SCR Catalyst Management

2005 Duke / WPCA NOx

Seminar

June 7, 2005

by

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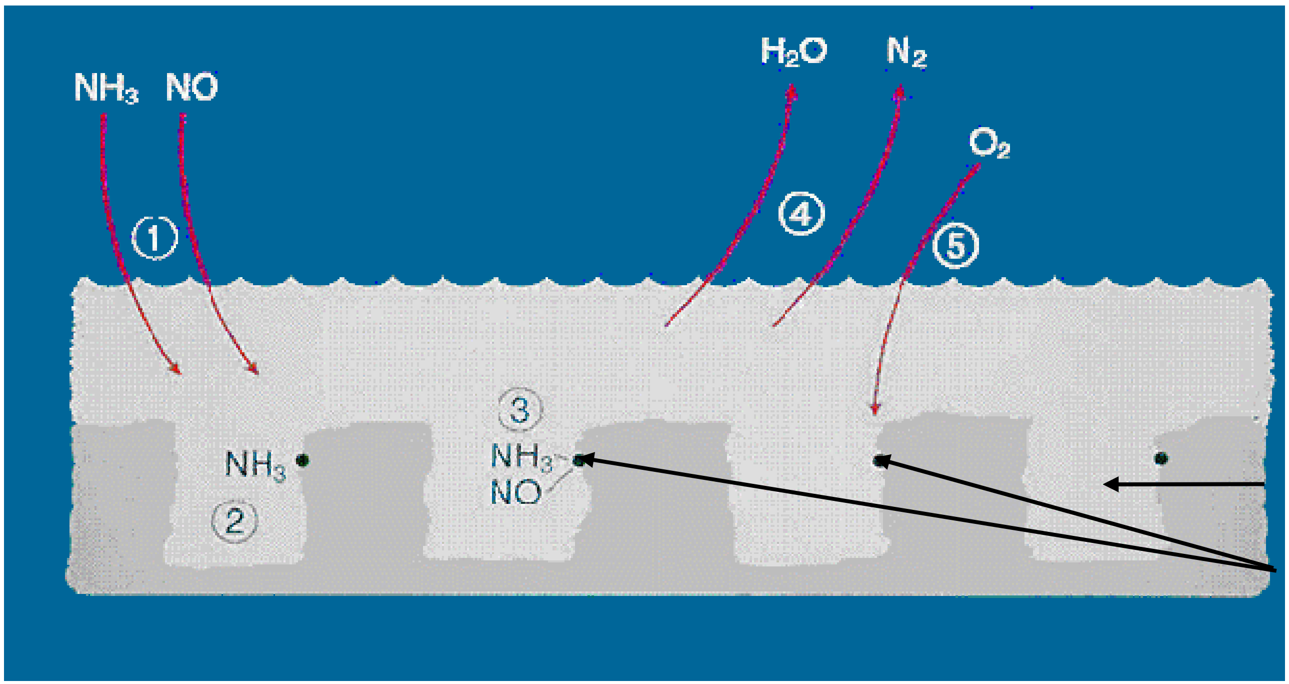
Outline

- DeNOx reaction
- Fuel impact
  - Ash
    - Amount
    - Particle size distribution
    - Minerals
    - Trace Elements
  - % Sulfur
- Catalyst sampling / analysis
- Inspections / housekeeping
- Catalyst replacement / cleaning
- Catalyst on line monitoring

The DeNOx Reaction

$$4\ NO + O_2 + 4\ NH_3 \Rightarrow 4\ N_2 + 6\ H_2O$$

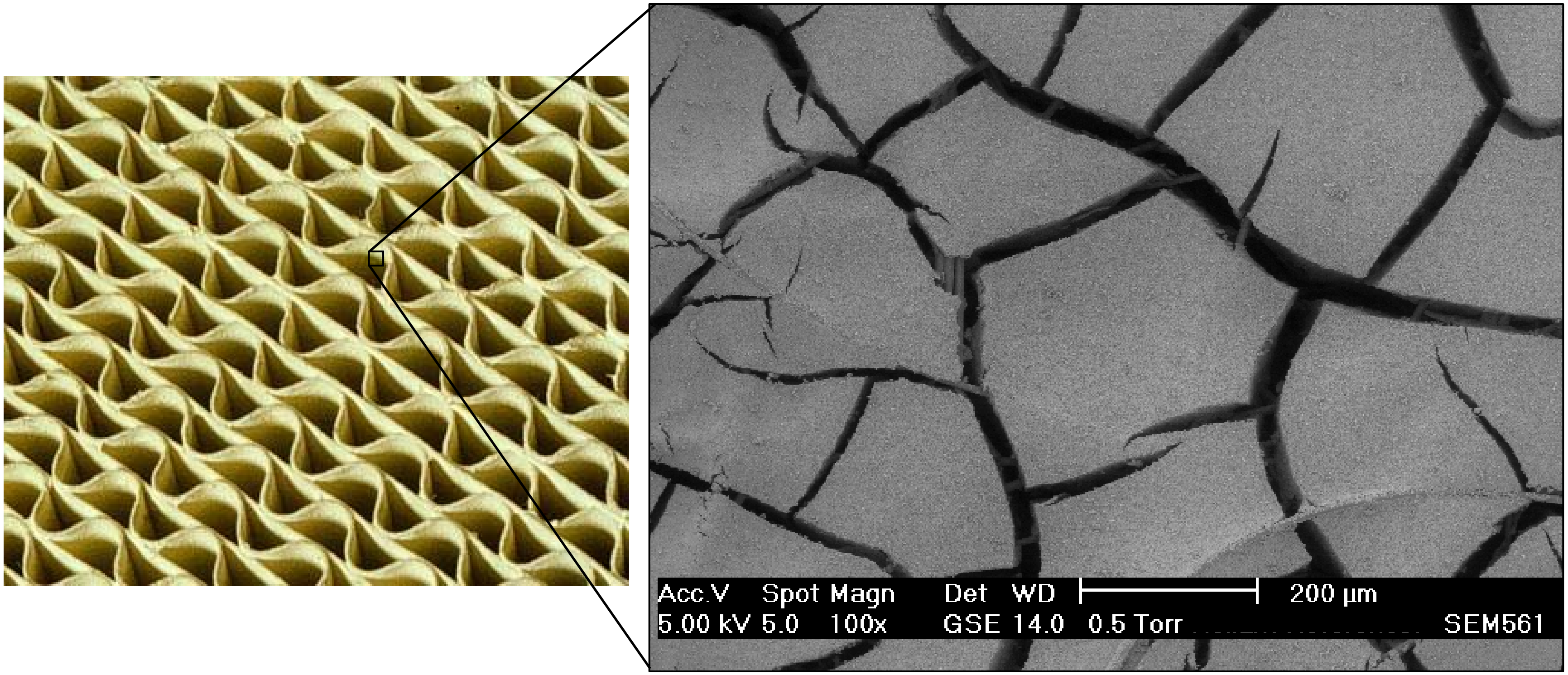
First order reaction – mass transport limited



DNX Catalyst: V_2O_5 and WO_3 on TiO_2

DeNOx reaction is diffusion limited

more highways = high diffusion rate = higher activity



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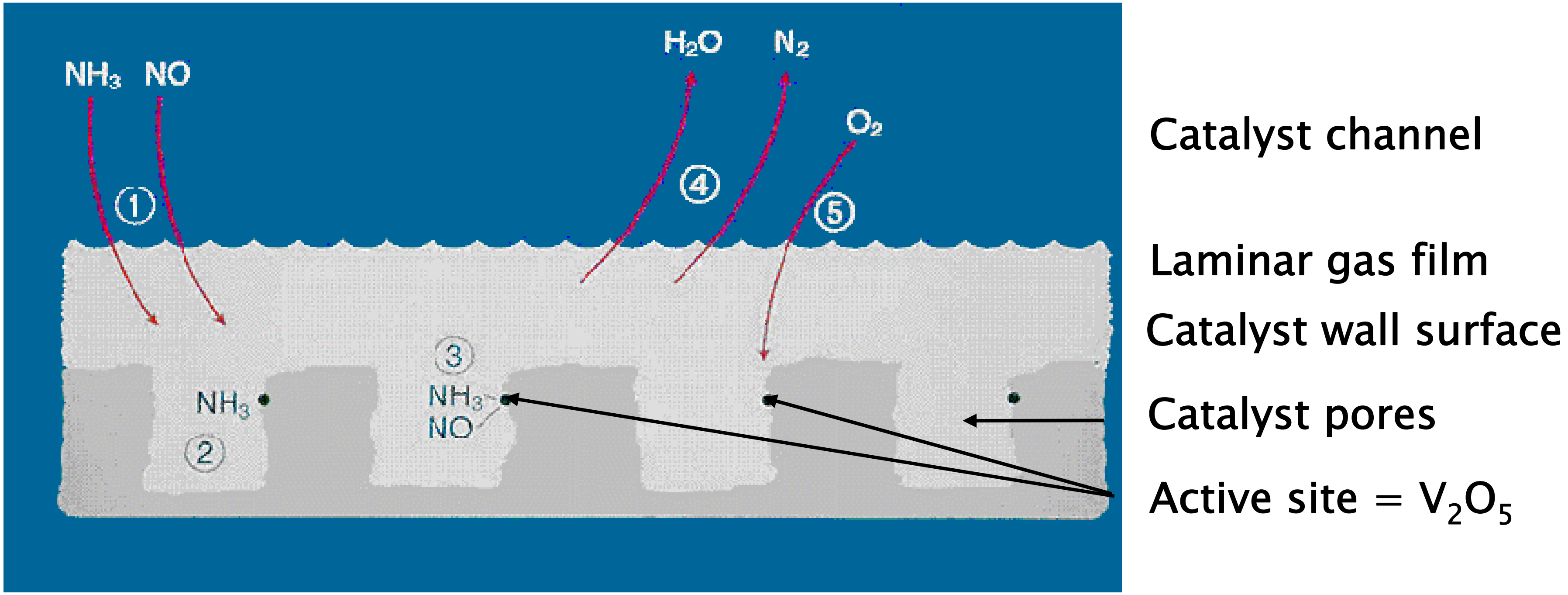
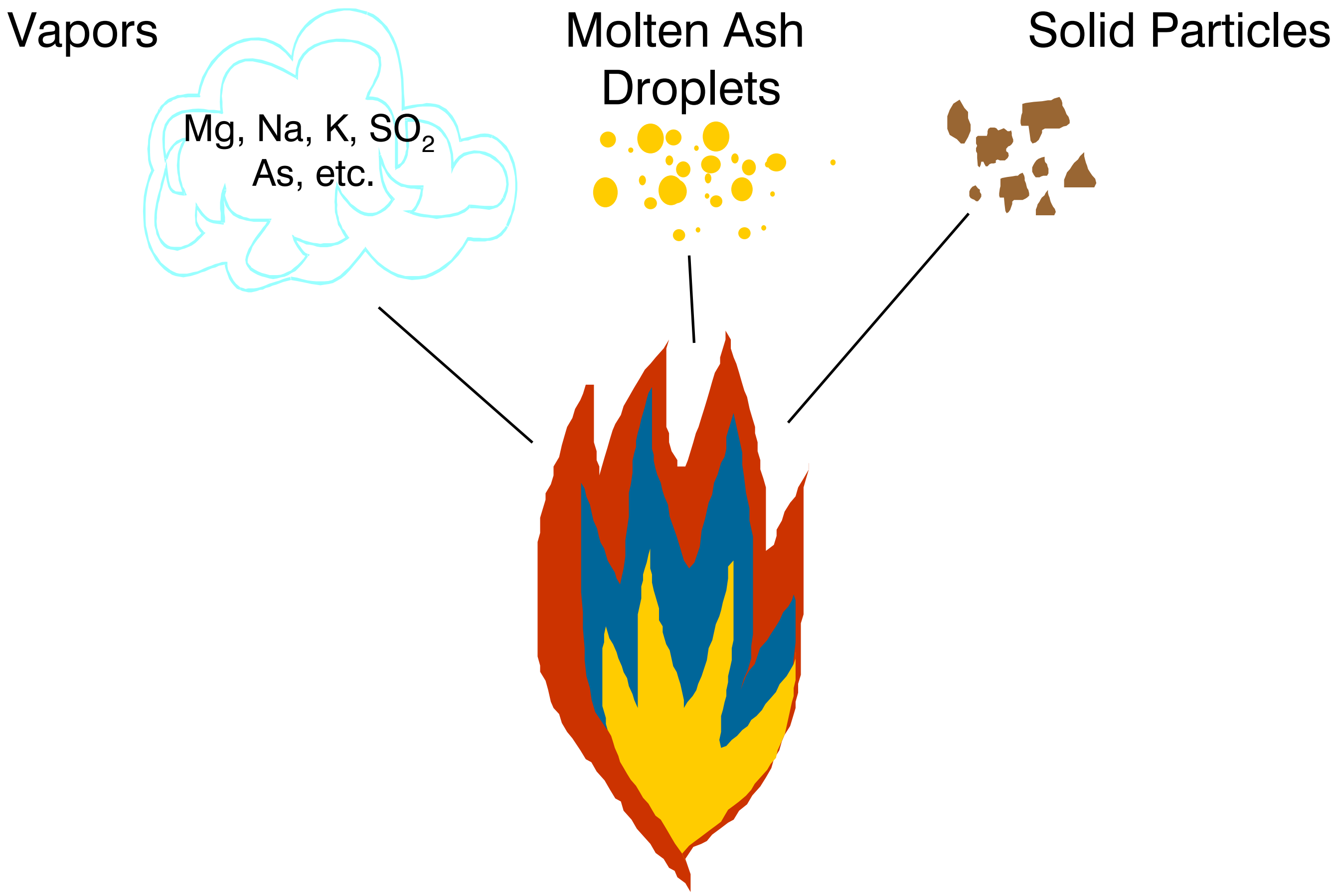


