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**JOHN F. KENNEDY SPACE CENTER  
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**CONTROL FOR NO<sub>x</sub> EMISSIONS FROM COMBUSTION SOURCES**

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**ABSTRACT**

The Environmental Program Office at the Kennedy Space Center is interested in finding solutions and to promote R&D that could contribute to solve the problems of air, soil and groundwater contamination. This study is undertaken as part of NASA's environmental stewardship program. The objective of this study involves the removal of nitrogen oxides from the flue gases of the boilers at KSC using hydrogen peroxide. Phase I of this study have shown the potential of this process to be used as an alternative to the current methods of treatment used in the power industry.

This report summarizes the research done during the 10-week summer program. During this period, support has been given to implement the modifications suggested for Phase II of the project, which focus on oxidation reactions carried at lower temperatures using an ultraviolet source. The redesign and assembly of the modifications for the scrubbing system was the main objective of this research.

# CONTROL FOR NO<sub>x</sub> EMISSIONS FROM COMBUSTION SOURCES

Maria E. Pozo de Fernandez, Ph.D.

## 1. INTRODUCTION

Over the years, the nature of the operations at the Kennedy Space Center including the use and handling of hazardous propellants and toxic substances have contributed to air, soil and groundwater contamination. Today better knowledge in the handling of hazardous and toxic materials and stringent regulations about their use and disposal has minimized the harmful impact and the risk that these substances pose to the environment. The Environmental Program Office through the Remediation Group at the Kennedy Space Center is interested in finding ways to obtain immediate and permanent solutions to these problems. Nitrogen Oxide (NO<sub>x</sub>) emissions are a primary criteria pollutant regulated by the USEPA. KSC is permitted to emit approximately 60 tons of NO<sub>x</sub> annually under their Title V air permit. NASA is pursuing R&D to minimize the detrimental environmental effects of KSC operations on the environment. This study is undertaken as part of NASA's environmental stewardship program.

This study involves the removal of nitrogen oxides from the flue gases of the boilers at KSC. The primary focus of the research is the conversion of NO<sub>x</sub> to nitrogen acids for the purpose of scrubbing them from the gas stream. NO is virtually non-soluble and NO<sub>2</sub> is only slightly soluble; however, nitrogen acids (HNO<sub>2</sub> and HNO<sub>3</sub>) are highly soluble and can be removed via scrubbing. Phase I of this study was completed in December 1998 and consisted of oxidation of the NO<sub>x</sub> at high temperatures (~930 °F). Phase II began in January 1999 and is expected to be completed by December 1999. Phase II will focus on oxidation at lower temperatures utilizing an ultraviolet (UV) light source. Key to the success of this study is optimizing the scrubber operation. The redesign included the following: 1. Conversion of batch to continuous reservoir flow. 2. Lower temperatures in the scrubber recirculation system. 3. Continuous and Batch caustic feed. 4. Providing for sampling and analysis in-line. 5. Increase recirculation flow rate.

Support was also provided in the coordination, implementation, assembling, logistics and follow-on procedures for the changes needed in the Reaction Zone of the Unit and in other areas of the project. This report summarizes the research done during the 10-week program at NASA-KSC. During this time the whole unit was assembled, with the exception of the UV lamps. Hydraulic tests were carried out at the scrubbing system.

## 2. BACKGROUND

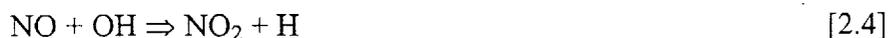
Laboratory studies have demonstrated that hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) when injected under proper conditions into hot gases of the exhaust stream it oxidizes nitric oxide (NO) into NO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub>. The formation of nitrogen acids allows for more inexpensive methods of post treatment for nitrogen removal, such as, scrubbing. Sulfur

dioxide can also be added to the combustion source to simulate the exhaust of an industrial power plant.

The primary reactions that are expected to occur during this process are as follows:



Hydroxyl-Radical Reactions:



Hydroperoxyl-Radical Reactions



To simulate the kinetics of the process, several parameters are needed, such as, activation energies, reaction temperatures, reaction intermediates and reactor flow regime, just to mention a few. Analysis of the reactions through reaction modeling determined that these reactions should take place within 0.1-0.3 seconds. The model used did not consider the effect of sulfur dioxide added to exhaust gases.

