REINHOLD ENVIRONMENTAL Ltd.

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Successful SCR Operation at Low Load for Coal Firing Plant

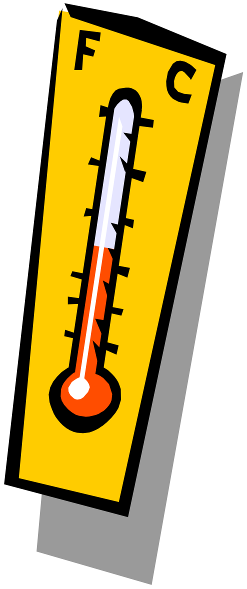
Mike Klump
Mitsubishi Hitachi Power Systems America, Ltd,

Co-author
Takuma Kurai

MITSUBISHI HITACHI POWER SYSTEMS, LTD.

Outline

- Advantage of Low Load Operation
- Approach for SCR Low Load Demands
- History of Basic Study on ABS Formation at MHPS
  - Laboratory Micro Reactor - Matsuda's Equation -
  - Basic Study on ABS Formation in Early1980's
- SCR Operation and Definition of MIT/MOT
- Review of MIT/MOT Model by Laboratory and Bench Test
  - Recovery Condition by Bench Scale Test
- Consideration of Low Load Operation at Actual Plant
- Further Study on Expected Impact of ABS on Activity



Advantages of Low Load Operation

- ❑Coal Power Plant is facing the requirement at Low load operation.
- ❑Environmental regulation is getting stringent even at low load

Condition:
Coal: Bituminous
Fuel Consumption: 650lb/MW
Fuel Cost: $0.035/lb

$500/h x 8,000 h/year = $4M/year

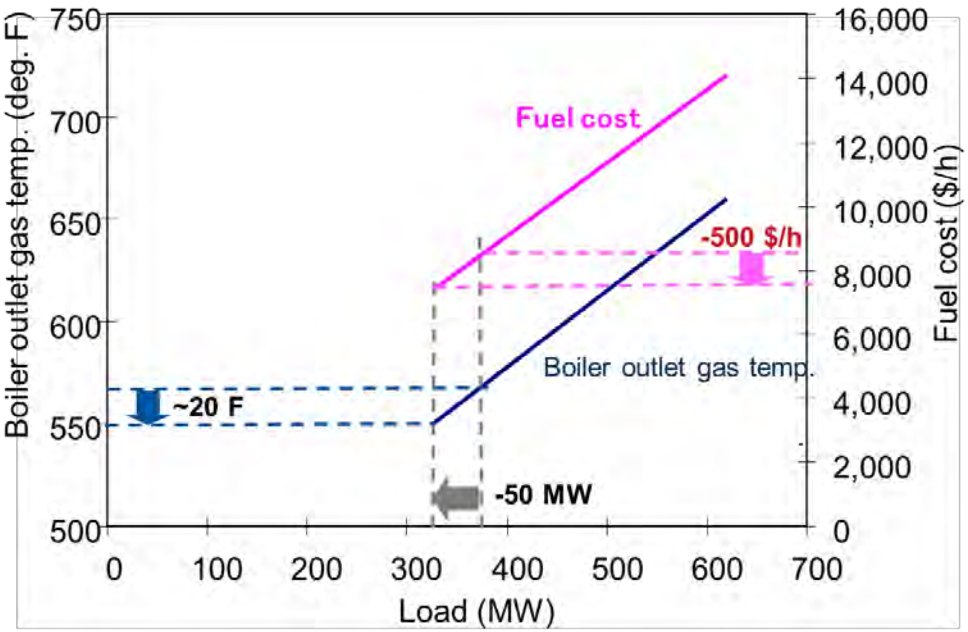
Benefits:

More flexibility for generation provides cost savings on fuel

- Lower loads = less wasted generation

Allows unit to operate without the need for economizer bypass

- No loss of boiler efficiency



Approx. $4M /year of cost saving by lowering MOT by ~20 F

Approach for SCR low load demands

SCR catalyst is being placed at sever condition of low load operation

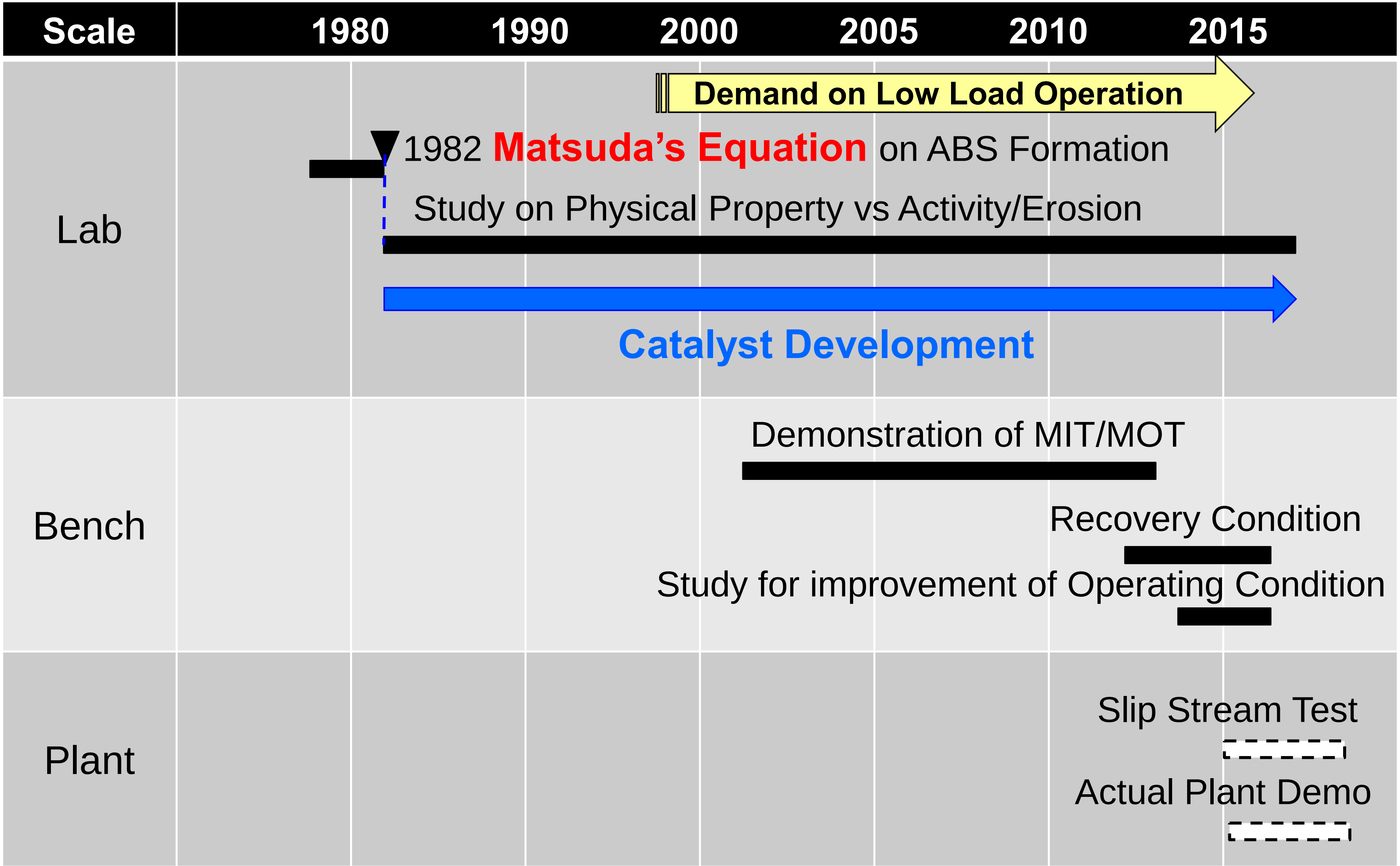
Because of ABS accumulate at low temperature

- SO_3 formed by coal combustion react with NH_3 as a reducing reagent for NOx to form ABS (Ammonium Bisulfate) by **Capillary Condensation** in catalyst pore structure to deteriorate

$$SO_3 + NH_3 + H_2O \rightarrow NH_4HSO_4 \text{ (ABS)}$$

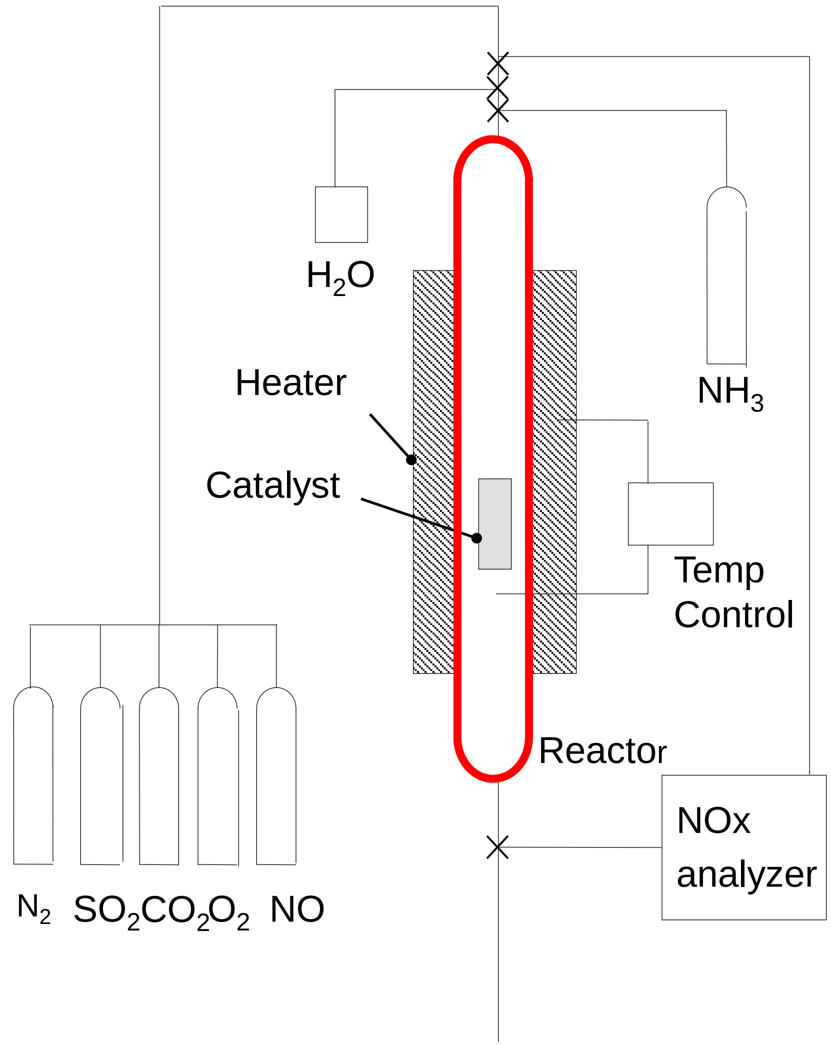
Contributor	How to Control ABS Formation
Temperature	Keep Temperature high
SO_3	Co-combustion with gas, Coal Blends, DSI etc.
NH_3	NH_3 free operation ?

