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A NEW SIMPLE APPROACH TO CAPACITY INCREASE OF REFINERY SULFUR PLANTS

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A New Simple Approach to Capacity Increase of Refinery Sulfur Plants (Case History: API Falconara Refinery)

Photo of the API Refinery in Falconara, outside Ancona, Italy
(api anonima petroli italiana S.p.A.)

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Introduction

The SURE™ Double Combustion technology has been in use in refineries since 1990 to provide increased sulfur plant capacity with oxygen at moderate operating temperatures. More recently, a unique adaptation of this technology has provided the client with even greater flexibility, while retaining the capacity improvement potential of this process. This paper describes the technology employed at the api anonima petroli italiana S.p.A (API) Falconara refinery, and the operating experience since start up in October of 1996. Special attention is paid to operation, emphasizing the points that may be useful in the operation of other units and to explore results that may be achieved in future projects.

Characteristics of the Plant before Revamp

The Claus units operating in the API Refinery before the application of oxygen to increase capacity had a maximum throughput of 42.5 LT/D each. Unit #3750 was built in 1983 and Unit #3800 was built in 1985. Both units were designed by Siirtec Nigi under license to Amoco.

As typical in refinery operations, the Claus Units operate downstream of an Amine Regeneration unit that is fed by several gas absorbers, and a liquid treating contactor. Refinery policy foresees frequent crude feed change. Therefore, quick modifications to plant throughput is required. Experience indicates that frequency in changes to Claus operations due to upstream units is at least once every four hours. Turn down capability for both units is 4:1, and both units have been designed to burn Amine Acid Gas and Sour Water Stripper gas.

The basic layout for each of the 2 plants is shown below.

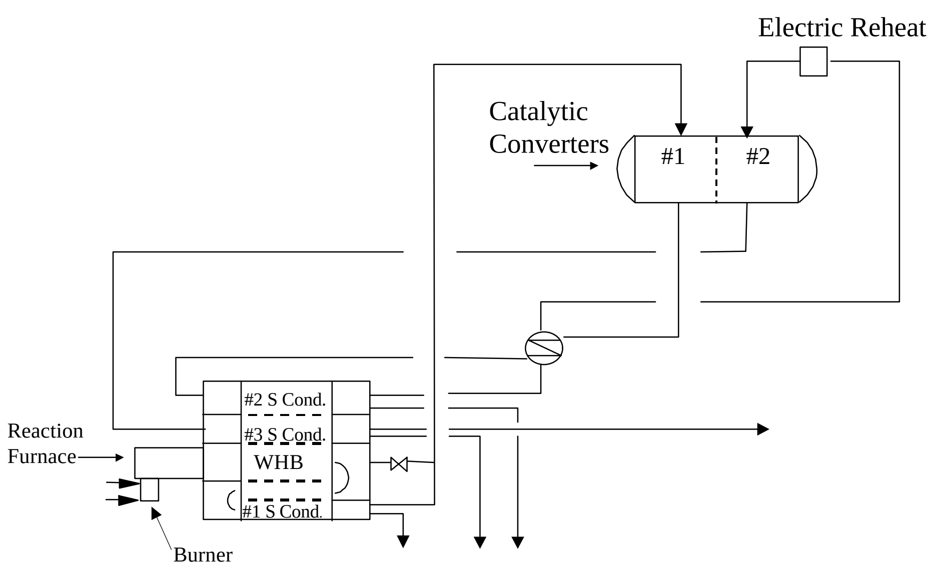


Figure 1 - Process Sketch of API Claus Plants

The plants consist of a thermal stage followed by 2 catalytic stages. As is often the case for smaller units the waste heat boiler and 3 sulfur condensers are integrated into a common vessel.

The gas composition of both amine acid gas (AAG), and Sour Water Stripper (SWS) off gas streams is typical for a refinery, and CO_2 concentration is negligible.

The design sulfur recovery is 95.0%, and actual recovery of 95.8% has been demonstrated.

Scope of Revamp

The objective of the revamp was to achieve the following targets:

- Increase the total capacity to 122.5 LT/D using ambient air plus oxygen, with provisions to achieve 160 LT/D in the future
- Increase the capacity for SWS off gas in the feed
- Improve operation to achieve a high service factor without decreasing overall sulfur recovery.

Additional restrictions for this project included:

- Minimize space requirements to fit new equipment within existing plot. The existing units are very compact to begin with, and very little space was available for the new equipment
- Minimize capital cost
- Minimize impact on refinery operations during revamp
- Complete tie-ins during a maximum 3-week window, which included shut down and start up operations.

To emphasize the tight plot space available, a photograph of the completed revamp is shown below.

