# NUCON International Inc.

## Control of Carbon Disulfide Emissions From Viscose Processes

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## ABSTRACT

The EPA has issued a proposed rule for control of hazardous air pollutants from cellulose manufacturing operations. Both the hydrogen sulfide and carbon disulfide emissions must be controlled.

An activated carbon based process has been developed which effectively removes both of these hazardous compounds with high efficiency. An impregnated activated carbon is used to remove hydrogen sulfide by converting it to sulfur on the interior surface of the activated carbon. The resulting waste is minimal and can be land filled at relatively low cost. A unique type of activated carbon is used to remove the carbon disulfide from the air stream and periodic regeneration of the carbon, using hot inert gas, recovers the carbon disulfide for reuse. This type of system has operated for several years with no safety problems associated with the low auto-ignition temperature of carbon disulfide.

Extensive laboratory tests have been conducted to optimize this process and the results are presented. A large system has been designed and installed and typical operating information is provided. Capital costs for systems of various sizes and configurations is given.

## INTRODUCTION

Several industrial products are manufactured by the viscose process, including sponges, sausage casings and rayon fibers. This process emits a hazardous air pollutant (HAP) carbon disulfide. USEPA is required by the clean air act to issue rules to control HAP emissions and recently published, for comment, the National Emission Standards for Hazardous Air Pollutants (NESHAP) for manufacturers using the viscose process. Carbon disulfide requires additional safety measures because of its very low autoignition temperature. Therefore, the proper emission control process must be chosen and safety precautions must be employed to prevent damage to equipment and injury to people.

In the effluent stream containing the carbon disulfide, hydrogen sulfide is always present.

The NESHAP also requires the control of this compound, even though it is not classified as a HAP. The presence of hydrogen sulfide complicates the emission control process because of its tendency to be converted to elemental sulfur.

Many processes have been used for removal of carbon disulfide and hydrogen sulfide from exhaust streams. The simpler ones, such as thermal oxidation, result in high operating costs for energy and for disposal of the sulfur oxides that are formed. The more capital intensive and complicated processes, such as activated carbon adsorption with steam regeneration, allow recovery and reuse of the carbon disulfide but are difficult to control and have high operating costs.

In the early 1990's, the first inert gas regeneration system for recovery of carbon disulfide was installed and operated. There were several problems with mechanical operation of the equipment and the process design, but a variety of changes have been made which improved the process and its operation.


## NESHAP

On August 28, 2000, USEPA issued a proposed rule titled "National Emission Standards for Hazardous Air Pollutants: Cellulose Products Manufacturing".[1] The proposed standards were intended to control the hazardous air pollutant emissions, such as carbon disulfide, carbonyl sulfide, ethylene oxide, methanol, methyl chloride, propylene oxide, and toluene. By defining "sulfides" as a category, the rule also requires control of hydrogen sulfide. The proposed standards were issued to implement section 112(d) of the Clean Air Act and will reflect the application of maximum achievable control technology (MACT).

Since two distinctly different cellulose-manufacturing processes are used (Viscose and Cellulose ethers) these two categories were separated in the NESHAP. This paper deals only with emissions from the Viscose manufacturing processes; Food Casings, Rayon, Cellophane, and Sponges.

MACT standards were designated based on present practice. They are shown in Table 1

### Table 1 Proposed MACT Floor

| Manufacturing Process | Emission Source | MACT Floor, % Control | |
|---|---|---|---|
| | | Existing Sources | New Sources |
| All | Wastewater | None | None |
| All | CS2 Unloading | 85 | 85 |
| All | Equipment leaks | None | None |
| Cellophane | Process Vents | 85 | 85 |
| Cellophane | Coating Processes | 95 | 95 |
| Food Casings | Process vents | 25 | 75 |
| Rayon | Process vents | 55 | 75 |
| Cellulosic Sponges | Process vents | 75 | 75 |