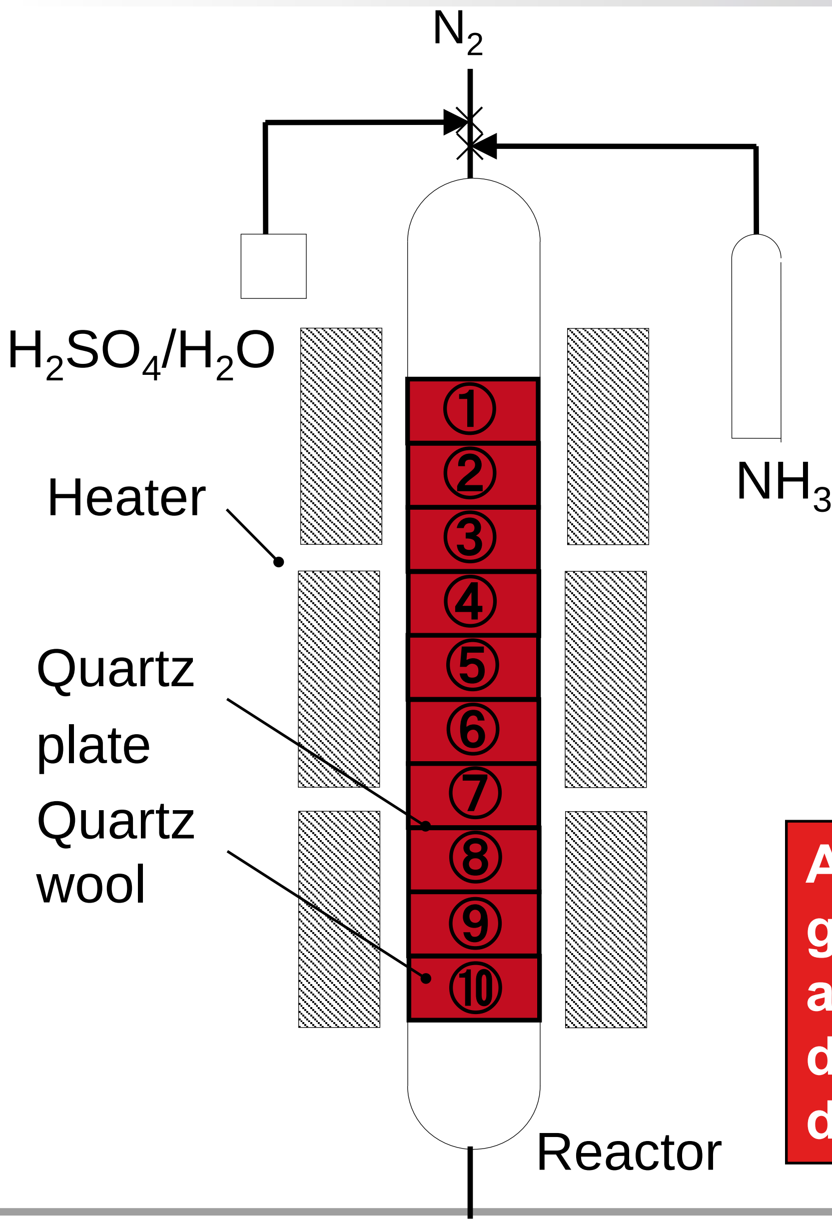
History of Basic Study on ABS Formation at MHPS



Laboratory Micro Reactor - Matsuda's Equation - (1)

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





Measurement Condition

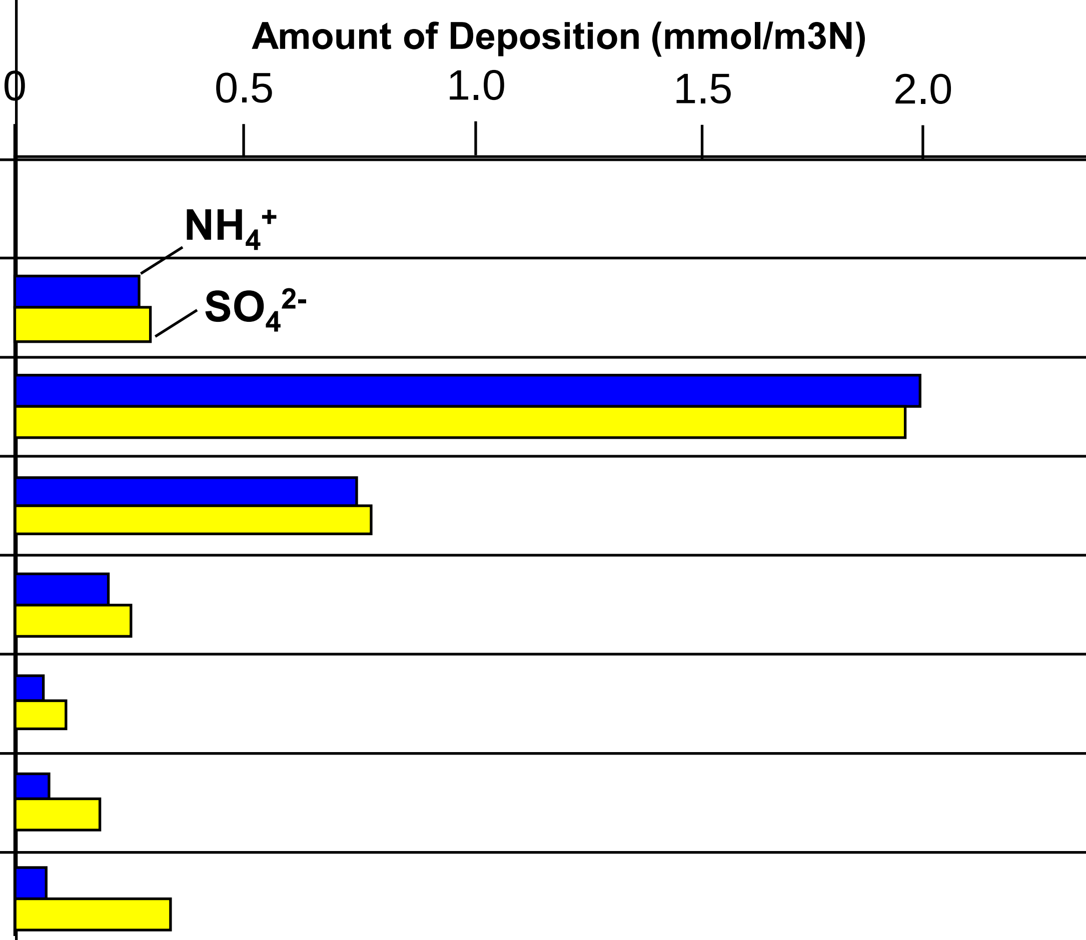
Item	Condition
Temperature Setting	Reactor Inlet: 550C Inlet ①: 360C Outlet ⑩: 100C
Duration Hours (h)	20
Inlet Gas Condition	5 sets of NH_3/H_2SO_4 Concentration

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

Laboratory Micro Reactor - Matsuda's Equation - (3)

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

Region	Temperature (Deg F)	NH_4^+/SO_4^{2-} (Mole Ratio)
1	673-613	-
2	613-556	0.91
3	556-509	1.00
4	509-466	0.95
5	466-432	0.77
6	432-397	0.26
7	397-361	0.14
8	361-316	0.11

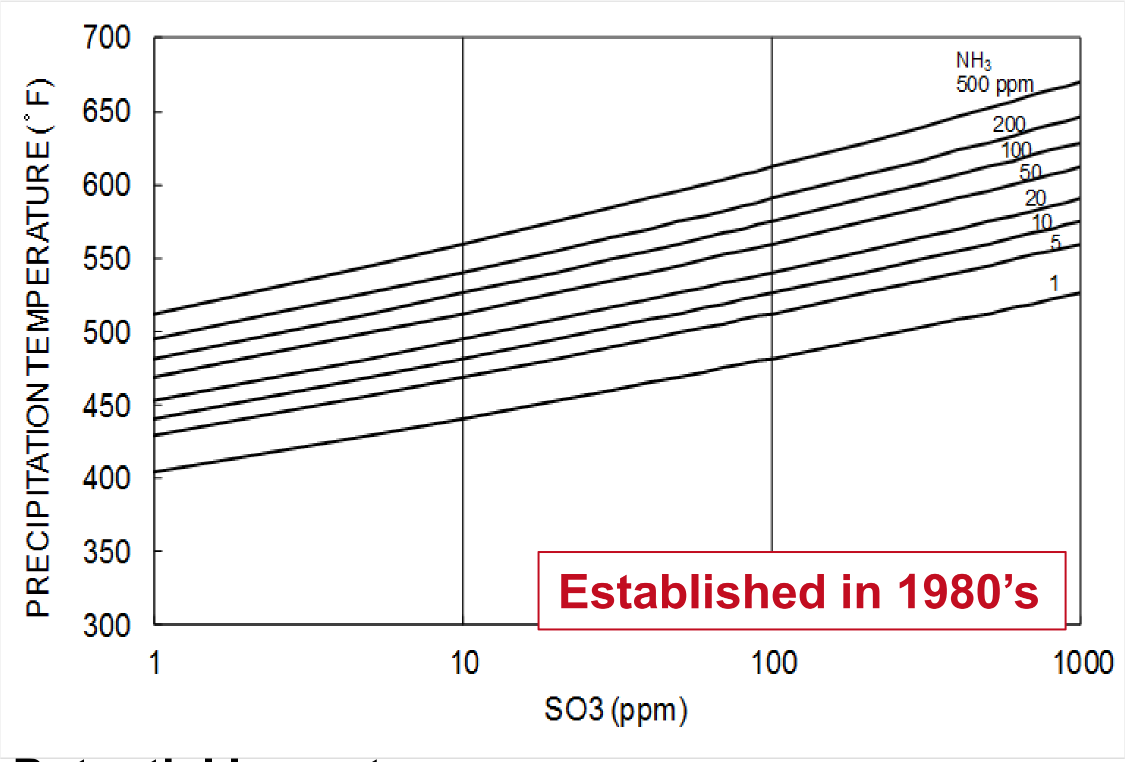


Based on 5 sets of examinations, MHPS found the following equation for ABS deposition

