Thermal Combustion Stage Criteria in SRU's Design

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Introduction

With the sulphur content of crude oil and natural gas on the increase and with the ever tightening sulphur content in fuels, the refiners and gas processors will require additional sulphur recovery capacity. At the same time, environmental regulatory agencies of many countries continue to promulgate more stringent standards for sulphur emissions from oil, gas and chemical processing facilities. It is necessary to develop and implement reliable and cost-effective technologies to cope with the changing requirements.

Oxygen enrichment is the most cost effective option to increase existing sulphur capacity. In general, commercially available technologies offer the low, middle and high levels of Oxygen enrichment, and these also represent the three incremental steps for capacity expansion from 25% to 150%, with equipment modifications and capital investments.

Using oxygen enrichment in the sulphur plant will increase the adiabatic flame temperature. This is because practically inert nitrogen is being replaced by reactive acid gases as the level of oxygen enrichment increases. Nitrogen moderates the temperature by absorbing heat. Commercial refractories are limited to a maximum temperature of about 3000°F so at higher levels of oxygen enrichment, the maximum refractory temperature may be exceeded depending on the composition of the feeds.

Recycling the cooled acid gas from the first condenser or staged combustions are employed to get around the refractory temperature limit. With either configuration, combustion zones operate comfortably below the maximum refractory temperature limit.

In a typical staged Combustion SRU revamp, a new reaction furnace and waste heat boiler are installed upstream of the existing reaction furnace, which then serves as the second combustion chamber. Occasionally, existing reaction furnaces and waste heat boilers cannot be reused because of original design limitations or plot space limitations or inadequate refractory.

For high level oxygen operation in the Claus unit, there are no practical refractories capable of withstanding the high temperatures produced in the furnace, therefore, a staged combustion process, or a recycle process, are employed to moderate the temperature so that a refractory lining can be used. In the double combustion process, the reactions occur in two stages. Inter-stage cooling is employed in order to not exceed the temperature limit of the refractory. In the recycle process, a portion of the cooled effluent from the reaction furnace is recycled to the reaction furnace to moderate the temperature.

Refractory lining has been used in air and oxygen applications in sulphur plant designs. However, due to increasing capacity, or a need for ammonia destruction, the sulphur plants have been operated near to the allowable limited refractory temperature, therefore, the possibilities of damaging refractory and ceramic materials have been increased significantly. In practice, the selected refractories have to have a proper grade of alumina, brick, castable, fiber and proper shape of ferrules based on specific feed compositions and combustion temperature for air and oxygen operations for lean or rich gases containing hydrogen sulfide and ammonia. The selection of the components and material grades for hot-face lining, back up lining, expansion joints and other parts has to be defined properly to eliminate refractory damages for different mode of operations.

In addition to that, the following items have high potential to damage the refractory.

1. Improper castable refractory installation
2. Installation of wrong shape ferrules.
3. Thermal shock due to improper refractory dry out
4. Rapid cooling during shut down
5. Ceramic cracking as a result of thermal, structural or mechanical stresses
6. Exposure to elevated temperatures by improperly using a higher level of oxygen or loss of temperature control system
7. Corrosive failure
8. Corrosion from improper turn down, which results cold spot and forms acids and undesired chemical reactions
9. Improper velocity at inlet and outlet of equipment
10. Erosion due to improper high loading under tension
11. Vibration as a result of improper design
12. Loss of burner from improper refractory selection

Acid Gas Feed Quality consideration

Oxygen Enrichment

Oxygen enrichment raises the flame temperature by eliminating the diluents effect of nitrogen in air. An economical source of Oxygen is the key in this case. A perfect example is the IGCC plant, where lean acid gas and inexpensive Oxygen are both present. Equipment sizes of a sulphur plant and, therefore, investment cost are lower when Oxygen enrichment is used.

Lean Acid Gas Feed

Lean (low H_2S content) acid gas feed often poses processing problems in an air-only Claus SRU in terms of unstable flame and inadequate contaminant destruction. Oxygen enrichment raises the reaction furnace temperature and provides for a more stable SRU operation in addition to increasing SRU's capacity.

