REINHOLD ENVIRONMENTAL Ltd.

2011 NOx-Combustion Round Table & Expo Presentation

February 7-8, 2011, in Birmingham, AL / Hosted by Southern Company

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Reinhold Environmental LTD.

2011 NOx Combustion Roundtable

Low Load Operation and the Affects on SCR Catalyst Performance

Presented by:

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SCR Product Manager

February 8, 2011

Birmingham, AL

Outline

- Reasons for Low Load Operation
- Concerns of Low Load Operation with Regards to Impact on SCR Catalyst Performance
- Advantages of Operating at Lower Loads with SCR's in Service
- Case Studies and Recommendations
- Conclusions

Reasons For Low Load Operation

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- New Environmental Regulations
  - More Stringent Emissions Levels Leading to Continued SCR Operation at Lower Loads
  - Year Round Operation of SCR's Required
- Load Cycling and Load Demand
  - SCR's Operating During Non-Peak Season
  - Weekend and Overnight Operation
  - Decreased Load Demand

Concerns of Low Load Operation

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How Does Low Load Operation Affect the Performance of My SCR Catalyst?

- Concerns
  - Ammonia Salt Formations
- Reactions
  - Ammonium Sulfate (Particulate)
    - $SO_3 + 2NH_3 + H_2O \rightarrow (NH_4)2SO_4$
  - Ammonium Bisulfate (“Sticky”)
    - $SO_3 + NH_3 + H_2O \rightarrow NH_4HSO_4$
- Potential Impacts
  - Reduced Catalyst Activity Area Due to Salt Pluggage
  - Pluggage of Downstream Equipment (i.e. Air Heater)

History of Development for Hitachi SCR Catalyst

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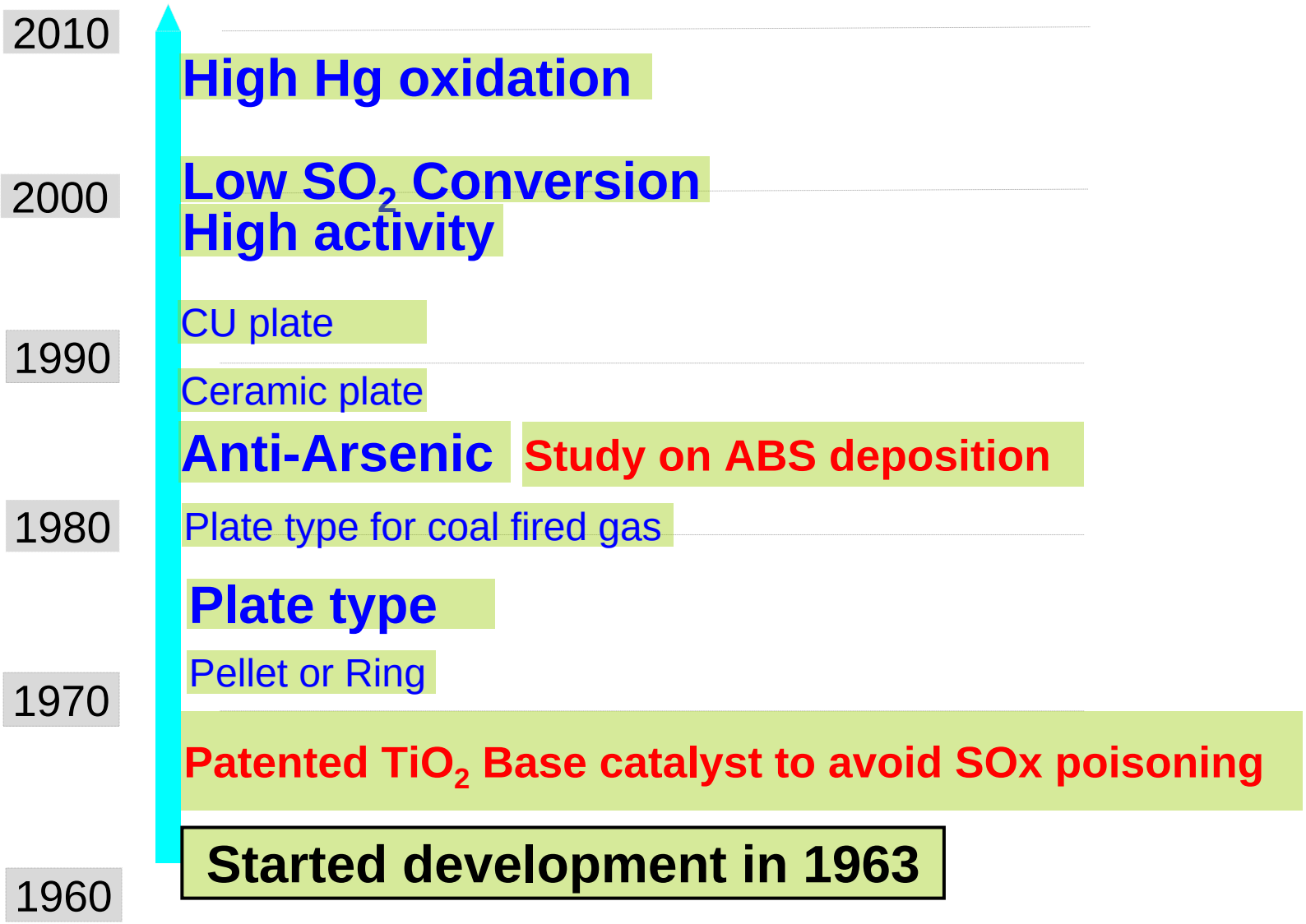
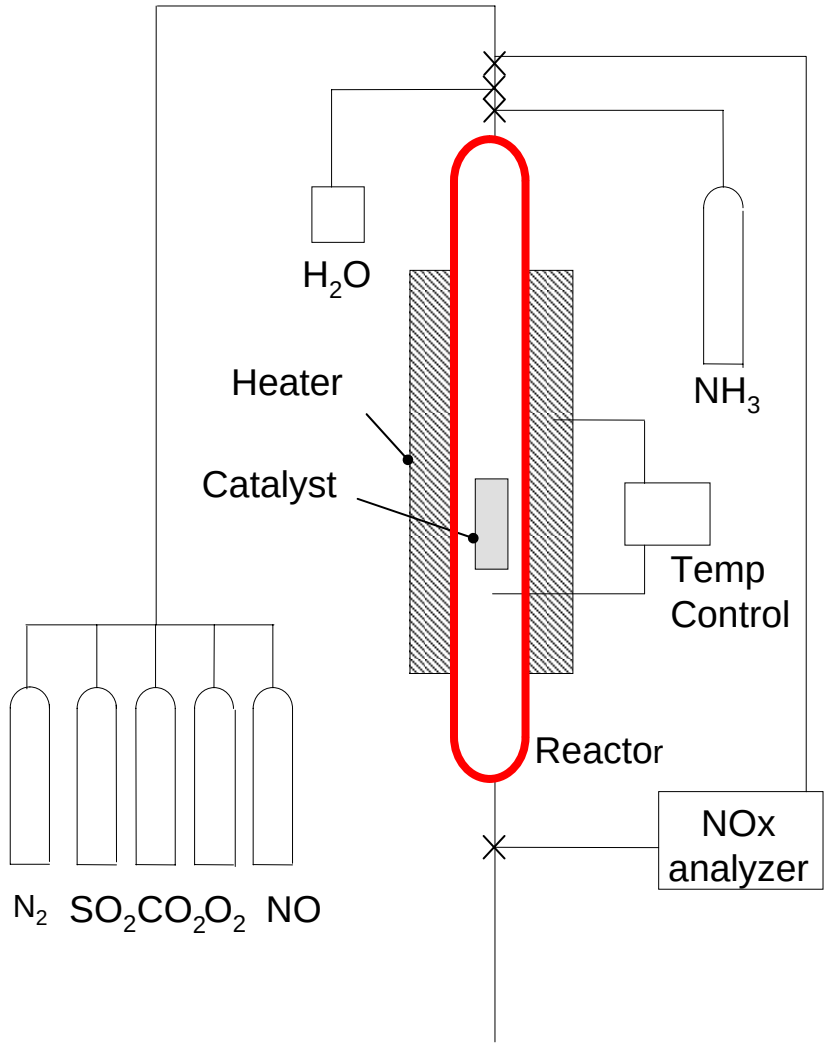
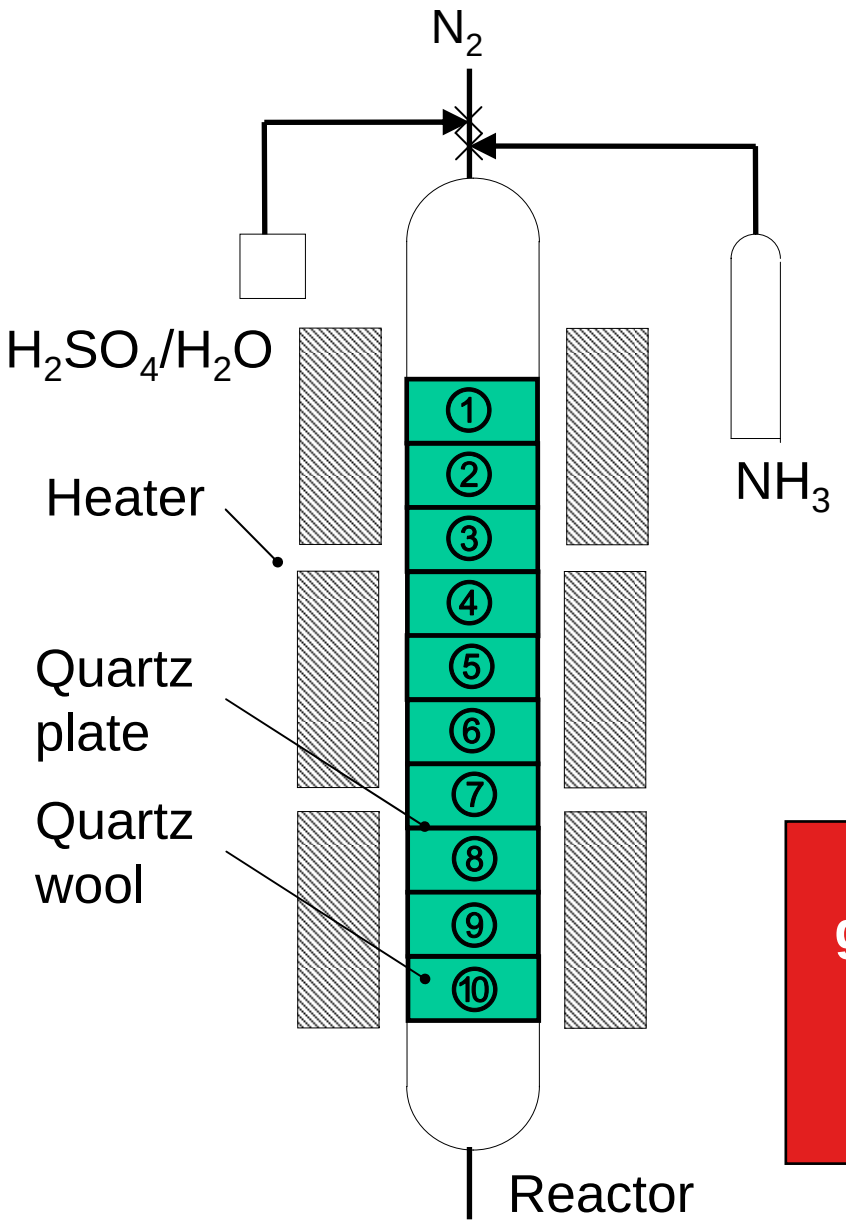


