

Ammonia Disposal — Coke Plants

By

H. A. GROSICK

*Chief Project Engineer — Coke Plant Section
Engineering and Construction Division
Koppers Company, Inc.*

THE DESTRUCTION OF coke plant ammonia by incineration is a subject that has received attention by many coke plant managers and operators during recent years. While ammonia destruction is receiving considerable attention now, it is not a new subject. Koppers Company, Inc., as early as 1956, practiced partial removal of ammonia from coke oven gas with combustion of this ammonia with coke oven gas in plant steam boilers. A paper¹ was presented as long ago as 1958 by Mr. E. V. Schulte of Koppers Company, Inc. on disposal of ammonia in coke plants. The primary purpose of this paper is to bring Mr. Schulte's 1958 paper up to date.

In 1958 the price of sulfate and the price of acid was such that the sulfate market was not considered good, and in new plants the destruction of ammonia looked attractive. Today the price of sulfuric acid is higher than it was in 1958 and the selling price of ammonium sulfate is considerably lower. Various losses resulting from production of ammonium sulfate have been reported by coke plants. These figures vary from \$10.00 to \$30.00 per ton of ammonium sulfate excluding capital costs. The price of ammonium sulfate used in the 1958 study was \$32.00 per net ton. Many plants today have been forced to dump excess sulfate on the export market at a new price of approximately \$8.00 per ton of sulfate. It is readily discernible with a return of this sort that the loss per ton of sulfate could approach \$30.00 per ton or more. The average coke plant produces approximately one ton of ammonium sulfate per 100 tons of coal carbonized. Based on the cost of today's acid and the selling price of sulfate today, the loss per ton of coal carbonized will be approximately 15 cents to 30 cents and the loss per ton of coke produced approximately 20 cents to 40 cents. In a plant carbonizing approximately 4800 tons per day of coal, the loss would be \$720 to \$1440 per day or \$263,000 to \$526,000 per year. It becomes quickly evident that another means of disposing of the ammonia in coke oven gas is certainly desirable.

The system of ammonia destruction proposed in 1958 as an alternate to sulfate production consisted of washing the ammonia from the coke oven gas by

means of water, distilling the ammonia from the water, dephlegmating the vapors to a concentration which could be burned, incineration of the vapors in a combustion furnace and venting of the products of combustion to the atmosphere by means of a stack. We are still proposing the same basic process of ammonia destruction today with improvements to be discussed in more detail later in this paper.

Coke plant managers, operators and research personnel experienced in by-product plant operations are well aware that the use of water washing for removal of ammonia from coke oven gas is not a new process. This process has been used for many years in some American plants and more widely in Europe for the recovery of ammonia as concentrated ammonia liquor and in the indirect process of ammonium sulfate production. It is only the destruction portion of the process and certain variations of the process in order to minimize operating difficulties and drastically reduce initial investment and operating costs which can be considered novel. Certain variations are also proposed as a direct result of the increased stringency of air and water pollution regulations. The interest in the incineration or destruction of coke plant ammonia now appears to be accelerating and one coke plant will begin incinerating the ammonia distilled from the crude ammonia liquor during the coming year. Koppers Company, Inc. expects to have a plant utilizing the total proposed process in operation within two years.

PROCESS DESCRIPTION

Figure 1 shows a by-product gas flow diagram of the proposed process. The gas flow through the primary coolers, exhausters and tar precipitators is conventional. However we do recommend that the gas outlet temperature from the primary coolers be carried as low as possible to minimize the amount of naphthalene remaining in the gas. It is also important that the efficiency of tar removal be maintained at a high level to minimize tar deposition in the naphthalene scrubbing system. To this end we would recommend that a spare tar precipitator be provided. This is also a good precaution for plants producing ammonium sulfate.