$(NH_3 + H_2SO_4 = NH_4HSO_4)$ $P_{NH3} \cdot P_{H2SO4}$ = 1.41x 10-12 Exp(-53000/RT) (Gas Phase Deposition)

Basic Study on ABS Formation in Early1980's (1)

Precipitation Temperature at Gas Phase



Reactions

Ammonium Sulfate (Particulate)

- $SO_3 + 2NH_3 + H_2O \rightarrow (NH_4)2SO_4$

Ammonium Bisulfate (ABS) ("Sticky")

- $SO_3 + NH_3 + H_2O \rightarrow NH_4HSO_4$

Potential Impacts

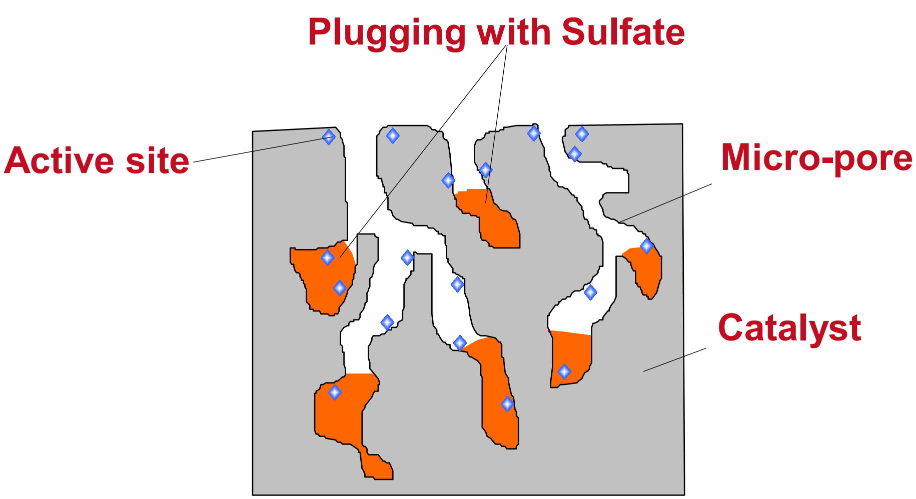
- ❑ Reduced catalyst active area due to salt pluggage
- ❑ Pluggage of downstream equipment (i.e. Air Heater)

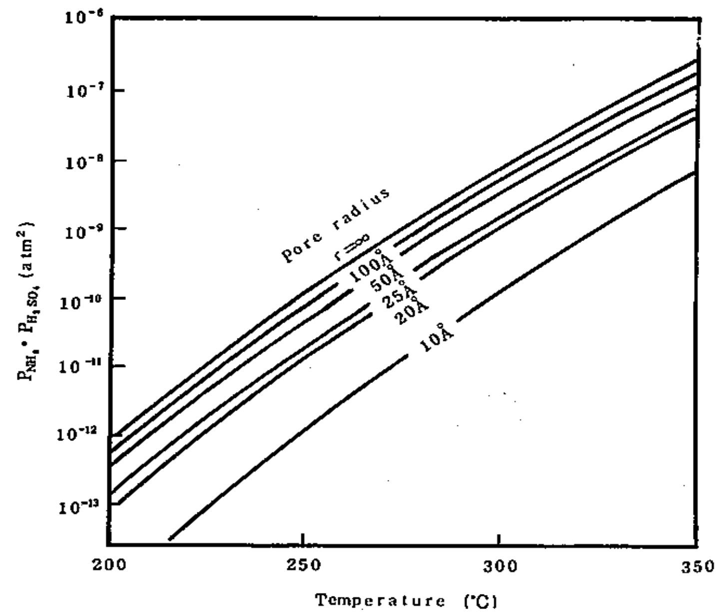
ABS formation is dependent upon NH_3 and SO_3 concentration

Ammonium Bisulfate Formation (ABS) in Catalyst Pore

- Formation of ABS causes plugging of the micro-pores in the catalyst through the process of <u>Capillary Condensation</u> and covers the catalyst surface where the active sites are located

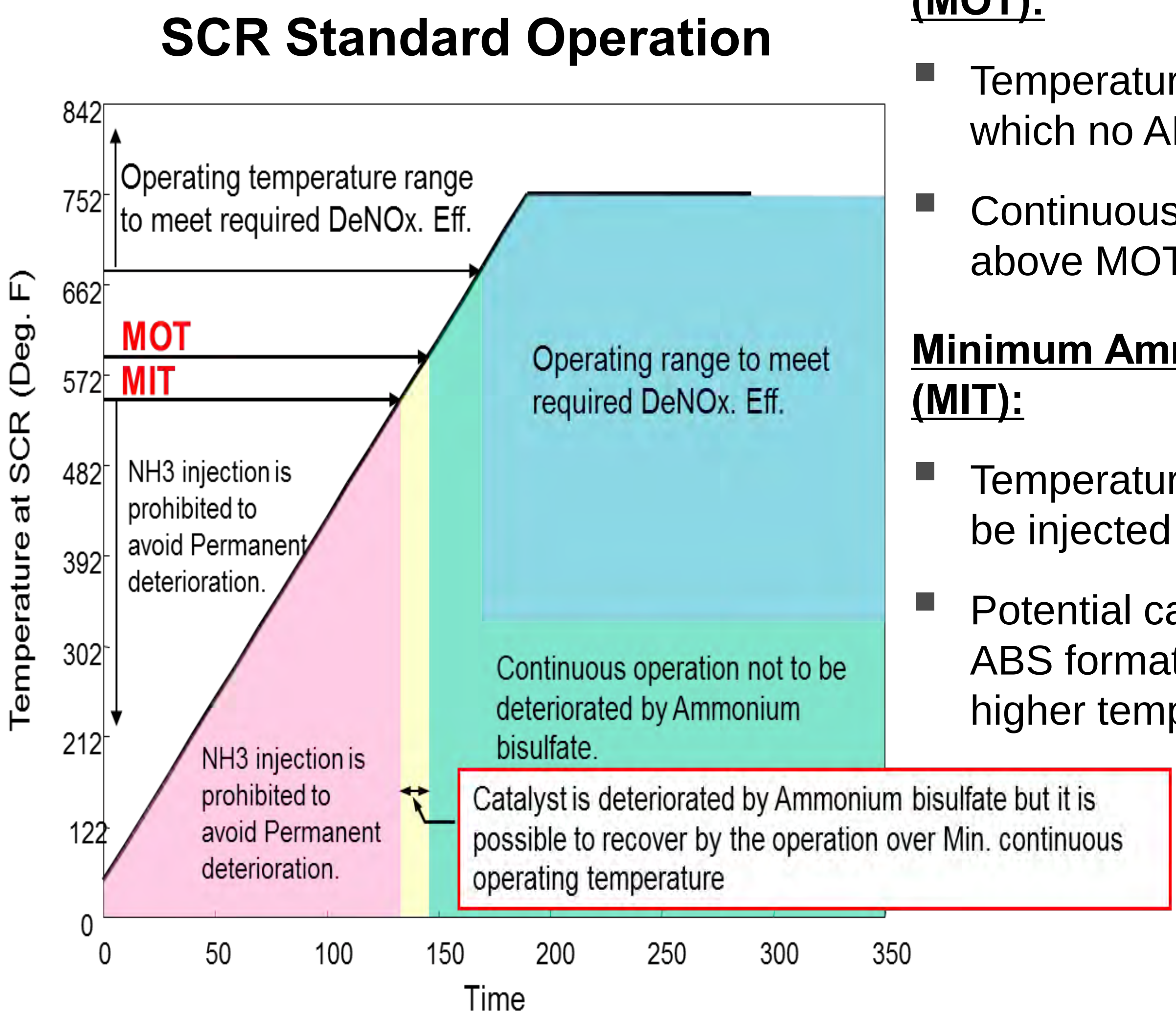
- This phenomenon causes decreased catalyst activity.





ABS formation temperature in catalyst is higher than formation temperature at gas phase, and is dependent upon pore radius.

SCR Operation and Definition of MIT/MOT



Minimum Continuous Operating Temperature (MOT):

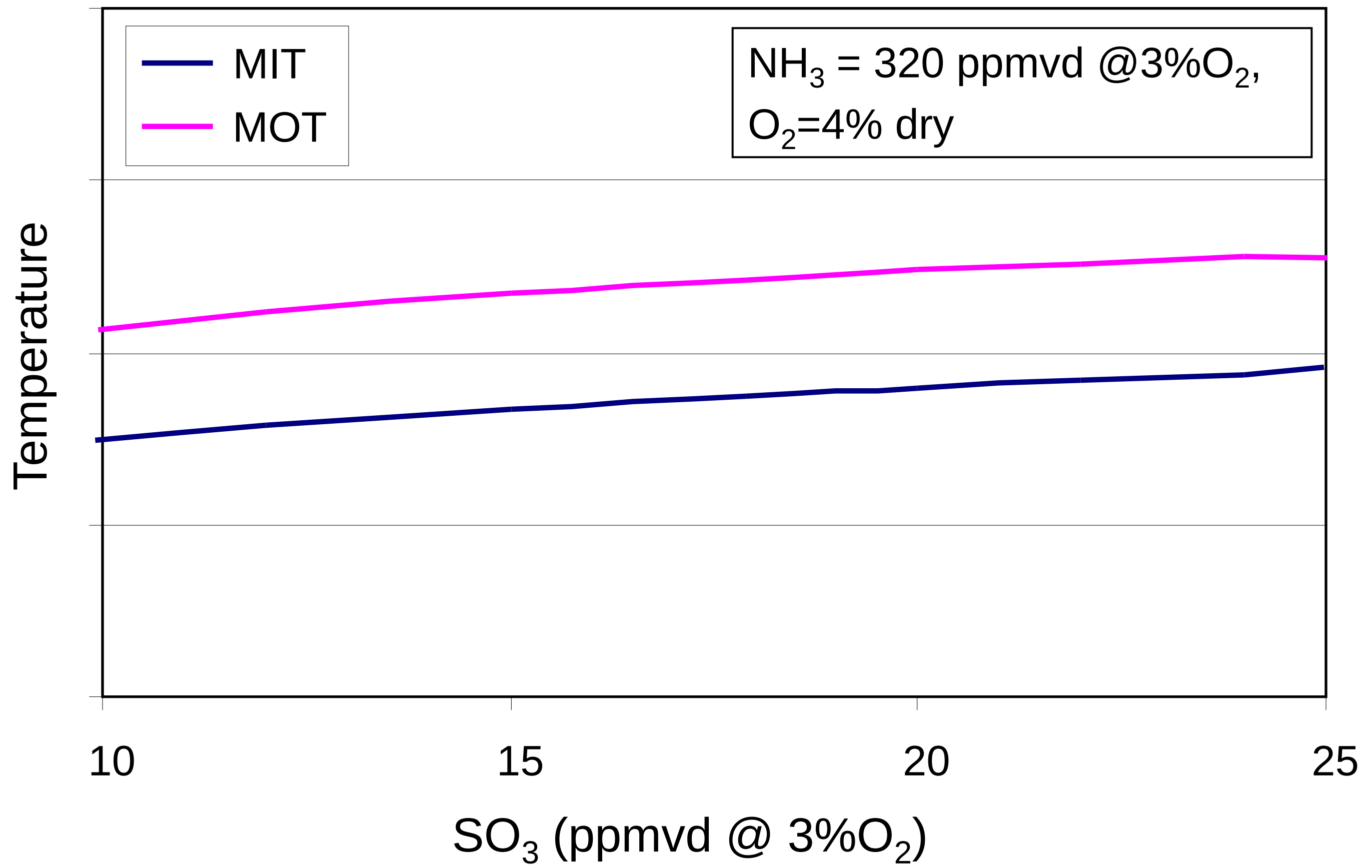
- Temperature at which SCR can be operated in which no ABS will accumulate on the catalyst.
- Continuous operation of the SCR must be above MOT.

