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SULFUR RECOVERY UNITS DESIGNED TO BE MORE RELIABLE

by

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Introduction

The age is upon us when minimizing air pollutant emissions must frequently take precedence over profit and production. Failures or reduced efficiency of an emission control system can cause an immediate reduction in the throughput rate of the total facility it serves. Sulfur recovery units in oil refineries and sour gas/oil production treating facilities are prime examples of where this situation might occur if improperly designed or operated.

A wealth of published information on the Claus sulfur recovery process is available to both the designer and the operator. A casual review of our sulfur recovery technical information files causes us to conclude that just about everything on this subject not considered proprietary has been documented, discussed, and published over the past ten years. Many good articles are available. Some of them are listed in the references for this paper and others are cited in those listed articles.

In addition to this published information, the typical Claus sulfur recovery design group will also have available an extensive documentation of proprietary technology and know-how. The Ortloff Corporation licenses such a body of technology from Amoco Production Company (formerly Pan American Petroleum Corporation) for use in conjunction with the know-how and design techniques we have developed over our seventeen (17) years of active work in the industry. Together this combination of licensed technology and Ortloff experience provides a sound and complete basis for design.

Current incentives justify the expenditure of much more effort and attention on the following aspects of Claus sulfur recovery units compared to what was thought to be optimum in the recent past.

- Designing for high sulfur recovery capability
- Designing for easy operation at optimum conditions over a wide rate range
- Designing for consistent operation near optimum conditions
- Designing for a high degree of reliability

Based on our past experiences and information gathered from the industry, we believe the last item, reliability, is one that has not received adequate attention. Claus sulfur recovery units do not generally enjoy a reputation for being highly reliable systems, even though several existing units do have very good downtime records. (1) Various failures occur and reoccur in a number of existing units that cause unscheduled outages and excessive downtime. This problem has been so severe that the managements of some oil refineries have chosen to install full capacity spare units.

The Ortloff Corporation initiated an intense Claus sulfur recovery unit design improvement effort in 1969. We began this effort by challenging ourselves to develop design and fabrication techniques that would eliminate the weaknesses responsible for the major outages and unscheduled maintenance requirements. We have accomplished that objective. The purpose of this paper is to share some of the solutions that were developed for some of the more common and significant problems that exist in many Claus sulfur recovery units which adversely affect their reliability and average stream efficiency.

Unscheduled Downtime - The Big Factor

Normal boiler inspection, equipment maintenance, and catalyst replacement requirements of a well designed and properly operated Claus sulfur recovery unit can usually be accomplished without causing a violation of air pollution limits if they can be performed on a scheduled basis. Most air pollution control authorities will allow flaring of the sulfur plant feed gas during relatively short downtime periods scheduled to do work that cannot be accomplished during a total facility turnaround. The unscheduled downtime resulting from equipment failures seems to be the major problem.

It was not difficult for us to prepare a priority list of the problems that caused unscheduled outages in the plants that we had designed and constructed. That information was readily available in the form of feedback from a few of our pre 1969 clients. The following items appeared at the top of our list.

- Failure of waste heat boiler tubes at the inlet tubesheet connection
- Damage resulting from heat generated by internal sulfur fires in the plant
- Frequent changeout of catalyst necessitated by heat damage, carbon contamination, and deactivation

We did not bother to survey the industry before attacking our task, but information gathered since that date indicates that our problems were common ones. Our discussion here will be limited to the items listed above even though our work on a number of other problems has resulted in significantly improving the reliability of our finished product.

Solving the Waste Heat Boiler Tube Failure Problem

At the time we began our study, we were designing the front tubesheet treatment for the waste heat boilers immediately downstream of our reaction furnaces using the general guidelines available to us. Figure 1 shows the general arrangement of tube, tubesheet, tube-tubesheet connection, and heat protection system that we used.

A carbon steel boiler tube was selected with a moderate amount of corrosion allowance. The tube was rolled into the tubesheet hole and seal welded as shown. A ceramic ferrule was installed in the tube extending slightly farther into the tube than the thickness of the tubesheet. The ferrule extended from the face of the tubesheet approximately three (3) inches. A castable refractory cover was installed over the tubesheet and around the ceramic ferrule extensions. This is a reasonably standard firetube type waste heat boiler front tubesheet treatment that has now been described and discussed by various authors. (2,3)