Experimental Apparatus – Laboratory Micro Reactor

Test Scale	Laboratory
Purpose	Evaluation of manufacturing catalyst for QC purpose, screening and checking catalyst deterioration
Type	Micro tube reactor
Condition	BHK Standard
Test Facility	 Outline of Laboratory facility



Experimental Method – ABS Deposition Temperature



Measurement Condition

Item	Condition
Temperature Setting	Reactor Inlet: 550C Inlet ①: 360C Outlet ⑩: 100C
Duration Hours (h)	20
Inlet Gas Condition	5 sets of NH_3/H_2SO_4 Concentration

After 20 hours duration, each part of glass wool and plate wall was removed and analyzed for NH_4^+ and SO_4^{2-} to determine the temperature of ABS deposition

Experimental results – Distribution of Deposited ABS

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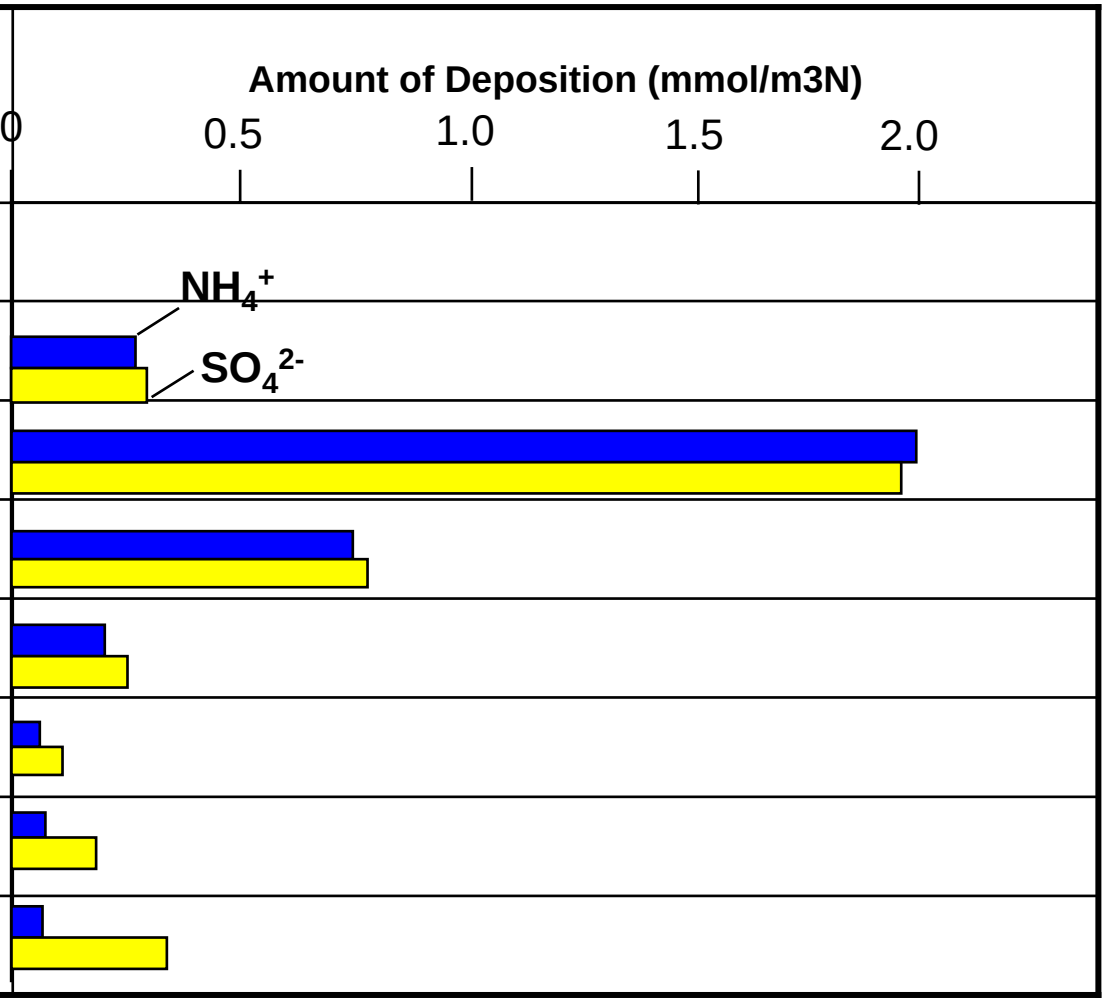
Example of Measurement Result (at SO_3=100ppm and NH_3=83ppm,H_2O=10%)

Region	Temperature (Deg C)	NH_4^+/SO_4^{2-} (Mole Ratio)
1	356-323	-
2	323-291	0.91
3	291-265	1.00
4	265-241	0.95
5	241-222	0.77
6	222-203	0.26
7	203-183	0.14
8	183-158	0.11



Based on 5 sets of examinations, Hitachi found the following equation for ABS deposition
($NH_3 + H_2SO_4 = NH_4HSO_4$) $P_{NH3} \cdot P_{H2SO4}$ = 1.41x 10-12 Exp(-53000/RT) (Gas Phase Deposition)

Concerns of Low Load Operation

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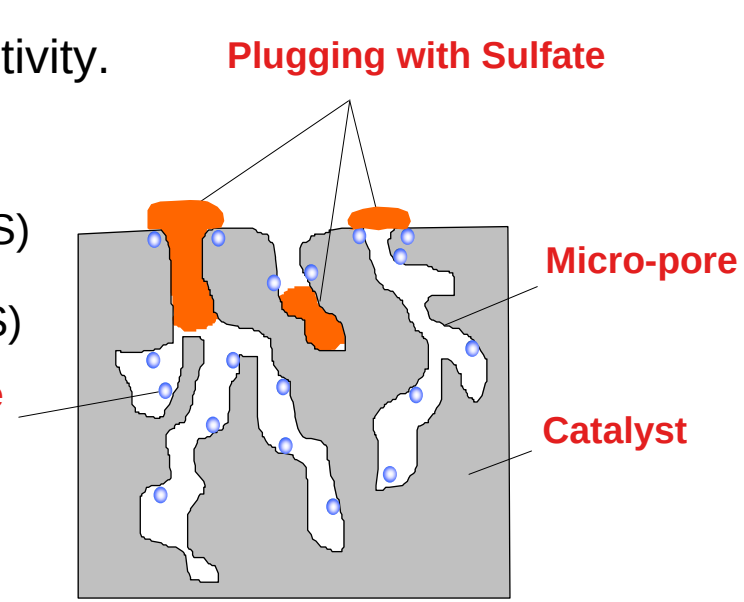
Concept of Ammonium Bisulfate Formation:

- Deposition of NH_4HSO_4 (Ammonium bisulfate or ABS) on the surface of the catalyst occurs when SO_3 in flue gas and NH_3 injected into flue gas though AIG reacts at lower than critical temperatures.
- The critical temperature depends on the concentrations of each.
- Deposition of ABS causes plugging of the micro-pores in the catalyst through the process of Capillary Condensation and covers the catalyst surface where the active sites are located as shown in sketch below.
- This phenomenon causes decreased catalyst activity.

Reactions:

$NH_3 + SO_3 + H_2O = NH4HSO_4$ (Ammonium bisulfate or ABS)

$2NH_3 + SO_3 + H_2O = (NH4)2SO_4$ (Ammonium sulfate or AS)



Therefore it is important to understand the SCR Catalyst's Minimum Continuous Operating Temperature (MOT) and Minimum Injection Temperature (MIT)

Definitions:

- Minimum Continuous Operating Temperature (MOT):
  - This is the temperature at which the SCR can be operated in which no ABS will accumulate on the catalyst.
  - Continuous operation of the SCR must be above MOT considering the lower side of temperature deviation across the catalyst/reactor.
- Minimum Ammonia Injection Temperature (MIT)
  - This is the temperature in which ammonia can begin to be injected into the SCR. Some activity deterioration may occur due to the formation of ABS, but this can be reversed by operation at or above the MOT.

