

# *Near-Zero Emissions Oxy-Combustion Flue Gas Purification*

## *Task 2: SO<sub>x</sub>/NO<sub>x</sub>/Hg Removal for High Sulfur Coal*

*Final Topical Report*

*January 1, 2009 to March 31, 2011*

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**December 2011**

**DOE Award No. DE-NT0005341**

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## **Abstract:**

The goal of this project is to develop a near-zero emissions flue gas purification technology for existing PC (pulverized coal) power plants that are retrofitted with oxy-combustion technology. The objective of Task 2 of this project was to evaluate an alternative method of SO<sub>x</sub>, NO<sub>x</sub> and Hg removal from flue gas produced by burning high sulfur coal in oxy-combustion power plants. The goal of the program was not only to investigate a new method of flue gas purification but also to produce useful acid byproduct streams as an alternative to using a traditional FGD and SCR for flue gas processing. During the project two main constraints were identified that limit the ability of the process to achieve the project goals. 1) Due to boiler island corrosion issues >60% of the sulfur must be removed in the boiler island with the use of an FGD. 2) A suitable method could not be found to remove NO<sub>x</sub> from the concentrated sulfuric acid product, which limits sale-ability of the acid, as well as the NO<sub>x</sub> removal efficiency of the process. Given the complexity and safety issues inherent in the cycle it is concluded that the acid product would not be directly saleable and, in this case, other flue gas purification schemes are better suited for SO<sub>x</sub>/NO<sub>x</sub>/Hg control when burning high sulfur coal, e.g. this project's Task 3 process or a traditional FGD and SCR.

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## Executive Summary:

The objectives of this project were to carry out an experimental program to 1) enable development and design of a near zero emissions oxy-combustion flue gas purification processes having a high CO<sub>2</sub> recovery for power plants burning high and low sulfur coals and, 2) to perform commercial viability assessment on the proposed technology.

The purpose of the Task 2 program was to investigate an alternative method of SO<sub>x</sub> and NO<sub>x</sub> removal from flue gas produced by burning high sulfur coal in oxy-coal power plants. In a typical power plant SO<sub>x</sub> is removed by reaction with lime or limestone producing disposable gypsum using a wet or dry-FGD at atmospheric pressure. The lime/limestone reagent cost, gypsum disposal cost, parasitic power plant load and equipment capital costs can be substantial especially in the case of high sulfur coal. NO<sub>x</sub> removal is typically achieved in an SCR which requires substantial capital investment and also requires ammonia reagent.

Instead of processing flue gas at low pressures, the proposed Task 2 processes aims to process flue gas at high pressure within the oxy-coal CO<sub>2</sub> processing unit (CPU) for production of useful-concentrated acid which can potentially be used as useful byproducts allowing for substantially reduced reagent costs, disposal costs and parasitic power loss.

In the Task 2 process a number of heterogeneous and homogeneous reactions are important for conversion of NO<sub>x</sub> and SO<sub>x</sub> to acids. The elevated pressure which would be present in the CPU is a key feature which enables the formation of acids in reasonable residence times by increasing the rates of important reactions. The enabling chemistry in the process involves NO<sub>x</sub> acting as a catalyst for conversion of SO<sub>2</sub> to SO<sub>3</sub>, which is then hydrolyzed to sulfuric acid. The proposed process chemistry takes place in three different gas/liquid contacting vessels. The performance of each of the three vessels was tested independently in small gas/liquid contactor to evaluate: 1) NO<sub>x</sub> absorption into sulfuric acid, 2) NO<sub>x</sub> desorption from sulfuric acid and 3) NO<sub>x</sub> catalyzed SO<sub>2</sub> oxidation to SO<sub>3</sub>.

The NO<sub>x</sub> absorption experiments showed a good ability of sulfuric acid to absorb NO<sub>x</sub>. The best absorption performance was seen when the NO:NO<sub>2</sub> ratio was 1:1, as is predicted in literature. Thermal desorption of NO<sub>x</sub> from concentrated sulfuric acid did not take place as required for producing a commercial purity of sulfuric acid with <5ppmw dissolved NO<sub>x</sub>. Further experimental results showed that concentrated sulfuric acid has a very strong affinity for NO<sub>x</sub> and could not be removed by catalytically stripping with activated carbon. Other methods, taken from the traditional sulfuric acid industry, were also investigated for NO<sub>x</sub> removal however, for a variety of reasons, none of the methods were appropriate for application within the Task 2 process given the program goals. Experimental data collected at a variety of conditions showed that SO<sub>2</sub> oxidation by NO<sub>x</sub> was an effective method of removing SO<sub>2</sub> from flue gas.

Results from the subcontracted Foster Wheeler boiler simulations showed that corrosion issues within the boiler island require that more than 60% of the fired sulfur be removed using a traditional FGD through processing of the recirculated flue gas. SO<sub>x</sub> must be removed from the primary ‘air’ stream as well as from a portion of the secondary ‘air’ stream (to address potential superheater/reheater corrosion issues). The main result of the Foster Wheeler simulations is that substantially less SO<sub>x</sub> is present in the flue gas as compared to the proposal assumption; this impacts the process design. Because no suitable method was identified for high efficiency removal of NO<sub>x</sub> from sulfuric acid within the Task 2 process, the Task 2 process design was changed from the original proposal version to reflect the scenario where all the captured NO<sub>x</sub> is produced with the ‘product’ sulfuric acid. Due to these process changes the ‘product’ sulfuric acid contains very high levels of dissolved NO<sub>x</sub>.

Although the SO<sub>x</sub> removal efficiency of the simulated process is high, the simulated removal efficiency of NO<sub>x</sub> from the compressed flue gas is only about 70%, meaning that roughly 120 ppm of NO<sub>x</sub> leaves the Task 2 purification process. This high level of NO<sub>x</sub> leaving the ‘NO<sub>x</sub> Absorber’ is attributed to the high concentration of NO<sub>2</sub> in the process and the relatively low effectiveness of sulfuric acid to absorb NO<sub>x</sub> when the NO<sub>2</sub>:NO ratio is much greater than 1. The Task 2 process exit levels of gas phase NO<sub>2</sub> can be scrubbed with water to improve overall NO<sub>x</sub> removal efficiency of the process to > 90%. However, this will increase the capital investment and generate additional acidic waste water.

Extremely high levels of NO<sub>x</sub> will be present in the produced sulfuric acid because NO<sub>x</sub> cannot be easily removed from concentrated sulfuric acid. It is unlikely that sulfuric acid distributors and customers would accept this type of out of spec acid because they would be unwilling to contaminate their storage and transport equipment. The sulfuric acid produced from the Task 2 process would most likely need to be neutralized due to the NO<sub>x</sub> contaminants in the acid.

As proposed, the potential advantages of the Task 2 process was the ability to capture SO<sub>x</sub> and NO<sub>x</sub> impurities, with high efficiency, convert them to useful products and to eliminate or reduce the need for traditional flue gas purification technologies (FGD and SCR). As a result of this program we have made the following major conclusions: 1) the boiler island FGD is still required for removal of the majority of the flue gas SO<sub>x</sub>, thus reducing the potential capital and operating costs savings 2) NO<sub>x</sub> capture rate of the Task 2 process is simulated to only be about 70% and 3) the sulfuric acid product contains very high levels of NO<sub>x</sub> so it will most likely need to be neutralized. Due to these factors, as well as other issues, it is concluded that other better options exist for removal of flue gas SO<sub>x</sub>, NO<sub>x</sub> and Hg, such as the Task 3 process and traditional atmospheric pressure treatment methods.

## **Approach:**

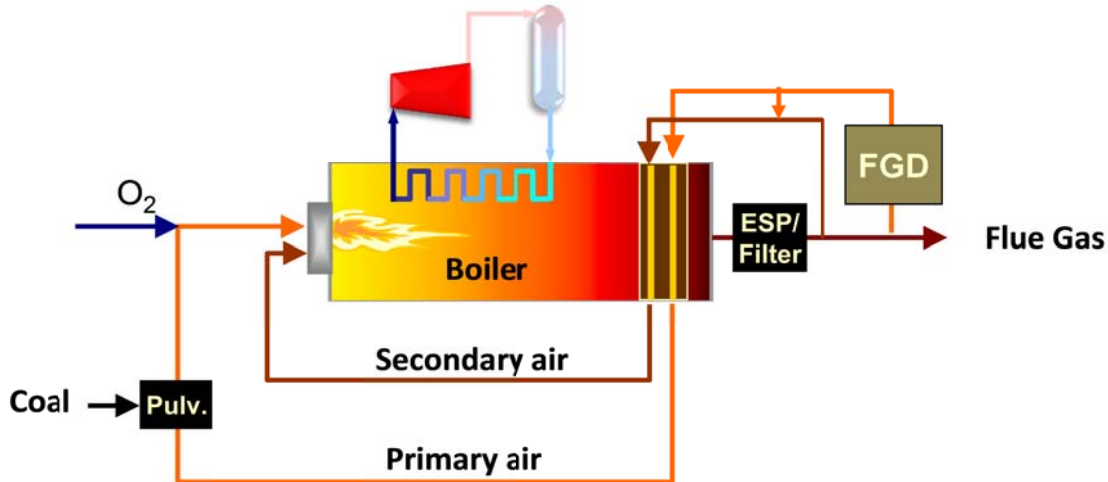
Efforts for technical and commercial feasibility assessments were divided into multiple different tasks involving experimental testing and process simulations by Praxair, power plant performance assessment by Foster Wheeler and commercial viability assessment by WorleyParsons, Canada. These activities were conducted in parallel. Initial process simulations of the sulfuric acid process were carried out with the assumption that all the sulfur in coal is converted to SO<sub>x</sub> in the boiler and the entire amount of SO<sub>x</sub> is present in the flue gas being sent to the CPU. Performance parameters of various unit operations in the sulfuric acid process were fixed by extrapolating literature data. The resulting process design package was used by WorleyParsons, Canada, to develop an initial commercial viability assessment.

In parallel, Praxair carried out experiments on a bench-scale system to develop performance data for various unit operations and Foster Wheeler conducted power plant simulations to define flue gas composition from an oxy-combustion power plant burning high sulfur coal. Based on these new test and simulation data, a revised process design was developed for WorleyParsons. The following paragraphs provide the detailed approach used for various tasks. In addition, technology, process and chemistry are described as background information.

## ***Technology Description:***

The purpose of the Task 2 project was to investigate an alternative method of SO<sub>x</sub> and NO<sub>x</sub> removal from flue gas produced by burning high sulfur coal in oxy-coal power plants. The process applies to oxy-combustion flue gas which is to be further compressed and processed for CO<sub>2</sub> capture and sequestration (CCS). Figure 1 shows a high level diagram of an oxy-combustion boiler for this application where two streams of recirculated flue gas are used to moderate boiler temperature. This figure shows the primary 'air' being treated in an FGD due to material of construction issues in the coal pulverizing and conveying equipment. Secondary air is shown here as not treated, but it may be partially treated for SO<sub>x</sub> removal depending on the allowable SO<sub>x</sub> levels in the boiler. Combustion energy is used to generate steam and a turbine is used for power generation. The flue gas produced from the boiler island is then treated in the CO<sub>2</sub> processing unit (CPU) for CO<sub>2</sub> compression and purification.





**Figure 1: Schematic of the Oxy-coal boiler island**

In a typical power plant SO<sub>x</sub> is removed by reaction with lime or limestone, producing disposable gypsum using a wet or dry-FGD at atmospheric pressure. The lime/limestone reagent cost, gypsum disposal cost, parasitic power plant load and equipment capital costs can be substantial especially in the case of high sulfur coal where all the flue gas must be treated for SO<sub>x</sub> removal. NO<sub>x</sub> removal is typically achieved in an SCR which requires substantial capital investment and also requires ammonia reagent.

The goal of this project was to develop a process which converts SO<sub>x</sub> and NO<sub>x</sub> to useful products in the compression train of an oxy-coal CPU to reduce reagent cost and parasitic power loss. Figure 2 shows high level diagram of the entire CPU process. Raw boiler flue gas enters the process and is cooled before a raw gas compression stage. Next the flue gas is treated in the proposed Task 2 process for SO<sub>x</sub> and NO<sub>x</sub> removal. Following the Task 2 process the flue gas is treated in a Cold Box cycle for CO<sub>2</sub> concentration into a CO<sub>2</sub> product which is further compressed to the final product pressure. The 'Cold Box Vent' stream is processed in a vacuum pressure swing adsorption (VPSA) process to recover CO<sub>2</sub> which is recycled to the raw gas compressor. The process vent gas, mostly composed of O<sub>2</sub>, N<sub>2</sub> and Ar is heated and expanded for power recovery.

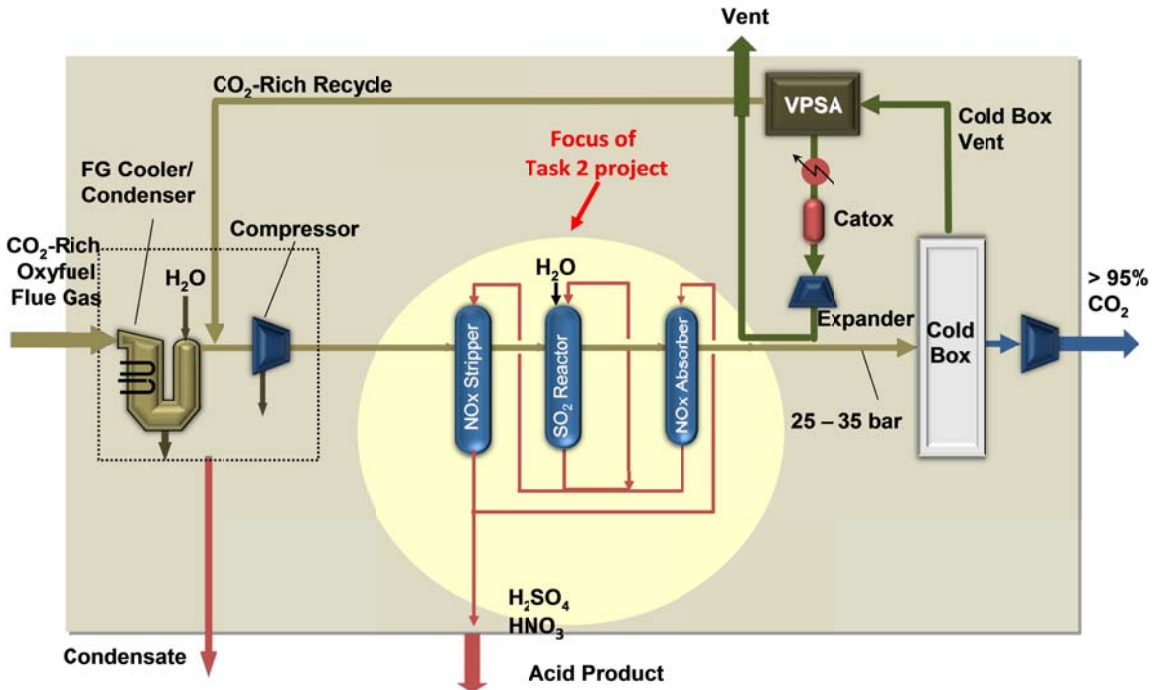


Figure 2: A CPU process using the Task 2 process for SO<sub>x</sub>/NO<sub>x</sub> purification

## Process Description

Figure 3 below shows the configuration of the Task 2 process for flue gas purification and conversion of SO<sub>x</sub> and NO<sub>x</sub> to concentrated acids. The process consists of three main vessels: the NO<sub>x</sub> stripper, the SO<sub>2</sub> reactor and the NO<sub>x</sub> absorber. Flue gas enters the process on the right after leaving the raw gas compressor, typically hot or warm without going through a compressor aftercooler, because hot or warm gas is needed in the NO<sub>x</sub> stripper. The original purpose of the NO<sub>x</sub> stripper was to thermally desorb NO<sub>x</sub> from NO<sub>x</sub> laden acid, to produce a sulfuric acid product which is substantially free of absorbed NO<sub>x</sub>. As experimental results show thermal desorption of NO<sub>x</sub> from sulfuric acid was not achieved and it was not possible to remove NO<sub>x</sub> from sulfuric acid to the extent needed for production of directly saleable sulfuric acid.

The second vessel is the SO<sub>x</sub> reactor with the primary purpose of SO<sub>2</sub> conversion to SO<sub>3</sub> and sulfuric acid. The operating temperature of this vessel is lower than the operating temperature of the NO<sub>x</sub> stripper, further energy needs to be removed from this vessel because the acid production reactions are exothermic. In this vessel water is added to control the concentration of the product acid and to ensure that no free SO<sub>3</sub> is formed (oleum).

Following the SO<sub>2</sub> reactor the last vessel is the NO<sub>x</sub> absorber. The purpose of this vessel is to absorb gas phase NO<sub>x</sub> from the flue gas stream into the liquid acid stream for 1) low NO<sub>x</sub> emissions and 2) to recycle NO<sub>x</sub> back to the front of the process for NO<sub>x</sub> concentration within the Task 2 cycle. Sulfuric acid has a high absorption capacity for

gas phase NO<sub>x</sub>; this vessel operates at as low temperature as is allowed by the available cooling utility for maximum NO<sub>x</sub> capture. Following the NO<sub>x</sub> absorber the Task 2-treated flue gas would proceed to the cryogenic processing unit of the CPU.

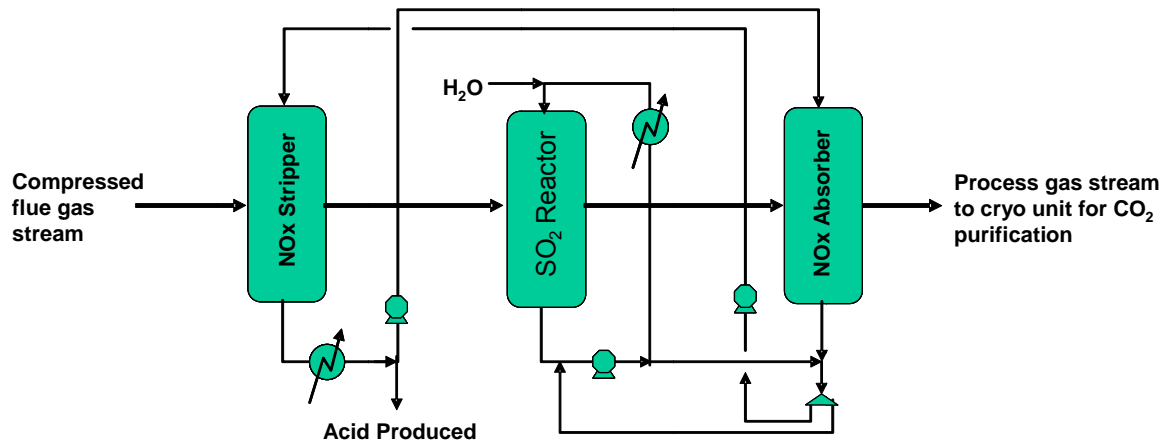


Figure 3: Schematic of the Task 2 process for SO<sub>x</sub> and NO<sub>x</sub> purification

### Chemistry Description

In the Task 2 process a number of heterogeneous and homogeneous reactions are important for conversion of NO<sub>x</sub> and SO<sub>x</sub> to acids. The elevated pressure which would be present in the CPU is another key feature which increases the rates of important reactions.

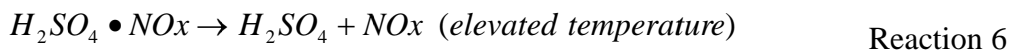
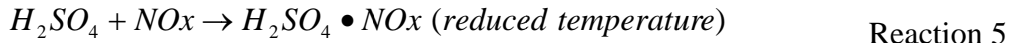
NO<sub>x</sub> in the flue gas is primarily NO (nitric oxide) with small amounts of NO<sub>2</sub>. Conversion of NO to NO<sub>2</sub> occurs homogeneously in the gas phase (Reaction 1) due to the presence of excess oxygen in the flue gas.



The formation of NO<sub>2</sub> is primarily important because it catalyzes SO<sub>2</sub> oxidation to SO<sub>3</sub> which in turn re-forms NO, Reaction 2. This reaction largely occurs in the liquid phase (involving some intermediate steps which are not shown) followed by the hydrolysis of SO<sub>3</sub> to form sulfuric acid, Reaction 3. Nitric acid may also be formed when NO<sub>2</sub> combines with water, however in this process NO is constantly re-formed, Reaction 4, making complete NO<sub>x</sub> containment difficult in a standard process (with water contact alone).



The important aspect of the proposed process is how these reactions are managed for production of concentrated acids. The proposed process used a scheme for NOx recycle which absorbs and desorbs NOx from sulfuric acid (Reactions 5 and 6) for NOx concentration in a central vessel where the Reaction 2 takes place. The process for NOx absorption and desorption is comparable to that used in the historic Lead Chamber Process for sulfuric acid manufacture.



Some valuable co-benefit can also be expected in this process: 1) sulfuric acid may be effective for Hg<sup>0</sup> capture in the form of HgSO<sub>4</sub> precipitate from gas streams 2) the gas leaving the entire process has already been dehydrated due to contact with the hygroscopic concentrated sulfuric acid product. This produces flue gas that is in theory dried to an appropriate level which can directly proceed to a cold box. This could simplify the process by eliminating the need for water and Hg beds, however Hg and water adsorbent beds would likely be required to protect against the possibility of getting any Hg or Water into the cryogenic CO<sub>2</sub> purification process due to the potential extreme consequences if there was any carryover into the coldbox.

### **Subtasks 2.1, 2.2 and 2.3 - Experimental Work:**

In the overall process, three separate gas/liquid contacting vessels are used to carry out the required reactions. The original proposal included an additional, catalytic reaction vessel to removing NOx from the product acid (no effective catalyst material was found and this vessel was removed from the process). The conditions inside each vessel differ in terms of process temperature and level of SOx/NOx impurities. Each of the vessels were tested separately in a single bench scale unit using preheated cylinder feed gases and preheated metered liquid acid (Task 2.2). The single gas/liquid contacting vessel consisted of a packed column monitored for temperature and pressure. The packed column contains roughly one equilibrium mass transfer stage. The effluent gas was analyzed for composition to determine reaction conversion, adsorption, desorption and reaction rates.

