In Situ Device for Real-Time Catalyst Deactivation Measurements*

(DOE Project 422FC2G05NT4229898)
Period Performance
5/1/05 to 5/31/07

Final Project Presentation
(via Web Meeting)

May 24, 2007

Project funding

U.S. Department of Energy (NETL)

Electric Power Research Institute

Southern Company

*** Patent Pending**

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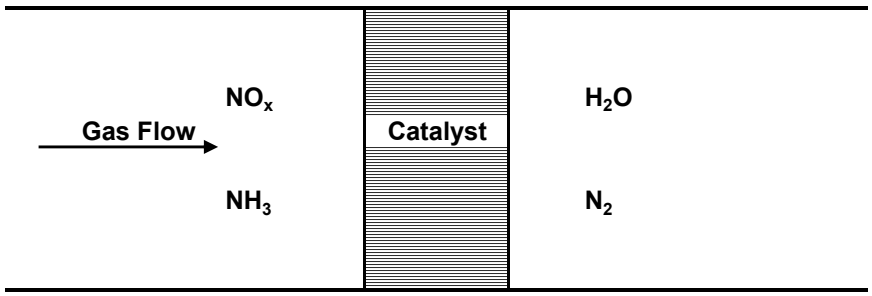
MP240

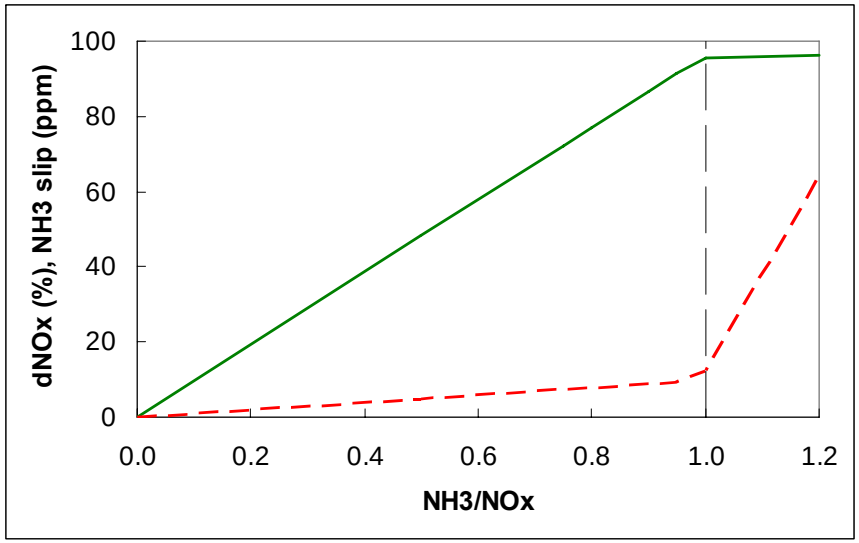
Presentation Outline

- Background
- Insitu Test Program
- Comparison of Insitu and Laboratory Results
- Low Load Operation
- Integrating the Insitu Results with CatReact™
- Commercialization Plans
- Demonstration (time permitting)
  - Insitu Test

Introduction

Overview of the SCR Process





$$NO + NH_3 + \tfrac{1}{4} O_2 \rightarrow N_2 + 1.5H_2O \qquad (1)^*$$

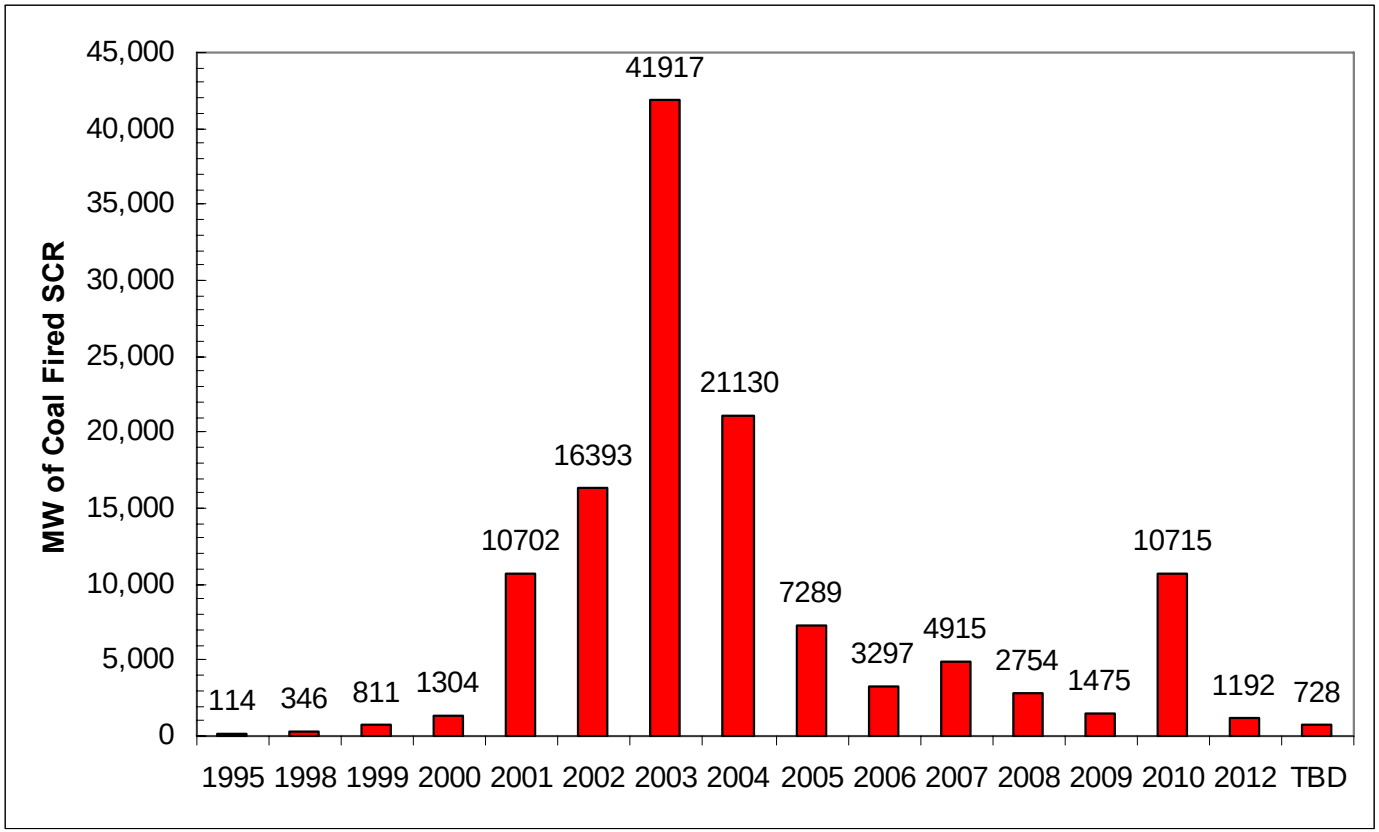
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 6H_2O \qquad (2)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (3)$$

* The vast majority of NO_x in coal-fired applications is in the form of NO, so reaction (1) dominates

Coal Fired SCR Installations

- **Over 100 GW Installed by the end of 2006**
- **Approximately 300 to 400 systems installed on pulverized coal fired boilers**



Catalyst Activity and Reactor Potential

Catalyst Activity (K)

- Measure of how active the catalyst material is for reducing NO_x

Reactor Potential (RP)

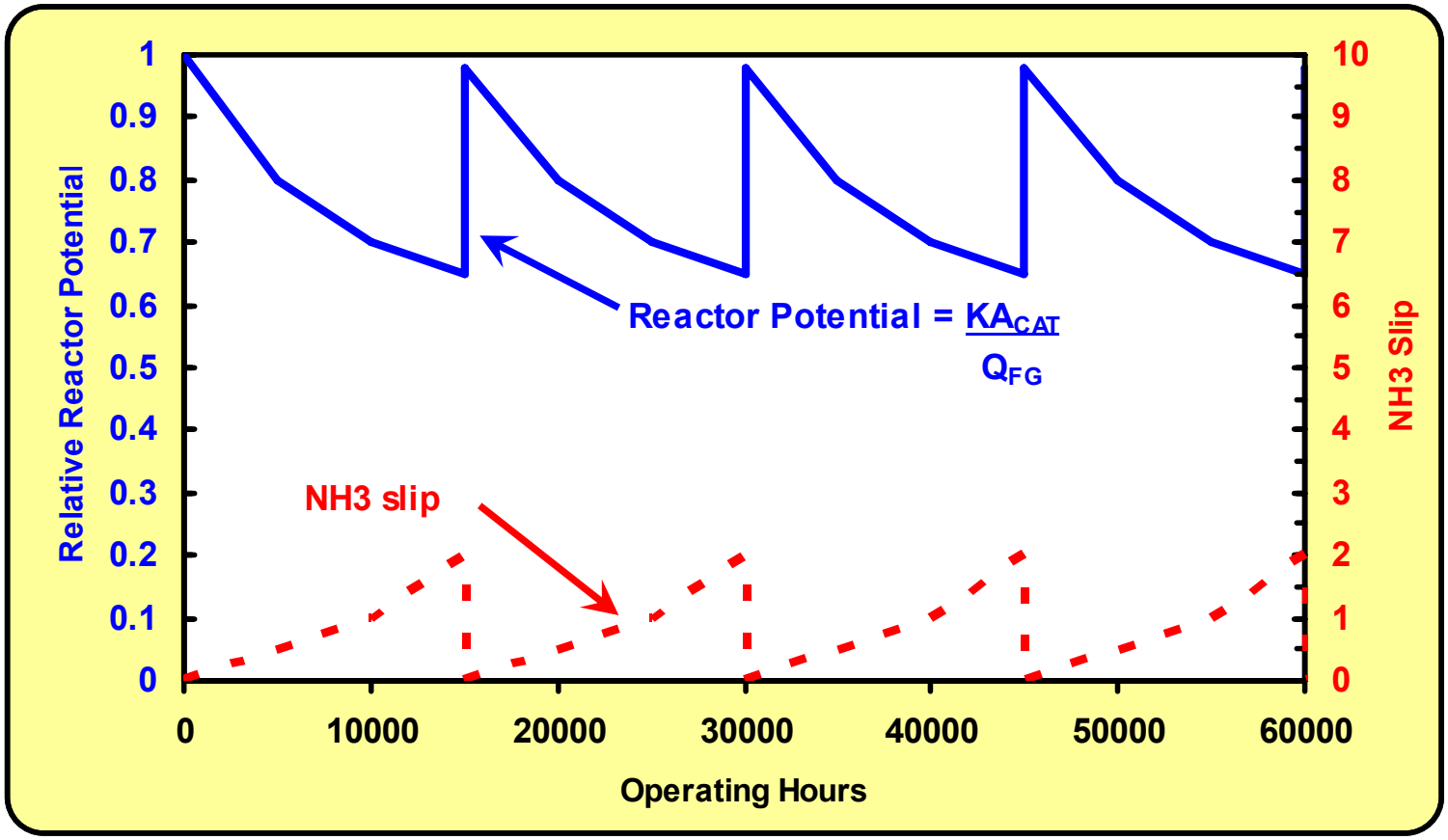
- Measure of the overall potential of the reactor to reduce NO_x
- Inherently accounts for both catalyst deactivation (K/K_0) as well as catalyst layer blockage, thereby providing a true assessment of the condition of the SCR reactor
- $RP = \frac{K}{A_{Vd}}(1-B)$ where,

