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REDUCE P_2O_5 COSTS 10% BY RECOVERING 95% OF THE ENERGY FROM YOUR SULFURIC PLANTS

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INTRODUCTION

The process steps involved in the production of sulfuric acid -- combustion of sulfur, oxidation of sulfur dioxide, reaction of sulfur trioxide with water, and dilution of sulfuric acid -- produce large quantities of heat energy. The removal of this heat is a process requirement; however, recovering the heat in useful form is controlled by economics and available technology. This energy resource can be used to meet the steam and electrical requirements of the phosphate chemical plant as well as to provide electrical power outside the fertilizer complex. The value received for the cogenerated power is a major factor in the cost competitiveness of each phosphate fertilizer site.

BACKGROUND

Since the early 1970's, there has been a major effort expended in developing methods to maximize the energy recovery from the sulfuric acid plant. Before this time, a typical sulfur burning acid plant recovered about 55% of the total heat as steam for turbine drives and process heating. About 40% of the heat was lost to cooling water in the acid coolers. Radiation losses and heat losses in effluent and product streams accounted for the remaining 5%.

By the late 1970's, Monsanto Enviro-Chem developed and successfully introduced technology that increased thermal efficiency from 55 to 70% and generated electrical power. This was achieved by the installation of the following energy enhancements:

- converting to suction drying tower
- increasing gas strength
- reducing plant pressure drop
- adding low temperature economizers
- preheating boiler feedwater
- installing steam superheaters
- installing a turbine generator

However, even with the above enhancements, more than 25% of the total heat is still removed in the acid coolers and rejected to cooling water.

In 1982, Monsanto Enviro-Chem research achieved a technological breakthrough which led to even greater energy efficiency by recovering the energy available in the strong acid system. The resulting invention, known as the Heat Recovery System (HRS), produces steam at pressures up to 10 bar to satisfy the process needs of the plant site or to generate electricity in a turbine generator. When the Heat Recovery System is installed in conjunction with the energy enhancements, 90 to 95% of the total available energy generated in the sulfur burning sulfuric acid process can be recovered. The Heat Recovery System is described in detail in the paper prepared by D. R. McAlister, et al., "A Major Breakthrough in Sulfuric Acid Heat Recovery".

The basis of the Heat Recovery System technology is the discovery that the acid concentration can be changed to a range where sulfuric acid exhibits low corrosiveness on commercially available alloys, while high absorption efficiency is maintained. To provide the necessary driving force to produce even low pressure steam, acid temperatures higher than a typical absorbing system are also needed. It has been discovered that at concentrations higher than 98%, sulfuric acid is less corrosive and readily available alloys can be used.

The Heat Recovery System is located before the interpass tower in a double absorption plant or before the absorption tower in a single absorption plant. In the case of a new plant, HRS can replace the interpass absorption tower. As shown in the attached flow diagram, sulfuric acid is circulated over the tower at about 99% strength and 165°C. Sulfur trioxide is absorbed from the gas entering the HRS into acid circulated over the tower, which increases the acid temperature to about 200°C and the concentration to nearly 100%. Concentrated, hot sulfuric acid leaving the tower is pumped through a boiler which cools the acid to 160°C and produces 3 to 10 bar steam. After product acid is removed, the remaining acid is diluted to 99%, which increases the temperature to 165°C, and the acid is recirculated to the tower.

The Heat Recovery System was demonstrated in a pilot plant in a 550 MTPD sulfuric acid plant for two years. This verified that high absorption efficiencies and low corrosion rates could be obtained under actual plant operating conditions including startups and shutdowns. The Heat Recovery System experienced high mechanical on-stream time, low corrosion rates, high absorption efficiency, and good operability. Detailed inspection of the equipment after the two years of operation confirmed corrosion rates of less than 1 mil (0.25 mm) per year in all equipment.

Earlier this year, Fenco Engineers, Inc., of Toronto, Canada, a licensee of Monsanto Enviro-Chem, was awarded a contract to design and build a 240 MTPD metallurgical sulfuric acid plant in Norway for Falconbridge Ltd. The Falconbridge plant will be the first built using Monsanto's Heat Recovery System and will recover the heat to produce 4300 kg/hr. of 8 bar steam. At the same time, it will also serve as the interpass tower. Start up is scheduled for August 1987.

APPLICATION

Phosphate fertilizer operations are a major energy resource. With the incorporation of HRS technology and energy enhancements in new or existing plants, 90 to 95% of the total heat can be recovered as steam for process needs or to generate electricity.

A typical 55% efficiency sulfuric acid plant will produce about 1.20 kilograms of steam per kilogram of acid. An additional 0.20 kg of steam per kg of acid can be produced with energy enhancements demonstrated in the 1970's, and another 0.50 kg of steam per kg of acid can be produced with HRS. Steam from the sulfuric plant is typically produced at 48 bar and 400°C. Steam from HRS is produced at a pressure between 3 to 10 bars. Normally a portion of the steam produced by the sulfuric acid plant is used in the fertilizer complex, and the excess steam is used to produce electricity in a turbine generator. As a point of reference, 400°C 48 bar steam condensed at 76 mm Hg will produce 242 KW-HR/MT in an 80% efficient turbine generator. Likewise, saturated 3 bar steam to 76 mm Hg condensing will produce 123 KW-HR/MT of steam.

