REINHOLD ENVIRONMENTAL Ltd.

2011 NOx-Combustion Round Table & Expo Presentation

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Reinhold Conference
NO_X Roundtable

Evonik Energy Services

The Benefits of Re-Calcination for Regenerated Catalyst Longevity

Mark Ehrnschwender

February 8, 2011

EVONIK INDUSTRIES

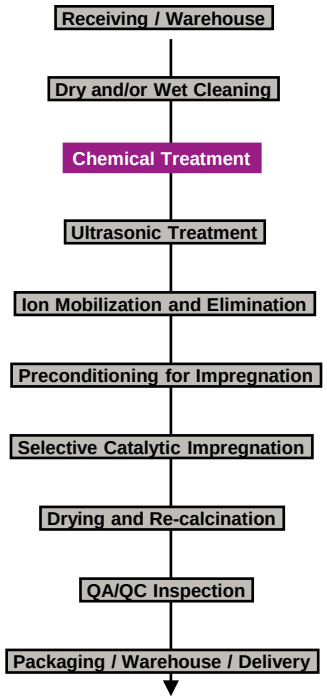
Nomenclature

- **Cleaning = Removal of physical restrictions such as blinding layers and large particle ash – can be done on-site as well as off-site.**
- **Rejuvenation = Removal of catalyst poisons without the need for replenishing catalytically active compounds – can sometimes be done in-situ, but is most commonly done either on -site or off-site.**
- **Regeneration = Removal of catalyst poisons plus restoration of catalytic activity by addition of catalytically active ingredients – can typically not be done in-situ or on-site, but should be done off-site to ensure required close process control.**
- **Re-Calcination = The heating of the catalyst for a prolonged period of time below the sintering point of the catalyst.**

Evonik‘s Bergkamen Power Station

Evonik‘s Fenne Cogeneration Plant

Catalyst Regeneration



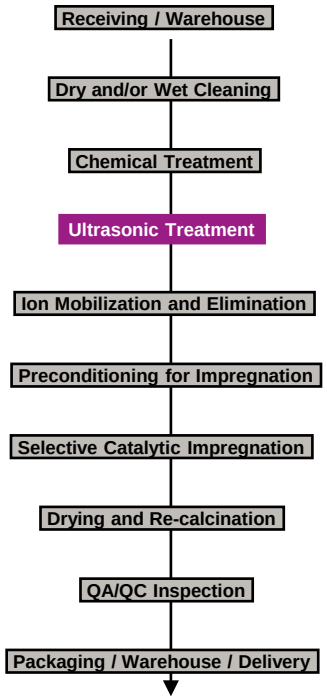
Evonik's Catalyst Regeneration Process

Evonik's Regeneration Process Steps

Multi-stage wet chemical treatment for poison removal:

- **Complex combinations of treatment time, pH, surfactants, chemical types, concentrations and temperature.**
- **Very precise process control to maintain stable process conditions including continuous removal of solids and replacement of spent solution.**
- **Tailored to avoid unwanted activation of metal ions (i.e. α-Fe_2O_3 to γ-Fe_2O_3) while maximizing their removal.**
- **Minimization of unwanted removal of active compounds (i.e. V_2O_5, WO_3) and damage to glass fibers.**

Catalyst Regeneration



Evonik's Catalyst Regeneration Process

Evonik's Regeneration Process Steps

Ultrasonic treatment:

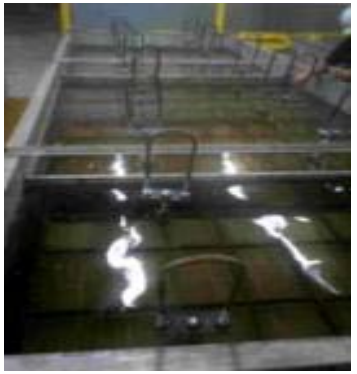
- **Time, pH, concentration and temperature controlled solution in the ultrasound.**
- **Very precise process control to maintain stable process conditions including continuous removal of solids and replacement of spent solution.**
- **Significant damage can occur to catalyst from ultrasonic energy, therefore ultrasound is only used when really needed.**

Catalyst Regeneration

Receiving / Warehouse
Dry and/or Wet Cleaning
Chemical Treatment
Ultrasonic Treatment
Ion Mobilization and Elimination
Preconditioning for Impregnation
Selective Catalytic Impregnation
Drying and Re-calcination
QA/QC Inspection
Packaging / Warehouse / Delivery

Evonik's Catalyst Regeneration Process

Evonik's Regeneration Process Steps



Ion mobilization and elimination:

- **More advanced, complex compounds but fewer chemicals used for cation mobilization.**
- **Highly effective cation elimination, especially of γ-Fe_2O_3 is very critical for achieving a low SO_2/SO_3 conversion rate.**
- **Critical for preparation for *Selective Impregnation*^{SM}**

Evonik's Patent Pending Process

Catalyst Regeneration

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Evonik's Catalyst Regeneration Process

