## FY-2001 Accomplishments in Off-Gas Treatment Technology Development

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Idaho National Engineering and Environmental Laboratory Bechtel BWXT Idaho. LLC

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Prepared for the U.S. Department of Energy Under DOE Idaho Operations Office Contract DE-AC07-99ID13727

#### **EXECUTIVE SUMMARY**

This report summarizes the efforts funded by the Tank Focus Area to investigate nitrogen oxide (NOx) destruction (a.k.a. deNOx) technologies and off-gas scrubber system designs. The primary deNOx technologies that were considered are staged combustion (a.k.a. NOx reburning), selective catalytic reduction, selective non-catalytic reduction, and steam reformation. After engineering studies and a team evaluation were completed, selective catalytic reduction and staged combustion were considered the most likely candidate technologies to be deployed in a sodium-bearing waste vitrification facility. The outcome of the team evaluation factored heavily in the establishing a baseline configuration for off-gas and secondary waste treatment systems.

Tests were conducted on a staged combustion process at MSE Technology Applications, Inc. to quantify NOx destruction efficiency, hydrocarbon emission, hydrocarbon destruction, and mercury speciation. Integrated tests were planned for a selective catalytic reduction (SCR) pilot plant that was installed on the EV-16 melter system at the Clemson Environmental Technologies Laboratory. The tests were postponed after the terrorist strike against the World Trade Center in New York and the Pentagon in Virginia. Limited data are available from a "shake down" run on the melter and SCR performed while personnel awaited the reopening of the nation's airports.

Enhancements were made to an existing kinetic model of a staged combustion process and kinetic models were written for the selective non-catalytic reduction (SNCR) process and a thermal destruction process. These models were used to determine the viability of these three technologies for NOx destruction. It was shown that the SNCR should efficiently destroy NOx when ammonia is used as the reductant and that thermal NOx destruction would have limited efficiency. An ASPEN model of the off-gas treatment system was written that is a tool for predicting impacts of scrubber performance on recycle to the melter feed, secondary waste generation, and off-gas composition. The model is an initial effort to understand the interrelationships between the unit operations in the off-gas treatment system.

The fate of mercury in the off-gas has a strong influence on decisions regarding potential air emissions and secondary waste generation, treatment, and disposal. Some preliminary answers to questions on mercury speciation and scrubbing efficiency were addressed by laboratory tests to determine mercury vapor/liquid equilibria as a function of temperature, off-gas composition, and scrub solution composition. Furthermore, mercury was added to the simulated waste fed to the research-scale melter (RSM) at the Pacific Northwest National Laboratory (PNNL) to observe mercury speciation and scrubbing efficiency. It was found that the mercury emissions from the melter are present primarily as elemental mercury vapors and that the ejector venturi scrubber successfully removed a substantial fraction of the mercury vapors from the off-gas. It is speculated that the mercury may have sorbed onto entrained particulates that were subsequently removed by the scrubber. Additional data are needed to validate the results and to broaden our understanding of the fate of mercury and the mechanism of mercury capture.

Recommendations are given for additional research and development on deNOx technologies, off-gas characterization, and the fate of mercury in the off-gas treatment system.

## **ACKNOWLEDGEMENTS**

The author recognizes and appreciates contributions to this report by John A. Del Debbio concerning mercury speciation in the research-scale melter off-gas. Efforts by those who have conducted much of the work reported in this document, who have provided technical guidance and review are also appreciated.

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#### INTRODUCTION

#### Statement of Need

The Idaho Nuclear Technologies and Environmental Center (INTEC) formerly reprocessed spent nuclear fuels to separate and recover the unused fissile material. During the course of reprocessing and incidental activities, more than a million gallons of sodium-bearing waste (SBW) was generated. Current research activities are exploring treatment methods and technologies that would convert the SBW into a chemically stable and environmentally-sound waste form. A viable candidate is the direct vitrification of the SBW. The process of vitrifying the SBW, however, would produce high concentrations of nitrogen oxides (NOx) in the off-gas stream. As is inherent with all melters, particle entrainment and volatilization of some waste constituents produce an off-gas that must be cleaned with high-performance scrubbing and particulate filtration prior to discharging the off-gas to the atmosphere.