The naphthalene scrubber is the next piece of equipment in the gas stream. This spray type unit counter-currently scrubs the naphthalene from the gas utilizing a wash oil of either the petroleum or creosote type. For purposes of this discussion we shall consider only the petroleum type wash oil utilized in conjunction

Presented at the Western States Blast Furnace and Coke Plant Association meeting, Chicago, Ill., January 29, 1971 and at the Eastern States Blast Furnace and Coke Oven Association meeting, Pittsburgh, Pa., February 19, 1971.

¹Proceedings Blast Furnace, Coke Oven & Raw Materials Committee of AIME Conference 1958.

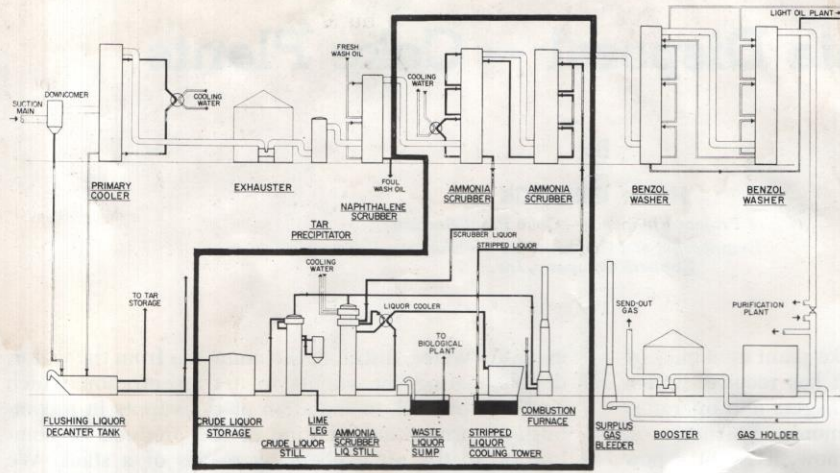


Fig. 1—Coal-chemical plant with ammonia destruction process

with a typical light oil recovery plant. This unit can be operated with or without gas cooling. Operation without gas cooling appears to be less troublesome and less expensive since there is little condensate to be separated from the oil and the heat transfer surface required for oil cooling is much greater than that required for water cooling in the first stage of the ammonia washer.

It is important that good naphthalene removal efficiency be maintained at all times so that naphthalene will not be precipitated in the scrubber liquor in the ammonia washers. This efficiency is dependent upon the temperature of scrubbing, the feed of fresh oil to the top stage of the scrubber, and the efficiency of naphthalene stripping in the wash oil still. In order to obtain better naphthalene stripping, the oil bled from the bottom of the naphthalene scrubber for one important example will be fed into a separate five-tray section at the top of the wash oil still. This oil will be stripped with the total steam and light oil vapors leaving the bottom section of the wash oil still. The wash oil feed to the wash oil purifier will be from the fifth tray of the wash oil still and will consist entirely of oil bled from the naphthalene scrubbing system. Any oil from the fifth tray not going to the wash oil purifier will overflow into the top tray of the bottom section of the wash oil still. In this manner, most of the tar which may be picked up by the wash oil in the naphthalene scrubber will be kept out of contact with the main wash oil stream. In the event a light oil plant is not included in the system, the naphthalene can be removed from the recirculated wash oil in a separate stripper.

The ammonia washers follow the naphthalene scrubber in the gas stream. These countercurrent multi-stage spray type washers are designed to remove approximately 98 per cent or more of the ammonia from the gas by washing with water. To improve ammonia removal, the liquor in the first gas stage is constantly recirculated through indirect type coolers. The foul scrubber liquor from the bottom stage of the first ammonia washer is pumped continuously through heat exchangers to the top tray of the scrubber liquor

still. Low pressure steam is utilized in this still to strip the ammonia from the scrubber liquor. The steam requirement is minimized by heat exchanger between the stripped liquor and the feed to the scrubber still. The vapors leaving the top tray of the still are dephlegmated to a concentration which can be successfully burned in a combustion furnace and vented to the atmosphere by means of a stack. The stripped liquor leaving the heat exchanger is further cooled in a cooling tower or by other indirect means and then recycled for further ammonia absorption. This system has a great advantage over use of fresh water to the scrubber in that all of the make up to the system is steam condensate and the blowdown from the system is quite small. Also if fresh water is used, it must be adequately treated or precipitates will form in the system giving much trouble in recirculating pumps and heat exchangers.