Phosphoric acid produced by the dihydrate process requires 2.87⁽³⁾ kg of 3 bar steam per kg of P₂O₅, which can be provided by HRS. Additional 3 bar steam, if required, would come from the main compressor turbine or be extracted from the turbine generator.

Steam flow diagrams for a 2200 MTPD sulfuric acid plant coupled with an 800 MTPD P₂O₅ plant, Figures 1, 2 and 3, show how the enhancements and HRS significantly increase power generation. Steam flows and power generation are summarized in Table 1.

TABLE 1 - STEAM AND POWER SUMMARY

	<u>55% CASE</u>	<u>70% CASE</u>	<u>90-95% HRS CASE</u>
<u>Steam Produced, (Kg/hr)</u>			
High Pressure (48 Bar)	110,000	128,000	128,000
Low Pressure (3 Bar)	--	--	46,000
<u>Power Generated, MW</u>			
From 48 Bar to 3 Bar Extraction	13.5	15.8	15.8
From 3 Bar to Condensing	1.1	3.2	8.5
Total	14.6	19.0	24.3

With HRS and the other energy enhancements and US \$0.05/KW-HR electricity, a total power credit of U.S. \$36 per ton of P₂O₅ produced is realized. This savings is based on the following calculation:

$$(24.3 \text{ MW})(1000 \text{ KW/MW})(\text{US } \$0.05/\text{KW-HR})(24 \text{ HR/DAY}) *$$

$$(2.75 \text{ MT H}_2\text{SO}_4/\text{MT P}_2\text{O}_5)/(2200 \text{ MTPD H}_2\text{SO}_4) = \text{US } \$36/\text{MT P}_2\text{O}_5$$

As shown on Graph 1, US \$14 per ton P₂O₅ (US \$0.05/KW-HR) results from HRS and other energy enhancements.

Based on an average production cost of US \$248⁽²⁾ per ton of P₂O₅ in the US, this is a cost reduction of nearly 6% due to HRS and other enhancements and 15% total electrical power credit. With higher power costs, such as US \$0.08/KW-HR electricity, the savings with HRS and enhancements would increase to US \$25 per MT P₂O₅ or 10% cost reduction. A fertilizer company with this cost savings has a strong competitive advantage and is in a much better position to withstand the current depressed fertilizer prices.

Of course, a major factor in determining the energy savings is the value of electricity, which varies as illustrated by the data in Table 2 from a survey conducted in April, 1986, by the National Utility Service in New York, New York.

TABLE 2 - ELECTRICAL POWER COSTS

<u>COUNTRY</u>	<u>US \$/KW-HR</u> ⁽⁵⁾
Germany	0.0700
United States	0.0659
Italy	0.0636
United Kingdom	0.0555
France	0.0487
Australia	0.0372
Canada	0.0354

In addition, data from a survey performed by Monsanto shows that the average power costs for the major fertilizer producing areas of Morocco and Tunisia in 1984 were US \$0.077 and US \$0.050, respectively.

These power costs are the average for each country. The actual cost of electricity can vary not only country to country, but sometimes from region to region or even city to city. This results in a wide range of prices paid for electricity within the same country. The difference is even more dramatic for the value of electricity exported from a fertilizer complex. For example, cogeneration is encouraged in some areas by regulations that require utilities to pay full value for exported power and discouraged in others resulting in exported power valued at only a fraction of the full value.

In the United States, the price that the fertilizer producer receives for the exported power is generally established by Federal guidelines and negotiations with the local utility. Even though the average guideline price for purchased power is US \$0.0659 KW-HR, some producers receive as little as US \$0.02/KW-HR and others receive more than US \$0.066/KW-HR. The sale price of power actually ranged from US \$0.0448/KW-HR to US \$0.1135/KW-HR in the United States in 1986. Since all producers compete in the same marketplace, those who obtain the highest price for their power have a competitive edge.

It follows that cogenerators need to work with their utilities, regulatory authorities, and politicians to obtain favorable results. In some cases, this will require new legislation.

The surest way to get the full value is to use the cogenerated electricity to offset purchases for the site energy needs. Site generated power can be used in the mining of the phosphate rock, beneficiation, storage and shipping of product, as well as to supply the sulfuric and phosphate fertilizer plants. In a completely integrated phosphate mine and chemical complex, the energy recovered with HRS and enhancements can normally supply all steam and electrical needs.