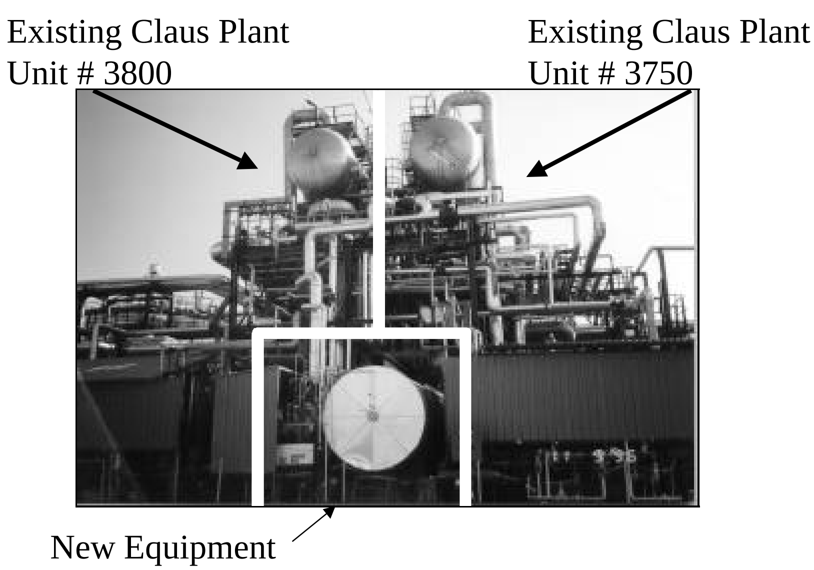


Figure 2 - Photo of Claus Plants with New Equipment at the API Refinery

Several alternatives had been studied, considering project objectives and the plant requirements. In the end, a solution based on the SURE™ Double Combustion process was selected.

The first phase revamp has been limited to the construction of one new thermal stage upstream of both existing Claus plants, increasing the total capacity up to 122.5 LT/D of H_2S in the feed gas. However, provisions have been made to install a second thermal stage to double the original capacity of both existing Claus units.

Overview of SURE™ Double Combustion Process

BOC Gases is a major supplier of industrial gases to refiners, including oxygen, nitrogen, and hydrogen. One important application for oxygen is the expansion of sulfur recovery capacity. BOC has developed technologies and equipment in this area, including the SURE™ Double Combustion process, to support its position as a supplier of oxygen.

At low levels, oxygen can be simply mixed together with the combustion air. However, in Claus sulfur recovery units, this method of introducing oxygen is normally limited to a maximum overall concentration of 28% oxygen. Therefore, BOC supplies SURE™ burners that are specifically designed for introducing oxygen directly into the Claus reaction furnace.

Even with a burner designed for higher concentrations of oxygen, the reaction furnace temperature would exceed the design limits of the refractory. Also, the capability of the existing waste heat boiler may limit oxygen usage, even before temperature limits are encountered. The Double Combustion process eliminates these problems, and allows operation at oxygen concentrations from 21% (100% air) up to 100% oxygen, <u>while maintaining safe conservative temperatures</u>.

The concept is simple. To limit temperature rise, the combustion reactions are carried out in two stages with intermediate cooling as shown below.

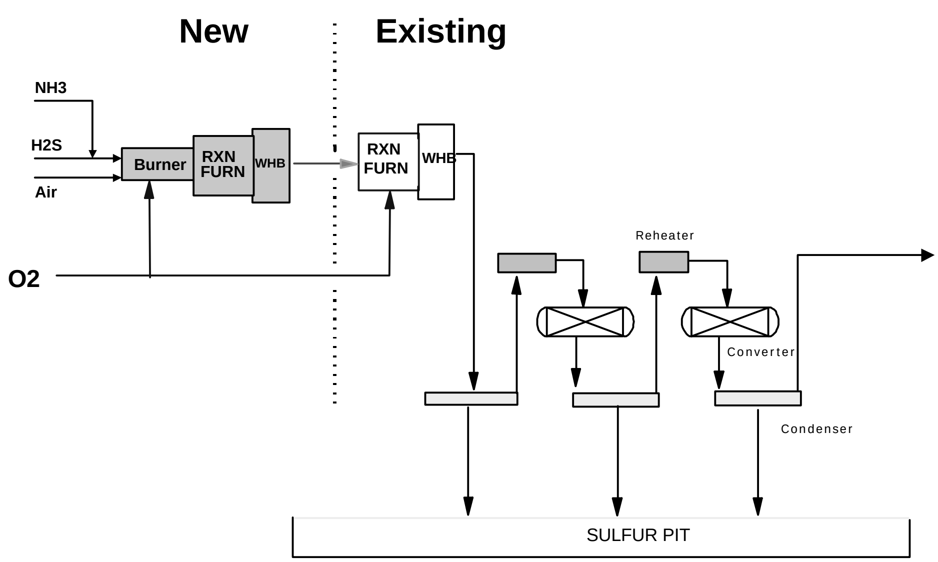


Figure 3 - Process Sketch of SURE Double Combustion

Acid gases are first subjected to a partial combustion at temperatures well below the safe operating temperature of the refractory, but at temperatures high enough to ensure complete ammonia and hydrocarbon destruction. This first stage of combustion is carried out without attempting to meet the overall stoichiometry requirements, or total oxygen demand. The gases are then cooled in a waste heat boiler, prior to entering a second reaction furnace where the remainder of the required oxygen is introduced.

Significantly, there is no sulfur condenser between the #1 waste heat boiler, and the #2 reaction furnace. Also, there is no burner in the #2 reaction furnace. By design, the gases exiting the #1 waste heat boiler, and entering the #2 reaction furnace, are substantially above the auto-ignition temperature under all normal, and turn down operating conditions. This concept is at the heart of the SURE™ Double Combustion process, and allows for a low pressure drop system, which is easy to control, and easy to install.