Minimum Ammonia Injection Temperature (MIT):

- Temperature in which ammonia can begin to be injected into SCR.
- Potential catalyst deterioration may occur by ABS formation, but this can be burned out at higher temperature at higher load.

Example of MIT/MOT

Example: MIT and MOT for Actual Plant



MIT: Minimum NH3 Injection Temperature

MOT: Minimum Operating Temperature

MHPS Approach of Study on Operating Condition of SCR

Lab

- MIT/MOT Reaction Model
- Simulated gas conditions

Implementation

- New Standard
- Operational Change

Bench

- Accuracy Evaluation
- Actual Flue Gas Conditions
- Recovery Condition Evaluation

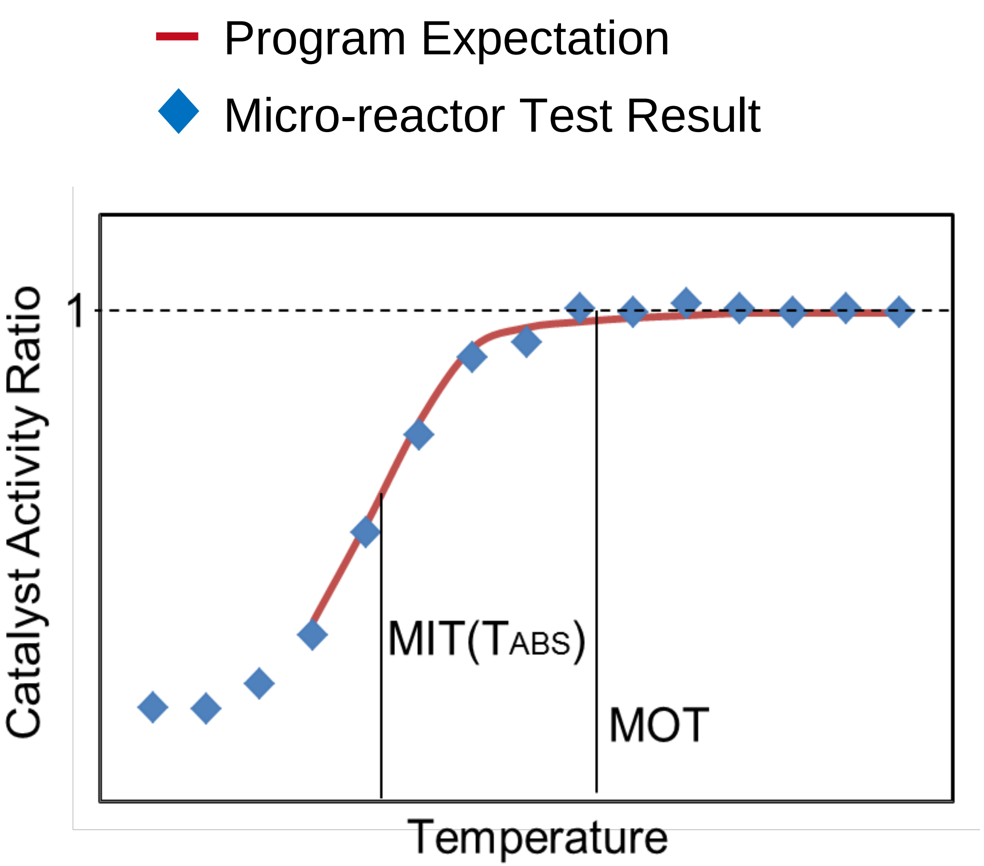
Plant

- Live Conditions
- Verify Reliable Operation
- Performance Monitoring

STEP by STEP approach had been taken focused on the accuracy of MOT/MIT measurement which is critical for plant operation.

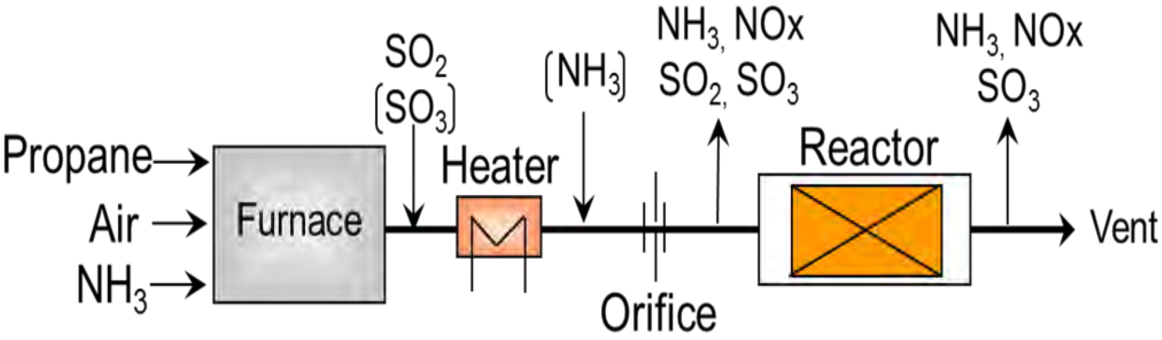
*Review of MIT/MOT Model by **Laboratory Scale Test***

Item	Test Condition
Inlet SO_3 (ppm)	20
Inlet SO_2 (ppm)	500
Inlet NOx (ppm)	200
NH_3/NO (-)	1.2



Established Model can expect how much catalyst deactivates at low temperature

Review of MIT/MOT Model by **Bench Scale Test** (1)



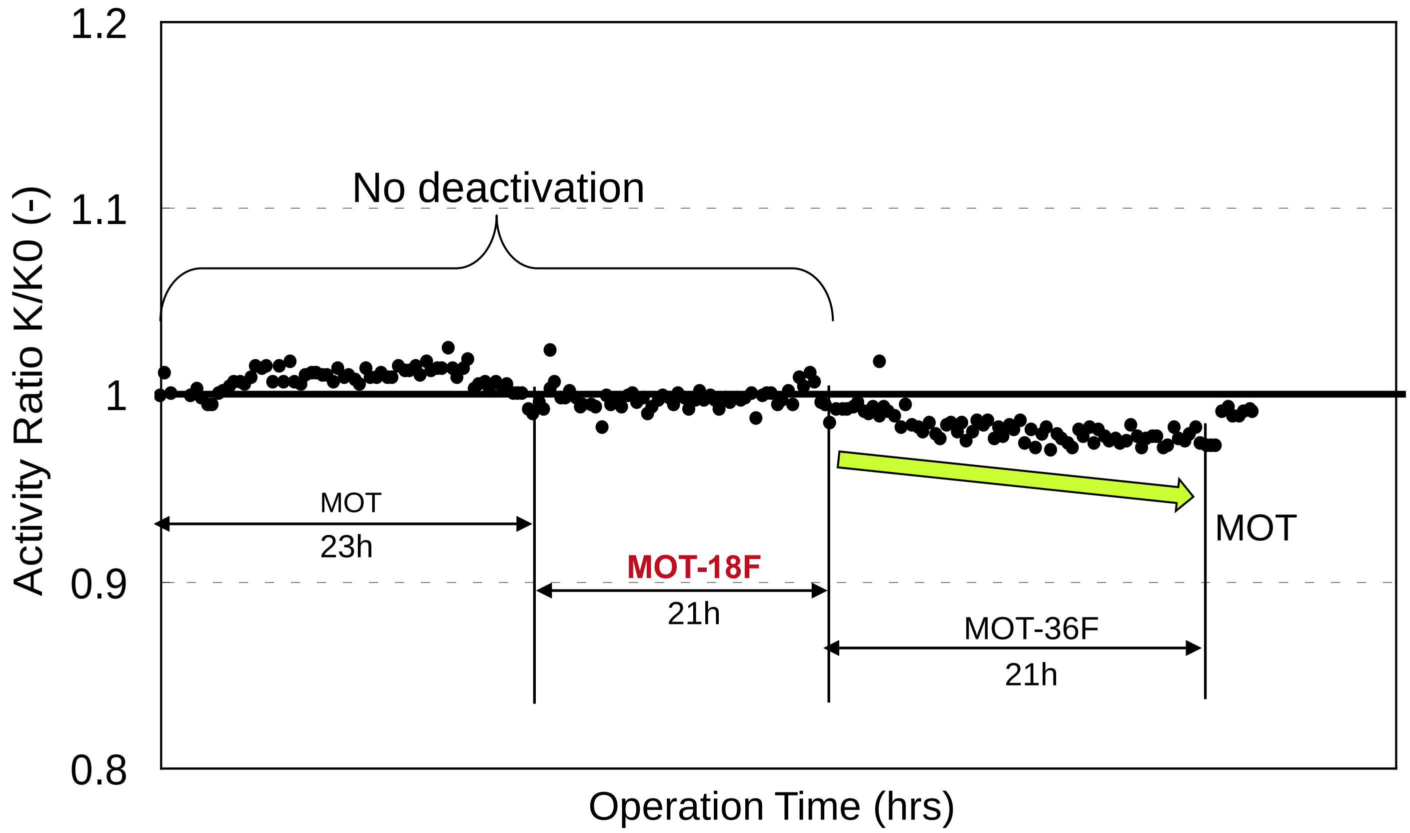
Catalyst Sample**(2.5" x 2.5" - 17.7")**