Evonik's Regeneration Process Steps

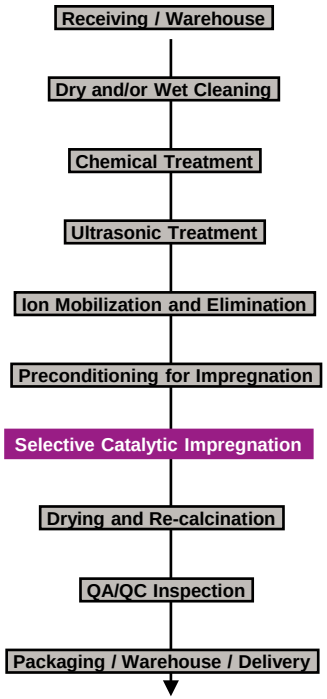


Pre-conditioning for *Selective Impregnation*[SM] :

- **Effective removal of all cleaning reagents and residual chemicals from the prior treatment.**
- **Controlled drying to a defined residual moisture content:**
  - **Catalyst module can hold up to 500 lbs. of water.**
  - **Catalyst drying after pre-conditioning / neutralization / rinsing and catalyst critical for correct impregnation.**

Evonik's Patent Pending Process

Catalyst Regeneration



Evonik's Catalyst Regeneration Process

Evonik's Regeneration Process Steps

***Selective Impregnation*^{SM} of catalytic activity:**

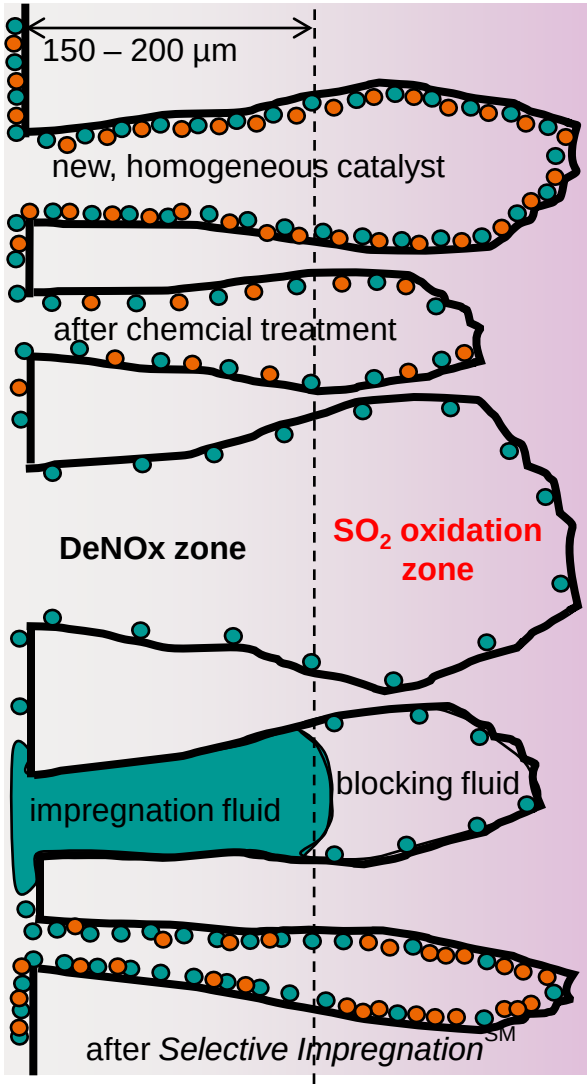
- **Patented one-step process for the replenishment of V_2O_5 and WO_3 or V_2O_5 and MoO_3 depending on catalyst type.**
- ***Selective Impregnation*^{SM} – the local distribution of active V_2O_5 on the catalyst surface is extremely critical for the effective reduction of the SO_2/SO_3 conversion rate.**

Evonik's Patented Process

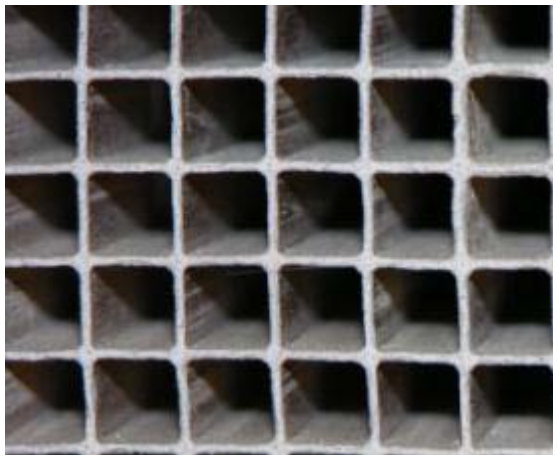
*Selective Impregnation*SM

***Selective Impregnation*SM is a patent pending process, which takes full advantage of these effects by:**

- **Removing an appreciable quantity of catalytically active compounds along with arsenic and other catalyst poisons.**
- **Selectively impregnating additional catalytically active compounds (Mo, V, W) only in the DeNOx zone.**
- **Actively preventing impregnation of any catalytically active compounds in the SO_2 oxidation zone by "sealing off" this area by means of a blocking fluid.**
- **Re-Calcination to catalytically activate impregnated metals (vanadium) and bond the strength metals into the catalyst (tungsten or molybdenum).**

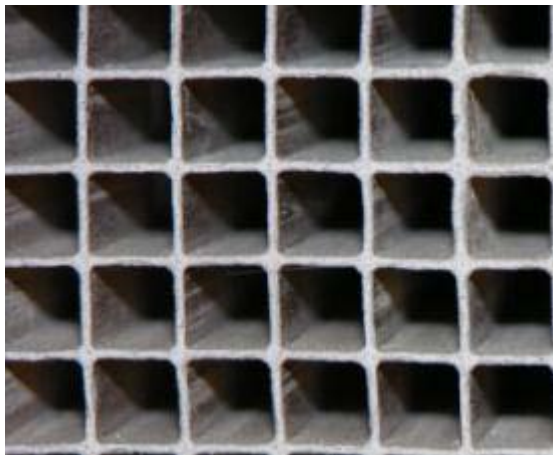


What reduces the strength metals?



