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Improving Furnace-Boiler System in Sulfuric Acid Plants

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ABSTRACT

This paper deals with the sulfur furnace and the associated waste heat boiler system in a sulfur burning sulfuric acid plant. The shortcomings and limitations of traditional sulfur furnace and waste heat boiler arrangements are reviewed.

An improved arrangement patented by *CECEBE Technologies Inc.* is presented and its benefits are discussed.

Case studies illustrating the improved arrangement are presented. This simple but very effective improved arrangement essentially eliminates the maintenance problem with the hot bypass valve while reducing pressure drop and increasing plant capacity at modest cost.

INTRODUCTION

The design of contact sulfuric acid plants has evolved over more than a century and the origins of many of the design choices are buried in old references. In the early days, the concept of chemical processes, as process engineers now understand them, had not been developed and the choices of materials and technologies were very limited. Many of the old practices have been copied without investigating the alternatives.

One such practice is the production of SO_2 gas needed in a sulfuric acid plant by combustion of sulfur in air and the recovery of the waste heat to generate valuable steam. This paper reviews the shortcomings of the traditional design practices and offers an improved furnace-boiler bypass arrangement which permits increased plant capacity, enhanced furnace and boiler performance, reduced maintenance and longer life for the bypass valve and better control of the inlet temperature to first converter bed.

SULFUR COMBUSTION IN SULFURIC ACID PLANTS

Chemical engineers are aware that sulfur is a good fuel and burns readily. They are also generally aware that in a sulfuric acid plant, the stoichiometric gas strength for making SO_3 is 14% SO_2. However, they are aware to a lesser degree that the stoichiometric limit for burning sulfur in air is 21% SO_2. In the late nineteenth century, the industry proceeded to produce sulfuric acid using 14% SO_2 and it took several decades before it was realized that excess oxygen would be required to drive the conversion to the higher efficiencies desired. With the extra air required to provide the excess oxygen, the gas strengths used in practice dropped to between 7 and 8% SO_2 compared to the 14% stoichiometric limit.

At that time, the choices for equipment and materials were very limited with only ceramics, steel, and cast irons available. The plants were also very small and in early 1900, for example, three 50 TPD plants in the Sudbury area of Canada were considered world scale plants. The burning of sulfur reliably was considered an achievement and energy recovery downstream of the combustion process was of secondary importance as there was little heat to recover in the small capacity plants. The acid plants therefore routed all of the process air required in the converter through the furnace and the boiler. With the low gas strengths, furnace temperatures were also low and it was possible to fabricate reliable valves which would allow bypassing of downstream boilers, especially as the sizes of the valves were very small, about two feet or less in diameter.

Today, acid plant capacities have risen to over 3000 TPD, gas flows have increased by a factor of about 100, and the heat that is contained in the furnace gases has become very valuable. The cost of downtime, maintenance and repairs is also much higher. As well, the gas strengths used in the acid plants have risen from 7-8% SO_2 to about 11-12% SO_2 thereby increasing the furnace temperature from 1500 ºF to well over 2000 ºF. This is beyond the limits of the high temperature alloys, creating acute materials problems. To further compound the difficulty, steam pressures now may run as high as 900 psi which makes cooling of the gases more difficult due to the corresponding higher boiling temperature of water.

SULFUR COMBUSTION IN OTHER INDUSTRIES

Other industries, mainly pulp and paper, also burn sulfur, to make sulfite solutions. Since this industry is concerned only with forming SO_2, the challenge is the 21% SO_2 limit on stoichiometric combustion of sulfur and how close it could be approached. The furnaces used in these applications routinely run with gas strengths approaching 18% SO_2. They avoid hot downstream valves as the gas stream is usually quenched with water or aqueous solution in a scrubber. Furnace temperatures are much higher as expected from the higher gas strengths. Furnace sizes are much smaller than in sulfuric acid plants. However, the routine ability to burn sulfur in air at higher concentrations than presently practiced in sulfuric acid plants is potentially very useful to sulfuric acid plant operators as demonstrated later in this paper.