In Task 2.2 each of the three main contacting vessels were tested independently by reproducing the conditions around each vessel in terms of feed gas composition and fluid temperatures. Because the conditions inside the vessels can vary depending on the experimental results, the experimental data was collected for a range of NOx, and SOx levels. Gases were delivered from cylinders and were heated to an appropriate inlet temperature. Reaction conversion and reaction kinetics were determined from the collected data for the conditions in each vessel. Figure 4 shows the general concept of this bench scale gas/liquid contacting system.

As mentioned above potential NO<sub>x</sub> removal catalysts were tested in a second small bench scale experimental system (Subtask 2.3).

**Figure 4: Schematic of the Task 2 Bench-Scale Unit**



**Figure 5: Photograph of the Task 2 experimental equipment setup**

### ***Subtask 5.1 - Process Simulation :***

Process simulations were completed for feed to the WorleyParsons subcontractor for comment on commercial viability, value of product acid, and Task 2 capex cost estimation. Two main process simulation iterations were completed: 1) at the beginning of the project (before experimental data was collected which was based on the limited literature data available) and 2) at the end of the project after the experimental data was collected and after feedback was received from Foster Wheeler and Task 5 activities on the expected on the flue gas composition.

### ***Subtask 5.3 - Commercial Viability of H<sub>2</sub>SO<sub>4</sub> Process :***

The WorleyParsons Toronto office has experience in the sulfuric acid industry designing sulfuric acid plants. Because WorleyParsons is involved in the sulfuric acid industry they have experience to provide feedback on the Task 2 process with respect to: 1) technical feasibility and commercial viability of the process, 2) assistance in developing a budgetary cost estimate, 3) commercial acid product viability based on the current acid market and logistical considerations.

## Results and Discussion

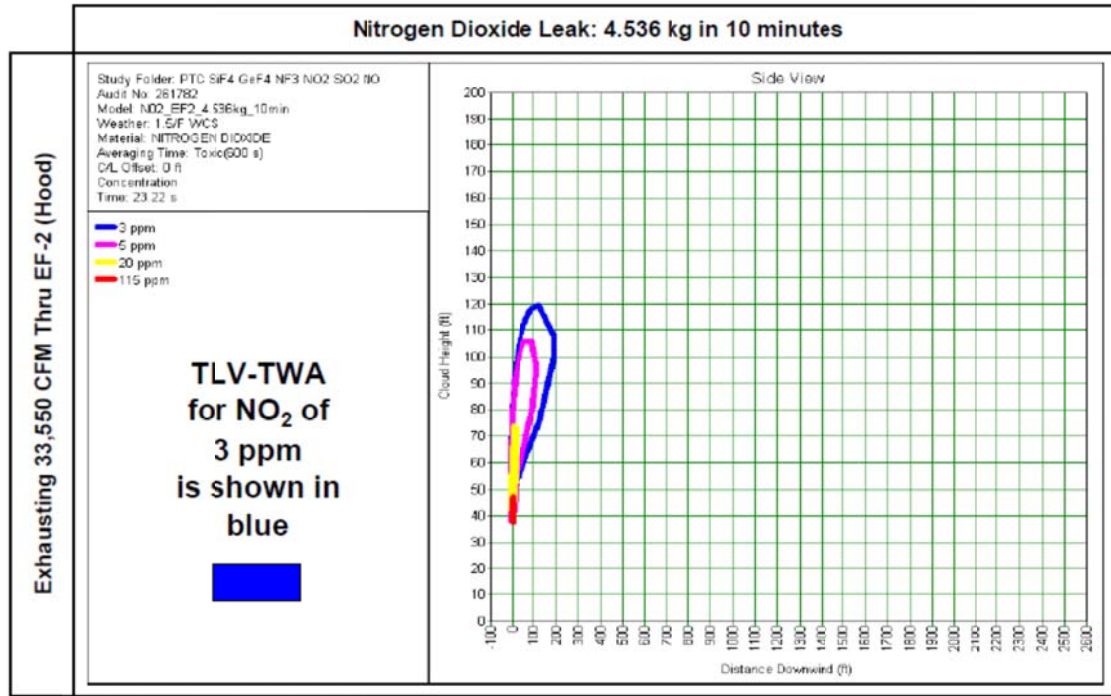
### ***Subtask 2.1: Experimental Apparatus Design and Construction***

Safety and corrosion were very important in physical design of the experimental system because the experiments involve contact of toxic gases with sulfuric acid, at elevated pressure and at elevated temperature. The heated sulfuric acid stream made for a unique challenge in terms of materials compatibility due to increased corrosion rates associated with high temperature sulfuric acid. Due to these unique considerations considerable time was spent on the design of certain pieces of equipment including the acid heater, acid cooler and reactor.

From a safety standpoint a decision was made to automate system shutdowns and to provide for remote system control due to the sulfuric acid and toxic gases used in the experiment. A programmable logic controller (PLC) was used to control the system which has added some system complexity to the project.

Due to a strong emphasis on safety at Praxair, significant efforts were spent to evaluate potential failure modes and to ensure that adequate protection existed for personnel and property during the commissioning and experimentation phase of the program. Due to the toxic nature of the gases involved in this experimentation ( $\text{SO}_2$ ,  $\text{NO}$  and  $\text{NO}_2$ ), it was deemed necessary to perform a dispersion analysis of a toxic gas release to make sure that the gas discharge plume from the fume hood exhauster is sufficiently dilute to ensure that there was not potential for injury in the worst case scenario.

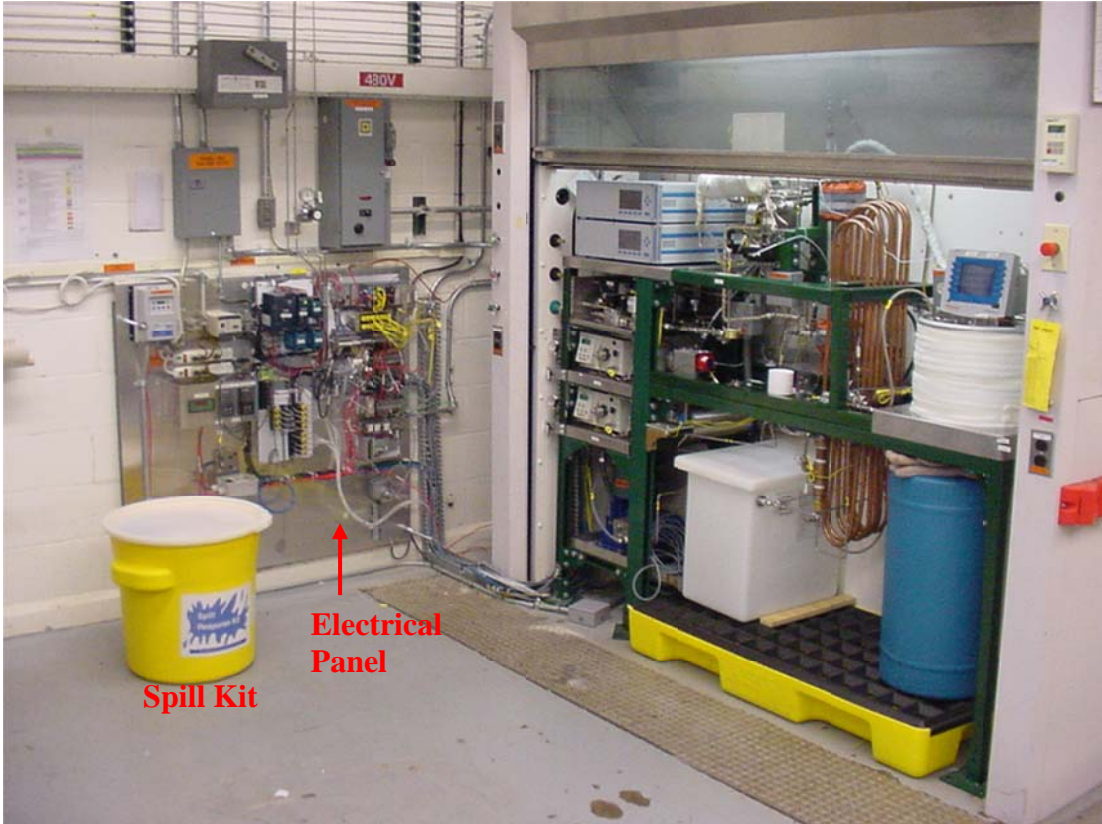
Refer to Figure 6 for a dispersion analysis case showing the hood exhauster plume following an  $\text{NO}_2$  cylinder leak. The plume shows the gas concentration in the area surrounding the hood exhauster and the extent of vertical and transverse movement of the plume. This analysis was performed for all toxic gases ( $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{NO}$ ) spanning a variety of potential cylinder leak/rupture scenarios. The plume analysis results showed that there was adequate dispersion of  $\text{NO}_2$  and  $\text{NO}$  due to the relatively small cylinder contents but that the dispersion of  $\text{SO}_2$  was not as complete. As a result of the plume analysis the  $\text{SO}_2$  cylinder size was decreased.



**Figure 6: Plume analysis for a 10min release of NO<sub>2</sub> through the fume hood exhauster**

Figure 7 shows the bench scale test unit constructed in subtask 2.1. The electrical and control connections are shown on the left along with an emergency spill containment kit. The experimental equipment is located in a fume hood, shown on the right. Sulfuric acid was stored in the fume hood while the toxic feed gases (SO<sub>2</sub>, NO, NO<sub>2</sub>) were stored in a dedicated vented gas cabinet (not shown). Figure 8 shows the computerized interface panel used to control the Task 2 experimental apparatus. From this interface gas flows, liquid flows, and process temperatures were controlled and monitored. Warnings, alarm conditions and analyzer readings were monitored and process data was recorded for later analysis.





**Figure 7: Bench Scale unit constructed as part of Subtask 2.1**

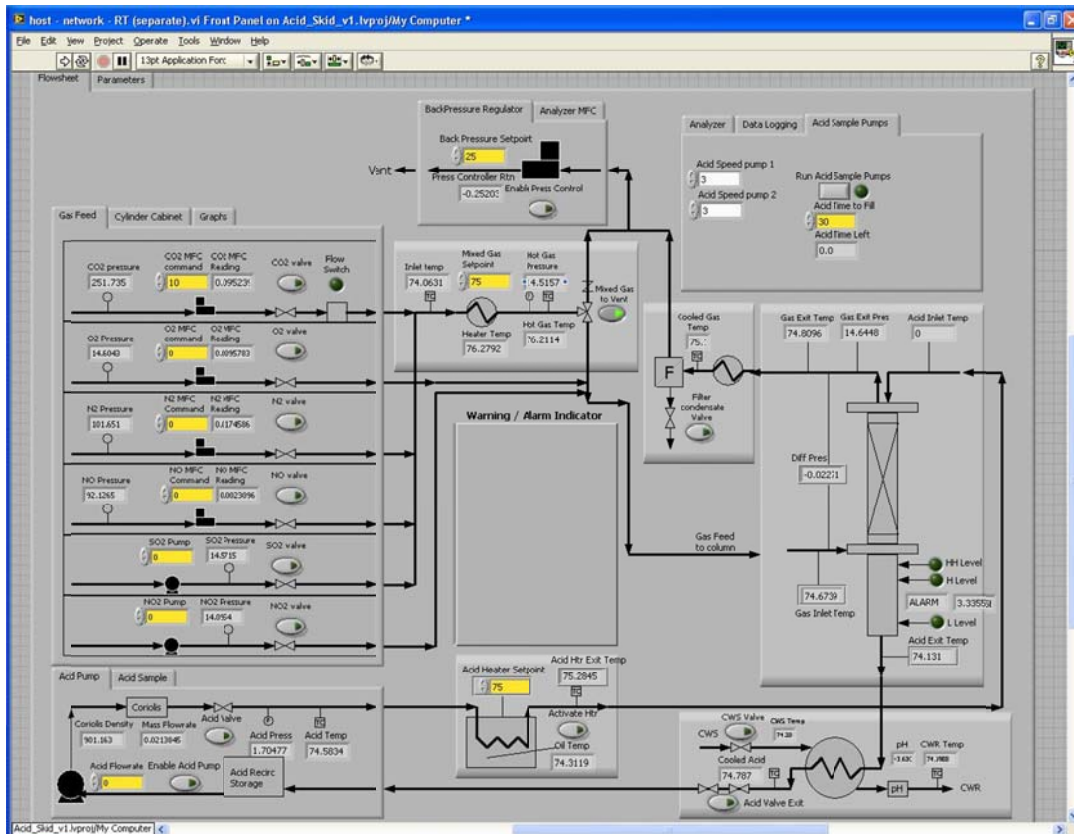


Figure 8: Computer interface control and monitoring panel for the Task 2 equipment

## Subtask 2.2: Data Collection in the Gas/Liquid Contactor

### General experimental, commissioning and NO oxidation reactions

The initial tests conducted in the bench scale experimental apparatus included:

- tests to understand the flooding behavior of the column
- tests to quantify the mass transfer performance of the gas/liquid contactor
- experiments to investigate the NO oxidation reaction kinetics in comparison to literature-reported data

The flooding behavior of the column was tested at atmospheric pressure and at elevated pressure with water to determine the operating limits of the system needed to avoid flooding during experimentation. Figure 9 shows the column limits at a fixed pressure as a function of gas flowrate. The column is less likely to flood at higher pressures due to the decreased superficial gas velocity through the column. These experimental results were used to calculate the flooding limits of sulfuric acid by accounting for the higher density and viscosity of this liquid.

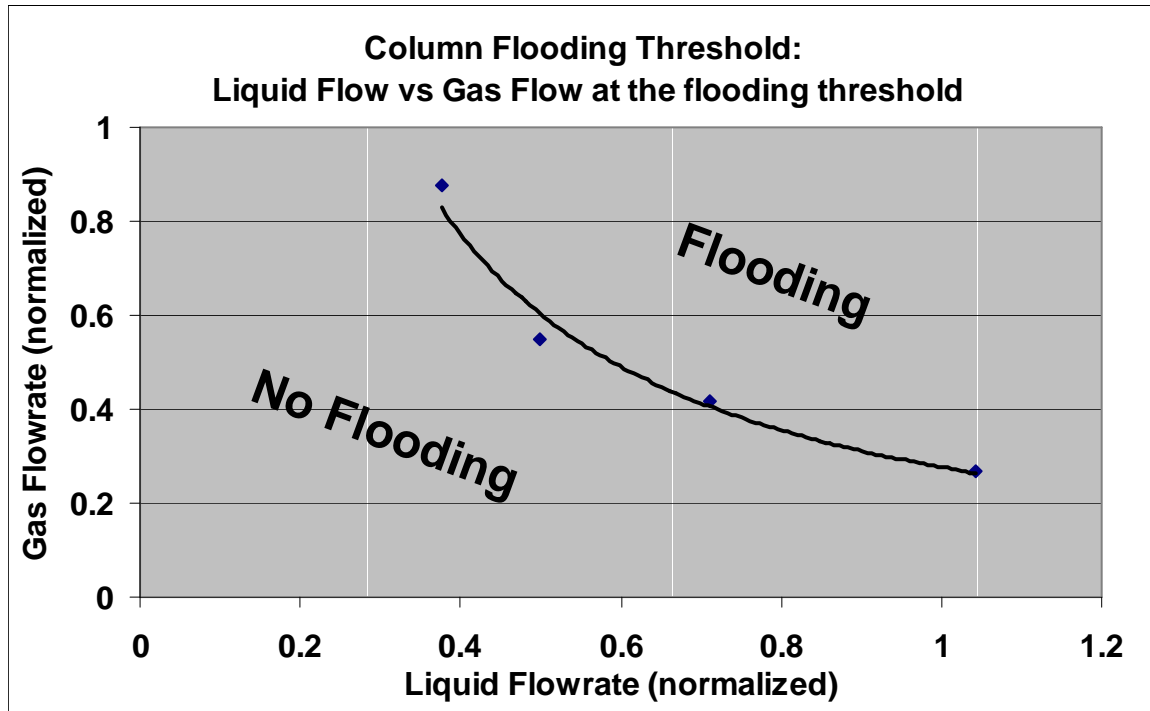


Figure 9: Experimental column flooding threshold

To determine the number of equilibrium column stages, a stream consisting of SO<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> was passed through the column counter current to water at various water flow rates. The uptake of SO<sub>2</sub> was determined by measuring the concentration of the exhaust gas. The same process has been simulated using a process simulator (Aspen Plus) for estimation of number of equilibrium stages vs. water flowrate. Process simulations include electrolyte interactions and the formation of acid species from CO<sub>2</sub> and SO<sub>2</sub> that enable accurate simulation of the system chemistry. In the laboratory and simulated contactor SO<sub>2</sub> and CO<sub>2</sub> are absorbed into the water, forming sulfurous acid and carbonic acid that affects the pH of the water exit stream as well as the ability of the water to absorb acid gas components.

Comparing experimental data and simulation data allows for the estimation of the number of equilibrium stages in the column. See Figure 10 showing the relationship between number of column stages (normalized) and liquid flowrate (normalized) for a fixed gas flowrate. The results of the commissioning testing of the gas/liquid contactor confirmed column that at the number of equilibrium stages in the column was roughly 1.0 at the average expected operating conditions during the SO<sub>x</sub>/NO<sub>x</sub> testing.

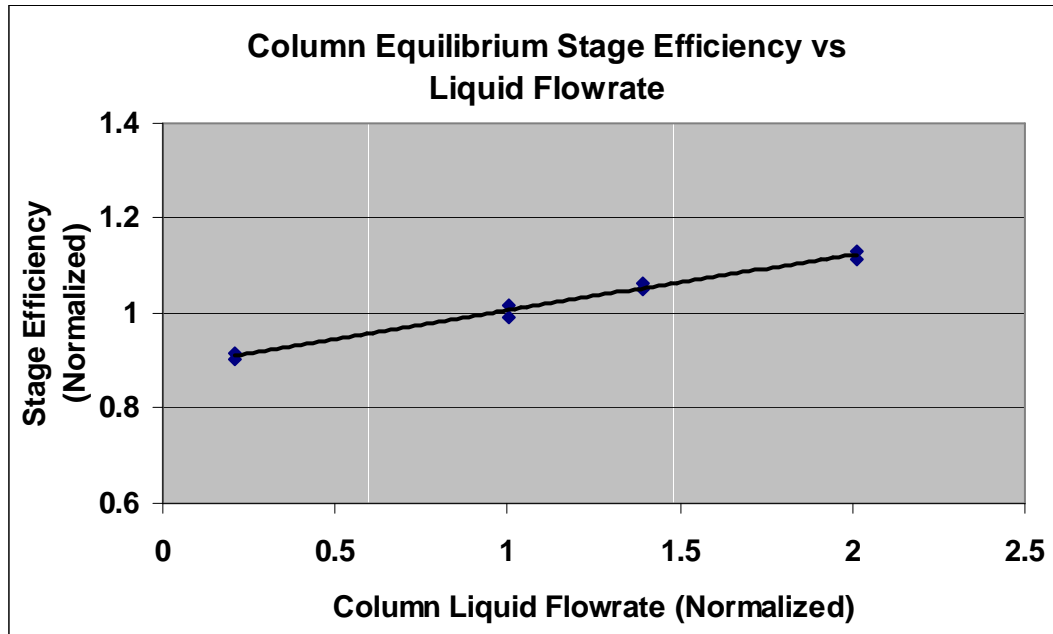


Figure 10: Experimental column stage efficiency

The bench scale apparatus had an empty chamber having a well-known volume that was used to determine the reaction rate of the NO oxidation reaction ( $\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$ ), Reaction 1. This reaction is well known to occur in the gas phase at the temperatures and pressures of interest in the carbon dioxide processing unit. The rate of the NO oxidation reaction was measured in the bench scale system for comparison against the literature-predicted reaction rate.

Figure 11 shows the conversion of NO due to the NO oxidation reaction for two flowrates. Nitric Oxide conversion depends on the flowrate and reaction pressure because these factors change the gas residence time and reactant concentrations (partial pressures) in the experimental apparatus. Figure 11 shows the experimentally observed reaction conversion vs. the literature-predicted reaction conversion at various pressures. Good agreement is shown between the laboratory measured conversions and kinetic rate law-predicted conversions. The cause of the larger discrepancy between experiment and prediction for the lower flowrate is likely due to the increased residence time in the tubing before and after the reaction volume. The ability to accurately predict the rate of NO oxidation is very important in the Task 2 effort because  $\text{NO}_2$  is required to catalyze  $\text{SO}_2$  oxidation for  $\text{SO}_2$  removal from the compressed flue gas stream.