The more troublesome waste heat boilers we had specified, purchased and installed in our Claus sulfur recovery plants prior to 1970 had suffered reoccurring tube end failures after no more than six to eight months of operation. Several careful inspections of the failures revealed the conditions shown in Figure 2. In some cases the ceramic ferrule and refractory cover around the end of the leaking tube had been damaged severely by the leaking water. At other tubes where leaks were small or had not yet developed, the refractory cover and ceramic ferrule were removed carefully to allow a close inspection of the metal surfaces behind these heat shields. The tube end extension beyond the face of the tubesheet and the seal weld would commonly be completely gone. The tube end was very thin at the hot face of the tubesheet, with the tube wall thickness tapering to original thickness at a point somewhat inside the back face of the tubesheet. The metal would be completely gone with no significant deposit of corrosion products in its place. The leaks would be observed at one of two places, either between the tube and the tubesheet where the seal weld had disappeared or through a rupture failure in the tube wall just beyond the seal weld inside the tubesheet.

Various retubing and repair procedures, some more successful than others, were developed through consultation with several groups. These will not be discussed here in detail for the sake of brevity. Considerable inspection data was obtained to ascertain the mechanism of the metal loss observed. Just one of the facts determined was that it is not necessary to have a high velocity hot gas flow in direct contact with these areas to experience the metal loss. In short, we concluded that the metal loss was simply due to high temperature sulfide corrosion. If carbon steel surface temperatures significantly exceed 700°F in the atmosphere that exists at this point in a typical sulfur recovery plant, sulfide corrosion occurs at a significant rate that increases rapidly as the temperature increases. The troublesome waste heat boilers we analyzed as a part of our study contained significant differences in the problem area design details. The tube service life for these boilers was also significantly different in that they ranged from less than one year to more than three years. Evaluation of these differences was helpful in pointing us toward a successful design approach.

Since the temperature of the gases entering these waste heat boilers is typically between 2200°F and 2500°F, the potential for having extremely high heat flux to surfaces in this area does exist. As you study the patterns of heat flow to and from the surface areas, it becomes evident that the area of the tube end where the seal weld is attached has to experience the highest surface temperature. Many factors become involved in determining the temperature that will exist at this point during operation. The more important of these factors are, referring back to Figure 1:

- Thickness of the tubesheet
- Diameter of the tubes
- Spacing (pitch) of the tubes
- Resistance to heat flow through the tube-tubesheet connection
- Resistance to heat flow through the ferrule wall and stagnant gas space between the ferrule OD and the tube ID
- Resistance to heat flow through the tubesheet cover refractory
- Process conditions (temperature, velocity, etc.) of the gas flowing through the ferrule into the tube
- Degree of steam blanking that occurs at the back surface of the tubesheet and at the outside surface of-the tube just beyond the tubesheet to reduce the effective heat transfer coefficient

We developed a calculation model to predict the maximum surface temperature that will exist in this problem area for any particular tube/tubesheet/protective system design. Actual operating temperatures have been measured with thermocouples attached to the tube ends and to the tubesheet surface. The values recorded have confirmed that our calculation model is accurate enough for design use. This calculation model is now used by Ortloff's designer to vary the factors under his control as factors dictated by specific project design requirements vary. This tool allows us to optimize boiler designs with considerations of cost versus service life, while utilizing carbon steel throughout in the construction of the waste heat boiler. Many of the exotic materials that are capable of resisting high temperature sulfide corrosion do not perform well in sulfur recovery plant service due to various other weaknesses.

The calculation model has been used to analyze several existing waste heat boiler hot end systems that experienced tube failures. A temperature profile can be calculated for the inside surface of a tube for the segment contained in the tubesheet. Figure 3 shows the temperature profile calculated for a centrally positioned tube in one existing "problem boiler" with the originally specified process and mechanical factors inputted. The tubes located in the center area of the tubesheet in this boiler had a service life of approximately six months. The model was also utilized to study the temperature profile improvement that could be obtained by changing various heat shielding and tube attachment details.

Changes in the refractory covering and ferrules improved the temperature profile, but the maximum temperature could not be reduced below about 900°F without introducing excessive process pressure drop at the waste heat boiler inlet. Therefore, we designed a replacement boiler that would have acceptable tube service life.

The temperature profile labeled "replacement boiler" on Figure 3 was calculated for the hot end tubesheet system specified in this design. As you can see, the replacement unit was designed very conservatively with a maximum calculated metal surface temperature of only slightly above 560°F when producing 435°F steam. The replacement unit was more expensive than the original item because it contained some 35% more surface area to accomplish the same process cooling duty. The shell volume per square foot of cooling surface was also larger, and some of the fabrication procedures were more costly. However, even a 50% greater initial cost for this one item can be very attractive additional investment if it allows long, troublefree service from the unit.