It will be noted that the crude ammonia liquor is kept entirely separate from the scrubber liquor recirculated through the ammonia washing system. This liquor is stripped in a conventional ammonia still equipped with lime leg and the vapors leaving this still are dephlegmated and mixed with the vapors leaving the scrubber liquor still for incineration. The waste liquor leaving the crude liquor still passes to the waste liquor sump after which it is further treated before disposal.

Figure 1 shows benzol washers immediately following the ammonia washers. This would be the recommended location for these washers; however, removal of light oil is not considered essential in the operation of the plant. In the case of a plant having no light oil recovery, it is obvious that operation of the naphthalene scrubbing system a design criterion is required to prevent deposition of naphthalene on the fuel gas and send-out gas lines. The arrangement showing the benzol washers indicates connection to a purification plant for H₂S removal before the gas passes to the holder for use as fuel gas and send-out gas. We still feel that a gas holder is the most reliable pressure controller and the best available means of minimizing the pressure surges created by the reversal of a large battery of valves.

CRITICAL OPERATING CONDITIONS

Even before a by-product plant as shown in this layout, is in complete operation, we are aware of certain operating conditions which are important to successful operation of this plant. These items are as follows:

Tar Removal

It is essential to good operation for this or any coal chemical recovery operation that the efficiency of tar removal be maintained at a high level. If an excessive quantity of tar gets through to the naphthalene scrubber, it is picked up by the wash oil recirculating system. In the recirculating system it can cause trouble in two ways. First it can be carried by the gas up into the mist suppressor causing plugging; and secondly, it can be carried over into the wash oil system causing difficulties in the light oil system. The wash oil system as described above has been designed to minimize problems caused by this tar, but even if no operating problems are encountered, frequent dumping of the wash oil purifier contents would be necessary and large quantities of make-up wash oil to the system would be required.

Naphthalene Removal

Naphthalene must be removed from the gas to such an extent that little or no naphthalene will precipitate in the ammonia waters. While a small amount of naphthalene in the scrubber liquor feed to the ammonia still might not cause serious difficulties, it is almost certain that large quantities of naphthalene would cause difficulties in the dephlegmator and heat exchangers and in the coke oven gas distribution system.

Cooling Water Temperature

The efficiency of ammonia removal by water washing in addition to the quantity of water used is inherently a function of the absorption temperature. For an ammonia removal efficiency of 98 per cent or better it is preferable for water and steam economy that the absorption be carried out at a temperature not exceeding 85 to 87 deg. F.; therefore, the maximum cooling water temperature should preferably not exceed 75 deg. F. In areas where the maximum service water temperature exceeds 75 deg. F. for an extended period it will probably be necessary to provide refrigeration or an alternate source of cooler water such as well water or city water.

POLLUTION PROBLEMS ASSOCIATED WITH AMMONIA DESTRUCTION

When discussing this ammonia destruction process with coke plant operators, the first question asked is invariably "How serious is the air pollution problem created by venting these combustion gases to the atmosphere?" It is well known that it is impossible to wash an ammonia from the gas with water without simultaneously washing out a portion of the H₂S, HCN and CO present in the gas. Of the acid gases removed, hydrogen sulfide is of particular importance since a portion of the H₂S absorbed with the ammonia will be distilled from the scrubber liquor with the ammonia vapor and burned in the combustion furnace to SO₂.

