Reinhold Environmental Ltd.

2009 NOx-Combustion Round Table & Expo Presentation

February 9 & 10, 2009, Cleveland, OH

SO2-SO3 Oxidation & Thin Wall Thickness

NOx Roundtable, Cleveland OH
February 10, 2009

Nick Macsata-Alstom Power Inc.
Tetsuo Kodama-Hitachi Zosen Corp.

We are shaping the future | ALSTOM

Agenda

- **SO$_3$ Formation and Impact on Performance**
  - Formation of SO$_3$
  - Impact on Performance
  - Factors Impacting SO$_3$ formation
- **Thin Wall Oxidation Reduction**
  - Test procedure
  - Adsorption of SO$_3$
  - Influence of NH$_3$
  - Surface Area (Area Velocity)
  - Temperature
- **Catalyst Manufacturing Types**
- **Thin Wall Stability**
- **Conclusion**

POWER SERVICE | ALSTOM

SO_3 Formation and Impact on Performance

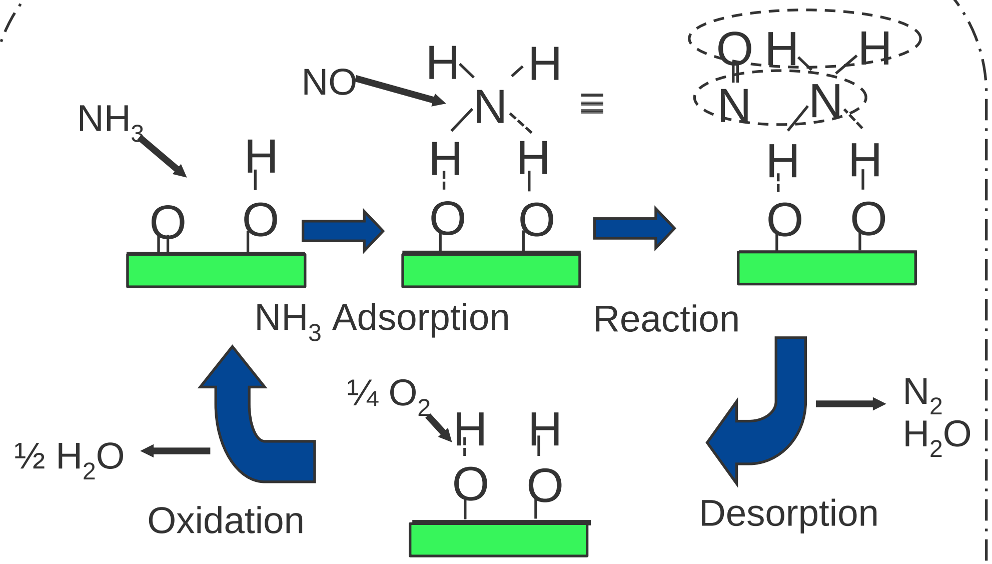
- **SO_3 Formation and Impact on Performance**
  - Formation of SO_3
  - Impact on Performance
  - Factors Impacting SO_3 formation

POWER SERVICE | ALSTOM

SO_3 Formation

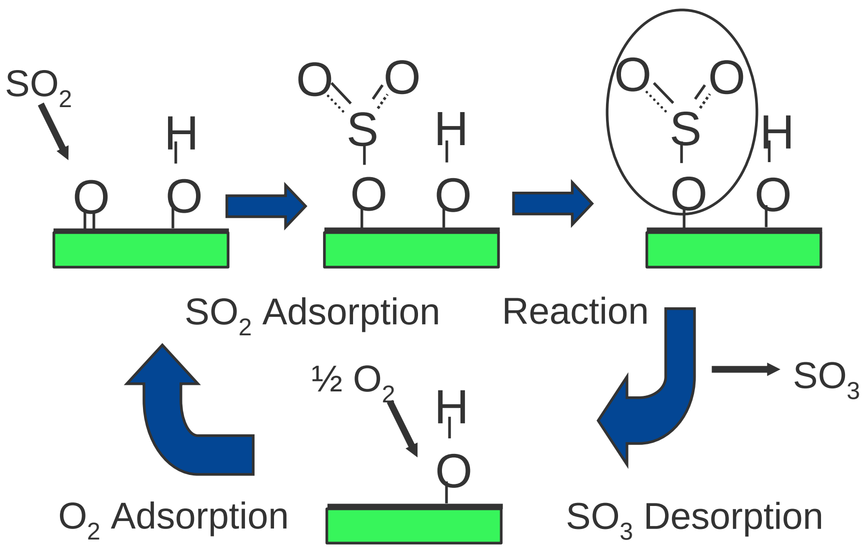
- During combustion, sulfur existing in fuel, is converted into SO_2
- At the Inlet of SCR reactor, SO_3 is contained approx. 1% of total SOx
- SO_2 is adsorbed with Vanadium, the main reagent in active SCR catalysts, and is oxidized into SO_3
- SO_2 oxidation rates are determined by the activity of the SCR catalyst

