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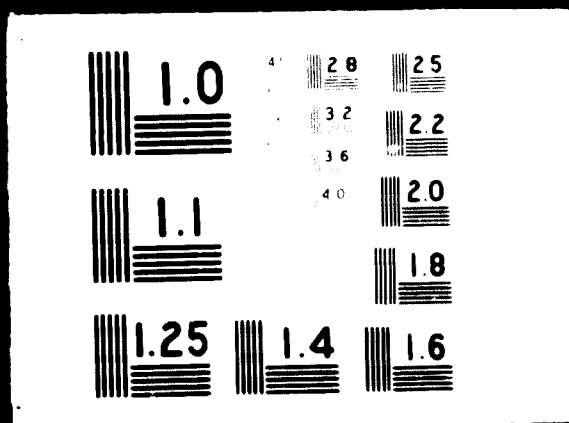
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6 August 1971

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Second Interregional Fertilizer Symposium

Kiev, USSR, 21 September - 1 October 1971
New Delhi, India, 2 - 13 October 1971

Agenda item III/4

POLLUTION CONTROL IN ACID PLANTS^{1/}

by

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Agenda item IIIA

SUMMARY

POLLUTION CONTROL IN ACID PLANTS^{1/}

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J. M. Connor

G. J. Dell

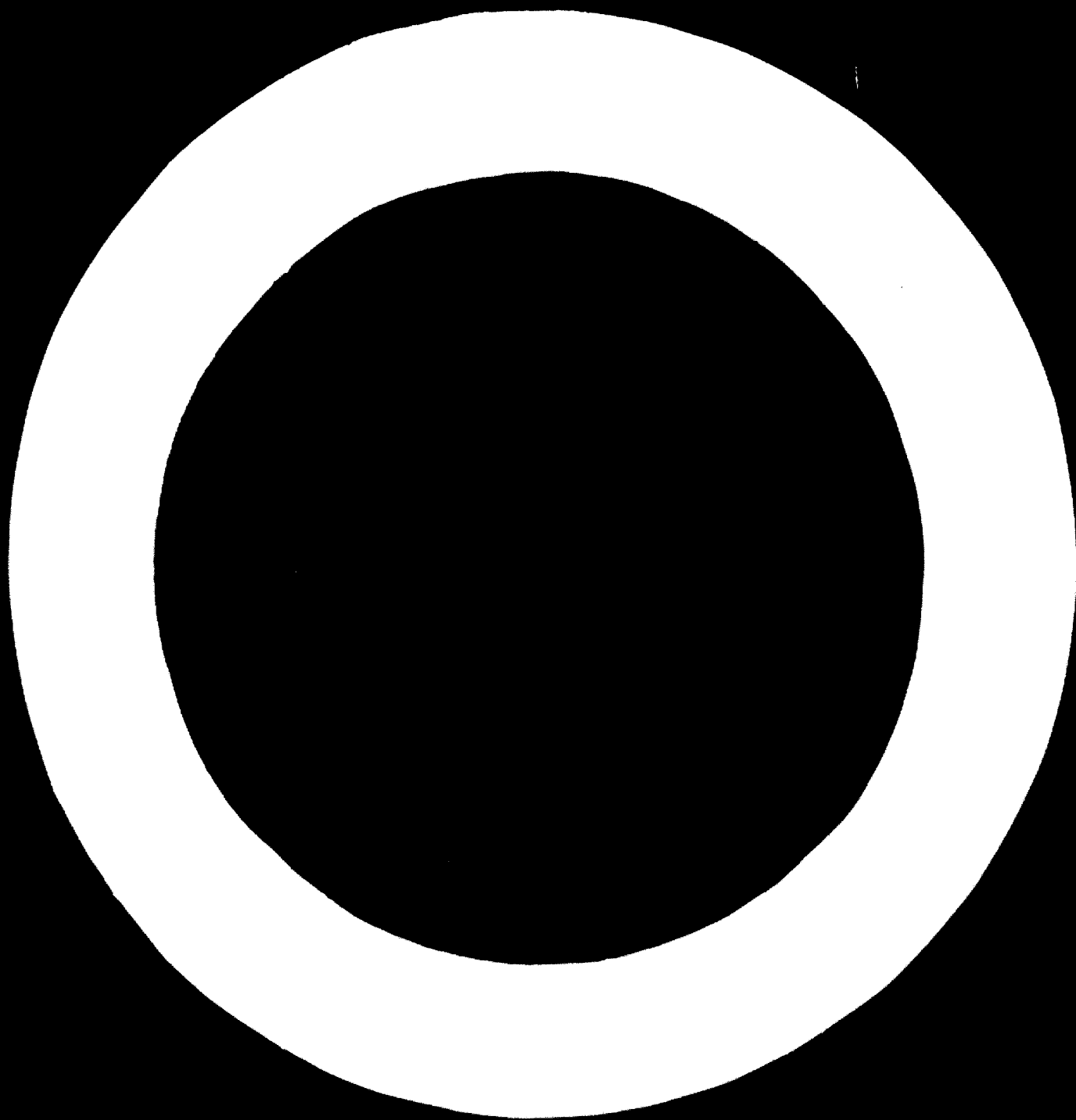
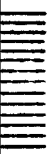
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The responsibility of the chemical plant designer and operator has undergone a dramatic change in recent years. No longer is his duty limited to obtaining the maximum return of product with a minimum direct expenditure of resources. Under the pressure of newly aroused community interest and, hopefully, the higher call of conscience, he now must in addition continually strive to reduce the discharge from the plant of all materials which can adversely affect the environment. This paper describes the extent of the pollution problem, and present and potential means for emission control, in the production of the three mineral acids which are the foundation of the fertilizer industry.

Sulfuric acid is now produced almost exclusively by the contact process wherein sulfur dioxide and air, generally from burning sulfur or roasting sulfide ores, are reacted at high temperature over a catalyst to yield sulfur trioxide. The latter is absorbed in water to produce sulfuric acid. Unconverted sulfur dioxide is discharged from the absorber in the tail gas at a concentration of approximately 2,000 ppm by volume in plants designed for the most economical operation.

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The plant design which has proven most successful in reducing sulfur emissions on a commercial scale has been the Dual Absorption System. After removal of sulfur trioxide in a primary absorption tower, the process gas flows to additional catalyst beds to convert a greater percentage of sulfur dioxide to the trioxide, so that the gas leaves a final absorption column with less than 500 ppm of sulfur dioxide. To reach still lower concentrations of oxides in the stack, treatment of the tail gas is necessary. Levels below 200 ppm can be reached by use of the technology already developed for removal of sulfur dioxide from power plant flue gases and even lower concentrations have been achieved with the use of absorbents in the pilot plant.

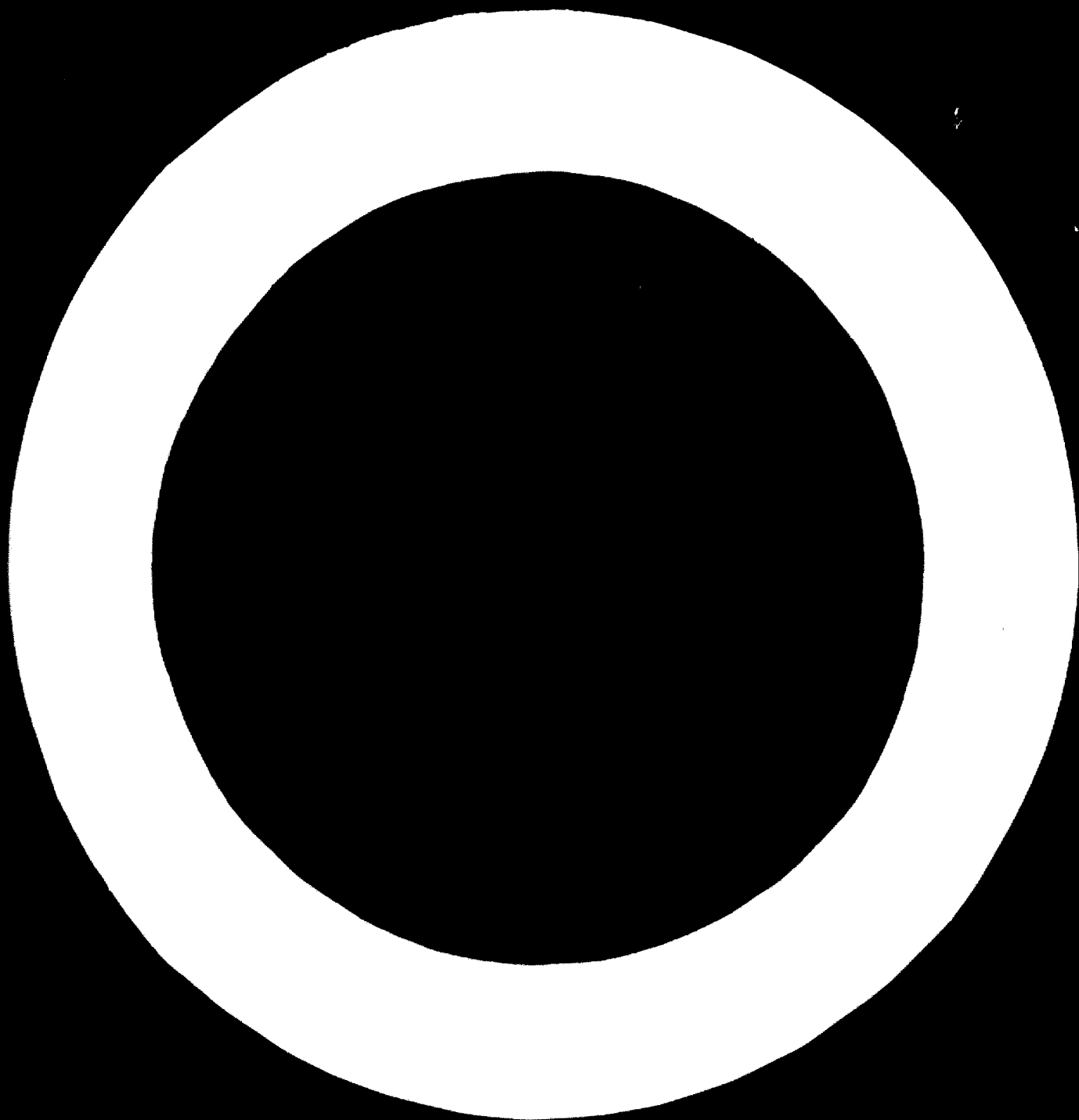
Phosphoric acid is made by reacting phosphate rock with sulfuric acid. This use consumes about 40 per cent of all sulfuric acid produced. Phosphate rock is a complex of calcium phosphates with varying amounts of other minerals and generally contains about three to five per cent of fluorine. On reacting with sulfuric acid, calcium in the rock precipitates as the sulfate and is removed by filtration. The fluorine present forms hydrofluoric acid which reacts with silicon dioxide to form fluosilicic acid. With Florida rock, about five per cent of the fluorine present is vaporized in the digester which now is normally exhausted and scrubbed with water in order to limit fluoride emission to the atmosphere. Scrubbers presently in operation reduce emissions from more than 2,000 ppm to the 10 ppm level. Equipment improvements should cut these losses in half.

Phosphoric acid is normally concentrated to 54% P_2O_5 in a vacuum concentrator where much of the remainder of the fluorine is vaporized. The overhead vapors are condensed by direct contact with cooling water which is circulated to large ponds where the fluorine eventually settles out. Alternatively, fluosilicic acid can be recovered from the overhead vapors and converted to valuable by-products.

The remaining acid critical to fertilizer production is nitric acid which is made by reacting ammonia with air to produce nitric oxide which reacts with additional air to produce nitrogen dioxide. The latter is absorbed in and reacts with water to produce nitric acid and additional nitric oxide which must be reoxidized for further absorption. The oxidation reaction is a relatively slow one so that increasingly larger equipment is required for reoxidation as the concentration of oxides is decreased. The value of the recovered oxides can only justify reducing the level in the vented gas to about 2,000 ppm of nitrogen oxides by volume. Concentrations below 700 ppm can be reached without too great a cost by increasing the size of the absorber.

