

## AOP-4 BACT Analysis Supplement

Apache Nitrogen Products, Inc.

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## Acronyms and Abbreviations

<b>Name</b>	<b>Description</b>
ADEQ	Arizona Department of Environmental Quality
ANPI	Apache Nitrogen Products, Inc.
AOP	Ammonia Oxidation Plant
AP-42	EPA's AP-42 Compilation of Air Pollutant Emission Factors
BACT	Best Available Control Technology
C.F.R	Code of Federal Regulations
CPI	Continuous Peroxide Injection
EPA	United States Environmental Protection Agency
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide
HNO <sub>3</sub>	Nitric Acid
HPI	Hydrogen Peroxide Injection
LoTOx <sup>®</sup>	Registered trademark name of the NO <sub>x</sub> control system developed by Linde
NH <sub>3</sub>	Ammonia
NO	Nitrogen Monoxide
NO <sub>2</sub>	Nitrogen Dioxide
NO <sub>x</sub>	Nitrogen Oxide
NSR	New Source Review
SNCR	Selective Catalytic Reduction

## 1 INTRODUCTION - PURPOSE AND SCOPE OF THIS SUPPLEMENT

The purpose of this supplement to the AOP-4 BACT Analysis submitted to the Arizona Department of Environmental Quality (ADEQ) in April 2020 is to provide an analysis of three additional control technology alternatives for reducing nitrogen oxide (NO<sub>x</sub>) emissions from the Ammonia Oxidation Plant 4 (AOP-4) at the Apache Nitrogen Products, Inc. facility in St. David, Arizona. The three additional control options that are addressed in this supplement are:

- Selective Non-Catalytic Reduction (SNCR);
- LoTOx<sup>®</sup>, a proprietary tail-end treatment technology developed by Linde; and,
- Continuous Peroxide Injection at reduced reagent injection rates.

On behalf of ANPI, Environmental Resources Management (ERM) has prepared this supplemental analysis consistent with the “top-down” approach as outlined in Chapter B of the United States Environmental Protection Agency (EPA) NSR Manual.

## 2. SUPPLEMENTAL BACT ANALYSIS FOR AOP-4 NO<sub>x</sub> EMISSIONS

### 2.1 Step 1 – Identify All Control Technologies

The objective in step 1 is to identify all control options with potential application to the source and pollutant under evaluation. According to Part I, Chapter B, Section IV.A of the EPA NSR Manual, the top-down BACT analysis should consider potentially applicable control techniques from all three categories: (1) Inherently Lower-Emitting Processes/Practices; (2) Add-on Controls; and (3) Combinations of Inherently Lower Emitting Processes and Add-on Controls. Furthermore, Part 1, Chapter B, Section IV.A.1 provides that applicants are expected to identify all demonstrated and potentially applicable control technology alternatives.

This supplemental analysis includes two additional potential control technology alternatives and a modification of a potential alternative that was evaluated in the April 2020 BACT Analysis:

- Selective Non-Catalytic Reduction (SNCR);
- LoTO<sub>x</sub><sup>®</sup>, a proprietary tail-end treatment technology developed by Linde; and,
- Re-evaluation of Continuous Peroxide Injection (CPI) at reduced reagent ratios.

#### 2.1.1 Selective Non-Catalytic Reduction (SNCR)

A selective non-catalytic reduction (SNCR) abatement system for NO<sub>x</sub> involves injection of an ammonia (NH<sub>3</sub>)-containing reagent directly into an exhaust stream at a suitable location. The injected NH<sub>3</sub> reagent must be effectively mixed into the exhaust gases, and reaction occurs in a "reaction zone" in the duct downstream of the injection. Since the system does not utilize a catalyst, the temperature regime in the reaction zone must be considerably higher than for catalytic systems in order to obtain beneficial NO<sub>x</sub> reduction levels. Generally, SNCR is an effective control in a relatively high and narrow range of reaction zone temperatures. Sources with stable temperatures in the range of 1,550 to 1,950°F, uncontrolled NO<sub>x</sub> concentrations above 200 ppm, and reaction residence times of at least 1 second can reach the higher reported control levels.<sup>1</sup>

Based on these process characteristics, SNCR systems are almost exclusively used on combustion processes such as fossil-fuel power plants, cement kilns, steel furnaces, and similar units. Control efficiency of SNCR systems vary depending on temperature, reaction zone residence time, the type of reagent used, and effective mixing of the exhaust stream with the reagent. Systems that use urea-based reagents reportedly achieve 25 to 60 percent reductions, while those that use NH<sub>3</sub>-based reagents (as would be the case for AOP-4) deliver 61 to 65 percent control.<sup>2</sup>

#### 2.1.2 LoTO<sub>x</sub><sup>®</sup>

The relatively new LoTO<sub>x</sub><sup>®</sup> control technology has been developed by Linde Gases Division based in Germany. DuPont is among the technology licensees in the United States. Figure 2-1 illustrates a typical flow diagram for LoTO<sub>x</sub><sup>®</sup>. The technology is based on the reaction between NO<sub>x</sub> and ozone gases that convert relatively insoluble NO and NO<sub>2</sub> species into higher oxides such as N<sub>2</sub>O<sub>5</sub> that are more soluble in water. In practice, a system to extract nearly pure oxygen from the atmosphere, and ozone generation system is installed on site. To ensure full-time operation of the LoTO<sub>x</sub><sup>®</sup> technology and produce sufficient ozone, it is typical practice to install dual (redundant) oxygen and ozone generators. The ozone is which is injected upstream of a gas scrubber using water as the circulating absorbent solution. The ozone reactions are rapid even at moderate gas temperatures and mixing of a gaseous reagent can be more

<sup>1</sup> EPA 2016, Control Cost Manual, Ch. 1, Selective Non-Catalytic Reduction, May 2016, Section 1.1

<sup>2</sup> EPA 2016, Section 1.1.

rapid than liquid-solution reagents. The reactions occur in the existing duct and within the scrubber itself. With sufficiently high ozone to NO<sub>x</sub> ratio, and sufficient residence time for reaction, control efficiency of 95 percent can be achieved. The control level achieved also depends on the wet scrubber design and operating practices. Technical information regarding the LoTOx<sup>®</sup> process is provided in Appendix E.

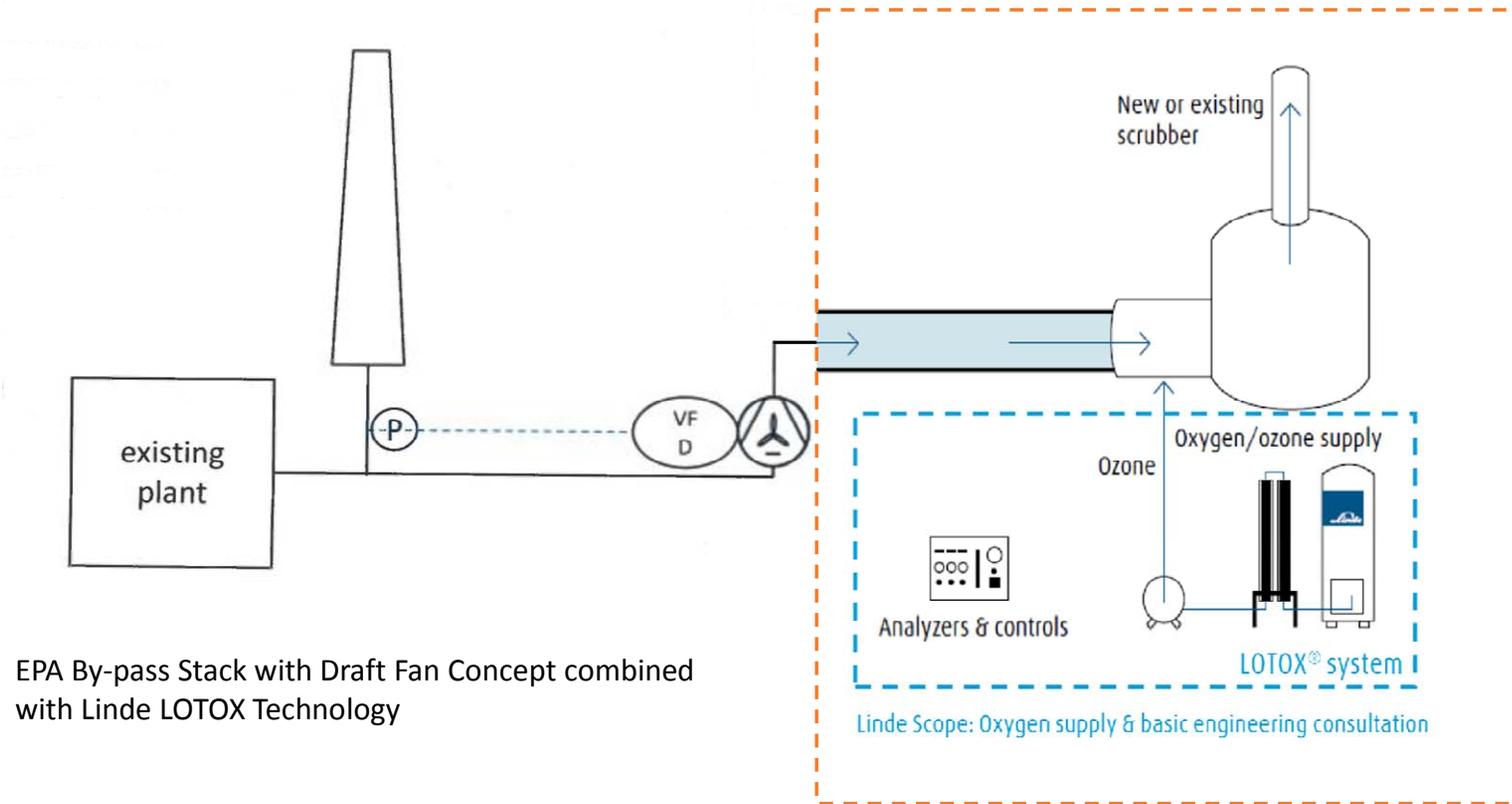
### **2.1.3 Continuous Peroxide Injection (CPI) at Reduced Reagent Ratio**

For nitric acid plants, peroxide injection control is typically implemented by injection of a supplemental scrubbing solution containing hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) into the circulating liquid stream in the extended absorption tower. This allows additional HNO<sub>3</sub> to be recovered from the tail gas by shifting the pH of the absorbing solution, and providing a second reaction path to form soluble HNO<sub>3</sub>. In practice, peroxide injection is used to control NO<sub>x</sub> emissions and avoid a colored tail gas plume during nitric acid plant startups. In suitable cases, it has potential applicability as a continuous control option, although a large reagent storage facility would be needed to accommodate the much higher level of consumption. The NO<sub>x</sub> control efficiency achieved depends primarily on the operating pressure and temperature of the absorption tower, the NO<sub>x</sub> concentration in the process gas, and the ratio of aqueous peroxide to gas-phase NO<sub>x</sub>; although a high excess of peroxide does not offer additional control benefit.<sup>3</sup>

Hydrogen peroxide injection is currently in use at ANPI to reduce NO<sub>x</sub> emissions in AOP-4 absorber tail gas during startup. From a process chemistry standpoint, the continual presence of H<sub>2</sub>O<sub>2</sub> in the extended absorption tower solution will make absorption of nitric acid more efficient, but this is not typical practice.

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<sup>3</sup> Thomas and Vanderschuren, *The Absorption-Oxidation of NO<sub>x</sub> with Hydrogen Peroxide for the Treatment of Tail Gases*. Chem. Engr. Sci. Vol. 51, No. 11, 1996.



EPA By-pass Stack with Draft Fan Concept combined with Linde LOTOX Technology

Figure 2-1. Illustration of LoTOx® Technology with By-Pass Stack for AOP-4

## 2.2 Step 2 – Eliminate Technically Infeasible Options

Step 2 is comprised of an evaluation of the technical feasibility of the control options identified in step 1. According to the EPA NSR Manual, Part 1, Chapter B, Section IV.B, “if the control technology has been installed and operated successfully on the type of source under review, it is demonstrated and it is technically feasible.”<sup>4</sup>

Two key concepts are important in determining whether a technology option is feasible: “availability” and “applicability.” As explained in Part I, Chapter B, Section IV.B of the EPA NSR Manual, a technology is considered “available” if it can be obtained by the applicant through commercial channels or is otherwise available within the common sense meaning of the term. An available technology is “applicable” if it can reasonably be installed and operated on the source type under consideration. A technology that is available and applicable is technically feasible. It should be noted that, with the exception of peroxide injection, the additional control alternatives have not been demonstrated in this sense for nitric acid plant tail gas treatment.

This case-by-case BACT analysis of alternative NO<sub>x</sub> controls must carefully consider the process-specific features of AOP-4. This includes consideration of physical, chemical, and engineering principles that may show that technical difficulties preclude successful use or deployment of the control option at AOP-4. Accordingly, the determination of technical feasibility is based on whether that control technology option can be reasonably installed and operated at AOP-4 and therefore considered “applicable.”

### 2.2.1 SNCR

The most apparent technical barrier to the use of SNCR for nitric acid tail gas treatment is the relatively high temperature regime that must be maintained for effective conversion of NO<sub>x</sub> in the absence of a catalyst. This high temperature requirement is why SNCR technology has been applied almost exclusively in fossil-fuel power plants and other combustion processes with high exhaust gas temperatures. In the AOP-4 tail gas path downstream of the extended absorber tower, the highest design temperature achieved is 1,250°F at the exit of the turbine gas heater, which is 300 °F to 700 °F below the range necessary for effective conversion.

The temperature and pressure conditions of the existing stream at this point are critical to the proper operation of the downstream high pressure expander that drives the Airco air compressor. Increasing the temperature of the tail gas as needed to operate SNCR would reduce the gas density, which will not allow the existing compressor to deliver the necessary discharge pressure. A further limitation is the maximum allowable inlet temperature to the high-pressure Expander, which according to specification is 1,350 °F.<sup>5</sup> So, increasing the tail gas temperature to accommodate SNCR at this location in the process is not considered feasible as it would make it impossible for the existing Steam Turbine/Air Compressor/NO<sub>x</sub> Expanders to operate within the pressure regime and heat balance that are inherent requirements of the design.

At another process location that may be considered for control retrofit, the exit of the low-pressure NO<sub>x</sub> Expander upstream of the final heat exchangers and tail gas stack, the tail gas is at the highest available design temperature of only 540°F. Therefore, to achieve acceptable SCNR operation at this location, a new NO<sub>x</sub> control train (tail gas reheat, reagent injection, reaction zone, heat recovery and tail gas cooling exchangers) must be designed and integrated with the heat balance of the entire process to greatly increase the tail gas temperature. The existing tail gas heat exchangers and stack and other components are not designed to accommodate such high operating temperatures and the large amount of added

<sup>4</sup> EPA NSR Manual 1990, Chapter B, Section IV.B.

<sup>5</sup> Apache Powder Co. Centrifugal Compressor Specification, 1978.

thermal energy. The higher temperature operating regime would have adverse effects on the performance and service life of the other high-pressure equipment along the tail gas exhaust path. More importantly the potential for mechanical failures of high-pressure components operating at much higher temperatures poses an unacceptable safety risk.

In combination, the issues described here are considered unresolvable for AOP-4 application of SNCR. Consequently, this alternative is considered technically infeasible, and therefore not addressed further in this analysis.

