**Final Report: Fiscal Year 1997
NO_x Selective Catalytic Reduction
Demonstration of Russian DeNO_x Catalysts
at MSE/WETO Facility**

**Yury Zundeleovich
Martyn Adamson**

April 1998

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (423) 576-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

FINAL REPORT: FISCAL YEAR 1997

NO_x Selective Catalytic Reduction

Demonstration of Russian DeNO_x catalysts at MSE/WETO facility

Yury Zundeleovich, Principal Investigator
Martyn Adamson, Project Manager

PURPOSE

The primary purpose of this work was for LLNL to coordinate, analyze and provide general technical support for testing of environmentally-benign catalysts for the selective reduction of NO_x with ammonia. The catalysts were developed at the Boreskov Institute of Catalysis (BIC) in Russia and the testing was performed in WETO facilities at Butte, Montana. In these tests, the performance of the Russian catalysts has been directly compared for effectiveness with a commercial Western selective catalytic reduction (SCR) catalyst.

TARGET PROBLEM

Catalysts currently used to convert/reduce NO_x at levels up to 10,000 ppm in thermal process off gas streams consist primarily of vanadium pentoxide, titanium dioxide, and zeolites such as ZSM-5. These catalysts are quite expensive, and the vanadium, copper and other metals that they contain prevents the disposal of these materials in California land fills (California has the most restrictive land fill disposal regulations in the nation and has therefore been chosen as the baseline for disposal criteria). Currently, NO_x in gas streams is usually removed by Selective Catalytic Reduction (SCR) which relies on the addition of ammonia to an oxygen-containing off gas that passes over the heated catalyst. The combination of ammonia and oxygen in the presence of the catalyst convert the NO_x to nitrogen, usually with an efficiency of 80-95%. A problem exists regarding the amount of ammonia that must be added to the off gas to effect the conversion of NO_x to nitrogen. If too little ammonia is added, the conversion efficiency of the NO_x will be reduced; if too much is added, ammonia will become an air pollutant itself (this condition is referred to as ammonia slip). In mixed waste thermal treatment off gas systems, it is difficult to determine how much ammonia must be introduced into the off gas because the amount of NO_x in the stream can change appreciably in a short time because of the variations in the waste being treated. Thus, the key requirement on an effective SCR process is that the catalyst will be capable of converting (destroying) excess ammonia; other requirements are that it will be at least as effective as existing Western catalysts, that it be land-disposable (environmentally-benign), and that it be relatively inexpensive.

Virtually any waste that is slated for treatment in an incinerator, or other thermal treatment system such as a melter is a target waste stream. There is approximately 40,000 m³ of mixed low level waste in the DOE inventory (includes current and projected volumes), but other mixed-TRU or non-mixed waste streams such as low-level contaminated waste could also be treated. For this particular technology, it is not so much the type of waste that is of concern, as the process. Thermal processes and in particular hot plasma systems produce

high levels of NO_x in the off gas. This is largely due to the nitrogen in the air in the combustion chamber being converted to NO_x at high temperatures ($> 1000^\circ\text{C}$). The amount of nitrates and some other N-containing constituents of the actual waste will also contribute to the amount of NO_x generated in an off gas stream.

BENEFITS

A new efficient, low cost catalyst that is not a RCRA hazardous waste itself as defined in 40 CFR 261 and does not contain materials listed in the California Code of Regulations, Title 22, Section 66261.24, or does not generate a RCRA hazardous waste through use and hence, can be disposed of in a non-RCRA landfill, or that substantially eliminates ammonia in the off gas stream, would be useable in the off gas system of almost any mixed waste thermal treatment facility. This would include DOE facilities such as the Waste Experimental Reduction Facility (WERF), Toxic Substances Control Act (TSCA) Incinerator, Transportable Vitrification System (TVS), Consolidated Incineration Facility (CIF), Advanced Mixed Waste Treatment Facility (AMWTF), and Plasma Arc Centrifugal Treatment-6 (PACT-6) at Western Environmental Technologies Office (WETO). In addition to mixed waste systems, the use of the described catalyst would have broad commercial applications to users such as coal fired power plants, which produce large quantities of NO_x in their operations.

TECHNOLOGY DESCRIPTION

Nitrogen oxides (NO_x) in gas streams from stationary sources are removed most efficiently by Selective Catalytic Reduction (SCR), a technique used widely in Japan and Europe, and which has lately become viewed as the best available control technology in the U.S. The process adds ammonia to an oxygen-containing exhaust stream that passes over the heated catalyst. SCR selectively reduces NO_x to nitrogen with an efficiency of 80 to 95%, depending on the nature of the feed. Performance depends on catalyst activity, the residence time, and the ratio of ammonia to NO_x in the exhaust. Depending on the catalyst formulation – the predominant SCR catalyst used today consists of vanadium pentoxide on a titanium dioxide support and is relatively expensive – SCR requires temperatures in the range 200° to 400°C , residence times of 0.05 to 0.5 seconds (gas hourly space velocities of 72000 h^{-1} to 7200 h^{-1}), and is subject to tight control over the ammonia- NO_x ratio, the ammonia being a pollutant itself. Newer zeolite catalysts such as copper ZSM-5 can use either ammonia or less polluting hydrocarbons. However, the vanadium and copper in these catalysts render them hazardous for land disposal in California and also complicate their possible use in mixed waste treatment facilities.

