

Oxygen enriched vs. Air-only Operation at Claus Units Field Tests are teaching Lessons - Especially in View of Ammonia Destruction

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Within the last 15 years Linde performed field operational tests at almost 20 Claus units in exclusive cooperation with the respective operators: European oil refineries. Respective test concept usually is to compare routine operation on air-only basis with oxygen enriched conditions – i.e. especially low-level enrichment (max. 28 vol-% oxygen in the process air). Linde's contribution was/is process know-how, hardware tailored for oxygen supply and dosing as well as analytical competence.

The paper given here presents a summary of test results in view of process intensification with some focus on ammonia (NH₃) topics: Beyond quantifying a larger than expected potential for capacity increase also other effects of oxygen enrichment were observed - encompassing decreasing fuel as well as hydrogen demand and improved ammonia destruction.

Nowadays in oil refineries considerable amounts of ammonia are sent into Claus units. Therefore the efficiency of ammonia destruction within the thermal Claus section is often in the focus of operators as ammonia breakthrough into the down-stream Claus section often results in salt precipitation at various "cold spots" in the path of the process gas and the condensed liquid sulphur product. By building up solid material ammonia salts have the potential to not only cause reduced plant availability, sulphur recovery efficiency and capacity but also enhanced maintenance effort and costs.

Measurements of ammonia concentrations in the Claus process gas showed that "conventional wisdom" – as disclosed in open literature – is not always in line with reality; i.e. obeying golden rules of thumb like esp. operating above certain temperature levels in the

Claus furnace without doubt provides a good lead but does not necessarily assure acceptably reduced ammonia concentrations in the Claus process gas.

INTRODUCTION

The basic concept of today's Claus process was developed and realised in the technical scale some 80 years ago by IG Farben in Germany. Using ubiquitous air as oxidant for the exothermal partial oxidation of hydrogen sulphide (H₂S), summarily described by



was and still is state of the art in Claus processing. Application of technical oxygen in order to enhance the performance of Claus units was coming up as late as in the 1980ies and gained momentum in the 1990ies mainly triggered by "Clean Fuels" programs. As corresponding demands called for considerably decreased sulphur content in (automotive) fuels more and more H₂S (and NH₃) was generated and had to be treated resp. recovered as harmless elemental sulphur. In many refineries installed sulphur recovery units were pushed to their limits – especially with respect to capacity and capability of NH₃ destruction. Thus intensification of the Claus process by easily adaptable and economic means was (and still is) of high interest. Oxygen enrichment which is - at least to a considerable extent - a low-investment solution not only serves these expectations; it also comes with a multitude of benefits for Claus operation. All this explains the high number of actually at least 200 Claus units being retrofitted/ equipped with technology based on additional use of technical oxygen. In the mid-1990ies in order not to miss this trend of increasing oxygen application in refineries Linde started to analyse the effects of process intensification by oxygen enrichment in more detail. Therefore an extensive trial campaign at a mid-size Claus unit was performed in Leuna/Germany [Ref. 1]. These activities were the basis for development of comprehensive capabilities necessary for preparation, realisation and evaluation of subsequent field tests at production sites of other interested Claus operators. Typically based on comparison of oxygen-enriched vs. air-only operation these test activities in refineries all over Europe started early in the new millennium and part of respective results – i.e. gained until 2007 - has already been published [Ref. 2].

OXYGEN ENRICHMENT – SOME BASICS

The basic concept of additional use of technical oxygen for Claus operation is to decrease the flow of process air and at the same time adding oxygen to such a degree that the total flow of enriched process air is lowered even though the same ("case A") or a higher ("case B" for capacity increase) amount of oxygen molecules is sent to the Claus furnace.

Corresponding to "case A" following diagram shows the decrease of process air flow in dependence of the degree of oxygen enrichment level:

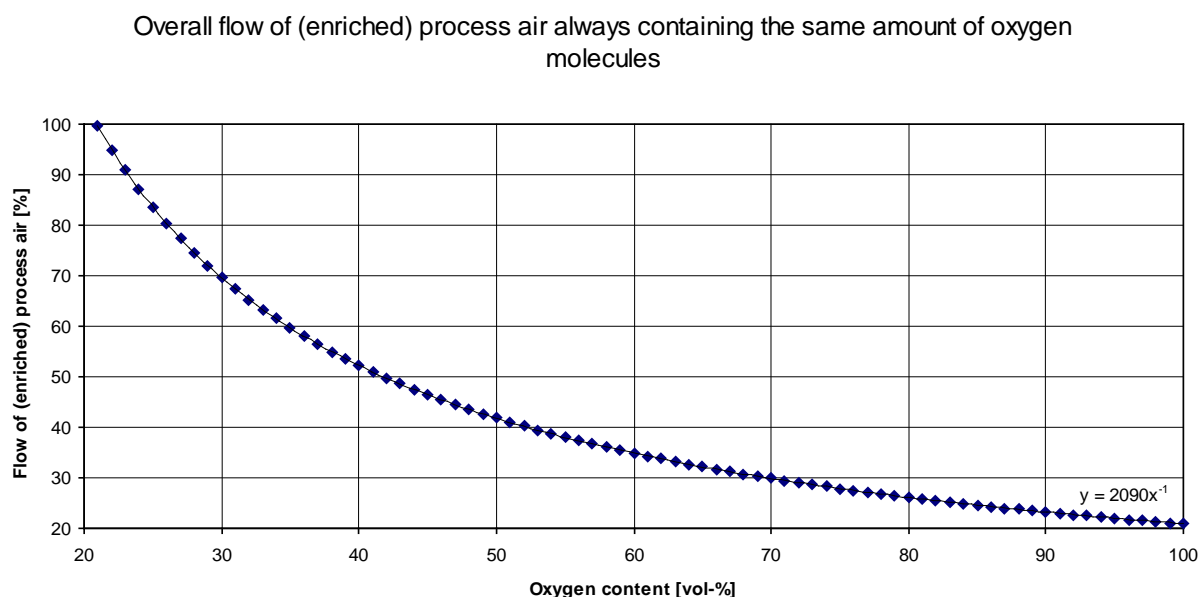


Fig. 1: The flow reduction is most significant at not too high oxygen enrichment levels – i.e. up to oxygen contents of say 40 vol-% in the enriched air stream, a range which is covered almost completely by low- and mid-level oxygen enrichment.

The decreased flow of process air (when enriched) is the very key for understanding oxygen enrichment's effects and potentials. An overview of the most important aspects of this effect is shown in the following table:

Reduced flow of process air by oxygen enrichment leads to reduced flow of process gas through the Claus unit →	Consequences for Claus operation
Additional volume available allowing for increased throughput of Claus feed (i.e. acid gas) without increasing the pressure drop	This measure directly translates into enhanced plant capacity. For concrete data see Fig. 3
Less inert nitrogen has to be heated up <ul style="list-style-type: none"> - in the Claus furnace - by the preheats of the catalytic Claus converters - by the down-stream off-gas incinerator 	Increased furnace temperature which in turn leads to important secondary effects pointed out in Fig. 7 Energy (CO ₂) saving Energy (CO ₂) saving
Enhanced residence time of process gas in reactors shifts slow reactions nearer to equilibrium <ul style="list-style-type: none"> a) in the Claus furnace e.g. $2 \text{ NH}_3 \rightarrow \text{N}_2 + 3 \text{ H}_2$ b) in the catalytic Claus converters esp. $\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2$ & $\text{CS}_2 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ H}_2\text{S} + \text{CO}_2$ 	Degree of ammonia destruction increases Efficiency of carbon sulphide hydrolysis (mainly in the 1 st catalytic stage and not seldom critical to optimised sulphur recovery efficiency) is enhanced
Less gas load on down-stream sections of the Claus unit	Potential bottlenecks in view of process gas throughput like tailgas treatments (e.g. amine scrubber column) or incinerators can be overcome

Fig. 2: shows some important consequences/potentials of decreased nitrogen content in the enriched process air.