Reactions at Catalyst's Active Sites



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

SCR Reaction at active sites



$$2SO_2 + O_2 \rightarrow 2SO_3$$

SO_2 Oxidation at active sites

POWER SERVICE | ALSTOM

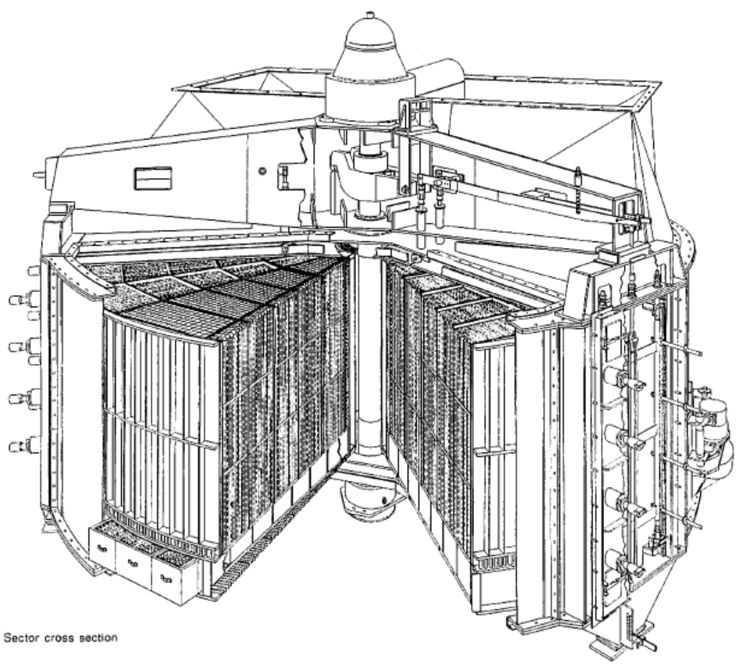
SO_3 Formation Impact

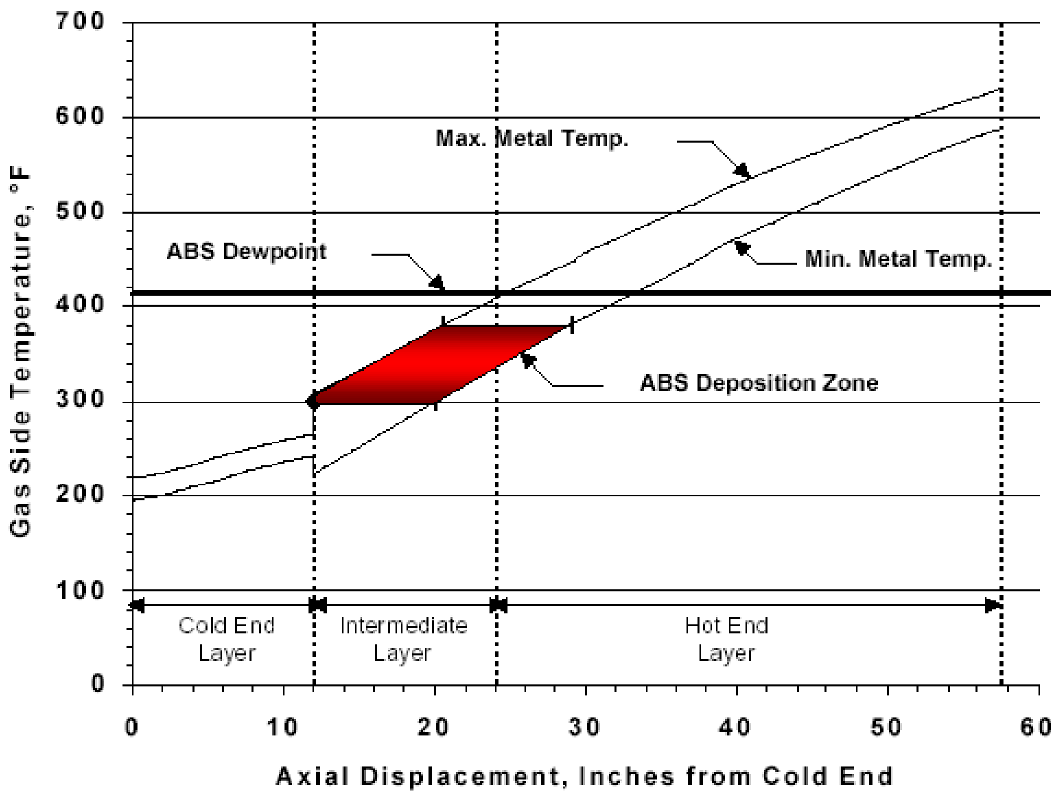
- Both Ammonium Sulfate, $(NH_4)_2SO_4$, and/or Ammonium Bisulfate, NH_4HSO_4, are formed within a critical temperature zone when flue gas contains various levels of SO_3
- Critical temperature zone typically occurs at the Air Pre-Heater
- The sulfur content found in most American coals results in Ammonium Bisulfate, NH_4HSO_4 formation
- Ammonium Bisulfate, NH_4HSO_4, causes Air Pre-Heater plugging

POWER SERVICE | ALSTOM

NH_4HSO_4 Impact on the Air Pre-heater

- “Sticky” Ammonium Bisulfate, NH_4HSO_4, causes Air Pre-Heater plugging





NH_4HSO_4 Impact on the Air Pre-heater

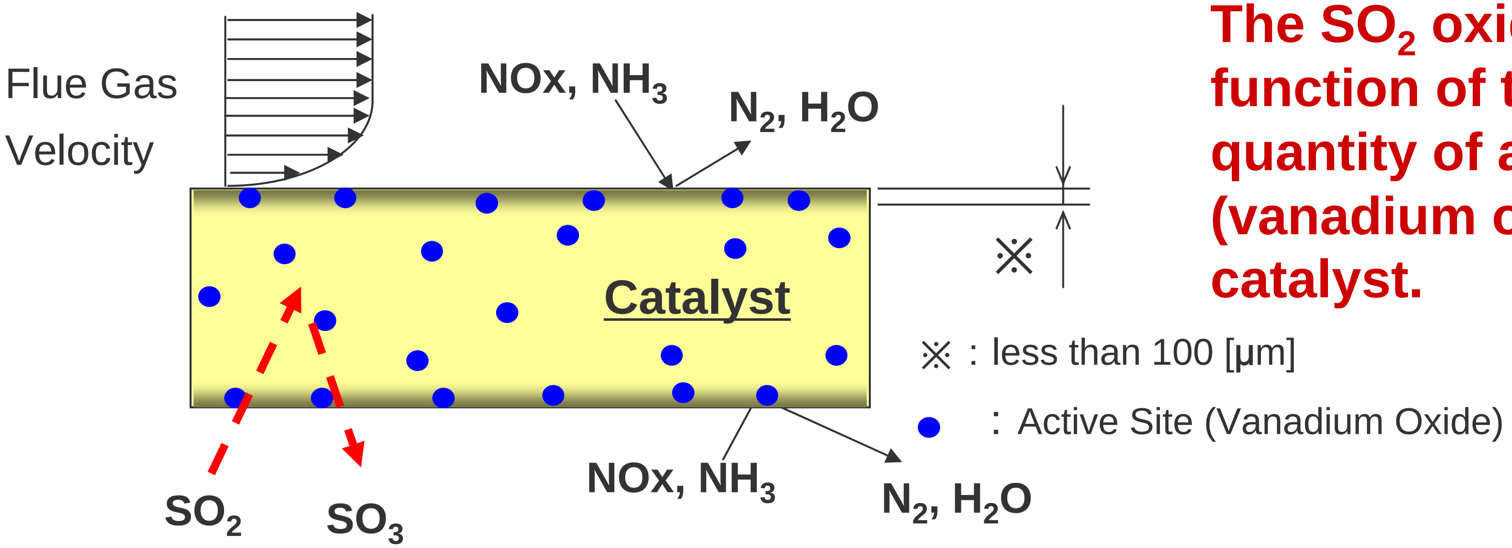
- “Sticky” Ammonium Bisulfate, NH_4HSO_4, causes Air Pre-Heater plugging

Cold End Layer (upper face)

Intermediate Layer (side view)

SO_3 Formation – Catalyst Mass

- The SCR reaction is a fast reaction that occurs within the 100 microns of a catalyst surface.
- Unlike the SCR reaction, SO_2 oxidation occurs **throughout** the catalyst mass.



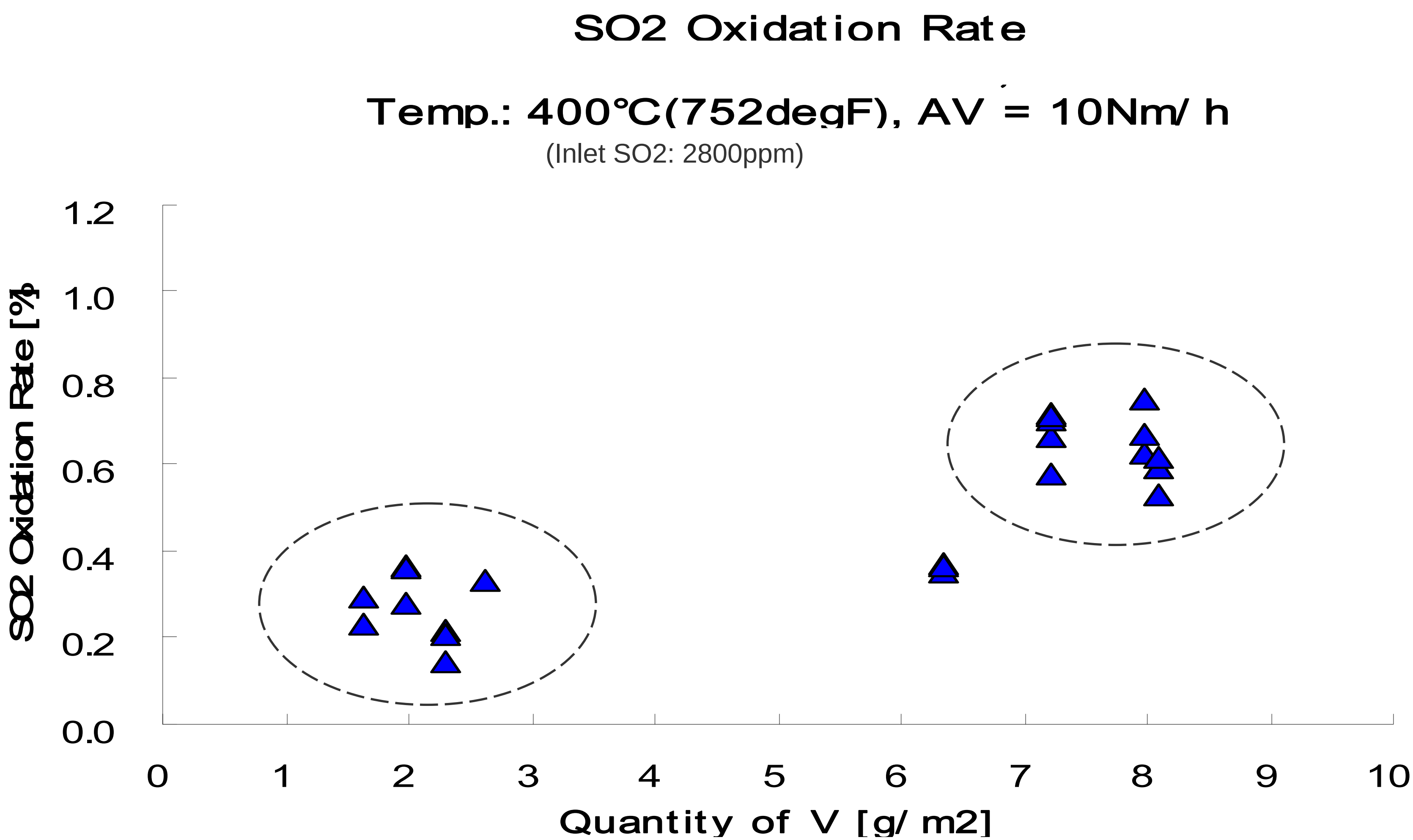
The SO_2 oxidation rate is a function of the total quantity of active sites (vanadium oxide) in the catalyst.

