

Utilization of Common Automotive Three-Way NO_x Reduction Catalyst for Managing Off-Gas from Thermal Treatment of High-Nitrate Waste – 13094

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ABSTRACT

Studsvik's Thermal Organic Reduction (THOR) steam reforming process has been tested and proven to effectively treat radioactive and hazardous wastes streams with high nitrate contents to produce dry, stable mineral products, while providing high conversion (>98%) of nitrates and nitrites directly to nitrogen gas. However, increased NO_x reduction may be desired for some waste streams under certain regulatory frameworks.

In order to enhance the NO_x reduction performance of the THOR process, a common Three-Way catalytic NO_x reduction unit was installed in the process gas piping of a recently completed Engineering Scale Technology Demonstration (ESTD). The catalytic DeNO_x unit was located downstream of the main THOR process vessel, and it was designed to catalyze the reduction of residual NO_x to nitrogen gas via the oxidation of the hydrogen, carbon monoxide, and volatile organic compounds that are inherent to the THOR process gas. There was no need for auxiliary injection of a reducing gas, such as ammonia. The unit consisted of four monolith type catalyst sections positioned in series with a gas mixing section located between each catalyst section. The process gas was monitored for NO_x concentration upstream and downstream of the catalytic DeNO_x unit.

Conversion efficiencies ranged from 91% to 97% across the catalytic unit, depending on the composition of the inlet gas. Higher concentrations of hydrogen and carbon monoxide in the THOR process gas increased the NO_x reduction capability of the catalytic DeNO_x unit. The NO_x destruction performance of THOR process in combination with the Three-Way catalytic unit resulted in overall system NO_x reduction efficiencies of greater than 99.9% with an average NO_x reduction efficiency of 99.94% for the entire demonstration program. This allowed the NO_x concentration in the ESTD exhaust gas to be maintained at less than 40 parts per million (ppm), dry basis with an average concentration of approximately 17 ppm, dry basis. There were no signs of catalyst deactivation throughout the 6 day demonstration program, even under the high steam (>50%) content and chemically reducing conditions inherent to the THOR process.

Utilization of the common Three-Way automotive catalyst may prove to be a cost effective method for improving NO_x emissions from thermal treatment processes that utilize similar processing conditions. This paper will discuss the details of the implementation and performance of the Three-Way catalytic DeNO_x unit at the THOR ESTD, as well as a discussion of future work to determine the long-term durability of the catalyst in the THOR process.

INTRODUCTION

Studsvik's patented THOR process is an attractive option for the treatment of liquid radioactive wastes

that contain high levels of nitrates. The reducing environment that is inherent to the THOR steam reforming process provides high conversion of nitrates and nitrites directly to nitrogen gas without the need to alter the process. At the heart of the THOR process is the Denitration and Mineralization Reformer (DMR). The DMR is a fluidized bed vessel designed to convert radioactive and hazardous liquid waste streams into dry, stable, solid granular products. The DMR is fluidized by low pressure, superheated steam. In addition to serving as the main energy source, coal is added to the DMR to produce a reducing environment inside the vessel. Excess amounts of coal are purposely added to the DMR such that a portion of the coal reacts with the steam Fluidizing Gas (FG) to create a reducing environment where long chain organics are broken down and nitrates and nitrites are reduced to nitrogen gas. The carbon from coal, organics from the coal and waste, and carbon monoxide and hydrogen gases created from the water-gas and water-gas shift reactions are oxidized by the oxygen derived from the nitrates and NO_x gases, thus reducing oxides of nitrogen to nitrogen gas. A small amount of auto-thermal gas (50% nitrogen, 50% oxygen by volume) is added to the bed as a means to control the amount of heat that is generated from the oxidation of the carbon and organics in the DMR bed to maintain the fluidized bed temperature.

