

Ammonia destruction in the reaction furnace

A study based on reaction fundamentals aids a comparison of the advantages of one-zone and two-zone SRU reaction furnace design in ammonia destruction

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Ammonia typically evolves from nitrogen-containing components in processing crude oil. Processing and handling sour gas and sour water containing ammonia in an environmentally acceptable manner has always been a challenge in refineries and is the focal point for many designs and patents. There are two main objectives that these designs and patents attempt to achieve: purifying ammonia-bearing sour water to prepare the water for further processing or discharge; and disposing of the ammonia once it has been removed from the sour water. Options for disposing of ammonia include destroying it, or selling it as a product if it meets purity standards. This article focuses on a common method for disposing of the ammonia: destroying it in the reaction furnace of a sulphur recovery unit (SRU). When directed to an SRU, nearly complete destruction of ammonia is needed to prevent plugging the SRU with ammonium salts.

The effectiveness of ammonia destruction is strongly influenced by the configuration and operation of the reaction furnace. The two hardware configurations considered here are one-zone and two-zone designs. The two-zone design that will be considered has one burner at the front of the first reaction chamber. These are two of the most common reaction furnace configurations used in SRUs. In this article, a brief introduction to each reaction furnace design is followed by a discussion of ammonia

destruction chemistry, and concludes with a case study illustrating how design and operating parameters affect ammonia destruction.

One-zone reaction furnace

The one-zone furnace, also referred to as a straight-through design, operates with all the amine acid gas (AAG) and sour water acid gas (SWAG) feed being mixed together, then fed to the furnace via a single burner (see **Figure 1**). This design is generally applied when the feed gas contains no ammonia, or small concentrations of ammonia, but with the addition of preheat and incrementally longer residence time it can also be used successfully when ammonia is present in higher concentrations.

A benefit of the one-zone furnace is that all the acid gas passes through the burner flame, thereby providing the maximum available heat for the destruction of contaminants such as hydrocarbons and ammonia. Insufficient destruction of hydrocarbons in the reaction furnace can have disastrous effects on the converter beds downstream, especially if they contain aromatics such as BTEX. Another bene-

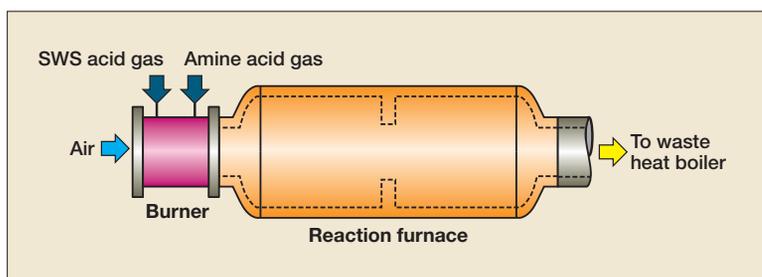


Figure 1 General layout of a one-zone reaction furnace

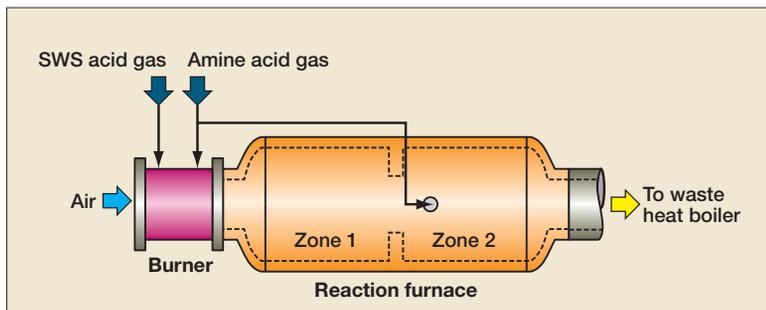


Figure 2 General layout of a two-zone reaction furnace⁴

fit is a more straightforward control scheme than in a two-zone furnace because the one-zone furnace controls do not have to address splitting gas between zones. As with any design, however, there are also some disadvantages.

Depending on feed gas composition, one-zone furnaces may experience problems with flame stability. Flame stability can be improved in a one-zone furnace by increasing the flame temperature by preheating the feed streams, including the combustion air. With very low quality, lean H_2S feeds, natural gas spiking is sometimes employed to maintain flame stability. In a one-zone furnace, there is no acid gas bypass available to increase the flame temperature. Lower flame temperatures can leave one-zone furnaces more susceptible to flame-out in the event of feed composition changes and can also lead to multiple operating and reliability issues caused by incomplete destruction of contaminants. By placing preheaters in the feed gas and air streams, this operating instability can be mitigated; however, it comes at the cost of adding capex for the equipment as well as opex for maintaining and operating that equipment.

Two-zone reaction furnace

An alternative furnace design is the two-zone one-burner furnace (see **Figure 2**), also referred to as a front side split. This design is generally applied when the ammonia content in the acid gas exceeds the nominal 2 mol% limit, but it can also be used in cases with less ammonia. The general layout directs all the ammonia-bearing SWAG to the front zone where it passes through the burner. The front zone operates at a higher temperature to encourage adequate ammonia and contaminant destruction. The AAG, which is rich in H_2S but contains relatively little ammo-

nia, comes from upstream acid gas removal units. It is split and directed to both the front-end and back-end zones. The relative fractional split between the zones is a primary unit control parameter. The Claus process only requires that one-third of the total H_2S be oxidised to SO_2 , which leaves the remaining two-thirds to act as a heat sink in the flame. Bypassing clean

AAG around the front zone burner flame increases the flame temperature by reducing the amount of non-combusting gas in the flame that is acting as a heat sink.