  B = catalyst blockage

  A_{Vd} = design area velocity (zero blockage)
- RP is the quantity utilized by catalyst management software programs such as EPRI's CatReact product in the evaluation of various catalyst management strategies

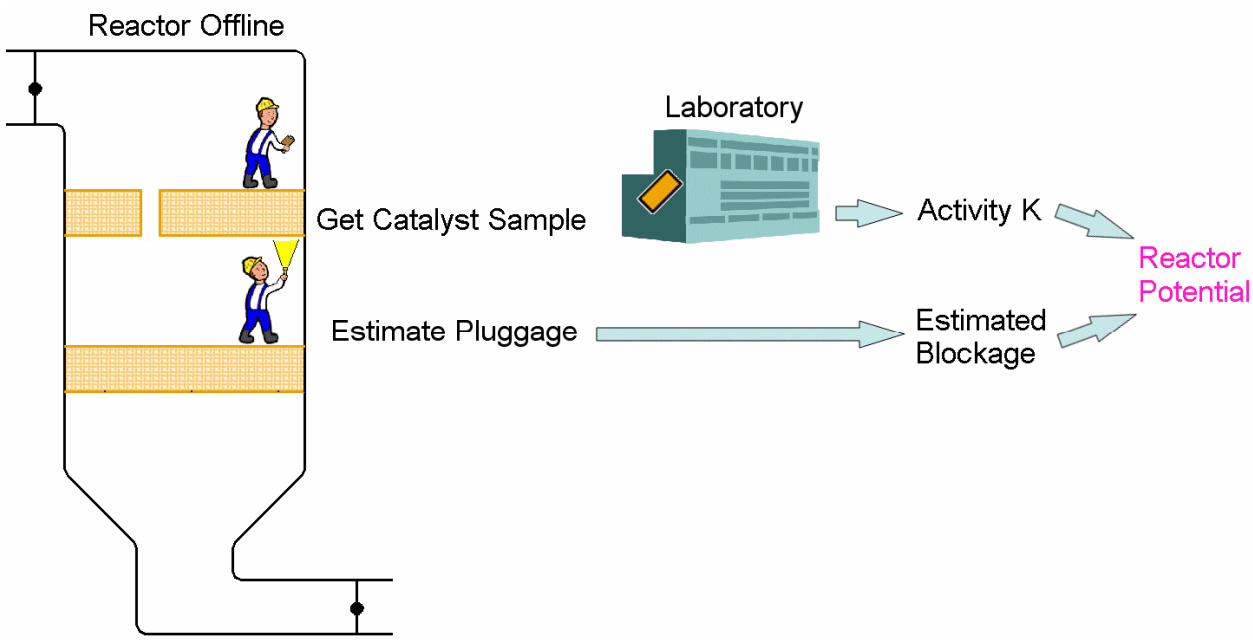
Catalyst Management

Managing the addition or replacement of individual catalyst layers to maintain the NO_x removal and NH_3 slip performance requirements throughout the lifetime of the plant



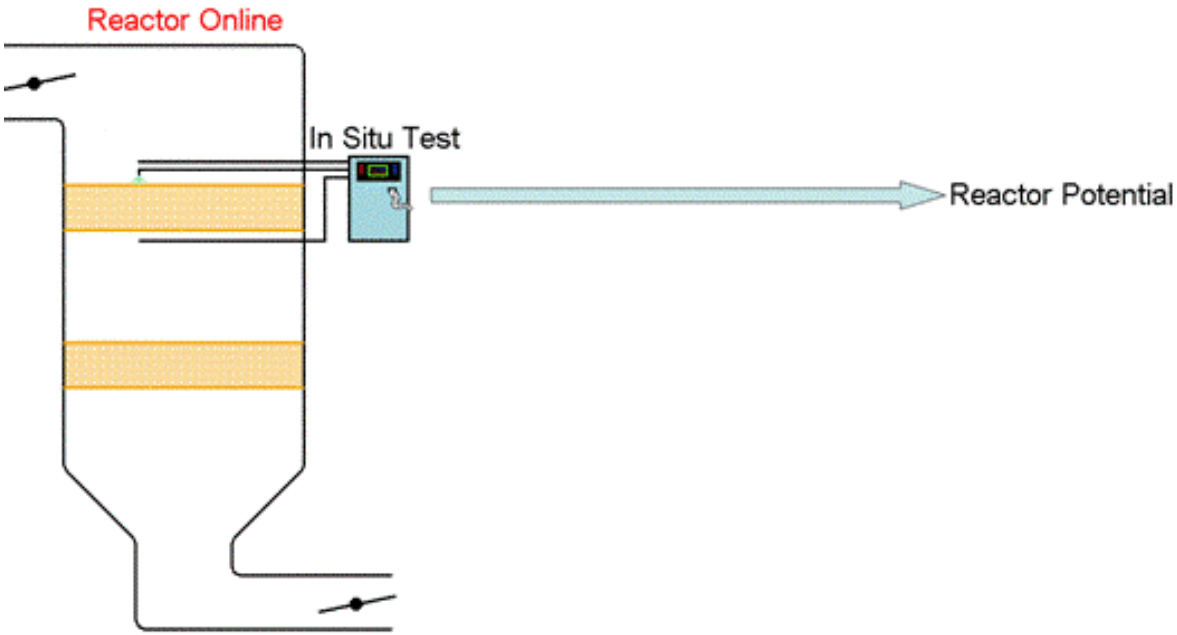
Laboratory Determination of Reactor Potential

- A catalyst sample is tested at the design A_V with $NH_3/NO_x = 1$, and then the activity determined from $K = -A_{Vd}\ln(1- \Delta NO_x)$ (Per VGB or EPRI Guidelines)
- An estimate of the blockage in the full scale reactor is then used to calculate the reactor potential: $RP = K(1-B)/A_{Vd}$
- With year round operation beginning in 2009 opportunities to obtain physical samples diminish



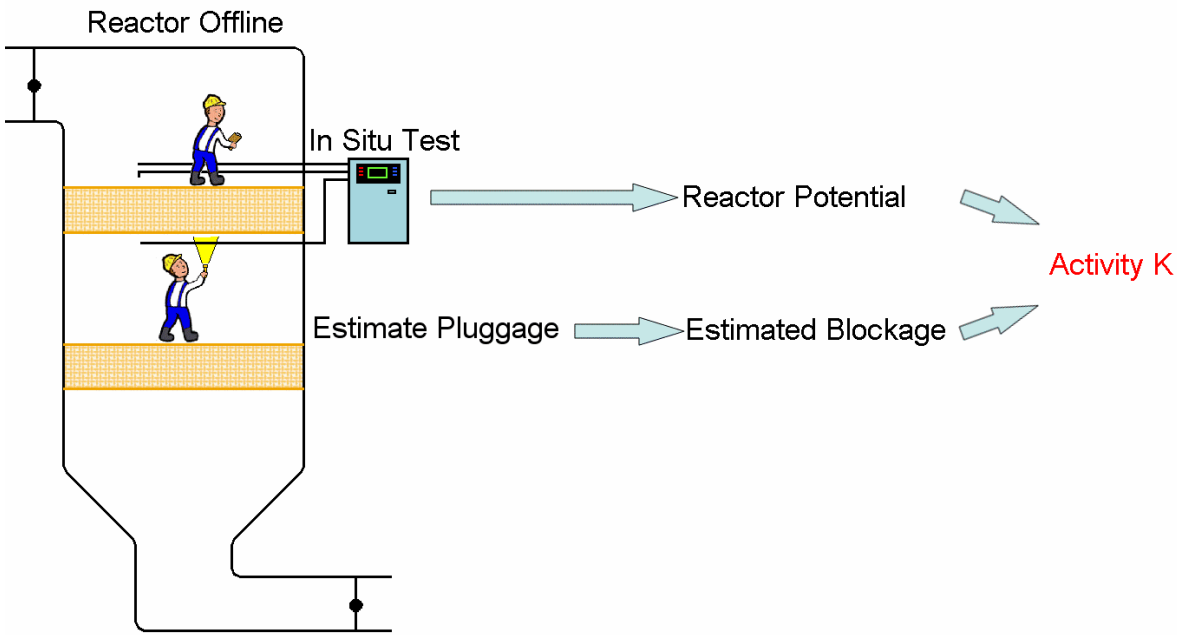
In Situ Reactor Potential

- $RP = K/A_{V,FS} = -\ln(1- \Delta NO_x)$, where $A_{V,FS}$ is the full-scale area velocity (accounting for blockage)
- An insitu measurement of the maximum NO_x removal across the layer yields a direct measurement of the reactor potential
- The insitu system will facilitate catalyst management with year round operation



In Situ Catalyst Activity

- **An in situ measurement of the maximum NO_x removal across the layer yields a direct measurement of the reactor potential**
- **To calculate the activity the full load A_V and an estimate of the blockage is needed; $K=RP*A_V/(1-B)$**



Experimental Program

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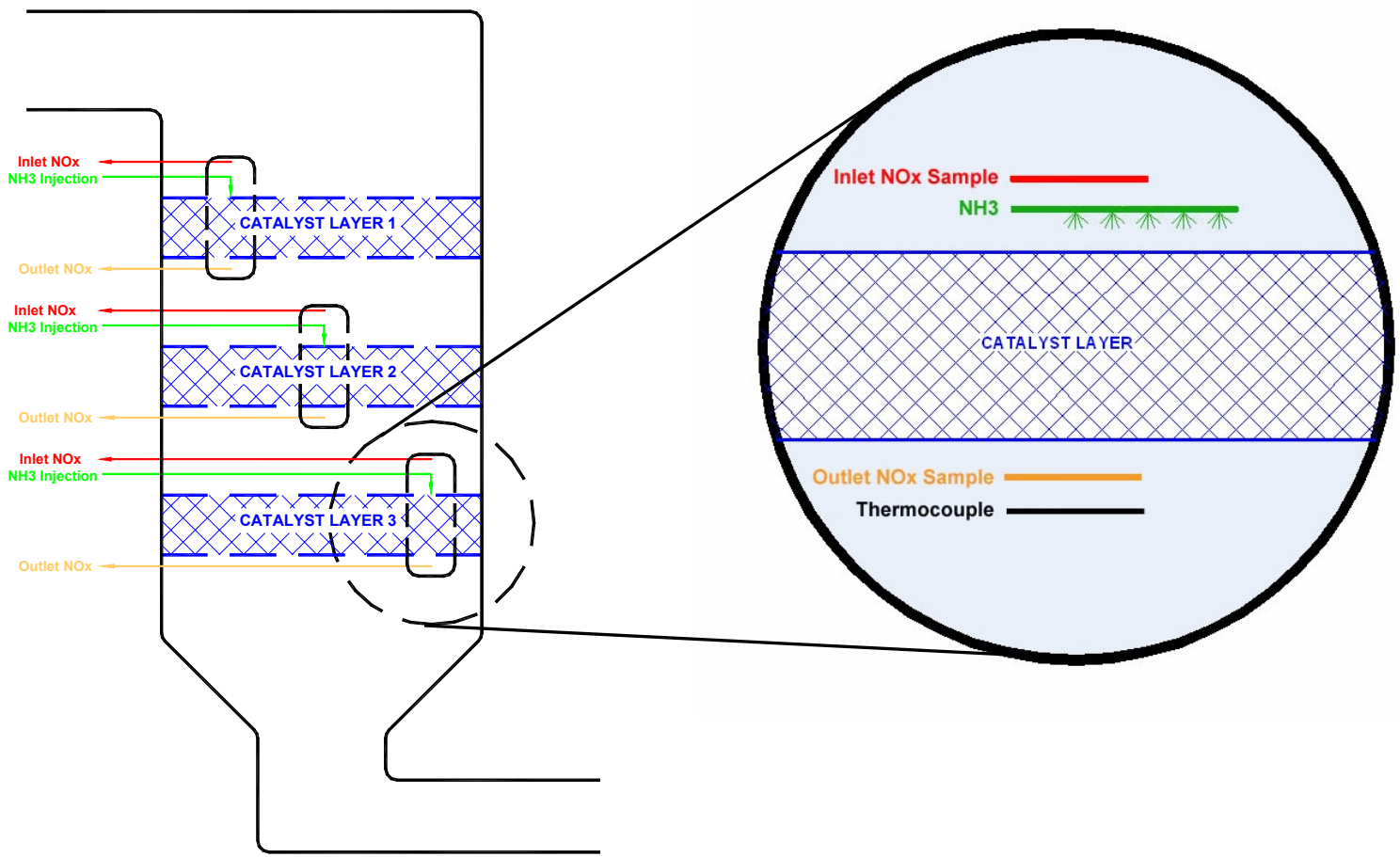
Experimental Program