The reduction of air flow when adding oxygen automatically implicates less nitrogen going into and through the Claus unit where nitrogen as an inert component takes up space and in addition dilutes the process gas. Therefore one effect of oxygen enrichment is a higher partial pressure of the reactants H_2S and SO_2 in the process gas and thereby a more pronounced temperature effect in the catalytic Claus stages where the so-called Claus reaction takes place:



As above reaction is exothermal the temperatures of the catalyst beds rise with the concentration of the reactants – i.e. as the ΔT over the catalyst bed rises also the outlet temperature of the first catalyst bed is increasing. This in turn speeds up the velocity of the hydrolysis of carbon sulphides (see above Fig. 2) which are kinetically limited reactions. Due to this acceleration less COS and CS_2 is passing the catalytic Claus section as well as the tailgas treatment (if without a hydrogenation/hydrolysis step) and being oxidised to SO_2 in the off-gas incinerator. Thereby decreased SO_2 emission can significantly contribute to the optimisation of sulphur recovery efficiency (SRE) of the Claus unit.

Of course such considerations have to be weighed against counteracting effects like e.g. enhanced COS generation in the Claus furnace due to increased furnace temperature.

But in general there are no indications that SRE drops with oxygen enrichment even though also other effects of negative impact on SRE do exist (see also Fig. 7).

However, it appears that in dependence of the given Claus design/configuration the application of oxygen enrichment may or may not have a favourable impact on the SRE of a Claus unit. This holds especially in view of the installed tailgas treatment; e.g. SCOT-like installations should perform better as enhanced partial pressure of H_2S works in favour of more efficient H_2S absorption.

CAPACITY INCREASE DUE TO OXYGEN ENRICHMENT

The capacity increase in Claus plants due to oxygen enrichment is a well proven effect. Tests applying oxygen enrichment showed time and again that especially with rich acid gas feed total capacities of > 130 percent can be realised when a concentration of 28 vol-% of oxygen in the enriched process air is applied:

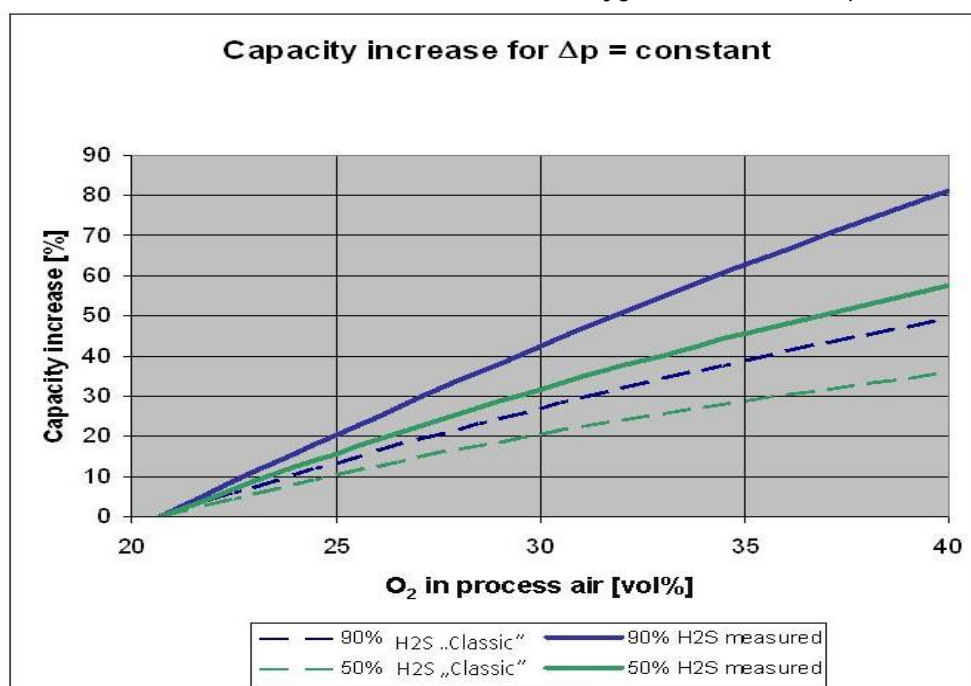


Fig. 3: shows the potential of oxygen enrichment with respect to capacity increase based on field tests in contrast to more conservative “Classic” values

This is worth mentioning as often lower degrees of capacity increase are offered by literature [see cit. in Ref. 2].

Capacity increase means that more Claus feed – esp. acid gas – can be sent into the Claus unit as at full load in the design case. In principle this could be accomplished easily by increasing the pressure of the feed gas. But optional measures in view of the acid gas like e.g. applying a blower compressing a gas high in H_2S are not favourable from an operational point of view. Therefore it is most interesting to increase the feed flow without increasing the total flow of process gas. The latter is the main limitation of Claus unit capacity as the pressure drop over a plant – by simplified theory based on a laminar gas flow - rises with the square of the gas flow. From an operational point of view this means that increasing the plant load increases the pressure drop. And at a certain value of the latter no more additional acid gas can be added as its pressure can't be enhanced to overcome the "resistance" – i.e. the built-up pressure drop - of the unit.

Oxygen enrichment allows for enhanced throughput of acid gas feed at constant pressure drop because the air flow is lowered. However – it has to be assumed that in reality the pressure drop over the unit doesn't rise in proportion with the square of the total gas flow. It appears that instead of the power of two values of < 2 apply, which can (at least partly) explain why capacity increase by oxygen enrichment in reality proves to be higher than expected [Ref. 2].

Even though a number of other beneficial effects are coming with oxygen enrichment its potential for considerable capacity increase was up to now the main driving force for operators to install this technology for revamp of existing Claus units. The enhanced flexibility of operation coming with oxygen usage not only holds when just one single Claus unit is operated at a site. In case of more than one Claus unit within the refinery by oxygen enrichment not only redundancy is added to the advantages but also the possibility to idle single plants in low load situations.

MODES OF OXYGEN ENRICHMENT

However - when applying oxygen enrichment the introduction of technical oxygen in parallel to reduced flow of process air is possible to a certain degree without the need to change anything of the hardware configuration of the existing Claus unit. But at a point – normally at approx. 28 vol-% of oxygen in the enriched process air – air-based Claus burners' design doesn't fit any more to the considerably reduced flow; i.e. capability for effective mixing is going down and especially the reduced gas velocity puts the burner material at the risk of overheating by a flame coming too close to the burner tip. Consequently when planning to operate beyond an oxygen concentration of 28 vol % it is inevitable to install a new burner or at least new burner lances. This measure comes with other, but normally only minor modifications of the Claus unit – typically the installation of a high quality furnace brick lining as the furnace temperature at oxygen concentrations of up to approx. 45 vol-% already rises to very high levels (e.g. 1500°C). Such temperatures challenge the stability of available material to its limits. This also means that when going beyond approx. 45 vol-% oxygen enrichment additional measures have to be taken in order to keep the furnace temperature at bay. One proven concept for realising high-level oxygen enrichment – i.e. beyond 45 vol% up to pure oxygen without any process air – is to keep the oxygen flow into the burner at lower level than necessary for achieving Claus stoichiometry (see reaction (1)). This is possible by adding oxygen not at once but stepwise allowing for intermediate removal of reaction heat – thereby keeping the temperature in the two subsequent combustion chambers ("double combustion") low enough; for more info on this technology see [Ref. 3].