SCR Reaction : $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$

SO_2 Oxidation : $2SO_2 + O_2 \rightarrow 2SO_3$

Reducing SO_2 Oxidation – Vanadium Content



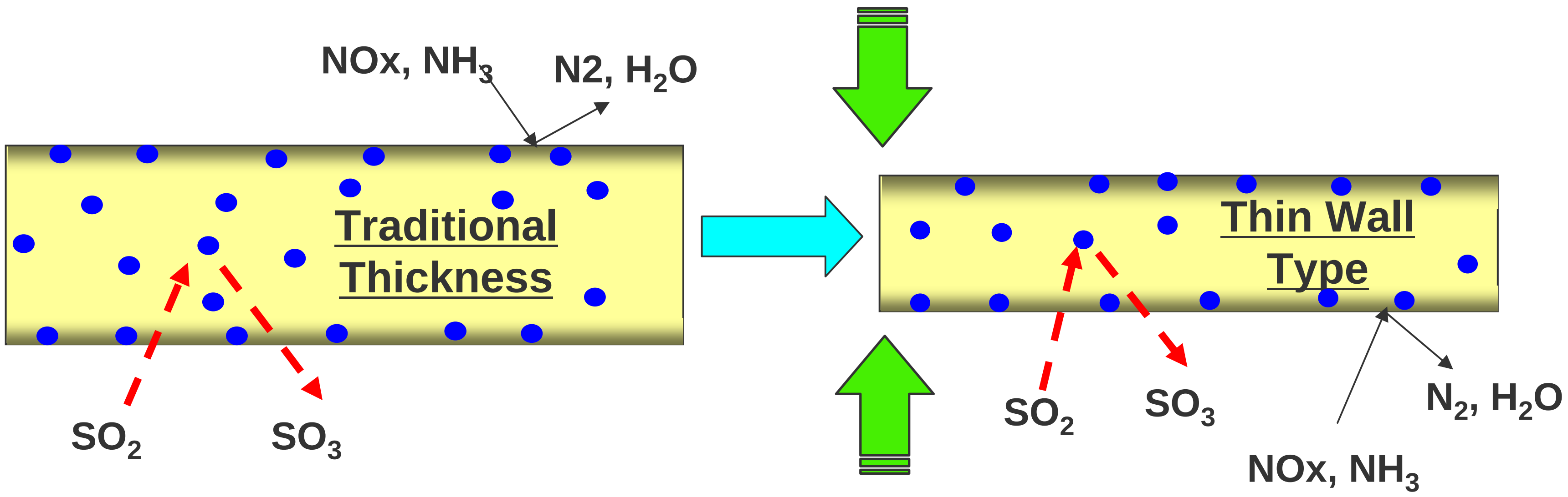
POWER SERVICE | ALSTOM

Reducing SO_2 Oxidation

•Although the thickness has been reduced, the "density" of the active site at the catalyst's surface has not changed.

•There is no differences in the NOx Reduction Rate after reducing the Catalyst thickness.

•**There IS a reduction in SOx Oxidation Rate!**



POWER SERVICE | ALSTOM

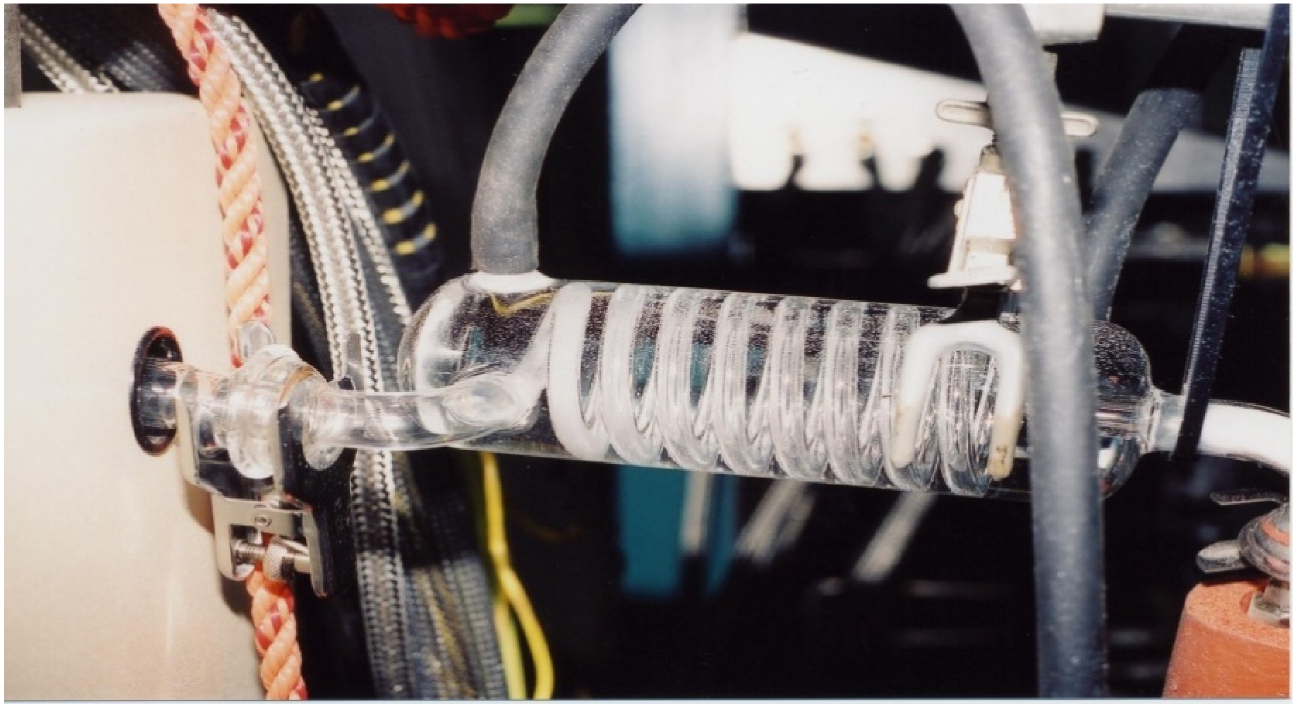
Thin Wall Oxidation Reduction

- **Thin Wall Oxidation Reduction**
  - Test procedure
  - Adsorption of SO_3
  - Influence of NH_3
  - Surface Area (Area Velocity)
  - Temperature