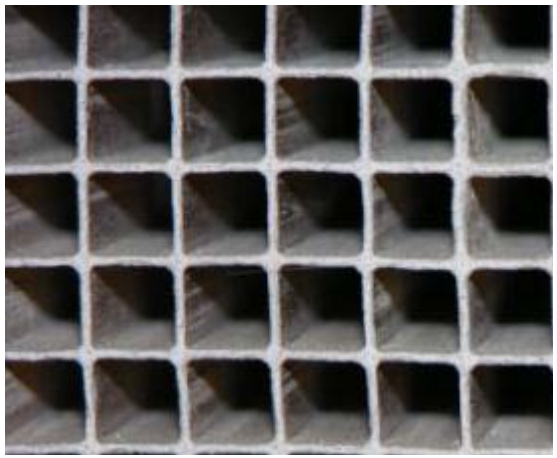
- **The catalyst de-activation compounds of Arsenic and Phosphorus.**
- **The removal of these compounds require more aggressive chemical treatment.**
- **Longer period of time being submerged in the solutions are required.**
- **Higher concentrations of cleaning solutions**
- **Ultrasonic cleaning is required to remove these compounds from the internal pores. Longer cleaning times are required.**

Effects of Chemical Treatment



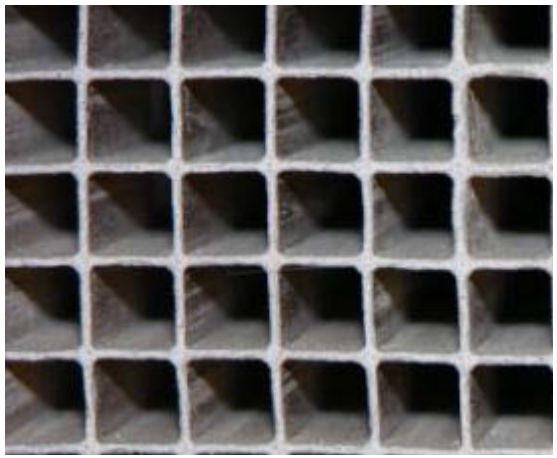
- **Catalyst looses strength during the treatment process.**
  - **Submerging the catalyst in a bath of liquid (even just water) will reduce the strength by 20% to 30% is normally observed.**
  - **Strength metals will be lost during the treatment. This has been observed to be in the 20% to 40% depending upon the treatment process utilized.**
  - **The above strength reductions are additive to the strength reduction.**

Re-Calcination



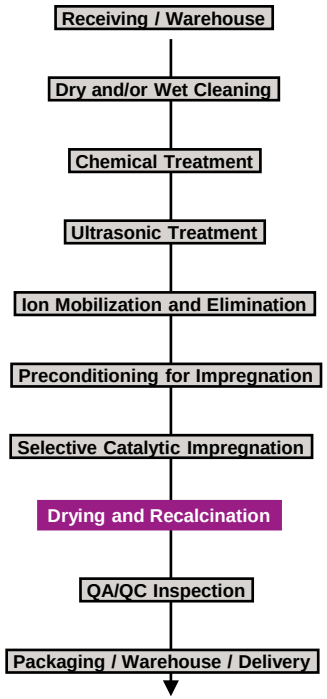
- **Evonik developed Re-Calcination to restore the strength in the catalyst after chemical treatment to regain strength and to stabilize / bond the impregnated metals on the catalyst.**
- **What is Re-Calcination?**
  - **Heating of the catalyst to elevated temperatures for prolonged periods of time. This temperature maintains the Anatase structure of the Titanium Dioxide material.**

