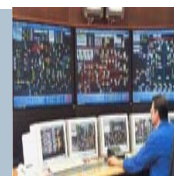
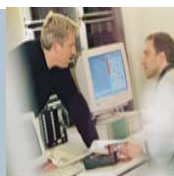


STEAG



**steag**

encotec  
America

# German Experience with Catalyst Regeneration

Hans Hartenstein  
STEAG LLC

**2007 NOx Round Table and Expo**

February 5 – 6, 2007

Cincinnati, Ohio

## SCR Catalyst Regeneration 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.**



STEAG's Bergkamen  
Power Station



STEAG's Fenne  
Cogeneration Plant

## SCR Catalyst Regeneration History

- **1983: Legislation – Flat rate NO<sub>x</sub> emission limit of 200 mg/Nm<sup>3</sup> (~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**



STEAG's Bexbach  
Power Station



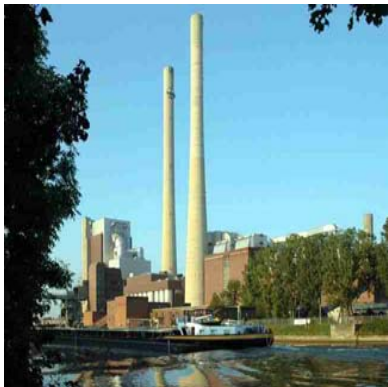
STEAG's Weiher  
Power Station

## SCR Catalyst Regeneration History

- **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.**



STEAG's Voerde  
Power Station



EnBW's Heilbronn  
Power Station

## 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).**



HEW's Tiefstack  
Cogeneration Plant

## SCR Catalyst Regeneration Processes

- **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.



EnBW's In-situ  
Rejuvenation Process

## SCR Catalyst Regeneration Processes

- **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.



HEW's On-site  
Rejuvenation Process



Integral's On-site  
Rejuvenation Process

## SCR Catalyst Regeneration Processes

- **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.



LPA Plugged Catalyst  
– STEAG's Voerde  
Power Station



Rejuvenated Catalyst  
– STEAG's Voerde  
Power Station

## STEAG's Catalyst Regeneration Needs

- **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<sub>2</sub>/SO<sub>3</sub> conversion rate of the catalyst of the Leuna and Godorf refinery units (same type of fuel, high-dust SCR).**
  - **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) SCR units due to increased use of world market coals and secondary fuels (sewage sludge, bone meal, pet coke, etc.).**



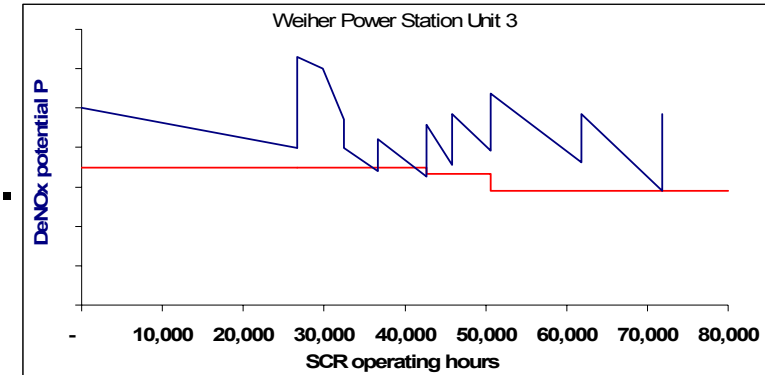
Weiher 6 x 6 Log  
Honeycomb Modules



Fenne  
Triple-decker Plate  
Modules

# Bexbach, Weiher and Fenne – Blinding Layers

- 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  $\text{CaSO}_4$  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.