A NO_x removal catalyst acquired from BIC in 1992 was a new iron/chromium/zinc mixed oxide honeycomb monolith which demonstrated in laboratory tests at LLNL very high activity ($> 95\%$) and the ability to convert excess ammonia to nitrogen, thus providing a convenient solution to the ammonia slip problem. Because this catalyst is predominantly iron oxide, it is far less expensive than either vanadia-titania or copper zeolite catalysts, but its chromium content is still problematic for land disposal. As a result of a small (\$21K) EM-50 funded contract negotiated between LLNL and BIC in 1993, an improved mixed oxide honeycomb monolith was delivered to LLNL in 1994 which contained copper oxide as an additional constituent. Although not intended to meet LLNL's low RCRA metal goals, this developmental catalyst (IC-44/I-700) proved capable of destroying ammonia slip over a much broader temperature range than the earlier catalyst. Under continued EM-50 funding (\$50K in FY96), BIC recently developed "environmentally-benign" NO_x removal catalysts intended to meet the soluble and total California threshold limits for RCRA metal

concentrations and possibly control the ammonia slip without generating NO_x . This development was completed in March 1996, honeycomb monoliths of three candidate environmentally-benign catalysts were fabricated, and then shipped to LLNL in April 1996.

At BIC, two methods were used to prepare candidate environmentally-benign catalysts for the selective catalytic reduction of NO_x :

- (i) Preparation of ceramic monolithic supports followed by wash coating with aqueous suspensions of active particles;
- (ii) Direct extrusion of green parts (honeycombs) containing active components.

Three monolithic support compositions were used: (i) α - Al_2O_3 + α - SiO_2 + Mg - Si - Al-O (magnesium aluminosilicate, (ii) α - Fe_2O_3 , and (iii) ZnO - Cr_2O_3 - Fe_2O_3 ; and five active wash-coating compositions (i) 3 w/o V_2O_5 + TiO_2 , (ii) 1.5 w/o V_2O_5 + TiO_2 , (iii) 5 w/o CuO + TiO_2 , (iv) 0.5 - 3 w/o CuO + H - ZSM-5 (zeolite), and (v) 0.1 - 1.7 w/o Co_2O_3 + H - ZSM-5 (zeolite). Each of the active coating materials was applied to supports in combination with γ - Al_2O_3 powder. Each of the various combinations was characterized by a variety of physical technologies and then tested for activity in a small flow reactor with high (7000 ppm) and low (500 ppm) concentrations of NO in the gas.

As a result of this work, three developmental catalysts were selected for fabrication into honeycombs of nominal dimensions 0.075 m x 0.075 m x 0.15 m. These were designated IC-45, IC-46 and IC-47. IC-45 is TiO_2 - V_2O_5 supported on a SiO_2 - Al_2O_3 monolith, IC-46 is TiO_2 - V_2O_5 supported on a ZnO - Cr_2O_3 - Fe_2O_3 monolith, and IC-47 is a composite oxide monolith consisting of V_2O_5 (0.17 w/o), CuO (0.24 w/o), WO_3 (~ 10 w/o) and TiO_2 plus traces of clay and mullite-silica fiber. With the exception of IC-46, the overall compositions were controlled so that California-listed metals (Cr, V, Cu, Zn) did not exceed their Total Threshold Limit Concentration (TTLC) values. In addition, a number of honeycombs were prepared from the monolithic catalyst IC-44 (ZnO - Cr_2O_3 - Fe_2O_3) impregnated with Cu^{2+} . This catalyst is designated IC-44/I-700, and it is intended to serve as our baseline for comparisons with the three advanced/developmental catalysts. This work is described in greater detail in reports prepared by Z. R. Ismagilov and his co-workers (Refs. 1-3).

PRIOR YEAR PROGRESS

Catalyst testing at MSE was not an independent activity but rather a part of the larger test of the Plasma Arc Waste Processing. As such, the catalyst test schedule necessarily followed overall MSE schedule and was subject to all changes and delays of the latter. Furthermore, due to shortage of technical personnel at MSE, construction of the catalyst testing rig was delayed as the numerous repairs of the PACT equipment was given first priority. Because of the downtime due to repair of the PACT equipment, uncertainties in the PACT test schedule, design bottlenecks pending resolution of DeNO_x demo issues related to analytical equipment and test strategy (parallel vs. serial), the DeNO_x testing schedule stretched into FY98. For the balance of FY97, work has been conducted on a best effort basis.

The following progress was made on the various work elements of this task since FY96. Final TTP were prepared and submitted as was the preliminary experimental plan. In a conference call between HQ (D. Valentich), the MSE/WETO Project Manager (J. Ruffner) and the MSE Project Manager (Dan Battelson), the Scope of Work for the Project and the distribution of effort between LLNL, MSE, and BIC was confirmed and an agenda for a

meeting with MSE personnel at Butte regarding the design and specifications for the catalyst testing enclosure was prepared. This meeting was held at Butte in February '97. Specifications for honeycomb catalysts were prepared and submitted to BIC. BIC's work on the advanced, environmentally-benign DeNO_x catalysts was monitored.

We first visited MSE in November '95 and viewed the Plasma Arc Centrifugal Treatment (PACT) system. We discussed and confirmed the goals and purposes of testing Russian honeycomb DeNO_x catalysts in a slip stream of the MSE PACT off-gas system in direct comparison with the existing commercial western SCR catalyst. We determined the inlet port location, the temperature, the flow, and the pressure drop for the slip stream. We outlined the instrumentation, control, and the support, piping/valving arrangement, and gas sampling port locations. The cost and scope of demo plan and cost-saving alternatives were also discussed.

