Balancing Energy Efficiency vs. Sulphur & Carbon Management in Middle Eastern Gas Processing Facilities

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ABSTRACT

Over the past several decades, governments world-wide have adopted increasingly strict clean air regulations on sulphur emissions from processing facilities, with a current industry benchmark of approximately 99.9% minimum recovery efficiency. However, this figure is on the rise with a greater number of facilities designing for higher sulphur removal rates, as evidenced by the World Bank Standard SO_2 emission specification, which currently sits at 150 mg/Nm^3 (equivalent to approximately 99.98% recovery efficiency).

While striving for increasingly lower sulphur emissions may be beneficial, it does not come free of cost. As sulphur recovery efficiency increases, the energy required to remove each additional kilogram of sulphur escalates. As energy consumption increases, so too do CO_2 emissions, which is an undesirable outcome in a time when carbon emissions reduction is among the top objectives for corporate environmental management programs. Not only is the environmental impact of greenhouse gas familiar and visible to the public, it also carries a high potential for future regulation.

This paper explores the relationship between SO_2 and CO_2 emissions in sulphur recovery facilities and investigates whether there is a point at which further increases in sulphur recovery efficiency results in diminishing returns, in terms of energy consumption and associated CO_2 footprint. Options for improving energy efficiency, thereby reducing carbon emissions, are discussed and views are presented regarding whether there are conditions under which carbon capture from sulphur recovery facilities can be a worthwhile endeavor.

This paper is an extension of a previous paper entitled “Dwindling Sulphur Emissions, at What Cost?” The purpose of the new work is to apply the basic principles developed in the original paper to examine the SO_2 and CO_2 emissions for a specific regional example.

INTRODUCTION

By the late 1980s, there were growing concerns that acid precipitation was damaging forests and aquatic ecosystems. As a result, governments world-wide began adopting increasingly strict clean air regulations on sulphur emissions from processing facilities. Flue gas from coal-fired power plants was, and still is, the primary source of SO_2 emissions contributing to these concerns. Nevertheless, sulphur recovery facilities in refineries and gas plants also came under scrutiny to substantially reduce their SO_2 impact on the environment. As a result, increased sulphur recovery emissions regulations have been imposed over the past three decades, via a stepwise approach.

Initial reductions in allowable SO_2 emissions from sulphur recovery facilities made a fairly significant impact on the global environmental landscape, as sulphur recovery efficiencies (SRE) increased from that which is achievable with a standard Claus sulphur plant (95-97% SRE), to 99% and above, which is achievable using various tail gas treating technologies. While additional SO_2 emissions reduction is beneficial for reducing the potential for acid rain, there is cause to question whether striving for ever higher recovery efficiencies (in excess of 99.9%) is actually leading to diminishing returns, in terms of increased energy consumption and associated carbon emissions. The current industry recovery efficiency benchmark is around 99.9%. However, this figure is on the rise with a greater number of facilities designing for higher sulphur removal rates, as evidenced by the World Bank Standard (WBS), which currently sits at 150 mg/Nm^3 (equivalent to approximately 99.98% recovery efficiency).

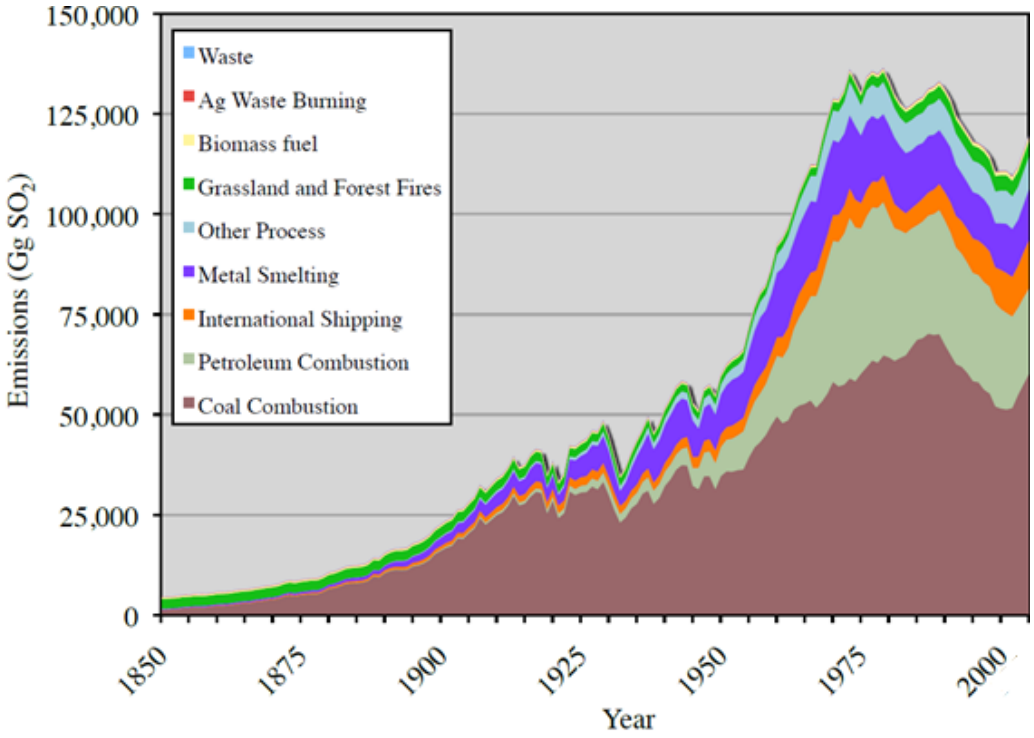
This paper explores the relationship between SO_2 and CO_2 emissions in sulphur recovery facilities and sets out to establish a reasonable balance between the two by investigating answers to the following questions:

1. How does increasing SRE positively impact global SO_2 emissions?
2. What is the corresponding negative impact on global CO_2 emissions?
3. Is CO_2 capture from SRUs a viable proposition?

GLOBAL SO_2 EMISSIONS

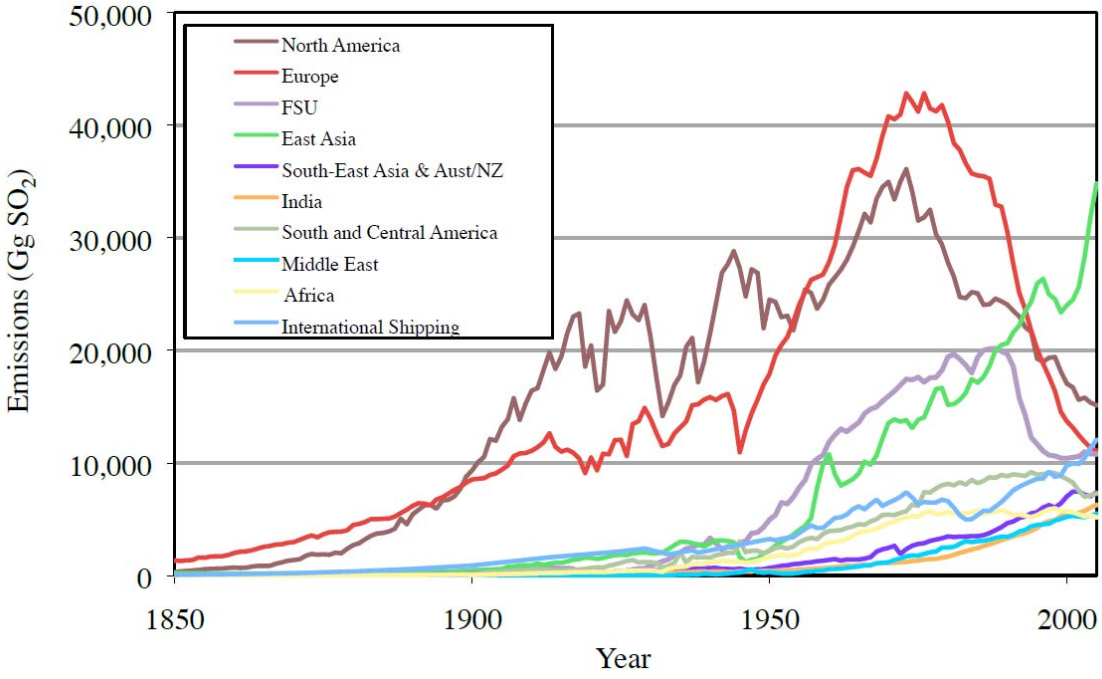
According to a recent study in the journal of *Atmospheric Chemistry and Physics,* global sulphur emissions peaked in the early 1970s and decreased until 2000, with an increase in recent years due to rising emissions in China, international shipping and developing countries in general.[1] Figures 1 and 2 illustrate estimated global anthropogenic SO_2 emissions from 1850 to 2005, by source and region, respectively. For reference, 1,000 Gg is equivalent to 1 million metric tons.

Figure 1. Global Anthropogenic SO_2 Emissions, by Primary Source



Source: Smith, SJ, J van Aardenne, Z Klimont, RJ Andres, A Volke, and S Delgado Arias. (2011). Anthropogenic Sulfur Dioxide Emissions: 1850–2005, Atmospheric Chemistry and Physics, 11:1101–1116.

Figure 2. Global Anthropogenic SO_2 Emissions, by Region

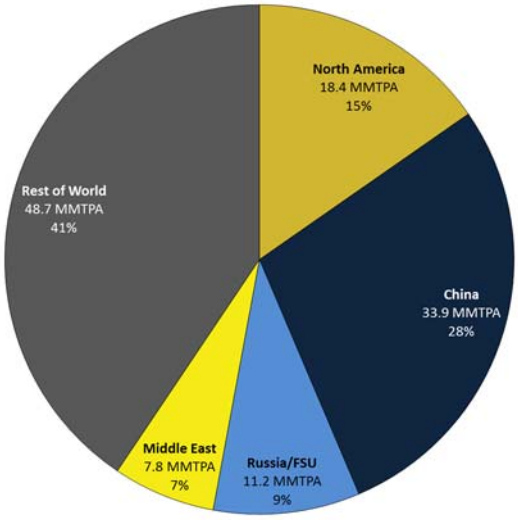


Source: Smith, SJ, J van Aardenne, Z Klimont, RJ Andres, A Volke, and S Delgado Arias. (2011). Anthropogenic Sulfur Dioxide Emissions: 1850–2005, Atmospheric Chemistry and Physics, 11:1101–1116.

Data from the referenced study do not extend beyond 2005, at which time, total SO_2 emissions were in the range of 115 million tons, up about 5 million tons from a dip in 2000. For the purpose of this paper, global anthropogenic SO_2 emissions are estimated at 120 million tons in 2013.

Figure 3 illustrates the distribution of current SO_2 emissions from the highest elemental sulphur-producing regions in the world. These regions are of particular interest due to the fact that they are some of the world's largest SO_2 emitters, while also possessing a large number of oil and gas facilities where large quantities of elemental sulphur are recovered.