Oxygen Control

Since the gases entering the #2 reaction furnace are above the auto ignition temperature, even small quantities of oxygen will react completely. A burner is not required, and an oxygen lance may be used to introduce oxygen into the #2 reaction furnace. There is minimal pressure drop through the system because there is still only one burner (the new BOC oxygen/acid gas burner in the #1 reaction furnace). Control of oxygen is also straightforward.   Oxygen is simply fed to the first and second reaction furnaces at a constant ratio between the two furnaces as indicated below:

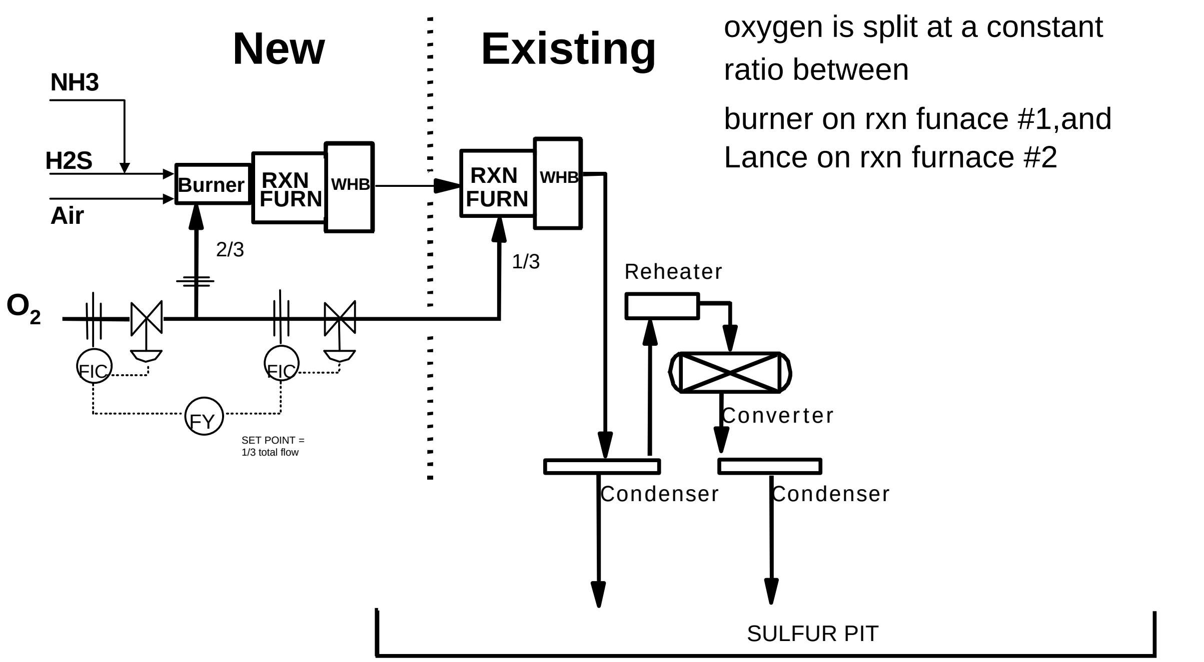


Figure 4 - Oxygen Control Sketch

Reaction Furnace Temperatures

Capacity requirements are satisfied by increasing the total flow of oxygen, relative to air as needed, but since only part of the oxygen flow goes to the #1 reaction furnace, temperatures remain well within design limitations. The temperatures in both reaction furnaces for a typical rich refinery gas with significant ammonia present are shown below, as overall oxygen concentration is increased from 21% (air only) to 100% (no air).

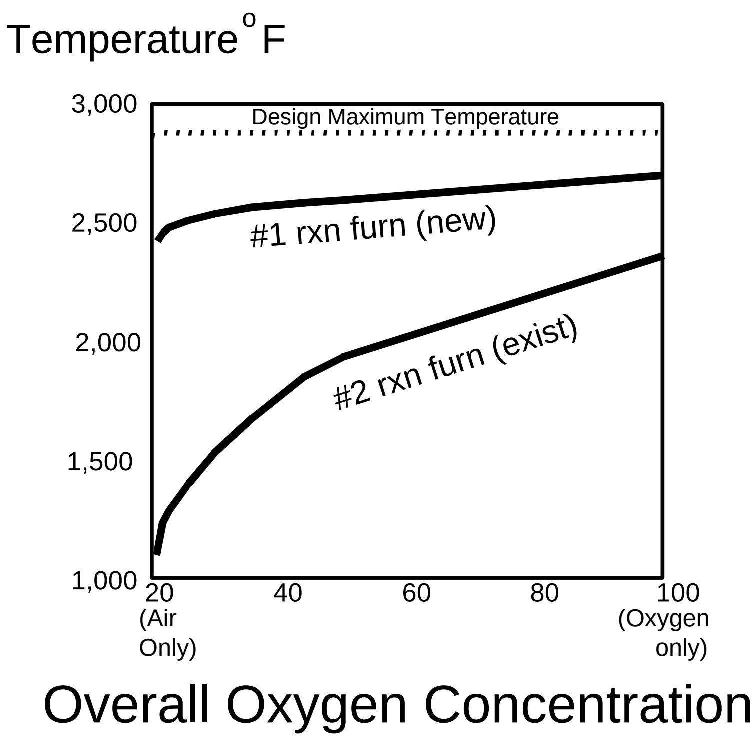


Figure 5 - Temperature Profile in Reaction Furnaces

As is evident from the figure, temperatures in the #1 reaction furnace are maintained at high levels to ensure satisfactory destruction of ammonia and hydrocarbons, but still well below the refractory design temperature limitations. The total flow, and therefore residence time, is essentially constant.

