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German Experience with Catalyst Regeneration

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SCR Catalyst Regeneration Nomenclature

STEAG's Bergkamen Power Station

STEAG's Fenne Cogeneration Plant

- **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.**

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SCR Catalyst Regeneration History

STEAG's Bexbach Power Station

STEAG's Weiher Power Station

- 1983: Legislation – Flat rate NOx emission limit of 200 mg/Nm^3 (~100 ppm) for all units ≥ ~100 MW regardless of age, fuel and capacity factor
- Mid to late 1980's: SCRS were installed on practically fossil fuel fired units in Germany to meet new legal emission requirements
- Mid to late 1990's:
  - Catalyst deactivation by plugging and catalyst poisons became a greater concern as the use of world market coal and "secondary fuels" increased
  - Buying new catalyst was economically unfavorable in light of deregulation and increasing catalyst cost
  - Several utilities including EnBW, HEW, SBW/STEAG began R&D on catalyst cleaning and rejuvenation

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SCR Catalyst Regeneration History

STEAG's Voerde Power Station

EnBW's Heilbronn Power Station

- 1995/1996: STEAG starts developing an on-site technique for LPA removal after Voerde's 760 MW Units 3 and 4 have major LPA problems and 4 honeycomb layers plug as a result of switching from indigenous to world market coal.
- 1996/1997: SBW (now STEAG) develops a patented on-site process for the removal of surface blinding layers and rejuvenation after a coal switch from Göttelborn to Ensdorf coal (Saar regional mine) caused the formation of strong surface blinding layers at Bexbach's 780 MW Unit 1 and Weiher's 725 MW Unit 3 due to high CaO content in the fly ash (similar to PRB) .
- 1996/1997: EnBW develops a simple in-situ process for the removal of ordinary fly ash pluggage and partial rejuvenation at the Power Plant Heilbronn.

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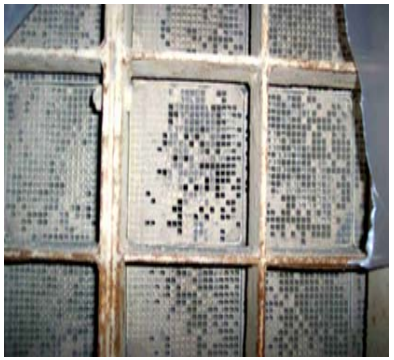

HEW's Tiefstack Cogeneration Plant

SCR Catalyst Regeneration History

- 1997/1998: SBW/STEAG perform first full-scale rejuvenations at Bexbach and Weiher (removal of blinding layers and mild catalyst poisons) and cleaning at Voerde (removal of LPA pluggage).
- 1997: STEAG's Leuna Cogeneration Plant burning 100% refinery residue including pet coke starts up with all 3 units having high-dust SCRs, which rely on regeneration for economically sustainable SCR operation.
- 1997/1998: HEW develops an on-site process for the removal of ordinary fly ash pluggage and rejuvenation at the Tiefstack Cogeneration Plant.
- 1998/1999: Integral develops an on-site cleaning and rejuvenation process at a coal- and oil-fired plant for the removal of vanadium blinding (oil-fired unit) and mild catalyst poisons (coal-fired unit).

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SCR Catalyst Regeneration Processes

EnBW‘s In-situ Rejuvenation Process

- BHK Process:
  - On-site process, which was used once at E.ON’s Mehrum Generating Station for one layer of BHK plate catalyst.
  - Process seems to be no longer marketed in Europe since no other known applications in Europe are known.
- EnBW’s In-situ Rejuvenation Process:
  - Process was further refined and optimized without overcoming its limitations of being performed in-situ, which is also its main advantage.
  - Still used in house within the EnBW/EDF group.
  - Technology sold to CESI/SCR-Tech for use in North America and to Envica/EKS for use elsewhere.
- Envirgy Process:
  - Spun off of Integral in late 2002.
  - Developed a cleaning process in 2003 together with Enerfab who markets the process in North America.