### 2.2.2 Continuous Peroxide Injection (CPI)

Given the status of peroxide injection at AOP-4 and other nitric acid plants, this technology can be considered “demonstrated in practice” and is an alternative control for AOP-4, although there is relatively little experience using CPI for continuous NO<sub>x</sub> control. Also, the effectiveness of reduced reagent ratio is subject to uncertainty, since it has only been evaluated at laboratory scale. On balance, this alternative is considered at this step to be available and applicable, and will be carried forward for more thorough evaluation.

### 2.2.3 LoTO<sub>x</sub><sup>®</sup>

The feasibility of retrofit LoTO<sub>x</sub><sup>®</sup> is affected by the existing compact arrangement of AOP-4 process block equipment, piping, and ductwork, with no physical ground space available nearby to locate oxygen and ozone generation units that would be the size of semi-truck trailer, or accommodate a large wet scrubber and ancillary pumps. Additionally, measures to compensate for the added pressure drop of a tail gas wet scrubber would be similar to those needed in for an end-of-pipe SCR system. There would need to be a variable-speed booster fan installed in the tail gas path, and a bypass stack to allow for unobstructed gas exhaust in the event of a booster fan or scrubber malfunction. The retrofit LoTO<sub>x</sub><sup>®</sup> installation would generally resemble the configuration shown for near-atmospheric SCR with an open bypass stack shown in Figure 4.3 of the April 2020 BACT Analysis. In this case the wet scrubber would replace the SCR module, and the wet scrubber would be considerably larger in volume.

To assess technical feasibility and potential costs, ANPI consulted with Linde Gases Division representatives in the U.S, and through them with the LoTO<sub>x</sub><sup>®</sup> technology team in Germany that designs systems for industrial customers. In an attempt to avoid the addition of a new wet scrubber, Linde initially suggested that the gaseous ozone might be injected in the existing AOP-4 acid absorber tower. However, due to the high pressure of the tower (approximately 280 psig, or higher), it was concluded after examination by Linde that there were no ozone generator systems that could deliver the reagent gas at sufficiently high pressure for injection.<sup>6</sup> Consequently, Linde examined the implementation of LoTO<sub>x</sub><sup>®</sup> with a separate ground-level scrubber, new stack, and redundant oxygen and ozone generator systems.

Separate from the installation practicality and configuration issues, a more critical feasibility consideration is the incorporation of an additional piece of equipment into the AOP-4 process stream while maintaining the system’s necessary operational characteristics. These considerations were discussed in depth in Sections 4.2.1 and 4.3.2 of the April 2020 BACT Analysis. This discussion described the critical balance of many factors that are unique to the Airco system design during transient startup and shutdown must be considered in determining the technical feasibility of implementing tail gas NO<sub>x</sub> control. ANPI made Linde aware of these pressure drop and stability factors for the added scrubber. Prior feasibility studies have stated that any modification to the Steam Turbine/Compressor/Expander gas flow, shaft rotating speed to or operating pressures requires an in-depth analysis to investigate whether safe and reliable system operation is possible. Specifically, turbine rotating speed within the range of resonant vibration

<sup>6</sup> Linde U.S. Industrial Gases, e-mail communication with ERM and ANPI, October 22, 2020. Copy provided in Appendix E.

frequencies must be avoided (as noted in the operating procedure) to reduce the chance of blade failures,<sup>7</sup> Lack of a compressor map to does not allow the AOP-4 operator to predict how pressure differences will affect steam turbine input and compressor rotating speed.<sup>8</sup>

In common with the SCR alternatives for AOP-4, there is the potential for uncontrolled release of untreated tail gas through the bypass stack. This stack is necessary to provide an unobstructed, alternate gas exhaust path during those events when the booster fan or scrubber malfunctions cause an instability in pressure drop losses through the scrubber and and exhaust stack. It is anticipated that periods of imbalance will likely occur during each AOP-4 startup, when the control of the booster fan (a variable speed unit) must be coordinated with pressure and flow transient conditions. In these events, the NO<sub>x</sub> emission rate from AOP-4 would no longer be controlled by the LoTOx<sup>®</sup> system. Events when the bypass stack would open can also cause pressure profile transients, with unpredictable effects on the turbine shaft speed and possible compressor surging.

Assuming that bypass emissions will occur throughout each 2-hour startup period occurring 8 times per year, this amounts to about 450 pounds per year of unabated NO<sub>x</sub> emissions.<sup>9</sup> These transient conditions would violate the expected performance level that would potentially apply to LoTOx<sup>®</sup> during startup and shutdown. There would also be unpredictable bypass emissions that would occur during process transients that affect the tail gas pressure conditions, and these would also violate a full-time NO<sub>x</sub> emission limit.

Primarily, there are too many unknowns and uncertainties regarding the effects of added pressure drop of any end-of-pipe abatement unit, such as a LoTOx<sup>®</sup> scrubber during startup transient operations. There are no other Airco systems currently in operation with end-of-pipe controls, and there is neither a reliable compressor map, nor field experience with this combination of technologies. Consequently, industry experts "cannot recommend any change to the system that would affect the rpm of this turbine, either under normal operation or during failure conditions (i.e. [booster] fan failure)."<sup>10</sup> In light of these uncertainties, ANPI would be encumbering a substantial risk of catastrophic equipment failure, especially during initial startups of a LoTOx<sup>®</sup>-controlled AOP-4 process. Under these circumstances there would be no available operator experience, no quantitative process operation or pressure map data, and no advice from the now non-existent system vendor.

After consideration of the anticipated technical barriers described above, Linde declined to offer detailed cost information or proceed with the development of an AOP-4 project. Even if the technical feasibility issues could be resolved, Linde estimated in general terms to ANPI that total capital expense for a retrofit system would range from 3 to 5 times higher than SCR alternatives for AOP-4.<sup>11</sup> Because the U.S. provider of LoTOx<sup>®</sup> has declined to offer ANPI a retrofit control project, this alternative is not considered available and applicable to AOP-4, and it is not further addressed in this analysis.

## 2.3 Step 3 – Rank Remaining Options by Control Effectiveness

Step 3 involves ranking all the technically feasible control alternatives that have been identified in Step 2. The control alternatives are ranked-ordered from the most to the least effective in terms of emission reduction potential. The additional control alternatives addressed in this supplemental analysis are ranked

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<sup>7</sup> Hickham 1999, pg. 19

<sup>8</sup> Advantech Feasibility Study, pgs. 24-25

<sup>9</sup> Based on 5-year averages of ANPI operating data, annual emissions average 106 tons per year, over an average operating period of 7,505 hours per year. Assuming 16 hours per year to be at baseline emission rate,  
(16 hrs/7,505 hrs) x 106 tons/yr x 2,000 lbs/ton = 452 lbs/yr

<sup>10</sup> Advantech Feasibility Study, 2015, pg. 3.

<sup>11</sup> Linde U.S. Industrial Gases, e-mail communication with ERM and ANPI, October 22, 2020. Copy provided in Appendix E.

below by the incremental reduction in residual tail gas NO<sub>x</sub> concentration (i.e. parts per million) reduction that would be achieved based on published information as described in Section 2.3. compared to the effective control provided by the existing refrigerated extended absorption. While refrigerated extended absorption does serve as a means to reduce tail gas NO<sub>x</sub>, it is also an inherent element of the AOP-4 process and in effect is the "baseline" control.

The implementation of CPI to supplement the performance of the existing refrigerated extended absorption, although at reduced reagent ratio, is considered a technically feasible option for AOP-4. Upon review of the April 2020 BACT Analysis, the agency requested support for the reagent input rate, or equivalently the reagent ratio, currently used for AOP-4 start up. As described in the prior analysis a control effectiveness of 65 percent is achieved at a peroxide solution input of 478 gallons per hour.<sup>12</sup> This reagent ratio has been implemented by ANPI based on USP recommendation and the measured relative speciation of NO and NO<sub>2</sub> in the absorber inlet gas.<sup>13</sup> Based on the USP recommended peroxide feed rate, the 50 percent diluted solution feed rate is 4,766 pounds/hour.

Technical literature, not specific to nitric acid plant conditions, is available on the relationships between NO<sub>x</sub> gas concentration and speciation, the peroxide to NO<sub>x</sub> ratio, and other variables.<sup>14</sup> This reference provides physical data relating the fractional absorption of NO<sub>x</sub> to the inlet concentration of H<sub>2</sub>O<sub>2</sub> in the absorbing solution. The relationship between total peroxide available in solution to the resulting NO<sub>x</sub> absorption is not linear. For purposes of identifying how reduced input of peroxide will affect NO<sub>x</sub> absorption from the AOP-4 gases, this data provides a basis for scaling the removal efficiency for NO<sub>x</sub> for different levels of reduced input of peroxide to the extended absorption scrubber. This results of the scaling exercise is summarized in Table 3-2a. The detailed graphical analysis is provided in Appendix E, with the economic analysis supporting material for this alternative.

**Table 3-2a. Estimated NO<sub>x</sub> Removal for Reduced CPI Levels for AOP-4**

Assumed Relative Reduction in CPI (%)	Peroxide Injection Rate (gal/hr)	Scaled Control Efficiency for NO <sub>x</sub> <sup>1</sup> (%)	Tons NO <sub>x</sub> Abated (tons/yr)
Current Operation	478	65	80
33	320	64	79
60	191	62	76
80	96	56	69

1 - Scaled control efficiency derived from NO<sub>x</sub> absorption data as a function of peroxide input concentration. Data set was for high nitric acid concentration (Thomas and Vanderschuren, 1996, Figure 2.)

Normal start up data shows tail gas NO<sub>x</sub> concentration with peroxide in the extended absorber column is nominally 80 ppm, and this concentration increases to approximately 180 - 200 ppm after the peroxide is depleted. This relative control effectiveness for alternative controls options is assumed to be in addition to that provided by refrigerated extended absorption operating alone. The ranking of potential control technology alternatives based on control effectiveness is as follows:

<sup>12</sup> CEMS data plot, AOP-4 start up, Appendix E, AOP-4 BACT Analysis, April 2020.

<sup>13</sup> In the case of AOP-4, the full capacity design case heat and energy balance shows that the tail gas contains 1042.8 lbs NO/h and 5,958.38 lbs NO<sub>2</sub>/hr. The resulting hydrogen peroxide injection requirement is:  $((1.7 * 1,042.8) + (0.4 * 5,958.38)) = 2,383$  lbs peroxide/hr.

<sup>14</sup> Thomas and Vanderschuren, Chem. Engr. Sci. 1996.

- |   |     |
|---|-----|
| ■ CPI at 33 percent reduced reagent ratio | 64% |
| ■ CPI at 60 percent reduced reagent ratio | 62% |
| ■ CPI at 80 percent reduced reagent ratio | 56% |

## 2.4 Step 4 – Evaluate Most Effective Controls and Document Results

After identifying and listing the available control alternatives by control effectiveness, the next step is the determination of the energy, environmental, and economic impacts of each option. Step 4 validates the suitability of the top control option in the listing for selection as BACT, or provides clear justification why the top candidate is inappropriate as BACT. In the event that the top candidate is shown to be inappropriate, due to energy, environmental, or economic impacts, the next most effective alternative in the listing becomes the new control candidate and is similarly evaluated.

### 2.4.1 Energy Considerations for CPI

Potential energy effects of implementing CPI can be evaluated from process information for the use of HPI during AOP-4 startup only. For the current HPI use during startup, the flow rate is less than 10 gallons per minute (gpm), based on ANPI process data. So the injection pump is fairly small, with an 8 horsepower rating. To provide for reduced injection rate, a new injection pump at a lower rating would require even less energy. Consequently, there are minimal added on-site energy requirements for CPI, compared to overall energy consumption of the ANPI facility.

The need to ship by truck or railcar large volumes of hydrogen peroxide does result in a substantial energy penalty for this alternative. Given the general lack of bulk chemical producers in Arizona, it is expected that the several hundred thousand additional gallons of peroxide would need to be shipped hundreds of miles from Southern California or the Gulf Coast. This incremental additional energy consumption is significant, given the relatively small amount of NO<sub>x</sub> that would be abated.

### 2.4.2 Environmental Considerations for CPI

There are a few substantive environmental considerations for expanded use of CPI at reduced reagent ratio. Per hour of operation, the levels of reduced reagent ratio considered in this analysis would consume between 96 and 320 gallons of aqueous hydrogen peroxide, which is an industrial grade solution that is diluted 1:1 with water. There would be normal safety and environmental precautions that must be taken to safely handle increased volumes of peroxide and avoid the risk of spills. Handling of railcar loads of a second reactive chemical (in addition to anhydrous ammonia) using a new unloading facility at ANPI represents an additional challenge for the facility to meet the environmental requirements to control and safely operate the peroxide off-loading and storage facilities.

Utilizing the current startup operation for HPI on AOP-4 on a continuous basis, even at reduced reagent ratio, still involves a large increase in the annual consumption of H<sub>2</sub>O<sub>2</sub> solution. ANPI does not produce this material, so it would need to be delivered by truck or rail. Based on the hourly rates of H<sub>2</sub>O<sub>2</sub> industrial grade solution consumption at various reagent ratios, the annual deliveries would increase between 360,000 and 1.2 million gallons per year. Although implementation of CPI at reduced reagent ratio somewhat mitigates the increase in delivery traffic, it is expected that the several hundred thousand additional gallons of peroxide would need to be shipped hundreds of miles from Southern California or the Gulf Coast. The energy use and pollutant emissions from the delivery vehicles are considered adverse environmental factors for CPI. The emissions from the added delivery vehicles required to implement CPI may more than offset the reduction in NO<sub>x</sub> at AOP-4.

### 2.4.3 Economic Considerations and Cost Analysis for CPI

Compared to SCR options evaluated previously, the total capital investment is much lower to implement continuous injection of peroxide solution. It is assumed that the equipment and piping that conveys the solution in to the Absorption Tower water feed stream would be essentially unchanged. This is because AOP-4 already has much of the hardware in place and operating during each AOP-4 startup. It is also assumed there would be no changes to the Extended Absorption column for this alternative. However, the higher rate of H<sub>2</sub>O<sub>2</sub> consumption would dictate that the available on-site storage must approximately double, which would require two new peroxide storage tanks. Estimated direct costs for the new tanks, upgraded injection controls, and other factored direct costs are just under \$224,000. Allowing for typical indirect costs of construction<sup>15</sup> the total capital investment is estimated to be \$296,400. These capital costs are assumed to be identical for any selected reagent ratio. Cost analysis tables are provided to supplement Appendix D for CPI and supporting information for the control option equipment cost, direct and indirect costs is provided in the supplemental Appendix E.

One potential disadvantage of CPI is that residual peroxide may remain in the nitric acid product due to "overdosing" of the reagent. Residual peroxide would be considered a contaminant of the nitric acid product and a reactivity hazard at any detectable concentration.<sup>16</sup> The adoption of CPI must assume that upgraded process controls must be installed to operate such that the reagent addition rate will respond to process changes, to ensure stable relative flow of the injected reagent.

Direct annual costs for this alternative include the normal levels of operating labor and maintenance defined by US EPA for acid gas scrubbing<sup>17</sup>. There are minimal additional utilities for this option, similar to the alternative of reagent injection at the rate now used for AOP-4 start up periods. A capital recovery factor is applied to allow for amortization of the invested capital cost over a period of 20 years at 5.5 percent interest.