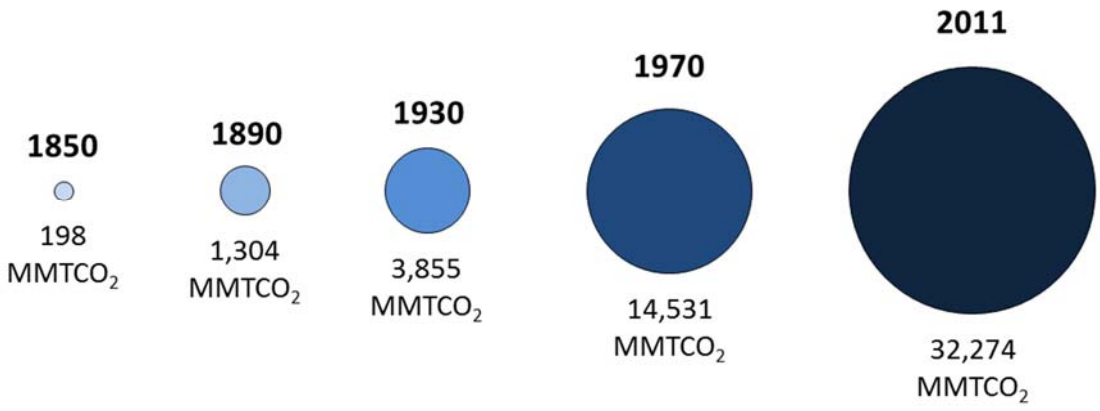
Figure 3. Anthropogenic SO_2 Emissions of World's Largest Sulphur-Producing Regions in 2013



GLOBAL CO_2 EMISSIONS

Carbon dioxide is the primary greenhouse gas emitted through human activities. In 2013, CO_2 accounted for about 82% of all anthropogenic U.S. greenhouse gas emissions. While CO_2 is emitted from a variety of natural sources, human-related emissions are primarily responsible for the increase that has occurred in the atmosphere since the industrial revolution. Global CO_2 emissions were 150 times higher in 2011 than in 1850, as illustrated in Figure 4.[2]

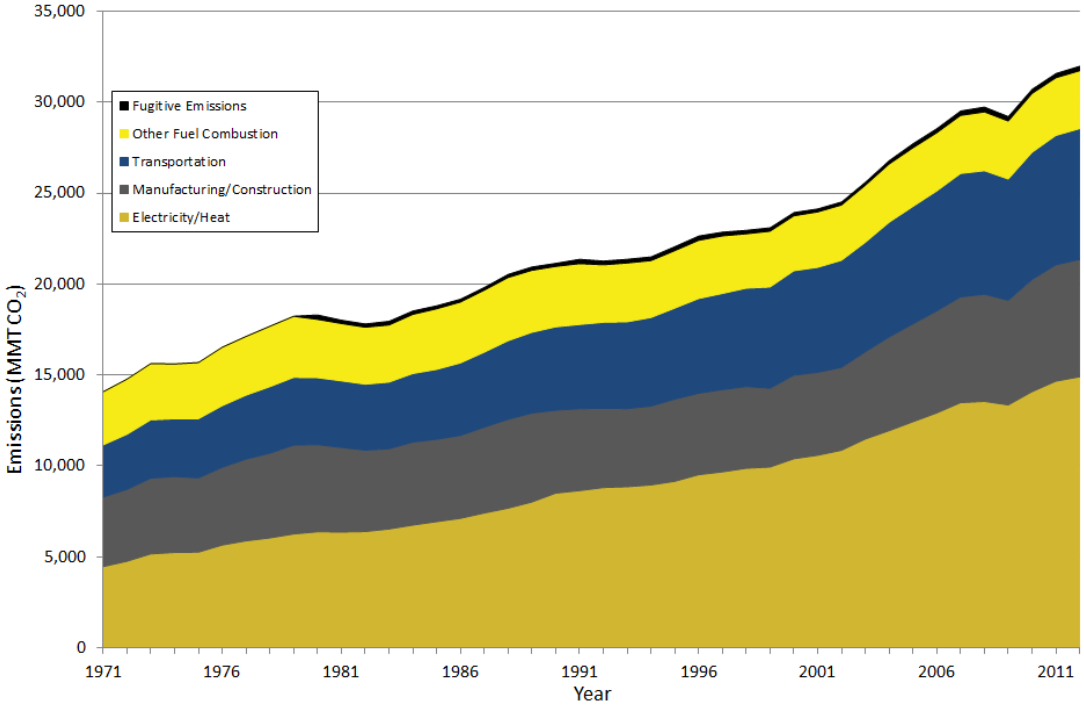
Figure 4. Global Anthropogenic Carbon Dioxide Emissions, 1850 to 2011



Source: Friedrich, Johannes and Damassa, Thomas, "The History of Carbon Dioxide Emissions," World Resources Institute Blog, May 21, 2014.

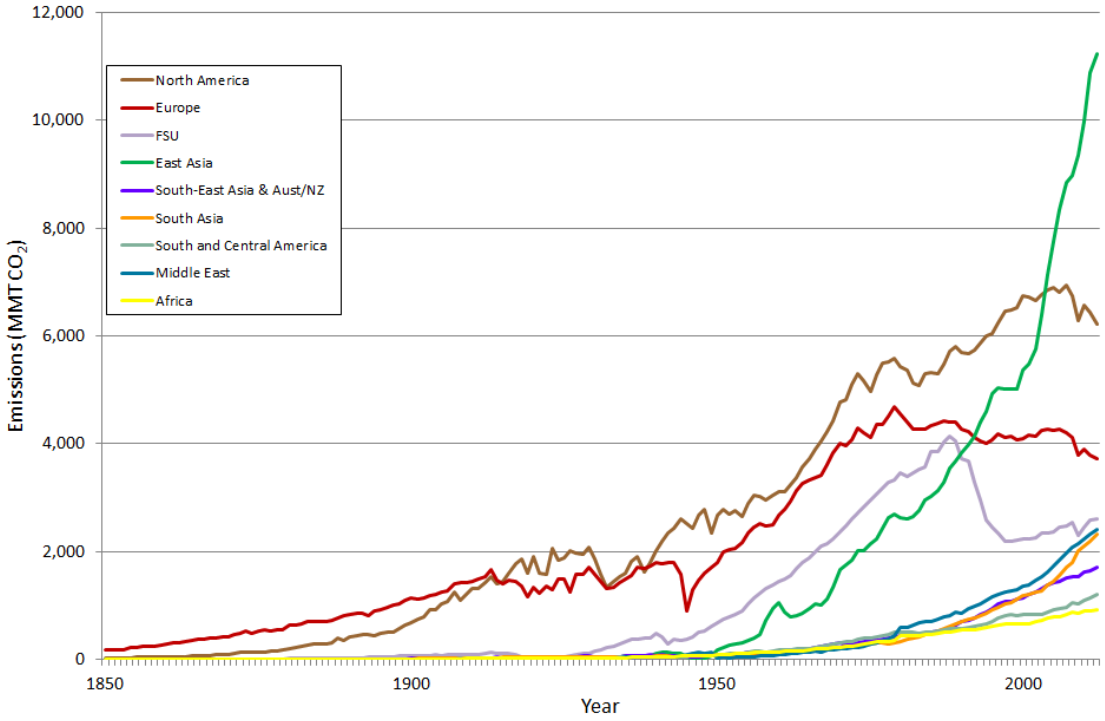
Figures 5 and 6 illustrate estimated historical global CO_2 emissions, by source and region, respectively.

Figure 5. Global Anthropogenic CO_2 Emissions, by Primary Source



Source: CAIT Climate Data Explorer. 2015. Washington, DC: World Resources Institute. Available online at: http://cait.wri.org.

Figure 6. Global Anthropogenic CO_2 Emissions, by Region

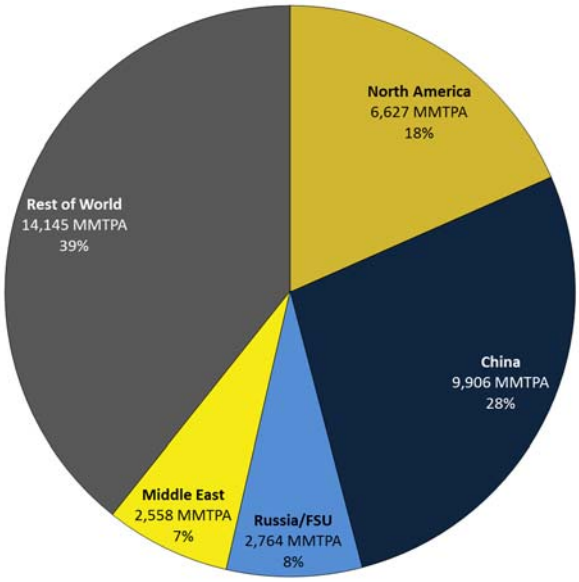


Source: CAIT Climate Data Explorer. 2015. Washington, DC: World Resources Institute. Available online at: http://cait.wri.org.

Current total anthropogenic CO_2 emissions are in the range of 36,000 MMTPA. Similar to SO_2 emissions, power generation is the number one source of carbon emissions (approximately 40% of world total), followed by transportation and industry (each approximately 20%). China leads the world in both SO_2 and CO_2 emissions. While many western nations have begun shrinking their carbon footprint, China's CO_2 emission rate is growing almost exponentially. For this reason, only a minor dip in global CO_2 emissions occurred around 2009 and has been on the rise ever since.

Figure 7 illustrates the distribution of current CO_2 emissions from the highest elemental sulphur-producing regions in the world. A comparison of Figures 3 and 7 reveals that the ranking of these regions is the same for both CO_2 and SO_2 emissions.

Figure 7. Anthropogenic CO_2 Emissions of World's Largest Sulphur-Producing Regions in 2013



TYPICAL SULPHUR RECOVERY FACILITY

To consider the impact that sulphur recovery facilities have on overall SO_2 and CO_2 emissions requires examination of the composition and flow of stack gas from a typical sulphur recovery unit. Thus, a hypothetical 1,000 MTPD sulphur recovery train has been considered, over a range of sulphur recovery efficiencies. Although 1,000 MTPD is larger than the typical average train size, this will not be important for the methodology utilized to evaluate impact on global emissions.

Considering that most refineries produce rich acid gas (H_2S > 85 mol%) and most gas plants produce relatively lean acid gas (40-50% H_2S), an average global concentration of 60 mol% is assumed. Feed gas flow and composition for the hypothetical plant are provided in Table 1.

Table 1. Feedstock for Hypothetical 1,000 MTPD Sulphur Recovery Train

	mol%	kmol/hr
Component		
H_2S	60%	1,300
CO_2	30%	650
Hydrocarbon (as C_1)	1%	22
H_2O	9%	195
Total	100%	2,166
Temperature, °C	54	
Pressure, barg	0.69	

To compare relative SO_2 and CO_2 emissions, simulations with this feedstock were generated for a range of sulphur recovery efficiency requirements. Sulsim®7 and ProTreat® were utilized for simulating the five SRE cases described below.

A. **97% SRE** – 97% recovery is based on a conventional 3-stage Claus unit.
B. **99.0% SRE** – 99.0% recovery is based on a sub-dewpoint process (2-stage Claus + 2 sub-dewpoint reactors), although it should be noted that a direct oxidation process would achieve similar SRE and stack gas flow/composition.
C. **99.3% SRE** – 99.3% recovery is based on a 2-stage Claus unit + TGTU (MDEA). This SRE is just beyond the upper limit of an achievable guarantee value for sub-dewpoint and direct oxidation processes; therefore, it was investigated as the entry point for an amine based TGTU.
D. **99.9% SRE** – 99.9% recovery is based on a 2-stage Claus unit + TGTU (MDEA).
E. **150 mg SO_2/Nm^3** – The World Bank Standard case (99.98% SRE) is based on a 2-stage Claus unit + TGTU (MDEA). A more selective solvent may be considered for this high recovery case, to reduce solvent circulation, but MDEA was used to allow consistent relative evaluation between all cases.

Process flow diagrams for the five SRE cases are provided in Figures 8-10.

