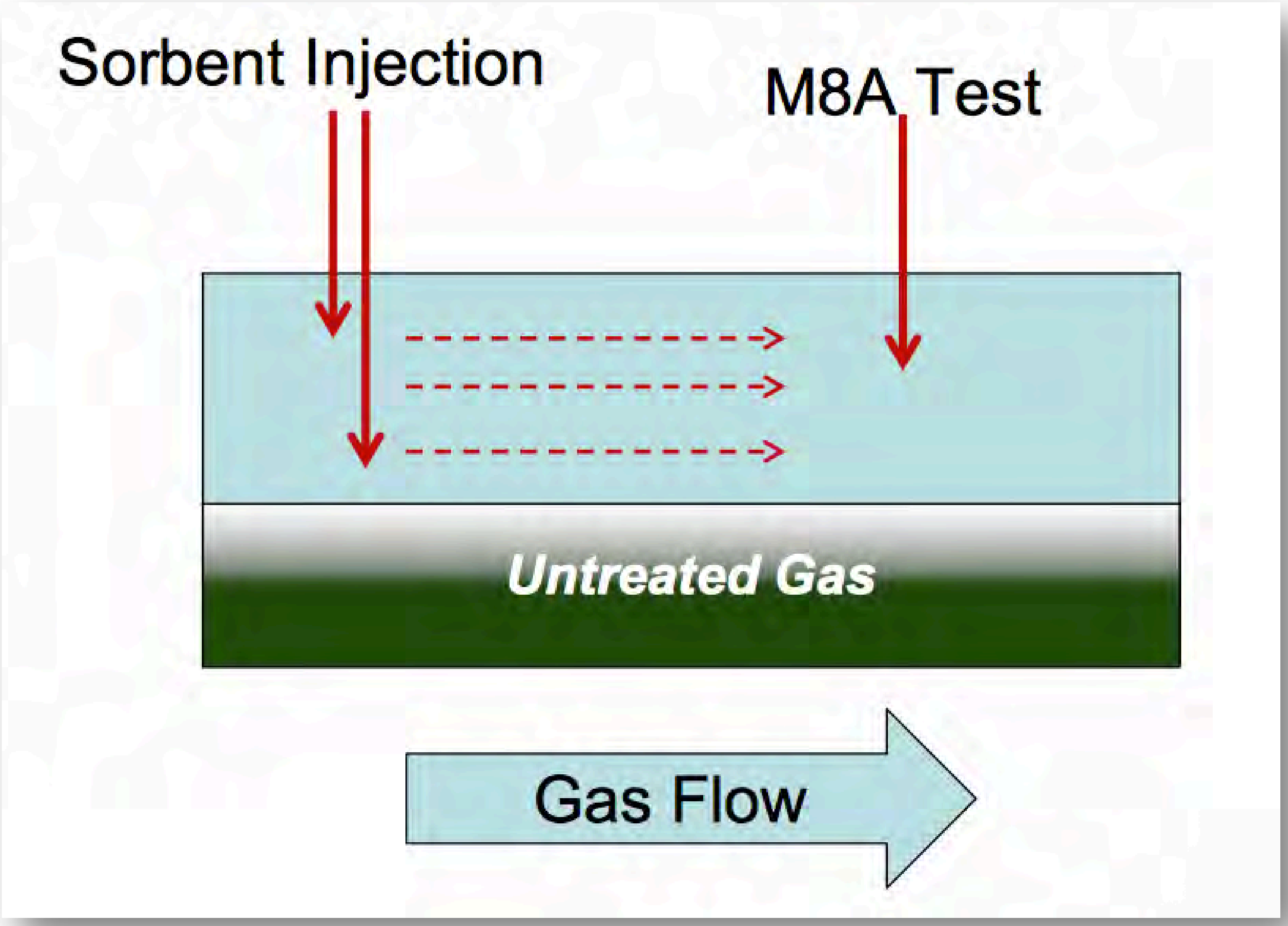
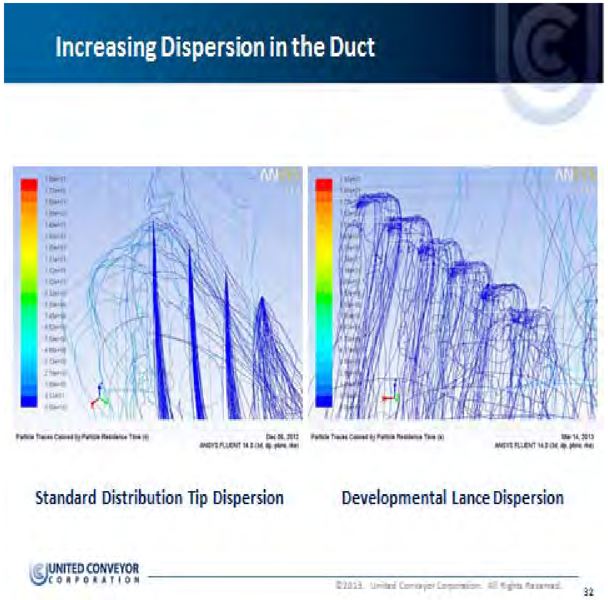


