



Operating Experience with SCR Catalyst Incorporating Valuable Additives Extracted from Used Petroleum Catalyst

SK Corporation



Background

A. The concept deployed in 1995 was followed by intensive development work in the areas of:

- ✓ Recyclability study of valuable metals extracted from used petroleum catalyst for SCR catalyst
- ✓ Catalyst composition refinement
- ✓ Material processing and manufacturing process

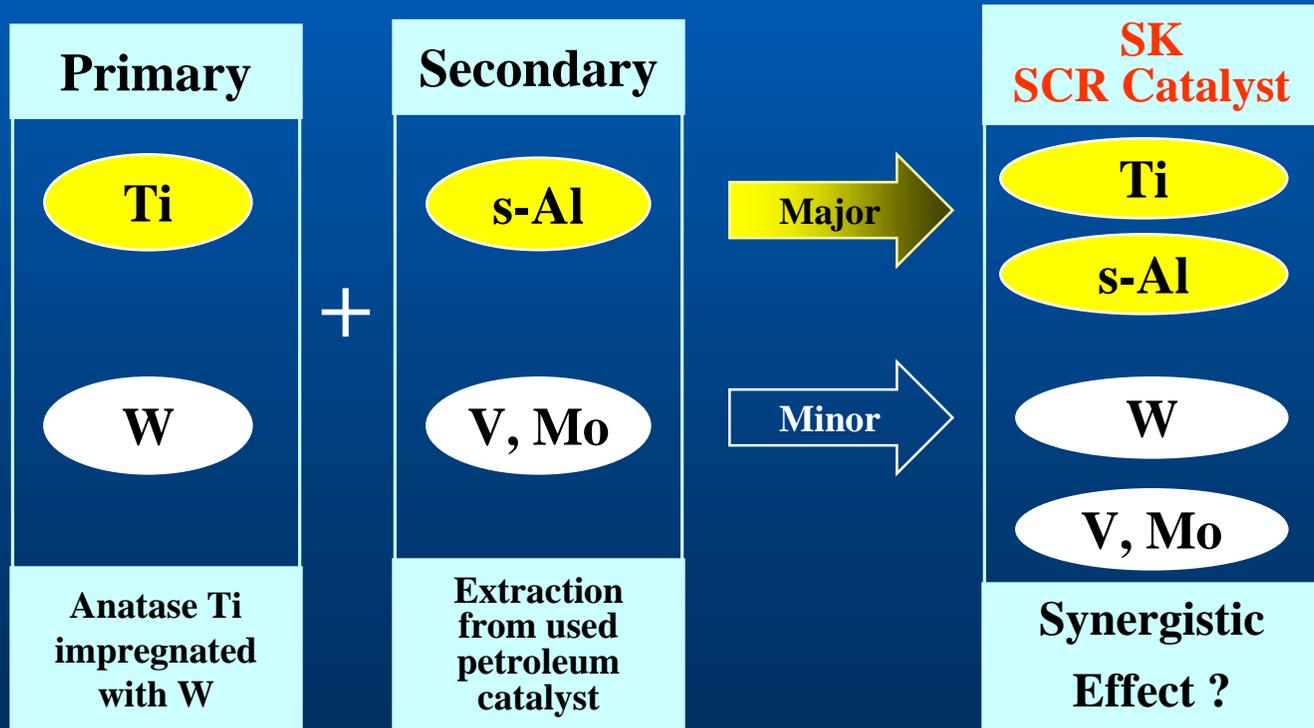
B. Commercial Installations

- ✓ LNG fired boiler
- ✓ Nitric acid plant
- ✓ Combined heat & power plant (B-C)
- ✓ Diesel application
- ✓ Coal fired power plant (Demo Test)

C. Recipient of Korea Excellent Technology Recognition Award

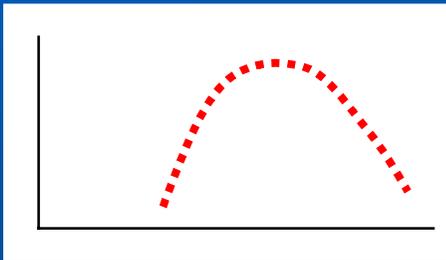
Description of SK SCR Catalyst

Synergy between Petroleum and SCR Catalysts



Synergistic Effects

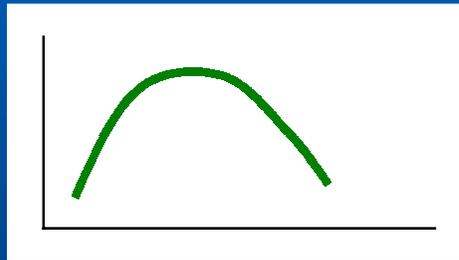
Commercially Available Ti/W



- ✓ High Surface Area Carrier
- ✓ SO₂ Resistance
- ✓ Thermal Resistance

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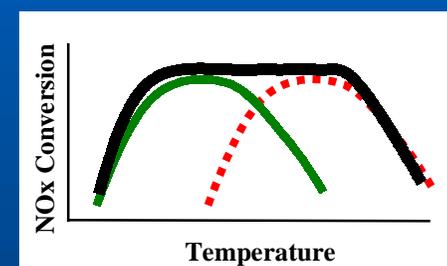
Components Extracted From Used Catalyst



