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WATER WALL BOILER FOR AIR AND OXYGEN FIRED CLAUS SULPHUR RECOVERY UNITS

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Abstract

This paper presents the basis of a new idea for the thermal combustion step of the modified Claus process in which acid gas combustion is carried out in a water-wall boiler instead of a refractory-lined reaction furnace. The critical components of this idea have already been practiced in other industries, which will be described later in this paper.

The adaptation of water wall boiler designs to Claus sulphur recovery units has been patented by WorleyParsons (June 2006, US Patent Number, 7,067,101). The water wall boiler may replace the conventional refractory-lined furnace and waste heat boiler when air, oxygen, or oxygen-enriched air is used as the oxidant. Thermal combustion can be performed in a single stage, without a recycle, for all levels of oxygen enrichment. This process is not commercialized yet, but WorleyParsons is looking for possible commercial applications.

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.

Two technologies are commercially available to get around the refractory temperature limit. COPE technology employs a recycle from the first condenser outlet to the reaction furnace burner to moderate the temperature. The BOC "SURE" Double Combustion process offered by WorleyParsons employs a two-stage combustion scheme with interstage cooling. A portion of the oxygen required for the process is



fed to the reaction furnace burner with the acid gas. The combustion products from the reaction furnace are cooled in a waste heat boiler. The balance of the required oxygen is introduced to a second furnace through oxygen lances to complete the combustion of the acid gases. With this configuration, both combustion zones operate comfortably below the maximum refractory temperature limit.

In a typical SURE™ Double 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.

In the conventional sulphur plant, hydrogen sulfide rich gases are processed through the reaction furnace (combustion chamber) followed by the waste heat boiler. The water wall boiler replaces the reaction furnace (combustion chamber) and the waste heat boiler, while the remaining of the equipment stay the same. Figure 3 represents the Claus sulphur recovery scheme by using water wall boiler.

Temperatures in a Claus unit can reach up to 2800°F (1538°C) when air is used in the process and up to 5000°F (2760°C) when oxygen is used. A refractory lining insulates the walls of the unit from the high temperature inside of the unit for operation with air. Such refractory linings are undesirable because of the time and expense required to install the lining, the time required to heat the lining during start-up of the unit, the time required to cool the lining during shutdown of the unit, and the expense and lost on-stream time and sulphur production caused by damage to or failure of the lining, which requires that the unit be shut down for repairs.

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 double 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

It would be beneficial to design a system to overcome the problems and limitations associated with refractory linings without resorting to two-stage combustion or recycle streams. A water-wall boiler could be employed to resolve this limitation.

