

COMMENTS ON PINEY POINT PHOSPHATE'S PROPOSED REPAIR LIST
BY R.C. "BILL" BERRY 758-4713
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SUMMARY

I have reviewed the list attached to Mr. Ivan Nance's letter dated December 17, 1996 to Mr. W. C. Thomas and feel that this list, together with statements contained in Mr. Nance's letter and the attached certification by Mr. Gerald W. Hartman, do not truly represent a repair effort but are, in fact, major modifications to the plant and may be alterations to the basic process under the guise of "repairs".

In my mind, repairs consist of replacing items that have broken or worn out with identical or very similar items. Repairs do not constitute changes in size, capacity or configuration. Several of the "repair" items on the repair and replacement list represent major changes in one or more of these categories.

Mr. Hartman's choice of words and punctuation in his certification could lead the reader to accept that there are no major changes but upon careful reading, it is apparent that the work to be performed might actually be a major process change.

Mr. Hartman applies the word "same" to capacity, design and emission limitations but after "design" includes in parentheses the words "double contact wet process".

The problem with this wording is that the plant was not designed to be, and is not now, a wet process sulfuric acid plant. It is, by definition, a "dry" process plant.

I am attaching a copy of a technical article titled "Alternatives in Sulfuric Acid Plant Design" that was published in Chemical Engineering Progress magazine in March of 1977 which discusses the various processes. On the first page, I have underlined a basic definition of the two processes.

Historically, wet process acid plants have used either smelter gases or oil refinery spent acids and sludges for feedstock and the line of demarcation between dry and wet plants was clear. It is my understanding, however, that Monsanto is now offering a sulfur burning process that does not strictly fit the criteria that the combustion air is dried immediately upon being drawn from the atmosphere and remains free of water throughout the rest of the process.

It is also my understanding that this new Monsanto process is the basis for

the application to build a totally new plant.

In the absence of a material flow diagram, it is not possible to tell if that is what is being contemplated in the proposed "repairs". As part of the review and approval process, a material flow diagram should be requested to be included as part of the submittal.

If an objection is raised that this information is proprietary, a simple diagram, without flow rates, showing the sequence in which the various gas and acid streams flow through the plant should be requested. This would show whether a major process change is involved.

Further reinforcing the suspicion that major process changes may be involved are the statements regarding changing the sizes, types and metallurgy of major pieces of equipment and ductwork.

These changes would indicate that the basic heat and material balance of the plant is being altered and that the changes are required as a result of different flows, temperatures and gas compositions.

These changes will be discussed in detail in the comments on each proposed change which will follow this summary.

If the proposed changes do, in fact, constitute a change from the original process upon which the emission limits were approved, it will be up to others to decide whether the changes are sufficient to require permit review and modifications.

I am attaching a material flow diagram from a plant that was built in North Carolina and which was one of my projects while I was Senior Project Manager with Monsanto Enviro-Chem Systems. This flow diagram is essentially the same as the flow diagram for the original Piney Point plant. The only appreciable difference between this plant and the existing Piney Point plant should be a second converter, and associated heat exchange equipment, which was added by a previous operator.

I am also attaching a technical article titled "Design Options For Sulfuric Acid Plants" written by Jack Rinckhoff and Lenny Friedman, both of whom are well recognized as experts in the field of sulfuric acid plants. This article gives an excellent overview of options and variations in sulfuric acid plant design and may assist in understanding and evaluating my comments regarding the list submitted by Piney Point Phosphates.

I first worked with Jack Rinckhoff in 1958 when he was with Chemical Construction Company which, at that time, was a major competitor of Monsanto in sulfuric acid plant design and construction.

Lenny Friedman was Senior Process Engineer on several of my projects while I was Senior Project Manager with Davy-McKee Corporation, the company which succeeded Davy Powergas.

My comments on the individual items detailed in Exhibit 1 to Mr. Nance's letter are as follow and are in the same order as presented:

1. Sulfur Burner: No comment.
2. Boiler Feedwater Heater: No comment.
3. Waste Heat Boilers: No comment.
4. Economizer: Unless gas flows or temperatures have increased, why is a larger economizer required?
5. Main Compressor: No comment.
6. No. 1 Converter: Replacement of the 1st pass section with "high temperature" materials raises several questions. The operating temperature, and temperature rise, of the gas through the 1st pass of a converter are determined by the catalyst characteristics and, to my knowledge, haven't changed since the use of Vanadium Pentoxide catalyst began. The original plant was designed for those conditions and the materials selected were appropriate for the conditions.

Have the temperatures changed?

Are they using a different catalyst?

Could it be that "high temperature" is also another term for corrosion resistant and that they are changing to 304 stainless steel which is "high temperature" but which would also be one of the choices for a wet gas plant?

- 7. No. 2 Converter:** No comment except that this converter was not included when the plant was originally built and was added by a previous operator to increase production from the original design capacity of 1500 TPD to the current 2000TPD.
- 8. Acid Towers:** The design of these towers needs to be reviewed since the efficiency of the towers, particularly the final tower, can have a major effect with regard to emissions. A reduction in size would indicate either reduced gas volume or a major increase in gas/acid contact efficiency.
- Relocation of two of the towers to new foundations is a major change. Why is this being done? Reference is made to safety considerations in Mr. Nance's letter. Are these towers part of the safety relocation and why are they unsafe in their present location?
- 9. Mist Eliminators:** My only comment here is that the eliminators should be defined and should be Brinks HE or equivalent eliminators in the final tower.
- 10. Heat Exchangers:** The reduction in size of a heat exchanger in a plant that is being "repaired" indicates that the heat and material balance of the plant is being altered since only a change in duty should allow reduction in size. There is no indication that the exchangers, as originally installed, were oversized.
- 11. Superheater:** No comment.
- 12. Condensate System:** The change in metallurgy may or may not indicate a process change since condensate is inherently corrosive under certain conditions and this change may only reflect a safety factor against future corrosion problems.
- 13. Cooling Tower:** This item also reflects a change in equipment sizing and could be related to either a change in the heat balance of the plant or to the different type of acid coolers being proposed since the proposed coolers have a better heat transfer coefficient.
- 14. Acid Coolers:** The coolers originally installed in the plant were cast iron

AX sections (see Rinckhoff/Friedman page 80) which are not very efficient. The proposed shell and tube coolers, which are assumed to be of stainless steel construction, are much more efficient but do create a concern regarding corrosion rates in the final product acid storage tanks.

I am attaching an article discussing corrosion in acid storage tanks and, at the bottom of page 66, have underlined a portion of a paragraph discussing this. I will have further comments on this subject in my review of item 16 on the list.

In any case, the inclusion of these totally different type coolers does not constitute a "repair".

- 15. Acid Pump Tanks:** The consolidation of the acid pump tanks is certainly a process change in that it alters the entire acid circulating system from what is known as a dual acid system to what is known as a mono acid system. On pages 79 and 80 of the article by Rinckhoff/Friedman, the difference in these systems, and the effect on the heat balance of the plant, is discussed.
- 16. Acid Storage Tanks:** The repair of these tanks in a proper manner is crucial. There is a special consideration in inspecting acid storage tanks that have been out of service for extended lengths of time and this was not recognized by the operators of the plant at the time of the major acid spill in 1989 that caused the evacuation of 400 people. I will address this in other comments that will follow the items on this list.
- 17. Plant Stack/
Water System:** No comment.
- 18. Pumps:** No comment.
- 19. Ducts:** Four new ducts to relocated towers are not repair items and we again find a change in metallurgy that is unexplained but could be related to a change in gas composition.
- 20. Misc. Pipe/Valves:** No comment.

21. SO2 Monitor: No comment.
22. Office: No comment.
23. Civil, Structural
Insulation, Electrical,
Painting: New piling and foundations for the new acid towers in their relocated positions are not repair items.
- Reference to a new MCC to be located adjacent to the existing MCC would imply that new equipment, in addition to that now in use, will be installed. Again, this is not a repair item.
24. Instrumentation: While complete replacement of the pneumatic instrumentation system with an electronic system does not constitute a repair, it is one of the few items listed where replacement rather than repair makes sense and is justified.