Vertical Issues



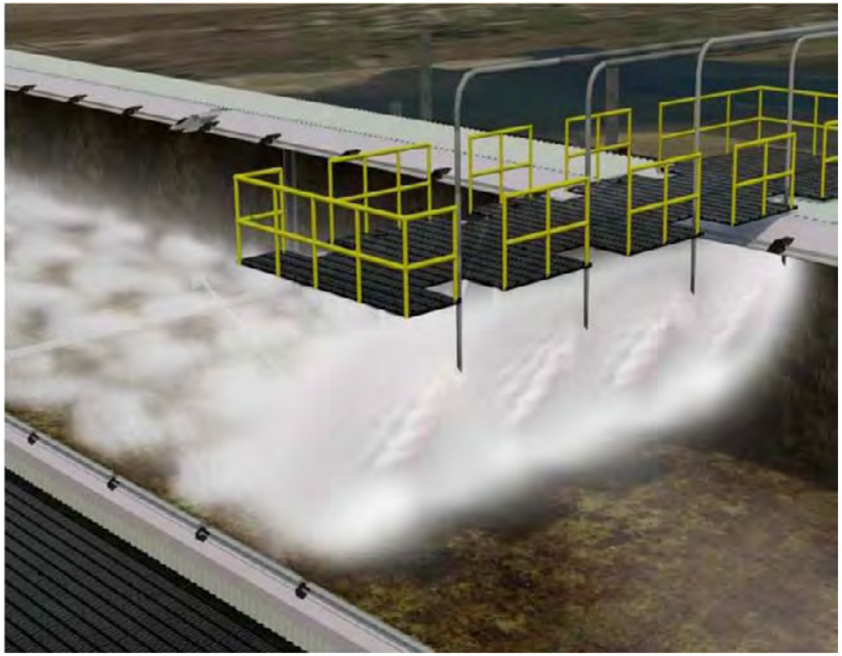
DSI Optimization - Distribution

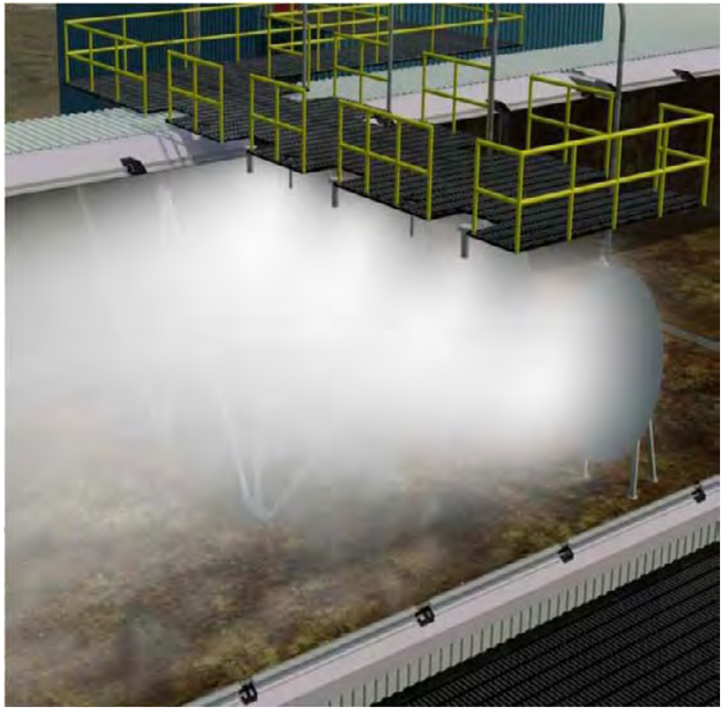
- **Distribution is critical to achieve good consistent performance**
- **Passive flue gas mixing is the key to overall system performance as multi port lances are not ideal due to pluggage**
- **United Conveyor's approach is incorporating a mixing device into the lance**
- **Both physical and CFD modeling have been performed developing this lance**