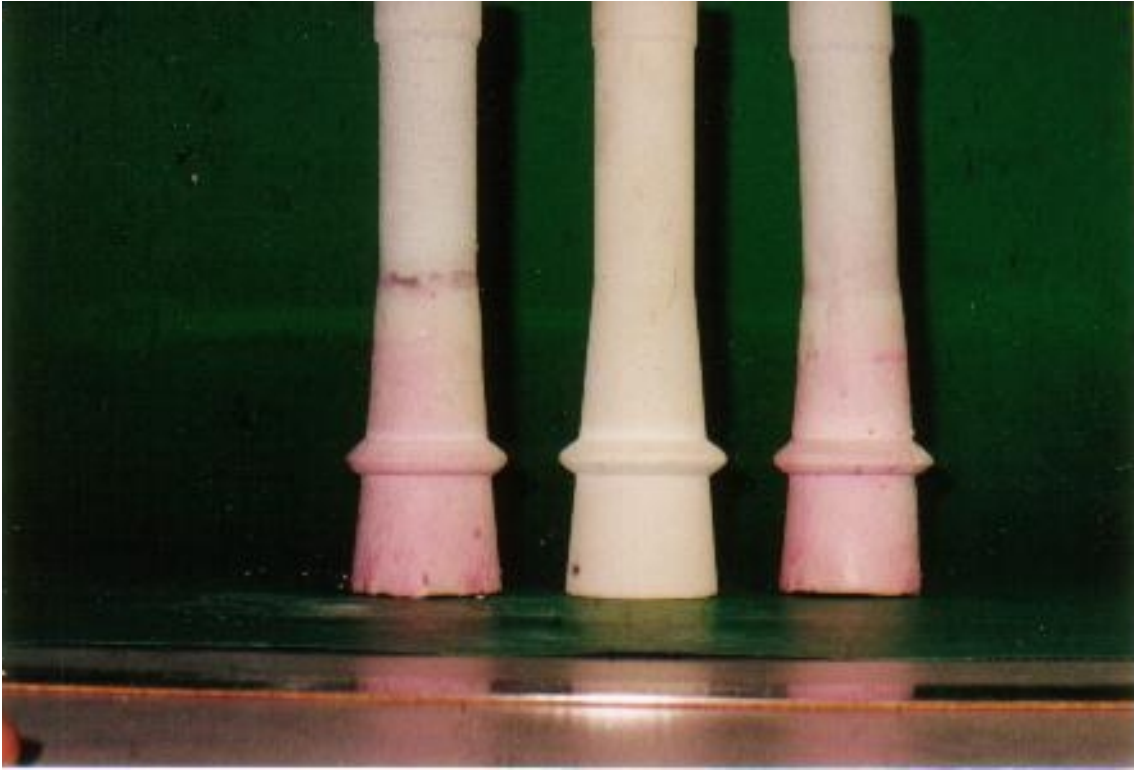
The water-wall boiler could replace the conventional refractory-lined reaction furnace and the waste heat boiler used in the modified Claus process when air, oxygen, or oxygen-enriched air is used as the oxidant. Thermal combustion is performed in a single stage, without a recycle, for all levels of oxygen enrichment.

The following photos illustrate refractory damage resulting from burner loss, from operating at an excessively high temperature with oxygen enrichment and from using the wrong refractory materials.



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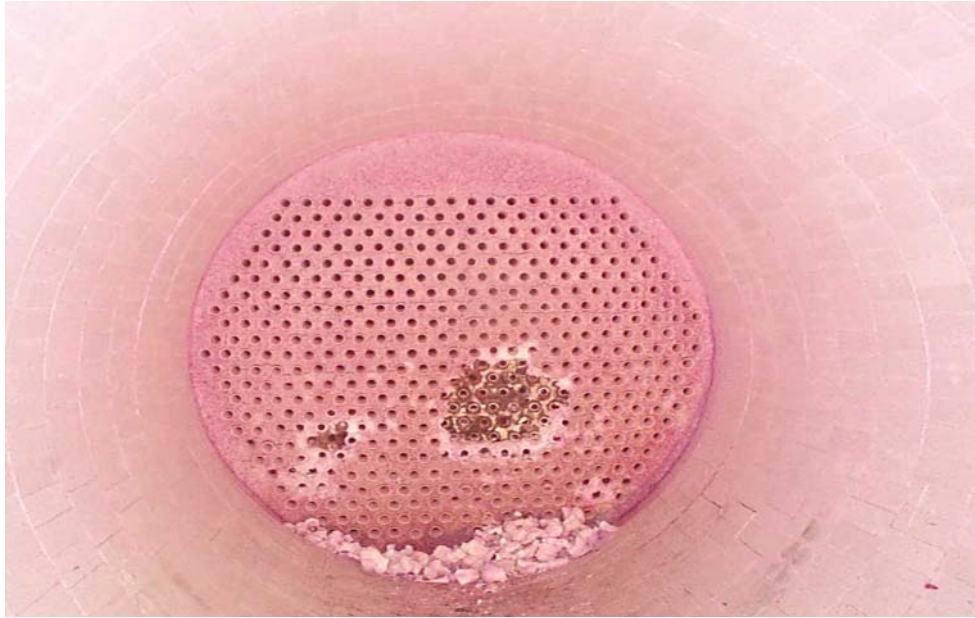