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SCR Catalyst Regeneration Processes

HEW's On-site Rejuvenation Process

Integral's On-site Rejuvenation Process

- HEW Process:
  - HEW and SAS founded KAS to further develop and market the HEW process for cleaning, rejuvenation and regeneration.
  - HEW sold its 50% share in KAS, (renamed Envica and later EKS) now markets the technology except for in North America where it was sold to CESI/SCR-Tech.
- Integral Process:
  - Process is being successfully marketed throughout Europe and Asia after further process refinements.
- KWH Process:
  - KWH developed a regeneration process in 2002/2003.
  - Process was used a few times in Germany but seems to have disappeared from the market with the sale and move of KWH to China.

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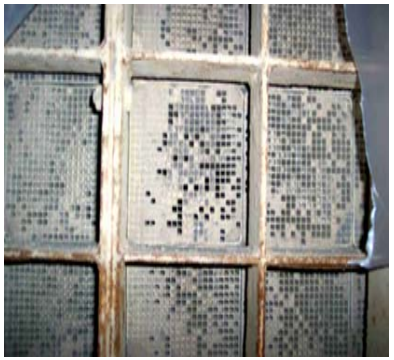
SCR Catalyst Regeneration Processes



LPA Plugged Catalyst – STEAG‘s Voerde Power Station

Rejuvenated Catalyst – STEAG‘s Voerde Power Station

- **STEAG/SBW Process:**
  - **Steag acquired SBW and obtained a license from Integral Umwelttechnik GmbH, Austria for STEAG’s fleet and for North America.**
  - **Merged technologies, know-how and experience for the development of a significantly optimized process.**
  - **Used up to now for in house rejuvenation and regeneration only.**
  - **On-site process for cleaning and rejuvenation.**
  - **Off-site process for cleaning, rejuvenation and regeneration.**
  - **Marketed in North America exclusively by STEAG since late 2006.**
  - **STEAG’s off-site regeneration facility will commence operation in Kings Mountain, North Carolina in summer 2007.**

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STEAG's Catalyst Regeneration Needs

Weiher 6 x 6 Log Honeycomb Modules

Fenne Triple-decker Plate Modules

- STEAG developed a regeneration process due to:
  - Perpetually frequent need for
    - Ca-based blinding layer removal and rejuvenation of the Bexbach, Fenne and Weiher catalyst.
    - Rejuvenation of V-based blinding layer removal and reduction of SO_2/SO_3 conversion rate of the catalyst of the Leuna and Godorf refinery units (same type of fuel, high-dust SCRs).
  - A more cost effective process for odd size modules.
    - Bexbach (9 x 18 log honeycomb modules)
    - Fenne (24 box triple-decker plate modules)
    - Weiher (6 x 6 log honeycomb modules)
  - Rapidly growing regeneration needs within STEAG's fleet of currently 24 (soon 26) SCRs due to increased use of world market coals and secondary fuels (sewage sludge, bone meal, pet coke, etc.).

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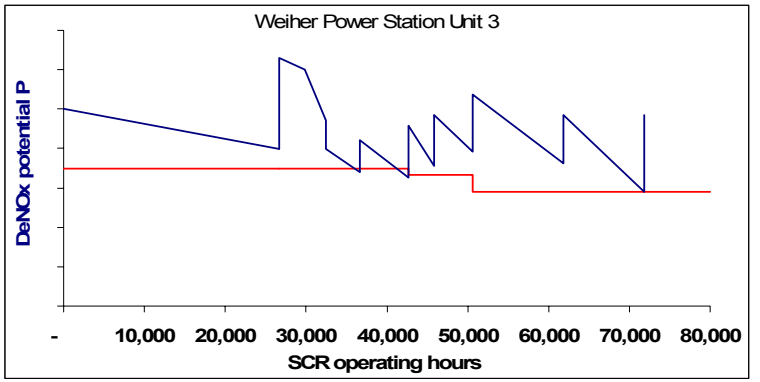
Bexbach, Weiher and Fenne – Blinding Layers

STEAG's Bexbach Power Station



- A coal switch to Ensdorf coal caused rapid deactivation due to unknown causes at the time.
- The formation of a very strong surface blinding layer mostly consisting of $CaSO_4$ and fly ash was found to be the cause.
- Ensdorf coal with a CaO content in the fly ash of around 10%wt. was determined to be the source.
- A patented, DI-water based rejuvenation process was developed and has been successfully applied to all catalyst layers at Bexbach, Fenne and Weiher since 1997.
- Since then the same catalyst layers have been successfully rejuvenated up to 3 times.