By far the largest component of annual direct cost is the purchase of large volumes of industrial grade H<sub>2</sub>O<sub>2</sub>. The effectiveness of NO<sub>x</sub> control at several different reagent levels was assessed in Section 2.3, using published literature describing the non-linear relationship between peroxide concentration and NO<sub>x</sub> absorption efficiency. The details of the evaluation of control efficiency at three selected levels of reagent input are provided in supplemental Appendix E. Based on current as-delivered 2020 pricing for ANPI, the continuous operation of the range of reduced injection rates considered for this alternative would consume between 360,000 and 1.2 million gallons per year, resulting in an estimated annual reagent solution cost of between \$1.54 and \$5.14 million per year. The reagent cost factor dominates the overall annualized control cost. The emission reductions achieved are not in direct proportion to the reagent ratio, as shown by published data.<sup>18</sup> However, the direct control costs are essentially proportional to the reagent injection rate.

The detailed cost estimation for this alternative is provided as a supplement to Appendix D. Cost estimates obtained prior to 2019 were scaled to 2020 dollars using Federal Reserve Producer Price Indices (<https://fred.stlouisfed.org/categories/32455>), with copies of the index plots provided in Appendix E of this report. Total annualized cost for this alternative is estimated to range from \$1.9 to \$5.5 million. The incremental control effectiveness that would be achieved, above that provided by the refrigerated extended absorption, was scaled from the current control level achieved by ANPI during startup (refer to Table 3-2a). Based on the upper bound annual baseline emissions of 122.9 tons per year (refer to Table

<sup>15</sup> EPA Control Cost Manual. Section 5.2. 1995, Chapter 1-Wet Scrubbers for Acid Gas, Section 1.5.1.

<sup>16</sup> Solvay Chemicals, Inc. *Nitric Acid with Hydrogen Peroxide: Reaction Hazards Technical Data Sheet*, 2005. Accessed at: <http://www.hydrogen-peroxide.us/chemical-catalyst-decomposition/Solvay-Hydrogen-Peroxide-Nitric-Acid-Hazards-2005.pdf>

<sup>17</sup> EPA Control Cost Manual. Section 5.2, 1995, Chapter 1-Wet Scrubbers for Acid Gas, Sections 1.5.1 and 1.5.2.

<sup>18</sup> Thomas and Vanderschuren, Chem. Engr. Sci. 1996.

1.1 in the April 2020 BACT Analysis) and estimated emission reductions, the cost effectiveness values range from of approximately \$27,500 to \$70,000 per ton abated, depending on the selected reagent ratio.

#### **2.4.4 Summary of Economic Considerations and Combined Alternatives**

Evaluation of the economic factors and control retrofit costs for the technically feasible control alternative indicates that CPI is cost prohibitive for AOP-4. In this case, total capital investment is not especially high because the existing Extended Absorber unit should not require internal modifications and the system for HPI injection currently operates on AOP-4. However, the high direct annual cost of purchased H<sub>2</sub>O<sub>2</sub> reagent solution to expand this operation from a few hours of startup per year to over 7,500 hours per year (based on 5-year operating history) drives the cost effectiveness results shown in Table 3-3a.

Table 3-3a summarizes the control effectiveness and the annualized control costs, environmental, and energy impacts for continuous CPI at three reduced reagent ratios. This evaluation considers the incremental reduction to apply to the residual emission rate after the benefit of the existing extended absorption system. The baseline emission rate, with refrigerated extended absorption combined with HPI during startup, is 123 tons per year, which equals the highest annual rate from a 5-year history of reported NO<sub>x</sub> emission data for the AOP-4 tail gas stack. The emissions reduction is then the product of the specified control effectiveness and the baseline emissions, which are not affected by the retrofit controls. The detailed control cost analyses for the tabulated summary are provided in supplemental tables in Appendix D.

**Table 3-3a: Summary of Cost Effectiveness Analysis for Added AOP-4 NO<sub>x</sub> Control Alternatives**

Control Alternative	Annual Emissions (tons/year)	Emission Reduction <sup>2</sup> (tons/year)	Economic Impacts			Adverse Environmental Impacts	Energy Impacts
			Total Annualized Cost (\$/year)	Average Cost Effectiveness (\$/ton abated)	Incremental Cost Effectiveness (\$/ton) <sup>3</sup>		
Continuous Peroxide Injection at Current Start Up Rate (Addressed in Prior BACT Analysis)	43	80	\$8.033 million App. D, Table D-5	\$100,498 App. D, Table D-6	\$9,854	Vehicle emissions and spillage risks with high number of long-distance reagent deliveries	Fuel consumption by delivery vehicles.  Minor increase in AOP-4 electricity consumption
Continuous Peroxide Injection 33% Reduced Rate	44	79	\$5.496 million App. D, Table D-5a	\$69,828 App. D, Table D-6a	\$12,647		
Continuous Peroxide Injection 60% Reduced Rate	47	76	\$3.424 million App. D, Table D-5b	\$44,908 App. D, Table D-6a	\$1,733		
Continuous Peroxide Injection 80% Reduced Rate	54	69	\$1.898 million App. D, Table D-5c	\$27,565 App. D, Table D-6a	—		

Notes:

<sup>1</sup> - Control effectiveness based on vendor performance specification for NO<sub>x</sub> concentration in treated tail gas. For alternatives with SCR combined with continuous HPI, the SCR control level applies to the residual emissions (43 tons per year) in the tail gas assuming operation of continuous HPI.

<sup>2</sup> - Baseline emissions are 123 tons per year. Emission reduction (tons/year) = 123 x (% control effectiveness)

<sup>3</sup> - The incremental cost effectiveness is the difference in annualized cost for the alternative and the next highest ranked alternative, divided by the difference in emission reductions.

## 2.5 Step 5 – Identify Recommended NO<sub>x</sub> Control Alternative

Consideration of the economic factors for CPI at reduced reagent ratios indicates that this alternative must be rejected as it is shown to be cost prohibitive. Continuous injection of H<sub>2</sub>O<sub>2</sub> reagent solution to the Extended Absorption tower is technically feasible, with relatively low total capital investment. However, the consumption of H<sub>2</sub>O<sub>2</sub> reagent solution, even at reduced reagent ratios for all operating hours, results in an estimated annual direct cost of almost between \$1.9 and \$5.5 million. Reagent expense alone accounts for 81 to 94 percent of the annualized control cost, depending on the reagent ratio. Further, the emission reduction benefit is reduced if peroxide is not present in excess, which also contributes to the resulting annualized cost range of \$29,685 to \$70,936 per ton abated.

Accordingly, this analysis concludes that there are no appropriate NO<sub>x</sub> control technology alternatives to the existing refrigerated extended absorption and HPI during startup for AOP-4.

**SUPPLEMENT TO APPENDIX D -  
CONTROL COST ANALYSIS TABLES FOR CPI  
ALTERNATIVES**

TABLE D-5

**TOTAL CAPITAL INVESTMENT AND ANNUAL COST CALCULATIONS  
HYDROGEN PEROXIDE INJECTION (HPI) - CONTINUOUS OPERATION**

Injection Rate Remains at Current Rate Used for Startup

Cost Item	Factor	Cost
<b>Direct Costs</b>		
Purchased Equipment Costs		
Two new H2O2 Storage Tanks (18,000 gal, 15 psig) <sup>1</sup>	A	103,000
Freight <sup>2</sup>	0.05 A	5,150
Sales Tax (prevailing west U.S. tax rates)	0.07 A	7,210
Purchased Equipment Cost (PEC)	PEC	115,360
Direct Installation Costs <sup>2</sup>		
Foundation and Supports/Construction	0.52 PEC	59,987
Instrumentation (updated injection system controls)	0.10 PEC	10,300
Electrical	0.01PEC	1,154
Upgrade peroxide piping and valves	0.30PEC	34,608
Insulation for new tank and piping	0.01PEC	1,154
Painting	0.01PEC	1,154
Direct Installation Cost		108,356
<b>Total Direct Costs (DC)</b>		<b>223,716</b>
<b>Indirect Costs</b>		
Installation for New Tanks and Ancillary Equipment <sup>2</sup>		
Engineering (tank foundation, injection control)	0.10 PEC	11,536
Misc. Construction & Field Expenses	0.10 PEC	11,536
Contractor Fees	0.10 PEC	11,536
Start-Up (trials, devel/test new startup and operating procedures)	0.3 PEC	34,608
Contingencies	0.03 PEC	3,461
Indirect Installation		72,677
<b>Total Indirect Costs (IC)</b>		<b>72,677</b>
<b>TOTAL CAPITAL INVESTMENT = DC + IC</b>		<b>296,393</b>
<b>Direct Annual Costs</b>		
Operating Labor <sup>3</sup>		
Operator (@ \$45/hr)	4 hrs/day	65,700
Supervisor	15% of operator	9,855
Total Operating Labor		75,555
Maintenance <sup>3</sup>		
Labor and Materials	0.5 TCI	148,196
Total Maintenance		148,196
H2O2 Reagent <sup>4</sup>		
Aqueous H2O2, 50% diluted industrial grade, 478 gal per hour	\$4.28/gal current vendor pricing	7,677,015
Operating time 7,505 hrs/yr, based on past 5-yr average for AOP-4	-----	
Utilities <sup>5</sup>		
Electricity - (kW) (@\$0.05/kwh)	10,000 kwh/yr	500
Total Additional Utilities		500
Miscellaneous <sup>6</sup>		
Permitting/Performance Tests - control efficiency testing for HPI	\$40000/yr	40,000
		40,000
<b>Total Direct Annual Costs (DAC)</b>		<b>7,941,266</b>
<b>Indirect Annual Costs</b>		
Administrative Charges <sup>2</sup>	0.03 x( Oper. Labor) + 0.4 (Ann. Maint Cost)	61,545
Property Taxes <sup>2</sup>	0.01TCI	2,964
Insurance <sup>2</sup>	0.01TCI	2,964
Capital Recovery Factor <sup>7</sup>	-----	0.0837
Capital Recovery	(CRF)(TCI)	24,808
<b>Total Indirect Annual Costs (IAC)</b>		<b>92,281</b>
<b>TOTAL ANNUAL COST = DAC + IAC</b>		<b>8,033,547</b>

<sup>1</sup> Cost for the storage tank derived from US Dept of Energy Process Equipment Cost Estim. Jan 2002, which provides 1998 costs for storage tanks. Adjusted to using Federal Reserve Economic Data Producer Price Index for Machinery and Equipment (2020): 1998 PPI = 145, 2020 PPI = 250; scaling ratio = 250/145 = 1.72

<sup>2</sup> These factors were taken from the EPA Cost Control Manual Section 5.2, Chapter 1, for wet scrubbing control of acid gases

<sup>3</sup> Operating labor factors were taken from the EPA Cost Control Manual for add-on pollutant control systems (2019), or ANPI internal estimates. Calculations assume workers are on shift 1,500 hours/year, with employees paid at the rate of \$45 per hour.

<sup>4</sup> Baseline case consumption of peroxide solution based on current ANPI operating data for hourly flow during startup, and current (2020) supplier costs for industrial grade hydrogen peroxide.

<sup>5</sup> Operation of small peroxide solution pump (8 gpm).

<sup>6</sup> These miscellaneous costs are comparable to costs for similar functions for comparable control equipment.

<sup>7</sup> The capital recovery factor was calculated assuming a 20-year equipment life and a 5.5% interest rate

**TABLE D-6**

**CONTROL COST EFFECTIVENESS  
HYDROGEN PEROXIDE INJECTION (HPI) - CONTINUOUS OPERATION**

**Injection Rate Remains at Current Rate Used for Startup**

	<b>Continuous HPI (Controlling NOX Only)</b>
Total Annualized Cost (refer to Table D-5)	8,033,547
Base Case Controlled Pollutant Emissions (tons/year)	123.0
Capture Efficiency (%)	100%
Incremental Control Efficiency above base case (%)	65%
Expected Emissions after Control (tons/year)	43
Expected Emission Reduction after Control (tons/year)	80
<b>Control Cost per Ton of Pollutant Removed (\$/ton)</b>	<b>100,498</b>

TABLE D-5a

**TOTAL CAPITAL INVESTMENT AND ANNUAL COST CALCULATIONS  
CONTINUOUS PEROXIDE INJECTION (CPI) - REDUCED REAGENT RATIO**

Injection Rate Reduced by 33% from Current Rate Used During Startup

Cost Item	Factor	Cost
<b>Direct Costs</b>		
Purchased Equipment Costs		
Two new H2O2 Storage Tanks (18,000 gal, 15 psig) <sup>1</sup>	A	103,000
Freight <sup>2</sup>	0.05 A	5,150
Sales Tax (prevailing west U.S. tax rates)	0.07 A	7,210
Purchased Equipment Cost (PEC)	PEC	115,360
Direct Installation Costs <sup>2</sup>		
Foundation and Supports/Construction	0.52 PEC	59,987
Instrumentation (updated injection system controls)	0.10 PEC	10,300
Electrical	0.01PEC	1,154
Upgrade peroxide piping and valves	0.30PEC	34,608
Insulation for new tank and piping	0.01PEC	1,154
Painting	0.01PEC	1,154
Direct Installation Cost		108,356
<b>Total Direct Costs (DC)</b>		<b>223,716</b>
<b>Indirect Costs</b>		
Installation for New Tanks and Ancillary Equipment <sup>2</sup>		
Engineering (tank foundation, injection control)	0.10 PEC	11,536
Misc. Construction & Field Expenses	0.10 PEC	11,536
Contractor Fees	0.10 PEC	11,536
Start-Up (trials, devel/test new startup and operating procedures)	0.3 PEC	34,608
Contingencies	0.03 PEC	3,461
Indirect Installation		72,677
<b>Total Indirect Costs (IC)</b>		<b>72,677</b>
<b>TOTAL CAPITAL INVESTMENT = DC + IC</b>		<b>296,393</b>
<b>Direct Annual Costs</b>		
Operating Labor <sup>3</sup>		
Operator (@ \$45/hr)	4 hrs/day	65,700
Supervisor	15% of operator	9,855
Total Operating Labor		75,555
Maintenance <sup>3</sup>		
Labor and Materials	0.5 TCI	148,196
Total Maintenance		148,196
H2O2 Reagent <sup>4</sup>		
Aqueous H2O2, 50% diluted industrial grade, reduced gal per hour	\$4.28/gal current vendor pricing	5,139,424
Operating time 7,505 hrs/yr, based on past 5-yr average for AOP-4	-----	
Utilities <sup>5</sup>		
Electricity - (kW) (@\$0.05/kwh)	10,000 kwh/yr	500
Total Additional Utilities		500
Miscellaneous <sup>6</sup>		
Permitting/Performance Tests - control efficiency testing for HPI	\$40000/yr	40,000
		40,000
<b>Total Direct Annual Costs (DAC)</b>		<b>5,403,675</b>
<b>Indirect Annual Costs</b>		
Administrative Charges <sup>2</sup>	0.03 x( Oper. Labor) + 0.4 (Ann. Maint Cost)	61,545
Property Taxes <sup>2</sup>	0.01TCI	2,964
Insurance <sup>2</sup>	0.01TCI	2,964
Capital Recovery Factor <sup>7</sup> 5.5% interest, 20 year service life	-----	0.0837
Capital Recovery	(CRF)(TCI)	24,802
<b>Total Indirect Annual Costs (IAC)</b>		<b>92,275</b>
<b>TOTAL ANNUAL COST = DAC + IAC</b>		<b>5,495,951</b>

<sup>1</sup> Cost for the storage tank derived from US Dept of Energy Process Equipment Cost Estim. Jan 2002, which provides 1998 costs for storage tanks. Adjusted to using Federal Reserve Economic Data Producer Price Index for Machinery and Equipment (2020): 1998 PPI = 145, 2020 PPI = 250; scaling ratio = 250/145 = 1.72

<sup>2</sup> These factors were taken from the EPA Cost Control Manual Section 5.2, Chapter 1, for wet scrubbing control of acid gases

<sup>3</sup> Operating labor factors were taken from the EPA Cost Control Manual for add-on pollutant control systems (2019), or ANPI internal estimates. Calculations assume workers are on shift 1,500 hours/year, with employees paid at the rate of \$45 per hour.