We obtained and reviewed with MSE/WETO personnel the bid from Oratech Controls Inc. for inexpensive EIT gas analyzers with electrochemical sensors. Due to the limited life cycle of the latter, it was decided to stick with conventional chemiluminescence type analyzers and absorb their higher cost. NO, NO₂ and NH₃ analyzer (Model 17) were ordered from Thermo Environment Instruments Inc. for the planned DeNO_x catalyst demonstration at WETO/MSE.

LLNL participated in discussions leading to development of design work packages for the catalyst enclosure, mechanical components, electrical components, and I&C. Upon our review correction and approval of the design work packages and the overall layout, all procurement/fabrication orders had been placed. All equipment and mechanical component had been shipped to MSE. Since MSE removed one section (out of two) of its existing catalyst, it was decided to match the new conditions (half the original residence time) by reducing the number of Russian catalyst blocks from the original 10 to 5 blocks.

Fabrication of the four batches of DeNO_x catalyst monolithic honeycombs (one "baseline" and three "environmentally-benign") was completed and the necessary paperwork to satisfy Russian/Siberian export control was processed. The four boxes of catalysts were shipped by air freight to LLNL in April '96 and the first batch of catalyst honeycombs (IC-44/I-700) was then shipped to MSE in Butte. Also, during the first week of April, the BIC Principal Investigator, Prof. Z. R. Ismagilov, paid a brief visit to LLNL to deliver the advanced catalyst development final report.

The catalyst enclosure complete with the piping and the instrumentation was fabricated and installed at the testing site with Russian "baseline" honeycomb catalyst in place. The inlet to the enclosure ("slip stream") was not connected to the main off-gas duct because of the Arc Plasma experiments being conducted. For the same reason, NO, NO₂ and NH₃ analyzer were not fully hooked up, the personnel to do that being involved in the Arc Plasma experiments. The catalyst testing, therefore, took place in FY97.

Specific objectives of the testing to be accomplished during FY97 included demonstrating: (i) that NO_x concentrations in off gas streams can be reduced by a minimum of 95% (assuming initial concentrations of NO_x of 2000 - 4000 ppm), (ii) that ammonia slip can be reduced by a minimum of 75%, and (iii) that spent environmentally-benign catalysts meet the requirements for disposal in a non-Resource Conservation and Recovery Act (RCRA) landfill. Initial (Phase I) testing was performed with the IC-44/I-700 baseline catalyst in the off gas slip stream in a special enclosure in early FY97. Phase II testing of two of the environmentally-benign catalysts were conducted later in FY97, as MSE's PACT-6 operating schedule allowed. Also during FY97, in conjunction with MSE personnel, LLNL planned possible long-term (≥ 1000 hours) testing of one of the Russian catalysts to obtain

data useful for service life comparisons. Complete technical requirements for the Russian DeNO_x testing are provided in the Mixed Waste Focus Area (MWFA) Technology Development Requirements Document (TDRD) "NO_x Selective Catalytic Reduction."

EQUIPMENT DESCRIPTION

Since installation in the summer of 1993, A Joy Environmental Systems, Inc., SCR DeNO_x reactor was used in the PACT-6 off gas treatment train. The Joy unit is skid mounted and contains two catalyst beds. The catalyst carriers are honeycomb-like monoliths of titanium dioxide impregnated with oxides of tungsten and vanadium. Aqueous ammonia is injected to effect NO_x removal in the reactor. The reactor typically operates with a gas inlet temperature of approximately 520 °F. The two catalyst beds in series are capable of well over 95% conversion.

The BIC catalysts are fabricated in monolithic blocks similar to the Joy catalysts. These blocks have a square cross section normal to a flow of 7.5 by 7.5 centimeters (cm). The length of each monolith is 15 cm. The cross sectional area of the catalyst monolith is approximately one-eighth of the cross sectional area of the Joy catalysts.

The five catalyst monoliths are installed in a reactor that takes a slip stream of the off gas past the point of ammonia injection but prior to entering the Joy unit. The slip stream flow rate is set at approximately 11% of the total off gas flow. In this configuration, the Russian catalysts were exposed to approximately the same mass flux as the catalysts in the Joy unit.

Five of the Russian monoliths are arranged in series in the slipstream reactor. A thermocouple and a sample probe are installed after each of the catalyst stages. The reactor body is insulated to lessen heat loss and to ensure the middle monolith can be operated at the temperature specified in the test plan. The inlet pipe to the reactor is wrapped with a high temperature electrical heater and is also insulated.

A mass flow block diagram in Fig. 1 shows the main off gas stream, the Joy DeNO_x reactor skid and the Russian DeNO_x reactor system incorporated into the slip stream.

The dependent variables that were measured were the concentrations of NO, NO₂, and NH₃ at the exit of each BIC catalyst block and at the exit of the Joy catalyst. The same species were also measured at the combined inlet to the same reactors. For the reactor containing the five Russian catalyst blocks, multiplexed valves could be switched manually to select a sample probe for a particular block. The samples from the probe were delivered through a heated line to a dilution box where they were diluted by a factor of 100. After dilution, the samples flowed to dedicated TECO analyzers within the process building.

TEST OUTLINE

Specification for testing BIC catalysts for SCR of NO_x at MSE, Inc. PACT-6 unit

The Joy Environmental Systems, Inc. DeNO_x unit for the Plasma Arc Centrifugal Treatment unit (PACT-6) is located at the very end of the off-gas treatment train prior to the stack. Prior to DeNO_x treatment, the off-gas undergoes quenching to 50°F, scrubbing, filtering, carbon bed adsorption, and is, therefore, essentially free of particulate, acid gases and poisons.