To demonstrate the viability of such process, researchers at NASA-KSC and the University of Central Florida (UCF) joint efforts to implement this process from a laboratory scale to a pilot plant scale. The experimental setting is located at the KSC Central Heat Plant (CHP).

Phase I of this project was performed on a 35 mmBTUH natural gas boiler. The fuel used consist mainly of methane and varying amounts of ethane, propane, butane, a sulfur-containing mercaptan added to natural gas, and inerts, such as, nitrogen, carbon dioxide and helium. When burning natural gas the major pollutant in the exhaust gases is mainly NOx. The percentage of NOx presence depends on the temperature of the combustion chamber as well on the fuel/oxygen ratio.

Part of the flue gas was diverted to the experimental apparatus consisting of different sections: Injection Zone, Reaction Zone, Quenching and Scrubbing. At the Injection Zone hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was injected to the system. Also NO and  $\text{SO}_2$  was added to the exhaust gases to simulate the composition of a flue gas from an industrial power plant. Once passed the Injection Zone the mixture of flue gas, NO,  $\text{SO}_2$  and ( $\text{H}_2\text{O}_2$ ) went through an auxiliary gas burner to bring the slip stream gases to the desired reaction temperature. From this point, the gases went through the Reaction Zone, where the conversion of NO to NOx and nitric acids took place. The Reaction Zone consisted

of a 12-inch diameter, 8-ft long stainless steel pipe, having sampling ports and thermocouples distributed along its length. Reactions could be carried out up to 500 °C. The reaction products and by-products passed then through the Quenching system, where water was added to cool off the gas mixture before entering the Scrubbing System. The scrubber was a packed column consisted of an 8-ft tall acrylic column with a 6-ft bed depth. 1-inch Hyflow 25-7 polypropylene rings were used as packing material. The scrubber had a 30x60x30 inch<sup>3</sup> reservoir, a 1¼ - inch PVC recirculation line with a Hayward diaphragm valve, a by-pass valve, a ½ HP submersible pump and reservoir drain and sampling port. Sodium bicarbonate was used to control the pH of the fluid at the reservoir.

Data Acquisition System (DAQ) using LabView software from National Instruments was used to obtain instant readings of the key parameters in the process. Figure 2.1 shows the schematics of the experimental system as the computer monitor displays it.