It is of interest to analyze the potential worldwide power generation from sulfuric acid. The basis for this analysis follows. HRS technology alone produces 0.5 kg 3 bar steam/kg acid and provides a net 2.4 KW/MTPD of acid (3.2 KW/MTPD for 10 bar steam). Energy enhancements on sulfur burning plants will produce 0.2 kg steam/kg acid and provide 2.0 KW/MTPD of acid. This is a total of 0.7 kg steam/kg acid and 4.4 KW/MTPD of acid. Based on IFA's reported sulfuric production for 1985, HRS plus enhancements would produce 1464 MW of electricity as shown in Table 3.

TABLE 3
POTENTIAL INCREASED POWER PRODUCTION(4)

	<u>FROM ENERGY ENHANCEMENTS AND HRS</u>				TOTAL POWER MW
	<u>BRIMSTONE</u>		<u>PYRITES AND OTHERS</u>		
	<u>PRODUCTION</u> <u>1000 TPA</u>	<u>POWER</u> <u>AVG. MW</u>	<u>PRODUCTION</u> <u>1000 TPA</u>	<u>POWER</u> <u>AVG. MW</u>	
Western Europe	13,609	164.1	12,499	82.2	246.2
France	3,770	45.4	540	3.6	49.0
West Germany	1,660	20.0	1,970	13.0	33.0
Spain	0	0.0	3,550	23.3	23.3
Africa	9,225	111.2	2,461	16.2	127.4
Morocco	3,960	47.7	0	0.0	47.7
South Africa	1,630	19.6	1,875	12.3	32.0
Tunisia	2,320	28.0	0	0.0	28.0
Asia	9,811	118.3	5,908	38.8	157.1
India	2,405	29.0	167	1.1	30.1
Japan	2,033	24.5	4,548	29.9	54.4
South Korea	1,650	19.9	450	3.0	22.8
Oceania	1,795	21.6	600	3.9	25.6
North America	29,947	361.0	8,999	59.2	420.2
United States	28,497	343.5	6,548	43.1	386.6
Latin America	6,666	80.4	1,079	7.1	87.5
Brazil	2,888	34.8	472	3.1	37.9
Mexico	2,988	36.0	260	1.7	37.7
Eastern Europe	5,630	67.9	4,292	28.2	96.1
USSR	14,000	168.8	12,000	78.9	247.7
China	887	10.7	5,800	38.1	48.8
Others	285	3.4	649	4.3	7.7
TOTALS	91,855	1,107.3	54,287	357.0	1,464.2

The typical cost for adding HRS to an existing plant for the 2200 MTPD case is US \$4.5 million, including the US \$1.0 million incremental turbine generator cost. This is US \$850/KW which gives about a 2 year payout with US \$0.05/KW-HR power. The comparable cost, if included as part of a new energy efficient plant, would be US \$3.5 million. This is approximately US \$660/KW, which gives about a 1.5 year payout. Payout is further improved if the steam can be used directly so the turbine generator cost is avoided.

Economics are obviously best for large sites and large sulfuric plants. However, many operators of small sulfuric plants will be able to develop economically attractive projects where the recovered steam has a high enough value. The 240 MTPD Falconbridge plant, which is being built in Norway, is a good example.

There are other special situations which favor installation of HRS. For example, where the interpass absorption tower in an existing plant must be replaced for maintenance reasons -- an HRS can be installed instead. With HRS, the tower replacement is turned into an earnings project.

Many phosphoric acid producers are at least considering conversion to the hemi-hydrate process, which consumes 1.1⁽³⁾ kg steam/kg P₂O₅ as compared to 2.87 kg steam/kg P₂O₅ for the di-hydrate process. Since less steam is required in the hemi-hydrate process, more steam can be taken to condensing in the turbine generator, resulting in an increase in power generation of 3.0 KW/MTPD of sulfuric acid produced. On a worldwide basis, this is an additional 1200 MW, giving a total potential of 2664 MW with HRS and enhancements. Many sites, and especially the smaller ones, will find that economics are improved by increasing energy efficiency in the entire phosphate complex.

CONCLUSIONS

Throughout this report it has been demonstrated that there is a definite competitive advantage for those who do incorporate HRS as part of their fertilizer complex. This advantage has been developed as an energy savings of US \$25/ton P₂O₅ in manufacturing cost. This cost reduction leads directly to greater profitability. Also, since this makes fertilizer producers self-sufficient in meeting their site electrical needs, they are no longer subject to power interruptions. This equates to higher on-stream time and reduced operating cost.

In the United States, those fertilizer producers who have rallied to obtain proper credit for cogenerated power, have seen the greatest returns. These producers have managed to generate profit during the last 2 years while many of their competitors sold their product at a loss.

Cogeneration benefits the electric power consumer as well as the cogenerator. Consumers long term will see lower electricity costs as the cogenerated power requires no continuous fuel usage. Also, construction of costly new electrical utility generating plants will be avoided. The cogenerated power is also a perfectly clean source of electricity. There is no coal or fuel oil burning, so there is no pollution.

Just as important is the conservation of non-renewable energy sources. For every 10 MW of cogenerated power, oil usage is reduced by 160,000 bbls. per year. At \$20/bbl for oil, this reduces foreign exchange requirements by US \$468 million per year worldwide. In many countries, this will improve the balance of payments.