Empirical data which we have obtained from operating plants indicate that the percentage of the H₂S in the gas removed along with the ammonia will approximate 12 to 15 per cent of the H₂S in the gas. In addition to this, a much smaller quantity of H₂S will be stripped from the crude liquor and also burned to SO₂ in the combustion furnace. This seems like a minor problem today when the majority of the coke plants in the United States are making no attempt to remove H₂S from the coke oven gas. This means that the total H₂S in the coke oven gas is burned to SO₂ and emitted to the atmosphere wherever this gas is burned. However, new air pollution codes are emerging almost continuously and it may be only a matter of time until gas purification (H₂S removal) is mandatory, and the SO₂ concentration in the stack gases has to be reduced. There are several possible answers to this problem, as follows:

a) Preheaters can be installed ahead of the ammonia stills. These units would be operated at a low steam rate and low temperature to remove and recycle the acid gases and a portion of the ammonia from the liquor before it is fed into the main still. The net result would be a buildup of the H₂S concentration in the gas to the ammonia washers such that the total H₂S from the ovens would then go on through the by-product plant to the H₂S removal plant.

b) Through dilution of the products of combustion. Our calculations indicate that if the products of combustion from the combustion furnace are vented directly to the oven stack, the concentration of SO₂ in the total stack gases will meet the most stringent codes we have seen to date, if the fuel gas has been purified (90 per cent removal of H₂S).

c) Recycling the products of combustion. We have been studying the possibility of recycling the combustion gases back into the suction main ahead of the primary coolers. This would entail a slight drop in the Btu of the coke oven gas, but the process has definite possibilities.

d) Processing the ammonia still vapors through a sulfur recovery unit. Calculations indicate that the dephlegmated ammonia vapors can be blended with the foul gas from an H₂S removal plant and sent to the sulfur recovery plant. Total sulfur recovery would be increased and it appears very probable that the tail gases from the sulfur recovery unit could be recycled into the suction main ahead of the primary coolers without serious difficulty. This approach could not be taken until such time as an H₂S removal plant for total gas is installed.

e) Use of ammonium phosphate solution. An ammonium phosphate solution is being used at present in one plant for the removal of ammonia from coke oven gas in conjunction with the production of anhydrous ammonia. Ammonium phosphate solution can also be used for low pressure operation in conjunction with ammonia incineration. The

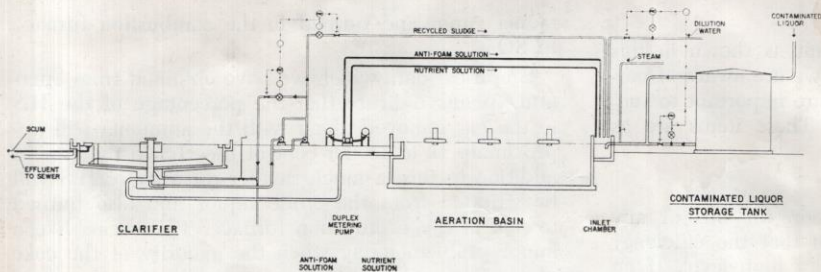


Fig. 2—Biological treatment plant

primary advantages of this system is that much smaller quantities of acid gases including H_2S are absorbed from the gas by the ammonium phosphate solutions. The primary disadvantages of this system compared to the water system is capital cost, since much stainless steel equipment is required when using phosphate solution.

Oxide of Nitrogen

Many potential customers have been concerned that the combustion of ammonia might produce an inordinantly high quantity of oxides of nitrogen. Extensive laboratory tests and equilibrium studies have shown that this is not a serious problem. The quantity of the oxides of nitrogen produced in this combustion per ton of coal carbonized will usually be only about 10 per cent of that produced in the battery itself by the combustion of coke oven gas in the heating system.

Any combustion process using air as the source of oxygen necessarily exposes a mixture of oxygen and nitrogen to high temperatures. Oxides of nitrogen, both NO and NO_2 , are formed. The concentrations developed are dependent upon many factors including the following:

- a) Combustion temperature
- b) Amount of excess air used
- c) Rate of cooling of combustion gases

In heating a battery of ovens, high temperature is necessary and this is the reason much higher concentrations of oxides of nitrogen are produced. In the ammonia combustion furnace, the flame temperature can be kept considerably lower.