SULFUR COMBUSTION THEORY

Sulfur is normally sprayed into furnaces in the form of fine droplets through a variety of nozzles, mainly using pressure atomization. Droplet size may reach as large as 1 mm. The droplets vaporize at temperatures above 840 ºF by taking heat from the gases surrounding them and from radiation. The rate of combustion is proportional to the heat flux from the hot gas to the boiling sulfur and higher gas temperatures are associated with higher rates of burning and smaller droplets and gas residence times in the furnace. For liquid fuels, the burning time of the droplet varies with the square of the droplet diameter. Therefore, smaller droplets are desirable and are produced by using higher pressures in pressure atomizers or smaller nozzles as well as by using two-fluid nozzles or rotary cup burners. The burning rate depends, to a lesser degree, on the excess oxygen available for combustion. The variation of furnace temperature versus the SO_2 gas strength is shown in Fig. 1.

In single absorption plants without air quenching, the gas strengths were about 7 to 8% SO_2 and furnace gas temperatures were around 1500 ºF where high quality stainless steels could be used. With the double absorption processes, the gas strengths are about 10.5 to 12% SO_2 and often the air is taken hot from the air blower which raises the furnace temperature to over 2000 ºF which is too hot for the available alloys. Special valves with some valve cooling and ceramic facings are normally used. These valves or jug dampers require frequent maintenance and repairs.

BOILER DESIGN

The acid industry has proceeded from small plants, in which the steam raising was not critical, to large plants in which high pressure steam is produced in large quantities. The disadvantage of generating high pressure steam is that it boils at temperatures close to the gas temperature required for the catalyst. Consequently the heat transfer surface in the boiler becomes large. Using modern cesium catalyst to lower the first catalyst bed ignition temperature further increases the size of the boiler.

Because the only temperature control on the boiler is through bypassing some of the hot gas around the boiler, the remaining gas must be overcooled in the boiler so that the mixture is at the required converter inlet temperature. The boiler hot bypass-valve normally leaks and therefore most designers assume a minimum 5% leakage in developing the boiler specifications. The higher boiler operating temperatures required to generate higher pressure steam and the hot gas bypassing increase the area and weight of the boiler.

A typical fire-tube boiler used in sulfuric acid plants is made of carbon steel, which is not able to withstand the hot gases from the furnace, even when the gas strength is low. The front tube sheet and the tube inlets are therefore protected by ceramic facings and ferrules which can accept much higher temperatures than found in the sulfur furnaces. The heat flux through the tube walls are, even at the hot end, well below critical flux values while the flux at the cold end is very low due to the small temperature difference between the gas and the boiling water.

CONVENTIONAL FURNACE-BOILER BYPASS ARRANGEMENTS

Fig. 2 shows a conventional boiler bypass and the flows and temperatures required for normal operations with 11.5% SO_2 gas. Fig. 3 shows another conventional arrangement in which two separate bypass lines are used, one for the air bypassing around the furnace and boiler, and another for the furnace gas bypassing only the boiler. With both air and hot furnace gas bypassing the boiler the temperature of the exit gas leaving the boiler is now higher than in the arrangement shown in Fig. 2, for the same converter gas inlet temperature and results in more efficient heat transfer. However, the furnace gas temperature is higher and the corrosive attack on the bypass valve is accelerated.

For a conventional 2000 STPD double absorption plant with 11.5% SO_2 gas to the converter and the blower located before the drying tower so that the dry air is cooled, the furnace temperature can be calculated for different furnace gas strengths and quantities of bypass air. The mixed gas temperature for the gas leaving and bypassing the boiler, which has to satisfy the first catalyst bed inlet temperature, can also be calculated. Fig. 4 shows the boiler inlet and outlet temperatures for four different furnace gas strengths.

Table 1 shows the furnace temperatures, boiler LMTD, the fraction of air bypassing the furnace and the pressure drop through the furnace and boiler for different furnace gas strengths. From Table 1 one can see that the furnace temperature rises as the gas strength increases. The driving force for heat transfer improves drastically, and the flow (and hence the flow resistance or pressure drop) decreases significantly.