The higher MACT floor standards for new sources was based on available technologies; condensers, biofilters and carbon adsorbers. Condensers can only be applied with very high concentration vent streams such as tank vents. Both biofilters and carbon adsorbers have been successfully used to control emissions from process vents at cellulosic sponge manufacturing operations

## HISTORICAL STUDIES

In the early 1990's, there was a considerable amount of activity associated with the control of carbon disulfide emissions. The USEPA funded a study (EPA-450/3-91-023)[2] titled "Carbon Disulfide Emission Control Options". Several emerging technologies were described which their advocates presumed could be used to control carbon disulfide emissions. Adsorption with activated and subsequent regeneration of the carbon with either steam or inert gas was a technology being applied at that time along with condensation in the case of concentrated streams.

A study published by Chemviron Carbon Company [3] in 1992, provided design parameters for recovery of carbon disulfide using steam regenerated carbon beds. The impact of concentration, relative humidity and temperature were quantified. At high relative humidities, the adsorption of water vapor on activated carbon interferes with the adsorption of the carbon disulfide and the capacity of the activated carbon is reduced. Relative humidity below 50% RH should be employed. Temperatures above 80 °F also significantly reduce the capacity of the activated carbon. If the concentration of carbon disulfide is at 2000 ppmv, the working capacity of the carbon is increased 2.5 times over that at 700 ppmv.

The Illinois Department of Natural Resources and Teepak Inc. sponsored a study performed by Argonne National Laboratory [4] to determine the best technology and associated costs of emission control from the Teepak viscose sponge manufacturing plant. Adsorption with activated carbon was considered to be the best technology for control of carbon disulfide emissions. A capital cost estimate was made based on airflow of 400,000 cfm and a carbon disulfide concentration of 100 ppmv. Several process schemes were evaluated including both steam and hot gas regeneration of activated carbon beds. The estimated capital cost of the installed plants was between $23 million and $26 million.

## EUROPEAN PLANT DESIGN

The Sulfasorbon Process developed by Lurgi [5] has had wide application for carbon disulfide emission control in Europe. It is an activated carbon based system with steam regeneration

Vertical cylindrical vessels, 6.5 ft diameter, hold the activated carbon. There are two

beds of carbon, each about 3 ft deep. The bottom bed contains an activated carbon that is impregnated to catalytically react the hydrogen sulfide with oxygen to form sulfur. The top bed is filled with a microporous activated carbon that has a high capacity for carbon disulfide. Eventually, the activated carbon in the bottom bed will be filled with sulfur and must be regenerated. This is done by washing the carbon, first with water to remove any sulfuric acid that is formed, and then with liquid carbon disulfide to dissolve the sulfur.

Unique process steps are used to improve performance and eliminate problems. To avoid autoignition of carbon disulfide at the beginning of the regeneration cycle, the beds are purged with nitrogen. To reduce the residual water on the carbon after regeneration, which would interfere with adsorption of carbon disulfide, a relatively hydrophobic activated carbon is used. In addition, the temperature of the solvent laden air (SLA) is increased to reduce the relative humidity. The typical effluent concentration of carbon disulfide is 25 ppmv while the hydrogen sulfide concentration is reduced to 1 ppmv. Removal efficiencies of 95 to 98% are reported.

## CARBON SYSTEM WITH INERT GAS REGENERATION

An inert gas regenerated carbon system was installed to control carbon disulfide emissions from a viscose operation in the early 1990's. While it did not meet the specified performance requirements during startup, several process changes were made which resulted in relatively good efficiency at a reduced SLA flow rate. The adsorption process is shown Figure 1.