OTHER COMMENTS

In addition to the comments on the individual items on the Piney Point Phosphate list, there are several items that are either an expansion of previous comments or are items that I feel should be addressed before the plant is allowed to be started up by any operator. These comments are as follow:

ACID STORAGE TANKS

I have previously indicated that the proper inspection of these tanks is crucial and particularly so in light of the 1989 spill.

The attached article on storage tanks discusses the problems with inlet location, iron content, storage temperature and other factors.

What was not discussed directly is what caused the 1989 failure.

In addition to the previously discussed considerations, there is a condition that can cause severe corrosion in tanks that sit in an empty condition. In empty tanks, the natural changes in air temperature and barometric pressure cause the tank to "breathe".

This causes moisture in the air to come in contact with residual acid that cannot be totally drained from the tank and in contact with the tank walls where condensate runs down and creates a very corrosive weak acid.

Since the center of the bottom of the tank is higher than the perimeter, this acid collects at the juncture of the sidewall and the bottom plate. As enough weak acid accumulates, it flows to the outlet elbow in the bottom of the tank where it sits and corrodes the elbow. This elbow is in a notch or box in the foundation of the tank and the back side of the elbow is under the tank where it cannot be inspected or checked for thickness.

The back, or long radius, side of the elbow is also subjected to the highest velocity when acid is being withdrawn from the tank and is, therefore, subject to scouring action that removes any passive film that otherwise might accumulate.

The elbow connects to the outlet shutoff valve of the tank and is, therefore, between the tank and the valve. The shutoff valve is useless if the elbow fails and this is what happened when the major acid spill occurred.

It is my understanding that the elbow was replaced after the spill but it is unknown how many times since the spill the tank has been sitting empty and subject to the same conditions that caused the failure.

As part of the "repairs", this elbow, and any others similarly located, should be replaced.

In addition, the tanks should be checked for thickness by ultra-sound testing and the critical welds in the tank shell should, in addition, be checked by X-ray for hydrogen or other inclusions. The X-ray examination should include, as a minimum, the intersections of vertical and horizontal welds in the tank shells and the weld connections between the tank shells and bottom plates.

Checking of the thickness of the tank shells will allow calculation of the hoop stress present when the tanks are in operation and will determine their suitability for continued operation.

ACID CIRCULATING SYSTEM

The other major environmental problem at the plant occurred when the Northern part of Manatee County was covered with SO₃ gas causing respiratory problems for many people.

I was told by a man who was an employee at the plant when the problem occurred that the plant operator failed to turn on the acid circulating pump on the final absorbing tower. This allowed raw SO₃ gas to be discharged directly to the atmosphere. This problem can occur when acid circulation is lost or reduced for any reason.

One solution to this problem would be to meter the flow going into the tower and interlock the meter to shut the plant down whenever acid flow fell below a predetermined level. The problem with this solution is that the large size of the piping would require that the meters for sulfuric acid service would be extremely expensive. Piney Point Phosphates would probably strongly oppose these meters on the premise that the meters could also fail and that the cost cannot be justified.

One other measure of acid flow is the amount of current going to the circulating pump motors. This current provides another means of preventing plant operation unless the proper amount of acid is being delivered to the absorbing towers.

Installation of undercurrent relays, with time delays, in the motor control equipment for the pumps would allow shutting down the main blower and sulfur pumps in the event of low acid flow whether this was caused by operator error, a broken pump shaft, worn or plugged impellers, closed pump discharge valves or any other reason. I will be happy to discuss this with you in more detail since it represents a relatively inexpensive means of providing insurance at a cost that should not be objectionable to a responsible operator.

EMISSIONS

When the capacity of a sulfuric acid plant is stated, this figure does not really mean too much unless it is related to the strength of the SO₂ gas leaving the sulfur furnace.

Because of this, a plant operator has the opportunity to, within certain limits, control the emissions from the plant to be whatever is necessary to satisfy testing requirements depending on how the limits are specified and how production is measured. There is latitude for the operator to "play games" with the emissions and those attempting to measure them.

The concept is not complicated but the explanation, and variables, can be lengthy and are best stated verbally. I will be happy to discuss this in detail.

AMMONIA SYSTEM

While a great amount of attention is being given to the sulfuric acid plant and the possibility of environmental and health problems associated with this plant, there is also a much more lethal system in the complex that presents a very real danger of catastrophic failure. This is the ammonia system that supplies the fertilizer plant in the complex. Ammonia gas, even in relatively low concentrations, can cause death and certainly severe respiratory problems.

To the best of my knowledge, the ammonia is still being stored in the original horizontal cylindrical pressurized storage tanks commonly referred to as "bullets". These tanks can reach a pressure of around 300 psig on a hot day and it is quite common to spray the exteriors of these tanks with water to hold the pressure down and prevent the relief valves from blowing off.

Installed integral to the outlets are excess flow valves that are designed to close if excess flow should take place for any reason, such as a broken ammonia pipe. The location of these valves, which are partly inside the tank, prevents inspection of the closing mechanism and, historically, the only way to test them for proper operation has been to return them periodically to the manufacturer for testing.

Further complicating this is the fact that fertilizer grade ammonia contains a small amount of water that can cause corrosion of the valves and their closing mechanisms, particularly when the tanks are not in regular operation. In addition, the water can also, over a period of time, corrode the interior of the tanks. This could be a particular possibility if the tanks have been left empty and open to the atmosphere where they could "breathe" high humidity ambient air either through tank openings or open ammonia pipes and valves.

Considering that there have been several plant operators and years of inactivity, there is the real possibility that these tanks have been neglected and could be in poor condition.

It is very important that these excess flow valves are tested prior to resumption of plant operation, or replaced with new valves, and that the tank shells are checked for corrosion and proper thickness.

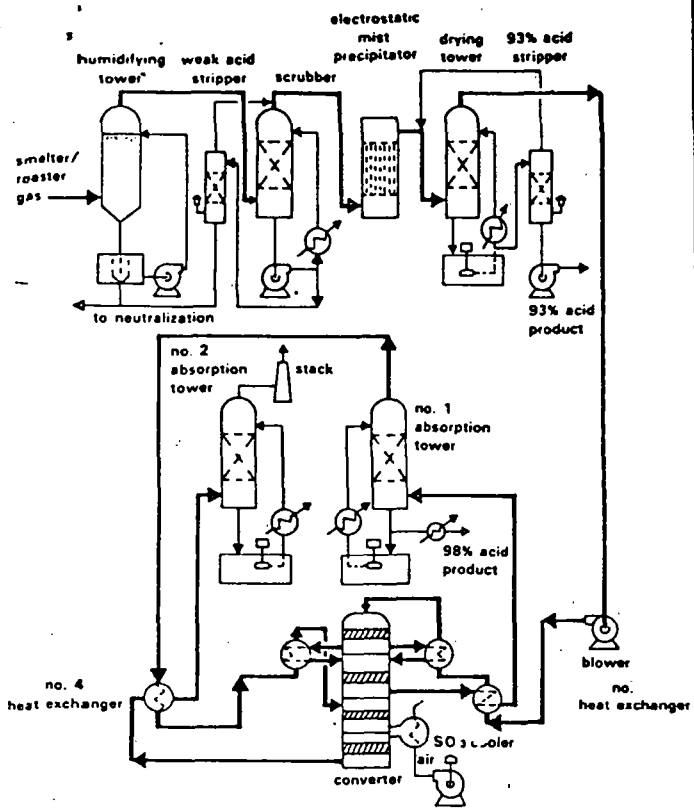
GENERAL

It is important to note that my comments are not intended to imply that there

is anything wrong with any new process that Piney Point Phosphates and Monsanto Enviro-Chem Systems may be intending to employ. My only objection is that there may be evidence that they are trying to introduce a new process under the guise of "repairs" and circumvent the appropriate approval processes.

My opinion is that the Piney Point Plant, in the hands of responsible operators and properly renovated and maintained, can be an asset to Manatee County. It can provide jobs and revenue, through taxes, that can be beneficial.

