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Catalyst Considerations for Dual Fuel Operation

WPCA/Duke Co-Firing Seminar 2019

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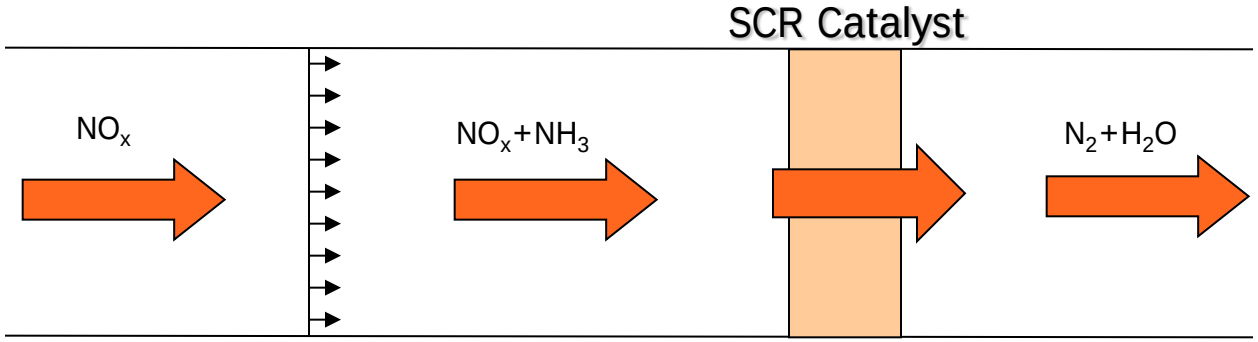
Agenda

- Basics
  - SCR Chemistry Primer
  - Performance Requirements (K/AV – Potential)
  - Coal SCR Management Plan
- Case examples
  - Cofiring
    - Special cases
  - Unit operating on full spectrum of 100% coal to 100% gas
  - Converting to 100% gas
- Other considerations
- Using the gas SCR advantages (Management Plans)

SCR Reaction Chemistry

Desired Reactions (goal: maximize activity):

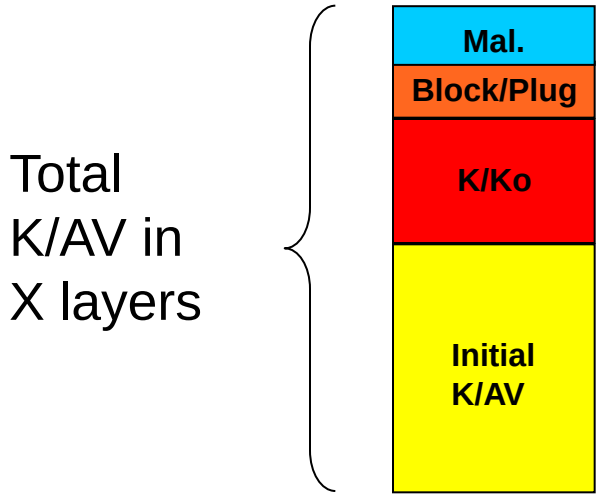
$4NO + 4NH_3 + O_2$	→ $4N_2 + 6H_2O$	(NO_x Reduction)
$NO + NO_2 + 2NH_3$	→ $2N_2 + 3H_2O$	(NO_x Reduction)
$6NO_2 + 8NH_3$	→ $7N_2 + 12H_2O$	(NO_x Reduction)
$Hg + 2HCl + ½O_2$	→ $HgCl_2 + H_2O$	(Hg Oxidation)



Undesired Reactions (goal: minimize activity):

$SO_2 + ½ O_2$	→ SO_3	(SO_2 Oxidation)
$4NH_3 + 5O_2$	→ $4NO + 6H_2O$	(Ammonia Oxidation)
$NH_3 + SO_3 + H_2O$	→ NH_4SO_4	(Ammonia Bisulfate)
$HgCl_2 + NH_3 + ¼ O_2$	→ $Hg + 2 HCl + ½ N_2 + ½ H_2O$	($HgCl_2$ Reduction by NH_3)
$HgCl_2 + SO_2 + H_2O$	→ $Hg + 2 HCl + SO_3$	($HgCl_2$ Reduction by SO_2)

Performance Requirements: A Quick Review

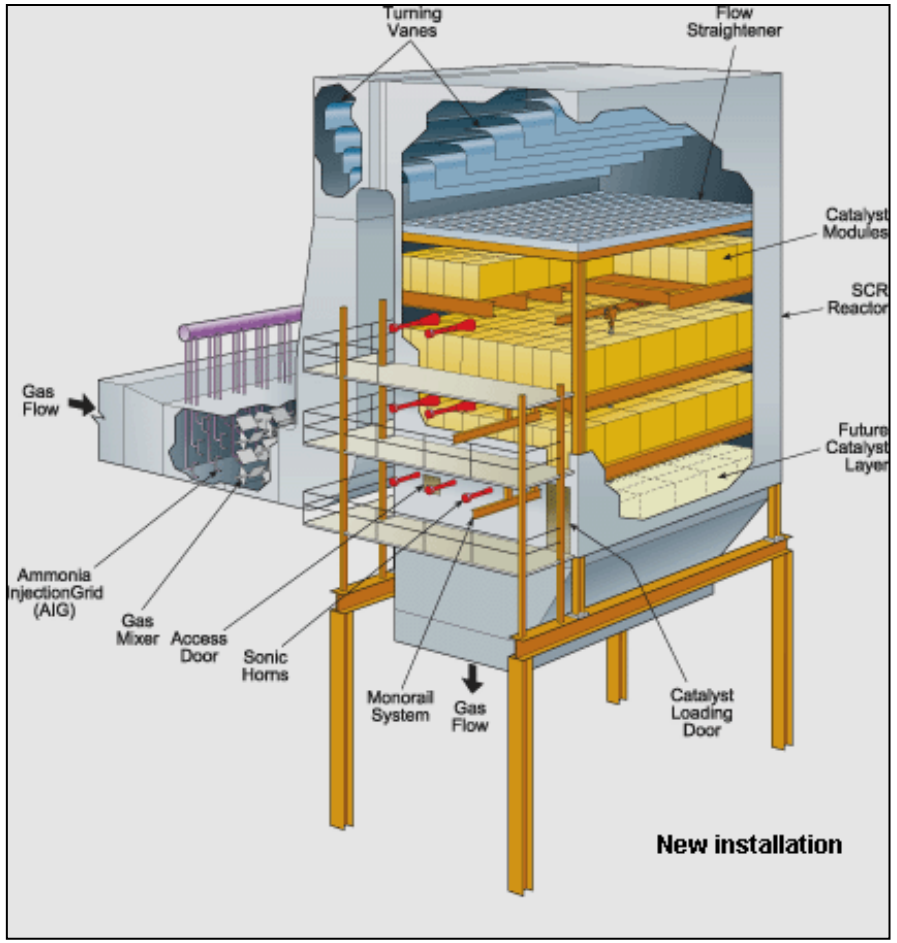


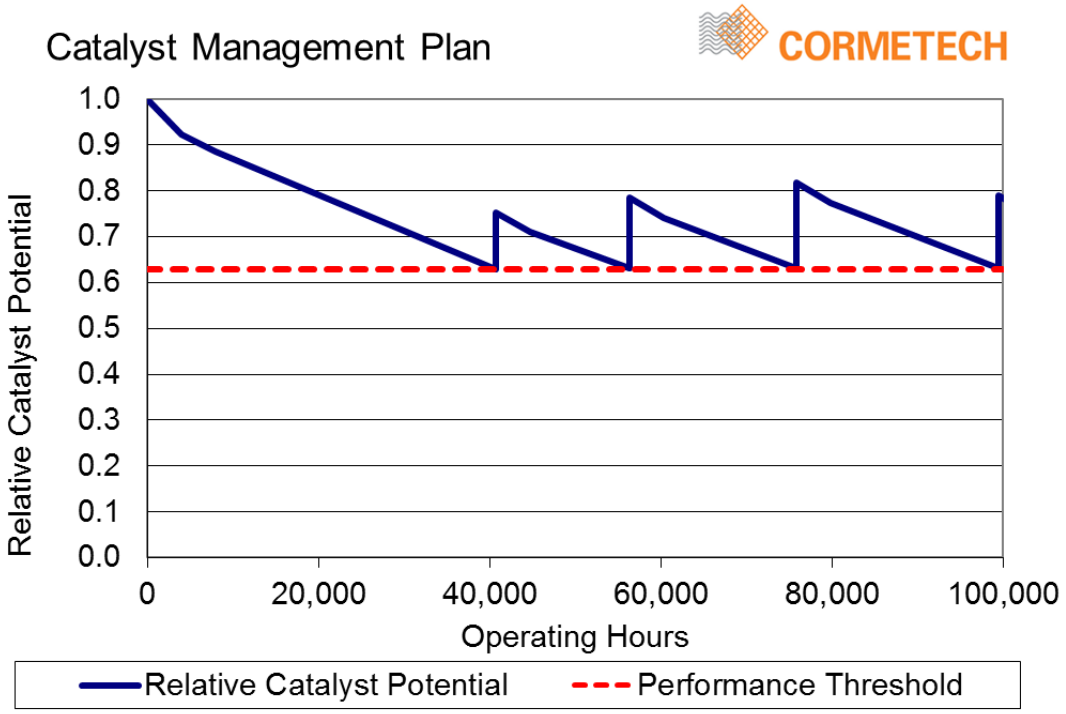
VGB/EPRI:

Potential = K/AV = - ln (1 – DeNOx) @ NH_3/NOx Ratio = 1

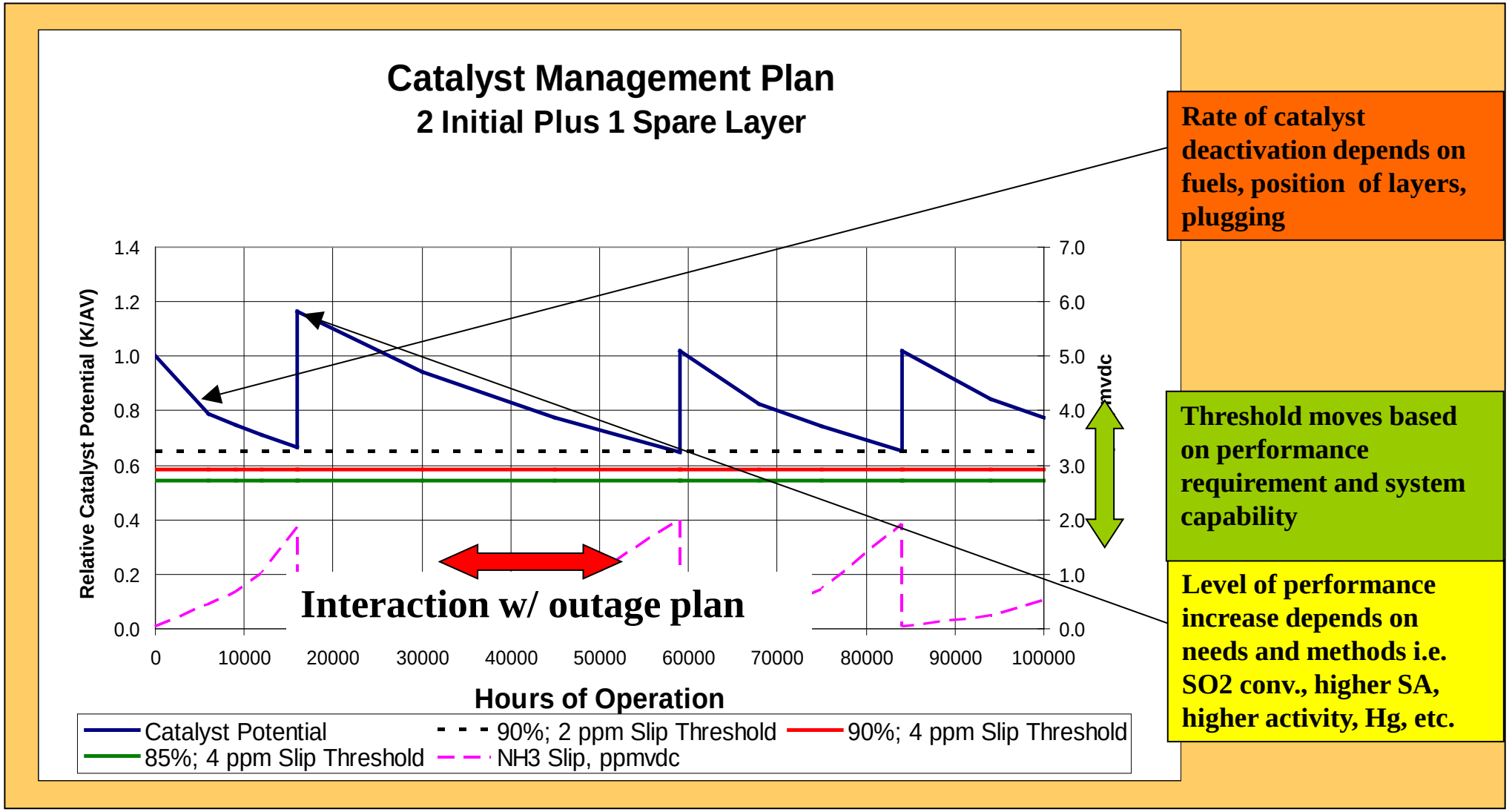
	Coal	Gas	Co-Fire
Inlet NOx	300 ppm	100 ppm	250 ppm
Outlet NOx	30 ppm	30 ppm	30 ppm
Relative K/AV	Current Basis	~35% lower	~15% lower

SCR and Management Curve





Catalyst Management Planning



Rate of catalyst deactivation depends on fuels, position of layers, plugging

Threshold moves based on performance requirement and system capability

Level of performance increase depends on needs and methods i.e. SO2 conv., higher SA, higher activity, Hg, etc.

Case 1: Co-fire - Assumptions

- Will still need to operate on 100% coal
- Natural gas will carry up to 50% load
- Coals fuel mix unchanged
- SCR performance requirements unchanged

  Stack NOx, Hg Oxidation, SO_2 Oxidation, NH_3 slip

Case 1: Co-fire
Check new SCR operating conditions

Leads to increased performance requirement

Higher flow

Lower Operating Temperature

Higher water content

Counteracts performance requirement increases

Lower Flow

Lower DeNOx requirement

Higher Oxygen

Higher Tolerance for NH_3 slip

Case 1: Co-fire
Check Minimum Load - ABS

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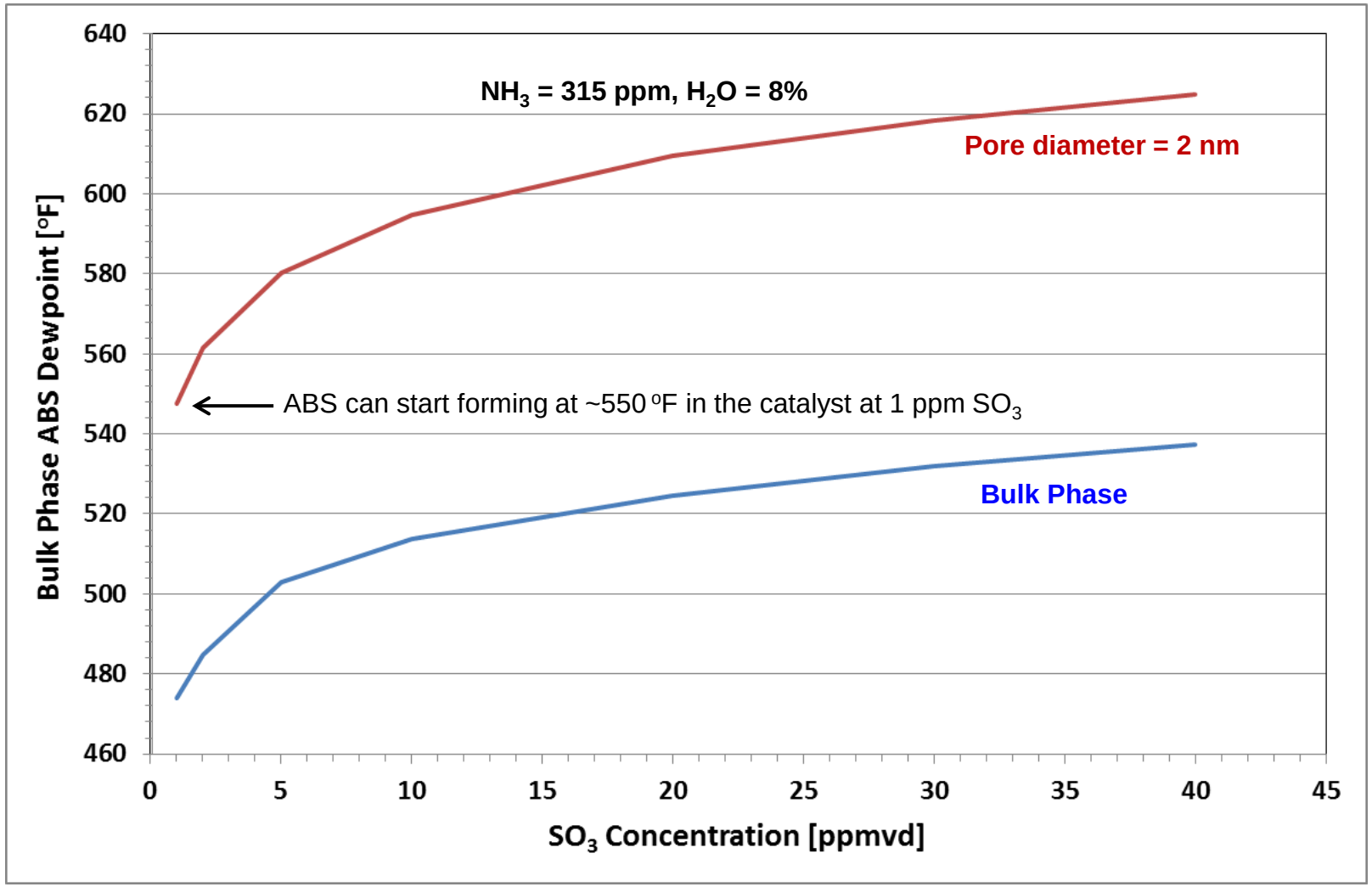
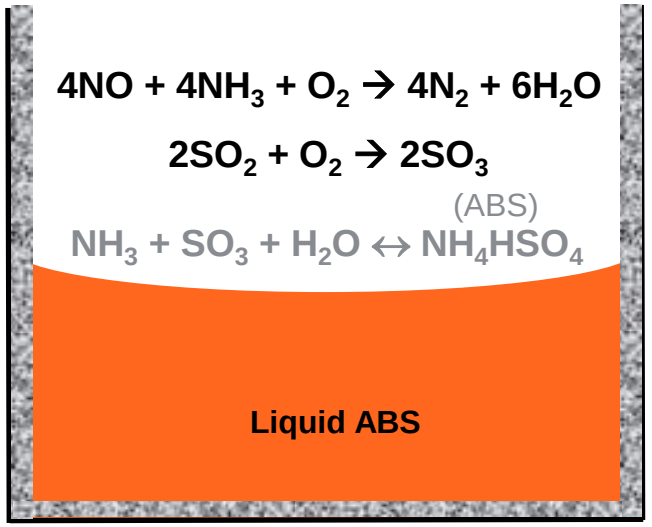