INTEC has had NOx release limitations imposed by the State of Idaho on the operation of the New Waste Calcination Facility that converted liquid high-level wastes into a more stable powder. It is anticipated that any new waste treatment processes would have similar, if not more restrictive, NOx release limitations. Furthermore, it is expected that the NOx concentrations in the melter off-gas will be sufficiently high to interfere with off-gas compliance monitoring for volatile and semi-volatile organic compounds, as required to obtain a Resource Conservation and Reclamation Act (RCRA) permit to operate the process. High NOx concentrations could degrade activated carbon, proposed as a mercury sorbent, and increase the potential for a carbon bed oxidation/combustion.

Technologies need evaluation and investigation to control emissions of NOx, mercury, radionuclides, particulates, and organic compounds in the off-gases from a waste vitrification facility.

#### State of the Art

#### **Deployed Technologies**

The following is a brief description on a few NOx destruction (deNOx) technologies that have been used in commercial and/or industrial applications. A more extensive explanation and review of the deNOx technologies is available in Reference 1.

#### Staged Combustion (NOx Reburning)

Staged combustion is a thermal treatment process that uses fuel-rich flame to produce the temperature (~1300°C) and a chemically reducing environment necessary to destroy the NOx species. The gases produced during combustion include products of incomplete combustion (PICs), unburned hydrocarbons, soot, etc. These pollutants are oxidized to harmless gases in an oxygen-rich stage. Interstage cooling is used to control the oxidation stage temperature (~1000°C) so that "thermal NOx" is not produced.

#### Selective Catalytic Reduction

Selective catalytic reduction (SCR) utilizes a gaseous reductant (ammonia) and a solid catalyst to selectively reduce NOx to nitrogen and water vapor. In this process, the off-gases are preheated to a temperature sufficient to initiate the reduction reaction and sufficiently hot to preclude the formation of ammonium nitrate; typically 200 - 350°C. Maximum process temperatures vary, depending on the catalyst, but typically range from 350 - 550°C. Ammonia can be supplied either as anhydrous ammonia or produced on demand via decomposition of urea. Unreacted ammonia in the SCR effluent, called ammonia slip, needs to be carefully controlled to minimize the possibility of forming ammonium nitrate,

which would condense on downstream equipment surfaces and in off-gas monitoring sample lines. The nitrate salt formation, however, can be mitigated by using a water scrub on the SCR effluent.

#### Selective Non-catalytic Reduction

Selective non-catalytic reduction (SNCR) is similar to the SCR in that either ammonia or urea is used as a reductant to selectively reduce NOx to nitrogen and water vapor. Without a catalyst to lower the activation energy for the reaction, the SNCR must operate at a significantly higher process temperature (850 - 950°C). Temperature control is important to ensure adequate NOx destruction without ammonium nitrate formation on the low end of the temperature range and avoiding NOx formation by ammonia burning on the other. As with the SCR, ammonia slip is a parameter that must also be controlled or mitigated.

#### **Undemonstrated Technologies**

#### Steam Reformation

Steam Reformation is a process whereby the off-gases are treated using superheated steam . The steam reacts with hydrocarbons and other carbonaceous materials to form carbon monoxide and hydrogen via the water-gas shift reaction. This destroys volatile and semivolatile organic compounds that are present in the off-gas. The carbon monoxide and hydrogen produce a reducing environment that causes nitrogen oxides to be degraded to nitrogen and water. To ensure that sufficient carbon monoxide and hydrogen are present, carbonaceous materials, such as charcoal or a soluble organic, are added to the reactor. A second stage is necessary to oxidize the hydrogen and carbon monoxide to form water and carbon dioxide.

A proposal received from Studsvik, Inc. would use a two-staged fluidized bed. The first bed for reducing the NOx and the second be for oxidizing the carbon monoxide and hydrogen. Since the process uses superheated steam, the reactions take place without a flame. The steam also helps to prevent combustible hydrogen mixtures from occurring.

Although this process has been used in waste treatment, including radioactive wastes and wastes with concentrated nitrate salts, it has not been demonstrated on a gaseous waste stream. One must note, however, that the off-gases produced during steam reformation of nitrate wastes had less than 100 ppm total NOx in the gaseous emissions.

#### Wet Electrostatic Precipitation

Wet electrostatic precipitation (WESP) functions by passing the off-gases between corona wires and collector plates, which ionize various species in the off-gas. The ions migrate in the electrical field toward the collector plate. In the process, they impart a charge on the entrained particles, which subsequently collide into the collector plates. The materials collected on the plates are rinsed off by water that is sprayed, coalesced, or condensed on the plates. Conventional operation of a WESP will oxidize NO to NO<sub>2</sub>, which is solublized in the rinsate. While conventional operation will remove NOx from the off-gas, it exacerbates secondary nitrate waste generation.