Item	Bench Scale Test Condition (Simulated Eastern Bituminous coal)
Inlet NOx	Approx. 400ppm
Inlet SO_3	Approx. 10 - 30 ppm
NH_3 / NOx	Approx. 0.9
MOT	Approx. 640 F
MIT	Approx. 580 F

Bench Scale test for reviewing MIT/MOT model was conducted with Newly developed TRAC® /CM catalyst

Test the Effect of Operating at between MOT and MOT-36

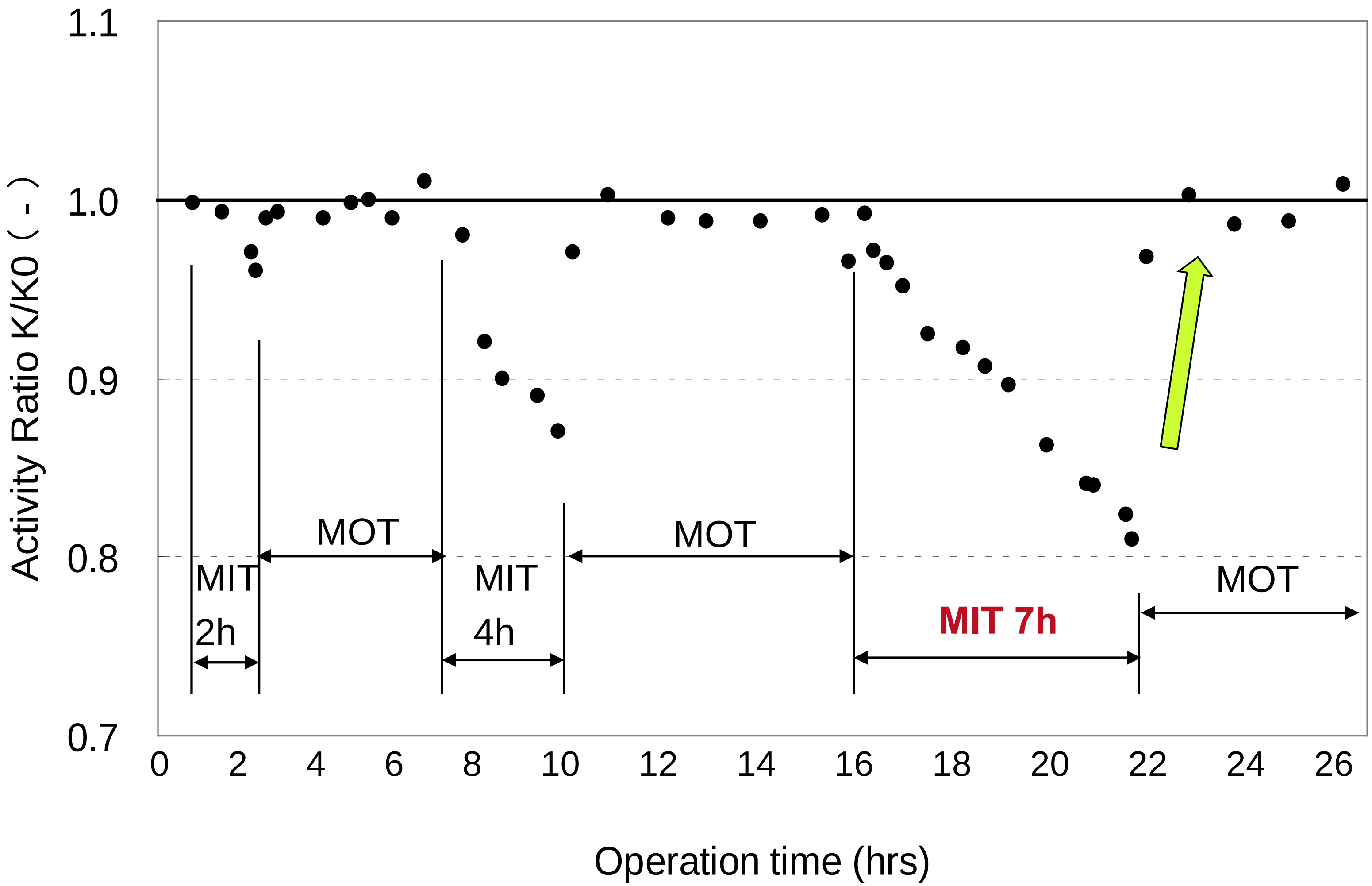
Test Pattern #1 : 23 Hr @ MOT, 21 Hr @ MOT-18, 21 Hr @ MOT-36, Recovery Time at MOT



No deactivation was observed at MOT-18F

Test the effects of MIT/MOT Cyclical Operation to Determine How Long Required to Run at MOT to Recover DeNOx Activity

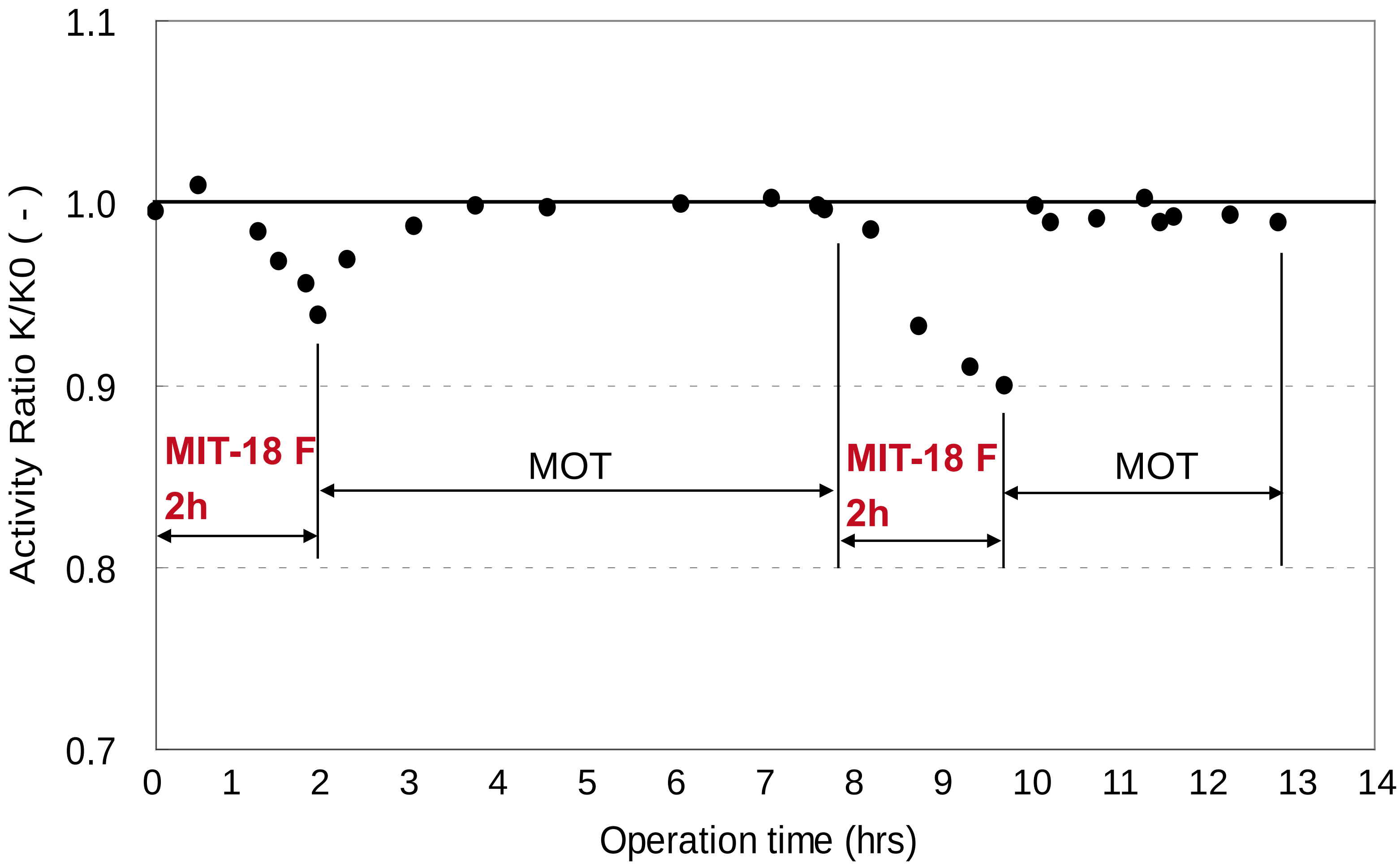
Test Pattern #2 : 2 Hr, 4 Hr, and 7 Hr Tests at MIT, Recovery Time at MOT



Although deactivation occurred at T_{ABS}, it was fully recovered by increasing temperature to MOT.