T < Dew Point

Catalyst Pore



Case 1: Co-fire
‘Stays the same’

Operating & Maintenance

- Inspections (AIG, turning vanes, catalyst plugging)
- Ash handling (sonic horns, soot-blowers, ash sweepers)
- AIG tuning
- Catalyst testing

Case 1: Co-fire 'Gets Better'

Lower SO_3 →

- Corrosion issues
- Less APH fouling

Lower emissions →

- SCR can stay in service to lower load
- Lower SCR inlet NOx translates to ability to achieve lower stack NOx
- Generally, Hg capture is same or better (Verification)

Cleaner Fuel/Lower Catalyst Deactivation Rate →

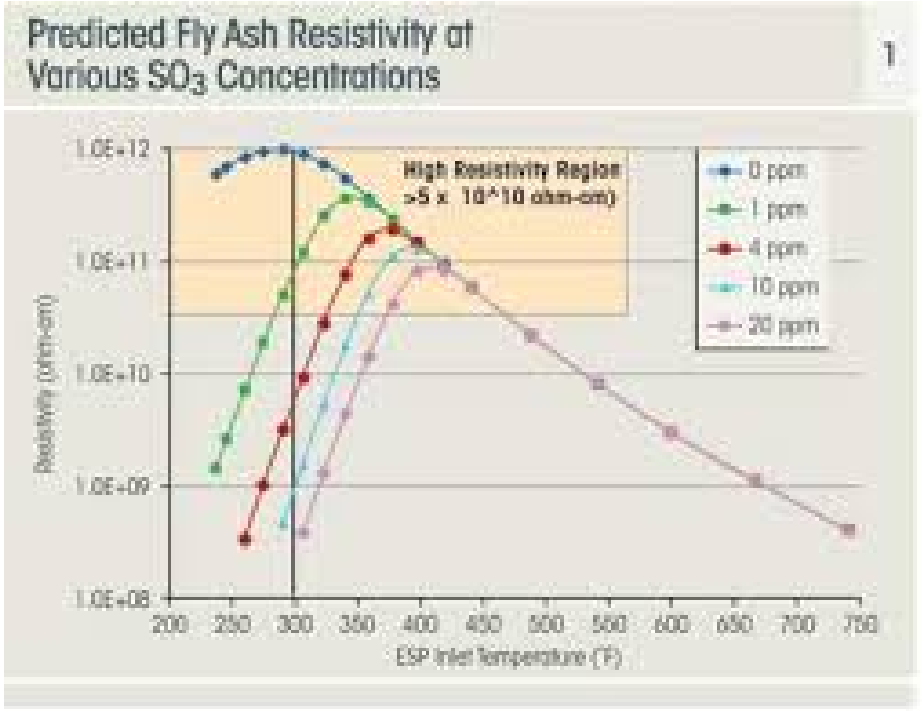
- Longer life cycle between layer changeouts

Case 1: Co-fire
‘Gets Better’ – Maybe?

Chemical Savings →

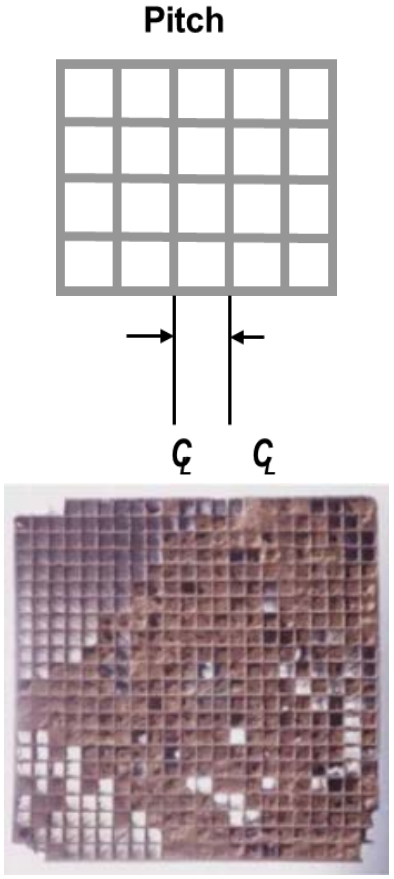
- Lower Boiler NOx means less ammonia
- Additive to mitigate Arsenic
- Additive to promote Hg Oxidation
- Additive to mitigate SO_3

✓ Check needs for ESP and SO_2 scrubber



Case 1: Co-fire
‘Gets Better’ – Maybe?

Lower ash loading → Less plugging?



- Wherever the box has piles of ash (duct floor, top of turning vanes, module/wall seals) are likely to still pile ash). This piling is often caused by low local velocities or eddies.
- Transition from low to full load will still ‘inundate’ the same areas of the SCR Box

→ Plugging may get better, but there may not by any improvement

Case 1A: Co-fire

No 100% Coal Operation

- ~~Will still need to operate on 100% coal~~
- Natural gas will carry up to 50% load
- Coals fuel mix unchanged
- SCR performance requirements unchanged

  Stack NOx, Hg Oxidation, SO_2 Oxidation, NH_3 slip

Case 1A: Co-fire
Check new SCR operating conditions

No 100% Coal Operation

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Leads to increased performance requirement