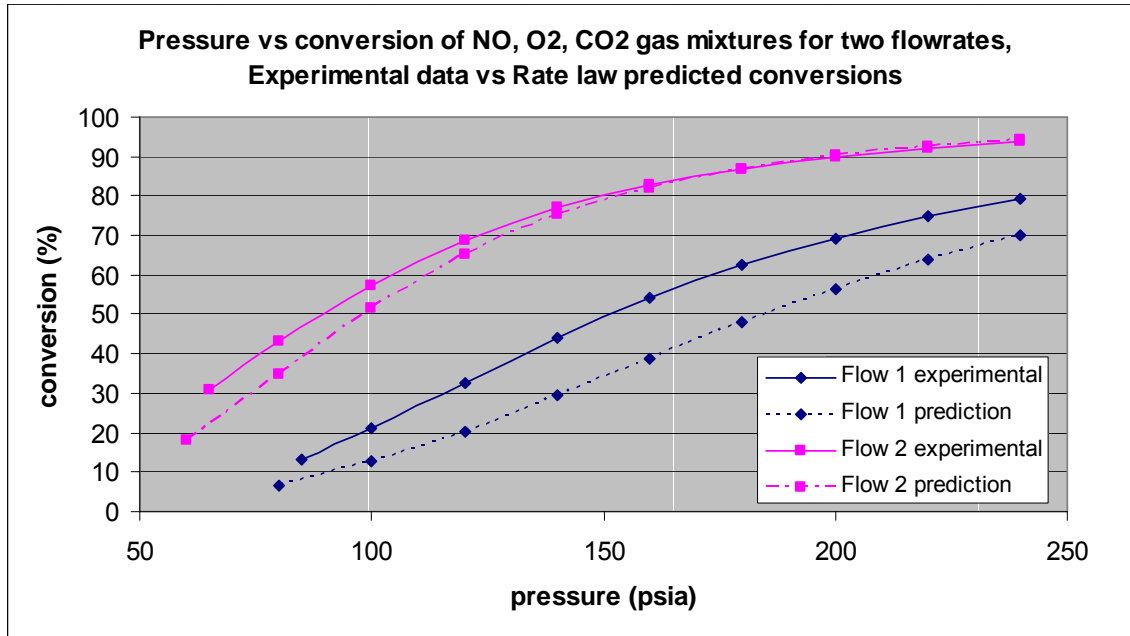


Figure 11: Percent conversion of NO to NO<sub>2</sub> in at various pressures and gas flowrates. Experimental results are compared to simulation results.

### NO<sub>x</sub> absorption and desorption with sulfuric acid

A number of tests were conducted to quantify the uptake of NO<sub>x</sub> into sulfuric acid. NO<sub>x</sub> – sulfuric acid interactions was very important in determining the feasibility of the proposed process. A number of tests were conducted to quantify NO<sub>x</sub> absorption behavior at various conditions:

- NO<sub>x</sub> absorption into sulfuric acid for various levels of NO<sub>x</sub> (800 - 6600ppmv total NO<sub>x</sub>)
- NO<sub>x</sub> absorption into sulfuric acid for various relative amounts of NO and NO<sub>2</sub>
- NO<sub>x</sub> absorption into sulfuric acid at various temperatures and pressures

Figure 12 and Figure 13 below show typical data collected for NO<sub>x</sub> absorption tests. In these particular tests various levels of NO<sub>x</sub> (1600-6600 ppm) are contacted with sulfuric acid. The absorption behavior of NO<sub>x</sub> into sulfuric acid is highly dependent on the ratio of NO to NO<sub>2</sub>. Maximum NO<sub>x</sub> absorption is observed when NO:NO<sub>2</sub> is around 1:1. At higher pressures (200 psia) maximum NO<sub>x</sub> absorption is observed when there is a slight excess of NO at the reactor inlet because the homogeneous reaction just described converts NO to NO<sub>2</sub> inside the gas/liquid contactor. This reaction pushes the NO:NO<sub>2</sub> ratio close to 1:1 when the gas is in actual contact with the column packing and liquid acid.

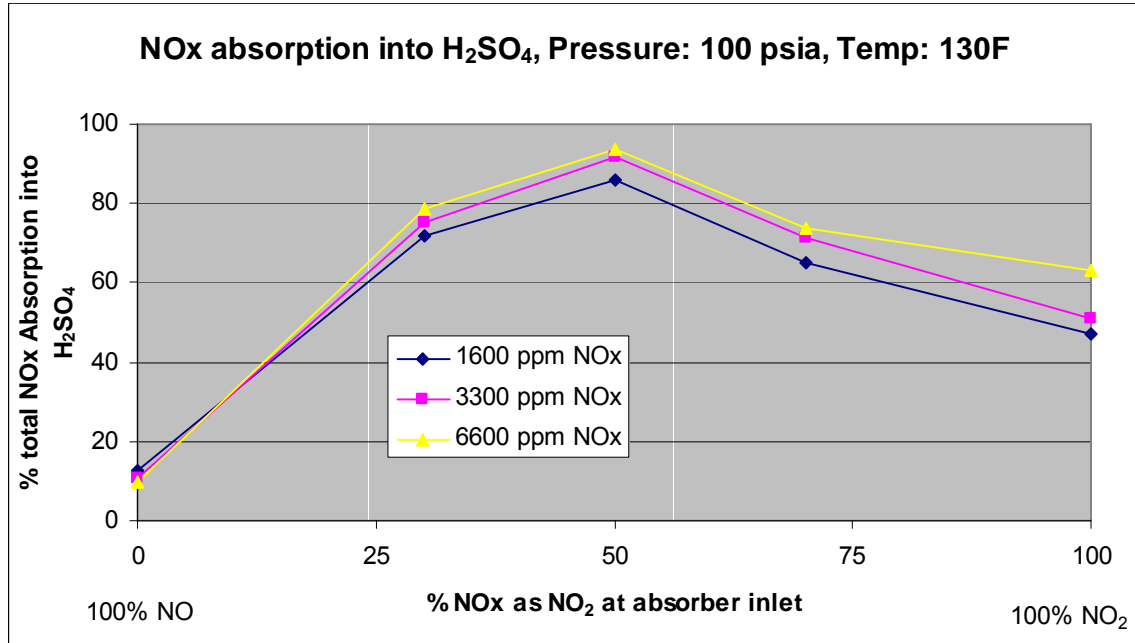


Figure 12: NOx absorption by H<sub>2</sub>SO<sub>4</sub>; 100 psia and 130 °F

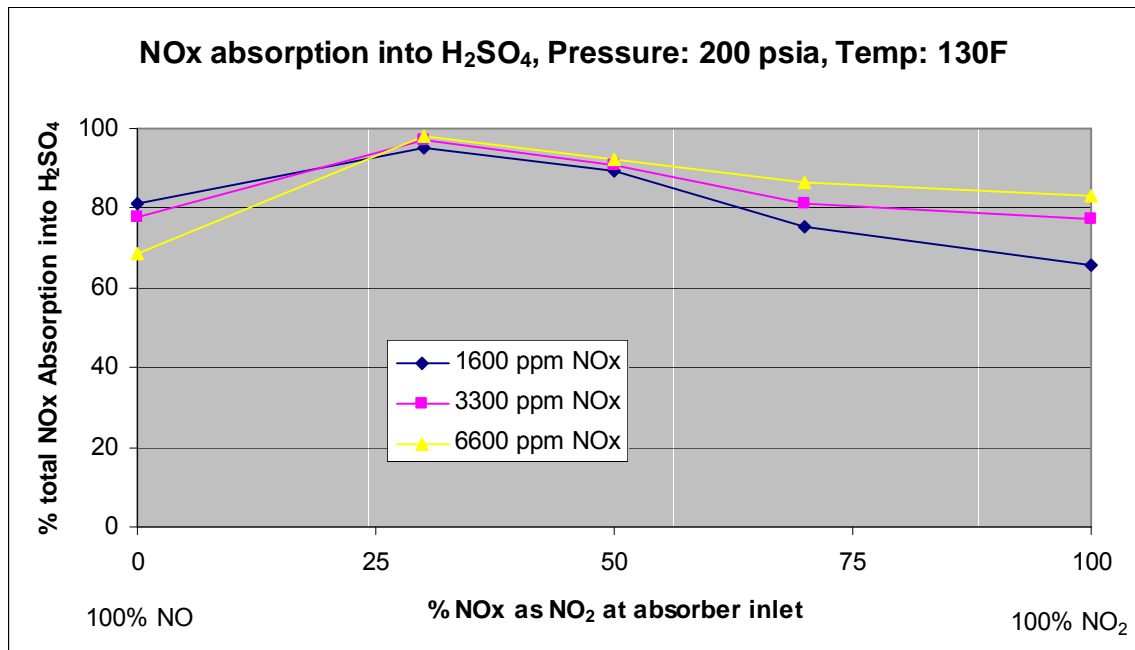


Figure 13: NOx absorption by H<sub>2</sub>SO<sub>4</sub>; 200 psia and 130 °F

Absorption/desorption experiments were conducted at increasingly higher temperatures of up to 235°F, see Figure 12 to Figure 16. The main important result that was determined from these graphs is that NOx absorption into 93wt% sulfuric acid remains high even at temperatures of up to 235°F at a relatively low pressure of 100 psia (Figure 16). The limited amount of literature information available near these conditions

which was consulted during the proposal phase of this program suggested that acid containing NO<sub>x</sub> would not absorb NO<sub>x</sub> and would even begin to desorb from acid at these temperatures. Because the sulfuric acid used in these experiments contained a substantial amount of dissolved NO<sub>x</sub> the gas leaving the gas/liquid contactor should have showed a gain in NO<sub>x</sub> if there was any net NO<sub>x</sub> desorbed from the acid.

The experiments that we conducted showed that sulfuric acid continued to absorb NO<sub>x</sub> at fairly high rates even at elevated temperatures of up to 235°F. NO<sub>x</sub> desorption from sulfuric acid is an important and necessary feature for production of relatively pure sulfuric acid and is also needed so too high of levels of NO<sub>x</sub> are not build up in the re-circulating acid stream. An inability to desorb NO<sub>x</sub> from sulfuric acid, as demonstrated experimentally, means that the sulfuric acid product will likely have very high levels of dissolved NO<sub>x</sub> and further there are implications on the ability of the Task 2 process to achieve a high NO<sub>x</sub> capture rate.

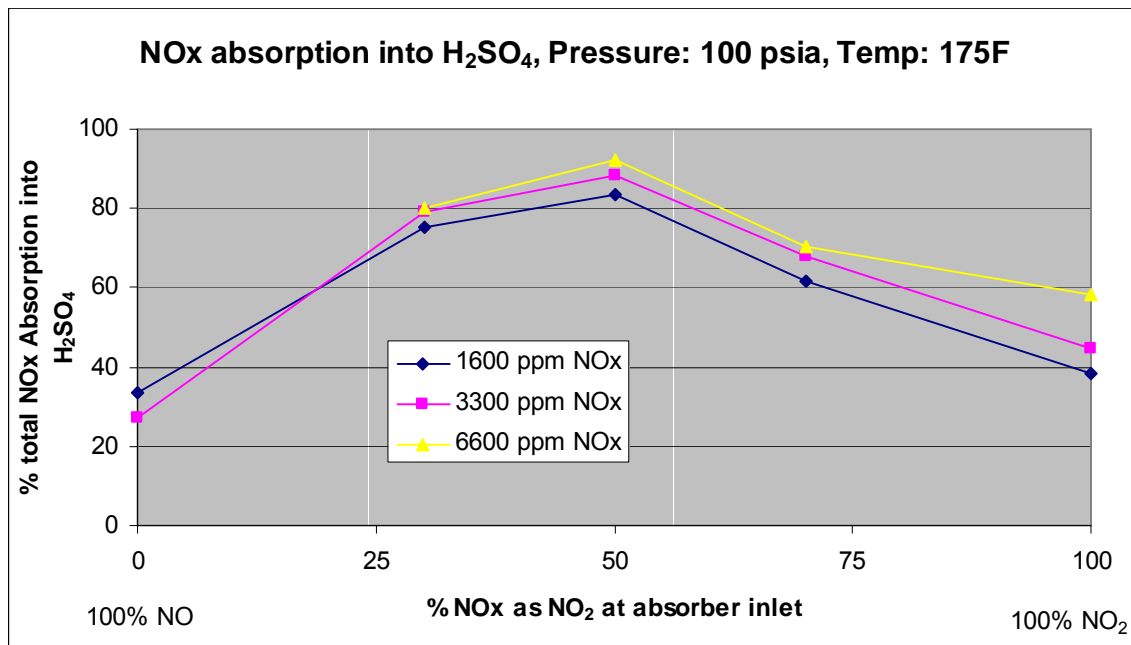


Figure 14: NO<sub>x</sub> absorption by H<sub>2</sub>SO<sub>4</sub>; 100 psia and 175 °F

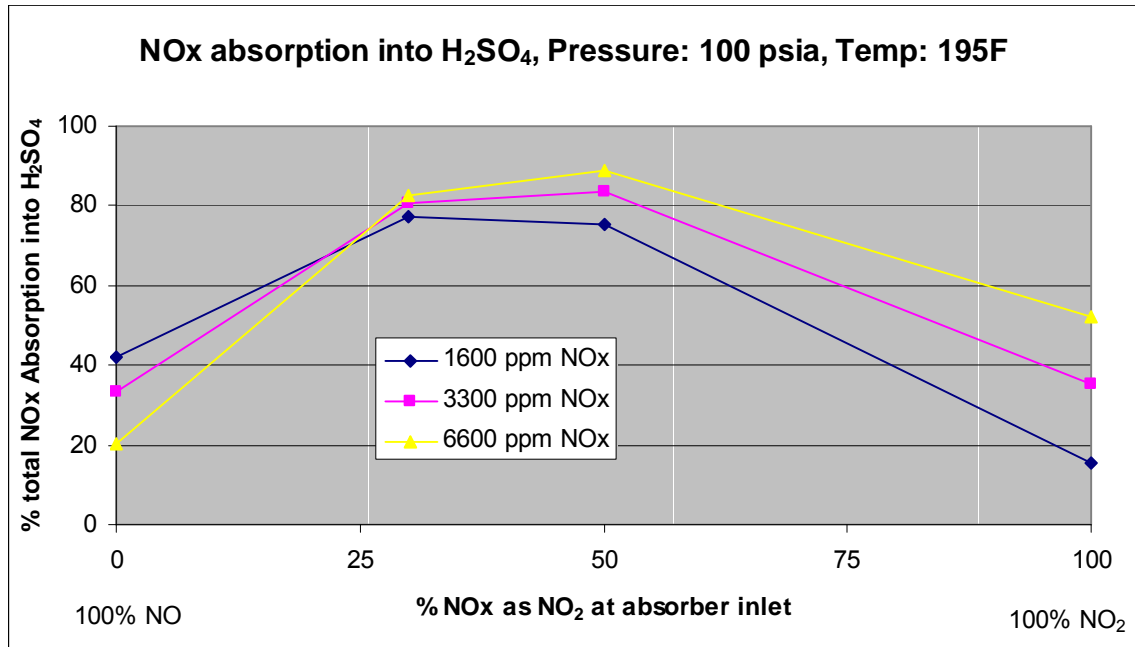


Figure 15: NOx absorption by H<sub>2</sub>SO<sub>4</sub>; 100 psia and 195 °F

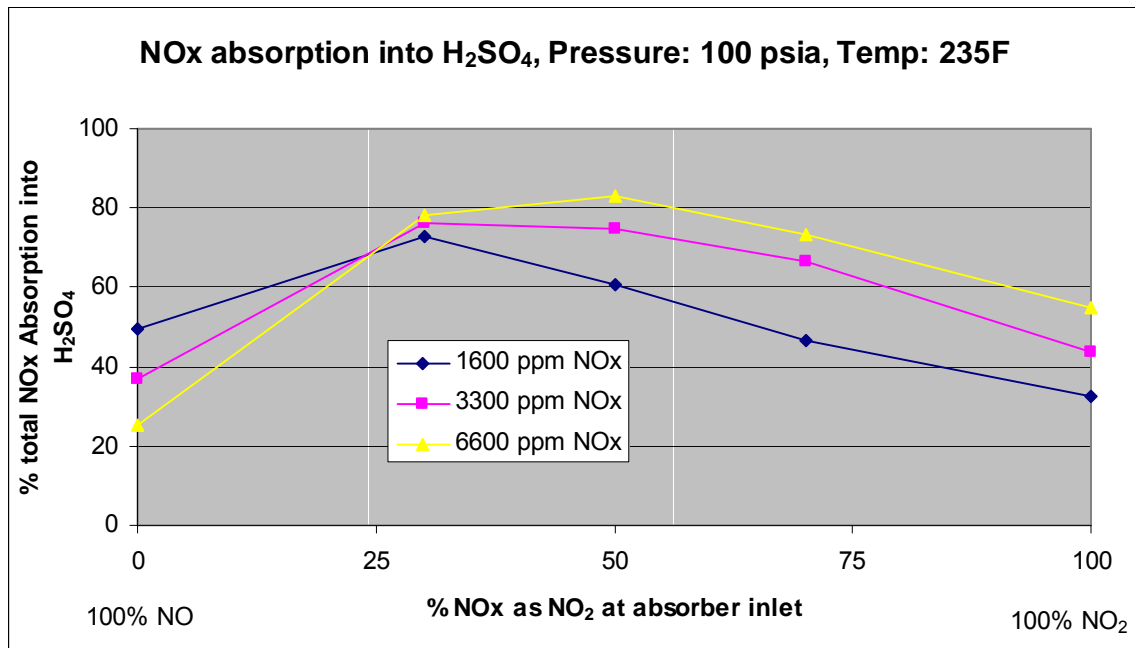


Figure 16: NOx absorption by H<sub>2</sub>SO<sub>4</sub>; 100 psia and 235 °F

As NOx absorption experiments were conducted at progressively higher temperatures it was expected that a significant amount of NOx would thermally desorb from the liquid acid. As described above the experimental data actually showed no ability of the acid to release NOx as it is heated at the conditions investigated experimentally. As an increasing number of experiments were conducted with the same batch of acid the NOx concentration in the acid batch continued to steadily rise according to the sulfuric



acid nitrite tests, see below in Figure 17. This again reinforces the observation that there is significant difficulty in removing NOx from sulfuric acid.

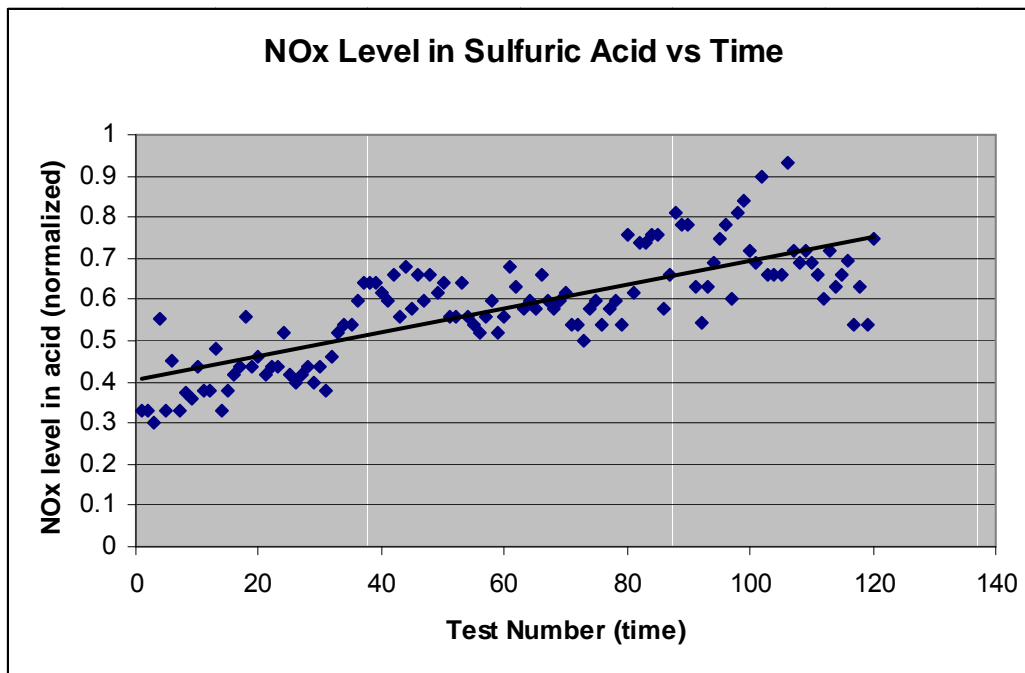


Figure 17: Accumulation of NOx in H<sub>2</sub>SO<sub>4</sub> during the test campaign

For some process conditions, generally at lower temperatures < 110°F, the gas/liquid contactor exhibited very significant pressure drop (>1psi), it was later determined that a solid substance was forming (H<sub>2</sub>SO<sub>4</sub> + NOx) and plugging up the column packing. Information from the literature regarding the Lead Chamber Process for sulfuric acid manufacture predicts the formation of a NOx-sulfuric acid mushy solid under certain process conditions (high acid concentration and high NOx levels). An experiment was conducted at atmospheric pressure under these conditions in clear glassware. The formation of a solid substance was visually observed confirming potential column plugging by these deposits. The pressure drop difficulties due to this solid formation was generally more frequently noticed at lower operation temperatures and higher NOx concentrations which would be similar to conditions in the NOx absorber vessel.

**SOx conversion and SOx/NOx reactions:**

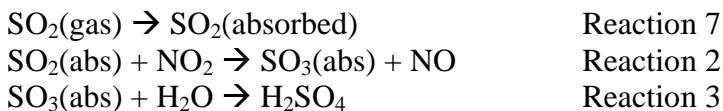
When designing a SO<sub>2</sub> reactor system for the Task 2 process there are a number of variables that could be manipulated to affect SOx containment, including temperature, NOx levels, SOx levels, residence time, acid flowrate, gas flowrate, etc. These variables can be adjusted by changing process parameters related to the SO<sub>2</sub> reactor, NOx absorber and NOx desorber to try to achieve high conversion of NOx and SO<sub>2</sub> to acids in the final process.

A number of key parameters were investigated as they relate to the SO<sub>x</sub> reactor to 1) determine their impact on the SO<sub>2</sub> oxidation/absorption performance and 2) to aid in the estimate of process conditions and physical dimensions of an SO<sub>2</sub> reactor in a commercial size CPU system.

Process characteristics experimentally investigated in Q4 2010 as they relate to the SO<sub>2</sub> reactor:

- SO<sub>2</sub> level in the gas feed
- Residence time (through varied vessel pressure and gas flowrate)
- Liquid acid flowrate
- NO<sub>2</sub> and NO levels
- Temperature

The conversion of SO<sub>2</sub> to SO<sub>3</sub> depends on the absorption of gas phase SO<sub>2</sub> into the sulfuric acid liquid (Reaction 1) followed by SO<sub>2</sub> reaction to SO<sub>3</sub> and hydration to sulfuric acid (Reactions 2 and 3). The relevant SO<sub>2</sub> conversion reactions responsible for sulfuric acid production are shown below.