Re-Calcination

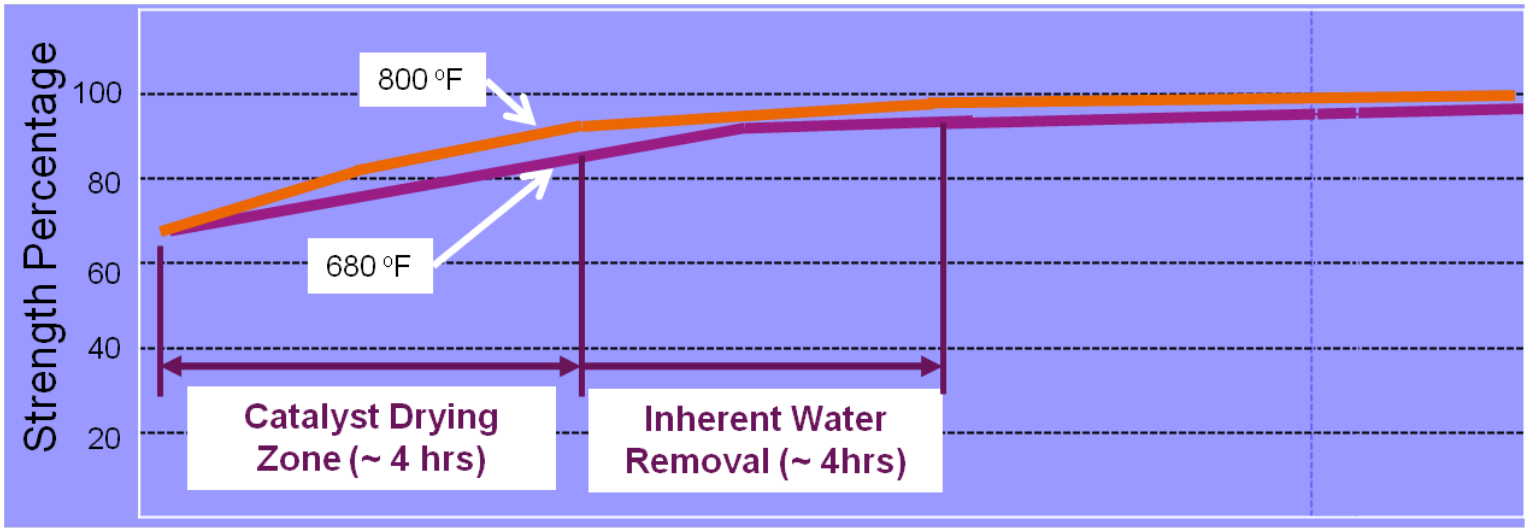


- **What is not Re-Calcination?**
  - **A simple drying step with lower 400 – 500 ^{o}F temperature heating.**
  - **A higher temperature heating of the catalyst with elevated temperatures above 850 ^{o}F.**

Catalyst Re-Calcination



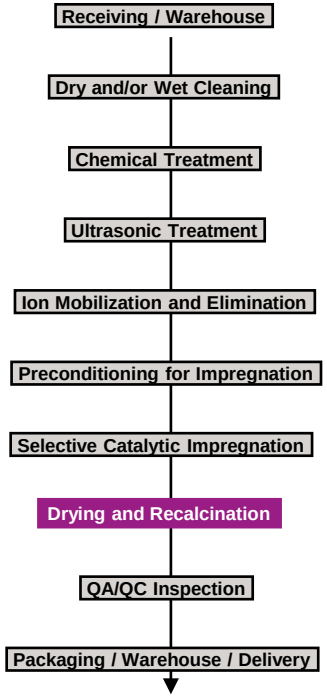
Evonik's Catalyst Regeneration Process



What happens in the Re-Calcination stage?

- **Catalyst Drying Zone (90% dry) – takes ~ 40% longer at 680 °F then at 800 °F.**
- **Inherent water removal takes about 150% longer at 680 °F.**
- **Strength metal bonding occurs in the later part of inherent water removal stage.**
- **Critical Re-Calcination issues - Controlled air circulation & moisture bleed.**

Catalyst Re-Calcination

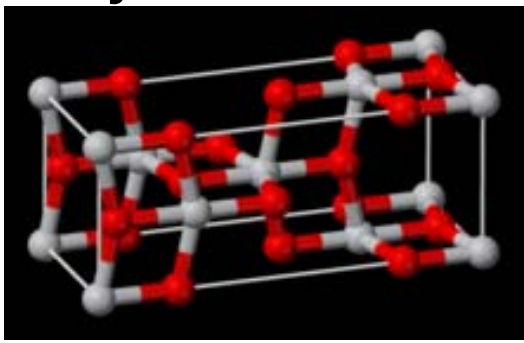


Evonik's Catalyst Regeneration Process

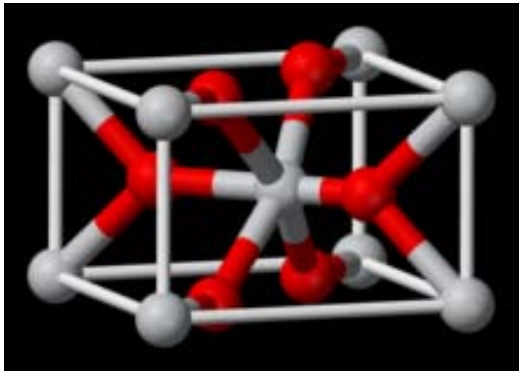
Why is the temperature important?

- **The Titanium Dioxide structure of catalyst is the Anatase crystal structure.**
- **Anatase crystal structure - very porous crystal structure to provide the surface area structure.**
- **Heating above 850 ºF to 900 ºF will cause the Titanium Dioxide crystal structure to change to Rutile crystal structure.**
- **The catalyst module will collapse (shrink) with excessive heat.**