MIT Determination

Precipitation Temperature of Ammonium Bisulfate at Gas Phase

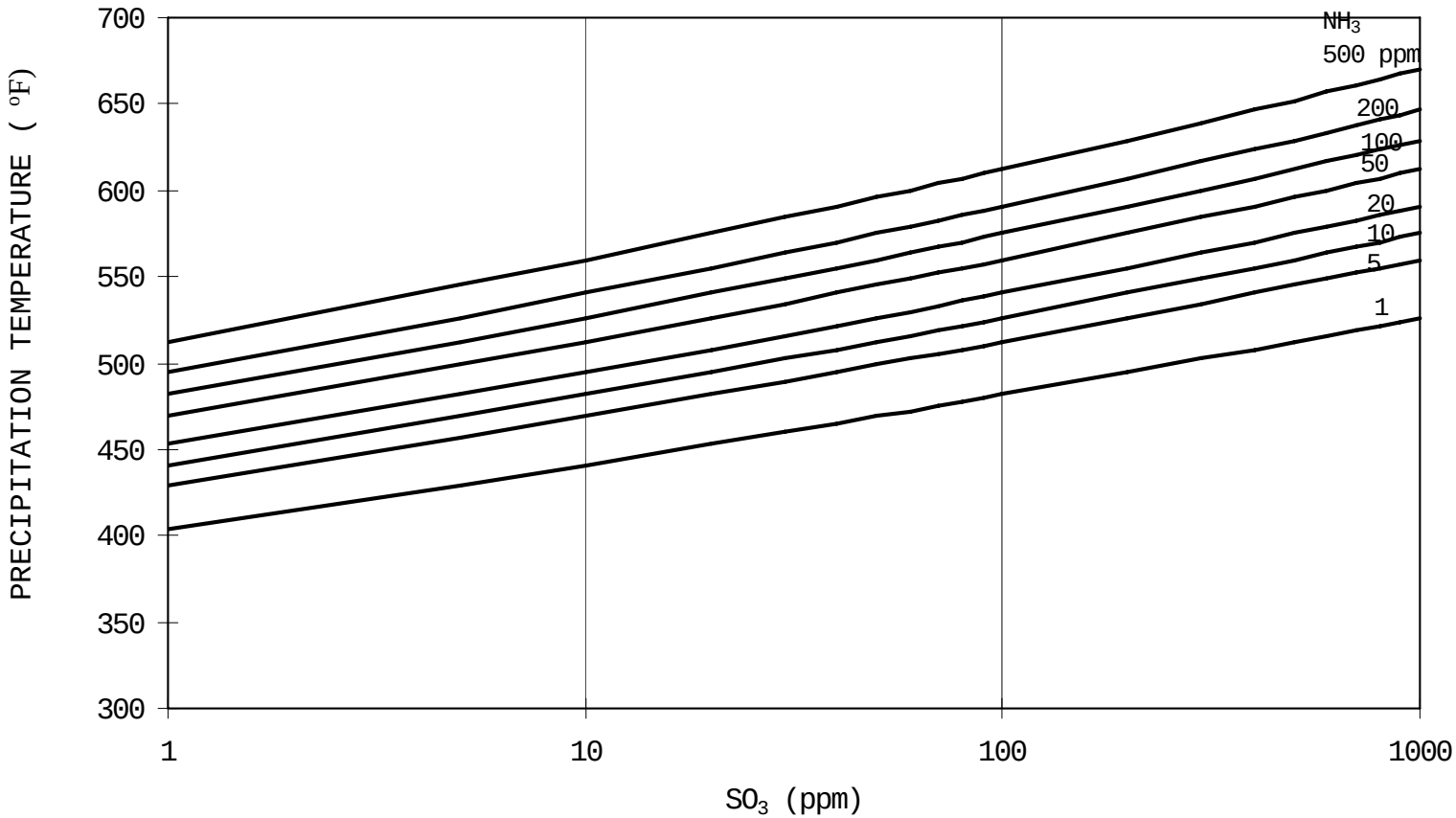


Fig.2 PRECIPITATION TEMPERATURE OF AMMONIUM BISULPHATE

MOT Determination

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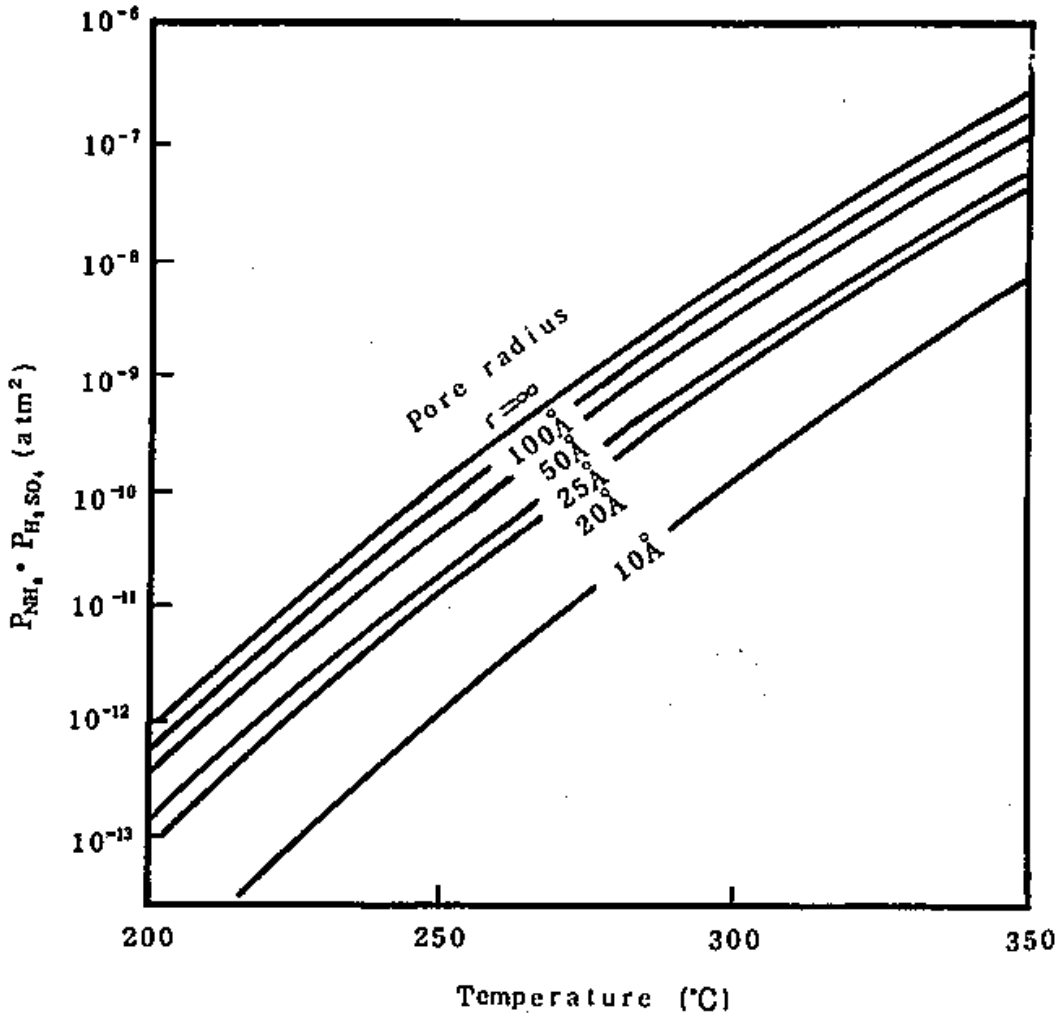
Based on Capillary Condensation of ABS



ABS formation is dependent upon pore radius.