POWER SERVICE | ALSTOM

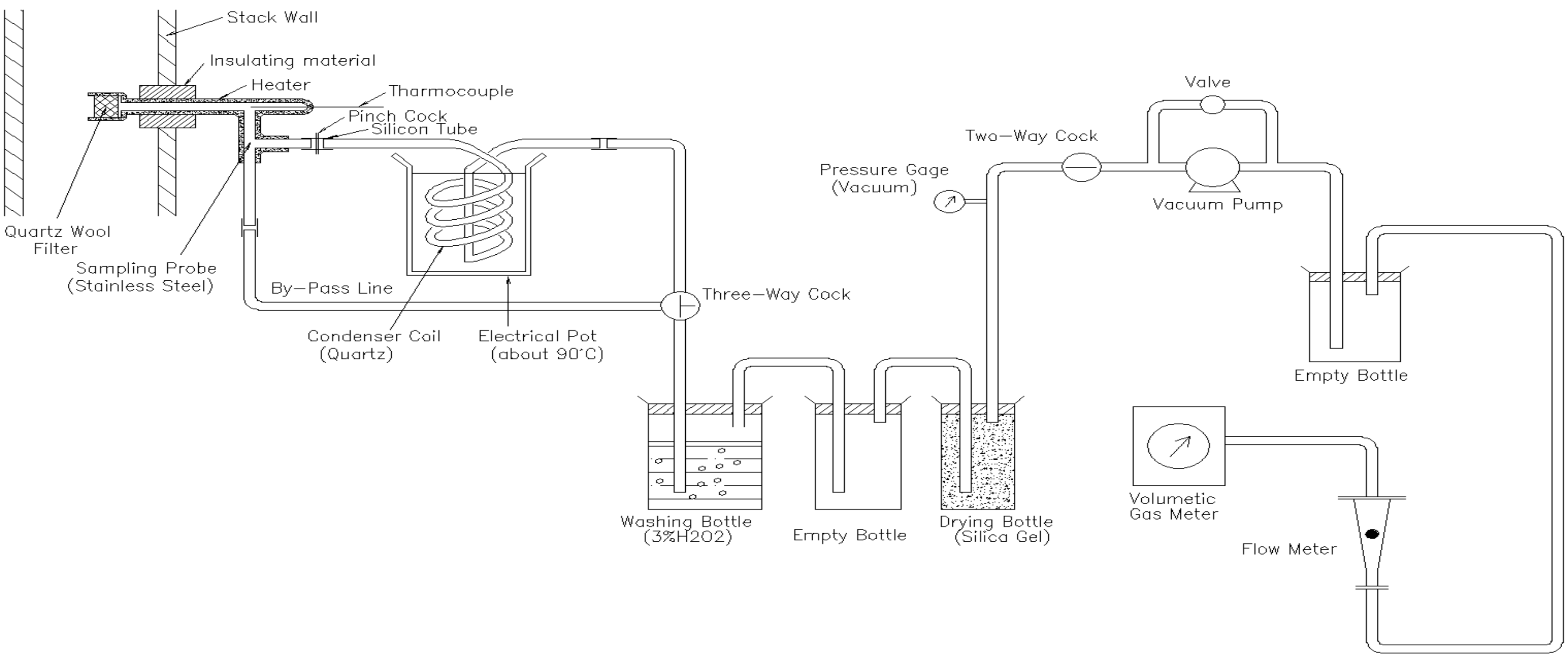
Measuring SO_3 for Determining SO_2 Oxidation Rate

- To measure SO_3, we utilized the "Helical Tube Capture Test"
- The Helical Tube is very effective for accurate measurement of SO_3



POWER SERVICE | ALSTOM

SO_3 Sampling Train for Testing



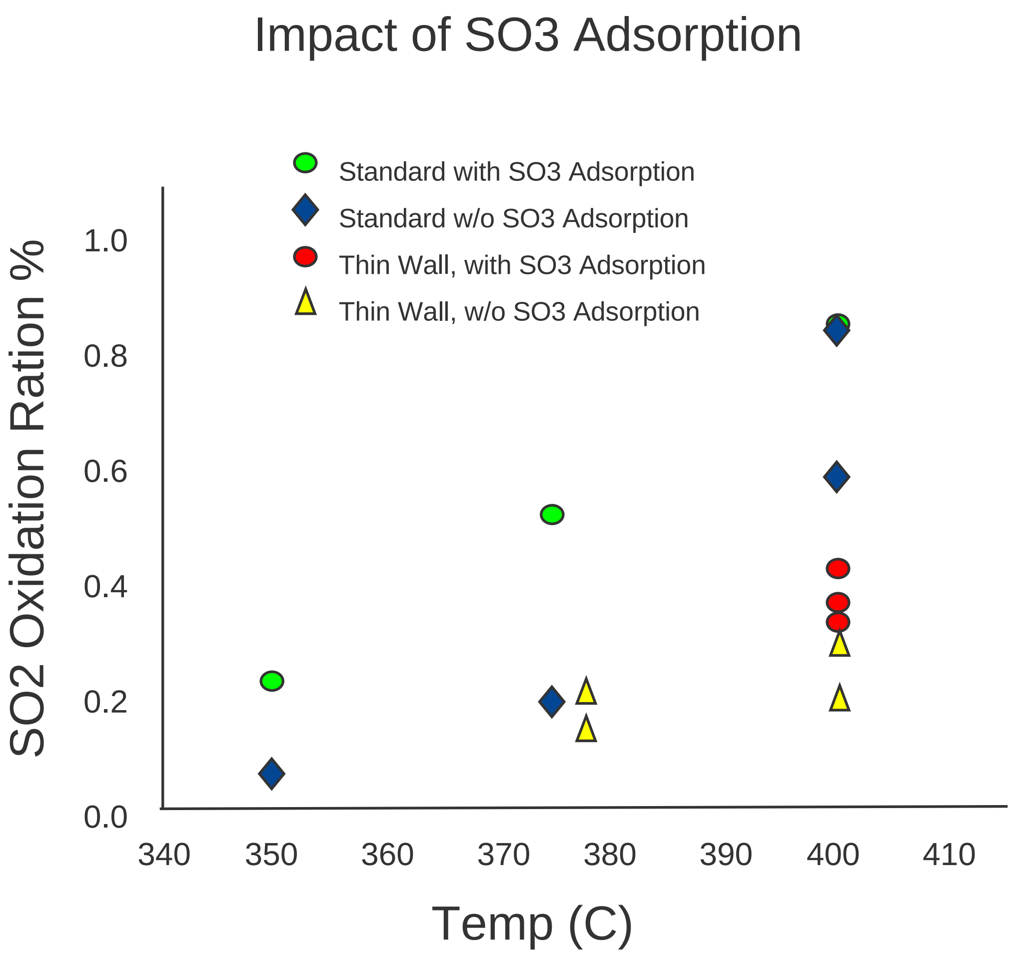
Schematic Diagram of Sampling Train for SO_3 measuring

Test Procedure

- A bench scale apparatus with 4 catalyst layers was used.
- The control catalyst was the K-Max substrate.
- The following parameters were controlled to simulate the actual gaseous operating conditions of the SCR reactor;
  - Gas composition,
  - Temperature,
  - Gas velocity and catalyst's area velocity,
  - NH_3 volume ratio.

POWER SERVICE | ALSTOM

SO_3 Adsorption & SO_2 Oxidation Rate



- At startup, SO_3 is adsorbed onto the catalyst layer for up to 50 hours
- Up to 50 hours there is a natural increase until saturation

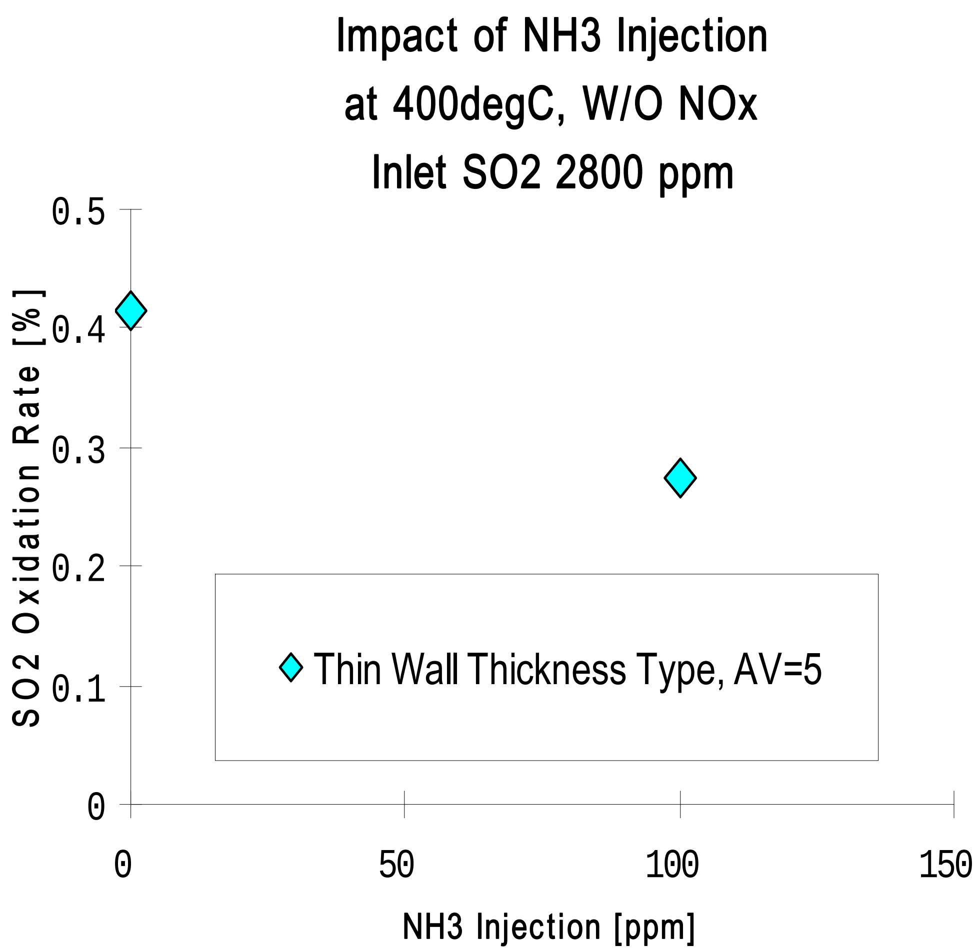
-This phenomenon is temperature dependent