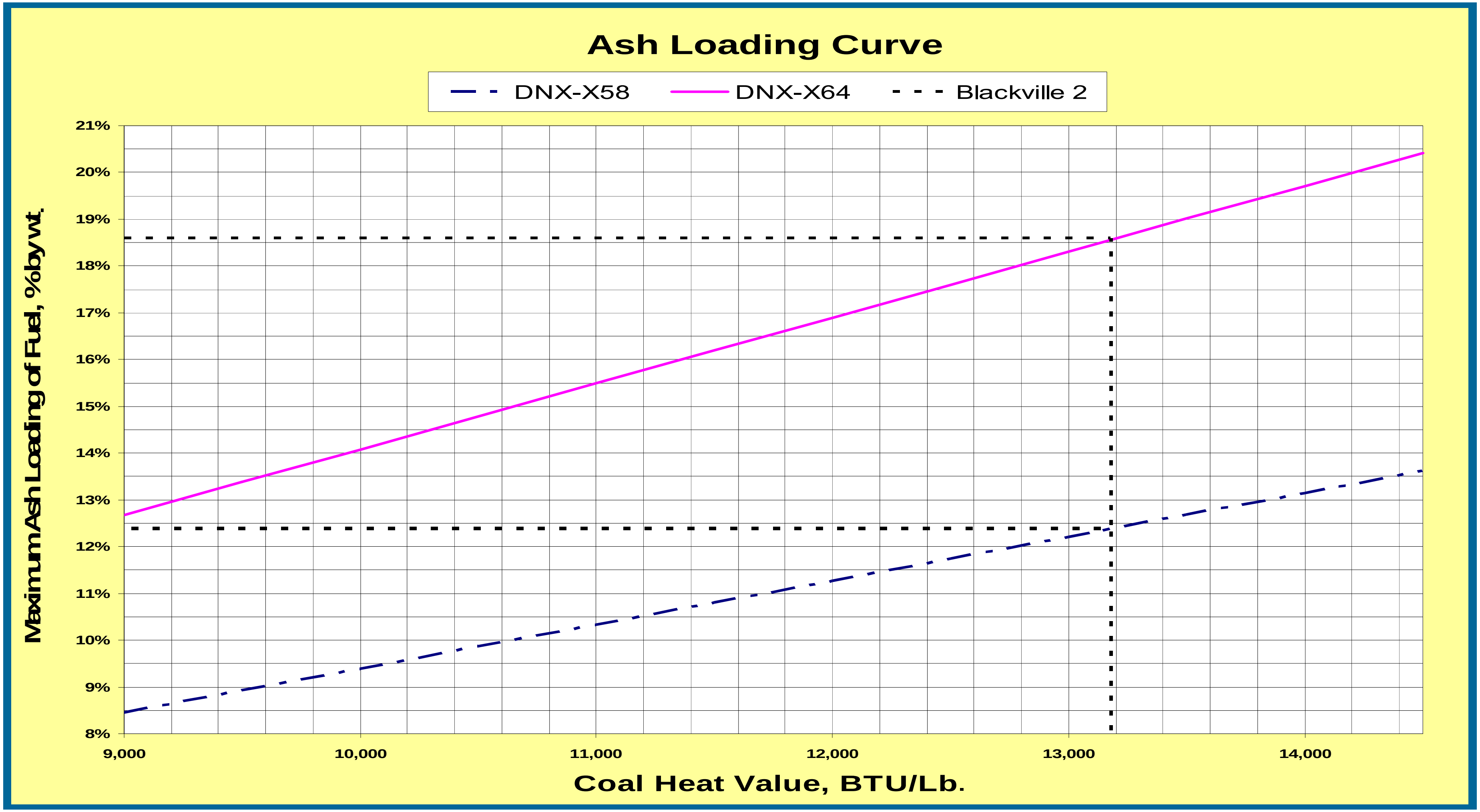
Catalyst deactivation results when one of the above is made less active.

Fossil Fuel Combustion



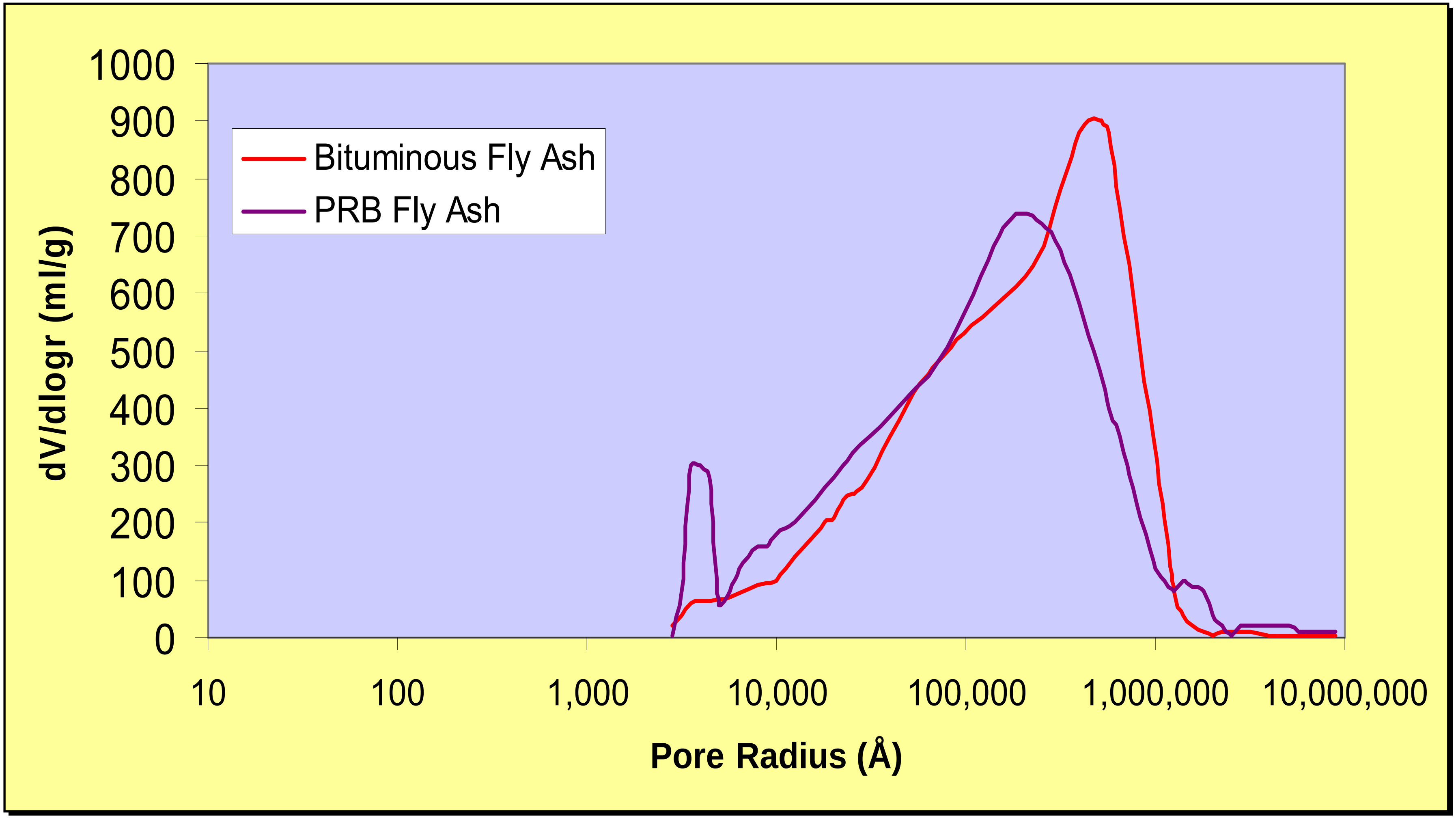
Fuel Impact - Ash

- **Catalyst pitch – amount of ash**



Fuel Impact - Ash

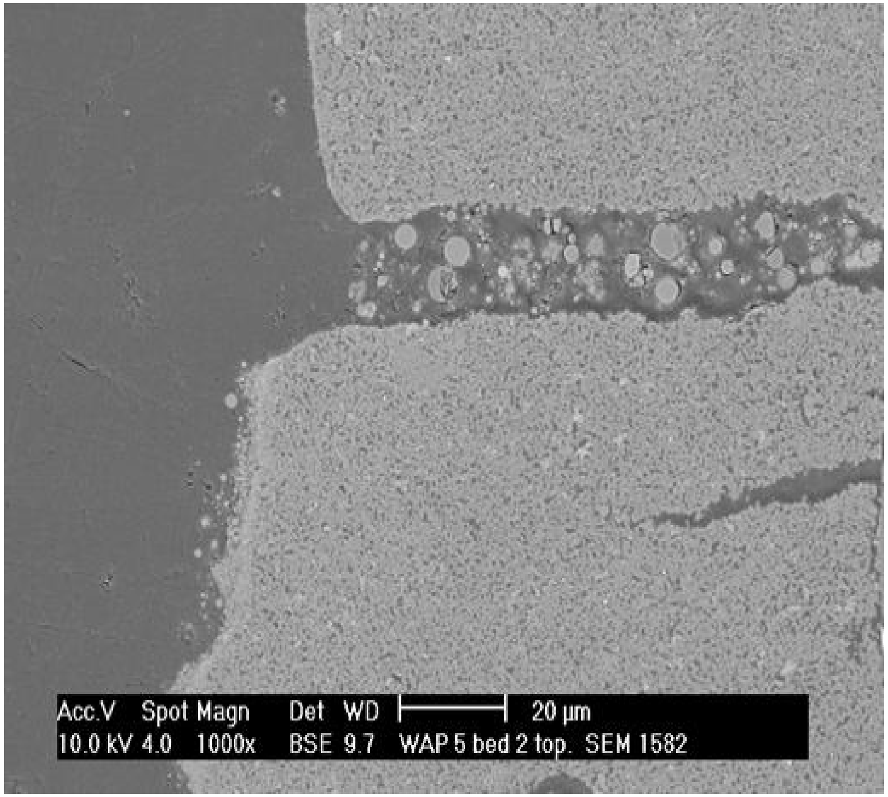
- **Catalyst pitch – particle size distribution**



Fuel Impact – Ash Mineral Analysis

Coal Ash Mineral Composition	Bituminous Coal
Al_2O_3, %	*22*
Fe_2O_3, %	*20.3*
SiO_2, %	*42.6*
SO_3, %	5
CaO, %	5.3
K_2O, %	1.4
MgO, %	0.9
Na_2O, %	0.9

- Al, Fe and Si impacts catalyst erosion
- Fe impacts SO_2-oxidation (+ / -)
- Si can also impact catalyst fouling



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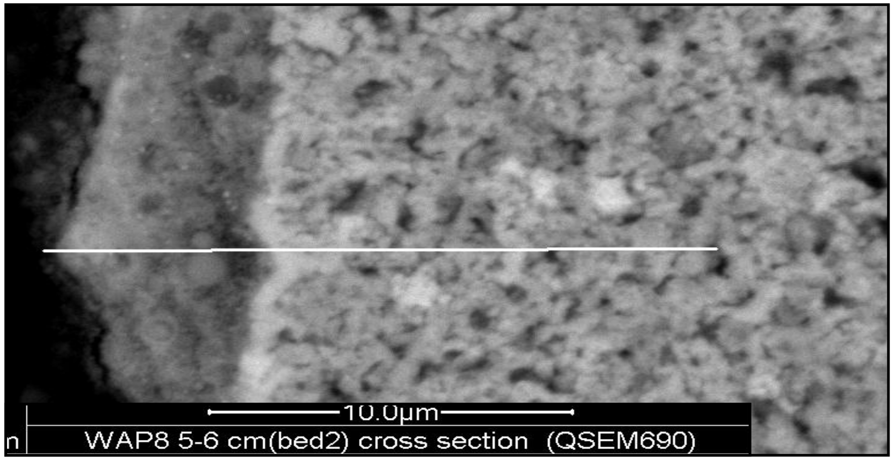
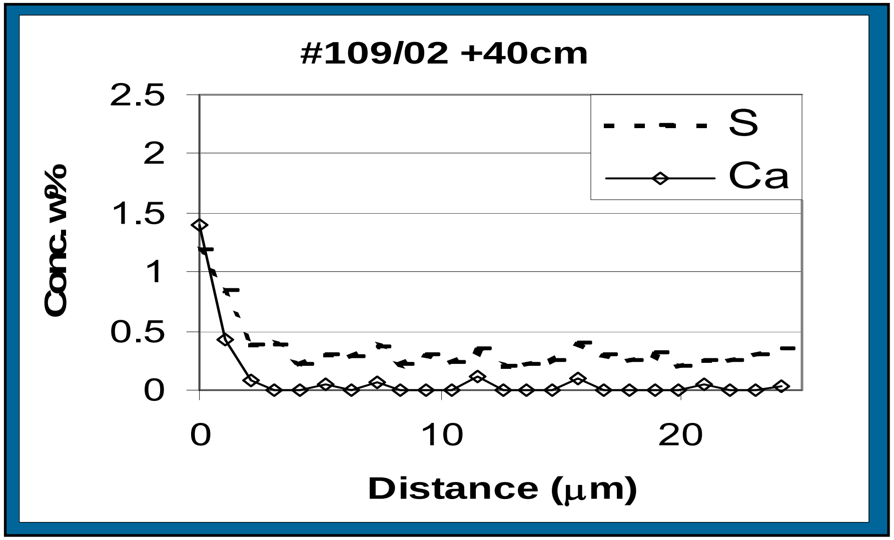
- $CaSO_4$ impacts catalyst fouling





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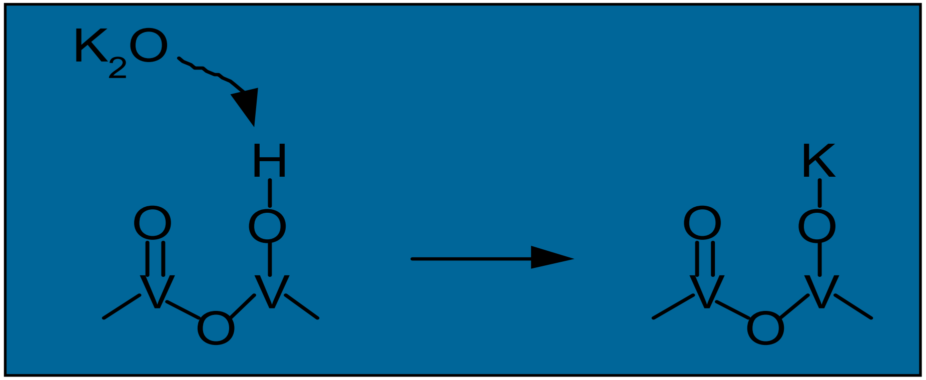
CaO, %	***5.3***
K_2O, %	***1.4***
MgO, %	***0.9***
Na_2O, %	***0.9***