Titanium Dioxide Crystal Structure

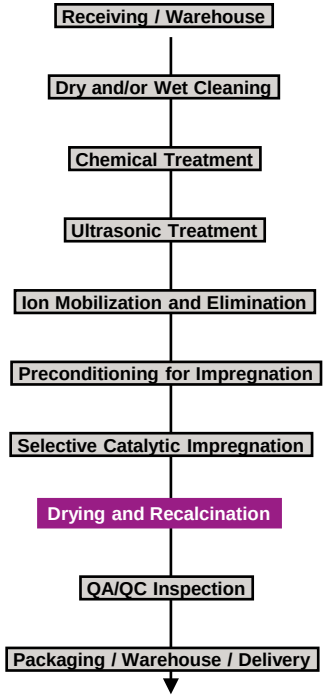


Anatase Crystal Structure



Rutile Crystal Structure

Catalyst Re-Calcination

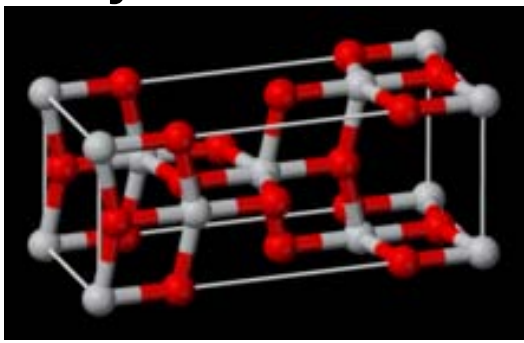


Evonik's Catalyst Regeneration Process

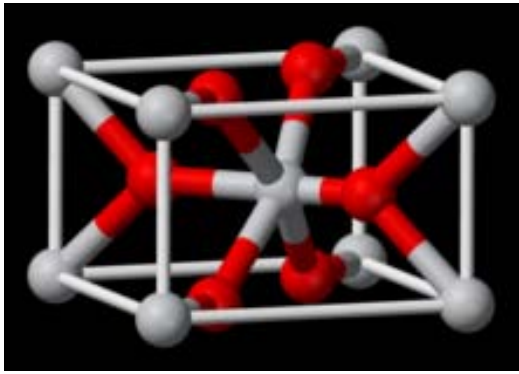
The goal of the Evonik Process?

- **High enough temperature to bond the strength metals to the catalyst.**
- **Drive off the crystalline water from the substructure.**
- **Not damage the Anatase crystal structure.**

Titanium Dioxide Crystal Structure

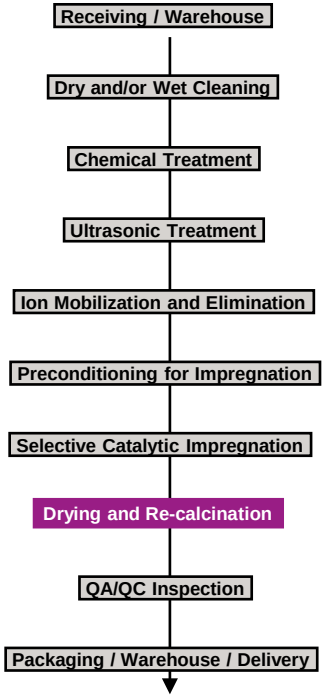


Anatase Crystal Structure



Rutile Crystal Structure

Catalyst Re-Calcination



Evonik's Catalyst Regeneration Process

Importance of Re-Calcination oven design:

- **Air circulation through the module is critical for even catalyst drying and less stress on the catalyst structure.**
- **Removal of the moisture from the furnace is also critical.**

- **The Re-Calcination is a function of temperature and time.**

Catalyst Re-Calcination

Receiving / Warehouse
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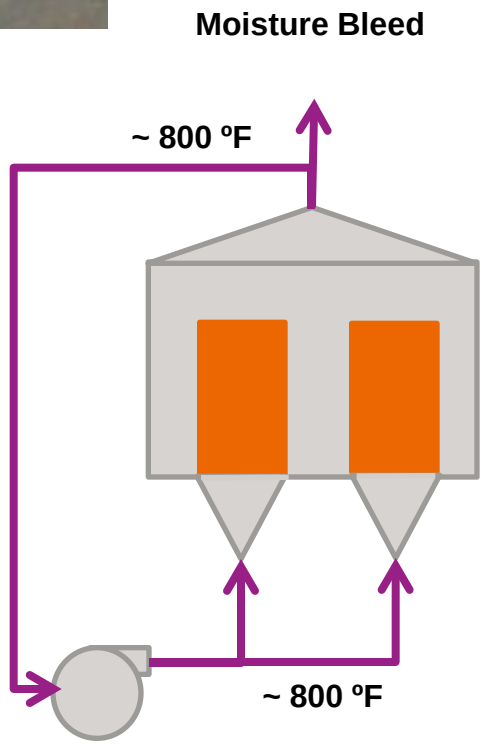
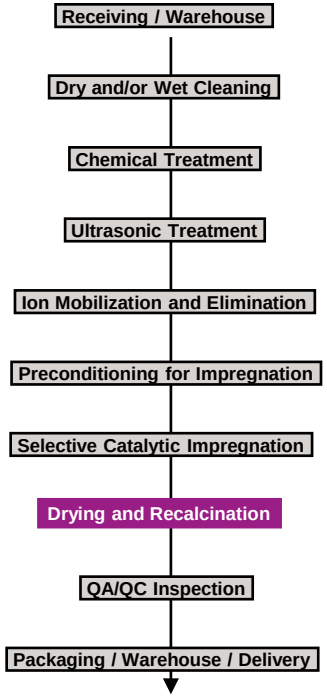
Evonik's Catalyst Regeneration Process

Importance of Re-Calcination oven design:

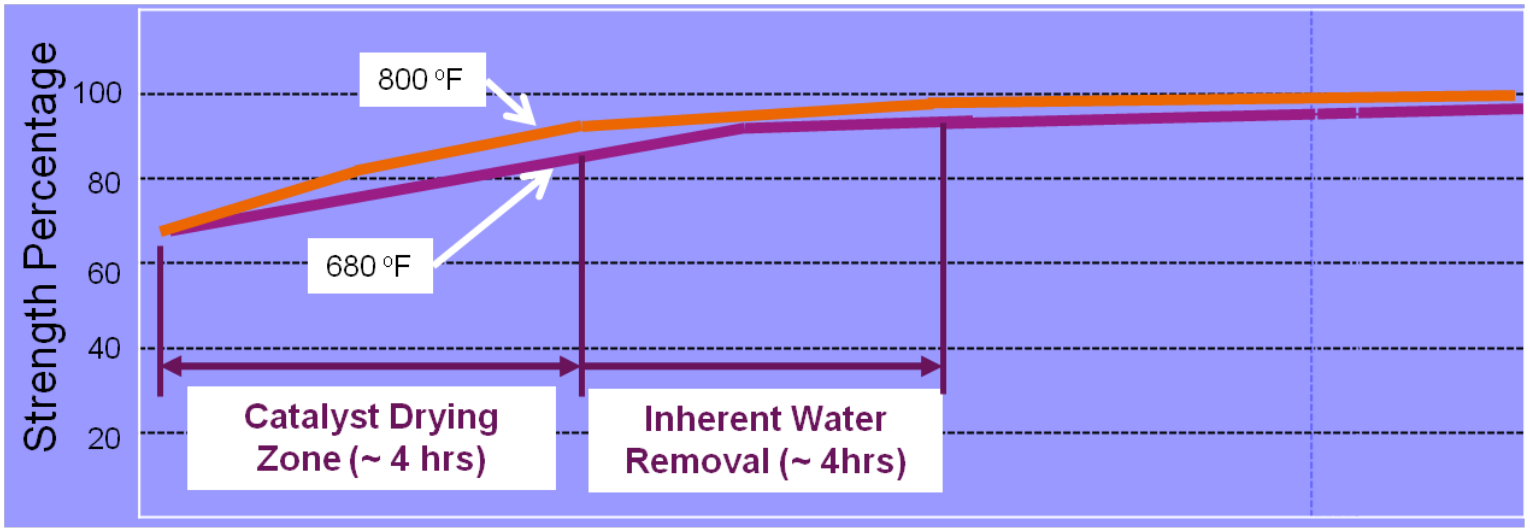
- **Air circulation through the module is critical for even catalyst drying and less stress on the catalyst structure.**
- **Removal of the moisture from the furnace is also critical.**
- **The Re-Calcination is a function of temperature and time.**
- **Minimize the operating cost.**