**Figure 1 Adsorption Process**



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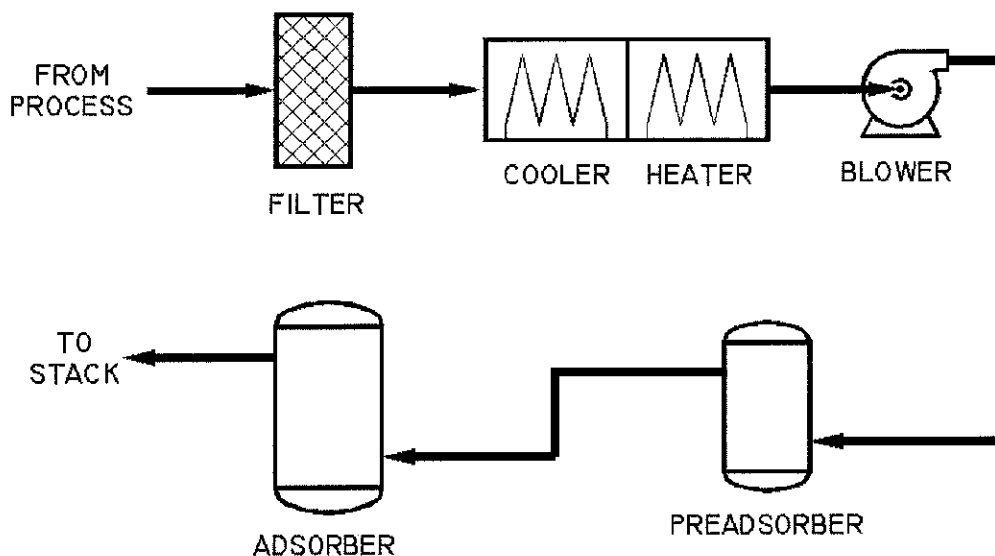
A filter is installed to remove any particulate matter that might be generated in the manufacturing process and transported to the solvent recovery unit (SRU). In order to reduce the relative humidity to around 30%, the SLA is cooled to 40 °F and reheated to 75 °F. The purpose of this step is to minimize the moisture on the carbon, which interferes with adsorption of carbon disulfide and requires energy for removal during the regeneration step. Since the pressure drop through the system is relatively high, a separate blower is supplied. The preadsorber, which contains an impregnated activated carbon, removes the hydrogen sulfide and any other sulfur gases that might be formed in the manufacturing process. The adsorber removes the carbon disulfide and clean air is exhausted to the stack. When the carbon becomes saturated with carbon disulfide and the outlet concentration begins to rise, the working adsorber is taken off line and the SLA is directed to an adsorber that has been regenerated.

Corrosion of the SLA cooler has been a problem. The SLA is saturated at 100 °F and the condensate generated in the SLA cooler is acidic. The fins and tubes of the cooling coils have been coated to reduce corrosion but they still need to be replaced almost annually. The regeneration process is shown in Figure 2.

**Figure 2  Regeneration Process**
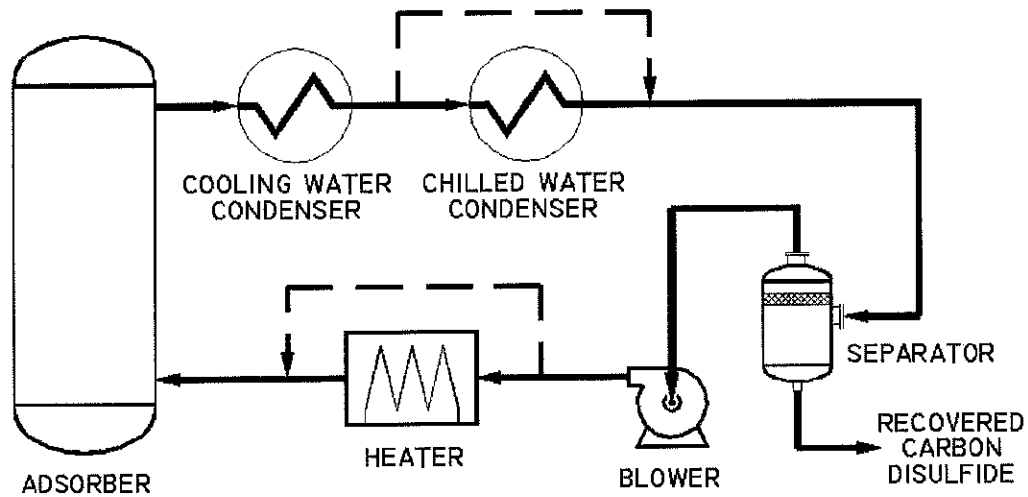


The gas is heated and then passes through the adsorber to remove the carbon disulfide and small amounts of adsorbed water. Condensing is done in two stages with cooling water and chilled water. The condensed liquids are separated and the gas is directed to the blower. After the heating cycle is complete, the heater is bypassed and the bed is cooled.