-At 400C There is a higher trend for SO_2 oxidation

-Thin Wall thickness maintains lowest rate of Oxidation

POWER SERVICE | ALSTOM

NH_3 Influence for SO_2 Oxidation



- 0.4mm-thick.
- No NOx in this test
- Entire catalyst surface is exposed by same concentration of NH_3 [ppm].
- Captured active sites by NH_3 limits the SO_2 oxidation.
- IMPACT: Lower rates of NH_3 results in Higher Rates of SO_2 oxidation

POWER SERVICE | ALSTOM

Definition of Area Velocity

Definition of Area Velocity:

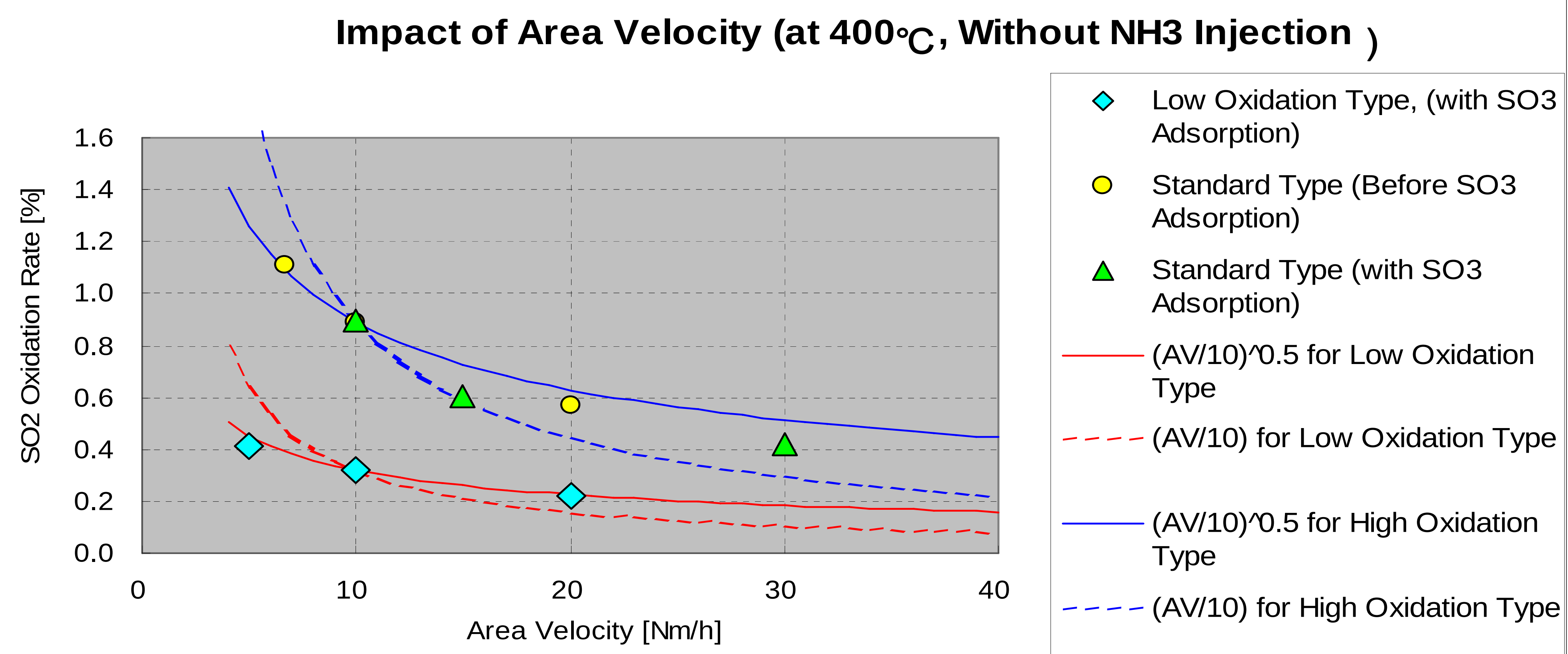
$$AV = Q / A$$

AV= Area Velocity [$Nm^3/m^2 \cdot hr$]

Q = Flue gas flow rate [Nm^3/hr]

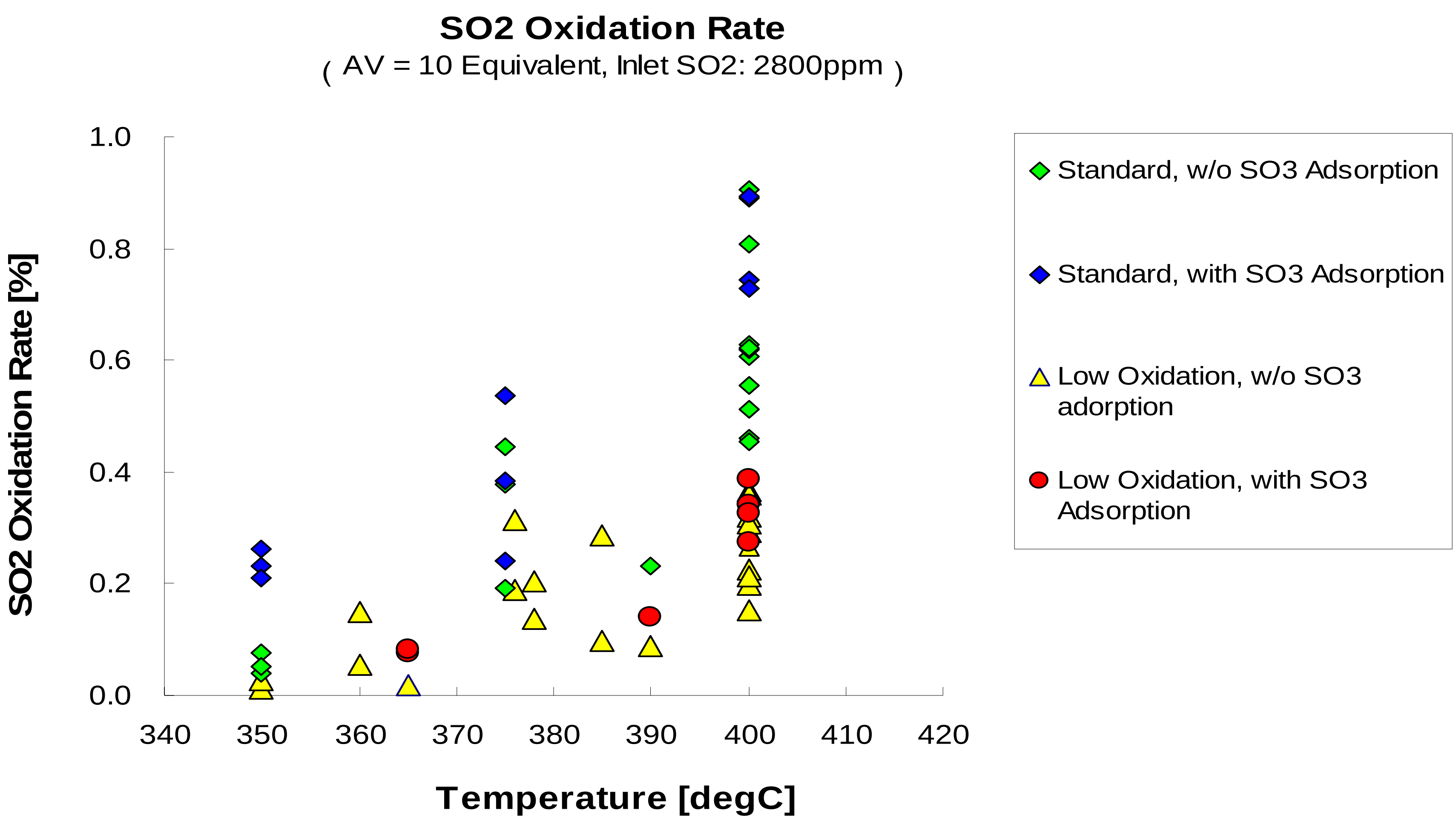
A = Contact Surface Area [m^2]