Figs. 4 shows that the difference between the gas temperature leaving the boiler and the boiling temperature of the water increases drastically with only modest increases in furnace gas strength. Thus, new applications using stronger gas will allow use of significantly smaller and less expensive boilers. In existing boilers, it is possible to bypass more gas around the boiler to avoid overcooling and there will be a further pressure drop reduction. This has the benefit of increasing the plant capacity.

In both of the above conventional bypass arrangements, the hot gas bypass ducting and valve are exposed to very high temperatures. Carbon steel ducting used for this service has to be brick-lined. The valve life is limited, despite the use of expensive heat and corrosion resistant alloys.

IMPROVED FURNACE-BOILER BYPASS ARRANGEMENTS(1,2)

By combining the cold air bypass around the furnace with the hot furnace gas bypass around the boiler as shown in Fig. 5 it is possible to get a colder mixed gas stream, which can be easily handled in a stainless steel valve. Such valves would operate at temperatures in the 900 - 1200 ºF range where the conventional materials are readily usable.

In Fig.5 the gas temperatures and flows are shown for the improved arrangement for a 13% SO_2 furnace gas. Boiler gas flows and temperatures for this case and for the conventional 11.5% SO_2 case are summarized in Table 2. Note that the area of the boiler for the improved bypass arrangement is significantly less than that of the conventional design or alternatively the gas flow and pressure drop through the furnace and boiler can be reduced.

There are several other interesting possibilities which can take advantage of this separate air stream. Since there is usually a large pressure drop around the furnace and boiler, it is possible to pass the separate air stream through other equipment on its way to the converter and provide cooling elsewhere in the process without increasing plant pressure drop, especially if the process stream being cooled is in parallel with another piece of equipment. The returning air, which would then be added to the bypass gas stream leaving the furnace, would be hotter. As a result, a larger boiler surface would be required and the boiler exit temperature would rise, but the heat recovered would show up as latent heat in the boiler. In this sense, heat suitable only for economizing could be transformed into heat adequate for evaporation in the main boiler. In many cases there may be too much low level heat for economizing and extra heat has to be rejected to the acid systems and then to the cooling tower.

By transferring heat to the separate air stream, such extra heat may be re-routed to vaporize boiler feed water in the boiler, where it shows up as latent heat. A flow arrangement showing an air heater using the bypass stream is presented in Fig. 6. Air is used to cool the gas between beds 3 and 4 of a single absorption plant. With this modification, all of the air previously used for dilution is available for use in all of the catalyst beds and not just the fourth bed.

OPERATING EXPERIENCE

The improved CECEBE furnace-boiler bypass arrangements have been running in two plants in the USA for several years, in one case for five years, and in another case for three years. The performance of these plants has improved and there has been no corrosion of the boiler bypass valves, eliminating a very expensive maintenance activity.

ADVANTAGES OF THE IMPROVED BYPASS SYSTEM

The improved CECEBE bypass arrangement offers the following advantages:

- ***Improved Boiler Performance and Reduced Emissions***: If the boiler is limited in capacity, the bed 1 inlet temperature may be operating hotter than optimum. The proposed bypass arrangement will improve boiler heat transfer capability and permit cooler gas to bed 1 which will improve conversion and reduce emission.

- ***Increased Plant Capacity***: With less gas flow through the furnace and boiler, the pressure loss in these two units will decrease significantly and will allow an increase in gas throughput and plant capacity for the cost of a valve and some gas ducting.

- ***Lower Operating Cost***: If increased capacity is not required then the bypass system will permit a lower pressure drop operation and reduce the blower horsepower and operating cost.

- ***Improved Reliability and Reduced Maintenance***: Plants having maintenance problems with the boiler bypass valve due to hot temperatures (over 2000 ºF) can improve the reliability of the valve because the cold bypass air reduces the temperature experienced by the valve to about 900 - 1200 ºF, significantly increasing its life.

- ***Additional Processing Options***: A secondary air stream is available which can be used for additional energy recovery and improvement of the balance between economizing and boiling in the steam system. By this method, flashing in economizers can be avoided while increasing steam recovery.

- ***Reduced Boiler Replacement Costs***: If the boiler is at the end of its service life, a less expensive boiler may be specified because of the better heat transfer offered by the proposed bypass arrangement.