<sup>4</sup> Consumption of peroxide solution based on current ANPI operating data for hourly flow during startup, and current (2020) supplier costs for industrial grade hydrogen peroxide.

<sup>5</sup> Operation of small peroxide solution pump (8 gpm).

<sup>6</sup> These miscellaneous costs are comparable to costs for similar functions for comparable control equipment.

<sup>7</sup> The capital recovery factor was calculated assuming a 20-year equipment life and a 5.5% interest rate

TABLE D-5b

**TOTAL CAPITAL INVESTMENT AND ANNUAL COST CALCULATIONS  
CONTINUOUS PEROXIDE INJECTION (CPI) - REDUCED REAGENT RATIO**

Injection Rate Reduced by 60% from Current Rate Used During Startup

Cost Item	Factor	Cost
<b>Direct Costs</b>		
Purchased Equipment Costs		
Two new H <sub>2</sub> O <sub>2</sub> Storage Tanks (18,000 gal, 15 psig) <sup>1</sup>	A	103,000
Freight <sup>2</sup>	0.05 A	5,150
Sales Tax (prevailing west U.S. tax rates)	0.07 A	7,210
Purchased Equipment Cost (PEC)	PEC	115,360
Direct Installation Costs <sup>2</sup>		
Foundation and Supports/Construction	0.52 PEC	59,987
Instrumentation (updated injection system controls)	0.10 PEC	10,300
Electrical	0.01 PEC	1,154
Upgrade peroxide piping and valves	0.30 PEC	34,608
Insulation for new tank and piping	0.01 PEC	1,154
Painting	0.01 PEC	1,154
Direct Installation Cost		108,356
<b>Total Direct Costs (DC)</b>		<b>223,716</b>
<b>Indirect Costs</b>		
Installation for New Tanks and Ancillary Equipment <sup>2</sup>		
Engineering (tank foundation, injection control)	0.10 PEC	11,536
Misc. Construction & Field Expenses	0.10 PEC	11,536
Contractor Fees	0.10 PEC	11,536
Start-Up (trials, devel/test new startup and operating procedures)	0.3 PEC	34,608
Contingencies	0.03 PEC	3,461
Indirect Installation		72,677
<b>Total Indirect Costs (IC)</b>		<b>72,677</b>
<b>TOTAL CAPITAL INVESTMENT = DC + IC</b>		<b>296,393</b>
<b>Direct Annual Costs</b>		
Operating Labor <sup>3</sup>		
Operator (@ \$45/hr)	4 hrs/day	65,700
Supervisor	15% of operator	9,855
Total Operating Labor		75,555
Maintenance <sup>3</sup>		
Labor and Materials	0.5 TCI	148,196
Total Maintenance		148,196
H <sub>2</sub> O <sub>2</sub> Reagent <sup>4</sup>		
Aqueous H <sub>2</sub> O <sub>2</sub> , 50% diluted industrial grade, reduced gal per hour	\$4.28/gal current vendor pricing	3,067,594
Operating time 7,505 hrs/yr, based on past 5-yr average for AOP-4	-----	
Utilities <sup>5</sup>		
Electricity - (kW) (@\$0.05/kwh)	10,000 kwh/yr	500
Total Additional Utilities		500
Miscellaneous <sup>6</sup>		
Permitting/Performance Tests - control efficiency testing for HPI	\$40000/yr	40,000
		40,000
<b>Total Direct Annual Costs (DAC)</b>		<b>3,331,845</b>
<b>Indirect Annual Costs</b>		
Administrative Charges <sup>2</sup>	0.03 x( Oper. Labor) + 0.4 (Ann. Maint Cost)	61,545
Property Taxes <sup>2</sup>	0.01 TCI	2,964
Insurance <sup>2</sup>	0.01 TCI	2,964
Capital Recovery Factor <sup>7</sup> 5.5% interest, 20 year service life	-----	0.0837
Capital Recovery	(CRF)(TCI)	24,802
<b>Total Indirect Annual Costs (IAC)</b>		<b>92,275</b>
<b>TOTAL ANNUAL COST = DAC + IAC</b>		<b>3,424,120</b>

<sup>1</sup> Cost for the storage tank derived from US Dept of Energy Process Equipment Cost Estim. Jan 2002, which provides 1998 costs for storage tanks. Adjusted to using Federal Reserve Economic Data Producer Price Index for Machinery and Equipment (2020): 1998 PPI = 145, 2020 PPI = 250; scaling ratio = 250/145 = 1.72

<sup>2</sup> These factors were taken from the EPA Cost Control Manual Section 5.2, Chapter 1, for wet scrubbing control of acid gases

<sup>3</sup> Operating labor factors were taken from the EPA Cost Control Manual for add-on pollutant control systems (2019), or ANPI internal estimates. Calculations assume workers are on shift 1,500 hours/year, with employees paid at the rate of \$45 per hour.

<sup>4</sup> Consumption of peroxide solution based on current ANPI operating data for hourly flow during startup, and current (2020) supplier costs for industrial grade hydrogen peroxide.

<sup>5</sup> Operation of small peroxide solution pump (8 gpm).

<sup>6</sup> These miscellaneous costs are comparable to costs for similar functions for comparable control equipment.

<sup>7</sup> The capital recovery factor was calculated assuming a 20-year equipment life and a 5.5% interest rate

TABLE D-5c

**TOTAL CAPITAL INVESTMENT AND ANNUAL COST CALCULATIONS  
CONTINUOUS PEROXIDE INJECTION (CPI) - REDUCED REAGENT RATIO**

Injection Rate Reduced by 80% from Current Rate Used During Startup

Cost Item	Factor	Cost
<b>Direct Costs</b>		
Purchased Equipment Costs		
Two new H2O2 Storage Tanks (18,000 gal, 15 psig) <sup>1</sup>	A	103,000
Freight <sup>2</sup>	0.05 A	5,150
Sales Tax (prevailing west U.S. tax rates)	0.07 A	7,210
Purchased Equipment Cost (PEC)	PEC	115,360
Direct Installation Costs <sup>2</sup>		
Foundation and Supports/Construction	0.52 PEC	59,987
Instrumentation (updated injection system controls)	0.10 PEC	10,300
Electrical	0.01PEC	1,154
Upgrade peroxide piping and valves	0.30PEC	34,608
Insulation for new tank and piping	0.01PEC	1,154
Painting	0.01PEC	1,154
Direct Installation Cost		108,356
<b>Total Direct Costs (DC)</b>		<b>223,716</b>
<b>Indirect Costs</b>		
Installation for New Tanks and Ancillary Equipment <sup>2</sup>		
Engineering (tank foundation, injection control)	0.10 PEC	11,536
Misc. Construction & Field Expenses	0.10 PEC	11,536
Contractor Fees	0.10 PEC	11,536
Start-Up (trials, devel/test new startup and operating procedures)	0.3 PEC	34,608
Contingencies	0.03 PEC	3,461
Indirect Installation		72,677
<b>Total Indirect Costs (IC)</b>		<b>72,677</b>
<b>TOTAL CAPITAL INVESTMENT = DC + IC</b>		<b>296,393</b>
<b>Direct Annual Costs</b>		
Operating Labor <sup>3</sup>		
Operator (@ \$45/hr)	4 hrs/day	65,700
Supervisor	15% of operator	9,855
Total Operating Labor		75,555
Maintenance <sup>3</sup>		
Labor and Materials	0.5 TCI	148,196
Total Maintenance		148,196
H2O2 Reagent <sup>4</sup>		
Aqueous H2O2, 50% diluted industrial grade, reduced gal per hour	\$4.28/gal current vendor pricing	1,541,827
Operating time 7,505 hrs/yr, based on past 5-yr average for AOP-4	-----	
Utilities <sup>5</sup>		
Electricity - (kW) (@\$0.05/kwh)	10,000 kwh/yr	500
Total Additional Utilities		500
Miscellaneous <sup>6</sup>		
Permitting/Performance Tests - control efficiency testing for HPI	\$40000/yr	40,000
		40,000
<b>Total Direct Annual Costs (DAC)</b>		<b>1,806,079</b>
<b>Indirect Annual Costs</b>		
Administrative Charges <sup>2</sup>	0.03 x( Oper. Labor) + 0.4 (Ann. Maint Cost)	61,545
Property Taxes <sup>2</sup>	0.01TCI	2,964
Insurance <sup>2</sup>	0.01TCI	2,964
Capital Recovery Factor <sup>7</sup> 5.5% interest, 20 year service life	-----	0.0837
Capital Recovery	(CRF)(TCI)	24,802
<b>Total Indirect Annual Costs (IAC)</b>		<b>92,275</b>
<b>TOTAL ANNUAL COST = DAC + IAC</b>		<b>1,898,354</b>

<sup>1</sup> Cost for the storage tank derived from US Dept of Energy Process Equipment Cost Estim. Jan 2002, which provides 1998 costs for storage tanks. Adjusted to using Federal Reserve Economic Data Producer Price Index for Machinery and Equipment (2020): 1998 PPI = 145, 2020 PPI = 250; scaling ratio = 250/145 = 1.72

<sup>2</sup> These factors were taken from the EPA Cost Control Manual Section 5.2, Chapter 1, for wet scrubbing control of acid gases

<sup>3</sup> Operating labor factors were taken from the EPA Cost Control Manual for add-on pollutant control systems (2019), or ANPI internal estimates. Calculations assume workers are on shift 1,500 hours/year, with employees paid at the rate of \$45 per hour.

<sup>4</sup> Consumption of peroxide solution based on current ANPI operating data for hourly flow during startup, and current (2020) supplier costs for industrial grade hydrogen peroxide.

<sup>5</sup> Operation of small peroxide solution pump (8 gpm).

<sup>6</sup> These miscellaneous costs are comparable to costs for similar functions for comparable control equipment.

<sup>7</sup> The capital recovery factor was calculated assuming a 20-year equipment life and a 5.5% interest rate

**TABLE D-6a**

**CONTROL COST EFFECTIVENESS  
CONTINUOUS PEROXIDE INJECTION (CPI) - REDUCED REAGENT RATIO**

**Reduce Injection Rate by 80%**

	<b>Continuous HPI (Controlling NOX Only)</b>
Total Annualized Cost (refer to Table D-5a)	1,898,354
Base Case Controlled Pollutant Emissions (tons/year)	123.0
Capture Efficiency (%)	100%
Incremental Control Efficiency above base case (%)	56%
Expected Emissions after Control (tons/year)	54
Expected Emission Reduction after Control (tons/year)	69
<b>Control Cost per Ton of Pollutant Removed (\$/ton)</b>	<b>27,565</b>

**Reduce Injection Rate by 60%**

	<b>Continuous HPI (Controlling NOX Only)</b>
Total Annualized Cost (refer to Table D-5b)	3,424,120
Base Case Controlled Pollutant Emissions (tons/year)	123.0
Capture Efficiency (%)	100%
Incremental Control Efficiency above base case (%)	62%
Expected Emissions after Control (tons/year)	47
Expected Emission Reduction after Control (tons/year)	76
<b>Control Cost per Ton of Pollutant Removed (\$/ton)</b>	<b>44,908</b>

**Reduce Injection Rate by 33%**

	<b>Continuous HPI (Controlling NOX Only)</b>
Total Annualized Cost (refer to Table D-5c)	5,495,951
Base Case Controlled Pollutant Emissions (tons/year)	123.0
Capture Efficiency (%)	100%
Incremental Control Efficiency above base case (%)	64%
Expected Emissions after Control (tons/year)	44
Expected Emission Reduction after Control (tons/year)	79
<b>Control Cost per Ton of Pollutant Removed (\$/ton)</b>	<b>69,828</b>

**SUPPLEMENT TO APPENDIX E -  
SUPPORTING MATERIALS FOR ALTERNATIVE EVALUATION  
AND CONTROL COST ANALYSES**

APACHE POWDER CO		REFERENCE NUMBER REQN 2006-1 03K101			
COMPRESSOR DATA		STEAM TURBINE	1 <sup>ST</sup> STG AIR COMP	2 <sup>ND</sup> STG AIR COMP	HI-PRESS EXPANDER
54	MODEL NO./SIZE				
56	TYPE	AXIAL	CENT	CENT	R.I.F.
57	NO OF STAGES	3	1	1	1
58					
59	IMPELLER DIA. INCHES	---	21.7	19.0	22.8
60	TIP SPEED @ MAX RPM, (19950 RPM) FT/SEC	---	1890	1654	1922
61	FIRST CRITICAL SPEED RPM		4500 TO 8500		
62	SECOND CRITICAL SPEED RPM"		26,000		
63	MAXIMUM CONT SPEED, RPM		19950		
64	MINIMUM CONT SPEED RPM		15100		
65	MAXIMUM ALLOWABLE INLET PRESS PSIG	475	6	65	200
66	MAXIMUM ALLOWABLE DISCH PRESS PSIG	0	65	125	28.3
67	HYDROTEST PRESS - INLET PSIG	850	0	97	595
68	HYDROTEST PRESS - DISCH PSIG	50	98	188	50
69	MAXIMUM ALLOWABLE INLET TEMP °F	800	AMBIENT	270	1350
70	MAXIMUM ALLOWABLE DISCH TEMP °F	---	400	500	755
71	INLET FLANGE: SIZE	4" IN	14X 62	20" IN	10" IN
72	RATING & FACING	400# RF	ACD DESIGN	150# RF	400# RF
73	LOCATION		TOP	TOP	---
74	DISCH. FLANGE: SIZE	30" IN	20	12" IN	---
75	RATING & FACING	CLASS 175 RF	150# RF	150# RF	---
76	LOCATION	END	SIDE	45 DEG	END
77					
78					
79	CONSTRUCTION		DOUBLE CASE		
80			OUTTER RAD SPLIT		
81	CASING TYPE	SEE	INNER HORIZ SPLIT	RAD SPLIT	
82	MATERIAL	TURB	STEEL	INCONEL	
83		DATA			
84	IMPELLER TYPE	SEE	OPEN	OPEN	OPEN
85	FABRICATION	SHEET	MILLED	MILLED	MILLED
86	MATERIAL	#12	Ti 6 AL-4V	Ti 6 AL-4V	A 286
87					
88	INTERSTAGE SEAL TYPE		LABYRINTH		
89	MATERIAL		STEEL		
90	DIFFUSER MATERIAL		STEEL	STEEL	
91	GUIDE VANE OR NOZZLE MATERIAL		STEEL	STEEL	INCONEL
92					
93	SHAFT MATERIAL		15-5 PH	15-5 PH	
94	SHAFT SLEEVE MATERIAL		17-4 PH	17-4 PH	
95	SHAFT SEAL TYPE		CARBON RING	CARBON RING	
96	BEARING HOUSING - SEPARATE OR INTEGRAL		INTEGRAL W INNER CASE	INTEGRAL W INNER CASE	
97	SPLIT		HORIZ	HORIZ	
98	MATERIAL		STEEL	STEEL	
99	JOURNAL BEARING: TYPE		TILT PAD	TILT PAD	
100	AREA SQ. IN.		8.44	6.5	
101	ACTUAL LOADING PSI		54.9	76.8	
102	ALLOWABLE LOADING PSI		300	300	
103	THRUST BEARING TYPE			TILT PAD DBL. ACT	
104	AREA SQ. IN.			10.9	
105	ACTUAL LOADING PSI			200	
106	ALLOWABLE LOADING PSI			300	
107					
108					

6-1-77  
11-76  
5/8



## NIITROGEN OXIDES (NOX) ABATEMENT WITH HYDROGEN PEROXIDE

### Introduction

Nitrogen oxides are major pollutants in the atmosphere and are a precursor to acid rain, photochemical smog, and ozone accumulation. The oxides are mainly nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), both of which are corrosive and hazardous to health.