Even though it is not possible to describe a total system design that is acceptable and also optimum for all applications, some general guidelines can be stated that we use in our design approach. The tubesheet thickness is very important. The tubesheet should be designed to have a thickness near the minimum required to satisfy the Power Boiler Code, ASME Section I. Larger diameter tubes and larger pitch are factors that also increase the ratio of cooling surface to heating surface that exists around the tubesheet. Larger diameter tubes allow installation of more substantial ferrules to provide more resistance to heat flow into the tube wall and tubesheet without severely restricting the tube entrance flow area. Particular attention must be given to the tube to tubesheet connection. A joint must be achieved that provides a minimal resistance to heat transfer between the tube wall and the tubesheet. The joint must also be water-tight to prevent the accumulation of deposits and the resulting "inchworm" type failures. (2, 3) When conditions and restraints are particularly severe, the tubes can be installed in the tubesheet with a full depth weld attachment as shown in Figure 4. This procedure causes the boiler to be more expensive, since it involves considerable additional welding and usually increases the diameter of the vessel. Even so, the additional expense is often justified by the large measure of increased reliability assurance it provides.

The first sulfur recovery plant waste heat boiler Ortloff designed using the procedure and methods discussed above was installed and placed in operation during November, 1971 at The Louisiana Land and Exploration Company's Wiggins Lake Production Treating Facility near Jay, Florida. The inlet end tubesheet of this unit was inspected for the first time during 1976 by personnel who now operate that facility. They have reported the tube ends, tube to tubesheet attachment welds, and the tubesheet surface were all observed to be in excellent condition with no detectable metal loss. The Ortloff Corporation has now designed and installed a total of eight Claus sulfur recovery plant waste heat boilers using our current design procedures. None of these units has suffered an inlet end tube failure. We therefore feel confident that modern Ortloff designed sulfur recovery plants will not experience this problem.

Solving the Sulfur Fire Heat Damage Problem

Traditional sulfur recovery plant designs and operating procedures have dictated the routing of combustion gases through the catalyst beds. This process is used to preheat the catalyst beds and bring all items of equipment up to normal operating temperature prior to the introduction of the H2S containing feed gas stream. During the early part of a warmup procedure, it is essentially impossible to generate an oxygen-free or low oxygen content combustion gas in the reaction furnace while adhering to the necessary refractory heating schedule. Even during the latter periods of a plant warmup it is not realistic, from a practical standpoint, to expect essentially oxygen-free and soot-free combustion gas to be generated at the warmup burners. A typical operating group, with the measurement and monitoring equipment normally available and used by them, will not control conditions that closely.

Since a significant quantity of elemental sulfur will exist in the catalyst and other accumulation points in a unit following typical unplanned shutdowns, sulfur fires or oxidation rates frequently occur during a startup procedure that cause localized temperatures to reach values of 1000°F to 1500°F. These excessive temperatures often occur in areas that are not being directly monitored by measuring and shutdown devices. Therefore, various sections of plant piping and equipment suffer some heat damage during essentially every startup. The most common eventual failure points have been catalyst bed support systems, catalytic reactor vessel shell and chamber divider plates, heat exchanger channels, and sulfur separators. The catalyst perhaps suffers most since it is mechanically damaged by heat, and its activity is decreased by the sulfate-producing conditions that exist.

In considering these problems we conclude that it would be very desirable to design sulfur recovery plants such that fuel gas combustion products would not have to be routed through the catalyst beds and other major portions of the unit for significant periods of time during normal startup, temperature maintenance, and shutdown operating procedures. In our attack on this problem we considered it absolutely necessary to bring all heat exchanger surfaces up to operating temperature during the startup procedure prior to introduction of feed gas. The accomplishment of this prerequisite required some innovative engineering but presented no real challenge. The steam generated in the waste heat boiler during the refractory warmup procedure has been utilized in various ways to preheat the heat exchange surfaces even when condenser passes were contained in separate vessel shells.

The true challenge appeared to be that of answering the question of whether the normal process stream could be routed to cold catalyst beds without accumulating a sufficient quantity of elemental sulfur in the catalyst as it warmed up to restrict flow through the beds. We calculated the catalyst heating rate versus the sulfur deposition rate for several typical plant designs using a number of reasonable assumptions. The calculated results indicated that the temperature of the top layer of catalyst would increase rapidly enough to reach reaction initiation temperature before a sufficient quantity of sulfur deposition occurred to completely deactivate or fill the void space in the catalyst layer. These results encouraged us sufficiently to try a plant startup with cold catalyst beds. The procedure was indeed successful.