- ✓ s-Al: SO₂ Resistance, Lower SO₂ Oxidation Rate
- ✓ V: Active Metal
- ✓ Mo: Arsenic Resistance

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SK SCR Catalyst



- ✓ Wide Temp. Window (NO_x Reduction)
- ✓ Lower SO₂ Oxidation Rate
- ✓ High Resistance to SO_x & Other Toxic Substances
- ✓ Thermal Resistance

Extraction of Components from Used Petroleum Catalyst

Used Petroleum Catalyst from hydro-desulfurization process



Physical & Chemical Treatment

Proprietary Additives



Extract Major Components

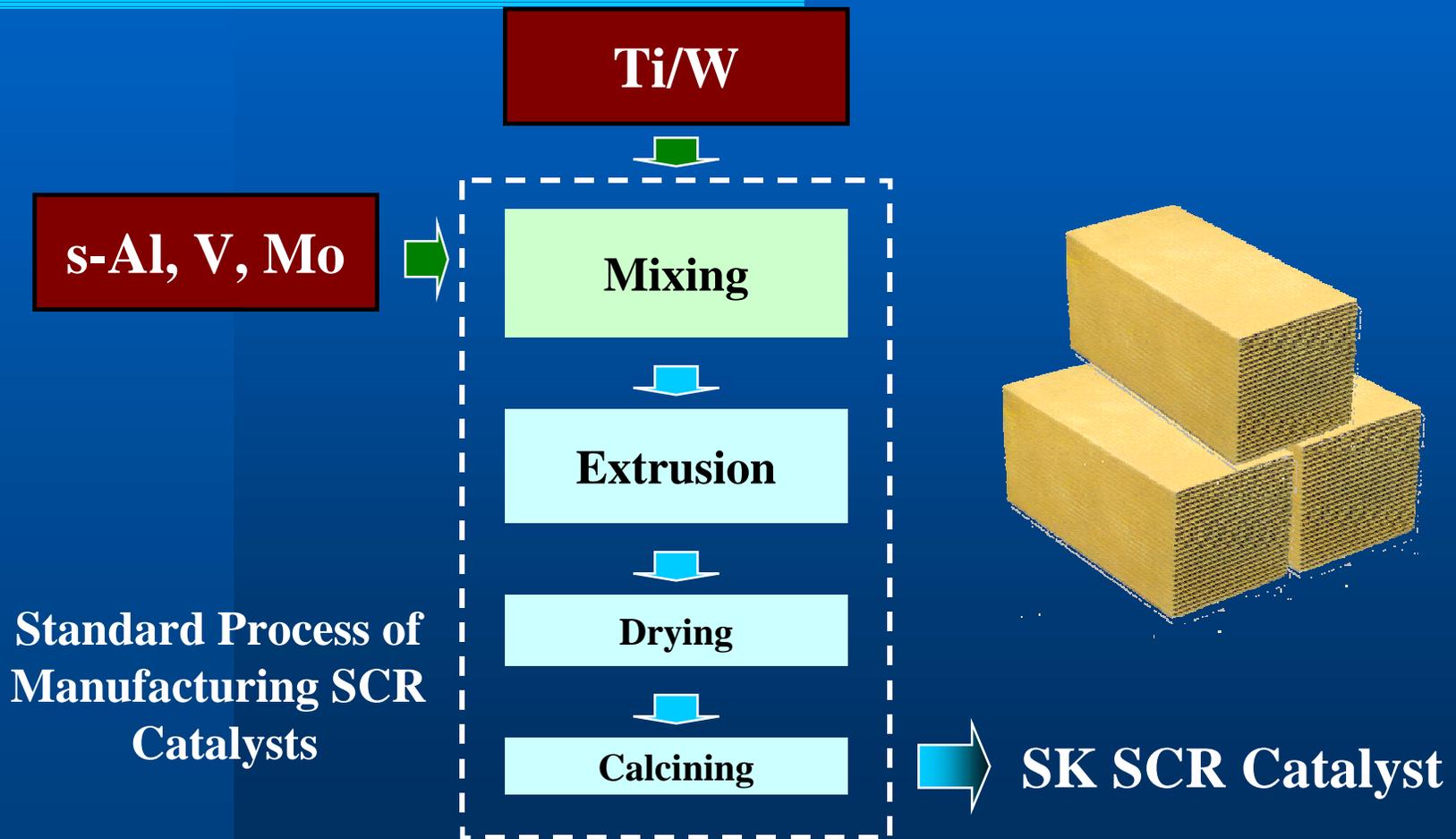


s-Al, V, Mo

Advantages of Catalyst with Additives

- Synergy between Petroleum and SCR catalyst
 - ✓ High resistance to SO_x and other toxic substances
 - ✓ Lower SO₂ oxidation rate
 - ✓ Wide temperature range
- Lower Cost
- Environmentally Friendly
(3R Campaign : Recycle/Reuse/Reduce)