- ***Reduced Ducting Costs***: Because of lower gas temperature, more expensive brick-lined carbon steel ducting can also be replaced with metallic ducting downstream of the SO_2 and cold air mixing location . This results in easier installation and lower costs.

- ***Better Furnace Performance***: Higher furnace temperature results in enhanced flame stability, improved combustion efficiency and increased burning capacity.

IMPLEMENTATION AND LIMITATIONS

The following points must to be considered before implementing this new technology:

- ***Brick-lining***: Furnaces are brick-lined and different quality bricks are usable to different temperatures. Before a drastic change in furnace operating temperature is proposed, the brick quality should be reviewed to make sure that the new conditions will not damage it. There may also be a merit in any re-bricking operation to use a higher quality brick so that the furnace can operate at a higher temperature.

- ***NOx Formation***: As furnace temperatures reach the 2300-2400 ºF range there is an increased risk of NO_X formation which will contaminate the acid product. The extent of such NO_X formation will vary from plant to plant, depending on gas mixing and hot spots as well as furnace residence time. The pick-up of NO_X in mist eliminators will vary to a degree with the type of mist eliminators used, high efficiency candles picking-up more NO_X. It is also possible to re-arrange the sulfur combustion into a stoichiometric or rich combustion step and a subsequent cooling step to minimize NO_X formation but this system is more complex and probably of little use in existing plants.

- ***Patented Technology***: This improved bypass concept is patented(1) by CECEBE Technologies Inc. and its use is possible on payment of royalty.

CONCLUSION

A simple but very effective bypass concept presented in this technical paper virtually eliminates the maintenance problems encountered with conventional designs. It also offers lower capital and operating costs, enhanced plant performance and increased plant capacity at modest cost.

ACKNOWLEDGMENT

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REFERENCES

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2. Cameron, G. M., Bhaga, D., “Sulphuric Acid Plant Maintenance and Upgrading”, SULPHUR 95, Abu Dhabi, United Arab Emirates, (Oct 15-18, 1995)