Demonstrate the viability of an in situ approach of monitoring catalyst activity in coal-fired SCR reactors

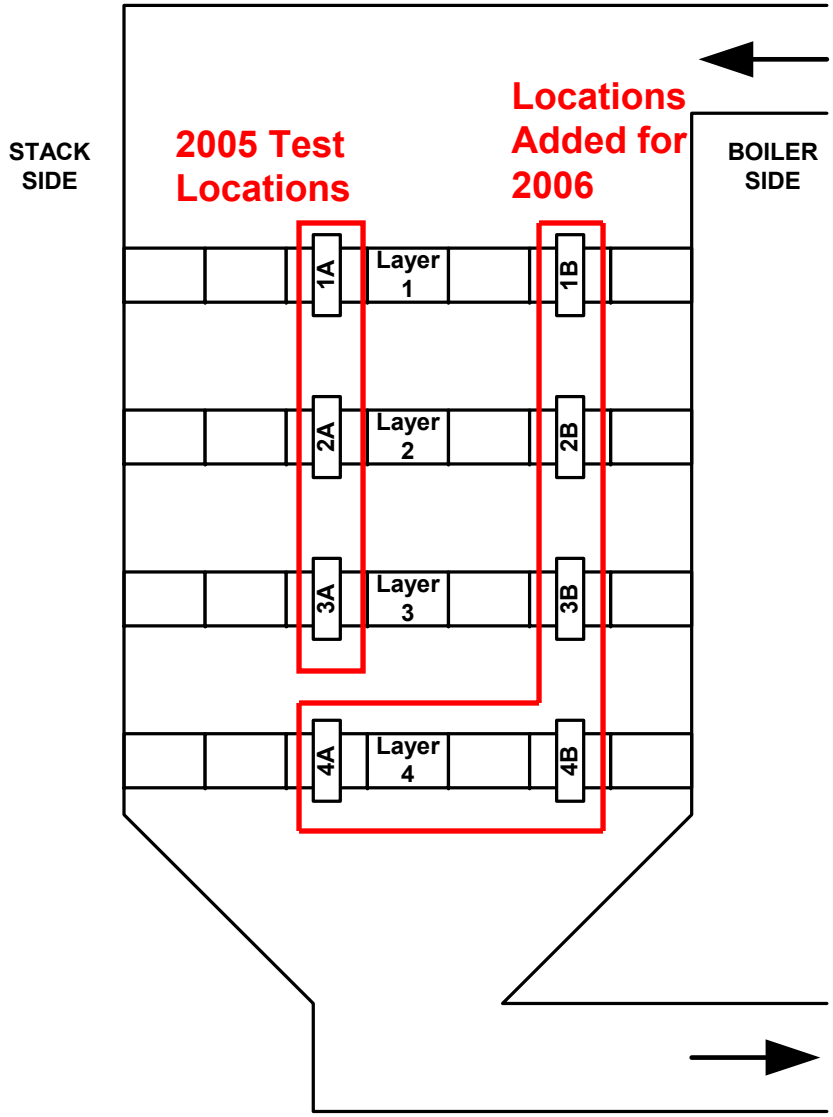
- **Design and install a prototype in situ system at a host utility site**
- **Conduct a test program to characterize deactivation rate for individual catalyst layers over two ozone operating seasons**
  - **2005 Ozone Season: Proof of Concept Hardware (3 modules)**
  - **2006 Ozone Season: More Commercial Hardware (8 modules)**
- **Utilize host unit operator's annual O&M catalyst sampling/analysis activities to validate the in situ deactivation measurements**
- **Demonstrate how the insitu results can be integrated with catalyst management software**

Multiple *In-Situ* Test Modules - General Approach



Demonstration Host Site Provided by Southern Company

- Alabama Power Company's Gorgas Unit 10
  - 700 MW
  - Alabama bituminous coal
- SCR on-line May 2002, ozone season operation
  - Two reactors
  - 3 + 1 configuration
  - Initial load: 3 layers honeycomb catalyst
  - Fourth layer of plate catalyst added prior to 2006 ozone season

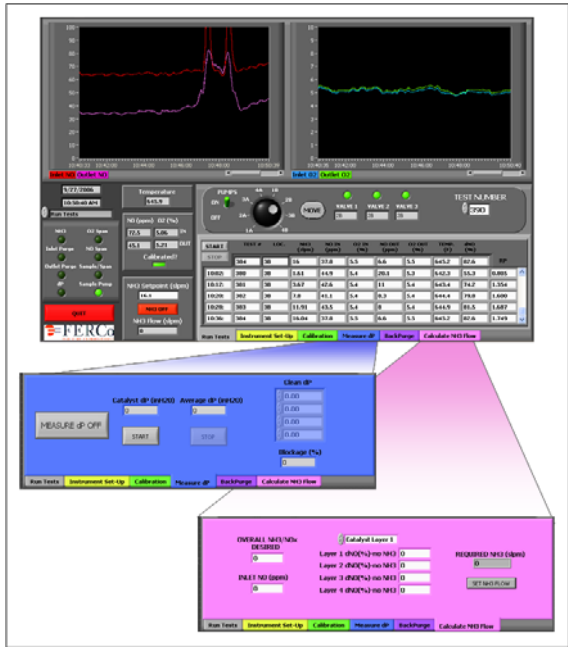


2005 Ozone Season: Proof of Concept Hardware

- **Manual Switching**
- **Electrochemical NO/O2 Measurement**

2006 Ozone Season: Commercial Equipment Design

- **Stationary NEMA 4 enclosure housing multi-position sampling valves**
- **Portable "cart" housing gas analysis instrumentation and control system**



Catalyst Arrangement

2005 Catalyst Arrangement

Reactor A		Reactor B
A1 - HC		B1 - HC
A2 - HC		B2 - HC
A3 - HC		B3 - HC
Spare		Spare

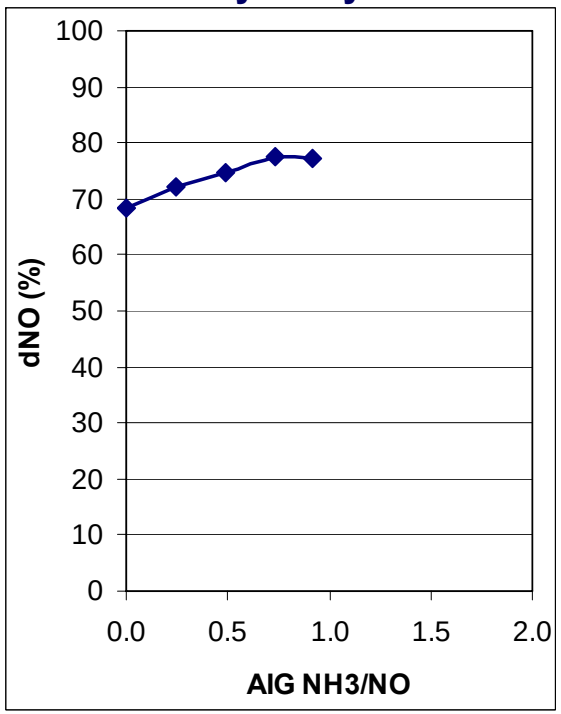
2006 Catalyst Arrangement

Reactor A		Reactor B
A1 – Plate (new)		**B1 – Plate (new)**
A2 - HC		B2 - HC
A3 - HC		B3 - HC
B1 - HC		A1 - HC

In Situ Test Protocol and Typical Test Results

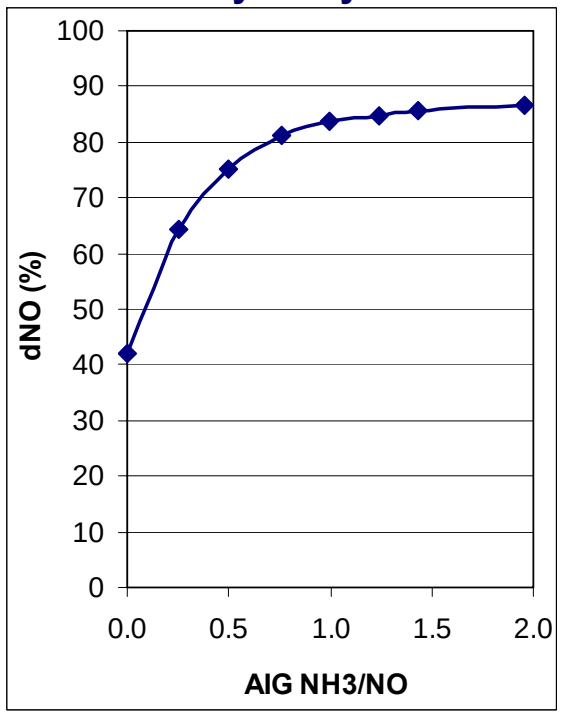
- Measure NO removal across test module without NH_3 injection
- Add NH_3 via test module AIG to point of maximum NO removal
- Calculate reactor potential from RP = -ln(1- ΔNO)