It is important to remove as much carbon disulfide from the activated carbon during the regeneration process as possible. The amount remaining at the end of the cycle (called the solvent heel) reduces the working capacity during the next adsorption cycle. The heel can be minimized by using a high regeneration temperature and by reducing the concentration of solvent in the recirculating inert gas stream. A heating temperature of 450 °F was used to minimize the heel. The design cooling temperature for the regeneration process was relatively low, 10 °F, in order to reduce the concentration of carbon disulfide as much as possible in order to increase the working capacity. The water adsorbed on the carbon comes off during the early stages of the heating cycle when the low temperature cooler is being bypassed. However, even the small amount of water left in later stages can plug the finned condenser coils and that has been a problem. Raising the temperature to thaw the cooler results in reduced working capacity.

Even though the adsorber is purged with inert gas before the heating step, some oxygen remains in the bed and some is adsorbed on the carbon. At this relatively high regeneration temperature, the oxygen is converted to sulfur dioxide and sulfuric acid is eventually formed through catalytic activity of the carbon. Since the sulfuric acid is not removed from the carbon during regeneration because of its high boiling point, it accumulates and eventually reduces the recovery efficiency and the carbon must be replaced.

It would be possible to wash the carbon while still in the adsorbers to remove the sulfuric acid but the mechanical design of this plant was inadequate to hold wet activated carbon. Therefore, the carbon had to be removed and replaced. Offsite reactivation of the spent carbon resulted in physical losses, which were costly, and in reduced performance of the carbon, which shortened the life of the reactivated material. Recent experience with activated carbon made from coconut shell charcoal indicates that less sulfuric acid is formed on that material and the life is extended considerably.

## NUCON LABORATORY STUDIES

In preparation for the design of a new carbon disulfide recovery system, several laboratory studies were performed. Some were undertaken to evaluate different process designs. Different activated carbons were evaluated. Carbon washing trials were run. These results were used to set final process and operating parameters.

In the installed plant, activated carbons made from coal, wood and coconut shells had been used with mixed success. A variety of materials were tested in the laboratory to determine the equilibrium adsorption capacity under adsorption conditions of 80 °F and 1700 ppmv concentration. The results are shown in table 2.

## Table 2  Equilibrium Adsorption of Carbon Disulfide

| Grade | Raw Material | Amount Adsorbed | |
|---|---|---|---|
| | | g/100g carbon | g/100ml carbon |
| GC 80-4 | Coal | 10.0 | 4.3 |
| GC 60-4 | Coal | 10.6 | 5.0 |
| GW 80-4 | Wood | 16.2 | 6.3 |
| G 50-4 | Coconut | 19.8 | 8.7 |
| G 60-4 | Coconut | 18.4 | 8.1 |
| G 60-3/5 | Coconut | 18.0 | 8.5 |
| G 40-3/5 | Coconut | 20.2 | 11.5 |

In general, activated carbons made from coconut shells show a higher capacity for carbon disulfide than those made from coal and wood. The reason is that the micropores are generally smaller in diameter. This factor also applies to the lower surface area coconut carbon (40 $CCl_4$ value), which has the smallest pores. The capacity on a volume basis is important because it dictates the size of the vessels. Since the density of granular coconut carbons is higher than that of pelleted carbons, the capacity on a volume basis is higher and the low activity granular coconut carbon shows the highest volume capacity. This material was selected for the adsorbers in the new system. This carbon is relatively unique because high surface area carbons are normally chosen for solvent recovery.