A typical composition (vol. %) of gas entering the DeNO_x unit is as follows:

N ₂	60-65
O ₂	7-15
CO ₂	5-10
Ar	8-10
H ₂ O	2-3
NO _x	2000-5000 ppm

Particulate < 0.01 mg/dry cm³

Additional moisture is introduced with ammonium hydroxide and is formed during SCR.

The Joy honeycomb catalyst elements used with PACT-6 are 6" x 6" in cross section and 31" long. There are two sets of catalysts in series in the NO_x reduction skid, each set consisting of two elements arranged side by side. The total cross section is, therefore, 6" x 12" (0.152 m x 0.305 m). Only one set of Joy catalysts with the overall length L = 31" (0.79 m) has been used in the tests. The catalysts are composed of titanium dioxide, vanadium pentoxide, tungsten trioxide, silicon dioxide and ceramic fiber.

The BIC catalyst blocks are 3" x 3" in cross section and 6" long. 5 BIC blocks in series producing comparable to the Joy catalyst overall length L = 30" (0.75 m) have been used in the tests.

Since the total cross section of Joy catalyst is 8 times that of the BIC catalyst, the off gas flow (260 scfm typical) had to be split accordingly with roughly 231 scfm going to Joy catalyst and 29 scfm (slip stream) going to BIC catalyst.

Prior to entering the Joy unit, the off-gas was preheated to 525°F (274°C). Using that temperature, the average gas flow across the Joy unit $Q = 462 \text{ cfm}$ ($785 \text{ m}^3/\text{h}$).

Assuming 50% honeycomb open area, the cross section area for gas $A_O = 0.5 \times 0.152 \times 0.305 = 0.023 \text{ m}^2$.

Actual gas velocity $V = Q/A_O = 785/0.023 = 34100 \text{ m/h} = 9.5 \text{ m/s}$.

Space velocity $SV = V/L = 34100/0.79 = 43200 \text{ h}^{-1}$ (or residence time of 0.083 s).

Prior to entering the BIC catalyst (IC-47) enclosure, the off-gas was additionally preheated, typically to 660°F (350°C). Using average (3-rd stage) temperature of 707°F (375°C), the average gas flow across the BIC unit $Q = 69 \text{ cfm}$ ($117 \text{ m}^3/\text{h}$).

Assuming 50% honeycomb open area, the cross section area for gas $A_O = 0.5 \times 0.075^2 = 0.0028 \text{ m}^2$.

Actual gas velocity $V = Q/A_O = 117/0.0028 = 41800 \text{ m/h} = 11.6 \text{ m/s}$.

Space velocity $SV = V/L = 41800/0.75 = 55700 \text{ h}^{-1}$ (or residence time of 0.065 s).

The catalysts performance was compared using a common basis such as the space velocity.

In the case of IC-47, for example, $SV = 45000 \text{ h}^{-1}$ was selected.

The tests conducted as part of WETO/MSE's imminent Controlled Emissions Demonstration (CED), covered three different catalyst formulations, IC-44/I-700, IC-47 and IC-45, in four distinct test series. IC-44/I-700 served as a baseline for performance comparison with the other Russian developmental catalysts that were intended to be environmentally-benign (IC-45 and IC-47). In each test series, the performance of a 5-block string of Russian DeNO_x catalysts were directly compared with the existing commercial (Joy) catalyst contained in a parallel enclosure.

In the first test series (DeNO_x-0), referred to as the Shakedown Test Series in the CED Test Component Master Plan, basic functionality of the various test components and

measurement systems in the off-gas train has been verified, including that of the Russian DeNO_x catalyst test enclosure and the existing commercial catalyst enclosure. The baseline DeNO_x catalyst IC-44/I-700 was in place during these tests which were conducted in two phases (cold and hot). The same catalyst, IC-44/I-700, remained in place for the second test series (DeNO_x-1), the objective of which was a detailed evaluation of catalyst performance and comparison with the existing commercial catalyst. This test series has been performed during the first part of the period devoted to the Organics Destruction Test referred to as 97-DURATION-1.

Upon completion of DeNO_x-1, catalyst IC-44/I-700 has been replaced with the environmentally-benign catalyst IC-47 and an identical set of detailed characterization tests has been performed during the latter part of the Organics Destruction Test period referred to as 97-DURATION-4. This test series were designated DeNO_x-2. Long-term performance of the same (environmentally-benign) catalyst would be evaluated by leaving it in place after the Organics Destruction Test and continuing its evaluation through the 1000-Hr Mass Test. This final test series (which was not conducted) would be designated DeNO_x-3.

Instead, in FY98 an additional run using catalyst IC-47 and a single run with catalyst IC-45 have been performed in a test series referred to as 98-DENOX-1.

Run test for DeNO_x - phase 0 "Shakedown"

Test Objectives:

1. Verify that the spaces between the cylindrical reactor enclosure and the rectangular Russian DeNO_x catalyst blocks are adequately filled to prevent the off-gas from bypassing the catalyst block channels. (cold test)
2. Verify that at a nominal off-gas flow rate (10 to 20 pounds per minute) the two flow orifices (in the main off-gas stream and in the slip stream) are capable of splitting the total stream between the JOY DeNO_x reactor and the Russian DeNO_x reactor in proportion of approximately 90% and 10%. (cold test)
3. Determine the extent and the accuracy of the JOY DeNO_x and the Russian DeNO_x reactors temperature control. (hot test)
 - (a) maximum sustainable temperature and the time to reach it
 - (b) temperature variation among individual blocks of the Russian DeNO_x reactor
 - (c) temperature variation between the JOY DeNO_x and the Russian DeNO_x reactors
 - (d) temperature response time (how long does it take to change the temperature ?)
4. Ammonia injection control as a function of NO_x concentration in the off-gas. Ability to maintain stoichiometric proportion between NO_x and NH₃. Preliminary testing of Russian DeNO_x catalyst NO_x destruction and ammonia slip control efficiency. (hot test at 275°C, plasma arc or gas cylinder as NO_x source)
5. Establish minimum (shortest) sampling lines for each Russian catalyst block and determine sampling time.
6. Gain operational experience for the system and obtain time estimate for DeNO_x - phase 1 and phase 2 tests.