Acid gas fired direct reheat has been extensively used in Claus units. Acid gas fired burners are usually operated far away from stoichiometry to minimize Oxygen slippage. When the acid gas is lean in hydrogen sulfide, the burner is usually designed for firing nearer to stoichiometry to reduce the amount of acid gas. Consequently, only an acid gas with stable composition should be used to avoid Oxygen slippage.

Acid Gas Bypass

The quantity of combustion air used in the Claus process is fixed at about one third of complete hydrogen sulfide combustion, as dictated by the requirement of the Claus reaction. The acid gas bypass scheme takes advantage of the fact that the furnace operates far away from complete combustion in the straight-through configuration. By bypassing part of the feed gas, the furnace will then operate nearer to complete combustion. Consequently, the flame temperature is increased. However, the amount of acid gas bypass is limited to two thirds of the total feed because it is undesirable to run the furnace under oxidizing conditions and operating beyond complete combustion will lower the flame temperature anyway.

Acid gas bypass is the most economical scheme since neither additional equipment nor operating cost is involved. The downside of this scheme is the contaminants in the feed gas, if present, will not be destroyed in the high temperature furnace zone. The detrimental effects of the contaminants on the back-end of the Claus plant, e.g. catalyst deactivation and equipment/line plugging, may jeopardize the smooth and continuous operation of the sulphur plant.

Feed Preheat

Both the combustion air and the acid gas can be preheated in order to raise the flame temperature. Usually, the combustion air is the first choice since it is more benign than the acid gas. Furthermore, there are the all important pressure drop considerations. The upstream amine unit often limits the available acid gas pressure.

The extent of combustion air preheat is basically an economic decision, i.e. available heating medium and metallurgy. Stream at a suitable pressure level is preferred over a fired heater due to ease of operation and lower investment cost. It is also desirable to use carbon steel rather than more exotic and expensive piping and equipment material.

The extent of acid gas preheat is further complicated by the possibility of thermal cracking of its constituents.

When applying preheat, it is important to ensure that the burner is properly designed in terms of both process performance and mechanical integrity.

Fuel Gas Supplement

Fuel gas can be added to raise the flame temperature. Of course, this is against conventional wisdom. Fuel gas, if not completely combusted, causes catalyst deactivation even plugging and off-color sulphur products. Even when it is completely combusted, the equipment sizes, investment and operating costs will be bigger and the overall sulphur recovery efficiency will be lower.

Fuel gas supplement has been applied successfully for operating the Claus unit at greater than ten to one turndown. In any case, when contemplating fuel gas supplement, investing in a high performance, high intensity and high cost burner is a must.

The relationship of adiabatic flame temperature versus SRU capacity increase at various Oxygen enrichment levels for a typical rich amine acid gas feed with no ammonia, for example 90% H_2S. The two major material limitations usually encountered in SRU Oxygen enrichment revamping implementation are: (1) piping material and burner for handling Oxygen/Oxygen enriched air, and (2) refractory of the existing reaction furnace in handling high Oxygen flame temperature. The most likely equipment limitation in determining achievable capacity expansion via Oxygen enrichment is the heat removal capacity of the existing WHB and the No. 1 sulphur condenser. The ultimate capacity increase for each individual case is dependent on acid gas compositions and existing equipment sizes.

The Claus process is undoubtedly the technology of choice for gases containing higher concentration of hydrogen sulfide and/or larger quantities of sulphur. Only when the hydrogen sulfide content drops below 30% and/or the amount of sulphur is less than about 10~30 tons/day (TPD) would other processes become economical.

The Effects of Oxygen Use on Ammonia and Hydrocarbon Destruction

If not properly destroyed, hydrocarbons in the acid gas feed often cause carbon laydown on catalyst, generation of undesired high concentration of COS and CS_2. In addition, ammonia in the acid gas feed often causes deposition of complex ammonia/sulphur salts in cooler parts of the plant. These undesired phenomena would either cause unscheduled plant shutdown or reduce sulphur recovery or shorten catalyst life. Oxygen enrichment raises the reaction furnace temperature which ensures complete destruction of heavy hydrocarbons and ammonia; reduces formation of COS and CS_2, and shortens gas residence time requirements for contaminants destruction.

In the case of lean acid gas feed contaminated with high levels of heavy hydrocarbons, Oxygen enrichment offers inexpensive and simple solutions to circumvent this otherwise unsolvable problem that requires costly processing technology.