STEAG's Weiher Power Station

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Bexbach, Weiher and Fenne – Blinding Layers

STEAG's Weiher Power Station

Regenerated Weiher 6 x 6 Log Honeycomb Modules

layer	26,631	32,868	36,681	42,627	45,853	50,560	61,526	72,000
1.1 1.2	A			B (reg)	B	B	B	A (reg)
2.1 2.2	B	B	C (reg)	C	C	C	D (reg)	D
3.1 3.2	C	A (reg)	A	A	E (new)	E	E	E
4.1 4.2	D (new)	D	D	D (reg)	D	F (new)	F	F

Addition of new honey-comb layer D.	Removal of layers A, C to regeneration, addition of regenerated layer A.	Removal of layer B to regeneration, addition of regenerated layer C.	Addition of regenerated layer B, regeneration of layer D.	Removal of layer A to regeneration, addition of new honey-comb layer E.	Removal of layer D to regeneration, addition of new honey-comb layer F.	Removal of layer C to regeneration, addition of regenerated layer D.

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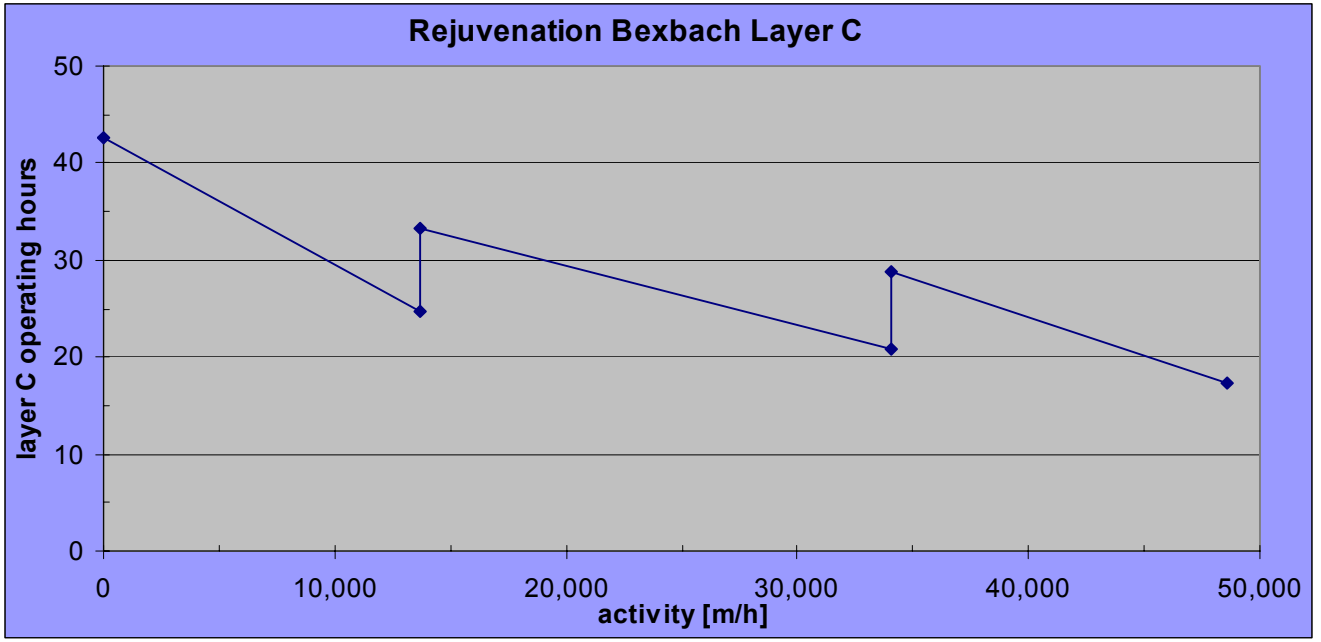
STEAG's Catalyst Regeneration Experience

Rejuvenation Tank at Weiher Power Station

Rejuvenation Tank During Catalyst Loading

- STEAG's regeneration process development was driven by:
  - Need for higher activity gains than possible through rejuvenation only.



  - More than 2 – 3 rejuvenations are not cost effective as the incremental gain in activity declines below the economic threshold. Full regeneration is needed.

