SCR-Catalyst Management

Dr. Dirk Porbatzki
UTG / Catalyst & Oil Management
We are Uniper

Our operations:
- Power Generation
- Commodity Trading
- Energy Storage
- Energy Sales
- Energy Services

Where we operate:
40+ countries around the world
4th largest generator in Europe

Employees: 13,000

Main activities:
- Gas fired plants 11.7GW
- Coal fired plants 9GW
- Energy storage Gas: 9bn m³
- Gas fields
- Gas pipelines & infrastructure
- Regasification
- Nuclear plants 2.5GW
- Hydroelectric plants 4.25GW
- Trading
- Energy sales (small to large customers, electricity & gas)
- Services

Company data: October 2016
Energy Services is bringing Uniper’s competencies to the global stage

- Front end engineering design
- Commercial evaluation
- Engineering Procurement and Construction tendering and project management
- Construction and site management
- Commissioning

Our core skills
- Owner’s engineer
- Project management
- Environmental management
- Electrical, mechanical and civil engineering
- Digital engineering
- Process engineering
- OEM independence
- Grid and Local energy system solutions

- Outage support
- Production support
- Maintenance and spares optimisation
- Field services
- Workshop services

- Planning, permit and impact assessment
- Decommissioning and dismantling
- Demolition

- Benchmarking
- Asset lifetime assessment & extension
- Asset risk management
- Compliance and standards
- Technical operational excellence

Value proposition
- Leading one-stop-shop energy solutions provider with services across the value chain and life-cycle
- Leveraging competencies in delivering bespoke customer solutions

Business at a glance
- Expertise across multiple technologies
- Services to more than 600 customers
- Active in more than 40 countries

1. Based on 2015
Uniper & India Power have formed a strategic partnership to develop and service the power sector

India Uniper Power Services
- 50:50 joint venture in power plant services
- A value-based service provider
- Offering a broad range of flexible and customised services
- Headquartered in Kolkata

The joint venture will combine strengths of strong partners with complementary scope and portfolio. Key service offerings:

- Plant operations and maintenance,
- Asset monitoring software and analytical tools,
- Fuel evaluation and optimisation (e.g. blending of Indian and Indonesian coals)
- Increasing flexibility of units; Lifecycle extension,
- Supply and integration of pollution control equipment and systems, etc.
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2. UTG Test Facilities
3. From Catalyst Testing to Catalyst Management
4. SCR-Impact on Downstream Equipment
5. Mercury Oxidation
SCR DeNOx Basics

Desired Reactions
4 NO + 4 NH₃ + O₂ → 4 N₂ + 6 H₂O
NO + NO₂ + 2 NH₃ → 2 N₂ + 3 H₂O
6 NO₂ + 8NH₃ → 7 N₂ + 12 H₂O

Hg + 2 HCl + ½ O₂ → HgCl₂ + H₂O

Undesired Reactions
SO₂ + ½ O₂ → SO₃ (SO₂ Conversion)
NH₃ + SO₃ + H₂O → NH₄SO₄ (Ammonia Bisulfate Formation)
HgCl₂ reduction by NH₃ and SO₃
Operating Temperatures

Catalytic (SCR)

Non catalytic (SNCR)

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]
Typical positions for SCR system installations
SCR-Fundamentals

Characteristics
- NO\textsubscript{x}\textsubscript{-} reduction below emission limit
- NH\textsubscript{3}\textsuperscript{-} consumption almost complete

Dr. Porbatzki, Uniper Technologies GmbH, India November 2016
Numerical example for NOx and NH3 conversion

NOx in : 243 ppmv  
NOx out : 29 ppmv

→ NOx conversion : 88 %

NH3 in : 215 ppmv  
NH3 out : 0,7 ppmv

→ NH3 consumption : 99,7 %
Uniper Technologies Know How for SCR Management

- Operation of 10 SCR pilot plants from 1985 - 1987
- Design and operation of a certified bench scale SCR test reactor since 1988
- Development of a MARA system for AIG tuning since 1989
- Design of a catalyst management system since 1990
- Commercial catalyst management services since 1992 at coal- and oil-fired units and waste incineration plants
- Experience from the operation of >40 SCR reactors in Uniper’s power plants
- More than 150 customers worldwide, mostly with several SCR reactors
- Detailed test results of almost all commercially available catalyst materials
- Design and operation of a bench test reactor in Columbus/Ohio 2004-2011
- Implementation of a lifetime database / calculation tool (LEONID) since 2004
- 80% of coal fired power stations in Germany use Uniper’s services
Why SCR Management?

- Catalyst in thermal power stations unavoidably deteriorate over time
- SCR catalyst is the most expensive “spare part” purchase in a power station
- Optimizing operation of installed catalyst volume by e.g. utilization of available design margins
- Forecasting the most economical catalyst replacement and regeneration schedules according to existing outage plans
- Best choice of appropriate catalyst material (price, technical properties)
- On time RFQ’s and PO’s for necessary new catalyst material or regeneration

→ Make rational financial decisions independent of catalyst suppliers / catalyst regenerators
Types of commercially available SCR catalyst

Honeycomb

Plate-type metal support
High Ash Content

Corrugated catalyst glass fiber support
Focuses of modern SCR Management in support of plant operations

- Fuel management i.e. co-firing of bio-fuel
- Catalyst management and regeneration
- Tuning of the ammonia injection system „MARA“-testing
- Gas flow optimization
- Gas entry
- Gas exit

Dr. Dirk Porbatzki, Catalyst Management, India November 2016
Uniper Kraftwerke GmbH - Scholven Power Station Unit F