### Stationary Source Focus

With the use of catalytic converters on automobiles, the initial regulatory focus of controlling mobile NOx emissions has reached the point where further restriction has become economically impractical. Consequently, the stationary sources of NOx emissions are now being subjected to more stringent standards in many areas of the U.S. These stationary sources include nitric acid manufacturing plants, manufacturers of nitrated materials such as fertilizer and explosives, and industrial manufacturers such as metallurgical processors, glass manufacturers, cement kilns and power generators where high processing temperatures are used. Because of the environmental concerns posed by air pollution, a great deal of research and money has been expended to develop methods for controlling NOx emissions.

### Regulations

Regulations concerning the limitation of atmospheric emission of NOx from industrial sources vary from region to region. Following the Clean Air Act amendments in 1990, the EPA has reviewed the current national standards, and has subsequently updated the standards pertaining to non-attainment areas. The EPA standard for new nitric acid manufacturing plants is three pounds of NOx per ton of nitric acid produced. This means that new plants must reduce NOx emission levels from 1500-3000 ppm to 200 ppm. The requirements for existing plants are complicated by controversy over methods for measuring ambient NOx levels, as well as the wide variations in state and regional requirements. Typically, existing nitric acid plants are allowed to produce 5.5 pounds of NOx per ton of nitric acid produced. Standards for other industries are being promulgated.

### Sources of Nitrogen Oxide

There are five major sources of nitrogen oxide.

1. Combustion of fuels: At high temperatures, oxygen and nitrogen present in air combine to form nitrogen oxides. Typical flue gas samples contain 100-1500 ppm of nitrogen oxides.
2. Nitric acid manufacturing: Waste gases which cannot be economically recovered in the final absorber usually contain 2-3% nitrogen oxides based on weight of acid produced.
3. Metal finishing operations: Metal surface treatment operations using nitrates, nitrites, or nitric acids, which evolve nitrogen oxides. Examples include bright dipping, phosphatizing, desmutting and pickling of stainless steel.
4. Chemical processes: Nitric acid, nitrates, or nitrites are used as reagents evolve nitrogen oxides. Examples include the production of explosives, plastics and dyes.
5. High temperature processes: Materials made at high temperatures, such as glass manufacturing, electric furnaces and cement kilns, which all evolve nitrogen oxides.

## Controlling NOx Emissions

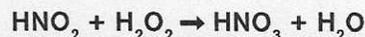
There are several methods for controlling NOx emissions. Gas scrubbing is one of the most common forms of NOx treatment, with sodium hydroxide being the conventional scrubbing medium. The absorbed NOx, however, is converted to nitrite and nitrate, which may present wastewater disposal problems. Scrubbing solutions containing hydrogen peroxide are also effective at removing NOx, and can afford benefits not available with NaOH. For example, H<sub>2</sub>O<sub>2</sub> adds no contaminants to the scrubbing solution and allows commercial products such as nitric acid to be recovered from the process. In its simplest application, H<sub>2</sub>O<sub>2</sub> (0.5-1 wt.%) and nitric acid (35-45 wt.%) are used to scrub both nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) – the chief components of NOx from many industrial sources. The reactions are rapid at moderate temperatures (30-80 deg-C), with about 1.7 and 0.37 lbs H<sub>2</sub>O<sub>2</sub> required per pound of NO and NO<sub>2</sub>, respectively. The chemistry controlling the process is outlined in Figure 1.

The Kanto Denka, Nikon and Ozawa processes also use hydrogen peroxide to remove NOx. The Kanto Denka process employs a scrubbing solution containing 0.2% hydrogen peroxide and 10% nitric acid while the Nikon process uses a 10% sodium hydroxide solution containing 3.5% hydrogen peroxide. The Ozawa process scrubs NOx by spraying a hydrogen peroxide solution into the exhaust gas stream. The liquid is then separated from the gas stream, and the nitric acid formed is neutralized with potassium hydroxide. The excess potassium nitrate is crystallized out and the solution is reused after recharging with hydrogen. A series of Japanese patents also describe efficient processes and equipment for reducing NOx to nitrogen using hydrogen peroxide and ammonia, but they must be carried out at higher temperatures.

Another approach to controlling NOx emissions involves its elimination at the source. This typically involves adding H<sub>2</sub>O<sub>2</sub> directly to HNO<sub>3</sub> contained in metal pickling baths, where

the H<sub>2</sub>O<sub>2</sub> reacts instantly with HNO as it is formed, thereby eliminating its decomposition to NO and NO<sub>2</sub>. In this way, the nitric acid is regenerated in-situ without the expense of scrubbers. Compared to urea, which is also used for in-situ control, the H<sub>2</sub>O<sub>2</sub> process affords true nitric acid recovery and does not degrade the quality of the finished product.

Figure 1. Controlling NOx Emissions



Compiled in part from FMC Technical Data, Pollution Control Release No. 119

## About USP Technologies

USP Technologies is the leading supplier of peroxygen-based technologies and services for environmental applications. We have been serving the water, wastewater and remediation markets for over 20 years and have offices and field service locations throughout North America. Our consultative approach to problem solving includes application assessment, technology selection and development of a tailored treatment approach. Our full service programs successfully integrate storage and dosing equipment systems, chemical supply, inventory and logistics management, and ongoing field and technical support. This approach provides cost-effective, "hands-off" solutions to our customers. USP Technologies also can provide access to experienced application partners for a turn-key program encompassing engineering, site characterization and technology selection, program implementation, execution and report generation.

## Getting Started

We look forward to supporting your treatment needs, whatever the scale of your requirements. To obtain a streamlined treatment solution tailored to your specific project, give us a call at (877) 346-4262.

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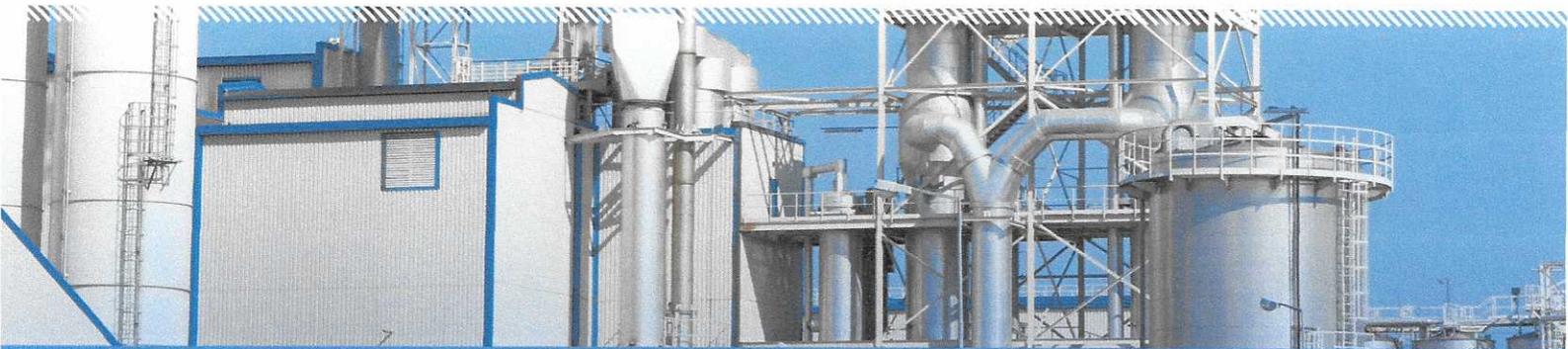
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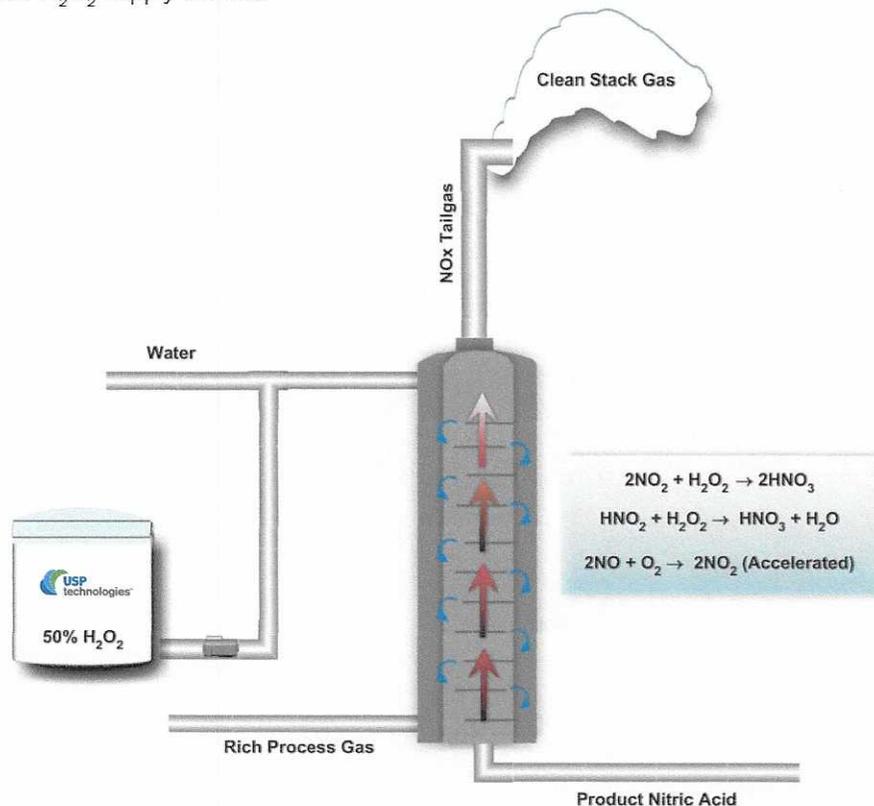
A TROJAN TECHNOLOGIES BUSINESS



## ELIMINATE VISUAL EMISSIONS DURING START-UPS

### NO<sub>x</sub> Control with Hydrogen Peroxide

This proprietary technology introduces diluted H<sub>2</sub>O<sub>2</sub> into the NO<sub>x</sub> absorber during start-ups to reduce emissions of NO<sub>x</sub> compounds such as NO and NO<sub>2</sub>. Removal of >90% is achieved, with the NO<sub>x</sub> being converted to high-quality HNO<sub>3</sub> product. The process is offered under license and is designed to minimize risk and disruption to operations. The license includes chemical storage and feed equipment, piping and instrumentation, process safety controls, installation and maintenance, training and documentation as well as H<sub>2</sub>O<sub>2</sub> supply service.



### Benefits

- **Effective:** Reduces NO<sub>x</sub> emissions from > 3,000 - 4,000 ppm to < 200 ppm
- **Versatile:** Always ready, covers a wide range of NO<sub>x</sub> concentrations and gas flow rates
- **Credits:** Produces high-quality nitric acid as the end-product
- **Low Risk:** Minimal capital investment needed as the equipment lease included in chemical price
- **Proven:** Operated on plant scale for over 15 years with > 30 successful start-ups per year
- **Safe:** Engineered through Process Hazards Analysis with built-in limit controls
- **Rapid:** Deployment within 2-3 months
- **Convenient:** License includes technology transfer package with start-up assistance
- **Ongoing:** Can be utilized for ongoing NO<sub>x</sub> emissions reduction

# ELIMINATE VISUAL EMISSIONS DURING START-UPS

## NO<sub>x</sub> Control with Hydrogen Peroxide

### Which Facilities Will Benefit

The process was designed to control concentrated NO<sub>x</sub> vapors emitted from stationary industrial sources such as manufacturing of nitric acid, fertilizer, explosives, and other chemicals that use nitric acid. The process eliminates visual NO<sub>x</sub> emissions during the start-up of Selective Catalytic Reduction (SCR) processes, thereby satisfying public and regulatory expectations. SCR processes, while very effective for removing NO<sub>x</sub> during normal operations, require high temperatures that are not typically achieved until 1-2 hours after the process has been started. It is during this interim period when visible NO<sub>x</sub> emissions occur and when H<sub>2</sub>O<sub>2</sub> feed is needed.

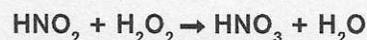
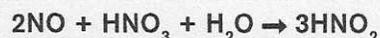
### Principle of Operation

The process entails injecting H<sub>2</sub>O<sub>2</sub> into the absorber feed water to provide a dilute solution containing 0.5 - 1 wt.% H<sub>2</sub>O<sub>2</sub>. This solution is passed through the absorber where NO<sub>x</sub> constituents are transferred from the vapor into the solution and oxidized to high-grade HNO<sub>3</sub>. The oxidation reactions are rapid at moderate temperatures (30-80 degrees C), with about 1.7 and 0.4 lbs H<sub>2</sub>O<sub>2</sub> required per lb of NO and NO<sub>2</sub>, respectively.

### Safety

A thorough process hazards analysis was performed on the process, which has resulted in several interlocks and controls being incorporated into the basic design. The process is used safely in over 30 start-ups per year at two HNO<sub>3</sub> manufacturing units. All piping, components, and controls needed to operate the process safely are included with the license and are installed by experienced H<sub>2</sub>O<sub>2</sub> specialists. The H<sub>2</sub>O<sub>2</sub> storage and feed systems are of modular design and are code-compliant, with years of safe operating history.