For the above benefits to be realized, the phosphate fertilizer producer must be assured of full value for cogenerated power. Otherwise, the necessary capital cannot be obtained. Considering the benefits to consumers, the general public, and the country as a whole, we believe this can be accomplished. However, it will require education of the general public to accept changes in electrical utility regulations.

In summary, the Heat Recovery System is a significant technological breakthrough that can dramatically improve the economics of producing phosphate fertilizers.

REFERENCES

1. McAlister, D. R., et al., "A Major Breakthrough in Sulfuric Acid Heat Recovery", paper presented at the 1986 annual meeting of AIChE, New Orleans, Louisiana.
2. "Cost of Making DAP in 1984 Found to Exceed Selling Price", Green Markets Fertilizer Market Intelligence Weekly, Vol. 9, No. 22, June 3, 1985.
3. "Phosphoric Acid by the Dihydrate Wet Process" and "Phosphoric Acid by the Hemihydrate Wet Process", SRI International PEP Yearbook 1985, Vol. 1, Max Sacks, ed., pp. 1-246 and 1-248.
4. "Preliminary Sulphur and Sulphuric Acid Statistics 1985", prepared for the IFA by The British Sulphur Corporation, Ltd., pp. 7-8.
5. 1986 Annual Survey of Utility Costs, prepared by the National Utility Service, New York, New York.