Test the Effects of MIT-18F/MOT Short Term Cyclical Operation on DeNOx Activity

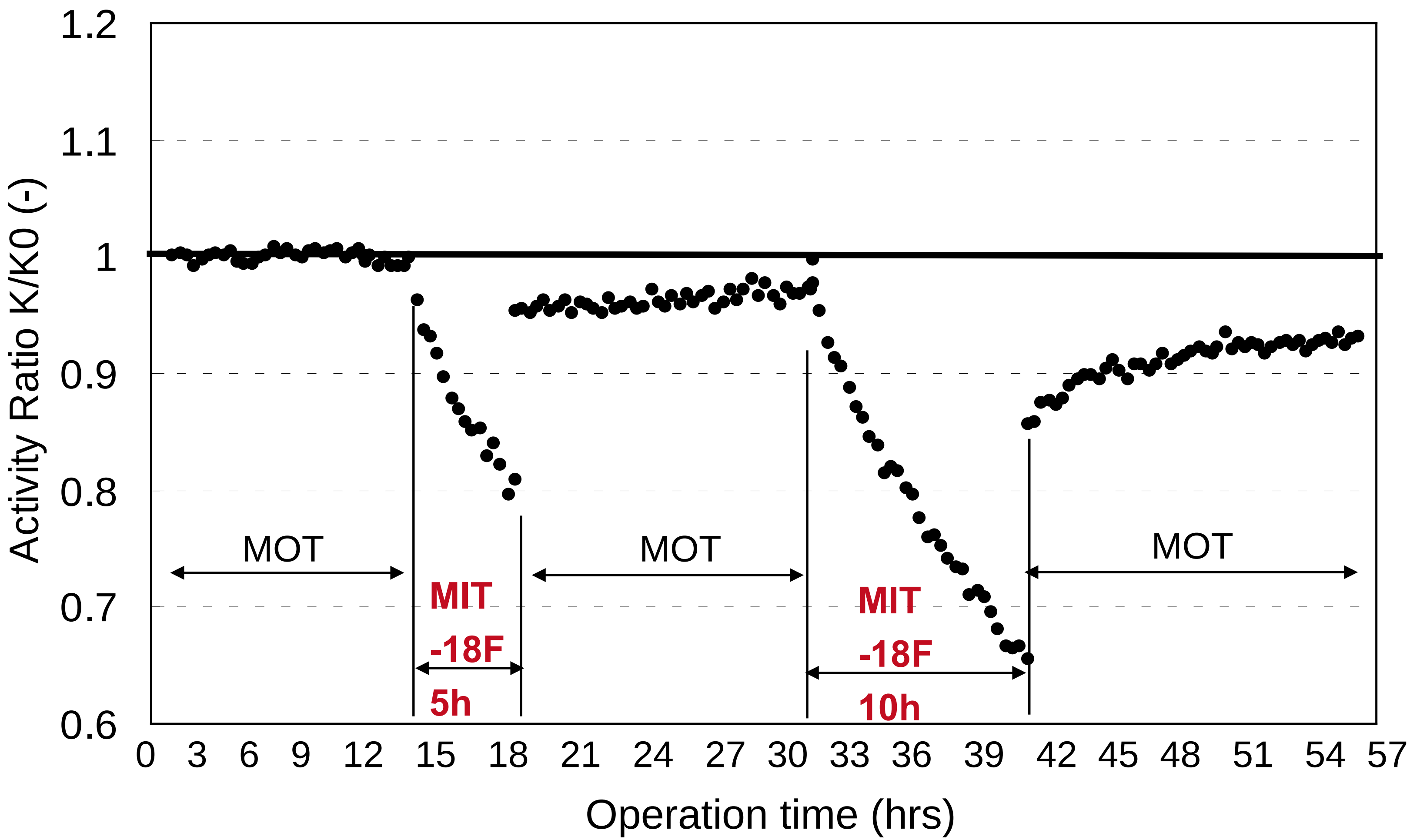
Test Pattern #3 : 2 Hr, Tests at MIT-18F, Recovery Time at MOT



Catalyst activity after short operating time (less than 2 hours) below T_{ABS} was fully recovered at MOT.

Test the Effects of MIT-18F/MOT Long Term Cyclical Operation on DeNOx Activity

Test Pattern #4 : 5 Hr and 10 Hr Tests at MIT-18F

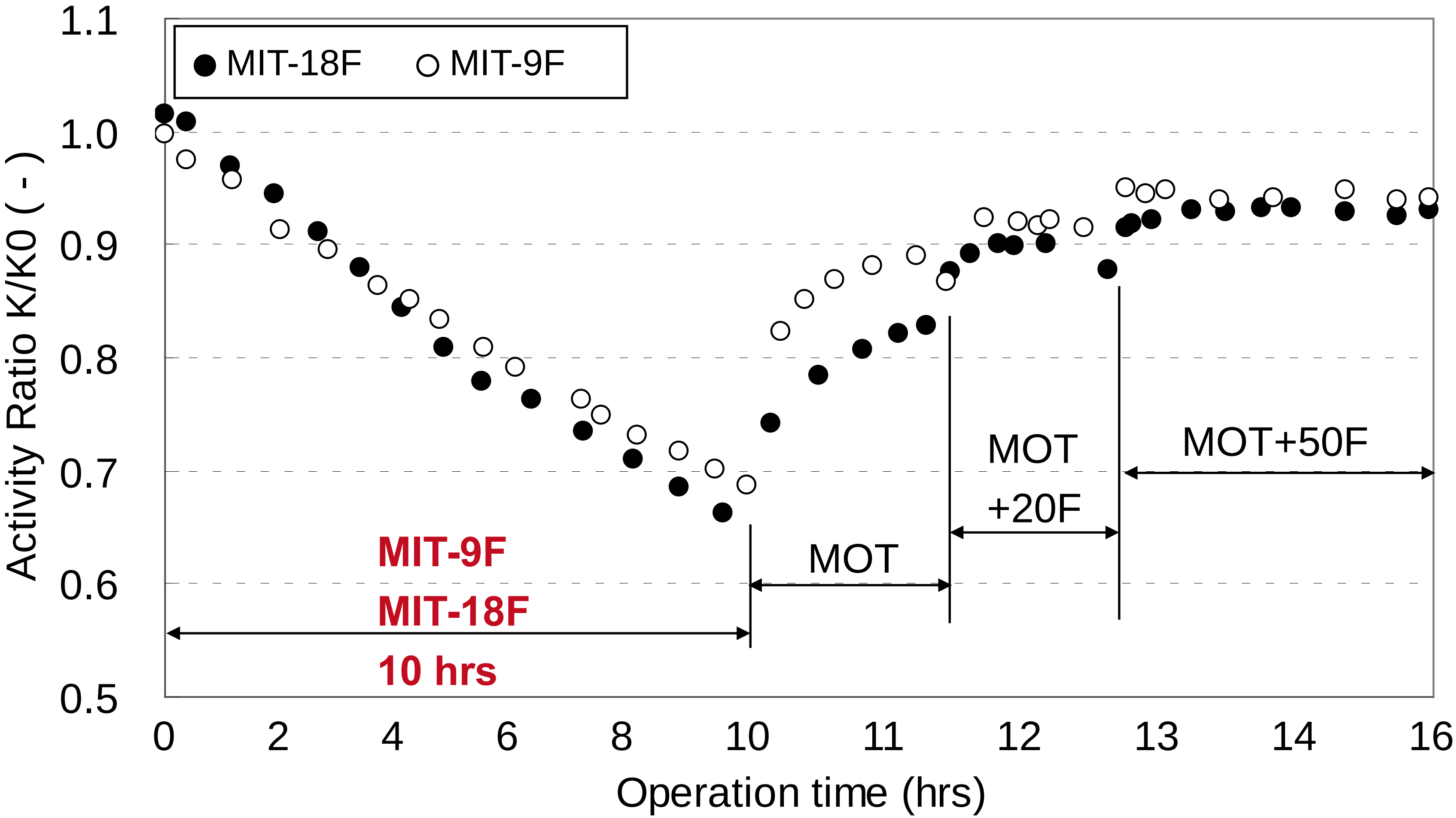


Catalyst activity after longer operating time (more than 5 hours) below T_{ABS} was not fully recovered at MOT.

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

Test Pattern #5 :10 Hr @ MIT -9 & -18,

Recovery Time @ MOT, MOT+20, MOT +50



Catalyst activity after longer operation (more than 10 hours) below TABS was not fully recovered even at temperatures above MOT.

*Review of MIT/MOT Model by **Bench Scale Test** (2)*

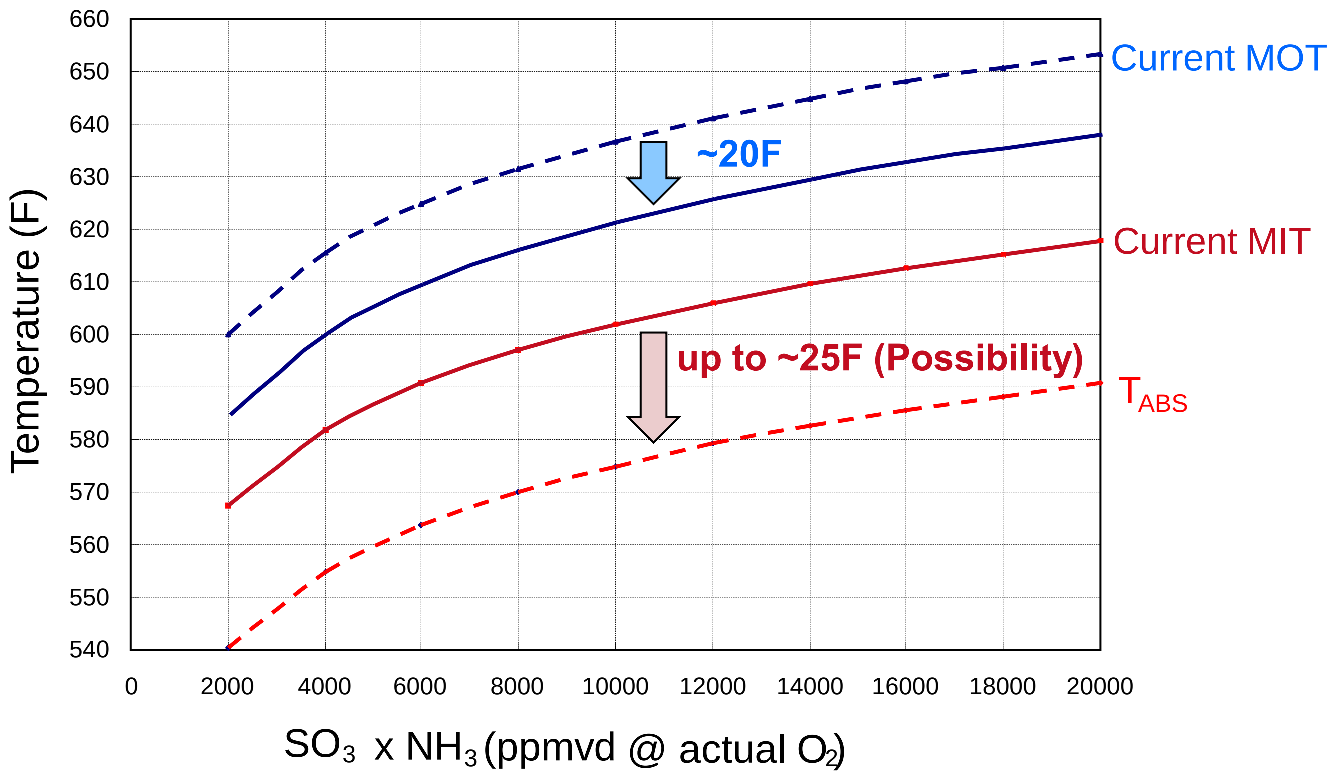
Summary of Bench Scale Test Results

Temperature	Bench Test Results
MOT	Not Deactivated
<MOT BUT >T_{ABS}	Not Deactivated at MOT-18^{o}F
T_{ABS} (Short Time)	Deactivated at T_{ABS} for 7 hours Fully recovered by MOT
< T_{ABS} (Short Time)	Deactivated at T_{ABS}-18^{o}F for 2 hours Fully Recovered by MOT
< T_{ABS} (Long Time)	Deactivated at T_{ABS}-18^{o}F for 5 and 10 hours Not able to be fully recovered by MOT/MOT+50^{o}F