- Ca, Mg, Na and K are all catalyst chemical poisons
- Acid soluble Na in ash >1.0%
- Acid soluble K in ash > 0.5%
- Risk is considered minor in bituminous coal, as most of the alkaline metals are not water soluble
- PRB, wood, straw fuel the risk is higher



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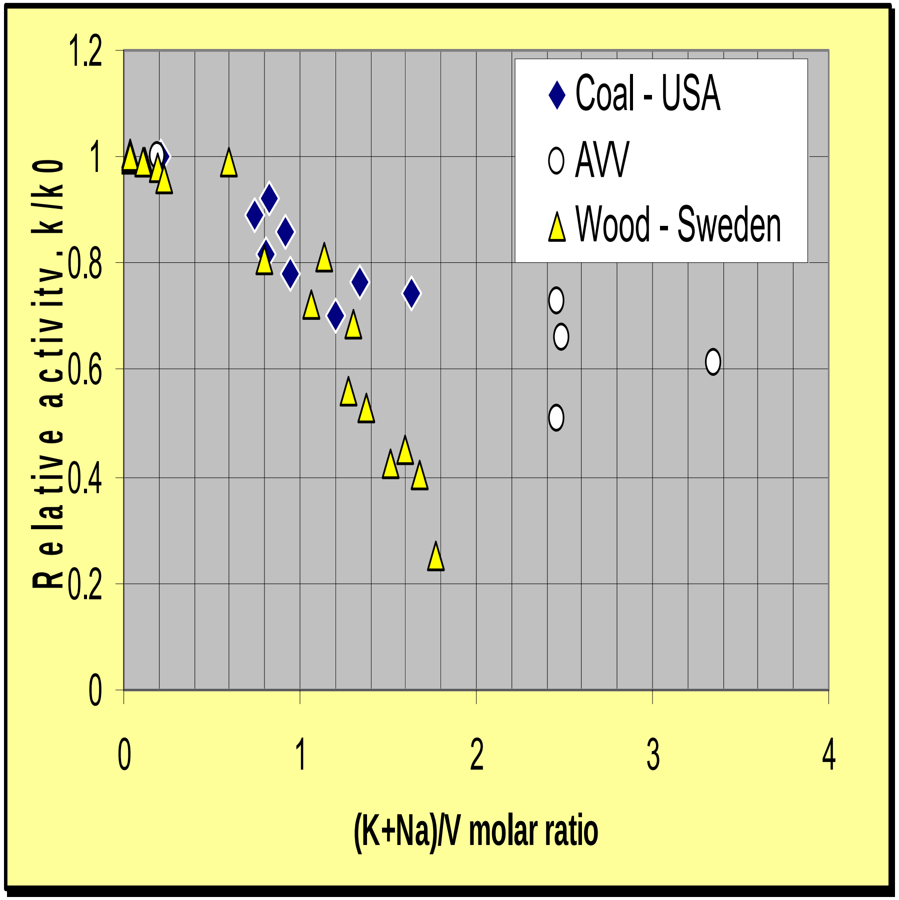
MgO, %	***0.9***
Na_2O, %	***0.9***

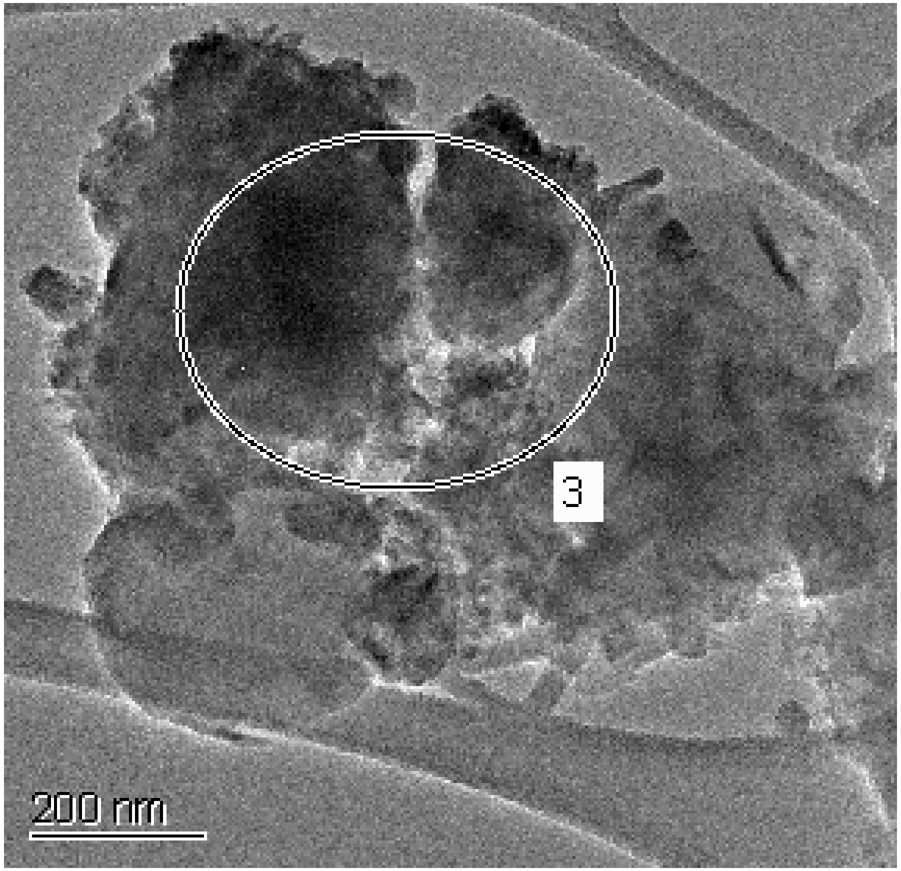
- SO_3 in the fuel reduces poisoning



Fuel Impact – Trace Elements

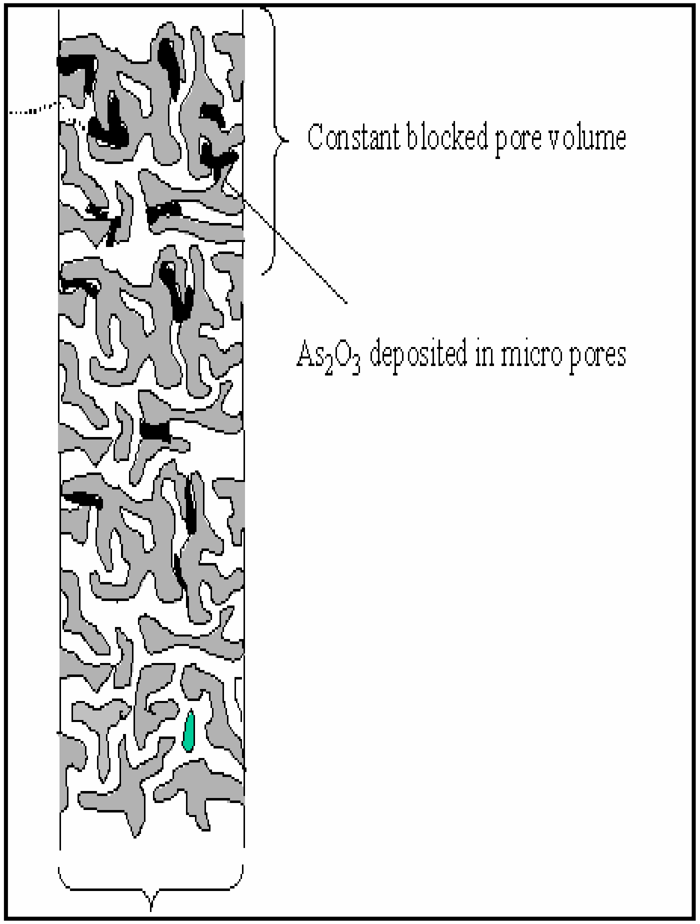
Coal Trace Elements	ppm
Arsenic ppm	*13*
Chrome ppm	43
Vanadium ppm	45
Copper ppm	21
Lead ppm	18
Mercury ppm	413
Nickel ppm	37

- As is a catalyst poison
- Mechanism – pore blockage



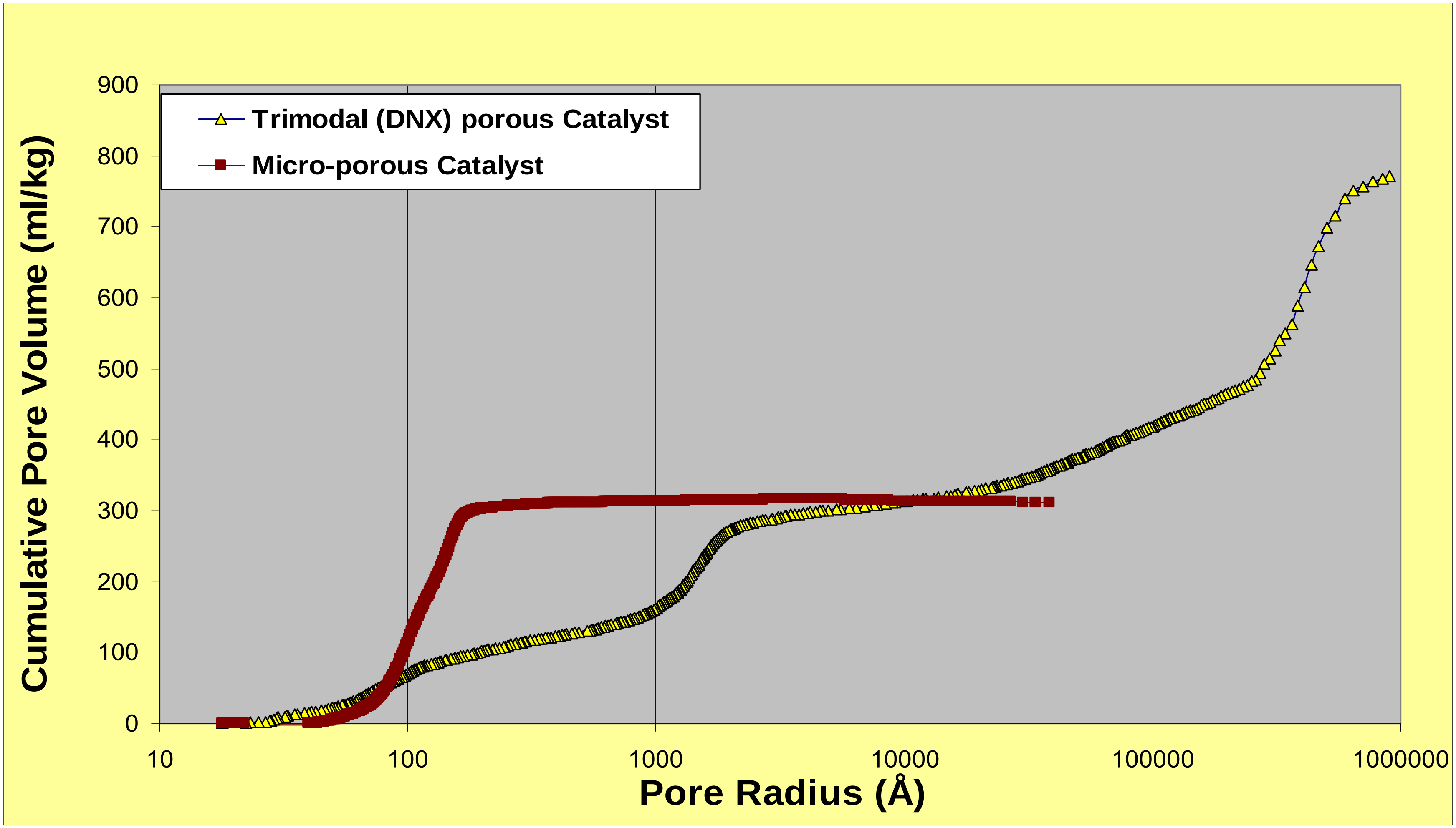
Fuel Impact – Trace Elements

- Arsenic poisoning mechanism
- As in coal is vaporized to As_2O_3,
- if the vapour pressure of As_2O_3 in the gas phase is higher than equilibrium, As_2O_3 will precipitate in the catalyst pores due to capillary forces,
- As condenses in the very small micro pores of the catalyst,
- As could react with the vanadium in the micro pores to form a vanadia-arsenate compound,
- this compound is so stable it inhibits V^{5+}-O-H reaction cycle.