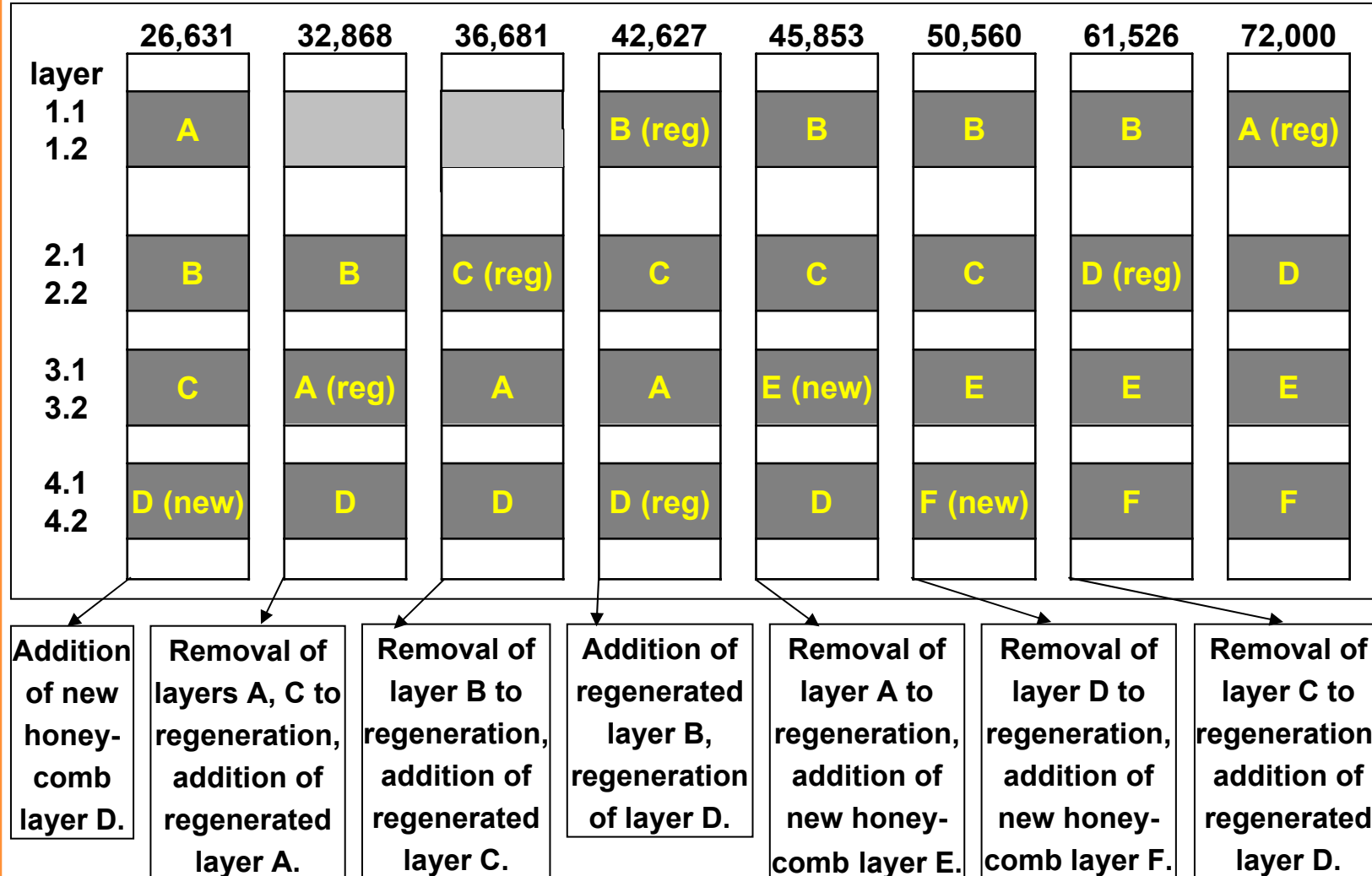


STEAG's Bexbach  
Power Station



STEAG's Weiher  
Power Station

## Bexbach, Weiher and Fenne – Blinding Layers



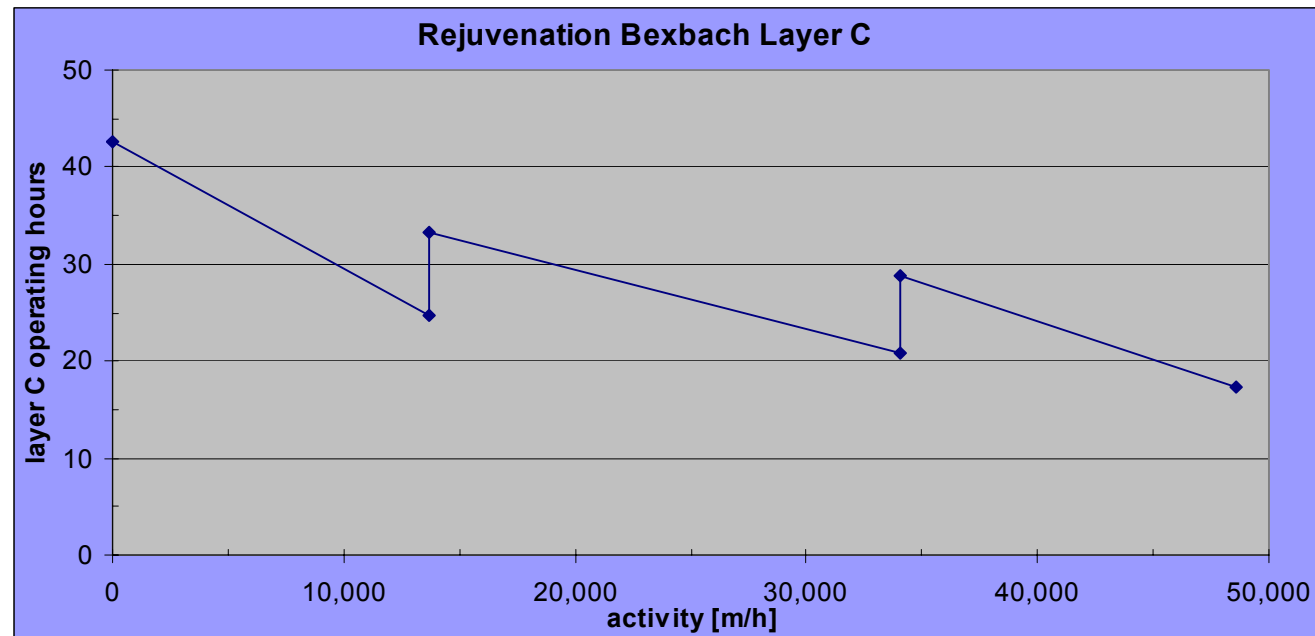
STEAG's Weiher Power Station



Regenerated Weiher 6 x 6 Log Honeycomb Modules

## STEAG's Catalyst Regeneration Experience

- 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.



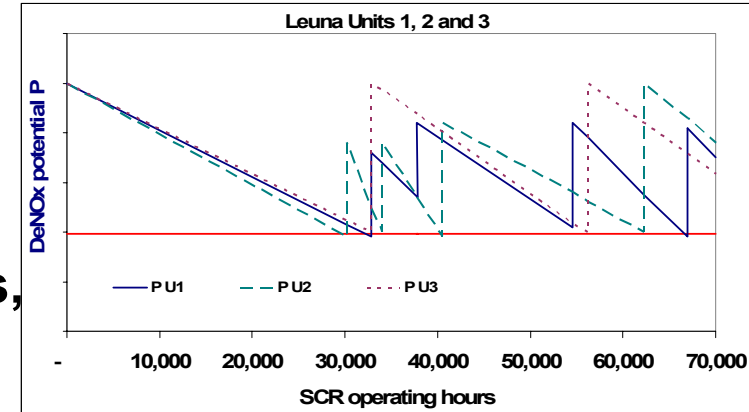
Rejuvenation Tank at  
Weiher Power Station