I feel, however, that considering the history of this plant, it is vital to all concerned that any efforts to put the plant in operation must be made with honesty and the full knowledge of all concerned and without even a hint of subterfuge. More than economic and political considerations are concerned with this issue. Lives are at stake.



▲Figure 2. Typical smelter/roaster gas wet process DC/DA sulfuric acid plant.

the same investment" (1) up to 13% more (2) than for a SC/SA plant. It seems unrealistic to expect to get an extra absorber, mist eliminator, acid cooler, and related piping and ducting at no cost. Therefore, consider 10% as a reasonable estimate for the added fixed capital requirement for a DC/DA plant. Then, if a 1,000 ton/day DC/DA battery limits plant were to cost \$8.5 million, its SC/SA counterpart would cost \$7.73 million, or a difference of \$770,000.

Advantages of DC/DA

However, comparing a DC/DA plant operating at 99.7% conversion efficiency to a SC/SA plant at 97%, both producing 1,000 ton/day of acid (100% basis), 350 days/yr., the sulfur consumed in the DC/DA plant will be nearly 3,200 tons, or \$175,000 less per year than in the SC/SA plant, if sulfur is valued at \$55/ton. Expressed another way, if both plants were fed exactly the same amount of sulfur and air, and if the product acid had a value of \$55/ton, the DC/DA plant would produce nearly \$540,000 worth of additional acid in a year than the SC/SA plant.

Some schemes have been developed for multiple (more than two) contact/multiple absorption sulfuric acid plants. If the hypothetical 1,000-ton/day DC/DA plant were extended to become a TC/TA (T = triple) plant at an added cost of, say, \$650,000, and achieved a conversion of 99.96%, it would "save" only about \$16,000/yr. in sulfur or "add" \$50,000/yr. in saleable acid production.

To evaluate comparative operating costs, however, one must recognize that a DC/DA plant will consume more energy and produce less "bonus heat steam" (a more appropriate term than "waste heat steam") for export than its SC/SA brother. This is partly because the gas return-

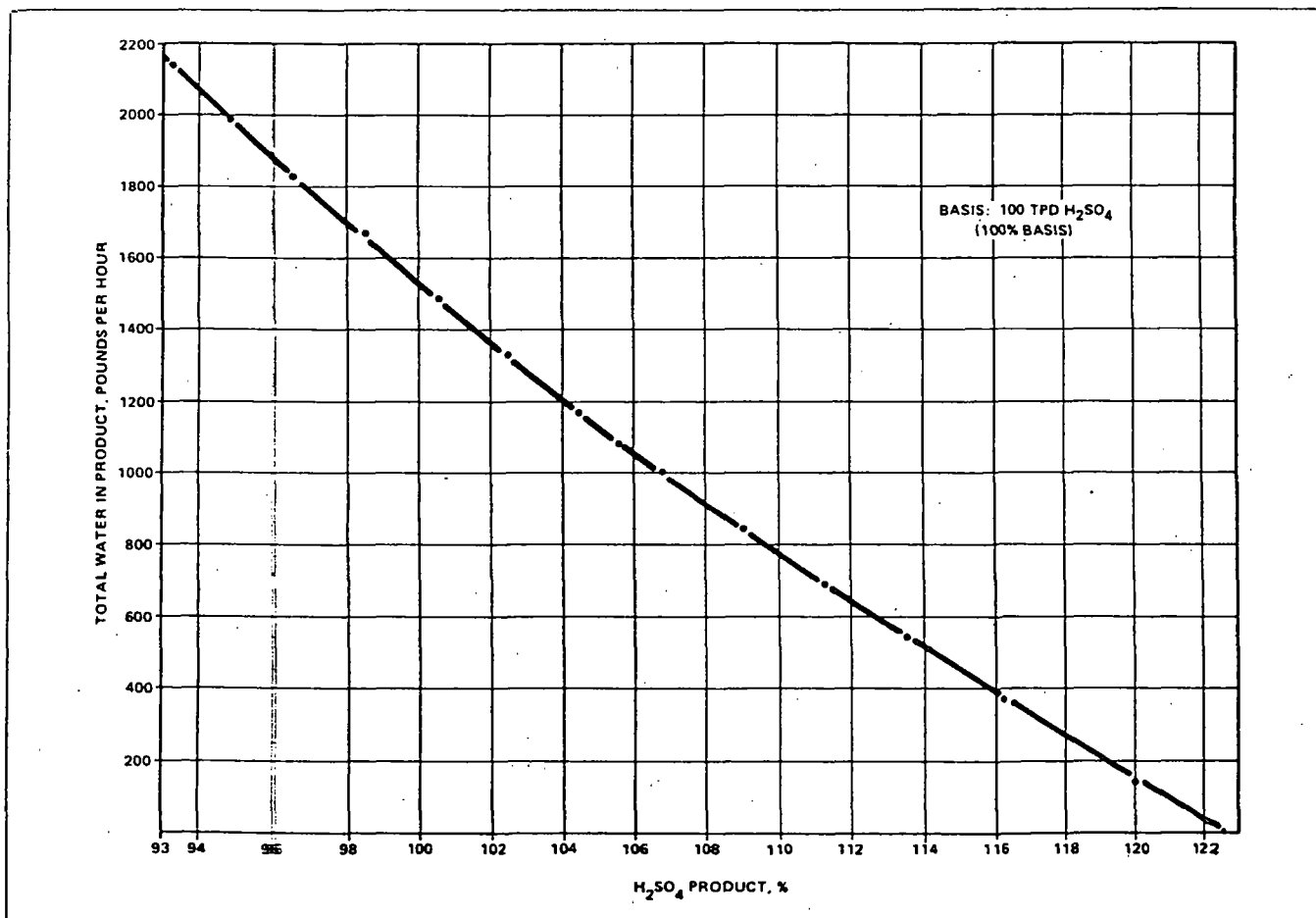


Figure 3. Total water present in product acid vs. product concentration.

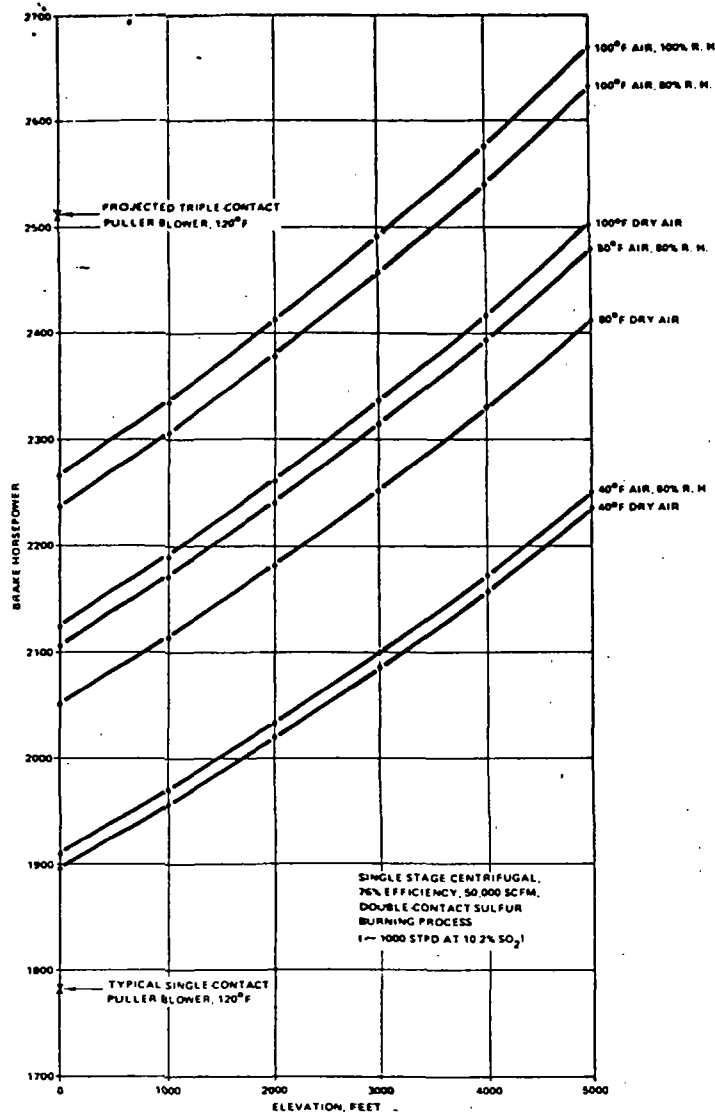


Figure 5. Brake h.p. requirements for pusher blowers.

unit operating cost for a DC/DA plant is only about 19¢/ton more than for an SC/SA plant. If your accounting philosophy permits you to reflect instead the extra \$540,000 worth of product that will be produced from the same amount of raw material, you may actually be able to find an 86¢/ton *advantage* in direct unit operating cost for DC/DA. Repeating this exercise for a hypothetical TC/TA plant produces very discouraging numbers that will not be reported here.

