

SULFURIC ACID - THE ENERGY SOURCE

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INTRODUCTION

Just as environmental issues controlled plant designs in the 1970's, energy is reshaping the sulfuric acid plant of the 1980's. The sulfuric acid plant that in the past did little more than provide acid and low pressure steam, is now a major factor in the supply of energy to a fertilizer complex and markedly effects production costs (energy exported from a sulfuric acid unit would presently be valued at \$36-\$42/ton P_2O_5). With current energy costs the result of dramatic increases over the past few years, and projections for the future indicating continued increases at an accelerated pace, the effect of the sulfuric acid units energy design will be reflected directly in fertilizer profit margins.

This work will review one of the more commonly used sulfur burning acid plant flow sheets, developed in the mid to late 1960's and still being used today, with little or no modification, for plants to be started up in the 1980's. The review is aimed at quantitatively evaluating the energy distribution within the plant to develop a clear understanding of where the energy comes from, where it goes, and what factors effect the quantity or quality of supply or loss. With this in mind, several modifications will be made to the basic flow sheet to reduce internal energy consumption and to recover more energy in a usable form. The modifications will include some of the more traditional alternates, such as single absorption with ammonia scrubbing verses double absorption, mono or dual acid systems, converter arrangement (3x1, 3x2, 2x2), and blower location. Other common choices include SO_2 gas strength, steam pressure and superheat, and absorption tower gas inlet temperatures. Some of the newer concepts

will also be evaluated and include, conventional verses open or radical flow converter, rankine cycle low level heat recovery, and co-current flow absorber designs. Each alternate will be analyzed from the energy, operations and economic view point, using todays factors and projections to the mid 1980's.

In the end, a flow scheme for the acid plant of the 1980's will be developed and compared to the basic, todays standard, flow sheet. It is hoped that this comparison will prompt both designers and operators into a more thorough evaluation of design and operating options, taking into consideration the present and future cost effects of energy.

BASIC FLOW SHEET

As Einstein said in his well known theory of relativity, our perception of the universe or its parts is relative to our position or basis. In the same vane, to evaluate the energy production or efficiency of a flow scheme we must have an established and well understood basis. In this way all comparisons or alternates can be compared to the basic flow sheet and judged relative to it. The ideal basic flow scheme would be the one most widely accepted by the fertilizer industry based on past installations and current commitments. This sulfur burning double absorption flow scheme can be characterized by a number of trademark type features; namely, blower before dry tower, mono acid system and 3x1 converter design. This design has been utilized essentially unchanged since the mid to late sixties and is shown in Figure 1 and discribed below.

GAS SYSTEM

Atmospheric process air at 90°F and 50% R.H. is drawn into the system through an inlet filter-silencer and enters the acid plant main blower. The main blower provides the suction to draw the air through the filter-silencer and the pressure to force it through the remainder of the plant. The blower has a pressure rise of 185" water with provision for a 30" water allowance for ash build-up on the first catalyst bed. Air heated to 183°F by the blowers heat of compression, enters the air drying tower and is dried by a circulating stream of 98% sulfuric acid. Heat is transferred from the air to the acid by the sensible heat difference between the acid and air, condensation and absorption of moisture in the air, and dilution of the acid. Dry air leaves the tower through an entrainment separator at the acid inlet temperature of 170°F and enters the sulfur furnace where sulfur is burned in air to produce a 10% SO₂ gas strength. The gas is heated by the heat of combustion of sulfur to 1820°F and is cooled in a waste heat boiler to 800°F producing 600 psig steam.

Conversion of 99.7% of the SO₂ to SO₃, required by environmental regulation, is accomplished over a vanadium pentoxide catalyst in a three by one converter arrangement using the double absorption process. In this system, the gas is reacted over three separate catalyst beds, with cooling after each, before entering the interstage absorption tower where the SO₃ reaction product is removed before the final conversion pass. Gas enters the first bed at 800°F and is heated by the heat of the oxidation reaction to 1128°F corresponding to a conversion of 62% of the SO₂. The gas from the first pass is cooled in a second waste heat boiler to the second bed inlet temper-

ature of 820°F. In the second bed the conversion is increased to 87% and the gas is heated to 950°F. The gas is cooled in a heat exchanger, reheating the gas returning from the interstage absorption tower, to the third bed inlet temperature of 830°F. After the third catalyst bed, the gas at 870°F with 95% of the SO₂ converted to SO₃ is cooled in a combination of gas to gas exchangers and an economizer to 420°F before entering the absorption tower. In the interstage absorption tower the SO₃ is removed from the gas by a circulating stream of 98% sulfuric acid. The gas leaves the tower, through a high efficiency mist eliminator, at the acid inlet temperature of 170°F and is reheated to 800°F before entering the last catalyst bed. Reheating of the gas is accomplished by using the heat available from gas cooling between the second and third beds, and most of the heat in the gas from the third bed. In the last catalyst bed conversion of SO₂ to SO₃ is increased to 99.7% and the gas is heated to 830°F. The gas is cooled in a superheater-economizer to 420°F and enters the final absorption tower where the remaining SO₃ is absorbed from the gas. The gas passes through a mist eliminator before being exhausted to the atmosphere via a stack.

ACID SYSTEM

The type of acid system used in this flow scheme is called the mono acid system. As the name implies, this system uses only one strength acid for the drying and absorption duties. If product acid concentrations other than the nominal 98% used in the system are required, a circulating diluter would be provided. In the drying tower circuit, process air is dried by a circulating stream of 98% sulfuric acid to less than 1mg water per

cubic foot of air. The acid enters the tower at 170°F and is heated by sensible heat transfer from the process air, condensation of moisture contained in the air, and the resulting dilution of the acid. The diluted acid leaves the tower at 198°F and enters the drying-intermediate absorber pump tank where it is intimately mixed with the return acid from the intermediate absorption tower. The reconstituted acid at 235 °F is pumped through an acid cooler before being returned to the drying tower.

The interpass absorption tower absorbs the sulfur trioxide produced in the first three catalytic stages. The SO₃ is absorbed by water contained in a circulating stream of 98% acid. Acid enters the tower at 170°F and is heated to 240 °F by sensible heat exchange from cooling the gas, and the heat of condensation of sulfur trioxide. Hot, concentrated interpass tower acid is intimately mixed with the diluted drying tower acid in the drying-intermediate tower pump tank. Water is added to the pump tank to control the acid concentration and a leveling line to the final tower pump tank transfers the acid produced to the final tower system. The recirculated 98% acid is pumped through the interpass acid cooler before being returned to the absorption tower.