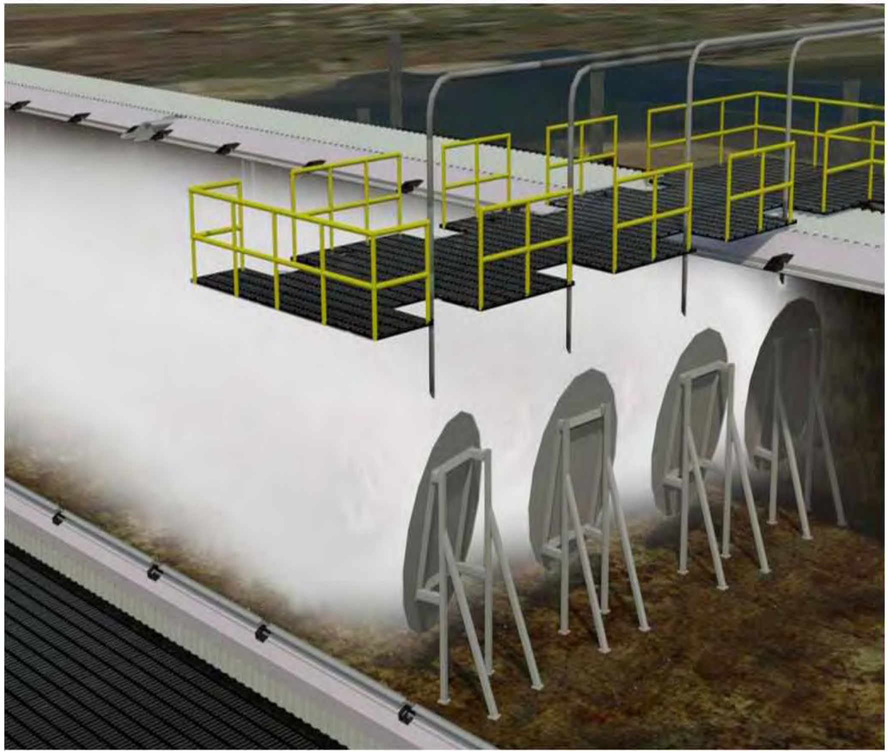
DSI Optimization - Distribution

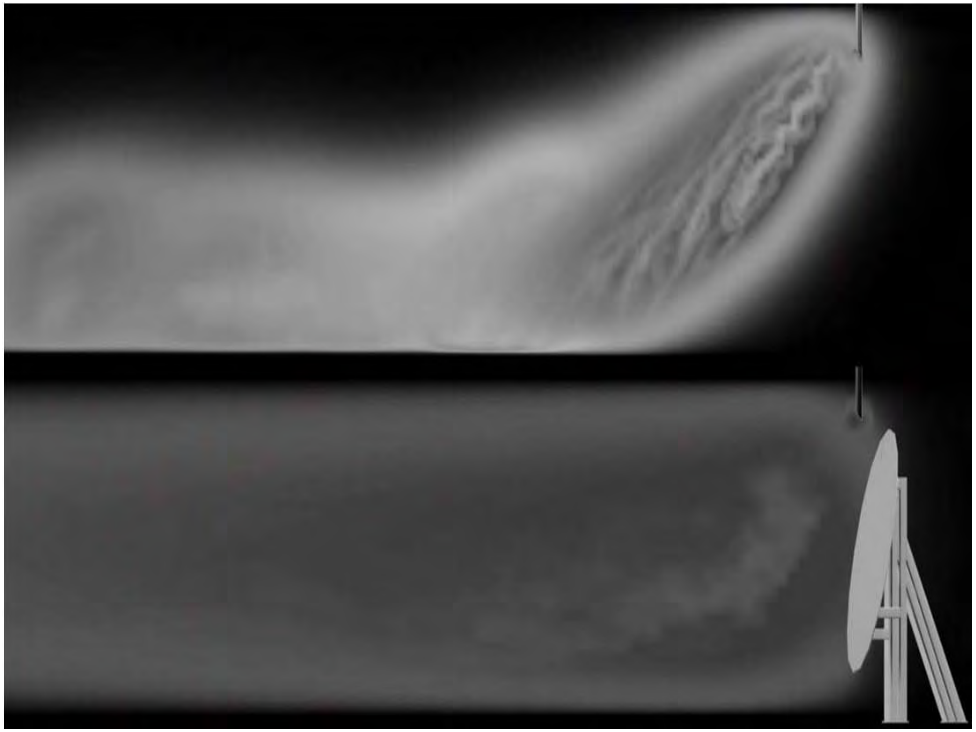
- **Another is duct mounted mixers such as the Babcock Power Delta Wing technology**





DSI Optimization - Distribution





Which gets us to Results Desired

Single or Dual Injection?

PRE-AIR HEATER HYDRATED LIME TREATMENT (SO3 BASIS)		
Treatment Mass Ratio HL:SO3	2.775 Lbs HL/LBs SO3	
SO3 Removal	73 %	

First Stage Hydrated Lime Performance

First Stage Hydrated Lime Results

POST-TREATMENT CONDITIONS AT AIR HEATER INLET DUCT				
Parameter	Wet Basis		Dry Basis	
SO3	0.0324	Lb/MMBTU	0.0324	Lb/MMBTU
SO3	201	Lb/hr	201	Lb/hr
SO3, Actual O2	14	ppm	15	ppm

STEP 4: Enter Air Heater Performance

ENTER AIR HEATER PERFORMANCE			
SO3 Loss Across AH	25	%	
Select Air Heater Leakage Basis from Drop-Down Menu	AH Leakage %		
Value for Leakage Basis	10.00	% AH Leakage	
% AH Outlet O2	5.24	%	