The next step in the test program was to perform column tests to determine the dynamic adsorption characteristics of the selected carbon. The carbon bed dimensions were 5" diameter, 24" long. The flow rate was 70-ft/min superficial velocity. The SLA contained 1700 ppmv carbon disulfide at 80 °F and 30% RH. The dynamic adsorption performance for Grade G 40-3/6 is shown in Figure 3 for new carbon and carbon after one regeneration.

**Figure 3, CS2 Outlet Concentration, Lab Test**
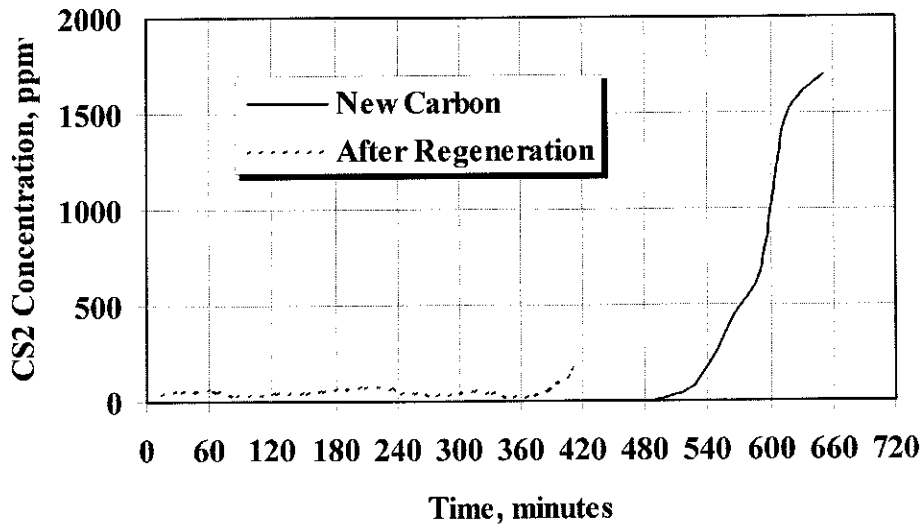


With new carbon, the time to breakthrough was just over 8 hours. After regeneration, it was reduced to just less than 7 hours. This is an indication that the regeneration was very effective. At the time of breakthrough after regeneration, the carbon had retained 12.5 g carbon disulfide /100 g activated carbon (working capacity).