Another disadvantage of triple contact is that the burning of liquid fuel (in compliance with EPA limits) to make up for the heat loss would in itself dump into the atmosphere fully 10% of the amount of SO₂ that the triple contact feature might hypothetically recover.

If, on the other hand, you belong to that endangered species who still dumps (or plans to dump) your excess bonus heat steam to the atmosphere, you may simply languish in the raw material savings and ignore the reduced thermal efficiency.

Much the same philosophy can be applied to pyrite burning and waste acid regenerating plants because both usually generate steam. The "value" of the various raw materials used in wet gas plants varies too widely from location to location to make any generalized comparison of DC/DA vs. SC/SA economics.

In any case, the effect on investment of applying double

contact technology to wet gas plants is, on a percentage basis, not as great as in dry gas plants. Since the cost of the purification section may typically be in the range of 40% of the cost for the entire plant and is unaffected by the type of contact process used, a 10% increase in the cost of the contact system would add only 6% to the cost of the whole plant.

The foregoing may seem somewhat academic, considering that current U.S. environmental regulations will apparently require that all future acid plants employ DC/DA, or some more advanced technology, for compliance. However, it may help to assuage the feelings of your management when they learn that their new acid plant is going to cost five or 10% more than the SC/SA plant that would have served their purpose several years ago disregarding inflation.

Water balance in wet gas plants

Following a wet gas purification system, the gas entering the drying tower will be saturated with water vapor. All this water will be taken up in the drying tower acid and will eventually appear in the product acid either as part of the sulfuric acid molecule or as the aqueous portion of the sulfuric acid solution.

The stronger the desired product strength, the cooler the gas must be made in the purification system. Cooling the gas costs money, both in heat exchange surface and in cooling water requirements. Of course, the water vapor that is not condensed in the purification system will be condensed in the drying tower, and the overall heat load will be the same. However, the LMTD on the drying acid cooler is usually much better than that on the purification liquor cooler. The additional heat can, therefore, be taken up in the drying acid cooler with a smaller increase in its size than would be required in the liquor cooler.

The multiplicity of types of heat exchangers and materials as well as the virtually infinite combinations of operating conditions make it necessary to evaluate each case as it arises, but optimization in this area should produce savings in investment and operating costs.

Figures 3 and 4 enable the convenient determination of the temperature to which a gas must be cooled to produce the desired acid, as illustrated in the following example:

Let us assume that gas strength (to the converter) is 7% SO₂, that the product (100% basis) is 200 ton/day as 98.5% plus 200 ton/day as 93.2%, and that the elevation is 2,000 ft.

By referring to Figure 3; 100 ton/day of 98.5% acid represents 1,670 lb./hr. H₂O, and 2 × 1,670 = 3,340; and 100 ton/day of 93.2% acid represents 2,140 lb./hr. H₂O, and 2 × 2,140 = 4,280. Thus, total H₂O in product is 7,620 lb./hr.

Decide what portion of the water you wish to add to the drying and absorption tower systems as liquid water for the purpose of strength control. For this example, say 15%. Then, 7,620 - (0.15)(7,620) = 6,477 lb./hr. permitted in gas.

By referring to Figure 4, at 2,000 ft. elevation, the correction factor is about 1.09. Thus, 6,477 ÷ 1.09 = 5,942 lb./hr. And dividing by 4 (hundreds of tons/day) = 1,486 lb./hr. H₂O permitted in the gas. Figure 4 shows that a 7% SO₂ gas will have to be cooled to 98°F.

Autothermality

In wet gas plants, it is always necessary to preheat the gas to the catalytic ignition temperature before introducing it into the converter. Most of the required heat is usually supplied by the heat of conversion of SO₂ to SO₃ (41,350 B.t.u./lb. mole). In cases where the gas strength (vol. % SO₂) is reasonably high (say over 5.5%), the heat of conversion is sufficient to supply all of the heat required.

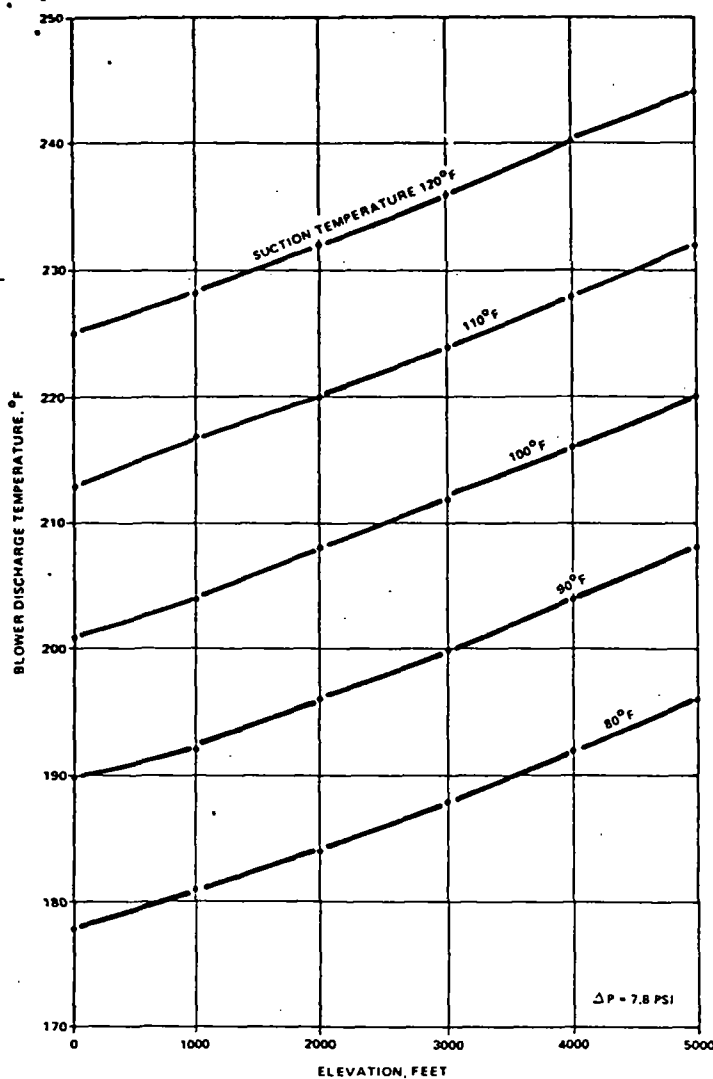


Figure 7. Puller blower discharge temperature at various elevations and suction temperatures.

since 1 h.p.-hr. = 2,545 B.t.u., then 178 h.p.-hr. = 453,000 B.t.u./hr.

The difference in the enthalpy of the air entering the furnace is determined as follows: 50,000 std. cu. ft./min. = 242,340 lb./hr. The temperature difference = 225 - 120 = 105°F, and specific heat = 0.25. Then, (242,340)(105)(0.25) = 6,361,000 B.t.u./hr. And, the net energy advantage for puller blower = 6,361,000 - 453,000 = 5.9 million B.t.u./hr.

One can substitute one's own dollar equivalents for energy costs, but at 2¢/kWh for electricity, this is nearly \$300,000/yr. Note also that the duty on the drying acid cooler and the cooling water system is reduced by around 5.7 million B.t.u./hr. in this example.