Refractory Damage from Burner Loss



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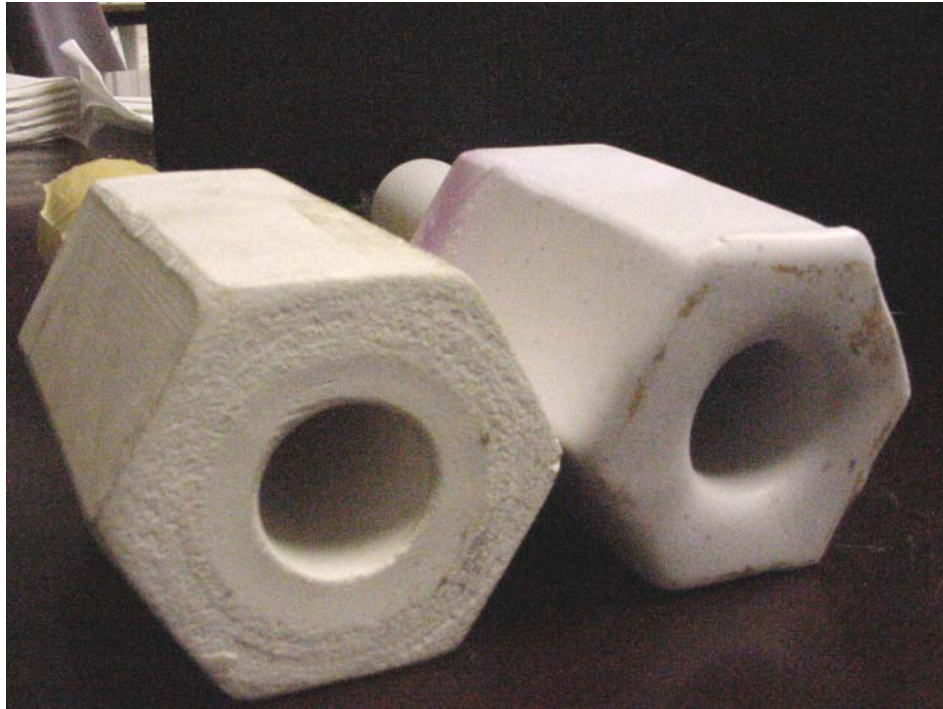