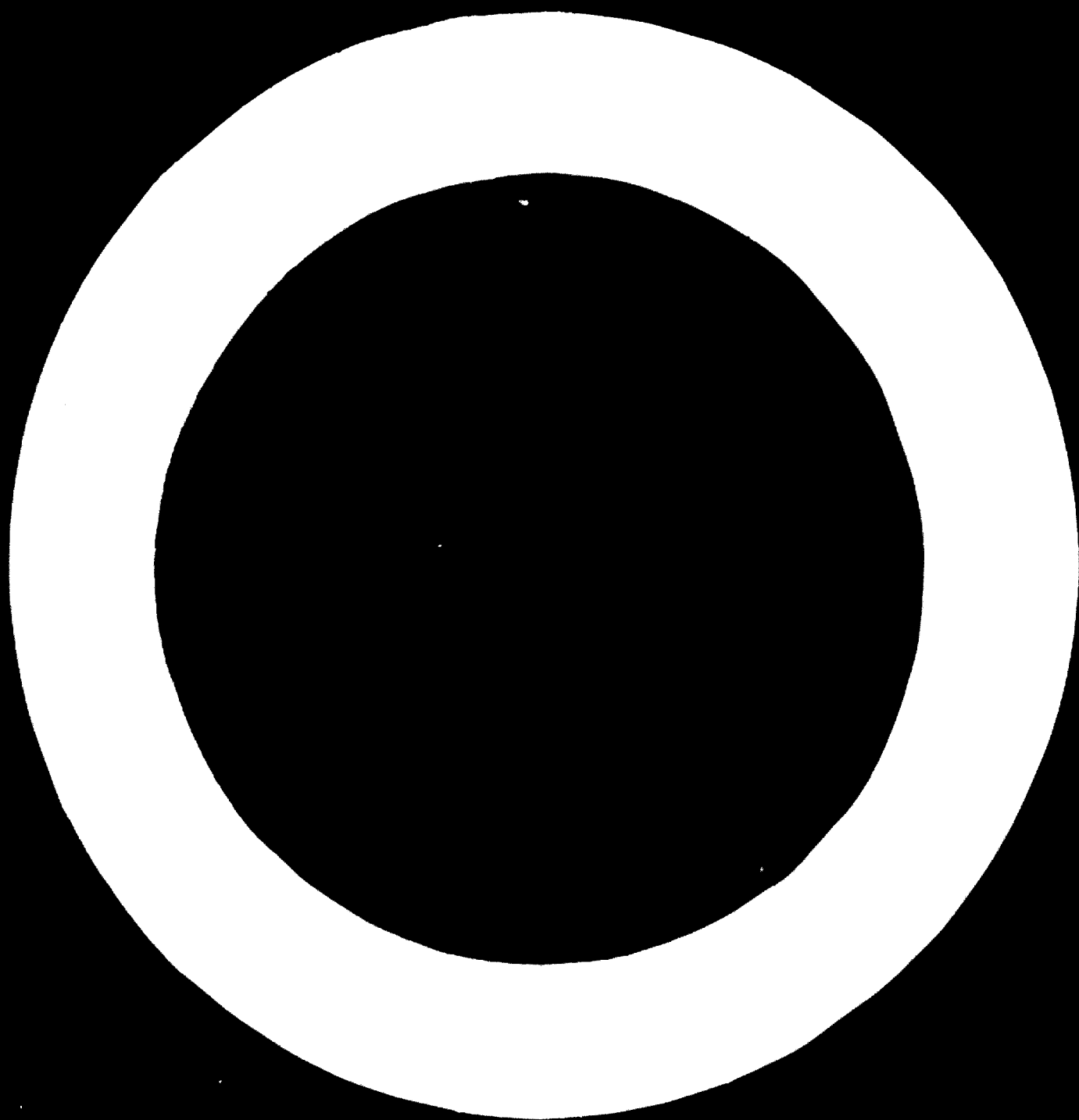
The most economical method now in operation for reducing the nitrogen oxides

content of the tail gas to below the 500 ppm range is by reaction of the oxygen and nitrogen oxides in the tail gas with fuel in a catalytic combustor. Operation at higher pressure can achieve equivalent results but would be more costly. Absorption of nitrogen oxides on molecular sieves has been demonstrated, but based on pilot testing, cannot justify the increased investment.



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I. INTRODUCTION

1. The responsibility of the chemical plant designer and operator has undergone a dramatic change in recent years. Now, in addition to his job of obtaining the maximum return of product with a minimum direct expenditure of resources, he must eliminate the discharge from his plant of any material which can adversely affect the environment. This new parameter has led to the study and incorporation into the plant of many designs which would previously have been rejected as uneconomical. This paper describes the extent of the pollution problem, and present and potential means for emission control, in the production of the three mineral acids which are the foundation of the fertilizer industry.
2. Plants for the production of sulfuric acid, phosphoric acid and nitric acid have been major contributors to atmospheric pollution in the past. The problems for each have been different and the approaches to solving these problems have of course varied. For sulfuric acid, incomplete conversion of sulfur dioxide to the trioxide is the fundamental difficulty. The greatest variety of approaches have been studied for this acid, and the plant design which has thus far proven most successful on a commercial scale has been the Double Absorption process. In phosphoric acid production, fluorides released during rock digestion and acid concentration are the main problems. These emissions can be minimized by use of properly designed scrubbers, and recovery can even provide a valuable byproduct. If no special provisions are made, the

nitric acid plant will discharge unabsorbed nitrogen oxides. These can most economically be eliminated by reaction with fuel in a catalytic combustor.

3. In all these cases, the development of solutions has followed detailed engineering evaluations of the variables involved and much progress has already been made. As will be noted, systems still under study will, when optimized, yield even further reductions in the amounts of pollutants discharged by these types of plants.

II. SULFURIC ACID PLANTS

4. Most sulfuric acid used in the fertilizer industry is produced by the Contact Process from sulfur dioxide generated by burning sulfur or metal sulfide ores. The dioxide is reacted with air over a catalyst at high temperature to yield sulfur trioxide which is absorbed in water to produce sulfuric acid. The majority of the plants now in operation were designed to convert between 96% and 98% of the SO_2 produced into sulfuric acid, the remaining SO_2 being discharged to atmosphere and constituting our major pollution problem. In fact, almost every sulfur based plant designed in the last ten years will convert at least 98% of the SO_2 into acid when properly operated at the design rate, but many are normally overloaded with resulting loss of conversion. Plants based on sulfide ores are usually designed for a slightly lower conversion efficiency than sulfur-based plants.

5. These plants, when operated at the best conditions, will discharge tail gas containing the unconverted SO_2 at a concentration of about 2,000 ppm by volume. Although this concentration was generally accepted for small plants, as individual plant capacity increased to 2,000 tons/day and the corresponding amount of SO_2 emitted increased to 34 tons/day, such discharge has become an increasingly severe local nuisance. Three general methods of mitigating this nuisance have been adopted:

Increased Stack Height

Modified Plant Design

Tail Gas Treatment

INCREASED STACK HEIGHT

6. This method plays some part in almost all control efforts. Considerable work has been done to establish the relationship between the ground level concentration of a pollutant, the height at which it is discharged, the quantity and concentration of the pollutant and the weather conditions. The Pearson-Bosanquet relationship has been widely adopted in the U. S. for determining the height of a stack required. Increasing the stack height does not reduce the total pollution but only spreads it over a greater area where it may be less obnoxious and harmful. The proper approach, and that now being adopted in many places, is to determine the stack height required for reasonable ground level concentration of the SO_2 after other methods of reducing the total emission have been applied.

MODIFICATIONS TO THE DESIGN OF THE ACID PLANT

7. Unquestionably the proper way to reduce pollution is to convert more of the SO_2 to acid. There are three ways that this can be done which have been or are being investigated currently as described below:

A Low Temperature Catalyst

8. Most catalysts available to the industry are active at about 440°C . With an 8% SO_2 feed gas, considerations of thermodynamic equilibrium limit the conversion obtainable at this temperature to 98.5%. If a catalyst would be developed which would be active at 300°C , the conversion might be increased to 99.97%.

The Double Absorption Process

9. If, after some of the SO_2 present is converted to SO_3 , this SO_3 is removed (by absorption) and the gas returned to the converter, the equilibrium conditions are changed and a greater proportion of the SO_2 can be converted. This process was first used in Germany in 1964 and although it initially spread rather slowly it is now being widely adopted. Plants designed according to this method are known to be operating in Germany, Belgium Japan, Australia, U.K. and U.S.A. It is probably true to say that most plants now being designed or built in industrial countries are adopting this method.

10. There are many variations of this process, the common feature being that an intermediate absorption stage is incorporated between two of the catalyst stages. A typical flowsheet is shown in Fig. 1 for a sulfur-burning plant. Sulfur is burned in dried air, cooled and fed to the converter in the same equipment as used for single absorption. After at least two stages of conversion and in some cases three stages, the gas leaves the converter and, after cooling, goes to the primary absorber where the SO_3 is removed and the bulk of the acid produced in the plant is formed. The gas from the absorber, after reheating, returns to the converter to pass through a further one or two stages, where because of the high O_2/SO_2 ratio and low SO_3 content, the possible equilibrium conversion is very high. This SO_3 is then absorbed in a second absorption tower.

The converter may contain three, four or five layers of catalyst in all depending on the concentration of SO_2 being used, and the degree of conversion required. 99.5% conversion using 10-12% SO_2 can be obtained in four stages arranged either two before and two after the primary absorber or three before and one after. If greater conversion is required, a third stage before the absorber may be included. Arrangements of heat exchangers vary depending on the designer and in some cases, the returning gas from the primary absorber is finally heated in an exchanger in parallel with the boiler after the first catalyst stage, an arrangement that ensures adequate heat is available even during upset conditions.

The Pressure Process

11. Traditionally, sulfuric acid plants operate at close to atmospheric pressure and, although the trend is towards higher pressure drop through the plant which raises the pressure at the converter slightly, this is not enough to affect equilibrium considerations. However, a substantial increase in operating pressure would not only increase the equilibrium conversion of SO_2 to SO_3 but would assist with the absorption of SO_3 . Anyone familiar with modern nitric acid plant technology must wonder why a similar system has not been applied to the sulfuric acid process but until now, the higher pressure could not be justified. Some patents have been recently published and a plant using this principle is now under construction in France.

12. Figure 2 shows a flow diagram for a potential pressure process. Other variations are possible. After drying, air is compressed to 60-100 psig and sulfur is burned in this air under pressure. The hot gas is cooled in a boiler to converter temperatures and passes through a multi-stage converter with interstage coolers before final cooling and absorption of SO_3 under pressure. The tail gas from the absorber tower is then heated by direct combustion of oil or gas and expanded in a gas turbine to provide the power for driving the compressor. The compressor-turbine unit is operated in the same way as a gas turbine controlled by the fuel supply rate. All the reaction heat developed in the sulfur furnace and converter is used for steam generation for export. If preferred, the tail gas may be heated in exchangers before expansion and the gas turbine combustion chamber eliminated. In this case, the steam available for export will be reduced, as will be the fuel requirements.

13. Whichever system is used, heat is rejected twice (in the gas going to the absorber tower and in the tail gas from the turbine) so that thermal efficiency will not be as good as in a standard acid plant. Present indications are that in plants of the capacities now being built, a pressure plant would be more expensive than a dual absorption plant but at very large capacities, the reduction in size of equipment possible with a pressure plant would make it economically attractive.

TAIL GAS TREATMENT

14. Instead of attempting to improve the dispersion of the SO_2 vented, or to improve the conversion, it is also possible to remove the SO_2 from the stack gas by after-treatment. A very large number of processes have been proposed over the last half century and interest has been considerably stimulated by studies of methods for removing SO_2 from power plant stack gas. Broadly these processes may be divided into three categories as described below:

Absorption with Byproduct

15. The usefulness of such a process depends on the value of the byproduct or the difficulty of disposing of it. Unfortunately, most byproducts are of no commercial value and may themselves result in a pollution problem (e. g. lime scrubbing to produce calcium sulfite; soda ash scrubbing to produce sodium sulfate).