FIGURE 1
55% EFFICIENCY CASE

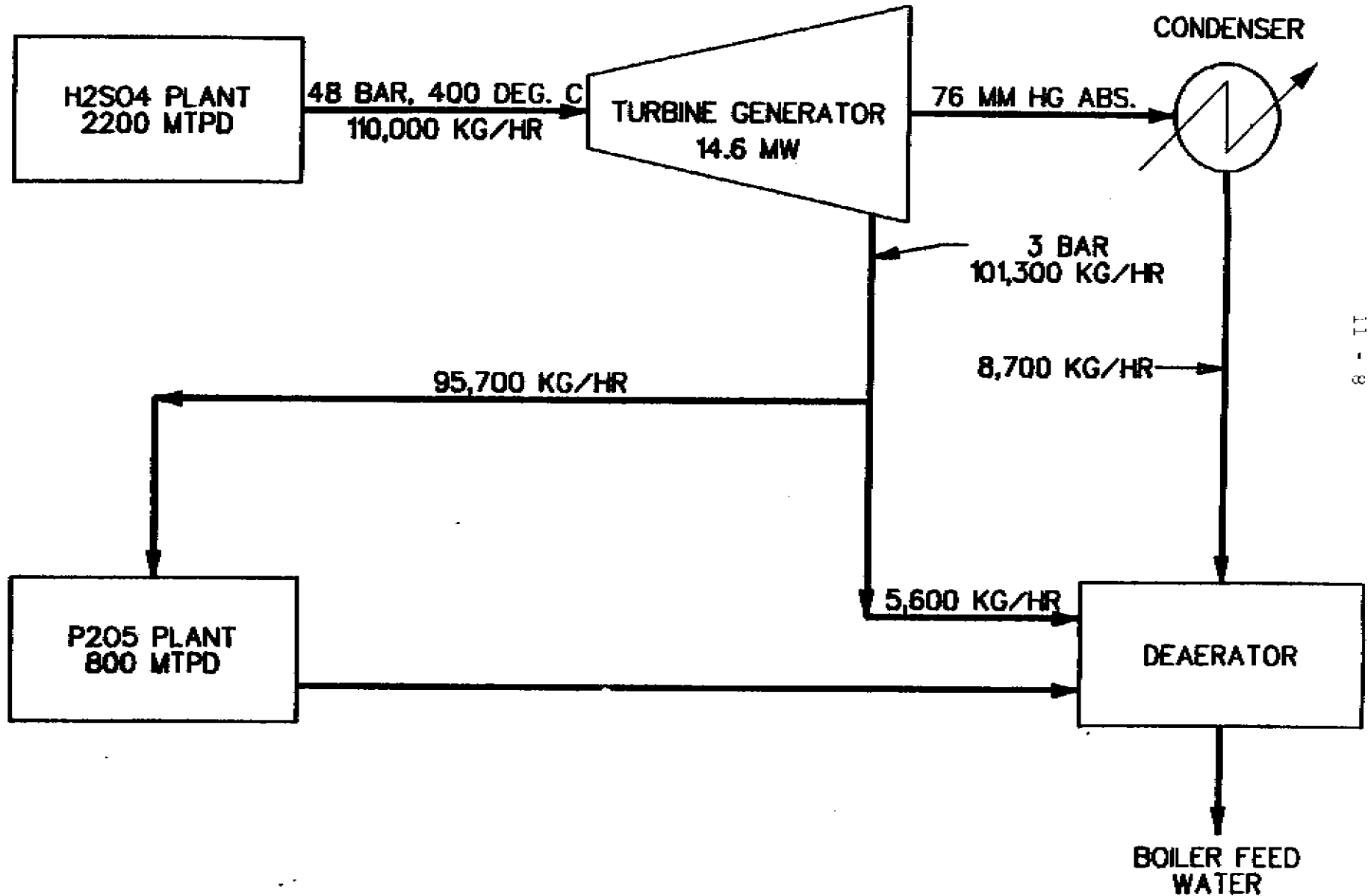


FIGURE 2
70% EFFICIENCY CASE