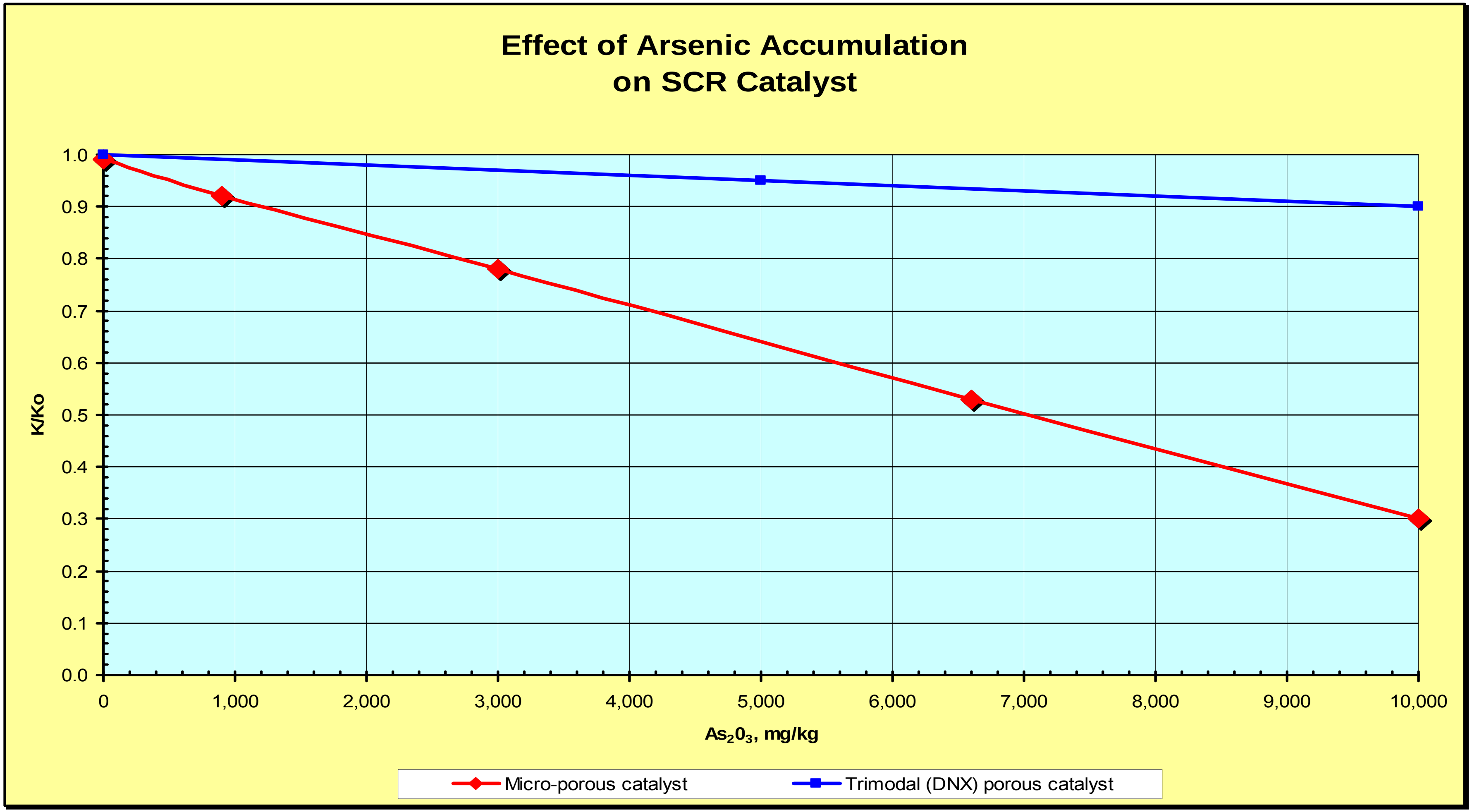
Fuel Impact – Trace Elements

- A catalyst with a diverse and accumulated larger pore volume



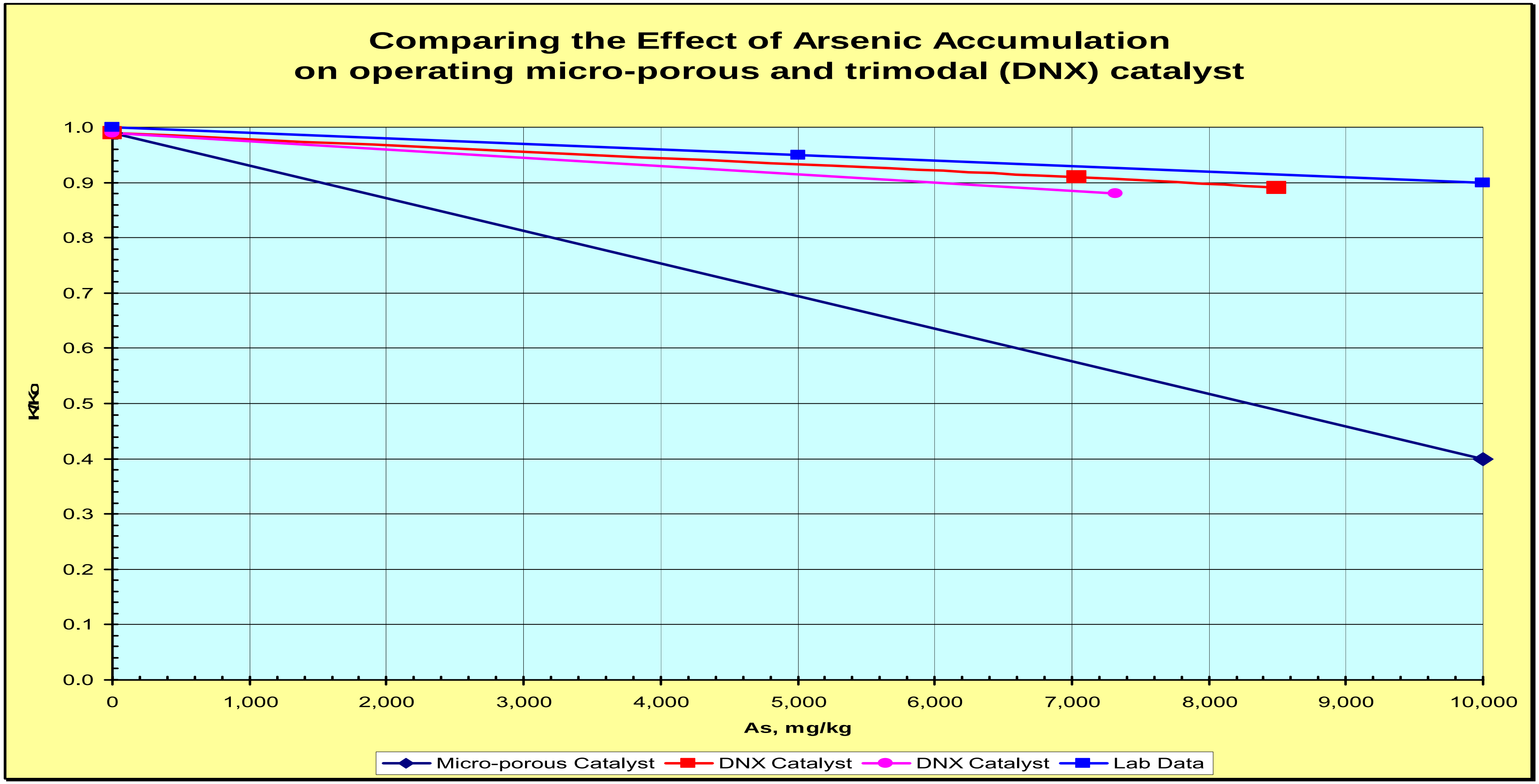
Fuel Impact – Trace Elements

- is more resistant to As poisoning



Fuel Impact – Trace Elements

- As containing fuel
  - Micro-porous catalyst increase CaO.
  - Use a catalyst with a diverse catalyst pore volume, w/ coal levels up to 25 ppm



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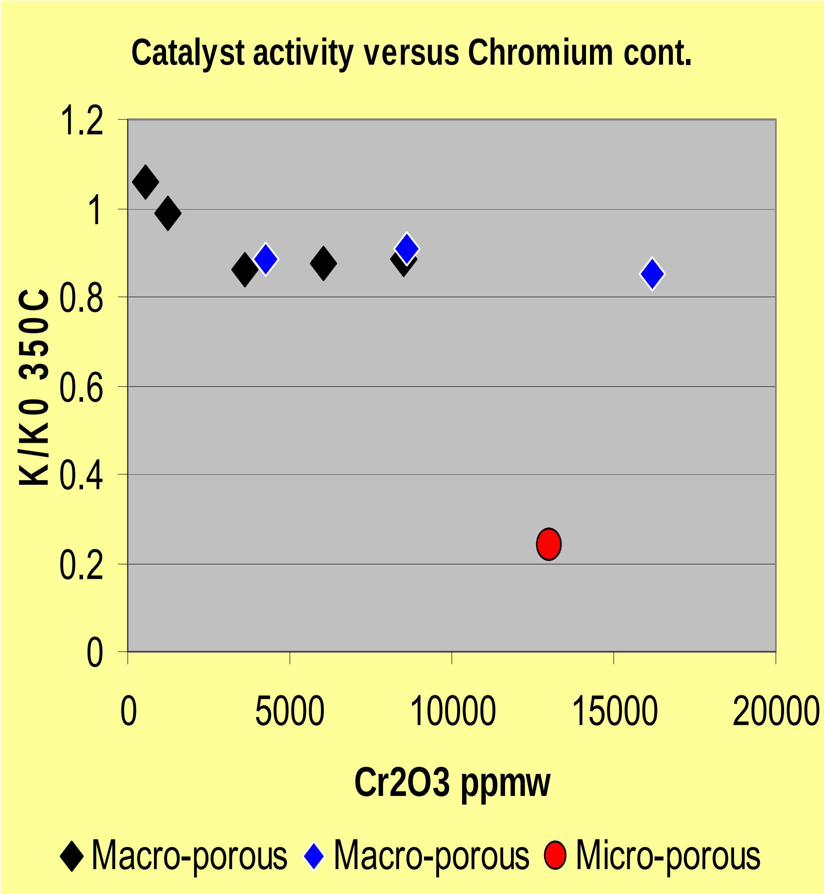
- Cr is a catalyst pore blockage poison



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Mercury ppm	**413**
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- $VOSO_4$ will accumulate on the on the catalyst surface
- Can deactivate catalyst, collapses active sites, if accumulation is high enough
- Increases SO_2- oxidation as V accumulates on the catalyst
- Oil, Pet coke

Fuel Impact – Trace Elements

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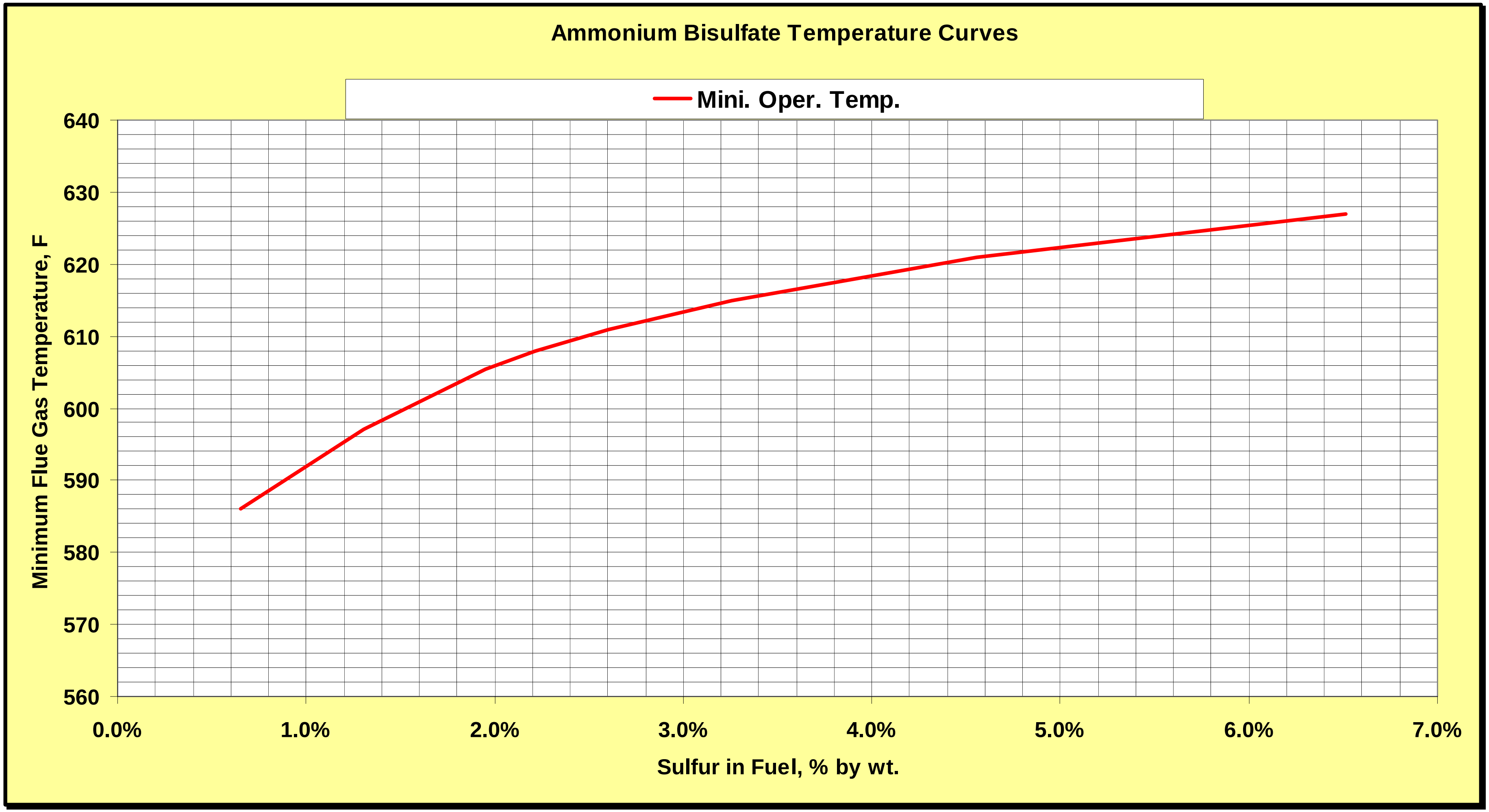
Arsenic ppm	**13**
Chrome ppm	**43**
Vanadium ppm	**45**
Copper ppm	***21***
Lead ppm	***18***
Mercury ppm	***413***
Nickel ppm	***37***

- Heavy and Base metals – antimony, chrome, copper, lead, mercury, nickel, tin, zinc
- Alkali Metals – cesium, lithium, rubidium
- Alkaline Earth Metals – barium, strontium
- Phosphorous

Fuel Impact - % Sulfur

- To prevent operating catalyst below Ammonium Bisulfate (ABS) formation temperature