Ortloff and others had designed a number of sulfur recovery plants wi th the capability of venting the fuel gas combustion products to the atmosphere upstream of the first catalyst bed. However, these venting systems typically contained valves that would never work when needed due to solid sulfur deposition and/or blinds that required pipefitter attention to utilize. Our experience told us that the typical operating group would not consistently use procedures that vented the combustion products rather than allowing them to traverse the plant unless systems were designed and installed that were reliable and easy to operate. Therefore, we developed special valve assemblies that would give long life, tight shutoff service, and easy operation. Our efforts have resulted in the use of trunion type valves with high temperature so ft seats as the heart of rather special jacketed assemblies. The valves can be automatically or manually operated. We install these valve assemblies for warmup vent and tail gas line block valves at the locations shown in Figure 5.

We give design details special attention to eliminate all possible points for sulfur accumulation in equipment and piping upstream of the warmup vent location to minimize sulfur burning in this small section of the plant. We install the block valve that prevents the flow of w armud combustion gases through the plant in the tail gas line. This location is chosen because the conditions there are the most friendly with respect to obtaining long term good service from the valve. The performance of the valve assemblies we now use has been excellent. The total design of the sulfur recovery unit must be tailored in some respects to provide good "cold startup" performance. For instance, the sulfur separators must be designed to give very good droplet separation performance. Poor se parator performance can allow excessive amounts of sulfur to reach the catalyst beds during the startup procedure.

Briefly, the operating procedure involves heating the reaction furnace with fuel gas on the desired warmup schedule while venting all combus tion products to the atmosphere. This allows easy operation with excess air and little attention. The waste heat boiler steam pressure rises to the operating level during the refractory warmup period and that steam is used, as needed, to bring all heat e xchanger surfaces in the plant to operating temperature. Just before switching from fuel gas combustion to feed gas, the tail gas block valve is opened and the vent valve is closed. The acid gas is immediately routed to the burner and the fuel gas is shu toff. The entire switchover operation requires routing the fuel gas combustion products through the catalyst beds and other equipment items for no more than 5 to 10 minutes. The catalyst bed inlet stream temperatures are maintained slightly higher than n ormal until the catalyst beds are up to operating temperature throughout, then reduced to the normal operating setpoints. This procedure can be reversed to bring the reaction furnace back on temperature maintenance with fuel gas combustion just as easily.

The design features that allow the above procedure to be used successfully and consistently have essentially eliminated the heat damage repair and replacement maintenance requirements with associated unscheduled outages in the plants we have installed si nce 1970.

Solving the Frequent Catalyst Changeout Problem

Many factors are recognized as being involved in determining the effective service life of a charge of sulfur recovery plant catalyst. Several compounds that are frequently contained in the feed gas stream can adversely affect the catalyst service life. (4) We cannot claim to have solved all of the problems that cause catalyst damage; we can only state that catalyst performance experience has been tremendously improved primarily as a pleasant side effect of the design and operating philosophy and procedure change discussed in the previous sections of this paper. We expected to eliminate the heat damage that had on occasions resulted in fused and glazed catalyst, loss of catalyst through damaged supports, etc. And, we have always believed that more damage than improvement resulted from the so-called regenerative burnoff procedures that others have used to improve the activity in the catalyst beds.

When we introduced our modern design features and procedures into our sulfur recovery plant designs in 1970, the sulfate contamination catalyst deactivation mechanism was not published, -- nor was it even clearly understood. However, we must now conclude that the essentially complete exclusion of oxygen from the catalyst beds throughout normal operating procedures is responsible for the notable improvement in maintaining high catalyst activity levels over long time periods in these plants. Efficient sulfur separators allow the plants to operate at bed temperatures down close to sulfur dewpoint without the excessive accumulation of elemental sulfur in the catalyst beds that reduces apparent activity. Periodic operation at higher temperatures to remove sulfur or other similar regeneration procedures discussed in literature (5) has not been required.

Some of the sulfur recovery plants designed and installed by The Ortloff Corporation since 1970 are listed along with comments pertaining to catalyst performance experience in Table 1. Only plants for which confirmed data could be obtained have been listed. As you can see, catalyst changeout in these plants could not be classified as a significant problem. It should also be noted that several of these plants receive a feed stream that has typically contained a significant quantity of propane and heavier hydrocarbon compounds. This is not true for the large split-flow plant listed, however. Split-flow configuration plants cannot tolerate the heavy hydrocarbons. In fact, special design features were incorporated into the gas treating system design which supplies the feed gas to this split-flow plant to minimize the hydrocarbon content of its feed stream. If sulfur recovery unit feed gas purity requirements are given proper consideration during the design of the total facility, catalyst damage and deactivation problems can be avoided.