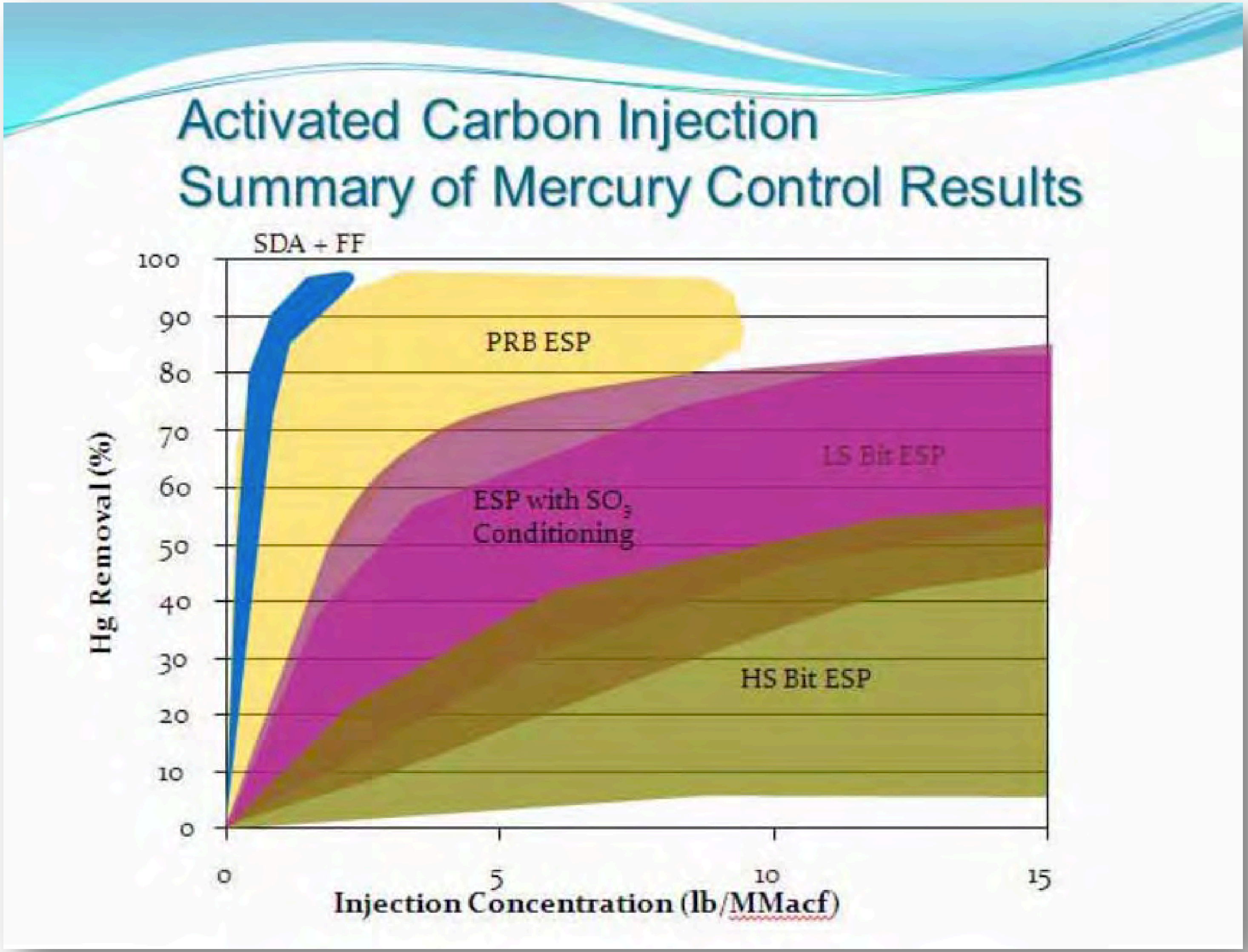
Dual Injection ups the Results

POST-TREATMENT CONDITIONS AT AIR HEATER OUTLET DUCT				
Parameter	Wet Basis		Dry Basis	
Flue Gas Flow, Actual O_2	75,237,011	wscf/hr	69,537,755	dscf/hr
Flue Gas Flow, Actual O_2	5,873,134	Lb/hr	5,620,471	Lb/hr
H_2O	252,663	Lb/hr	0	Lb/hr
H_2O, Actual O_2	7.3	%	0	%
O_2	290,948	Lb/hr	290,948	Lb/hr
O_2	5.24	%	5.65	%
SO_2	4.60	Lb/MMBTU	4.60	Lb/MMBTU
SO_2	28,464	Lb/hr	28,464	Lb/hr
SO_2, Actual O_2	2304	ppm	2507	ppm
H_2SO_4	0.0268	Lb/MMBTU	0.0268	Lb/MMBTU
H_2SO_4	166	Lb/hr	166	Lb/hr
H_2SO_4, Actual O_2	9.4	ppm	9.1	ppm

Other Reagents?