The THOR process has been demonstrated in numerous test programs to 1) convert a variety of radioactive waste streams into dry granular products that retain radionuclide species in a mineral structure, 2) convert greater than 98% of the nitrates and nitrites in the waste stream to nitrogen gas, and 3) destroy essentially all of the organic contents of the waste stream through their conversion to carbon dioxide and water vapor [1]. While this has proved to be more than satisfactory for projects within the U.S., greater nitrate conversions are required for most projects in Europe due to its comparatively stringent gas emission regulations. For one French project in particular, nitrate destruction efficiencies of greater than 99% were required to meet the gas emissions requirements for NO_x gas. Any nitrates that are not reduced to nitrogen gas in the DMR fluidized bed thermally decompose into NO_x gases, mostly in the form of NO. The amount of NO_x present in the DMR outlet gas proved to be too high for the applicable French emissions regulations. This issue was partly due to the extremely large inventory of nitrates in the waste stream (7.23 M), as well as the inability of the DMR to achieve higher NO_x destruction efficiencies than approximately 98% [1].

In a recent ESTD conducted by Studsvik in April of 2012, multiple methods were explored in attempts to increase the level of NO_x reduction in the DMR, and lower the emission rate of NO_x gases from the process. These methods included: increasing the coal feed rate to the DMR to create a more reducing environment (lower oxygen fugacity), varying the operating temperature to optimize the gas phase equilibrium point for NO_x reduction, and varying the size of the granular coal pieces feed to the DMR. Varying the operating temperature of the DMR bed was shown to be the only technique that provided improved NO_x destruction in the DMR; however, NO_x emissions were still too high. As NO_x emissions could not be satisfactorily controlled through process adjustments, Studsvik explored options in supplemental off-gas treatment systems. It was ultimately decided that a typical off-gas treatment catalyst would be a simple yet cost-effective option for achieving the elevated level of NO_x destruction in the ESTD.

Catalysts are commonly utilized for process gas after treatment, especially in the automotive and coal

power industries. Selective Catalytic Reduction (SCR) catalysts can be found in the off-gas treatment systems of coal power plants and diesel automotive engines. In these applications ammonia (NH₃) is injected into the gas stream to react with NO_x over the catalyst to form nitrogen and water vapor. Under the right temperature and pressure these catalysts can provide NO_x destruction efficiencies of greater than 95%, even at incoming NO_x levels of less than 100 parts per million (ppm). [2]

Another common NO_x reduction catalyst is known as a Three-Way Catalyst (TWC). Traditionally, TWCs are used in rich-burn or stoichiometric (spark ignition) engines for simultaneous conversion of oxides of nitrogen, carbon monoxide, and hydrocarbons [3]. However, this type of NO_x reduction technology is becoming more and more prevalent for industrial applications.

As the DMR process gas contains excess amounts of Hydrogen (H₂), Carbon Monoxide (CO), and Volatile Organic Compounds (VOCs) that would be used by the TWC to catalyze the reduction of NO_x to nitrogen gas, TWCs were deemed to be the most appropriate type of catalysts to be used in the ESTD. After some consideration, a decision was made to install a set of typical automotive TWCs downstream of the DMR to destroy the remainder of NO_x in the process gas.

THREE-WAY AUTOMOTIVE CATALYSTS

The TWC technology was developed for the automotive industry in the mid to late 1970s to provide a simplified solution for meeting the requirements of the U.S. Clean Air Act Amendment of 1970 [3]. A typical automotive TWC consists of a non-catalytic substrate that is coated with a washcoat and catalyst coating. The substrate provides the structure and shape of the catalyst, and is typically formed into a honeycomb structure made of a metallic or ceramic material (see Figure 1).

- 1 Catalyst Layer Containing Platinum and Rhodium,
- 2 Ceramic or Metal Substrate.