Mode of O ₂ enrichment O ₂ content in the process air [vol-%]	Measures for implementation of O ₂ enrichment technology	
Low-Level 21 up to 28	Only: Implementation of oxygen supply train (see Fig 8)	
Mid-Level 28 up to 45	Implementation of oxygen supply train + Installed air based burner to be modified or substituted by a new burner (see example in Fig. 5)	
High-Level (e.g. Double Combustion) 45 up to 100	Implementation of oxygen supply train + Substitution of air based burner by new burner + Various revamp measures in dependence of applied technology (e.g. installation of a second Waste heat boiler, re-design of liquid sulphur drainage system etc.)	

Fig. 4: shows the three different modes of oxygen enrichment and the typical measures necessary for their implementation into an existing air-based Claus unit being operated with acid gas feed rich in H₂S.

Burners designed for application of enrichment levels higher than 28 vol % often feed the pure oxygen by dedicated piping into the flame zone – i.e. as a stream of pure oxygen and not pre-mixed with process air as is typical for technology based on low-level enrichment. The type shown by the following picture is one example of such a burner with integrated oxygen lances being applied in a few dozen reference cases.



Fig. 5: Multiple lance Claus burner of the SURE™ type – here designed for a revamp up to mid-level enrichment

OXYGEN ENRICHMENT FOR PROCESS INTENSIFICATION

When revamping an existing Claus unit by implementation of oxygen enrichment corresponding effort is dictated by the maximum enrichment level which is expected to be necessary – often deduced from the expectation of needed capacity in the future (see Fig. 3) or sometimes driven by other considerations, e.g. with respect to redundancy in case more than one Claus unit is in operation within the refinery. Corresponding effort for such a revamp is – as indicated in Fig.4 – strongly dependent on the envisioned mode of oxygen enrichment:

Low-level enrichment can be implemented swiftly with only minor effort and correspondingly low investment – of course always dependent on plant size and local conditions – which in most cases can be expected to be less than € 500,000.

In contrast high-level enrichment which has the potential to more than double the capacity of an existing Claus unit comes with considerably higher effort – but still comparing favourably with the erection/operation of an additional Claus unit in case an oxygen source is available. Due to the higher oxygen demand for this option, it normally excludes tank supply based on delivery of liquid oxygen – as very common for supply of Claus units equipped with low-level oxygen enrichment – and calls for either a nearby large-scale oxygen production unit available for pipeline connection or the erection of a dedicated on-site oxygen supply unit.

TEMPERATURE INCREASE DUE TO LOW-LEVEL OXYGEN ENRICHMENT

A high enough temperature in the Claus furnace is critical to sustain a reliable plant operation which includes e.g. the total destruction of trace compounds coming with the acid gas feed like e.g. highly persistent hydrocarbons as benzene, toluene and xylenes (BTX). With that respect in oil refineries normally sufficiently high furnace temperatures are reached as corresponding acid gases typically are very rich in the fuel H_2S . However – a further increase of Claus furnace temperature often proves to be very advantageous (see Fig. 7) from an operational point of view. This can be realised by application of low-level enrichment to such a degree that the limitations given in the thermal Claus section (i.e. max. temperature endurance of refractory and waste heat boiler) in the vast majority of cases are not gaining critical importance.

Below diagram shows the temperature increase achieved in the Claus furnace during one field test with low-level oxygen enrichment. The temperature profile is very typical for the test procedure which is typically applied; this especially holds for the temperature increase of some $130^\circ C$.

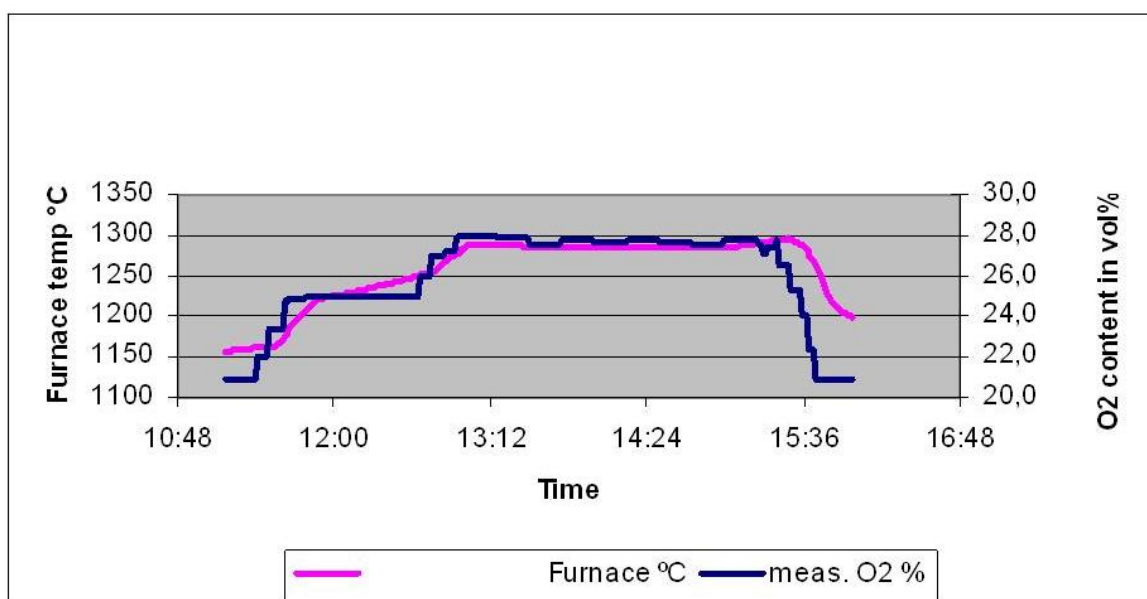


Fig. 6: Claus furnace temperature always rises with the degree of oxygen enrichment; besides the diagram outlines the circumspect approach by step-wise increase of oxygen content in the process air up to 28 vol-%, being characteristic for the test procedure usually applied.

The temperature increase in the Claus furnace triggers a number of secondary effects which have considerable impact on Claus operation:

General effects of increased temperature within the Claus furnace e.g.	Consequences for Claus operation/performance
Reactions are speeded up like e.g. $\text{SO}_2 + 2 \text{NH}_3 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} + \text{H}_2\text{S}$	Degree of ammonia destruction increases, thereby probability of salt build-up decreases (see Fig. 13)
Cracking reactions are gaining importance; esp. $\text{H}_2\text{S} \rightarrow \text{S} + \text{H}_2$	Enhanced hydrogen content in the process gas, thus reducing hydrogen demand – i.e. if a reducing tailgas-step is operated and/or reduction of fuel demand for incineration of off-gas [Ref. HP].
The partial oxidation of H_2S in the Claus furnace according to $\text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$ is shifted to the right thereby leading to more sulphur product.	This not very pronounced effect is among the factors which are in favour of an enhancement of sulphur recovery efficiency (SRE). However – as also negative effects in this respect are caused by oxygen enrichment (e.g. enhanced partial pressure of water in the process gas impacting the equilibrium of the Claus reaction (8) by shifting it to the left) SRE has proven to be quite indifferent to oxygen use.
Increased flame stability	More reliable plant operation

Fig. 7: Temperature effects in Claus furnace

FIELD OPERATIONAL TESTS WITH LOW-LEVEL OXYGEN ENRICHMENT

Even though there are certainly more than 2000 Claus units in operation globally they are all different in one way or another. Differences are in feed composition, plant size, composition of plant components, process parameters, gas flow modifications, gas (pre) heating, applied tailgas treatments etc.