16. One such process is, however, of considerable interest to the fertilizer industry and has been applied to several fertilizer based acid plants during the last twenty or more years. This is to scrub with ammonia and then release the SO_2 from the resulting ammonium sulfite solution by adding sulfuric acid. The resulting ammonium sulfate solution, though no longer a valuable byproduct in itself, can usually be incorporated into any solid or liquid fertilizer produced. Alternatively, either nitric or phosphoric acid may be used instead of sulfuric to release the SO_2 and produce an ammonium

phosphate or nitrate solution. In any case, the solution will contain some ammonium sulfate from the acid mist and vapor in the tail gas and oxidation in the solution.

17. This process is illustrated in Fig. 3. Several plants of this type were built, often at fertilizer plants producing ammonium sulfate where it provided an easy method of recovering additional sulfuric acid to add to the product. With the declining popularity of this fertilizer material, the process lost ground until requirements of pollution control brought it once more into view. Recent plants using the process have been built in Roumania, Czechoslovakia and U.S. and probably in other areas.

18. Most of the earlier plants used single stage scrubbing to reduce the SO_2 concentration to about 500-800 ppm. The current generation of plants uses two stages of scrubbing and sometimes a third washing stage to recover ammonia. In any case, the scrubbing solution is a mixture of ammonium sulfite and bisulfite with a weaker, more alkaline solution in the second stage than in the first. This weaker solution is used as makeup to the first stage and a bleed of product solution is taken from this stage for recovery of SO_2 . Provision is made to add ammonia to both stages so that the pH in each stage may be independently controlled.

Absorption with Regeneration

19. These processes (many of which have been developed) always require heat for regeneration of the solution. Many of the processes developed

for power plant stack treatment are in this category and two such processes have received considerable publicity and are in advanced stage of development. A sodium sulfite-bisulfite process is in operation on a sulfuric acid plant in the U.S. A magnesium oxide scrubbing process with regeneration of SO_2 , developed by Chemical Construction Corporation, is being erected in New England for a power plant.

Adsorption on Solid Adsorbents

20. Although no process using solid adsorbents has yet been installed, several manufacturers of resins and molecular sieves are known to be investigating the problem. In many cases, adsorbents of this type will remove not only SO_2 but any remaining SO_3 acid vapor and acid mist. It may be more difficult to regenerate these sulfate forming compounds than the SO_2 . Regeneration would normally involve passing the air required for the combustion of sulfur through the resin before its use in the furnace so that the regenerated SO_2 is recycled to the acid plants. The economical use of relatively expensive adsorbents will require the use of an automatically timed adsorption-regeneration system and this type of system for the large gas flows normally encountered in acid plants will require some development work itself. Solid adsorbents have the capability of reaching very low SO_2 concentrations (10-50 ppm have been mentioned) but there appears to be a considerable amount of development work involved.

THE PROBLEM OF EXISTING PLANTS

21. Upgrading an existing plant to meet new reduced pollution standards is much more difficult and expensive than designing a low pollution plant in the first place. For this reason, it is probable that as regulations impose standards which are impossible to achieve by minor operating improvements, the older and smaller plants will be replaced by the later designs. However, where a medium sized well maintained plant is in operation and effluent standards must be improved, there are several alternates open to the operator.
22. If the fertilizer plant is producing an ammonia fertilizer and is, therefore, already handling anhydrous or aqueous ammonia, the ammonia scrubbing process described above is one which should be considered first. It does not require any modification within the acid plant itself and can, therefore, be added with the minimum disturbance to current operations. Although it should be located as close to the plant as possible, its only connections to the plant are the tail gas duct and a small line for the return of SO_2 , both of which are cold. It is a simple plant to operate and properly located can be handled by the acid plant operators. Like most other scrubbing processes, being essentially independent of the acid plant, it can handle increased pollutant loads normally associated with plant starts and upset conditions.
23. There are several ways in which an existing plant can be converted to double absorption. Some of these are illustrated in Figs. 4 and 5. The

gas from the stack must be reheated before entering the secondary converter and while some of this heat is obtained in a feed/effluent exchanger additional heat is required. Fig. 4 shows how this can be obtained from the existing plant by means of a new exchanger whereas in Fig. 5 this heat is obtained from a fuel-fired furnace and exchanger. This system will be most useful where several acid plants are combined for one dual absorption addition or where the location of the additional plant is remote from the main plant.

SO₃ AND ACID MIST

24. All the foregoing has been concerned only with SO₂ emission, which represents by far the greatest pollution caused by sulfuric acid plants. However, SO₃ and sulfuric acid vapor, though smaller in quantity are possibly more dangerous. The reason they are given so little attention in this paper is that the problem is largely solved and the solutions have already received a lot of attention.

25. SO₃ is a gas present due to incomplete absorption. In most well operated plants, the absorption is so efficient that it does not represent a problem. If SO₃ is present in the stack gas it will combine with water in the atmosphere to form acid mist. Acid mist is formed in the absorption tower by the reaction of SO₃ with water vapor which may be present due to water or hydrocarbons in the sulfur, inefficiency in the drying tower, or in metallurgical type plants, poor performance of the mist precipitators.

26. Acid mist can usually be removed by the proper selection of stainless steel, teflon or fiberglass filters and several proprietary makes are available. The most efficient require a relatively high pressure drop but will remove mist down to 0.5 microns with an efficiency of about 90%, and most filters will remove all mist particles above 3 microns. In selecting a filter it is, therefore, important to know the mist size that will be encountered and this is the difficulty. The mechanism of mist formation is not fully understood but it is well known that the mist almost always produced in a plant manufacturing oleum is very fine.

27. Scrubbing methods do not usually remove acid mist and may produce it if the SO_3 or acid vapor content of the gas is high. Mist should be removed by filtration before the gas is treated in a scrubbing tower.

III. PHOSPHORIC ACID

28. Wet process phosphoric acid is the principal source of phosphates for fertilizers. It is produced by reacting ground phosphate rock with sulfuric acid and filtering out the calcium sulfate (gypsum) which is precipitated. Practically all phosphate rock used to manufacture this acid contains three to five percent of fluorine and is generally characterized by the formula $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ or $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. The reaction of this fluorapatite with acid is shown as:

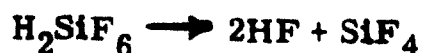


29. The hydrofluoric acid produced then reacts with silicon dioxide (SiO_2) in the rock to produce fluosilicic acid (H_2SiF_6) as follows:



In plants that use rock deficient in silica for the above reaction, the hydrofluoric acid is not converted to fluosilicic acid and severe equipment corrosion problems are generally encountered.

When vaporized, fluosilicic acid disassociates as follows:



30. During digestion, 5 to 30 percent of the fluorine present in the rock is volatilized, principally as silicon tetrafluoride (SiF_4) and will be exhausted with the reactor vapors. The amount of fluorine vaporized depends principally upon the type of rock used but to some extent upon the digester temperature and concentrations. These vapors are the primary source of

harmful emission to the atmosphere in a phosphoric acid plant.

31. In order to minimize pollution, the digester is normally vented to the first of a two-stage scrubbing system or to a prescrubbing section of a multi-stage system. In modern installations, exhaust from other parts of the plant such as the filter, open acid or slurry launders, filtrate seal tanks, hot wells, and vents of acid storage tanks, which will evolve small amounts of fluorides, are collected and combined with the prescrubbed digester gases. The exhaust gas from all these sources are then scrubbed to control and limit the fluoride emission to the atmosphere. Modern plants using Florida rock will vent about 5,000 NM³ of air (per ton of P₂O₅) containing less than 10 ppm of fluorides.

Concentrated Acid

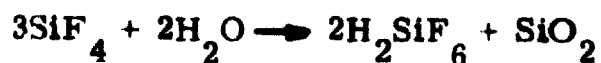
32. The 30% P₂O₅ acid remaining after removal of the gypsum contains up to 75% of the original fluorine content of the rock. It may be treated with a sodium salt such as sodium carbonate to precipitate sodium fluosilicate which is settled, filtered and washed and sold as a by-product. Generally the untreated acid is concentrated to 54% P₂O₅ under vacuum as shown on Figure 7. Much of the fluorine present is released in the overhead steam generated in this step.

33. The overhead vapors are generally condensed by direct contact with water circulated to a gypsum pond where the fluorides settle out. In an increasing number of plants, the vapor is scrubbed before condensing to recover by-product fluosilicic acid. About 40% of the fluorine fed to the

plant is released during acid concentration and 85 to 90% of this can be recovered as a 15 to 25% solution of fluosilicic acid.

Scrubbers

34. SiF_4 vapor is the major pollutant from wet process acid plants where the P_2O_5 content of the acid is 28 to 32%. In scrubbing with water, the tetrafluoride reacts to form fluosilicic acid and silica:



35. The silica forms as a gel and will stick to most surfaces building up on unirrigated ducts, fan blades, packing, etc. To avoid costly shutdowns for cleaning, the preferred equipment for absorbing fluoride vapors is the open spray tower that tends to be self-cleaning.

36. Cyclonic spray scrubbers with water injected from the outside of the cylindrical spray chamber have proven to be quite effective as a means of capturing the SiF_4 and HF in the vent gas. The simplicity of design, low gas pressure drop, low water rate, ease of servicing spray nozzles, even with the plant operating, and their non-clogging characteristics, have made them a popular choice in the fertilizer industry.

37. Each scrubbing stage will remove 75 to 95% of the fluorides in the gas stream. Figure 9 illustrates a typical two-stage installation for this type scrubber which would reduce emissions to 5 ppm of fluorine by volume.

38. The cross-flow spray chamber with an irrigated packed section of "Tellerettes" has also been extensively used to control fluoride emissions

from wet process phosphoric acid plants. Figure 8 depicts a typical unit. The fluoride rich gases are first contacted with sprays to remove the major part of the fluorides. Any airborne liquids or solids are removed by an irrigated baffle. The gas, now lean in fluorides, passes to a crossflow packed bed for final cleanup. Any moisture entrainment is removed from the gas stream by the final one to two feet of the bed which is not irrigated. The solids handling capacity for this type of scrubber is lower than the cyclonic spray tower, so that increased maintenance is required.

Gypsum Pond

39. The slurried byproduct gypsum, scrubbing water and condensing and cooling water effluent from a phosphoric acid plant are normally channeled to a gypsum pond where the gypsum settles out and the water cools by evaporation. This water is recycled to the plant for re-use. Recent investigations indicate that only a small part of the fluorides sent to the ponds revaporizes causing some secondary atmospheric pollution. The remainder apparently precipitates so that, after several years, the concentration stabilizes at approximately 0.6% F by weight.

IV. NITRIC ACID

40. Nitric acid is manufactured by reacting ammonia with air to produce nitric oxide which reacts with additional oxygen to form the dioxide. The latter is absorbed in and reacts with water to produce nitric acid plus additional nitric oxide which must be reoxidized for further absorption. The oxidation of nitric oxide is a relatively slow reaction and becomes the controlling mechanism as the concentration remaining in the tail gas is reduced, requiring increasingly larger equipment to accomplish further reductions in concentration. Without treatment, most plants discharge tail gas containing 1500 to 3000 ppm by volume of nitrogen oxides, which is equivalent to approximately two to three percent of the plant production. Since a major portion of the oxides are in the form of the red dioxide, the vented gas has a distinct yellow to red color. This color is a sharp contrast to the colorless gas containing equivalent concentrations of pollutants which, in the form of nitric oxide alone, which can be unknowingly discharged from utility plants, incinerators and automobiles.

Dilution and Decolorization

41. Efforts at pollution abatement in nitric acid plants were initially directed at eliminating the visible color of the plume. In Europe, particularly, it became the practice to mix additional air or steam with the tail gas in order to dilute the oxides to a level that would not be visible. While this method reduces the concentration of oxides to a somewhat safer level in the immediate vicinity of the plant, the total quantity discharged remains the same. Similar

local protection is afforded by providing increasingly high vent stacks. Several countries now specify minimum elevations at which particular concentrations of oxides can be discharged.