Refractory Damage from Burner Loss



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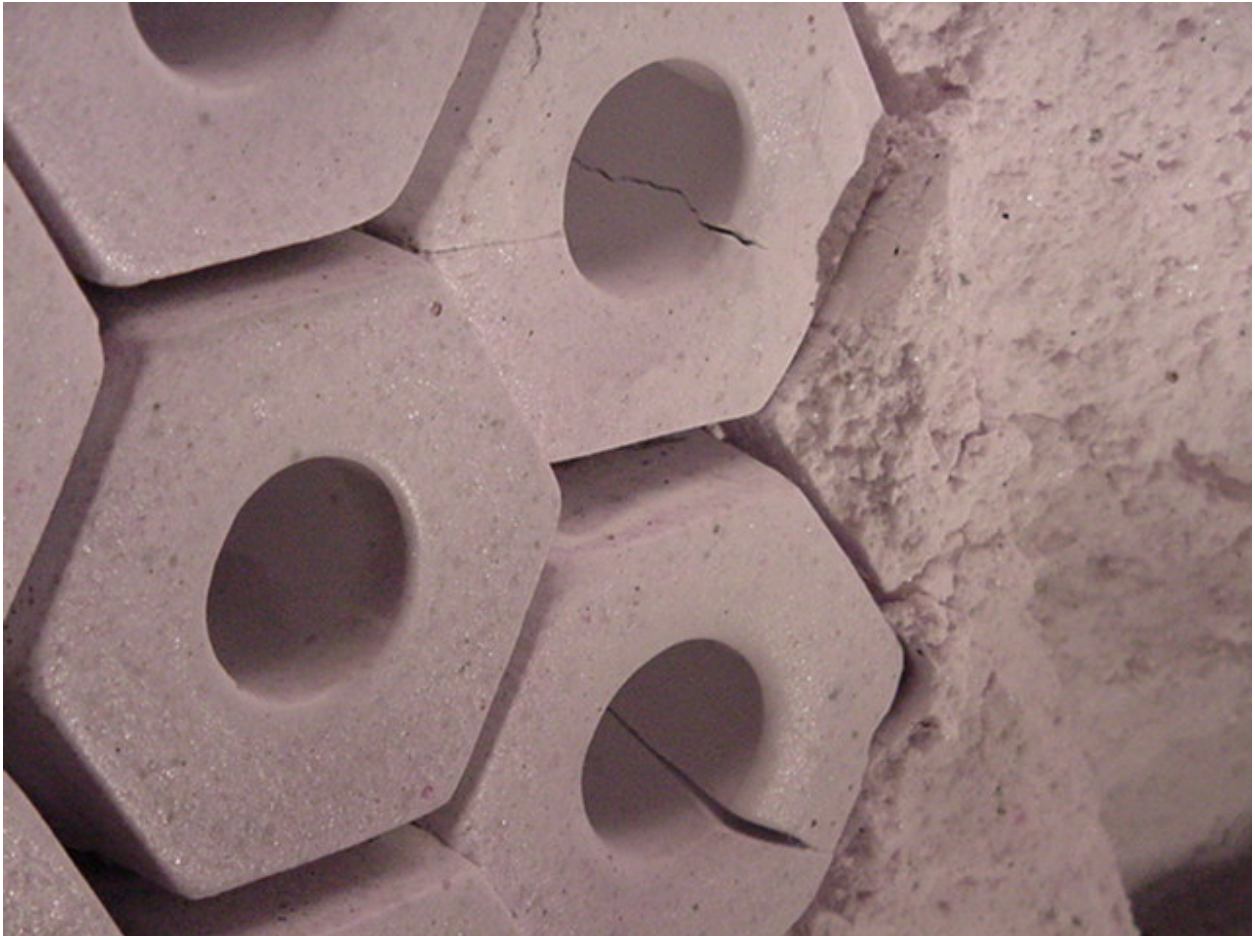


Refractory Damage from High Temperature Operation



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Refractory Damage from High Temperature Operation



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Refractory Damage from Wrong Material of Construction



Background

The first U.S. refinery Claus sulphur recovery plant was commissioned in California in 1949, and early involvement quickly established WorleyParsons predecessor, the Ralph M. Parsons Company (RMPCo), as a leader in sulphur technology by using Scotch Marine waste heat boilers in sulphur plants. In this configuration, process combustion gases pass through a relatively large firetube, surrounded by boiler water, before returning through the smaller tubes where most of the heat transfer is accomplished. Acid gas is center-fired in a relatively short refractory-lined combustion chamber, with the firetube accounting for most of the residence. Scotch Marine boilers have been in operation in Claus sulphur recovery units since the 1950s.

An advantage of the Scotch Marine design is that inlet tube sheet temperatures are reduced considerably by virtue of the limited cooling achieved in the firetube and lack of direct radiation. However, it is likely a more expensive design than prevailing straight-through configurations, and there are practical limits with regard to size and steam side pressure so Scotch Marine waste heat boilers have found limited application in Claus sulphur recovery units in recent years.

Figure 1 represents a schematic diagram of a Scotch Marine boiler.