Nevertheless – as experienced in various European refineries - low-level oxygen enrichment normally is always applicable without having to replace any hardware; i.e. exceptions are very rare. The by far most critical part where operational problems may occur is within the thermal Claus section where burner behaviour, endurance of refractory and capability of the waste heat boiler deserve particular watchfulness. Just in one out of 18 cases low-level oxygen enrichment couldn't be realised up to the max. enrichment level of 28 vol-%. The reason here was that the Claus furnace started to emit an intensive humming noise at a level of approx. 26 vol-%. This observation was attributed to the installed Claus burner and explained by development of a self-oscillation due to the reduced air flow. In that very case further testing was omitted in fear of build-up of the resonance effect to vibration of the whole thermal Claus installation and possible damage to the refractory especially.

In case a Claus operator likes to see his very unit running with low level oxygen enrichment – which is not a rare occurrence - a field test can be staged with only minor effort and at low cost; mainly because all the equipment necessary is related to oxygen supply/injection – see Fig. 8 - and can be rented. In order to prepare the Claus unit for such tests only one small modification is necessary. This is the installation of a stud at the pipe of the main process air – a procedure which can be performed during a few hours of plant idling and if need be even during plant operation by hot tapping. As soon as the oxygen injector is inserted into this stud the plant is prepared for tests with oxygen enrichment – typically performed within one week - at any appropriate time.

HARDWARE FOR SUPPLY AND INJECTION OF OXYGEN

In order to realise envisioned test operation an oxygen supply train has to be added, its typical lay out shown by the following scheme :

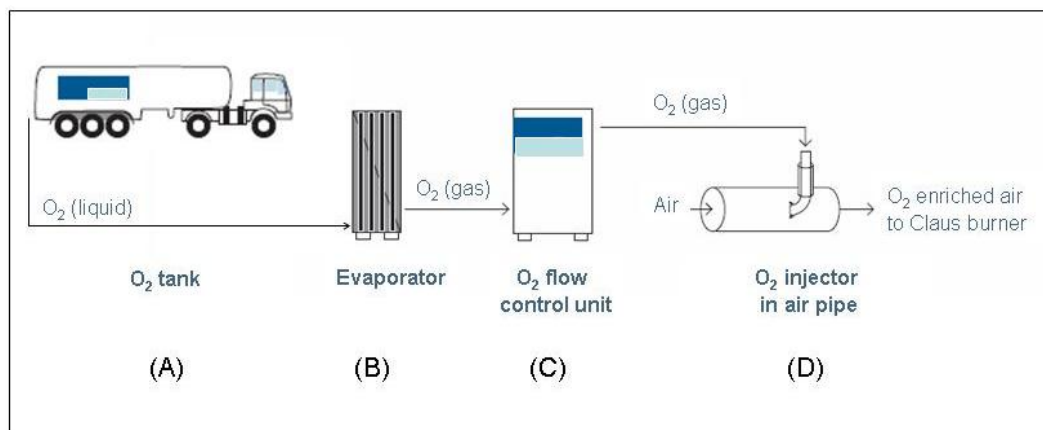


Fig. 8: Set-up of an oxygen supply train based on liquid oxygen (LOX) as typically applied for field operational tests with low-level enrichment

In refineries which operate Claus units exclusively on basis of air-only processing in most cases no oxygen source – like a gas pipeline or a stationary tank containing liquid oxygen (LOX) - is available nearby those plants.

For test operation refiners often prefer mobile tanks filled with LOX as oxygen source because this supply equipment can be swiftly removed from the premises. The following picture shows a truck supplying gaseous oxygen (GOX) to an oxygen flow control unit during Claus trials:



Fig. 9: Shown truck with integrated evaporation system is a mobile storage and evaporation system for LOX to supply GOX.

When handling oxygen within a refinery safety considerations of course are of utmost importance. Looking at the oxygen supply train shown by Fig. 8 this not only holds for the tank/evaporation system but also in view of oxygen control and injection.

Corresponding hardware – (C) and (D) in Fig. 8 - looks simple and straight-forward. But it is worth a closer look to avoid difficulties in operation and safety risks due to faulty design. Therefore a few important topics will be discussed here.

The injection of oxygen is done directly into the pipe for the process air to the Claus furnace. As the air pipe is normally made of carbon steel it is mandatory that high levels of oxygen concentration are safely kept away from the carbon steel wall. This is because in the long run the oxygen would react with the carbon and slowly remove it from the steel. The result then is brittle steel which may fail without warning. The problem here is that the damage becomes visible only when it is too late to prevent it. Therefore injection has to be done by adequate devices, e.g. the one shown in Fig. 10. This oxygen injector is

designed using CFD (computational fluid dynamics) and ensures both good mixing of the combustion air with the injected oxygen at very short distance and that high concentration oxygen is safely kept away from the inner surface of the carbon steel pipe.

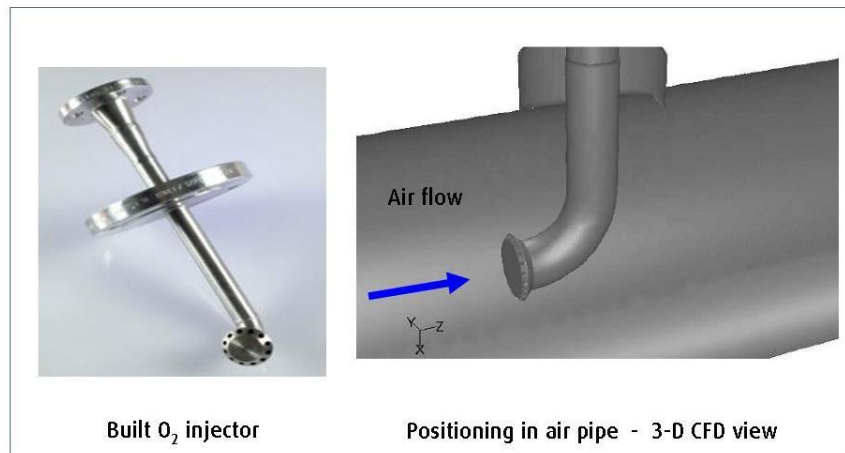


Fig. 10: OXYMIX™ oxygen injector – a circular arrangement of holes in the head of the injector provides for oxygen jets directed against the flow of process air thereby serving both safety and good mixing.

Another important equipment is the control and safety cabinet required to meter the oxygen into the process air. Of course the main item there is the flow control valve. But in addition the safety features are of high importance. Any major deviation of the actual O_2 flow must be alarmed and – if the situation cannot be corrected – oxygen flow has to be interrupted in a suitable way. Just switching off the oxygen at high enrichment levels would almost necessarily lead to a failure of the Claus plant, primarily due to too high temperature in the incinerator. As the oxygen for enrichment is provided from a liquid oxygen tank temperature control in the piping must be provided to avoid any cryogenic oxygen entering the air duct. And during shut-down periods an absolute separation between oxygen source and Claus plant has to be ensured which includes safeguarding against creeping gas flows. The picture of a device in kind is shown in Fig. 11:



Fig. 11: FLOWTRAIN® for metering oxygen into Claus plants and to fulfil the safety requirements

Arrangements for oxygen supply and injection as shown in Fig. 8 are the typical set-up used for tests but quite often are applied later on for routine operation as well; esp. in cases when no nearby oxygen source like an air separation unit or access to an oxygen pipeline is existing. The only difference then typically is a stationary LOX tank rather than a truck.