MATS

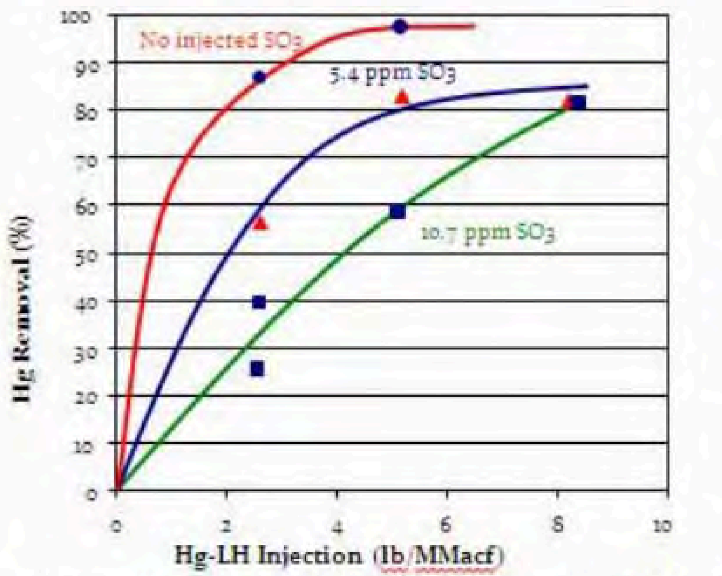
Activated Carbon Summary



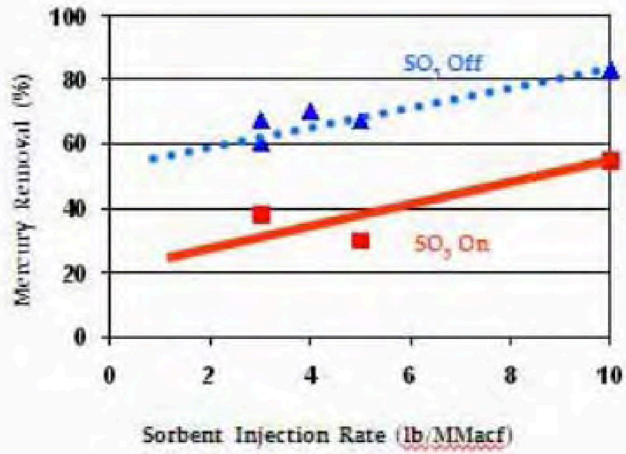
What Happens when SO_3 is present

SO_3 Injection and PAC Effectiveness

- SO_3 is used to condition fly ash for better capture in ESPs
- Typical injection targets < 10ppm in gas phase
- Any SO_3 in gas phase appears to affect Hg capture