Impact of Area Velocity @400degC(752degF)



POWER SERVICE | ALSTOM

Impact of Temperature for SO_2 Oxidation Rate



POWER SERVICE | ALSTOM

Testing Summation

1) SO_2 oxidation rate depends on the catalyst's Vanadium Content

2) Adsorption rate increases after the initial ~50hrs of operation

3) NH3 impacts oxidation rates, More NH3=Less Oxidation

4) As temperature increases, SO2 Oxidation increases

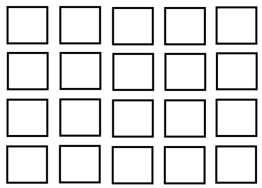
5) As Area Velocity increases SO2 Oxidation decreases

6) Thin Wall catalysts maintained the lowest rates of oxidations for all the aforementioned variables

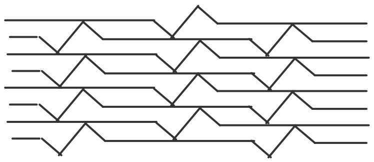
Catalyst Manufacturing Types

- **Catalyst Manufacturing Types**

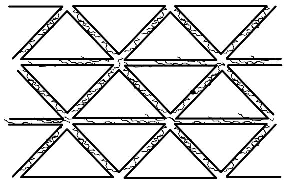
Catalyst Manufacturing History and Variation



Extrude Honeycomb



Plate



Triangular Corrugated

’70

’80

’90

’00

Extrude Type

Plate Type

Triangular /Metal Plate

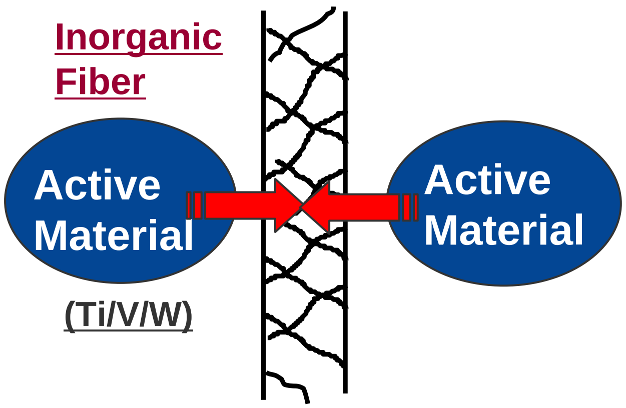
Triangular /Hybrid

POWER SERVICE | ALSTOM

Corrugated Catalyst Manufacturing

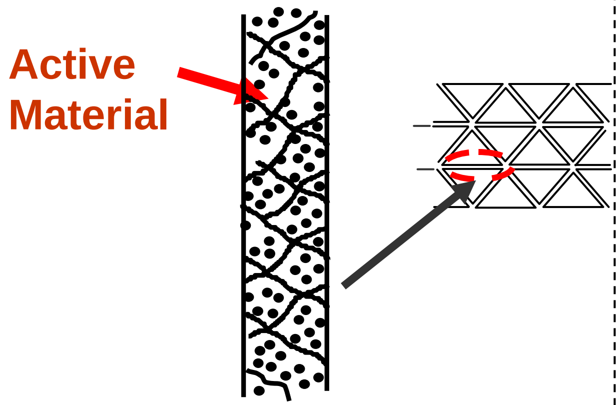
(1) Catalyst Active Material are impregnated inside of the Fiber Matrix.

(2) Both Active Materials and Fibers are united after calcification.



The Fiber Matrix contains inner room, Active materials can be impregnated into this space.

(1) Impregnation of Active Materials



After the calcination process, both Fiber Sheet and “Ceramic” Active Materials are united.

After completion, we cannot separate them.

(2) United strongly after Calcinations

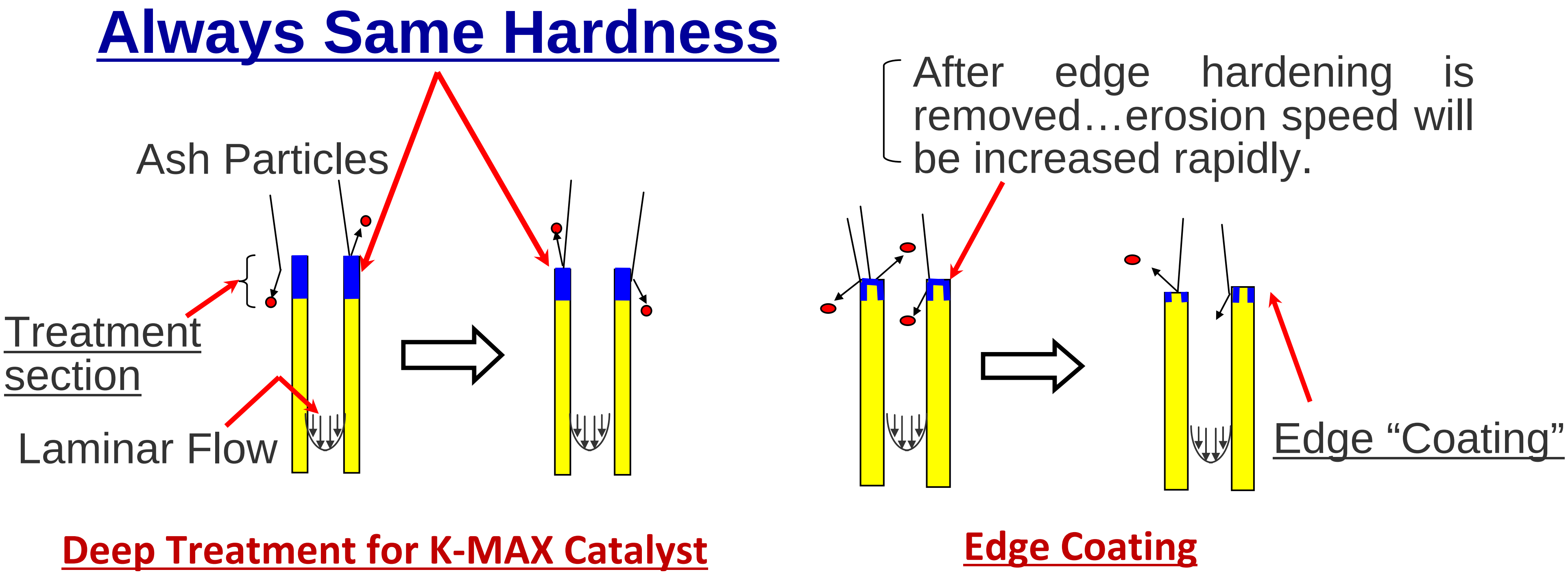
POWER SERVICE | ALSTOM

Thin Wall Stability

- **Thin Wall Stability**

POWER SERVICE | ALSTOM

Deep vs. Edge Hardening

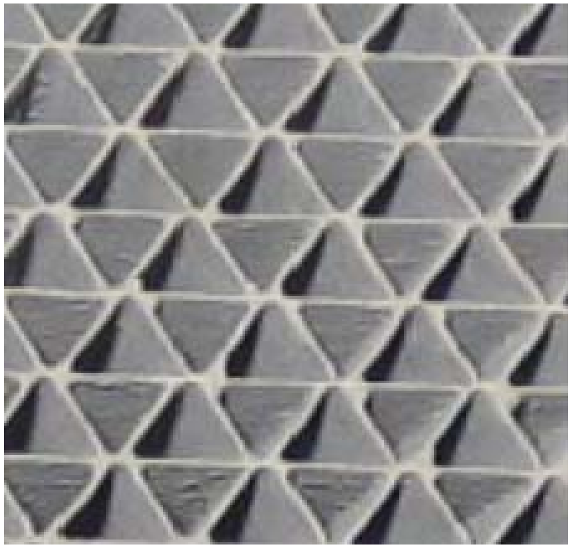


- Since this "Hardening Treatment" is applied not only the surface but also the inside of catalyst monolith, the erosion speed is the same.