The major change to the system as a result of the shakedown tests was the addition of the electric heat wrap that allows the middle block of the Russian DeNO_x reactor to operate at the specified test temperature. It has also become evident that, due to system heat losses, the inlet temperature to the Joy catalyst cannot be raised much above the nominal 272°C at

which it is commonly operated. The heaters for the Joy catalyst were specified to achieve approximately this input temperature.

Test matrix for DeNO_x - phase 1 and phase 2

Test Objectives

According to our TTP(SF23MW35), the general objective of the tests was to directly compare the performance of the Russian DeNO_x catalysts with the performance of an existing commercial SCR catalyst (JOY) based on vanadia-titania. This had to be accomplished by measuring NO, NO₂ and NH₃ levels before and after each catalyst at representative feed gas compositions (total NO_x level, NH₃:NO_x ratio) and flow rates and at recommended catalyst operating temperatures. From these measurements (i) the rate and extent of NO_x reduction over a range of conditions including the maximum and minimum conceivable off-gas flow rates would be derived, (ii) information on the ability of the catalysts to minimize ammonia slip would be determined, and (iii) information relative to the ease of disposal of spent catalysts (particularly in California) would be obtained.

The test plans for phase 1 ("baseline" IC-44/I-700) and phase 2 ("environmentally benign" IC-47) catalyst are shown in the Table below and, except temperature, are identical. The temperature (equal for all 5 blocks) and the ammonia/nitrogen oxides ratio NH₃/NO_x are two independent parameters which will be varied.

Temperature T was varied on three levels and NH₃/NO_x, on two levels.

The third independent parameter, the space velocity $SV = V/L$ (h⁻¹) was fixed. Here $V = Q/A_0$ (m/h) is the gas volumetric flow per catalyst open area A_0 (m²) and L (m) is total catalyst length prior the gas sampling point. For each combination of T and NH₃/NO_x, the concentrations of NO, NO₂, and NH₃ were determined after each block and compared with their inlet values. Thus, the effect of T, SV and NH₃/NO_x ratio on NO_x destruction and NH₃ slip control was established.

Gas volumetric flow Q is fixed	Temp. level 1 250°C (phase 1) 300°C (phase 2)	Temp. level 2 275°C (phase 1) 350°C (phase 2)	Temp. level 3 300°C (phase 1) 400°C (phase 2)
NH ₃ /NO _x ratio: 1 to 1	for blocks 1-5: NO, NO ₂ , NH ₃	for blocks 1-5: NO, NO ₂ , NH ₃	for blocks 1-5: NO, NO ₂ , NH ₃
NH ₃ /NO _x ratio: 1.5 to 1	for blocks 1-5: NO, NO ₂ , NH ₃	for blocks 1-5: NO, NO ₂ , NH ₃	for blocks 1-5: NO, NO ₂ , NH ₃

This test series were initiated with a nominal level of NO_x (ca. 3000 ppm) at a nominal off-gas feed rate (ca. 2 lb/min).

RESULTS AND DISCUSSION

Scope

The first series of tests (designated 97-DURATION-1) in which the baseline catalyst IC-44/I-700 performed side by side with the Joy catalyst consisted of 6 sweeps. This 6 sweeps covered the temperature ranges of 240°C to 278°C and 241°C to 295°C, respectively, for Joy and IC-44/I-700 catalysts. At the above temperatures the space

velocities (nominally fixed) varied from 26700 h⁻¹ to 30600 h⁻¹ for Joy and from 26900 h⁻¹ to 38200 h⁻¹ for IC-44/I-700 catalysts.

The second and third series of tests (designated 97-DURATION-4 and 98 DENOX-1) in which the new environmentally benign catalyst IC-47 performed side by side with the Joy catalyst consisted of 5 sweeps. This 5 sweeps covered the temperature ranges of 283°C to 303°C and 319°C to 379°C, respectively, for Joy and IC-47 catalysts. Again, at the above temperatures the nominally fixed space velocities varied from 40400 h⁻¹ to 42300 h⁻¹ for Joy and from 41100 h⁻¹ to 55100 h⁻¹ for IC-47 catalysts. (98 DENOX-1 series also included one sweep involving the IC-45 catalyst. The initial results—35% reduction efficiency for NO_x and 52% reduction efficiency for ammonia—showed such poor performance that the test matrix was not run.)

To complicate the matter, the inlet concentration of the NO_x species, as well as the inlet concentration of ammonia, varied widely. The temperature at the exits of the catalysts also varied, partially due to the concentration variation, and partially due to the limited ability to control the temperature profile in this system.

Because only one sample at a time could be taken from the five sample ports in the Russian catalyst enclosure, and because a minimum of 10 minutes was required to obtain one sample, the inlet concentration to the reactor could vary by a factor of two during a sample sweep. This made it almost impossible to attribute the outlet concentration seen at any particular catalyst block to a concentration of NO_x or ammonia at the inlet to the reactor. Since a meaningful superficial analysis of the data was in doubt, it has been proposed in the MSE Final Report—FY97 Controlled Emissions Demonstration that "a kinetic model be constructed of the Russian catalyst, and the data used to validate the model. This particular task is beyond the scope of MSE involvement; however, if conclusions are to be made that the Russian catalyst performs as well or better than the Joy catalyst, the above work will probably be necessary."