Overall Process Control Scheme

With no burner in the #2 reaction furnace, and temperatures above the autoignition temperature, there are no minimum flame temperatures, or minimum acid gas flows, to maintain. There is a smooth transition from air only operation, through partial oxygen enriched air, all the way to 100% oxygen. Air is fed only to the first reaction furnace burner, while oxygen is fed at a constant ratio to both the first reaction furnace burner, and directly to the second reaction furnace. Even the richest acid gases found in refining applications, can be processed with 100% oxygen using this process. Control for the process is extremely safe and simple.

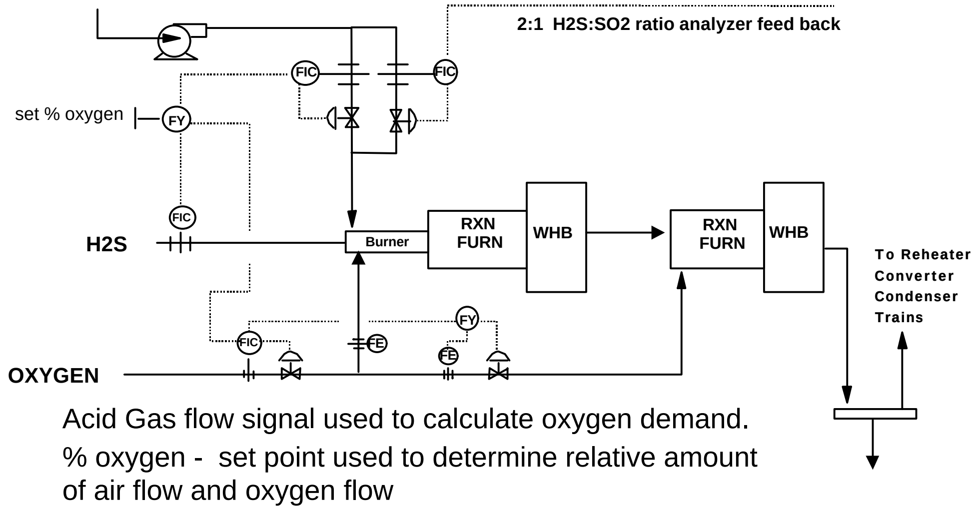


Figure 6 - Overall Plant Process Control with Oxygen

A typical Claus plant control scheme employs acid gas flow (feed forward), and H_2S/SO_2 ratio in the tail gas (feed back) to determine oxygen demand, and set the air flow. Control of the SURE™ Double Combustion process is very similar. The acid gas flow (feed forward) continues to provide the primary signal for oxygen demand. However, the oxygen demand signal now goes to an additional controller which has per cent overall oxygen enrichment (21% to 100%) as a set point. It then controls both the flow of air and the flow of oxygen. At 21%, the control scheme is essentially the same as a conventional air based plant. As the enrichment level set point is increased, proportionately more oxygen flow is called for, with an equivalent reduction in air flow (negative bias). All air goes to the #1 reaction furnace burner, and any oxygen called for is split at a constant ratio between the #1 reaction furnace burner, and the separate #2 reaction furnace lance.

Double Combustion at the API Refinery

The API refinery at Falconara, just outside Ancona on the Adriatic coast of Italy, employs the SURE™ Double Combustion process in a rather unique manner. The concept was developed by Siirtec Nigi, SpA in conjunction with Parsons Energy & Chemicals Group, Inc. (Parsons).

Siirtec Nigi is an Italian Engineering Contractor, with the design of approximately 70 Claus sulfur plants to its credit, including 5 Claus oxygen enrichment projects. Many of these projects are located in Italy, including the original design of the existing Claus plants at the API refinery. All 5 of the oxygen enrichment projects use SURE™ burner technology.

Parsons is BOC's Engineering partner for the application of SURE™ technologies in the expansion of sulfur plants with oxygen.

Engineers at Siirtec Nigi worked with their counterparts at Parsons, to provide their client, API, with a means to provide the capacity expansion and redundancy required within a very limited plot space. Parsons then developed the basic engineering design package, and Siirtec Nigi provided the detail design, fabrication, and installation of all equipment for the project at API.

The new #1 reaction furnace is rather conventional, and similar to the existing units, except that it uses the SURE™ burner for oxygen service. A photo of the burner installed at API is shown below:

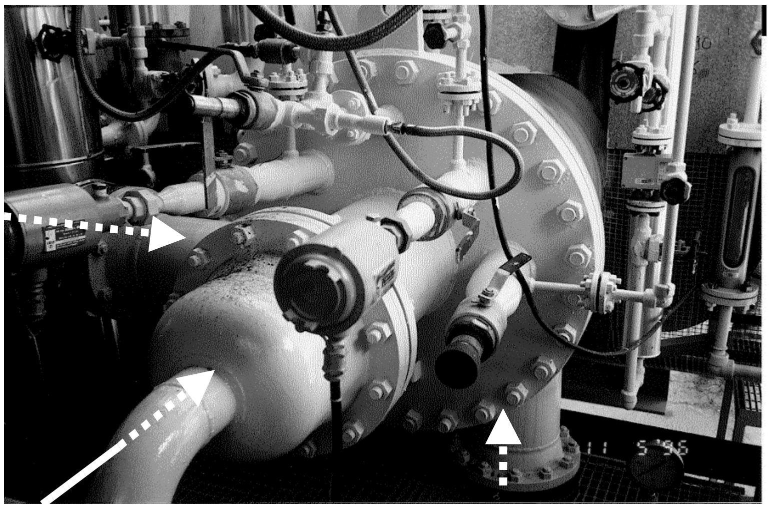


Figure 7 - Photo of BOC Burner Installed at the API Refinery

The SURE™ oxygen burner, like the one at API, has been received well by the refining industry. It is a simple, compact unit, which provides proper mixing for destruction of ammonia and hydrocarbon contaminants while operating with or without oxygen. There are currently 10 burners in operation, with orders in place for another 8 burners to be used in projects currently underway.   Two burners will be used in a gas processing application. Two will be used in refinery SRU's dedicated to a gasification project (API). The remaining burners are all used in typical refinery SRU expansion projects. Clients include major oil companies like BP, Shell, Chevron, and Agip.

The SURE™ oxygen burner is a tip mix type burner, which promotes dissociation reactions. As such, it is capable of the highest enrichment levels possible of any burner currently available. For example, at Valero in Corpus Christi, oxygen with the SURE™ burner alone, and without further process modification, increases capacity by 67% over air operation. Nonetheless, the SURE™ Double Combustion technology provides further benefits in terms of still higher capacity increase potential (150% increase) and, more importantly, operation at moderate temperatures.

In the Double Combustion process, the #1 waste heat boiler follows the BOC burner and new reaction furnace. At API. it is provided as the first pass of a new multi function heat exchanger. Rather than directing the hot gasses from the #1 waste heat boiler to one of the existing reaction furnaces, or providing a separate vessel for the #2 reaction furnace, the head of this multi-function heat exchanger was extended to provide residence time, and this then became the #2 reaction furnace.

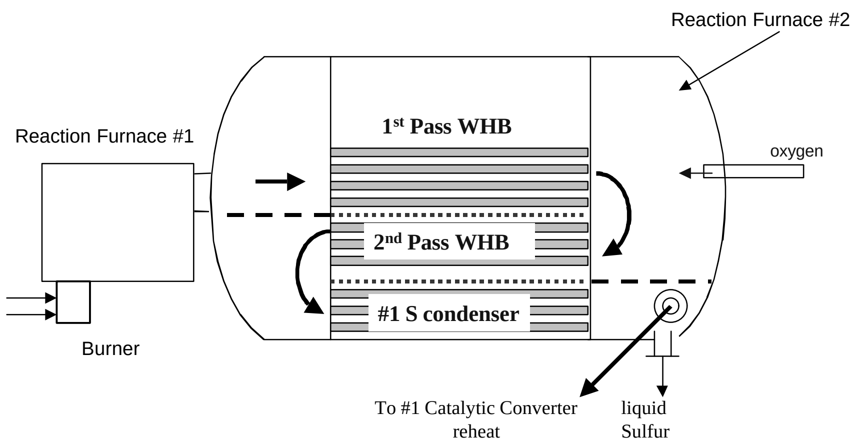
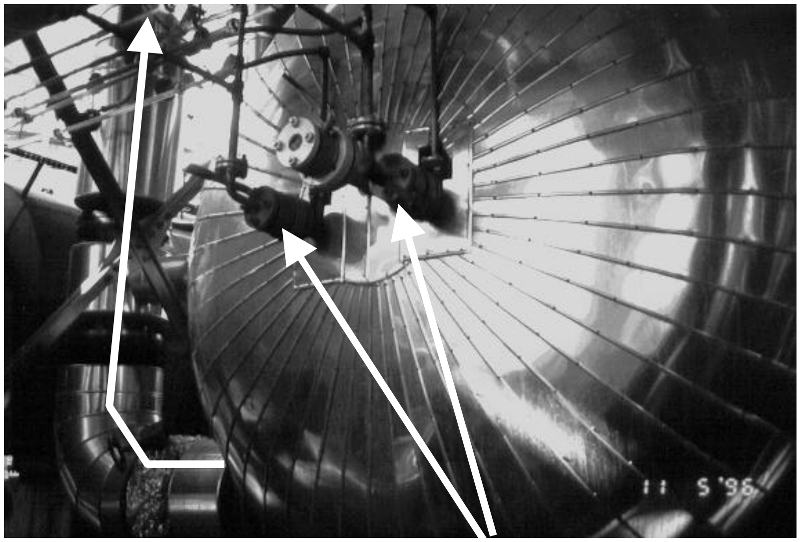


Figure 8 - Sketch of Multi Pass Waste Heat Boiler with Integral #2 Reaction Furnace

All of the air, all of the acid gas (including sour water stripper gas), and most of the oxygen is introduced through the BOC burner into the #1 reaction furnace. Therefore, all of the ammonia and hydrocarbons are destroyed in the #1 reaction furnace and, in fact, most of the Claus reaction has also taken place. The residence time requirement for the #2 reaction furnace is, therefore, much less than that for the #1 reaction furnace. The amount of extension required for the head of the multi-function heat exchanger to provide this residence time proved to be quite modest.