POWER SERVICE | ALSTOM

Deep Hardened Application

Deep Hardening for Catalyst



(1) <u>Catalyst End Facing Incoming Gas</u>

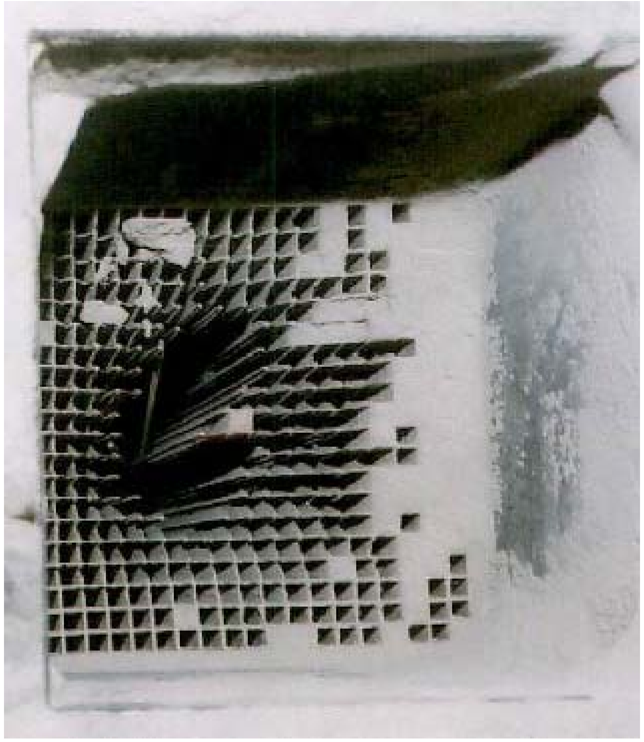
(after several years operation in Taiwan Plant)

POWER SERVICE | ALSTOM

Deep vs. Edge Hardening

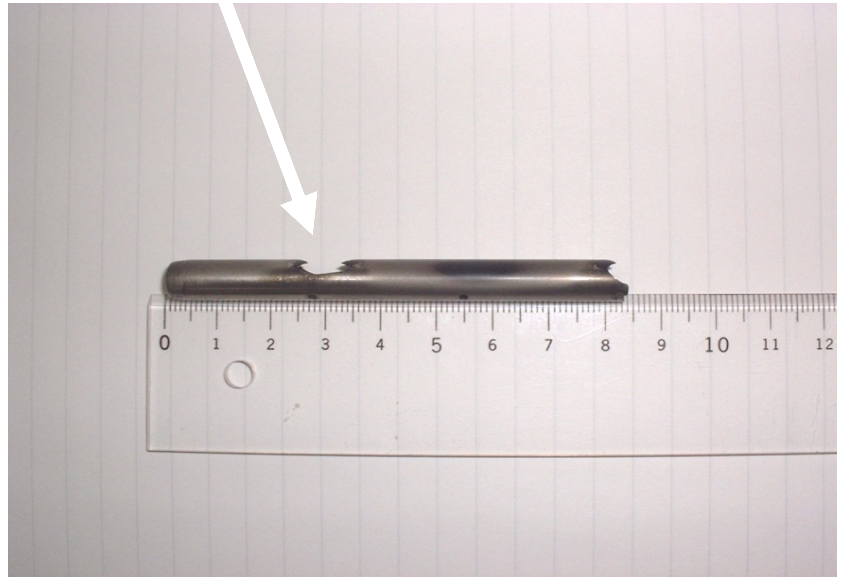
Deep Hardened Catalyst

Edge Hardened Catalyst



POWER SERVICE | ALSTOM

Thin Wall Toughness

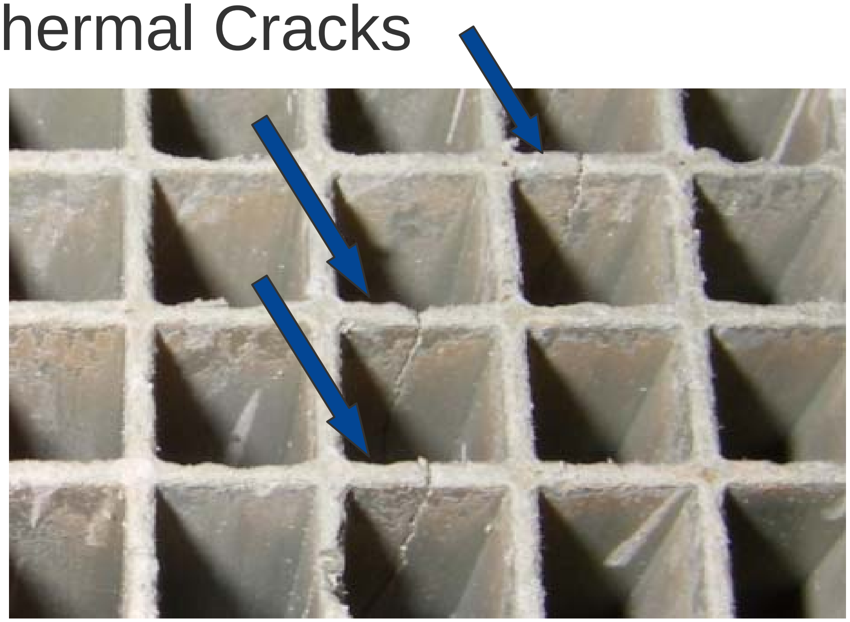


- At Ontario Power, during a performance test <u>the Stainless Steel tube</u>, located above the catalysts, <u>was broken by flyash erosion</u>. There was NO damage to the catalyst.

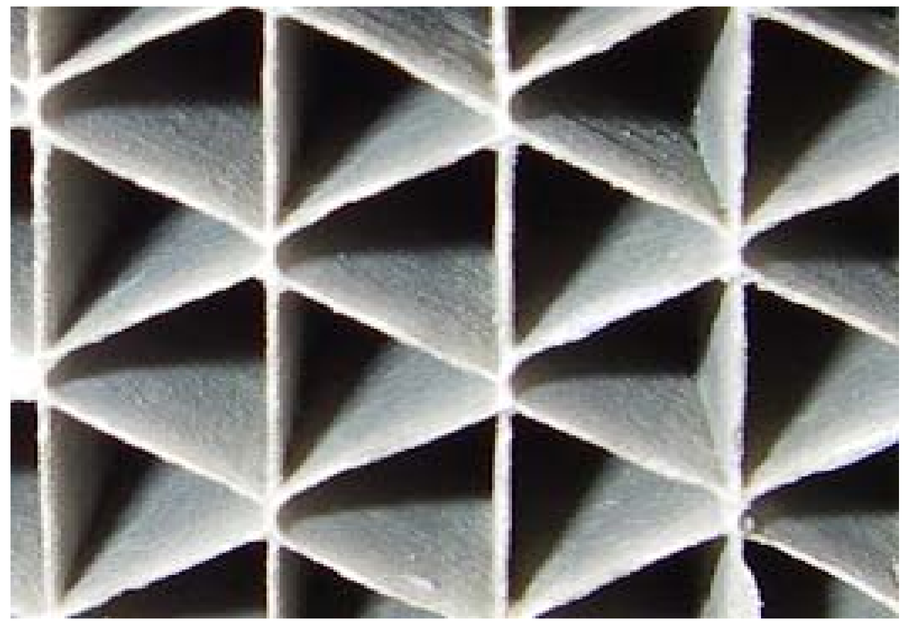
Fiber Matrix Tough

- Inside a SCR system the temperature change can be up to 100 deg F
- Typical Catalysts can receive “Thermal Shock”
- Thin Wall fiber matrix resists “Thermal Shock”