T_{ABS} : ABS Formation Temperature at gas phase as same temperature as Minimum NH3 Injection Temperature

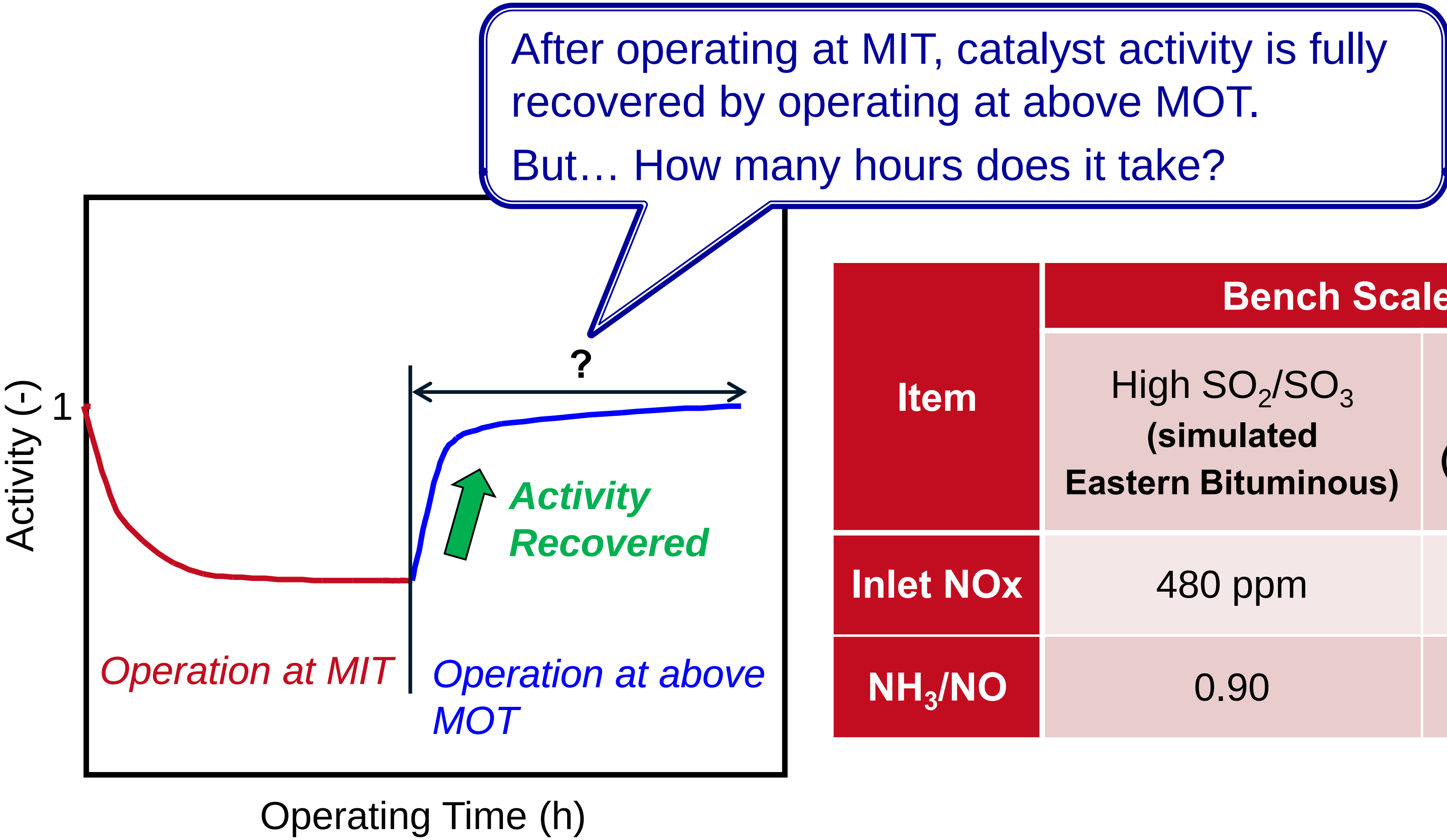
*Review of MIT/MOT Model by **Bench Scale Test** (3)*

- Bench test results show good match with MOT and T_{ABS} calculation.
- <u>No deactivation was observed at MOT-18 F</u>.
- Newly developed TRAC® /CM catalyst have <u>better pore structure</u> for ABS formation.



<u>For newly developed SCR catalyst, MOT can be reduced by ~20F</u>
without any impact on reliable operation.

Recovery Condition by **Bench Scale Test** (1)

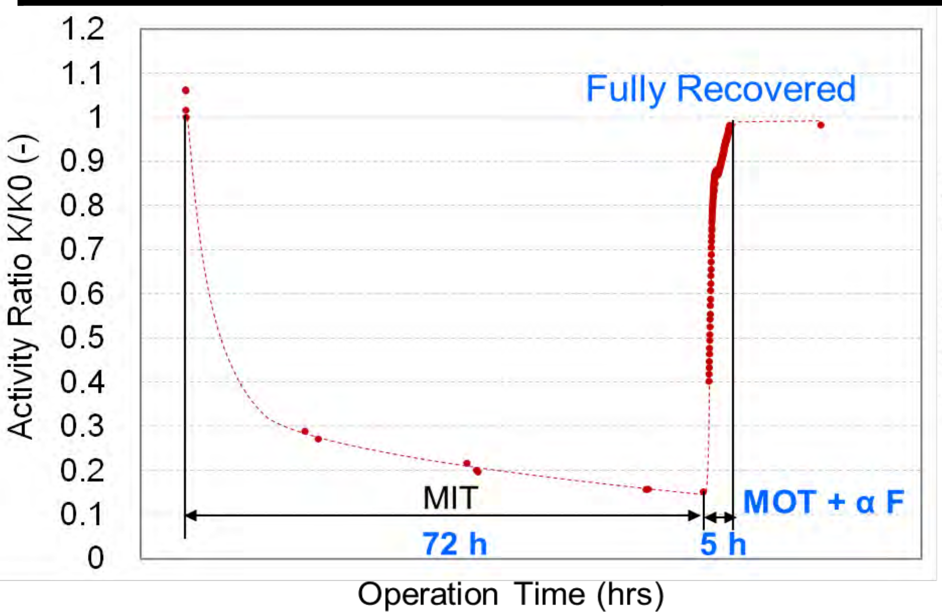


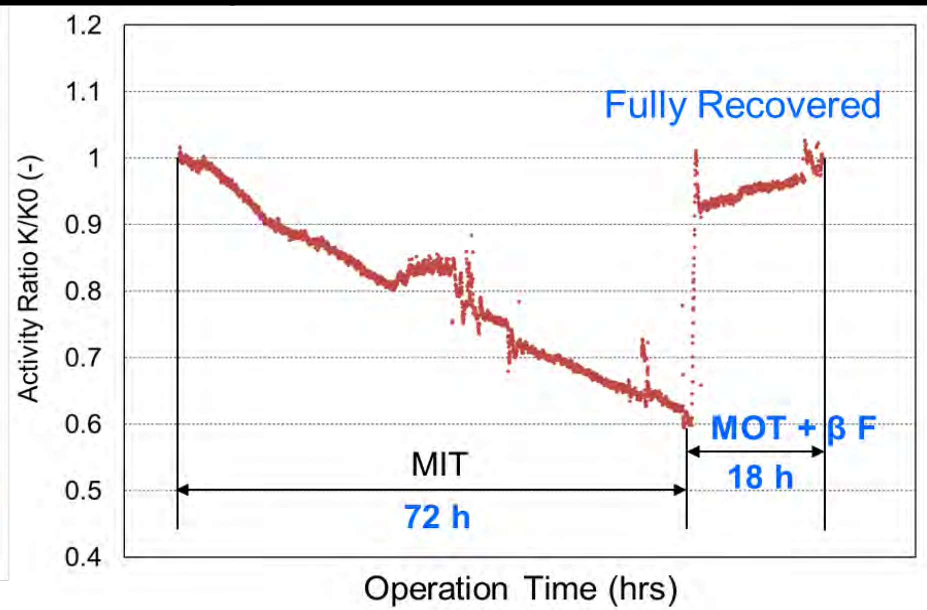
Item	Bench Scale Test	
	High SO_2/SO_3 **(simulated Eastern Bituminous)**	Low SO_2/SO_3 **(simulated PRB)**
Inlet NOx	480 ppm	200 ppm
NH_3/NO	0.90	0.85

Bench Scale test for confirming recovery condition was conducted under both of high and low SO_2/SO_3 condition

*Recovery Condition by **Bench Scale Test** (2)*

Item	High SO_2/SO_3 (Eastern Bituminous)	Low SO_2/SO_3 (PRB)
Allowable Operation Time at Low Load (MIT)	**72 hours**	**72 hours**
Recovery Temperature (F)	**≥ MOT + α F**	**≥ MOT + β F**
Recovery Time (hrs)	**≥ 5 hours**	**≥ 18 hours**