The final absorption tower absorbs the SO₃ formed in the last catalyst stage. The acid is also heated by condensation of SO₃ and by cooling the gas. The system includes the final absorption tower, final tower pump tank, pump and acid cooler. Acid concentration is controlled by adding water with the acid produced being withdrawn before the acid is returned to the tower. If 98% is the desired product acid concentration, the acid is cooled to storage temperature and pumped to storage. If concentrations

other than 98% are required, ie., 93%, 96%, then a circulating diluter would be required. The dilution system consists of a pump tank, pump, and acid cooler. Heat of dilution is removed by the acid cooler while temperature excursions, due to improper dilution ratios are prevented by diluting the product acid in a large circulating stream of cooled acid.

ENERGY DISTRIBUTION

For a sulfur burning acid plant, heat enters the plant from five sources and is removed by three main systems. Heat enters from the heat of compression of the gas by the main blower, the heat of combustion of sulfur, the heat of reaction (oxidation) of sulfur dioxide to sulfur trioxide, the heat of condensation of water and sulfur trioxide, and the heat of dilution of the acid. Heat is removed from the gas to the steam system, from the acid to the cooling water system and by heat losses to the atmosphere. A second look at the basic flow sheet with a step by step analysis of the energy inputs and outputs of each sub-system will not only provide an understanding of where the energy comes from and where it goes, but will highlight areas for increased energy production or conservation. A plant capacity of 2000 STPD will be used so actual numbers can be compared. These are summarized in table 1 and discussed below.

Air used for combustion of sulfur and oxidation of SO_2 to SO_3 enters the plant through a filter-scilencer and is boosted in pressure by the main blower. The blower consumes 4200 horsepower while raising 100M scfm of moist air 200 inches water gauge. The heat of compression of the machine increases the air temperature from 90°F to

183°F while adding 11.3 MMBTU/hr to the air. The blowers heat of compression is the first input of energy into the plant and comes from electric power or steam energy.

The air from the blower must be dried before contacting sulfur trioxide containing gases to prevent corrosion of plant equipment. This is accomplished in the air drying tower where the moist air is contacted with a circulating stream of 98.5% acid that enters the tower at 170°F. The air is dried and the acid is heated to 198°F by the sensible heat transfer of 1.9 MMBTU/hr from the gas to the acid, by 7.7 MMBTU/hr from condensation of the moisture contained in the air, and by the dilution of the acid to 98%. At this point in the system, with the dry air ready to enter the sulfur furnace, 11.3 MMBTU/hr of energy has been transferred to the gas by the blower and 9.6 MMBTU/hr has been transferred from the gas to the acid system during the air drying process.

Sufficient air is drawn into the plant and enters the sulfur furnace where it oxidizes sulfur to sulfur dioxide and maintains a 10% SO₂ concentration at the exit of the furnace. To produce 2000 STPD of acid (100% basis) with 99.7% conversion or recovery, 54.6 M pounds per hour of sulfur heats the incoming 170°F air to 1820°F and transfers 218 MMBTU/hr of energy to the gas. This is the major heat input into the plant and the easiest to recover since the quantity is large and the temperature level is high. The majority of this energy is recovered by the furnace waste heat boiler which cools the gas to the converter inlet temperature of 800°F and transfers 134 MMBTU/hr to the steam system.

Ten percent SO_2 gas is contacted with the first bed of catalyst resulting in the conversion of 62% of the SO_2 to SO_3 . The heat of reaction transfers 44.6 MMBTU/hr to the gas and heats it from 800°F to 1128°F . The majority of this energy is recovered in a second waste heat boiler that cools the gas to 820°F before it enters the second catalyst bed. Gas cooling between the first and second catalyst beds transfers an additional 40.7 MMBTU/hr to the steam system. The oxidation reaction continues in the second catalyst bed with the conversion increasing to 87% and the gas heated to 950°F . Conversion in the second bed adds 18.0 MMBTU/hr to the gas. The gas is cooled to the third bed inlet temperature of 830°F by a gas to gas heat exchanger. All of the heat available from gas cooling between the second and third beds, 16.6 MMBTU/hr, is utilized in reheating the gas returning from the interpass absorption tower. Additional reaction takes place in the third catalyst bed increasing the conversion to 95%, the gas temperature to 850°F , and transferring 5.8 MMBTU/hr to the gas. After the third catalyst pass the gas is cooled to 507°F , reheating the gas returning from the interpass absorption tower, and further cooled in an economizer to 420°F before entering the interpass absorption tower. The economizer recovers 10.5 MMBTU/hr, heating boiler feed water.

Sulfur trioxide is absorbed from the gas by the water contained in a circulating stream of 98.5% sulfuric acid that enters the interpass absorption tower at 170°F . The acid is heated by the sensible heat from cooling the gas, 420°F to 170°F , and the heat of condensation of SO_3 . Hot acid, at 240°F , leaves the tower at 99.3% concentration with 33 MMBTU/hr added to it from gas cooling and 92 MMBTU/hr added from SO_3 condensation. The absorber

acid mixes with the drying acid in the drying-intermediate pump tank. Water is added to maintain the acid concentration at 98.5% and the acid produced flows via a leveling line to the final tower pump tank. The mixed acid at 235°F is pumped through an acid cooler, one for each tower service, and recirculated to the towers. Sulfur dioxide gas leaves the interpass absorption tower at 170°F and must be heated to 800°F before entering the forth and final catalyst bed. Gas to gas heat exchangers are used for this, utilizing the heat available between the second and third beds and cooling the gas from the third bed to the interpass absorber economizer. Overall the interpass system results in the transfer of 10.5 MMBTU/hr to the steam system via the economizer and the transfer to the acid system of 33 MMBTU/hr from the gas and 92 MMBTU/hr from SO₃ condensation.