Higher flow

Lower Operating Temperature *

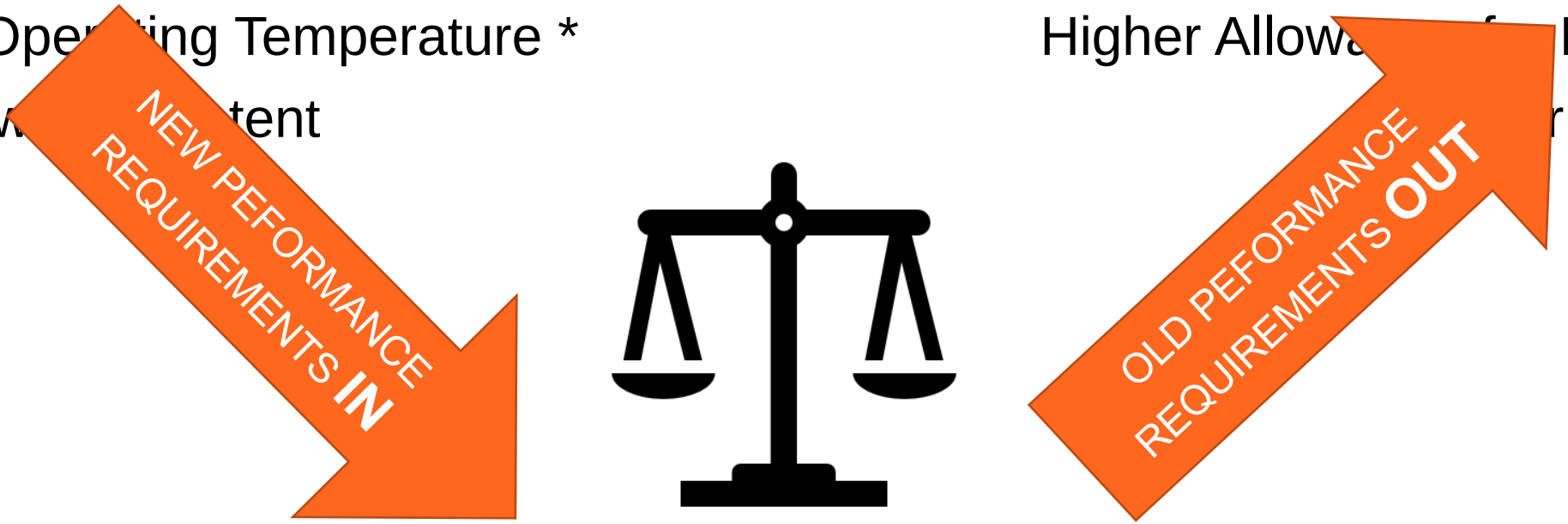
Higher water content

Counteracts performance requirement increases

Lower DeNOx requirement

Higher Allowable NH_3 slip

Lower oxygen



Case 1A: Co-fire

No 100% Coal Operation

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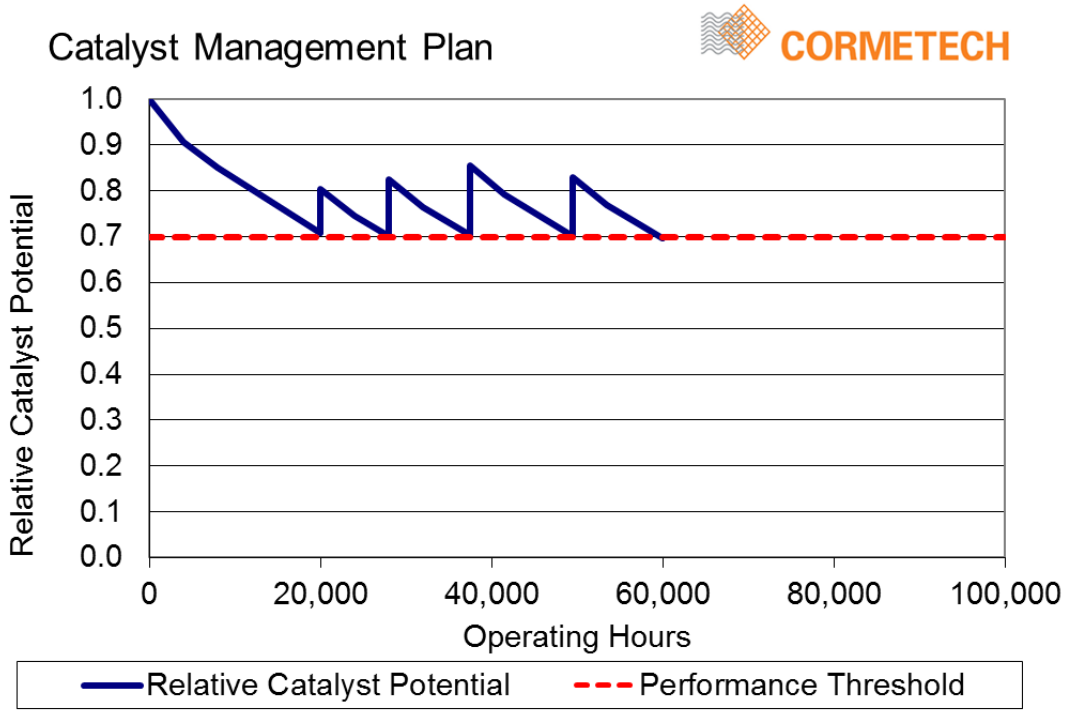
There is opportunity to move the unit's performance threshold lower on a permanent basis.

If the performance requirement is lower, take advantage of it.



Case 1B: Co-fire

Firing on gas only for extended periods

- Will still need to operate on 100% coal
- Natural gas will carry up to 50% load
- Coals fuel mix unchanged
- SCR performance requirements unchanged

  Stack NOx, Hg Oxidation, SO_2 Oxidation, NH_3 slip
- Operation on gas may extend indefinitely

Case 1B: Co-fire

Firing on gas only for extended periods

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‘Isn’t Sulfur always bad?’

Sulfate promotes activity

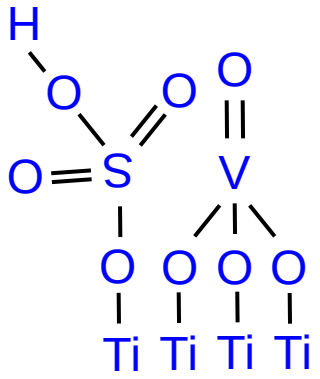
→With time and temperature on 100% gas, sulfate is lost in catalyst

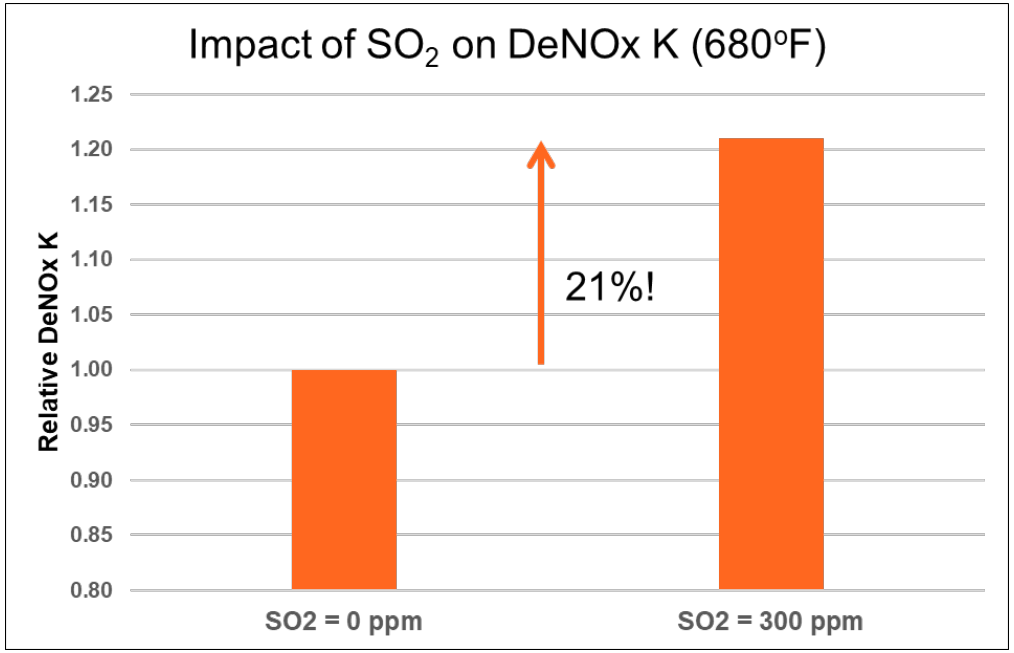
→With loss of sulfate comes loss of activity, K

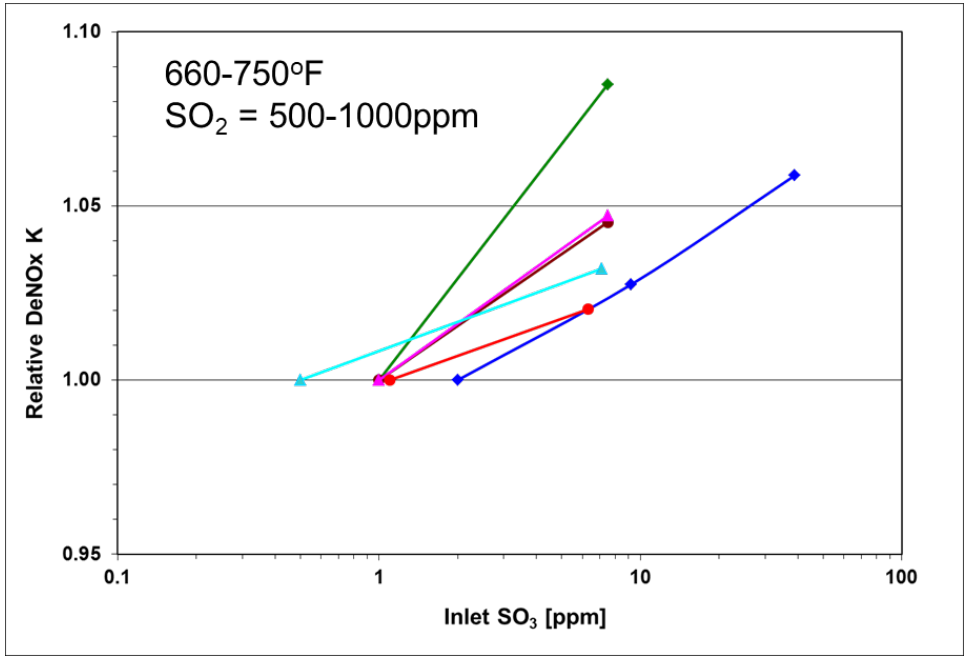
→With loss of K, then understanding ‘new’ and temporary K/AV or potential requirement is needed!

Adsorbed Sulfate Promotes Activity

- Adsorbed sulfate: good for DeNOx activity.
  - Formed by SO_3 adsorption on catalyst.
  - Sulfate enhances surface acidity → promotes NH_3 adsorption.