Catalyst Layer 1



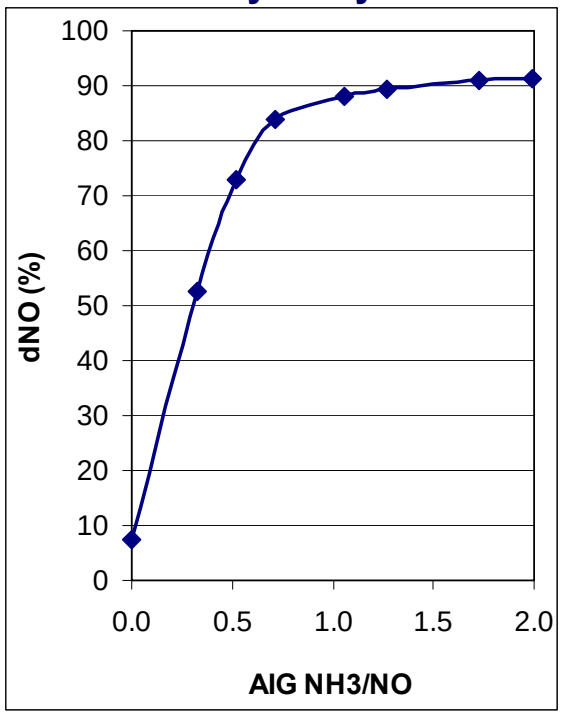
- dNO maximum = 77.3%

Catalyst Layer 2



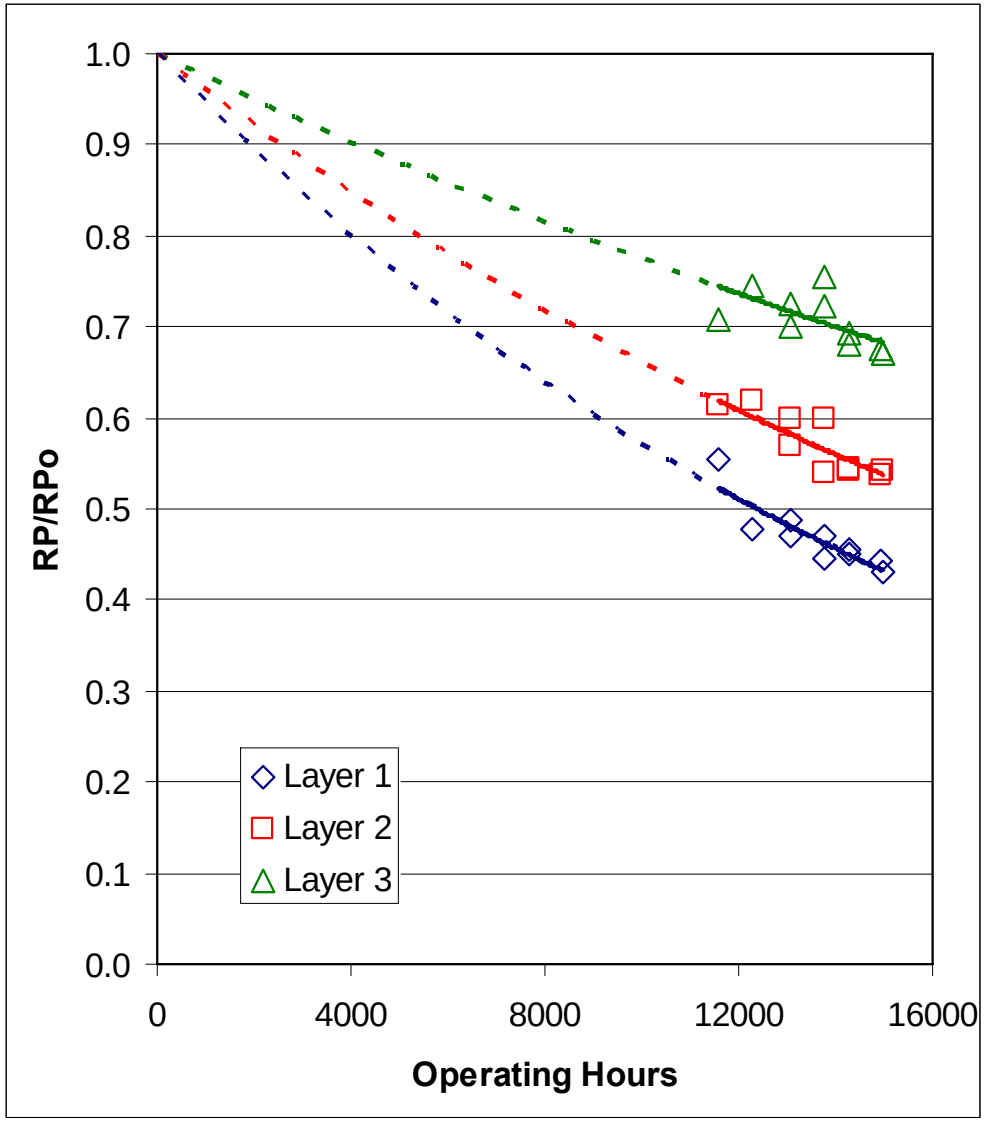
- dNO maximum = 86.6%

Catalyst Layer 3



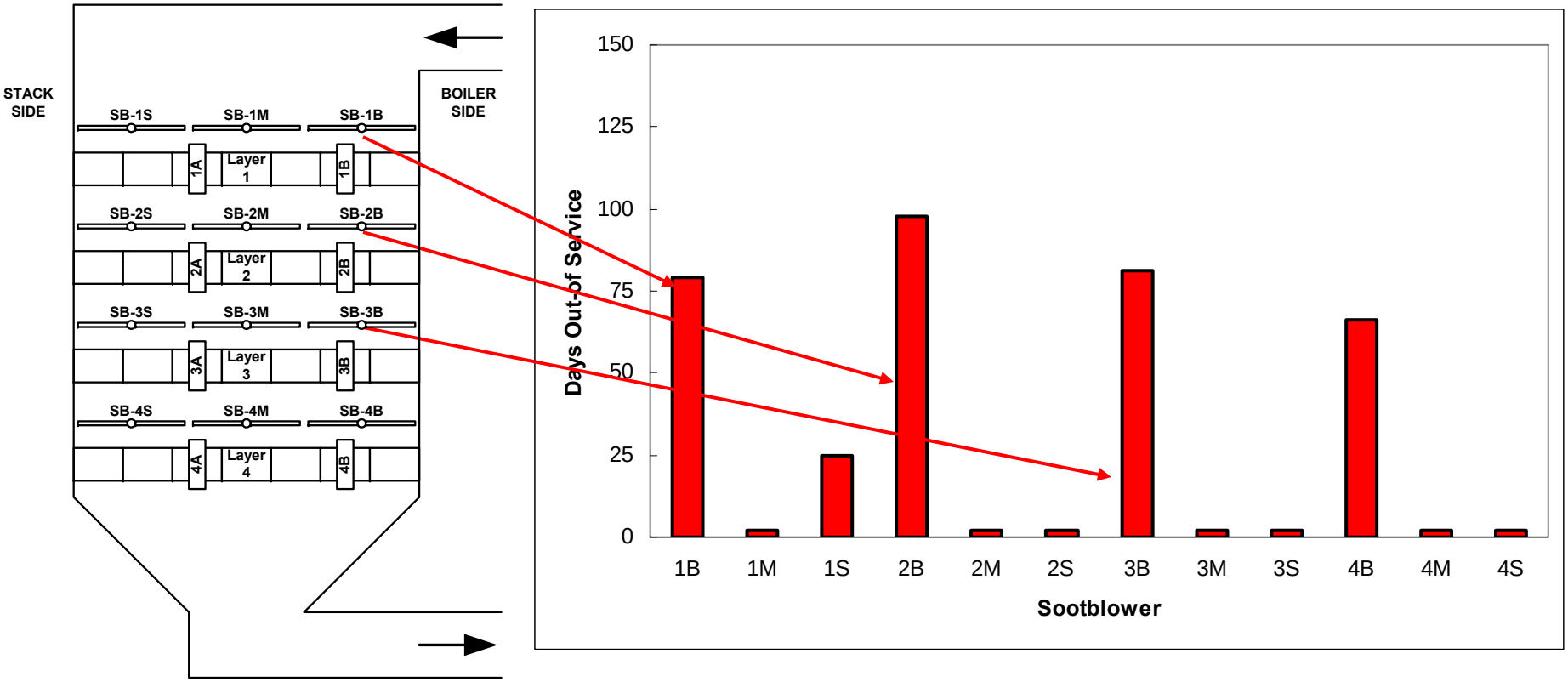
- dNO maximum = 91.3%

In Situ Reactor Potential Results – 2005



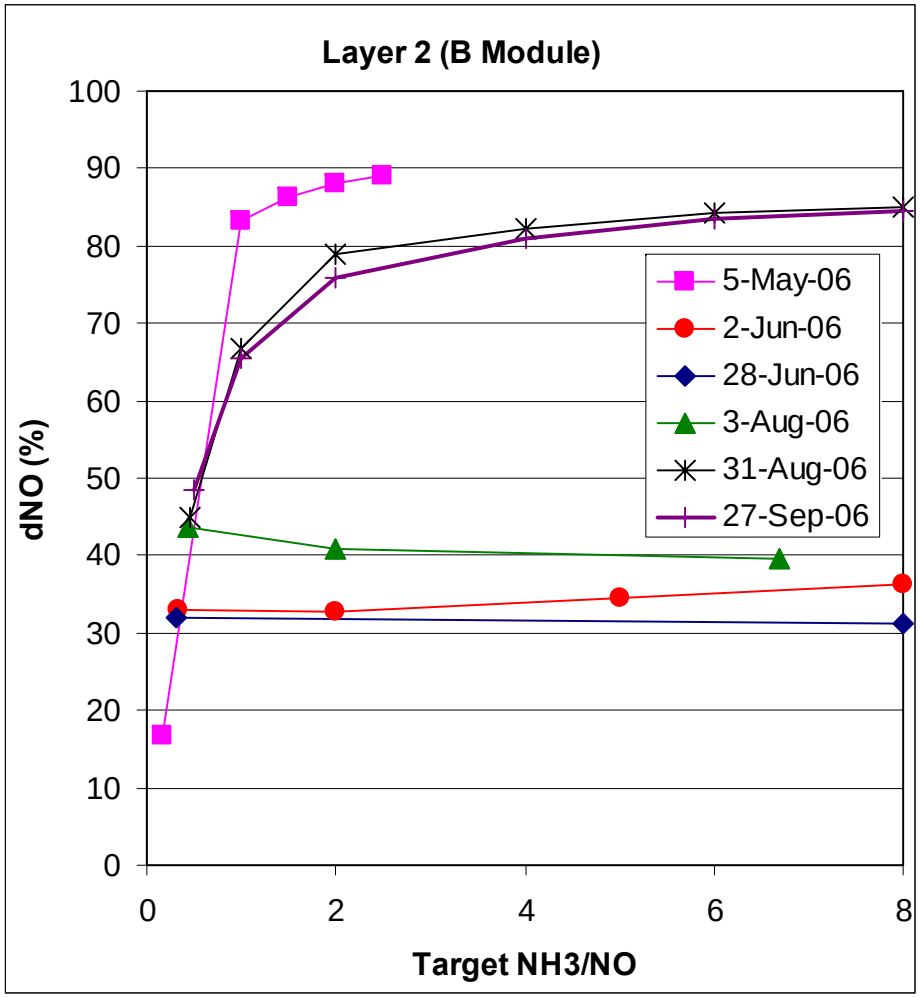
Sootblower Issues

- **A number of the sootblowers in the SCR reactor were out of service for a significant portion of the 2006 ozone season**



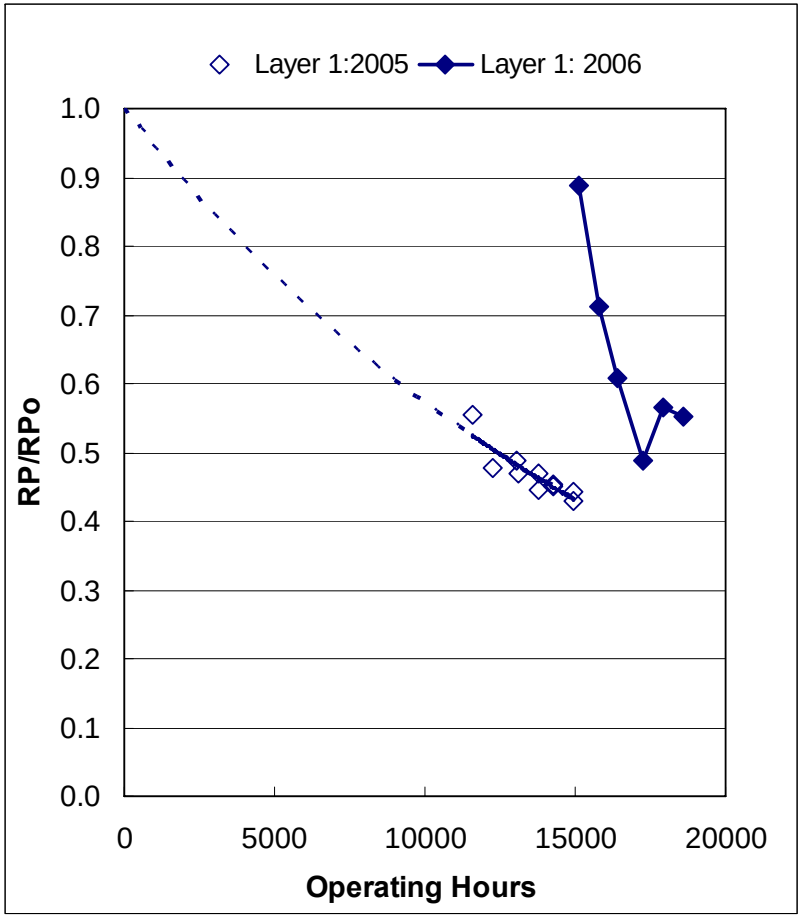
Sootblower Issues

- **The sootbower issues compromised the 2006 Ozone Season data at some of the test locations**