A unique process design for regeneration was used in the lab tests. Rather than condensing the carbon disulfide as a means of purifying the regeneration gas stream, a separate activated carbon bed was used to adsorb it. The process flow diagram is shown in Figure 4.
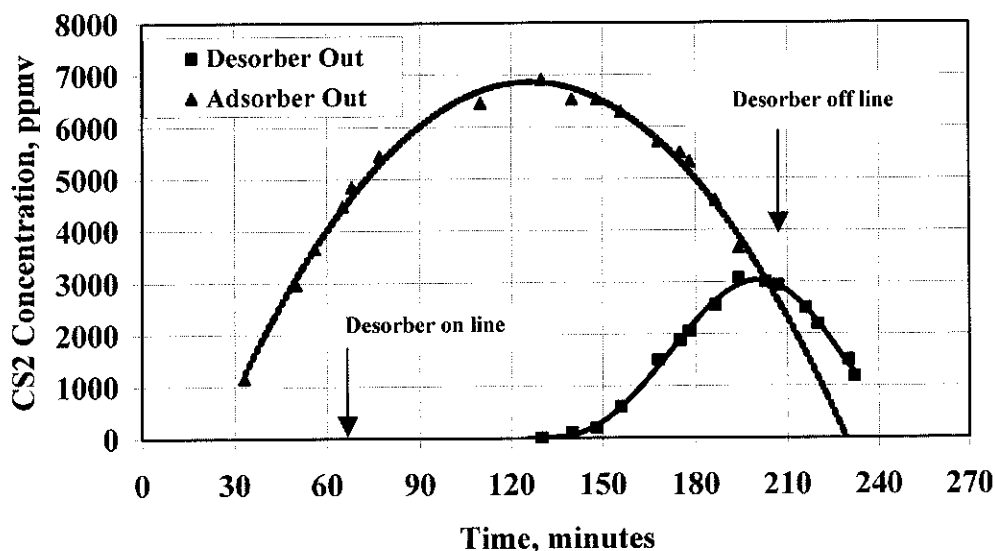
**Figure 4  Laboratory Regeneration Process**
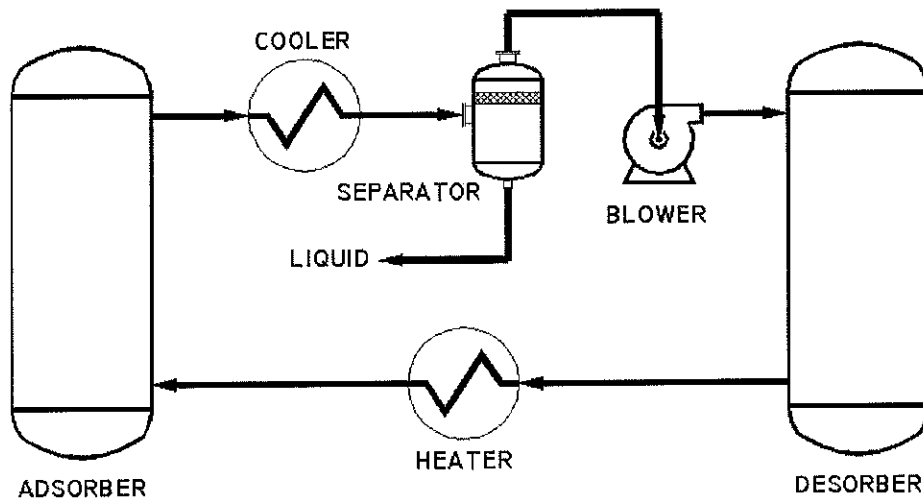


When the adsorber is being regenerated, the cooled gas passes through the desorber where the solvent is removed. The relatively clean gas then passes through the heater and back to the adsorber. Since the concentration of carbon disulfide in the regeneration gas is much higher than that in the SLA, the capacity of the desorber bed carbon is very high. In fact adsorption studies show that a high surface area carbon made from coal has a good capacity under these conditions and releases it very easily during regeneration. The desorber is regenerated by the same process as the adsorber except that the carbon disulfide is condensed in the cooler and the gas from the fan is passed to the heater directly.

The concentration of carbon disulfide in the regeneration gas during a typical regeneration is shown in figure 5.

**Figure 5  CS2 Concentration, Laboratory Regeration**



The desorber was placed on line when the solvent concentration began to rise rapidly, which is an indication that the water has been desorbed from the bed and condensed in the cooler. While the outlet concentration in the regen gas from the adsorber rises to relatively high levels, it is not high enough to be condensed at the cooler operating temperature of 40 °F. The heating of the adsorber was continued until the outlet temperature was within 50 °F of the inlet temperature. At that time, the desorber was taken off line and cool gas was introduced to the adsorber.

The alternating adsorption, adsorber regeneration and desorber regeneration steps were continued until the working capacity was duplicated on three separate runs. This was an indication that the experiment had reached dynamic equilibrium. At that point the working capacity of the adsorber was 12.5 g carbon disulfide/100g carbon. The difference between that number and the 20 g/100g equilibrium capacity is attributed to the unused capacity at breakthrough and the heel of solvent left on the bed.

Trials were performed to determine the effectiveness of washing the carbon to remove the sulfur compounds that built up on the adsorber carbon with time. Spent carbon from the operating unit was analyzed. It contained 6% sulfuric acid and 9% free sulfur. Washing trials using concentrated caustic and rinsing with water proved that essentially all the acid and sulfur could be removed from the carbon and that the capacity to adsorb carbon disulfide was restored to new carbon levels.