The amount of excess air used can be well controlled in either combustion system. Less excess air means less oxides of nitrogen.

Slow cooling of the combustion gases means lower concentrations of oxides of nitrogen. The cooling is not rapid in either furnace.

Stream Pollution

The system for destruction of ammonia has not changed the age-old problem and stream pollution associated with coke plants. The main pollutant, since the first by-product coke plant was built, has been and remains the excess flushing liquor make which we shall call crude ammonia liquor. For many years it was standard practice to strip both the free and the fixed ammonia from the crude ammonia liquor and introduce the ammonia vapors back into the gas stream ahead of the saturators thereby increasing

the ammonium sulfate production. Lime was utilized to free the fixed ammonia. In some plants liquor was dephenolized either before the ammonia still or in conjunction with the ammonia still.

Some years ago, many plants discontinued the use of lime on their stills since it was an unprofitable operation and in recent years many plants have discontinued distillation of the crude ammonia liquor entirely. Since this liquor cannot generally be disposed of in any waterway adjacent to the plant site, it has become very common to dispose of this liquor in the quenching station. This practice has intensified the air pollution problem and it will soon be mandatory to discontinue this method of disposal. Our recommended method for handling this crude ammonia liquor today is to distill both the free and the fixed ammonia from the liquor and follow with treatment in an activated sludge type waste disposal plant.

Figure 2 shows a flow diagram of this process. Extensive laboratory tests were run over an extended period of time with actual coke plant liquor to establish parameters for the design of this plant. In this plant the waste liquor from the waste liquor sump is first transferred to a large storage tank so that the composition of liquor fed to the aeration basin will not be subject to sudden variations. The liquor is fed continuously from this tank and mixed with a controlled amount of dilution water as it enters the aeration basin. A nutrient is also added. The aeration basin is designed for from 12 to 24 hours retention time depending upon the composition of the feed, its pretreatment, and the amount of dilution water used. The aeration basin is kept in a constant state of agitation and aeration under controlled temperature and the overflow passes to a clarifier where the sludge is collected and the clarified effluent overflows to a point of disposal. The sludge is recycled to the aeration basin with a small bleed-off to the sanitary sewer. Some results established by a comprehensive long range research program include the following:

- 1) When treating undistilled crude ammonia liquor, only the phenol and BOD can be reliably removed.
- 2) When treating distilled liquor, the phenol can be removed consistently to less than two tenths of one part per million and removal of thiocyanate and BOD was consistently in excess of 90 per cent.
- 3) The temperature of the liquor in the aeration basin must be maintained between 70 and 100 deg. F.

- 4) The color of the effluent deepens and will not meet effluent color standards. Color standards can be met by subsequent treatment with activated carbon or possibly soil percolation where space permits.

In summary, economics are dictating changes to the methods of removal of ammonia from coke oven gas

and its disposal. A method of removing the ammonia from the gas by water washing and its destruction by burning is for economic reasons being considered and adopted. The minimizing of both stream and air pollution is becoming of increasing importance and methods to comply with these newer regulations are being made available for adoption.

Scrap Preheating Systems For Electric Furnaces Developed By Loftus Engineering

Three advanced types of scrap preheaters for electric furnaces have been introduced to the steel production industry by Loftus Engineering Corporation, Pittsburgh, Pa., a subsidiary of Western Gear Corporation.

The first of the new systems and the first in the industry, a direct-fired type of furnace, soon will go on-stream at Bethlehem Steel Corporation's plant at Steelton, Pa. Specifications for the Bethlehem operation call for preheating scrap to an average of 1500 deg. F. for a three-bucket charge to a 200-ton electric arc furnace.