When running field operational tests with oxygen enrichment the development of critical parameters like temperature increase in the furnace, the waste heat boiler, the 1st catalytic converter and of course the

behaviour of the Claus burner can be observed closely and in a safe manner as long as the increase of oxygen addition is realised in a patient and step-wise manner. Such an approach – as shown in Fig. 6 – also offers the opportunity of process gas sampling at different enrichment levels, e.g. to compare the efficiency of ammonia destruction correlated to different furnace temperatures.

AMMONIA IN CLAUS UNITS

Crude oils which are composed of a complex mixture of hydrocarbons always contain a certain amount of N-bearing compounds. As typical especially for sour crude the concentration of the latter is often lower than of S-bearing compounds and the C-N-bond is considerably stronger than the C-S-bond. Nevertheless in all refinery processes which are generating H₂S from organic compounds – esp. cracking processes and hydrotreatment – also ammonia (NH₃) is generated. As this base is highly soluble in water most of it (but not always quantitatively) ends up in condensing process water and by increasing the pH also enhances the solubility of H₂S. This so-called sour water normally is treated in a sour water stripper (SWS) in order to drive out dissolved H₂S and NH₃ from the aqueous liquid phase. In most cases the SWS applied is of the 1-stage type generating a gas phase mainly consisting of H₂S, NH₃ and water – typically in quite similar concentration – which very often is sent to the Claus unit to recover the respective sulphur and get rid of the ammonia in one go. This concept is very straightforward but its applicability stands and falls with the efficiency of NH₃ destruction in the Claus furnace. A serious breakthrough of NH₃ through the thermal Claus section can cause severe troubles which always start with precipitation of ammonia salts at “cold spots”.

Many Claus operators struggle with the consequences of such build up of solids which can add up to a multitude of troublesome effects. Ammonia salts have the potential to reduce performance characteristics of the Claus unit and also come with increased operating and maintenance effort (see Fig. 13) [Ref. 2].

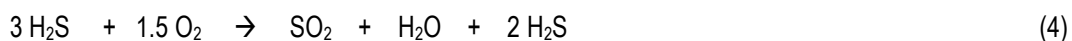
Measuring the NH₃ concentration in the process gas – especially when different modes of Claus operation are being compared – gives a good lead for identification of the most favourable way of processing.

Please note that it is not possible to give a general recommendation on the max. Tolerable NH₃ concentration in the process gas down-stream the thermal Claus section. This is due to the fact that individual Claus trains – i.e. the whole way down from the Claus furnace to the off-gas incinerator – show different susceptibilities towards NH₃ in dependence of Claus design and size and esp. of technology of the respective Claus tailgas-treatment.

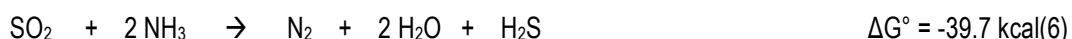
AMMONIA DESTRUCTION IN THE CLAUS FURNACE

In a Claus unit, the additive ammonia is destroyed inside the Claus furnace only – not in down-stream sections of much lower temperature.

While the Claus furnace is a very complex reaction system, the crucial oxidants are oxygen and SO₂. As established through ASRL, oxygen reacts faster with H₂S (4) than with NH₃ (5):



On these grounds it appears to be highly probable that the oxidation of NH₃ by SO₂ (6) is at least of similar importance as NH₃ oxidation by O₂:



High precision thermochemical calculations confirm that the equilibrium of (6) is nearly exclusively on the side of the products under standard conditions and is shifted even further to the right (entropy) at the temperatures present in the Claus furnace [Ref. 4].

An additional potential pathway consuming NH₃ is its decomposition into nitrogen and hydrogen.



As the cleavage of NH_3 according to reaction (7) is an endothermic process an increase of the Claus furnace temperature should favour (7). However, ASRL studies show that the reaction is severely inhibited (i.e. very slow) in presence of appreciable amounts of water and H_2S . As the latter are major constituents of the gas mixture being present in any Claus furnace, reaction (7) can be considered to be kinetically slow. But it can be expected that with increasing temperature (7) is gaining in importance.

Field experience is summed up by the "T³-rule" which states that ammonia consumption rises with increasing temperature, more efficient mixing ("turbulence") and enhanced residence time. In practice this means that in order to achieve complete NH_3 destruction not only a high Claus furnace temperature is required but also a burner with excellent mixing performance as well as a furnace chamber of adequate size.

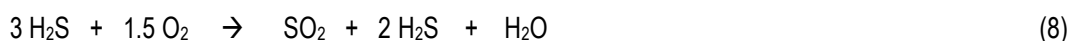
For additional information on the subject of NH_3 destruction see [Ref. 5].

AMMONIA SALTS

Once residual NH_3 has left the waste heat boiler of the thermal Claus section there is no way of NH_3 destruction. But as NH_3 is a potent base it can react with acids contained in the process gas. These so-called "acid base reactions" can lead to solid salts if the vapour pressure of the salt components is sufficiently low. This happens when the temperature is below a certain threshold which is dependent on the type of anion of the ammonia salt. Under Claus conditions ammonia salts (typical component of such salts is the NH_4^+ ion) which would be generated by ammonia and the weak acids H_2S or CO_2 are not stable – i.e. all components stay in the gas phase. But due to the presence of stronger acids like namely SO_3 and SO_2 - which are not present in the Claus feed but both being produced in the Claus furnace – ammonia salts can build up at "cold spots" of all Claus sections downstream the Claus furnace.

The latter sulphur oxides occur in very different concentration and besides of that the vapour pressure of their respective ammonia salts differs to a considerable extent.

With respect to Claus operation the very strong acid SO_3 can be addressed as a trace compound because its generation in the Claus furnace is limited to quite low levels. This only minor occurrence is mainly due to the partial oxidation condition within the Claus furnace where oxygen molecules are mainly consumed by H_2S in a matrix of a considerable surplus of this highly reduced compound:



As above reaction (8) is very fast not a great many of oxygen molecules is left for subsequent further oxidation of the oxidation product SO_2 according to



However, e.g. 2-digit-ppmv concentrations ex the thermal Claus stage have been found [Ref. 1] and in presence of a high enough concentration of ammonia the build-up of ammonium sulphate salts occurs according to.



As ammonia sulphates (shown in reaction (10) is ammonium bisulphate) are characterised by very low vapour pressure they can build up at quite hot locations and are stable in environments – like waste heat boilers (see Figure below) - where ammonium sulphites do not build up :

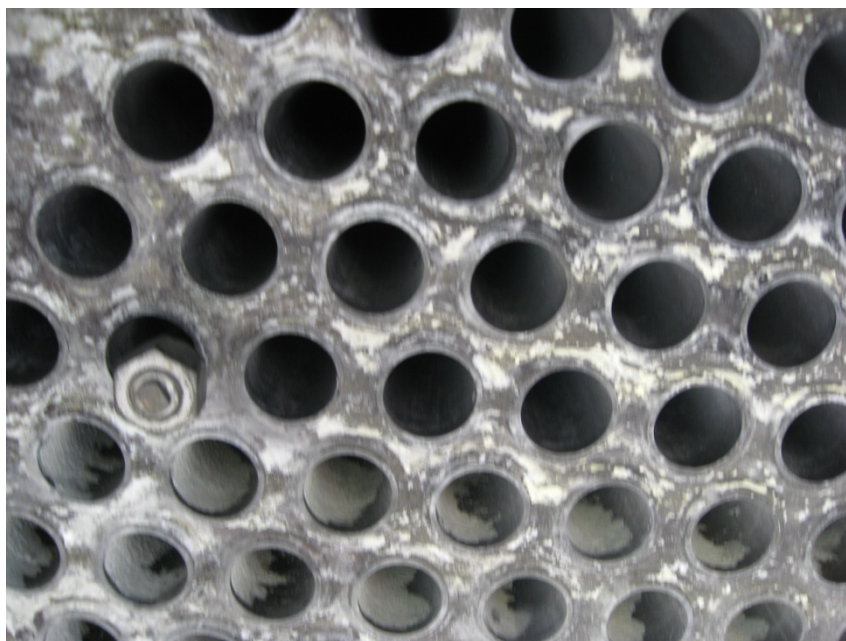


Fig. 12: Ammonium salts with very low vapour pressure – i.e. ammonium sulphates – typically accumulate in the tubes of waste heat boilers (see the white material in the lower, non-cleaned tubes).