Figure 8. Process Flow Diagram for Case A, 97% SRE

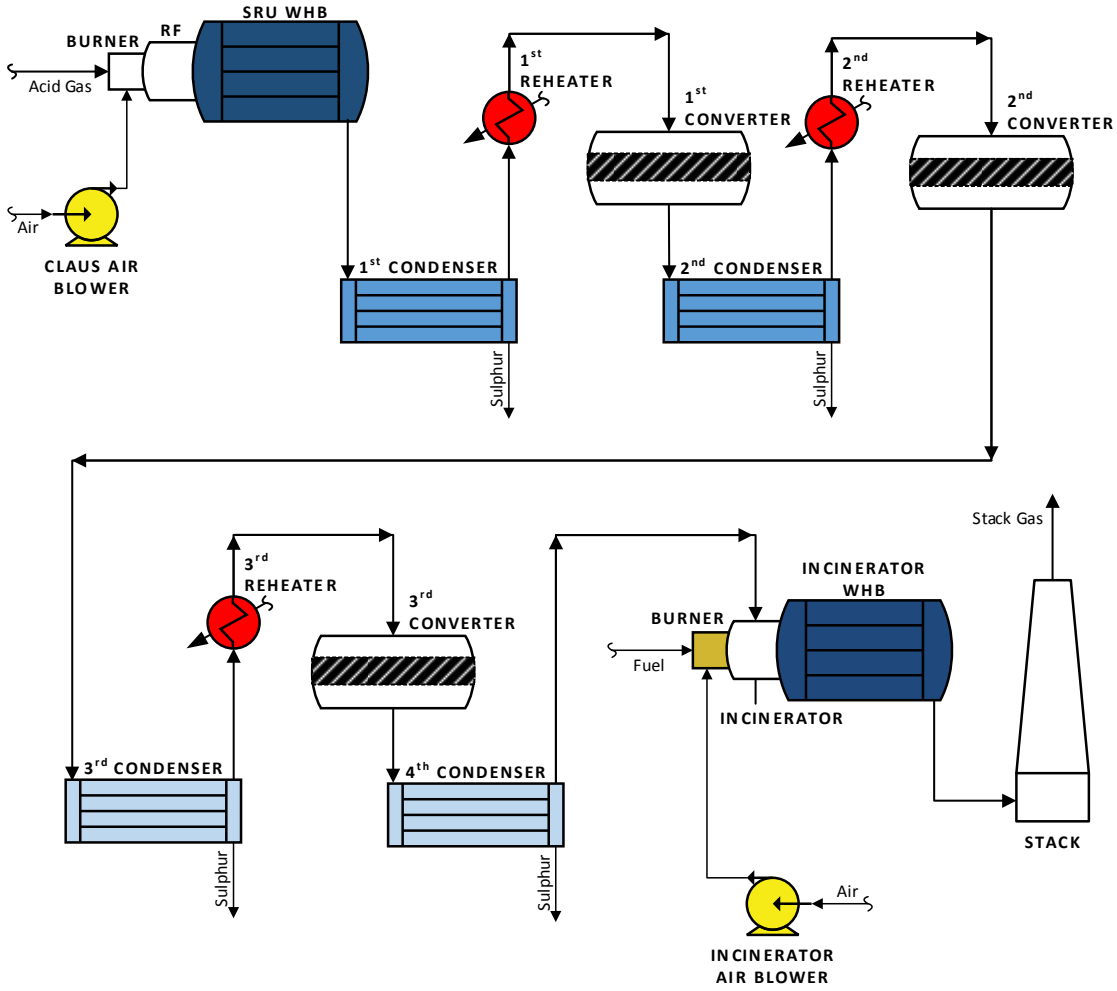


Figure 9. Process Flow Diagram for Case B, 99.0% SRE

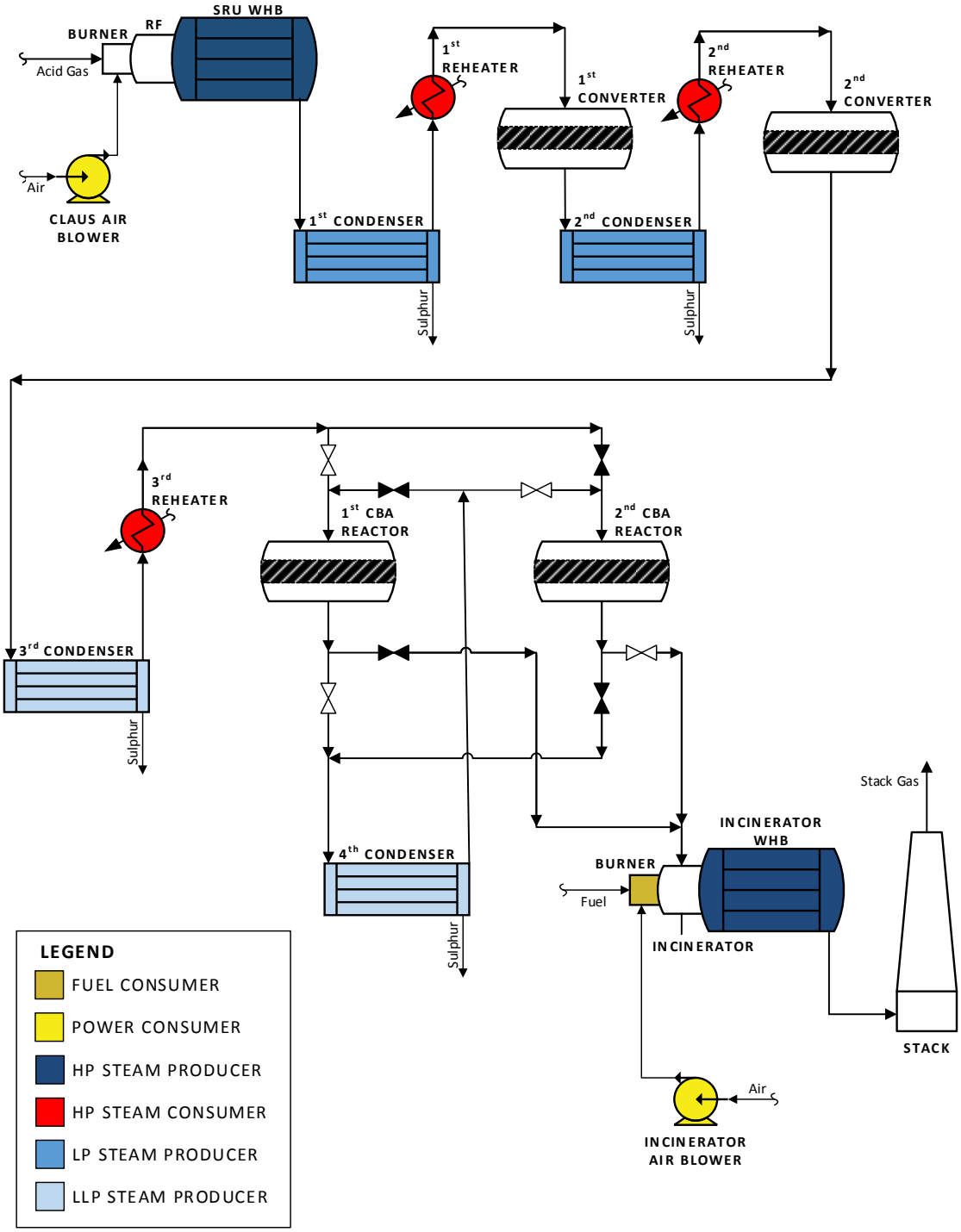
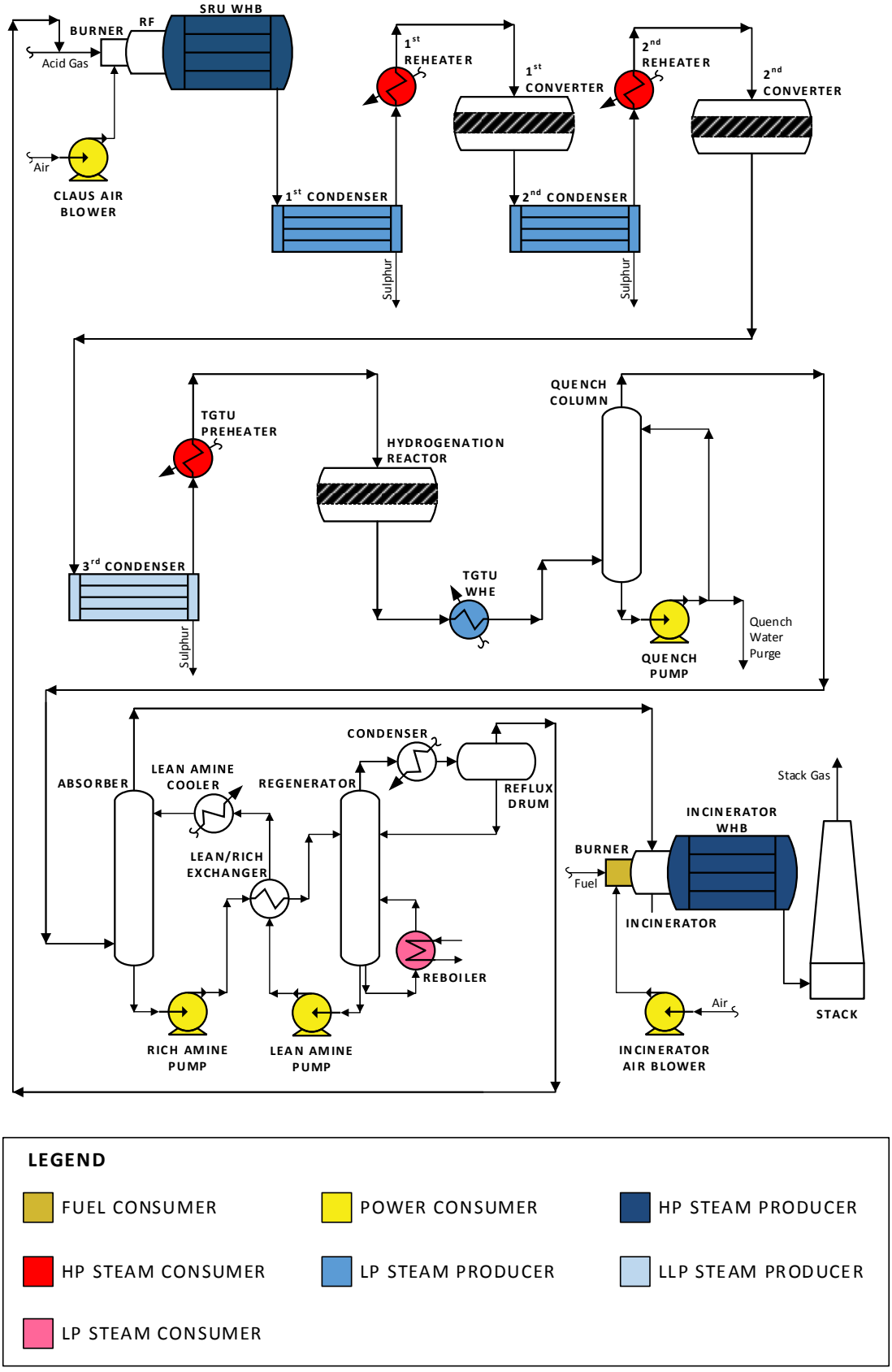


Figure 10. Process Flow Diagram for Cases C-E, 99.3 – 99.98% SRE



A standard design basis was employed for all cases to allow relative comparison on a consistent basis. Key design parameters are provided below.

- Sulphur Recovery Unit
  - Air-only operation
  - HP steam (40 barg) produced in SRU waste heat boiler (WHB)
  - 2 Claus beds (3 for 97% SRE case) with promoted activated alumina catalyst
  - 2 additional sub-dewpoint beds for 99.0% SRE case
  - LP steam (3.5 barg) produced in 1st & 2nd sulphur condensers
  - LLP steam (1.0 barg) produced in 3rd & 4th sulphur condensers
  - HP steam (40 barg) consumed in SRU reheaters

- Tail Gas Treatment Unit
  - HP saturated steam (40 barg) consumed in preheater
  - Low temperature hydrogenation catalyst
  - LP steam (3.5 barg) produced in TGTU waste heat exchanger (WHE)
  - MDEA solvent (lean temperature of 50°C for all except Case E, which was reduced to 40°C to achieve ultra-high SRE using MDEA)
  - LP steam (3.5 barg) consumed in regenerator reboiler

- Incinerator
  - Operated at 815 °C (upper limit, required for achieving <5 mg/Nm^3 TRS)
  - 2% excess O_2 in stack gas
  - Natural gas fired (LHV of 8,953 kcal/Nm^3)
  - HP saturated steam (40 barg) produced in incinerator waste heat boiler
  - No sulphur pit ejector routed to incinerator

The SO_2 and CO_2 content of the incinerator stack gas were compared for the range of SRE cases, as summarized in Table 2. For the amine-based TGTU cases, amine circulation rate and TGTU absorber overhead H_2S concentration are also provided for information.