Quantitatively, based practical experience, the “SURE” burner has proved to be very effective in destroying ammonia and hydrocarbons in Claus plants. Outside of their application in Claus plants, oxy-fuel burners are widely used in the metals and minerals and in the chemical and refining industries to burn a wide range of fuels, including gases, liquids, and pulverized solids. One of their most attractive features is their ability to burn heavy residual hydrocarbons cleanly.

Two major effects in using Oxygen or Oxygen-enriched air in place of air for combustion are higher temperatures and higher flame speeds. The degree of change depends on the degree of Oxygen enrichment, but in the case of pure Oxygen, temperatures may increase by 1,000°C and flame velocities by 10 times in round numbers. The combination of these two effects is to produce a hotter, shorter, more intense flame much better suited to the rapid destruction of combustible materials.

The destruction of individual feed components in a Claus unit cannot be considered in isolation, since there is considerable molecular interaction. Both hydrogen sulfide and ammonia dissociate quite readily and the higher the temperature, the higher the level of dissociation. The result is that when Oxygen is used, the hydrogen level in the reaction furnace increases greatly over that achieved in air-based systems. Most of this hydrogen will subsequently recombine with sulphur in the Waste Heat Boiler (WHB), including hydrogen produced from ammonia dissociation. The ammonia must effectively be burned; therefore, even if the mechanism of destruction is initially dissociation, in order to preserve the Claus Stoichiometry downstream of the WHB.

It is possible to speculate that the hydrogen remaining in the gas after the WHB will be higher if the level in the reaction furnace before the boiler is higher. This must be true if the quench rate in the boiler remains constant. The effect may be small however, and in the case of up rating with Oxygen, where the WHB sees a higher load, a fall in quench rate may reduce it still further.

Heavy hydrocarbons such as BTX can be present in the feed to Claus units in certain cases; and their propensity for cracking thermally to produce carbon is well understood. Little, if any, published data on the effect of Oxygen on BTX destruction in a Claus environment is currently available; however, it is known that Oxygen is very efficient in burning these materials in other environments.

It is also possible to design the “SRUE” Claus burner so that feed stream contaminants are preferentially destroyed; and making use of the much higher reaction rates which are available even in plants operating with only moderate enrichment levels. Qualitatively, therefore, Oxygen should have a beneficial effect on the destruction of heavy hydrocarbon contaminants such as BTX.

Three general parameters may be said to control the destruction of feed stream contaminants in Claus units, temperature, mixing and residence time. Temperature may be the most important parameter;

and mixing is an essential parameter to ensure that all the contaminant molecules reach a high enough temperature and promote reaction where appropriate. A study of the Claus system using a kinetic CFD model indicates that residence time is important, particularly to sulphur forming reactions, but while Oxygen is present, the system is dominated by hydrogen combustion. In such a system, molecules like ammonia compete poorly for Oxygen and the initial step in its destruction is likely to be dissociation. The higher temperatures generated with Oxygen use clearly favor this; and since the ammonia is often contained in a stream separate from the main Claus feed stream, it is possible to maximize the benefit through the burner design.

The key parameter considered when applying the Claus process is to maintain a stable flame at the burner. However, if the feed gas contains contaminants, a much higher flame temperature will be required to destroy the undesirable compounds in the furnace so that they do not cause operational difficulties downstream.

Others (Cyanide, Mercaptans)

These contaminants can be destroyed in the Claus furnace based on the same considerations as given for aromatic hydrocarbons above. They are detrimental to the wet oxidization and non-regenerative processes due to spent chemical disposal and odor problems.

It cannot be over emphasized that a well-designed burner and reaction furnace, which promotes good mixing of the reactants, is essential for complete destruction of undesirable feed contaminants.

Low-Level Oxygen Enrichment (< 28% O_2)

For a desired capacity increase of up to 20% to 25% of the original design sulphur processing capacity, low-level Oxygen enrichment technology is adequate. Low-level Oxygen enrichment is accomplished by injecting pure Oxygen or Oxygen-rich air into the combustion air; i.e., Oxygen is premixed with combustion air upstream of the burner. No equipment modification is required in the existing SRU, other than providing the tie-in point for Oxygen injection in the combustion air line. An SRU capacity increase of approximately 20% to 25% is achievable with low-level Oxygen enrichment. The capital cost investment is mainly in the installation of an Oxygen supply system, which is usually an Oxygen supply line added to the reaction furnace burner.