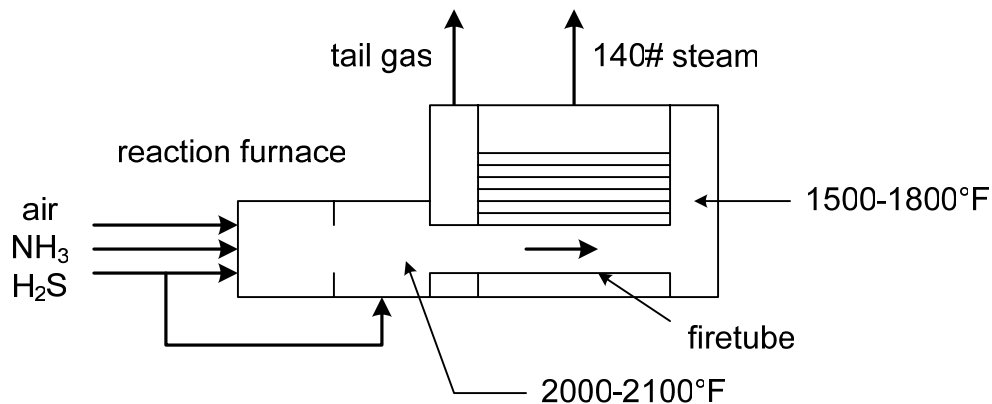


Figure 1. Scotch Marine boiler scheme

Water Wall Boiler Description

The water-wall boiler is designed with a radiant section, using water-wall tubes, capable of withstanding a bulk gas temperature of up to 5000°F (2760°C). Sufficient furnace volume is provided to achieve the residence time required for completion of the conversion reactions. A refractory-lined section may be employed to hold the temperature at a desired level to complete the conversion reactions. The combustion products are cooled to about 650°F (343°C) in the convection section of the water-wall boiler. The water-wall boiler may produce saturated and/or superheated steam.

The water-wall boiler eliminates problems associated with refractory maintenance. Fast boiler startup and heating rates are not concern with water-wall designs. The entire furnace expands and contracts uniformly as a unit. This eliminates relative expansion problems that occur at the interfaces between water-cooled walls and refractory casing. For a given volume, the water-wall boiler has lower furnace



area heat release rates and heat fluxes because the front and rear water cooled walls provide additional effective surface area.

This process can be used for new Claus plants as well as for the revamp of existing Claus units for air and/or oxygen operation.

Oil and gas-fired packaged steam generators are widely used in chemical plants, refineries and cogeneration systems. Power plant industries have converted their conventional steam generation to water wall boiler to achieve a higher efficiency, better performance, lower pressure drop, maintain uniform temperature distribution, reduce NO_x and soot formation, lower maintenance. The result is a more reliable operation at a lower cost. Water wall boilers have been used successfully for other applications such as gasifiers for major oil and gas companies and power plants and IGCC units. Water Wall Boiler is advanced technology, well proven, well known and established technology in a very large scale in the current industry. Water wall units are in operation currently in gasifiers using technology developed by Shell and by Future Energy.

Custom-designed steam generators for modified Claus sulphur plants are considered where the feed gas is a hydrogen sulfide rich feed gas stream, is increased by combusting hydrogen sulfide in one stage with an oxidant which is an oxygen rich gas stream comprised of air, oxygen or a mixture of air and oxygen.

The boiler is designed as a furnace to achieve the proper combustion with minimum pressure drop by adjusting the boiler height, tube spacing, tube counts, high efficiency, low operating cost, proper material selection and without flame impingement concerns. The water-wall boiler could replace the conventional refractory-lined reaction furnace and waste heat boiler and can be designed with partial or no refractory depending on the application.

The water-cooled furnace could be used in any new sulphur plant design where the units operates on air or oxygen enrichment or any combination of air plus oxygen instead of conventional reaction furnace. The water-wall furnace can be used in any revamp sulphur unit where there is a need for increasing capacity up to 250% by replacing the existing reaction furnace and waste heat boiler with a new water-wall boiler, which is capable of achieving up to 5000°F (2760°C) combustion temperature. The remaining existing equipment could be kept in place without any modification if they are sized properly.

Some existing sulphur plants have space limitations for additional or new equipment. Using a water wall boiler may help with space restrictions at the plants.