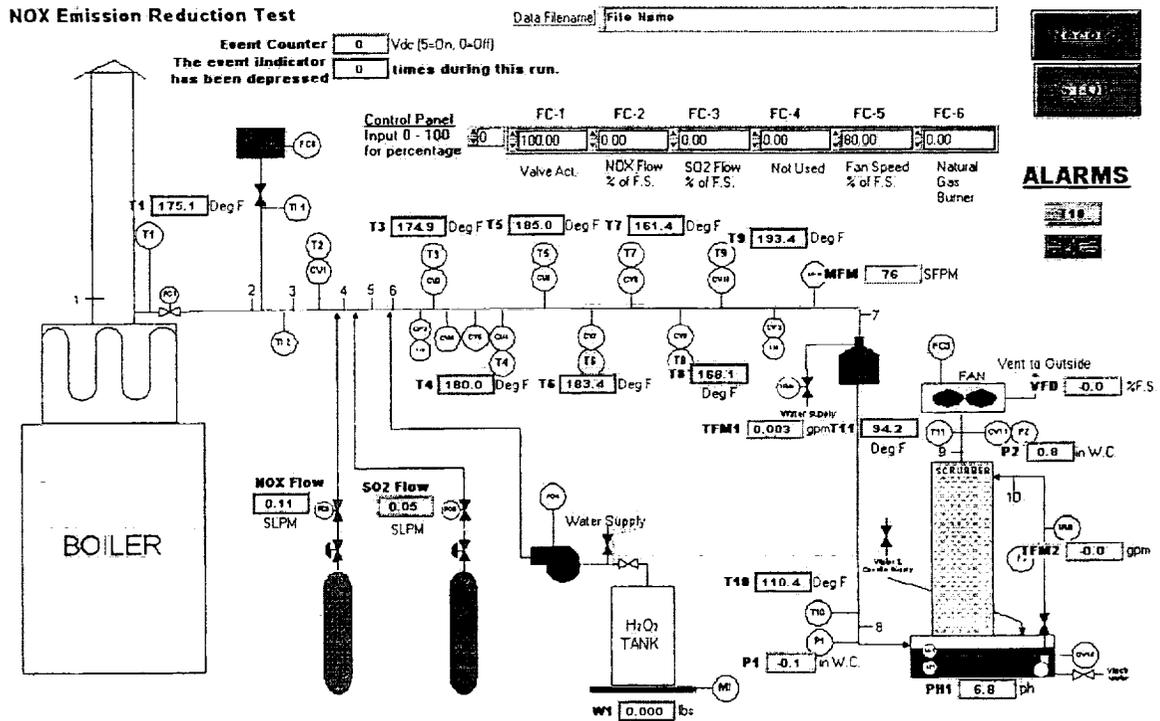


Figure 2.1. Schematics of the Experimental Process (Phase I)

Several runs were made with this experimental configuration changing the following variables: Reaction temperature, NO, SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> concentration, NO/ H<sub>2</sub>O<sub>2</sub> ratio, SO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> ratio and residence time.

The results obtained during Phase I were encouraging but some modifications would be required in order for the system to perform to the optimum expected values. The conversion from NO to NO<sub>x</sub> worked very well, getting conversions greater than 96% for NO/ H<sub>2</sub>O<sub>2</sub> ratios of 1:1. Conversion from NO<sub>2</sub> to nitric acids was not as high as expected. Operating the reactor at high temperatures and having the surface of the stainless steel reactor without any type of coating could have been part of the problem. Some authors believe that iron can act as a catalyst leading to reverse reactions. The removal of the nitric acids by the scrubber was not as efficient as expected. The scrubbing system was never optimized for the kind of removal required by the process. The submersible pump provided was under-specified, since the rates of liquid flow recommended for optimal scrubbing operation were never achieved. The implementation of these modifications led to Phase II of the project.

### 3. EXPERIMENTAL

Based on the results obtained during Phase I, several modifications were proposed for Phase II of the project. The sections to be re-designed are the Reaction Zone and the Scrubbing System.

**Reaction Zone:** The modifications proposed for the reaction zone were as follows:

1. Coating of the reaction zone pipe:

It was proposed to coat the interior of the 12-inch diameter, 8-ft long stainless steel pipe with a boron-nitride paint to prevent the release of iron during the reaction. From findings in the literature it has been suggested that the use of this kind of paint will help in the NO<sub>2</sub> to nitric acids conversion. The paint selected was high temperature ceramic boron nitride paint from Carborundum.

Before the pipe could be sent to the paint shop, it was necessary to dismantle the apparatus previous configuration. In order to do that, several groups within KSC needed to perform several tasks in an orderly manner. First the "insulators" needed to take care to remove the insulation in order to have access to the pipe. Once the insulation was out, the bolts that held the pipe flanges in place, the thermocouples and sampling ports needed to be removed. This turned out to be a big problem, since some of the bolts were corroded and "frozen" in place. Once this task was accomplished, personnel from "Heavy Equipment" needed to move the pipe to the paint shop. To carry out the whole process until the pipe finally arrived to the paint shop took several weeks.

The process of painting the pipe with the boron-nitride paint was not as simple as one could think. On a first attempt the pipe was painted without any prior surface treatment. It turned out that the paint did not adhere well to the surface of the pipe and it did not have a smooth finish as expected. The paint could be easily scratched from the surface. Also, there were brown spots (pitting) all over the interior surface of the pipe, which were not expected to appear. It was proposed to re-paint the pipe but this time the surface to be painted was sandblasted in order to provide a better surface preparation for adhesion.

Thin coats of paint were added to the surface, letting them dry well before each application. This time, the pipe interior surface looked smoother and the paint showed good adhesion. Still the brown spots appeared this time. After some debate, it was demonstrated that the "brown spots" were signs of corrosion occurring at the surface of the pipe. The facility where the pipe was painted did not have a "controlled environment" room, meaning that the pipe was exposed to humidity and heat, which are quite high during the summer months in Florida. To prove this point, two identical smaller pipes were painted and one was let dry outdoors and the other one was placed inside in an air-conditioned room. The first pipe showed signs of corrosion the very first day, whereas the second pipe seemed fine. By talking to the vendor, pitting should not occur at all. He also suggested that the pipe should be heated at a high temperature prior painting the surface. This would ensure that the surface would have the "enamel" type finish desired. It was concluded that even with the corrosion spots, the pipe was ready to be put back in place. Figure 3.1 shows surface finish of the reaction zone prior to be taken back to the Central Heat Plant (CHP).