Catalyst Re-Calcination



Evonik's Catalyst Regeneration Process

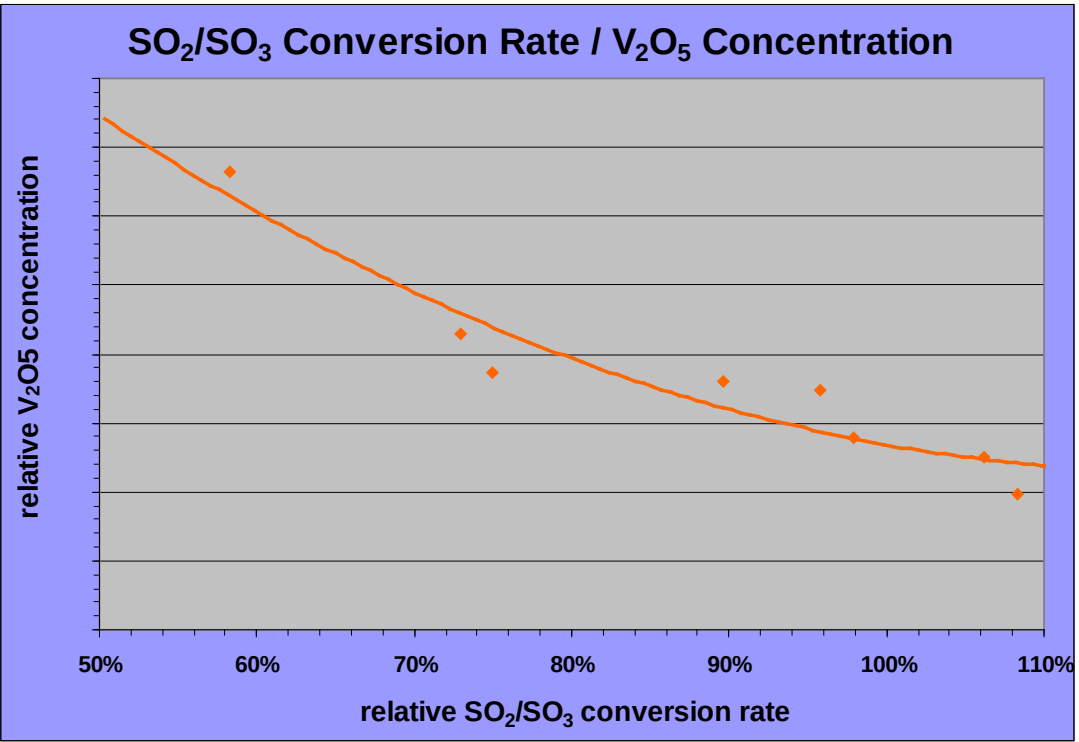


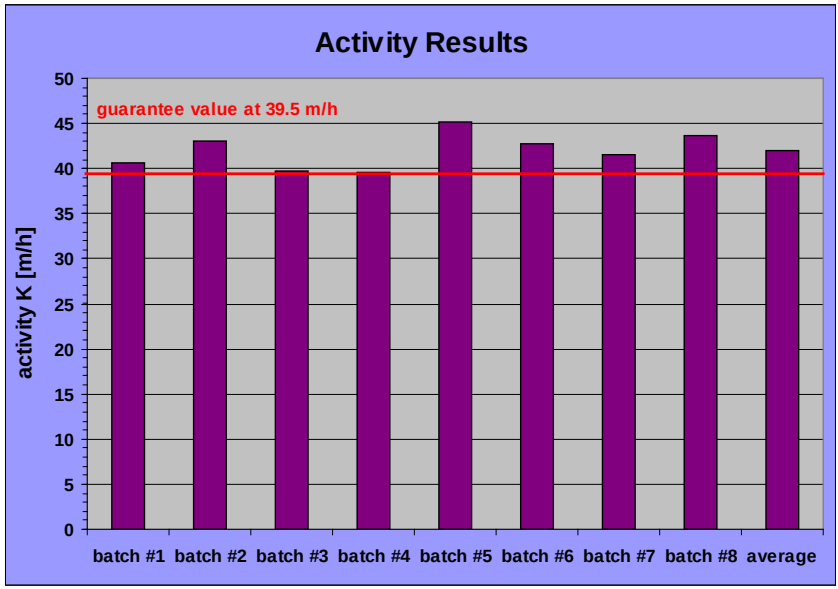
What happens in the Re-Calcination stage? Furnace Design

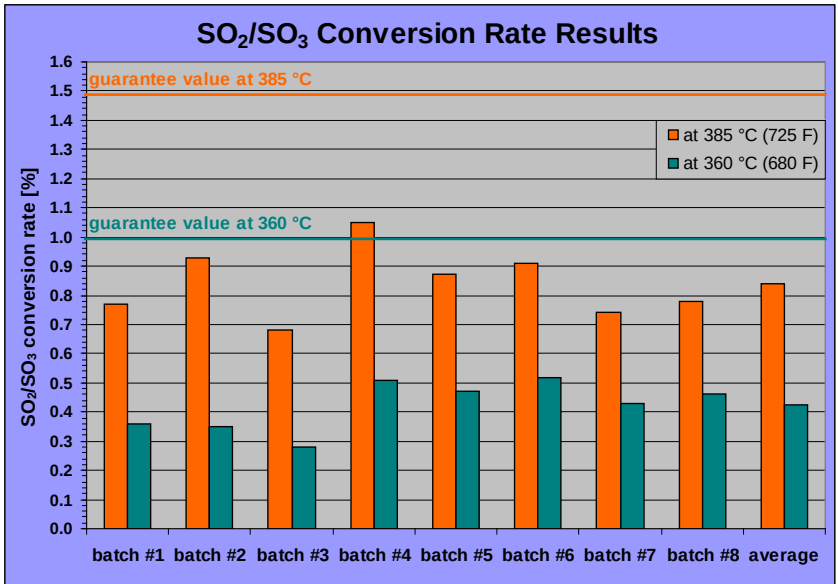
	Evonik's Furnace circulation	Traditional Furnace no circulation
Catalyst Drying	4 hrs	9 - 12 hrs
Inherent Water	Add'l 4 - 5 hrs	Add'l 12 – 15 hrs
Metals Bonding	8 hrs	24 hrs

Selective Impregnation[SM]

The value of Evonik's patent pending *Selective Impregnation*[SM] process is a significantly lower SO_2/SO_3 conversion while still reinstating the full or close to full activity.