SK SCR Catalyst Production Process



Standard Process of
Manufacturing SCR
Catalysts

Comparison of SCR catalysts

Manufacturer	Company A	Company B		SK
Type	Honeycomb	Honeycomb	Metal Plate	Honeycomb
Active Components	V/W/Ti	V/Mo/Ti		V/Mo/W/s-Al/Ti
Substrate	Extruded Monolith	Extruded Monolith	S.S.	Extruded Monolith
BET SA (m ² /g)	90	50 ~ 80		80 ~ 90
Operating Temp (°F)	400 ~ 750	340 ~ 800	570 ~ 840	380 ~ 840

Patent Protection

- The proprietary technology for manufacturing SCR catalysts using used petroleum catalysts is patented in U.S. and Europe.
- Several related patents are pending

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(81) Designated States: DE, JP, US.

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(12) **United States Patent**
Ku et al.

(11) Patent No.: **US 6,171,566 B1**
(45) Date of Patent: **Jan. 9, 2001**

(54) SELECTIVE CATALYTIC REDUCTION FOR THE REMOVAL OF NITROGEN OXIDES AND CATALYST BODY THEREOF	4101288	31977	Shirashi et al.	425239
	4108700	41977	Osamoto et al.	252430
	4048312	91977	Matsubara et al.	252461
	4182337	101977	Nishikawa et al.	252485
(75) Inventors: Don chul Ku, Young Woo Kim, Young Jack Choi, all of Taejeon (KR)	4195183	41978	Nakajima et al.	425239
	5128314 *	71991	Golbenger et al.	28216-R
	5343551 *	81991	Carroll	43528
(73) Assignee: SK Corporation, Seoul (KR)	5866100 *	21999	Ogushi et al.	512905

(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: **09/462,763**

(22) PCT Filed: **Jul. 10, 1997**

(86) PCT No.: **PCT/KR97/00135**

§ 371 Date: **Jan. 10, 2000**

§ 102(c) Date: **Jan. 10, 2000**

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(52) U.S. Cl. **423229.1, 502305, 502312, 502313, 502314, 502315, 502316, 502321, 502322**

(58) Field of Search **423229.1, 502305, 502312, 31A, 314, 315, 316, 321, 322**

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,903,572 H1976 Hindri et al. 352-92