## OPERATING PLANT DESIGN

Plant designs for both the viscose sponge and the sausage casings have been made. Both use the adsorption process design illustrated in Figure 1. The regeneration process uses the desorber concept as shown in Figure 4. In addition, the desorber bed has its own regeneration circuit so it can be regenerated while the adsorber is being cooled.

The design basis for both of these plants is shown in Table 3

**Table 3  Plant Design Basis**

| Design Parameter | Sponge Plant | Food Casing Plant |
|---|---|---|
| Airflow, scfm | 40,000 | 120,000 |
| SLA Temperature, °F | 100 | 85 |
| Relative Humidity, % | 100 | 80 |
| Carbon Disulfide Concentration, ppmv | 1700 | 200 |
| Hydrogen Sulfide Concentration, ppmv | 5 | 150 |

The SLA conditioning train consists of a particulate filter, a glycol cooler condenser, a seam reheater and a preadsorber. After the SLA passes through these components, the temperature is 70 °F, the water dew point is 40 °F and all the sulfur gases have been removed. The blower, which generates about 30 in. water differential pressure, raises the temperature of the SLA to about 80 °F. The SLA then passes to the adsorbers, which are sized for 30,000 scfm each. When the carbon disulfide breaks through an adsorber, the valves are switched to direct the SLA to a newly regenerated adsorber. For the sponge plant, the adsorption cycle length is expected to be 18 hours for each adsorber, while for the food casing plant it is expected to be 48 hours. The regeneration system is designed for a cycle time of 9 hours, which gives a substantial standby time. In both cases, an additional adsorber is supplied so that carbon washing can be performed without shutting the system down. For the food casing plant, 2 additional adsorbers are provided to cover emergency shutdowns of the SRU regeneration system for as much as 48 hours.

Estimates have been made for the capital costs for the two cases. They are shown in Table 4. The cost estimate for the nitrogen desorption case from the Argonne study (400,000 scfm) is also shown.

**Table 4  Estimated Capital costs.**

| Application | Food Casings | Sponges | Food Casings |
|---|---|---|---|
| Air Flow Rate, scfm | 120,000 | 40,000 | 400,000 |
| Equipment Cost | $8,300,000 | $4,000,000 | $15,300,000 |
| Utilities Equipment Cost | $1,500,000 | $800,000 | $2,500,000 |
| Installation Cost | $2,000,000 | $1,700,000 | $7,700,000 |
|  |  |  |  |
| Total Installed Cost | $11,800,000 | $6,500,000 | $25,480,000 |

The major operating costs are the electric utilities, nitrogen and preadsorber bed carbon. An estimate of those costs is shown in table 5.

**Table 5  Estimated Annual Operating Costs**

| Application | Sausage Casings | Sponges |
|---|---|---|
| SLA Flow Rate, scfm | 120,000 | 40,000 |
| Steam and power costs | $1,200,000 | $650,000 |
| Nitrogen costs | $50,000 | $30,000 |
| Replacement carbon | $135,000 | $75,000 |
| | | |
| Total operating costs | $1,385,000 | $755,000 |

The stated operating costs do not include labor. Since the system is automatically operated, the operator of the manufacturing equipment line can monitor the SRU. In addition to that effort, approximately 1 man-day per week is required for standard maintenance and repair activities.

## SUMMARY

At the present time, all manufacturers of cellulose products by the viscose method are meeting the proposed NESHAP standards. However, for new facilities, more stringent control requirements will be applied. The timetable for enforcement of the new rule is not known.

While there are a number of options available for control of emissions from viscose manufacturing operations, the one most widely used has been activated carbon adsorption. Recent improvements in an inert gas regeneration process have resulted in relatively trouble free operation. This process design can be applied to all levels of concentration and flow rates encountered in the three major applications, food casings, sponges and rayon.

One manufacturer investigated all control options and decided to install an inert gas regenerated activated carbon system.

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