In the past, many air blowers have been placed in the pusher position to protect the blower itself from acid mist carryover from the drying tower. Modern mist eliminating devices have substantially eliminated this problem.

Upgrading existing plants

Existing SC/SA plants can be upgraded to DC/DA performance levels in either of two ways:

1. *Add-on facilities.* This method basically collects the stack gas from an existing SC/SA plant, reheats it by burn-

ing fuel, passes it through an additional conversion stage, then absorbs the newly-formed SO₂ in a final absorption tower before emitting the gas to the atmosphere.

2. *Revamping existing facilities.* When sufficient process heat is reliably available (as in most dry gas plants and high SO₂ strength wet gas plants), and when existing equipment is of suitable design, it is often possible to convert an SC/SA plant into a DC/DA plant. The job requires addition of gas-to-gas heat exchangers, a new absorption tower, mist eliminator, acid cooler, and duct revisions. Some revisions may also be required on the blower and inside the converter.

Again, the plethora of existing plant designs and requirements makes it necessary to refrain from generalization and to consider each case in detail on its own merits. A number of forward-thinking producers have built SC/SA plants that have been specifically designed in every respect to allow for future upgrading to DC/DA with minimal cost and interruption to operations.

In conclusion

Scientists and engineers have responded admirably in supplying the technology needed to meet recent environmental and energy shortage challenges. Double contact technology will probably dominate the world sulfuric acid manufacturing scene for the near future. Multiple contact and other as yet undemonstrated technologies are available to be applied if and when needed. As with so many endeavors in our increasingly technological world, the manufacture of sulfuric acid is transforming from an art to a science. Those involved in this metamorphosis will perform accordingly or perish. #

Literature cited

1. Atmospheric Emissions from Sulfuric Acid Manufacturing Processes, U.S. Dept. of Health, Education, and Welfare, Cincinnati, Ohio (1965).
2. Kronseder, J. G., "Economics of High Conversion Sulfuric Acid Plants," AIChE 61st Annual Meeting, Los Angeles, Calif. (December, 1968).



R. W. Reidel, senior process engineer for The Ralph M. Parsons Co., has more than 17 years engineering and manufacturing experience in heavy basic and fine chemicals for industry and agriculture. He holds a B.S.Ch.E. from Grove City College.



J. K. Knight, senior project engineer for The Ralph M. Parsons Co., has more than 30 years experience in plant and project engineering in the chemical manufacturing industry. This includes extensive work in sulfur and sulfuric acid facilities. He holds a B.S. degree in mechanical engineering from the Univ. of Utah and is a registered mechanical engineer in California.



R. E. Warner, senior process engineer for The Ralph M. Parsons Co., has been responsible for the design of 23 operating sulfuric acid plants. His background includes process engineering and operation of petroleum refineries, sulfur recovery units, and sulfuric acid plants throughout the world. Warner earned his B.S.Ch.E. from Pennsylvania State Univ.

Table 1. Applicable heats for comparing effect of increasing steam production.

	Heat, million B.t.u./hr.		Increase
Dried Air, @ 110°F.....	2.0....	—
Dried Air, @ 160°F.....	—	5.1....	+3.1
Blower, Before D.T.....	0.0....	—
Blower, After D.T.	—	4.3....	+4.3
Combustion of Sulfur.....	108.9....	108.9....	
Conversion to SO ₃	35.9....	35.9....	
Loss to Interstage	-18.4....	-18.4....	
Loss to F.A.T. -450°F....	-20.1....	—
Loss to F.A.T. 400°F.....	—	-17.4....	+2.7
Total Heat to Steam	108.3....	118.4....	+10.1

This is referred to as a mono acid system with both the dryer and absorber operating with 98% acid.

The temperature of the air or gas leaving the drying tower is nearly the same as the temperature of the acid entering the tower. This temperature has an effect on several operating factors in the plant.

A higher acid inlet temperature will reduce the acid cooling duty because more heat is picked up by the air or gas stream.

In a sulfur burning plant, a higher acid inlet temperature will result in an increase in steam production because the air going to the furnace is hotter. An increase from 110° to 170°F in the temperature of the air going to the sulfur furnace will increase the total steam production in a double catalysis plant by about 3.5%.

Mono or dual acid system. If a product in the range of 93 to 96% is desired, it can be withdrawn from a drying tower system operated at the desired concentration, or 98% acid can be withdrawn from a mono acid system and diluted in a separate dilution system.

The temperature rise resulting from the dilution of 98% acid is high, and a recirculated system with a cooler is normally used to avoid excessive temperatures in the diluter. In the case of a dual acid system, this heat of dilution occurs in the drying tower system. The acid circulation rate is high, so the temperature rise is small.

The overall installed cost of a mono acid system is generally slightly less than that of a dual acid system. This is primarily due to the reduced acid cooler costs resulting from the higher temperature level in the acid drying system. The total reaction heat is the same in either case, and the only difference in the total acid heat duty is the result of the higher acid inlet temperature to the drying tower with the mono acid system.

There are relative merits and disadvantages in each of the systems. In the mono acid system, an extra circulating system is required for the diluter if a product acid strength less than 98% acid is required. A common pump tank is used for the drying and absorption tower in the mono acid system, eliminating the need for cross transfer between these acids. A mono acid drying tower can be operated hotter to permit greater steam production and to reduce the acid cooling duty.

Acid coolers. In the normal double catalysis sulfuric acid plant, the heat to be removed from the acid system is usually at least 80,000 B.t.u./hr./daily ton of acid production. The actual heat load depends on several factors, including product acid strength, humidity of gas entering drying tower, and whether a single or a double catalysis plant is used.

A number of different types of acid coolers are in use today. The plant location, with respect to availability and quality of cooling water as well as atmospheric temperature and humidity, will have an effect on the selection of the type of cooler.

The early acid plants in the 1930s and 40s generally used trombone-type coolers. These were banks of horizontal runs of cast iron pipe (usually 6 in. in diameter) with return bends mounted one above the other on posts, and with a water distribution trough on top. The heat transfer coefficient for these coolers is low compared to more modern designs, and the space required is excessive. They had the advantage that leaks could be patched with chemical putty and a pipe clamp, and that external scale could be easily chipped off.

The well-known AX sections currently offered by Pentex were introduced in the 1940s and soon became the standard in the acid industry. They are S-shaped cast iron sections with internal fins designed for stacking, with a water distribution pan on top of each stack. These provide a better heat transfer coefficient and more efficient water distribution, and they require much less plot area than the trombone coolers. Leaks cannot be easily patched, and usually a complete stack is replaced when a leak develops in one of the sections.

The certainty that any cast iron acid cooler will eventually have leaks led to the development and introduction in the early 1970s of acid coolers of stainless steel and Teflon. There have been some problems with these units, however, and some questions about their serviceability remain to be answered.

The stainless steel shell and tube units offered by Chemetics are furnished with anodic protection. Acid is cooled in the shell side by water flowing through the tubes. The units can be installed either horizontally or vertically and require very little plot area. Two shells in parallel may be required for absorber acid cooling in large plants, but normally only one shell is needed for each duty. A high chloride content in the cooling water may cause some problems. It will, at the least, require the use of a higher alloy and increase the cost of the cooler.

The Teflon tube bundle type of acid cooler offered by Du Pont is normally installed in an annular section of the pump tank. Cooling water flows through the tubes of several bundles in parallel while the acid flows through the annular section around several bundles in series. Some failures have occurred as a result of abrasion and excessive pressure. It appears that repetition of these can be avoided by added safety features and by careful operation.

In a comparison of installed capital costs, the trombone coolers are the most expensive and the other three are in the same general price range.

Product acid. Any strength of sulfuric acid can be produced in the plant. As indicated above, some concentrations, such as 93 to 96%, 98 to 99%, and 20 to 40% oleum, can be withdrawn directly from the appropriate circulating system. A separate dilution system is required for strengths below 93%, or below 98% if a mono acid system is used. Intermediate acid strengths may be produced by blending two product strengths. Higher strength oleums or liquid SO₃ can be produced if an oleum reboiler and additional equipment is provided.