Besides any kinetic limitations of Reaction 2 the rate of SO<sub>2</sub> oxidation also depends on the mass transport limitations of absorbing gas phase SO<sub>2</sub> into the liquid as well as solubility limits of SO<sub>2</sub> in sulfuric acid. Based on the results of the NO<sub>x</sub> experimentation it is expected that mass transfer resistance is not limiting in these experiments because some NO<sub>x</sub> experiments were able to achieve up to 98% NO<sub>x</sub> absorption at similar gas and liquid flow conditions (roughly one equilibrium mass transfer stage).

### SO<sub>2</sub> solubility in sulfuric acid

According to literature, the solubility of SO<sub>2</sub> in sulfuric acid can be predicted using a simple Henry's law relationship:  $P_{SO_2, Gas} * H = C_{SO_2, Liq}$  [2]. At a fixed temperature and acid concentration the maximum solubility of SO<sub>2</sub> in sulfuric acid is determined by the partial pressure of SO<sub>2</sub> in the gas phase (for the binary system involving SO<sub>2</sub> and acid). Experimental data has been collected in our system with high partial pressures of CO<sub>2</sub> and high levels of NO<sub>x</sub> in the acid. Experimental results indicate that the solubility of SO<sub>2</sub> in sulfuric acid is decreased by a factor of about 10 over the ideal binary case. The specific reason for this substantial decrease in SO<sub>2</sub> solubility is not clear however it is believed to be due to the high partial pressure of CO<sub>2</sub> and/or the high levels of NO<sub>x</sub> in acid. Figure 18 shows the estimated maximum solubility of SO<sub>2</sub> in concentrated 95wt% sulfuric acid as a function of SO<sub>2</sub> partial pressures for the model binary system (blue line). The estimated solubility limits in our system with a high CO<sub>2</sub> partial pressure and NO<sub>x</sub> dissolved in acid is shown by the pink line.

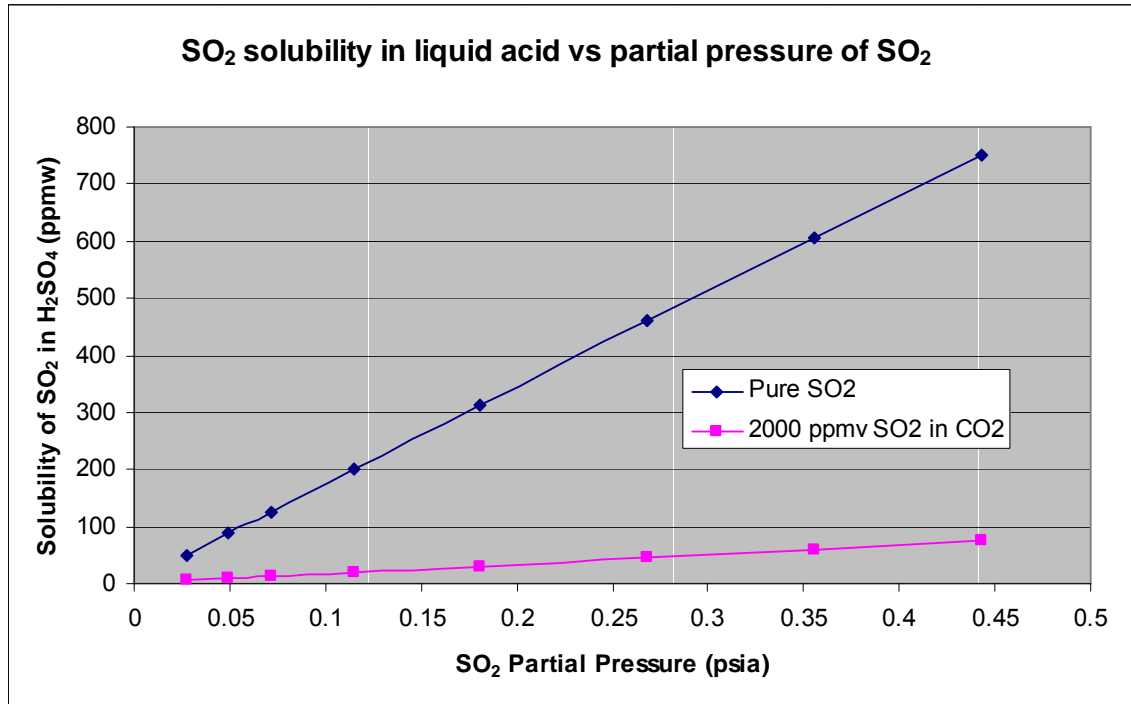


Figure 18: Equilibrium solubility of SO<sub>2</sub> in 95wt% sulfuric acid vs. partial pressure of SO<sub>2</sub>.

It is important to note that when SO<sub>2</sub>-containing gas is contacted with sulfuric acid SO<sub>2</sub> will be absorbed even in the absence of Reaction 2 due to SO<sub>2</sub>'s solubility in sulfuric acid. Therefore removal of SO<sub>2</sub> from the gas phase may not necessarily be attributed to SO<sub>2</sub> conversion to SO<sub>3</sub> (Reaction 2). Direct measurement of SO<sub>2</sub> content of the liquid sulfuric acid was not possible in our experimental apparatus because as soon as the liquid pressure is reduced much of the SO<sub>2</sub> desorbs from the acid. For this reason SO<sub>2</sub> reaction and absorption must be measured indirectly by changing gas/liquid contactor conditions such as (flowrate, pressure, SO<sub>2</sub> and NO<sub>x</sub> levels, etc.) and monitoring the gas SO<sub>2</sub> levels.

### Effect of SO<sub>2</sub> level on SO<sub>2</sub> absorption and reaction

Experiments were conducted at constant pressure, temperature, total gas flowrate, NO<sub>x</sub> gas level and liquid flowrate with varying SO<sub>2</sub> level to estimate the SO<sub>2</sub> reaction rate in our system. Figure 19 shows the experimental total absorption result for the experiments (in blue) along with the vapor liquid equilibrium (VLE) predicted absorption of SO<sub>2</sub> into sulfuric acid (in pink) for concentrations of SO<sub>2</sub> of up to about 2200 ppm.

At low inlet gas concentrations of SO<sub>2</sub> the total absorption of SO<sub>2</sub> as denoted by the experimental blue line approaches that which is predicted by VLE absorption because the low concentration of liquid phase SO<sub>2</sub> limits the actual SO<sub>2</sub> oxidation rate (Reaction 2). At higher concentrations of gas inlet SO<sub>2</sub> the liquid concentration of SO<sub>2</sub> is higher and the SO<sub>2</sub> reaction rate (Reaction 2) is faster; this increases the spread between the blue and pink lines.

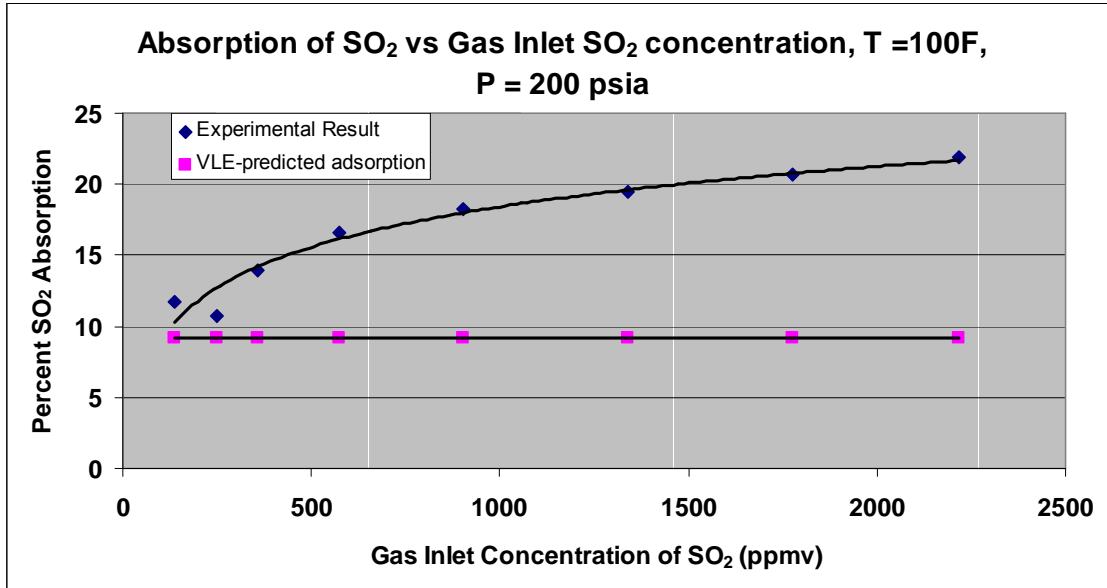


Figure 19: Percent SO<sub>2</sub> adsorption vs. inlet gas concentration of SO<sub>2</sub>.

### Effect of residence time on SO<sub>2</sub> absorption

Experiments were conducted in the gas/liquid contactor at 100°F with a CO<sub>2</sub> gas feed containing about 2100 ppm SO<sub>2</sub> and a liquid sulfuric acid feed containing an excess of dissolved NO<sub>x</sub>. Data was collected for various gas feed rates (10, 20 or 30 slpm) and various pressures (100, 150 and 200 psia) to investigate the effect of residence time on SO<sub>2</sub> absorption. In all experiments the liquid flowrate was kept constant. Figure 20 shows the effect of residence time on the absorption of SO<sub>2</sub>. An increase in residence time has a nearly linear effect on increasing SO<sub>2</sub> absorption. A decrease in reaction rate is observed at high SO<sub>2</sub> conversions, which is believed to be due to a decrease in the rate of Reaction 2 as the SO<sub>2</sub>(abs) concentration decreases ( $Rate_{rxn2} \sim k \cdot Conc_{SO_2} \cdot Conc_{NO_2}$ ), as was shown above in Figure 19. The concentration of absorbed NO<sub>2</sub> is in excess and should not limit the reaction rate at the conditions investigated here.

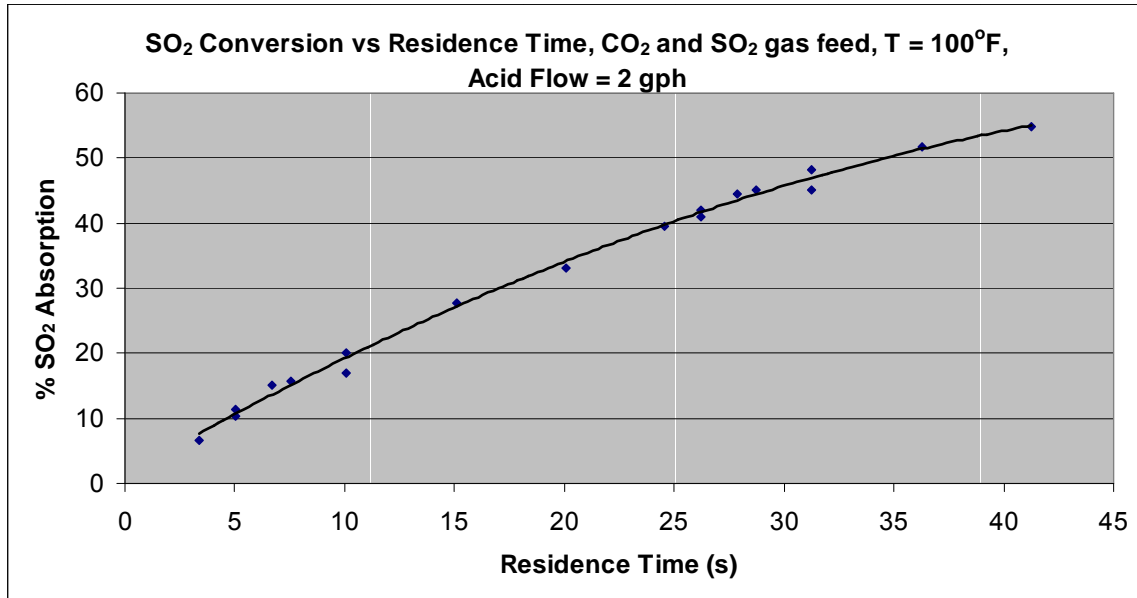


Figure 20: Impact of residence time on SO<sub>2</sub> absorption in H<sub>2</sub>SO<sub>4</sub> in absence of NO<sub>x</sub>.

A second set of data was collected with roughly 800 ppm of NO<sub>x</sub> added to the contactor feed gas, the results are shown below in Figure 21. The experimental data shows that the addition of 800ppm of gas phase NO<sub>x</sub> serves to increase the rate of SO<sub>2</sub> absorption by roughly 10%. Gas phase NO<sub>x</sub> is readily absorbed by sulfuric acid, as previously shown, the added gas phase NO<sub>x</sub> increases liquid phase NO<sub>x</sub> resulting in an increased reaction rate.

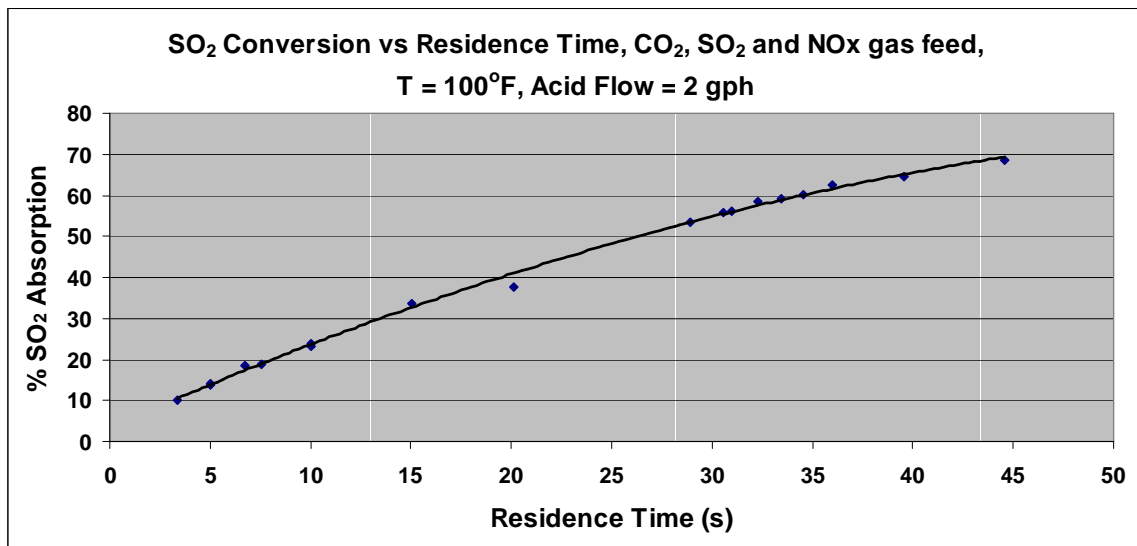


Figure 21: Impact of residence time on SO<sub>2</sub> absorption in H<sub>2</sub>SO<sub>4</sub> in presence of NO<sub>x</sub>

In Figure 22 some of the data from Figure 20 and Figure 21 are shown together with the VLE predicted contribution to SO<sub>2</sub> Absorption. The VLE-predicted absorption is calculated based on the inlet gas composition, gas flowrate, acid flowrate and system

pressure and is not residence time dependent. It is, however, plotted versus residence time for comparison with the corresponding experimental data points (shown in green and blue). The difference between the blue and pink data and the green and pink data corresponds to the amount of SO<sub>2</sub> oxidation (Reaction 2) taking place; the presence of gas phase NO<sub>x</sub> allows for a faster reaction rate. As residence time is increased SO<sub>2</sub> absorption also increases due to Reaction 2.

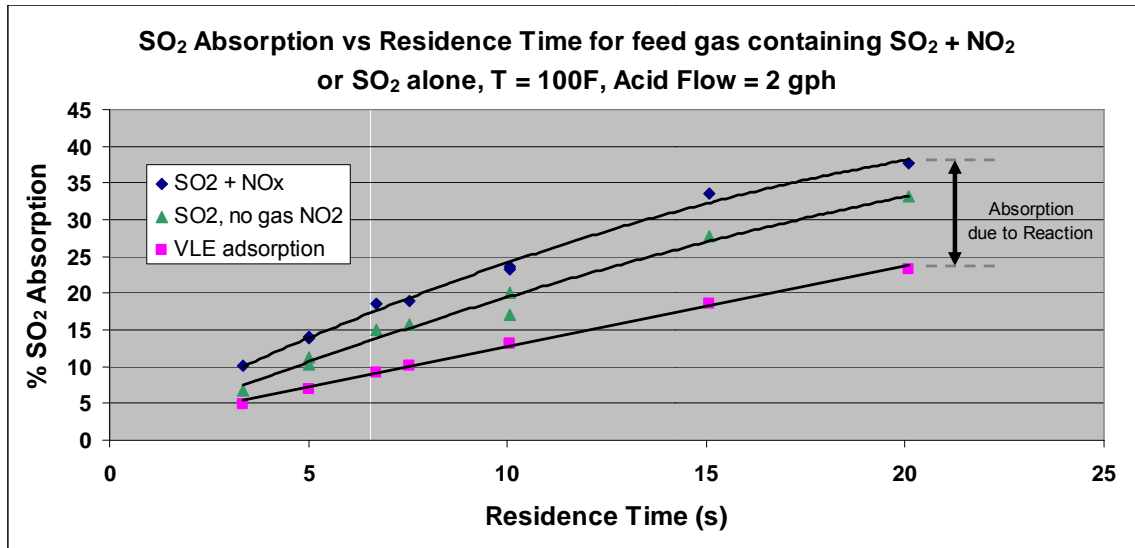


Figure 22: Increase in SO<sub>2</sub> absorption in H<sub>2</sub>SO<sub>4</sub> by reaction with NO<sub>2</sub>

### Effect of liquid flowrate on SO<sub>2</sub> absorption rate

Most of the SO<sub>2</sub> oxidation experiments were performed using a constant acid flowrate of 2.0gph to try to fix the gas/liquid mass transport performance of the reactor (Reaction 1). Fixing the liquid flowrate essentially fixes the gas/liquid interfacial area inside the gas/liquid contactor available to absorb SO<sub>2</sub> (Reaction 7); this helps to remove the mass transport effects as pressure or flowrate and residence time are changed (at constant temperature). The area available for gas/liquid contact can be changed by altering the liquid flowrate, or by changing the column packing material (which was not an option in our system).

Figure 23 shows the effect of varying acid flowrate on SO<sub>2</sub> adsorption. The distance between the experimental data (blue line) and the VLE adsorption line (pink) indicates the amount of SO<sub>2</sub> converted to SO<sub>3</sub> via Reaction 2. A decrease in acid flowrate from 2.0 gph to 1.0 gph reduces the SO<sub>2</sub> absorption capacity and results in a roughly linear decrease in SO<sub>2</sub> absorption (blue curve) which follows the VLE-prediction. For an acid flowrate of 1.0 and 2.0 gph the liquid’s SO<sub>2</sub> capacity is relatively low, meaning that the SO<sub>2</sub> concentration in the liquid is very similar and the resulting SO<sub>2</sub> reaction rate is similar.

As acid flowrate is increased above 2.0 gph the increase in liquid SO<sub>2</sub> capacity starts to appreciably reduce the gas and liquid phase SO<sub>2</sub> concentrations resulting in a

reduced rate of SO<sub>2</sub> reaction. This means it is expected that the distance between the blue and pink curve starts to close at higher acid flowrates, which is observed in Figure 23.

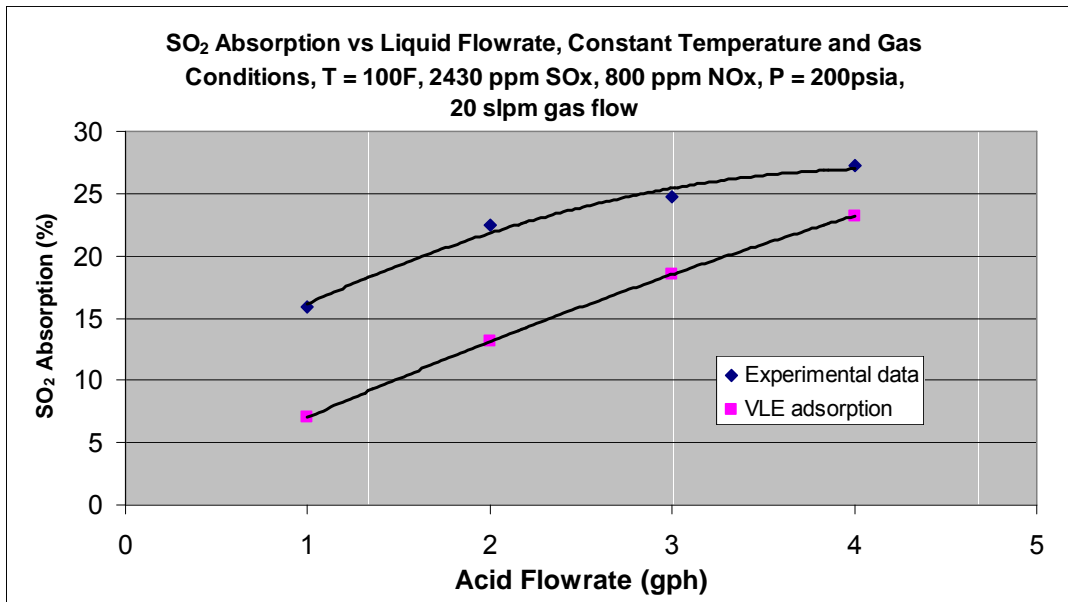


Figure 23: Effect of acid flowrate on SO<sub>2</sub> absorption.