SO_3 Impact on DeNOx Activity: Sulfated vs. De-Sulfated Catalyst States

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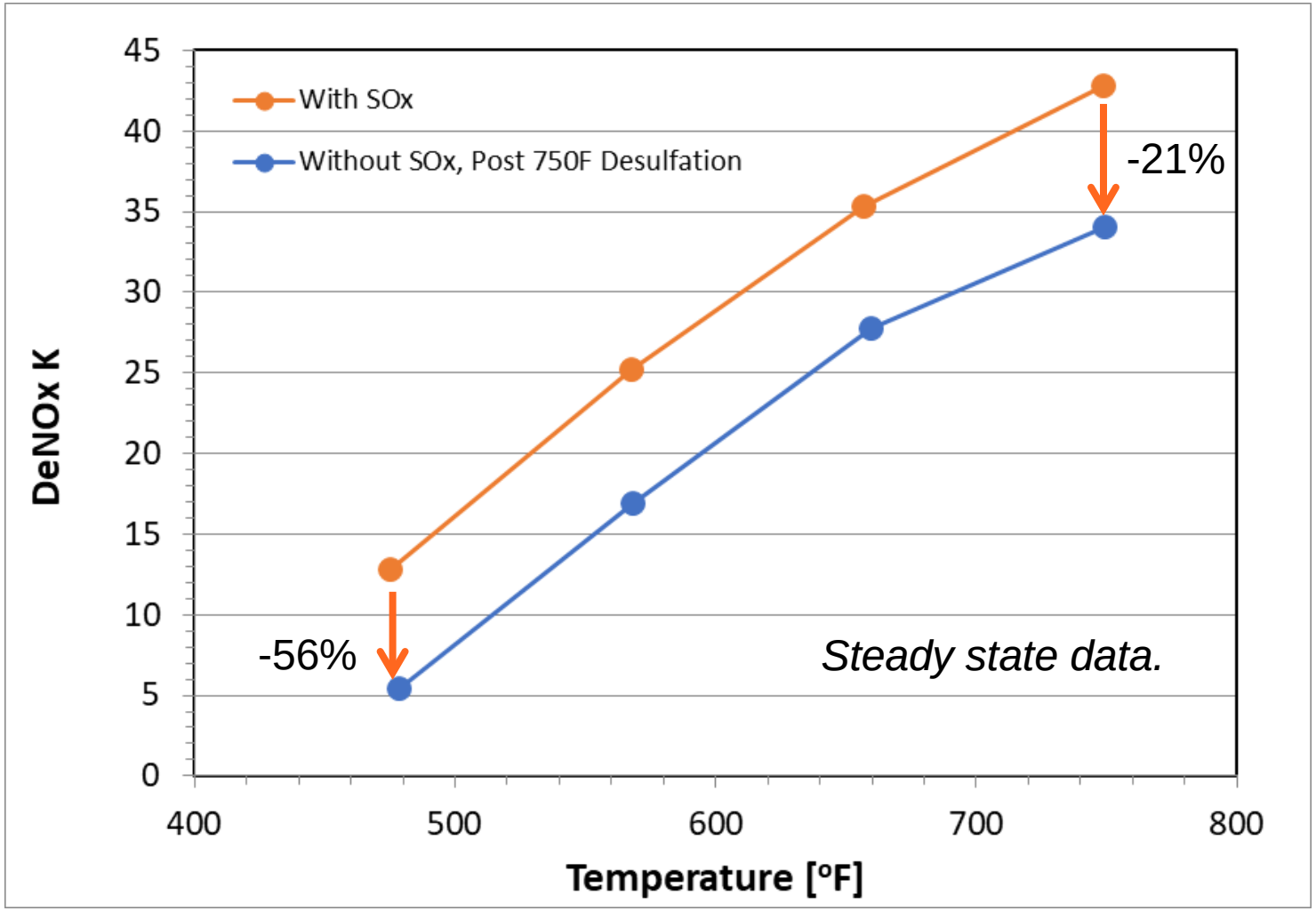
Data set for two “states”:

- After 750ºF aging “with SOx” to fully sulfate.
- After 750ºF soak “without SOx” to fully desulfate.

Sulfate has a big impact!



SO_3 Impact on DeNOx Activity: Impact of Re-Sulfation

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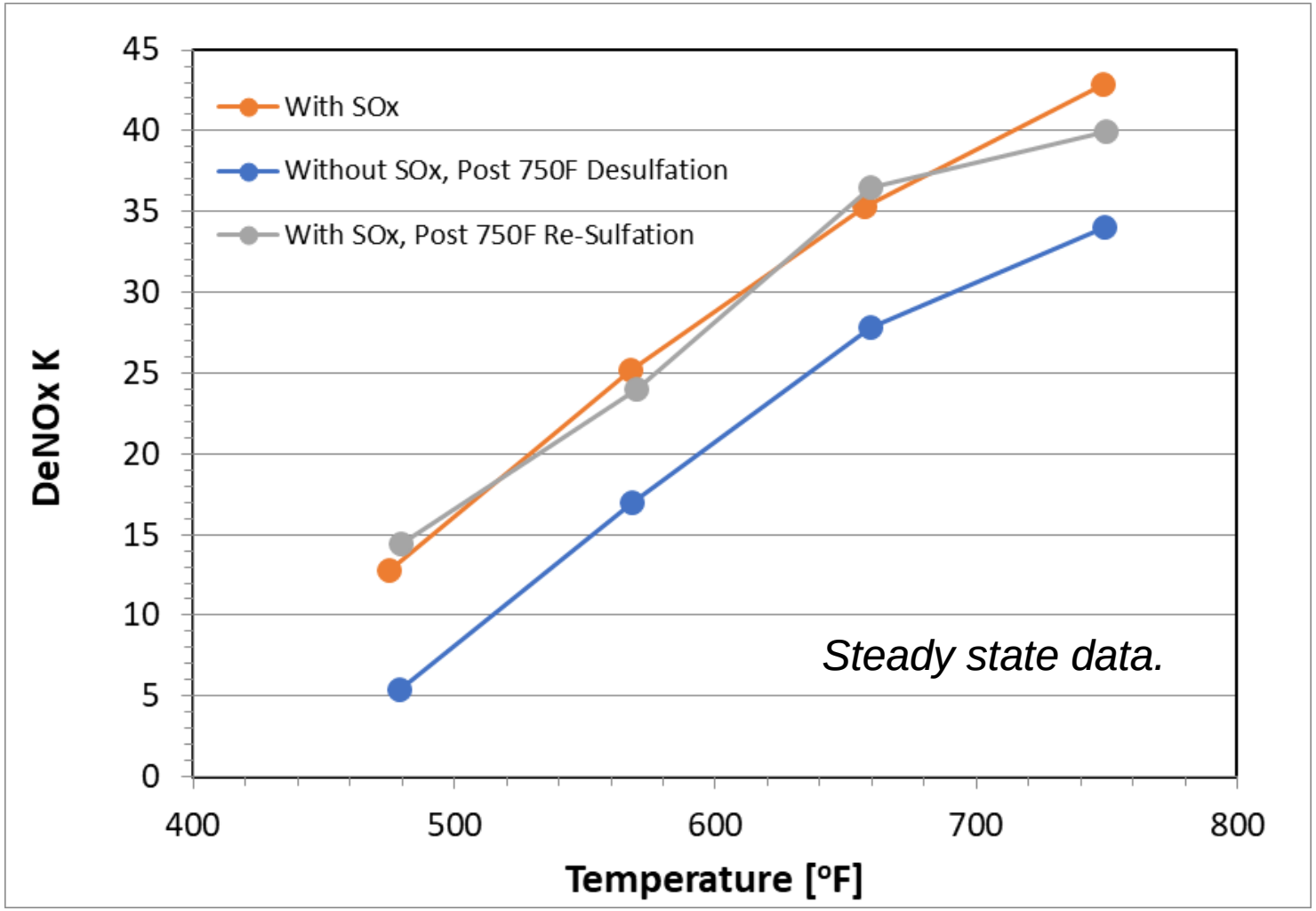
Aging catalyst again at 750ºF “with SOx” restores the DeNOx activity.



Simulation: Sulfate Desorption Transient
Fully Sulfated State → No SOx Flow

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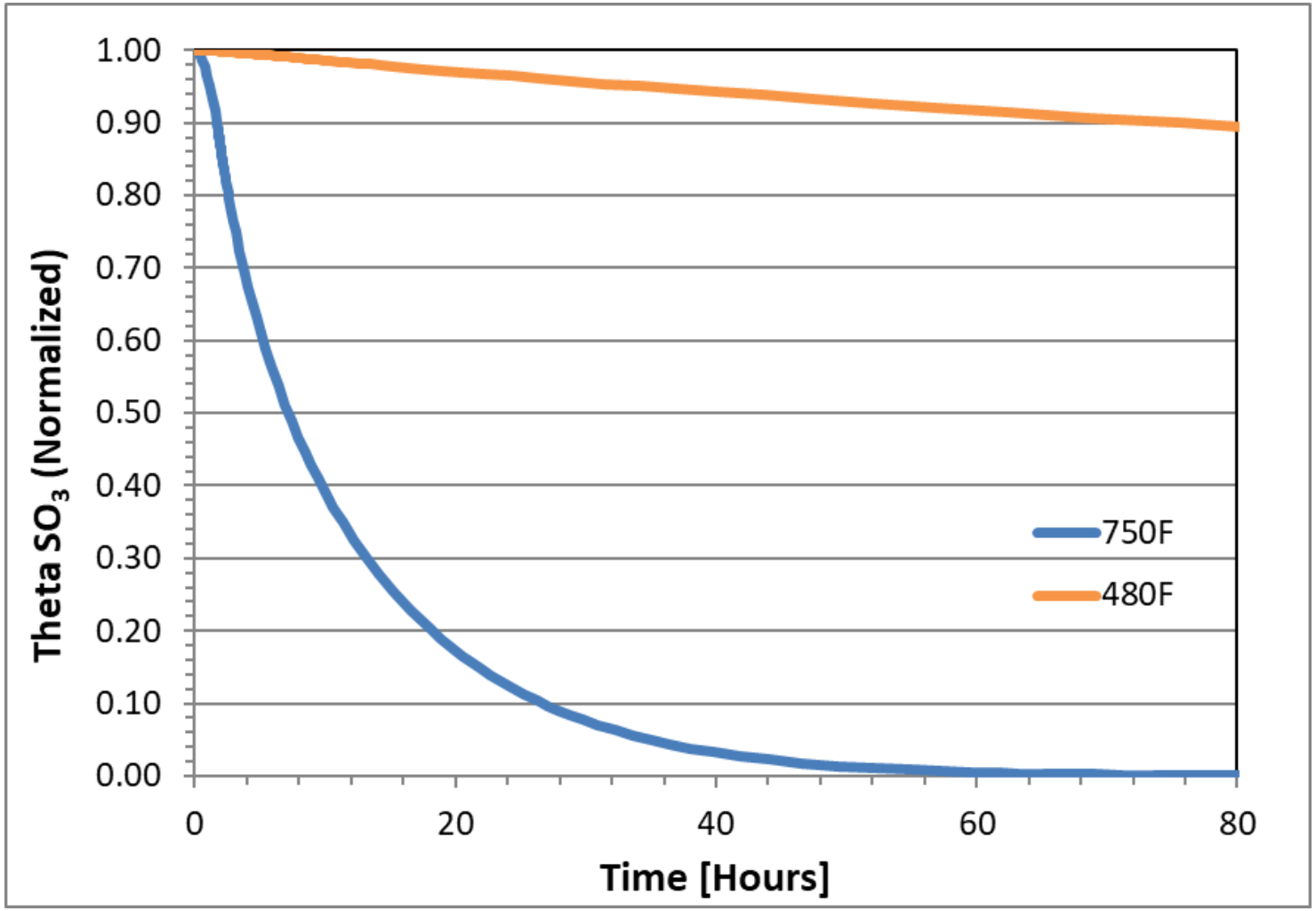
At 750ºF:

Sulfate desorption is fast.

At 480ºF:

Sulfate desorption is slow.



Case 1B: Co-fire

Firing on gas only for extended periods

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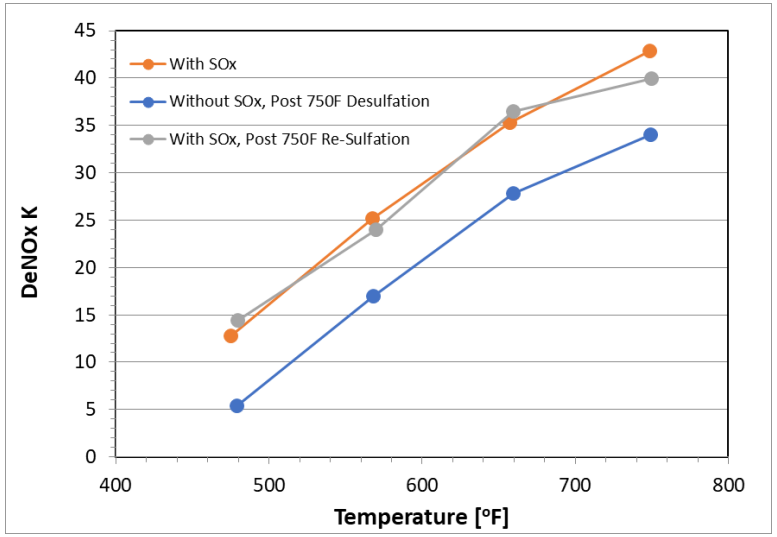
Firing on gas only *at low load* should not be defining case (Lower flow, lower deNOx)

Check steps added:

→Some thought into transition from 50% load gas to full load coal or co-firing

→Consider transition from 100% gas to co-fire requirements on downstream equipment



Case 2:
100% coal to 100% load gas

I want it ALL

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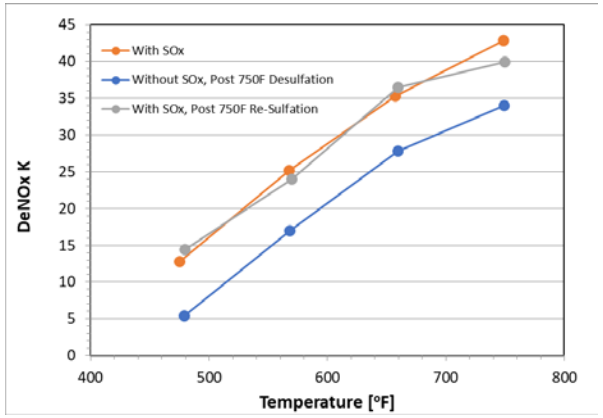
- Will still need to operate on 100% load coal
- Natural gas will carry up to 100% load!
- Coals fuel mix unchanged
- SCR performance requirements unchanged

Stack NOx, Hg Oxidation, SO_2 Oxidation, NH_3 slip



Case 2:
100% coal to 100% load gas

100% Gas
100% Coal

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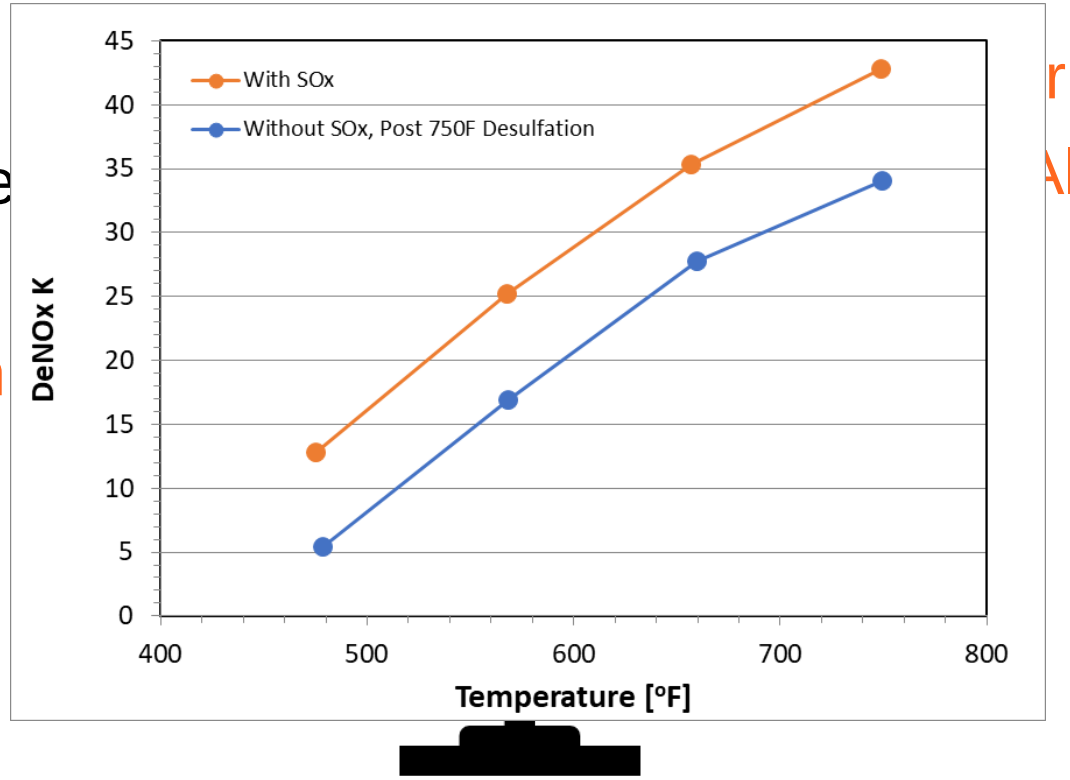
Leads to increased performance requirement

Higher flow

Lower Operating Tempe

Higher water content

Catalyst Desulfurization



Counteracts performance requirement increases

r DeNOx requirement

llowance for NH_3 slip

Lower Flow

Higher oxygen

Case 2:
100% coal to 100% load gas

100% Gas
100% Coal

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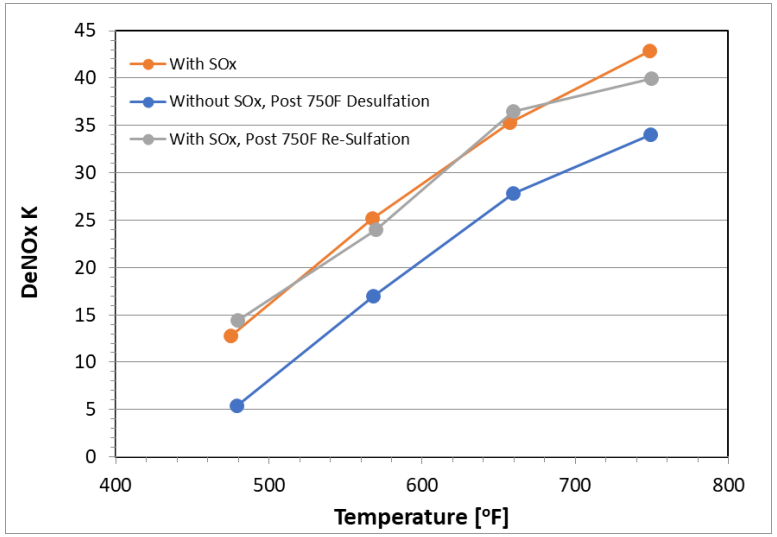
Same check steps added:

→Need strategy for transition from full load gas to full load coal or co-firing

→Are there is transition requirements on downstream equipment to consider



Case 3:
Conversion from Coal Operation to Gas operation

All new SCR performance requirements

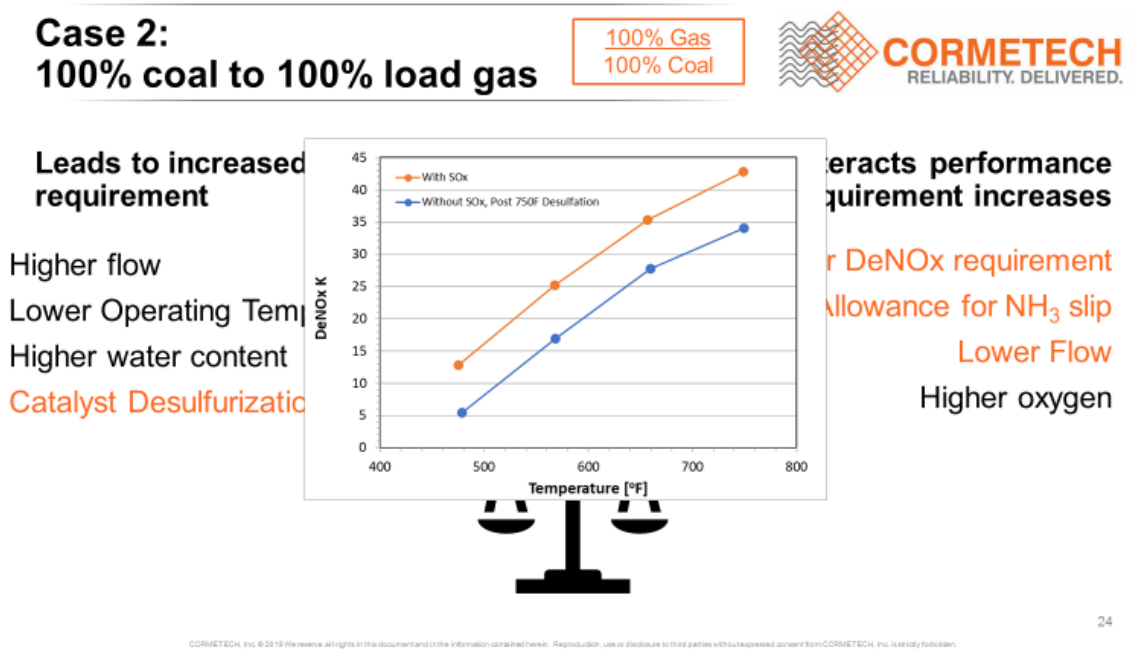
Stack NOx, ~~Hg Oxidation, SO2 Oxidation~~, NH_3 slip

Permitting?

CO/VOC emissions issues?

→ Same Catalyst Bed,

Same performance issues



Other considerations

- NH_3 system valve/controls sizing
- CEMs & Instrumentation
- Impact of AIG performance

Quick Reminders

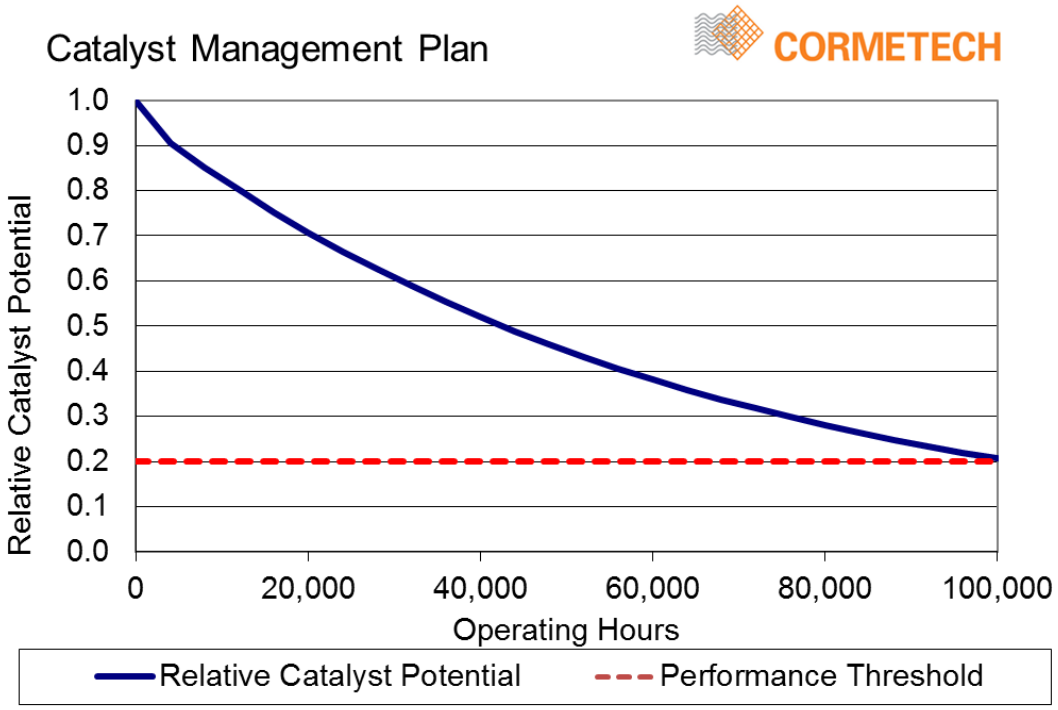
- Impacts of lower SOx on downstream equipment
- Transient issues on downstream equipment with fuel changes

Catalyst Management Planning

‘Bookend’ cases of SCR management

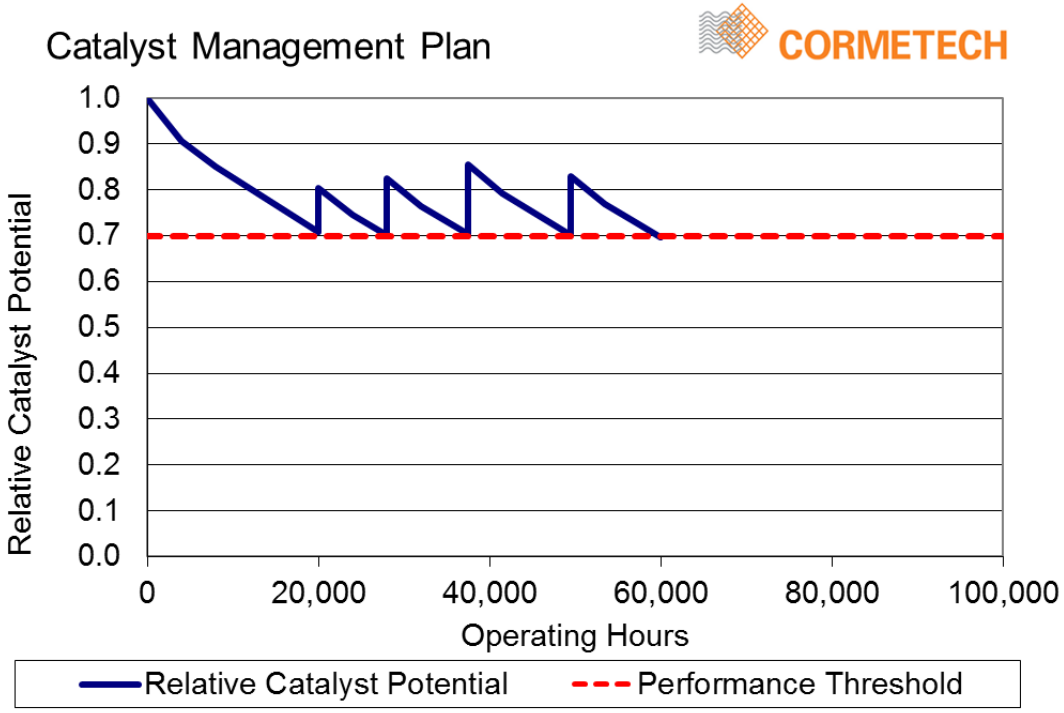
‘Friendly fuels’