Final conversion of SO₂ to SO₃ is accomplished on the forth bed of catalyst. Sulfur trioxide conversion is increased to the required 99.7%, the gas is heated to 830°F, and 3.4 MMBTU/hr is added to the gas. So after four beds of catalyst and 99.7% conversion a total of 71.8 MMBTU/hr has been transferred to the gas by the heat of reaction of SO₂ to SO₃. The gas is cooled by a superheater-economizer to 420°F, transferring 41.2 MMBTU/hr to the steam system, before entering the final absorption tower. At this point the remaining heat contained in the gas stream is either transferred to the acid system or lost to atmosphere in the stack gas. The final tower, like the interpass tower, absorbs the SO₃ in the gas in water contained in a circulating stream of 98.5% acid. Acid enters the tower at 170°F and is heated to 228°F by cooling the gas from 420°F to 170°F and by condensation of SO₃. Acid from the final tower mixes with the acid produced by the drying-intermediate system and water (to control concentration) in the final tower pump tank. The acid at 230°F is pumped through

a cooler before being recirculated to the tower. A portion of the cooled acid is withdrawn as product, cooled to 110°F (3.3 MMBTU/hr) and transferred to 98% acid storage. If 93% product acid is required, 98.5% acid, withdrawn from the final tower system, is diluted in a circulating diluter. The acid is diluted in a large stream of cool acid to limit the temperature rise to 40°F, ie. 110°F to 150°F. Heat of dilution, 6.4 MMBTU/hr, is removed by an acid cooler. Product 93% acid at 110°F is transferred to 93% acid storage.

A review of table 1 shows that a total of 405.4 MMBTU/hr of heat energy enters the sulfuric acid plant, with 55.8%, 226.4 MMBTU/hr, recovered in the steam system, 40.6%, 164.4 MMBTU/hr going to the acid system and 3.6 %, 14.6 MMBTU/hr, lost to atmosphere. In the basic flow sheet all the heat recovered in the acid system is rejected to the atmosphere as warm air and water vapor via a water cooling tower while adding a requirement for 1000 hp input for cooling tower fans and circulating pumps. Heat losses directly to atmosphere from hot equipment, ducts and lines are a function of insulation type and thickness. The steam system is the only area where energy is recovered for use and, as can be seen in table 2, not all of it is available for export. Some is used to drive the main blower and boiler feed water pump and some to heat cold make-up water to 220°F for deaeration. The remaining high pressure steam can be used to produce electric power for in plant or export via a turbo generator, off set electric power input by turbine drives, or let down to low pressure across a valve. The basic plant design lets down excess steam across a valve.

If values are placed on steam and electric power at todays cost, 1982 and 1986 costs a basis for judging the

energy efficiency of this or alternate schemes is established.

<u>ITEM</u>		<u>VALUE</u>		
Steam	\$/1000lbs	1980 4	1982 7	1986 14
Electricity	\$/KW	0.03	0.05	0.10

These values were calculated based on january 1980 forecasts of the cost of oil and natural gas in the 1980's. Using these cost figures the value of energy exported from the basic acid plant can be evaluated at todays and future conditions.

<u>ITEM</u>	<u>CREDIT (COST) \$MM</u>		
Steam	1980 6.4	1982 11.2	1986 22.4
Electricity	(0.3)	(0.5)	(1.0)
Net Credit \$MM	6.1	10.7	21.4

It's obvious from the above table that the value of energy produced by the sulfuric acid plant is significant and is increasing in value at an astounding rate. This is the main reason the plant design of the 1980's must be different than the design of the 1960's and 1970's.

The energy distribution, presented above, is helpful in indicating areas for improvement in the basic system

design. A number of these areas are described below:

1. Main Blower - The acid plant main air blower converts input power into heat in the air stream. With the blower located ahead of the drying tower the blower's heat of compression, 11.3 MMBTU/hr is transferred to the acid system. If the blower were to be located after the air drying tower the heat of compression would be transferred to the steam system. This is an area for energy efficiency deserving further evaluation.
2. Gas Concentration - A significant amount of heat energy lost by the gas is in the sensible heat transfer from the gas to the acid towers. One way to reduce this loss, would be to reduce the total gas volume. An increase in the SO₂ gas concentration of 1%, from 10% to 11% should be evaluated to determine whether the energy credits offset the environmental emission risk of a higher gas concentration.
3. Gas Temperatures To Acid Towers - Another means to reduce the heat loss to the acid system in the absorption towers is to reduce the gas inlet temperature. If the gas were cooled to 350°F instead of 420°F, 15.8 MM BTU/hr would be recovered into the steam system with a corresponding reduction in acid cooler system size. The value of the energy recovered must be compared to the increased surface area and cost of the required heat exchange equipment to establish

an optimum tower inlet temperature.

4. Alternate Absorber Design - In items 2 and 3 above, two methods of reducing the heat loss from the gas system to the acid system are listed. A third scheme utilizing a co-current flow interstage absorber rather than the more common counter-current design offers still greater advantages. With the co-current, either packed or venturi, tower design, the gas and acid leave at the same temperature. So instead of transferring 33 MMBTU/hr from the gas to the acid by cooling the gas from 420°F to 170°F in a counter-current tower, only 21 MMBTU/hr is lost to the acid system since the gas (and acid) leave the tower at 285°F. A minimum recovery of 12 MMBTU/hr would be transferred to the steam system and when combined with a lower inlet temperature to the tower, further efficiencies could be achieved.
5. Single Absorption - Elimination of the intermediate absorption system would, obviously, eliminate the energy loss in that system. The double absorption process was applied in order to meet environmental emission standards and not because it is energy efficient or economically sound. The single absorption system can regain the energy and economics lost to the double absorption process when applied with suitable emission controls. In many cases, ammonia scrubbing has been used successfully to reduce emissions from a

single absorption plant to acceptable levels. An energy savings of 800 hp for the main blower and the recovery of 45 MMBTU/hr of energy to the steam system makes an evaluation of this alternate of great interest.

6. Acid System - In basic design, all the energy transferred to the acid system is removed by cooling water and lost to atmosphere. This is 41% of the total energy input to the system. As energy costs increase, recovery of this low level energy becomes more and more attractive. Systems utilizing boiler feed water heating, water heating, rankine-cycle electric power generation and steam generation using vapor recompression are in use around the world to some degree and should be evaluated.

7. Boiler Feed Water - As seen in table 2, a significant amount of energy, in the form of steam, is used to preheat cold boiler feed water for deaeration. This coupled with the excessive blowdown required with softened water or the high cost of demineralized water indicates the need for improvement. The return of condensate would not only permit the economic use of demineralization, but would recover an additional 6 MMBTU/hr by reducing boiler blowdown losses and 6 MMBTU/hr in feed water heating requirements. In addition the use of heat available from the acid system to provide the remaining feed water heating duties would recover 10 MMBTU/hr in low pressure steam for export.

8. Electric Power Generation - The basic design uses a part of the high pressure steam produced to drive the main blower and boiler feed water pump, with the remainder let down across a valve to low pressure user requirements. This was economically sound in the past, but with current and projected energy costs, the use of co-generation systems are increasing with many evaluations showing ROI's of less than one year.