Non-conventional variants of the WESP involve the use of reagent gases that are injected into the gas stream through corona nozzles. The resultant "cold plasma" can ionize and react with the NOx to form nitrogen gas. One such variant is a process known as plasma-enhanced electrostatic precipitation (PEESP)<sup>2</sup>.

#### **ACCOMPLISHMENTS**

### **Staged Combustion Test**

MSE Technology Applications, Inc. (MSE) was contracted by the U.S. Department of Energy (DOE) Transuranic and Mixed Waste Focus Areas to conduct a test of a staged combustion process known as the John Zink NO<sub>X</sub>idizer<sup>TM</sup>. The NO<sub>X</sub>idizer<sup>TM</sup> has a fuel-rich combustion stage followed by an interstage cooler and an oxidation stage. The tests were conducted to determine:

- the NOx destruction and removal efficiency, when the  $NO_X$ idizer<sup>TM</sup> was fired with propane
- the total hydrocarbon emission and hydrocarbon destruction efficiency
- the fate of mercury and mercuric chloride vapors.

Nitric acid was injected into a flameless oxidizer to generate NOx for the tests at concentrations in the simulated flue gas up to 40,000 ppmv. Elemental mercury was injected into a vaporizer and combined with chlorine gas to generate a mixture of elemental and halogenated mercury vapors. Benzene was vaporized into the flue gas as an indicator of hydrocarbon destruction efficiency. The NO<sub>x</sub>idizer<sup>TM</sup> destroyed 92-97% of the NOx, over 99.7% of the benzene, and reduced the mercury vapors to elemental mercury. A detailed description of the test and the results are available in Reference 2.

Although the primary funding source for the staged combustion test was independent this project's funding, oversight and technical direction were provided by INEEL to ensure that the data would be useful to the current evaluations. Subsequent tests should use a flue gas that is more complex and representative of the off-gasses expected from the melters that could be used for the direct vitrification of sodium-bearing wastes and calcines stored at the Idaho Nuclear and Environmental Center (INTEC).

#### **SCR Procurement and Installation**

A competitive bid was awarded to Born Environmental Services to design and fabricate a skid-mounted selective catalytic reduction (SCR) system. It is equipped with a fan to pull a slip stream of pilot plant melter off-gas into the SCR unit. It is instrumented for SCR inlet, outlet and mid-bed temperature and flow rates of the off-gas and ammonia addition.

The skid was installed at the Clemson Environmental Technologies Laboratory (CETL) for the second planned melter run (mid-September). Some preliminary testing was conducted to confirm that the SCR bed did catalyze a reaction between NOx and ammonia as evidenced by a rise in the mid-bed temperature and limited SCR outlet gas composition monitoring. Total NOx concentrations in the melter off-gas, after scrubbing, were only 2 – 4% of the expected concentration for extensive time periods. Over a two hour period, the NO concentration rose to over 10,000 ppmv (near projected levels) and decayed down to a few hundred ppmv. This phenomenon could not be explained. Equipment operation and the melter cold cap appeared to be in a steady state condition. Addition surveillance and data are required to determine if the phenomenon is real and to identify the causal factors. For much of the time that data are available, the NOx levels in the SCR influent stream were low enough that they would not pose a threat to mercury sorption beds (activated carbon) nor would it interfere with maximum achievable control technology (MACT) compliance sampling/monitoring. It is possible that a deNOx operation can be eliminated from the off-gas treatment design if the causal factors for the low NOx emissions can be explained and exploited.

The integrated test with the EV-16 melter was postponed to FY-2002 after the terrorist attacks on the World Trade Center in New York and the Pentagon in Virginia.

## **Kinetic Modeling**

Kinetic modeling is important for determining the operating parameters, estimating the performance, and the setting the physical dimensions of deNOx equipment. Kinetic modeling accounts for dominant reaction pathways and rate limiting steps in predicting the conversion or destruction of NOx species.

#### **Staged Combustion**

An existing staged combustion model has been used to model the  $NO_X$ idizer<sup>TM</sup> performance when fired with natural gas. This model was enhanced to interface with a spreadsheet program. Further enhancements are recommended so that the model can be validated with operating. The recommendations are given in Reference 1.