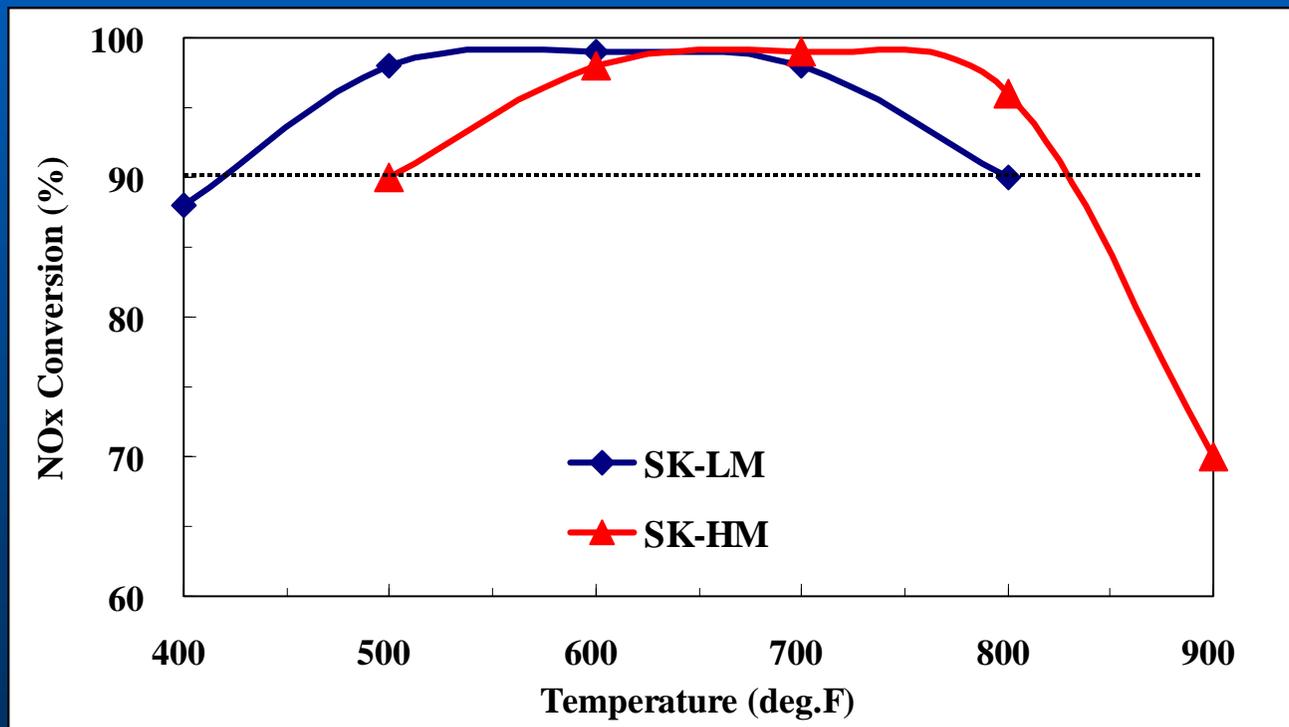
ABSTRACT

A selective catalytic reduction body for the removal of nitrogen oxides (NO_x) comprising about 5 to 80% by weight of vanadium, about 0 to 60% by weight of molybdenum, about 0 to 20% by weight of nickel and about 0 to 20% by weight of cobalt, which catalytic body is economically favorable in production cost and superior in removing the nitrogen oxides from exhaust gas, can keep its activity high for a long time by virtue of excellent thermal resistance and poison resistance to sulfur oxides and other chemicals, exhausts oxygenated ammonia and heavy metal by ash at the lowest amount, and allows the catalyst volume necessary to obtain the same removal degree and the pressure loss authorized to be minimized.