Fig. 1: Furnace Temperature versus Gas Strength

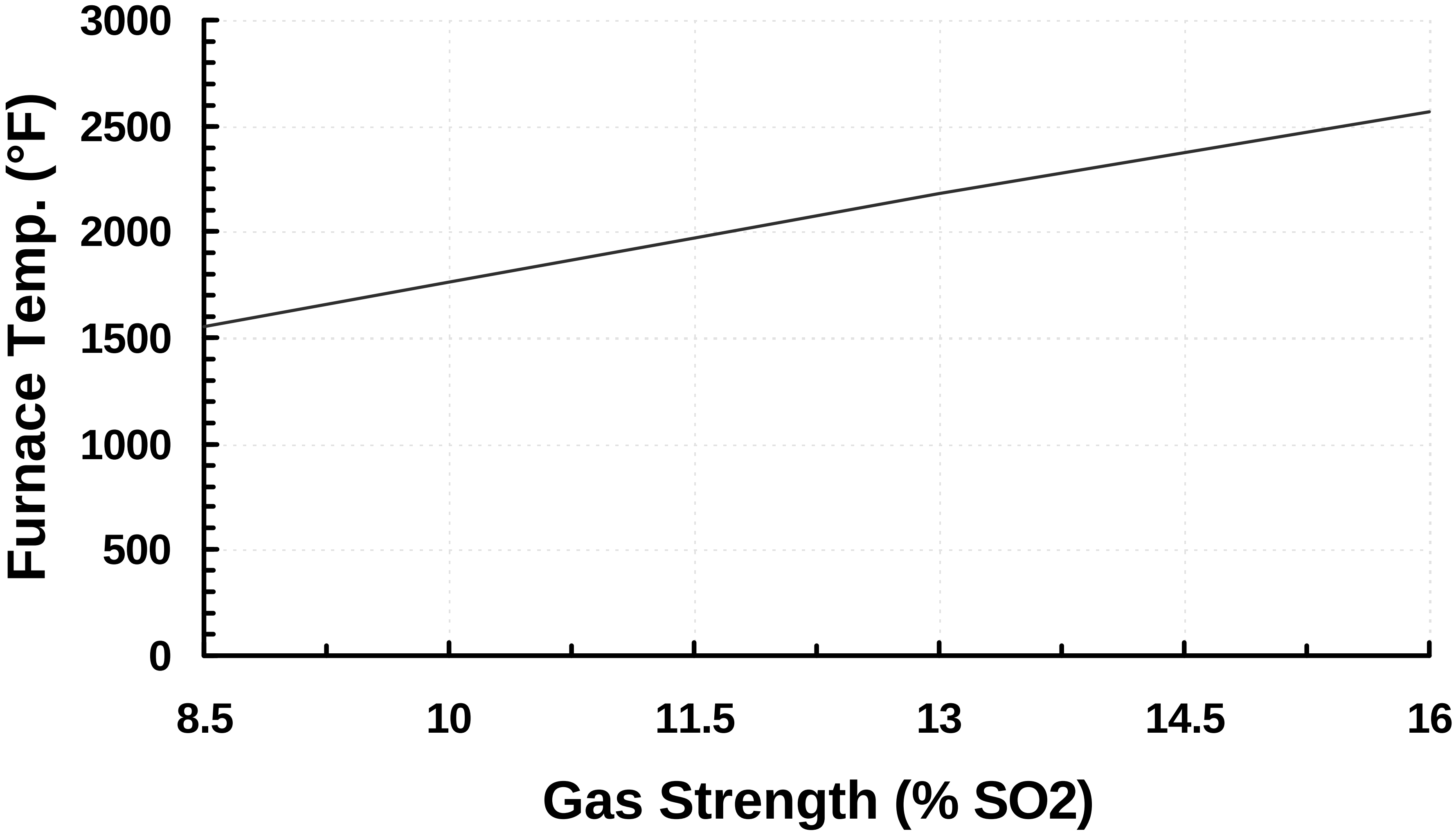
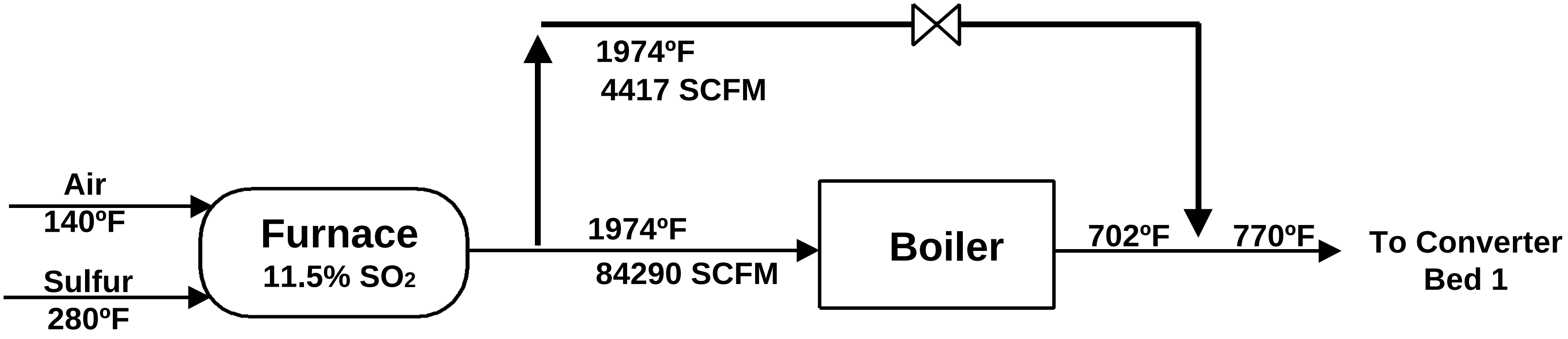