Influences on MIT/MOT

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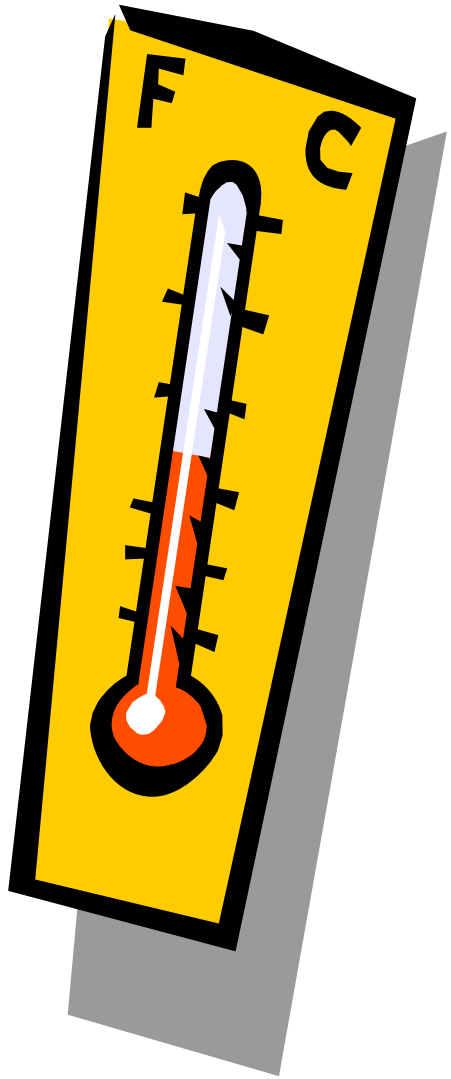
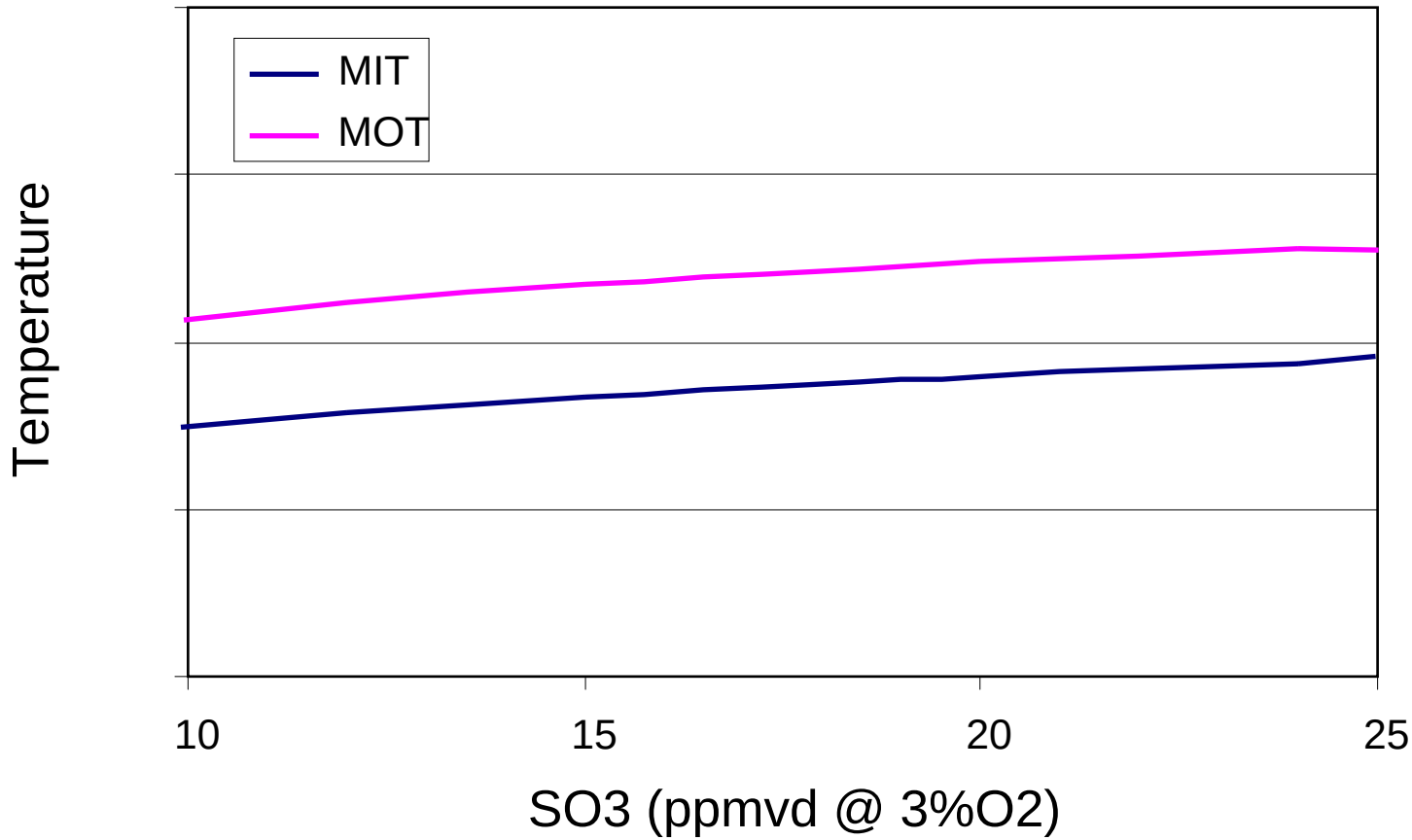
- **Major Factors That Affect MIT/MOT**
  - NH_3 Concentration:
    - Based on required NOx reduction
  - SO_3 Concentration:
    - Sulfur content in the fuel
    - SO_2 to SO_3 conversion across the catalyst
  - H_2O in flue gas
  - Catalyst Pore Size
  - SCR Operating Temperature (Load)



Example of MIT/MOT

Example: MIT and MOT for Actual Plant



NH3 = 317.8 ppmvd @3%O2, O2=3.9% dry

MIT: Minimum NH3 Injection Temperature
MOT: Minimum Operating Temperature

Affect of NH_3 and SO_3 on MIT/MOT

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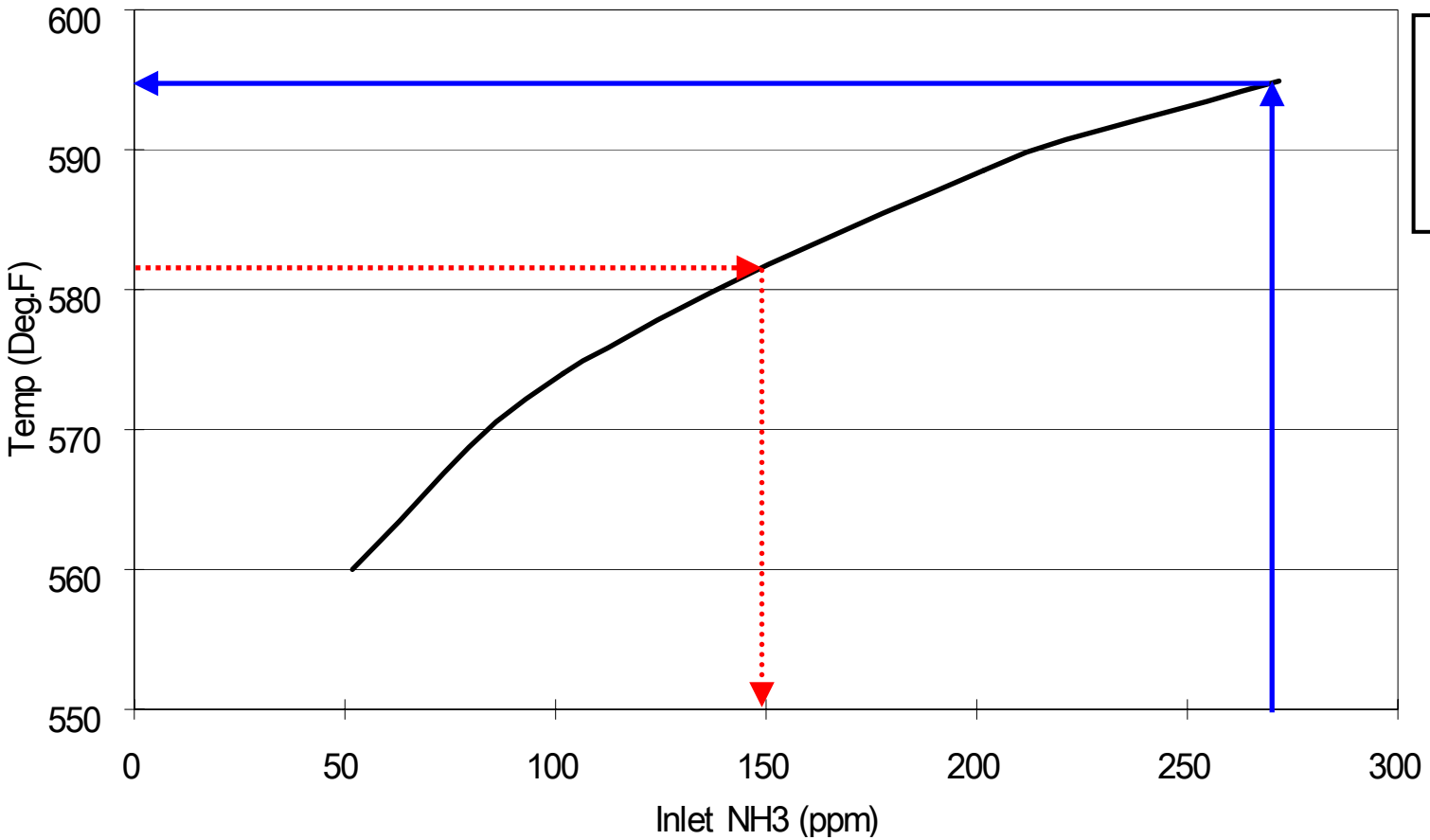
Example: MOT for Actual Plant