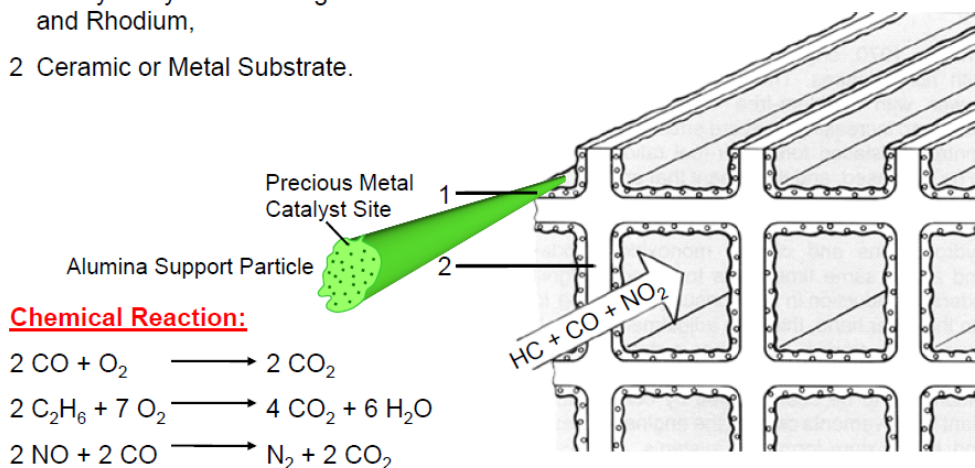


Figure 1. Simplified Diagram of a Channeled Monolith TWC [3]

The washcoat is typically made of alumina and/or silica and a rare earth metal oxide such as cerium oxide. The cerium oxide can release or capture oxygen in the gas stream. The washcoat helps to provide a large surface area by forming a porous, rough and irregular surface that enhances gas diffusion into the

catalyst layers. The catalytic coating consists of precious metals; Platinum (Pt) and/or Palladium (Pd) are used for the oxidizing catalyst, and Rhodium (Rh) is typically used for the reducing catalyst. The Pt and Pd sites are responsible for dissociating the hydrocarbons and carbon monoxide molecules, while Rh is responsible for dissociating the nitrogen oxide molecules. [4]

O₂ molecules are attracted to the Pt and Pd sites where they attach and share an electron bond with the Pt/Pd site. CO, H₂, and VOCs are also attracted to the Pt/Pd sites. The CO, H₂, and VOCs react with the oxygen molecules and desorb as water vapor and Carbon Dioxide (CO₂), leaving a clean Pt/Pd site that is available to absorb oxygen and reducing gas molecules. NO molecules are attracted to the Rh sites, where they dissociate such that the nitrogen and oxygen atoms each share an electron bond with rhodium. The nitrogen atoms combine and desorb as nitrogen gas (N₂). The oxygen atoms remain on the rhodium site until they react with H₂, CO, or VOCs from the gas phase, and then desorb as water vapor and CO₂, leaving a clean rhodium site (see Figure 1, above). Sometimes the precious metal catalysts are added in separate layers with the Pt/Pd layer underneath the Rh layer. This promotes interaction between the Rh sites and the reducing gases (H₂, CO, and VOCs) and helps to improve NO_x conversion across the catalyst. [3]

If there is not sufficient free oxygen (O₂) in the gas stream, then the H₂, CO, and VOCs that are attached to the Pt/Pd sites will not fully react and desorb as water vapor and CO₂, thus leaving the oxidizing catalyst sites (Pt/Pd) covered and inactive. On the other hand, if there is not a sufficient amount of reducing gases (CO, H₂, and VOCs) available to react with the dissociated oxygen molecules at the Rh sites, then the reducing catalyst sites will remain covered and inactive. Providing too much free oxygen can result in the same issue, as the reducing gases (H₂, CO, and VOCs) will preferentially react with the free oxygen in the gas stream, leaving little or no reducing gases to react with the oxygen molecules on the Rh sites. Therefore, cerium oxide is typically included in the washcoat to help stabilize the operation of the TWC as engine exhaust varies between slightly lean (deficient of H₂, CO, and VOCs) and slightly rich (deficient of free oxygen). During lean operation cerium acts a reductant such that Ce₂O₃ (+3 oxidation state) reacts with oxygen to form CeO₂ (+4 oxidation state). Then during rich operation cerium acts as an oxidizer such that CeO₂ reacts with the reducing gases to form Ce₂O₃ and CO₂ and water vapor. [3, 4]