Leuna Cogeneration Plant

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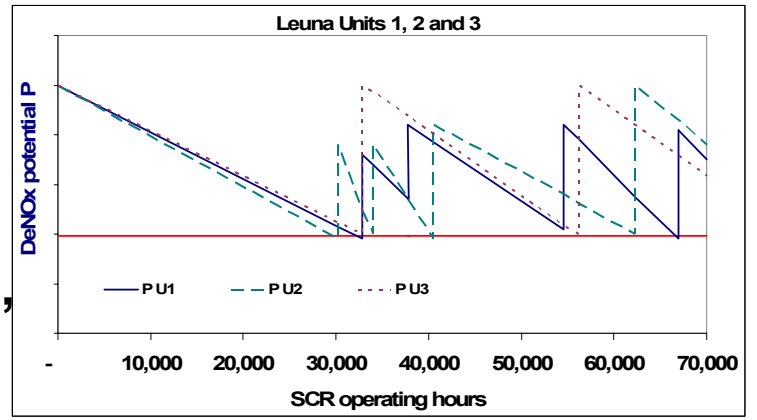
Leuna and Godorf – Vanadium Pore Pluggage

STEAG's Leuna Cogeneration Plant

- High-dust SCR in combination with the refinery residue fuel (S ≤ 6%wt.) highly problematic.
- Very rapid deactivation at times, highly dependent on fuel mix.



STEAG's Godorf Cogeneration Plant

- The formation of a very strong pore pluggage mostly consisting of vanadium and fly ash as well as poisoning depending on fuel composition was found to be the cause.
- Unit operation would be uneconomical without catalyst regeneration due to highly variable catalyst exchange frequencies and cost.

hours	0	30,178	32,813	33,994	37,772	40,470	54,570	56,198	62,256	67,000
U1	A	A	E (reg)	E	E	E	B (reg)	B	B	B
	B	B	B	B	D (reg)	D	D	D	D	F (reg)
U2	C	G (new)	G	G	G	A (reg)	A	A	I (new)	I
	D	D	D	F (reg)	F	F	F	F	H (reg)	H
U3	E	E	C (reg)	C	C	C	C	E (reg)	E	E
	F	F	H (new)	H	H	H	H	C (reg)	C	C
out for regen.	C	F	A	A, B	B	E	H	A, F	A, D	
					G used elsewhere					