### Effect of NO<sub>x</sub> level on SO<sub>2</sub> adsorption and oxidation rate

Experiments were also performed to determine the effect of increasing NO<sub>x</sub> content in the gas feed on SO<sub>2</sub> reaction rate. Experiments were conducted at constant temperature (100°F), constant gas flowrate, constant pressure (200 psia or 150 psia) and constant liquid feed rate. At each pressure two sets of data were collected for feed gases containing NO<sub>2</sub> and NO + NO<sub>2</sub>. Figure 24 and Figure 25 show the impact of increasing NO<sub>x</sub> level on SO<sub>2</sub> adsorption rate. A relative NO<sub>x</sub> level of 1 corresponds to about 800ppm of NO<sub>x</sub>. As NO<sub>x</sub> feed to the reactor is increased with other factors held constant the increase in SO<sub>2</sub> adsorption is directly attributable to an increase in SO<sub>2</sub> oxidation rate, Reaction 2. The presence of NO<sub>x</sub> is expected to increase the rate of SO<sub>2</sub> reaction because NO<sub>x</sub> is required for SO<sub>2</sub> oxidation. Furthermore if NO<sub>x</sub> feed to the reactor is composed of a mixture of NO and NO<sub>2</sub> the reaction rate is enhanced further. Figure 24 shows that the NO<sub>x</sub> enhancement is significantly greater in the higher pressure case.

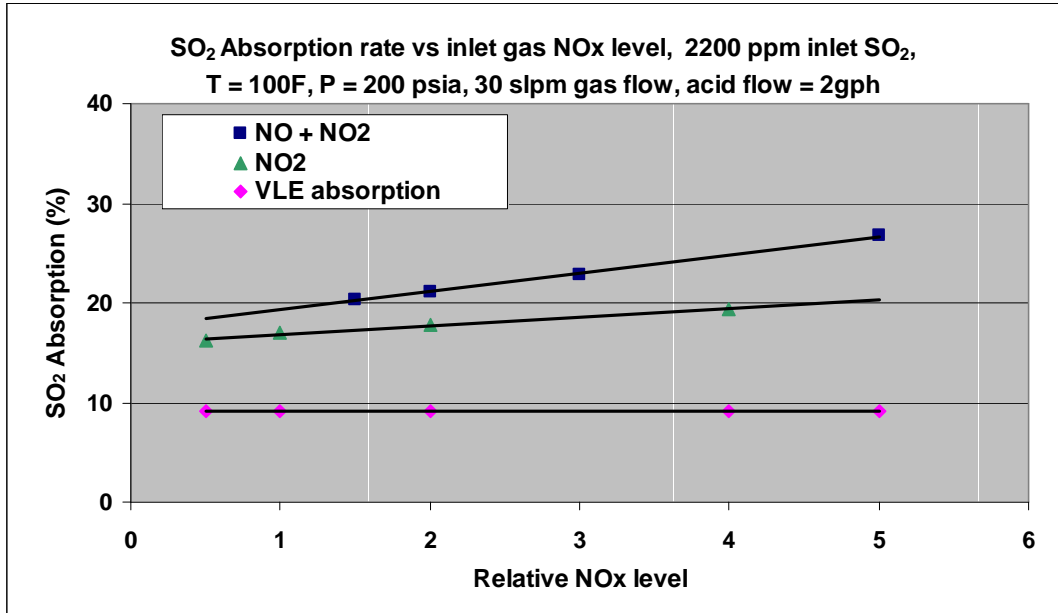


Figure 24: SO<sub>2</sub> absorption in H<sub>2</sub>SO<sub>4</sub> vs. NO<sub>x</sub> concentration in feed at 200 psia .

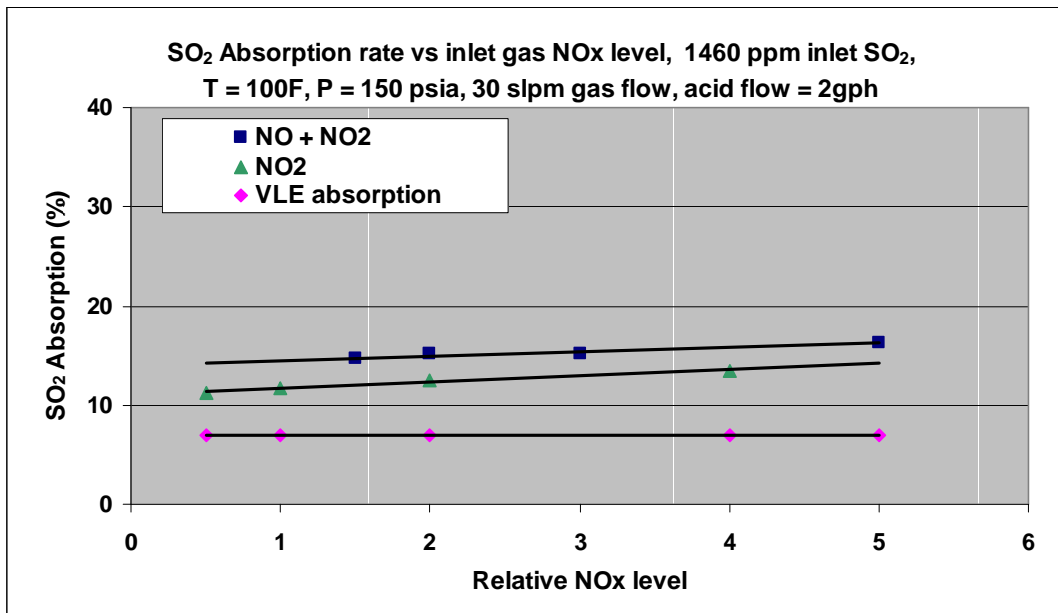


Figure 25: Absorption in H<sub>2</sub>SO<sub>4</sub> vs. NO<sub>x</sub> concentration in feed at 150 psia

**Effect of reaction temperature on SO<sub>2</sub> reaction rate**

With a fixed reaction volume and a fixed liquid flowrate an increased reaction temperature changes residence time, NO<sub>x</sub> oxidation kinetics, reduced SO<sub>2</sub> solubility, and potentially the SO<sub>2</sub> oxidation kinetics, etc. As reaction temperature changes in the bench scale system any change in these properties is observed as a changed SO<sub>2</sub> reactor outlet conversion.



An increase in reaction temperature is observed to modestly decrease the SO<sub>2</sub> reaction rate, as shown below in Figure 26. The reduced SO<sub>2</sub> reaction rate is expected to be due to a reduced SO<sub>2</sub> solubility in H<sub>2</sub>SO<sub>4</sub> which is predicted in the literature. Between 100°F and 180°F about a 3 fold decrease is expected based on a decrease the Henry’s law constant.

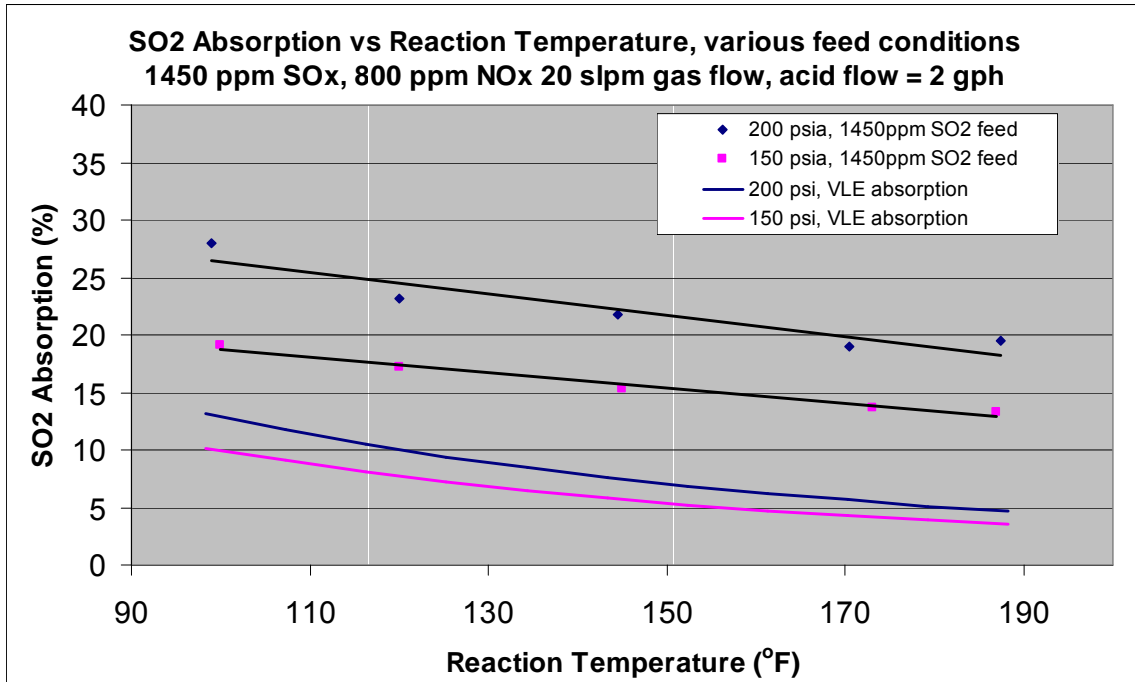


Figure 26: Impact of temperature on SO<sub>2</sub> absorption in H<sub>2</sub>SO<sub>4</sub>

### Subtask 2.3: NO<sub>x</sub> Removal with Activated Carbon

#### Carbon testing for NO<sub>x</sub> removal from sulfuric acid

In Project Year 1 (2009) a number of activated carbons were tested for their effectiveness to catalyze NO<sub>x</sub> removal from NO<sub>x</sub> contaminated sulfuric acid at atmospheric pressure. The carbons were tested for NO<sub>x</sub> removal by bubbling N<sub>2</sub> or air through a vessel containing carbon and sulfuric acid spiked with NO<sub>x</sub>. A sulfuric acid sample was taken periodically and tested for NO<sub>x</sub> concentration to determine the rate of NO<sub>x</sub> removal.

The purpose of the experiment was to determine if a particular carbon in the presence of oxygen can catalyze NO<sub>x</sub> removal from the acid at a faster rate than is observed with simple stripping of the NO<sub>x</sub>, when an inert gas, N<sub>2</sub>, is bubbled through the sulfuric acid.

Figure 27 shows a plot of NO<sub>x</sub> concentration vs. time using Carbon 1. This set of data shows the results of trying to remove NO<sub>x</sub> by stripping with N<sub>2</sub> and air. The rate of

NOx removal is shown to be significantly faster when N<sub>2</sub> is used for NOx removal as opposed to air.

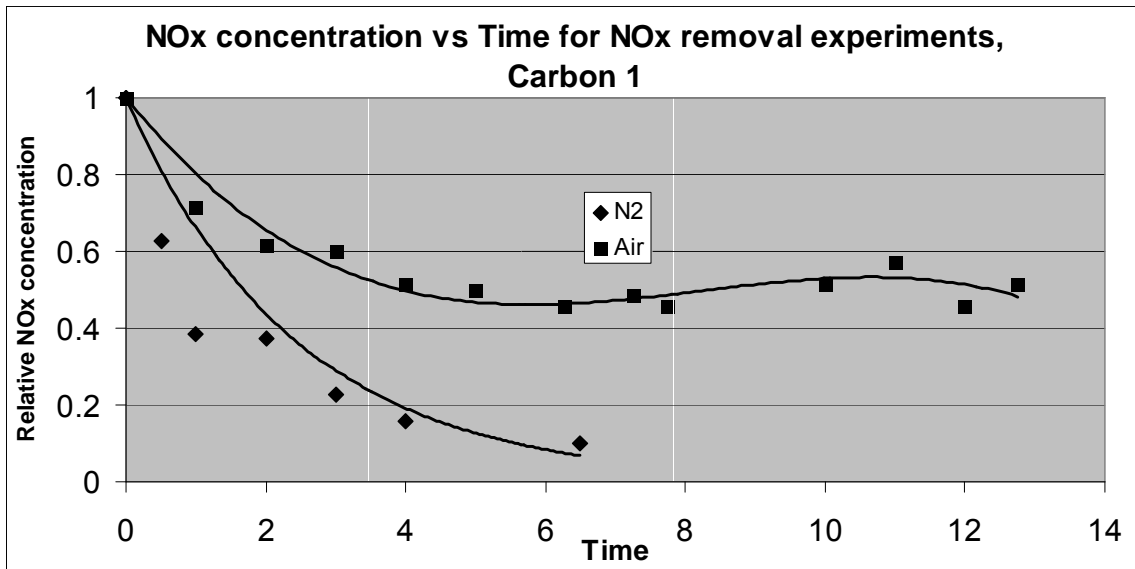


Figure 27: Stripping performance of N<sub>2</sub> and air for NOx removal from sulfuric acid

The results of all 5 tested carbons show the same result in which NOx removal is slower in the presence of carbon and oxygen. The presence and type of the carbon does however impact the rate of NOx removal because there are significant differences in the rate of NOx removal between the carbons tested. See Figure 28 which shows the relative rate of NOx removal for the different carbons.

The identity of the carbon has a significant effect on the rate of NOx removal in the presence of N<sub>2</sub> and Air. Some carbons had significantly better performance than others with carbons 1 and 2 having the best performance. Carbons 4 and 5 show little effectiveness for NOx removal using N<sub>2</sub> as the stripping gas; even less ability is observed for NOx removal in the presence of air. In all cases the rate of NOx removal is slower in the presence of O<sub>2</sub> indicating that NOx removal may be somehow slowed by some type of oxidative chemistry. This result is opposite of what was expected and means that this method of NOx removal from the circulating acid and/or the product acid is not viable as a method for selective NOx removal.

	Relative NOx removal rate	
	N2	Air
Carbon 1	1.00	0.65
Carbon 2	0.92	0.13
Carbon 3	0.29	0.14
Carbon 4	0.04	0.00
Carbon 5	0.15	0.00

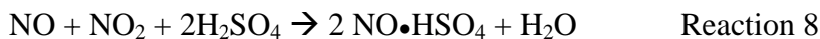
Figure 28: Relative rate of NOx removal for various carbons using N<sub>2</sub> and air

## Subtask 2.4 Byproduct Purification

At the completion of Subtask 2.3, and associated Milestone M4, it was concluded that the candidate catalysts for the NO<sub>x</sub> stripping reactor would not be able to remove NO<sub>x</sub> from concentrated sulfuric acid to produce acid of appropriate purity for sale in the standard industrial market. The NO<sub>x</sub> removal was much too slow to be of any value in the proposed process. Based on these results it was decided that the NO<sub>x</sub> stripping reactor should be removed from the process and that other technologies should be evaluated for NO<sub>x</sub> removal from the product sulfuric acid.

In the proposal the performance of the NO<sub>x</sub> stripping reactor was identified as the most likely Task 2 process risk. This possibility was considered when the proposal was written and Task 2.4 was included in the original proposal to address this possibility through evaluation of alternative NO<sub>x</sub> removal methods. In this scenario the evaluation of the alternative NO<sub>x</sub> removal methods is required by Subtask 2.4 to satisfy Milestone M7. The approach taken was to evaluate methods of NO<sub>x</sub> removal used in the contact-process-based sulfuric acid industry and to rule out those methods that are not appropriate due to the Task 2 process reliance on lead chamber based chemistry.

NO<sub>x</sub> absorption into sulfuric acid occurs most substantially when NO and NO<sub>2</sub> are in a 1:1 ratio, forming nitrosylsulfuric acid (NO•HSO<sub>4</sub>), see Reaction 8. The absorption behavior of NO<sub>x</sub> mixtures at various temperatures and pressures has been the subject of much of the experimental data collected in Task 2 and was discussed above. Absorbed NO<sub>x</sub> is very important to the Task 2 process because it is required for SO<sub>2</sub> conversion to sulfuric acid in the process. However nitrosylsulfuric acid is also a contaminant to the final product sulfuric acid and should be removed to the extent possible, ideally down to a level of < 5ppmw, to ensure the product sulfuric acid is useful, and hopefully saleable, to sulfuric acid consumers.



Nitrosylsulfuric acid contaminant in sulfuric acid is commonly referred to as ‘nitrates’ and has a limit in typical sulfuric acid of 5 to 10 ppmw. The presence of nitrates discolors sulfuric acid and can accelerate corrosion of steel equipment. High NO<sub>x</sub> levels have also been suspected of attacking the protective coating in tank cars.

In the past, NO<sub>x</sub> levels as high as 30 ppmw (as NO<sub>3</sub>) have been acceptable in product sulfuric acid. Current requirements are much lower at 5 ppmw or less. Sulfuric acid destined for use in the sulphonation industry requires low nitrate levels. If the acid contains high nitrate concentrations a dark black, rather than honey colored, acid slurry is formed which is cause for rejection of the acid.

High concentrations of NO<sub>x</sub> in the product acid may pose an occupational health problem if NO<sub>x</sub> is subsequently released in the process, usually as a result of diluting the acid. The reaction of NO<sub>x</sub> and dissolved iron can impart a purple color to the acid which gives the impression that the acid is otherwise off-spec.

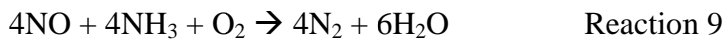
There is an expectation from acid distributors and customers that NO<sub>x</sub> levels need to be below 5 ppm even if the presence of NO<sub>x</sub> does not have any impact on the process in which the acid is used. This acid will probably go into a common storage tank with acid from other sources. Customers or acid distributors would not want to risk contaminating their entire inventory of acid because of one off-spec shipment. Acid with high NO<sub>x</sub> concentrations can be utilized in the phosphate fertilizer industry, the largest consumer of acid, with potential for no impact on the fertilizer production process.

## NO<sub>x</sub> Control Strategies

NO<sub>x</sub> control strategies for traditional contact sulfuric acid plants are broadly divided into two categories: 1) NO<sub>x</sub> removal from the feed gas prior to entering the contact plant and 2) NO<sub>x</sub> removal from the liquid acid. In a traditional sulfuric acid plant NO<sub>x</sub> is not involved in the desirable chemistry of the plant because SO<sub>2</sub> is directly oxidized to SO<sub>3</sub> on a solid catalyst in the gas phase. Therefore it is typically advantageous and less expensive to remove NO<sub>x</sub> to the extent possible before it enters the process and has the opportunity to contaminate the product sulfuric acid.

## Gas Phase NO<sub>x</sub> Removal

In the context of a contact sulfuric acid plant the most desirable location to remove NO<sub>x</sub> is before the flue gas enters the contact plant, this is done with the use of a selective catalytic reduction (SCR) unit or a selective non-catalytic reduction (SNCR) unit [1]. The SCR process involves the reaction of NO and NO<sub>2</sub> with ammonia or urea in the presence of a catalyst to form nitrogen and water, reactions 2 and 3. The approach and equipment are essentially the same as in a power plant's SCR.

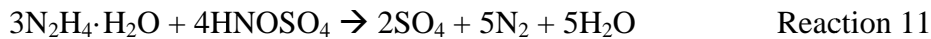


Traditional SCR and SNCR technologies are not of interest in the context of the Near Zero Emission Oxy-Combustion Flue Gas Purification program because the goal of the program is to evaluate other more cost effective technologies for flue gas purification. Furthermore NO<sub>x</sub> cannot be removed before the Task 2 flue gas purification scheme because the Task 2 process relies on NO<sub>x</sub> for SO<sub>2</sub> conversion to H<sub>2</sub>SO<sub>4</sub>.

## NO<sub>x</sub> Removal from Liquid Acid

One approach for NO<sub>x</sub> treatment in the liquid phase processes is to reduce NO<sub>x</sub> in the product acid by the addition of strong reducing reagents to destroy NO<sub>x</sub> compounds in the acid. The most common reducing agent used is hydrazine (H<sub>2</sub>N<sub>4</sub>), hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) or dihydrazine sulfate ((N<sub>2</sub>H<sub>2</sub>)<sub>2</sub>H<sub>2</sub>SO<sub>4</sub>) because they are the most effective reducing agents. Other reducing agents are urea (NH<sub>2</sub>CONH<sub>2</sub>), hydroxyl-ammonium sulfate ((NH<sub>2</sub>OH)·H<sub>2</sub>SO<sub>4</sub>) and hydroxylamine (NH<sub>2</sub>OH). Reagents that are non-hydrazine based are typically not used with concentrated sulfuric acid because their

reaction rate is too slow to be practical. The reaction between hydrazine hydrate and nitrosylsulfuric acid is as follows:



The elimination of NO<sub>x</sub> using hydrazine is affected by several factors:

- Acid Strength – reaction rate is higher in 93% H<sub>2</sub>SO<sub>4</sub> than 98% H<sub>2</sub>SO<sub>4</sub>
- Acid Temperature – reaction rate increases with increasing temperature
- Excess Hydrazine – the reaction rate is roughly proportional to % excess hydrazine
- Sulfur Dioxide – the presence of SO<sub>2</sub> reduces the reaction rate
- Residence time

Hydrazine chemicals are the most common and effective chemicals for NO<sub>x</sub> destruction in sulfuric acid but these chemicals are extremely toxic and are possible carcinogens. Hydrazine compounds are used to remove similar levels of NO<sub>x</sub> from sulfuric acid in contact plants as would be seen in the Task 2 process, however the total flowrate of acid requiring treatment is typically small because NO<sub>x</sub> concentrates in a very specific location in contact sulfuric acid plants where the rate of acid accumulation is low (candle filter drains in mist eliminators). In a traditional contact sulfuric acid plant only a small stream of acid is treated and added back to the process.

When hydrazine is used some amount of excess hydrazine is typically needed to achieve adequate destruction of NO<sub>x</sub>, however it is important that no excess hydrazine remains in the product acid. Typically a secondary hydrogen peroxide addition is used to consume the excess hydrazine. Treatment of sulfuric acid using hydrazine or hydrazine related compounds is expensive due to the cost of the reagent, the cost of installing an engineered hydrazine storage and delivery system, and the cost of the ozone supply and treatment system. In the context of the Task 2 process these costs are expected to be prohibitively expensive (hydrazine for example is more expensive and more toxic than ammonia).

A second approach for removal of NO<sub>x</sub> from liquid sulfuric acid involves the dilution of concentrated sulfuric acid containing nitrosylsulfuric acid. Nitrosylsulfuric acid has a very high solubility in concentrated 93wt% sulfuric acid but has a fairly low solubility in sulfuric acid of 60wt% concentration and below. Nitrosylsulfuric acid concentrations in the candle filters of a traditional contact sulfuric acid plant is typically 5wt% to 20wt%.