3 Claims, No Drawings

Catalyst Performance

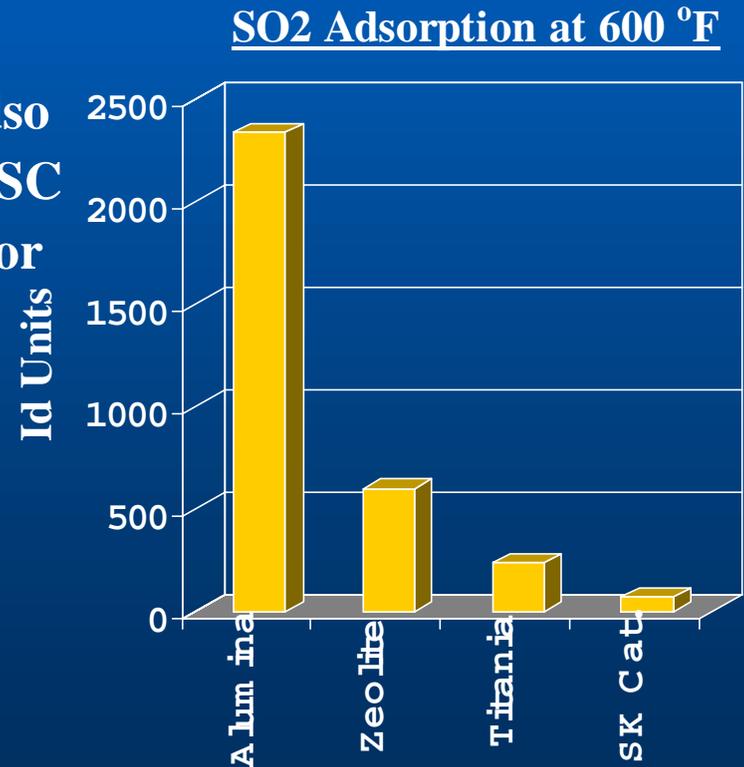
NO_x Conversion



Catalyst Performance

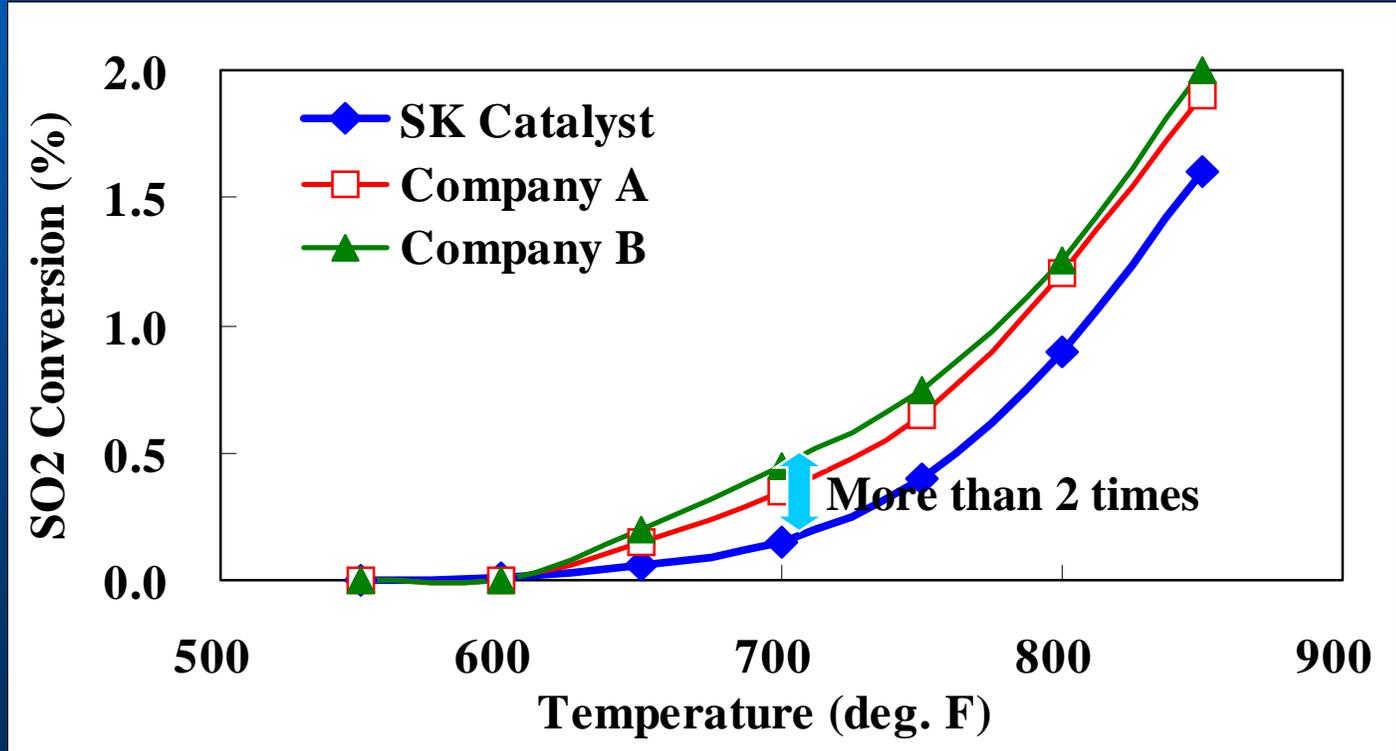
SO2 Adsorption

- Substantially reduced SO2 adsorption on the surface of SK's SCR catalysts results in two major effects:
 - ✓ Less SO2 oxidation rate
 - ✓ Higher poison resistance to SO2



Catalyst Performance

SO₂ Conversion



Applications

SCR for NamHae Chemical Plant

Application Information

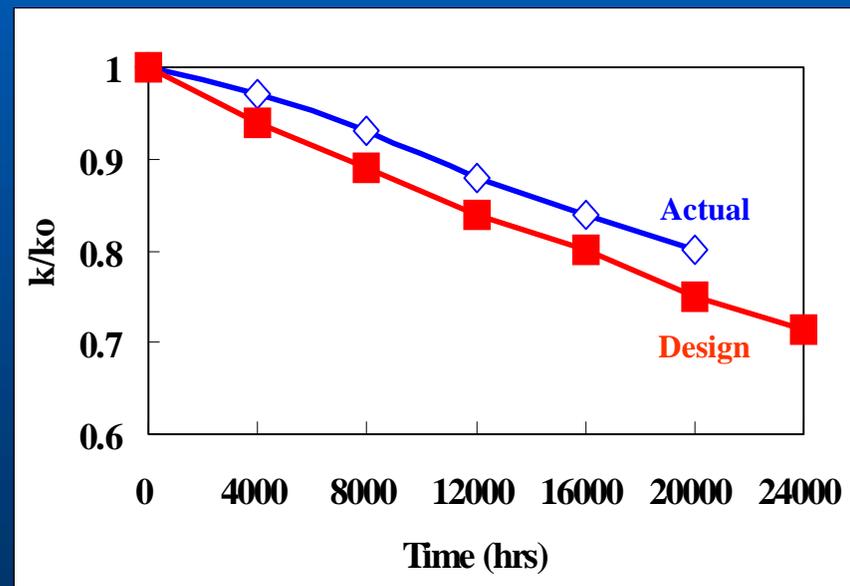
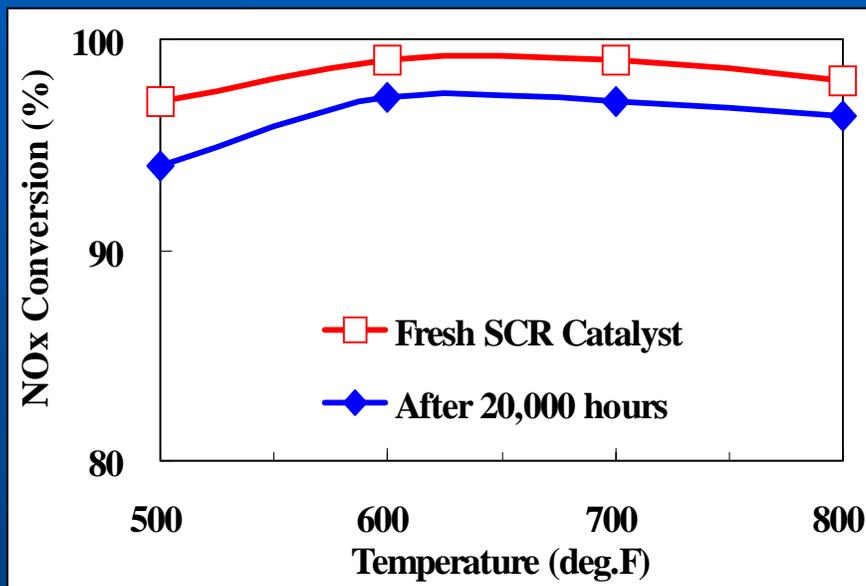
- Installation Date : 1999. 09
- Plant : Nitric Acid Plant
- Operating Temp. : 570°F
- NO_x Inlet (@4%O₂) : 2,300ppm
- Reducing Agent : Aq. Ammonia (25wt.%)