Table 2. 1,000 MTPD Hypothetical Sulphur Train Process Parameters

	97% SRE		**99.0% SRE**		**99.3% SRE**		**99.9% SRE**		**150 mg SO_2/Nm^3**	
Incinerator Stack Gas Composition										
	mol%	**kmol/hr**	**mol%**	**kmol/hr**	**mol%**	**kmol/hr**	**mol%**	**kmol/hr**	**mol%**	**kmol/hr**
O_2	2.00%	16.97	2.00%	162.70	2.00%	123.48	2.00%	123.72	2.00%	123.73
N_2	59.95%	4857.64	59.89%	4874.31	71.42%	4411.07	71.45%	4421.84	71.46%	4422.81
CO_2	10.75%	**870.64**	10.88%	**885.69**	13.69%	**845.35**	13.75%	**850.63**	13.75%	**851.19**
SO_2	0.48%	**38.95**	0.16%	**12.97**	0.15%	**9.04**	200 ppmv	**1.24**	45 ppmv	**0.28**
H_2O	26.82%	2172.97	27.07%	2203.06	12.75%	787.60	12.78	790.93	12.78	791.20
Total	100%	8102.17	100%	8138.73	100%	6176.54	100%	6188.37	100%	6189.22
Key TGTU Process Parameters										
MDEA Circ. Rate (m^3/hr)	---		---		176		264		1,026	
TGTU Absorber Ovhd H_2S (ppmv)	---		---		2,609		345		74	

When considering the carbon footprint of a sulphur recovery facility, it is important to look beyond the obvious CO_2 content of the stack gas. It is also essential to take into account the equivalent CO_2 emissions associated with all of the major energy producers and consumers in the facility. Table 3 summarizes the energy balance for each case. These values are used to generate equivalent CO_2 values for further evaluation of the facility's overall CO_2 footprint.

Table 3. Energy Balance Information for 1,000 MTPD Hypothetical Sulphur Recovery Train

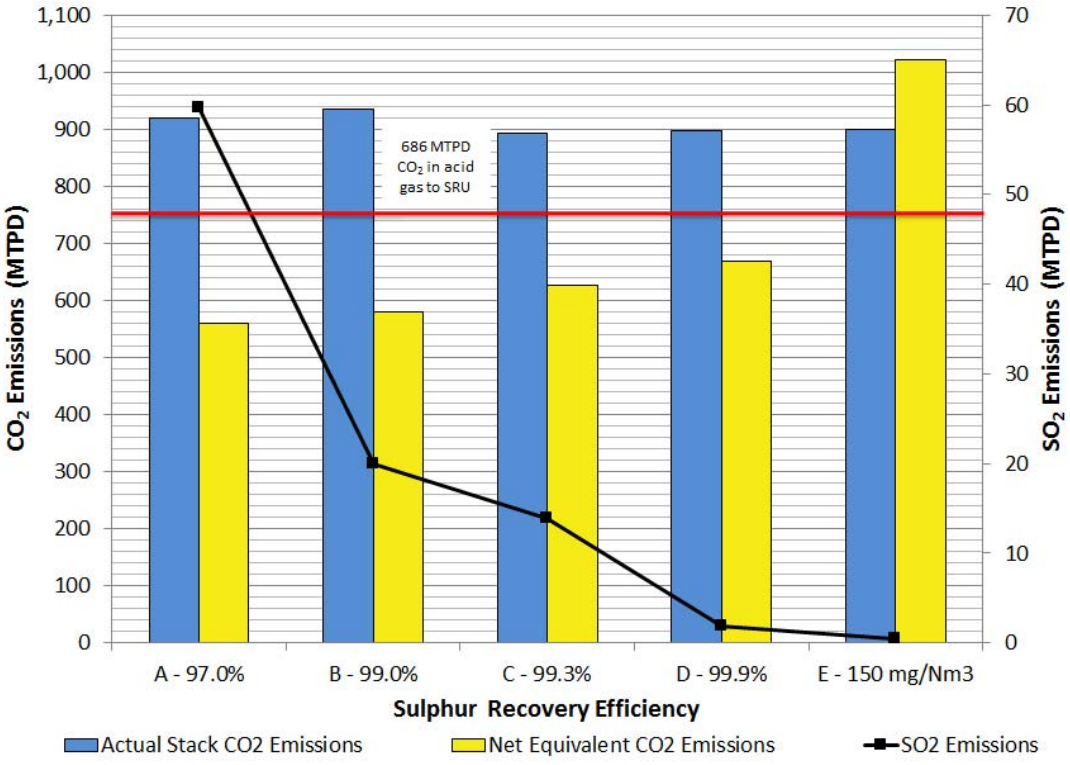
	97% SRE	99.0% SRE	99.3% SRE	99.9% SRE	150 mg SO_2/Nm^3
Major Power Consumers					
Claus Air Blowers	1,516 kW	1,520 kW	2,001 kW	2,012 kW	2,014 kW
Quench Pumps	N/A	N/A	75 kW	75 kW	75 kW
Amine Pumps	N/A	N/A	83 kW	126 kW	486 kW
Incinerator Air Blowers	246 kW	247 kW	196 kW	196 kW	196 kW
Incinerator Fuel	4,213 Nm^3/hr	4,531 Nm^3/hr	3,677 Nm^3/hr	3,789 Nm^3/hr	3,803 Nm^3/hr
HP Steam Producers					
SRU WHE	53,921 kW	54,044 kW	55,256 kW	55,586 kW	55,561 kW
Incinerator WHB (815°C)	40,460 kW	40,615 kW	30,379 kW	30,424 kW	30,429 kW
HP Steam Consumers					
1st & 2nd SRU Reheaters	7,376 kW	7,210 kW	7,604 kW	7,638 kW	7,678 kW
3rd SRU Reheater	2,352 kW	1,350 kW	N/A	N/A	N/A
TGTU Reactor Preheater	N/A	N/A	4,382 kW	4,401 kW	4,423 kW
LP/LLP Steam Producers					
1st & 2nd Sulphur Condensers	19,544 kW	19,620 kW	20,255 kW	20,353 kW	20,431 kW
3rd Sulphur Condenser	4,954 kW	4,092 kW	5,282 kW	5,307 kW	5,329 kW
4th Sulphur Condenser	2,677 kW	4,185 kW	N/A	N/A	N/A
TGTU Hydrogenation WHE	N/A	N/A	3,592 kW	3,609 kW	3,622 kW
LP Steam Consumers					
Regenerator Reboiler	N/A	N/A	12,266 kW	18,610 kW	86,820 kW
Net Energy Balance					
	66,228 kW produced	65,082 kW produced	49,896 kW produced	42,795 kW produced	25,892 kW consumed

IMPACT OF SULPHUR RECOVERY FACILITIES ON GLOBAL SO_2 & CO_2 EMISSIONS

While SO_2 emissions have an immediate impact near the pollution source, it is believed that CO_2 is more likely to have long-term effects on the global environment. Thus, local communities have strong incentives to reduce SO_2 emissions from SRUs in oil and gas operating facilities but CO_2 emissions are still not regulated in most parts of the world. For this reason, SO_2 and CO_2 emissions from sulphur recovery facilities will be explored on both a global and regional basis.

Figure 11 illustrates SO_2 and CO_2 emissions from the hypothetical SRU for each of the cases described above. CO_2 in flue gas is shown, along with a net equivalent CO_2 value that is calculated based on the information provided in Table 3 (see Appendix for net CO_2 equivalent calculation methodology). Because a sulphur recovery facility is normally an energy exporter, net CO_2 equivalent is lower than the actual CO_2 value in the flue gas for all except Case E. It is important to remember that the TGTU for the WBS case (Case E) utilizes generic MDEA, rather than a highly selective solvent. The use of proprietary selective solvents will be discussed later in this paper.

Figure 11. SO_2 and CO_2 Emissions from Hypothetical Sulphur Recovery Facility



As shown in Figure 11, SO_2 emissions decrease substantially from Case A to D, while net CO_2 emissions only increase by about 20%. However, in increasing sulphur recovery from Case D to the WBS specification, there is only a very minor decrease in SO_2 emissions with a significant corresponding CO_2 increase of more than 50%. The dramatic increase in CO_2 emissions for only a marginal decrease in SO_2 emissions can be more clearly illustrated with the correlations provided below.

When increasing SRE from 99.0% to 99.9%:

- Every 1 ton of SO_2 reduction results in 5 tons of CO_2 emissions, or
- Every 1 ton of S reduction results in 10 tons of CO_2 emissions

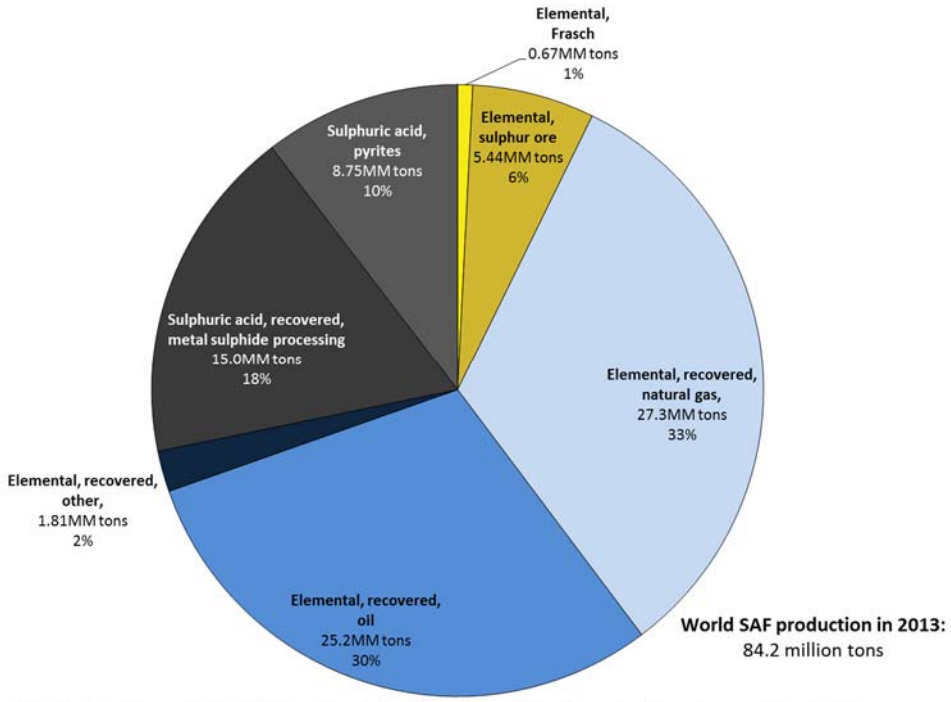
When increasing SRE from 99.9% to 150 mg/Nm^3 (99.98%):

- Every 1 ton of SO_2 reduction results in 240 tons of CO_2 emissions, or
- Every 1 ton of S reduction results in 480 tons of CO_2 emissions

The impact of increasing SRE to ultra-high values, in excess of 99.9%, clearly has a significant impact on energy consumption and CO_2 emissions, which begs the question as to whether the minor SO_2 reduction benefit is justified. This question can be addressed by looking at how the above figures for a single sulphur recovery train translate to the global SO_2 and CO_2 landscape. To do this, it is first necessary to review current world sulphur production figures so that the hypothetical sulphur recovery facility can be scaled up accordingly.