When sulfuric acid containing NO<sub>x</sub> is diluted the nitrosylsulfuric acid is hydrolyzed and NO<sub>x</sub> fumes are released. In sulfuric acid the heat of dilution is substantial and enhances the NO<sub>x</sub> removal effect when NO<sub>x</sub> containing sulfuric acid is diluted because the diluted acid is substantially warmed. The released NO and NO<sub>2</sub> is of very high concentration and must be captured, for example by contact with water to make a dilute nitric/nitrous acid solution. Low concentration sulfuric acid has no value and is typically prohibitively expensive to concentrate to a saleable concentration of 93wt% or greater.

## **Subtask 2.5 Mercury Removal Research**

The Near Zero Emission Oxy-Combustion Flue Gas Purification proposal included the use of a wet scrubbing process for the removal of mercury from the process gas stream. The scrubbing process uses sulfuric acid at concentrations greater than 80 wt.% H<sub>2</sub>SO<sub>4</sub>. The mercury in the process gas reacts to form mercury sulfate which precipitates and would be removed from solution by clarification and filtration. There is some risk involved with the process since it was not originally designed as a high pressure process gas containing mercury.

Moderate levels of mercury containment, about 90%, are typically seen in mercury removal technologies for the sulfuric acid industry. This level of Hg containment may be adequate prior to the Task 2 process in the case that any sulfuric acid product needs to be saleable from a mercury impurity standpoint. However in a CPU process a very high level of mercury containment (> 99.9%) is absolutely essential prior to the flue gas entering the coldbox due to the potential severe consequences of mercury in the coldbox. This extremely high level of mercury containment is likely not possible through mercury containment that is designed for sulfuric acid manufacture. Two main scenarios exist:

- 1) If the acid product from the Task 2 process is saleable some Hg removal may be needed upstream of the Task 2 process. A mercury guard bed would also be needed downstream of the Task 2 process to ensure that no mercury makes it to the CO<sub>2</sub> purification coldbox.
- 2) If the acid product is not saleable the sulfuric acid product will likely be neutralized, in which case it is likely that the neutralization product will be landfilled and the mercury content will not be an issue. In this scenario a single Hg adsorbent bed would be used prior to the cold box.

Worley Parsons has offered some mercury control alternatives to the wet scrubbing method in the proposal since this method is not widely used in the sulfuric acid industry. The mercury containment methods described below are alternatives to mercury containment that would be needed upstream of the Task 2 process for control of mercury in the potential sulfuric acid product.

Alternative processes such as adsorption of mercury on activated carbon or selenium filters are used in the traditional sulfuric acid industry for control of mercury in the sulfuric acid product. These processes do not involve circulating scrubbing solutions and only passing the process gas through a fixed bed of material. Two parallel units are recommended to allow one unit to be taken out of service for servicing and replacement of the materials while the other unit remains on line. There is an ongoing operating cost associated with replacing the material and disposing or recycling of the spent material. The design of the equipment is simply a pressure vessel designed to hold the required material. Little in the way of ancillary equipment would be required.

### Activated Carbon

The adsorption properties of activated carbon have been used for removal of heavy metals (among them mercury), organic pollutants (such as dioxin and furans) and acid gases (HCl, SO<sub>2</sub>). Three filter designs are typically utilized and are categorized based on the flow configuration as follows: cross flow, counter-cross flow and cross-current flow. However, the cross-flow carbon filters are most common. The adsorption capacity of the carbon filter is sensitive to humidity in the gas stream and is limited by temperature. Tight control over temperature is needed to avoid volatilization and release of mercury and to avoid creation of “hot spots”. The cross-flow design is used to minimize this risk by distributing the gas equally. Carbon monoxide sensors are installed to detect the formation of fires in the bed. The typical values reported in literature of mercury adsorption efficiency for activated carbon range between 12% and 20% of the carbon weight. Research is always geared towards increasing the porosity of the carbon to increase this efficiency. The pressure drop across the filter depends on the size of the filter bed and the amount of carbon used. If the gas contains particulate the pressure drop will increase eventually requiring replacement and renewal of the bed.

The spent carbon can be thermally treated in rotary kilns to re-establish its adsorption features. Steam is used to create a reducing environment in the activating kilns and avoid oxidation of carbon. Alternatively, the spent carbon can be disposed of in an appropriate landfill. The technology is widely used in the power industry and to remove organic material and heavy metals from off-gas streams at incineration sites in Europe. The main advantages and disadvantages of the activated carbon filter are listed in Figure 29.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>▶ Modular construction</li> <li>▶ Minimum ancillary equipment</li> <li>▶ High removal efficiency and low mercury output</li> <li>▶ Common reagent</li> <li>▶ Simple to operate and maintain</li> </ul>	<ul style="list-style-type: none"> <li>▶ Relatively low loading value</li> <li>▶ Disposal of contaminated carbon</li> <li>▶ Sensitivity to temperature and humidity</li> <li>▶ Side reactions</li> </ul>

Mercury removal efficiency is >90%.

**Figure 29: Advantages and disadvantages of the activated carbon filter**

The cost for activated carbon is approximately \$2100/tonne of carbon. The replacement of the carbon bed will depend on the gas flow and mercury content of the gas. Sizing the unit in terms of carbon loading will take into account the frequency of carbon replacement and maintenance cost. A typical mercury adsorption system would consist of parallel columns such that a column could be taken out of service to replace carbon when it becomes fully loaded. Sufficient isolation would be provided to enable the work to be done safely while the other column remains in operation. For this application an activated carbon loading of 10,000 lb would be loaded into a 1900 mm (6.3 ft) diameter column with a carbon bed height of about 3050 mm (10 ft) high. The activated carbon would be able to adsorb about 1500 lb of mercury before needing to be replaced.

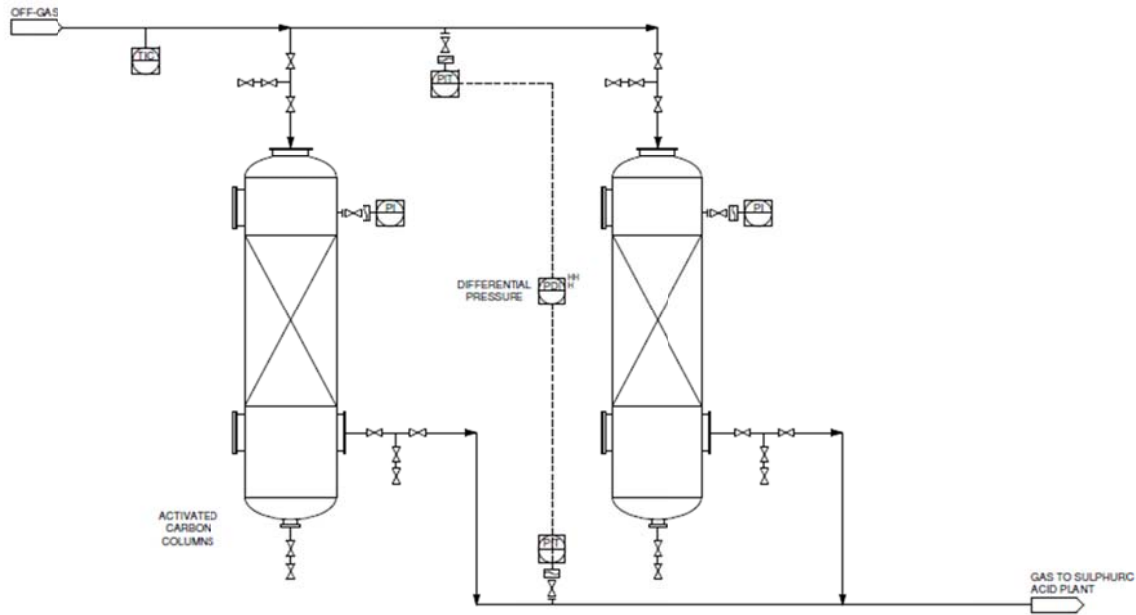
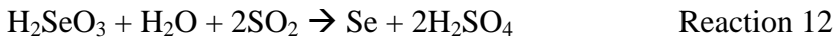


Figure 30: Activated carbon mercury removal system

### Selenium Filter

Selenium filters were developed by Boliden (currently Outotec) to target and remove elemental Hg from metallurgical off-gases based on the affinity between selenium (Se) and Hg. The filter consists of porous inert material (stainless steel or ceramic grains impregnated with metallic Se) soaked with selenious acid that reacts with water vapor and sulfur dioxide in the process gas to precipitate selenium (Reaction 12). Consequently, Se reacts with elemental Hg vapor in the gas to form mercury selenide, HgSe, (Reaction 13). The Hg removal process is summarized by the following reactions:



The key to the operation of the selenium filter is the speciation of the mercury in the gas. Mercury must be present as elemental mercury for the selenium filter to be effective. Once the mercury and selenium react, the resulting compound has a much lower vapor pressure than either elemental mercury or HgS which ensures low residual mercury levels in the gas as shown in Figure 31.



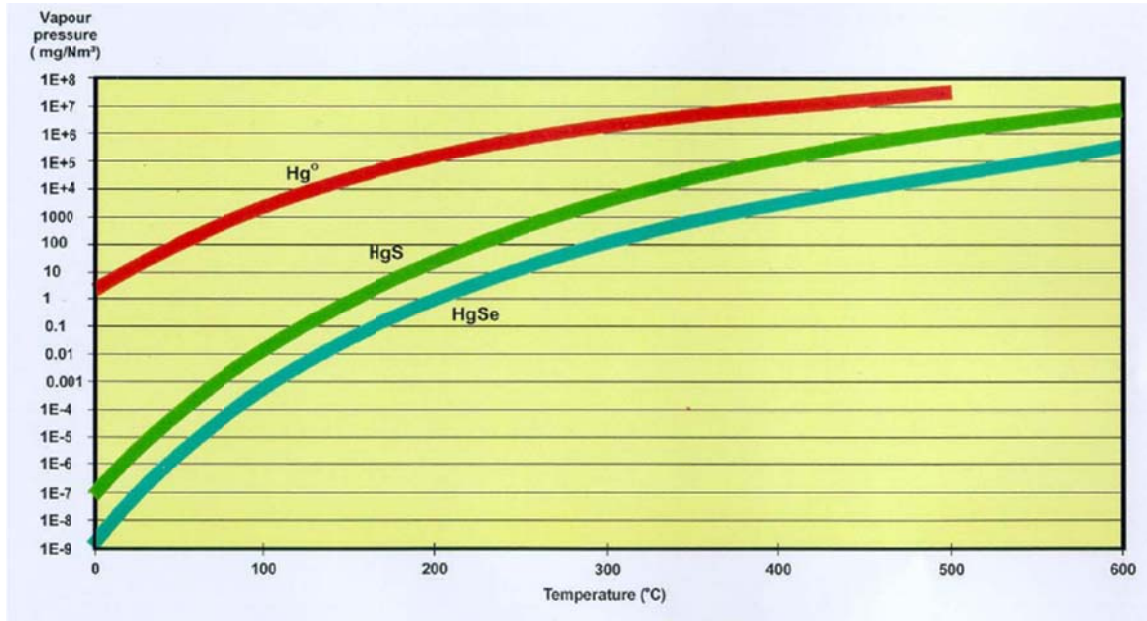


Figure 31: Vapor pressure for Hg, HgS and HgSe

The filter generally consists of two layers or beds. The first layer acts as a dust filter while the second filter is the active medium in which the above reactions take place and HgSe is formed. A schematic of the selenium filter is shown in Figure 34.

The selenium filter continues to be effective until the level of mercury in the filter reaches 10-15%wt. The filter can then be treated to recover Hg and regenerate Se. The selenium filter method is suited for low to medium Hg concentrations in the process gas. The filter operates efficiently up to 9 mg/m<sup>3</sup>. Higher Hg concentration decreases the lifetime of the filter requiring more frequent regeneration of Se, making its operation costly. At lower Hg concentrations, the removal efficiency is decreased because of reduced molecular collisions between Hg and Se.

The temperature of the gases entering the selenium filter is limited to 120°C to avoid decomposition of HgSe in the filter and to enhance the rate of formation for HgSe. Dust loading below 9 mg/m<sup>3</sup> is recommended to avoid frequent filter washing and reduce downtime. Water degrades active selenium and the relative humidity in the off-gas needs to be controlled to avoid formation of water droplets.

The selenium filter has been used in metallurgical off-gas applications as well as from geothermal off gases. In geothermal applications, the steam generated underground contains non-condensable gases such as CO<sub>2</sub> and contaminants such as mercury and hydrogen sulphide (H<sub>2</sub>S). The off-gases are treated in a selenium filter to remove mercury which would otherwise be vented to atmosphere. Typical operational parameters for a selenium filter are listed in Figure 32. A summary of advantages and disadvantages of the selenium filter method is presented in Figure 33.

Item	Operating Parameter
Flow rates through standard filter sizes	535 to 53500 m <sup>3</sup> /h
Effective Hg removal range	Up to 9 mg/m <sup>3</sup>
Recommended residence time	2 seconds or more
Operating temperature	120 °C
Removal efficiency	>90 %
Pressure drop	50 mmH <sub>2</sub> O
Dust contamination	Up to 9 mg/m <sup>3</sup> for feasible operation
Typical filter material usage	1 m <sup>3</sup> of filter material to convert 50 kg of Hg to HgSe
Average lifetime	5 years (depending on mechanical construction of filter, Hg content in flue gases and pressure drop)
Mercury Selenide disposal	Landfilled or processed for Hg recovery and Se regeneration

Figure 32: Typical Operational Parameters for a Selenium Filter

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>▶ Modular construction</li> <li>▶ No liquids to pump, spill or treat</li> <li>▶ High mercury removal efficiency</li> <li>▶ Easy regeneration and recovery processes</li> <li>▶ Selective for mercury, no side reactions or catalytic activity</li> </ul>	<ul style="list-style-type: none"> <li>▶ Selenium cost is expensive</li> <li>▶ Disposal or regeneration of the selenium filter</li> <li>▶ High mercury loading may require frequent filter washing</li> <li>▶ Lowering the relative humidity involves higher costs by addition of heat exchanger, fan for compression</li> <li>▶ Low dust loading required</li> <li>▶ Low temperature required</li> <li>▶ There is a possibility of forming other selenium compounds in the filter that would reduce the Hg removal effectiveness</li> </ul>

Figure 33: Advantages and disadvantages of the selenium filter

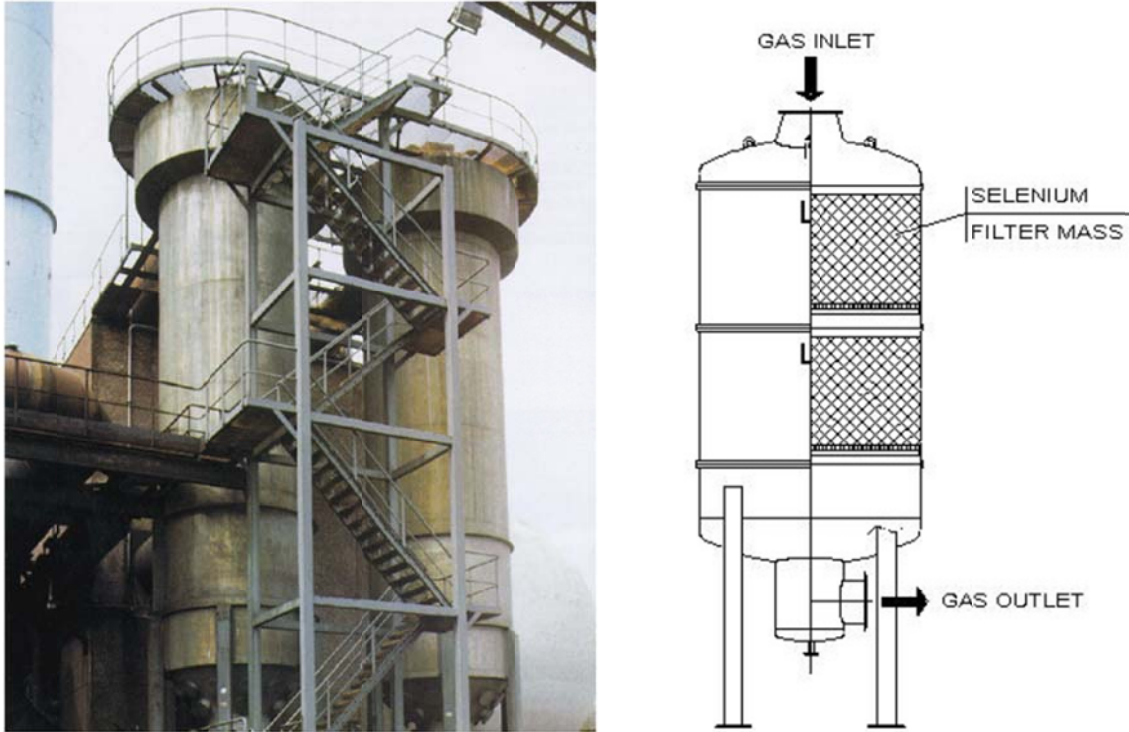


Figure 34: Typical selenium filter arrangements

In addition to the operational Selenium disadvantages described above the selenium filter approach would likely not be possible in an Oxycoal CPU because of any potential interactions of selenium with the materials in the CPU coldbox. For example heavy metals in general are known to react destructively with aluminum metal.

### Subtask 5.1 Process Simulation

Process simulation of the final Task 2 process scheme required manual iteration using different simulation tools and experimental data due to the complexity of the process simulation and the inability of any available single process simulation tool (e.g. Unisim, AspenPlus, etc.) to accurately predict the thermodynamics, chemistry and reaction behavior of the Task 2 process. The main difficulties in simulating the Task 2 process are related to 1) gas and liquid phase reactions occurring in mass transfer columns (reaction-distillation type problem), 2) general sulfuric acid adsorptive characteristics (e.g., moisture and CO<sub>2</sub>), 3) the unique chemistry that occurs between sulfuric acid and NO<sub>x</sub> (with this third item being the most complex and sensitive aspect of the system).

The procedure used for simulating the system was to first use a standard process simulation software (Honeywell Unisim) for high level mass and energy balance of the system. In this mass and energy balance simulation simple reactors and component splitters were used to look at the process at a high level. The main purposes being to 1) estimate the required acid recirculation rates needed to manage the system temperatures

(for thermal management and for rough vessel sizing), 2) investigate the acid concentrations in the system (moisture management), and 3) in the case of the final simulation iteration, to determine the need for any process changes from a high level mass and energy balance perspective.

Following the mass and energy balance simulation some more detailed reaction modeling was performed to model the NO oxidation behavior of the system to fine tune the NOx conversion assumptions in the various vessels. Next experimental data is used to update the assumed NOx absorption and desorption behavior as well as the SO<sub>2</sub> oxidation behavior. These revised assumptions were then used to update the mass and energy balance simulation for the next iteration.

The low pressure flue gas conditions and composition used in the final Task 2 process simulation was taken from the Foster Wheeler report High Sulfur Bituminous Coal case. Specifically the flue gas for the “Reduced SOx” case was used because it represents the case which is most commercially relevant at this time. In the two high sulfur bituminous coal cases a traditional FGD has been used to remove SOx from the primary air stream. In the “Reduced SOx” case a portion of the secondary air stream has also been treated for SOx removal. The “Reduced SOx” case addresses potential corrosion issues on the superheater/reheater that are possible with a SOx content of above 4000ppm SOx, as described in more detail in the Foster Wheeler report. The “Reduced SOx” case represents the highest levels of SOx that Foster Wheeler would be comfortable with in this oxy-combustion scenario given the corrosion issues and their boiler experience.

The Flue gas from the “Reduced SOx” case leaves the boiler island and is compressed in 5 intercooled-centrifugal compressors (no aftercooler is needed) to an appropriate pressure for treatment in the Task 2 process and subsequently in the cold box portion of the CPU process. The gas conditions entering the Task 2 process are shown below in Figure 35. In the compression train a negligible amount of SO<sub>2</sub> is lost through NO<sub>2</sub> catalyzed-oxidation because the residence time in the intercoolers is low. However, roughly 15% of the NOx is lost in the last 2 intercoolers through NO oxidation and contact with water. From Figure 35 it is notable that the inlet gas concentration has only 12 times more SO<sub>2</sub> than NOx, on a molar basis, which reflects the much lower SOx levels in the gas stream as compared to the gas composition assumed in the proposal. It is also important to note that in this ‘Reduced SOx’ case the SOx levels fed to the Task 2 process are not very different from the SOx level expected in the flue gas from the low sulfur coal case.

Temperature (F)	203.7
Pressure (psia)	377.6
Mole flow (lbmol/hr)	23373
mass flow (lb/hr)	980940

Mole Fraction	
CO <sub>2</sub>	0.831545
O <sub>2</sub>	0.040943
Ar	0.031863
N <sub>2</sub>	0.086433
SO <sub>2</sub>	0.004198
NO	0.000335
NO <sub>2</sub>	0.000067
H <sub>2</sub> O	0.004260
SO <sub>3</sub>	0.000000
CO	0.000356

Figure 35: Pressurized flue gas composition for feed to the Task 2 process

As discussed above the Task 2 related experimentation and literature review has found no method for selective removal of NO<sub>x</sub> from the Task 2 process (appropriate to maintain the ability to produce concentrated sulfuric acid as was assumed in the proposal process). With no method to remove NO<sub>x</sub> from concentrated sulfuric acid the “NO<sub>x</sub> Stripping Reactor” has been removed from the process. In this final process design every mole of product sulfuric acid could contain up to about 0.08 mole NO<sub>x</sub> (assuming 100% NO<sub>x</sub> capture). This is an extremely high level of NO<sub>x</sub> that would introduce significant safety considerations related to depressurization and handling of the product acid.