Results

	<u>Design</u>	<u>After Installation</u>
▪ NO _x Outlet	100 ppm	< 70 ppm
▪ NO _x Reduction	96%	> 97%
▪ Pressure Drop	1.2" W.C.	0.8" W.C.

SCR for NamHae Chemical Plant

Durability



SCR for Diesel Engine Application

Application Information

- Installation Date : 2000. 07
- Plant : Diesel Engine
- Fuel : Diesel
- Operating Temp. : 570°F
- NOx Inlet (@13%O2) : over 300 ppm
- Reducing Agent : Anhydrous Ammonia

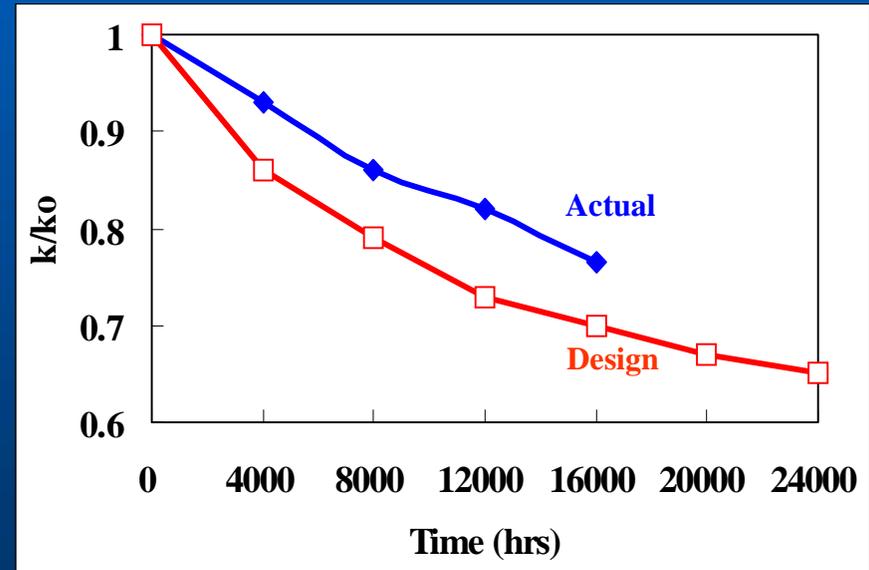
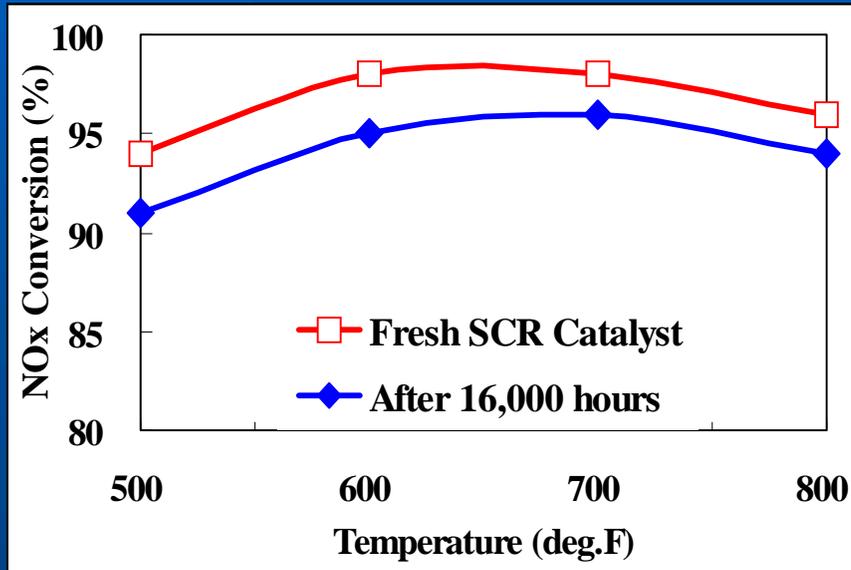


Results

	<u>Design</u>	<u>After Installation</u>
▪ NOx Outlet	60 ppm	< 15 ppm
▪ NOx Reduction	80 %	95 %
▪ NH3 Slip	< 10 ppm	3 ppm
▪ Pressure Drop	4.0" W.C.	3.1" W.C.