ALTERNATE SYSTEM EVALUATION

It is fairly easy to sit here, at the start of the 1980's, look back, and criticize the design of the 1960's and 1970's. A design developed during a period of cheap energy, that today would be rated extremely poor. It must be realized, however, that many of the energy efficiency improvements listed above are not new, but have been around for many years waiting either for improvement in materials or technology or more likely for the economic picture to change and make them more attractive. This change has come in the form of energy costs and the analysis presented below reflects an evaluation of systems for energy improvement based on current and projected energy costs along with an assessment of operating risks.

INTERNAL ENERGY IMPROVEMENT

Using the energy distribution analysis of the basic flow scheme as a guide, the first step in energy efficiency improvement is to evaluate systems for reduced internal

energy consumption. The main blower stands out as a major user of high level energy. In the basic flow sheet the blower uses 4200 hp in compressing 100 scfm of air to 200 inches water. The energy consumed by the blower is a function of the volume of gas moved and the plant pressure drop or resistance. A reduction in blower energy consumption would require a reduction in gas volume resulting in higher SO₂ gas strength, or a decrease in plant pressure drop necessitating larger equipment. Blower horsepower is a direct function of gas volume so a 10% reduction in volume will result in a corresponding horsepower savings. A decrease in gas volume would have secondary effects also. It would reduce the energy lost to the acid towers and save capital cost by permitting smaller gas volume sized equipment. Overall the operating savings would amount to 420 hp and 6 MMBTU/hr. In terms of today's and future costs the savings by reducing gas volume 10% are shown below.

Capital Savings	\$ 1.25	MM	
	1980	1982	1986
Operating Savings	0.27	0.47	0.94
\$ MM 1year			

Of course, a reduction in gas volume corresponds to an increase of SO₂ gas concentration of 10% (from 10% to 11%). These are two main limits on increases in gas strength; they are overall conversion efficiency and overheating of the first catalyst bed resulting in accelerated vanadium loss. Subtle catalyst advances in the past five years have permitted operation, at high efficiency, with lower ignition temperatures and higher gas strengths. Many of the plants, designed along the lines of the basic flow

sheet with 10% SO₂ gas strength, have, in fact been operating consistently in the range of 10.5% to 11% SO₂. Experience has shown that 11% SO₂ is close to the upper limit with today's catalysts but is an acceptable design limit.

Overall acid plant pressure drop has been increasing with increasing plant size. Capital cost savings were balanced against main blower power requirements with clean plant pressure drops increasing from 75-85 inches water in the 1950's to 185-220 inches water in the mid to late 1970's. With the energy cost guidelines as outlined above, a new evaluation of plant pressure drop can be made for the 1980's design. Figure 2 presents the results of this evaluation showing overall plant pressure drop for a three year ROI based on today's, 1982 and 1986 energy costs. The plant pressure drop decreases from 180 to 158 to 110 with increasing energy costs, with judgement indicating an optimum for 1980's design at 105 inches water clean at a incremental capital cost of \$2.0 MM and an operating cost savings of \$0.7 MM/year.

Opening up the plant to reduce pressure drop is justified so the next step is to indicate the most advantageous ways of doing it. A review of the acid plants pressure profile indicates that 79 inches water is consumed by the boilers, economizers and heat exchange equipment, 40 inches water clean with a 30 inch water allowance for dirt build-up in the first catalyst bed is the loss for the catalyst system, 46 inches water pressure drop for the towers and mist eliminators, with the remaining 20 inches water for entrance and exit, duct, and miscellaneous losses. Reducing duct velocities from the 80-100 ft/sec along with improved equipment arrangement and multi-miter bends would

save about 5-7 inches water. Very little savings can be achieved in the drying-interpass-final tower-mist eliminator systems since the towers are already oversized based on good mass transfer-packed tower design principles and the mist eliminators are designed for maximum efficiency at minimum pressure drop. The resistance in the heat exchange system can be reduced significantly, but only at the expense of increased capital cost. The investment cost for heat exchange equipment varies by the following relationship:

$$\text{Initial Cost} = K(\Delta P)^{-0.24}$$

In addition each of the exchangers would have its own cost per square foot relationship and therefore its own value for the constant K. So to achieve the maximum reduction in pressure drop at a minimum incremental capital cost, an optimization analysis would be required to establish the optimum pressure drop for each exchanger. The converter system offers a potential savings of 25-30 inches water. There are two methods available to obtain this savings; using a conventional converter design with the diameter increased to provide a minimum of one foot catalyst bed depth, or the radical flow converter design with the catalyst in vertical candles, also with one foot thick bed depth. Both systems would accomplish about the same pressure drop savings and offer the side benefit of increased surface for dirt, ash, (pressure drop) build-up. If the basic plant's converter is opened up from 40 ft to 56 ft a pressure drop savings of 30 inches water can be achieved along with an increase of plant on-stream time between screenings of 100 percent (12 months to 24 months). This is the maximum savings that can be achieved with present catalyst systems and would cost about \$0.8 MM in increased capital.

Very little savings can be achieved in the three tower-mist eliminator systems required by the double absorption process, but a savings of 30-40 inches water can be obtained by the use of the single absorption process with a suitable emission control scrubber. The single absorption plant would not require the gas to gas interpass heat exchangers, acid tower or mist eliminator which account for 60-70 inches water pressure drop in the basic flow sheet. A net pressure drop savings of 30-40 inches water is obtained with the remainder for steam superheaters and the emission control ammonia scrubber. Single absorption-ammonia scrubbing systems have been in successful operation in modern plants since the mid 1930's. The main drawback to the use of ammonia scrubbing has been the disposal of the ammonium sulfate by-product. Over fifteen years experience with plants in Europe, in the U.S. (Texas) and more recently in Florida has demonstrated that ammonium sulfate solutions can be fed directly to the phosphoric acid reactor (attack) system with ammonia recovered in the phosphoric acid and the sulfate offsetting fresh sulfuric acid feed. All of these plants produced only nitrogen grade fertilizer. Plant tests have indicated a problem with zero nitrogen grades when using nitrogen containing phosphoric acid. A system has been developed by Friedman, et al, patent pending, for converting the ammonium sulfate to ammonium phosphate, eliminating the ammonium sulfate disposal problem. A system similar in some respects to the Friedman, et al, process has been in use for a number of years in Romania. Therefore, with the assumption that the by-product ammonium sulfate or phosphate can be utilized in the fertilizer plant, the single absorption-ammonia scrubbing system becomes a viable alternate with the savings shown below as compared to the basic scheme:

Capital Cost Savings	\$3 MM		
	<u>Credit \$MM/yr</u>		
Operating Credit	1980	1982	1983
Steam	1.34	2.3	4.6
Electric Power	0.16	0.26	0.53
Net Credit \$MM/yr	1.5	2.56	5.13

In summary, substantial economic improvement over the basic flow sheet can be achieved by the adoption of one or more methods for reduced internal energy consumption. Each of the methods presented has been demonstrated commercially and offers little or no risk. Internal energy improvement described above has centered on reducing the input power required by the main blower by reducing gas volume and/or plant pressure drop. Alternates have included increased SO₂ gas strength, reduced duct velocities, lower pressure drop heat exchange equipment, open or larger diameter converter and elimination of the interpass system by using the single absorption ammonia scrubbing process. The operating cost savings shown is real and increases with rising energy costs.