#### **Selective Non-catalytic Reduction**

Since selective non-catalytic reduction (SNCR) has not been applied to off-gas streams with NOx concentrations as high as will be seen in the melter off-gas, a model was written to describe the operation and to predict whether an SNCR could achieve the level of NOx destruction that will be required. Published data indicate that the fractional destruction was low; primarily due to the relatively low concentration of NOx in the SNCR influent. Reported SNCR effluent levels are acceptable.

The SNCR model predicts that satisfactory NOx destruction can be achieved and that the fractional destruction of NOx will be sufficiently high to make this a viable technology. Furthermore, the influence of reducing gases in the influent (carbon monoxide, hydrogen, and methane) were explored to determine if slight increases in these minor constituents would result in significant changes in NOx destruction. None of the reducing gases was as effective as ammonia. With ammonia, the NOx is virtually eliminated within a temperature range of 870- 1040°C.

#### **High Temperature Decomposition**

A kinetic model was written to determine if NOx could be satisfactorily destroyed by heating the off-gas to a temperature where the NOx would decompose. It was found that the minimum achievable NOx level would be near 4000 ppmv at a temperature near 1840°C. The extreme temperature and comparatively low NOx destruction ( $\leq 90\%$ ) do not warrant further investigation of this proposed deNOx technology.

## **Scrubber System Design and Modeling**

Scrubber selection for melter off-gas treatment is an important aspect of the system design. To minimize secondary waste, the off-gas treatment system will likely have an acidic scrubber upstream of the deNOx equipment and a caustic scrubber downstream. The "blow down" from the acidic scrubber will be recycled to the melter feed makeup tank to return volatile salts and radionuclides to the melt, thereby reducing the quantity of secondary waste that will be generated and minimizing the radioactivity of the waste. The efficiency of a scrubber and the nature of the secondary waste that it generates influences the design of upstream and downstream equipment. For this reason, an ASPEN model was written to provide a tool for evaluating the impacts that scrubber selection and operation will have on melter operation and secondary waste treatment. To more fully understand the inter-relationships between the scrubber and other unit operations, the ASPEN model was written with modules for upstream and downstream equipment. This tool has already been used to predict stream compositions and validate anticipated offgas and secondary waste compositions. An extensive discussion on the model capabilities and limitations is available in Reference 3.

#### **Baseline Flowsheet Selection**

Competent individuals were identified in the Applied Technology, Engineering, Waste Management Technology, and High-Level Waste programs and invited to participate in a review and down selection of

off-gas treatment technologies. Engineering prepared four Engineering Design Files (EDF) on staged combustion, SCR, SNCR, and steam reformation deNOx technologies. Applied Technology funded a Value Engineering session to down select the technologies and to propose a baseline off-gas treatment flowsheet.

During the review and down selection processes, the technical feasibility, implementation cost, operability, secondary waste generation, safety, and stakeholder perception were scored. Each criterion was assigned a weighting factor so that the deNOx technologies could be objectively ranked using a sum of the weighted scores. The weighting factors had been determined early in the meeting and kept "secret" as the technologies were scored to avoid biasing the team member responses. To minimize the influence of dominant personalities on the team, the scoring was done via a localized computer network that ensured anonymity. The team ranked SCR the highest  $(3.6 \pm 0.4)$ , staged combustion second  $(3.5 \pm 0.4)$ , SNCR third  $(3.2 \pm 0.6)$ , steam reformation last  $(2.6 \pm 0.6)$ . Statistically, the first three technologies are indistinguishably ranked. A consensus of the team established staged combustion as the baseline technology although it is recognized that development should continue on SCR until sufficient data are obtained to eliminate on technology from consideration. More detail concerning the evaluation and down selection process is available in Reference 4.

Ancillary equipment include an acidic scrub upstream of the combustor to remove entrained and volatilized particulates. A basic scrubber would be located after the combustor to remove acidic gases (mostly halogens). A slip stream of the acidic scrub will be recycled to the melter feed mix tank and a slip stream of the basic scrub would be grouted as secondary waste.

## Mercury Vapor/Liquid Equilibria

Preliminary mercury vapor/liquid equilibria tests were conducted to screen parameters that could influence the equilibrium between the off-gas and a scrub solution. A test apparatus was set up to bubble a purge gas through a mercuric chloride solution at  $70^{\circ}$ C and to collect condensable constituents in a separate flask. It was determined that the  $NO_2$  concentration in the purge gas, the nitric acid concentration in the solution, and the solution temperature influenced the vapor/liquid equilibria, but variations in the solution chloride concentration (0.009 - 0.109 molar) had no appreciable impact.