Previously the melting of cold scrap, a vital steel-making resource, had been excessively costly in terms of time and energy requirements. Both time and energy factors can be reduced with installation of one of the new scrap preheaters, which, in addition to the direct-fired type at Bethlehem, Steelton, include an external combustion furnace and a vortex-hood-type. Each system basically consists of a combustion chamber, a hot air duct from the combustion chamber to a refractory-lined preheat hood, modified clamshell charging buckets, a transfer car, and a waste heat exhaust system.

In the external combustion type, the design uses a typical blast furnace stove combustion chamber,

fueled by natural gas, with an excess air system to control flame temperature to about 2400 deg. F.

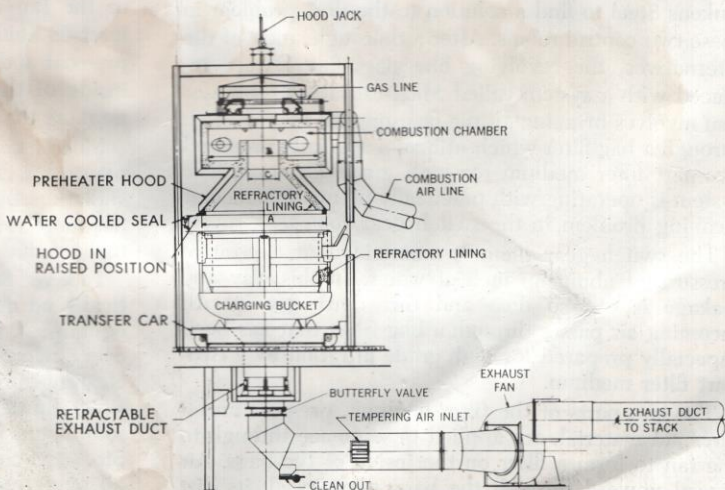
The direct-fired system has the burners in the preheat hood and combustion air blowers adjacent to the preheat stations. Flexible hoses, which facilitate raising and lowering the preheat hood, supply fuel and combustion air through headers to the burners.

In the newly-patented vortex system, burners are arranged tangentially around a combustion chamber of annular ring shape, mounted above the preheat hood. Combustion products flow through a centrally-located vortex down into the preheat hood, and to the scrap bucket. A major feature provides for direct introduction of tempering or diluting air to the vortex, not through the burners as in the other systems.

According to Loftus Engineering, while total savings from scrap pre-heating will vary with each installation, direct savings and lower operating and maintenance costs will result in average savings of about \$2 per ton of steel produced. Savings as high as \$4 per ton are not uncommon, considering that these savings are in part derived from reduced labor costs through increased production.

Added production is a major factor, since by doing a large part of the preheating work outside the furnace, a corresponding reduction in tap-to-tap time is realized, allowing for additional heats. A plant now producing four heats a day without preheat can produce six heats a day with a Loftus preheating system, an increase of 25 to 30 per cent of plant capacity.

Vortex-type scrap preheat system shows in schematic form, position of combustion chamber with tangential arrangement of burners above preheat hood. Tempering or diluting air is introduced directly to the Vortex



Air Filtration System For Electric Furnace Switch Gear At Lukens Steel

With so much emphasis on air pollution, many industrial firms are faced with the problem of "room pollution". Not just with so called clean rooms but increasingly for rooms that contain highly sensitive and sophisticated equipment such as switch gear, motor controls, M-G sets and instrumentation. These rooms must be kept free of dust and grime for such equipment to operate properly. This is especially true for industries whose basic operations develop large quantities of dust emissions.

Collection equipment located at the source of dust generation, that limits fugitive dust to allowable levels, does not always meet the needs of sensitive switch gear instruments and control systems. Dust that does escape the collecting system tends to rise to the upper levels of enclosed buildings where much of the complex equipment is often housed.

The steel industry, because of all the processes utilized, is especially cognizant of its problems of keeping motor controls, computer areas, and sophisticated control equipment operating in a clean atmosphere.