The best possible yield of sulfuric acid, and maximum possible benefit of the Task 2 process, would be achieved if all the coal sulfur could be sent to the CPU in the form of SO<sub>2</sub> and if all the SO<sub>2</sub> was converted to concentrated, pure, saleable sulfuric acid in the Task 2 process, however as described this is not feasible given the input from FW (this was the assumption in the proposal). In the other extreme, the Task 2 process, as currently configured, cannot produce concentrated acid if the SO<sub>2</sub> concentration to the CPU is too low because the water vapor in the CPU leaving the raw gas compression train would be more than is necessary to produce 93wt% sulfuric acid and the acid product would be too dilute (sulfuric acid concentration is typically too energy intensive to be viable).

As described above a mass and energy balance simulation was first completed with Honeywell Unisim. The mass and energy balance simulation alone was able to identify a necessary minor process change that is due to a significantly lower SO<sub>x</sub> concentration (and higher water concentration relative to the SO<sub>x</sub> level) in the flue gas. The inlet gas contains roughly equivalent molar amounts of SO<sub>2</sub> and water; this amount of moisture is already enough to make 100wt% sulfuric acid; only about 30% more water is required to make 93wt% sulfuric acid. This small amount water is added to the ‘SO<sub>x</sub> Reactor’ however it is not enough to hydrolyze all the SO<sub>3</sub> that is formed in the ‘SO<sub>x</sub> Reactor’ vessel. A stream of the circulating ~93wt% sulfuric acid going to the ‘NO<sub>x</sub>

Stripper’ is added to the ‘SOx Reactor’ vessel to supply the extra water required to ensure the sulfuric acid concentration in the ‘SOx Reactor’ vessel does not exceed 100%. Sulfuric acid exceeding 100% concentration (oleum) contains un-hydrolyzed SO<sub>3</sub>, which would introduce significant additional safety considerations and material of construction issues. The updated process configuration is shown in Figure 36.

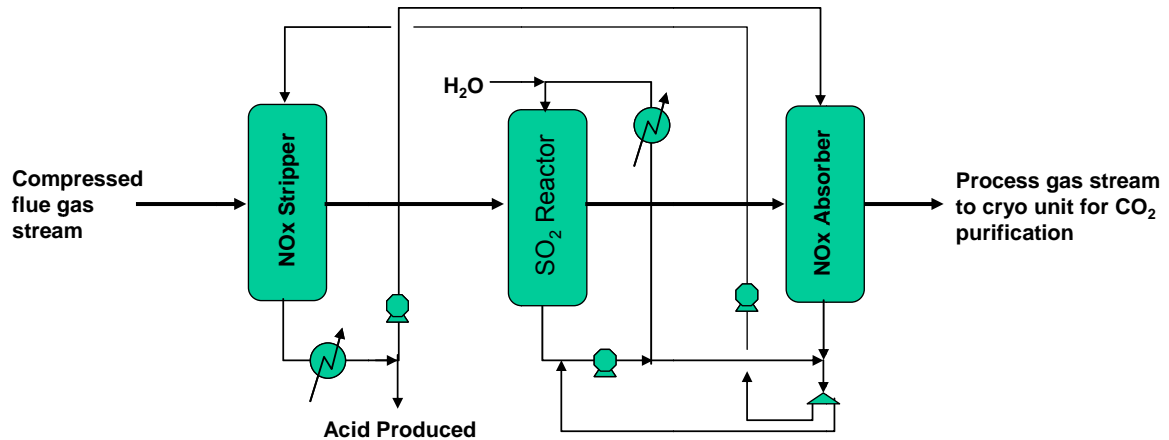
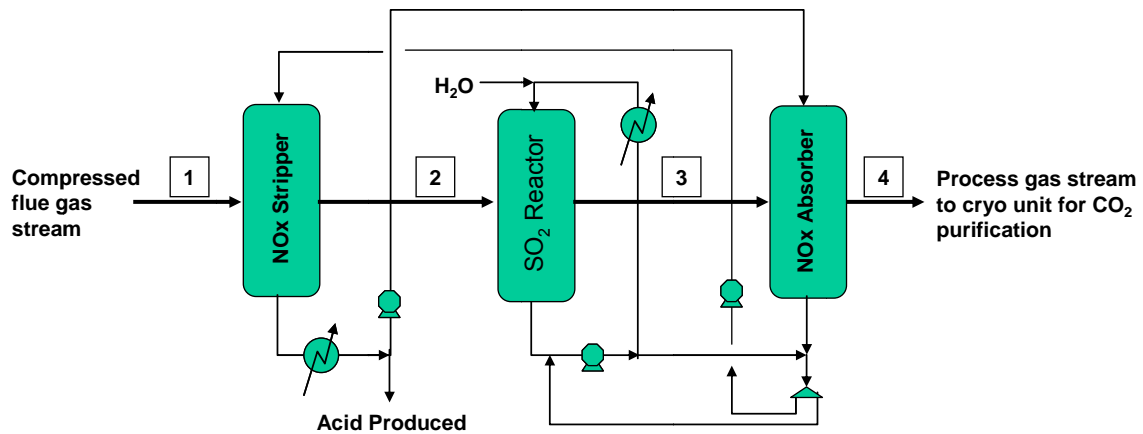


Figure 36: Process schematic of the final Task 2 process

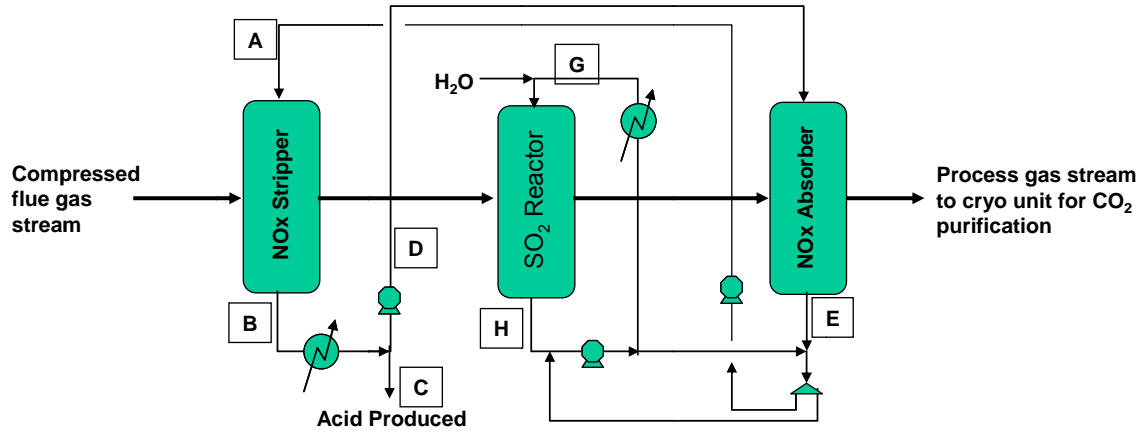
With this updated flowsheet configuration iterations were made between the simulation tools and experimental data to estimate the performance of each of the three vessels. Acid recirculation rates and gas flowrates are used to estimate vessel size and reaction residence times. A high level stream summary of the gas and liquid streams is given in Figure 37 and Figure 38.



Gas Stream	1	2	3	4
Temperature (F)	203.7	170.3	109.7	104.7
Pressure (psia)	377.6	374.6	371.6	368.6
Mole flow (lbmol/hr)	23373	23422	23321	23117
mass flow (lb/hr)	980940	985852	979574	971063

Mole Fraction				
CO <sub>2</sub>	0.831545	0.829799	0.833402	0.840744
O <sub>2</sub>	0.040943	0.040522	0.038798	0.039129
Ar	0.031863	0.031797	0.031935	0.032216
N <sub>2</sub>	0.086433	0.086251	0.086626	0.087389
SO <sub>2</sub>	0.004198	0.003770	0.000038	0.000038
NO	0.000335	0.000282	0.000244	0.000001
NO <sub>2</sub>	0.000067	0.007087	0.007428	0.000121
H <sub>2</sub> O	0.004260	0.000138	0.001172	0.000003
SO <sub>3</sub>	-	-	-	-
CO	0.000356	0.000355	0.000357	0.000360

Figure 37: Stream summary for gas streams of final process simulation



Liquid Stream	A	B	C	D	E	G	H
Temperature (F)	122	199	100	100	112	100	145
Pressure (psia)	390.0	377.6	377.6	377.6	371.6	374.6	374.6
Mole flow (lbmol/hr)	2773	2705	135	2570	2773	10692	10692
mass flow (lb/hr)	212554	207594	10380	197214	205726	881225	888043

Mass Fraction	A	B	C	D	E	G	H
H2SO4	0.893	0.919	0.919	0.919	0.881	0.918	0.921
H2O	0.047	0.056	0.056	0.056	0.056	0.029	0.027
NOx	0.060	0.025	0.025	0.025	0.063	0.053	0.052

Figure 38: Stream summary for liquid streams of final process simulation



The gas stream conditions for the process are shown in Figure 37 and the liquid stream conditions are shown in Figure 38. The simulated stream results show that in the 'NOx Stripper' a large amount of NOx is desorbed from the NOx-loaded acid. The gas leaving the NOx stripper contains about 7300 ppm of NOx with about 96% of the gas phase NOx being NO<sub>2</sub>. A small amount of SO<sub>2</sub> is reacted in the 'NOx Stripper' with the majority of SO<sub>2</sub> being reacted in the SO<sub>2</sub> reactor. The acid produced from the 'NOx Stripper' is has the lowest concentration of NOx in the process at about 2.5wt%.

The majority of gas SO<sub>2</sub> reacts in the 'SO<sub>2</sub> Reactor' because this vessel is larger and has much more circulating acid. The rate of SO<sub>2</sub> conversion to SO<sub>3</sub> is dependent on the amount of NOx containing acid present. In the 'NOx Absorber' NOx is absorbed by sulfuric acid for recirculation. The gas phase NOx leaving the 'SO<sub>2</sub> Reactor' contains roughly 7600ppm NOx. Roughly 98.5% of gas phase NOx is absorbed into the liquid acid in the 'NOx Absorber'. The absorption rate of NOx is not higher because the concentration of NOx in the acid is very high and because most of the gas phase NOx here is NO<sub>2</sub>. Although 98.5% NOx absorption seems fairly high, 98.5% absorption of 7600ppm NOx means that roughly 120ppm of NOx is leaving the Task 2 process. This means that the NOx capture rate for the Task 2 process is only about 70%.

Literature and experimental data show that maximum absorption rates for NOx are achieved when equal molar amounts of NO and NO<sub>2</sub> are contacted with acid that is substantially free of absorbed NOx. In the 'NOx Absorber,' and in the rest of the process, gas phase NOx is mostly composed of NO<sub>2</sub> due to the size of the 3 vessels (large residence time) and due to the fast gas phase reaction rate of NO to NO<sub>2</sub> at the process conditions. The vessels size cannot be decreased to reduce the amount of gas phase NO<sub>2</sub> because vessel size is determined by the acid and gas flowrates in the process.

For these reasons the NOx capture rate of the Task 2 process actually ends up being fairly low. The relatively high levels of NOx leaving the Task 2 process would likely present other material of construction and process issues in the downstream equipment such as the cold box and VPSA unit. The NO<sub>2</sub> present in the treated gas from the acid process can be scrubbed by water to improve the overall NOx removal efficiency to > 90%, while protecting the downstream equipment. This will require additional capital investment and it will also generate additional acidic waste water.

### ***Subtask 5.3 Commercial Viability of H<sub>2</sub>SO<sub>4</sub> Process***

#### **Sulfuric acid market**

Of all heavy industrial chemicals, sulfuric acid is said to be the one produced in the largest tonnage. As well, sulfuric acid is perhaps the most fundamentally important chemical that it plays a part in virtually all manufactured goods.

### World Production

In 2008, the world sulfuric acid production was estimated to be 205 million tonnes. The breakdown in terms of sources is as follows:

- Elemental sulfur 64%
- Smelter gas 28%
- Pyrites 7%
- Other 1%

Sulfuric acid produced from the oxy-combustion flue gas purification process falls in to the ‘Other’ category.

### Consumption

The breakdown in terms of consumption worldwide is as follows:

- Phosphate Fertilizer 48%
- Single Super Phosphate (SSP) 8%
- Ammonium Sulfate 7%
- Copper Leaching 4%
- Titanium Dioxide Production 3%
- Animal Feed 3%
- Technical Uses 2%
- Nickel Leaching 1%
- Other 24%

### World Trade

The majority of sulfuric acid is produced and consumed is relative close proximity to each other. In 2007, only 16 million tonnes of acid was traded on the international markets. This is only about 8% of the total world production. Some of this world trade in sulfuric acid does enter the USA market mainly to meet demand in the fertilizer industry.

### Prices

Historically, the price for sulfuric acid has remained fairly constant, particularly through the 1980’s and 1990’s (Figure 39). In the late 1990’s, there is a slight drop in prices because of the world recession. As the world came out of the recession we see the price of sulfuric acid increasing in-line with the general increase in manufacturing and country GDP.

The run up in the price of elemental sulfur and sulfuric acid beginning in 2007 saw the price for these commodities reach unprecedented levels which were unsustainable. When the world-wide recession hit at the end of 2008, prices collapsed to below the levels prior to the run up in prices. Figure 39 shows the Producer Price Index (PPI) for sulfuric acid to the end of 2008 and the sudden downturn in prices.

Sulfuric acid prices for May-June 2009 were \$0 to \$30 per tonne, US Gulf external (Figure 40). The traded market for sulfuric acid remains essentially stalled.

Suppliers are focusing on balancing the market in terms of supply and demand. In

early 2009, involuntary producers of sulfuric acid announced cutbacks in metals production because consumption of the by-product sulfuric acid had declined. In late 2009, some idle production has come back on-line but there still remain producers that are shut down due to labor issues and supply of concentrate.

The prices reported in the press are generally spot market prices which are subject to fluctuations based on supply and demand. Most producers and consumers of sulfuric acid have entered into ‘long-term’ contracts where the price of sulfuric acid is fixed and not subject to a lot of volatility. It is assumed that acid produced from flue gas purification plants will be marketed and sold according to the terms of long term contracts that are negotiated considering the current cost of acid.

For the purposes of this study, a price of \$50 per tonne of acid (100% basis) is assumed.

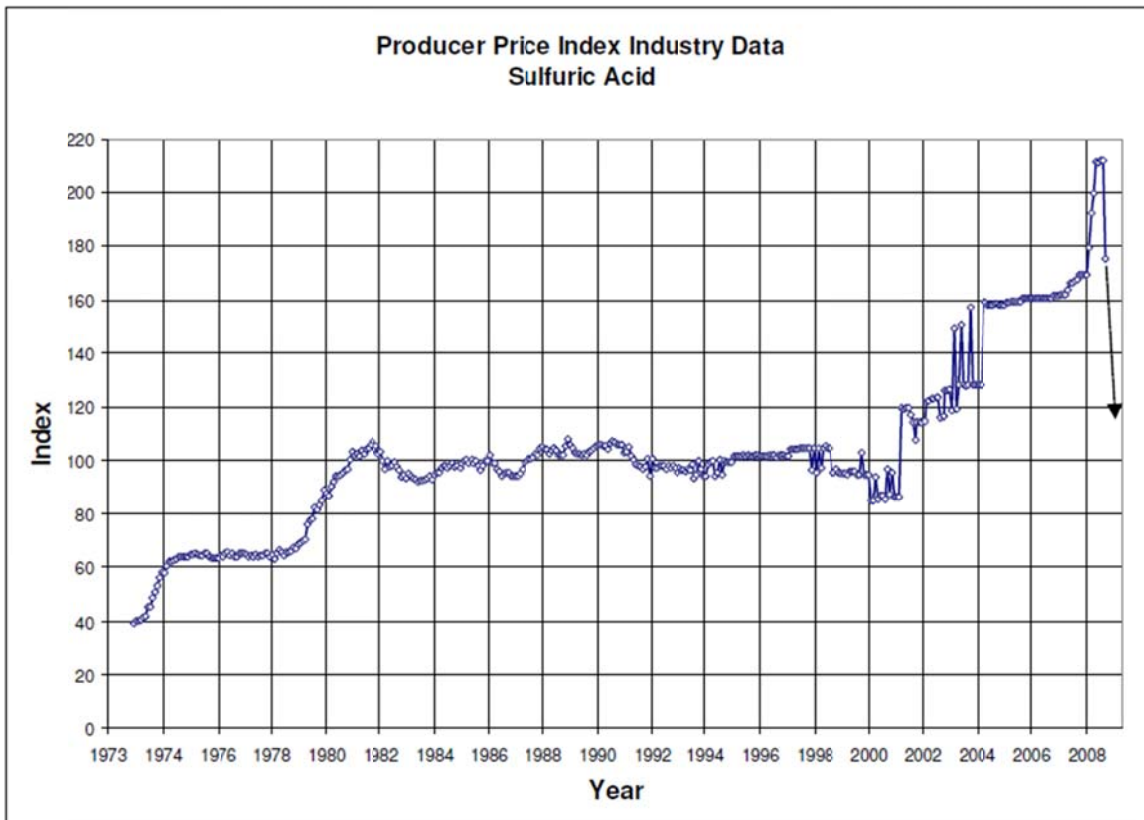


Figure 39: US Bureau of Labor statistics – producer price index for sulfuric acid

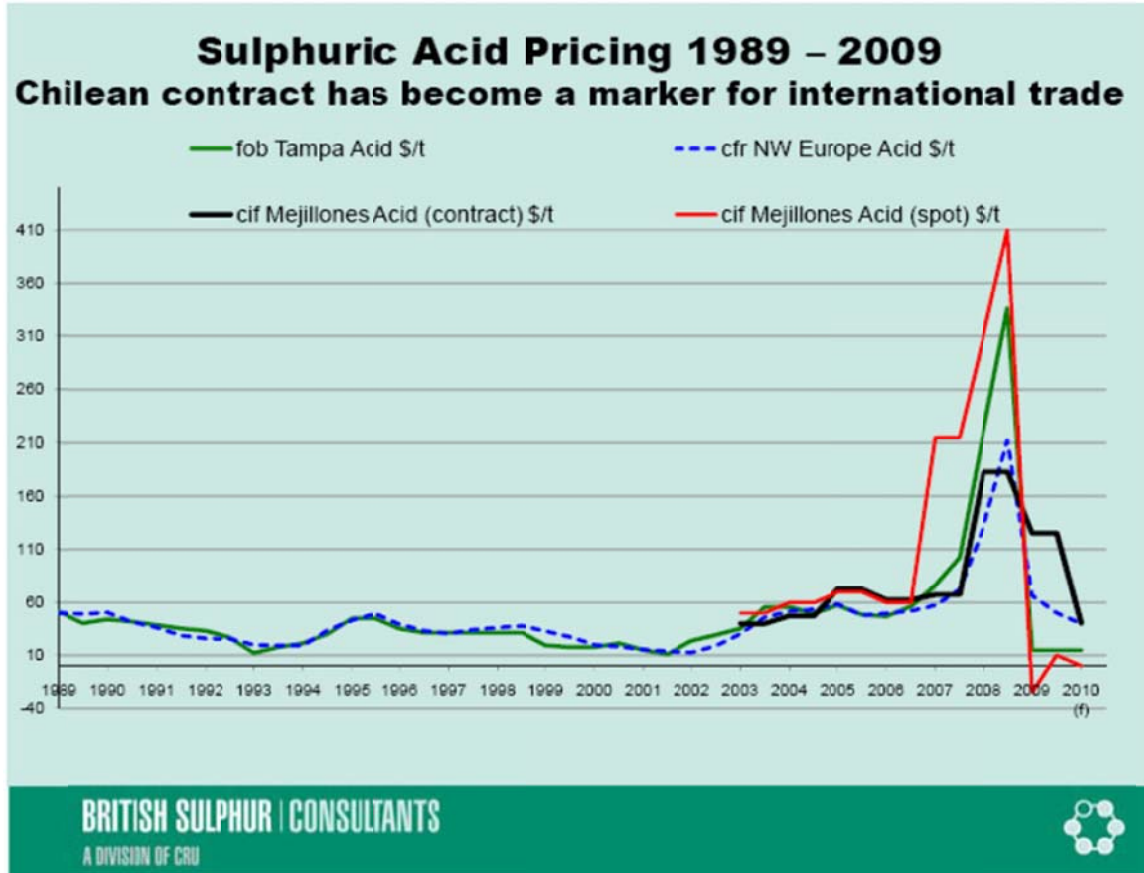


Figure 40: Sulfuric acid pricing 1989-2009

**USA and North American Market**

In 2008, the breakdown of the USA sulfuric acid market is as follows:

<u>Production</u>	Smelters	2,300,000 tonnes
	Sulfur Burning	28,000,000 tonnes
<u>Recycled</u>		3,150,000 tonnes
<u>Net Imports</u>		2,500,000 tonnes
<u>Total Supply</u>		35,950,000 tonnes

The USA does import sulfuric acid primarily into the Florida region to meet demand of the phosphate fertilizer industry. This excludes the acid that is imported from Canadian producers.

The production from the proposed facility is 325 MTPD or 118,625 tonnes per year (365 days/year). This represents 0.3% of the total supply of acid in the USA market for 2008.

Figure 41 shows the sulfuric acid producers for North America. Most production and hence consumption is located in the eastern USA with concentrations in the Florida and Gulf Coast areas. Production and consumption of acid in the western USA is

centered on the mining and metals, fertilizer, and petroleum (acid regeneration) industries.

### **New Production**

The following new production is scheduled to come on line in the next year or two in the USA:

Freeport McMoran (Safford):	420,000 MTPA
Martin Midstream (Beaumont):	150,000 MTPA
Southern States Chemicals (Wilmington):	150,000 MTPA

The new sulfuric acid plant for Freeport McMoran supplies an acid leach project in Arizona. The Martin Midstream plant is being built to supply local demand and consumption of sulfuric acid. Southern States Chemicals supplies sulfuric acid along the east coast and is building a new plant to replace two smaller older plants while increasing production two-fold.