The normal operating temperature of most acid streams in the plant is too high to be delivered to storage tanks, and product acid coolers are required. The only exception is 93% acid, which is normally cooled to about 110°F for use in the drying tower.

Steam system

When acid is produced from sulfur, considerable excess heat is generated that is usually used to produce steam.

With a 6 lb./sq.in. pressure rise across the blower, the air is heated about 90°F by the blower. With a blower before the drying tower, the acid cooling duty is increased by this heat. With a blower after the drying tower, this added heat goes to the furnace and boiler to produce more steam.

With a blower after the drying tower, there has been some concern about acid carry-over from the tower, which would result in sulfate accumulation on the blower impeller and casing. This did cause an occasional problem before the present mesh-type entrainment separators were available. However, the "wet gas" type of acid plants operating with smelter gas, spent acid, or H₂S have always operated with the blower after the drying tower and their operating records, even before entrainment separators, were good. With a suitable separator after the drying tower, carry-over to the blower is essentially eliminated.

Blower pressure rise. It was indicated earlier that the design basis pressure drop through a clean sulfur burning plant has increased from 40 to 160 in. over the past 40 years. There was good economic justification for increasing the gas velocities and the allowable pressure drop across boilers and exchangers to reduce the size and cost of the plant. With the present concern over the energy shortage, however, it may be time to reverse the trend toward higher pressure drop in acid plant design.

Another pressure consideration is the allowance for pressure build-up in the plant during the operating period between plant turnarounds. This allowance, which is normally specified as about 1 lb./sq.in., is intended to permit the plant to continue to operate at its rated capacity throughout the operating cycle. It is used by some operators, however, to operate considerably above design rates when the plant is clean. This can adversely affect the life of the plant by operating at temperatures well above design.

In a brand new plant, when all of the heat transfer surfaces in the acid and steam systems are sparkling clean, this overcapacity can probably be achieved while maintaining normal temperatures in the plant. This can be very misleading and it has, on occasion, provided a false impression of the future potential overcapacity of the plant.

It is generally impractical to specify much more than 1 lb./sq.in. dirt factor in blower pressure rise. In most cases, the major portion of the pressure increase in the plant occurs in the first catalyst bed. The catalyst is supported on castings, and it is impractical to select a material or a design for these castings that will withstand a pressure of 1 lb./sq.in. more than the clean plant resistance for an extended period without sagging.

In the normal sulfur burning plant design today, the pressure drop through the catalyst beds in the converter is about one fourth of the total pressure drop in a clean plant. This pressure drop through the catalyst could be cut in half by increasing the converter diameter by 15%. This not only reduces the gas velocity by 25%, but it also reduces the total depth of the catalyst beds by 25% since the total volume of catalyst required remains the same. The increase in pressure drop across the catalyst bed resulting from entrapment of foreign matter will also be reduced since the surface area of the bed in the above case will be increased by one third.

Blower driver. The main blowers in sulfur burning acid plants are usually operated with a turbine driver because steam is available in the plant. A turbine drive is convenient for throttling for operation at reduced rates. The pressure drop through the plant is essentially all friction loss, and it therefore varies as the square of the gas flow. With a turbine drive, the blower speed and the resulting gas pressure rise are reduced as the gas flow is decreased.

With a motor-driven blower, it is generally uneconomical to consider any sort of variable speed drive. The simplest way to reduce gas flow is to throttle at the inlet of the blower, generally with a butterfly damper.

With a constant speed driver, the pressure rise across the blower increases with reduced gas flow. This is the reverse of the plant requirement, and the excess pressure must be wasted across the throttling damper. For this reason, the constant speed motor drive becomes very inefficient at reduced operating rates.

The efficiency at reduced rate can be greatly improved by the use of adjustable inlet guide vanes for throttling. These are installed in the inlet of the blower. As they are closed, they impart a spin to the incoming gas in the direction of impeller rotation. This has an effect similar to reducing the impeller diameter, thus reducing the pressure rise across the blower and the required horsepower input.

Sulfur burning

Molten sulfur is very similar to a light fuel oil, and there should be no difficulty in achieving efficient combustion. It is probably for just this reason that sulfur burning is frequently given less consideration than it deserves. In an 1,800 ton/day sulfuric acid plant, the heat release in the sulfur furnace is just under 200 million B.t.u./hr., resulting from the combustion of 49,000 lb./hr. of sulfur. This requires a large furnace with well-designed burners.

There are two important considerations: furnace operating temperature, and sulfur burner design.

Furnace operating temperature. The sulfur furnace is normally operated at a temperature in the range of 1,700 to 2,000°F, depending on several factors. Burning sulfur in dry air to produce a gas containing 10% SO₂ will give a temperature rise of about 1,600°F. If the blower is ahead of the drying tower, the furnace temperature with a 10% SO₂ gas may be as low as 1,725°F if 93% acid at 100°F is delivered to the drying tower.

For the same gas strength, the furnace temperature will be higher if a higher drying acid temperature is used, as in the mono-acid system, or if the air is preheated by using it for cooling, or if the blower is after the drying tower.

The upper limit of 2,000°F is usually accepted as a safe temperature for entering the fire tube boiler following the furnace as long as the hot tube sheet is protected with castable refractory and ceramic ferrules.

This higher furnace temperature is generally achieved by bypassing a portion of the air around the furnace and boiler, resulting in a higher SO₂ concentration in the furnace gas. This higher furnace temperature with the cold air bypass has two major advantages. It reduces the size of the waste-heat boiler following the furnace by increasing the temperature differential at both ends of the boiler and by reducing the gas flow through the boiler. It also provides a flow of cold bypass air to reduce the operating temperature of the boiler hot gas bypass damper, which is used to control the temperature of the gas going to the converter. With no cold bypass, this damper must operate with gas at the furnace temperature.

Sulfur burner design. In the early acid plants, solid sulfur was charged to a rotary kiln where it melted and was burned from the walls of the kiln. Some unburned sulfur vapor was carried with the gas and burned in a subsequent combustion chamber after admission of additional air. The development of sulfur melting facilities led to the use of pressure atomizing spray burners in a number of different arrangements. The current design is usually a horizontal cylindrical furnace operating with a combustion air pressure of 5 to 6 lb./sq.in. gauge and with as many as five or six pressure atomizing sprays. The sprays normally operate at about 75 lb./sq.in. gauge. If the pres-

not uniformly distributed, so that part of the catalyst bed is hindered, and the remainder of the catalyst on the bed is overloaded and does not provide maximum conversion.

The scaling can be avoided by metallizing the surfaces with aluminum, usually during fabrication of the vessel. It consists of sandblasting to white metal, followed immediately by flame spraying of aluminum to 10 mil. thickness. This is an expensive operation, and a decision must be made as to how much of the interior surface should be metallized.

Heat exchangers are affected by scaling in two ways. Scale on the tubes acts as insulation and reduces the heat transfer rate. Scale also roughens surfaces and blocks gas flow passages to increase the pressure drop across the exchangers.

The amount of scaling that takes place is related to the operating temperature. With gas temperatures below 900°F, scaling of carbon steel is generally not serious. With higher temperatures, some precautions should be taken. Low chrome-moly tubes have been used, but in some plants, these have shown evidence of scaling. More recently, Alonized tubes have been used successfully.

Acid attack of gas-to-gas exchangers is always the result of bad operation elsewhere in the plant, which should be corrected at its source. In sulfur burning plants, corrosion on the tube side is the result of excessive moisture in the gas, usually from a leak in a boiler or in the steam jacketed sulfur piping. Similar corrosion may also occur during plant heat-up with direct firing. Water from combustion of hydrocarbons combines with SO_3 retained in the catalyst, and the resulting acid condenses in the cooler portions further on in the plant.