NOx=300ppm

NH3/NO=0.9

Low SO3

For Continuous Operation

Affect of NH_3 and SO_3 on MIT/MOT

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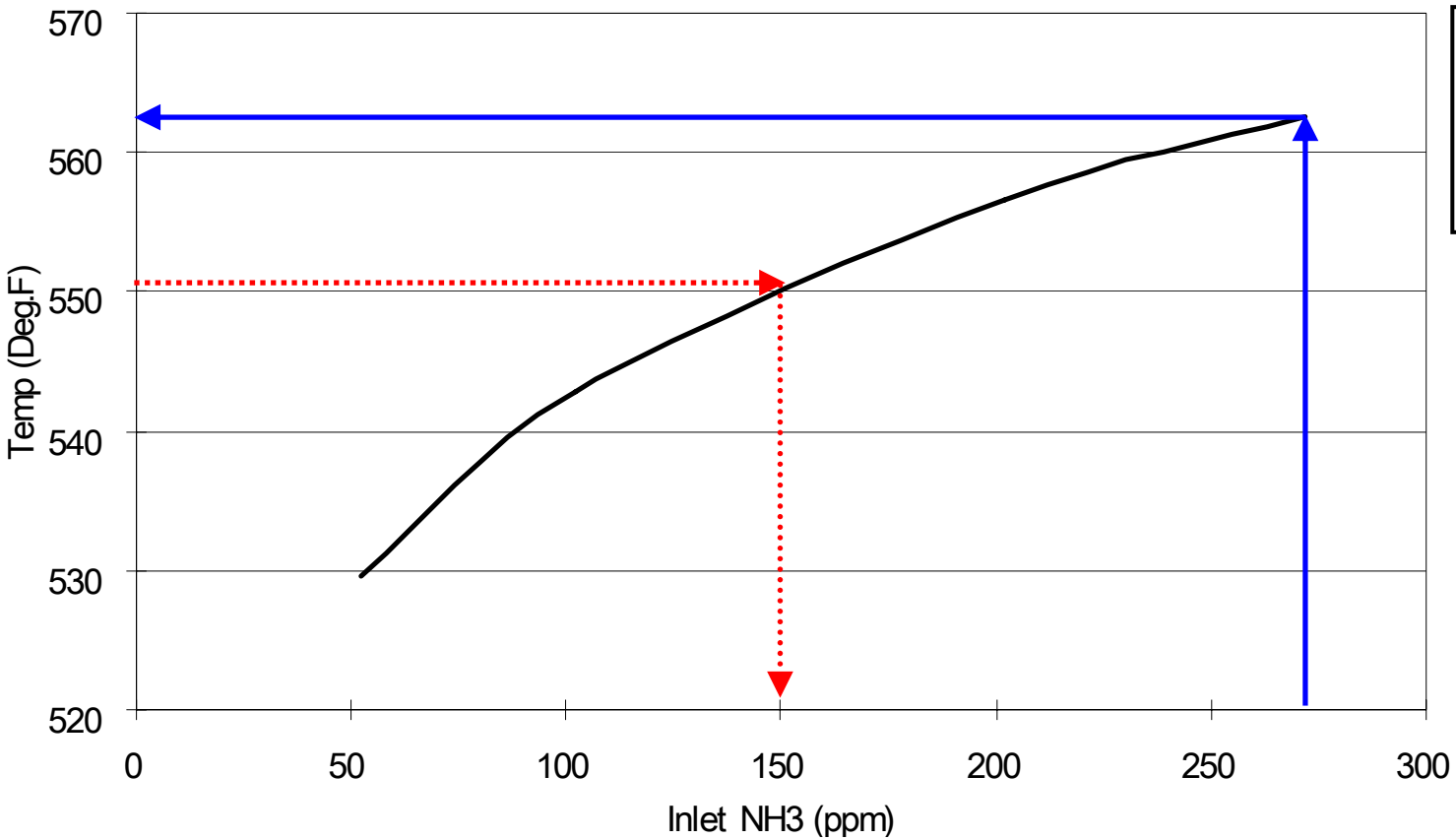
Example: Between MIT and MOT for Actual Plant



NOx=300ppm

NH3/NO=0.9

Low SO3

For Recovery, one to two times longer than the amount of time operated at the lower temperature is required to operate at MOT

Affect of NH_3 and SO_3 on MIT/MOT

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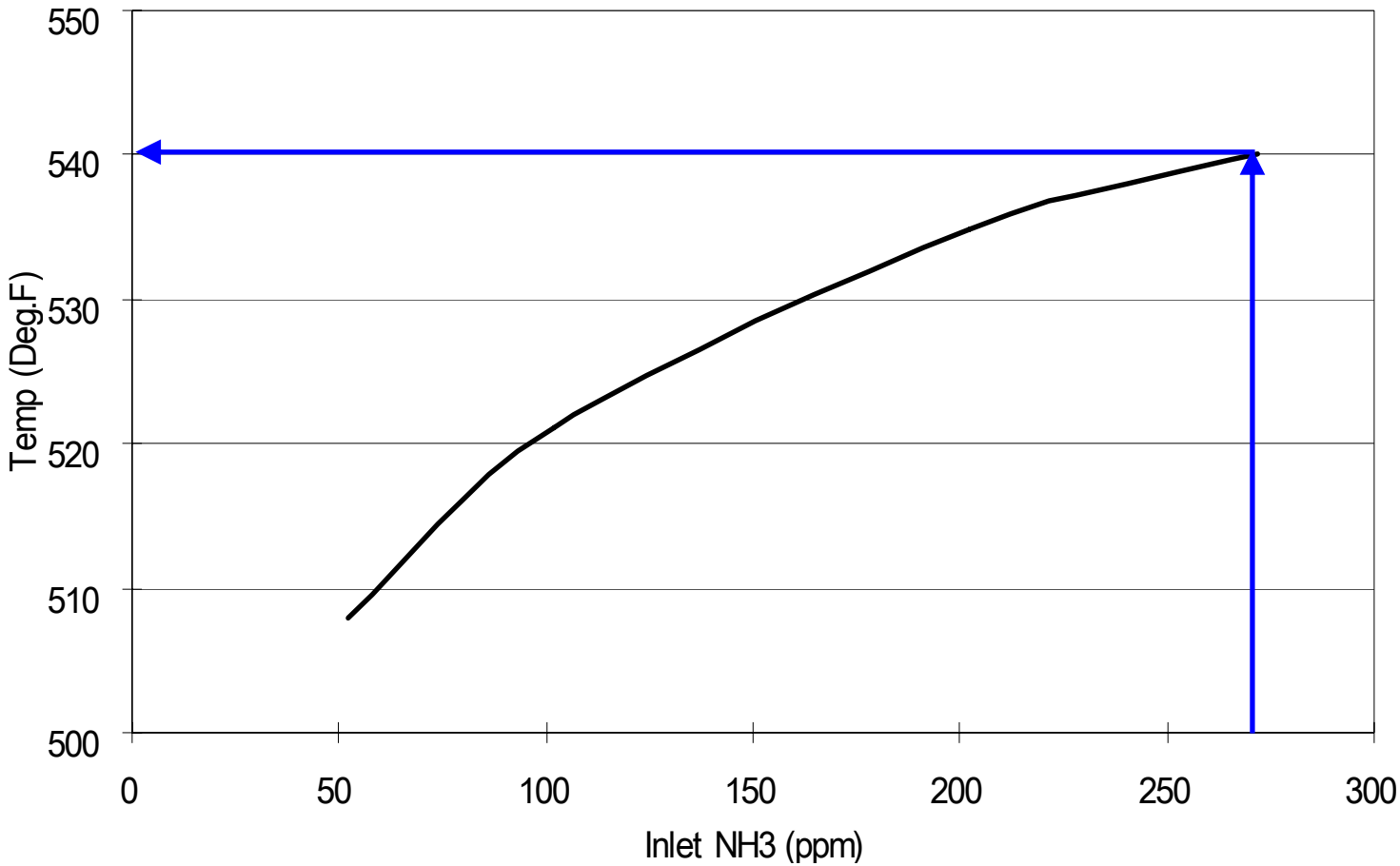
Example: Below MIT for Actual Plant



NOx=300ppm

NH3/NO=0.9

Low SO3

For Recovery, one to two times longer than the amount of time operated at the lower temperature is required to operate at MOT plus α deg. F

Affects of Pore Size on MIT/MOT

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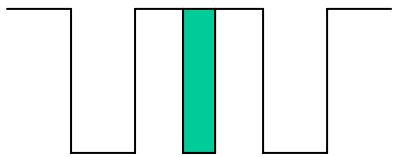
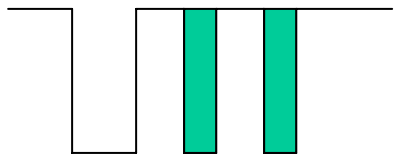
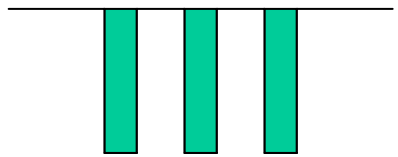
Relation between Pore Size and Deterioration by ABS

Catalyst	A	B	C
Pore Size	Large	Medium	Small
Deterioration by ABS	Small	Medium	large
Recovery of Deterioration by ABS	Easy	Medium	Difficult
Model			

SCR MIT and MOT are determined by NH_3, SO_3 concentration in flue gas, but also depends on the catalyst pore structure such as pore diameter and total volume.