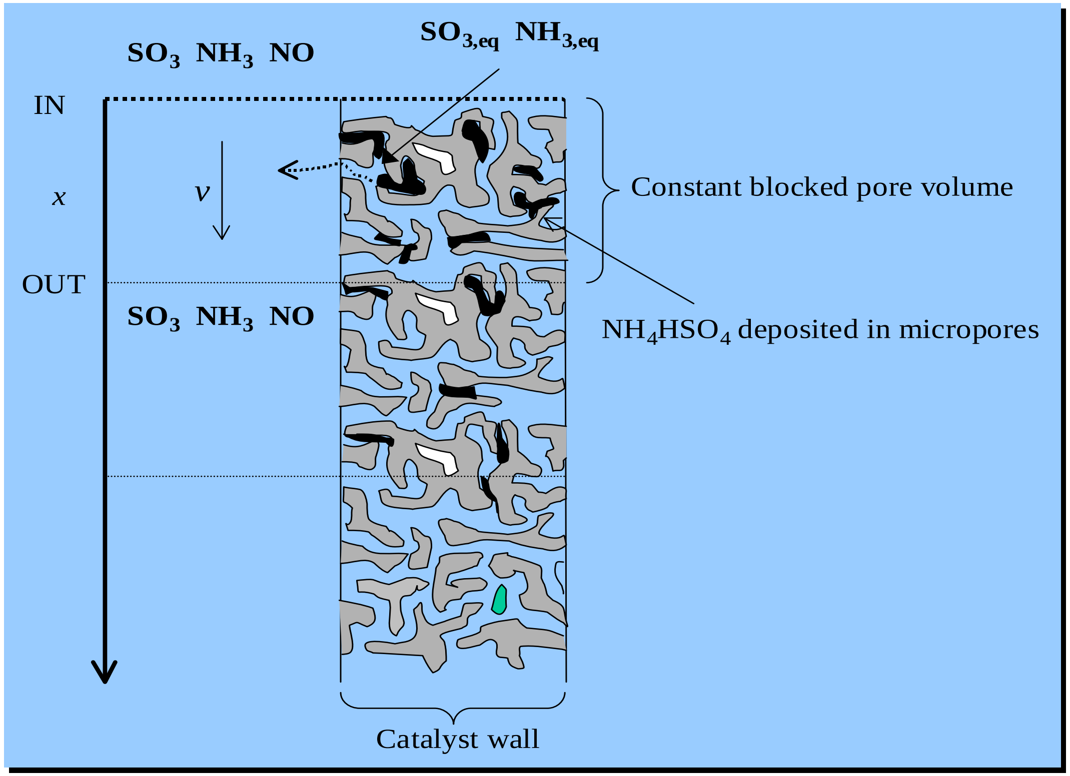


Fuel Impact - % Sulfur

- ABS – NH_4HSO_4

$$NH_{3(g)} + H_2SO_{4(g)} \rightarrow NH_4HSO_{4(liq)} \text{ (mp.147°C)}$$

- Mechanism
  - Pore blockage by capillary condensation.



Fuel Impact - % Sulfur

- Mechanism - ABS dew point calculation

NH_3 concentration
$SO_3 + H_2SO_4$ concentration
H_2O concentration
Pore size distribution

$\rightarrow$ T_{dew}

Clausius/Clapeyron equation:

$$\ln\left(P_{NH_3} \cdot P_{H_2SO_4}\right)_{eq,bulk} = 27.97 - \frac{26671}{T[K]}$$

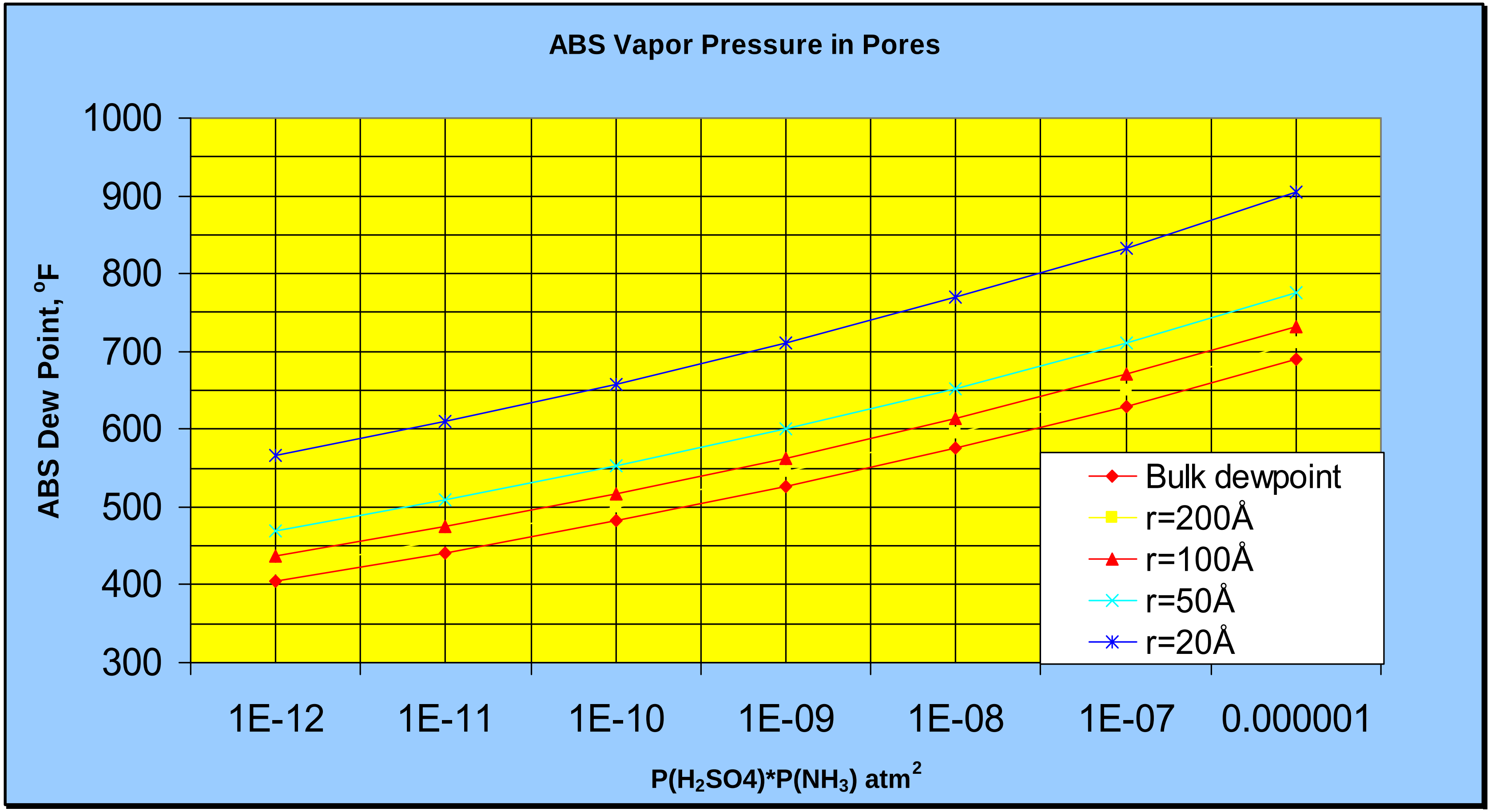
Matsuda, S., 1982

Kelvin equation:

$$\ln\frac{\left(P_{NH_3} \cdot P_{H_2SO_4}\right)_{eq,pore}}{\left(P_{NH_3} \cdot P_{H_2SO_4}\right)_{eq,bulk}} = -\frac{2 \cdot \sigma \cdot M}{\rho \cdot r_{pore} \cdot R \cdot T}$$