Corrosion on the shell side of the exchanger by acid in the gas returning from the interstage absorber was a serious problem in the early double absorption plants. Lurgi solved it by a simple method that is practically fool-proof; by preventing condensation of sulfuric acid vapor from the gas. Gas leaving the interstage absorber is saturated with sulfuric acid vapor at essentially the temperature of the acid entering the tower (6 to 8 mg. H_2SO_4 /std. cu. ft.). If the duct wall is cooler than the gas, some of this acid vapor will condense. Lurgi overcame this problem by jacketing this duct and passing some of the hot gas going from the converter to the absorber through the jacket.

Others have tried steam tracing this duct with disastrous results in some cases. Apparently, some areas were left cold so that acid condensed and then very seriously attacked the duct in the heated areas.

Instrumentation

There is frequently a question as to the degree of instrumentation desired or required in a sulfuric acid plant. There is the glamor of data logging and computer control vs. the practicality of a simpler installation.

A very limited number of instruments is required to provide essential information for control of acid plant operation. These include furnace and converter temperatures, acid strengths, and boiler levels. Other instruments are helpful in monitoring the operation, such as ammeters, pressure gauges, and additional temperature points. There are still other data, such as pressure drops, that should be logged regularly so that long-term trends can be spotted or to help in troubleshooting if the unexpected upset occurs.

Pollution control agencies require measurements of production rate, stack gas flow, and SO_2 emission. The plant accountants may want measurements of utility consumptions and product and byproduct deliveries.

Remote manual operators for dampers and throttle valves permit the operator to stay in the control room, but

they also probably limit his inspection trips through the plant.

Automatic control can easily be applied to most operations in the plant, but it may reduce the operators' interest in the operation and limit his ability to take over in case of instrument failure.

A sulfur burning acid plant is usually a very steady operation once it is lined out at the desired capacity. Full automatic controls would be very hard to justify, but certain safety features are a necessity. These include sulfur feed shut-off for low boiler water level and low blower air pressure and alarms for such items as pump failure, high furnace temperature, or low and high boiler water level. Automatic control of acid strength and pump tank levels is fairly easy to justify because it may help to avoid a messy spill or a bad stack.

In a plant operating with metallurgical gas, the concentration of SO_2 in the gas entering the converter is not constant. This is especially true of gas from copper converters. The variations in SO_2 content affect the converter temperatures and the instantaneous acid production rate. In these plants, automatic control of converter temperatures as well as acid strength and pump tank levels may be necessary to assure compliance with emission regulations.

Start-up heater

The use of an indirectly fired start-up heater will prolong the life of the catalyst and of the plant. If the heating is by direct firing, the gas contains moisture from combustion of the hydrocarbon fuel. This moisture will combine with any SO_3 remaining in the plant, especially in the catalyst. The resulting acid then condenses in the cooler portions of the plant, where it corrodes the cast iron and steel and softens the catalyst, voiding the manufacturer's guarantee.

The damage caused by direct firing can be kept to a minimum by suitable purging of the plant before shut-down to eliminate SO_3 from the converter. The purging is most effective if the catalyst is kept hot, and it may be necessary to fuel fire in the sulfur furnace after the sulfur is shut off to keep the temperature high enough for effective purging.

The use of an indirectly fired start-up heater reduces the time required for reheating a plant from dead cold. A longer heating time is required with direct firing since at least two or three "dry blows" are necessary to heat the catalyst sufficiently to minimize acid formation and condensation on the catalyst even after good purging on shut-down.



J. B. Rinckhoff, who earned his B.S. degree from Lafayette College, is principal engineer, sulfuric acid, for Davy Powergas, Inc. Prior to 1970, he held a similar position with Chemico in its New York office.



L. J. Friedman, a supervising engineer specializing in sulfuric acid and sulfur processes for Davy Powergas, Inc., earned his B.S.Ch.E. from Polytechnic Institute of Brooklyn. He has done graduate work in nuclear engineering at SUNY at Buffalo and in business administration at Pace College Graduate School.

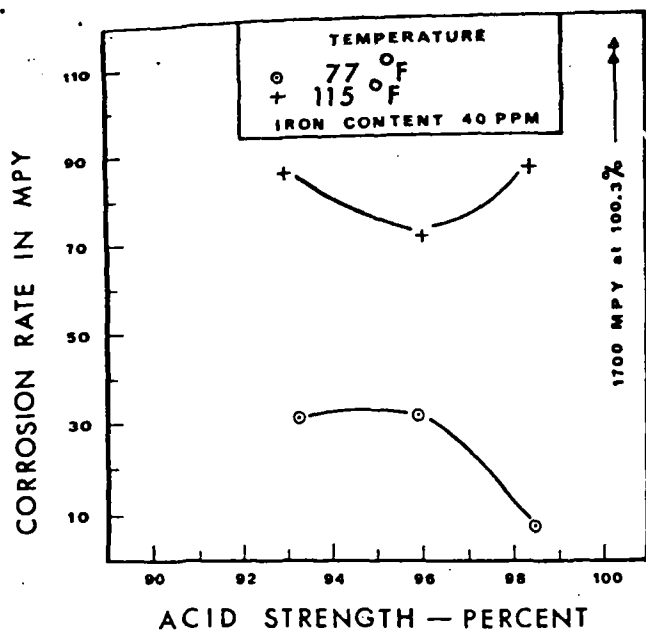


Figure 2. Corrosion rate of carbon steel in concentrated sulfuric acid as a function of acid strength.

be added to the list of corrosion rate determining factors. In addition to all these, two new factors have been identified: the iron contamination level of the acid stored; the copper content of the steel used in the construction of the tank.

In general, the lower the acid strength the more corrosive it becomes, with 77% H_2SO_4 , a commonly accepted practical limit for storage in an unprotected carbon steel tank. However, at around 100% strength, sulfuric acid again becomes extremely corrosive. Figure 2 illustrates the influence of acid strength in otherwise identical conditions. This is laboratory data obtained using commercial steel and plant acid with controlled agitation and iron content. Ninety-six per cent strength was chosen as being commonly used for product acid in the European sulfuric acid industry. It is apparent from the data that at 77°F., 98.5% H_2SO_4 is considerably less corrosive than either 93.5 or 96% acid. However, at 100°F., 98.5% acid becomes much more corrosive, approaching the corrosivity of the other two acid strengths examined. The implication of the latter result is to strongly suggest that in cold climates 98% acid only be heated to the minimum temperature sufficient to prevent its freezing.

Figure 3 illustrates the very strong influence of temperature on the corrosivity of 93.5% acid. The practical implications are that good product acid cooling is very important in prolonging tank life, and that in warmer climates the corrosion allowance on a tank has to be increased for a given lifespan. Alternatively, the case for installing anodic protection is greater in warmer climates.

Figure 4 indicates the influence of the level of iron contamination in 93.5% acid on its corrosivity. It is apparent that low iron content acid has a strong affinity for more iron, stronger than acid containing higher iron levels, a fact that was previously unknown. Modern sulfuric acid plants using stainless steel cooling equipment produce acid containing 5 to 10 parts/million iron compared to higher levels, especially in the summer, using cast iron cascade coolers. Therefore, storage tanks may now experience more corrosive conditions than in the past.

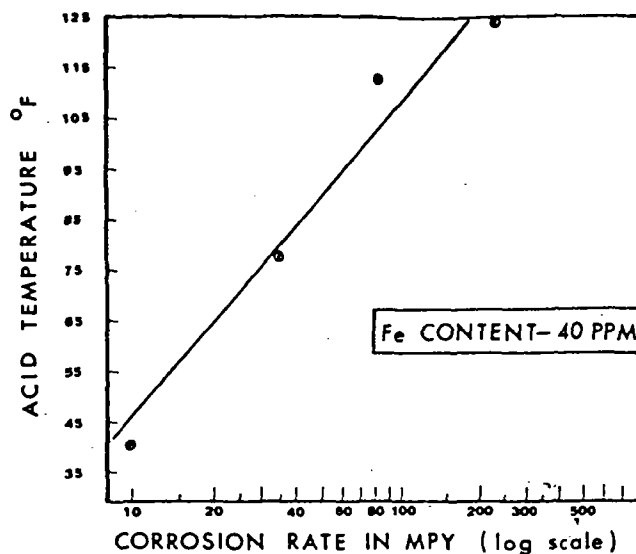


Figure 3. Effect of acid temperature on the corrosion rate of carbon steel in 93.5% sulfuric acid.