High allowance for deactivation



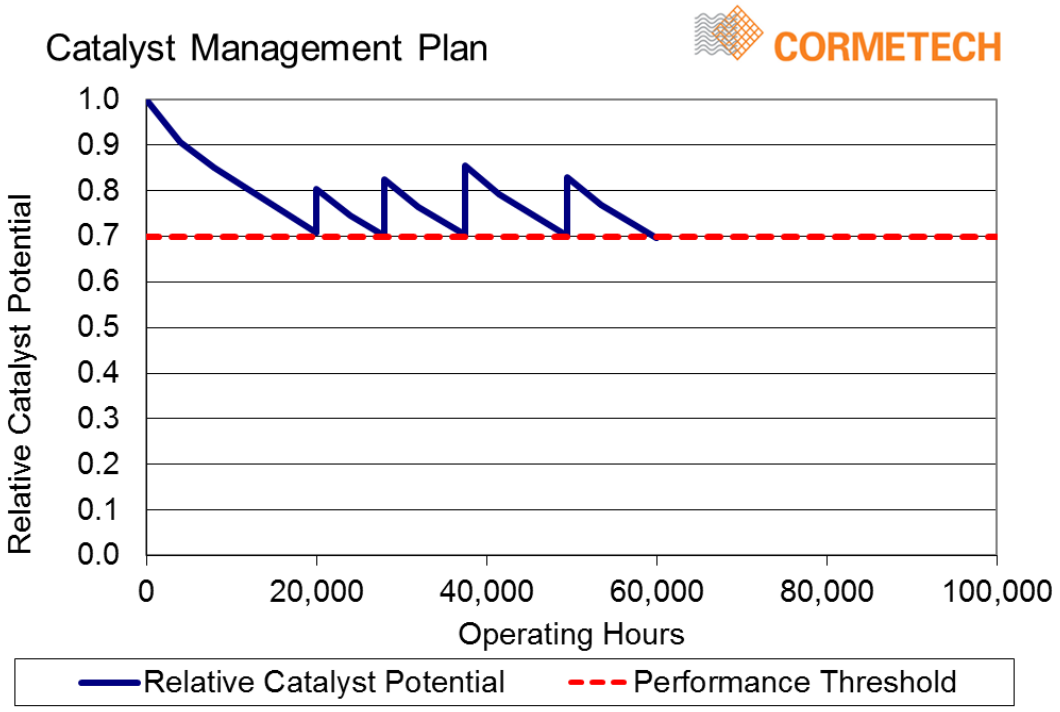
SCR unfriendly fuels

Catalyst changeouts 1 year to 18 months

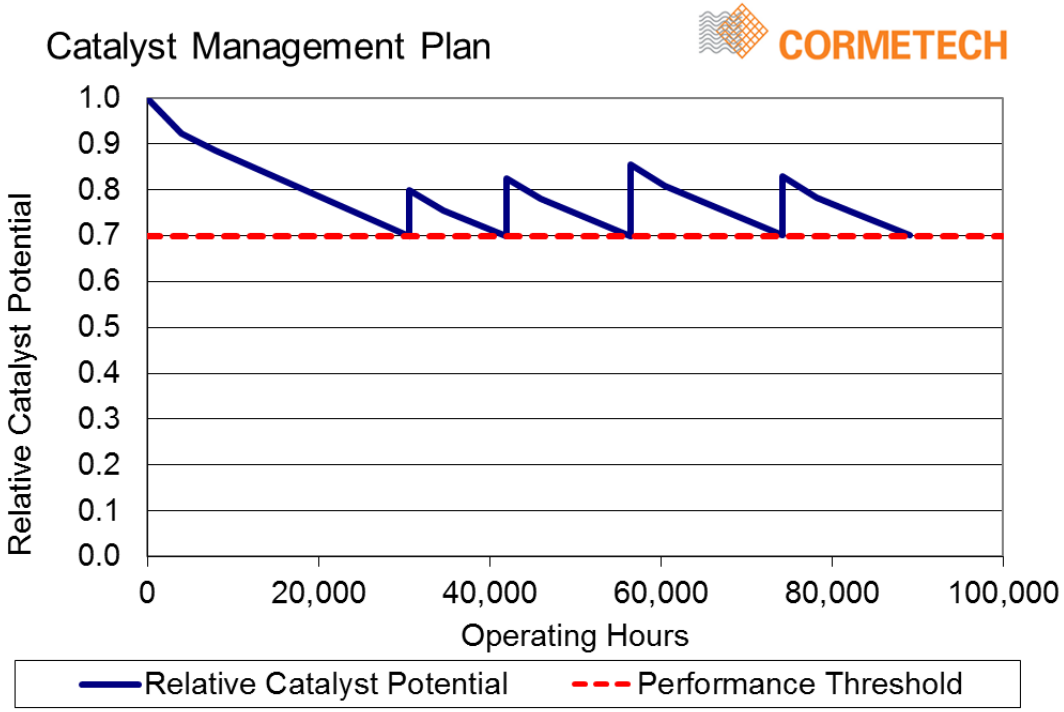


20% reduction in deactivation rate

Current
Action every 9-10k hours



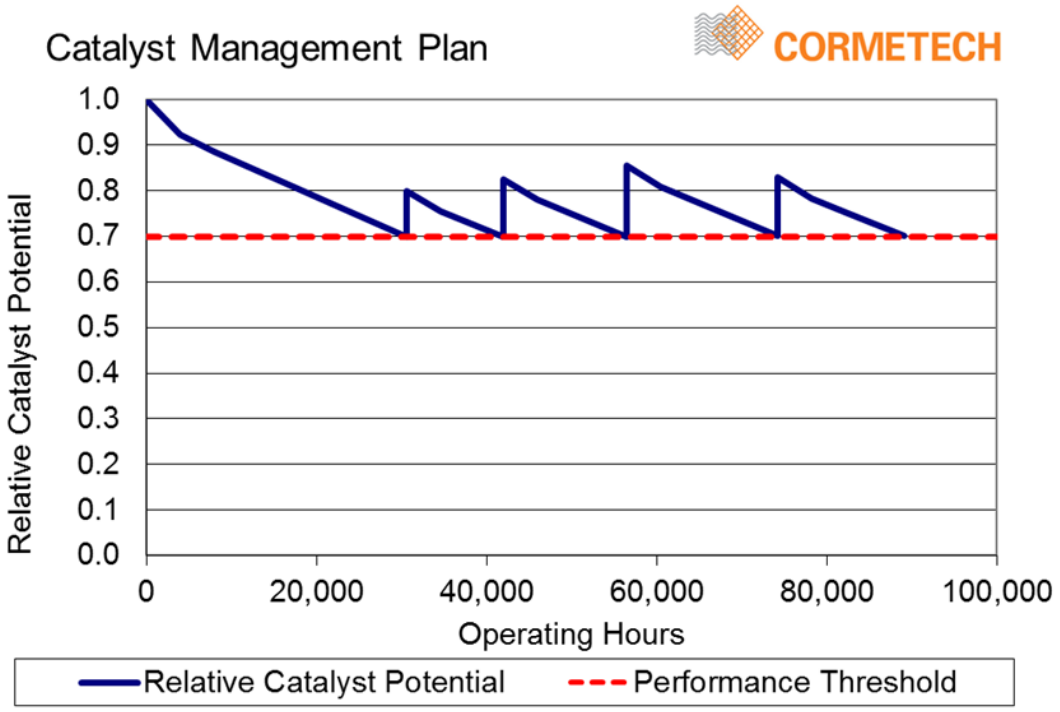
20% reduction in deactivation
Action every 14-15k hours



20% reduction in deactivation rate + Lower K/AV by 10%

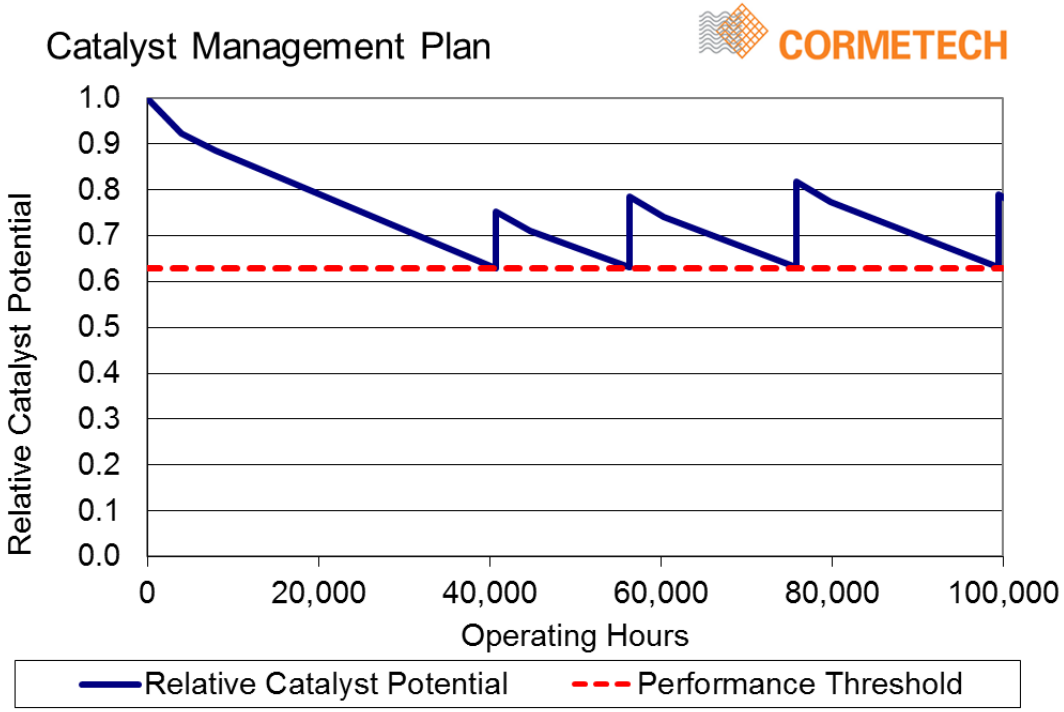
20% reduction in deactivation

Action every 14-15k hours



Add lowering K/AV by 10%

Action every ~20k hours



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