### Principle of Operation



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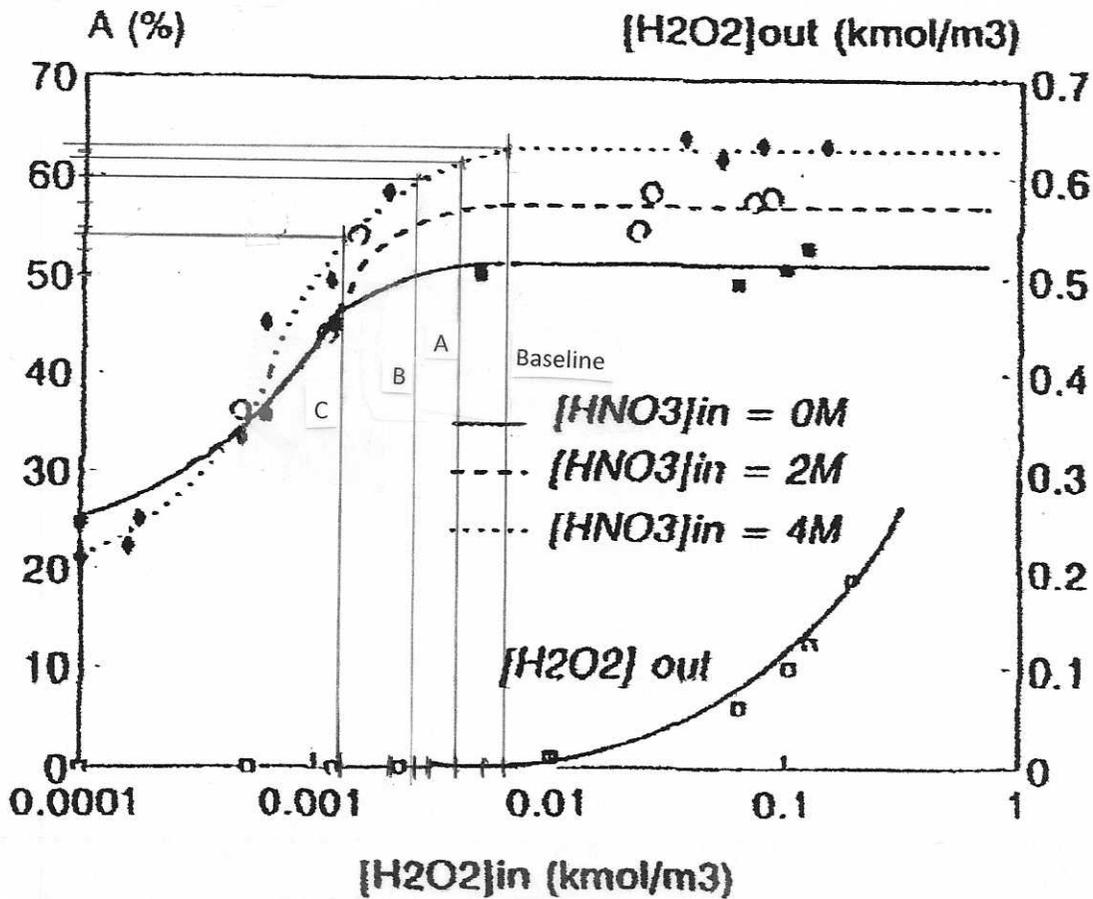
Phone: (404) 352-6070 or (877) 346-4262

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Figure 2. Fractional absorption of NOx and outlet concentration of H<sub>2</sub>O<sub>2</sub> versus inlet concentration of H<sub>2</sub>O<sub>2</sub> - Recycle mode - OR = 66 % - (p<sub>NOx</sub>)<sub>in</sub> = 500 Pa



From Thomas and Vanderschuren, *The Absorption-Oxidation of NOx with Hydrogen Peroxide for the Treatment of Tail Gases*. Chem. Engr. Sci. Vol. 51, No. 11, 1996.

Case	Percent Reduction in H <sub>2</sub> O <sub>2</sub> Input	H <sub>2</sub> O <sub>2</sub> In (X-axis value) <sup>1</sup>	A % (Y axis value) <sup>2</sup>	Scaled H <sub>2</sub> O <sub>2</sub> Injection Rate (gal/hr) <sup>3</sup>	Scaled Absorption Efficiency (%) <sup>4</sup>
A	33	0.004	62	320	64
B	60	0.0024	60	191	62
C	80	0.0012	54	96	56

Baseline coordinates on Figure 2 corresponding to H<sub>2</sub>O<sub>2</sub> absorption at no excess input: H<sub>2</sub>O<sub>2</sub> In = 0.006, and A = 63

1 - X-axis value obtained by scaling the baseline flow on Figure 2 (X=0.006) by the percent reduction in assumed H<sub>2</sub>O<sub>2</sub> input; e.g. 0.006 x (1-33) = 0.004, and plotting this scaled value on the X-axis

2 - Y-axis value is read from the linear scale "A (%)", corresponding to the "H<sub>2</sub>O<sub>2</sub> In" X-axis value

3 - The scaled injection rate is the baseline startup rate (478 gal/hr) reduced by the assumed percent reduction in rate for each case.

4 - On Figure 2 the baseline absorption level is 63% this is used to scale down the observed ANPI control efficiency for H<sub>2</sub>O<sub>2</sub> injection at the normal startup level = 65%. For each Case, these are the scaled absorption efficiencies for the cost analysis:

A: 65% (62/63) = 63.96%

B: 65% (60/63) = 61.90%

C: 65% (54/63) = 55.71%

S0009-2509(96)00131-5

## THE ABSORPTION-OXIDATION OF NO<sub>x</sub> WITH HYDROGEN PEROXIDE FOR THE TREATMENT OF TAIL GASES

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Department of Chemical Engineering, Faculté Polytechnique de Mons, Mons, Belgium

**Abstract** - Absorption of NO<sub>x</sub> up to partial pressures of 500 Pa was experimented at 20°C and atmospheric pressure with aqueous and nitric acid solutions containing hydrogen peroxide. Various NO<sub>x</sub> oxidation ratios in the gas phase, and different concentrations of nitric acid and hydrogen peroxide in the scrubbing liquid were investigated.

It was shown that the absorption rate was enhanced by H<sub>2</sub>O<sub>2</sub> but remains constant if increasing excess quantities of H<sub>2</sub>O<sub>2</sub> are used. Absorption of NO<sub>x</sub> into H<sub>2</sub>O<sub>2</sub> is considerably catalyzed by nitric acid. A mathematical model was developed in which all these experimental observations were included, and overall kinetic parameters for different NO<sub>x</sub> species were determined. Favorable agreement was shown between the model predictions and the experimental results obtained both in a laboratory-scale and a pilot-scale absorption column.

### INTRODUCTION

The reduction of NO<sub>x</sub> in flue gases of boilers, nitric acid plants and all concerned reactors receives nowadays considerable attention due to new stringent laws for a clean environment. For that purpose, both dry and wet treatment techniques are largely used and studied.

In case of wet processes, the major obstacle to absorption is the very low solubility of nitric oxide NO. An obvious way to make more soluble the mixture of nitrogen oxides is to oxidize NO to NO<sub>2</sub> in the gas phase by means of ozone or chlorine dioxide. Oxidation can be also performed in the scrubbing liquid by adding oxidizing agents such as potassium permanganate, sodium chlorite or sodium hypochlorite. A comprehensive review of the various reactive solvents investigated for the absorption of NO<sub>x</sub> was presented recently (Jethani et al., 1990).

The use of hydrogen peroxide in the liquid phase was already investigated experimentally (Adrian and Verilhac, 1976, Deo, 1988, Buck et al., 1991) and largely patented (Downey, 1980, Uguine Kuhlmann, 1974, 1975, 1976), though never thoroughly studied. It appeared to us really interesting to better understand the effect of this reactant as it has a number of attractive environmental properties: easy to handle, non-toxic and non-polluting. A major advantage of this oxidizing agent is that the absorption-oxidation of NO<sub>x</sub> results in the production of nitric acid which can be recovered or recycled in the process.

Despite its rather high cost, hydrogen peroxide could be competitive for the treatment of tail gases from nitric acid plants, pickling units, nitration reactors or catalyst calcinators. Thanks to the low investment required, an acid scrubbing process with H<sub>2</sub>O<sub>2</sub> would be of particular interest for retrofit to old plants of which the NO<sub>x</sub> emission exceeds current standards.

### REACTIONS INVOLVED DURING NO<sub>x</sub> ABSORPTION

The mechanism of NO<sub>x</sub> absorption can be represented as in figure 1.

Main nitrogen oxides species to be considered in liquid and gas phases are: NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, HNO<sub>2</sub> and HNO<sub>3</sub>. The most important chemical reactions that occur during NO<sub>x</sub> scrubbing in water or diluted HNO<sub>3</sub> are quite well described in the literature (Counce and Perona, 1983, Joshi et al., 1985, Newman and Carta, 1988).

In the gas phase, the oxidation of NO to NO<sub>2</sub> is a limiting step in the manufacture of HNO<sub>3</sub> because of the very low solubility of NO. Other species such as dinitrogen trioxide (N<sub>2</sub>O<sub>3</sub>) and tetraoxide (N<sub>2</sub>O<sub>4</sub>) are produced rapidly by gas-phase equilibria.

Nitrous acid is also formed in the gas phase but the

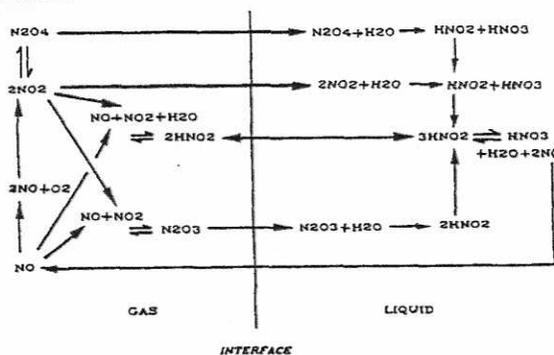


Figure 1. Mechanism of NO<sub>x</sub> absorption into water and dilute nitric acid solutions

literature does not clearly explain whether this formation is achieved at equilibrium or not. Moreover, considerable disagreement exists among the various reported data about the kinetics of  $\text{HNO}_2$  formation.

In the liquid phase, highly soluble compounds  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  dissolve and react rapidly with water to produce nitrous and nitric acids. It is also the case of the less soluble species  $\text{NO}_2$ . Nitric acid is stable in the liquid phase whereas aqueous nitrous acid can desorb directly or can be decomposed with the release of  $\text{NO}$ .

When  $\text{H}_2\text{O}_2$  is present in the liquid phase, the decomposition of  $\text{HNO}_2$  is prevented as it is oxidized to  $\text{HNO}_3$ . This oxidation obviously increases the overall absorption rate.

### EXPERIMENTATION

Our experimental system includes an insulated scrubber, a temperature controlled liquid supply, a gas supply and a gas sampling part. The  $\text{NO}_x$  scrubber is a small glass column of inside diameter 0.045 m packed with 10 mm glass Raschig rings, the height of the packing material being 0.455 m.

The partial pressure of  $\text{NO}_x$  in the gaseous mixture, made of humidified nitrogen and different  $\text{NO}_x$  species, can vary from 10 to 500 Pa. The total gas flow rate is equal to 1  $\text{m}^3/\text{h}$  ( $0.175 \text{ m}^3/\text{s m}^2$ ). Gas analysis is performed continuously by a chemiluminescence analyser which gives the total  $\text{NO}_x$  and the "chemical" nitric oxide contents. The partial pressures of "chemical" nitric oxide  $\text{NO}^*$  and nitrogen dioxide  $\text{NO}_2^*$  are defined as:

$$P_{\text{NO}^*} = P_{\text{NO}} + P_{\text{N}_2\text{O}_3} + 0.5 P_{\text{HNO}_2} \quad (1)$$

$$P_{\text{NO}_2^*} = P_{\text{NO}_2} + 2 P_{\text{N}_2\text{O}_4} + P_{\text{N}_2\text{O}_3} + 0.5 P_{\text{HNO}_2} \quad (2)$$

$$\text{with } P_{\text{NO}_x} = P_{\text{NO}^*} + P_{\text{NO}_2^*} \quad (3)$$

The proportion of high oxidation state  $\text{NO}_x$  species in total  $\text{NO}_x$ , called the oxidation ratio  $OR$ , can be varied between 2 and 95%. To characterize the experimental results, two parameters are calculated from the analyses performed in the gas at the ends of the column:  $A$ , the overall fractional absorption of  $\text{NO}_x$  and  $S$ , the absorption selectivity of tetravalent nitrogen oxides, defined as the ratio of chemical nitrogen dioxide absorbed to the total  $\text{NO}_x$  absorbed.

Two modes of scrubber operation were used in the experiments: recycle and non-recycle of the scrubbing solution. In the non-recycle mode (NRM), the whole scrubbing liquid is fed to the top of the column by means of a volumetric pump. The liquid flow rate is fixed to 0.51 l/min ( $5.34 \cdot 10^{-3} \text{ m}^3/\text{s m}^2$ ). In the recycle mode (RM), the feed of fresh scrubbing solution represents only 1.4% of the total liquid flow rate. When a steady state is reached in the column, samples of liquid are withdrawn for titration. The  $\text{H}_2\text{O}_2$  concentration is determined by means of iodometric and colorimetric (using a titane complex) methods.

All experiments were conducted at atmospheric pressure and at a temperature of  $20 \pm 0.5^\circ\text{C}$ .

### RESULTS

Absorption of  $\text{NO}_x$ , diluted with nitrogen up to partial pressures of 500 Pa, was performed using aqueous and nitric acid solutions containing  $\text{H}_2\text{O}_2$  (Thomas et al., 1996). The absorption rate was determined for various  $\text{NO}_x$  oxidation ratios in the gas phase and for different concentrations of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  in the scrubbing liquid.

Figure 2 presents the overall fractional absorption and the outlet peroxide concentration as functions of the inlet peroxide concentration for absorption runs performed with recycled aqueous solutions of hydrogen peroxide of increasing concentrations, the oxidation ratio of  $\text{NO}_x$  in the gas being 66% (continuous lines). Two zones can be identified in this figure. In the first zone,  $A$  increases rapidly over a very small range where the outlet oxidizing agent concentration is zero and the consumption is total; as the oxidizing agent becomes in excess (second zone), the absorption rate remains constant. A small excess is sufficient to obtain the maximum absorption rate. Similar results were obtained if nitric acid is added to the scrubbing solution (dotted lines), the absorption efficiency increasing with the concentration of  $\text{HNO}_3$ . These findings, confirmed for other oxidations ratios, prove that the kinetics of the overall absorption process of  $\text{NO}_x$  is zero order with respect to the hydrogen peroxide concentration. This overall zero order dependence in  $\text{H}_2\text{O}_2$  is not due to controlling mass transfer resistance in the gas phase as increasing absorption rates are observed for increasing acidities, for equal inlet  $\text{NO}_x$  partial pressure and oxidation ratio and the same hydrodynamic conditions (gas flow rate) (see also fig.3 and 4). Such independence of the  $\text{NO}_x$  absorption rate relative to the concentration of  $\text{H}_2\text{O}_2$  has already been observed by Shah (1976) for tetravalent nitrogen oxides.

Figure 3, giving the outlet concentration of  $\text{NO}_x$  in the gas phase for a constant inlet partial pressure of 500 Pa, illustrates the benefic influence of the oxidation ratio of  $\text{NO}_x$ : as nitric oxide alone is sparingly soluble, the increasing occurrence in the gas phase of high oxidation state  $\text{NO}_x$ , more soluble and more reactive in water, results in higher absorption efficiencies, therefore lower outlet concentrations of  $\text{NO}_x$ . Moreover, this figure summarizes in a very good way the major effects of the use of hydrogen peroxide for  $\text{NO}_x$  absorption using recycled nitric acid

solutions of increasing molarity. Without H<sub>2</sub>O<sub>2</sub>, the outlet NO<sub>x</sub> increases with the concentration of HNO<sub>3</sub> in the liquid phase. In this case, the nitric acid is likely to oxidize the nitric oxide in the liquid phase producing gaseous NO<sub>2</sub> which can desorb from the solution (Carta and Pigford, 1983). As hydrogen peroxide is added to the solution, this phenomenon can obviously not occur because of the oxidation of the intermediate species HNO<sub>2</sub> into HNO<sub>3</sub>. The outlet NO<sub>x</sub> is then decreasing with the rise of the HNO<sub>3</sub> content.