Fig. 2: Conventional Boiler Bypass Arrangement



Basis: 2000 STPD, 11.5% SO_2, 99.7% Conversion Efficiency

Fig. 3: Conventional Furnace - Boiler Bypass Arrangement

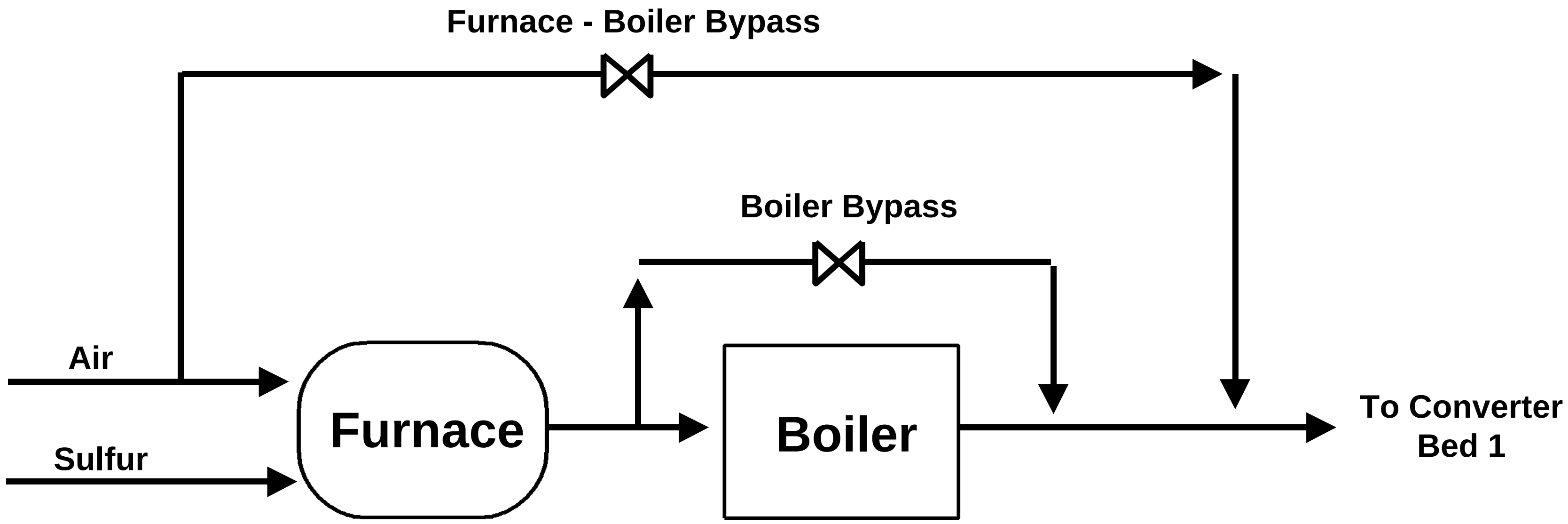
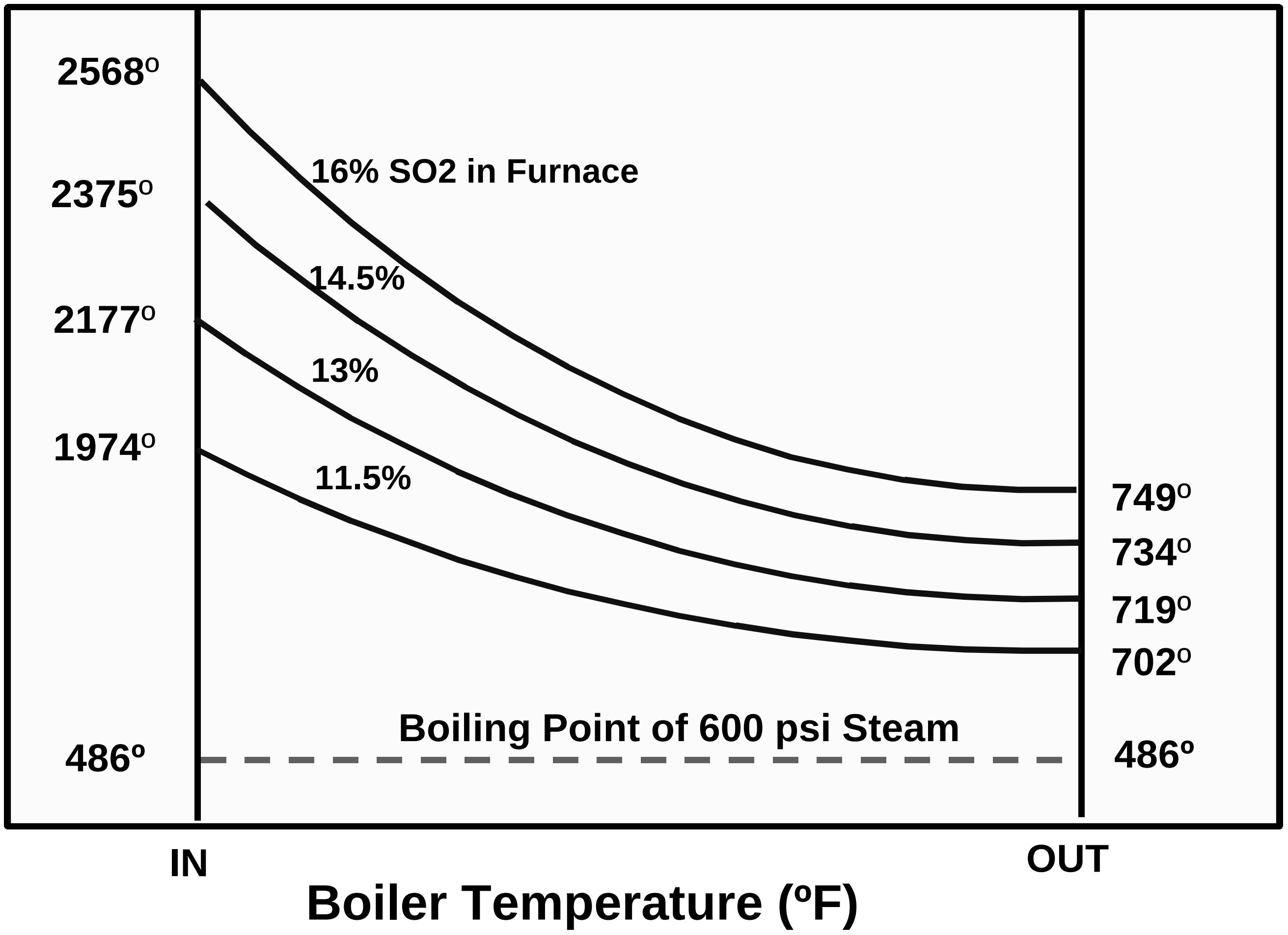
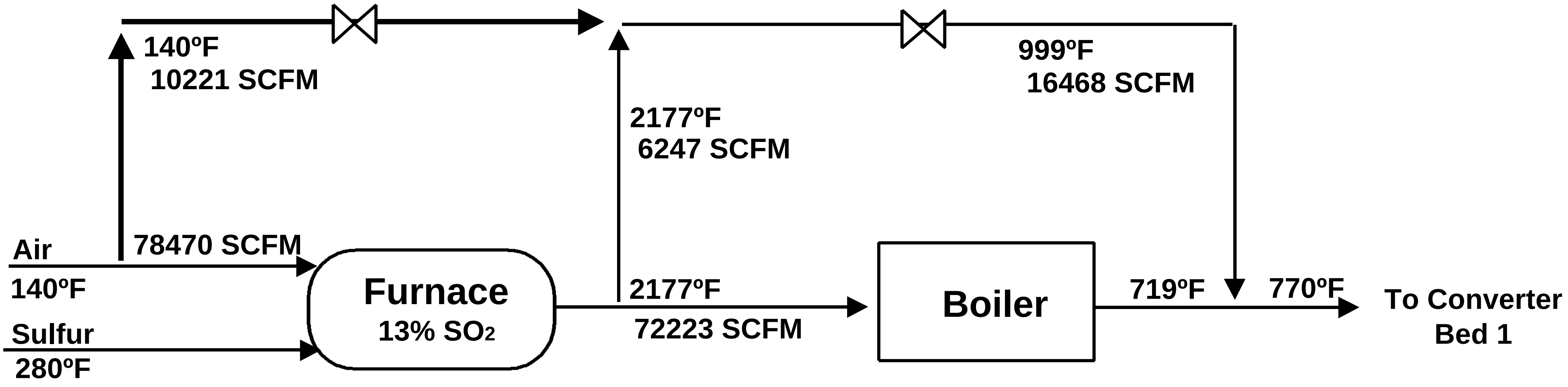