Medium-Level Oxygen Enrichment (28% to 45% O_2)

For a desired capacity increase of up to 75% of the original design sulphur processing capacity, medium-level Oxygen enrichment technology is required. The combustion air piping in a conventional SRU is not suitable for handling Oxygen-rich air above 28% Oxygen. The burner designed for air-only operation might not withstand the higher combustion temperature. In any case, direct injection of Oxygen through separate nozzles from combustion air is recommended; hence, special burners designed for direct Oxygen injection should be installed.

The burner is designed for efficient combustion in SRUs with Oxygen enrichment. It can be used in either end-firing or tangential-firing designs. The excellent mixing characteristics of the Oxygen burner, coupled with the higher combustion temperature attained in Oxygen enrichment operation, allow the existing reaction furnace to be used with only minor modifications to accommodate the new burner.

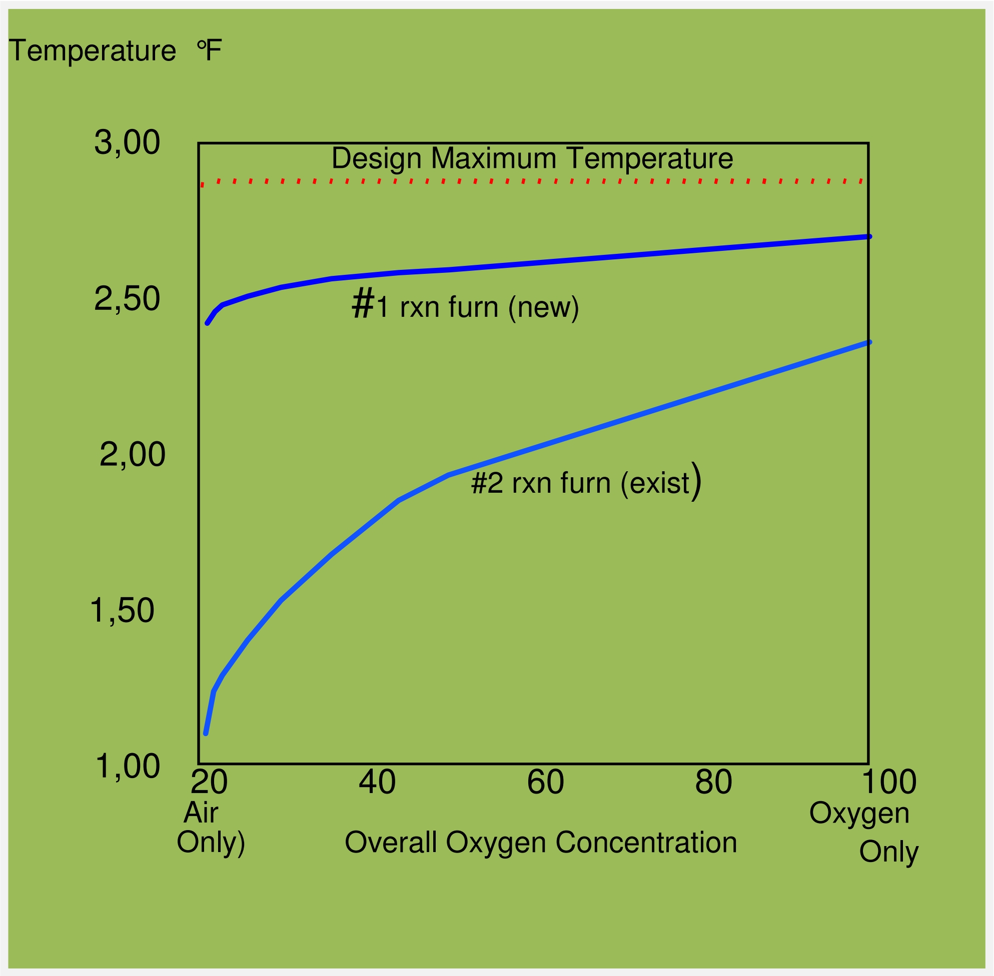
Oxygen enrichment considerably raises the reaction furnace temperature, which ensures complete destruction of undesired heavy hydrocarbons and ammonia, reduces formation of COS and CS_2 and shortens gas residence time requirements for contaminant destruction.