42. In the United States, the equivalent effect of eliminating color from the tail gas resulted from the introduction by Chemical Construction Corporation of the catalytic combustor. This device was first provided in 1954 as an improved means of heat and power recovery. In order to raise the temperature of the tail gas to 670°C and take full advantage of high temperature gas expanders available, a fuel gas is added to the tail gas and the mixture passed over a catalyst to effect reaction with the small amount of oxygen remaining. It was found that the catalyst simultaneously reacted nitrogen dioxides with the fuel to yield nitric oxide and, to a limited extent, nitrogen. (In order to reduce the oxide completely to nitrogen, it was necessary to first eliminate all oxygen.) Since danger from nitric oxide emission itself was not yet recognized, the additional equipment and fuel required for total abatement could not be justified, and the decolorizing type of combustor became more or less standard in the U.S. in the 1960's. Figure 10C is a flow diagram of a typical plant with full power recovery using a catalytic combustor.

43. The catalyst used for the service has generally been platinum or palladium supported on nichrome wire or on alumina in the form of pellets or a honeycomb structure. When a waste hydrogen or carbon monoxide stream is available for fuel, little difficulty is experienced with operation, even at

medium temperatures. The preferred fuel, however, is natural gas and this requires much greater attention to catalyst design as well as a substantially higher ignition temperature, in excess of 510°C in some cases. While the combustors for larger plants were designed to discharge directly into expanders at 670°C in order to obtain the maximum advantage of the high temperature, for plants smaller than 200 T/D nitric acid capacity, high temperature expanders were not available. In order to decolorize the tail gas in such plants, it was necessary to provide a waste heat boiler after the combustor to cool the gas back to about 510°C.

Oxide Destruction

44. With increasing knowledge of the dangers of nitrogen oxide emission, community pressure for total elimination of the oxides mounted. In 1964, only one nitric acid plant in the U. S. was attempting to operate in a manner to actually destroy the oxides. This was being done in a catalytic combustor by providing sufficient fuel to react with all the oxygen and nitrogen oxides in the tail gas. With natural gas as the fuel, final temperatures in excess of 850°C were reached, and the effluent was cooled in a waste heat boiler. Great difficulty was experienced in developing suitable mechanical designs and control systems for the high temperature involved, and it took years before the operation could be considered satisfactory.

45. In order to minimize the problems of high temperature design and control, Chemico developed the Dual Combustion system. (Fig. 10 D) Only part of the tail gas is heated to the ignition temperature and reacted with fuel

to yield an intermediate temperature. The remaining cold tail gas quenches this effluent back to the ignition temperature, the mixture then flowing to a second catalyst bed to react with the remaining fuel. The gas leaves this second bed free of oxides and oxygen, and at the expander inlet temperature. The first plants designed with Dual Combustors did not operate properly because of failure of the catalyst chosen. More recent experience, with improved catalyst and slightly modified operating conditions, has proven the suitability and desirability of the process. In 1969, the client who had experienced the initial difficulty with the system chose the Dual Combustion process for his two new plants in preference to single high temperature bed designs which he had also operated. While theoretically the catalytic combustor should effectively eliminate all oxides, in actual operation there will be some leakage through the catalyst. Abatement will also decrease as the catalyst loses activity, or if insufficient fuel is used. It has generally been indicated that little difficulty would be met in holding emissions to below 300 ppm on a reasonably long term basis.

46. Although catalytic combustion is the only abatement method now in operation at nitric acid plants, the difficulty experienced with combustor catalysts, and the still uncertain life of the new ones offered, has led to renewed interest in other methods of minimizing nitrogen oxide emissions.

Absorption

47. The most obvious means of reducing nitrogen oxide emissions is by providing additional capacity in the absorption tower. The increased cost for improved absorption varies with other plant parameters but rises asymptotically as lower levels of oxides are sought. A recent study showed the effect of changing oxygen content, acid concentration and operating pressure upon the cost of reducing the concentration of oxides in the tail gas. It was indicated that, with a compressor discharging at 9.2 atmospheres, oxide content should be held to the range of 1500 to 2000 ppm for economic reasons alone and that below the 500 ppm range the cost of reducing oxides by increasing the size of the absorber becomes excessive. By increasing the operating pressure, oxide emission can be reduced to the 300 ppm level, but at a relatively high cost. Alternative methods for reducing oxide emission involving absorption and adsorption in various media have been continuously studied and proposed. Early atmospheric pressure plants frequently provided absorption towers using soda ash solution following the water absorbers. At such low pressures these only served to reduce the oxides to the 3,000 ppm level and left the producer with a problem of disposing of the sodium nitrate-nitrite mixture formed.

Adsorption

48. Adsorption was studied most completely for recovery of the dilute oxides produced by the high temperature pebble heaters of Farrington

Daniels' Wisconsin process. Silica gel was the chosen adsorbent and required three successive beds for dehydration, oxidation and adsorption respectively. A small demonstration plant was built by the FMC Corporation for the U.S. Government in 1953 and operated for eighteen months. The data obtained proved the process feasible but not economically justified at the time.

49. With the development of engineered molecular sieves, new studies on adsorption of nitrogen oxides were begun. Research at the University of Florida yielded new data and patents and continued improvement in physical characteristics and adsorption properties of the sieves have led to hope that an economical material may be in sight. Based upon the latest data available, however, the cost for a pair of adsorption beds would be significantly higher than for a catalytic combustion system and cannot compete economically for a new plant so long as steam produced by the latter has value.

Existing Plants

50. All the data presented above refer basically to the design of new plants. Eliminating pollutants from existing plants presents different problems depending on the specific installation. A plant without power recovery, for example, would require the addition of tail gas heaters as well as combustors and waste heat boilers and, if large enough, a tail gas expander and compressor -- virtually a whole new plant. In such a case,

an adsorption system could prove the more economical approach to abatement. Similarly, a plant operating with a 510°C expander would more easily accept a single high temperature combustor bed plus boiler rather than a Dual Combustor system. The latter, however, might be preferable for a plant with a high temperature expander despite requiring a modification to the existing tail gas heaters. Again, for all cases of high pressure plants, if an intermediate range of emission is allowed, an additional absorption section could be the most economical answer.