Fig. 4: Boiler Temperatures versus Gas Strength



Note: Not to Scale

Fig. 5: Improved CECEBE Furnace-Boiler Bypass



Basis: 2000 STPD, 13% SO_2, 99.7% Conversion Efficiency

Fig. 6: Improved CECEBE Bypass with Heat Recovery

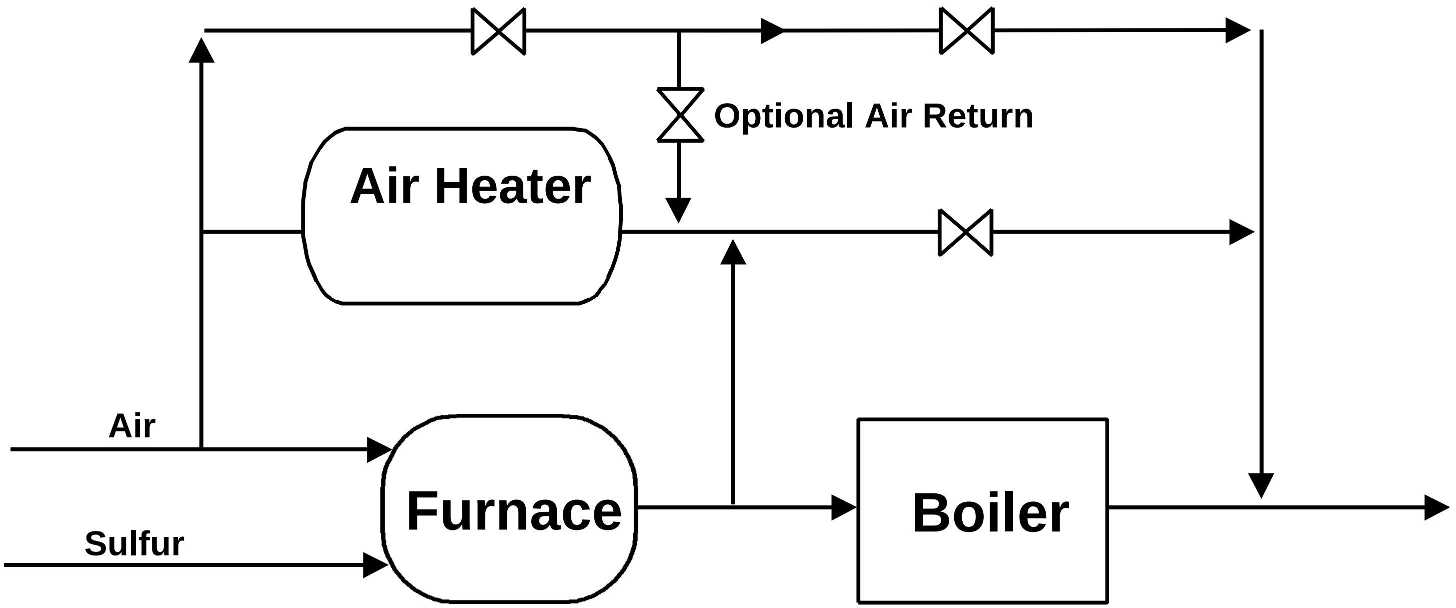


Table 1: Effect of Higher Gas Strength and Air Bypass

Gas Strength (%SO_2)	**11.5**	**13**	**14.5**	**16**
% Air Bypass	**0**	**11.5**	**20.7**	**28.1**
Furnace Temp. (ºF)	**1974**	**2177**	**2375**	**2568**
Boiler LMTD (ºF)	**653**	**729**	**802**	**873**
Furnace & Boiler DP (in. WC)	**30**	**24**	**17**	**11**

Table 2: Comparison of Bypass Arrangements

Case	Conventional Bypass	Improved Bypass
Gas Strength (%SO_2)	11.5	13
Boiler Inlet Temp. (ºF)	1974	2177
Boiler Outlet Temp. (ºF)	702	719
Bed 1 Inlet Temp. (ºF)	770	770
Gas Flow to Boiler (SCFM)	84300	72200
Boiler Area (Ft²)	25800	23100
Furnace - Boiler DP (in W.C.)	30	24