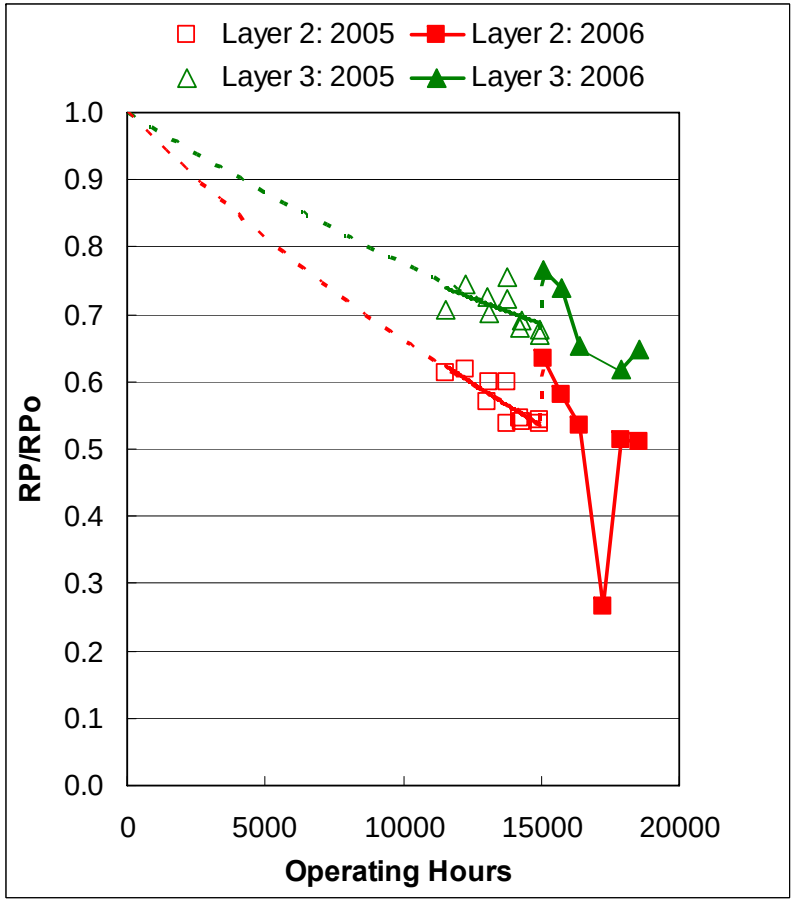


In Situ Reactor Potential Results – 2005 & 2006

Layer 1



Layers 2 & 3



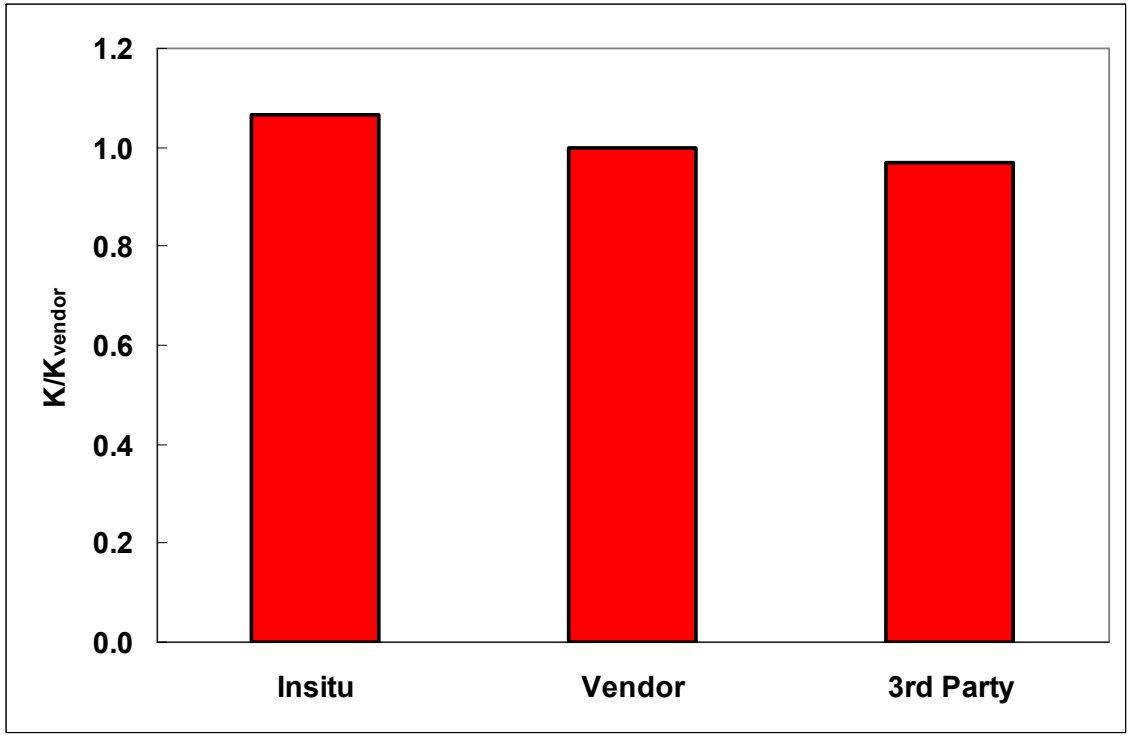
Lessons Learned

- Replace the 3 rotary valves with a single valve that can provide NH_3 and sample at the inlet and outlet of each test module
- Address corrosion issues with stainless steel lines near the ports
- Work with Brand-Gaus to make the NO_x analyzer less flow sensitive
- Incorporate an ammonia scrubber ahead of the analyzers to prevent ABS deposition