The TWC application in the THOR process is a unique concept. To this point, essentially all research and testing of TWCs has been focused on automotive applications. Compared to automotive applications, the THOR process gas is significantly different, especially with respect to the high steam (55% to 65%) and high reducing gas (1% to 2% H₂, ~0.5% CO, ~0.5% VOCs) concentrations [1]. Typical spark ignition engine exhaust contains 10% to 15% water vapor, 1% to 2% CO, and <0.25% Hydrocarbons/VOCs. The performance of a TWC has never been tested in such a high steam environment, with little to no free oxygen in the gas stream. In addition to the differences in process gas composition, the TWC for the THOR process was to be operated with a focus on maximizing NO_x reduction. With an oxidation unit located downstream of the TWC, the sole purpose of the TWC would be to reduce NO_x to the lowest possible level. The following sections discuss the implementation of the TWC in the THOR ESTD configuration, and the performance this Catalytic DeNO_x Unit (CDU) in the THOR process.

STUDSVIK'S CATALYTIC DeNO_x UNIT (CDU)

A simplified flow diagram of the THOR ESTD is shown in Figure 2 below. In order to minimize project costs, it was decided that the CDU and downstream oxidation unit would be sized such that only a slip stream of the process gas from the DMR would be used to demonstrate the capability of the off-gas treatment system. As shown in the figure, the process gas stream downstream of the Product Separation Filter (PSF) was split into two off-gas streams, with approximately 55 scfm flowing to the CDU and the remainder (~300 scfm) flowing to secondary oxidation unit. The purpose of the secondary oxidation unit was to reduce the concentration of CO and VOCs in the secondary off-gas stream such that all gas emissions from the ESTD system were in compliance with the regulatory requirements of the test facility.