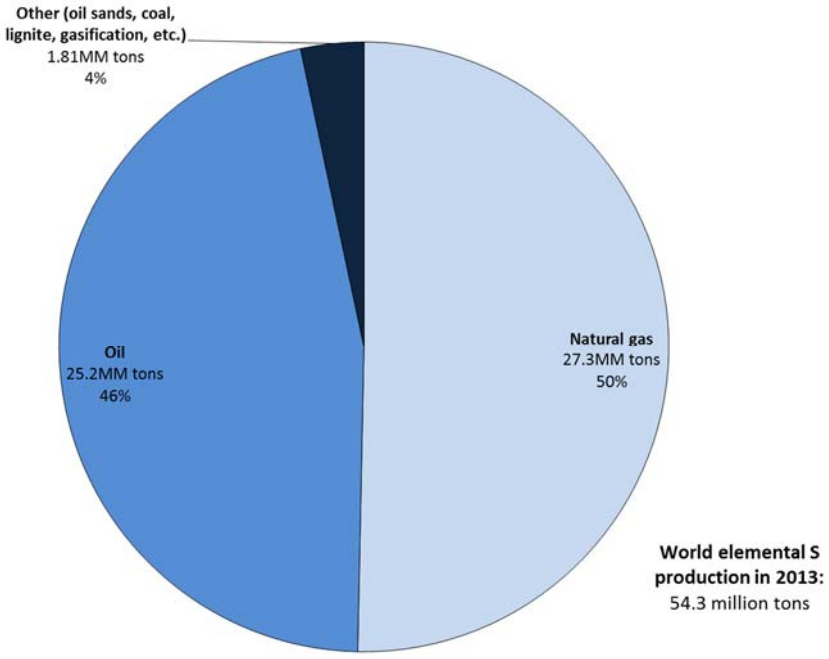
As shown in Figures 12 and 13, world elemental sulphur production in 2013 was approximately 54.3 million tons. The roughly equivalent split between sulphur from oil and natural gas validates the previous premise of 60 mol% H_2S in the acid gas. Thus, the hypothetical SRU provides a reasonable basis for predicting emissions from SRUs worldwide.

Figure 12. World Production of Sulphur in All Forms (SAF) in 2013, by Source



Source: British Geological Survey . 2015. *World Mineral Production 2009-2013*. Available online at: http://www.bgs.ac.uk/mineralsUK/.

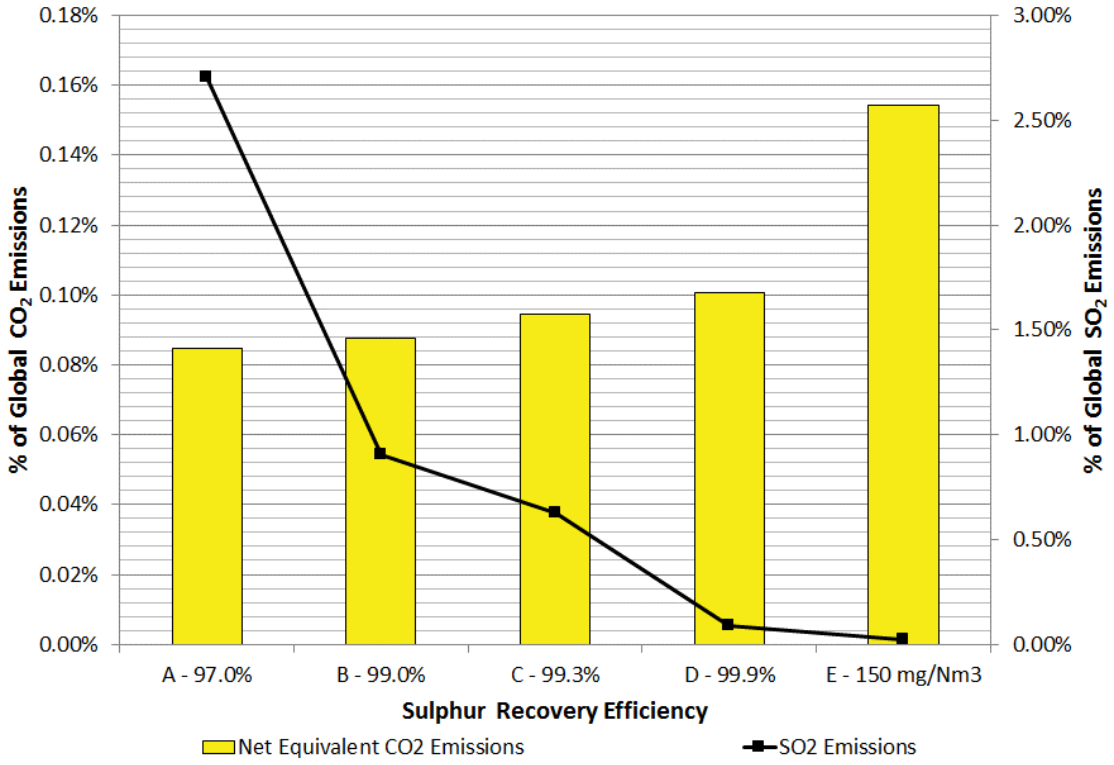
Figure 13. World Production of Elemental Sulphur in 2013, by Source



Source: British Geological Survey . 2015. *World Mineral Production 2009-2013*. Available online at: http://www.bgs.ac.uk/mineralsUK/.

Scaling up from the 1,000 MTPD hypothetical sulphur plant to a global production of 54.3 MMTPA gives SO_2 and equivalent CO_2 emissions (as % of world totals) as shown in Figure 14.

Figure 14. Global Contribution to SO_2 and CO_2 Emissions from SRUs Worldwide



Assuming a world average sulphur recovery efficiency in the range of 99.5 – 99.9%, Figure 14 illustrates that sulphur recovery facilities contribute somewhere around 0.3% of global SO_2 emissions and less than 0.1% of global CO_2 emissions. Increasing recovery efficiency from 99.3% to 99.9% with an amine based TGTU (Case C to Case D) only very slightly increases CO_2 emissions but substantially reduces SO_2 emissions. For this reason, if amine-based tail gas treating is employed, it is certainly worthwhile to design for at least 99.9% SRE, from both an energy efficiency and CO_2 footprint perspective. Similar to what was observed in Figure 11, increasing SRE to greater than 99.9% achieves little benefit with respect to SO_2 emissions but has a significant detrimental impact on CO_2 emissions.

Table 4 provides tabulated data from Figure 14, as well as SO_2 and CO_2 emission data for the most significant sulphur producing regions in the world. The range of actual emissions contributed by local SRUs is shaded, based upon assumed average SRE for sulphur recovery facilities in that particular region.

Table 4. SO_2 and CO_2 Emissions from Global Sulphur Recovery Facilities in 2013

	World	North America	Russia & FSU	Middle East	China
Elemental Sulphur Production					
MMTPA	**54.3**	**15**	**11**	**9**	**7**
MTPD	**148,767**	**41,096**	**30,137**	**24,658**	**19,178**
SO_2 Emissions from all SRUs (MMTPA)					
If 97% SRE	3.24	0.90	0.66	0.54	0.42
If 99.0% SRE	1.08	0.30	0.22	0.18	0.14
If 99.3% SRE	0.75	0.21	0.15	0.13	0.10
If 99.9% SRE	0.10	0.03	0.02	0.02	0.01
If 150 mg/Nm³ SO_2	0.02	0.01	0.005	0.004	0.003
Anthropogenic SO_2 from all Sources (MMTPA)	**120**	**15.1**	**10.0**	**5.5**	**32.7**
SRUs Contribution to Total Global or Regional SO_2 Emissions					
If 97% SRE	2.70%	5.93%	6.57%	9.77%	1.28%
If 99.0% SRE	0.90%	1.98%	2.19%	3.26%	0.43%
If 99.3% SRE	**0.63%**	1.38%	1.53%	2.27%	0.30%
If 99.9% SRE	**0.09%**	0.19%	0.21%	0.31%	0.04%
If 150 mg/Nm³ SO_2	0.02%	0.04%	0.05%	0.07%	0.01%
CO_2 Emissions from all SRUs (MMTPA)					
If 97% SRE	30.5	8.4	6.2	5.0	3.9
If 99.0% SRE	31.5	8.7	6.4	5.2	4.1
If 99.3% SRE	34.0	9.4	6.9	5.6	4.4
If 99.9% SRE	36.3	10.0	7.4	6.0	4.7
If 150 mg/Nm³ SO_2	55.5	15.3	11.2	9.2	7.2
Anthropogenic CO_2 from all Sources (MMTPA)	**36,000**	**5,900**	**2,250**	**2,200**	**8,300**
SRUs Contribution to Total Global or Regional CO_2 Emissions					
If 97% SRE	0.08%	0.14%	0.27%	0.23%	0.05%
If 99.0% SRE	0.09%	0.15%	0.28%	0.24%	0.05%
If 99.3% SRE	**0.09%**	0.16%	0.31%	0.26%	0.05%
If 99.9% SRE	**0.10%**	0.17%	0.33%	0.27%	0.06%
If 150 mg/Nm³ SO_2	0.15%	0.26%	0.50%	0.42%	0.09%

As would be expected, SRUs located in some of the world's most significant sulphur-producing regions contribute a greater percentage to regional SO_2 and CO_2 emissions than the world average, due to a high level of industrial activity in those locations. For example, contribution from Middle Eastern SRUs to local SO_2 emissions is in the range of 2-3%, an order of magnitude greater than the contribution of all SRUs to the world average. Middle Eastern SRUs contribute greater than 0.2% of local CO_2 emissions, approximately double the world average. China is an exception, with a lower contribution of SO_2 and CO_2 emissions from sulphur recovery facilities, which results from the large quantities of these pollutants emitted from coal-fired power plants. When compared to the world average, North American SRUs have a less significant impact on local SO_2 emissions due to relatively high recovery efficiency requirements in the region.

A SPECIFIC REGIONAL EXAMPLE

The authors were interested in validating some of the regional figures above with real world data; thus, an investigation of the sulphur facilities in Abu Dhabi was undertaken. Middle Eastern sulphur production at the end of 2015 was 14.3 million tons per annum (~24% of world total), making it the largest sulphur producing region in the world. This figure is more than 60% greater than the 2013 Middle East production figure provided in Table 4, owing primarily to the start-up of several large sulphur recovery facilities in the UAE and Saudi Arabia. The UAE accounts for roughly 50% of Middle Eastern capacity; hence making it one of the important countries of focus. Current installed sulphur production capacity exceeds 24,000 MTPD and normal production is around 80% of this figure. However, for the purpose of simplifying the analysis, it is assumed that all sulphur recovery facilities are operating at 100% of design rates.

The first sulphur plants in UAE were built in the early 1990s and the most recent plants were started up in 2015. Similar to the rest of the world, sulphur recovery emissions specifications in the UAE have tightened over the years. Yet older plants remain grandfathered and are permitted to continue operating with higher emissions, in accordance with regulations that were applicable at the time of construction. Thus, a wide range of sulphur plant technologies and recovery efficiencies exist throughout the country.