The water wall boiler has several advantages as follows:

1. The furnace front, rear, side walls and floor are completely water-cooled and are of membrane wall construction, resulting in a leak proof enclosure for the flame.
2. The thermal combustion step of the modified Claus process is carried out in a water-wall boiler instead of a refractory-lined reaction furnace to reduce issues with refractory design and installation.
3. The entire furnace expands and contracts uniformly avoiding casing expansion problems.
4. The current refractories commonly used in sulphur plants are limited to 3000°F (1650°C) combustion temperature, where oxygen used there is a need for intermediate cooling in stages or to provide cooled recycle gas to protect the refractory lining. The water wall boiler eliminates this temperature limitation.



5. Using a water wall boiler will eliminate the other problems such as low temperature corrosion and limits on the startup rates for refractory dryout.
6. The water wall boiler will reduce the furnace exit temperature, which helps lowering the radiant heat flux and tube failures. In a natural circulation boiler, tubes are vertical and the gas flows horizontally. Natural circulation moves the steam-water mixture through the evaporator tubes, where the gas temperature is low act as downcomer tubes, while the rest of the tubes in the radiant and convection section act as risers carrying the steam-water mixture to the steam drum. Steam temperatures could be controlled using an inter-stage de-superheater or a spray attemperator, which injects water into steam to control its temperature.
7. The membrane wall design acts as a gas tight enclosure for the flue gases and minimizes problems associated with thermal expansion and movement of the various parts of the furnace. In the membrane wall design, the entire furnace operates at a uniform temperature, so all the combustible components are reacted and differential expansion is minimal.
8. The size of the tube and pitch are optimized depending for the generation of low or high-pressure steam. CO formation could be reduced by using water cooled boiler instead of conventional furnace.
9. The water wall boiler can generate very high steam pressure beyond conventional Claus unit limit.
10. The water wall boiler is capable of processing the amine acid gas containing up to 100% by volume of hydrogen sulfide.
11. The water wall boiler will generate the high-pressure steam in the range of 250 to 750 psi.
12. The water wall boiler reduces heat losses compared to conventional reaction furnaces.

When a water wall boiler replaces the reaction furnace and the waste heat boiler in the conventional sulphur recovery units, a preliminary cost estimate indicates that the total installed cost using water wall boiler versus reaction furnace and waste heat boiler is about half for air operation and about 40% lower cost compared to the conventional configuration when using 100% oxygen enrichment.

A schematic diagram of the water wall boiler is shown in Figure 2.

The design feature includes a radiant section, using water wall tubes, capable of withstanding the 4,000 °F inlet gas temperature. Sufficient furnace volume (conversion zone) shall be provided to achieve the required residence time/ temperature. The conversion zone may consist of water wall tubes and/ or a refractory lined section depending on gas temperature. Refractory is only acceptable below 3,000 °F. Following the conversion zone, a convection section will cool the gas to the desired outlet temperature.