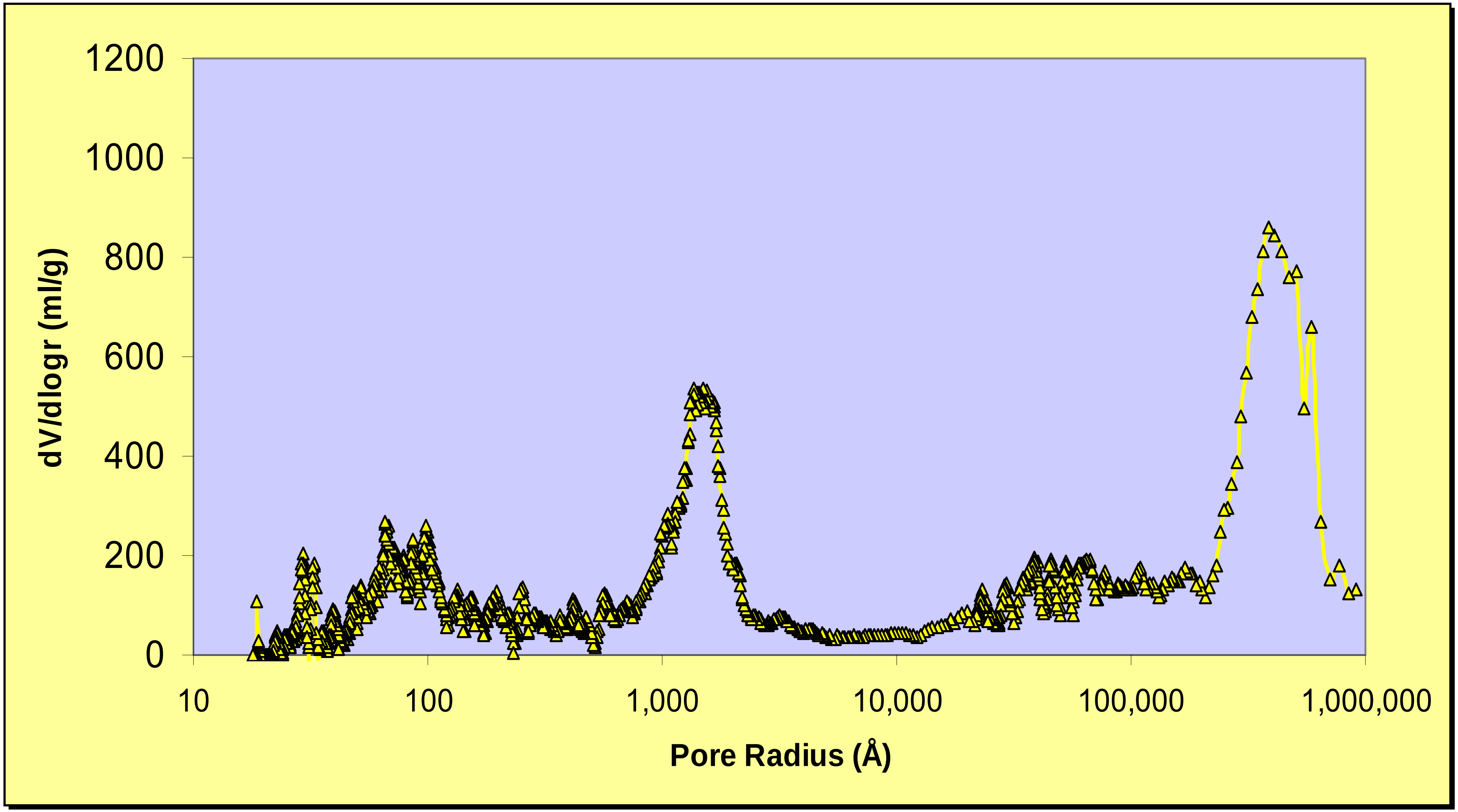
Fuel Impact - % Sulfur

- ABS dew point temperature depends on the catalyst pore distribution



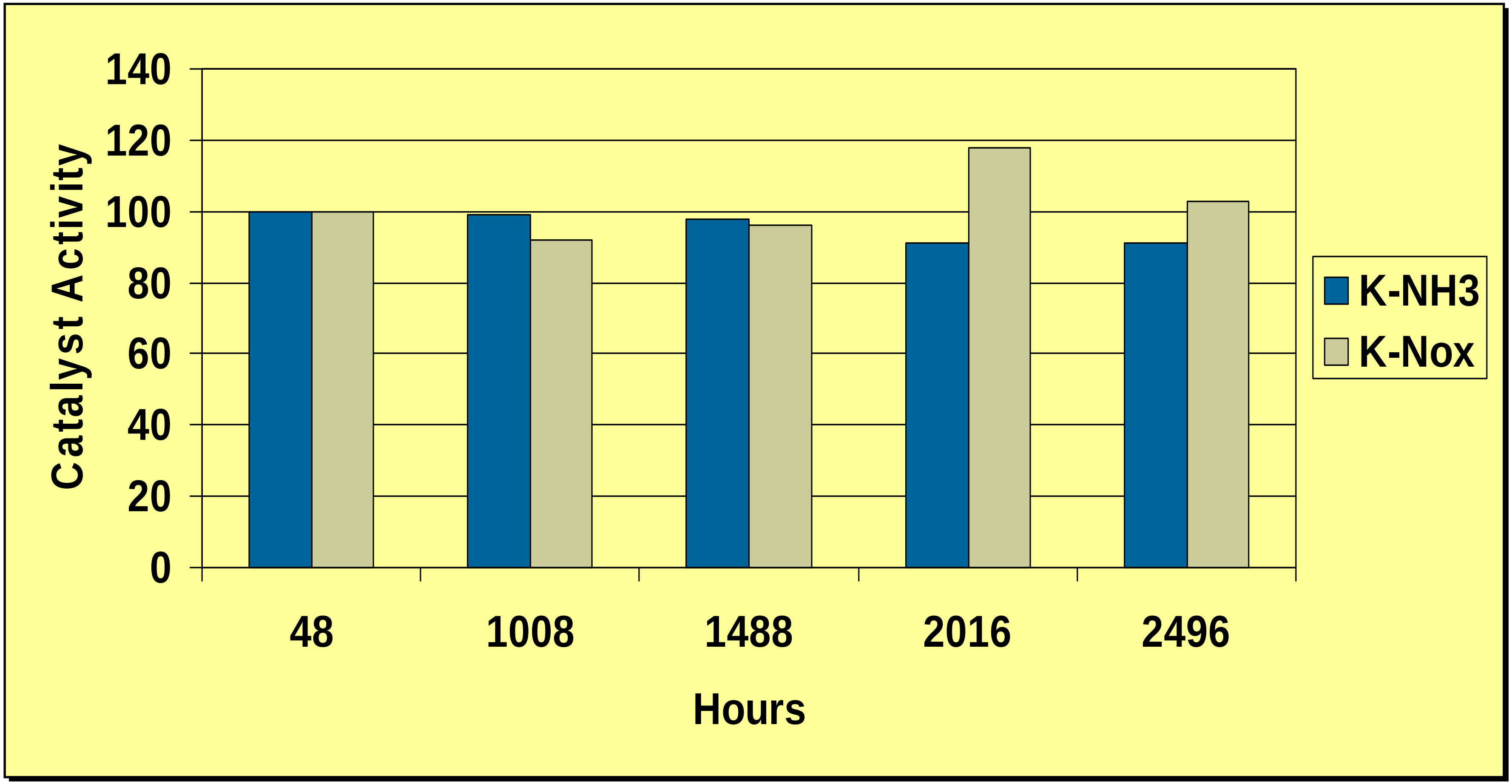
Fuel Impact - % Sulfur

- A diverse pore volume should allow operation below the ABS dew point

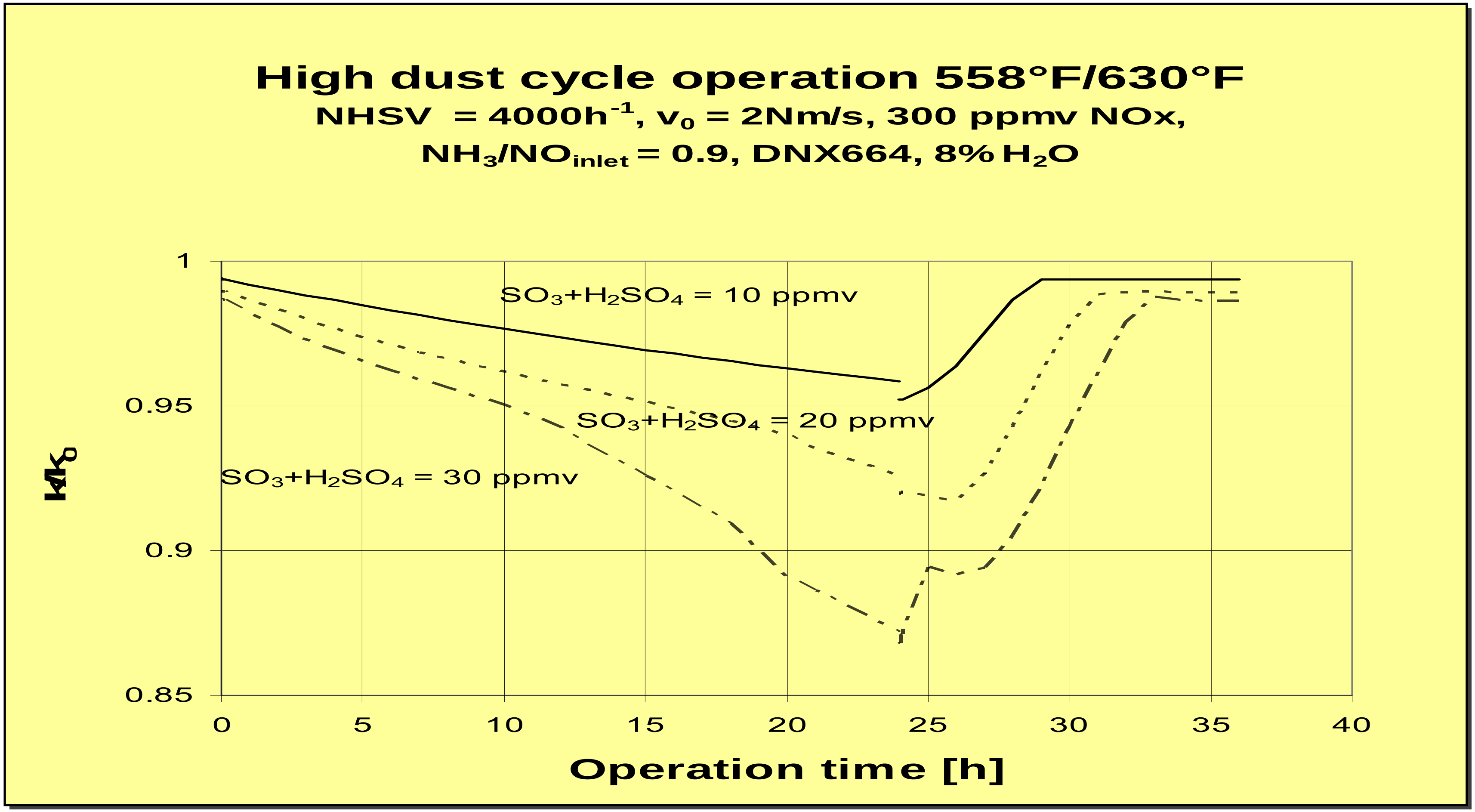


Fuel Impact - % Sulfur

- Cycle operation below and above the ABS dew point



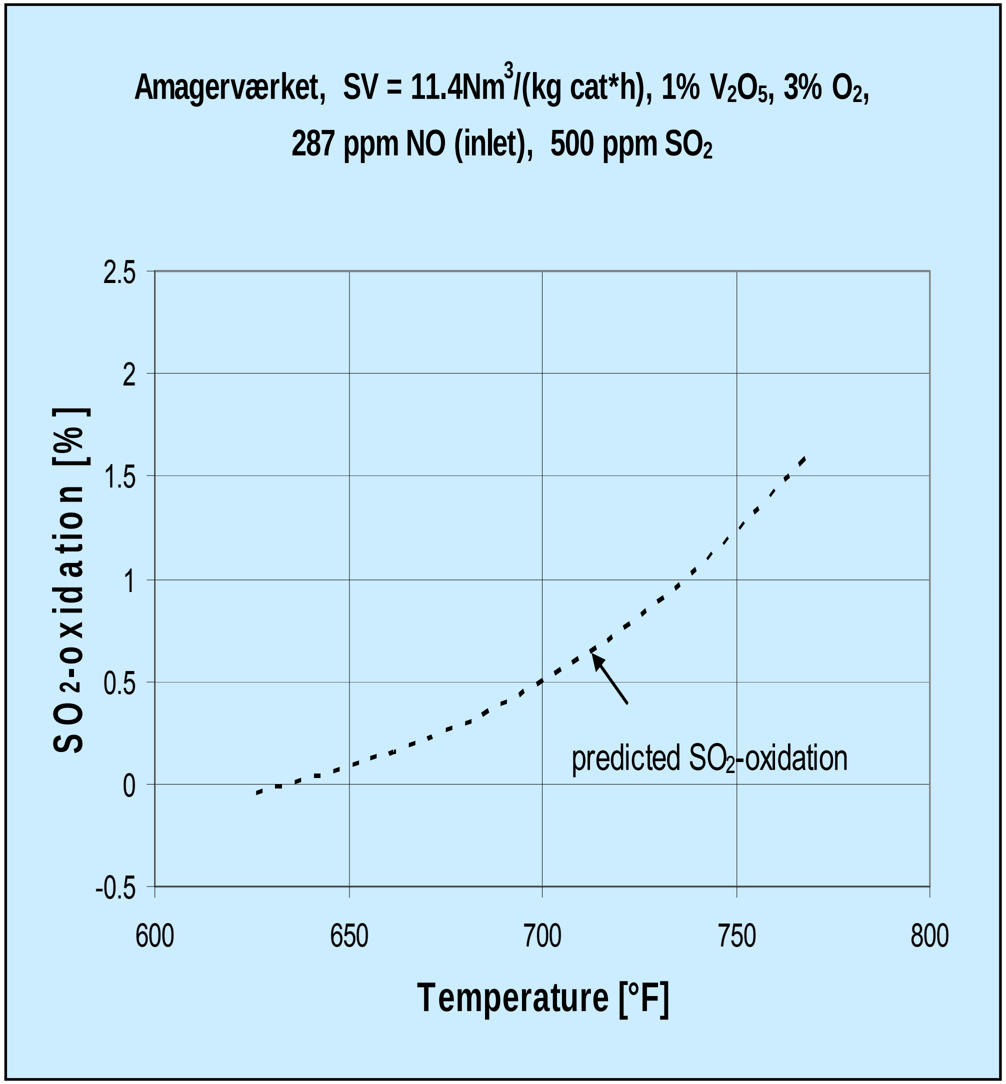
Fuel Impact - % Sulfur



- Five (5) SCR nightly operate below ABS dew point, up to 300 continuous hours, within 10 degrees F of the ABS bulk dew point temperature.

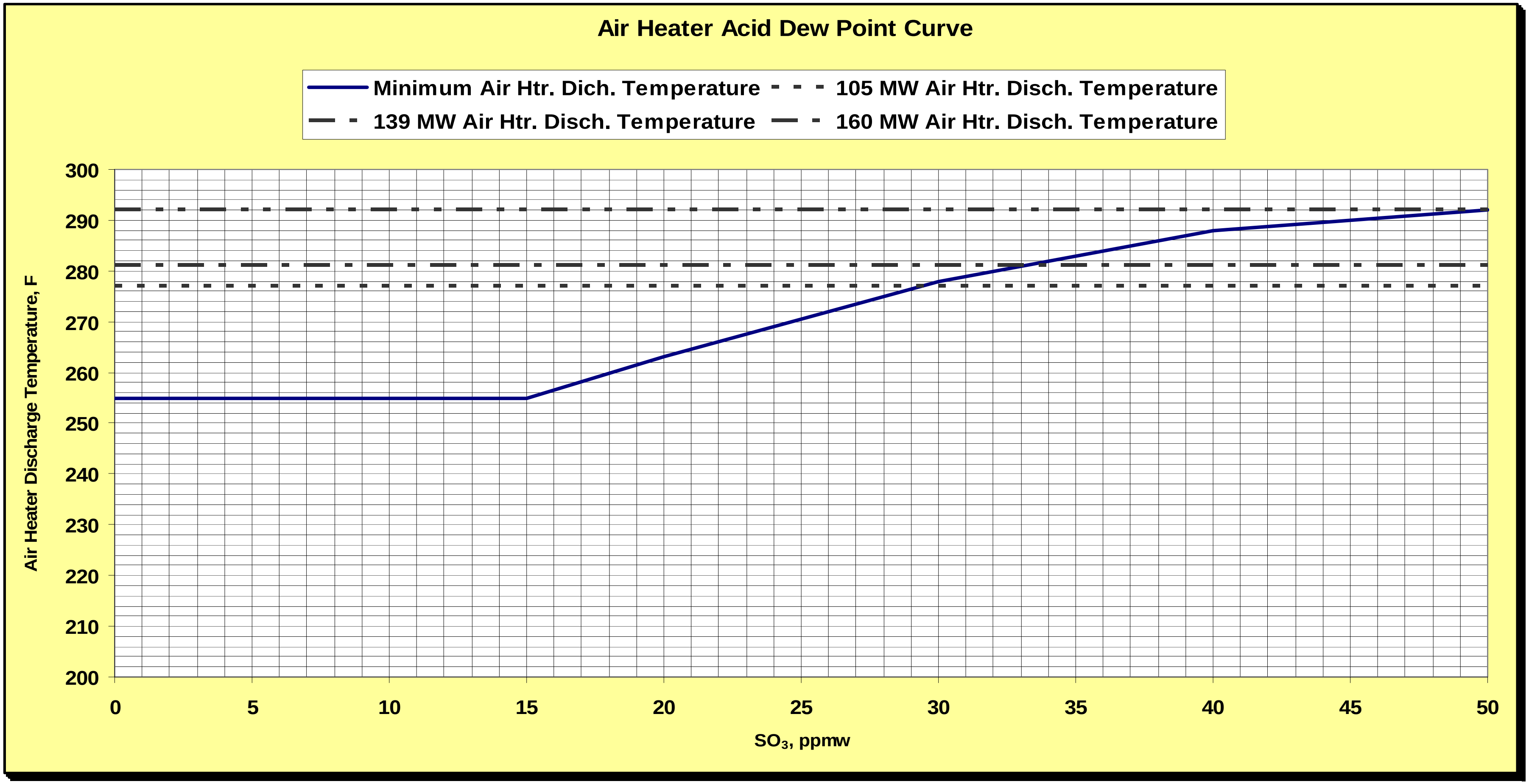
Fuel Impact - % Sulfur

- Managing SO_2-oxidation
  - Fuel
    - SO_2 concentration
    - Ash composition
  - Boiler
    - Excess O_2
  - Catalyst
    - Distribution of vanadium
    - Diverse pore structure



- Current SO_2- oxidation experience
  - High dust guarantees < 0.1%
  - Operating experience < 0.1%

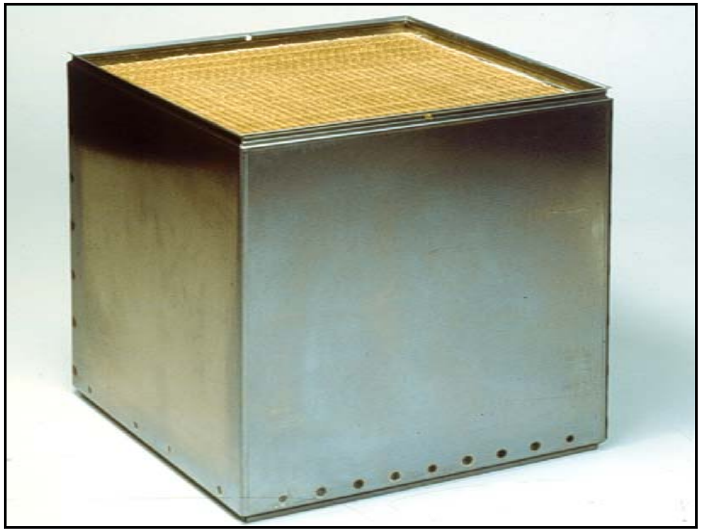
Fuel Impact - % Sulfur



- A 2.5 % sulfur coal, SO_2-oxidation of 0.5% increases SO_3 content > 10 ppm thereby increasing the acid dew point temperature.