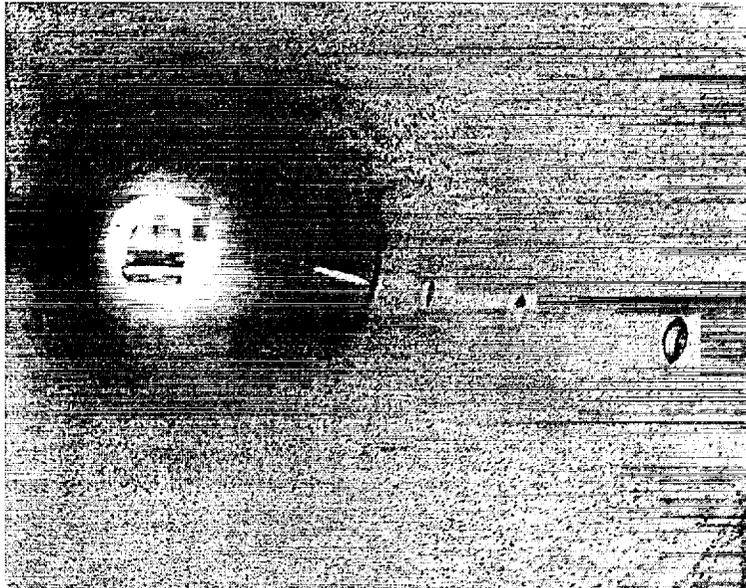


Figure 3.1. Reaction Zone surface

## 2. Use of UV lights:

It was suggested to use UV light as a heat source to carry the reaction at lower temperatures. Two UV lamps were bought from Calgon in Canada. In order to accommodate the lamps, a spool was designed and plates were welded to ensure the proper alignment of the lamps. The spool was made of a 12-inch diameter, 2-foot long stainless steel pipe having end slotted flanges to be bolted between the Injection Port and the Reaction Zone. It took several weeks before the spool was ready to send to the paint facility due to a delay on shipment of the plates that needed to be welded to support the lamps. Once the welding was finished, the spool was sent to the paint facility where its interior was sandblasted and coated with the ceramic boron nitride paint as it was done

for the reaction zone. Since the spool was made of a new pipe, it did not show as much pitting as the reactor zone did. The method for painting the spool was the same as the one used to paint the other pipe. Once the spool was painted, both the spool and reaction zone were delivered to the CHP plant to be mounted in place. This time, special precaution was taken to use anti-seize compound in the bolts used, to prevent rusting. Figure 3.2 shows the spool and reaction zone in place. The picture also shows the thermocouples in place, the new sampling ports and part of the system with the new insulation.

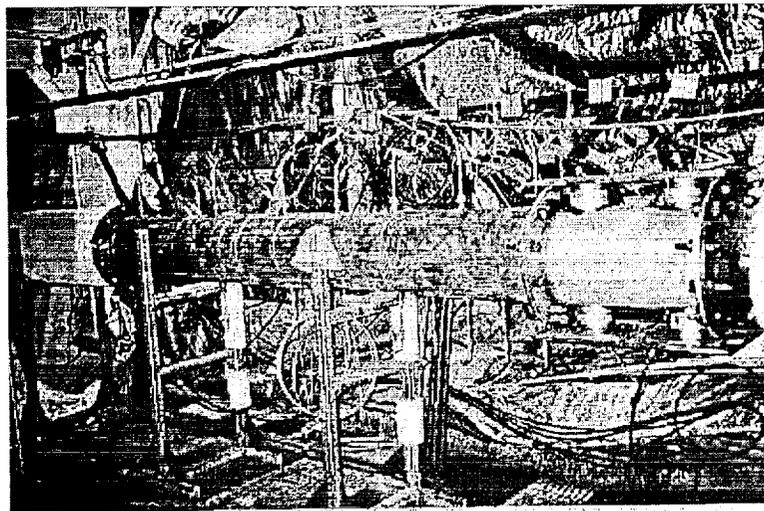


Figure 3.2. Reactor zone and spool in place

Once the whole unit was in place, new insulation was placed over the reaction zone. The delivery of the lamps was delayed for almost two months. Several problems in the fabrication of the lamps itself and its power supply system delayed the shipment. The lamps and power supply were delivered during the final week of the Summer Program. Figure 3.3 shows the reaction zone and spool with the UV lamps in place.