FIGURE 1
DUAL ABSORPTION SULFURIC ACID PLANT

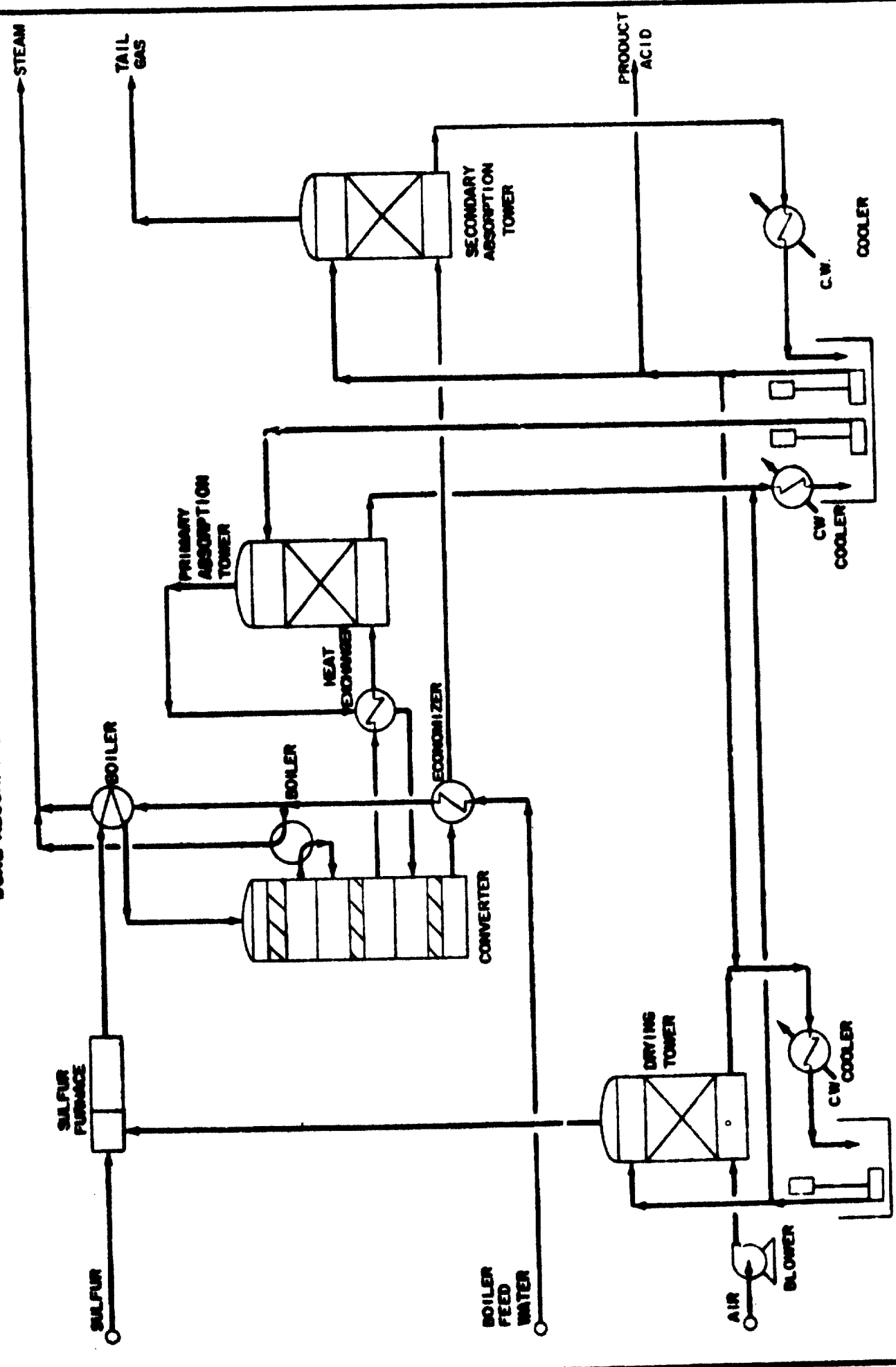


FIGURE 2
PRESSURE PROCESS

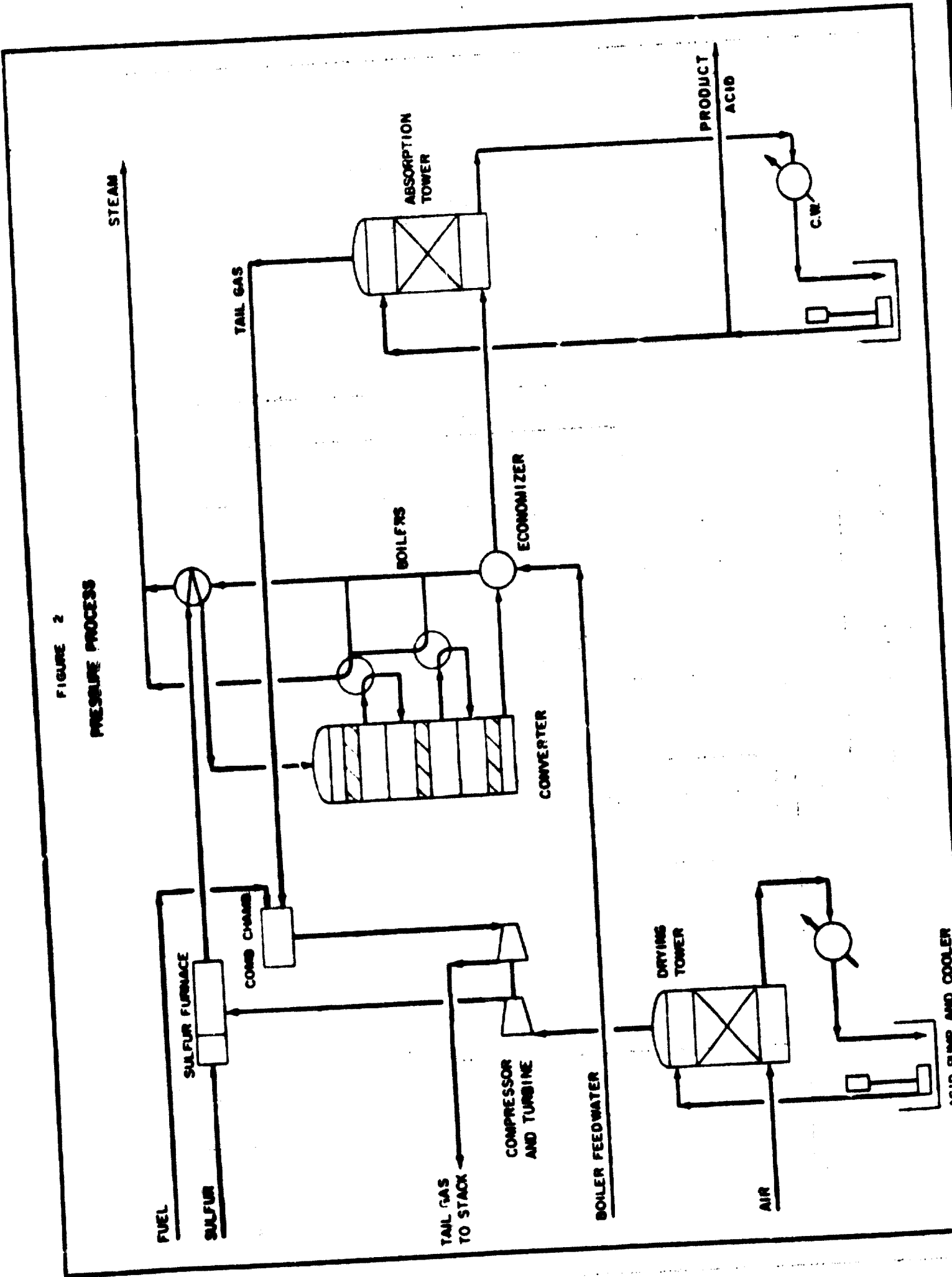
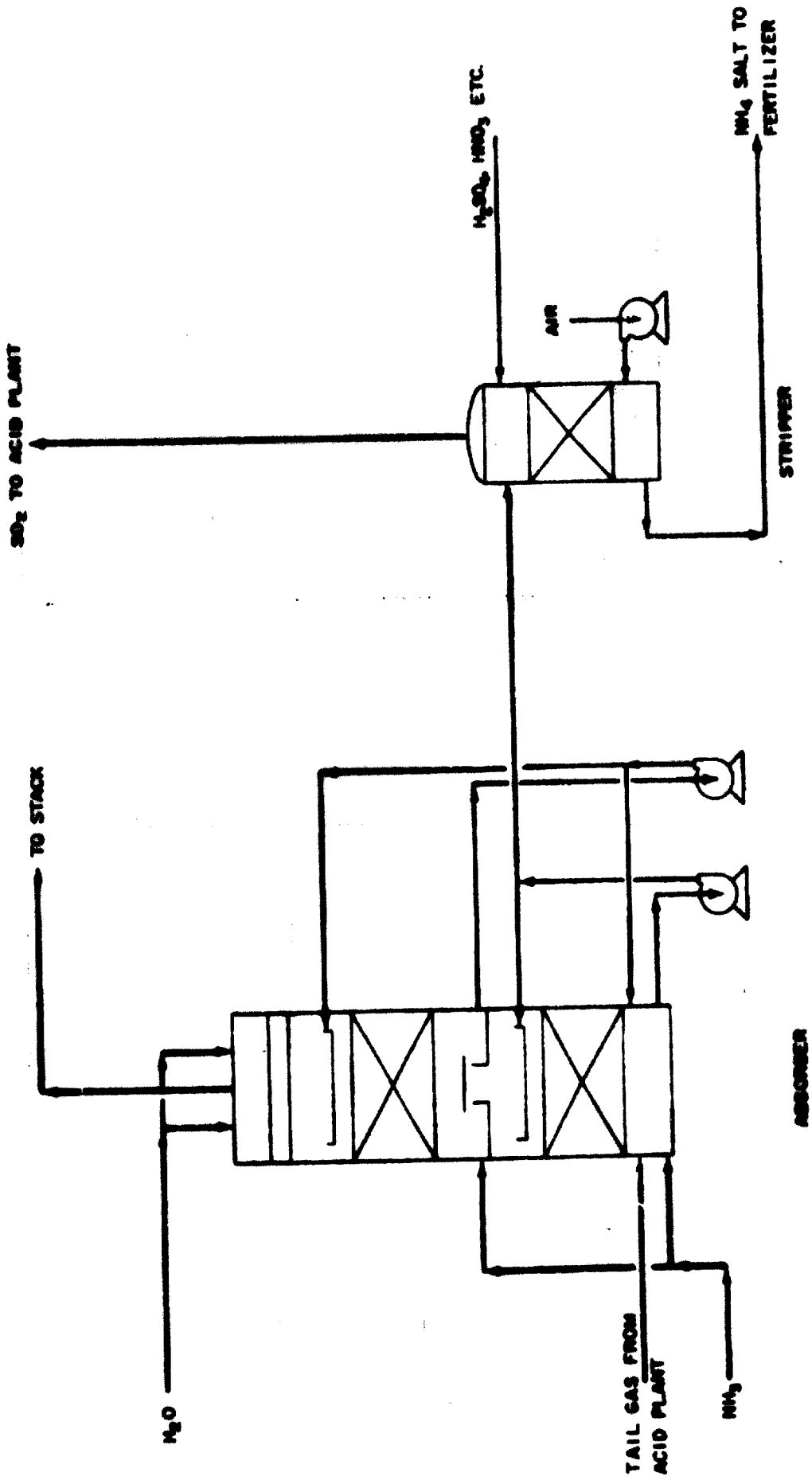