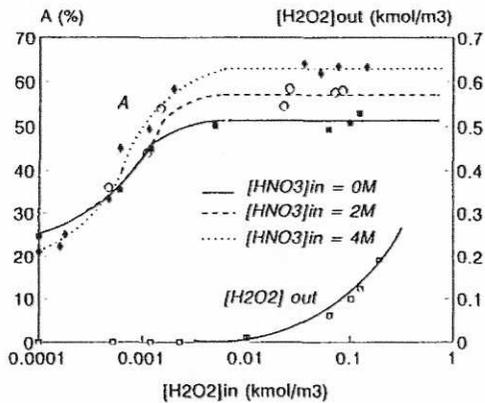


Figure 2. Fractional absorption of NO<sub>x</sub> and outlet concentration of H<sub>2</sub>O<sub>2</sub> versus inlet concentration of H<sub>2</sub>O<sub>2</sub> - Recycle mode - OR = 66% - (p<sub>NO<sub>x</sub></sub>)<sub>in</sub> = 500 Pa

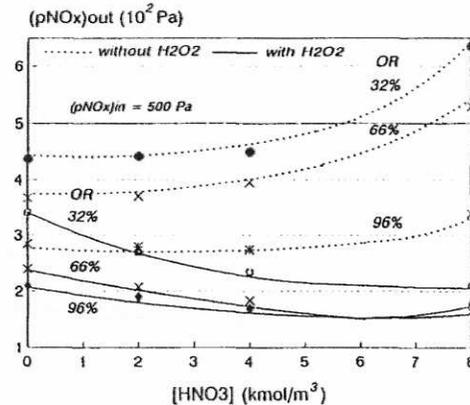


Figure 3. Outlet concentration of NO<sub>x</sub> with and without H<sub>2</sub>O<sub>2</sub> versus the acid concentration - Inlet partial pressure of NO<sub>x</sub> = 500 Pa

Another important result that can be inferred from these experiments is that, in presence of H<sub>2</sub>O<sub>2</sub>, absorption of dilute NO<sub>x</sub> is possible into fairly concentrated nitric acid solution up to 8 kmol/m<sup>3</sup>. Therefore an appreciable advantage of the use of H<sub>2</sub>O<sub>2</sub> for NO<sub>x</sub> absorption would be the possibility to carry out the gas treatment while producing rather concentrated nitric acid.

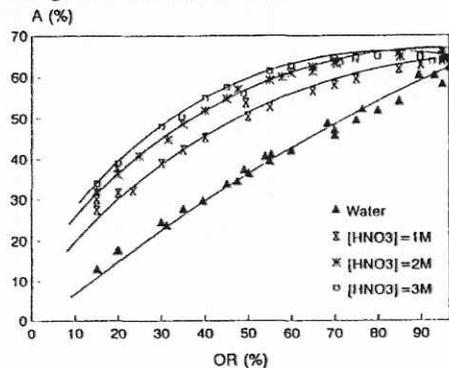


Figure 4. Effect of nitric acid on the absorption of NO<sub>x</sub> into solutions of hydrogen peroxide

nitric acid solutions containing H<sub>2</sub>O<sub>2</sub>. Deo (1988) observed in fact that the scrubbing efficiency for NO<sub>2</sub> alone and for NO/NO<sub>2</sub> mixtures increases marginally with nitric acid concentration up to 40%.

Thanks to numerous experiments, we have also shown that the specific consumption of hydrogen peroxide is stoichiometric with regard to the different absorbed species. Evaluation of this parameter requires only knowledge of the proportions of NO<sub>x</sub>(II) and NO<sub>x</sub>(IV) in the total NO<sub>x</sub> absorbed, that can be inferred from the selectivity index *S* defined above (Thomas et al., 1996).

#### MODELING OF NO<sub>x</sub> ABSORPTION INTO NITRIC ACID SOLUTIONS CONTAINING SMALL EXCESS OF HYDROGEN PEROXIDE

A mathematical model was developed to simulate the NO<sub>x</sub> absorption process with HNO<sub>3</sub> solutions containing H<sub>2</sub>O<sub>2</sub> (Thomas and Vanderschuren). In this model, gas phase equilibria were assumed to be achieved in the bulk gas, the gaseous film and at the interface. Equilibrium constants and solubilities were taken from Schwartz and White (1981). As gaseous nitrous acid is highly soluble, the fact that the formation rate of HNO<sub>2</sub> in the gas phase is not precisely established can induce very bad final results. To avoid this problem, we decided to regroup the trivalent species N<sub>2</sub>O<sub>3</sub> and HNO<sub>2</sub> into one single effective compound N<sub>2</sub>O<sub>3</sub><sup>\*</sup>.

Figure 4 compares the values of the fractional absorption of NO<sub>x</sub> obtained in water and nitric acid solutions of different concentrations (1, 2 and 3 kmol/m<sup>3</sup>) containing a small excess of H<sub>2</sub>O<sub>2</sub>. In these experiments, the oxidation ratio of NO<sub>x</sub> ranged from 15 to 96% and the scrubbing solution was not recycled. It appears clearly that the absorption rate is enhanced sharply with the nitric acid concentration. We concluded that the increase of NO<sub>x</sub> absorption efficiencies is due to the increase with the acidity of the rates of oxidation reactions in the liquid phase, these reactions being catalyzed by hydrogen ions (Thomas et al., 1996).

This fact was already mentioned in some previous studies for nitrous acid oxidation (Halfpenny and Robinson (1952)) and for NO<sub>x</sub> abatement with

The theory of absorption accompanied by fast irreversible reactions was applied with a two-film approach in order to calculate the absorption rates. As the reactions of dissolved NOx species with H<sub>2</sub>O<sub>2</sub> seem to be zero order with respect to H<sub>2</sub>O<sub>2</sub> and are second order with respect to NO<sub>2</sub> and first order with respect to N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>3</sub>, the following expressions for the absorption rates were used:

$$R_{NO_2} = \sqrt{\frac{k_{2NO_2} D_{NO_2}}{H_{NO_2}^3}} P_{iNO_2}^{1.5} \quad \text{and} \quad R_j = \frac{\sqrt{k_{1j} D_j}}{H_j} P_{ij} \quad j=N_2O_3^*, N_2O_4 \quad (4)$$

The factors preceding  $p_{ij}$  (with an order dependency) are essential for the design of scrubbing towers. We called them the Overall Kinetic Parameters (OKP). The OKP's were preferred to conventional Hatta numbers because they overcome the uncertainties about the solubilities of different NOx species (Henry constants). Moreover they do not contain the coefficients  $k_L$  and therefore they are theoretically independent on the hydrodynamic conditions prevailing in the column.

The absorption of NO, of which the rate remains very low and is not substantially enhanced by increasing excess of H<sub>2</sub>O<sub>2</sub> or by the presence of HNO<sub>3</sub> in the liquid, could be simulated thanks to the expression:

$$R_{NO} = k_{LNO} C_{iNO} \quad (5)$$

In this specific case corresponding to absorption with fast kinetics (Hatta numbers greater than 3), it is important to notice that the volumetric absorption rates are only dependent on the effective surface area  $a$  because they do not include the liquid mass transfer coefficients  $k_L$ . A precise determination of  $a$  was achieved by absorbing dilute CO<sub>2</sub> into concentrated sodium hydroxide solutions, corresponding to the fast regime. The kinetic constant for the reaction between CO<sub>2</sub> and OH<sup>-</sup> was given by Nijsing et al (1959).

Dividing the column into incremental volumes, the simulation was made for given OKP's, element by element, computing the partial pressures of NOx species leaving one element and concentrations of the liquid entering it. Going from bottom to top, we obtained finally the NOx removal performances,  $A$  and  $S$ , of the packed tower.

In order to determine the OKP values relative to the various NOx species, numerous experiments were conducted. The scrubbing liquids were aqueous or nitric acid solutions containing small excess of H<sub>2</sub>O<sub>2</sub> flowing in a single pass through the column. Large ranges of operating conditions for total NOx partial pressure (10-500 Pa), oxidation ratio in the gas phase (2-95 %), and nitric acid concentration (0-4 kmol/m<sup>3</sup>) in the liquid phase were investigated.

For these conditions, the simulation gave low gradients of partial pressures of NOx species in the gas phase, which confirms that the gas mass transfer resistance is not controlling.

For the minimization of the mean deviation between experimental and calculated values, a grid method was used with the following objective function:

$$OF = \frac{1}{N} \sum_{i=1}^N (0.5 |A_{i,exp} - A_{i,calc}| + 0.5 |S_{i,exp} - S_{i,calc}|) \quad (6)$$

Parameters  $A$  and  $S$  were included in this function with equal weights as both played equal important roles in this minimization.

For a given nitric acid molarity, the overall kinetic parameters of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> were first determined from approximately 30 absorption tests with gases containing from 10 to 500 Pa of tetravalent NOx at a maximum oxidation ratio close to 95%. By completing with some 40-50 test runs made in a large range of partial pressures of NOx and oxidation ratios, the value of the OKP relative to N<sub>2</sub>O<sub>3</sub>/HNO<sub>2</sub> was then assessed (Thomas and Vanderschuren). For NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>, we found OKP values which, roughly, do not vary with the nitric acid concentration and are close to those obtained in water without H<sub>2</sub>O<sub>2</sub> by Komiyama and Inoue (1980) or Jethani et al (1992). On the contrary, the OKP of N<sub>2</sub>O<sub>3</sub>\* increases regularly with the acidity.

Favorable agreement was obtained between the model predictions and the experimental observations for a large range of operating conditions.

As a typical example, figures 5(a) and 5(b) compare the computed values of parameters  $A$  and  $S$  to the experimental ones, for a nitric acid concentration of 3 kmol/m<sup>3</sup>. The predictions seem to be excellent for all absorption rates. Experiments made with high oxidation ratios and absorption selectivities of NOx (IV) close to 100% are perfectly simulated. For lower selectivities, the model gives slightly too greater values of  $S$ .

The quality of our simulation is even good for aqueous solutions as for nitric acid solutions containing small excess of H<sub>2</sub>O<sub>2</sub>, the average absolute error (mean value of OF) being quite low (less than 5%).

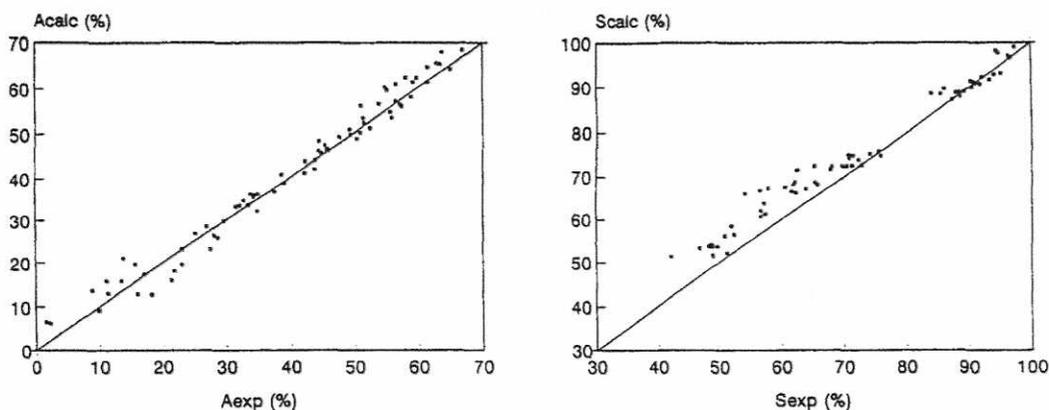


Figure 5. Calculated versus experimental absorption efficiencies and absorption selectivities - Nitric acid concentration =  $3 \text{ kmol/m}^3$

### VALIDATION OF THE MODEL

As said before, the theory assumes that the overall kinetic parameters are not functions of the hydrodynamic conditions achieved in the column. This assumption will be verified and the OKP values validated if the model developed hereabove can work with fair success in predicting the  $\text{NO}_x$  removal efficiency of a pilot-scale column. Therefore we investigated the absorption of  $\text{NO}_x$  with  $\text{H}_2\text{O}_2$  in a 2 meters high tower with an inside diameter of 0.215 m, packed with 25 mm plastic Pall rings.

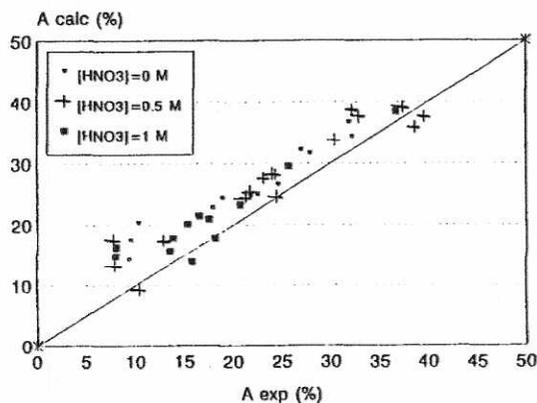


Figure 6. Calculated absorption efficiencies vs experimental ones for the pilot-scale column

A screening series of tests was conducted at  $20^\circ\text{C}$  with a total gas flowrate of  $128 \text{ m}^3/\text{h}$  ( $0.979 \text{ m}^3/\text{s m}^2$ ) and a liquid flowrate varying between 0.4 and  $0.7 \text{ m}^3/\text{h}$  ( $0.0031$  to  $0.0054 \text{ m}^3/\text{s m}^2$ ). Various compositions were used in the gas phase (partial pressures of  $\text{NO}_x$  and oxidation ratios) and in the liquid phase (nitric acid concentration equal to 0, 0.5 and  $1 \text{ kmol/m}^3$ ).

The column was operated with nonrecycle of the absorbing liquid. The experimental response variables were  $A$  and  $S$ . For simulation, the specific gas-liquid area was taken from Linek et al (1984).

As shown in figure 6, taking into account of a possible error in estimating the specific area of the packing, there is a fairly good agreement between results of the experiments and the simulation.

### CONCLUSIONS AND PROSPECTS

A mathematical model for  $\text{NO}_x$  absorption into aqueous solutions of nitric acid containing hydrogen peroxide has been developed in which original features, experimentally observed, have been included:

- catalytic effect due to  $\text{HNO}_3$  on the  $\text{NO}_x$  absorption with  $\text{H}_2\text{O}_2$ ;
- $\text{NO}_x$  absorption accompanied by chemical reaction of zero order with respect to small excess of  $\text{H}_2\text{O}_2$ ;
- equal important roles played by quantity absorbed  $A$  and selectivity of absorption  $S$ .

For simulation and design of  $\text{NO}_x$  scrubbers which will be operated with  $\text{HNO}_3$  solutions containing  $\text{H}_2\text{O}_2$ , enhancement factors of the mass transfer rates in the liquid phase for the different  $\text{NO}_x$  compounds have been determined at room conditions.

In order to be able to simulate this gas treatment process in industrial conditions, we plan to study the effect of the temperature by achieving similar investigations at  $10$  and  $30^\circ\text{C}$ .