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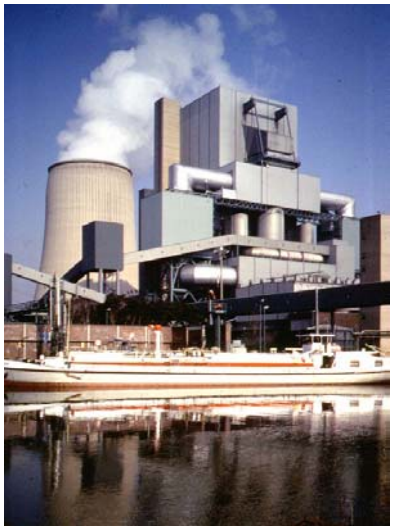
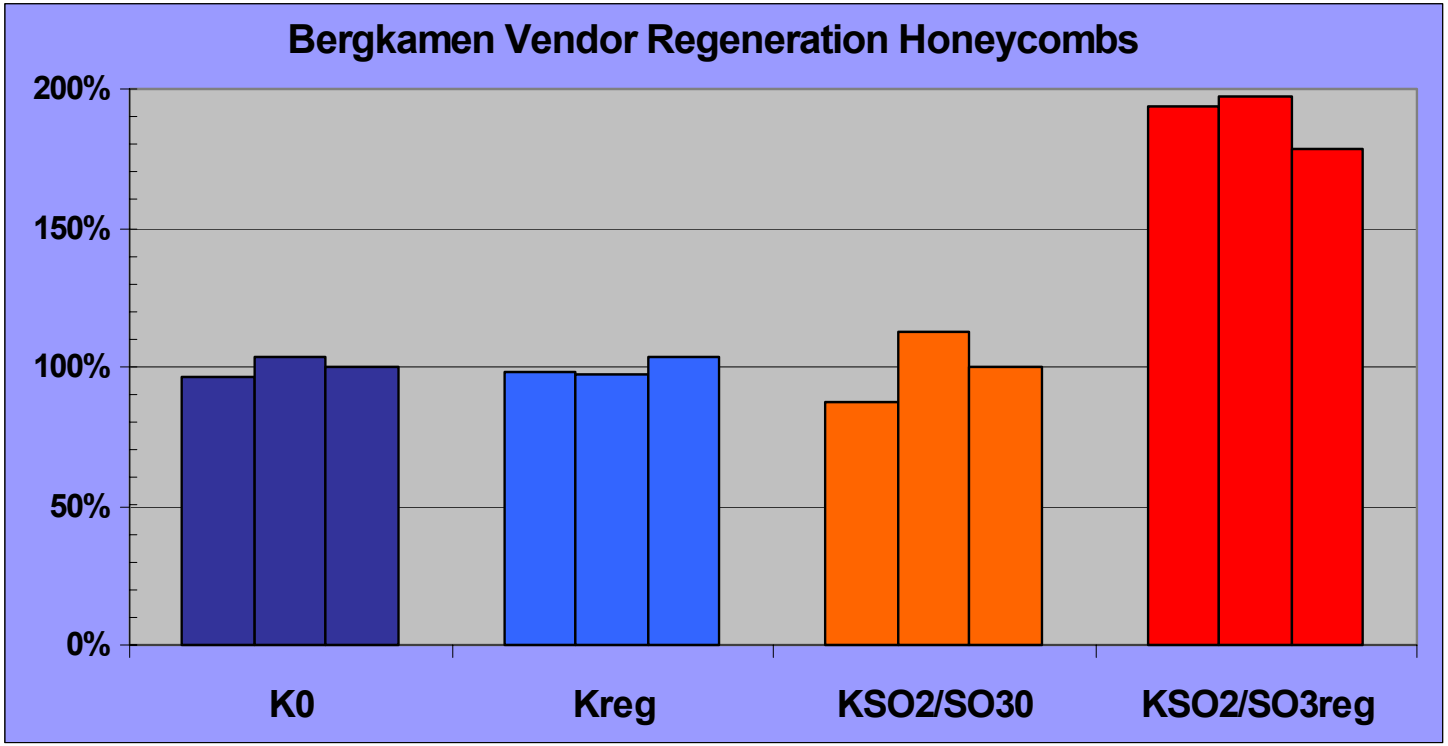
STEAG's Catalyst Regeneration Experience



STEAG's Bergkamen Power Station

STEAG's Bergkamen Power Station

- STEAG's regeneration process development was driven by:
  - Suspicions of increases in SO_2/SO_3 conversion rate when regenerated by commercial regeneration vendors.