FIGURE 3
AMMONIA SCRUBBERS



ACID PUMP AND COOLER

FIGURE 4
ADD-ON DUAL ABSORPTION SULFURIC ACID PLANT
CONVERTER HEAT OPTION

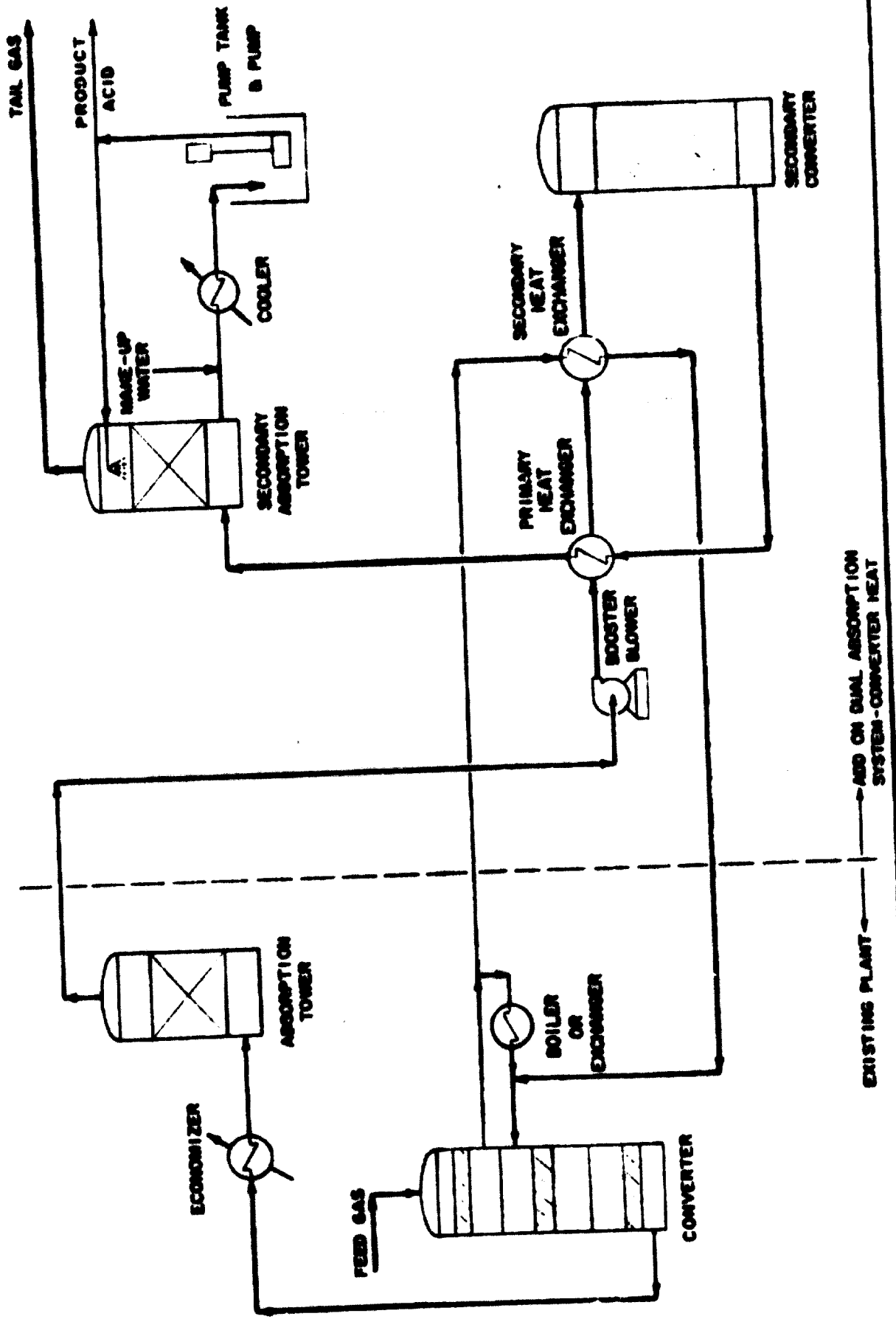


FIGURE 5
ADD-ON DUAL ABSORPTION SULFURIC ACID PLANT
OUTSIDE HEAT OPTION

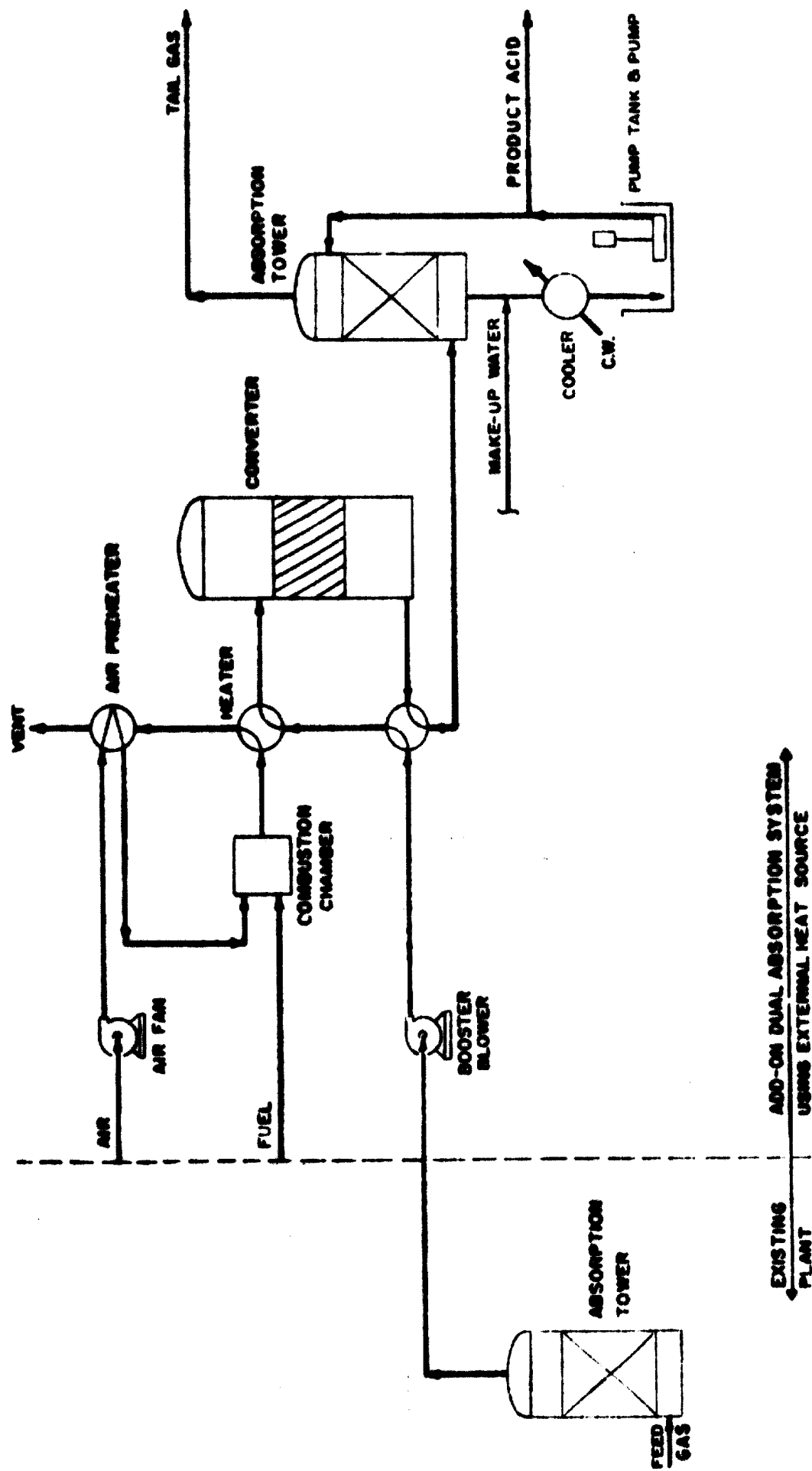


FIGURE 6
PHOSPHORIC ACID DIGESTION-FILTRATION
FUME CONTROL

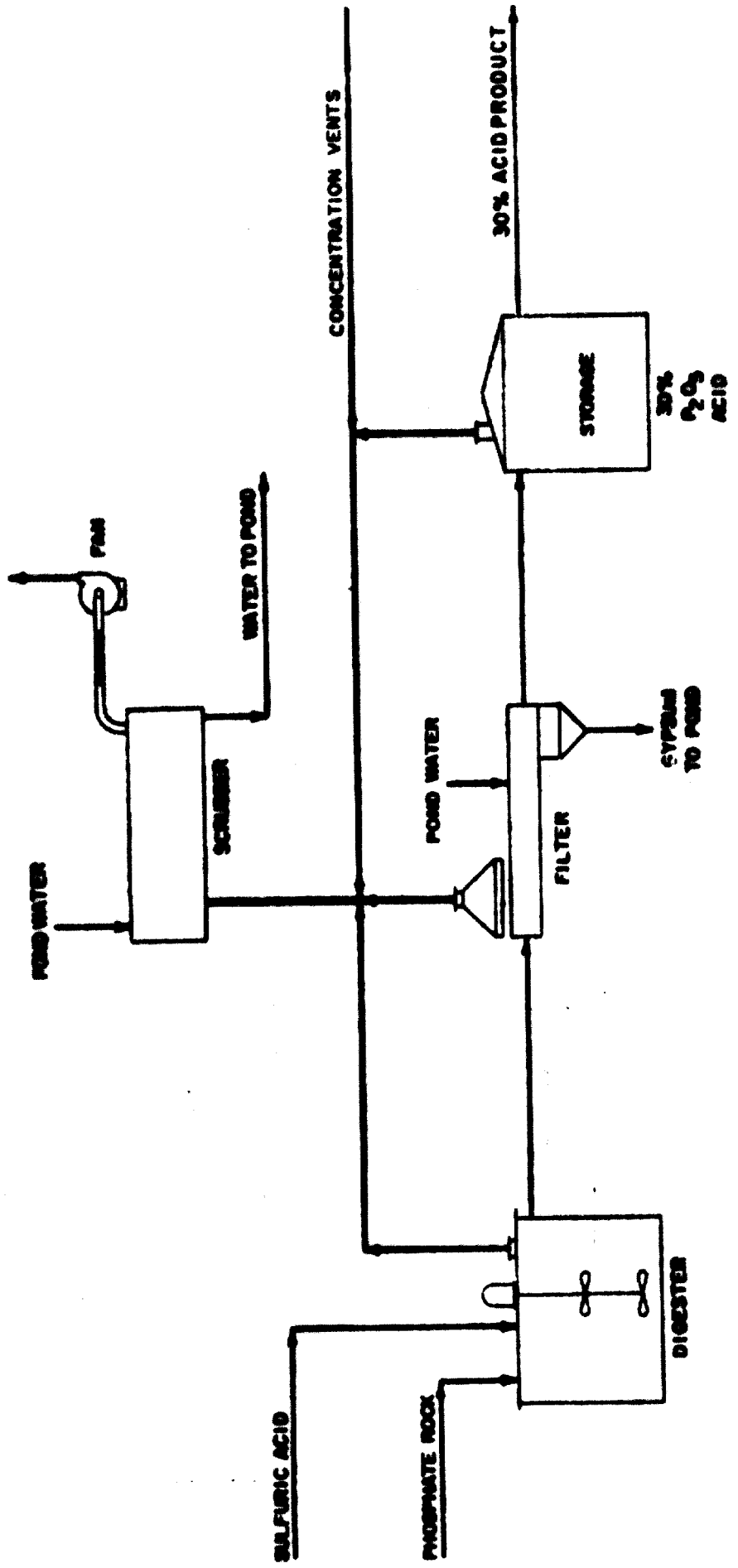