The capital cost investment is mainly in the installation of an Oxygen supply system and a new Oxygen-compatible burner.

High-Level Oxygen Enrichment (> 45% O_2)

For a capacity increase of up to 150% of the original design capacity, high-level Oxygen enrichment is applicable. The thermal section of the existing SRU must be modified and/or have new equipment added, depending on which Oxygen enrichment technology is chosen.

The attached chart represents the limitation of the temperature in the reaction furnace using high level of oxygen enrichment.



SRU Burner & Reaction Furnace Evaluation

Low-level Oxygen enrichment is accomplished by injecting pure Oxygen or Oxygen-rich air into the combustion air; i.e., Oxygen is premixed with combustion air upstream of the burner. No burner modification is required in the existing SRU, other than providing the tie-in point for Oxygen injection in the combustion airline. For medium-level or high level Oxygen enrichment with rich H_2S, the burner designed for air-only operation might not withstand the higher combustion temperature. In any case, direct injection of Oxygen through separate nozzles from combustion air is recommended; hence, special burners designed for direct Oxygen injection should be installed.

For lean H_2S acid gas and high Oxygen enrichment, single combustion is adequate; therefore, there is no need for an additional reaction furnace if the refractory lining is adequate, only burner needs to be replaced.

The existing reaction furnace should be evaluated for low level of Oxygen no changes or concern is required. For medium or high level of Oxygen, the following factors should be considered if: the modification for sulphur plant has high content of H_2S, a new reaction furnace is required as a first combustion chamber; and, the existing reaction furnace will be used as a second combustion chamber, if the existing reaction furnace is well maintained and the refractory lining is adequate. The following are the Oxygen enrichment impacts the burner and reaction furnace design:

- Higher Combustion temperature, then existing refractory lining should be evaluated. In many cases, the refractory system will need to be upgraded to accommodate higher operating temperature. The maximum operating temperature is limited by refractory to about 2700 °F to 2900 °F (for short time excursions).
- If the burner needs to be replaced to a new one, the size of the existing nozzle should be evaluated for the new burner location.
- If the reaction furnace contains a choke ring or checker wall, it should be evaluated for flame impingement with a new burner flame characteristics.
- Higher partial pressure of elemental sulphur, SO_2 and H_2O vapor, leads to higher sulphur dew points.
- Producing more H_2, which is beneficial in TGU as a reducing agent, can be used as a fuel in the incinerator.
- Increase the efficiency of down stream Claus catalytic reactors.
- Better destruction of ammonia, HCN, heavy hydrocarbons and BTEX, or any contaminants, requires a higher combustion temperature.
- The gas volumetric is about the same, no changes in residence time.
- Oxygen line should be provided to the unit; therefore, burner management system ESD system, and oxygen demand controls should be added or modified for Oxygen supply.
- Purging requirements will be different and should be considered.
- Pilot /ignition requirement should be evaluated.
- Acid Gas piping pressure drop and instrumentation should be evaluated to maintain the pressure profile throughout the unit.

- The plot plan is to be evaluated if the burner is replaced.
- The location for the flame scanners should be evaluated with the burner replacement for the replacement or relocation. RATE recommends IRIS S-550 type flame scanners since it will not be effected as the results of pipe x-raying, heats and radiation on the site and seems more robust for the sulphur plants.
- The flow meters and control valves on the acid gas lines should be evaluated for a higher flow rate and turndown issues.
- The existing refractory should be evaluated for a higher combustion temperature in the reducing atmosphere. The principle of using double combustion for processing rich H_2S acid gas is that 90% alumina refractory with silica, at reducing atmosphere, has a maximum temperature limitation, and using 94% alumina refractory with magnesium is very sensitive to thermal shock at reducing atmosphere and may not be very cost effective, but it will handle higher combustion temperature. The melting point of 90% alumina with silica and 94% alumina with magnesium is about 3400℉ and 3500℉ respectively. However, the ferrules should be evaluated for this combination.