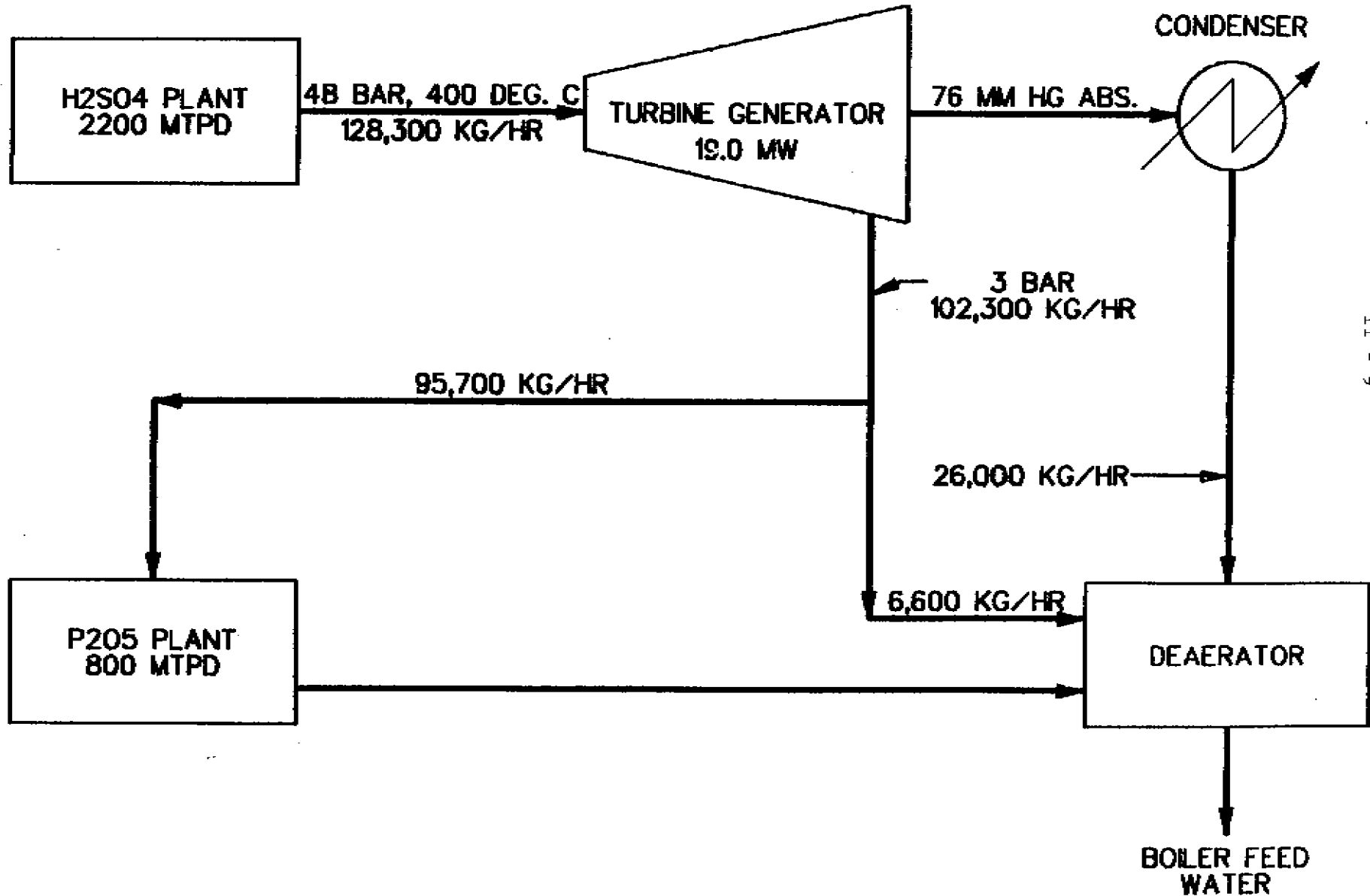
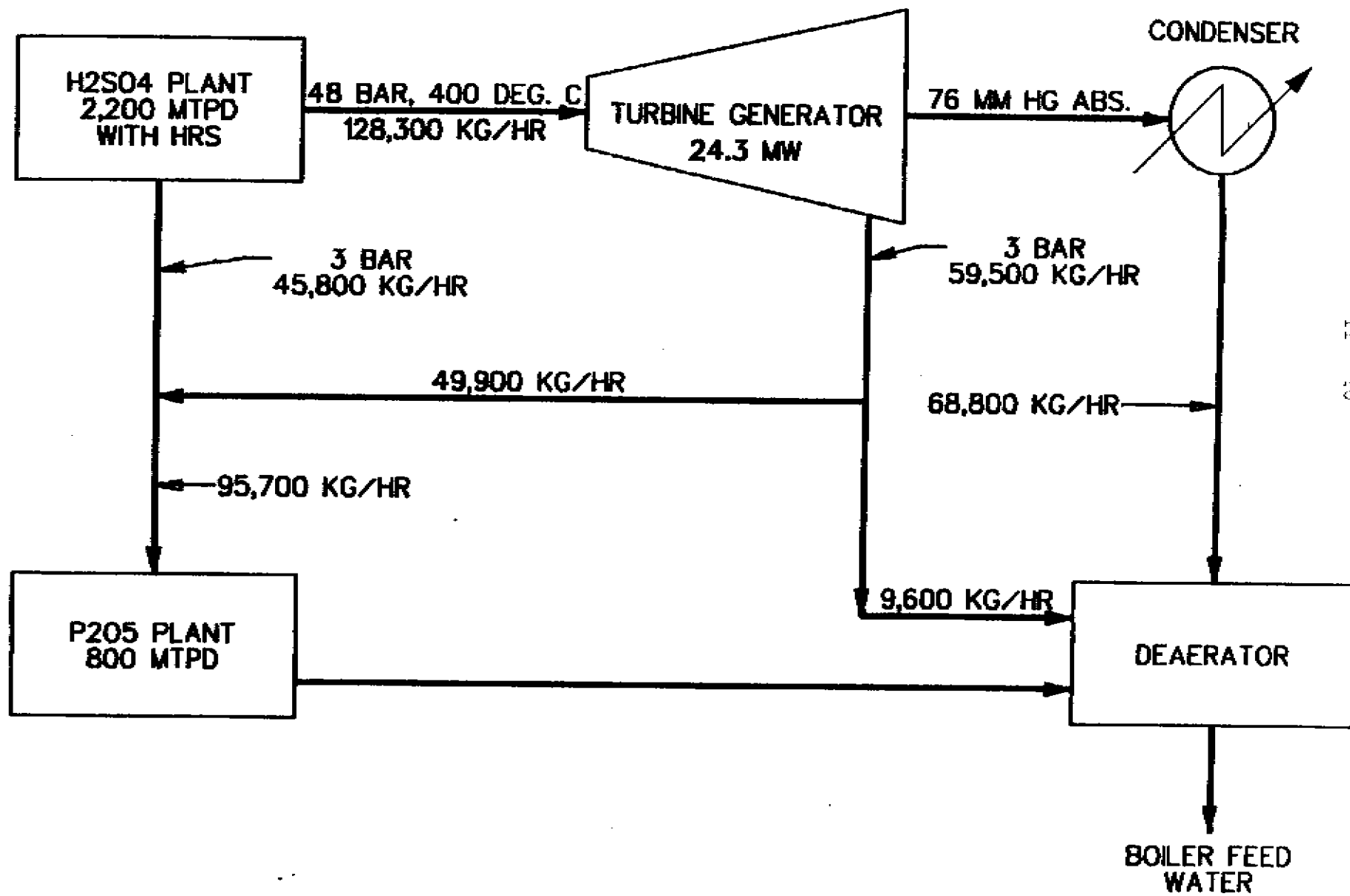
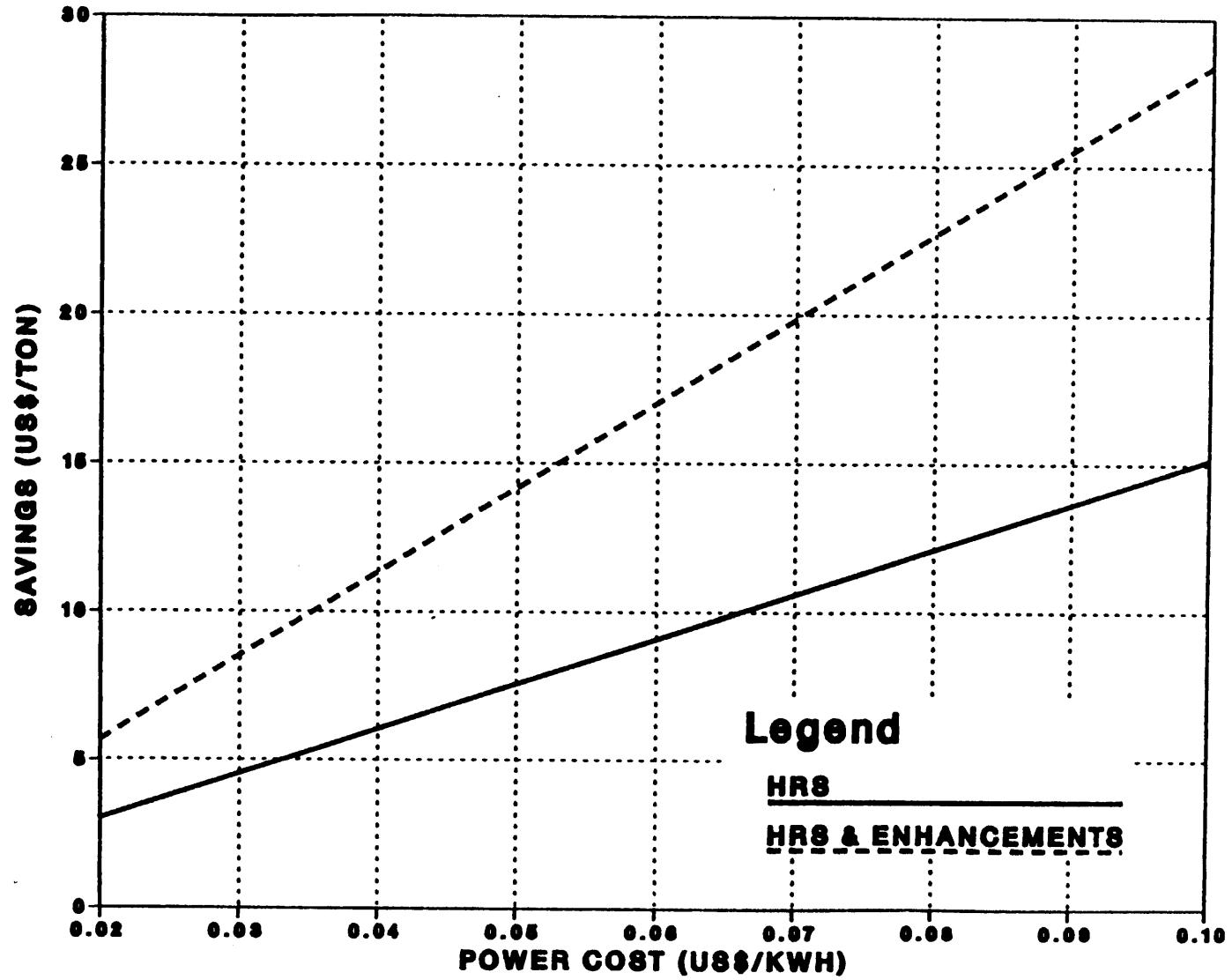