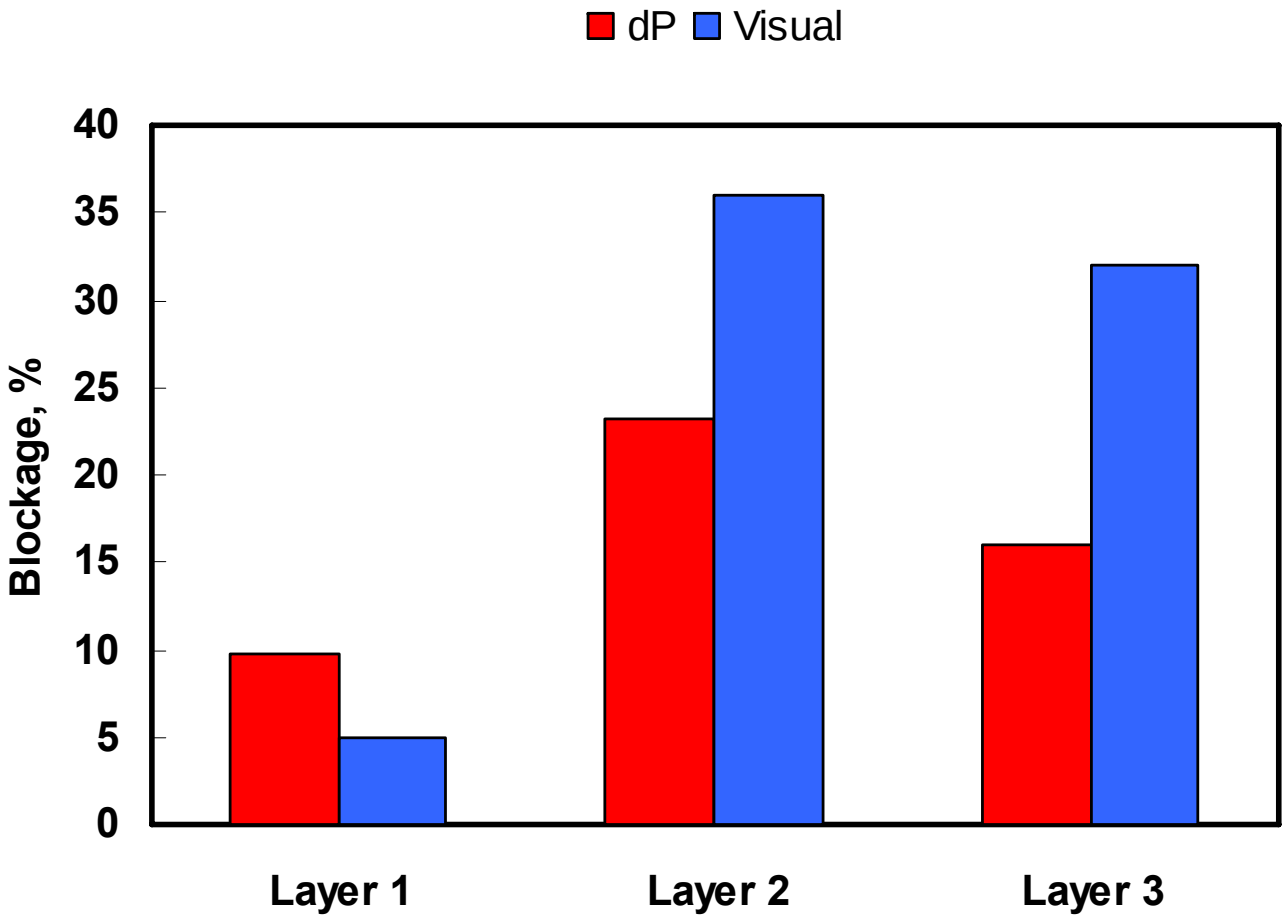
Insitu - Laboratory Comparison

New Plate Catalyst Measurements

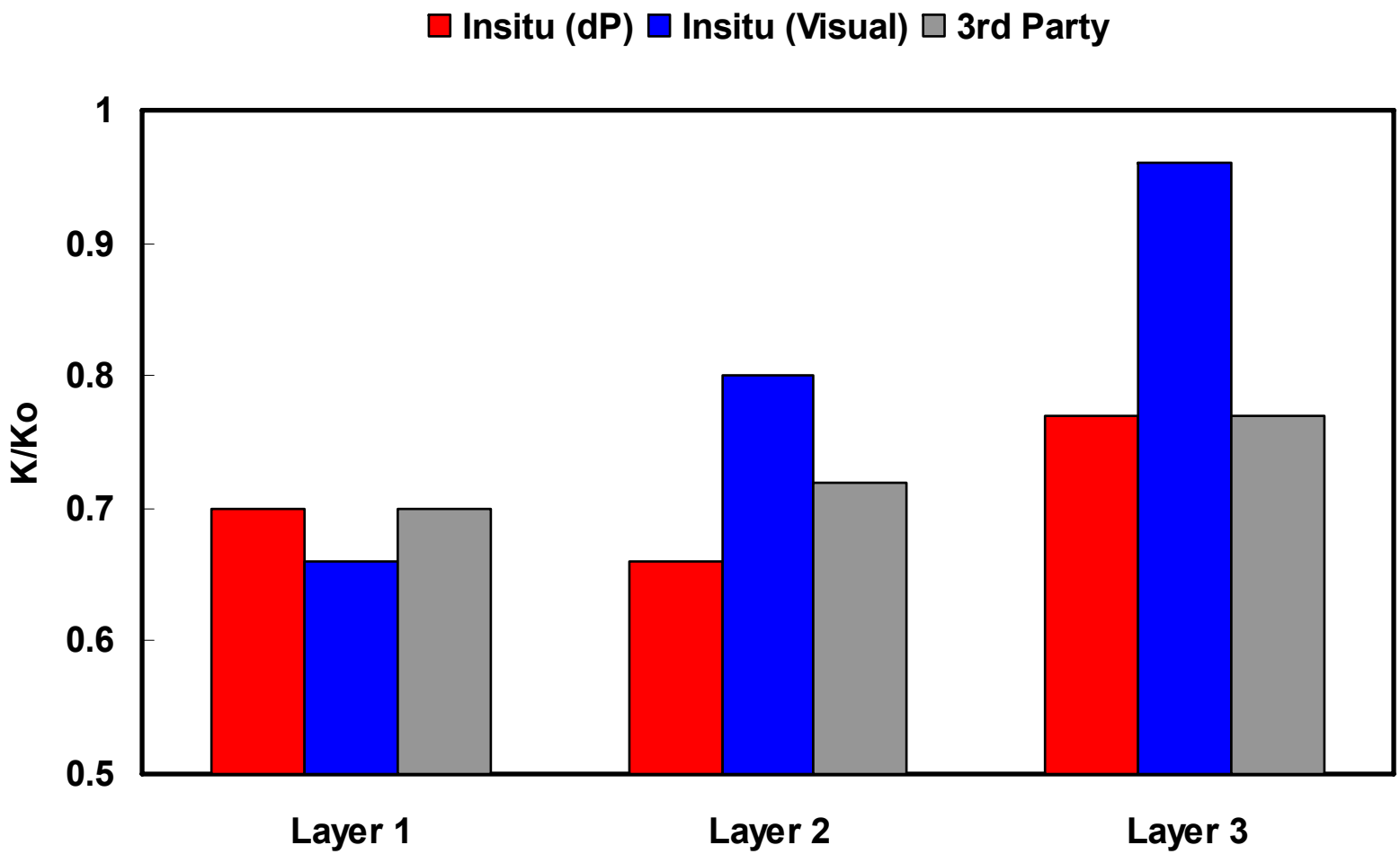
- Plate Catalyst added to Layer 1 at the beginning of the 2006 Ozone season
- Activity measurements available from the catalyst vendor and a 3rd party Laboratory
- Insitu measurements made after 120 hours of operation
- Provides a direct comparison of Catalyst Activity without the complication of dealing with blockage



End-of-Season Comparison: Blockage (2006)

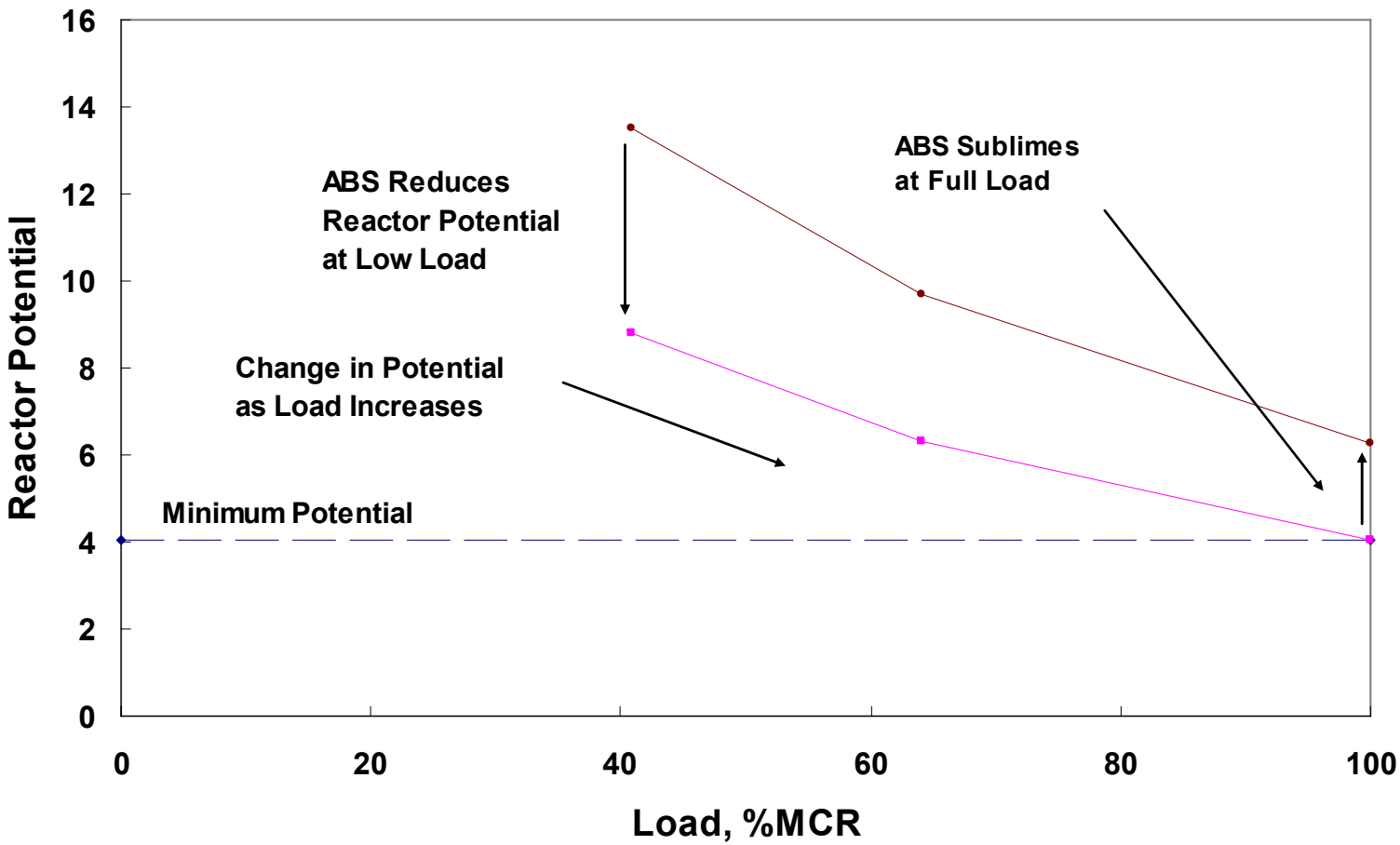


End-of-Season Comparison: K/K_0 (2006)



Low Load Operation

Reactor Potential Changes with Load and ABS deposition



Integrating the Insitu Measurements with CatReact™

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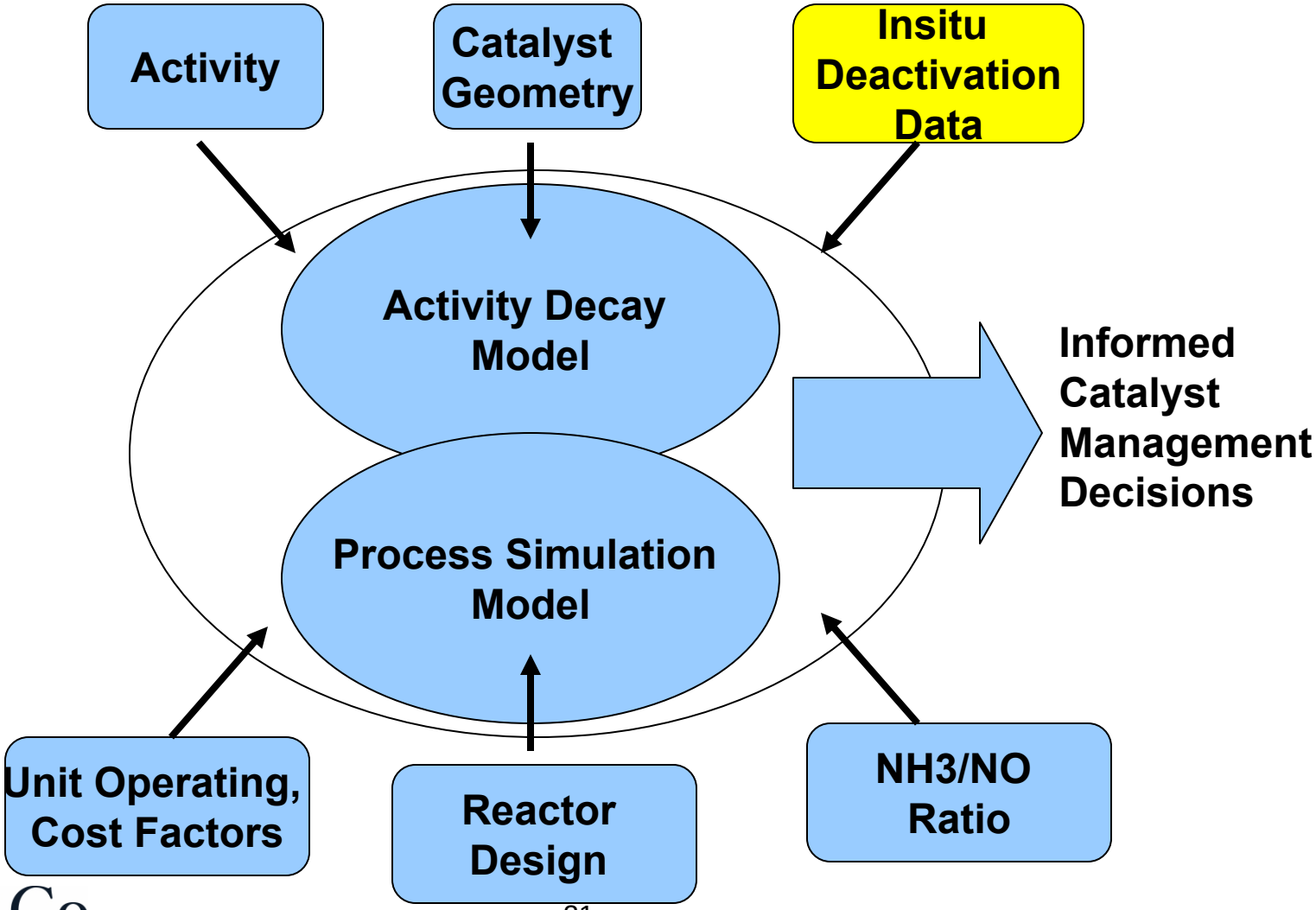
CATREACT™

- EPRI Product ID#1014740
- Available to Program #73 Funders
- Non-Funders End-use License Available
- Excel Based Catalyst Management Software

CATREACT: SCR PROCESS MODEL & CATALYST EVALUATION TOOL



CatReact™: Excel Workbook

Worksheet	Function
Input Buttons	Buttons to access sheets below, input scenario, run calculation
Unit Data	Unit size, coal type, etc.
SCR Data	SCR process design and operating data
Catalyst Data	Specific catalyst data
Time Factors	Start time, year when annual operation begins, date for the summary report
Economic Factors	Discount rate, cost of electricity, etc.
Planned Outages	List of planned outage dates and durations
Capacity Factors	Capacity factors by year
Deactivation	Catalyst layer deactivation rates
Output Data	Output from the calculations
Blank Sheet	User can paste results from multiple model runs