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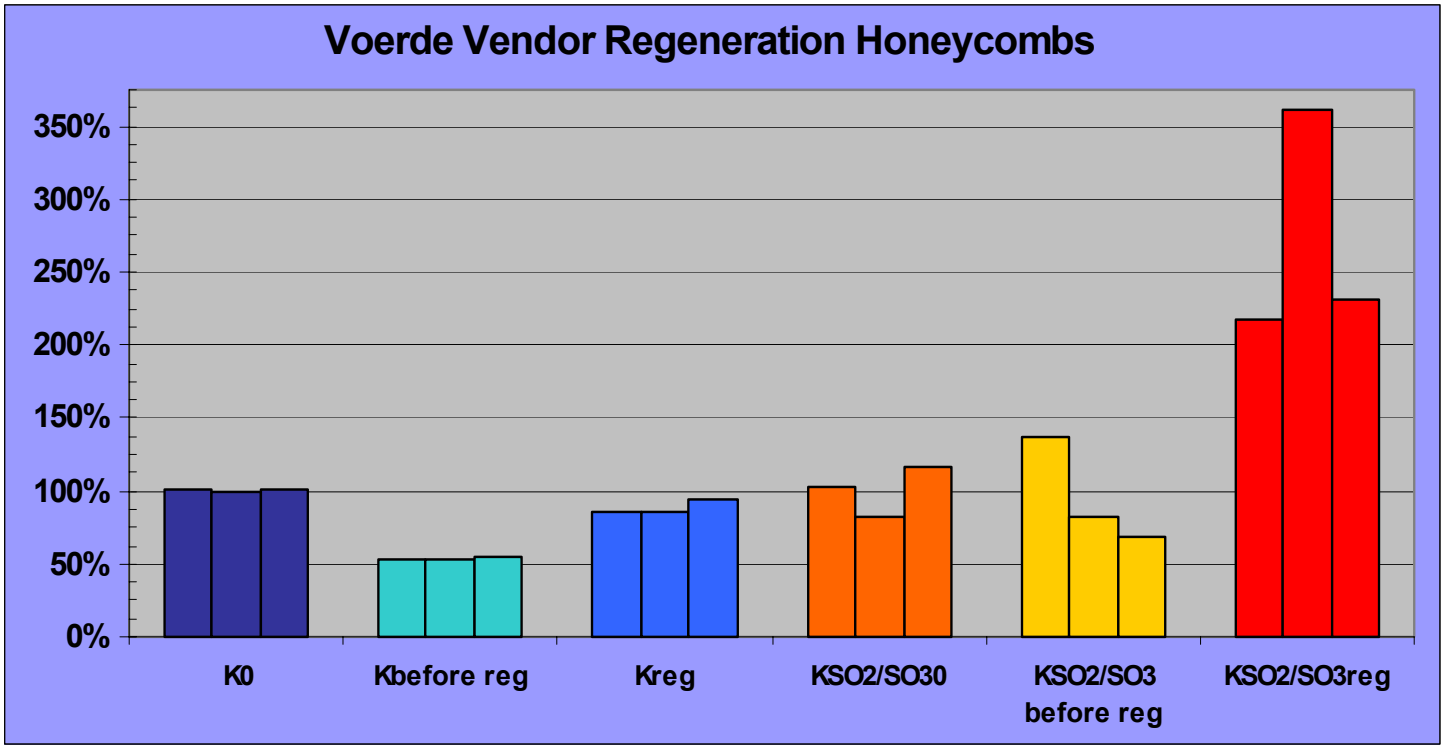
STEAG's Catalyst Regeneration Experience

STEAG's Voerde Power Station

STEAG's Voerde Power Station

- Further investigation confirmed the problem:
  - Other utilities reported similar observations.
  - Unwanted and/or unpredictable increases were considered very undesirable for STEAG's SCRs.



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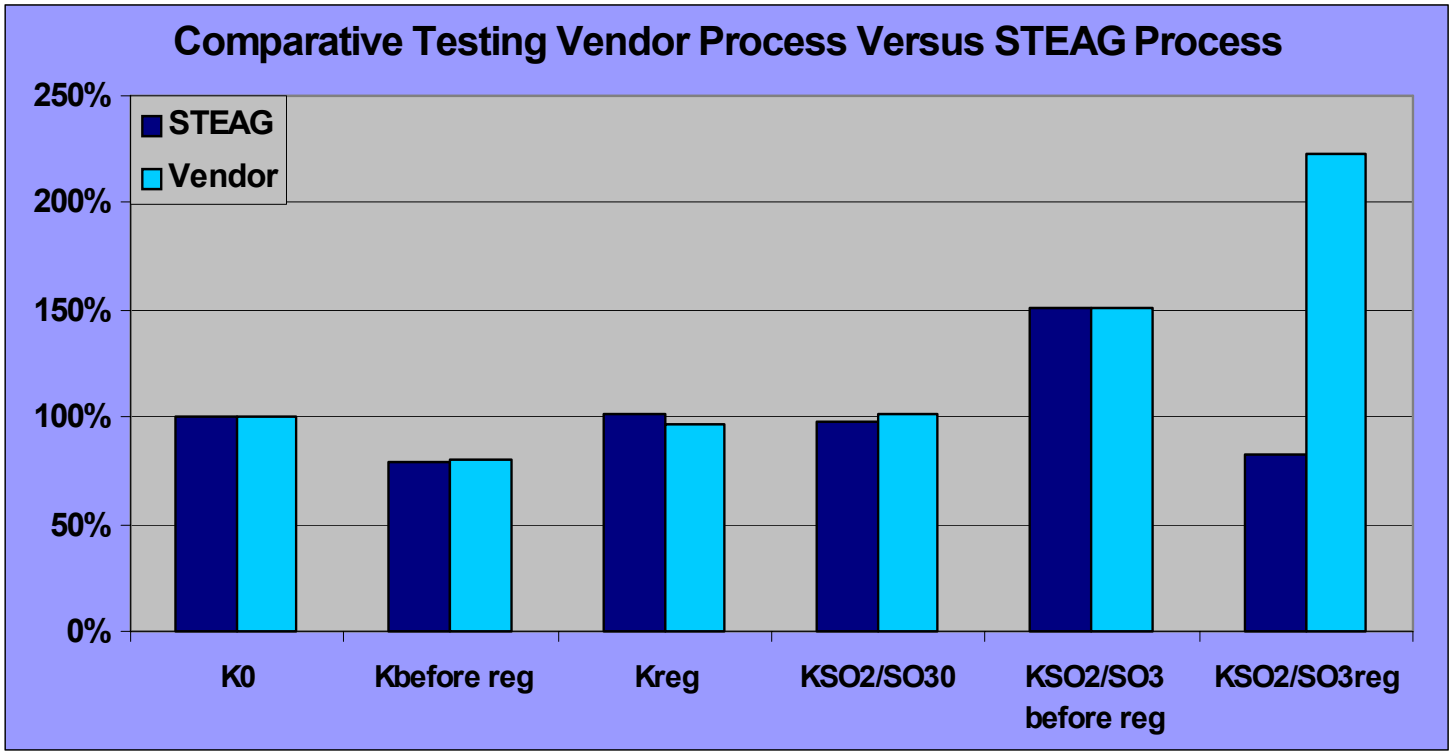
STEAG's Catalyst Regeneration Experience