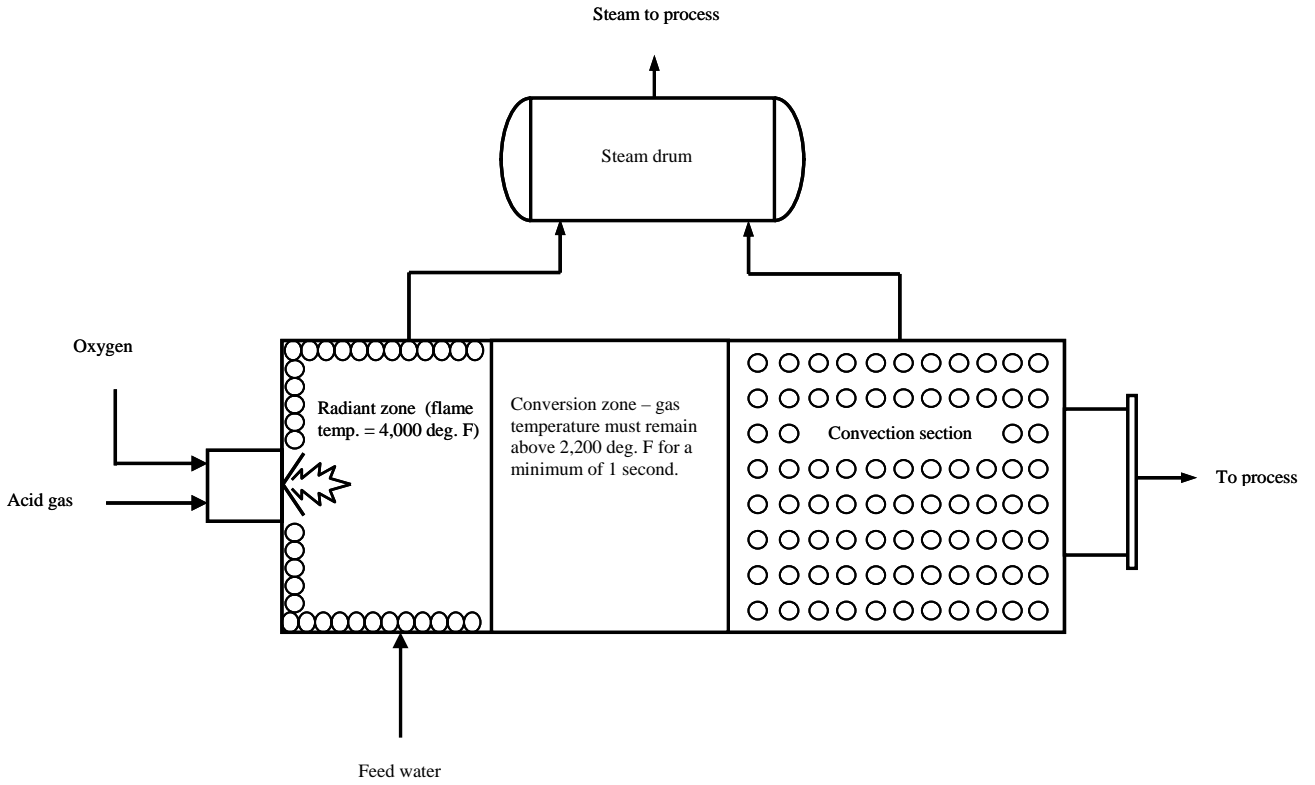


Figure 2. Water Wall Boiler Scheme



Conclusion

The water Wall Boiler is an alternative solution for the production of sulphur in conventional sulphur plants for air operation, enriched air with oxygen, or 100% oxygen enrichment for any rich or lean hydrogen sulfide stream with or without ammonia from sour water stripper for complete ammonia destruction and any other contaminants such as hydrocarbons. The sulphur recovery efficiency is the same as conventional sulphur recovery units where a reaction furnace and waste heat boiler is used.

The water wall boiler process has the following advantages:

1. Water Wall Boiler Replaces refractory-lined reaction furnace of the modified Claus process
2. Processing the acid gas combustion of hydrogen sulfide-rich or hydrogen sulfide-lean with or without contaminants such as hydrocarbons and ammonia.
3. Flexibility of mode of operation with air only, on oxygen-enriched air, or on oxygen only, which involves only the Oxygen supply system.
4. Eliminate the requirements of shutting down and isolating a recycle loop when Oxygen enrichment is not being used; this further improves the safety of the process.
5. Generate very high steam pressure beyond conventional Claus unit limit
6. Provide plant flexibility for turndown, ability to handle different feeds, and changes in production rate
7. Provide high reliability and easy maintenance
8. Reduce Capital and Operating Costs
9. Reduce Plot Space with fewer modifications, less impact on downstream equipment
10. Eliminate staged process or any recycle process to moderate the refractory temperature and eliminate a recycle blower or ejector.