SPECIFY CATALYST EVENTS

Example: 3+1 Catalyst Layout

EPRI

Case 1

- Input Buttons
- Unit Data
- SCR Data
- Catalyst Data
- Time Factors
- Economic Factors
- Planned Outages
- Capacity Factors
- Catalyst Deactivation
- Output Data

Reset All Forms

CATREACT

Initiate Calculaton

Calculate

☐ *Check for Changes*

1	1+1	1+2
2	2+1	2+2
3	3+1	3+2
4	4+1	

Calculation Scenario					
	Layer 1	*Layer 2*	*Layer 3*	*Layer 4*	*Layer 5*
Startup	1	1	1		
Event 1				1	
Event 2	1				
Event 3		1			
Event 4			1		
Event 5				1	
Event 6	1				
Event 7		1			
Event 8			1		
Event 9				1	
Event 10	1				
Event 11		1			
Event 12			1		
Event 13				1	
Event 14	1				
Event 15		1			
Event 16			1		
Event 17				1	
Event 18	1				
Event 19		1			
Event 20			1		

Note: Numbers signify Catalyst Type

CATALYST DEACTIVATION: INPUT TEMPLATE

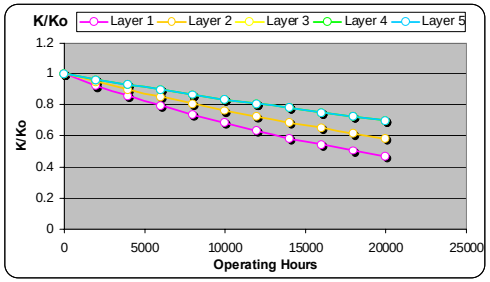
Case 1

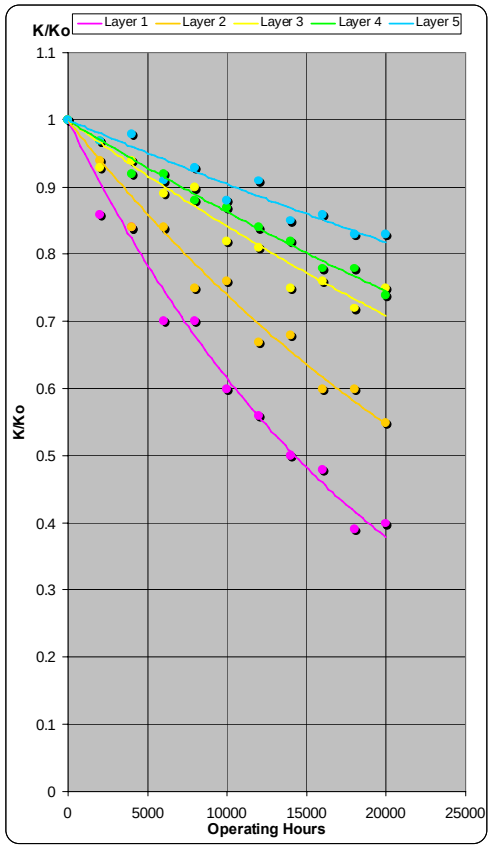
- Input Buttons
- Unit Data
- SCR Data
- Catalyst Data
- Time Factors
- Economic Factors
- Planned Outages
- Capacity Factors
- **Catalyst Deactivation**
- Output Data

Catalyst Deactivation Worksheet

	Deactivation Rates	T Values				
		Layer 1	Layer 2	Layer 3	Layer 4	Layer 5
	Default Low Arsenic	28000	40000	60000	60000	60000
	Default High Arsenic	18000	23000	30000	30000	30000
	Fit Vendor EOL Estimate	26291	37558	56337	56337	56337
	User Supplied	21319	34756	62016	69854	104506
Vendor	Used in the Calculations	26291	37558	56337	56337	56337

	e-t/T Time	Actual Deactivation Data or Vendor Curves				
		Layer 1	Layer 2	Layer 3	Layer 4	Layer 5
		K/Ko	K/Ko	K/Ko	K/Ko	K/Ko
1	0	1	1	1	1	1
2	2000	0.86	0.94	0.93	0.97	0.97
3	4000	0.84	0.84	0.94	0.92	0.98
4	6000	0.7	0.84	0.89	0.92	0.91
5	8000	0.7	0.75	0.90	0.88	0.93
6	10000	0.6	0.76	0.82	0.87	0.88
7	12000	0.56	0.67	0.81	0.84	0.91
8	14000	0.5	0.68	0.75	0.82	0.85
9	16000	0.48	0.60	0.76	0.78	0.86
10	18000	0.39	0.6	0.72	0.78	0.83
11	20000	0.4	0.55	0.75	0.74	0.83
T		21319	34756	62016	69854	104506





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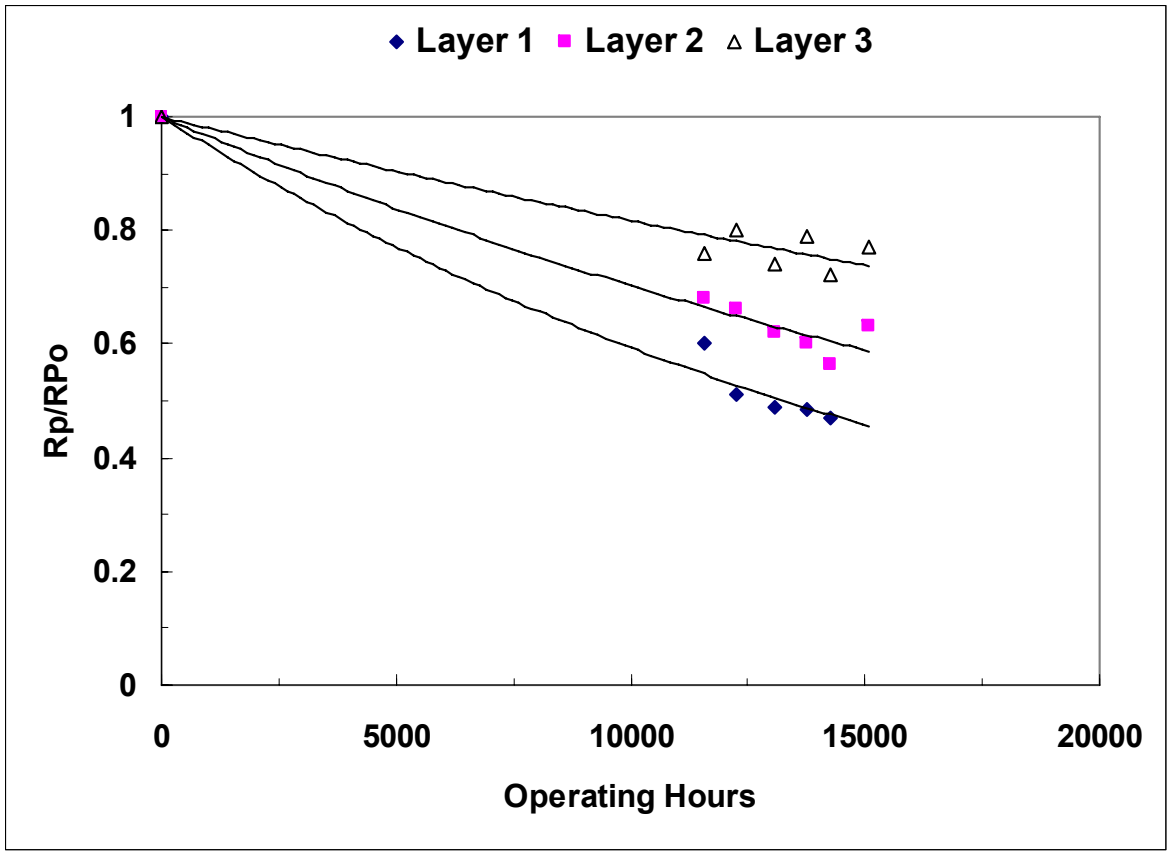
Insitu Data for CatReact™

- Just used the 2005 data and 1st measurement in 2006
- Insitu inherently accounts for blockage



CatReact Test Cases

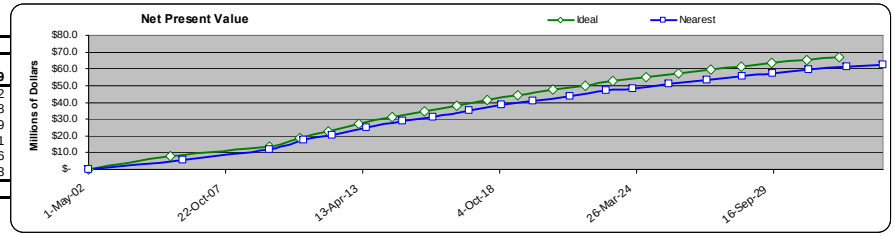
1. <u>Minimize Pressure Drop</u>
   - 3+1 Honeycomb (Design Condition)
   - 3+0 Honeycomb
   - 3+1 Plate in the 1st Layer

2. <u>3+1 (Plate in Layer 1)</u>
   - Explore more coordination with planned outages
   - Change catalyst late or early

CatReact™ Output

Case 1-Insitu

Summary Report	Ideal	Nearest
As of Date	12/31/22	12/31/22
Total Cost NPV	$ 50,792,012	$ 45,137,569
Catalyst NPV	$ 14,103,532	$ 13,068,692
Reagent NPV	$ 18,635,501	$ 19,070,008
Labor NPV	$ 667,086	$ 618,139
Electricity NPV	$ 16,431,786	$ 9,040,281
NOx Credit NPV	$ -	$ 2,365,086
dP NPV	$ 954,108	$ 975,363
Catalyst Layers Installed	12	11