In contrast to ammonium sulphates corresponding sulphites can only build up at much lower temperatures – typically below 148°C – and therefore need the presence not only of water and ammonia but also SO₂ which occurs in the process gas not as a trace (like SO₃) but in the one-digit percent range:



(Shown in reaction (11) is ammonium bisulphite)

In order to avoid salt precipitation according to (10) and (11) the most promising measure is in minimising the ammonia content in the process gas – preferably aiming at complete ammonia destruction within the Claus furnace.

The consequences of the build-up of ammonia salt deposits can be a comprehensive range of troubles from minor up-sets, remarkable maintenance/repair effort and sometimes even unscheduled shut-down of the Claus unit (CU). Corresponding causalities and chains of consequences are summarised in the following table:

Typical locations	Primary effects	Secondary (and higher) effects
Waste heat boiler (WHB) tubes (see Figure above)	Δp (\uparrow) \rightarrow	CU capacity (\downarrow)
Sx condenser tubes (general)	Δp (\uparrow) \rightarrow	CU capacity (\downarrow) Often temperature is increased to vaporise the salts => Sx vapour in process gas (\uparrow) => Sulphur recovery efficiency (\downarrow)
Coalescers see below picture b)	Δp (\uparrow) \rightarrow	CU capacity (\downarrow)
Analysers down-stream catalytic stages; esp. air demand analyser (ADA)	Malfunction (optics turn turbid) \rightarrow	Bad control of process air => Sulphur recovery efficiency (\downarrow)
Sulphur (liquid) run down lines and resp. seal legs	Blockage \rightarrow	Effort for maintenance (\uparrow)
Steam ejector (liquid sulphur degassing gas export); see below picture c)	Δp (\uparrow) \rightarrow	Effort for maintenance (\uparrow)
WHB down-stream thermal incineration	Δp (\uparrow) \rightarrow	CU capacity (\downarrow)
Cold spots in general	Build-up of corrosive environment by the salt layer	Corrosion rate (\uparrow) see below picture d) of a carbon steel pipe corroded by ammonium salt deposits

Fig. 13: Ammonia salt precipitation/plugging – an exemplary selection of typical consequences (see also [Ref. 6])

The following pictures show exemplary cases of ammonia salts found in Claus units:

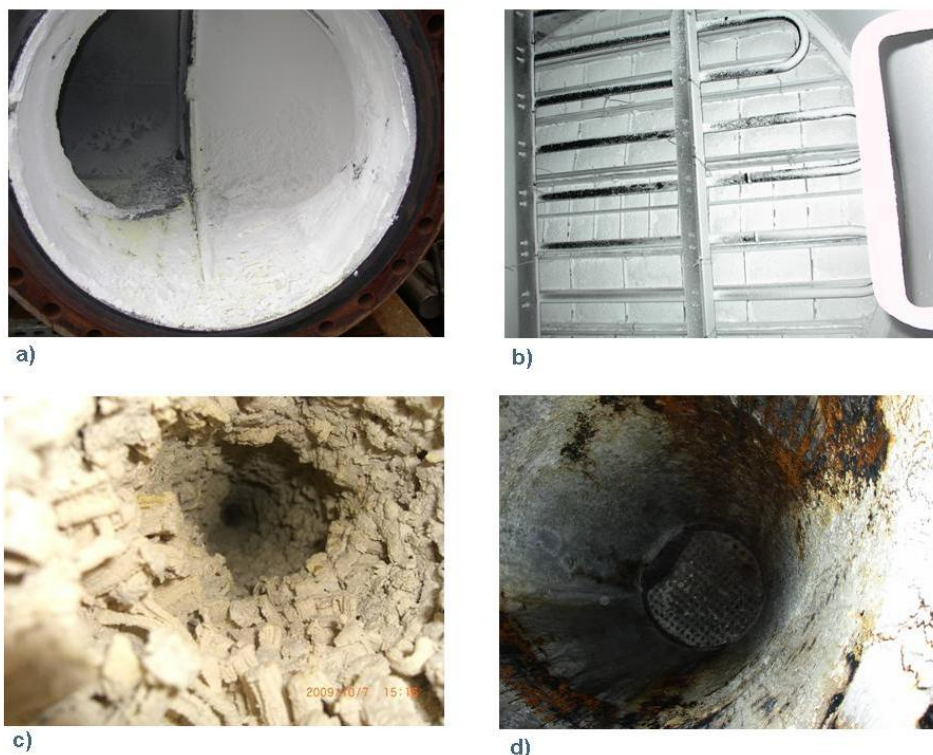


Fig. 14 a-d: Ammonia salt deposits as found in pipes (a) and d)), a coalescer (b)) and in a steam ejector (c)).

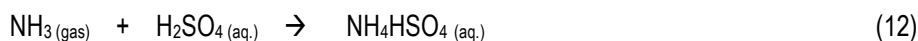
SAMPLING AND ANALYSIS OF NH₃

In order to get quantitative information on the efficiency of NH₃ destruction in the Claus furnace the most reliable method is by analysis of the process gas right downstream the thermal Claus section. However, no online analysers for measurement of NH₃ at ppmv concentrations at this location are commercially available. This appears to be due to the challenging operation conditions, esp. caused by the properties resp. composition of the process gas within this Claus section where high H₂S, SO₂, sulphur and water contents prevail. Therefore manual sampling and subsequent measurement in a laboratory has to be applied in order to get quantitative information on the actual situation.

Due to its characteristic properties – NH₃ is highly soluble in water and is the only known gaseous base which can occur in the Claus process gas – the only methods applied to manually sample/analyse NH₃ in Claus process gas are based on wet chemistry; i.e. using aqueous solutions of low pH for gas absorption.

Sampling

Between the waste heat boiler of the thermal Claus section and the reheat of the first catalytic Claus converter a measured gas portion of a slip-stream of process gas is taken out by a tube, passing the gas through an impinger bottle filled with a known volume of diluted sulphuric acid. In this solution water, elemental sulphur and ammonia are absorbed - the latter quantitatively according to



a)



b)

Fig. 15 a/b: Gas sampling and sample preparation (a) yield aqueous samples of usually yellowish-milky appearance as shown in the impinger bottle right after sampling of NH₃ (b).

Analysis

After sampling the NH₄⁺ ions dissolved in the liquid represent the NH₃ molecules which were present in the gas portion taken from the Claus process gas. In order to get a quantitative value of respective NH₃ content the concentration of NH₄⁺ in the measured aqueous solution has to be determined. This analysis can be performed by various methods; e.g. ion chromatography or photometric absorption. The typically yellowish milky appearance of the aqueous sample - which is due to small particles of elemental sulphur – in dependence of the analytical method applied can exclude direct analysis of the liquid; e.g. when applying photometric detection methods only clear and colourless solutions can be analysed which calls for a pre-treatment of the yielded liquid - like e.g. distillation – in order to get such a clean solution.