INCREASED ENERGY EXPORT

In the previous section alternates were presented to reduce internal energy consumption; this section proceeds to the next step and reviews flow schemes for recovering and exporting additional energy in usable forms. Here again, a walk through using the basic process energy distribution as a guide, starting with the main blower and following the flow through the gas, steam and acid systems. Then looking at auxiliaries such as feed water heating, co-generation and heat recovery from acid cooling.

The main blower is the single largest consumer of easily recoverable energy from an acid plant. In the previous section methods were reviewed to reduce the blowers energy consumption, either by reducing plant volume or pressure drop. It was also noted, in the basic design energy distribution that 11.3 MMBTU/hr is transferred by the blower to the gas stream, and lost to the acid-cooling water system. A majority of the acid plants in the world operate with blowers located after drying towers, so an evaluation of the energy effects of this new blower location is warranted. With the blower located after the drying tower an inlet silencer is not required and the atmospheric air is heated to 170°F by the acid system, transferring 9.4 MMBTU/hr to the gas and reducing the acid cooling duty by 11.3 MMBTU/hr as compared to the basic design. Blower input horsepower and gas discharge temperature are increased to 4800 hp and 275°F due to the higher inlet temperature and suction pressure. The increased blower discharge temperature transfers an additional 12.4 MMBTU/hr to the gas. Energy transferred to the gas at this point in the system is easily recoverable as high pressure steam in the furnace boiler so the net effect of locating the blower after the drying tower is to increase the horsepower 14% and recoverable energy 12.4 MMBTU/hr, while reducing acid cooler duty 11.3 MMBTU/hr. The capital cost is essentially unchanged since the increased cost of the boiler and steam system due to its higher heat removal duty is offset by the elimination of the inlet silencer and the reduction in the acid and cooling water systems.

Main Blower Location

Capital Cost Increment \$0

Credit \$MM/yr

Operating Credit	1980	1982	1986
Net Steam-Electric	0.48	0.83	1.67

With operating credits like these why would anyone locate the blower ahead of the dry tower? The answer goes back many years, to a time before good entrainment separators were developed. At that time, acid entrainment from the drying tower caused excessive blower vibration, in the order of one to five times per year, causing a shut down to soda ash wash the blower. With steam worth less than \$1/1000 lbs., this operating nuisance and corresponding down time could be avoided by giving up the energy operating cost credit and locating the blower before the drying tower. In addition, a major acid plant designer adopted this blower location as an industry trademark type feature and is staying with it even with todays economics. With the advent of modern entrainment separation devices, reducing acid carry-over to negligible levels, the industry can no longer afford the luxury of avoiding a minor operating nuisance and giving up \$0.48 MM/yr to \$1.67 MM/yr in operating credits.

Drying of the process air in the system is required to prevent corrosion of carbon steel equipment and duct-work. Adequate drying, to less than 1 mg/scf, can be achieved with 98% acid at 170°F, 96% acid at 140°F or 93% at 110°F. When 98% acid is used for drying, the acid strengths for the drying and absorber services are the same and the system is called the mono acid system. The mono acid system is utilized in the basic flow sheet and has been described elsewhere. The use of 93% acid for drying is required for all acid plants except sulfur burners. Since different acid strengths are used for the drying and absorbing duties the system is called the dual acid system. The dual acid system is required in plants where the moisture content of the incoming gas is too great to permit the production of 98% acid or when SO₂ is

present in the incoming gas. The dual acid system prevents SO_2 in the gas to the drying tower from being absorbed in the acid and stripped in the absorber causing a by-passing of part or all of the catalyst system. For sulfur burners either mono or dual acid system would be satisfactory. The dual acid system has one process advantage. Since both 93% and 98% acid are used in the system product acid of either strength can be withdrawn directly from the system, eliminating the need for a dilution system. The initial investment cost for both systems is about the same with the main difference being an energy edge of 6.3 MMBTU/hr for the mono acid system due to the air leaving the drying tower at 170°F instead of 110°F .

There has been a lot of discussion over the years about the number of catalyst beds before and after the inter-stage absorption system in double absorption plants. Each acid plant designer has his own favorite arrangement and promotes it vigorously. Theoretical calculations indicate very slight differences in conversion efficiencies for the three most common arrangements with 3x2 showing a slight edge of 3x1 with a slim margin over 2x2. Ten to fifteen years of operating history however, has shown no discernible difference in conversion efficiency between those three converter arrangements, and since converter arrangement has little or no effect on energy, the debate will be left to the designers advertising and marketing people.

The basic flow sheet energy distribution indicated the large amount of energy lost to the acid system in the absorption towers. Three methods have been suggested to recover additional energy to the steam system. They are

elimination of the interpass absorption system by the use of the single absorption process with an emission control scrubber, co-current absorber design and cooling the absorber inlet gas to a lower temperature.

Single absorption-ammonia scrubbing has been discussed above, and offers the greatest potential savings; including \$3 MM in capital cost, 800 hp for the main blower and about 45 MMBTU/hr of energy to the steam system.

A significant energy recovery can be achieved within the double absorption process by the use of a co-current absorber design for the interpass tower. Co-current absorbers have been in operation in sulfuric acid plants for about ten years with excellent performance. Their use has mainly been in metallurgical plants in the U.S., where recovery of additional heat offsets fuel requirements, and in Europe where energy costs are higher than in the U.S. With the basic flow sheet design 33 MMBTU/hr is lost to the acid system by gas cooling in the interpass absorber. The use of a co-current absorber design, either packed or venturi, would permit the recovery of 12 MMBTU/hr to the steam system.