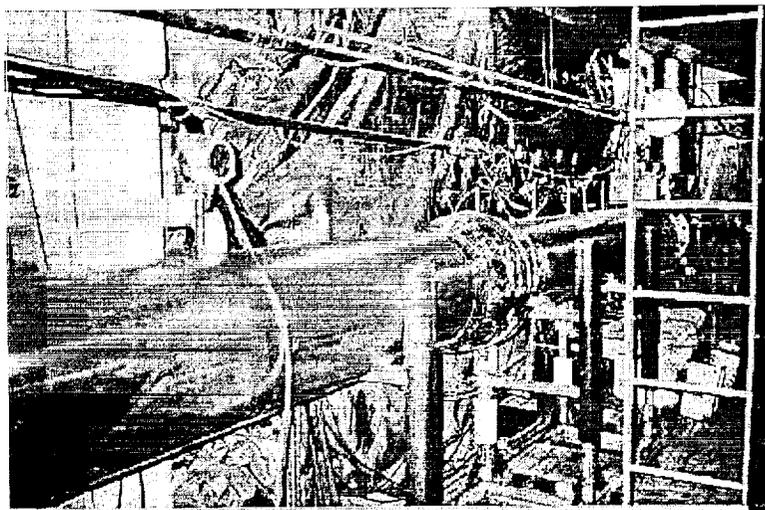


Figure 3.3. System with insulation and UV lamps in place

**Scrubbing System:** Gas absorption is a mass-transfer operation where a soluble vapor is absorbed by means of a liquid in which the gas is more or less soluble. This operation is commonly known as scrubbing. The apparatus used in gas absorption is the packed tower. The packed tower has gas inlet and distributing space at the bottom, liquid inlet and distributor at the top, gas and liquid outlets at top and bottom, and it is filled with solids of different shapes called *packing material*. The purpose of the packing material is to provide a surface for good contact to favor the mass transfer between the liquid and the gas. The packing could be placed inside the tower in a random manner or in order. The packing should be inert to the fluids used in the process.

A configuration of the tower previously mentioned is *counter-current* since the liquid and the gas flow in opposite directions. A good contact between the liquid and the gas is important to obtain the desired efficiency of the process. The optimum liquid and gas flow rates through the column depend on many factors, such as, the type of packing, the depth of the packing, number of packing stages, etc. Two common problems that are present in packed towers are *channeling* where the packing surface could be dry or covered by an stagnant film of liquid, and *flooding* when the column is filled with liquid.

Every packed column has its own *hydraulics*, meaning the points of loading and flooding which limits the flow rates within the tower. To characterize a scrubber several factors has to be taken into consideration, such as, components to be separated, type of packing, characteristics of the packing, mass transfer properties of the components to be separated, temperature of operation, gas and liquid flow rates within the column, just to mention a few.

The scrubber used during Phase I of the project was designed and manufactured by Rauschert Industries, Inc. Based on the parameters supplied, they estimated the size, material, packing material, optimum gas and liquid rate within the column and the operation temperature. The scrubber specifications were given in section 2. The packing material selected by the vendor was 1-inch Hyflow 25-7 polypropylene rings. This packing material is proprietary, meaning that its characteristics and hydraulic behavior can not be found in the open literature. Once the vendor specified the unit, it recommended 500 scfm for the gas rate and 35 gpm for the liquid rate. Since the recirculation pump provided with the unit was under-specified the maximum liquid flow achieved was approximately 15 gpm, which proved to be too low for the scrubber operation.

An attempt was made to get information from the vendor in relation to the hydraulics of the packing material to perform calculations to obtain the optimal relationship for the gas and liquid rates at the temperature of separation. For a given system and packing material a characteristic curve relating the HTU (height of transfer unit) and gas flow rate can be obtained. With the gas flow rate and mass transfer data the optimum liquid flow rate can be obtained. Unfortunately, the system used in the scrubber is quite complex, since there are several components present and also sodium bicarbonate is added to the reservoir to maintain a favorable pH. The changes made in the scrubber were based on the original design but providing some improvements. (See Figure 3.4)