SCR for Diesel Engine Application

Durability



SCR for Samsung Corning Power Plant

Application Information

- Installation Date : 2001. 04
- Plant : Combined Heat & Power Plant
- Fuel : Bunker-C Oil
- Operating Temp. : 600°F
- NO_x Inlet (@13%O₂) : over 1,200 ppm
- Reducing Agent : Anhydrous Ammonia

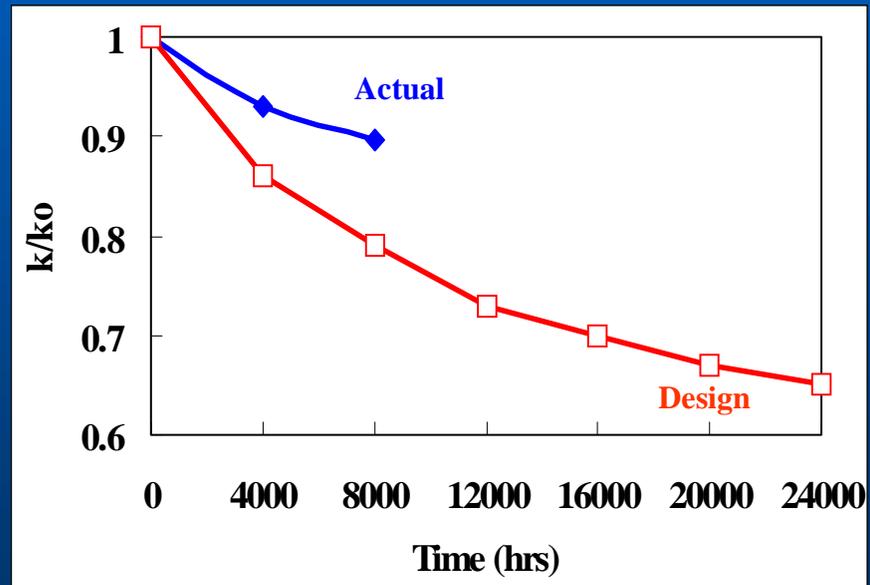
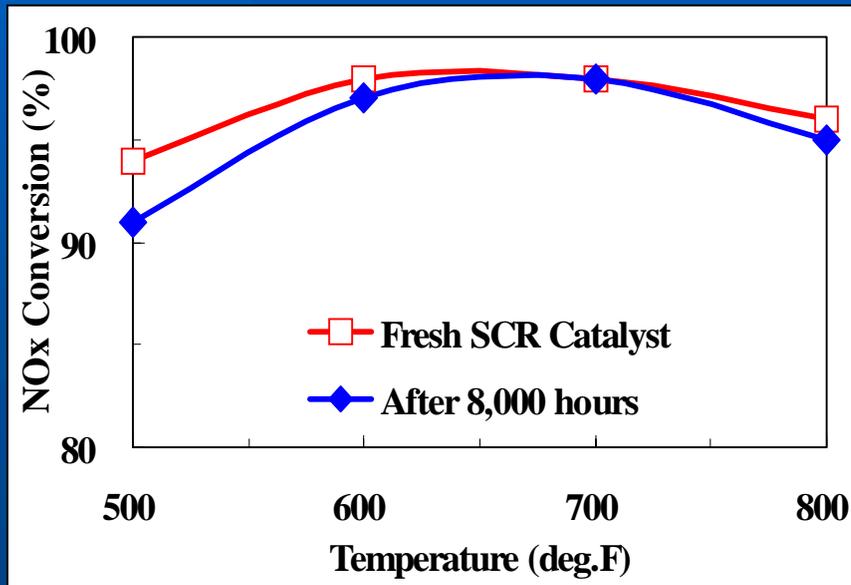


Results

	<u>Design</u>	<u>After Installation</u>
▪ NO _x Outlet	450 ppm	< 240 ppm
▪ NO _x Reduction	63%	80%
▪ NH ₃ Slip	< 10 ppm	3 ppm
▪ Pressure Drop	4.0" W.C.	3.1" W.C.