The third method of reducing the sensible heat loss in the absorber acid system is to cool the absorber inlet gases further. In the basic flow sheet the gas is cooled to 420°F, a common value based on 1960's economics. Basically the choice of the absorber inlet temperature has always been, and still is, one of economics, balancing the value of the extra energy recovered against the added capital cost for larger heat exchange equipment (economizers). Many still believe that absorber inlet temperature is determined based on acid dew points, which is

not the case except in the few plants burning H_2S or dark sulfur in the contact section of the plant. Designer advertising men have promoted this false view for many years. The proof that dew point has little or no effect is as follows: present economizers operate with cold side gas exit temperatures of $420^{\circ}F$ and water side temperatures of $220^{\circ}F$ - $230^{\circ}F$. A review of the heat transfer coefficients shows coefficients of about 10 for the gas and about 1500 for the boiler feed water. Therefore the gas side wall temperature will be essentially the water temperature of about $230^{\circ}F$ and the gas temperature has little effect on the wall temperature. Plants have been operating with economizer wall temperatures of around $230^{\circ}F$ for years without dew point problems so lowering the gas temperature from $420^{\circ}F$ to $350^{\circ}F$ should not effect acid condensation. The energy savings for a $350^{\circ}F$ temperature would be 15.8 MMBTU/hr over the basic design. Based on 1982-1986 energy costs a 3 year ROI can be achieved at an absorber inlet temperature of $300^{\circ}F$ with a savings of 27 MMBTU/hr over the basic flow sheet. The combination of a $300^{\circ}F$ absorber inlet temperature and the co-current absorber design would recover 39 MMBTU/hr of heat to the steam system with a corresponding reduction in the acid-cooling water systems.

Even with all the savings described above, the energy lost to the acid system would still be greater than 100 MMBTU/hr or 25% to 30% of the energy produced by the plant. The increasing value of this large quantity of low level energy makes recovery more attractive each day. A number of schemes have been in commercial practice around the world where the energy crunch has been in effect longer. These systems include boiler feed water heating, water heating for in plant or town heating, vapor re-

compression for production of low pressure steam, water chilling by an absorption type refrigeration system, and rankine cycle freon systems producing electric power. Heating water whether for boiler feed, in plant use, vapor recompression or refrigeration systems, is the simplest recovery method for low level acid cooler heat. Water heating requires little more than shell and tube acid cooler, good water (preferably demin) to prevent water side fouling at higher temperatures, and larger acid coolers due to the reduced delta T. Water heating, to about 200°F or higher has been in use in the U.S. and Europe since the early 1970's. Two 900 STPD plants at N.L. Industries in New Jersey have been heating boiler feed water since 1973-74 and plants in Europe have been providing in-plant, greenhouse and town heating for many years. The use of hot water for vapor recompression or absorption refrigeration is a logical extension of the alternate uses of 200°F water. Rankine cycle, freon systems, have been in use in Japan for a number of years. The use of a hot fluid to boil freon and generate electric power is not new, however, one potential problem in acid systems would have to be overcome before the system could be recommended for use. There is always the potential for an acid cooler leak. With water systems the cooler is designed to leak from acid to water where damage would be minimized and easily detected. Acidified water can be either neutralized or replaced at little cost. With the freon system, leaks of acid to the freon side would cause major damage to the turbogenerator, so the system would have to be designed to leak freon to the acid. Freon leak to the drying and interpass absorber acids would result in the release of freon to the gases entering the converter. The combination of oxygen, vanadium catalyst, 800°F - 1100°F temperature, and chlorinated-fluorinated hydrocarbon-

freon, could cause temperature excursions and poisoning of the catalyst. The advent of rankine cycle freon systems must still await the technical development of a method to protect the catalyst in the event of an acid cooler leak.

An economic evaluation of acid heat recovery requires an extensive review of in plant uses for hot water. Along with boiler feed water heating other potential uses include dryer air preheating, filter wash water heating and even as an evaporator heating medium. These are too important and complex to be discussed in this paper and are the subject of a future work directed solely to recovery and use of low level acid cooler heat.

A part of the export energy in the form of steam is consumed within the plant to preheat the 100% make-up cold, softened boiler feed water and in boiler blowdown. The use of demineralization for feed water treatment would recover the 6 MMBTU/hr lost to boiler blowdown but the initial cost, about .5 MM, of the demin system along with the acid and caustic chemical requirements would make it uneconomical. If steam condensate (about 70%-80%) could be collected and returned to the boiler system, with suitable checks to prevent contamination, the demin system size can be reduced and its installation economically viable. The use of demin water has the side advantages of cleaner steam resulting in lower maintenance, the recovery of steam condensate treatment chemicals, and the ability of the plant to operate at higher steam pressures with negligible blowdown. Return of condensate would also reduce feed-water heating requirements by 6 MMBTU/hr. This in combination with the use of acid heat for the remaining feed water heating duty would recover for export 16 MMBTU/hr.

The steam system recovers 56%-70% of the energy produced by the acid plant as high pressure steam. A portion of the high pressure steam is used to drive the main blower and boiler feed water pump exhausting at the low pressure requirement of 35 psig, with the remainder let down across a valve. This system was fine in the days 10 mil power and \$1/1000 lbs. steam, but today the efficient recovery of the energy in the acid plants steam is an economic necessity. The first area that effects energy recovery from steam is the pressure of the high pressure steam. Essentially all plants built in the 1970's have 600 psig high pressure steam. This is for a number of reasons; first, 600 psig is the normal pressure break point for the use of softened water, and since essentially all plants were on 100% make-up, demineralizers could not be justified; in addition, 650 psig is also a break point for turbines. For these reasons steam pressure above 600 psig were not used. With current and future energy cost projections, recovery of condensate and the use of demineralized feed water an increase in the plants steam pressure to the next turbine break point of 900 psig would be economically justified by the 20% increase in recoverable energy from the steam.

The advantage of operation at higher steam pressures is lost if excess high pressure steam is let down across a valve. A number of plants have installed turbines, both within and outside the acid plant, to recover some of this energy. A more efficient system would be to take all the high pressure steam to a turbogenerator producing electric power, for use anywhere within the fertilizer complex, and low pressure steam. Excess low pressure steam can be condensed (heat of condensation recovered, of course) through the turbogenerator producing more power, instead of being blown-off to atmosphere. From an energy standpoint the

use of a turbogenerator at the basic flow sheet condition would produce about 8.9 MW of power with 4.2 MW export over and above the total acid plant requirement. In addition there would be only one turbine in the plant and that would be a high quality efficient unit that is a part of the turbogenerator package. In the event of turbogenerator failure outside power could be purchased to operate the plant. The energy recovered by the turbogenerator system is compared to the base case below:

	<u>Capital Cost \$1.3 MM</u>		
	Net Operating Credit \$ MM		
	1980	1982	1986
1. Base Case	6.1	10.7	21.4
2. Base Case w/turbogenerator	7.8	13.5	26.9

From the above it can be seen that the installation of a turbogenerator system has less than a one year payout in 1980 and looks even better in the future. The use of higher pressure steam, say 900 psig would increase the savings by 20%-30% and it too would have less than a one year payout.