Waste Heat Boiler and Steam Drum Evaluation

Hot gases leaving the reaction furnace are cooled in the waste heat boiler by generating steam. The existing waste heat boiler and steam drum should be evaluated, for low level of Oxygen, no changes or concern is required. For medium or high level of Oxygen with rich H_2S content the existing waste heater could be used as a second pass waste heat boiler and a new waste heat boiler should be added as a first pass waste heat boiler.

For lean H_2S acid gas and high Oxygen enrichment, single combustion is adequate therefore, there is no need for the additional waste heat boiler, if the existing waste heat boiler is well designed and well maintained.

The following is the Oxygen enrichment impacts the waste heat boiler design.

- Higher operating temperature, resulting in higher heat duty, which requires more cooling.

- Having more sulphur vapor from reaction furnace needs more heat for redistribution.
- Recombination of CO to COS, and H_2, S_2 to H_2S releases additional heat in front of several feet of boiler tubes, which is not predicated by some simulator. It increases the heat flux near the critical tube to tube sheet weld (maximum metal temperature), and inlet tube sheet refractory and ferrules, maximum heat flux in tubes requiring mechanical attention.
- Improved heat transfer as the result of higher radiant film coefficient.
- Steam drum size, downcomer/riser size and number, nozzle sizes, associated piping and instrumentation should be evaluated.
- Relief capacity, BFW /steam rate will be increased.
- Mass velocities should not be exceeded or heat flux issues may arise, which may cause vapor blanketing of the tubes and high temperature in the tube and tube-sheet.
- The peak heat flux occurs at the outlet of the ceramic ferrules; therefore, the heat flux should be limited to a maximum 50,000 to 70,000 Btu/hr-ft^2 to prevent eddying.
- The temperature of tube to tube-sheet weld should be limited and evaluated for the possibility of sulfidic corrosion of carbon steel.

Conventional Configuration for High Capacity Expansion

The conventional configuration involves the addition of a new reaction furnace burner, reaction furnace and WHB boiler upstream of the existing reaction furnace. Gas effluent from the new waste boiler is routed to the existing reaction furnace, which serves as the second thermal stage. With this configuration the staged Combustion technology allows SRU capacity to be expanded at considerably lower costs compared to building new air-based SRUs. The operator could save substantial initial investment cost even for new SRUs if Oxygen is available or can be imported across the fence. Moreover, Oxygen enrichment reduces the plot area required and, in fact, for operating facilities limited by plot space, Oxygen enrichment might be the most viable option for SRU capacity expansion.

Occasionally, existing reaction furnaces and WHBs cannot be reused because of original design limitations. In these cases, a two-pass WHB with an extended head can be designed in which the extended head serves as the second-stage reaction furnace and the second pass serves as the second WHB . This two-pass WHB configuration effectively reduces capital cost and conserves plot space requirement. In addition, operators could realize the following benefits:

The new reaction furnace/WHB can be installed while the existing SRU is still in operation. The new equipment can be tied in with the existing reaction furnace/WHB during a short period shutdown or during the SRU turnaround time, thus minimizing the loss of plant throughput while the technology is implemented.

The simple piping for the Oxygen design reduces the possibility of accidental H_2S emission and equipment failure compared to other commercially available processes.

The design does not require shutting down and isolating a recycle loop when Oxygen enrichment is not being used; this further improves the safety of the Oxygen process.

Changing the mode of operation between air-only and Oxygen enrichment is simple and smooth for the Oxygen process, which involves only the Oxygen supply system. The SRU itself is always ready to receive Oxygen.