Theory

Such a model, described below, was derived at LLNL with the assumptions of isothermality and the first-order reaction with respect to NO concentration. A few percent of NO₂ in the inlet gas flow had little effect on the overall catalyst performance and were excluded from the analysis. The selective catalytic reduction of NO by NH₃ in the presence of O₂ primarily involves two chemical reactions:

Reaction (1) indicates that the minimum (stoichiometric) NH₃/NO ratio is 1. Reaction (2) is an unwanted side reaction which takes place usually above 400°C. As the temperature is increased further, the more rapidly increasing rate of NH₃ oxidation (higher activation energy) more than offsets the increased rate of NO reduction, resulting in a net decrease of NO conversion and hence the bell-shaped conversion versus temperature curve. The first-order reaction may, therefore, not be valid at higher reaction temperatures (>400°C) where NH₃ oxidation rate becomes significant. The model still correctly predicts the NO removal rate within the experimental range covered in these tests where NH₃ is not the limiting reactant (NH₃/NO ratio > 1).

The first-order rate of disappearance of NO follows the equation

$$dC_{\text{NO}}/dt = -kC_{\text{NO}} \quad (3)$$

where C_{NO} is the concentration of NO, k is the first-order rate constant, and t is the contact or residence time. Integration of (3) yields the expression from which the rate constant k is determined:

$$\ln(C_{NO}/C_0) = -kt \quad (4)$$

Here C_{NO} is the concentration of NO leaving the reactor (or i -th stage of it) after spending there the time t . C_0 is the concentration of NO entering the reactor. If the NO reduction can be described by the first-order process, then the data plotted as $-\ln(C_{NO}/C_0)$ versus the residence time t should fit a straight line with a slope equal to the first-order rate constant k . Defining fractional conversion as $X_{NO} = (C_0 - C_{NO})/C_0 = 1 - C_{NO}/C_0$, the reaction rate equation predicting NO conversion takes the form:

$$X_{NO} = 1 - \exp(-kt) \quad (5)$$

The temperature dependent term k in Eq. (5) varies with temperature according to Arrhenius' law:

$$k = k_0 \exp(-E/RT) \quad (6)$$

where k_0 is the frequency factor, E is the activation energy, $R=1.987 \text{ cal/mol} \cdot ^\circ\text{K}$ is the gas constant, and T is the absolute temperature. Since Arrhenius' law can also be written:

$$\ln k = -E/RT + \ln k_0, \quad (7)$$

a plot of $\ln k$ versus $1/T$ yields a straight line with a slope of $-E/R$ and an intercept of $\ln k_0$.

For a given set of the experimental data, Eq. (5) should be capable of predicting NO conversion for any combination of temperature T and space velocity SV (SV is reciprocal of the residence time t) within the range covered by the experiments. For any given space velocity a plot of conversion X_{NO} versus temperature can be generated on the basis of Eq. (5) and the data obtained at the same space velocity can be plotted in the same graph to validate the model. Furthermore, the model can be used to adjust the data obtained at one space velocity (residence time t_1) to be viewed on the plot based on a different space velocity (residence time t_2).

Consider Eq. (5) for two different residence times t_1 and t_2 and other conditions equal:

$$1 - X_1 = \exp(-kt_1) \quad (8)$$

$$1 - X_2 = \exp(-kt_2) \quad (9)$$

Dividing (9) by (8):

$$(1 - X_2)/(1 - X_1) = \exp(k(t_1 - t_2)) \quad (10)$$

Upon rearranging (10), an expression for calculating new conversion X_2 for different residence time t_2 is obtained:

$$X_2 = 1 - (1 - X_1)\exp(k(t_1 - t_2)) \quad (11)$$

It is easily seen that when $t_1 = t_2$, $X_2 = X_1$.

NO conversion

The experimental results processed according to the above procedure are plotted below.

Fig. 2. 97-DURATION-1. Rate constant k determined for the IC-44/I-700 catalyst on the basis of Eq. (3). C_i designates NO concentration at the exit of i -th block; C_0 designates common (to the Joy and the IC-44/I-700 catalysts) NO concentration at the inlet to the catalysts' enclosures.

Fig. 3. 97-DURATION-4 and 98-DENOX-1. Rate constant k determined for the IC-47 catalyst on the basis of Eq. (3). C_i designates NO concentration at the exit of i -th block; C_0 designates common (to the Joy and the IC-47 catalysts) NO concentration at the inlet to the catalysts' enclosures.

Five dots (besides the one at the origin which refers to the enclosure inlet) on the plots in Figs 2 and 3 are referred to NO concentration at the exit of the five catalyst blocks within the enclosure. The plots with the number of dots less than five are obtained from runs with NH_3/NO ratio < 1 . In these cases NO conversion due to NH_3 deficiency was artificially low near the end of the catalyst train. Therefore, all such data was excluded.

As is seen in Figs 2 and 3, the linearity of the plots is obvious, thus validating the first-order reaction assumption.

The data for Joy catalyst has been processed similarly. However, with only two points available (the inlet and the outlet) linearity of the plots became automatic. Since these plots are trivial, they are not shown.

The next step is to determine the temperature effect on the rate constant k by plotting $\ln k$ versus $1/T$ according to Eq. (7).

Fig. 4. Plot of $\ln k$ versus $1/T$ using k values for the IC-44/I-700 catalyst shown in Fig. 2. Approximate values for the temperature (on the top) and the rate constant (on the right) as well as the sweep numbers are shown for convenience. Three small tables list the curve fit parameters for the three consecutive parts of the plot.