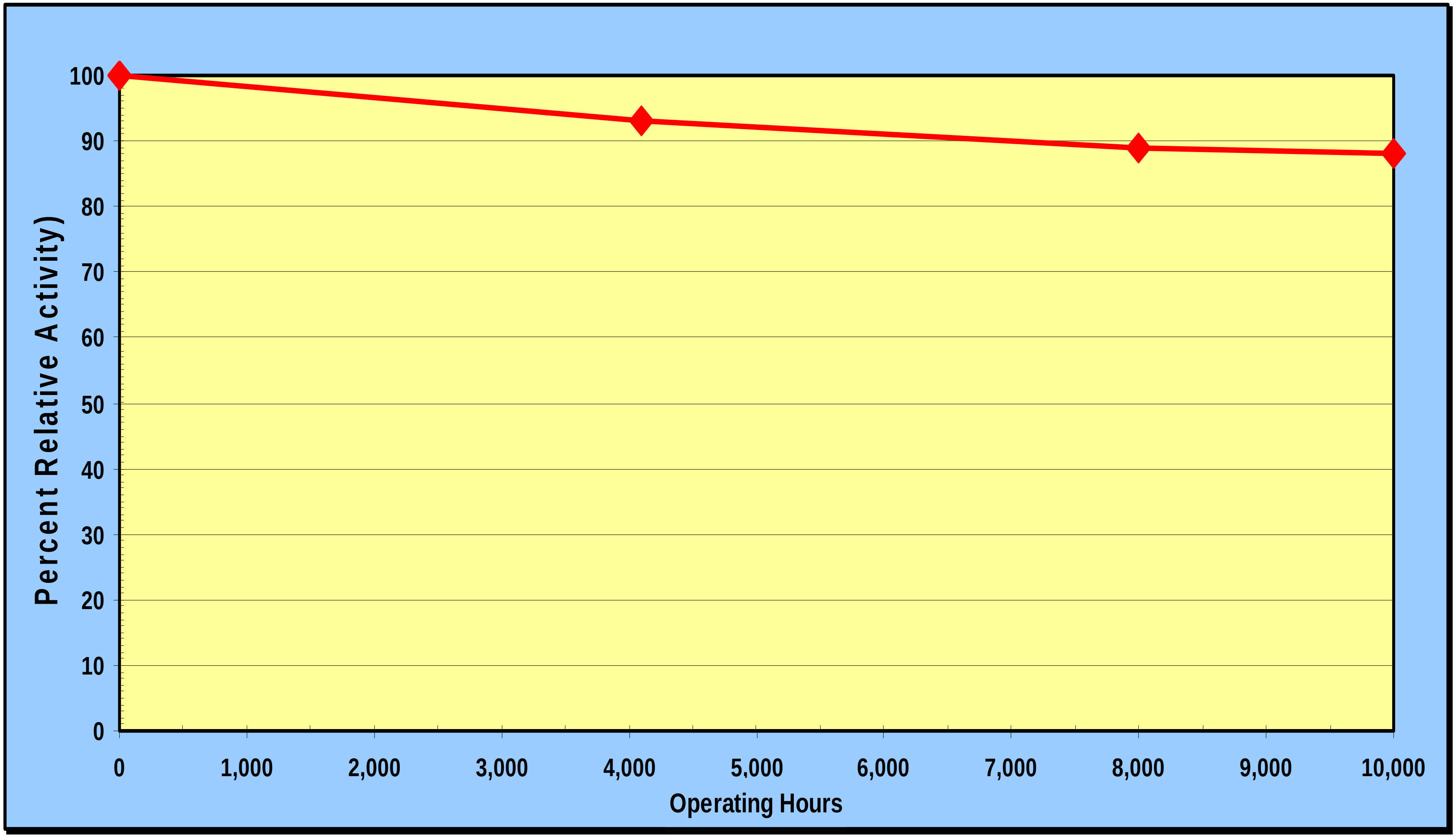
Catalyst Testing

- **Catalyst testing – Elements / Plates**
  - **When?**
    - Annual
    - End of ozone season
  - **Where should you sample?**
    - 1st layer
    - Look at flow model results
    - Area of highest dust loading
  - **What analysis should you request?**
    - Activity – STD / Unit Conditions
    - Chemical
    - Surface



Catalyst Testing

- Activity Analysis Results



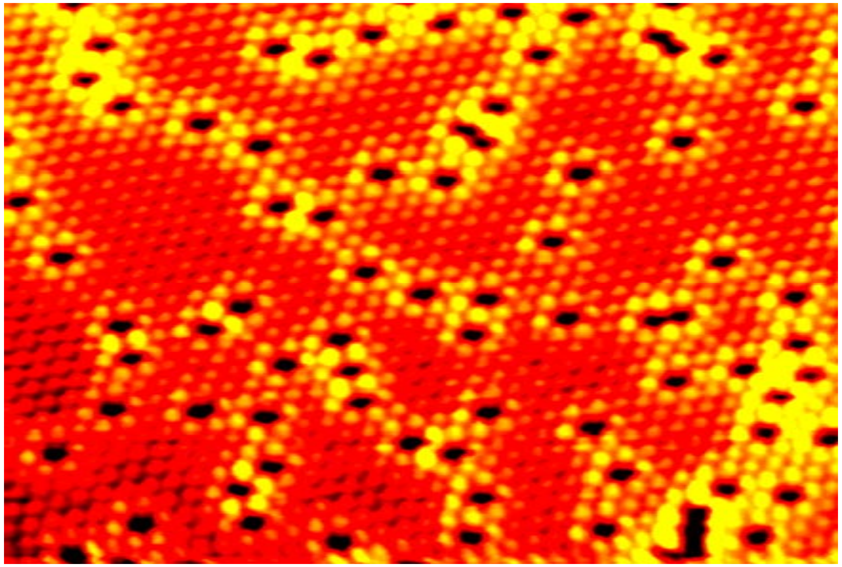
Catalyst Testing

- Chemical Analysis
  - Look at catalyst poisons

Sample	Reference	Reactor A		Reactor B	
		Original Layer 1	Duplicate Layer 1	Original Layer 1	Duplicate Layer 1
Al, %	1.12	1.52	1.43	1.76	1.67
As, ppm	< 10	6,070	6,315	4,805	4,170
Ca, %	2.56	2.53	2.43	2.69	2.45
Fe, %	0.04	0.68	0.58	1.16	0.93
$K_{soluble}$, ppm	165	1,475	1,600	1,775	2,100
Mg, %	0.06	0.08	0.08	0.09	0.1
$Na_{soluble}$, ppm	545	1,380	1,210	1,400	1,330
P, ppm	1,680	1,605	2,000	1,570	2,000
Si, %	5.24	5.78	5.69	6.32	6.05
S, %	0.03	0.55	0.57	0.58	0.59

Catalyst Testing

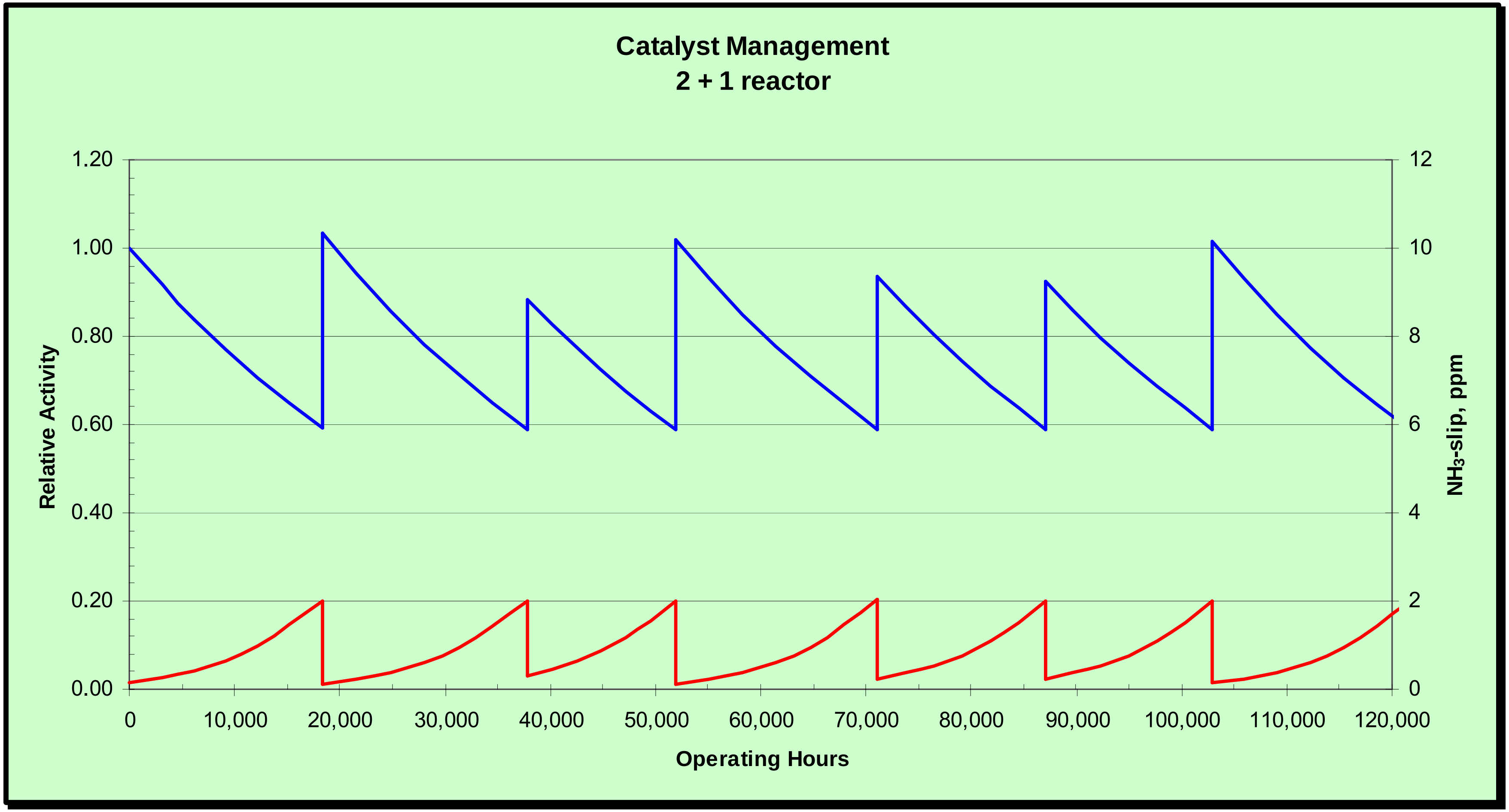
- Surface Analysis
  - Internal surface area (BET) pore volume



	Reference sample		Reactor A		Reactor B	
	A	B	Layer 1	Layer 3	Layer 1	Layer 3
Surface area BET, m^2/g	70	68	68	65	65	64

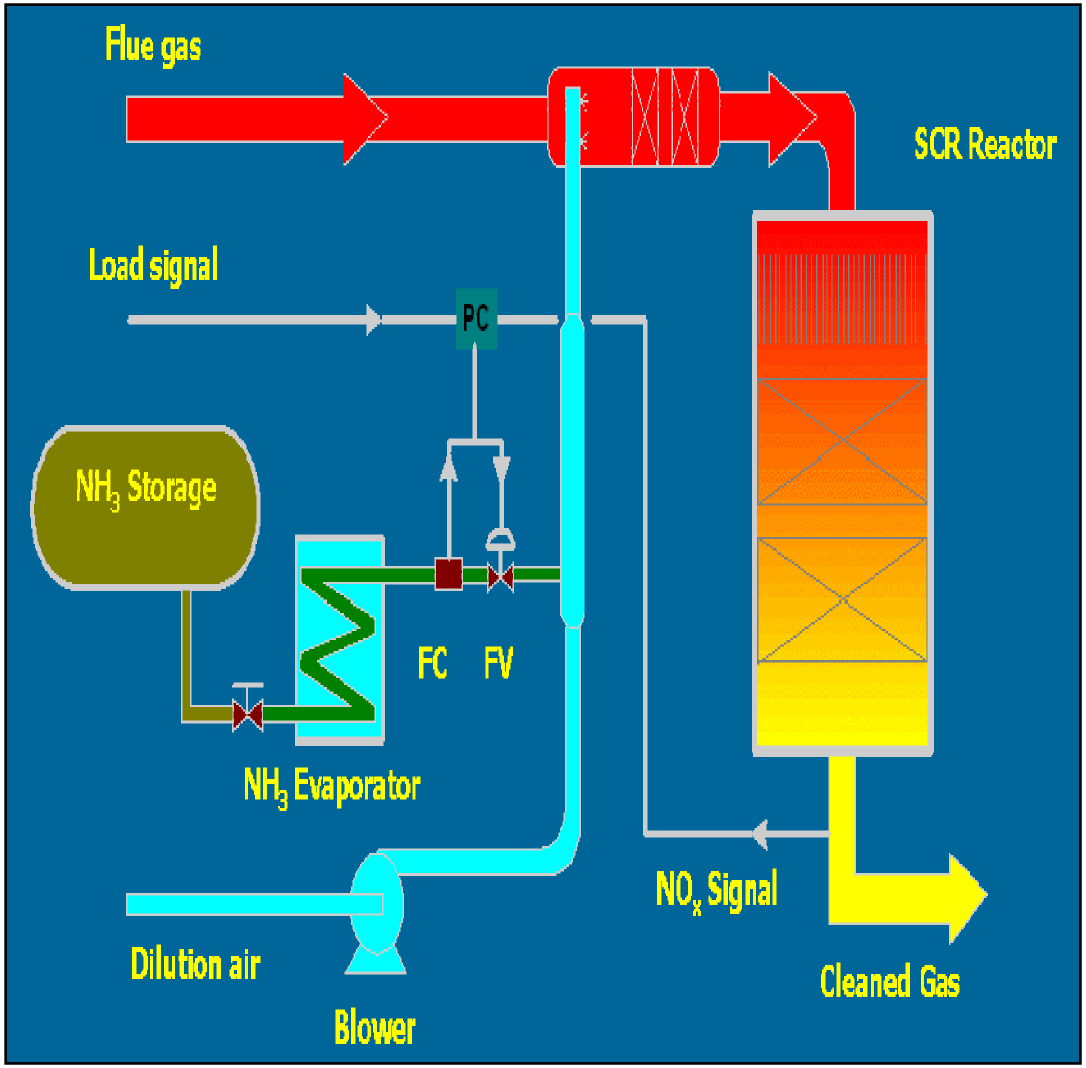
Catalyst Testing

- Reactor specific catalyst management curve
  - To predict future catalyst additions



Inspection / Housekeeping

- When / what should you inspect?
  - At least annually
    - Inlet duct
    - AIG / Mixer
    - Turning vanes
    - Rectifier
    - SCR catalyst
    - Outlet duct
  - Take advantage of short outages
  - Take a quick look before start up in the spring
  - Remove / prevent ash pile build up on catalyst



Catalyst Replacement – Case 1 (New)

- 600 MWe
- 85% operation, 7500 hours
- SCR layout, 2+1
- DeNOx efficiency, 90%
- Ammonia-slip, 2ppmvdc
- SO_2-oxidation, 0.5%