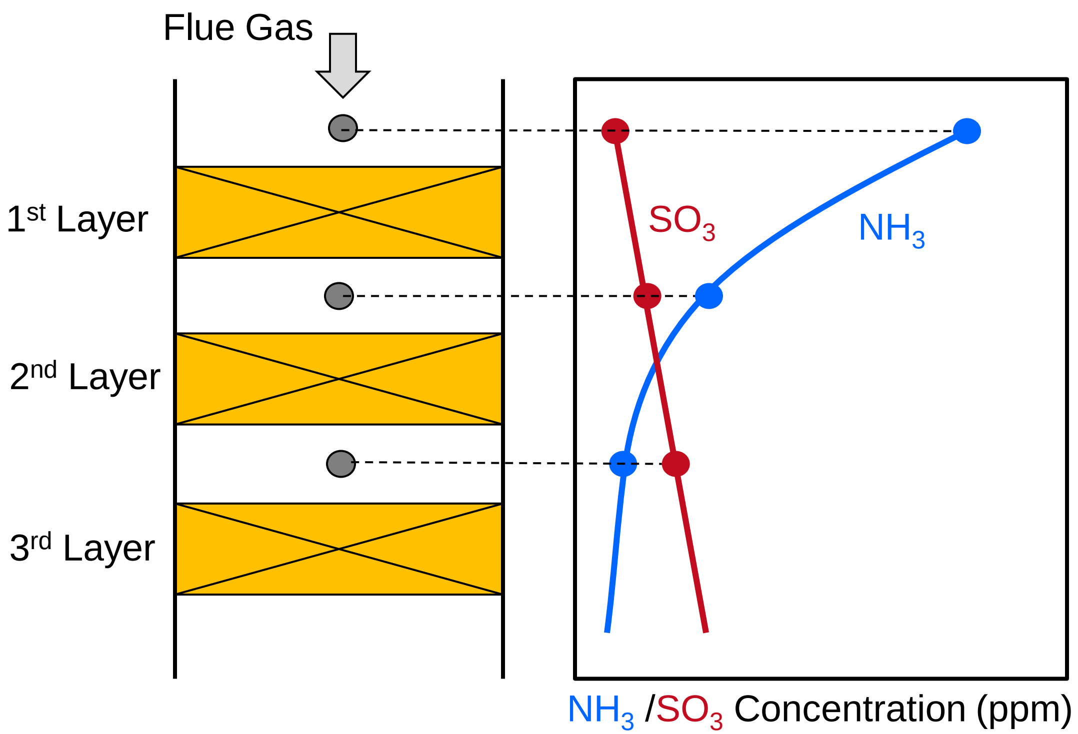


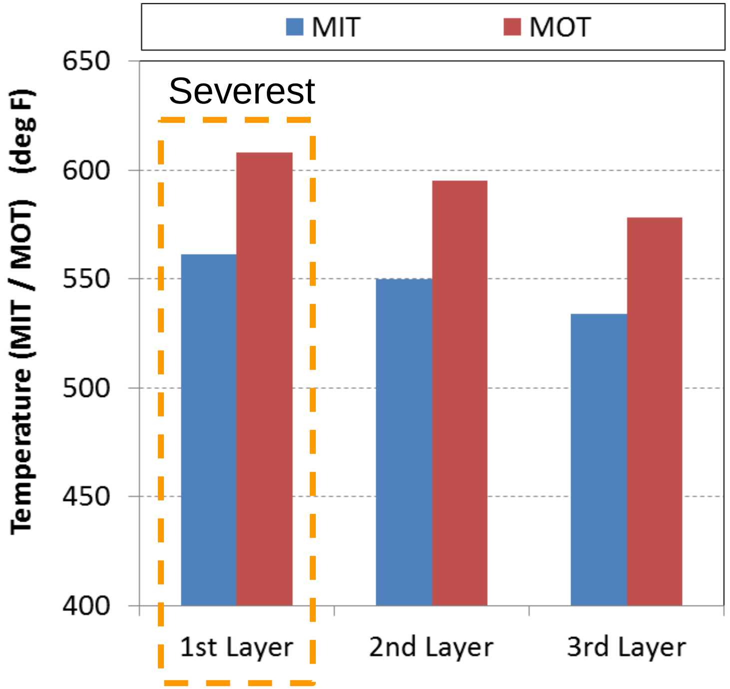


Allowable operation time at MIT is able to be increased to 72 hours
Recovery time should be related to the recovery temperature above

*Consideration of Low Load Operation **at Actual Plant***

Design Condition : NH_3/NO =0.9, NOx removal = More than 88%





- 1st layer is critical for ABS formation
- Real effect of ABS formation on catalyst activity should be considered based on the calculation with multi-layer structure for actual plant

Further Study on Expected Impact of ABS on Activity(1)

- ABS formation depends on SCR design flue gas condition
- Impact of ABS formation on catalyst activity is related to pore structure
- Performance across all layers shall be based at each layer inlet condition

SCR Design Condition

- Catalyst Type
- Area Velocity
- Temperature
- SO_3 @each layer
- NH_3 @each layer

→

Expected Performance

- Expected Plugged Pore Structure Portion

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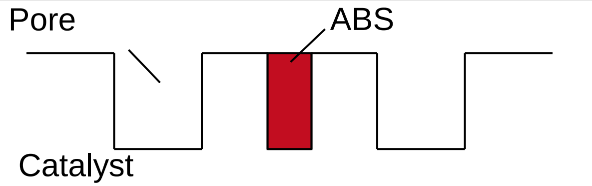
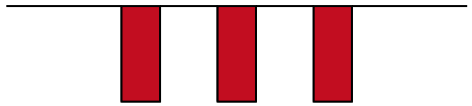
- Expected Activity Loss

Further Study on Expected Impact of ABS on Activity(2)

<table>
<tr><th>Catalyst</th><th>Catalyst A</th><th>Catalyst B</th></tr>
<tr><td>Pore Size</td><td>Large</td><td>Small</td></tr>
<tr><td>Deterioration by ABS</td><td>Small</td><td>large</td></tr>
<tr><td>Recovery</td><td>Easy</td><td>Difficult</td></tr>
<tr><td>Model</td><td>
</td><td></td></tr>
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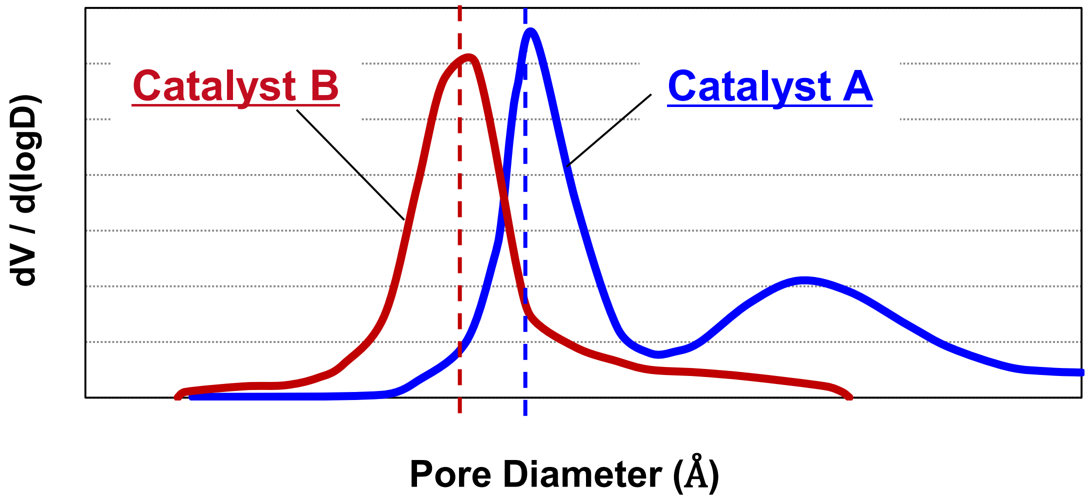
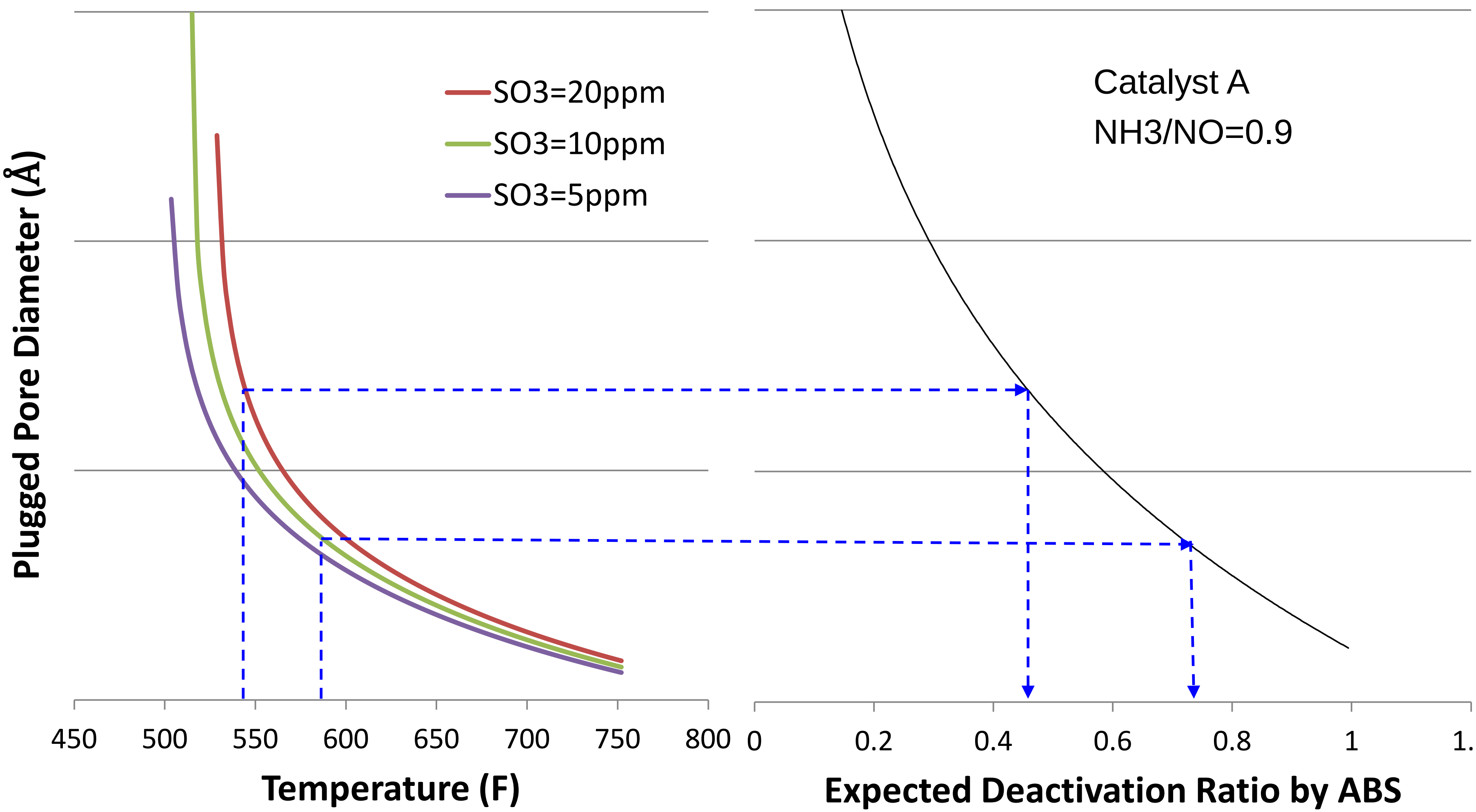


Pore structure of catalyst can be controlled while keeping activity and erosion resistance for coal firing plant

Further Study on Expected Impact of ABS on Activity(3)



Effect of ABS could be calculated based on catalyst base data with activity, pore structure in order to expect deterioration at low load

Summary and Conclusion

1. MOT calculated by ABS formation reaction model is well corresponding to the test results obtained at both laboratory and bench scale test facilities.

2. DeNOx activity could be recovered at proposed recovery condition for both high sulfur and low sulfur coal firing flue gas condition.

3. Multi-layer calculation shall be needed to determine real effect of ABS formation

4. Further study on low load operation will be done at Slipstream reactor testing and actual plant for a reliable operation