Fig. 4 indicates that the temperature effect on the rate constant for IC-44/I-700 catalyst, very strong at low temperature, weakens above 275°C and levels off around 300°C . These results are consistent with the position of the maximum on the conversion versus temperature curve for this catalyst provided by BIC and shown in Fig. 5.

Fig. 5. Boreskov Institute of Catalysis test results for their IC-44/I-700 and IC-47 catalysts.

Fig. 6. Plot of $\ln k$ versus $1/T$ using k values for the IC-47 catalyst shown in Fig. 3. Approximate values for the temperature (on the top) and the rate constant (on the right) as well as the sweep numbers are shown for convenience. The table lists the curve fit parameters for the plot.

Fig. 7. Plot of $\ln k$ versus $1/T$ for the Joy catalyst using the data from 97-DURATION-1, 97-DURATION-4 and 98-DENOX-1 runs. Approximate values for the temperature (on the top) and the rate constant (on the right) are shown for convenience. The table lists the curve fit parameters for the plot.

Fig. 6 shows a moderate temperature effect on the IC-47 catalyst rate constant in the range of 320°C to 380°C which is indicative of approaching the maximum on the conversion versus temperature curve. According to Fig. 5 provided by BIC, the maximum on the conversion versus temperature curve for IC-47 is around 400°C.

Similar to IC-47, Fig. 7 shows a rather moderate temperature effect on the Joy catalyst rate constant in the range of 240°C to 297°C hinting at possible leveling off beyond 300°C. However, the maximum on the conversion versus temperature curve for Joy has never been verified due to the limited capacity of the main off gas preheater. A scatter of the data in Fig. 7 is associated with low accuracy of the rate constants k determined for the Joy catalyst on the basis of only two data points (inlet and outlet). In the case of the Russian catalysts, up to six data points were available (inlet and five sampling ports after each block) which helped to balance out fluctuations of inlet NO concentration and permitted us to use partial information provided by the runs with NH_3/NO ratio < 1 .

Once the temperature effect on the rate constant k has been determined for each catalyst type, their conversion versus temperature curves can be generated on the basis of Eq. (5) and compared to the data. In order to generate a curve, a space velocity (or residence time) must be fixed in Eq. (5). Space velocities in the 97-DURATION-1 series of tests varied from 26700 h^{-1} to 38200 h^{-1} , hence a common $\text{SV} = 30000 \text{ h}^{-1}$ was selected for all 6 sweeps of the 97-DURATION-1 series. In the 97-DURATION-4 and 98-DENOX-1 series the space velocities covered the range of 40400 h^{-1} to 55100 h^{-1} , thus a common $\text{SV} = 45000 \text{ h}^{-1}$ was selected for the 5 sweeps of those series. The observed conversion data associated with their actual space velocities were adjusted to the above fixed space velocities using Eq. (11). Figs. 8 and 9 show the observed and adjusted conversion data plotted together with the predicted conversion versus temperature curves.

Fig. 8. Predicted NO conversion at $\text{SV}=30000 \text{ h}^{-1}$ as a function of temperature for Joy and IC-44/I-700 catalysts. The data from 97-DURATION-1 runs adjusted to $\text{SV}=30000 \text{ h}^{-1}$ are shown for comparison. The sweep numbers are shown for convenience.

Fig. 9. Predicted NO conversion at $SV=45000\text{ h}^{-1}$ as a function of temperature for the Joy and IC-47 catalysts. The data from 97-DURATION-4 and 98-DENOX-1 runs adjusted to $SV=45000\text{ h}^{-1}$ are shown for comparison. The sweep numbers are shown for convenience.

As is seen in Figs. 8 and 9, with the playing field leveled through data point adjustment, the IC-44/I-700 and IC-47 conversion went up and that of Joy, slightly down. The increase of activity with temperature is well pronounced for all catalysts over the temperature ranges covered in the tests and the leveling off for IC-44/I-700 and IC-47 tends to occur at temperatures predicted by BIC (Fig. 6).

Note that the curves for the Joy and the IC-47 catalysts appear very similar (the IC-47 curve starts where the Joy curve ends) which, perhaps, is not surprising since the compositions of both catalysts are similar. Unfortunately, we have no high temperature data to find out whether the Joy's curve would follow the IC-47 curve into the range of higher temperatures, or, as the IC-44/I-700 curve did, would level off.

Since only the data obtained with adequate (stoichiometric or greater) NH_3 feed went into determination of the rate constants, the computed conversion versus temperature curves in Figs. 8 and 9 predict maximum conversions and are unique. They cannot be applied to runs with various degree of NH_3 deficiency as evident in Fig. 8 and, especially, in Fig. 9 where the data points falling below the prediction are those with NH_3/NO ratio <1 .

This simple first-order kinetic model offers a means of predicting NO conversion in a broad (but limited to the temperature range explored) space velocity–temperature field, as the example in Fig. 10 illustrates.

Fig. 10. Prediction of NO conversion for the Joy, IC-44/I-700 and IC-47 catalysts as a function of space velocity and the temperature (within the range covered in the tests).