FIELD TESTS WITH OXYGEN ENRICHMENT IN VIEW OF NH_3 DESTRUCTION

The destruction of NH_3 within the Claus furnace operated in the air-only mode is already a quite efficient process:

Claus feed in refineries typically contains a considerable amount of ammonia – i.e. often within the one-digit percent range in the combined streams of acid gas and SWS gas and sometimes beyond. The factor of NH_3 decimation is within the range 100 – 1000 which can be stated because the NH_3 concentration in the process gas down-stream the waste heat boiler is typically seen within the range of say 80 – 500 ppmv (dry values). The latter values – even on the low side and below – can give reason to considerable operating troubles and maintenance effort.

When performing field trials with low-level oxygen enrichment the opportunity to improve the efficiency of ammonia destruction is often of interest because virtually every Claus unit can be expected to react in a different way. Therefore NH_3 measurement with and without oxygen addition was often performed in European refineries in Claus units of /with different

- sizes (10 – 140 tons of daily sulphur production);
- tailgas treatments (SCOT/RAR; SubDewPoint; Superclaus; Euroclaus and also without tailgas treatment);
- temperatures of feed streams (incl. process air) to the Claus furnace
- loads (but never low loads);
- acid gas split flow arrangements (see Figure below);
- burners;
- NH_3 contents in the feed.

(Interestingly in air-only mode of respective Claus units NH_3 was always detectable in the process gas down-stream the waste heat boiler – even in cases where no SWS gas had been added to the Claus feed)

With respect to these multifaceted preconditions from a more scientific point of view it does not appear to be acceptable to compare the performance of all respective Claus units in a single sweep.

However - by trying a practical approach in the following it was made a selection out of all field tests performed; this was realised by applying specific criteria to be fulfilled in order to be selected:

- Appreciable NH_3 content in the Claus feed
(i.e. within the range of 3-10 vol-% of NH_3 in the combined Claus feed);
- Once-through operation mode (i.e. no split-flow arrangements);
- High H_2S content in acid gas.

To allow for an overview of the results gained according to above criteria in below Fig. 16 is plotted the performances with respect to NH_3 destruction comparing air-only operation vs. oxygen enriched operation mode:

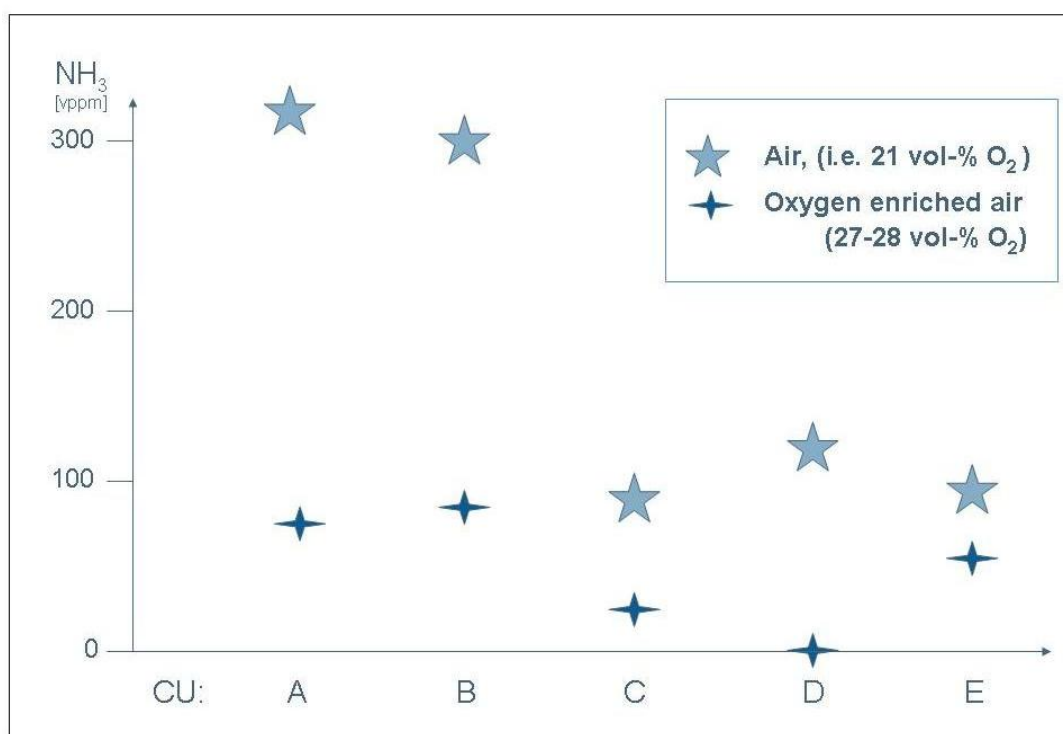


Fig. 16: shows how different Claus units (CU) reacted to oxygen enriched operation with respect to NH₃ destruction efficiency – NH₃ concentrations (dry) found in the process gas sampled between waste heat boiler of the Claus furnace and preheat of the first catalytic Claus converter.

In general terms the NH₃ measurements presented in Fig. 16 show that by application of low-level oxygen enrichment the degree of NH₃ destruction can be improved in every case. However, the improvement of NH₃ destruction can be of only minor significance (Claus unit E) but in most cases an improvement factor of better than 3 was found which in one case mounted up to more than one order of magnitude.

Especially remarkable are results gained at Claus unit A, where due to preheat of feed going into the Claus burner the furnace temperature of 1290°C was reached in air-only mode.

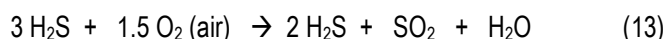
However, furnace temperatures of "1,232-1,288°C" are generally considered necessary for complete destruction of ammonia (see [Ref. 7]). This led to the expectation of at least very low NH₃ concentrations in the process gas of Claus unit A. However – the experimental result of 330 ppmv couldn't be discussed away and stands firm especially as the respective plant experienced troubles due to ammonia salt effects. Interestingly even by substantial temperature increase when applying oxygen enrichment (1440°C) the NH₃ concentration couldn't be reduced below 80 ppmv, a value other Claus units already reach in the air only mode. In sharp contrast to these findings in case of another plant (Claus unit D) it was possible to boost NH₃ destruction to completion by applying low-level oxygen enrichment - in this case by an enrichment level of only 25 vol-% at a furnace temperature of 1300°C (when increasing the enrichment level further to 28 vol-% thereby yielding a furnace temperature of 1340°C the degree of NH₃ destruction was – not at all surprisingly - still total).

Acid gas split-flow and NH₃ destruction

Besides the application of oxygen also other technologies can be used to improve the efficiency of ammonia destruction within the Claus furnace (for an overview refers to [Ref. 8]).

The underlying concept is normally to bring the ammonia into a very hot environment, preferably in presence of an oxidant and high turbulence. Such conditions prevail especially in the flame zone of a Claus furnace – where temperatures well above 2000°C can be assumed. Therefore sending the SWS gas stream through the main Claus burner and thereby into the flame zone already goes a long way. But the efficiency of ammonia destruction can be increased even further when feed components are minimised which do not take part in reactions and - due to their heat capacity - reduce the flame resp. furnace temperature in the up-stream part of the Claus furnace.

One way of leaving out such gas components which are behaving as inerts in the hot zone is to send only part of the acid gas to the burner. This is possible because in course of the substoichiometric combustion process typical for Claus operation only one third of the whole H_2S amount needs to be oxidised to SO_2 according to



In case of the acid gas split-flow technology according to Fig. 17 a considerable part (in theory up to two thirds) of the acid gas – i.e. mainly H_2S – is by-passed around the Claus burner. In this mode of operation the by-passed H_2S doesn't contribute to cooling in the first furnace section as it would do if all the acid gas would be sent to the Claus burner. In addition the partial pressure of the available oxidants – i.e. especially oxygen and SO_2 – is higher thereby also favouring more efficient ammonia destruction.