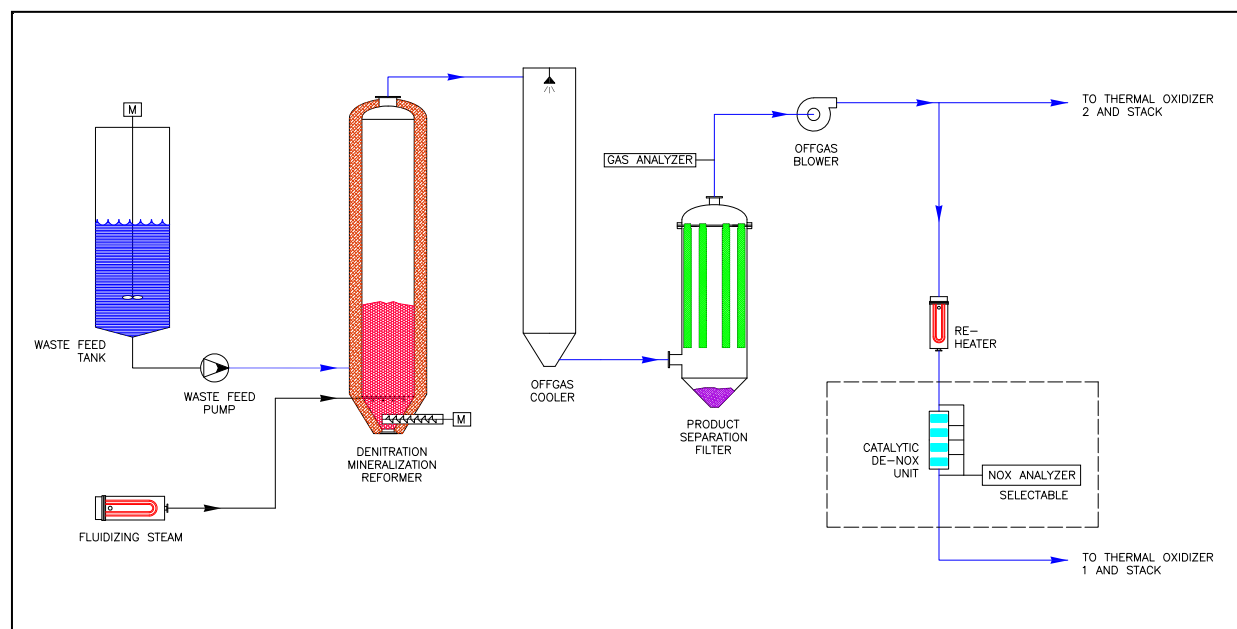


Figure 2. Simplified Process Flow Diagram of the THOR ESTD System for Treating Nitrate Waste

The CDU was a custom-built horizontal vessel that utilized four monolith Three-Way catalyst sections arranged in series with a gas mixing section in between each catalyst section. Figure 3 shows the internal details of the CDU and Figure 4 is a photograph of the installed CDU. The outer shell of the CDU was constructed of 8 inch NPS 304 stainless steel spool pieces and was approximately 4 feet in overall length. Each of the metallic substrate catalyst pieces was 6.375 inches in diameter and 3.5 inches in length. The annular gaps between the outer diameter of the catalyst monoliths and the inner diameter of the 8" pipe were filled with compressed layers of Kaowool insulation to prevent process gas from bypassing the catalysts. The gas mixing sections, located in between each catalyst section, were filled with corrosion-resistant ceramic saddles to improve gas mixing and contact time. No operational issues specific to the CDU vessel were encountered during the test program. In the ESTD, a slip stream that consisted of approximately 55 scfm of the total process gas flow was treated inside the CDU for approximately 138 hours of operating time. This slip stream was equal to approximately 15% of the total process gas flow in

the ESTD.

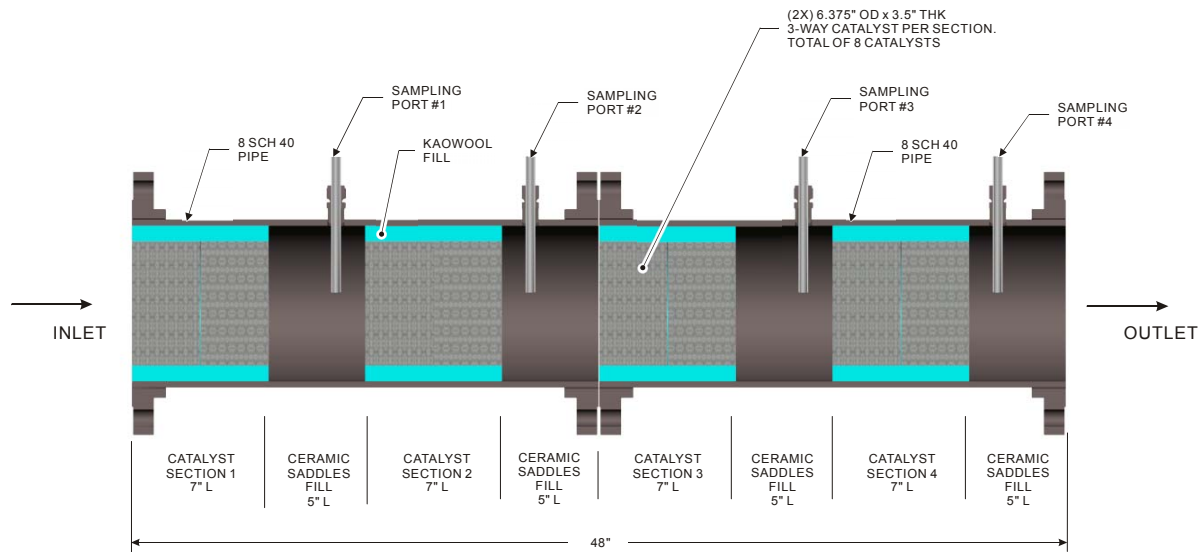


Figure 3. Section View of Catalytic De-NO_x Unit.



Figure 4. Photograph of the installed Catalytic De-NO_x Unit.