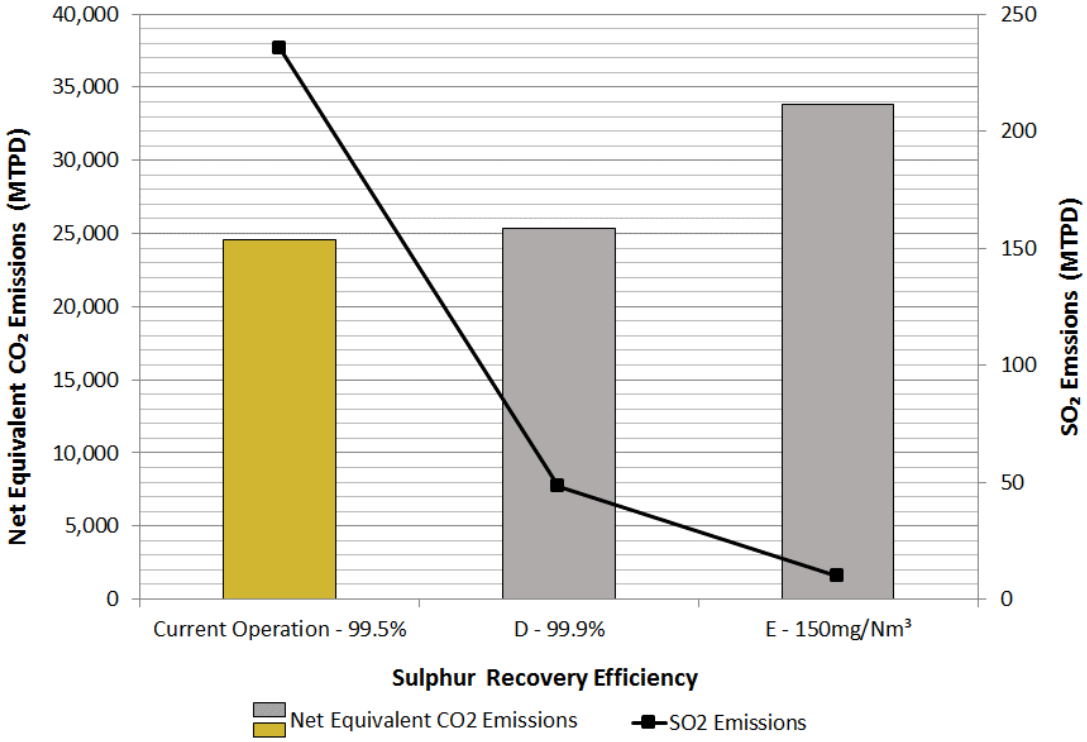
A survey of the major SRUs in the UAE reveals the current operating conditions summarized in Table 5, assuming operation at 100% of design rates. The average sulphur recovery efficiency of these facilities is 99.5%, which is greater than Case C but less than Case D. At this recovery efficiency, total SO_2 emissions are approximately 235 MTPD (85,800 MTPA), which is less than 0.1% of total global SO_2 emissions. Actual CO_2 emissions are approximately 31,000 MTPD which is also less than 0.1% of total global CO_2 emissions. Equivalent CO_2 emissions are approximately 20% lower than actual due to the fact that at 99.5% SRE, a sulphur recovery facility is a net energy exporter, as demonstrated previously.

Table 5. SO_2 and CO_2 Emissions from UAE Sulphur Plants

	Total Sulphur Processing Capacity	Average SRE	Emissions at 100% of Design Rate		
			SO_2	Actual CO_2	Equivalent CO_2
Current Operating Condition	24,065 MTPD	99.5%	235 MTPD	30,630 MTPD	24,550 MTPD

Figure 15 illustrates predicted SO_2 and equivalent CO_2 emissions from UAE sulphur plants if overall average SRE were increased by applying Case D or E technologies. Similar to the trend observed previously, as SO_2 emissions decrease, equivalent CO_2 emissions increase. At recovery efficiencies greater than about 99.9%, equivalent CO_2 emissions increase at a disproportional rate to the corresponding reduction in SO_2 emissions.

Figure 15. SO_2 and Net Equivalent CO_2 Emissions from UAE SRUs - Current Operation and Increased SRE Cases



A high level analysis reveals that a capital investment of nearly $1 billion USD would be required to increase the average SRE of UAE sulphur recovery facilities to roughly 99.9%, which basically involves installation of amine-based tail gas treating on all existing SRUs which are not currently equipped with such facilities. These modifications would decrease SO_2 emissions to about 20% of the current figure, or approximately 50 MTPD (18,250 MTPA). While this is a substantial reduction, the incremental energy requirements would still require consideration. As a result of the additional energy consumption, for every ton of SO_2 reduction, approximately 5 tons of equivalent CO_2 would be produced.

When contemplating total SO_2 emissions from sour gas treating facilities, SRE achieved in the sulphur plant is not the only area of consideration. Another important aspect is the significant quantity of SO_2 that can be released during start-up, shutdown and upset conditions, when sour gas must be flared. Current sour gas processing capacity in the UAE exceeds 7 BSCFD. Figure 16 illustrates the number of days of sour gas flaring equivalent, at various rates and H_2S concentrations, to match the current equivalent annual SO_2 emissions from UAE sulphur plants (85,500 MTPA).

Figure 16. Sour Gas Flaring to Release 85,800 Metric Tons SO_2 - Equivalent to Normal Annual SO_2 Emissions from All UAE SRUs

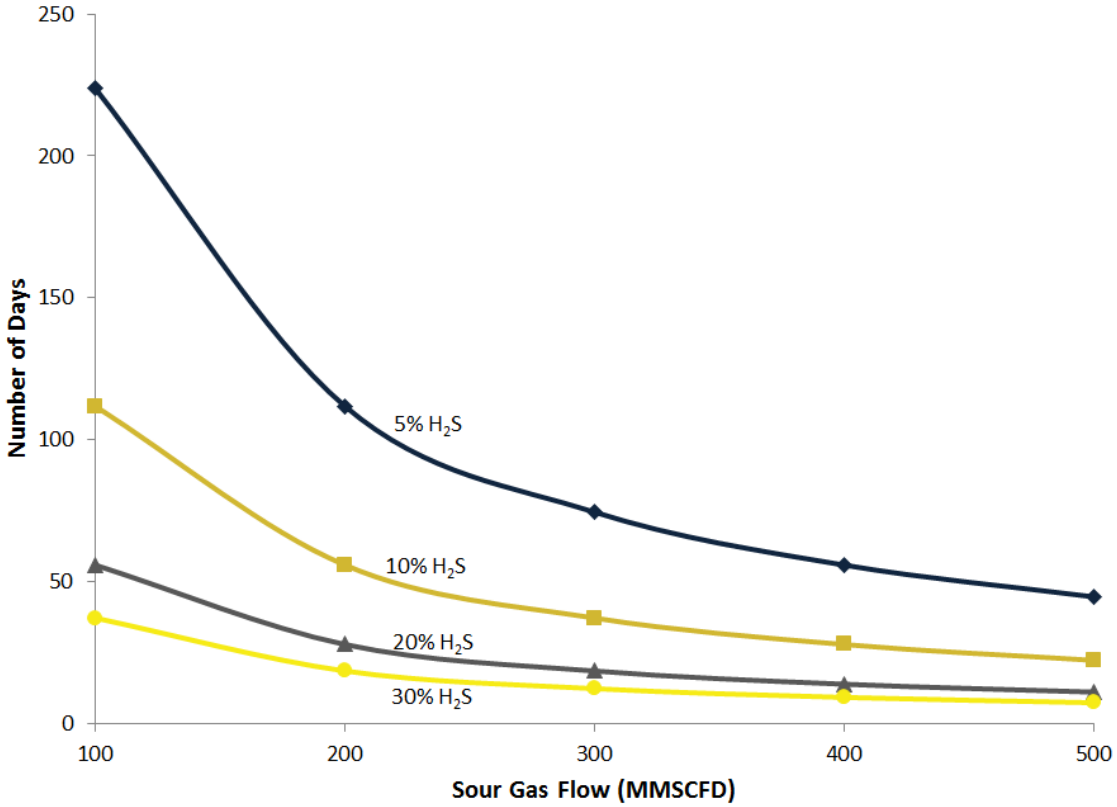


Figure 16 shows that for a highly sour gas field, it would only take a few days of flaring, at relatively low rate, to release as much SO_2 as is emitted from all UAE SRUs in an entire year. While sour gas flaring isn't something that is planned, it can occur during initial start-up and in facilities that achieve low reliability and/or availability. Thus, in some cases, it may be more beneficial to direct efforts toward improving availability/reliability of existing assets rather than upgrading existing SRUs to achieve higher sulphur recovery efficiency during normal operation. Development and implementation of well management programs that facilitate sour gas diversion or containment, in the case of planned or unplanned outages, would also be highly beneficial for minimizing total SO_2 emissions from the facility as a whole.

POSSIBILITIES FOR REDUCING CO_2 FOOTPRINT OF SRUs

As demonstrated above, sulphur recovery facilities do not contribute a great deal to global CO_2 emissions. However, in large facilities with stringent SO_2 emissions specifications, it is still advantageous to minimize the quantity of CO_2 emitted for every ton of SO_2 removed. This is because, in addition to designing and/or operating an environmentally responsible facility, a reduction in carbon footprint also provides an improvement in energy efficiency, which translates to reduced operating cost. Some potential measures that might be considered to achieve these objectives are described below.

Incinerator Operating Temperature

As described above, the hypothetical sulphur plant examined in this paper has an incinerator operating temperature of 815°C, which is higher than the temperature required by most SRUs. Such a temperature would only be required when the total reduced sulphur (TRS) specification in the stack gas is extremely low (<5 mg/Nm^3). Incinerator operating temperature can be optimized, depending upon various stack emission specifications. This topic is explored in detail in a paper by Sulphur Experts,[3] which concludes that a range of temperatures from 650°C to 815°C may be acceptable, depending on local environmental regulations.

Table 6 and Figures 17 and 18 illustrate the CO_2 impact of reducing incinerator operating temperature from 815°C to 650°C, which is the minimum temperature required for H_2S oxidation. Figures 17 and 18 illustrate only the CO_2 footprint of the incineration system and not the entire SRU/TGTU, e.g. equivalent CO_2 for: fuel consumed in burner, plus power consumed by blowers, minus HP steam produced. Figure 17 considers the employment of an incinerator WHB (as per the hypothetical SRU design) and Figure 18 considers incinerator operation without any form of waste heat recovery.

Table 6. Hypothetical Sulphur Plant (99.9% SRE) – Impact of Incinerator Operating Temperature

	815°C Incinerator		**760°C Incinerator**		**650°C Incinerator**	
Incinerator Stack Gas Composition						
	mol%	**kmol/hr**	**mol%**	**kmol/hr**	**mol%**	**kmol/hr**
O_2	2.00%	123.72	2.00%	117.70	2.00%	107.38
N_2	71.45%	4421.84	71.54%	4211.62	71.70%	3851.56
CO_2	13.75%	850.63	14.02%	825.45	14.56%	782.30
SO_2	200 ppmv	1.24	211 ppmv	1.24	231 ppmv	1.24
H_2O	12.78	790.93	12.42%	731.24	11.71	629.01
Total	100%	6188.37	100%	5887.24	100%	5371.50
Key Incinerator Process Parameters						
Fuel Gas Consumption (Nm^3/hr)	3,789		3,256		2,344	
Combustion Air (kmol/hr)	2,600		2,324		1,850	
HP Steam Production (kg/hr)	39,111		32,933		22,345	

Figure 17. Impact of Varying Incinerator Operating Temperature on Hypothetical SRU **w/ WHB**