Summary

An experienced and knowledgeable designer who will dedicate sufficient attention to design details can eliminate the most common Claus sulfur recovery plant maintenance problems. Stringent enforcement of pollution emission regulations now make it imperative that these units be designed and fabricated for a high degree of reliability.

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4. Goar, B. Gene, "Feed Gas Impurities can Create Claus Plant Problems", Paper presented at The Gas Conditioning Conference, Norman, Oklahoma, March, 19 74.

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FIGURE 1

TYPICAL WASTE HEAT BOILER INLET END TUBE/ TUBESHEET TREATMENT DETAIL

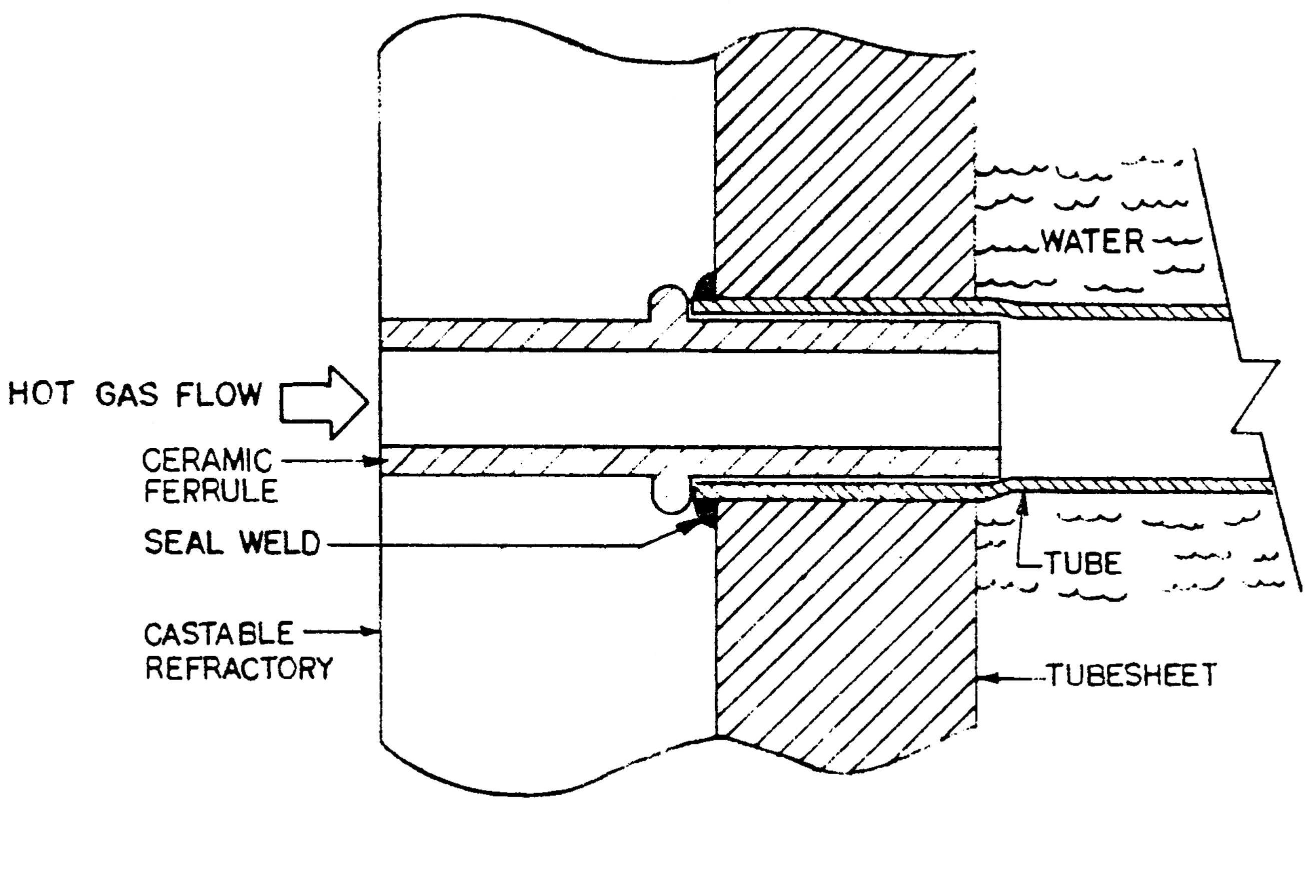


FIGURE 2

TYPICAL TUBE END DETERIORATION AND FAILURES

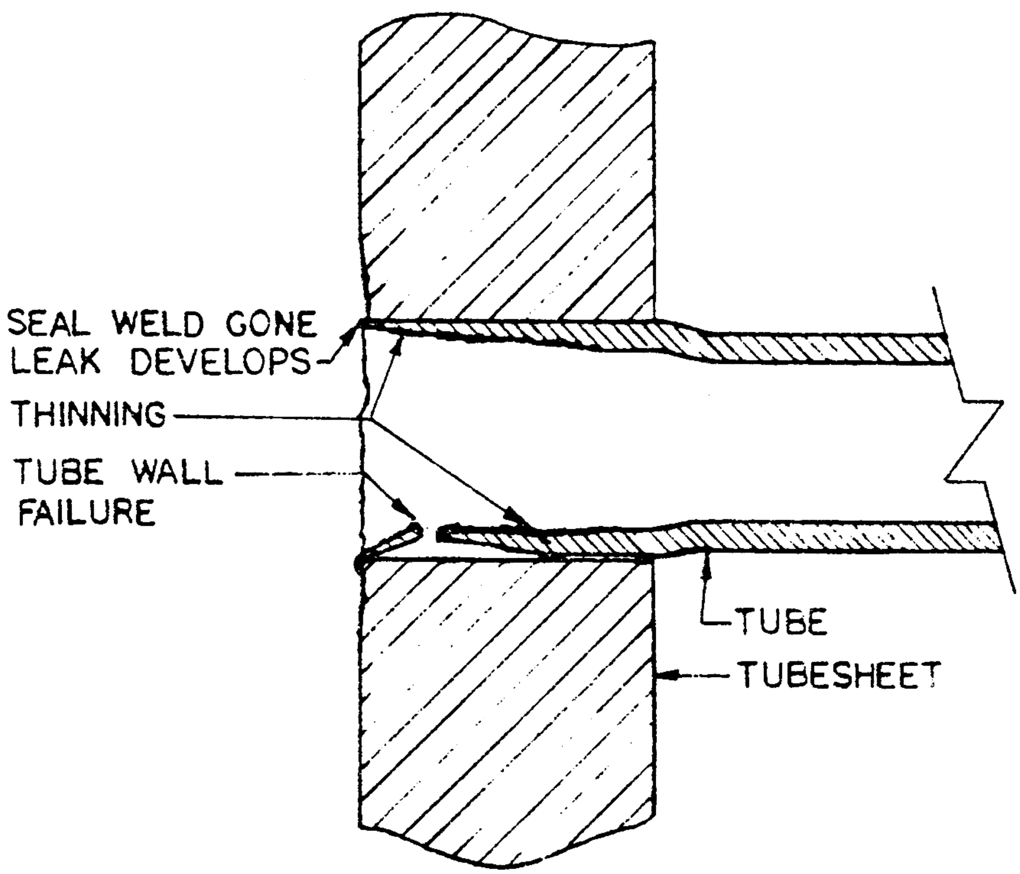


FIGURE 3

CALCULATED TEMPERATURE PROFILE FOR SEGMENT OF TUBE HELD IN INLET TUBESHEET

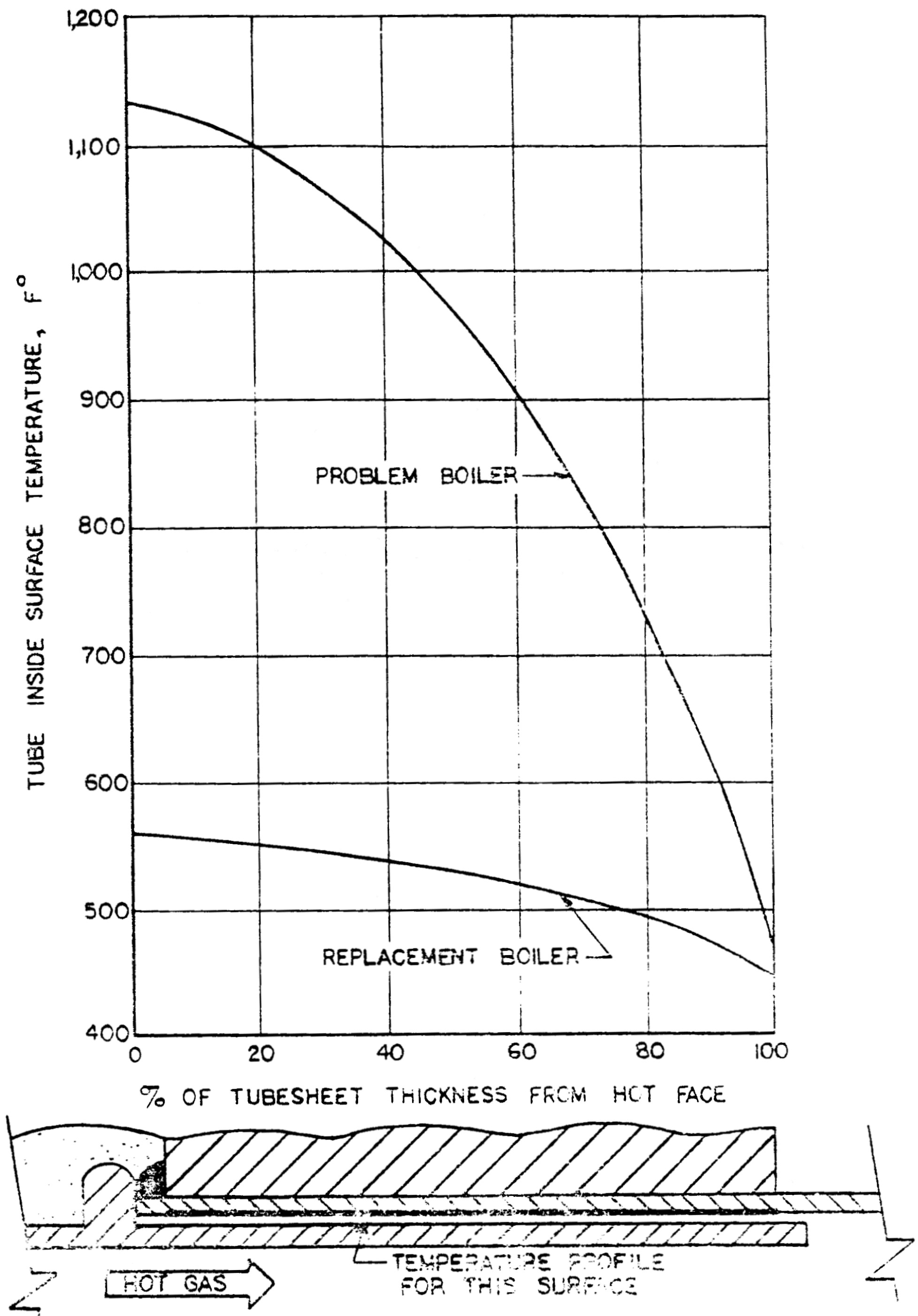
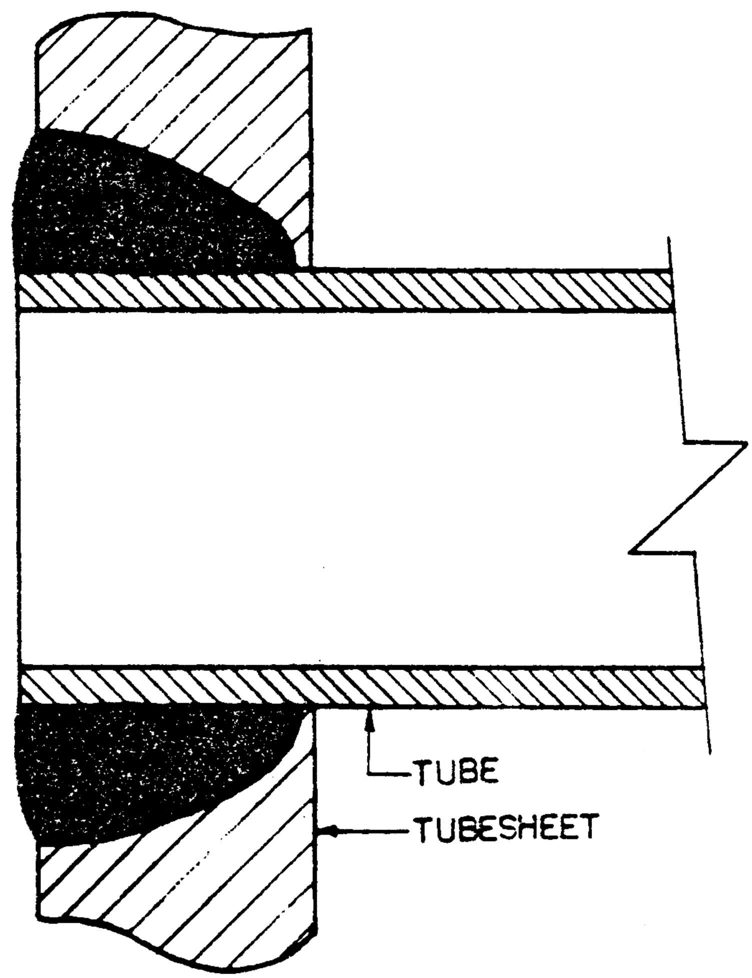