The four sampling ports shown on Figure 3 provided the means to monitor the NO_x concentrations, temperatures and pressures at the outlet of each catalyst section of the CDU. Pressure and temperature indicators were installed at each sampling port and all sampling ports were connected to a manifold that isolated and directed sample gas to either a gas analyzer instrument or a sampling port for independent

sample collection and analysis. The temperature indicators monitored the temperature in between each catalyst sections to ensure that CDU temperatures remained within normal operating ranges. The pressure indicators monitored the pressure drop across each section of the CDU, providing indications of the extent of flow restriction in the CDU. The gas analyzer instruments used to measure CDU NO_x concentrations in the ESTD included a Chemiluminescence NO_x analyzer and Fourier Transform Infrared Spectroscopy (FTIR). The on-line Chemiluminescence NO_x analyzer provided a continuous measurement of the NO_x concentrations in the CDU throughout the test program. Via the operation of the gas manifold, the sampling point for the NO_x analyzers were switched between the four catalyst sections. The default sampling point, at which the CDU gas was measured for the vast majority of the test program, was located at the outlet of the fourth catalyst sections, which represents the gas outlet of the CDU. Periodic sampling of the CDU gases via FTIR instrumentation and Tedlar bag sample collection were performed to verify the gas measurements reported by the on-line NO_x analyzer. Analytical results of the Tedlar bag and FTIR samples indicated that the NO_x measurements from all three instruments were in good agreement with each other. The NO_x destruction efficiency for the CDU was determined using the on-line CDU outlet NO_x measurement and the NO_x measurements recorded at the outlet of the PSF.

The normal operating temperature range for the CDU was between 540°C and 650°C. According to vendor specifications, the catalyst media is rated for a maximum operating temperature of 650°C, and an operating temperature of at least 540°C is optimal for NO_x destruction. Operational data indicated that maintaining the temperature in the first two sections of the CDU vessel at approximately 580°C resulted in the best NO_x destruction efficiency across the CDU. As the CDU vessel was not provided with a means to control its own temperature, the temperature inside the CDU was controlled through the operation of the Re-heater (see Figure 2 above) that was installed directly upstream of the CDU. The Re-heater was a circulation heater of stainless steel construction that increased the temperature of the incoming process gas from approximately 210°C to approximately 440°C. The oxidation and NO_x reduction reactions that occur across the catalyst are exothermic processes, and therefore the regional temperature inside the CDU was proportional to the extent of catalytic reactions occurring in each catalyst section. The heat created from the NO_x reduction reactions in combination with the oxidation reactions from the small concentration of free oxygen in the inlet gas contributed to a significant temperature increase across the first two sections of the CDU. As the majority of the catalytic reactions occurred in the first two sections of the CDU, the temperature inside the last two CDU sections were typically approximately 50-80°C lower than the first two sections. This occurrence was not surprising as the CDU was intentionally oversized to account for any unanticipated negative impacts to the catalyst media, such as suppression of catalytic reactions from steam or catalytic poisoning. However, there was no decline in catalytic activity observed during the test program.

NO_x Destruction Performance

The addition of the CDU to the THOR ESTD test system proved to be a cost effective method for achieving NO_x emissions that met applicable French regulations. With the addition of the CDU to the off-gas treatment system, the overall NO_x destruction efficiency of the THOR ESTD test system (as determined at the outlet of the CDU) was increased to > 99.9% (average of all testing) with a range of 99.86% to >99.98%. The overall NO_x destruction performance of the THOR ESTD process resulted in

CDU NO_x emissions ranging from 7 to 37 ppm (wet basis), with an average of 17 ppm (wet basis). Even with the use of a direct fired thermal oxidizer downstream of the CDU that increased NO_x content in the stack gas by a factor of 5 to 10, the stack gas from the THOR ESTD system was shown to be in compliance with French regulations.