It will be noted that the corrosion rates reported in Figures 2, 3, and 4 are significantly higher than previously reported. The tests in this case were carried out in stirred acid. It is believed that previous tests have been carried out in stagnant acid and, as discussed below, the degree of turbulence in a tank will substantially influence its corrosion rate. The data presented here is probably more representative of turbulent areas within the tank or the behavior of a tank with constant recirculation of acid.

Because of better scrap sorting, changes in steel making practice, and tighter specifications for steel plate chemical composition, the level of tramp copper in carbon steel plate has been reduced progressively in the last 20 years. The level is now below 0.1%. It is well known that very small additions of copper to steel markedly affect the corrosion rate of carbon steel in sulfuric acid. When the influence of this variable was studied (1), it was concluded that as little as 0.25% copper content in the steel halved corrosion rates in commercial sulfuric acid.

The practical significance of this is that recently constructed storage tanks may corrode faster than tanks constructed in the past. The steel in one 25 year old tank within C.I.L. was recently analyzed at 0.4% Cu. A copper bearing steel was not specified in its construction.

Finally, turbulent acid is considerably more corrosive than stagnant acid. The rate of acid throughput in the tank may, therefore, be expected to influence corrosion rates. In a recent test, a continuously measuring corrosion meter was placed in a 93% acid storage tank. Fluctuations in corrosion rate were recorded between 15 mils/yr. when the contents of the tank were nominally stagnant, and 150 mils/yr. when acid was being simultaneously drawn from and put into the tank.

The rate of general corrosion in a tank can be reduced to very low levels by anodic protection or membrane or brick lining the tank. Anodic protection will reduce the general corrosion rate to typically 3 mils/yr. or less, depending on local circumstances.

A membrane lining, e.g., a baked phenolic resin, if correctly applied and cured, will eliminate corrosion entirely, but has a limited life (5 to 7 years in 93% acid) and cannot be used for 98% acid storage tanks.

Brick lining is an economic solution only for very small tanks.

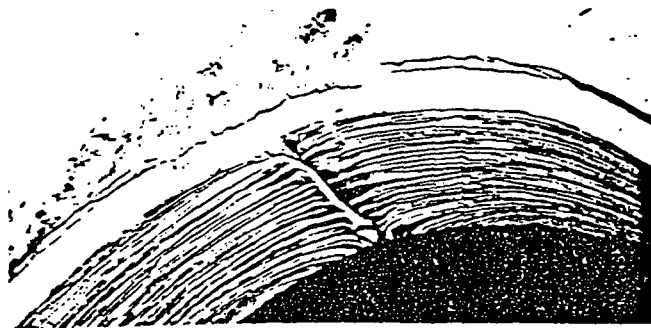


Figure 6. Grooving in the side man-hole of a storage tank.

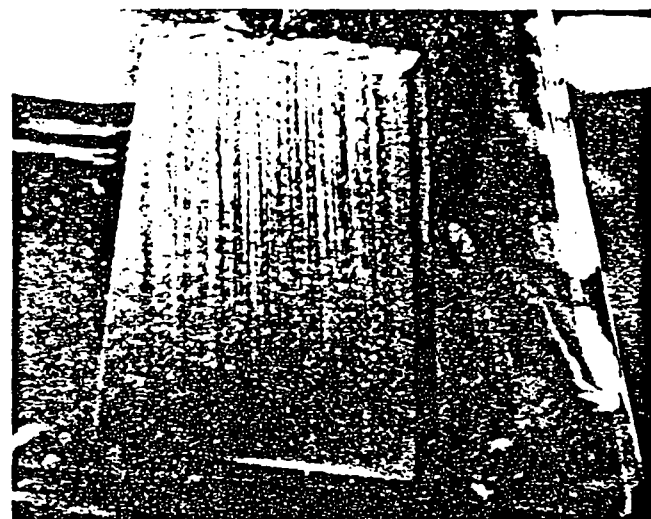


Figure 7. Grooving produced in the underside of an inclined plate immersed in 93% acid for several days.

enough hydrogen bubbles to effect grooving.

Almost all tanks the authors have inspected have had blistering of the floor plates and/or sidewalls. These blisters are usually in the size range 2 to 12 in. in diameter. In some cases they have ruptured and in these cases corrosion takes place at an accelerated rate within the blister.

The explanation for these blisters is well known. In the corrosion process, hydrogen is first produced in atomic form. Two atoms then combine to form a gaseous hydrogen molecule. Some of the hydrogen atoms, however, do not combine to form hydrogen bubbles, but diffuse singly into the steel.

If there is a lamination in the plate then these hydrogen atoms diffuse to the lamination and combine there to form hydrogen gas. This gas is trapped within the plate and pressures of several thousand atmospheres build up slowly until the steel bulges to form a blister and eventually ruptures.

As with hydrogen grooving, blistering can be prevented by suppressing the corrosion reaction producing the hydrogen. Thus, tank lining or anodic protection would be effective. (In an anodically protected tank, any hydrogen is evolved at the cathodes suspended in the acid.)

Ultrasonic examination of plate before tank fabrication would reveal laminations, but this is not proposed as an

economic method of preventing blistering in a tank. With a reasonable tank inspection frequency, blisters can be detected and repaired before serious damage occurs. It should be remembered that an unburst blister contains pure hydrogen that will explode if a grinding tool is used. A lamination can be the reason for an abnormally low thickness reading when testing a tank's thickness ultrasonically. A layer of weak, highly corrosive, sulphuric acid can form at the acid/air interface in a tank either by roof openings being left open and rain entering, or simply by "breathing" of damp air into the tank as the acid level falls and absorption of the moisture by the highly hygroscopic acid.

In tanks where there is a large throughput of acid, the weak acid is continually being mixed in with strong acid as acid is discharged into the tank. Also the acid never remains at the same level for very long so attack is never concentrated at one level. However, horizontal grooves have been observed in tanks and some operators are known to have air drying trains attached to the tank vent system. Other operators agitate the contents of the tank either by air sparging or by recirculation of the contents.

The general conclusion is that weak acid attack is only a minor contributor to the overall rate of corrosion of a tank and that special precautions are not warranted for tanks where acid is being added to and drawn from a tank at regular intervals.

Tank linings obviously eliminate weak acid attack and C.I.L. experience of anodic protection system operation is that the passive film formed when the tank is full of acid provides protection for a number of days on the wet walls when the acid level falls.

There are many references in the literature to the effectiveness of anodic protection in reducing the corrosion rate of carbon steel in strong sulfuric acid to very low levels, typically 1 to 3 mils/yr. (3, 4) The quality of the acid in terms of iron content is also improved, an important feature where the acid is being marketed either to industries requiring low iron content for product purity such as in alum manufacture or in a market situation in which acid quality can be the key to a sale.

In an anodic protection system, reference electrodes, immersed in the acid, sense the potential of the tank in contact with the acid and feed back the value of this potential to a controller. The control circuit compares this potential value with a preset value and, if necessary, triggers a power stage to apply current to the tank via cathodes suspended in the acid from the tank roof. In this manner the potential of the tank is held continuously in the passive range. The passive film remains intact even when acid drains from the tank and is reinforced very quickly when the tank is refilled. Only water washing of the tank would completely destroy the passive film. Power consumption is minimal and maintenance costs are very low.

Figure 8 shows the comparative corrosion rates of anodically protected and unprotected carbon steel exposed at various heights in a 10,000 ton, 93% acid storage tank. Of interest is that the ratio between protected and unprotected corrosion rates remains virtually unchanged from the tank base, where specimens were continuously immersed, to the upper levels where fluctuation in acid level left specimens alternately immersed and exposed to humid air drawn into the tank. This bears out the assertion that the passive film remains intact when acid drains from the tank.

In a tank of this size, assuming acid remained in the tank for an average of one week, this protected corrosion rate would correspond to an iron pickup of 1 to 2 parts/million.