FIGURE 7
PHOSPHORIC ACID CONCENTRATION
FUME CONTROL

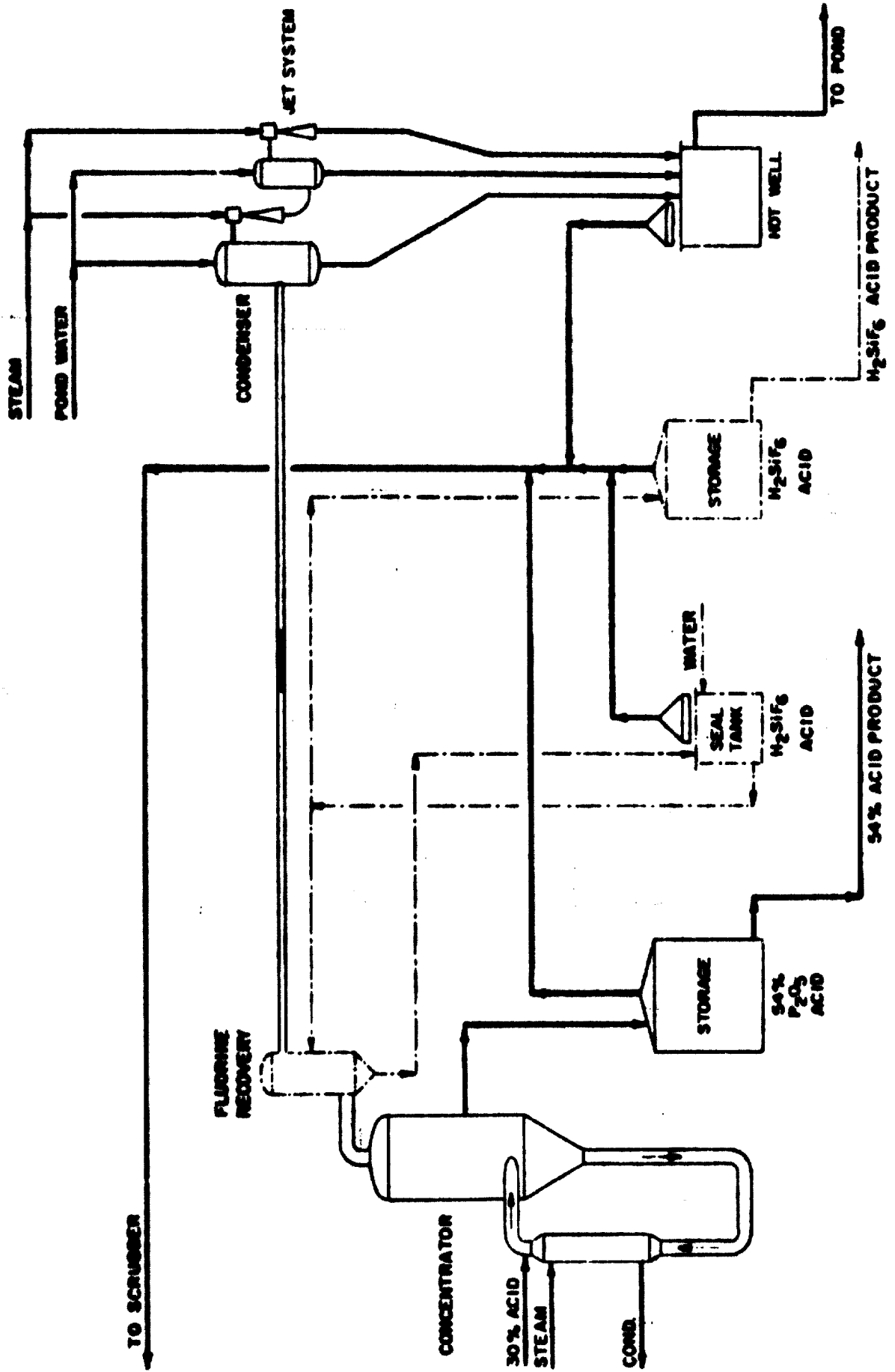


FIGURE 6
TYPICAL CYCLONIC SCRUBBING SYSTEM

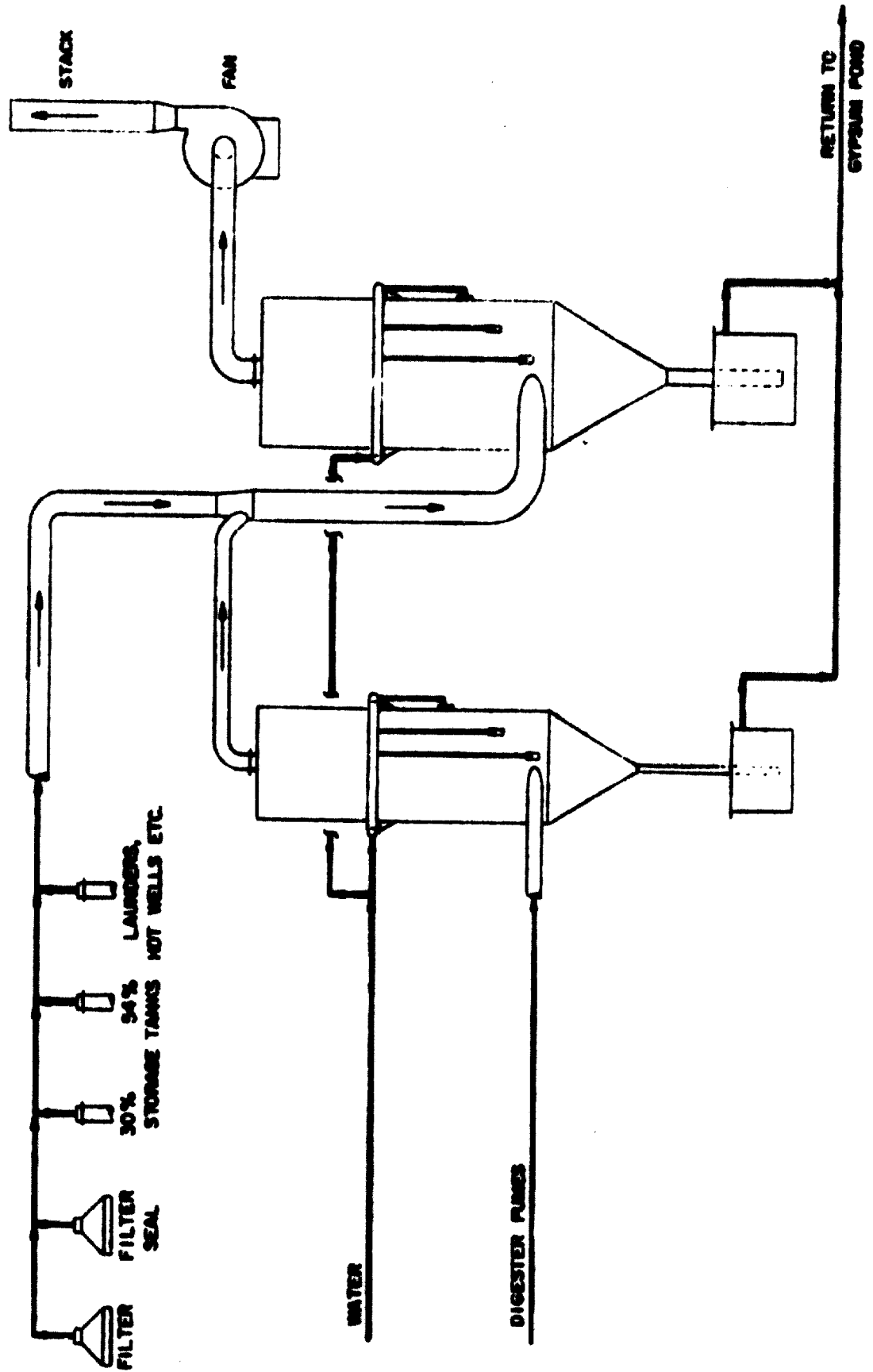


FIGURE 9
TYPICAL CROSSFLOW SPRAY-PACKED BED SCHEMATIC

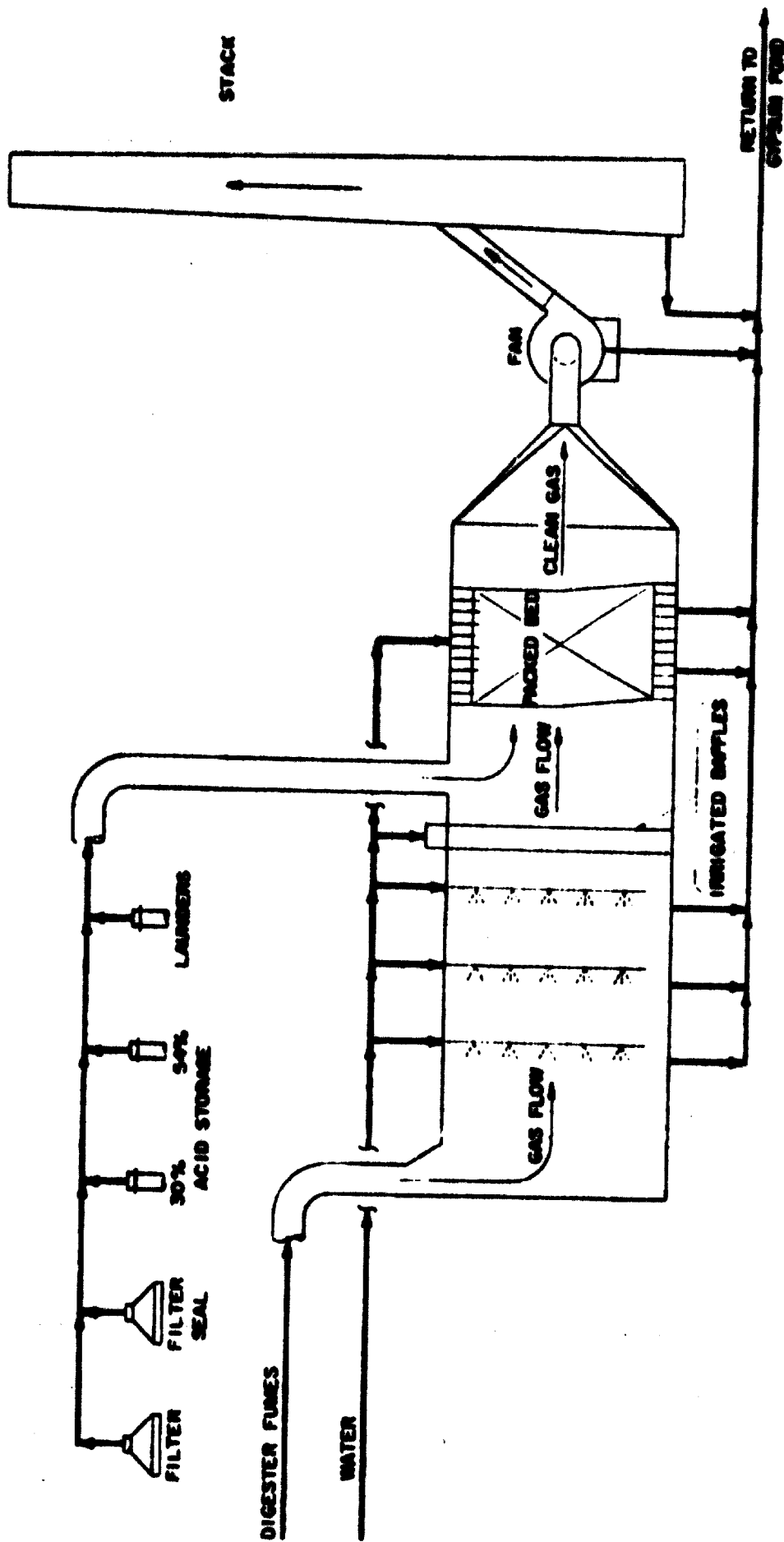


FIGURE 10 A
NITRIC ACID PLANT

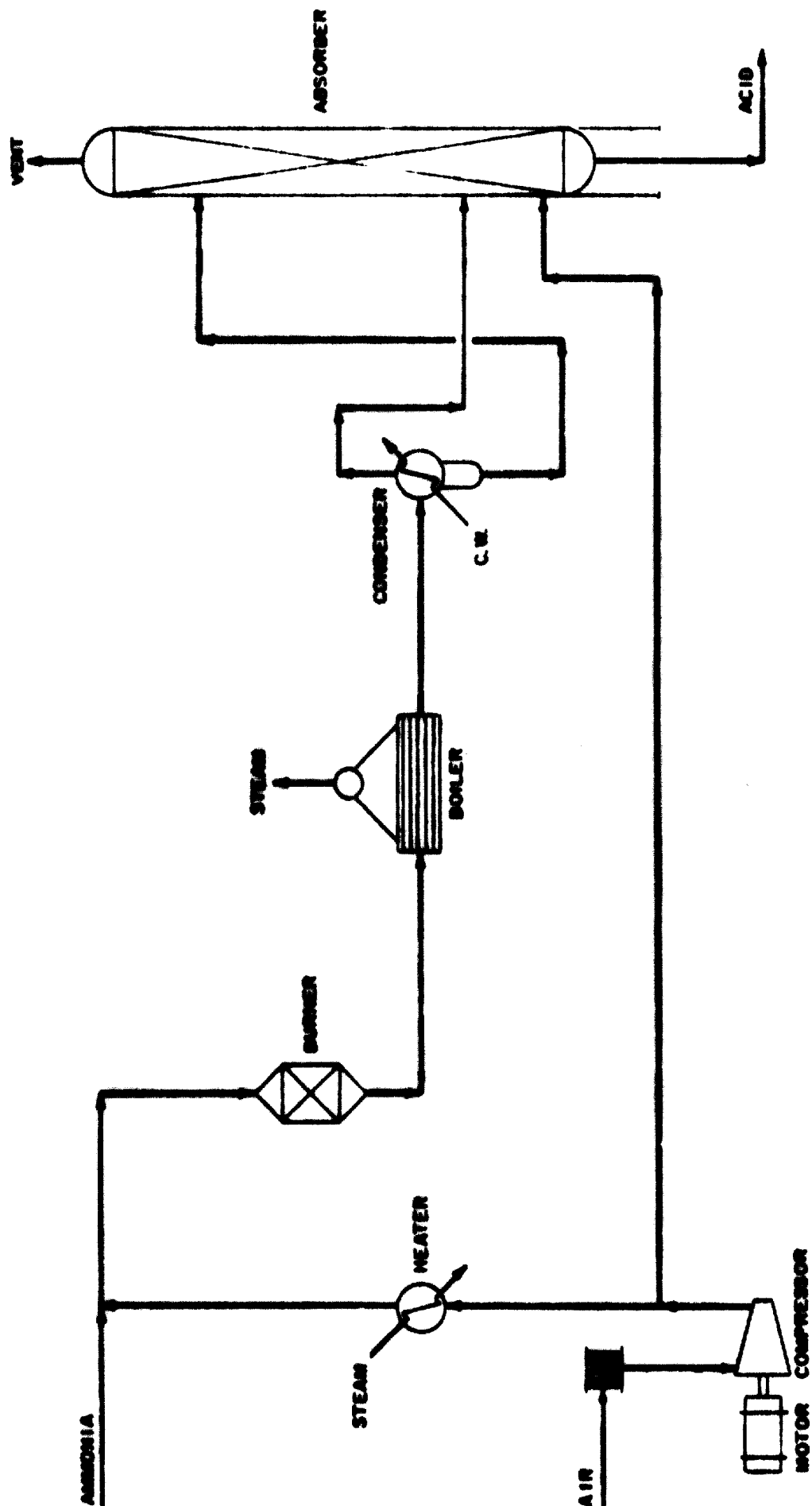


FIGURE 10 B