Thermal Cracks



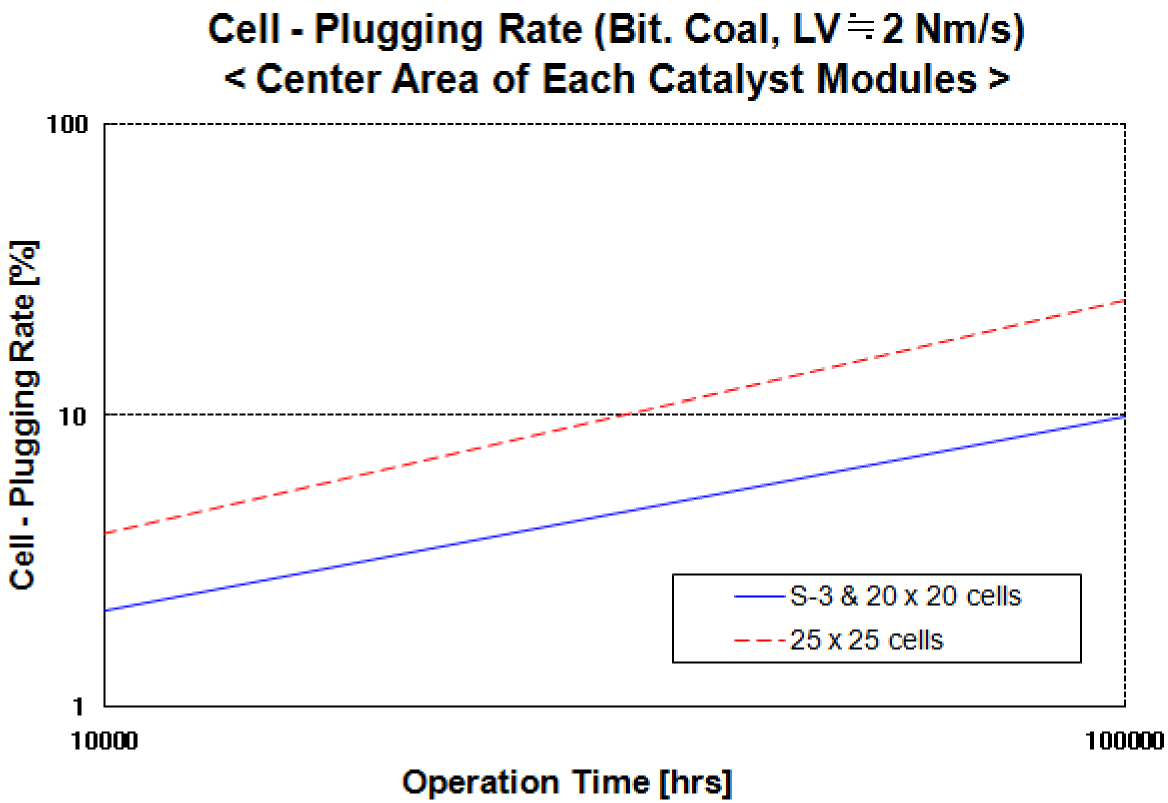
Operated
Extruded Type Cat.

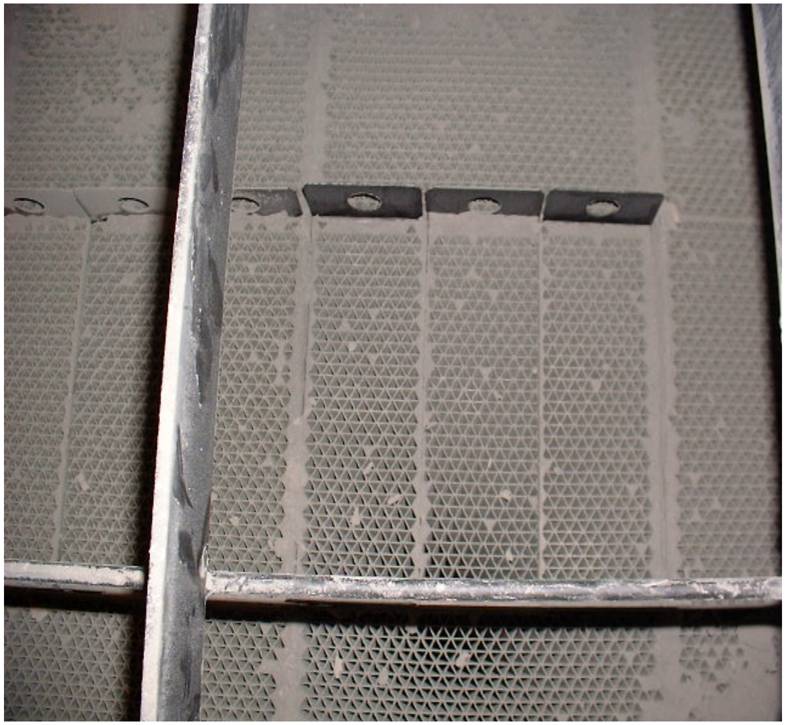


Operated
Thin Wall

High Density, Thin Wall, Low Plugging

Thin Wall catalyst provides high geometric surface area, it's plugging rate is less than the 25x25 cell honeycomb catalyst, which has similar density.





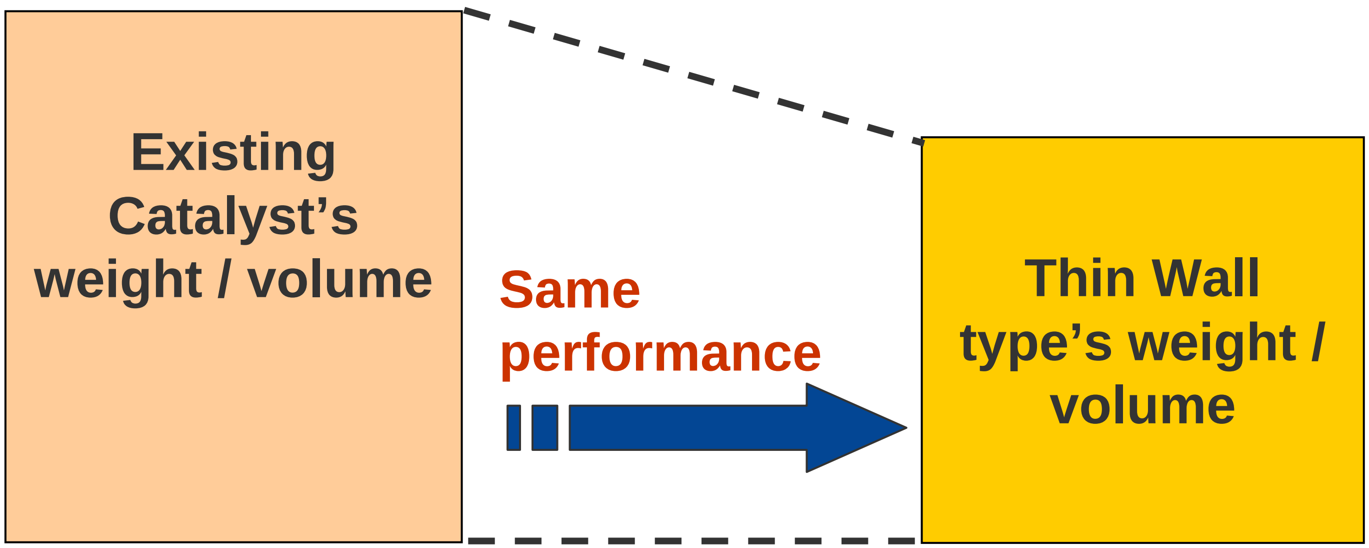
POWER SERVICE | ALSTOM

Additional Thin Wall Advantages

HIGH SUBSTRATE DENSITY

“Thin Walls = Less Total Volume” and “Light Weight”

We can achieve the same Area Velocity (= same SCR Performance) w/o any modifications of Reactor



POWER SERVICE | ALSTOM

Additional Thin Wall Notes

- **Thin Wall Catalysts <u>can</u> be Regenerated**
  - **Regeneration of Thin Wall Catalyst requires special consideration**
    - **Regeneration techniques may vary from traditional regeneration techniques**
    - **Requires careful washing**
    - **Apply Chemical treatment to remove poisoning**
    - **Re-apply a Chemical treatment of active materials**
- **Thin Wall Catalyst washing is not recommended by users without guidance**
  - **This is due to the wide variation in customer washing techniques**
  - **To ensure proper protection of the Active materials when considering washing, consult your catalyst manufacturer**

POWER SERVICE | ALSTOM

Conclusion

- Ammonium Bisulfate at Pre-heater is one of the biggest issue regarding the SCR Catalyst due to SO_3 formation
- Wall Thickness influences the SO_2 oxidation
- Thin Wall Thickness maintains the NO_x reaction, while minimizing the SO_2 oxidation
- Thin Walls using Fiber Matrix manufacturing technology are as, if not more durable than traditional catalyst manufacturing methods
- Fiber Matrix corrugated catalysts have less plugging, and higher density than traditional catalysts, while minimizing SO_2 oxidation

Questions? Comments?

Please visit the ALSTOM booth for any further discussions, and to view actual catalyst materials.

Thank you!

K-MAX CATALYST

POWER SERVICE | ALSTOM