Acknowledgement

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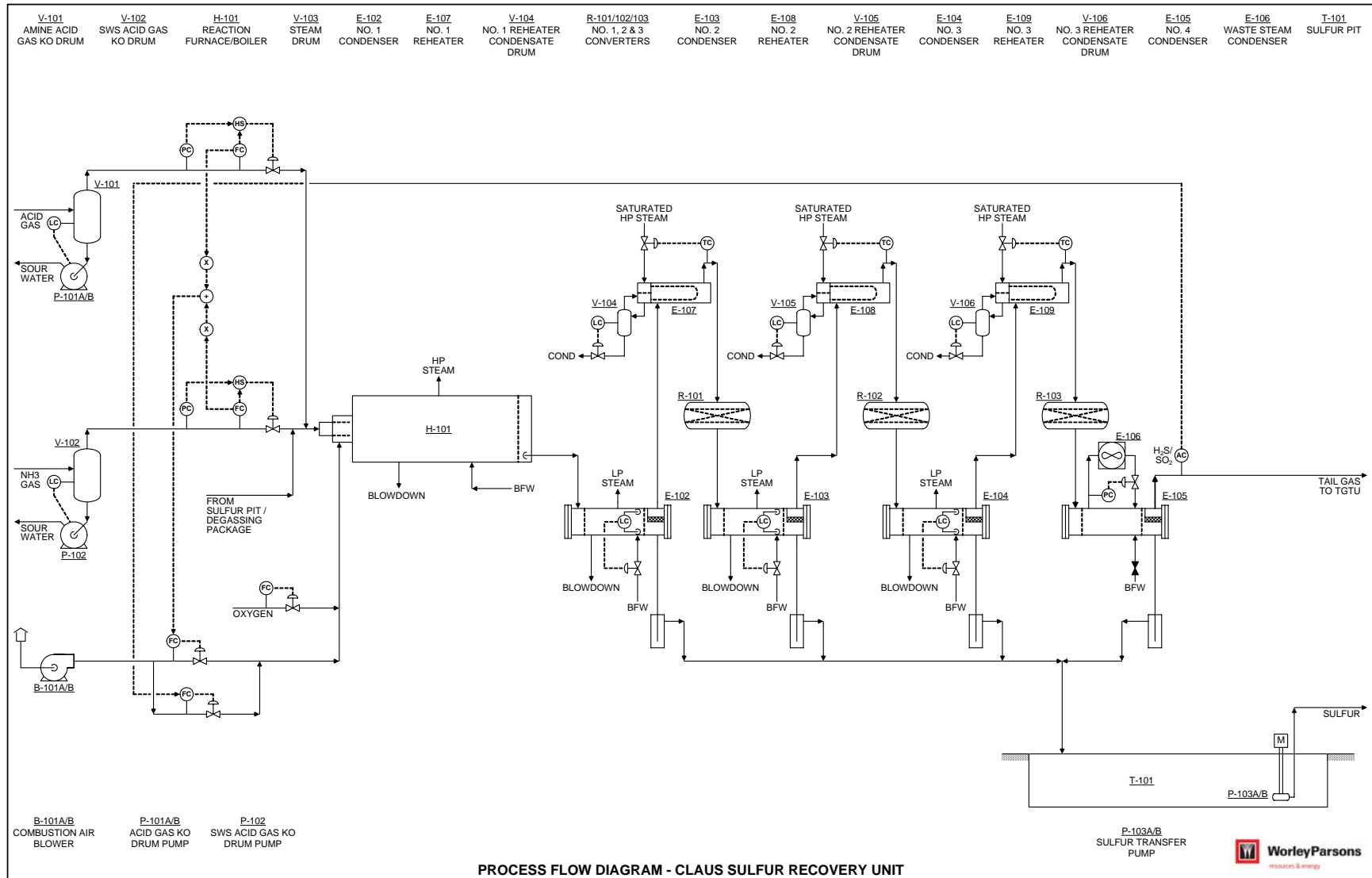


Figure 3. Water Wall Boiler Process Flow Diagram