Ameren Labadie Data: DOE DE-FC26-03NT41986 and EPRI PRB, ESP

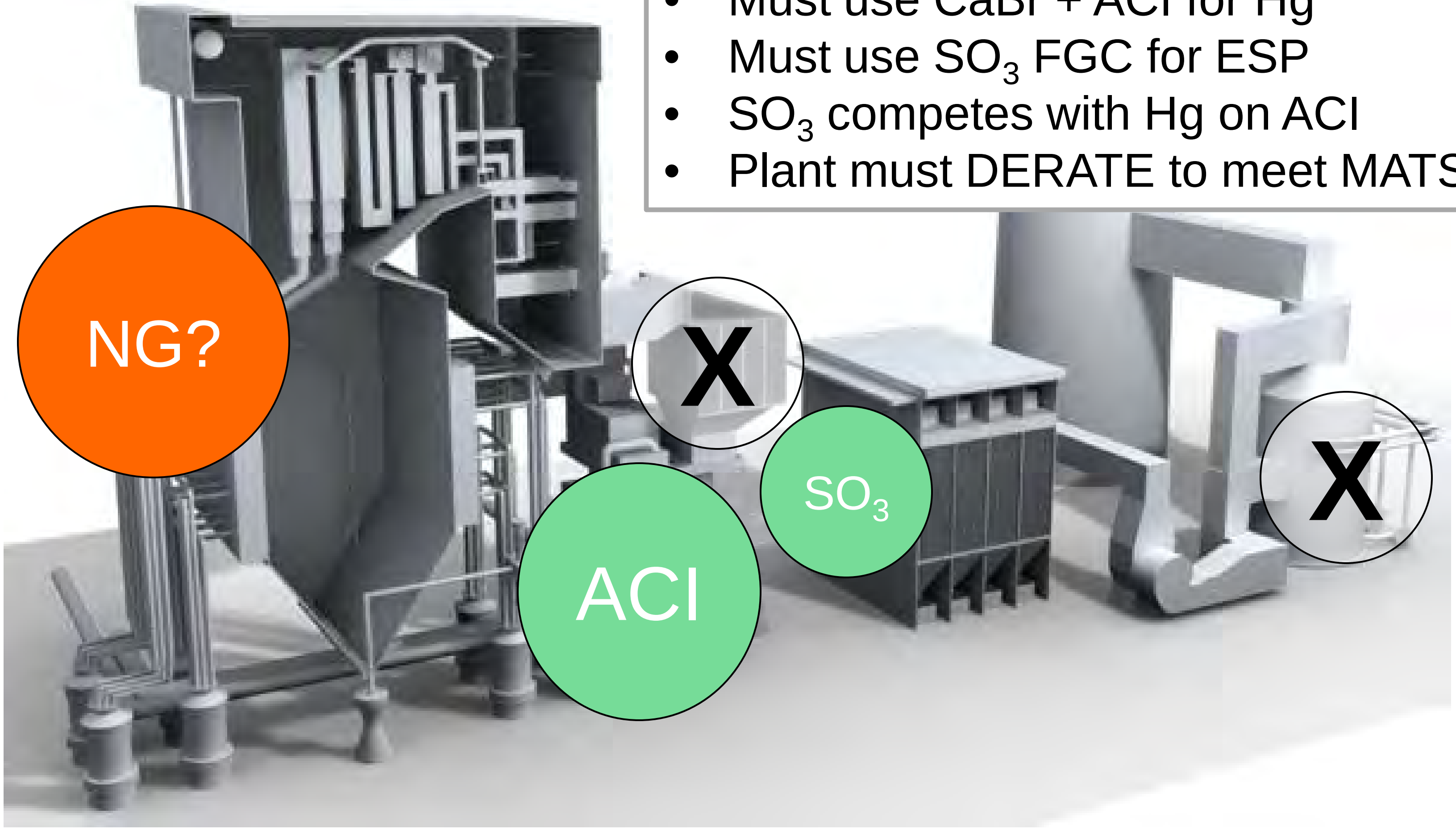


Mississippi Power Plant Daniel
Low sulfur bituminous coal

One Typical MATS Problem

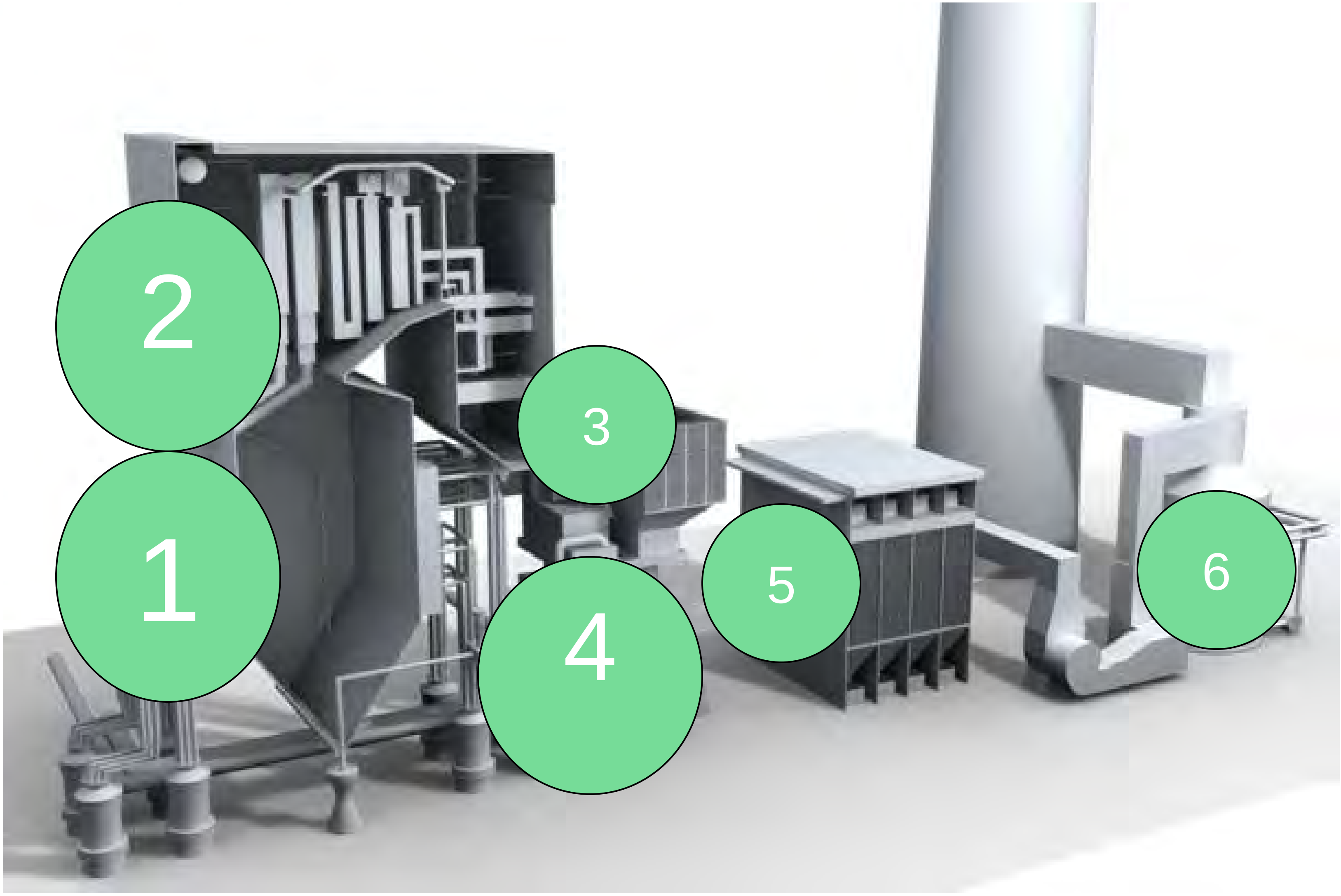
Plant Issue:

- No SCR/No FGD burning PRB
- Must use CaBr + ACI for Hg
- Must use SO_3 FGC for ESP
- SO_3 competes with Hg on ACI
- Plant must DERATE to meet MATS



Summary & Conclusions

So Where do we End Up?



Summary & Conclusion

BREEN
SMART SCIENCE • CLEANER ENERGY

- **Reagents & Sorbents are a part of our life**
- **Reagents are not necessarily stand alone compounds. What one does may very well affect the performance of another.**
- **Regardless of the above, proper distribution and residence time are key to optimizing the cost and performance of all reagents.**

Thank You – Questions?