Oxygen lances were provided directly in this extended head to introduce the remaining oxygen required to satisfy stoichiometry, in accordance with the Claus reaction and the Double Combustion process. Design of the oxygen lances, including number of lances, diameter, length, position in the head, and orientation was defined using criteria every bit as rigorous as the SURE™ burner design used in the #1 reaction furnace. In particular, Computational Fluid Dynamic modeling (CFD) was employed. Use of this powerful tool ensured proper mixing, the avoidance of flame impingement on the heat exchanger tube sheet, and complete consumption of oxygen (to prevent oxygen breakthrough). Oxygen lances are shown in the photo below:

To Catalytic Converter



Oxygen Lances

Figure 9 - Photo of Oxygen Lances on End of API Waste Heat Boiler

The gases exiting the extended head go through the second pass of this multi-function heat exchanger, which acts as the #2 waste heat boiler.

The plant design called for only 50 psig steam generation from the waste heat boilers. At API it was possible, therefore, to add a third pass to this multi-function heat exchanger which acts as the #1 sulfur condenser.

This is a convenience, but not a requirement of the system. For example, at the Shell project currently under design, a sulfur condenser pass is not included in the multi-function heat exchanger. It does include a pass for each waste heat boiler, and the #2 reaction furnace in the extended head, as in the API project. Eliminating the sulfur condenser pass allows generation of medium or high pressure steam, if that is required, or desirable.

API Plant Configuration

As indicated above, there are two parallel sulfur trains at the API refinery. Each has two catalytic converters, and the combined tail gas from both trains goes to a single Tail Gas Treating Unit. This Tail Gas Treating Unit was also designed by Siirtec Nigi. It is of the type where hydrogenation is followed by amine treating. Hydrogen sulfide from the amine unit is recycled to the sulfur plant feed.

While there are plans to eventually add SURE™ Double Combustion to both trains, the initial installation included only a single new reaction furnace plus multi-function heat exchanger. However, this new equipment was placed between the two trains, and tied into both, so that either train could be increased in capacity.

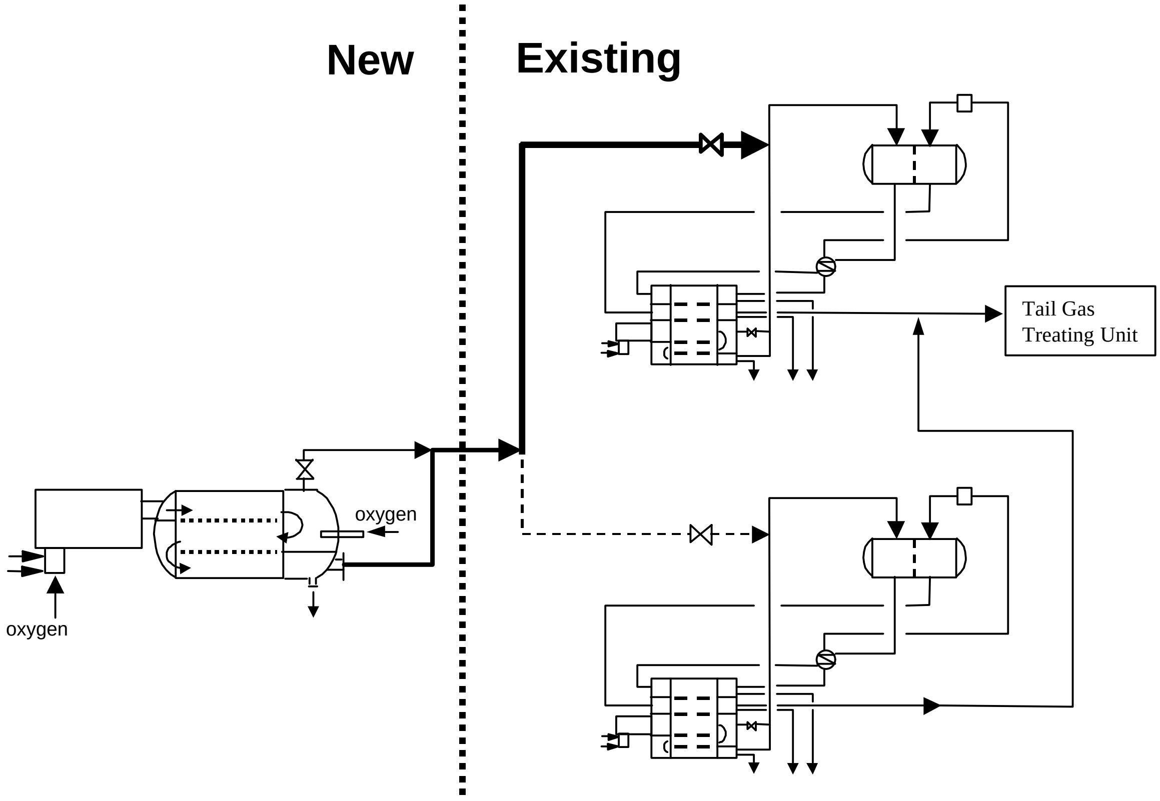


Figure 10 - Process Sketch of API Configuration

This not only provided the required increase in capacity, but also provided some redundancy. When either of the existing trains is out of service for any reason, the remaining train can be increased to approximately double its original capacity by using oxygen in the new reaction furnace and multi-function heat exchanger.

The method of reheat for gases going to the #1 catalytic converter bed is hot gas bypass. Therefore, some gases coming from the #1 waste heat boiler are diverted to heat up gases coming from the #1 sulfur condenser. For the new equipment, retaining the hot gas bypass method of reheat means taking gases directly from what is effectively the #2 reaction furnace. In order to keep the temperature of this diverted gas within reasonable limits, using a very conservative design, the overall level of oxygen enrichment is confined to approximately 40%, which results in a capacity increase of just under 100%. The design capacity for the train using the new equipment, while operating on oxygen, is 80 LT/D. The air based capacity of each train remains at 42 LT/D. Therefore, the total maximum capacity for both trains operating is 122 LT/D (80 + 42 LT/D).