Ideal Change Analysis

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5		Date	Operating Hours	Total Cost	dNOx	NH3slip	Cost Components: Catalyst	Reagent	Labor	Electricity	NOx Credits	dP	SO2 Conv	dP	RP/RPo(used)	RP/RPo (new)
							hrs	$ 10^6	%	ppm	$ 10^6	$ 10^6	$ 10^6	$ 10^6	$ 10^6	$ 10^6	%	in H2O		
1	1	1			Start	5/1/2002	0	$ -	85	0.1	$ -	$ -	$ -	$ -	$ -	$ -	0.5%	1.3		1.00
			1		Event 1	8/2/2005	13,252	$ 8.10	85	1.9	$ 1.80	$ 3.45	$ 0.09	$ 2.64	$ -	$ 0.13	0.7%	1.7	0.60	0.93
1					Event 2	7/16/2009	27,288	$ 13.76	85	1.9	$ 3.29	$ 5.74	$ 0.16	$ 4.29	$ -	$ 0.29	0.7%	1.7	0.60	0.86
	1				Event 3	10/3/2010	37,003	$ 18.58	85	1.9	$ 4.69	$ 7.34	$ 0.22	$ 5.96	$ -	$ 0.36	0.7%	1.7	0.60	0.86
		1			Event 4	11/24/2011	46,760	$ 22.94	85	1.9	$ 6.02	$ 8.76	$ 0.28	$ 7.44	$ -	$ 0.44	0.7%	1.7	0.60	0.82
			1		Event 5	2/21/2013	56,719	$ 27.06	85	1.9	$ 7.26	$ 10.12	$ 0.34	$ 8.82	$ -	$ 0.51	0.7%	1.7	0.60	0.81
1					Event 6	6/20/2014	67,368	$ 31.03	85	1.9	$ 8.43	$ 11.49	$ 0.40	$ 10.12	$ -	$ 0.58	0.7%	1.7	0.60	0.90
	1				Event 7	10/7/2015	78,504	$ 34.81	85	1.9	$ 9.53	$ 12.83	$ 0.45	$ 11.34	$ -	$ 0.65	0.7%	1.7	0.60	0.87
		1			Event 8	1/21/2017	88,886	$ 38.27	85	1.9	$ 10.56	$ 14.00	$ 0.50	$ 12.49	$ -	$ 0.71	0.7%	1.7	0.60	0.81
			1		Event 9	4/6/2018	98,474	$ 41.44	85	1.9	$ 11.53	$ 15.02	$ 0.55	$ 13.57	$ -	$ 0.77	0.7%	1.7	0.60	0.81
1					Event 10	6/27/2019	108,983	$ 44.52	85	1.9	$ 12.45	$ 16.08	$ 0.59	$ 14.59	$ -	$ 0.82	0.7%	1.7	0.60	0.90
	1				Event 11	11/17/2020	120,228	$ 47.48	85	1.9	$ 13.30	$ 17.13	$ 0.63	$ 15.54	$ -	$ 0.88	0.7%	1.7	0.60	0.87
		1			Event 12	3/6/2022	130,643	$ 50.18	85	1.9	$ 14.10	$ 18.05	$ 0.67	$ 16.43	$ -	$ 0.92	0.7%	1.7	0.60	0.81
			1		Event 13	4/18/2023	140,195	$ 52.66	85	1.9	$ 14.86	$ 18.85	$ 0.70	$ 17.28	$ -	$ 0.97	0.7%	1.7	0.60	0.81
1					Event 14	8/8/2024	150,704	$ 55.06	85	1.9	$ 15.58	$ 19.67	$ 0.74	$ 18.07	$ -	$ 1.01	0.7%	1.7	0.60	0.90
	1				Event 15	11/30/2025	161,955	$ 57.37	85	1.9	$ 16.24	$ 20.49	$ 0.77	$ 18.81	$ -	$ 1.05	0.7%	1.7	0.60	0.87
		1			Event 16	3/19/2027	172,372	$ 59.48	85	1.9	$ 16.87	$ 21.21	$ 0.80	$ 19.51	$ -	$ 1.09	0.7%	1.7	0.60	0.81
			1		Event 17	5/30/2028	181,921	$ 61.41	85	1.9	$ 17.46	$ 21.83	$ 0.83	$ 20.17	$ -	$ 1.12	0.7%	1.7	0.60	0.81
1					Event 18	8/20/2029	192,430	$ 63.29	85	1.9	$ 18.02	$ 22.47	$ 0.85	$ 20.79	$ -	$ 1.15	0.7%	1.7	0.60	0.90
	1				Event 19	1/11/2031	203,682	$ 65.09	85	1.9	$ 18.54	$ 23.12	$ 0.88	$ 21.37	$ -	$ 1.19	0.7%	1.7	0.60	0.87
		1			Event 20	4/29/2032	214,098	$ 66.74	85	1.9	$ 19.03	$ 23.68	$ 0.90	$ 21.91	$ -	$ 1.22	0.7%	1.7	0.60	0.81

Nearest Outage Analysis

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5		Date	Operating Hours	Total Cost	dNOx	NH3slip	Cost Components: Catalyst	Reagent	Labor	Electricity	NOx Credits	dP	SO2 Conv	dP	RP/RPo (used)	RP/RPo (new)
							hrs	$ 10^6	%	ppm	$ 10^6	$ 10^6	$ 10^6	$ 10^6	$ 10^6	$ 10^6	%	in H2O		
1	1	1			Start	5/1/2002	0	$ -	85	0.1	$ -	$ -	$ -	$ -	$ -	$ -	0.5%	1.3		1.00
			1		Event 1	2/1/2006	14,688	$ 5.91	68	2.00	$ 1.76	$ 3.65	$ 0.08	$ -	$ 0.27	$ 0.14	0.7%	1.7	0.57	0.90
1					Event 2	7/24/2009	29,874	$ 12.08	65	2.00	$ 3.25	$ 6.12	$ 0.15	$ 1.65	$ 0.60	$ 0.31	0.7%	1.7	0.56	0.83
	1				Event 3	11/30/2010	40,755	$ 17.44	61	2.00	$ 4.64	$ 7.90	$ 0.22	$ 3.31	$ 0.98	$ 0.39	0.7%	1.7	0.56	0.82
		1			Event 4	2/1/2012	50,064	$ 20.26	78	2.00	$ 5.95	$ 9.24	$ 0.28	$ 3.31	$ 1.01	$ 0.47	0.7%	1.7	0.58	0.82
			1		Event 5	6/7/2013	61,893	$ 24.87	65	2.00	$ 7.18	$ 10.84	$ 0.34	$ 4.68	$ 1.28	$ 0.55	0.7%	1.7	0.56	0.79
1					Event 6	11/14/2014	73,522	$ 29.11	67	2.00	$ 8.32	$ 12.30	$ 0.39	$ 5.95	$ 1.51	$ 0.63	0.7%	1.7	0.57	0.87
	1				Event 7	2/1/2016	83,208	$ 31.45	85	1.80	$ 9.40	$ 13.45	$ 0.44	$ 5.95	$ 1.51	$ 0.68	0.7%	1.7	0.61	0.88
		1			Event 8	7/18/2017	96,018	$ 35.36	62	2.00	$ 10.41	$ 14.87	$ 0.49	$ 7.07	$ 1.76	$ 0.76	0.7%	1.7	0.56	0.78
			1		Event 9	11/6/2018	106,488	$ 38.74	65	2.00	$ 11.35	$ 15.95	$ 0.54	$ 8.12	$ 1.97	$ 0.81	0.7%	1.7	0.56	0.78
1					Event 10	2/1/2020	116,352	$ 40.70	81	2.00	$ 12.24	$ 16.91	$ 0.58	$ 8.12	$ 1.98	$ 0.86	0.7%	1.7	0.59	0.89
	1				Event 11	8/3/2021	129,528	$ 43.94	62	2.00	$ 13.07	$ 18.11	$ 0.62	$ 9.04	$ 2.18	$ 0.93	0.7%	1.7	0.56	0.84
		1			Event 12	1/5/2023	141,050	$ 46.81	63	2.00	$ 13.84	$ 19.08	$ 0.65	$ 9.90	$ 2.37	$ 0.98	0.7%	1.7	0.56	0.78
			1		Event 13	2/1/2024	149,496	$ 48.29	85	1.98	$ 14.57	$ 19.76	$ 0.69	$ 9.90	$ 2.37	$ 1.01	0.7%	1.7	0.60	0.81
1					Event 14	7/17/2025	162,273	$ 50.90	67	2.00	$ 15.25	$ 20.71	$ 0.72	$ 10.65	$ 2.50	$ 1.06	0.7%	1.7	0.57	0.87
	1				Event 15	1/25/2027	174,688	$ 53.33	62	2.00	$ 15.88	$ 21.57	$ 0.75	$ 11.36	$ 2.66	$ 1.10	0.7%	1.7	0.56	0.83
		1			Event 16	6/20/2028	186,022	$ 55.52	62	2.00	$ 16.47	$ 22.31	$ 0.78	$ 12.01	$ 2.80	$ 1.14	0.7%	1.7	0.56	0.78
			1		Event 17	9/5/2029	196,379	$ 57.51	65	2.00	$ 17.03	$ 22.94	$ 0.81	$ 12.63	$ 2.93	$ 1.18	0.7%	1.7	0.56	0.79
1					Event 18	2/15/2031	208,092	$ 59.43	67	2.00	$ 17.55	$ 23.61	$ 0.83	$ 13.21	$ 3.03	$ 1.21	0.7%	1.7	0.57	0.87
	1				Event 19	8/26/2032	220,517	$ 61.28	62	2.00	$ 18.03	$ 24.26	$ 0.85	$ 13.74	$ 3.15	$ 1.24	0.7%	1.7	0.56	0.83
		1			Event 20	2/1/2034	232,848	$ 62.60	54	2.00	$ 18.48	$ 24.87	$ 0.87	$ 13.74	$ 3.36	$ 1.28	0.7%	1.7	0.54	0.76

Note: In the above output tables "black" entry dates correspond to planned outages
"red" entry dates correspond to special outages just to add or replace catalyst

Case Study No. 1

	Case 1a					Case 1b					Case 1c				
	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5
Start	1	1	1			1	1	1			1	1	1		
Event 1				1		1					3				
Event 2	1						1							1	
Event 3		1						1				1			
Event 4			1			1							1		
Event 5				1			1				3				
Event 6	1							1						1	
Event 7		1				1						1			
Event 8			1				1						1		
Event 9				1				1			3				
Event 10	1					1								1	
Event 11		1					1					1			
Event 12			1					1					1		
Event 13				1		1					3				
Event 14	1						1							1	
Event 15		1						1				1			
Event 16			1			1							1		
Event 17				1			1				3				
Event 18	1							1						1	
Event 19		1				1						1			
Event 20			1				1						1		

Summary Report	3+1	3+0	3+1Plate
As of Date	12/31/22	12/31/22	12/31/22
Total Cost NPV	$ 45,137,569	$ 63,359,330	$ 49,755,460
Catalyst NPV	$ 13,068,692	$ 16,667,577	$ 15,302,859
Reagent NPV	$ 19,070,008	$ 19,942,226	$ 19,581,103
Labor NPV	$ 618,139	$ 788,363	$ 684,325
Electricity NPV	$ 9,040,281	$ 10,249,495	$ 9,757,481
NOx Credit NPV	$ 2,365,086	$ 14,920,096	$ 3,476,486
dP NPV	$ 975,363	$ 791,573	$ 953,206
Catalyst Layers Installed	11	14	12

Commercialization

Will Be Offered by FERCo in 2007

- **Patent Applied For**
  - **U.S. Patent Application 20050255605, Filed April 21, 2005.**
- **Technical Presentations**
  - **2005 EPRI SCR Workshop**
  - **2006 DOE Environmental Controls Conference**
  - **2006 EPRI SCR Workshop**
  - **2007 Reinhold NOx Roundtable**
- **Technical Exhibits**
  - **2006 Mega Symposium**
  - **2006 Reinhold NOx Roundtable**
  - **2007 Reinhold NOx Roundtable**

Commercialization (continued)

Knox✓ Online Catalyst Activity Test System

- **Implementation**
  - **One utility has incorporated the ports for the Insitu System on two new SCR Systems being built**
  - **The insitu technique has been integrated into a SCR pilot plant at a FERCo client with remote testing via the WEB**
  - **FERCo plans to offer the first three commercial systems at basically cost**
  - **The hardware has been redesigned based on the 2006 Ozone Season results**

Conclusions

- The *in situ* technique directly measures the Reactor Potential. The Reactor Potential is the parameter that determines the overall performance of the SCR reactor. With the laboratory activity measurement, an estimate of the catalyst blockage is needed to determine Reactor Potential.

- Measurements can be made on a layer-by-layer basis within the reactor. This provides a larger data set upon which to quantify deactivation rates compared to once a year physical sampling.

- There was excellent quantitative agreement in the *in situ* and laboratory activity measurements of a new layer of plate catalyst installed at the start of the 2006 ozone season.

- The *in situ* results can be easily integrated into catalyst management software such as EPRI's CatReact™ Program to aid in making informed catalyst management decisions.

- The insitu technique can be used to monitor the decrease in Reactor Potential when operating below the " Minimum Operating Temperature"

- The technique will be offered by FERCo in 2007 and marketed under the name Knox✓

THANK YOU

- FERCo appreciates the support of all of the organizations that provided funding to allow us to successfully complete the project.
- We would also like to thank Southern Company for all of their support throughout the project.