SCR for Samsung Corning Power Plant

Durability



SCR for Coal-Fired Boiler (Demo Plant)

Application Information

- Installation Date : 2001. 08
- Plant : Coal Fired Boiler
- Fuel : Coal (High Dust)
- Operating Temp. : 750 °F
- NO_x Inlet : 300 ~ 400 ppm
- Reducing Agent : Anhydrous Ammonia

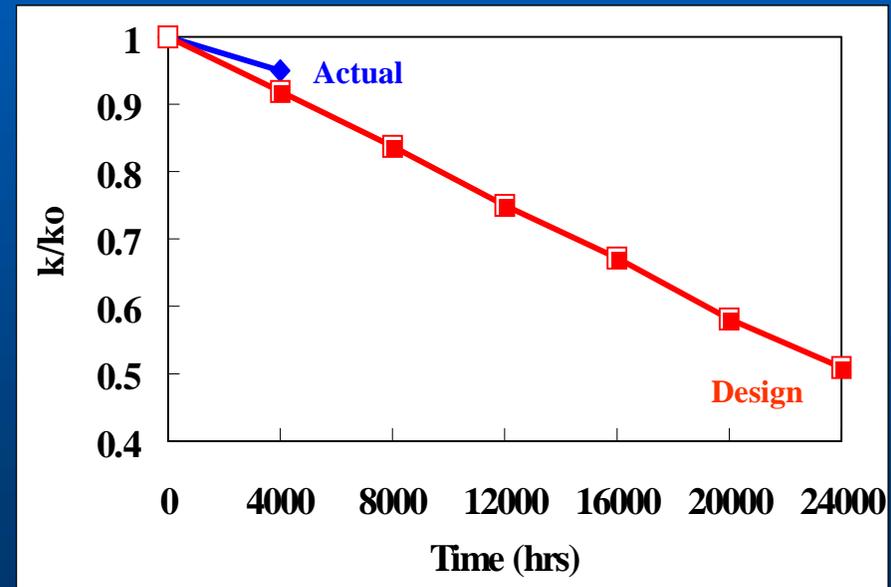
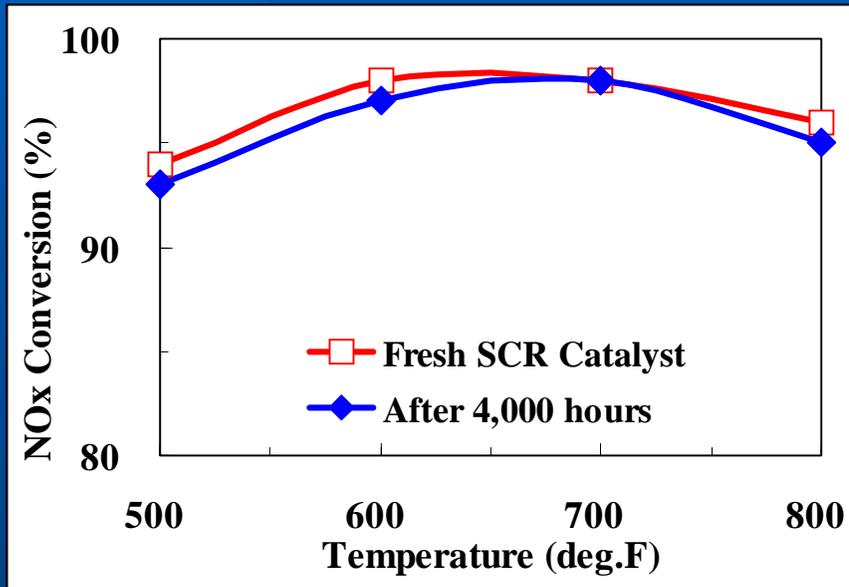


Results (After Installation)

- NO_x Outlet < 20 ppm
- NO_x Reduction over 95 %
- NH₃ Slip under 3 ppm
- Pressure Drop under 2" W.C.

SCR for Coal-Fired Boiler (Demo Plant)

Durability



SK SCR Catalyst Specification

Model	SK-20	SK-25	SK-30	SK-35	SK-40	SK-50
Normal Pitch, mm	7	6	5	4	3.5	3
Number of cells	20x20	25x25	30x30	35X35	40x40	50x50
Cell Density (cpsi)	11.5	18	26	35	46	72
Face Dimension, mm	_____ 150 x 150 _____					
Max. Length, mm	_____ 1,000 _____		_____ 800 _____		_____ 800 _____	
Application	Coal	Coal,Oil MSW*	Oil,Gas MSW	Oil & Gas	Gas	Gas

*MSW: Municipal Solid Waste

QA/QC Program & Standards

- Raw material quality is continuously monitored and evaluated by Q/C team and SK LABZone test service in accordance with SK quality assurance guidelines (ASTM, ANSI and NIST standards).
- SK Quality Management System is certified by ISO 9001, BS EN ISO 9001, KS A 9001, and approved by Lloyd's Register Quality Assurance Ltd.



Micro-Reactor



Pilot Research Facility



Module

Conclusion

Proven Performance

- Synergy between Petroleum and SCR catalysts
- High NO_x removal efficiency
- Wide temperature window
- Low SO₂ oxidation rate (High resistance to SO_x)
- Mechanical strength, thermal and chemical stability

Operational Benefits

- Environmentally Friendly
- (3R Campaign : Recycle/Reuse/Reduce)
- Lower Cost
- Longer Operating Life