**NOMENCLATURE**

a	= gas-liquid interfacial area per unit volume (m <sup>2</sup> )
A	= overall absorption efficiency = ((p <sub>NOx</sub> ) <sub>in</sub> - (p <sub>NOx</sub> ) <sub>out</sub> )/(p <sub>NOx</sub> ) <sub>in</sub>
c <sub>ij</sub>	= interfacial concentration of component j (kmol/m <sup>3</sup> )
D <sub>j</sub>	= diffusivity of component j (m <sup>2</sup> /s)
H <sub>j</sub>	= Henry's law constant (Pa m <sup>3</sup> /kmol)
k <sub>1</sub>	= first-order rate constant (s <sup>-1</sup> )
k <sub>2</sub>	= second-order rate constant (m <sup>3</sup> /kmol s)
k <sub>l,j</sub>	= mass-transfer coefficient in the liquid phase for the component j (m/s)
M	= molarity of nitric acid solution (kmol/m <sup>3</sup> )
n	= number of experiments
OKP	= overall kinetic parameter
OR	= oxidation ratio of NO <sub>x</sub> in the gas phase = (p <sub>NOx</sub> - p <sub>NO*</sub> ) <sub>in</sub> /(p <sub>NOx</sub> ) <sub>in</sub>
p <sub>ij</sub>	= interfacial partial pressure of the component j (Pa)
p <sub>j</sub>	= partial pressure of the component j (Pa)
R <sub>j</sub>	= absorption rate for the species j (kmol/m <sup>2</sup> s)
S	= absorption selectivity of tetravalent nitrogen oxides = ((p <sub>NO2*</sub> ) <sub>in</sub> - (p <sub>NO2*</sub> ) <sub>out</sub> )/((p <sub>NOx</sub> ) <sub>in</sub> - (p <sub>NOx</sub> ) <sub>out</sub> )

## subscripts:

in	= inlet of the column
out	= outlet of the column
exp	= experimental value
calc	= calculated value

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**ACKNOWLEDGMENTS**

The authors acknowledge for the support of the National Fund for Scientific Research of Belgium which gave a fellowship to one of them (D.Thomas).

## LoTOx™ System.

### Low temperature oxidation for NOx control.

#### Process Description

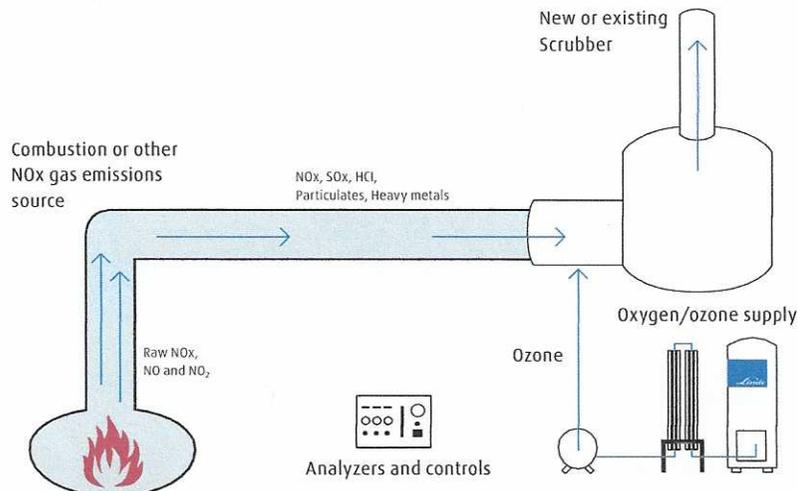
The Low-Temperature Oxidation (LTO) process is a patented process for removal of NO<sub>x</sub> and other pollutants from waste gas streams.

Linde's LoTOx™ technology is an end-of-pipe system that removes NO<sub>x</sub> by adding ozone to oxidize insoluble NO and NO<sub>2</sub> to N<sub>2</sub>O (a highly soluble species of NO<sub>x</sub>) which can be effectively removed by a variety of Air Pollution Control (APC) equipment, such as wet or semi-dry scrubbers or wet electrostatic precipitators (WESP). LoTOx™ can be used as a stand-alone treatment system, where inlet NO<sub>x</sub> levels are moderate, or can be used cost effectively as a polishing system in conjunction with combustion modifications such as Low NO<sub>x</sub> burners (LNB) or other post-combustion technologies such as Selective Non-Catalytic Reduction (SNCR) for NO<sub>x</sub> removal. Ozone is generated on site and on demand from oxygen and is either completely consumed in the LoTOx process or residual ozone is destroyed in the scrubber system. NO<sub>x</sub> capture in wet scrubbers results in a dilute nitric acid stream which after neutralization is either sent for waste water treatment or for recovery as a valuable by-product in large industrial and utility systems. Calcium nitrate, a valuable commercial fertilizer, can be produced as a saleable product in systems using lime scrubbers. NO<sub>x</sub> capture in a dry/semi-dry scrubber results in a waste stream of nitrates mixed with other solids such as particulate matter, sulfides, chlorides, etc.

#### LoTOx™ System Chemistry

Gas Phase Reactions	Relative Reaction Rate
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	Fast
$2\text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$	Fast
$\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$	Slow
$\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2$	Very Slow
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{+2} + \text{O}_2$	Fast
Liquid Phase Reactions	Relative Reaction Rate
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	Very Fast

- Ozone is highly selective for NO<sub>x</sub> relative to other combustion products
- NO<sub>x</sub> is rapidly converted to water soluble species
- The resulting N<sub>2</sub>O<sub>5</sub> is readily absorbed by aqueous scrubbing solutions or adsorbed by dry/semi-dry scrubber adsorbents.



**Overall Benefits**

- Lowest Achievable Level of NOx Emissions
- Easily Tuned for Variable Loads
- Low Temperature Operation
- Fully Automated
- No Secondary Gaseous Pollutants Generated
- Consistent Reliable Performance Regardless of Fuel Type
- No Effect of Particulate Matter on NOx Removal
- Simultaneous Oxidation of Hg and other Contaminants
- Easily integrated with existing wet scrubbers

**Applications**

- Utility Boilers (Coal, Petcoke, Lignite fired)
- Industrial Boilers (Gas, Coal, No. 6 Oil)
- Kilns, Furnaces and Ovens (Lead, Iron Ore, Zinc/Copper, Glass, Cement)
- Waste Combustors (Bio-waste, tires, industrial wastes)
- Acid Gas Streams (Exhaust from pickling and chemical processes)
- FCC Off Gas (licensed to Dupont™ Belco® Clean Air Technologies)
- Incinerators (Municipal, Industrial)

**Commercial Application**

Systems using the patented LTO process have been installed in a number of challenging applications where particle and metals laden waste gas streams have had to be treated to very low NOx levels to meet national or local air quality requirements. More than 30 full scale commercial systems have been installed across a range of different market segments, including; gas, coal and petcoke fired boilers; a metals furnace, a stainless steel pickling plant, sulphuric acid plants and multiple FCC regenerator offgas treatment plants. Flue gas volumes treated range from 6300 Nm<sup>3</sup>/hr to 620000 Nm<sup>3</sup>/h; inlet NOx levels range from 60 to 6000 (more typically 100–600) mg/Nm<sup>3</sup> with typical outlet NOx levels required in the range from 20 to 90 mg/Nm<sup>3</sup>. Under design conditions a total of over 7 million Nm<sup>3</sup>/hr of polluted air is treated in the systems resulting in the removal of more than 15,000 MT of NOx each year.

Linde modular ozone and oxygen supply systems enable quick and easy retrofit of the LoTOx process into customer's existing APC systems without significant changes or additional major process equipment. The small, modular system footprint allows flexibility of the equipment layout to meet unique spatial requirements for a variety of applications and industries. Custom-designed LoTOx™ systems are commercially used in treating large gas streams containing NOx and have demonstrated consistent performance to remove NOx on combustion systems fueled by natural gas, oil, and coal. The NOx removal performance does not deteriorate with respect to time in spite of heavy dust loading and the presence of other contaminants. The on-site generation of ozone to treat NOx results in a highly responsive control system for treatment of single point sources with variable loads or fuels, or multiple point sources combined into a single treatment system.

**The LoTOx PSO**

- Feasibility study and demonstration
- Process license
- Basic engineering package, detailed engineering support, startup and troubleshooting with and without process guarantees
- Oxygen and/or ozone (Gas) sales
- Complete Turn-key LoTOx system along with co-operation partner

**Demonstration**

Linde has developed a LoTOx™ Demonstration system that has been successfully used to demonstrate performance of LTO on customer processes, and to develop detailed process and operating data for use in designing full scale installations. Contact Linde's Chemical Industry Markets Team to inquire about scheduling a demonstration at your facility.

**Linde AG**

Gases Division, Seitnerstrasse 70, 82049 Pullach, Germany  
Phone +49.89.7446-0, Fax +49.89.7446-1230, [www.linde-gas.com](http://www.linde-gas.com)

## LOTOX®

Leading the market for abatement efficiency, flexibility and cost competitiveness

Our LOTOX® solution delivers the highest NOx removal capabilities commercially available, achieving efficiency rates in excess of 95%. This is a low-temperature oxidation process, which employs ozone to oxidise nitrogen oxides (mainly NO and NO<sub>2</sub>) – known as NOx – to higher oxides of nitrogen such as N<sub>2</sub>O<sub>5</sub>. These oxides are not only very soluble but also reactive, so they can be easily removed along with other hazardous pollutants using conventional wet or dry scrubbers.

- ☒ The NOx oxidation process is not affected by other contaminants such as acid gases and particulates, resulting in very robust performance even with dirty and challenging gas streams.

The ozone is produced from oxygen on site and on demand, which means that hazardous chemicals no longer need to be stored.

### Benefits at a glance

- Configurable NOx removal rates scaling from 30% to 95%-plus
- Effective treatment of a wide range of nitrogen oxides and harmful pollutants – also in conjunction with various APC equipment
- Future-proof solution capable of meeting evolving NOx regulations
- Low CAPEX when inlet NOx is of moderate level and existing APC equipment can be used
- Transparent costs with ozone consumption reflecting removal efficiency

- No need to interfere with / modify existing combustion equipment or to reheat the flue gas to high temperatures
- No need to store hazardous chemicals required for traditional abatement processes
- Valuable by-products such as nitric acid, calcium nitrate and mixed nitrates

### **Turnkey solution**

A LOTOX<sup>®</sup> installation consists of an oxygen supply stream, on-site ozone generation equipment, analysers and controls. We deliver a LOTOX<sup>®</sup> site license, also supplying a wide range of solutions tailored to individual needs – covering everything from gas supply through to end-to-end turnkey installations. In some regions, we also supply ozone. We can even run on-site trials with our mobile demonstration unit to establish proof-of-concept before you invest in LOTOX<sup>®</sup>.

### **Proven technology**

LOTOX<sup>®</sup> is already successfully deployed across a wide range of industries and exhaust streams, including gas and coal-fired boilers, lead recovery furnaces, stainless steel pickling operations, sulfuric acid regeneration plants, fluidised catalytic cracking (FCC) regenerators and pet coke boilers. This proven and growing list of reference projects underscores our leading experience in industrial ozone applications.

Contact us today for more information on our reference projects or to discuss a demonstration at your facility.

#### **Chemistry Team Contact**

Ask the chemistry team

Contact us [\(/en/processes/emissions\\_solutions/contact](/en/processes/emissions_solutions/contact)



## Main take-aways

LOTOX® is preferred to alternative technologies (SNCR/SCR) when:

- > 90 % NOx removal is required
- An additional polishing step is required to “boost” existing SNCR/SCR
- Temperature conditions are too low for SNCR/SCR < 200 °C [390 °C] (down to 60 °C [140 °F])
- Flue gas is dirty (high particulate levels) and challenge for the SCR catalyst
- Customer has an existing wet scrubber or wet electrostatic precipitator
- Production process demands robust and reliable performance
- Quick and flexible start up is required
- Site footprint is a constraint
- Customer case makes economic sense (O<sub>3</sub> generator is the major cost component)



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# Budgetary Estimate

Making our world more productive

## Linde LoTOx Budgetary Estimate (+ or -30%).

<b>Customer:</b>	ERM/Apache Nitrogen
<b>Site:</b>	Arizona, US
<b>Contact:</b>	Bob Farmer
<b>Phone:</b>	602-499-9474
<b>Email:</b>	<a href="mailto:bob.farmer@erm.com">bob.farmer@erm.com</a>
<b>Linde Representative:</b>	Walter Renz

<b>Assumptions</b>			
Operating days	days/year	360	
Daily operation	hours/day	24	
Desired NOx emissions	mg/m <sup>3</sup>	10	

<b>Customer Operating Conditions</b>		
Temperature point of injection	F	125
Pressure point of injection	psi(g)	12.50
Flue gas flow rate (dry)	scfm	26,160
Current NOx emissions	ppmv	220
% NO	%	100%

<b>Ozone requirements &amp; NOx removal</b>		
Ozone required	kg/h	30
NOx Removal %	%	95%
Annual NOx removed	T/year	173

Linde scope  
 Scope ownership to be defined  
 Customer proposal\*

<b>Design Assumptions</b>		
O2 required	TPD	8
Power required	kW	228
Cooling water required	gph	13,209



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## RE: Apache/ERM/Linde Discussion on LoTox NOx Abatement

Walter Renz <Walter.Renz@linde.com>

Thu 10/22/2020 8:19 AM

To: Bob Farmer <Bob.Farmer@erm.com>; David Lenhart <David.Lenhert@linde.com>; Jana Haisley <Jana.Haisley@linde.com>  
Cc: Stephanie Domanski <Stephanie.Domanski@linde.com>; Heinz-Dieter Obermeyer <Heinz-Dieter.Obermeyer@linde.com>; Jackson Sia <JSia@apachenitro.com>; TJ Raica <traica@apachenitro.com>

**CAUTION:** This email originated from outside of the organization. Do not click links or open attachments unless you recognize the sender and know the content is safe.

Hello Bob:

We've conferred with our folks in Linde Germany and, unfortunately, have come to the conclusion that the Apache plant is not be a good candidate for LoTox after all. The core issue is the higher pressure of the absorber column where we hoped to inject the ozone. We checked with our ozone equipment partners in Europe and found there is no standard equipment available that could provide the required flow and pressure to feed O3 here.

The alternative would be to try to add a treatment system including wet gas scrubber and heat exchangers at the end of the pipe. This would be significantly more involved and require a higher capital investment (perhaps 3-5X?). We really don't think this would be a cost-effective solution for Apache.

Sorry we couldn't come back with a more positive assessment. We do want to thank you and the folks at Apache for giving us the chance to evaluate this opportunity.

Best Regards,  
Walter

---

**From:** Bob Farmer <Bob.Farmer@erm.com>

**Sent:** Thursday, October 15, 2020 11:43 AM

**To:** Walter Renz <Walter.Renz@linde.com>; David Lenhart <David.Lenhert@linde.com>; Jana Haisley <Jana.Haisley@linde.com>

**Cc:** Stephanie Domanski <Stephanie.Domanski@linde.com>; Heinz-Dieter Obermeyer <Heinz-Dieter.Obermeyer@linde.com>; Jackson Sia <JSia@apachenitro.com>; TJ Raica <traica@apachenitro.com>

**Subject:** Re: Apache/ERM/Linde Discussion on LoTox NOx Abatement

\*\*\* Please note the message below originated on the Internet. Please use caution when replying or opening links or attachments. \*\*\*

Walter -

I've checked again the absorber tower pressure. During the call, I was looking at the wrong call-out on the PFD. The absorber tower is actually under fairly high pressure, which promotes acid gas absorption. A better value to work from is that the pump discharge pressure for make-up scrubbing water injected to the column is 280 psig. That should be shown also on the PFD that was sent.

I'd open it up for the ANPI folks if they want to provide better tower pressure information.

Thanks for the reply.  
Bob Farmer  
ERM  
(602) 499-9474 cell

---

**From:** Walter Renz <Walter.Renz@linde.com>

**Sent:** Thursday, October 15, 2020 5:52 AM

**To:** Bob Farmer <Bob.Farmer@erm.com>; David Lenhart <David.Lenhert@linde.com>; Jana Haisley <Jana.Haisley@linde.com>

**Cc:** Stephanie Domanski <Stephanie.Domanski@linde.com>; Heinz-Dieter Obermeyer <Heinz-Dieter.Obermeyer@linde.com>

**Subject:** RE: Apache/ERM/Linde Discussion on LoTox NOx Abatement