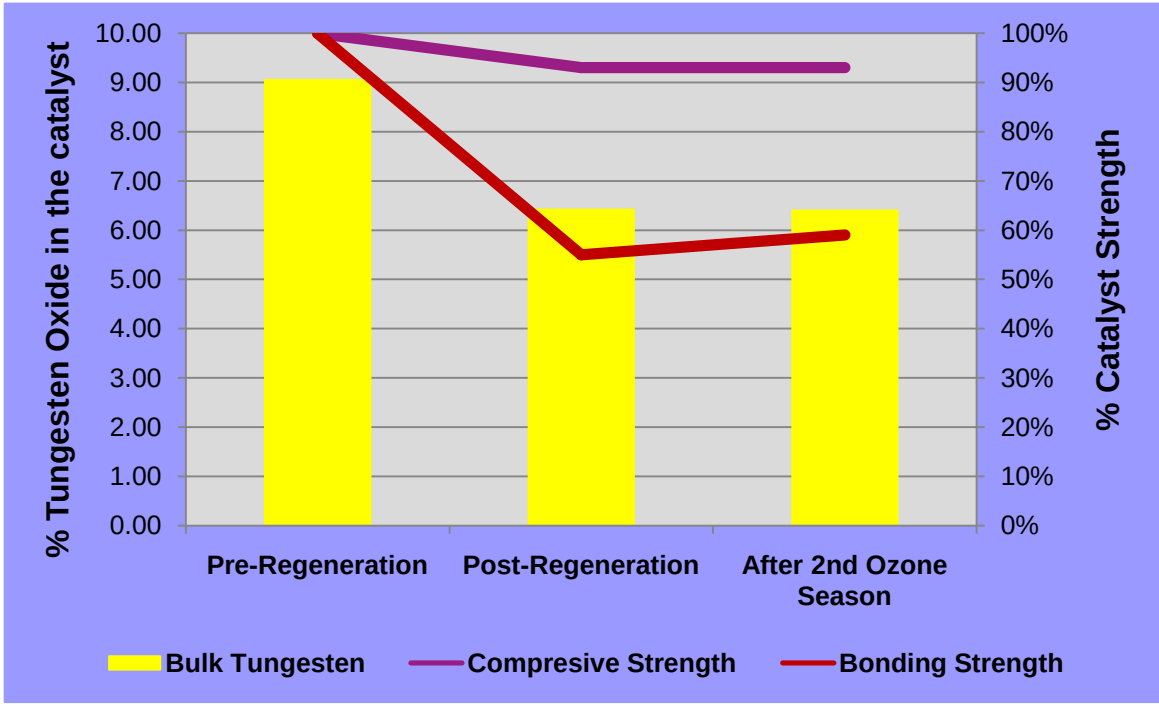




Re-Calcination

Mechanical Strength Problems With The “Old” Process

- After regeneration the WO_3 level was reduced by ~30% in the bulk material and the glass fibers were severely damaged by the harsh treatment with no WO_3 replenishment and no Calcination.
- Compressive strength was reduced ~8% from pre-regeneration level.

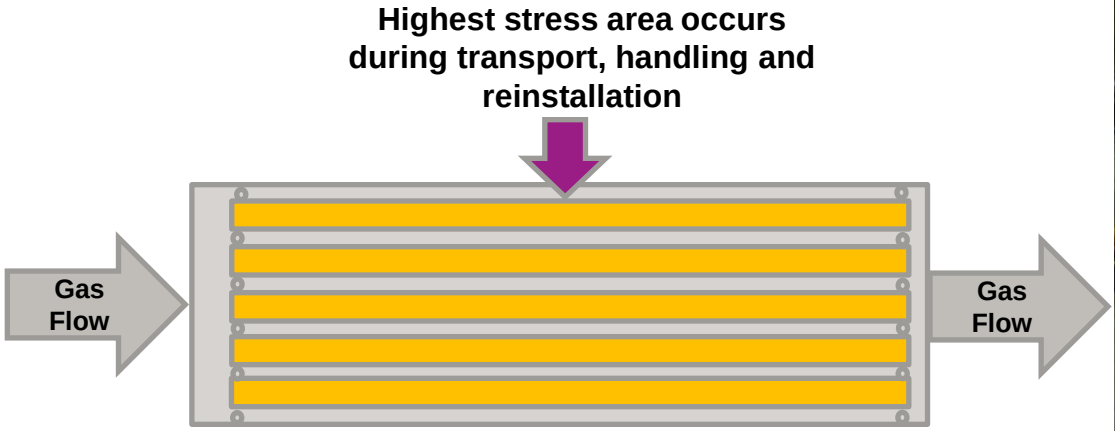


- Transversal bend strength was reduced by more than 50% from original pre-regeneration level.

Lost mechanical strength cannot be regained during SCR Operation - The catalyst in this example may not be suitable for another regeneration

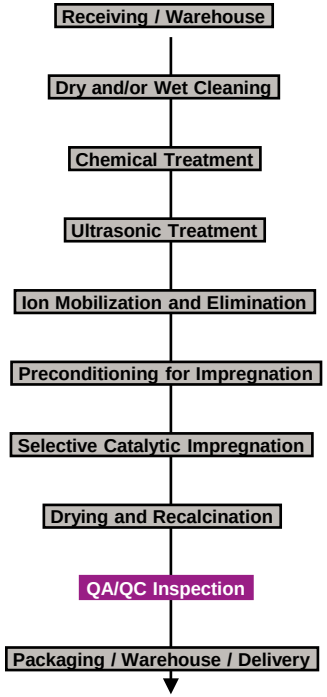
Re-Calcination

The value of one-step *Selective Impregnation*[SM] and catalyst Re-Calcination:



- **Catalyst is weakest during & after the regeneration process prior to the Re-Calcination.**
- **Catalyst has it's greatest stress during the transportation, handling and reinstallation of the catalyst. Catalyst needs to be at full strength during these times.**

Catalyst Regeneration



Evonik's Catalyst Regeneration Process

Evonik's Regeneration Process Steps

Quality Assurance / Quality Control:

- **XRF capabilities: What is the chemical composition of the final catalyst product?**
- **Bench and micro scale catalyst testing capabilities in Kings Mountain, NC and VGB Certified bench in Herne, Germany.**
- **Catalyst structural integrity testing capabilities.**

Re-Calcination benefits

Conclusions

- **Catalyst regeneration is a viable process with over 12 years of experience.**
- **In 2009, Evonik completed the 4th regeneration of a layer of catalyst of our Bexbach Power Station after over 100,000 hrs of operation. This catalyst is back in-service with the expect removal in 2016 (over 25 years of catalyst service). Selective Impregnation℠ and Re-Calcination are the key to longevity of catalyst.**
- **The Evonik Selective Impregnation℠ and Re-Calcination providing much lower SO_2/SO_3 conversion rate of our Bexbach catalyst by more than 60% while maintaining an activity of over 93% of initial K_0.**
- **Catalyst's chemical composition can be optimized to reduce the SO_2/SO_3 conversion rate or increase the Activity of the catalyst.**

Questions?

Evonik has over 260,000 sq.ft. of space with a storage capacity of over 16,000 MW's of catalyst