SUMMARY

In summary, the energy exported from the basic sulfuric acid plant flow sheet can be increased significantly by the methods outlined above. The dollar savings is in the millions today and in the tens of millions in 1986. Two flow schemes are the result of the energy analysis, one based on the double absorption process and the other single absorption with ammonia scrubbing. A 1980's energy efficient design using the single absorption-ammonia

scrubbing process is described below:

1. Mono acid system
2. 11% SO₂ gas strength
3. Blower after drying tower
4. 900 psig steam system
5. 300°F gas temperature to absorber
6. Ammonia scrubbing
7. Demineralized boiler feed water
8. Use of acid heat for boiler feed water heating
(no credit for other acid heat recovery systems)
9. 1.05 inch water clean blower discharge pressure
10. Motors for all plant drives
11. All steam to turbogenerator exhausting at 35 psig

Based on the above criteria, the following comparison to the basic flow sheet was developed:

	Captial Cost	Operating Credits		
		\$ MM/yr		
	Savings	1980	1982	1986
Basic Flow Sheet		6.1	10.7	21.4
Single Absorption/AS	\$2 MM	11.3	19.5	39.0

Should an acid heat recovery system be added to recover part or all of the 100 MMBTU/hr from the acid system, substantial additional operating credits can be obtained. The energy and economic draw backs of the basic flow scheme, as shown above, are not surprising and would appear to be the panacea all are looking for.

Some operations, however, can not tolerate ammonium sulfate or phosphate in their systems and must stay with the double absorption route. For these situations a 1980's

double absorption design can also be developed based on the following:

1. Mono acid system
2. 11% SO₂ gas strength
3. Blower after drying tower
4. 900 psig steam system
5. 300°F gas temperature to absorbers
6. Co-current interstage absorber design
7. Demineralized boiler feed water
8. Use of acid heat for boiler feed water heating
(no credit for other acid heat recovery systems)
9. 105 inch water clean blower discharge pressure
10. Motors for all plant drives
11. All steam to turbogenerator exhausting at 35 psig

With the outlined criteria, the following compares this design to the basic flow sheet:

	Capital Cost	Operating Credits		
		\$ MM/yr		
	Savings	1980	1982	1986
Basic Flow Sheet		6.1	10.7	21.4
Double Absorption 1980's	(\$2.5 MM)	10.2	17.6	35.5

The 1980's double absorption process, although requiring more capital than the basic design or 1980's single absorption design, still shows significant operating cost advantages over the basic flow sheet. The tables indicate the design for today should be the energy efficient one with an overall payout of less than one year. It is hoped that designers and operators will more fully consider the cost of energy when evaluating the design and operating options of any plant modification or new sulfuric acid plant installation.