Advantages of Low Load Operation

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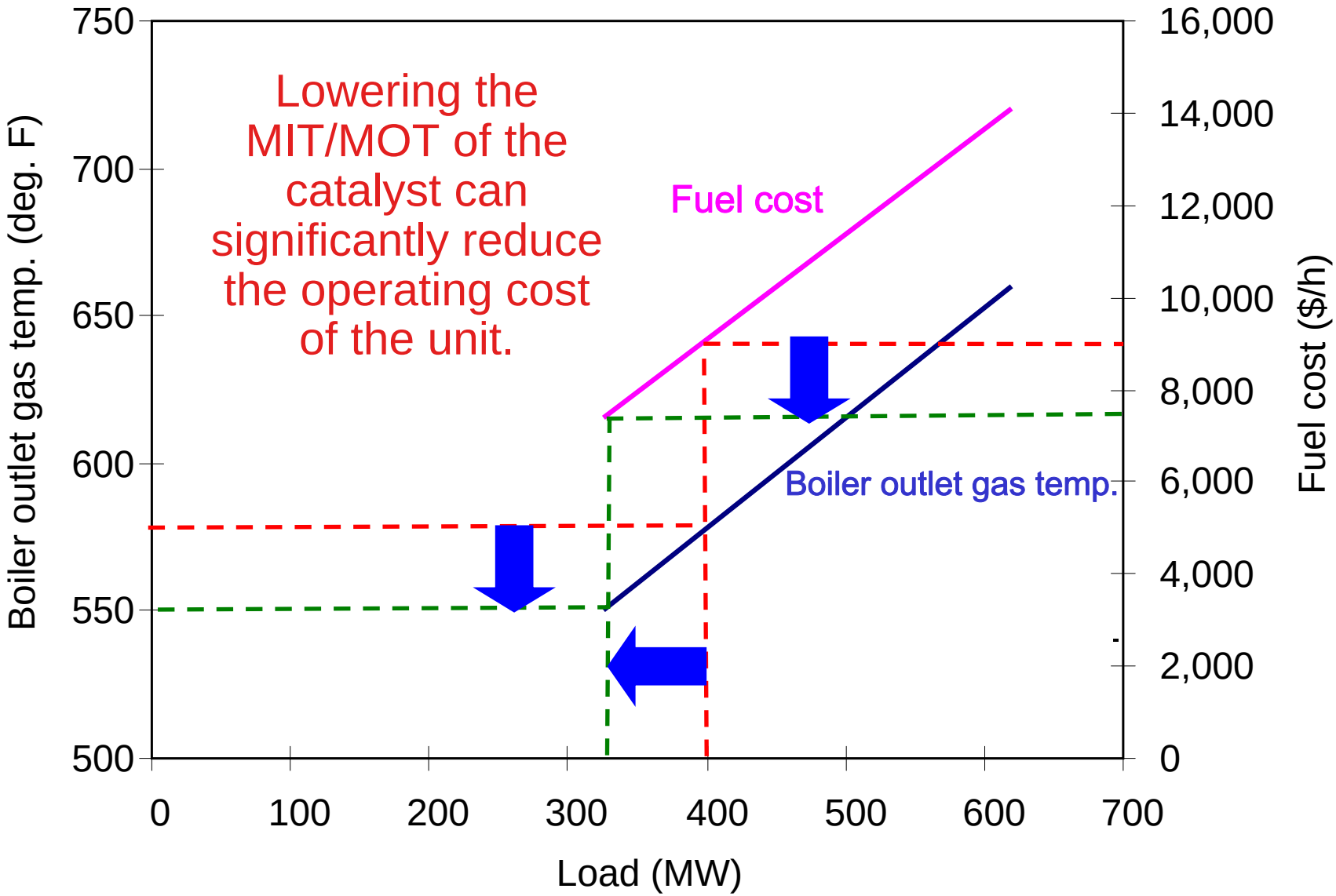
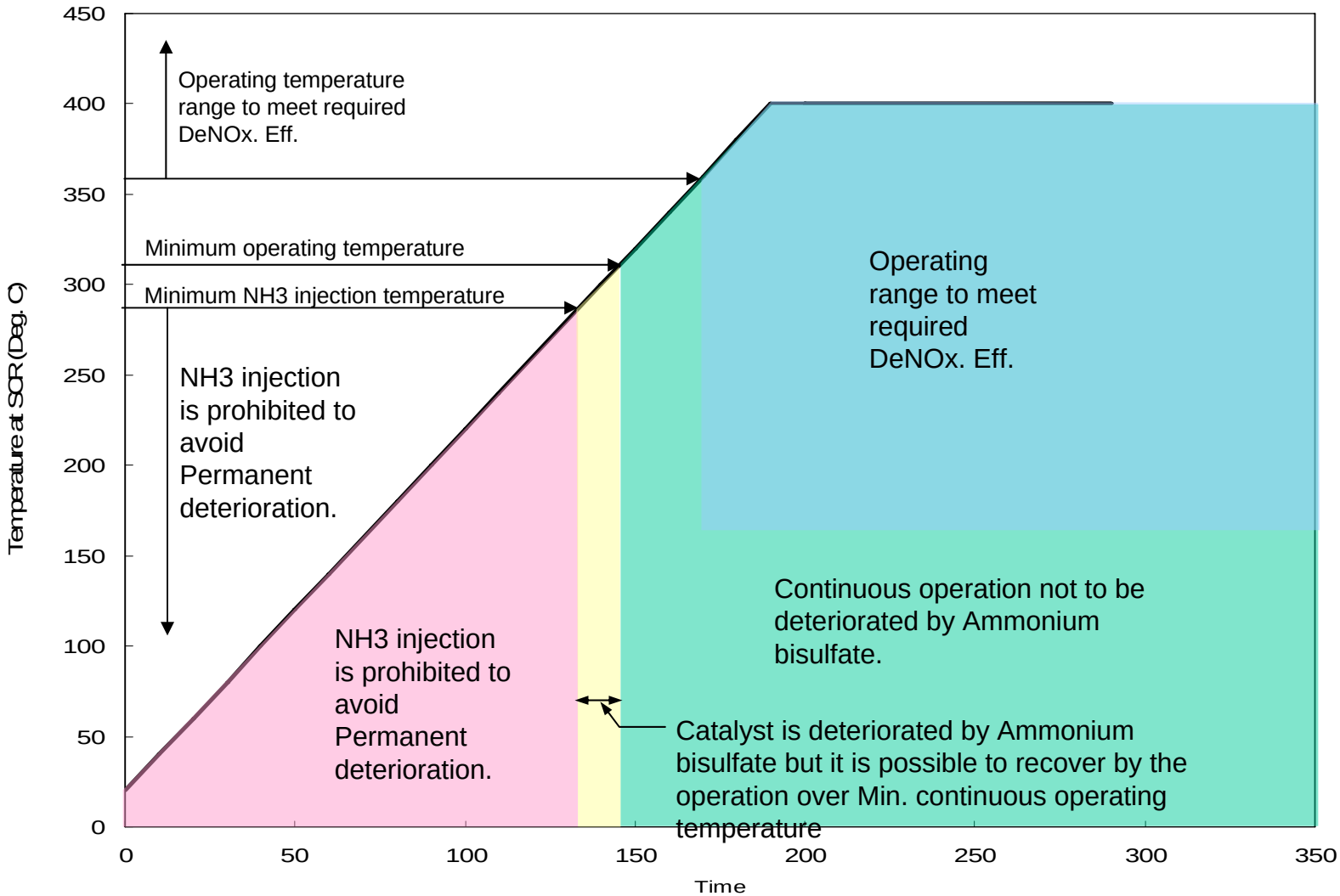
What Are the Advantages of Being Able to Operate My SCR at Lower Loads?

- Provides Cost Savings on Fuel
  - Lower loads = less wasted generation
- Allows Unit to Operate without the Need for an Economizer Bypass
  - No loss of boiler efficiency
  - No maintenance concerns
- Allows Operation with Higher Sulfur Fuels
  - As more FGD's come on line this becomes an increasing issue

Advantages of Low Load Operation



Operating Standard



Operating Temperature

Case Studies at Bench Scale Reactor

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- Test the effect of operating at between MOT and MOT-36 (still above MIT)
  - Test Pattern #1: 23 Hr @ MOT, 21 Hr @ MOT-18, 21 Hr @ MOT-36, Recovery Time at MOT
- Test the effects of running for different cycle times at MIT to determine how long is required to run at MOT to recover catalyst activity
  - Test Pattern #2: 2 Hr, 4 Hr, and 7 Hr Tests at MIT, Recovery Time at MOT
- Test the effects of running below MIT for different cycle times and determine what times and what temperatures are required to run to recover catalyst activity
  - Test Pattern #3: 2 Hr, Tests at MIT-18F, Recovery Time at MOT
  - Test Pattern #4: 5 Hr and 10 Hr Tests at MIT-18F
  - Test Pattern #5: 10 Hr @ MIT -9 & -18, Recovery Time @ MOT, MOT+20, MOT +50
- Further testing to be done

Affect of Operation Time at MOT to MOT-36F on DeNOx Activity

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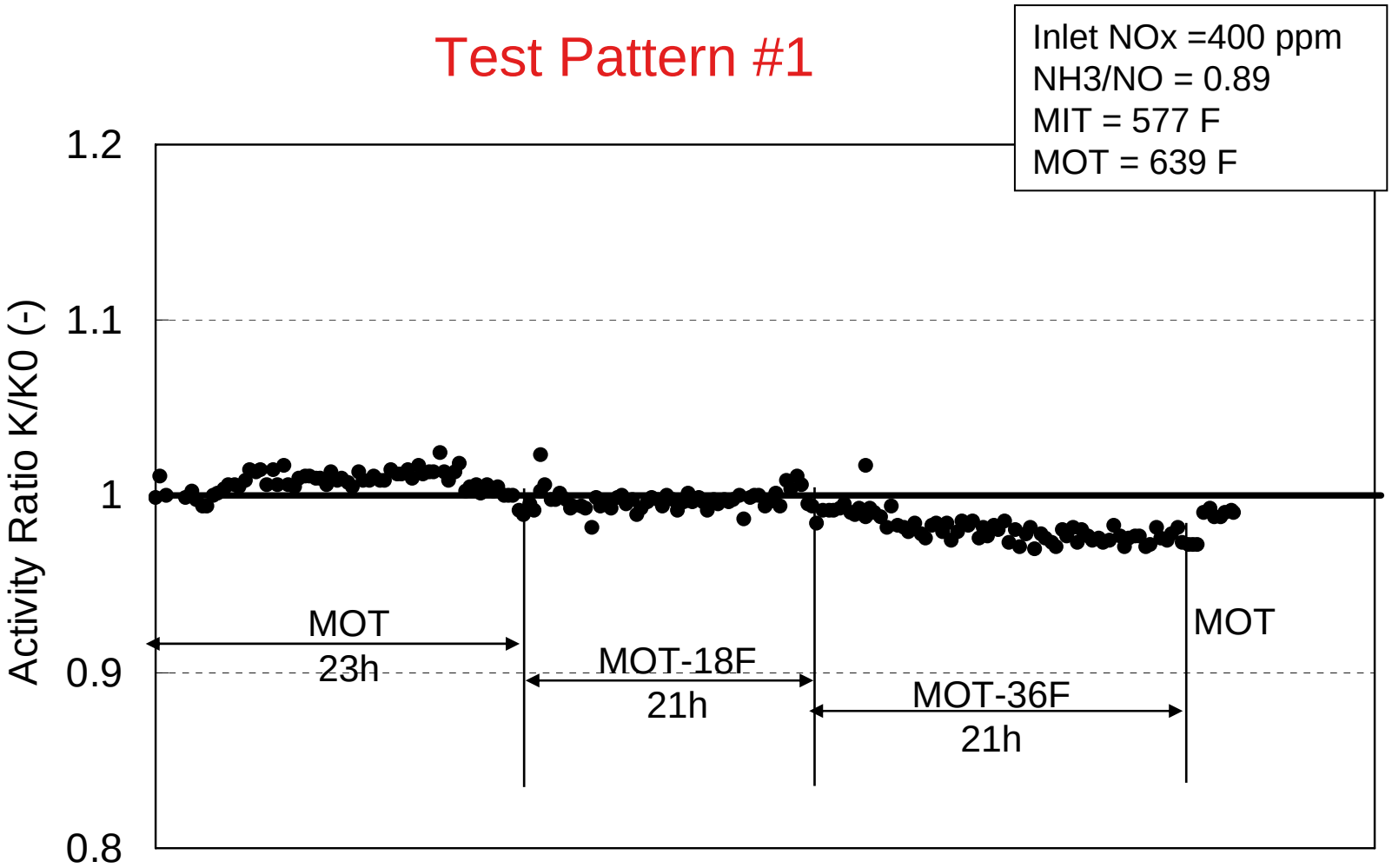