## **Research-Scale Melter Off-Gas Mercury Speciation**

Schemes to control mercury in the melter off-gas cannot be established without an understanding of the speciation and behavior of mercury in the off-gas environment. Test plans were modified to incorporate mercury into the simulated sodium-bearing waste so that mercury could be studied. The RSM and ancillary equipment were reconfigured to ensure employee safety during operation with mercury in the feed and to monitor the speciation of the mercury in the off-gas under differing melter redox conditions.

Mercury monitoring consisted of measuring and speciating mercury at the following sampling locations: (1) between the film cooler and the ejector venturi scrubber (EVS), (2) between the EVS and the high-efficiency mist eliminator (HEME) and (3) downstream of the HEME. Preliminary results indicated the following:

With glycollic acid as the reductant, at location (1) the total mercury concentration for one sampling period was 16,536 ug/m³. The elemental mercury was 14,016 ug/m³. This indicates that 15% of the total mercury was oxidized (possibly HgCl₂). Sampling location (2) resulted in 2643 ug/m³ total mercury (an elemental mercury measurement was not taken). This indicates that 84% of the total mercury was removed by the EVS. Sampling location (3) indicated no detectable mercury of any speciation. This indicates at least 99% mercury removal for the EVS/HEME.

- With sugar as the reductant, at location (1) the total mercury was 12,701 ug/m³. At location (2) the total mercury concentration was 2352 ug/m³. This indicates that 82% of the total mercury was removed by the EVS. Speciation was inconclusive. No samples at location (3) were taken.
- With no reductant, the total mercury at location (1) was 1916 ug/ m³ and the elemental mercury was 528 ug/ m³. This indicates that 72% of the total mercury was oxidized. No other samples were taken.

These results are to be considered estimates to be verified by additional sampling during future pilot runs. The data hint that the scrubbers may efficiently remove mercury, enough so that mercury sorption beds may not be required except as a guard against unexpected releases during upset conditions and noncompliance with MACT mercury release limits. At this time, the data are insufficient to determine the mechanism for mercury removal in by the scrubber. If sufficient data can be obtained to explain the mechanisms for mercury scrubbing, then the mechanisms could be exploited in equipment design and operation.

#### Research-Scale Melter Off-Gas Scrubber Performance

During the second run on the Research-Scale Melter (RSM-2) at Pacific Northwest National Laboratory (PNNL), the off-gas scrub solutions were changed out after the melter had come to steady state operation. The normal scrub solution used on the RSM is caustic. It is expected that the first scrubber in the full-scale waste melter facility would be acidic from the sorption of NO<sub>2</sub>. Therefore, the scrub solution was changed out with an acidic solution after the melter came to steady state. The fresh scrub was monitored to determine the accumulation of water, dissolved solids, undissolved solids, hazardous metals (inlcuding mercury), and halides. Efficiency of NOx and SOx removal were also measured. Data are still pending. It was noted that the scrub solution was partially neutralized from 1 N nitric acid to approximately 0.6 N by solids carried over from the melter. The scrub and mist eliminator acidity is plotted in Figure 1 and particulate accumulation is shown in Figure 2.

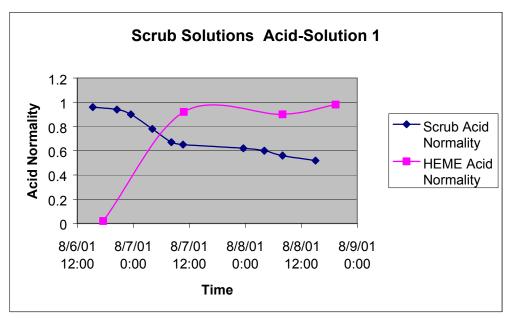


Figure 1. RSM scrub and HEME solution acidities.

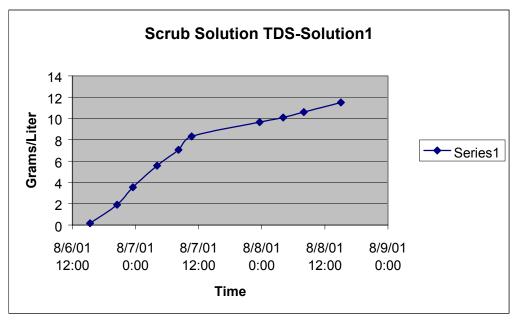


Figure 2. Total dissolved solids accumulation in the RSM scrub solution

#### RECOMMENDATIONS

## **Staged Combustion**

Since the testing to date at MSE has involved simple off-gas (air, water, NOx, mercury, and benzene), data are not available on the formation or destruction of dioxins, furans, or other halogenated hydrocarbons. MSE has a melter that can be fired with natural gas or propane to produce a more realistic melter off-gas than would be produced by thermal decomposition of nitric acid (current practice). Polyvinyl chloride (PVC) or other halogenated organics could be charged to the melter to produce a variety of off-gas compositions focused around the operation of a waste melter.