Lukens Steel Company, one of the country's largest specialty plate steel producers, had such a problem. They needed reliable atmospheric filtering systems for two control rooms that contain controls for three electric arc melt furnaces, high voltage mercury tube rectifiers and de-gasser controls. Formerly clean air was introduced to the control rooms after being filtered by a revolving fiberglass filter. Constant positive pressure was kept in the control room by revolving the filter to keep the resistance to air flow at the designed level. Because of the location of the filtering system and the conditions of air contamination in this area this type of cleaning system proved to be inadequate and undependable. Replacement of the filter rolls after contamination and constant cleaning of the rooms and controls made maintenance time and costs prohibitive.

The Johnson-March Corporation was called in by Lukens Steel to find a solution to the dust problem in these two control rooms. After a thorough study of the alternatives, the revolving fiberglass filters were replaced with a system called Maxi-Filtration. This system involves bringing all the charging air for the room through a bag filter which utilizes a specially prepared two-part filter medium for high grade filtration. The system is operating with practically no maintenance or cleaning problem in the switch gear rooms.

The switch gear room is maintained at a positive pressure of about an inch of water. In this way any leakage is out so dust and dirt don't get in. All incoming air passes through a bag filter that has been especially prepared for high grade filtration by a two-part filter medium.

The two parts of the filter medium, pre-coat and a filter aid material, are applied in sequence through to the fan to form a filter on the inside of the bags. Air forced upward through the bags deposits all its dirt

on the filter medium. When this filter is first installed a pressure drop through the filter of about an inch and a half of water is experienced. Over a period of months as dirt is collected, this slowly increases. When a pressure drop of five inches of water is reached, the filter is shaken down and a new filter medium is placed in the filter by repeating the initial installation process. The frequency of recharging depends upon individual plant conditions of air contamination. Usual applications last one to three years before recharging is required.

The operation of the equipment is very simple. Except for preparation of the filter medium, there is virtually no maintenance. In nearly a year and a half of operation the filter medium has been changed twice. Once after about nine months of operation and second time, after about six months. The difference is thought to be due to the considerable amount of moisture that was taken in during a very wet winter period. It is believed that if a hood were provided over the air intake to cut down atmospheric moisture, that the filtering medium might last longer. However, this is of little concern because the entire cleaning and recharging process requires less than four hours. Even if the unit is recharged considerably more frequently than every six months, it would not be anywhere near such a problem as was the cleaning of the switch gear room, and the maintenance of switch gear previously.

The recharging cycle is simple. The fans are turned on, the bags are shaken down and the old filter medium and the collected dust are gathered in the hopper. When this has been discharged to a collecting bin or box under the unit, a thorough shaking completes the cleaning of the bags. The bags are inspected, tensions adjusted if necessary and any damage to the bags is repaired. During the initial start-up the bags are, of course, installed and checked for tightness and tension. With the blower running, the desired weight of the pre-coat is blown into the system until the pressure differential across the unit stabilizes at one and half inches of water. With the fan still running, the filter aid is injected into the system through the fan in the same manner and is added to the pre-coat. Operation of the fan must be maintained at this point for at least 48 hours, preferably for a week so that both the pre-coat and the filter aid are allowed to settle on the inside of the bags. The unit is out of operation for no more than a four-hour period for the entire process.

Since electrical dependability is the essence of this plant, this factor alone was sufficient to justify the installation. But the modest investment in the equipment has more than paid off in terms of the reduced maintenance and longer trouble-free switch gear operation.

Lukens Steel reports that they now have practically no maintenance or cleaning problem with the equipment. If the filter medium had to be replaced every two or three months, it still beats all previous cleaning problems. Replacing it every six months is no burden. It represents a maximum of three or four hours work that is easily accomplished. Lukens Steel switch gear, rectifiers and motor controls now all operate in a good, clean atmosphere.