Affect of MIT/MOT Cyclical Operation on DeNOx Activity

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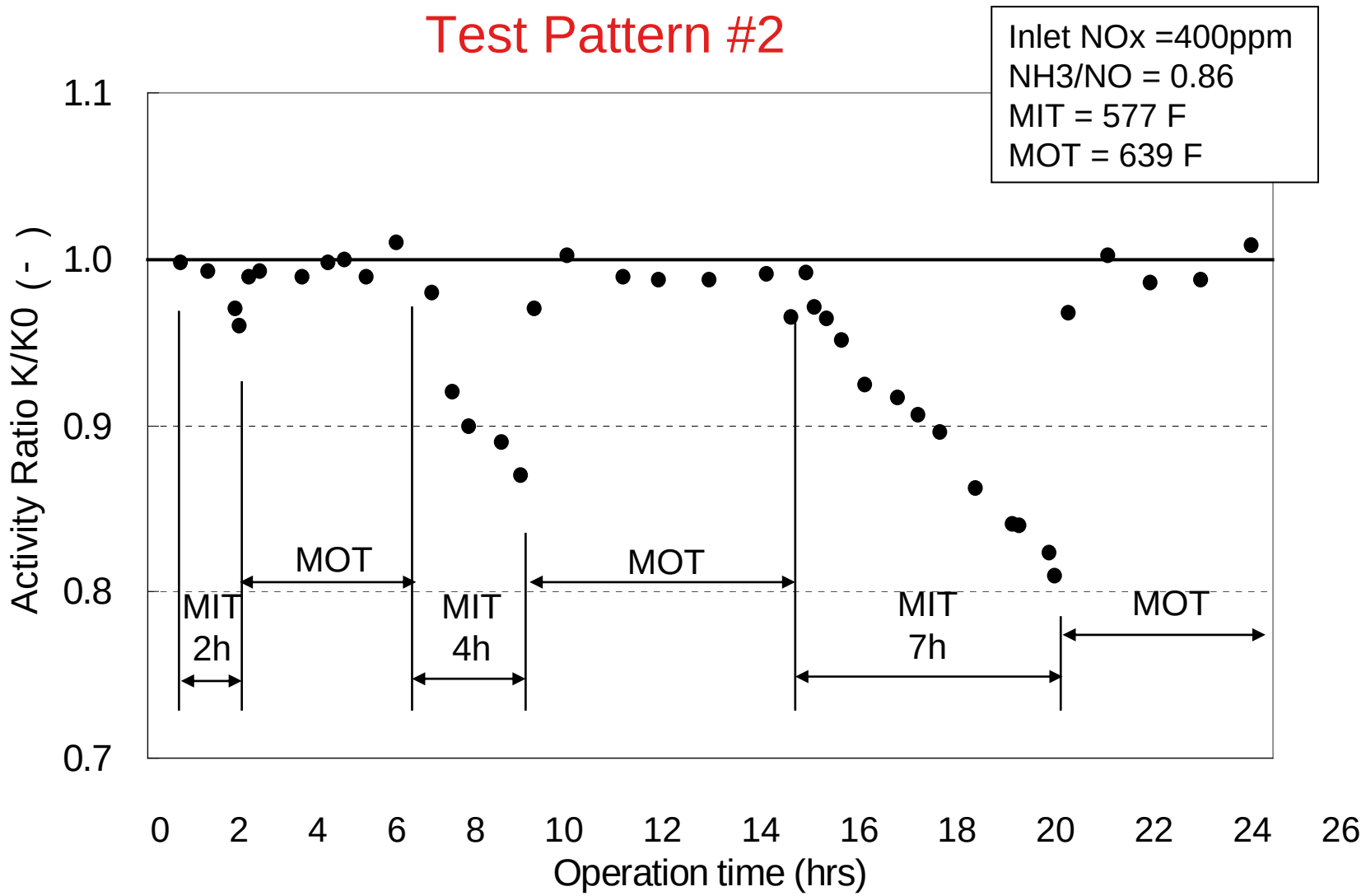

Affect of MIT-18F/MOT Short Term Cyclical Operation on DeNOx Activity

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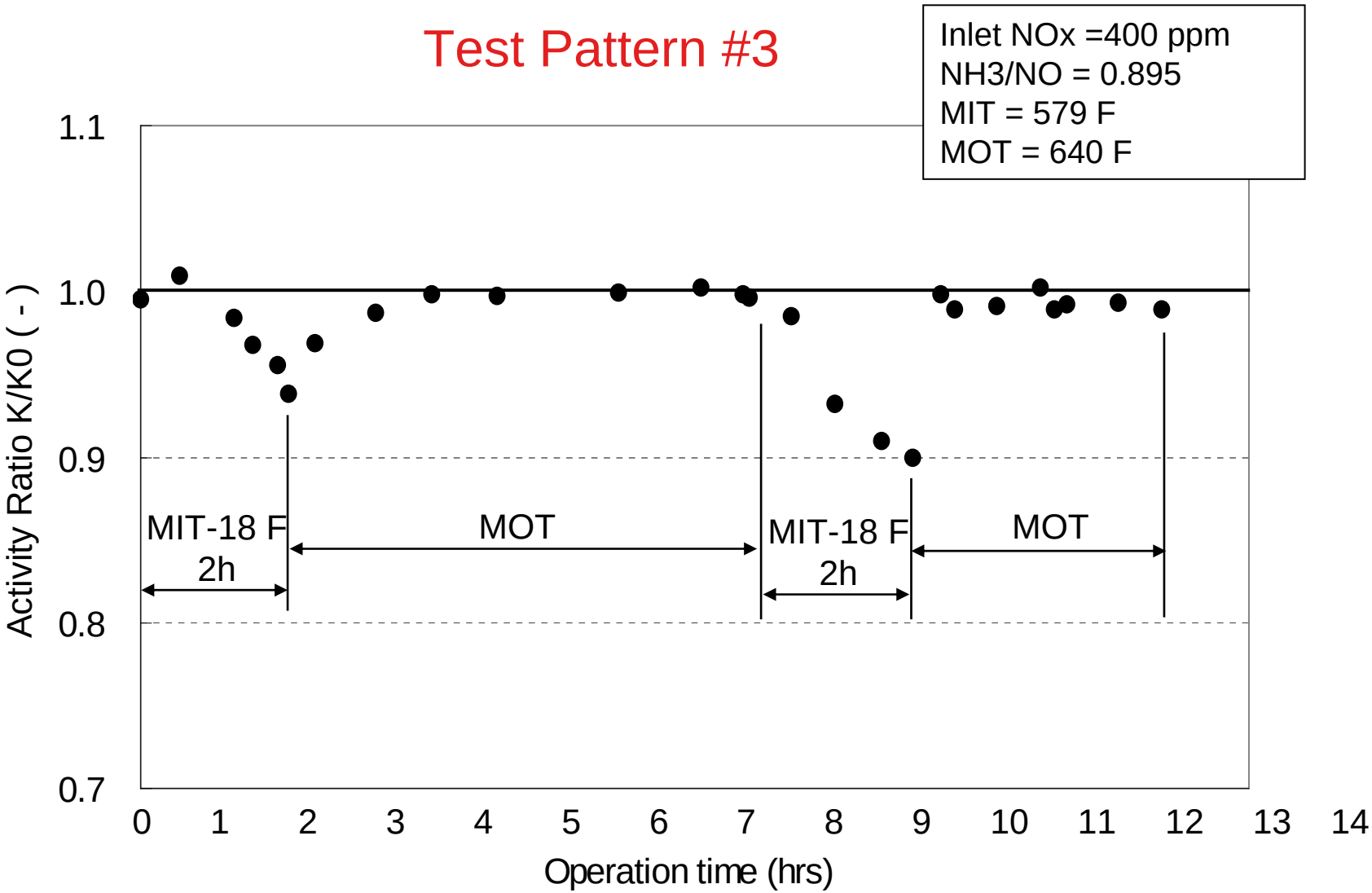