FIGURE 1

BASIC FLOW SHEET

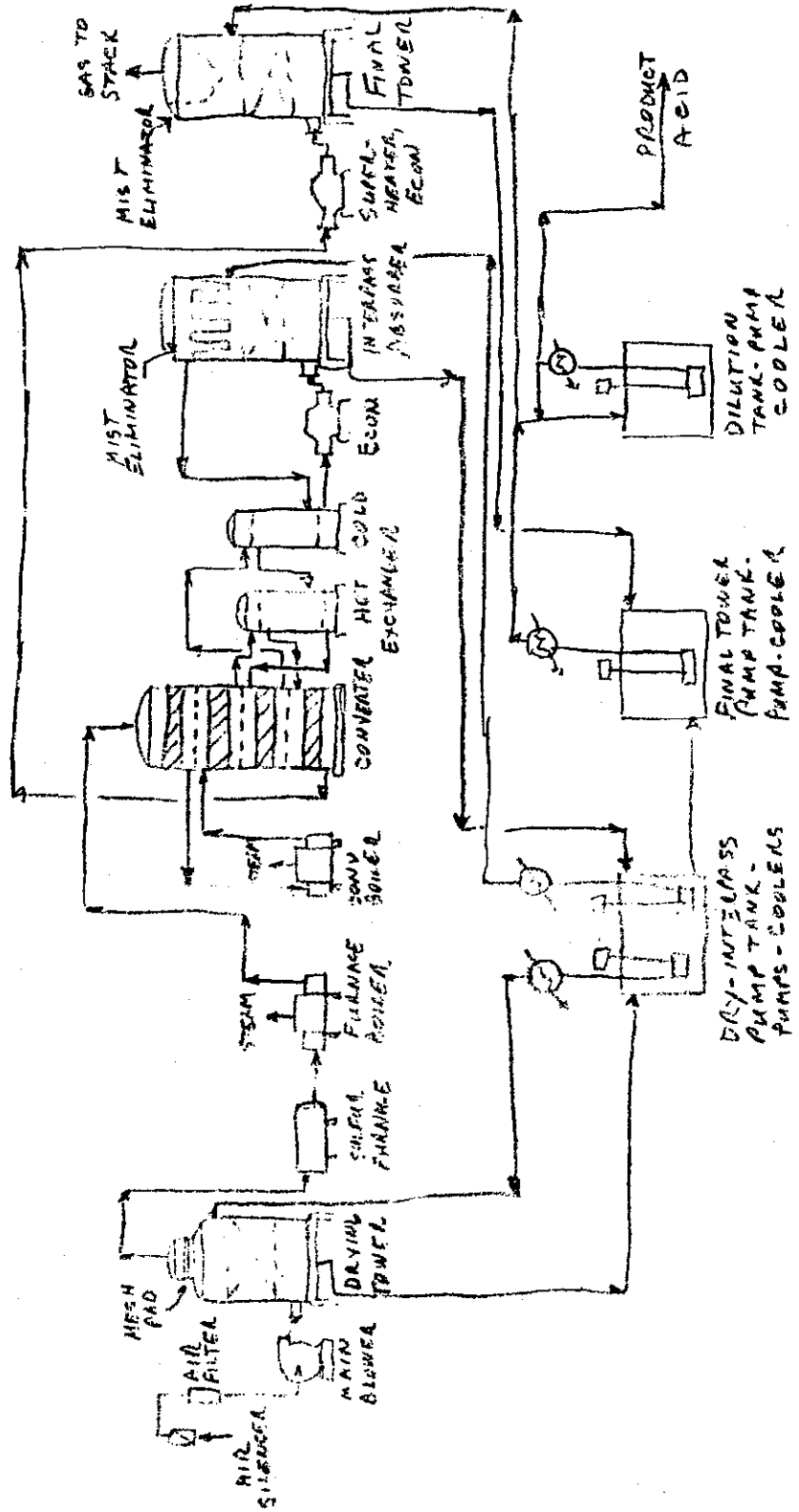
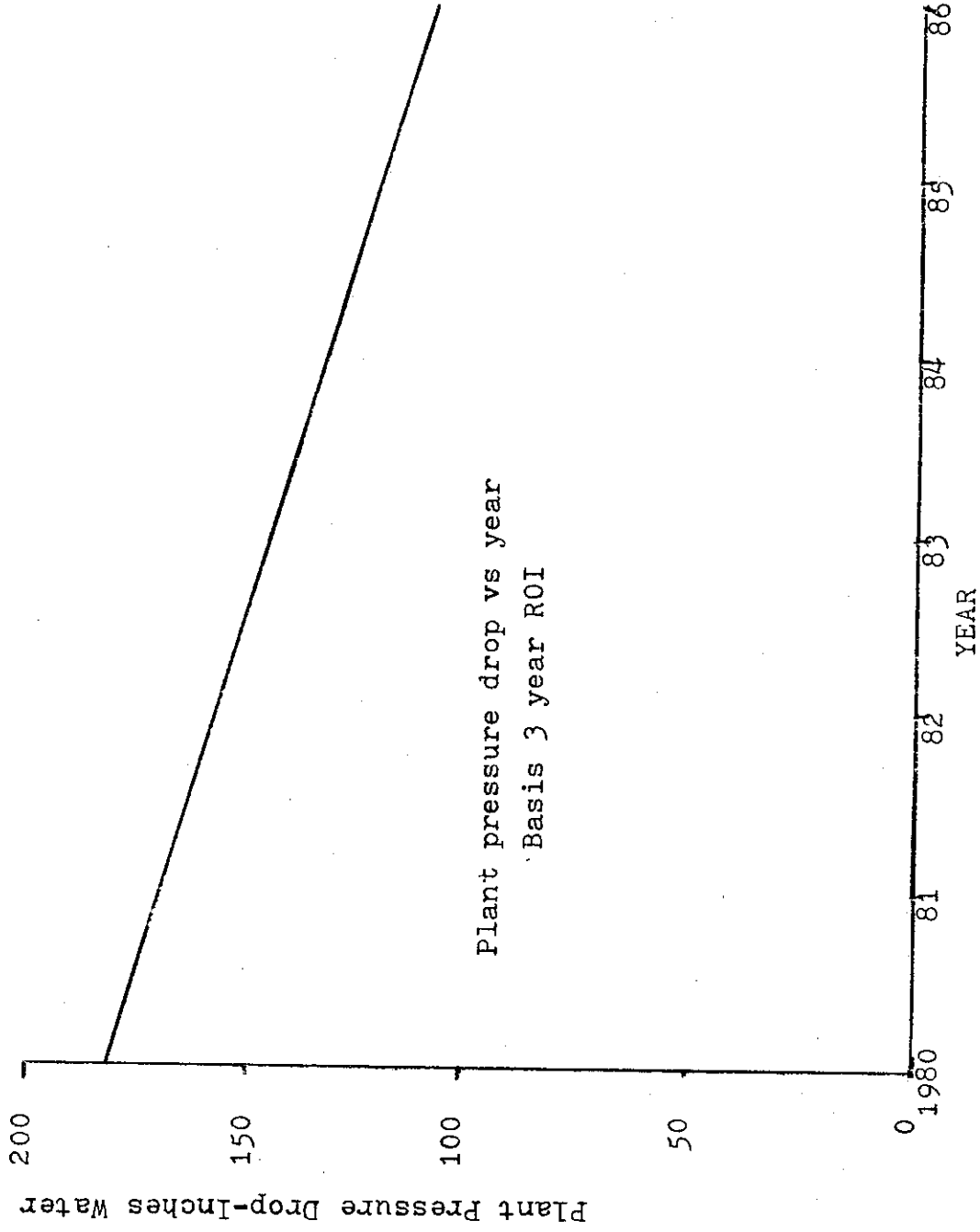


FIGURE 2

OVERALL PLANT PRESSURE DROP EVALUATION



Note: Plant pressure drop includes 15 inches water dirt build-up.

TABLE 1

BASIC FLOW SHEET ENERGY DISTRIBUTION

ITEM	ENERGY INPUT, MMBTU/hr	ENERGY REMOVED		
		STEAM	ACID	ATM
Main Blower (power)	4200hp			
Main Blower Heat	11.3			
Dry Tower Gas Cooling			1.9	
Dry Tower Water Cond.			7.7	
Sulfur Furnace	218.1			
Furnace Boiler		134		4
#1 Catalyst Bed	44.6			
Converter Boiler		40.7		1.2
#2 Catalyst Bed	18			
#3 Catalyst Bed	5.8			
Interpass Economizer		10.5		0.3
Interpass Tower Gas Cooling			33	
Interpass Tower SO ₃			92	
#4 Catalyst Bed	3.4			
Superheater Economizer		41.2		1.3
Final Tower Gas Cooling			25.3	
Final Tower SO ₃ Cond.			4.5	
Stack				7.8
<hr/>				
Sub Totals (SO ₃ Cond.)	301.2	226.4	164.4	14.6
(H ₂ O Cond.)	96.5			
	7.7			
<hr/>				
Totals MMBTU/hr	405.4	405.4		

TABLE 2

BASIC FLOW SHEET ENERGY USE

1. Steam System

a) Total high pressure steam produced	200,425 #/hr
b) Heat lost to blowdown	5.7 MMBTU/hr
c) Heat for cold BFW, 70°F-220°F	9.9 MMBTU/hr
d) Net export steam Hp & LP	190,415 #/hr
e) High pressure export	76,225 #/hr
f) Low pressure export	114,190 #/hr
g) Export steam, #/hr/STPD acid	95.2

2. Import Electric Power

a) Battery limits	350 Hp
b) Offsites - Cooling tower, etc.	1050 Hp
c) Total import electric	1400 Hp