The CDU demonstrated NO_x destruction efficiencies ranging from 85% to 98% during the ESTD testing program. The main purpose of the ESTD test program was to obtain the necessary process and operational data to be used for the design of a full-scale waste treatment system while examining various operational and design parameters. These parameters included DMR waste feed composition, level of reducing environment in the DMR (determined by DMR outlet gas H₂ concentration), DMR operating temperature, and waste feed rate (throughput). The NO_x destruction efficiency of the CDU in the ESTD has been averaged over each applicable test period and provided in Figure 5 below. The process gas entering the CDU contained small amounts of oxygen (0% to 0.4%) with excess amounts of reducing gases: 0.7% to 1.2% H₂, 0.3% to 0.5% CO, and 0.3 to 0.5% VOCs; and the total process gas flow rate to the CDU ranged from 53 to 57 scfm. It is known that all reducing gases (H₂, CO, and VOCs) contribute to the NO_x reduction reactions that occur on the TWC [3, 4]; however, the strongest correlation exists between CDU NO_x reduction efficiency and VOCs in the process gas (Correlation Coefficient of 0.82). Therefore, the average VOC molar flow rate for each test period has been calculated and plotted with the CDU NO_x reduction efficiencies in Figure 5, along with a second plot that shows CDU NO_x reduction efficiency as a function of the molar flow rate of VOCs in the process gas. According to the test data, a VOC molar flow rate of >0.3 mole/min (process gas VOC concentration of approximately 0.47 %) resulted in high NO_x conversion (>90%) in the CDU under normal steam reforming conditions.

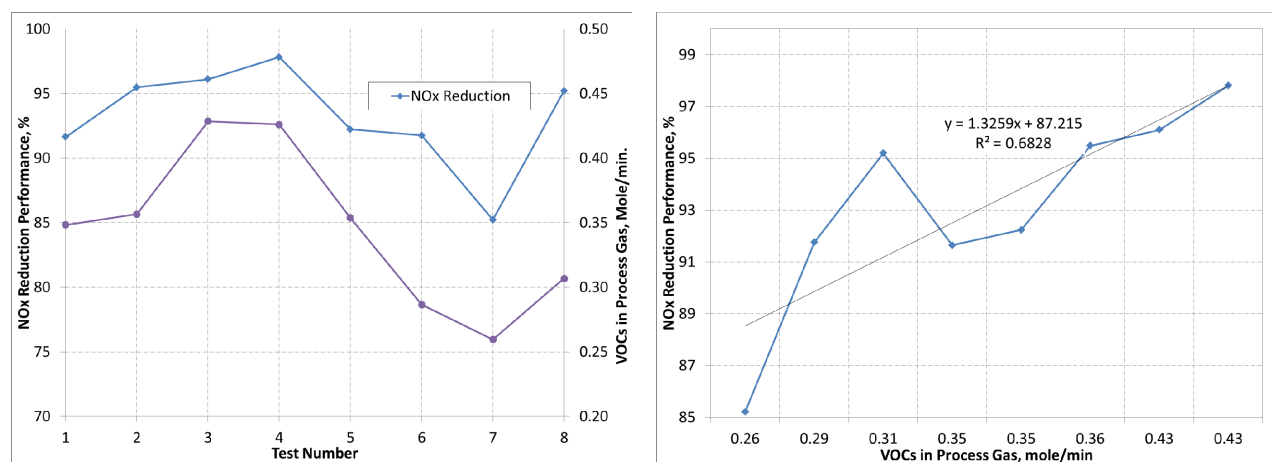


Figure 5. CDU NO_x Destruction Performance Compared to VOCs in Process Gas

For this particular waste stream, essentially all of the VOCs in the process gas are from the organic content (~30% by mass) of the coal that is added to the DMR. The organic content of the coal is volatilized and broken down into small chain organics like methane in the DMR fluidized bed. The majority of the VOCs from the coal flow out of the DMR with the process gas, with a small fraction being

oxidized in the DMR. Therefore, the CDU performance could be enhanced by adding more coal to the DMR, and operating with a higher nominal H₂ concentration and higher overall molar flow rate of VOCs in the process gas. Another viable option would be to inject Natural Gas (NG) directly upstream of the CDU to supplement the reducing gases that are already present in the process gas. While testing has shown that neither modification of operating parameters (coal addition) nor the introduction of auxiliary NG injection are required, both of these options will be considered during detailed design of the full-scale DMR and off-gas treatment system.