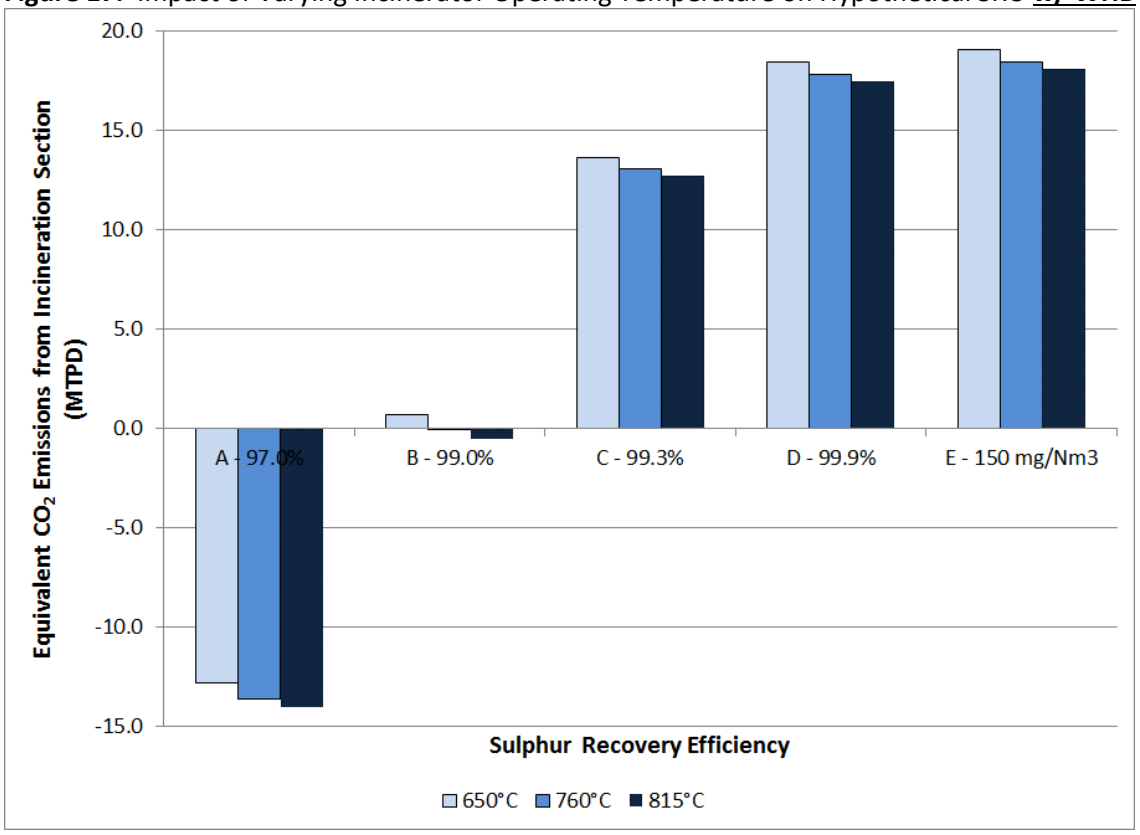


Figure 18. Impact of Varying Incinerator Operating Temperature on Hypothetical SRU **w/o WHB**

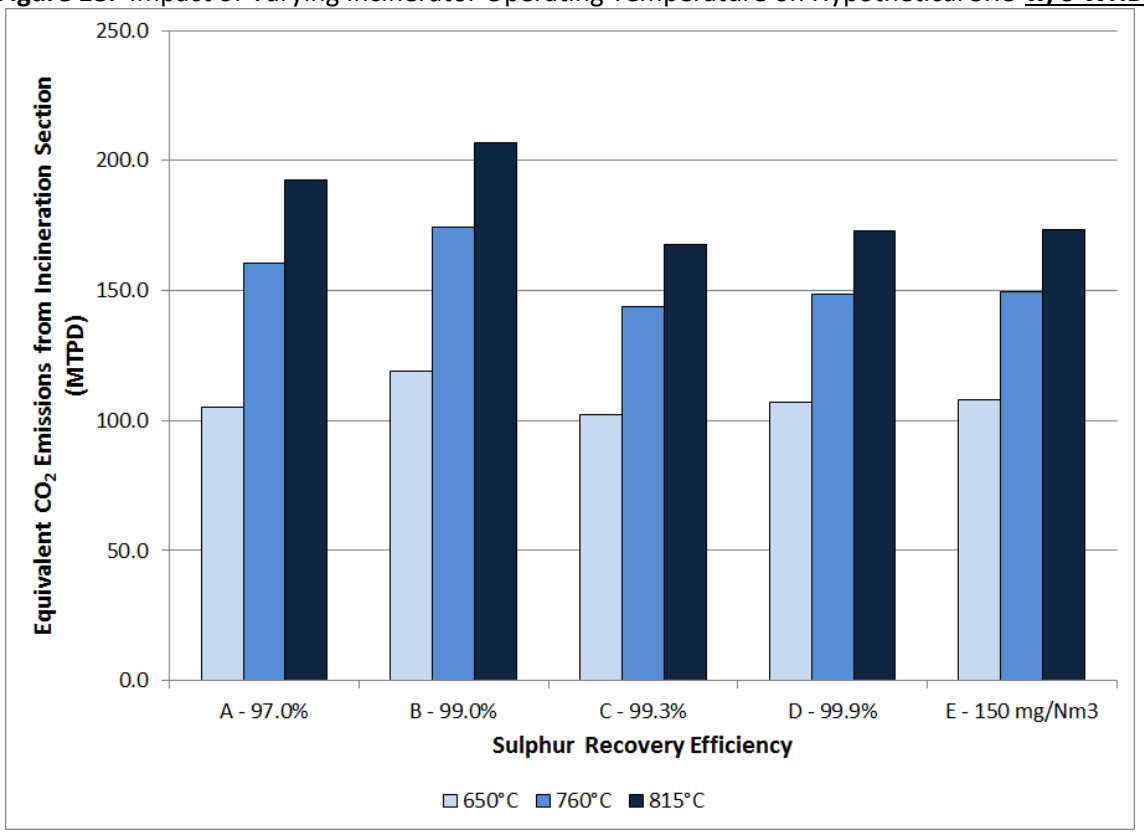


Figure 17 shows that when an incinerator WHB is employed, higher operating temperature is actually advantageous in terms of both energy efficiency and CO_2 footprint. This is due to the higher temperature driving force in the WHB, which increases efficiency of steam production. Figure 18 shows that when a WHB is not employed, the opposite is true; energy efficiency and CO_2 footprint are negatively impacted as operating temperature is increased.

It is interesting to note that when an incinerator WHB is employed, the incineration system for the Claus SRU (Case A) becomes a net energy exporter with a negative CO_2 footprint, due to the heating value of the H_2S in the tail gas. For a sub-dewpoint or direct oxidation unit (Case B), with lower H_2S concentration in the tail gas, the system is essentially energy and CO_2 neutral. For amine-based tail gas treating systems, H_2S content in the tail gas is low enough that the incineration system is a net energy consumer. As illustrated in Figure 18, with no WHB the incineration system is always a net energy consumer, regardless of H_2S content in the tail gas, because none of the waste heat is recovered.

Employment of Incinerator WHB

Comparing Figures 17 and 18, it is evident that inclusion of a WHB to recover waste heat from an SRU incinerator is highly advantageous in terms of energy efficiency. Equivalent CO_2 emissions are an order of magnitude greater when waste heat recovery is not employed. Thus, in general, incinerator WHBs should be considered to optimize the energy efficiency of new SRU designs. It is important to note that the efficiency of such systems is limited by the minimum allowable stack gas temperature, which is dictated by the acid dewpoint in this stream. The acid dewpoint is dependent upon the sulphur recovery efficiency of the facility; however, the TGTU bypass scenario will always dictate the maximum acid dewpoint that can be experienced in an off-design operating scenario. A typical minimum incinerator WHB outlet temperature is 315 - 350^{o}C, although this value may be increased for large facilities and/or in cold climates where heat losses in the stack can be substantial. During turndown conditions, the WHB outlet temperature will be lower than the design value and this must be taken into account when ensuring that the stack temperature is always maintained above the acid dewpoint.

Sulphur Pit Vent Recycle to SRU Reaction Furnace

In many sulphur recovery facilities, sulphur pit vent and/or degassing vent streams are routed to the incinerator, where H_2S in the streams is oxidized to SO_2, directly impacting emissions. As an alternative, these streams can be recycled to the reaction furnace in the SRU where most of the H_2S can be recovered as elemental sulfur, significantly reducing emissions. Table 7 shows the SO_2 emissions impact of routing the degassing vent to the incinerator versus to the front end of the SRU and illustrates the huge benefits associated with recycle, especially as recovery efficiency requirements increase.[5]

Table 7. Contribution of Degassing Vent to Total SRU SO_2 Emissions[5]

Sulphur Recovery Efficiency	Degassing Vent - % of Total Stack SO_2 Emissions, When Routed to:	
	Incinerator	Front of SRU
95% SRE	0.5%	0.03%
97% SRE	0.9%	0.03%
99% SRE	2.7%	0.03%
99.9% SRE	22.0%	0.03%

Such a substantial reduction in SO_2 emissions can be accomplished at very little cost, in terms of CapEx, OpEx and CO_2 footprint, as this is typically achieved via employment of a steam ejector which utilizes medium pressure for motive force. Thus, routing sulphur degassing vapors to the front end of the SRU should be considered as a first course of action to reduce SO_2 emissions, prior to the consideration of tail gas treating options that would have a considerable impact on the facility's energy balance and CO_2 footprint.

It should be noted that there are many critical safety and reliability considerations which must be taken into account when determining the location for sulphur degassing vent recycle into the front of the SRU. These considerations are discussed at length in the literature[5] and will not be addressed further in this paper.

Selective Solvents for Tail Gas Treating

When a particular sulphur recovery application calls for ultra-high recovery efficiency (99.9%+), it is typically prudent to consider TGTU solvents which are highly selective to H_2S. This is because these types of solvents reduce amine circulation rate and regeneration energy requirements due to their ability to slip a greater percentage of the CO_2 in the tail gas. A recent study[4] demonstrated that amine circulation rate and associated regeneration steam required for one particular proprietary solvent is roughly 50% of that required for MDEA under the same operating conditions.

Table 3 shows that the MDEA circulation rate for Case E is approximately four times that required for Case D. With the employment of a selective proprietary solvent, Case E SO_2 emissions can be achieved at approximately 50% of the MDEA circulation rate, cutting the reboiler energy consumption in half. This would convert the facility into a net energy exporter, rather than consumer, with overall net energy balance of approximately 18,000 kW (produced) instead of 26,000 kW (consumed). This would result in a CO_2 emissions reduction of approximately 25%. Thus, for ultra-high recovery efficiency, selective solvents should be seriously considered to achieve the optimum solution, in terms of CapEx, OpEx and CO_2 footprint.

Acid Gas Injection

Acid gas injection (AGI) schemes are employed in some sour gas processing facilities to avoid sulphur production in relatively remote regions where sulphur handling logistics would be difficult and/or where extremely sour gas would result in enormous quantities of elemental sulphur production. Other than the CO_2 that leaves with the sales gas, the injected acid gas

stream contains all of the CO_2 in the raw gas. Thus, injecting acid gas back into the reservoir, rather than routing it through a sulphur recovery unit, will completely eliminate CO_2 emissions from the process plant. Equivalent CO_2 emissions associated with AGI power consumption would need to be considered, which is dependent upon the quantity of acid gas and reservoir injection pressure. However, given that CO_2 in the raw gas makes up the majority of CO_2 emissions from the facility (as shown in Figure 11), it is likely that acid gas injection would result in an overall carbon footprint reduction for a sour gas processing facility.

It is important to note that AGI schemes require numerous HSE considerations due to the high H_2S partial pressures which result from compressing acid gas to the elevated pressures required for injection into a reservoir. Depending on the reservoir and acid gas conditions, AGI may not be feasible in some cases.

In summary, to optimize energy efficiency and minimize CO_2 footprint of a new sulphur recovery facility, all of the above options should be evaluated. Existing facilities may consider optimizing incinerator operating temperature, routing degassing vapors to the front of the SRU and/or carrying out a TGTU solvent swap. However, the revamp of an incinerator to include waste heat recovery and/or implementation of AGI in an existing facility would be more complex options that may not be feasible.

CO_2 RECOVERY FROM SULPHUR RECOVERY FACILITIES – IS IT VIABLE?

Because sulphur recovery units are typically energy exporters, they are actually quite responsible facilities in terms of environmental carbon impact. As a result, SRUs around the world contribute only a tiny fraction to global CO_2 emissions. However, there remains interest in certain parts of the world to capture CO_2 from these types of facilities. One may ask what the drivers might be. Two primary possibilities are described below.