Rejuvenation Tank  
During Catalyst  
Loading

## Leuna and Godorf – Vanadium Pore Pluggage

- High-dust SCR in combination with the refinery residue fuel ( $S \leq 6\%wt.$ ) highly problematic.
- Very rapid deactivation at times, highly dependent on fuel mix.
- 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 B	A B	E (reg) B	E B	E D (reg)	E D	B (reg) D	B D	B D	B F (reg)
U2	C D	G (new) D	G D	G F (reg)	G F	A (reg) F	A F	A F	I (new) H (reg)	I H
U3	E F	E F	C (reg) H (new)	C H	C H	C H	C H	E (reg) C (reg)	E C	E C
out for regen.		C	F	A	A, B	B	E	H	A, F	A, D
						G used elsewhere				



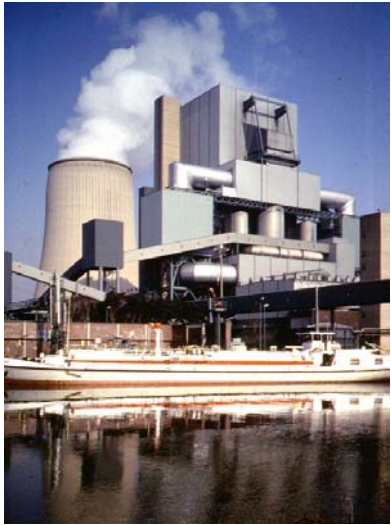
STEAG's Leuna  
Cogeneration Plant



STEAG's Godorf  
Cogeneration Plant

## STEAG's Catalyst Regeneration Experience

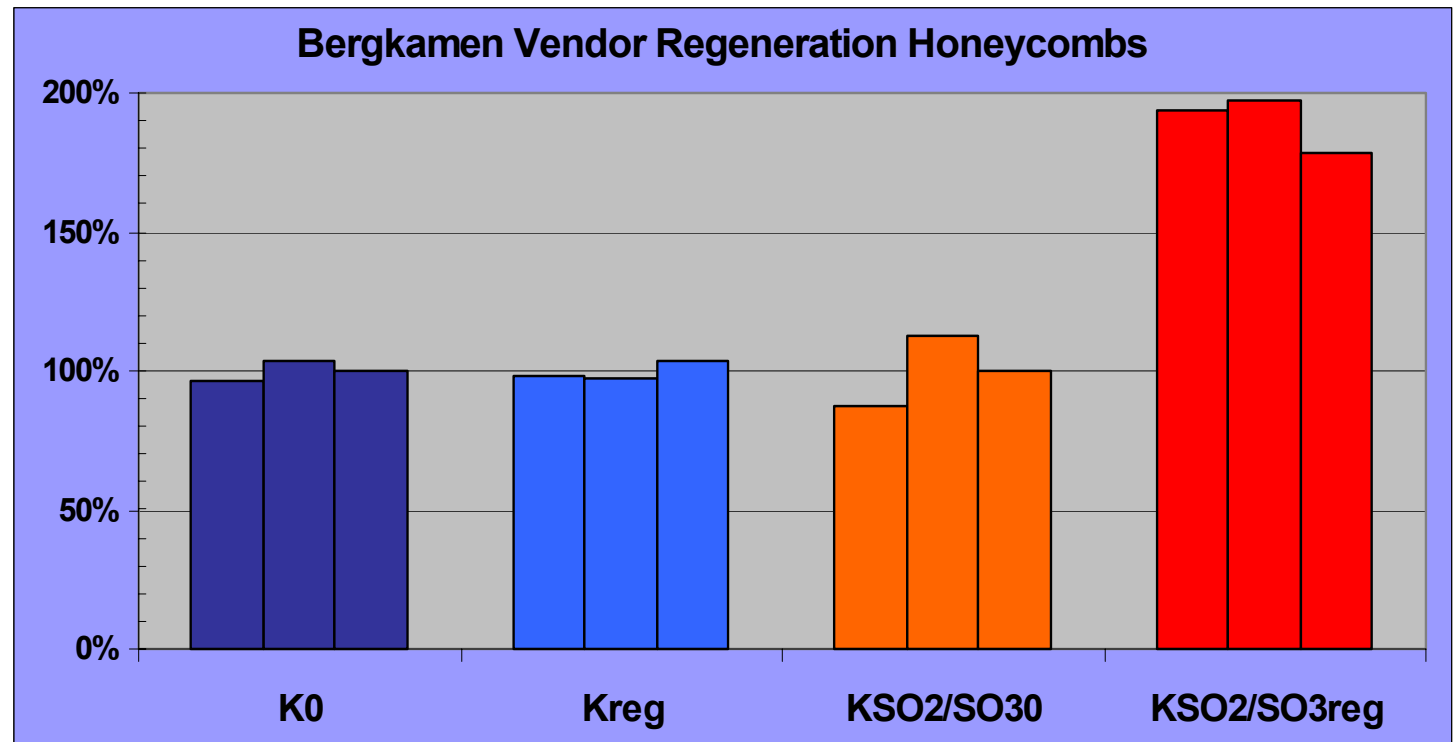
- STEAG's regeneration process development was driven by:
  - Suspicions of increases in  $\text{SO}_2/\text{SO}_3$  conversion rate when regenerated by commercial regeneration vendors.