NITRIC ACID PLANT
WITH POWER RECOVERY

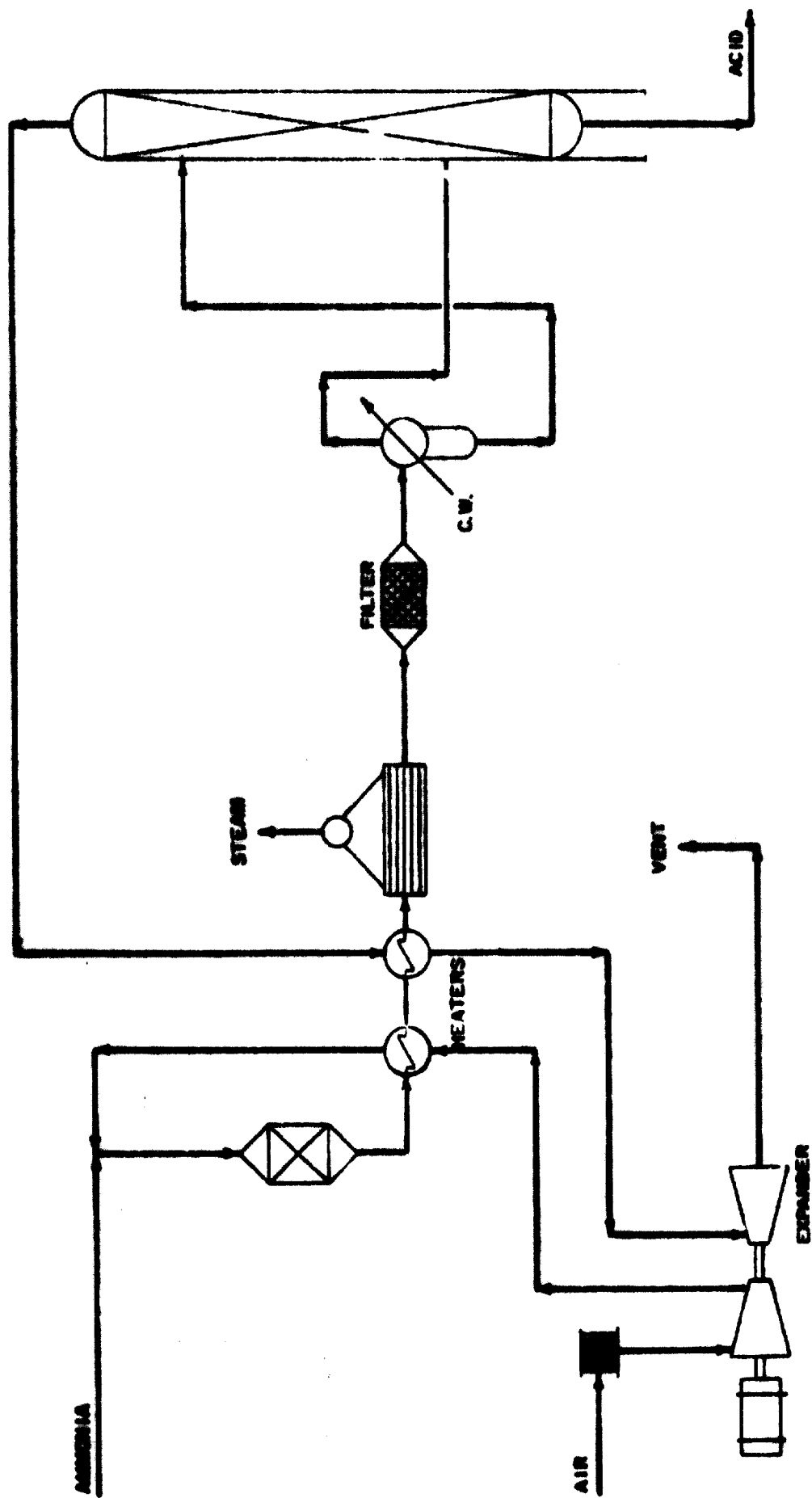


FIGURE 10 C
NITRIC ACID PLANT
WITH CATALYTIC COMBUSTOR

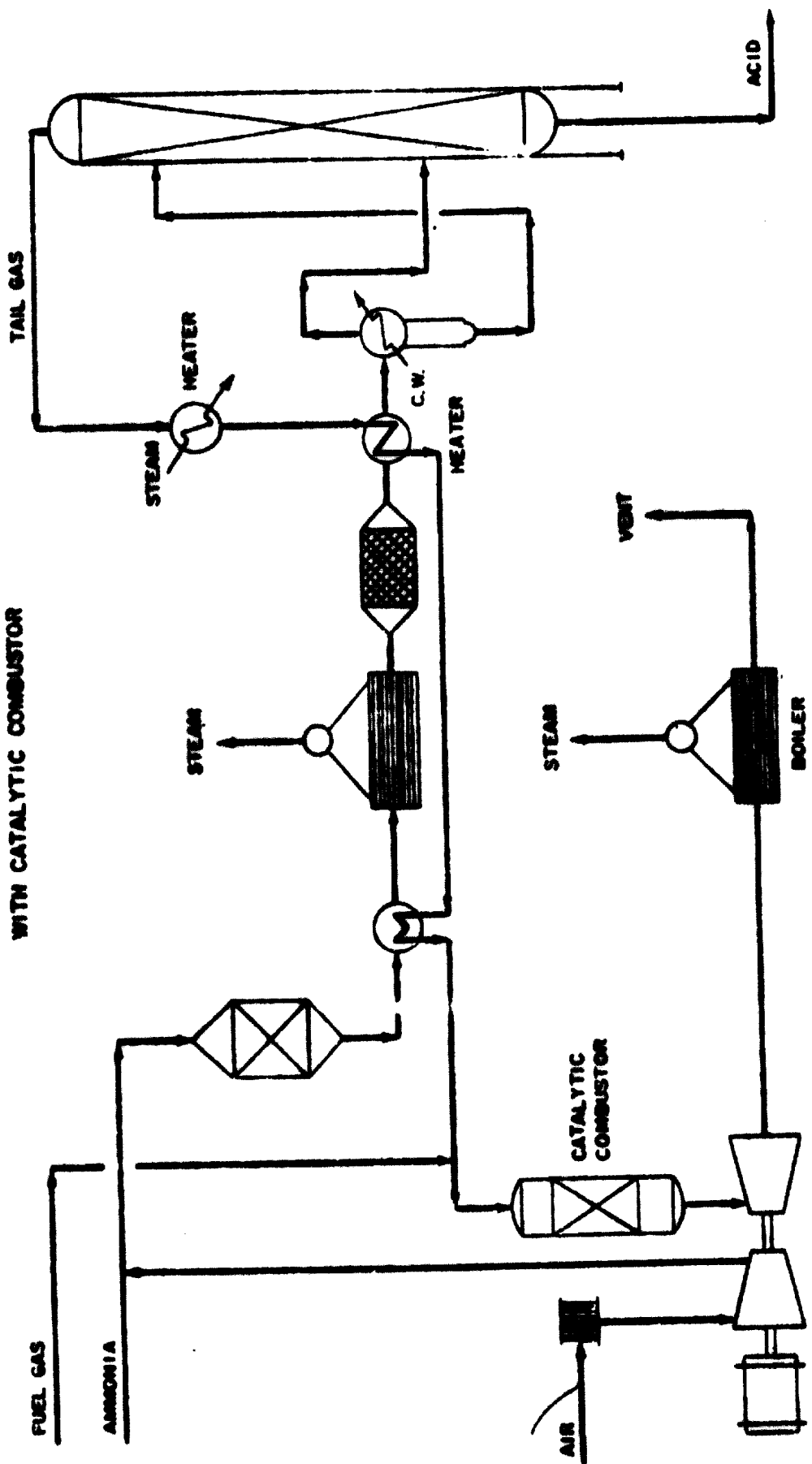
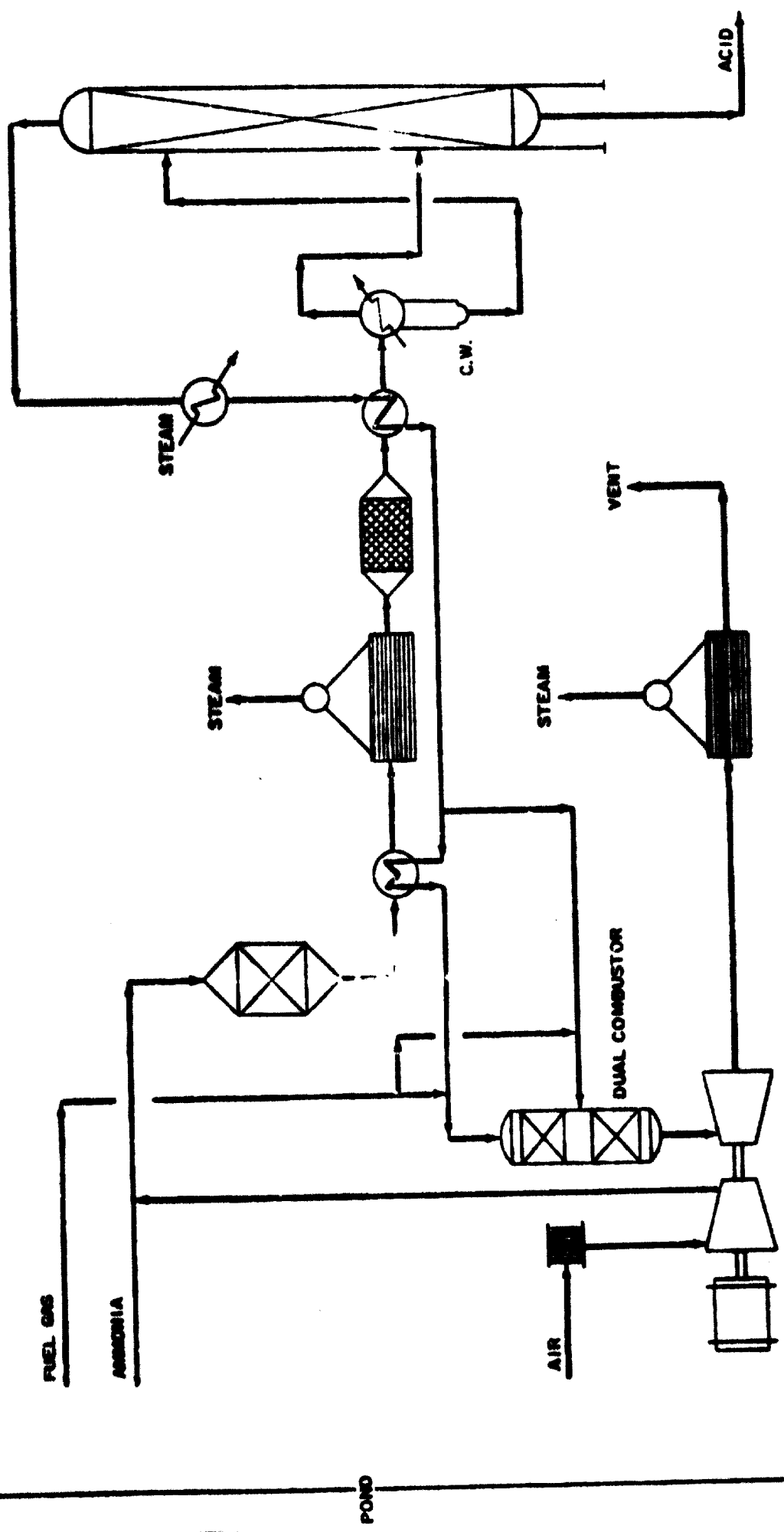
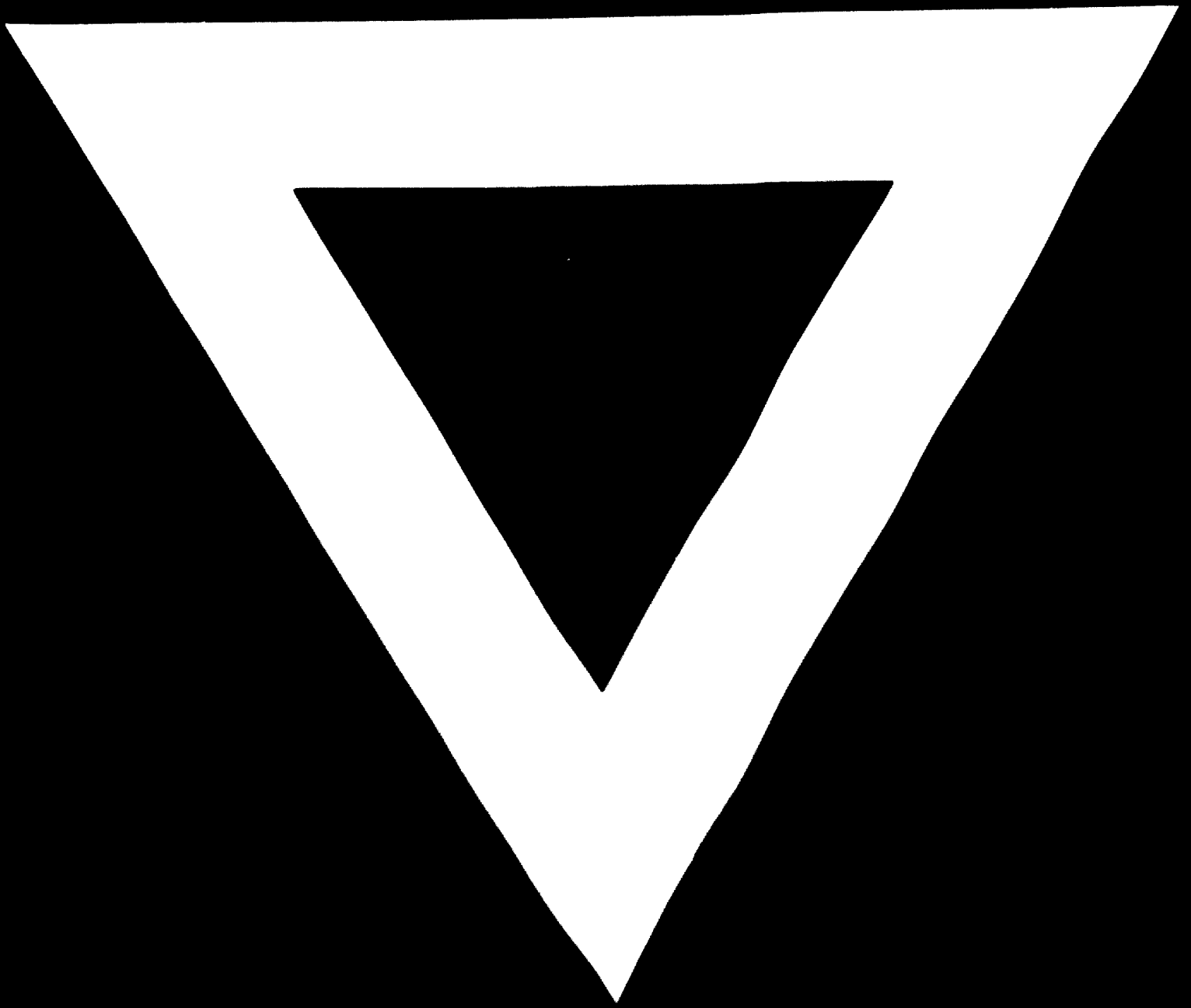


FIGURE 10 D
NITRIC ACID PLANT
WITH DUAL COMBUSTION SYSTEM





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