Before Treatment

During Treatment

- STEAG's regeneration process was benchmarked against commercial regenerators in Europe:
  - R&D was focused on getting the SO_2/SO_3 conversion rate under control while regaining full activity.



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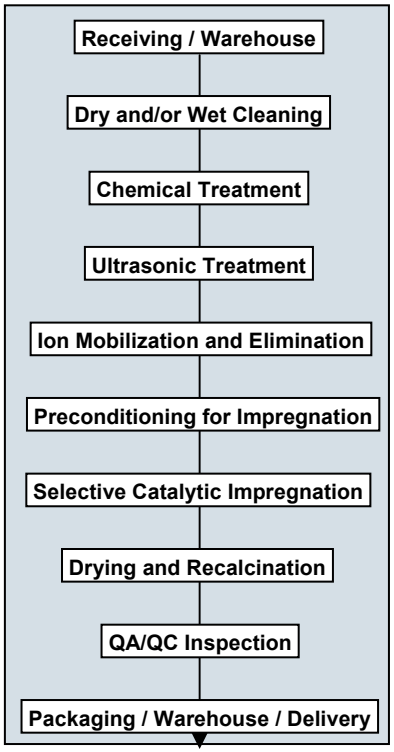
STEAG‘s Patented Regeneration Technology



STEAG’s Catalyst Regeneration Process

- STEAG’s patented regeneration technology is based on effective:
  - Removal of physical restrictions (fly ash and LPA).
  - Removal of catalyst poisons (As, P, Na, K, $CaSO_4$, etc.).
  - Protection of components essential for maintaining the catalyst’s structural integrity and mechanical strength (i.e. WO_3).
  - Full activity restoration through replenishment of the catalyst’s active components (V_2O_5, MoO_3, WO_3).
  - Recalcination for best impregnation success and mechanical strength protection.

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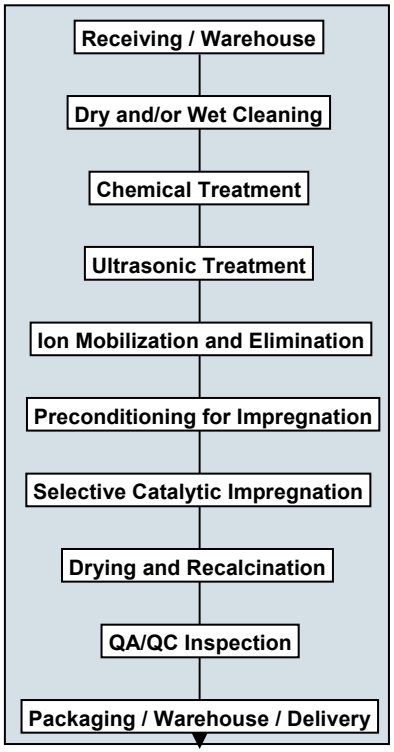
STEAG's Patented Processes (continued)