STEAG's Bergkamen  
Power Station



STEAG's Bergkamen  
Power Station



## STEAG's Catalyst Regeneration Experience

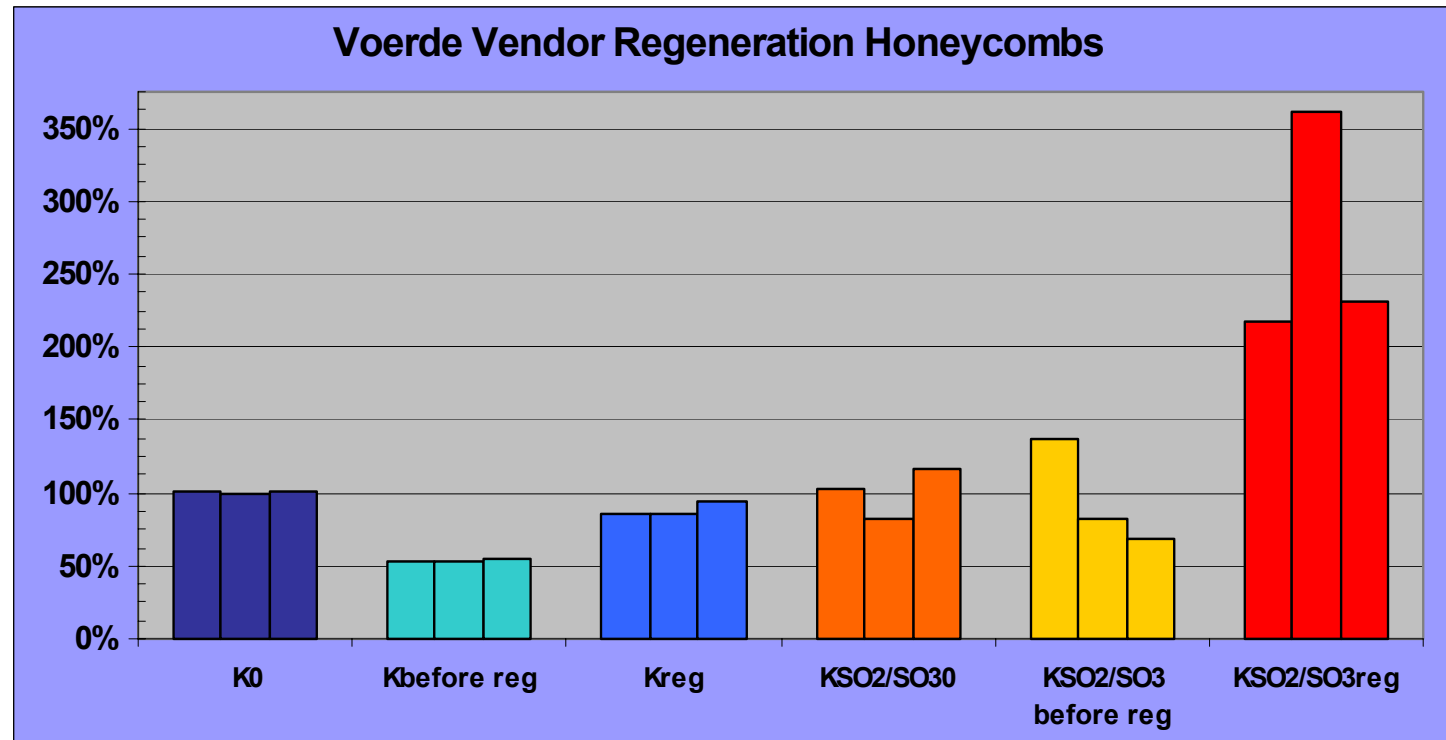
- Further investigation confirmed the problem:
  - Other utilities reported similar observations.
  - Unwanted and/or unpredictable increases were considered very undesirable for STEAG's SCRs.