Ammonia slip

Ammonia slip control relies on the reaction:

Reaction (11) is rather slow and requires low enough space velocity to be of practical significance. In a series of tests at LLNL in 1993-1994 with BIC mixed oxide catalysts similar to the IC-44/I-700, reaction (11) was shown to destroy, in the absence of NO, over 90% of NH_3 at 275°C and $\text{SV} \approx 9000 \text{ h}^{-1}$. The rate constant with respect to ammonia k_a at 275°C was around 6 s^{-1} . It is easy to see that, e.g., at $\text{SV} = 36000 \text{ h}^{-1}$ (which was typical in 97-DURATION-1 tests of the IC-44/I-700 catalyst) the same catalyst would have removed less than 50% of the excess NH_3 . Still, even that level of ammonia slip control has not been achieved during the 97-DURATION-1 tests suggesting that supposedly identical to its predecessor, the IC-44/I-700 catalyst has a somewhat different composition, porosity, etc.

The new environmentally benign formulations such as IC-47 and IC-45 as well as the Joy catalyst never held a claim of being capable of controlling ammonia slip by way of reaction (11). 97-DURATION-1 and the 97-DURATION-4 tests confirmed that none of them did. Yet, the tests produced evidence that in the main DeNO_x reaction (1), IC-47 activity with respect to ammonia is vastly superior to that of Joy.

As Fig. 11 indicates, the activation energy E_a with respect to ammonia for IC-47 catalyst is 3 times that of Joy. Consequently, if both catalysts operated in the same temperature range, then the IC-47 activity would be expected to increase much faster with temperature than that

of Joy. As is seen in Fig. 11, the IC-47 rate constant k_a with respect to ammonia would have exceeded that of Joy around 330°C and at still higher temperature (assuming E_a for Joy remained constant) the rate constant k_a for Joy would have fallen far behind. The activation energy constancy is usually associated with the constancy of reaction mechanism which is defined in this case by the reaction (1). The only major reason for the apparent increase of the activation energy E_a for Joy would be the onset of a parasitic reaction (2). This reaction also consumes NH_3 but produces NO instead of N_2 . That would be indicative of reaching a maximum on the NO conversion versus temperature curve rendering the whole issue of NH_3 control immaterial. In the absence of high temperature data for the Joy catalyst, any other assumption appears less probable.

Fig. 11. Plot of $\ln k_a$ versus $1/T$ for the IC-47 and the Joy catalysts using the data from 97-DURATION-1, 97-DURATION-4 and 98-DENOX-1 runs. Approximate values for the temperature (on the top) and the rate constant (on the right) are shown for convenience. The tables list the curve fit parameters for the plots.

Fig. 12 shows the observed and adjusted NH_3 conversion data plotted together with the predicted NH_3 conversion versus temperature curves for Joy and IC-47 catalysts. As before, the curves were generated on the basis of Eq. (5), this time with respect to NH_3 . Since only the data obtained with adequate (stoichiometric or greater) NO feed went into determination of the rate constants k_a , the computed conversion versus temperature curves in Fig. 12 predict maximum NH_3 conversions. The data points falling below the prediction are those with NO/ NH_3 ratio < 1 . The superior performance of the IC-47 catalyst in the high temperature range is evident.

Fig. 12. Predicted NH_3 conversion at $\text{SV}=45000 \text{ h}^{-1}$ as a function of temperature for the Joy and IC-47 catalysts. The data from 97-DURATION-1, 97-DURATION-4 and 98-DENOX-1 runs adjusted to $\text{SV}=45000 \text{ h}^{-1}$ are shown for comparison. The sweep numbers are shown for convenience.

TCLP ANALYSIS

After 97-DURATION-1, the IC-44/I-700 catalysts were removed. Toxicity Characteristic Leaching Procedure (TCLP) analysis was performed on one of the removed catalyst blocks. The IC-44/I-700 catalyst failed to pass the TCLP analysis for one metal, chromium. The concentration for chromium was 7.66 mg/liter, which is above the TCLP limit of 5.0 mg/liter.

The second Russian catalyst, IC-47 was installed and tested during 97-DURATION-4. TCLP analysis was performed on one of the spare IC-47 catalyst blocks that was not installed in the DeNO_x unit. The IC-47 catalyst passed the TCLP analysis.

A sample taken from an unused spare Russian Type IC-45 catalyst was submitted to the MSE-HKM Laboratory for EPA analysis. The catalyst passed the TCLP analysis.

CONCLUSIONS

The IC-47 catalyst is capable of reducing NO_x emissions well in excess of 95% at space velocities up to 50000 h^{-1} (residence time 0.07 s).

When ammonia feed does not exceed the stoichiometric requirements, the IC-47 catalyst can control ammonia emissions exceptionally well (due to its high activity with respect to reaction (1)) and far better than the existing Joy catalyst. Since, however, only reaction

(11) can control ammonia emissions in excess of the stoichiometric requirements, both catalysts would produce ammonia slip due to their low activity with respect to this reaction.

Spent IC-47 catalyst is not a hazardous waste as defined in 40CFR 261. It will meet the disposal requirements of California Code of Regulations, Title 22, Section 66261.24 and will be able to be disposed of in a non-RCRA landfill.

Neither the service life nor the cost of the new catalyst has been determined.

REFERENCES

1. "Technologies for the Efficient Removal of Nitrogen and Sulfur Oxides from Effluent Gas Streams," research report prepared under LLNL contract B239611 by Z. R. Ismagilov, et al, Boreskov Institute of Catalysis, Novosibirsk, Russia, 1992.
2. "DeNO_x Catalysts for Improved Off-Gas Treatment," final report prepared under LLNL contract B239737 by Z. R. Ismagilov, Boreskov Institute of Catalysis, Novosibirsk, Russia, August 1994.
3. "Application of Catalysts to Treatment of Off-Gases and Mixed Wastes," final report prepared under DOE contract by Z. R. Ismagilov, Boreskov Institute of Catalysis, Novosibirsk, Russia, April 1996.