FIGURE 4

FULL DEPTH WELD TUBE TO TUBESHEET ATTACHMENT



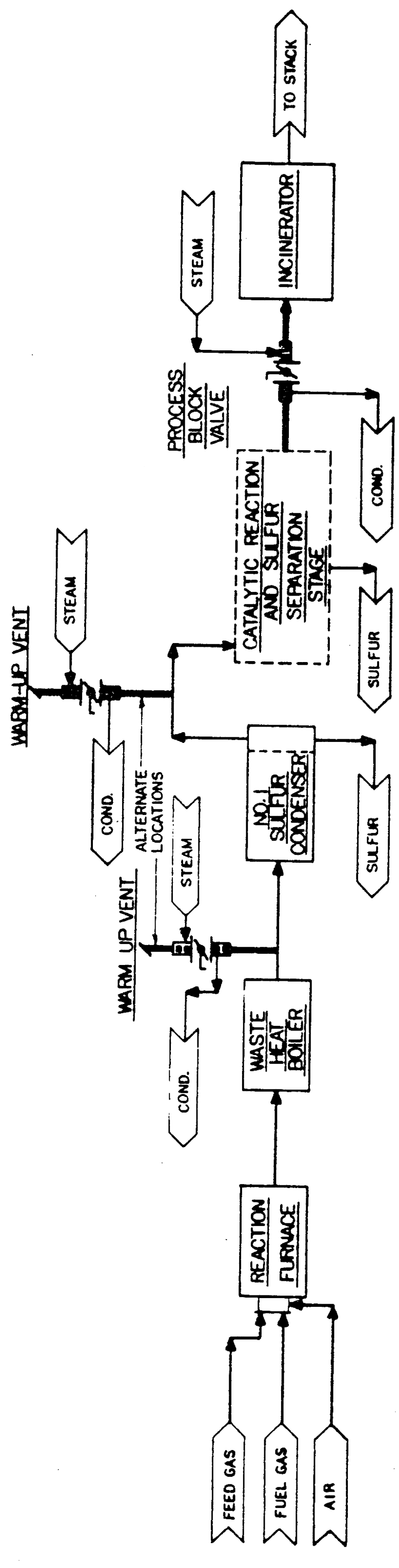


FIGURE 5

STARTUP VENT AND BLOCK VALVE ARRANGEMENT

TABLE 1
CATALYST PERFORMANCE DATA
FROM SOME MODERN SULFUR RECOVERY PLANTS
DESIGNED AND CONSTRUCTED
BY
THE ORTLOFF CORPORATION

Owner	Plant	Type Process	Size L.T./Day	Startup Date	Plant Recovery Performance: Original Guarantee	Plant Recovery Performance: Recent Test	Catalyst Replacement Dates
The Louisiana Land & Exploration Company	Wiggins Lake No. 1, Escambia Co., Florida	Straight-Through	44	1971	96.0%	96.30%	1976 (1)
The Louisiana Land & Exploration Company	Wiggins Lake No. 2, Escambia Co., Florida	Straight-Through	44	1972	96.0%	97.10%	1976 (2)
The Louisiana Land & Exploration Company	Wiggins Lake No. 3, Escambia Co., Florida	Straight-Through	142	1973	96.0%	97.10%	1976 (2)
Phillips Petroleum Company	Chatom Plant, Chatom, Alabama	Straight-Through	190	1974	96.0%	>96.0%	(3) (4)
Mallard Exploration, Inc.	Big Escambia Creek No. 1, Escambia Co., Alabama	Split-Flow	440	1974	96.0%	97.07%	(3) (4)
Exxon Company, U.S.A.	Blackjack Creek, Santa Rosa Co., Florida	Straight-Through	81	1975	99.80% (5)	99.84% (5)	(4)
Cosden Oil and Chemical Company	Big Spring Refinery, Big Spring, Texas	Straight-Through	38	1974	94.3%	>95.0%	(4)

Notes:
(1) Original charge of activated bauxite catalyst replaced with pure activated alumina.
(2) Original charge of activated alumina catalyst replaced during planned turnaround. Plant had not failed to pass a permit renewal performance test.
(3) First catalytic reactor contains sulfate deactivation resistant alumina catalyst.
(4) Original charge of activated alumina catalyst remains in service.
(5) Combined performance of Claus unit plus SCOT tail gas cleanup unit.
(6) Information on this page current as of March 1977.