FIGURE 3
90-95% HRS CASE



GRAPH 1 - P2O5 PRODUCTION COST SAVINGS



TA/86/11 Reduce P2O5 costs 10% by recovering 95% of the energy from your sulfuric plants by C.A. Johnson & R.M. Smith, Monsanto Enviro-Chem Systems, Inc., United States.

.DISCUSSION : (Rapporteur B. Christensen, Superfos, Denmark)

Q - Mr. P. ORPHANIDES, Duetag, France

1. What type of boiler have you used in the 550 t/d pilot plant (form, materials)?
2. What was the type of concentration control equipment? (Make, working principle etc...)?
3. What have you foreseen to avoid acid dilutions below 99% due to maloperation of the acid concentration control system?
4. What have you foreseen to detect water/steam leaks to the acid from the boiler at a very early stage? (I presume acid pressure being lower than steam pressure).

A - 1. In the pilot plant we used a thermal siphon boiler. The acid was in the tubes and we used a natural circulation to obtain the circulation. In Foreskill plants, though we are going to use what will be called a kettle type boiler, that will lay horizontally, the acid would be pumped through the boiler.

Regarding materials we installed 6 different tube materials in the boiler, and it was quite a range of common materials: 304 stainless steel, 316 stainless steel, 310 stainless steel, and all of these worked very well, none had excessive corrosion. However, we have found that some were slightly better than others and we would choose those.

2. We are using conductivity, but it is a new system, it is called a toroidal conductivity measurement, somewhat like a magnetic flowmeter, the coils are outside of the pipe, outside of the acid flowstream. There are two very good advantages to this. One is that you do not have the maintenance problem with the old reference cells. Second you get essentially no drifting, so it stays to the set point very closely.
3. First of all we are installing 2 conductivity controls so that you do have duplicate readings and obviously that can give an indication of a problem, but, more importantly, we demonstrated on the pilot plant that we can measure corrosion rate continuously with an electrical device, and we actually have that incorporated as part of the design; so, if for any reason the instantaneous corrosion rate goes up, an alarm sounds and you must take care of it, whatever the reason would be.

4. We are using an acoustical emission measuring instrument for that. This is a system that was developed by Monsanto Co. for protecting equipment throughout chemical plants and this system actually is constantly monitoring the sound level, a sound frequency in the boiler, and, when the acid and the water come together, you get a dramatic change in the sound being emitted and that sounds an alarm. So we have a system that instantaneously will tell if there is a leak in the system.