STEAG's Voerde Power Station

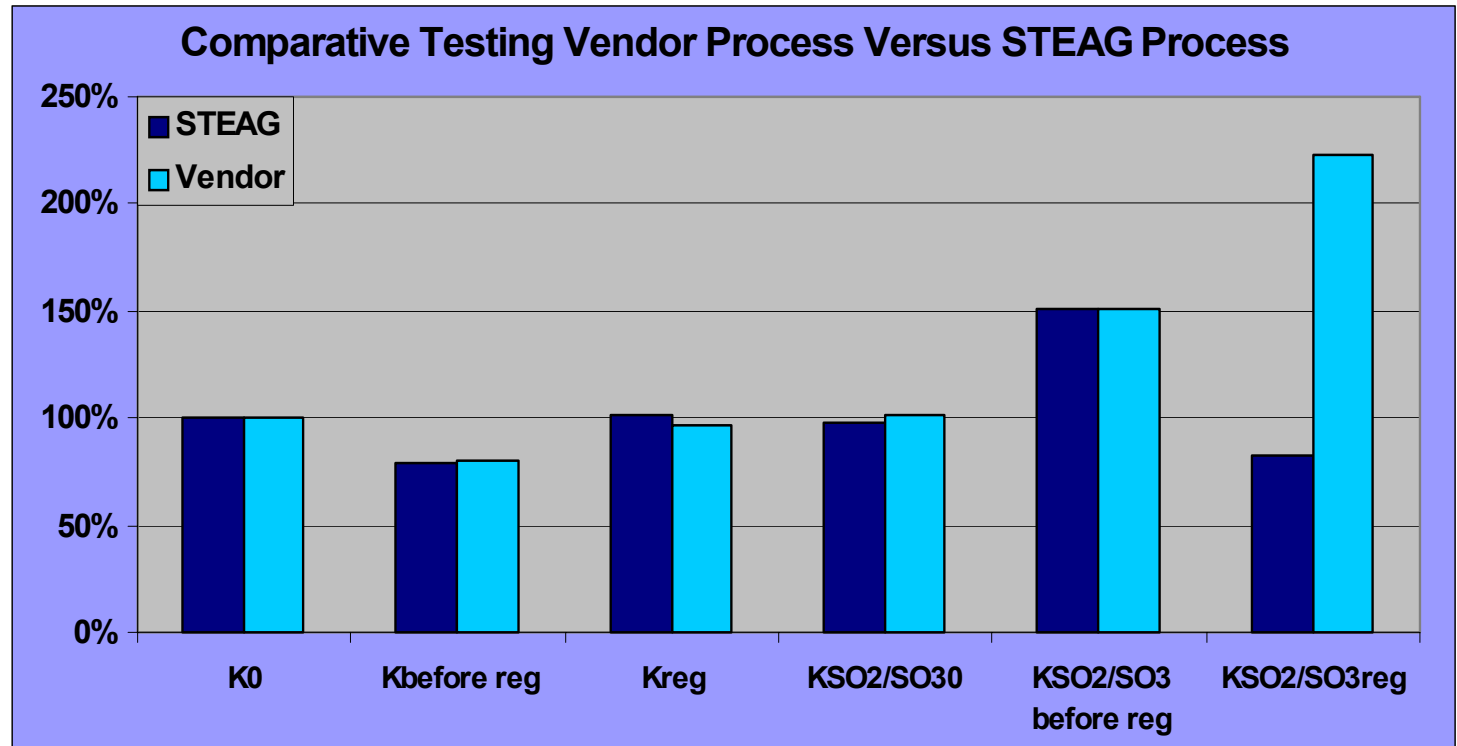


STEAG's Voerde Power Station



## STEAG's Catalyst Regeneration Experience

- STEAG's regeneration process was benchmarked against commercial regenerators in Europe:
  - R&D was focused on getting the  $\text{SO}_2/\text{SO}_3$  conversion rate under control while regaining full activity.



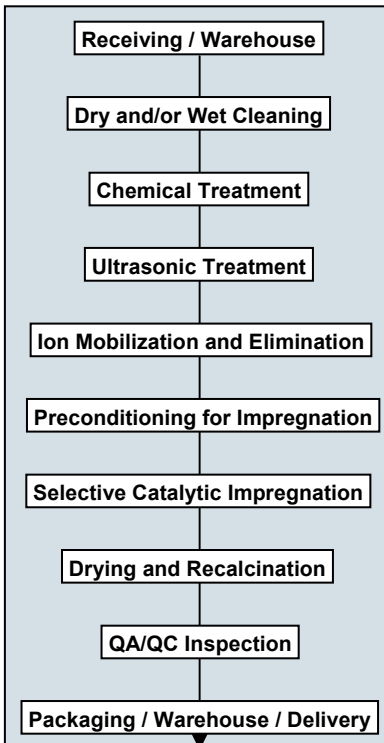
Before Treatment



During Treatment

## STEAG's Patented Regeneration Technology

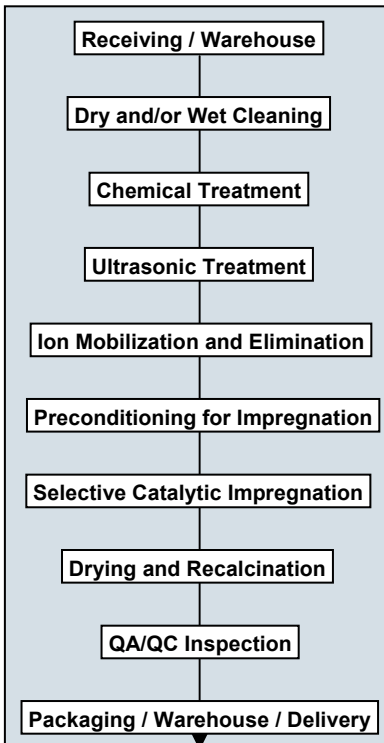
- STEAG's patented regeneration technology is based on effective:
  - Removal of physical restrictions (fly ash and LPA).
  - Removal of catalyst poisons (As, P, Na, K,  $\text{CaSO}_4$ , etc.).
  - Protection of components essential for maintaining the catalyst's structural integrity and mechanical strength (i.e.  $\text{WO}_3$ ).
  - Full activity restoration through replenishment of the catalyst's active components ( $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ).
  - Recalcination for best impregnation success and mechanical strength protection.