Additional data are also needed to validate kinetic models of the staged combustion process. Enhancements should be made to the model to include a more representative fluid dynamics and to incorporate propane combustion kinetic expressions. After the enhancement, the model can be used to investigate means to minimize off-gas dilution so that the size of downstream equipment can be reduced.

## **Selective Catalytic Reduction**

Testing with the SCR skid needs to be completed to demonstrate the ability to respond to changing NOx inlet conditions and to quantify NOx destruction as a function of temperature, residence time, and ammonia slip. The formation and control of nitrous oxide  $(N_2O)$  may become a very important issue as  $N_2O$  is recognized as a resilient molecule that is suspected to contribute significantly to ozone depletion. Some SCR operations have been known to form nitrous oxide in the process of destroying NO and  $NO_2$ .

No data are currently available on how the catalytic activity will be affected by mercury vapors in the offgas or on the possible accumulation of ammonium sulfate salt on the catalyst. The latter could be very important if melter operation and formulations are designed to decompose much of the sulfate salts that have limited solubility in the glasses. Additionally, there has been some speculation that the catalysts may catalyze oxidation of minor off-gas constituents such as carbon monoxide, hydrocarbons, and halogenated organics. A thorough investigation would involve exposure of a variety of SCR catalyst materials to a melter off-gas stream containing mercury, hydrocarbons, halogenated organics, and sulfur dioxide. It is recommended that further SCR studies be conducted on a lab scale and the pilot plant scale to fill the knowledge gaps.

Kinetic models should be developed of the SCR process that accurately describe the catalysis of the deNOx reactions for the variety of catalysts that may be tested.

## **Selective Non-Catalytic Reduction**

SNCR technology should not be forgotten, since it offers the distinct advantage over staged combustion in that the off-gas dilution is negligible (like SCR). However, it has not been conclusively shown to effectively destroy products-of-incomplete-combustion and other minor constituents in the off-gas that may be of regulatory concern. The relatively narrow temperature range at which SNCR is effective makes it likely that a staged process would have to be used. Should SNCR appear to become more attractive as data are collected on the staged combustion and SCR technologies, then it is recommended that this technology be thoroughly investigated.

#### **Steam Reformation**

No recommendations are made at this time because the technology was ranked last during the value engineering session to evaluate the deNOx technologies. Should this technology be deployed for off-gas treatment elsewhere, then it is advisable to reconsider our position. It should be noted that steam reformation is an integral part of the liquid waste pretreatment for the PNNL low-level waste vitrification process.

## Mercury Vapor/Liquid Equilibria and Off-Gas Speciation

The data obtained on mercury vapor/liquid equilibria (VLE) and the speciation of mercury in the melter off-gas are limited in scope and quantity. Additional data need to be obtained to describe a family of mercury VLE curves that will be useful in predicting scrubber performance and mercury emissions. The scope of the data need to be broadened to include VLE with caustic solutions. This will enable mercury capture to be predicted for a caustic scrubber as well as an acidic scrubber. Preliminary data from the RSM run hint that the scrubbers may efficiently remove mercury, enough so that mercury sorption beds may not be required except as a guard against unexpected releases during upset conditions and noncompliance with MACT mercury release limits. If sufficient data are obtained to explain the mechanisms for mercury scrubbing, then the mechanisms could be exploited in equipment design and operation.

To help ensure that the behavior and destiny of mercury in the melter off-gas is well understood, additional monitoring and sampling need to be performed during melter operation.

#### **Off-Gas Characterization**

The variability of the off-gas stream in composition and flow rate must be understood to allow for the selection and sizing of off-gas treatment equipment. It is recommended that additional effort be expended to monitor the off-gas composition after the scrubber on pilot-plant melter systems to determine the recorded NOx concentrations are authentic and to determine the causal factors for variations in off-gas composition and flow rates. The design of the film cooler, quench, and scrubber will impact the design of downstream deNOx equipment.

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