- New catalyst SOR = 1.0
- New catalyst deactivation = 13% per 10,000 hours
- New catalyst cost based on actual 2005 cost

Catalyst Replacement – Case 1 (New)

Catalyst Layers	New	Hours	New Catalyst Cost	Sealing Cost	Freight Cost	Removal Cost	Installation Cost
Spare	X	32,000	$1,407,375	incl.	$60,000	$0	$250,000
First	X	73,500	$1,407,375	incl.	$60,000	$250,000	$250,000
Second	X	102,500	$1,407,375	incl.	$60,000	$250,000	$250,000
Spare	X	136,000	$1,407,375	incl.	$60,000	$250,000	$250,000
First	X	169,500	$1,407,375	incl.	$60,000	$250,000	$250,000
Second	X	202,000	$1,407,375	incl.	$60,000	$250,000	$250,000
Sub - Total			$8,444,250	$0	$360,000	$1,250,000	$1,500,000

Total Cost over 27 years: $11,554,250

Catalyst Replacement – Case 2 (New / Clean)

- 600 MWe
- 85% operation, 7500 hours
- SCR layout, 2+1
- DeNOx efficiency, 90%
- Ammonia-slip, 2ppmvdc
- SO_2-oxidation, 0.5%

- New catalyst SOR = 1.0
- New catalyst deactivation = 13% per 10,000 hours
- New catalyst cost based on actual 2005 cost

- Clean catalyst SOR = 0.95
- Clean catalyst deactivation = 15 per 10,000 hours
- Damaged catalyst replacement = 10%
- Clean catalyst cost based on actual 2005 cost

Catalyst Replacement – Case 2 (New / Clean)

Catalyst Layers		Hours	Cleaning Catalyst Cost	New Catalyst Cost	Sealing Cost	Freight Cost	Removal Cost	Installation Cost
Spare	N	32,000	$0	$1,407,375	incl.	incl.	$0	$250,000
First	C	73,500	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Second	C	125,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Spare	C	151,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
First	C	174,500	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Second	C	196,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Sub - Total			$6,836,875	$2,111,065	$250,000	$500,000	$1,250,000	$1,500,000

Total Cost over 27 years	$12,447,940	Savings over New Catalyst, year =	($34,373)
w/o damaged catalyst	$11,744,250	Savings over New Catalyst, year =	($7,308)

Catalyst Replacement – Case 3 (Clean)

- 600 MWe
- 85% operation, 7500 hours
- SCR layout, 2+1
- DeNOx efficiency, 90%
- Ammonia-slip, 2ppmvdc
- SO_2-oxidation, 0.5%

- Clean catalyst SOR = 0.95
- Clean catalyst deactivation = 15% per 10,000 hours
- Damaged catalyst replacement = 10%
- Clean catalyst cost based on actual 2005 cost quotation

Catalyst Replacement – Case 3 (Clean)

Catalyst Layers	Cleaned	Hours	Cleaning Catalyst Cost	New Catalyst Cost	Sealing Cost	Freight Cost	Removal Cost	Installation Cost
Spare	X	32,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
First	X	70,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Second	X	95,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Spare	X	123,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
First	X	149,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Second	X	176,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Spare	X	194,000	$1,367,375	$140,738	$50,000	$100,000	$250,000	$250,000
Sub - Total			$8,204,250	$844,428	$300,000	$600,000	$1,500,000	$1,500,000

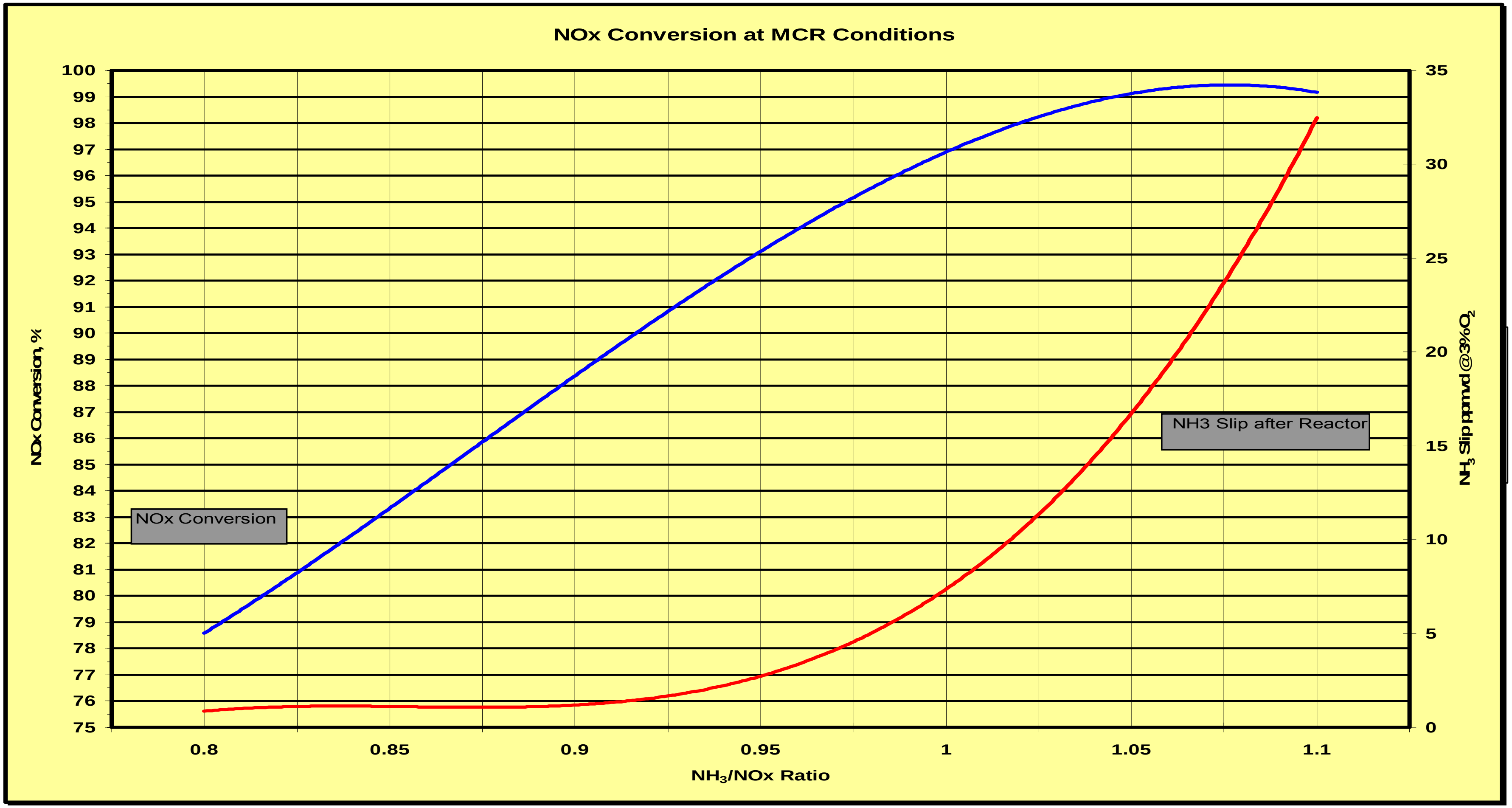
Total Cost over 27 years	$12,948,678	Savings over New Catalyst, year =	($53,632)
w/o damaged catalyst	$12,104,250	Savings over New Catalyst, year =	($21,154)

On Line Catalyst Monitoring

Measurements	Units	Daily	Daily	Daily	Daily	Daily
Unit load	MWe					
Flue gas flow	SCFM					
Oxygen in flue gas	% wet					
Flue gas temperature	^{o}F					
NOx inlet	ppm wet					
NOx outlet	ppm wet					
Ammonia consumption	lb/hr					
Ammonia valve position	%					
Dilution air flow	SCFM					
Ammonia slip	ppm wet					
Ammonia in fly ash	ppm wet					
Pressure drop reactor	Inch WG					
Pressure drop 1st layer	Inch WG					
Pressure drop 2nd layer	Inch WG					
Pressure drop 3rd layer	Inch WG					
Pressure drop APH	Inch WG					
Catalyst life	Hours					

On Line Catalyst Monitoring

- NOx conversion graph
  - Data can allow estimate of conversion and slip



On Line Catalyst Monitoring

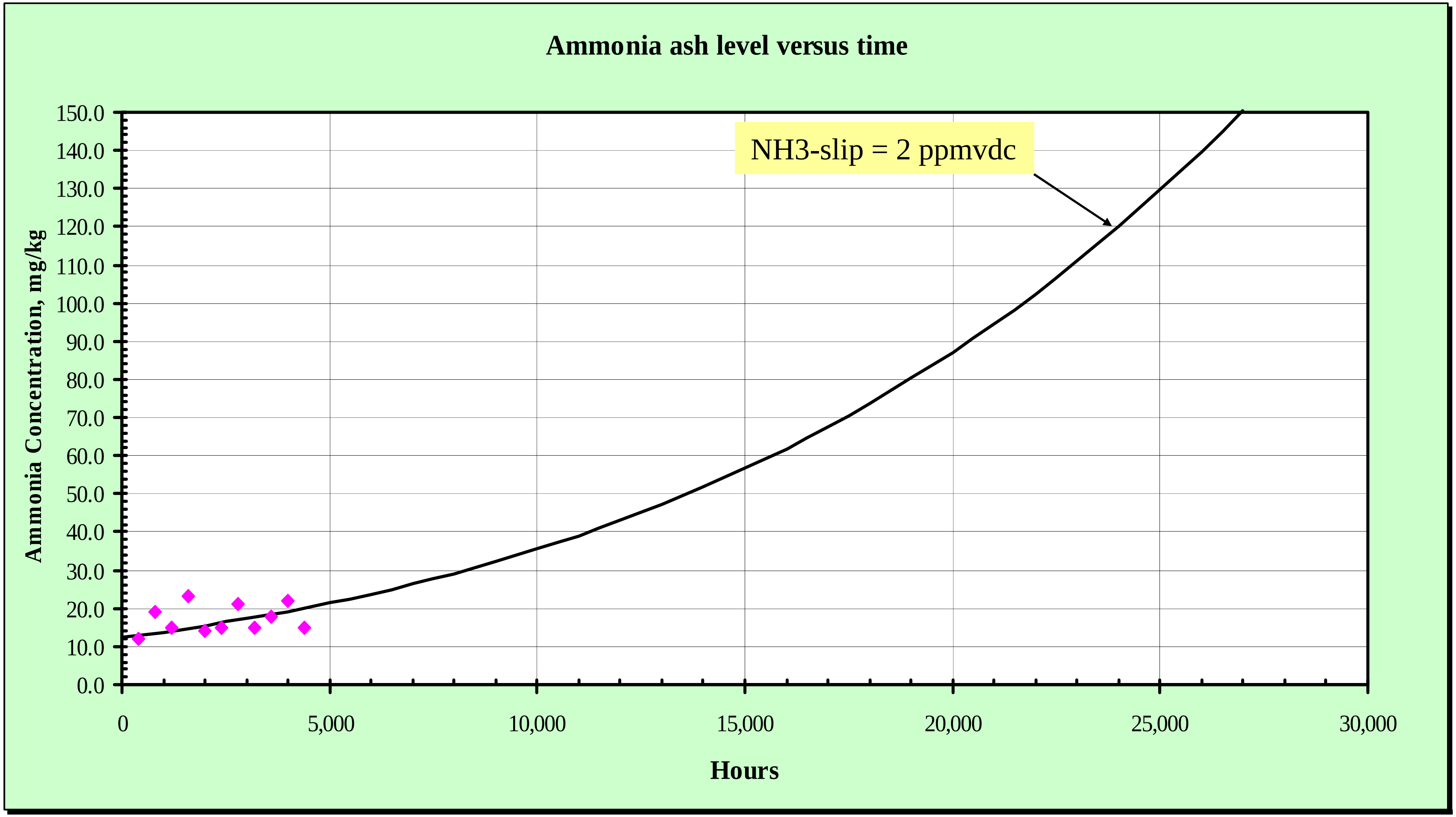
- Ammonia slip / Ammonia on fly ash
  - How does ammonia get on the ash?
    - Acidic ashes attract ammonia
    - SO_3 attracts ammonia
  - Without acid sites, ammonia will remain as gas
  - Other factors that play a role
    - LOI (especially in PRB coal, very highly ammoniated ash)
    - Structure, mineralogy of ash
    - Local concentrations of NH_3
  - Rule of Thumb: 2 ppm slip yields 100 ppm on ash
  - ***Ammonia levels in ash are known to be quite variable***

On Line Catalyst Monitoring

- Ammonia slip / Ammonia fly ash sampling
  - Where should I measure?
    - Different ammonia levels in fly ash hoppers
    - Pick the hopper with the highest level
  - How often should I measure?
    - For best results sample hopper once a day
    - Combined samples for once a week ammonia analysis
    - Graph results

On Line Catalyst Monitoring

- Performance test generated curve



Summary

- Catalyst may be impacted with a fuel switch
  - Ash loading
  - ABS
  - Catalyst poisons
  - SO_2-oxidation
- Catalyst sampling / analysis
  - At least annually – activity, chemical analysis, and pore volume
- Inspection
  - At least once per year
  - Quick look in the spring
  - Take opportunities

Summary

- Housekeeping
  - Keep catalyst clean / free of pluggage
- Catalyst replacement / cleaning
- Catalyst On Line Monitoring
  - Monitor catalyst / system performance
  - Monitor NH_3-slip
    - Analyzer
    - Fly ash sampling – daily samples combined for weekly analysis

Summary

- Catalyst may be impacted with a fuel switch
  - Ash loading
  - ABS
  - Catalyst poisons
  - SO_2-oxidation
- On line monitoring
  - Monitor catalyst / system performance
  - Ammonia ash sample - daily sample / combined samples for weekly analysis
- Off line monitoring
  - Catalyst sampling / analysis @ least annually – activity, chemical analysis, and pore volume
  - Inspection
    - Complete inspection annually
    - Quick look in the spring
    - Take opportunities
- Housekeeping
  - Keep catalyst clean / free of pluggage

Summary

- Keep care of your investment to prevent this ……………………