- **Unit Capacity**: 740 MW
- **Fuel**: Hard Coal

**DENOx Plant**
- **Type of Process**: High Dust SCR
- **Capacity**: 2 x 1,200,000 m³/h STP
- **Arrangement**: High Dust
- **Type of Catalysts**: Honeycomb 7-pitch
- **4 catalyst layers x 314 m³**
- **NOx removal**: 78%
- **Commissioning**: 1989
Example: Catalyst Sampling (plates)

- One layer of catalyst modules
- 12x9 modules \( \times 1 \times 2 \times 1 \text{ m}^3 \sim 216 \text{ m}^3 

\textbf{X: pull positions (plates)}

- Representative samples over the cross section

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inspection door
Visual Inspection of AIG, SCR Reactor

Visual reactor inspection and SCR catalyst sampling often provides valuable first hand information about the SCR reactor and reasons for potential performance problems.

plugged NH$_3$-injection system

flue gas bypass

plugged honeycomb catalyst

March 2009 | Dep. VAU | Bo

plugged plate-type catalyst

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Example: Catalyst Inspection - Plugging & Piles
Example: Catalyst Inspection - Erosion
Catalyst Deactivation

- Deactivation by heat
  - sintering
  - rutilization

- Accumulation of catalyst poisons
  - alkali metals
  - As, Ti, Pb
  - others

- Erosion pluggage

- Prevention of gas diffusion by the formation of surface layers
  - accumulation of dust particles
  - formation of dense surface layers
  - bounding agents (free lime, sulfate, phosphate)
  - low melting compounds
  - coal properties, ash composition

- Pore blockage
  - \((\text{NH}_4\text{)}\text{HSO}_4\)
  - micro particles

- Plant operation
  - soot blower
  - start-up/shutdown
  - airheater washing
  - tube failure
  - temperature
  - excess air
Catalyst Testing under power plant conditions

- Determination of the realistic NOx reduction capability fully transferable to the full scale plant according to VGB standard S302
- Calculation of catalyst activity and potential of each catalyst layer and whole SCR reactor
- Potential forecast in combination with the calculated minimum potential
- Optimized catalyst reloading / regeneration strategy

Bench-Reaktor, front side
Example: Long Term Deactivation of High Dust Catalyst (best case)

- 260 MW dry ash boiler
- tangentially fired
- imported coal
- 10 % ash
- district heating

app. 22 % loss / 100,000 h

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Example: Long Term Deactivation of High Dust Catalyst (real case)

app. 60 % loss / 100,000 h
Example: Long Term Deactivation of High Dust Catalyst (worst case)

- 740 MW dry ash boiler
- tangentially fired
- local domestic coal
- sewage sludge co-firing
- 10% ash

appr. 70% loss / 15,000 h

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Potential forecast – compliance with NO\textsubscript{x} and NH\textsubscript{3} limits

- Minimum potential 4.18 incl. 23% safety margin, 90% NO\textsubscript{x} removal, 2 vpm NH\textsubscript{3}-slip
- Forecast.

Note: No data from new 1st layer available!

Next replacement required ~58,000 h
Catalyst Deactivation

- Catalyst deactivation causes ammonia slip
- NOx emission values remain stable
- NH\textsubscript{3} slip causes increased ammonia in fly ash concentrations
- NH\textsubscript{3} slip causes air heater fouling (pressure drop) and corrosion
Catalyst Deactivation - Detection of Mechanisms (e.g. XRF Analysis)

- Chemical analysis of catalyst surface and bulk gives informations about the reasons for deactivation (e.g. poisoning, surface layer blinding)
- Understanding of catalyst deterioration mechanisms allows countermeasures! (e.g. CaO addition at arsenic poisoning)
**SCR Impact on Downstream Equipment, example: SO₂ to SO₃ conversion**

- Sulfuric acid plume, visible ~2 ppm SO₃
- AH / corroded heat exchanger plates
- AH / plugged heat exchanger plates (cold end)

**SO₂ conversion:**
- Acid emissions
- Corrosion
- Plugging (increasing pressure loss)
Example: SO$_2$ to SO$_3$ Conversion Rate throughout a Catalyst Lifetime

- Experience shows that SO$_2$ to SO$_3$ conversion does not decrease throughout a catalyst lifetime.

- Conversion can increase if iron is present in/on the catalyst surface. Data has shown that conversion decreases in the presence of H$_2$SO$_4$ (originated by SO$_3$ and moisture) by mobilizing iron into the micropore system.

- The iron can have different sources: fly ash, metal grid (plate type catalysts), modules metal structure, corroded particles carried over by the flue gas, ...
SO$_2$ conversion; Ammonia (bi)sulphates

ABS dew point
- Important low load / partial situations
- Affected by partial pressures of NH$_3$ and SO$_3$, both can vary over lifetime
- Note: graph not valid for SCR-catalyst pore systems due to different conditions inside/outside the pores (pressure dependancy)
Catalyst management – Leonid database and calculation tool
Catalyst Management

- Development of catalyst replacement strategies (lifetime, position, volume)
- Inspection and sampling of catalyst in SCR DeNOx plants
- Activity tests in bench- and micro-scale reactors
- Determination of the deactivation causes and forecast of the catalyst potential/lifetime
- Determination of the main reasons for activity loss (chemical and physical effects)
- Determination of opportunities and limitations for catalyst regeneration
- Determination of \( \text{SO}_2/\text{SO}_3 \) conversion rate in bench-scale reactor
- Measurement of pressure loss of catalyst in bench-scale reactor

Summary

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**Future Aim: Advanced catalyst management considering the Hg-oxidation on catalysts**

- Example: Influence of catalyst deactivation (increased NH₃-slip) on Hg oxidation and possible effects (Leonid database and calculation tool)
  - Shifting Hg-active layers downstream
  - Effect: Possibly lower total Hg oxidation rate