### **Outlook**

The long-term outlook for sulfuric acid production and consumption in the USA is flat. One consulting firm anticipates a 1.5 million tonnes per year increase in acid consumption through to 2020. During the same period production is predicted to increase only 0.15 million tonnes per year. The difference between overall production and consumption is made up by acid imports. Current acid import is approximately 2.5 million tonnes per year.

Long term predictions of acid production, consumption and prices should be used with caution since they are essentially guesses. This problem with these predictions is illustrated by the fact that no one foresaw the run-up in prices and shortages that were seen in 2007 and 2008.

If this technology is widely adopted in the USA, there is the potential to produce 350,000 to 1,800,000 tonnes per year of acid if 10 to 50 plants are built over the next 10 years. This additional production will partially reduce the amount of acid imported into the USA each year. The degree to which this occurs will depend on many factors such as the location of the plant, transportation cost, the cost of imports, etc.

The remaining acid production will simply displace ‘voluntary’ acid produced by burning sulfur. The market will set the ‘involuntary’ acid price such that producers that burn sulfur to produce acid will be forced to cut-back production.

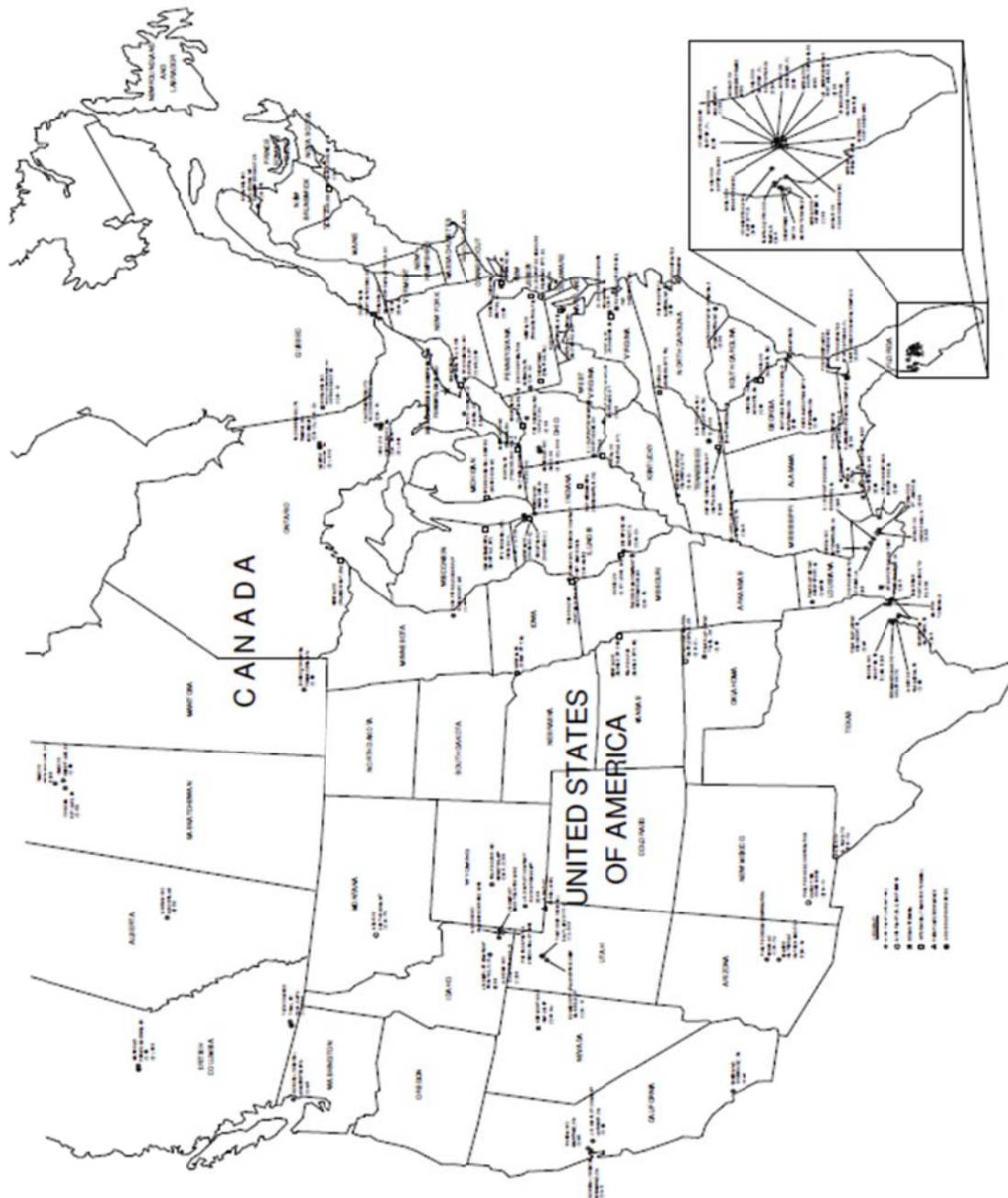


Figure 41: North American sulfuric acid producers

**Pennsylvania and Illinois Acid Markets**

Norfalco, a North American supplier and distributor of sulfuric acid were contacted to obtain information on the sulfuric acid markets in the Pennsylvania and Illinois markets. Figure 42 shows Norfalco’s North American Distribution network.

There is plenty of competition in the Pennsylvania and Illinois markets so it would not be difficult to sell the entire production of sulfuric acid from a number of potential Oxy-Combustion power plants that could be using the Task 2 technology. The 'local market' refers to the sulfuric acid market that can be served by truck transportation. Variations in the local market can be overcome by shipping the acid by rail tank car which opens up a larger market area. The cost of providing loading facilities for both truck and rail is more but provides more flexibility and options for disposing of the acid.

Norfalco recommend that a producing facility maintain 3 to 4 weeks of acid storage capacity. This amount of storage helps to mitigate risks related to market and production fluctuations. This study has currently assumed a 5000 MT storage tank giving ~10 days storage capacity. The amount of storage that will be required will depend on many factors which at this stage are based on very loose assumption about the plant size, location, market, etc.

Norfalco indicate that it is extremely difficult to predict pricing one year to the next and predicting prices 4 to 5 years from now is nearly impossible.

Companies that starting up acid production facilities that are not already acid producers often choose not to market the acid themselves due to the resources required to do it properly. Many companies instead opt to sell to specialist such as Norfalco that already have the infrastructure in place, market knowledge/awareness, transportation emergency response capabilities and a large customer base to spread out supply risks. The income from the sale of product acid is more consistent and predictable when this approach is used.

Norfalco offer a free service to sulfuric acid producers/suppliers where they share information on the sulfuric acid market, distribution business and market projections. This service can be used in the future when the technology is being proposed for a specific customer or site.

### **Transportation and Logistics**

As stated earlier, the majority of sulfuric acid is produced and consumed in close proximity to each other. The majority of the acid imported into the USA is from Canada. The acid is produced from the various smelters in northern Ontario and Quebec. This 'involuntary' acid is transported in large quantities by rail tank car into the markets in the northeast USA.

The primary restriction on the distribution of sulfuric acid is the high cost of transportation. The importation of Canadian smelter acid is a bit of an exception but it works because the acid is produced at low cost and large quantities of acid are transported.

In the eastern USA, there are two main importers of acid; Norfalco and Chemtrade Logistics. Both companies have extensive infrastructure for the storage, handling, transportation and distribution of sulfuric acid.

Over long distances, sulfuric acid is shipped by tank car in unit trains from the producers to terminals where it is stored and distributed to local customers by tank car or tank truck. Rail-to-truck transfer facilities avoid the need for storage facilities.

In North America, there are many producers and distributors of sulfuric acid. Some producers market their acid directly into the local market while others utilize distributors/traders. Some of the main producers and traders in the sulfuric acid market are:

<u>Company</u>	<u>Region</u>
Norfalco	Eastern USA
Chemtrade Logistics	Eastern USA
Southern States Chemicals	Eastern USA
Martin Midstream	Texas, US Gulf Coast
SATCO Florida,	US Gulf Coast, South-East USA
Rhodia	Across the USA (Acid Regeneration)
DuPont Chemical Solutions	Across the USA (Acid Regeneration)
PVS Chemicals	North, North-East USA



Figure 42: Norfalco Supply and Distribution Network for Sulfuric Acid

### Acid Production and Marketing

The acid produced from the purification of oxy-combustion flue gases is small in comparison to the entire USA market for sulfuric acid. The acid produced is considered



‘involuntary’ acid because it is a byproduct of another process and the operator has little choice but to continue to produce the acid.

There should be no problem in ‘disposing’ of the acid produced from a typical facility in the local market. Factors that will impact on the ability to market the acid are:

- Acid is produced at a marketable concentration (i.e. 93 to 98% H<sub>2</sub>SO<sub>4</sub>). The market for lower acid concentrations is smaller and the acid may need to be shipped further to consumers who can use the acid.
- Acid is produced free of impurities that may limit consumers who can use the acid.
- Location of the plant relative to consumers and other producers

If Praxair’s technology is applied to a facility located in the eastern USA, there should be no problem in marketing and selling the acid, if it is of appropriate purity. The acid produced would likely displace the production of ‘voluntary’ acid or acid that is shipped into the area from more distant producers.

The production and marketing of sulfuric will not be part of the core business of the owner and operator of a power generating plant. Therefore, it is unlikely that the owner will spend the time and resources to market, sell and distribute sulfuric acid to local consumers.

The most likely scenario, with acid of appropriate purity, is that an established sulfuric acid trader and marketing company will be engaged to remove and distribute the acid under a long term contract. As mentioned above in the byproduct purification section, if the acid is not of appropriate purity (with acid containing high levels of NO<sub>x</sub>, for instance) an acid distributor would be unwilling to accept the acid because the acid would typically have to be mixed in storage vessels with other high purity acid. The distributor would not want to risk contaminating their entire inventory of acid because of one off-spec shipment.

### **Commercial Byproduct Viability**

The high level of NO<sub>x</sub> in the sulfuric acid product makes the acid unmarketable to conventional customers. The only potential customers for acid containing these levels of extremely high NO<sub>x</sub> are customers dealing with nitration reactions this segment of the sulfuric acid market is a very small share and the demand for acid from these industries is small, such that the quantity of acid produced here would certainly overwhelm this limited market.

The high NO<sub>x</sub> levels in the potential sulfuric acid also introduces corrosion and safety issues making any potential customers for this acid more unlikely to accept the product. Any dilution of acid will liberate NO<sub>x</sub> which becomes a safety and hygiene issue.

Disposal (neutralization) of the product acid with limestone is the most likely possibility however when diluting and neutralizing the acid stream NO<sub>x</sub> would be

released and would have to be captured in a closed system process containing an elaborate vent and scrubbing system. Disposing of the product sulfuric acid defeats the purpose of Task 2 concept because this arrangement would still require limestone purchase and gypsum disposal,

### **Capex Estimate**

WorleyParsons completed an initial capex estimate in year 2 of the project based on the proposal process where it was assumed that the maximum level of SO<sub>x</sub> could be sent to the CPU and that concentrated saleable (high purity) sulfuric acid could be produced with a very high conversion of SO<sub>x</sub> to sulfuric acid. The details of this capex estimate are shown in Appendix A. This initial capex estimate for the idealized proposal scenario showed a relatively low capex.

A second capex estimate was not performed due to the technical process issues as well as the commercial byproduct viability issues discussed above related to purity, small potential market size, and acid product safety.

### **Commercial Process Viability**

The investigated Task 2 concept does not constitute a commercially viable process given the program goals of producing concentrated saleable sulfuric acid from oxy-combustion flue gas. Due to acid purity issues the produced acid would need to be neutralized on site with careful attention given to the disposition of NO<sub>x</sub>. Other better alternatives for SO<sub>x</sub> and NO<sub>x</sub> removal include traditional removal options via wet-FGD and SCR or the Task 3 process. Foster Wheeler feedback on the high sulfur coal case indicates that a substantial FGD must already be included in the boiler island so there is not potential for a large capex or opex benefit as compared to the traditional SO<sub>x</sub>, NO<sub>x</sub> removal options.

Aside from the assumed performance of the process simulation there are still questions related to the viability of the process in a scaled up version related to potential corrosion of process equipment given the very high levels of NO<sub>x</sub> and safety issues related to NO<sub>x</sub>. Other technical issues include: The relatively low simulated NO<sub>x</sub> capture rate and potential column plugging given the plugging issues experienced during experimental testing.

## Conclusions:

The Task 2 experimental apparatus performed as designed and the experiments involving SO<sub>x</sub>, NO<sub>x</sub> and sulfuric acid were conducted in a safe manner without incident. The NO<sub>x</sub> absorption experiments showed a good ability of sulfuric acid to absorb NO<sub>x</sub>. The best absorption performance was seen when the NO:NO<sub>2</sub> ratio was 1:1, as is predicted in literature. For some NO<sub>x</sub> absorption experiments, formation of a solid white material was observed. This white substance is predicted in lead chamber process literature and was known as ‘chamber crystals’.

Higher temperature NO<sub>x</sub> desorption experiments up to 235°F showed that instead of desorption high levels of NO<sub>x</sub> would still absorb into sulfuric acid that already contained thousands of ppm of dissolved NO<sub>x</sub>. An inability to remove NO<sub>x</sub> from sulfuric acid by thermal desorption (or any other method) means that NO<sub>x</sub> would continue to build up to very high levels in the re-circulating sulfuric acid in the process. Very high NO<sub>x</sub> levels in the acid would limit the NO<sub>x</sub> removal efficiency of the Task 2 process. Collection of this experimental data was necessary to arrive at these conclusions because there was no experimental data in the literature collected at relevant conditions.

As part of Subtask 2.3 activated carbons were investigated as NO<sub>x</sub> removal catalysts. The activated carbons showed a poor ability to catalytically remove NO<sub>x</sub> from sulfuric acid. Some literature data indicated that an oxygen containing gas would help strip NO<sub>x</sub> from sulfuric acid. However experimentally it was found that the presence of oxygen actually made NO<sub>x</sub> removal from sulfuric acid more difficult as compared to the comparison case where N<sub>2</sub> was used to strip NO<sub>x</sub> from acid.

In Subtask 2.4 other traditional methods of NO<sub>x</sub> removal from sulfuric acid were studied for product purification. The candidate methods were taken from the sulfuric acid industry. Two methods for liquid phase NO<sub>x</sub> removal from sulfuric acid were explored. Gas phase NO<sub>x</sub> removal prior to the Task 2 process (via a typical SCR unit) is not an option for this project because the Task 2 concept depends on NO<sub>x</sub> for conversion of SO<sub>2</sub> to sulfuric acid.

The relevant liquid phase removal options are: NO<sub>x</sub> destruction with hydrazine (or a hydrazine related reagent) and NO<sub>x</sub> removal through acid dilution. NO<sub>x</sub> destruction with hydrazine may be a technically feasible option for NO<sub>x</sub> removal from concentrated sulfuric acid. However, treatment of acid with hydrazine would add significant complexity, safety, operating cost and capex requirements to the process. A second method of liquid phase NO<sub>x</sub> removal involves dilution of the concentrated sulfuric acid, from about 93wt%, to roughly 60wt% sulfuric acid. Re-concentration of acid is energy intensive and would add significant complexity, capital and operating cost to the process.

Because no suitable method was identified for high efficiency removal of NO<sub>x</sub> from sulfuric acid within the Task 2 process (in Subtask 2.3 or 2.4), the process design has been changed to reflect the scenario where all the captured NO<sub>x</sub> is produced with the

‘product’ sulfuric acid. Due to this process change the ‘product’ sulfuric acid contains very high (percent levels) of NO<sub>x</sub> dissolved in the sulfuric acid. The produced acid will have to be neutralized for disposal as a waste stream. Extra capital equipment would still be required from a safety standpoint to capture NO<sub>x</sub> fumes generated during neutralization, for example.

Feedback from WorleyParsons has indicated that the sulfuric acid trade is active in the region of the US where high sulfur coal is mined and typically used (Illinois and western Pennsylvania). The acid market in these locations could easily absorb the volume of acid which would be produced from a number of power plants equipped with a hypothetical Task 2 process; however the purity of the acid would be a problem due to the high NO<sub>x</sub> levels in the acid. Acid distributors and customers would be unwilling to accept acid having high levels of impurities, regardless of the price (or credit), because they would not want to risk contaminating their storage and transport equipment.

### **Process Simulation**

Flue gas flow and composition from Foster Wheeler’s high-sulfur-coal boiler simulations has been used with Task 2 experimental data to complete an updated process simulation of the Task 2 SO<sub>x</sub>/NO<sub>x</sub> purification equipment. The SO<sub>x</sub> content of the flue gas is significantly lower than the proposal process due to boiler constraints. The process configuration has changed to deal with the lower SO<sub>x</sub> concentration.

While the SO<sub>x</sub> removal efficiency of the simulated process is high, >99%, the simulated removal efficiency of NO<sub>x</sub> from the compressed flue gas is only about 70%, meaning that roughly 120 ppm of NO<sub>x</sub> leaves the Task 2 purification process. This high level of NO<sub>x</sub> leaving the ‘NO<sub>x</sub> Absorber’ is attributed to the high concentration of NO<sub>2</sub> in the process and the relatively low effectiveness of sulfuric acid to absorb NO<sub>x</sub> when the NO<sub>2</sub>:NO ratio is much greater than 1. The high levels of NO<sub>2</sub>, and corresponding low levels of NO seen in the process simulation stream results, are due to contactor vessel size, the speed of the NO oxidation reaction, and the inability to selectively remove NO<sub>x</sub> from the product sulfuric acid. The overall NO<sub>x</sub> removal efficiency can be improved to >90% by installing a water scrubber downstream of the acid process.

Sulfuric acid produced from the Task 2 process is still simulated to be ~93wt% (with respect to water and H<sub>2</sub>SO<sub>4</sub>). The acid produced from the process is predicted to contain roughly 2.5wt% NO<sub>x</sub>, which is a very high level of NO<sub>x</sub> impurity compared to the NO<sub>x</sub> impurity spec in commercial grade acid of <5ppmw.

In summary, the sulfuric acid process can remove >99% SO<sub>x</sub> and >90% NO<sub>x</sub> from the oxy-combustion flue gas. However, the acid produced would not meet commercial specs and it must be disposed of by neutralization. As a result, overall value of this technology is lower than the activated carbon process being developed under Task 3. Therefore, Praxair has decided not to continue further development on this technology at this time.

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## Appendix A Budgetary Cost Estimate

A budget cost estimate was developed based on a preliminary process design and equipment sizing.

### ***Basis of Estimate***

The following describes the scope and basis of the cost estimate for the Near Zero Emission Project Sulphuric Acid Process:

- No bulk material quantity take-offs were generated.
- Best guess allowances or factors were used to estimate bulk materials.
- Accuracy: Order of Magnitude (+/- 50%)
- Currency: US Dollar
- Labour Rate: \$85 per hour
- Escalation: None (i.e. 2010 pricing)
- North American cost base
- Contingency: 25%
- Storage tank capacity (5000 MT or ~10 days storage for 470 MTPD capacity)

### ***Costing***

#### **Direct Costs**

The following direct costs were included in the estimate:

<b>Equipment</b>	A preliminary budget quote was obtained for the columns only.
<b>Site Development</b>	A greenfield site free of contamination and existing structures has been assumed so minimal site development is required.
<b>Civil and Structural</b>	Allowances were made for concrete work and acid resistant coating for an acid containment area. Allowances were also made for equipment support steel, duct support bents, pipe support brackets, platform steel and pipe rack steel.
<b>Buildings</b>	It has been assumed that the sulphuric acid process will be housed in a building to protect the equipment from the elements.
<b>Electrical</b>	The electrical cost was factored from the Process Equipment cost, in accordance with in-house experience. Power will be supplied to the terminals of the main breaker on the MCC.
<b>Insulation</b>	The insulation cost was factored from the Process Equipment cost, in accordance with in-house experience.
<b>Instrumentation</b>	The instrumentation cost was factored from the Process Equipment cost, in accordance with in-house experience. The cost of the control system and control room has been

**Piping**

excluded and are assumed to be part of the overall site system.

The piping cost was factored from the Process Equipment cost, in accordance with in-house experience.

**Indirect Costs**

The following indirect costs were included in the estimate:

- Construction Indirects
- Spares
- Freight and Logistics
- Engineering, Procurement and Construction Management (EPCM)
- Commissioning and Startup
- Vendor's costs
- Owner's costs
- The following have been excluded from the estimate:
  - Utility Systems (i.e. cooling water, instrument air, plant air, etc.). These utilities are assumed to be supplied to the sulphuric acid process from systems installed for the entire complex.
  - First fills
  - Reagents
  - Taxes and Duties
  - License fees
  - Insurance

**Summary of Estimate**

Based on the assumptions stated in the previous sections, the preliminary order of magnitude cost of the Near Zero Emission DOE Project Sulphuric Acid Process is as follows:

**Process Plant****Direct Costs**

Process Equipment	\$3,588,000
Civil Works	\$18,000
Concrete	\$287,000
Structural Steel	\$305,000
Architectural	\$18,000
Piping	\$269,000
Insulation	\$108,000
Coating and Linings	\$72,000
Instrumentation	\$359,000
Electrical	\$287,000

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<b>Total Direct Costs</b>	<b>\$5,311,000</b>
<b><u>Indirect Costs</u></b>	
Construction Indirects	\$1,062,000
Spares	\$186,000
Freight and Logistics	\$398,000
EPCM	\$797,000
Commissioning and Startup	\$212,000
Vendors	\$106,000
Owner's Costs	\$797,000
<b>Total Indirect Costs</b>	<b>\$3,558,000</b>
<b><u>Contingency</u></b>	<b>\$2,217,000</b>
<b><u>Storage and Loading</u></b>	
<b>Direct Costs</b>	
Tank, Loading Station, Civil Works, etc.	\$1,340,000
<b>Indirect Costs</b>	
Construction, EPCM, Freight, etc.	\$355,000
Contingency	\$424,000
<b>Total Storage/Loading Cost</b>	<b>\$2,119,000</b>
<b><u>Total Installed Cost (+/- 50%)</u></b>	<b>\$13,205,000</b>