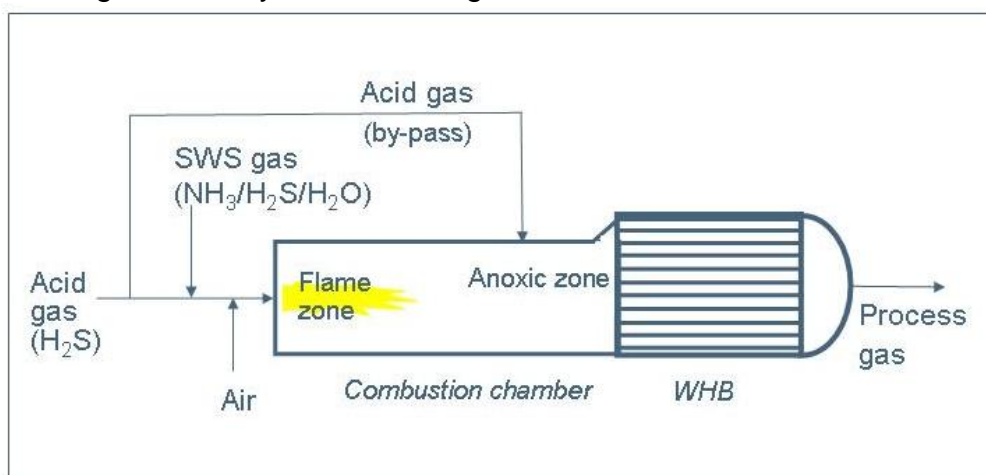


Fig. 17: Acid gas split-flow - By-passing part of the acid gas around the very hot flame zone into the downstream section of the combustion chamber

The split-flow concept shown above is certainly older than oxygen enrichment and applied in a great many of cases. As it can allow for furnace temperatures of well above 1400°C it is very efficient as long as all the ammonia is passing through the burner into the flame zone; i.e. as long as the acid gas comes without any or only with very minor NH_3 content described split-flow can be expected to work very efficient with respect to ammonia destruction.

BUT it is often overlooked that in acid gas in not only exceptional cases NH_3 is being present. In dependence of the operation mode of the up-stream amine scrubber regenerator NH_3 concentrations in the therein generated acid gas can – in extreme cases - mount up even to percent levels.

The following case example shows that already much lower ammonia concentrations in the acid gas can render the split-flow concept useless - if not counteractive:

At one German Claus unit (see Fig. 16: Claus unit C) bedevilled with severe ammonia problems especially in the SubDewPoint section (see Fig. 14 a originating from this plant) a revamp by implementation of a split-flow according to Fig. 17 was realised. When about half of the acid gas (containing 500 ppmv of ammonia) was bypassed around the Claus burner – a not unusual degree of split-flow - measurements showed that the ammonia content in the process gas with 110 ppmv exceeded the initial value of 80 ppmv. The latter ammonia concentration had been found during the previously applied air-only based once-through operation mode; i.e. by application of the split-flow the concentration of residual ammonia did increase by more than one third. Moreover, compared with the oxygen enriched operation mode (once-through) the split-flow was less efficient by a factor of almost four.

Such finding indicates that only a minor amount of the NH_3 by-passed with the acid gas was destroyed on its way through the second (anoxic) part of the Claus burner. This most unintended effect of the split-flow can hardly surprise as this ammonia contingent doesn't experience the very hot flame zone and in addition

is not intensely mixed with the very hot gas ex Claus burner containing SO₂, the most important reaction partner of ammonia according to (6).

Above case example allows for a conclusion as follows:

Air based Claus technologies for optimised ammonia destruction in the furnace which are based on by-passing part of the acid gas around the Claus burner are perfect in theory. In practice – as could be shown by measurements – such solutions can even counteract by leading to increased ammonia content in the process gas. Such effects can be expected if NH₃ shows up in the acid gas; and as appreciable amounts of ammonia in the acid gas like e.g. 1000 ppmv are not uncommon and considerable higher concentrations have been seen this aspect deserves to be considered when the application of acid gas split flow is envisioned.

OUTLOOK & CONCLUSION

In oil refineries from a general perspective the challenges facing sulphur recovery installations will continue to rise. Main reasons for this foreseeable tendency can be seen in decline of crude oil quality, tightening regulations and also in the pressure on refiners to operate ever more profitable in order to be competitive.

Such summary can be deduced from major trends as follows:

On the one hand as an average the sulphur content in the crude oil used in refineries is growing – not dramatically but in a steady manner [Ref. 9].

In addition requirements on fuel quality are still on the rise – e.g. the up-coming step-wise reduction of sulphur content in oil-based fuel for ocean going vessels [Ref. 10]. Last but not least to be mentioned is a tendency in refineries towards processing of more heavy resp. heavier fractions for conversion processes like (hydro) cracking [Ref. 11].

Focussing on oxygen enrichment as a versatile option to answer above mentioned challenges in view of respective repercussions on Claus installations – especially increasing load of H₂S and NH₃ - the following statements are offered:

- Field tests comparing air-only operation with low-level oxygen enrichment are an interesting and proven means to find out on an experimental basis how an individual Claus train - incl. downstream installations - reacts to additional oxygen use; esp. in terms of capacity increase, energy saving and ammonia destruction.

In addition the results gained by such tests provide a good basis for estimations with respect to applicability of higher levels of enrichment at the very plant.

- In terms of capacity increase by revamp of existing Claus units the three different modes of oxygen application – i.e. from low-level to mid-level up to high-level enrichment - cover a considerable spread: Ranging from more than 30 % to max. 150 % of additional Claus capacity; i.e. already the application of low-level oxygen enrichment bears a considerable potential in terms of capacity increase –even in appreciable excess of 25 percent which are not seldom offered as the maximum value.
- Implementation of oxygen enrichment at existing Claus units is not only a versatile answer to increasing loads of H₂S and NH₃ coming as Claus feed. In addition this kind of revamp technology reduces energy demand of the Claus train - especially for incineration of off-gas - thereby bearing the potential of counterbalancing operational expenditure due to oxygen cost to a considerable degree.
- Expect ammonia to be present up to an appreciable amount not only in SWS gas but also in the acid gas coming from amine scrubbers. This is a very important point – especially when selecting a technology for optimisation of NH₃ destruction.
- Oxygen enrichment applied in a once-through operating mode - i.e. without by-passing any acid gas around the Claus burner - is not susceptible to occurrence of NH₃ in the amine acid gas.
- Ammonia measurements performed during field tests with and without low-level oxygen enrichment have shown that ammonia destruction always improved in efficiency - in most cases at

least by a factor of 3 but also by more than one order of magnitude. Therefore – especially in cases of severe operational problems due to ammonia salts - permanent application of oxygen can be the preferable option.

- High temperature in the Claus furnace does often - but not always - come with highly efficient ammonia destruction - In other words: The "T³-rule" applies – i.e. besides the temperature aspect also a high residence time and an excellent mixing quality of the Claus burner has to be appreciated as well.
- Field tests with low-level oxygen enrichment can easily and swiftly be realised as the only hardware modification at the Claus unit itself is the installation of a stud for oxygen injection onto the process air pipe. The costs for such tests are very low.
- Availability of major (esp. for new units) and medium investment (esp. for revamps) in oil refineries is often limited. As the effort for implementation of oxygen enrichment – esp. in the low- and mid-level mode - is quite limited it appears save to state that the number of cases with oxygen application at Claus units will increase further.

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