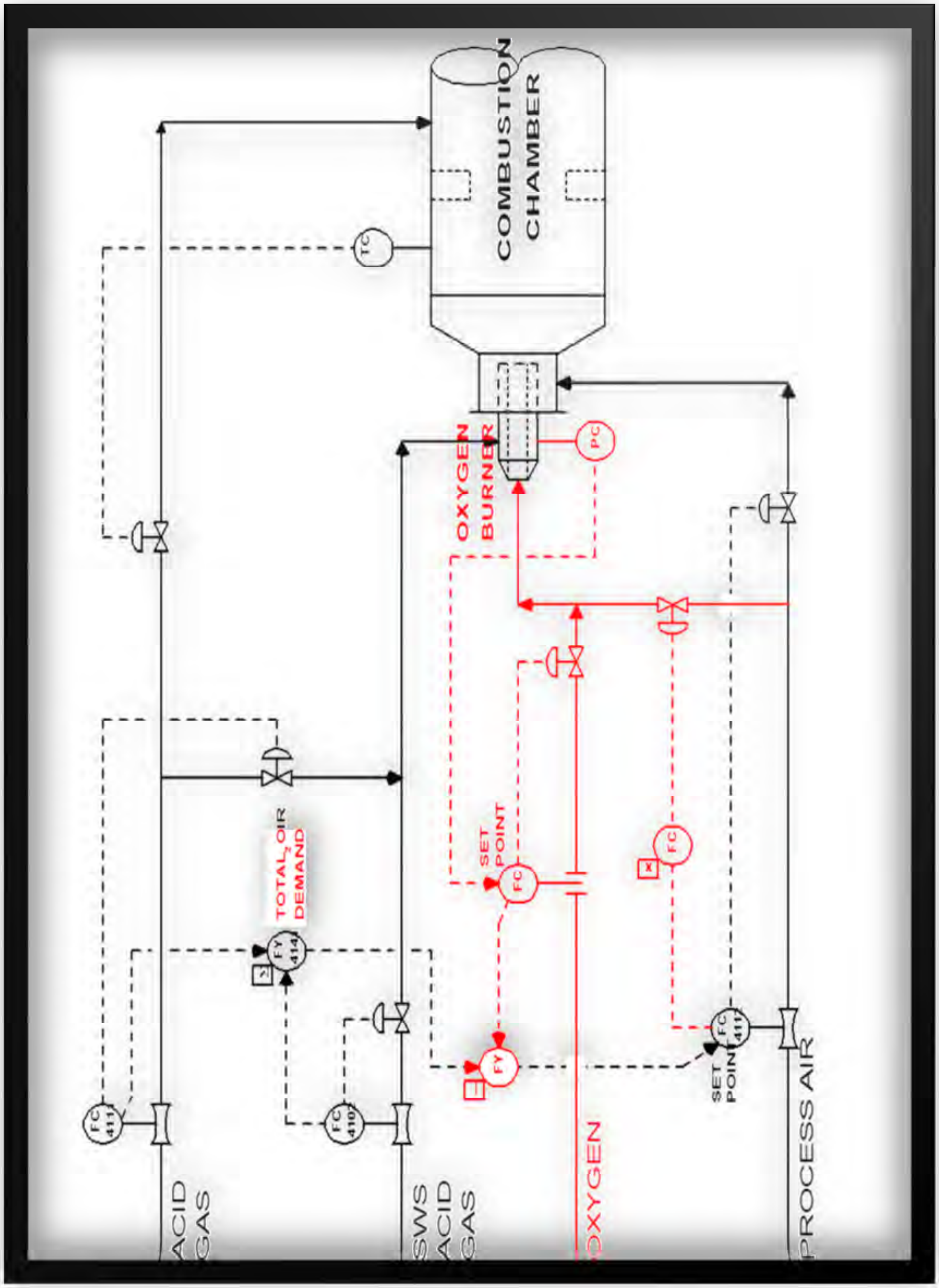
Configuration for High-capacity Expansion

When multiple SRU trains are involved, one set of common new equipment (burner, reaction furnace and WHB) can be shared by the various trains. The effluent of the new WHB is split and routed to each of the existing Sulphur condensers. The new equipment could be installed onsite while the SRU is in operation. Only a short downtime is needed to tie in the new equipment for high-level Oxygen enrichment. Typically, the revamp tie-in work has been accomplished within 1 to 2 weeks, which is normally within the schedule of a routine plant maintenance shutdown.

Provide 300% Additional Capacity for Two Existing Parallel Trains

The new reaction furnace/WHB can be designed to provide up to 150% additional sulphur processing capacity for each of the two existing parallel SRUs resulting in a total additional capacity of 300%. This operation mode would require the reaction furnace/WHB to be operated with Oxygen during normal operation. If the new equipment is shut down, the existing reaction furnaces can be operated with up to 28% Oxygen-enriched air and can still provide 125% of the original design capacity. This configuration and operation mode minimize the loss of sulphur processing capacity and still maintain more than half of the total required capacity if any one of the two trains is down or if the new equipment system is down.

The following drawing represent the control system modification using oxygen enrichment.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