BOC Gases and Parsons are currently in the design phase of a project for Shell Oil at the Anacortes refinery in the state of Washington. That sulfur plant does not use hot gas bypass for reheat. Using an approach very similar to the API expansion project, operation at 100% oxygen is possible, and is being incorporated into the design. This results in a capacity increase for the single train of 150% over current capacity (2 1/2 times original capacity).

In summary, the changes to the basic SURE™ Double Combustion scheme at API are as follows:

- The #1 waste heat boiler and #2 waste heat boiler are combined as separate passes in a common vessel
- A new #2 reaction furnace is integral with the waste heat boiler vessel
- Oxygen lances are installed directly into the extended head of the multi-function heat exchange vessel
- Hot gases are taken directly from the #2 reaction furnace section of the multi-function heat exchange vessel to provide reheat for gases leaving the new #1 sulfur condenser
- The new reaction furnace and waste heat boiler (including a new #2 reaction furnace) are placed between two parallel Claus trains so that it can increase the capacity of <u>either</u> train

Results of this configuration include:

- No modifications required to the existing Claus plants
- New Equipment required minimal plot space
- Either plant may continue to operate on air exactly as before the revamp
- New Equipment may be used in conjunction with both existing plants, or independently with either one. This provides flexibility, and redundancy equal to a spare plant

API Operating Experience

At API, as with most Italian refineries, flexibility has proven to be more important than continuous operation at higher capacity. This is due to the fact that the refineries process a variety of crude oils depending largely on the price differential between sweet and sour crudes. Oxygen is supplied as liquid, which is quite expensive.

The new Double Combustion equipment is easily brought on line as needed, and has been operating approximately 60% of the time. Of this, oxygen is employed approximately 20% of the time. The process has worked completely as expected, and there has been no evidence of oxygen breakthrough when operating with oxygen in the extended head of the multi-function heat exchanger. Temperatures are easily controlled with a maximum temperature of approximately 2500 ^{o}F in the new #1 reaction furnace. Increasing overall capacity up to 122 LT/D (80 + 42 LT/D), by operation at 40% oxygen enrichment, has been accomplished as often as required since October 1996.

The new equipment was opened for inspection during the summer of 1997, and it was noted that, while there was some slight refractory damage (cracking on the tubesheet refractory), it was consistent with, and no more severe than, past experience with the air based furnaces. The #2 reaction furnace in the extended head showed no refractory damage whatsoever.

One very interesting aspect of the API project is the use of air as the purge gas in the oxygen lances, when oxygen is not required. Since the gases in the extended head of the multi-function heat exchanger are always above the auto-ignition temperature, there is always a flame in the extended head. There is a view port in this extended head, and the chamber is always illuminated by the flame.

The new integral reaction furnace / heat exchange vessel is the key aspect to this new approach for the SURE™ Double Combustion technology. Operation of the plant has verified the effectiveness of this equipment and the design of the oxygen lances in the integral reaction furnace section. Specifically, residence time is sufficient, and the introduction of oxygen is done in a fashion that provides proper mixing.

- Overall conversion is essentially the same as with air operation
- There are no local hot spots, and the refractory was found to be in good condition
- There is no evidence of oxygen breakthrough
- Temperature in the #2 reaction furnace is easily controlled by varying the flow rate of oxygen

Economics of the API Project

The total installed cost for the revamp at the API Refinery, escalated to a 4th quarter 1997 basis, was just under 2 MM USD. As stated earlier, plot space is severely limited, and there is no room available for a new sulfur plant.

The Tail Gas Treating Unit (TGTU) was installed at the same time as the expansion. However, had it been possible, and had a new air based sulfur plant been installed, a larger TGTU would have also been required. While the TGTU, as built, does not have capacity for the additional flow from a third air based plant, it is able to process the extra throughput when achieved through oxygen enrichment.

If space had been available, it is estimated that the cost on the same basis (4th quarter 1997) for a new third sulfur plant, using the same configuration as the existing plants, plus the incremental cost for a larger TGTU, would have been approximately 5 MM USD. Adding a third sulfur plant after the TGTU is already in place is more expensive because it requires an additional TGTU. Therefore, if the TGTU was already in place, or if the third sulfur plant was built in a distant location so that it could not use the same TGTU, the cost for a third sulfur plant plus TGTU would be approximately 7 MM USD.

The unit cost for liquid oxygen is high when compared to the cost of oxygen from an on-site generation facility. However, given the sporadic demand for the higher sulfur plant capacity, even with the higher cost for liquid oxygen, the total annual cost for oxygen is estimated to have been well below 200,000 USD.

Clearly, the revamp project using the SURE™ Double Combustion technology has been an economic success as well as a technical success.