FUTURE ANALYSIS AND EVALUATION

While Three-Way catalysts have been used since the 1980s to control automotive emissions of hydrocarbons, CO and NO_x, their performance had not been assessed with off-gases from radioactive processes that contain high steam (>50%) contents. Now that the ESTD has been completed, the next step in qualifying the Three-Way catalysts for use in the THOR process and similar thermal treatment technologies is performing detailed analysis of the post-test catalyst media. While the test operations did not reveal any apparent signs of catalyst deactivation or material degradation, the post-test catalysts must be laboratory tested and analyzed to determine long term catalyst performance, causes of catalytic deactivation, projected service life, and catalyst design optimization. Lab-scale or bench-scale catalyst performance testing using both the used (THOR) and new catalyst samples under controlled laboratory conditions would provide the data necessary to quantify any losses in performance after aging. Characterization and analysis for chemical and physical properties of the post-test catalyst would identify likely root causes for catalyst performance degradation and/or poisoning. The ultimate goal of these analyses will be to determine the expected service life for the catalysts in the THOR process. The expected service life will be an important factor in selecting the most suitable Three-Way catalyst during full-scale design of the waste treatment facility.

SUMMARY AND CONCLUSIONS

A Catalytic De-NO_x Unit (CDU) that utilizes four sections of a common automotive three-way catalyst had been successfully installed and tested in Studsvik's recent THERMAL ORGANIC REDUCTION (THOR) technology demonstration program. Although Studsvik's THOR steam reforming process has been tested and proven to effectively treat radioactive and hazardous wastes streams with high nitrate contents to provide high (>98%) destruction efficiencies of nitrates and nitrites, an additional off-gas treatment system was required in a recent test program to reduce NO_x emissions to within stringent regulatory limits. The CDU performed extremely well in providing the additional destruction efficiencies of NO_x in the process system. The destruction efficiencies of NO_x in the CDU ranged between 85% and 98% throughout the test program, and the NO_x destruction performance of THOR process in combination with the Three-Way catalytic unit resulted in overall system NO_x reduction efficiencies greater than 99.9% with an average NO_x reduction efficiency of 99.94% for the entire demonstration program.

While Three-Way catalysts have been used for many years to control automotive emissions of hydrocarbons, CO and NO_x, their performance had not been assessed with steam reforming applications with high steam contents in the process gas. After their performance has been verified to a greater degree,

Three-Way catalysts will be used in conjunction with the THOR process to provide extremely high levels of NO_x destruction, should they be required by off-gas emissions regulations outside of the U.S. The ESTD testing that has been performed by Studsvik has shown that Three-Way automotive catalysts are a cost effective method for improving NO_x emissions from high steam content thermal treatment processes.

REFERENCES

- [1] W. S. Roesener, H. L. McShane, A. L. Foster, and K. Song, “THOR Steam Reforming Pilot Plant: AREVA Malvésí Lagoon Waste Treatment Demonstration Test Report,” Studsvik Test Report AML-TR-4 (2012).
- [2] T.J. Toops, K. Nguyen, A. L. Foster, “Deactivation of Accelerated Engine-Aged and Field-Aged Fe-Zeolite SCR Catalysts,” *Catalysis Today*, 151 (2010) 257-265.
- [3] J. J. Mooney, “The 3-Way Catalytic Converter: a) Invention and Introduction into Commerce – Impacts and Results b) Barriers Negotiated,” 2007, California Air Resources Board Chairman Invitational Seminar Series.
- [4] E. Belcastro, “Life Cycle Analysis of a Ceramic Three-Way Catalytic Converter,” Thesis, Virginia Polytechnic Institute and State University, April 23, 2012.