Enhanced Oil Recovery

CO_2 injection into partially depleted oil reservoirs has been widely accepted as an effective technique for enhanced oil recovery (EOR) for over 40 years. It is estimated that approximately 80% of the world's reservoirs could qualify for some level of CO_2 injection.[6] If there is one region where EOR has the potential to be optimized and implemented on a large scale, it is likely to be the Middle East. In particular, the UAE is among the highest in the world in carbon dioxide emissions per capita and is also one of the world's top oil producing nations. The combination of these factors would incentivize the capture of CO_2 from refinery and sour gas plant SRUs for EOR. Most gas processing facilities in the region are quite large (1 BSCFD and greater) and CO_2 content in the raw gas feed is substantial, potentially making them attractive candidates for CO_2 capture.

Improved Acid Gas Quality

Sour gas processing facilities often produce acid gas with low H_2S concentration, which is referred to as "lean acid gas." Lean acid gas feed to an SRU can be problematic due to low reaction furnace temperature and a tendency for flame instability. Removing CO_2 from the acid gas benefits the SRU in several ways. Higher H_2S content increases reaction furnace temperature, which improves flame stability and enhances contaminant destruction. Lower CO_2

content reduces volumetric flow through the entire SRU/TGTU, reducing the size of equipment in the case of a new facility, or providing the opportunity to debottleneck an existing unit. CO_2 removal upstream of the SRU can be achieved via two principal methods:

- Selective sour gas treating, followed by CO_2 removal downstream
- Bulk sour gas treating, followed by acid gas enrichment

In either case, CO_2 in the raw gas from the reservoir is removed from the acid gas that flows to the SRU. The CO_2 stream may be routed to the incinerator (for subsequent emission to the atmosphere) or captured for further use, such as EOR.

Methods for CO_2 Capture

When it comes to capturing CO_2 from SRUs in sour gas treating facilities or refineries, there are 3 basic options:

1. From sour gas - As described above, where CO_2 is captured upstream of the SRU/TGTU and does not flow through the units.
2. From TGTU – CO_2 is captured downstream of the low pressure TGTU absorber after flowing through the SRU and TGTU, and the benefits described above are not realized.
3. Post Combustion – CO_2 is captured downstream of the SRU/TGTU incinerator, after flowing through the SRU/TGTU. Although the benefits of CO_2 removal from acid gas are not realized, CO_2 concentration is higher at this point in the process due to additional CO_2 produced in the combustion reactions in the incinerator.

Generally speaking, option 1 is the most attractive means of capturing CO_2 due to high operating pressure, which increases CO_2 partial pressure and improves capture efficiency. This type of process would typically emit less than 1 ton of CO_2 equivalent for every 10 tons of CO_2 captured. Although operated at low pressure, Option 3 would typically be the next best option due to higher CO_2 partial pressure than Option 2. This is because CO_2 formed in the combustion of natural gas in the incinerator increases its partial pressure, as well as increasing the total quantity of CO_2 available for capture. This type of process would typically emit 1-2 tons of CO_2 equivalent for every 10 tons of CO_2 captured. Option 2 is typically the least attractive option due to lowest CO_2 partial pressure. For this type of process, equivalent CO_2 emission can exceed 5 tons of CO_2 for every 10 tons of CO_2 captured, depending on the solvent selection and process scheme employed.

SUMMARY & CONCLUSIONS

Revisiting the questions posed at the outset of the study gleans the following conclusions.

1. How does increasing SRE positively impact global SO_2 emissions?

Although SO_2 emissions from sulphur recovery facilities contribute less than 5% of the global total, a significant positive impact is observed as SRE approaches 99.9%. Above 99.9%, energy consumption increases drastically for very little reduction in SO_2 emissions. Even when proprietary, highly-selective solvents are employed, there is a significant energy increase required to achieve the WBS emission standard (99.98% SRE). Therefore, it is questionable whether there is good reason to consider SO_2 emissions specifications in excess of 99.9%.

Possible exceptions may be the case of very large sulphur recovery facilities that would have substantial SO_2 point source emission rates (ton per day basis) and/or facilities that are located in environmentally sensitive regions. Additionally, there may be opportunities to relax SRE requirements below 99.9% for smaller SRUs (<50 MTPD), which have only a minor point-source emission impact, even at lower SRE. This philosophy has already been adopted in some parts of the world.

2. What is the corresponding negative impact on global CO_2 emissions?

The study revealed that sulphur recovery facilities have an essentially inconsequential impact on global CO_2 emissions. However, it would be irresponsible to unnecessarily increase the carbon footprint of the facility by not enhancing the design via the use of selective solvents, optimized incinerator design/operation or perhaps even considering acid gas injection rather than sulphur recovery. Implementing such measures would also improve energy efficiency of the facility, thereby improving overall project economics.

3. Is CO_2 capture from SRUs a viable proposition?

The study demonstrated that it is generally preferable to optimize the design of a sulphur recovery facility to minimize its carbon footprint rather than to incur costs associated with capturing CO_2 from this source. However, some parts of the world requiring EOR may have different incentives/drivers which would make CO_2 capture from sour gas processing facilities attractive. Also, in some sulphur-critical regions of the world (e.g. Middle East, Russia/FSU), sulphur plants can be extremely large in size and contribute a higher percentage to regional CO_2 emissions, potentially increasing their environmental responsibility to consider CO_2 capture. Although CO_2 capture from power generation facilities is likely to have a greater impact on global emissions, there is often resistance toward the use of amines in these types of facilities due to lack of experience. Oil and gas processing facilities which are intimately familiar with these types of processes may therefore be more likely to consider their employment.

In closing, although it is not the intent of this paper to comment on the general state of world SO_2 and CO_2 emissions, China's recent surge is striking and cannot be ignored. Unfortunately, as this paper has illustrated, reduced emissions from oil and gas production facilities will not solve this growing concern. Instead, the focus will need to be directed toward power generation facilities, as already demonstrated by some western countries that have successfully begun to reduce their environmental impact by reversing the trajectory of SO_2 and CO_2 emissions.

ACKNOWLEDGMENT

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NOMENCLATURE

°C	degrees Celsius	**mg**	milligram
AGI	acid gas injection	**MMT**	million metric tons
barg	bar gauge	**MMTPA**	million metric tons per annum
BSCFD	billion standard cubic feet per day	**mol%**	mole percent
CapEx	capital expenditure	**MTPD**	metric tons per day
CBA	Cold Bed Adsorption	**N_2**	nitrogen
CO_2	carbon dioxide	**Nm^3**	normal cubic meters
EOR	enhanced oil recovery	**O_2**	oxygen
FSU	Former Soviet Union	**OpEx**	operating expense
Gg	Gigagram	**ppmv**	parts per million by volume
H_2O	Water	**RF**	reaction furnace
H_2S	hydrogen sulphide	**S**	sulphur
HP	high pressure	**SAF**	sulphur in all forms
hr	Hour	**SO_2**	sulphur dioxide
HSE	health, safety and environment	**SRE**	sulphur recovery efficiency
kcal	Kilocalorie	**SRU**	sulphur recovery unit
kg	Kilogram	**TGTU**	tail gas treating unit
kmol	Kilomole	**TRS**	total reduced sulphur
kW	Kilowatt	**UAE**	United Arab Emirates
LHV	lower heating value	**WBS**	World Bank Standard
LLP	low pressure	**WHB**	waste heat boiler
LP	low pressure	**WHE**	waste heat exchanger

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APPENDIX

Methodology for Calculating Equivalent CO_2 Emissions from Fuel, Electricity and Steam Consumption and/or Production

The combustion of fuel for direct heating applications, or for generating electricity and/or steam, results in the production of carbon dioxide, CO_2. Due to their varying energy densities, the equivalent amount of CO_2 emitted by each of the activities listed above – otherwise known as the CO_2 emissions factor – will depend on the type of fuel used. For this study, natural gas is selected as the fuel of choice and it is assumed to have a composition of 100% methane, CH_4.

Emissions factors are reported in terms of kilograms of CO_2 produced per kilowatt-hour of heat energy, electricity or steam generated (kg CO_2/kWh).

CO_2 Emissions Factor for Direct Combustion of Natural Gas

The reaction equation for the complete combustion of methane is,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

and its enthalpy of combustion at standard conditions is approximately 55.5 MJ/kg.

The complete combustion of 1 kg or 62.3 moles of CH_4 (molar mass of 16.04 g/mol) will produce 62.3 moles or 2.74 kg of CO_2 (molar mass of 44.01 g/mol). Therefore, 2.74 kg of CO_2 are emitted for every 55.5 MJ of heat energy released, which is equivalent to **0.18 kg CO_2/kWh of heat energy**.

CO_2 Emissions Factor for Steam Generation from Natural Gas

Natural gas can be burned in the furnace of a boiler to generate heat that is then used to boil water to produce saturated steam. However, not all of the heat that could theoretically be generated from combustion is released and not all of the heat that is generated is effectively transferred to the water. A typical steam boiler has an efficiency of about 85%, i.e. for every 1 kWh of heat energy, only 0.85 kWh of steam energy is produced. It is assumed that the boiler efficiency is the same for both low pressure and high pressure steam production.

Given that 0.18 kg of CO_2 are produced per kWh of heat energy from natural gas combustion,

$$\frac{0.18 \ \frac{kg\ CO_2}{kWh\ of\ heat\ energy}}{0.85 \ \frac{kWh\ of\ steam\ energy}{kWh\ of\ heat\ energy}} = 0.21 \ \frac{kg\ CO_2}{kWh\ of\ steam\ energy}$$

the emissions factor for steam generation is approximately **0.21 kg CO_2/kWh of steam energy**.

CO_2 Emissions Factor for Electricity Generation from Natural Gas

For this study, it is assumed that electricity is generated in a steam-electric power station. In this case, natural gas is burned to produce heat to convert water to steam, which in turn spins a steam turbine to generate electricity. The electrical efficiency of a conventional steam-electric power station fueled by natural gas is 33%, i.e. for every 1 kWh of heat energy, only 0.33 kWh of electrical energy is produced.

Given that 0.18 kg of CO_2 are produced per kWh of heat energy from natural gas combustion,

$$\frac{0.18\ \frac{kg\ CO_2}{kWh\ of\ heat\ energy}}{0.33\ \frac{kWh\ of\ electrical\ energy}{kWh\ of\ heat\ energy}} = 0.55\ \frac{kg\ CO_2}{kWh\ of\ electrical\ energy}$$

the emissions factor for electricity generation is approximately **0.55 kg CO_2/kWh of electrical energy**.

Calculating Equivalent CO_2 Emissions

The amount of CO_2 emitted from any of the above activities is calculated by simply multiplying the corresponding emissions factor by the amount of energy generated. For example, if the Claus Air Blower consumes electricity at a rate of 100 kW,

$$100\ kW * 24\ \frac{kWh}{kW\ \cdot day} * 0.55 \frac{kg\ CO_2}{kWh\ of\ electrical\ energy} * \frac{1\ tonne}{1000\ kg} = 1.32\ TPD\ CO_2$$

it is associated with an equivalent emission of 1.32 tons per day of CO_2.

Some processes in the sulphur recovery unit produce steam as a byproduct that can be used elsewhere in the gas plant or refinery, lowering the load on the facility's steam boiler. As a result, less fuel needs to be burned and less CO_2 is consequently emitted. This 'savings' in CO_2 emissions can also be calculated as shown above. For example, if the SRU waste heat boiler produces steam with a duty of 2500 kW,

$$2500\ kW * 24\ \frac{kWh}{kW\ \cdot day} * 0.21 \frac{kg\ CO_2}{kWh\ of\ steam\ energy} * \frac{1\ tonne}{1000\ kg} = 12.6\ TPD\ CO_2$$

it saves the plant from emitting an equivalent of 12.6 tons per day of CO_2.