Future Operations at API

A gasification project is currently underway at the API refinery. Acid gases from that project will be processed in two new 75 LT/D sulfur plants. On-site generation of oxygen is part of the gasification project, making available oxygen at a much lower cost than the liquid currently used in the refinery sulfur plants. The new sulfur plants have been designed for continuous operation with 100% oxygen. This allows for much smaller sulfur plants, and the capital savings have greater economic value than the cost of oxygen required. The hydrogen sulfide concentration in the feed gas to these new gasification sulfur plants is much lower than in the refinery sulfur plants. Therefore, SURE™ Double Combustion is not required to reduce temperature in the reaction furnace. One hundred percent oxygen can be accommodated in a conventional Claus configuration using BOC burners.

As stated earlier, future plans have always considered application of Double Combustion to both refinery sulfur plants to increase capacity further, from the current 122 LT/D (80 + 42 LT/D) to 160 LT/D (80 + 80 LT/D). Installation of the second train of Double Combustion equipment, consisting of a new reaction furnace and multi function heat exchanger, is likely to go ahead once inexpensive oxygen is made available from the gasification project.

Implications for New Grass Roots Sulfur Plants

Often, when considering new grass roots Claus sulfur plants, it is anticipated that future capacity requirements may exceed current capabilities. This is particularly true in today's environment where anticipated regulations will require more hydrotreating to meet product specifications, and further reductions in allowable emissions from refineries are likely. At the same time, the sulfur content of the crude supply continues to increase. Further, it is often desirable or necessary to provide full redundancy to avoid limiting plant production. For example, it is not uncommon to build three 50% plants.

Planning for expansion with oxygen in the future, or building two 50% plants (instead of three 50% plants), and providing the required redundancy with oxygen, clearly has merit in these situations. Using the adaptation of Double Combustion developed for API, a new plant can easily provide full redundancy (twice air capacity), at an insignificant capital cost, by simply incorporating modest design modifications to the conventional waste heat boiler, which is required in any case. The sketch of process flows is shown below. Basically, the Double Combustion waste heat boiler would contain additional heat transfer surface area and a slightly extended head, when compared to the conventional waste heat boiler.

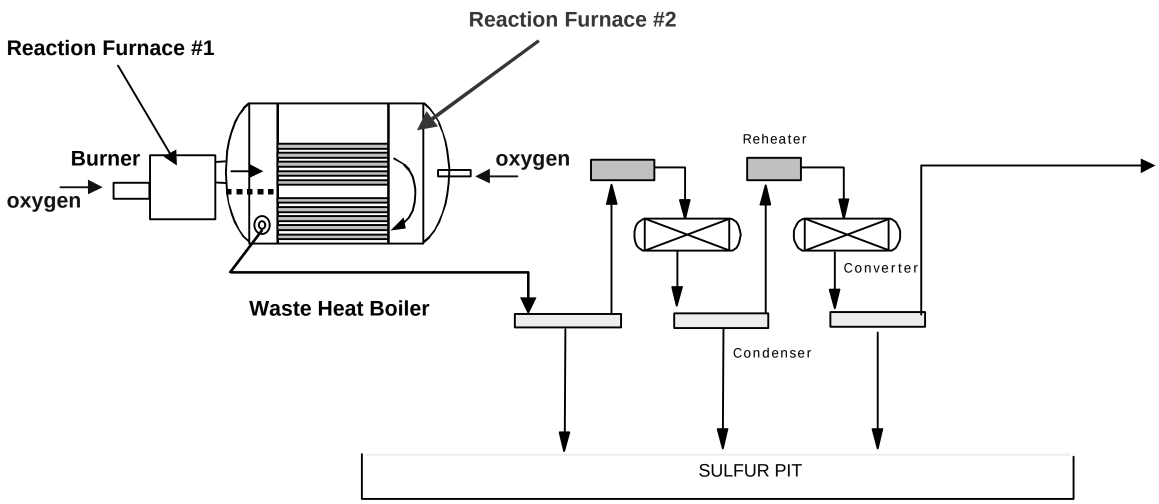


Figure 11 - Double Combustion Applied to New Claus Plants for Redundancy

For new construction, the difference between a conventional waste heat boiler, and a multi-function heat exchanger that is suitable for application of Double Combustion, is truly insignificant within the budget scope of a new sulfur plant. The plant will be ready to provide the additional capacity without further modification or expense. Once oxygen is supplied to the plant, it will be able to provide the additional capacity while operating within the same <u>modest</u> temperature regimes.

An alternate approach has been to only provide a burner, which can be converted to oxygen service in the future. At first glance, this may appear to be an equal or an even less expensive option but, in fact, it is not. For a typical refinery gas, a tip mix burner that maximizes the endothermic dissociation reactions, and allows maximum oxygen concentrations without exceeding refractory limits, still reaches its limit at about 75 - 80% increase in capacity (compared to 150% increase with Double Combustion). That means in order to provide full redundancy, or twice the air capacity with oxygen, the original air based plants must be built approximately 15% larger than actually required. Even allowing for economies of scale, this represents a 10% increase in capital cost requirement (pre-investment) for the air based plants. Further, and perhaps more important, when actually trying to achieve that increased capacity with high concentrations of oxygen, the reaction furnace will have to operate near its refractory mechanical limits. This, of course, leaves no room for typical upset conditions such as slugs of hydrocarbons in the feed, etc.

The Double Combustion approach not only requires less capital (both at time of original construction, and in the future when additional capacity is required), but also provides greater capacity -- up to 2 1/2 times air based capacity, <u>while continuing to operate at moderate temperatures</u>. This makes the SURE™ Double Combustion process the obvious choice for providing redundancy, or future capacity requirements in new grass roots sulfur plants.