**STEAG's Catalyst  
Regeneration  
Process**

## STEAG's Patented Processes (continued)

- 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.



**STEAG's Catalyst  
Regeneration  
Process**

## STEAG's 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<sub>2</sub>/SO<sub>3</sub> 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.



STEAG's Catalyst  
Regeneration  
Process



STEAG's Patents  
for Catalyst  
Regeneration

# Catalyst Regeneration



encotec  
America

## STEAG's Regeneration Experience

- Experience gained and regeneration performance was tested and verified within our own pool of almost 10,000 m<sup>3</sup> of SCR catalyst.

- 3,220 m<sup>3</sup> for STEAG's SCR fleet in Germany

- Single layers regenerated up to 4 times

- 680 m<sup>3</sup> for various third parties in Europe

- Some of STEAG's SCR's depend and solely rely on successful catalyst regeneration for adequate SCR operation and economical unit operation, e.g. Leuna and Godorf Cogeneration Plants.

13000130381

(12) United States Patent  
Dörer 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 OXIDIZING FLUE GASES

(75) Inventors: Hans-Kurt Dörer, G. Inghert, Georg K. Sch. Schmidt, Walter Bartsch, Egidio W. Watsch, et al. of DE

(73) Assignee: SasolEnergy GmbH, Sandstracker (DE)

(\*) Priority: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/242,893

(22) PCT Filed: Jan. 8, 1999  
(86) PCT No.: PCT/DE99/01448  
(371) Date: Mar. 8, 1999  
(370) Date: Mar. 8, 1999

(87) PCT Pub. No.: WO/99/04228  
PCT Pub. Date: Dec. 23, 1999

(93) Foreign Application Priority Data  
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1997 (DE) 197 23 796  
1997 (DE) 197 23 796

(52) Int. Cl. B01D 53/04  
(51) Field of Search: 423/22, 423/23, 423/24, 423/25, 423/26, 423/27, 423/28, 423/29, 423/30, 423/31, 423/32, 423/33, 423/34, 423/35, 423/36, 423/37, 423/38, 423/39, 423/40, 423/41, 423/42, 423/43, 423/44, 423/45, 423/46, 423/47, 423/48, 423/49, 423/50, 423/51, 423/52, 423/53, 423/54, 423/55, 423/56, 423/57, 423/58, 423/59, 423/60, 423/61, 423/62, 423/63, 423/64, 423/65, 423/66, 423/67, 423/68, 423/69, 423/70, 423/71, 423/72, 423/73, 423/74, 423/75, 423/76, 423/77, 423/78, 423/79, 423/80, 423/81, 423/82, 423/83, 423/84, 423/85, 423/86, 423/87, 423/88, 423/89, 423/90, 423/91, 423/92, 423/93, 423/94, 423/95, 423/96, 423/97, 423/98, 423/99, 423/100, 423/101, 423/102, 423/103, 423/104, 423/105, 423/106, 423/107, 423/108, 423/109, 423/110, 423/111, 423/112, 423/113, 423/114, 423/115, 423/116, 423/117, 423/118, 423/119, 423/120, 423/121, 423/122, 423/123, 423/124, 423/125, 423/126, 423/127, 423/128, 423/129, 423/130, 423/131, 423/132, 423/133, 423/134, 423/135, 423/136, 423/137, 423/138, 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## 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  $\text{SO}_2/\text{SO}_3$  conversion rate differs significantly, depending on the regeneration process used.**



STEAG's Herne  
Cogeneration Plant



STEAG's Walsum  
Cogeneration Plant

STEAG

steag

encotec  
America



?Questions?

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