Affect of MIT-18F/MOT Long Term Cyclical Operation on DeNOx Activity

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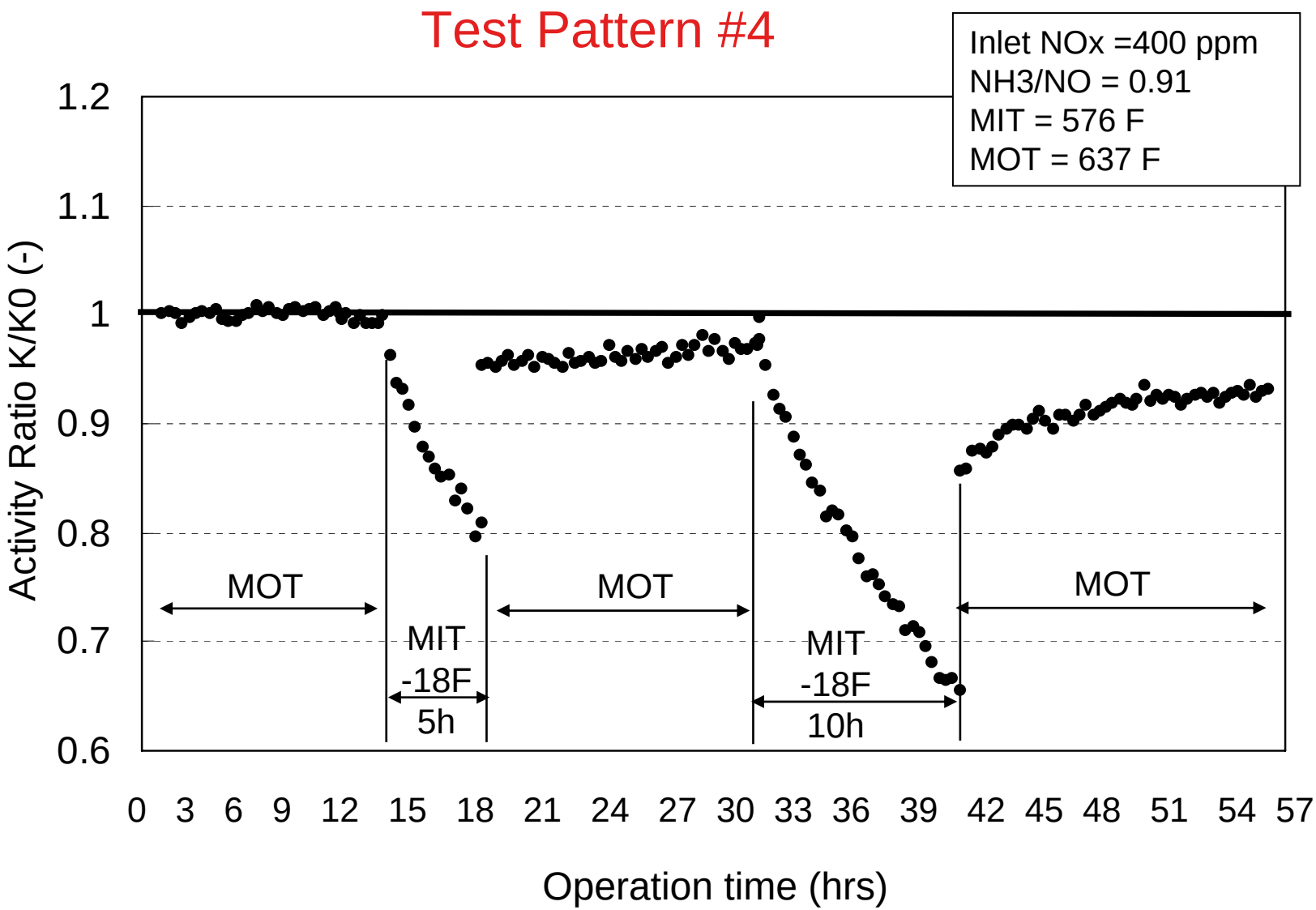

Affect of Long Term Operation at MIT-9F and MIT-18F on DeNOx Activity with >MOT Recovery Temperature

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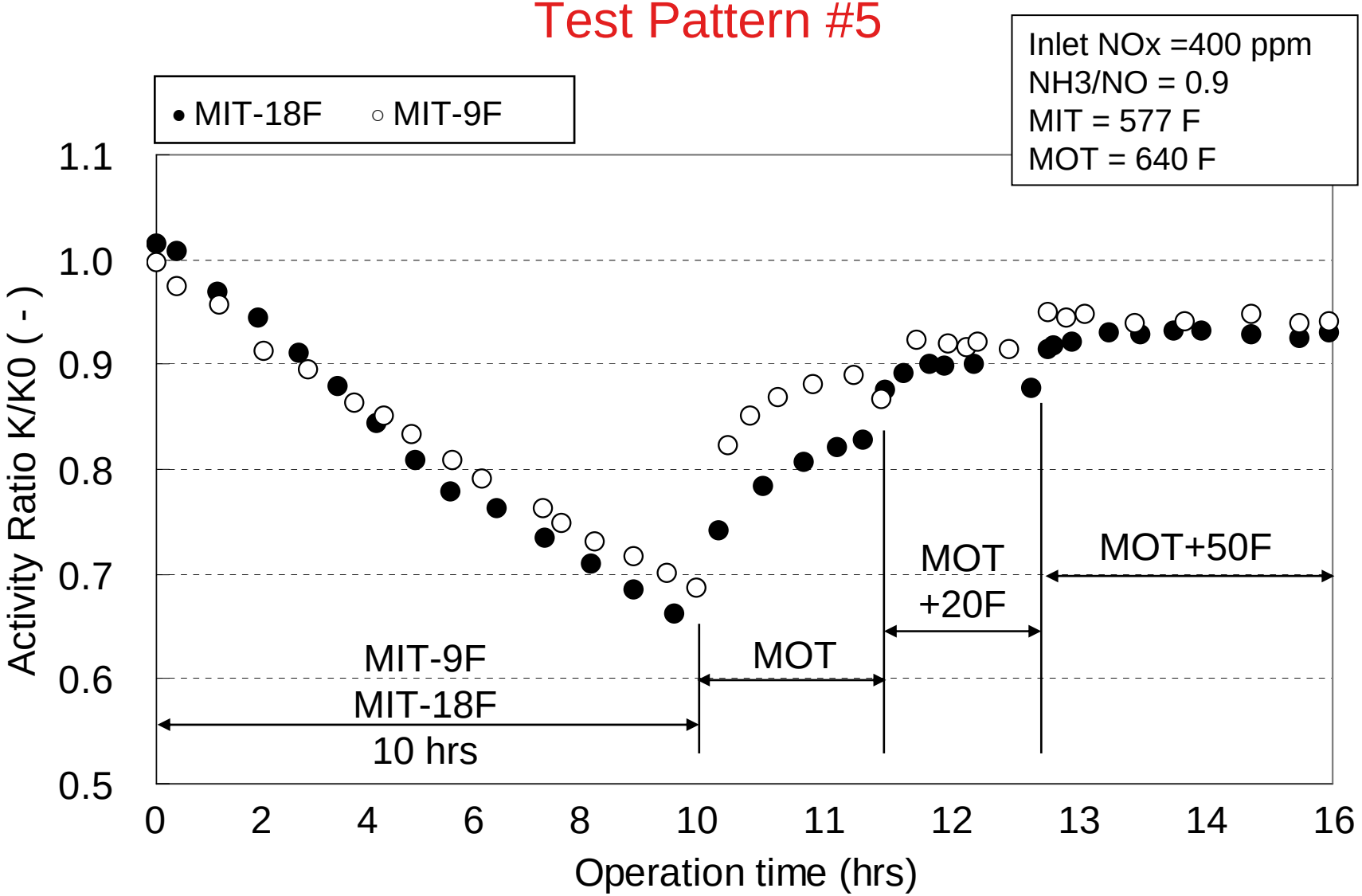
Test Pattern #5



Conclusions

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SCR Temperature	Deactivation	Recoverable
MOT	NO	N/A
<MOT BUT >MIT	SOME	YES
MIT (Short Time)	SOME	YES
< MIT (Short Time)	YES	YES
< MIT (Long Time)	YES	???

NOTE: IT IS NOT RECOMMENDED TO RUN AT OR BELOW MIT FOR EXTENDED PERIODS OF TIME!

Conclusions and Recommendations

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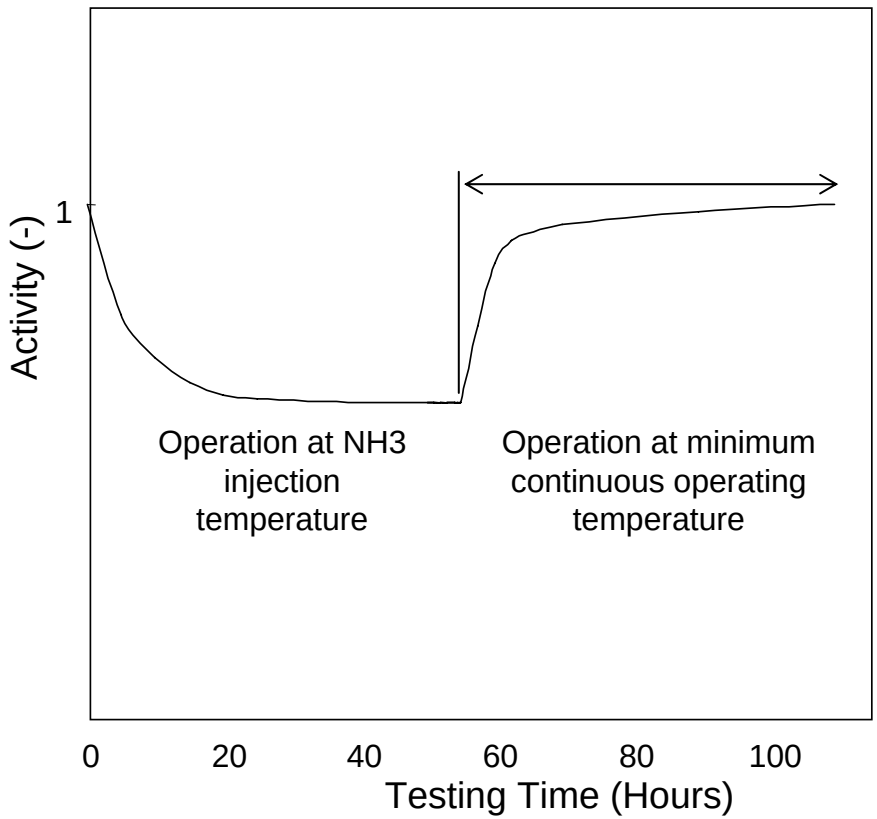
Countermeasure

- Do not inject ammonia below ammonia injection start temperature
- Operate at minimum continuous operating temperature



For every 1 hour of operation between minimum injection temperature and minimum operating temperature you should operate for approx. 1-2 hours at or above the minimum operating temperature to recover the catalyst activity.

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QUESTIONS