Q - Mr. E. UUSITALO, Kemira Oy, Finland

1. Which are the strictly controlled acid concentrations and how do you control them in practical big scale acid production? Have you some automatic control system and what happens when you are working outside of the limited conditions for instance in start-up and shut-down periods?
2. In your own opinion, what is the probability that you succeed with your first client and who is taking the responsibility in the first case, you or your client?

- A - 1. The first question also relates to concentration control and acknowledges that is a very important area. I discussed the instrument we use but I would like to mention another point on that. You noticed we add the water after the boiler and before we go into the tower; so we add the water and then within just hundredths of a second we measure the concentration and so we get a very quick response time. That is one thing that makes this process different from almost all of the normal sulphuric processes. Normally the pump tank gives you a long response time, so it is hard to control concentration. With quick response you can do it extremely well.

The next point was on start-up and deviations. What happens if we do get some corrosion? With the materials that we select we are able to drop acid concentration down to the 97% range for reasonable periods of time, and may be the corrosion rate increases up to a rate of 1 mil per year, but, if you only do that for short periods it is not really significant when you look at the total. So you are able to have variation away from the normal without disastrous results.

2. We think that the probability to succeed is extremely high and because of that we have offered this generally for sale. I mentioned the one we have also in Norway. We have sold two others to a client that I am not able to announce yet, but we are openly selling it, we have confidence in it. Now, in the very early units we are selling, we are giving guarantees with a lot of Monsanto-commitment, and a lot of liability on Monsanto.

Q - Mr. A. MOULDI, ICM, Tunisia

1. To our knowledge HP steam production in a single absorption Monsanto unit is such that the steam/acid ratio is 1.2. In the paper you indicate a ratio of 1.4 for the units built between 1970 and 1982.

Why do the units started in 1970, 1972 and 1979 only follow 1.2?

What are the changes to be achieved profitably to increase the ratio from 1.2 to 1.4?

2. What is the effect of air humidity on the recovery rate of a HRS unit and on the time for repaying investment in that unit (in particular in the sites with a very high air humidity)?

A - 1. The first question relates to the comments that I made in terms of steam production in normal sulphuric plants. I intended to say in my paper that it ranges from 1.1 to 1.3, so I did not mean to say 1.4, if I did. Now, there are several factors that affect that rate, and one of them that is rather critical is, what is the temperature of the boiler feedwater returned to the site. That can vary quite a lot. Obviously another factor is the ambient temperature, but we are finding that very normally we can get up to 1.3. What we would need to do at your particular plant is to see: are there other enhancements that should be included, such as boiler feedwater heating, increasing gas strength, f.ex. in single absorption plants such as yours, sometimes we eliminate the air dilution after the third pass and provide instead a superheater or economizer and by raising the gas strength you get more steam recovery in the plant. So we would need to look at the specifics on it, but we consistently can get up to a 1.3 ratio.

2. The next question concerns the effect of humidity and this does have an impact because we are recovering the energy in the absorption tower. Obviously you must have some system of getting the energy that is released in the drying tower into the absorption tower to get full recovery. We have made a number of flowschemes on that. With some of them we have lost on an average 3 or 4% of the energy due to the high humidity in some areas. We are still working with new flowschemes where at least our new plants have been able to almost completely avoid that problem, but on existing plants it may or may not be economical to re-pipe the systems completely to eliminate the loss.

Q - Mr. M. BAKLOY, SCPA, France

1. Could you consider a direct heating of phosphoric acid for P2O5 concentration?
2. Producing electricity has some manufacturing cost which should be taken into account in the repayment calculation. How high are these costs? It seems that the repayment in 2 years does not consider the financial charges. Could you confirm?

A - 1. We are aware that there is opportunity in using the heat from the sulphuric acid plants for directly heating the phosphoric acid in the evaporation area. But we are not experts in the phosphoric acid field; so we have not considered that very fully. We think the benefit of going to the heat recovery system that we have though is that it does generate steam,

which is very flexible, and it can be incorporated into the flow schemes of many different plants, but I am also sure that work will continue in the area of direct heating of phosphoric acid evaporation plants...

2. In the calculation of return on investment you are right. What we have defined is simple pay-back. We have just defined that as a term and it does not include the interest expense or the depreciation or the other costs. It is more of a cash flow evaluation rather than a true return calculation. All it is saying is that over a two year period you will receive that much in electricity. We have tried to do it right, but it gets very complicated when we have to define the taxes, the depreciation period, and so forth. Obviously, for each project you would have to look at it on a much more rigorous basis.

Q - Mr. E. SEITZ, Lurgi, Germany

Were there any precautions taken for the process water of the test plant?

A - The process water is actually more critical on the boiler side than it is on the acid side. Obviously, when you are using stainless steels, you must keep low chloride in the boiler feed water, or else you run into troubles. On the acid side, you must consider silicon, that can give fouling on the tubes. Too much chloride could be a problem, so we have established limits on these. In most cases typical water is satisfactory, but when there are areas, where that would be troublesome, then we would have to look for some type of treatment. And so we would have to look at it on case by case, but it is not very sensitive to water quality.