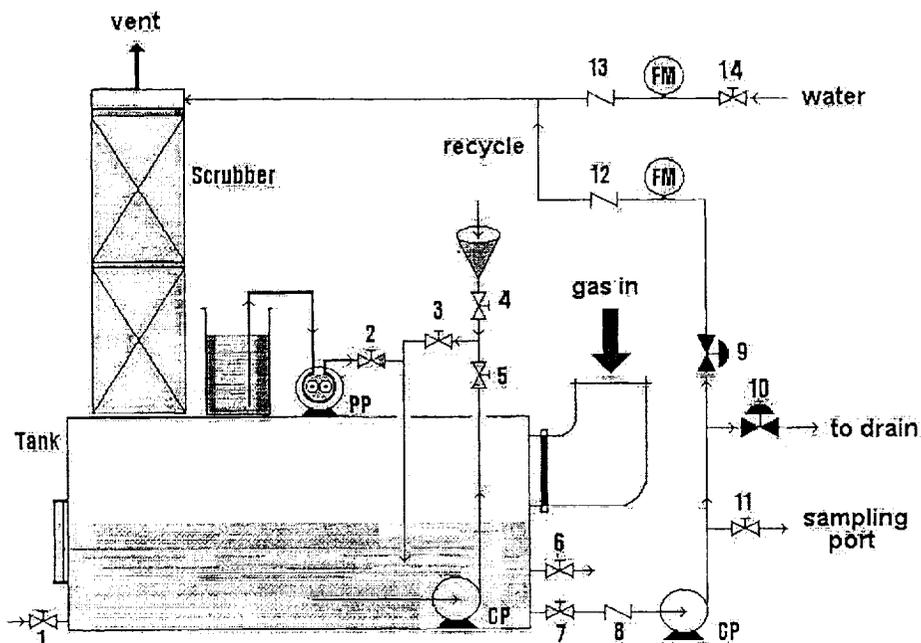


Figure 3.4. Schematics of the Scrubber Modifications

First, the scrubber was re-designed for continuous operation having inlet, outlet and recirculation lines. Fresh water was introduced in the system through the inlet line. Two Hayward diaphragm valves control the flow through the outlet line and the recirculation line in the system. Mass flowmeters hooked up to the DAQ provided accurate flow measurement at the inlet, outlet and recirculation lines. The lines were made of 1¼ - inch PVC pipe and fittings. Check valves were placed in each line to prevent back-flow. Liquid recirculation was provided through a new 1-HP pump, able to deliver 35 gpm if desired. The system was tested for leaks and it worked fine.

A continuous and batch caustic feed was also added to the system, to provide versatility in the operation mode. For continuous operation, a reservoir for the caustic solution was connected to a peristaltic pump to deliver the solution at a given rate. If it is needed, a funnel was provided to introduce sodium bicarbonate to the reservoir in large quantities. The submersible pump at the reservoir provides continuous mixing of the tank fluid and the caustic solution added to the tank. Figure 3.5 shows the actual scrubber with the modifications.

**Variables:** Once the UV lamps are connected and the whole system is ready for operation, several parameters will be varied. The parameters to be varied are as follows:

- 1) Reaction temperature: Test will be carried at three temperatures 350, 400 and 450 °F.
- 2) Location of Injection point: It is very important during the first test to locate the optimum position for the injection of H<sub>2</sub>O<sub>2</sub>.
- 3) NO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> ratio.
- 4) SO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> ratio.
- 5) pH of the scrubber reservoir solution.
- 6) Recycle flow at the scrubber.

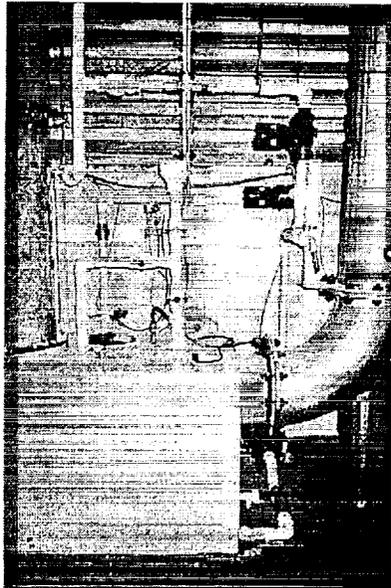


Figure 3.5. Actual Scrubber with Modifications

#### 4. CONCLUSIONS

The objectives during this study were accomplished. The modifications suggested for Phase II of this project were implemented. Once the UV lamps are properly connected, the whole unit will be ready for testing. The scrubber modifications are in place and the unit will be able to deliver the required liquid flow rate of 35 gpm. A continuous/batch caustic feed was added to the system.

#### 5. REFERENCES

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