STEAG's Catalyst Regeneration Process

- Developed patented processes that are fully flexible:
  - Dry and/or wet mechanical cleaning (as needed).
  - Multi-stage wet chemical treatment for poison removal.
  - Ultrasonic cleaning (only if needed and appropriate).
  - Ion mobilization, elimination and preconditioning for impregnation.
  - Selective replenishment of V_2O_5, MoO_3, and WO_3 as needed (in case of full regeneration only).
  - Multi-stage drying.
  - Recalcination (only in case of regeneration needed).
  - Repair of mechanical (e.g. erosion) damage (if needed).
  - Packaging.

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STEAG's Catalyst Regeneration

STEAG's Catalyst Regeneration Process

(19) Bundesrepublik Deutschland Deutsches Patent- und Markenamt

(10) DE 102 22 915 A1 2004.01.15

(12) Offenlegungsschrift

(51) Int Cl.: B01D 53/86

(71) Anmelder: Saar Energie GmbH, 66287 Quierschied, DE

(72) Erfinder: Schneider, Peter, 66299 Sulzbach, DE; Baetuck, Walter, 66571 Eppelborn, DE

(54) Bezeichnung: Verfahren und Vorrichtung zur erneuten Aktivierung wabenförmig aufgebauter Katalysatorelemente für die Entstickung von Rauchgasen

STEAG's Patents for Catalyst Regeneration

- Technology based:
  - Experience and own know-how developed since 1997
- STEAG's own patents (German and U.S.)
  - Use of DI-water for cleaning, rejuvenation and regeneration.
  - Aeration of vat during treatment.
  - Reduction of SO_2/SO_3 conversion rate.
  - Selectively distributive replenishment of catalytically active ingredients.
- STEAG owns a license for the process developed by Integral Umwelttechnik, Austria including use of their patents for STEAG's own SCR fleet and in North America.

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STEAG's Regeneration Experience

- Experience gained and regeneration performance was tested and verified within our own pool of almost 10,000 m³ of SCR catalyst.
  - 3,220 m³ for STEAG's SCR fleet in Germany
  - Single layers regenerated up to 4 times
  - 680 m³ for various third parties in Europe
- Some of STEAG's SCRs depend and solely rely on successful catalyst regeneration for adequate SCR operation and economical unit operation, e.g. Leuna and Godorf Cogeneration Plants.

(12) United States Patent
Dürr et al.

(10) Patent No.: US 6,387,836 B1
(45) Date of Patent: May 14, 2002

(54) METHOD FOR RENEWED ACTIVATION OF HONEYCOMB-SHAPED CATALYST ELEMENTS FOR DENITRATING FLUE GASES

FOREIGN PATENT DOCUMENTS

ABSTRACT

4 Claims, No Drawings

STEAG's Patents for Catalyst Regeneration

(12) United States Patent
Bodin et al.

(10) Patent No.: US 6,484,733 B2
(45) Date of Patent: Nov. 26, 2002

(54) PROCESS FOR REGENERATING USED DENOX OR DEDIOXIN CATALYTIC CONVERTERS

U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS

ABSTRACT

26 Claims, No Drawings

STEAG's Herne Cogeneration Plant

STEAG's Walsum Cogeneration Plant

Summary and Conclusions:

- Catalyst is viewed and treated by STEAG as a commodity, however not all catalyst types are suitable for all applications.
- Each type of catalyst has its distinct advantages and disadvantages. The selection of the best catalyst type requires an economic evaluation on a case by case basis.
- The use of new versus regenerated catalyst depends solely on market conditions and prices. The prices of regenerated catalyst varied between 25% and 65% of new catalyst, depending on the price of new catalyst and the type of regeneration process used and required.
- As other German utilities, STEAG also found no difference in longevity or deactivation rate between regenerated and new catalyst. However, the SO_2/SO_3 conversion rate differs significantly, depending on the regeneration process used.

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?Questions?

STEAG's catalyst regeneration: 10 years of in-house experience