The percentage of AAG being bypassed to the second chamber depends on the desired flame temperature as well as the concentration of H_2S in the gas. The temperature of the front zone should be kept high enough to ensure adequate ammonia destruction, generally in the range 2300–2700°F (1260–1480°C). The maximum temperature is governed by the refractory lining's upper temperature limit. Generally, no more than 60% of the total H_2S in the SRU feed should be bypassed to ensure the atmosphere in the front zone does not operate in the oxidising region and cause NOx levels to increase. If the atmosphere in the furnace operates in this oxidising region, substantial amounts of NOx and SOx can be produced which, under the right conditions, can form hot aqua regia, an extremely corrosive material capable of dissolving even gold and platinum. The controls for the amount of acid gas bypass are generally based on the flame temperature in the front zone as well as the concentration of H_2S in the AAG feed.

One of the benefits of a well-designed two-zone furnace is improved ammonia destruction over the one-zone furnace. To a large extent, greater ammonia destruction results from higher flame temperatures. This temperature control advantage in the front zone comes from the ability to bypass some of the amine acid gas around the front burner, relieving some of the cold acid gas load on the flame. When the heat sink of cold uncombusted acid gas is removed from the flame by bypassing it to the back zone, the flame temperature can be greatly increased. High temperatures are known to benefit ammonia destruction. The benefit derives from improved

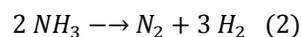
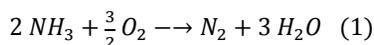
kinetics for the complex and somewhat counter-intuitive ammonia destruction mechanism described in the next section.

One of the negative aspects of the two-zone design is that the fraction of AAG that is being bypassed to the second zone does not pass through the burner flame at all. Thus, any contaminants that may be present are not subjected to the high temperatures of the flame. This can pose a problem if the contaminant levels in the clean AAG become excessive. Another negative is that the portion of the acid gas that is bypassed has a much shorter residence time, making it harder to achieve equilibrium of the Claus reaction in the furnace. Finally, since the two-zone design has an additional control point for splitting the clean acid gas flow between the zones, the control system will be inherently more complex. There are also safety concerns associated with bypassing acid gas around the front zone. If too much is bypassed, the temperature of the front zone can exceed the refractory thermal limits and compromise the integrity of the reaction furnace lining, and therefore the furnace wall itself.

Two-zone furnaces also require a relatively large nozzle on the side of the reaction furnace vessel to allow the bypassed acid gas to enter the back zone. This nozzle has accompanying mechanical challenges associated with construction and maintenance of the refractory lining, which are avoided in the one-zone furnace design.

Ammonia destruction pathways

Adequate destruction of ammonia is extremely important for reliable SRU operation because insufficient destruction can lead to precipitation of ammonium salts of sulphide, bisulphide, sulphate, sulphite, and bicarbonate. This typically occurs downstream in the sulphur condensers where temperatures are lower. It can also cause catalyst deactivation. There are two ammonia destruction pathways that are commonly assumed to dominate in the reaction furnace:

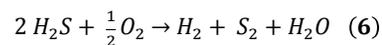
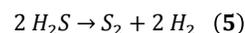
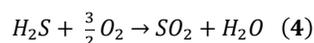
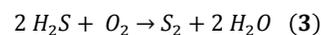


The first pathway (Reaction 1) is the oxidation

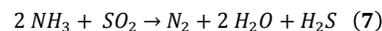
of ammonia to free nitrogen and water. The second (Reaction 2) is thermal cracking to free nitrogen and hydrogen. Both pathways are well documented and both occur in the reaction furnace. However, there is another pathway that has been reported by Alberta Sulphur Research Limited⁶ (ASRL), which usually dominates in an operating plant.

The influence of hydrocarbons and other contaminants in sulphur plant feeds will be set aside so the main focus can be placed on the reactions involving H_2S and ammonia. It is well established that H_2S is present in significant quantities in the front zone where ammonia destruction takes place and where H_2S oxidises to SO_2 . The kinetics of H_2S oxidation have been shown by ASRL^{3, 6} to be much faster than the reaction between ammonia and oxygen. Most, if not all of the oxygen present in the flame environment is consumed by H_2S long before ammonia even has a chance to react. It being the case that oxygen is rapidly consumed predominantly by H_2S , one must ask the question as to what oxidises ammonia? ASRL has shown that a pathway for this oxidative reaction begins with H_2S oxidation, then proceeds to ammonia oxidation as follows:

H_2S oxidation (very fast reactions)



NH_3 oxidation (fast reaction)



This mechanism proposes that because the reaction rate of H_2S with oxygen is so much faster than between ammonia and oxygen, the H_2S consumes oxygen first, producing SO_2 according to Reaction (4). The SO_2 then oxidises ammonia according to Reaction (7). In the ProTreat simulator, the furnace model is based on reaction kinetics. It uses this mechanism together with data from ASRL's recent work. This kinetic furnace model also predicts the extent of destruction of aliphatic and aromatic

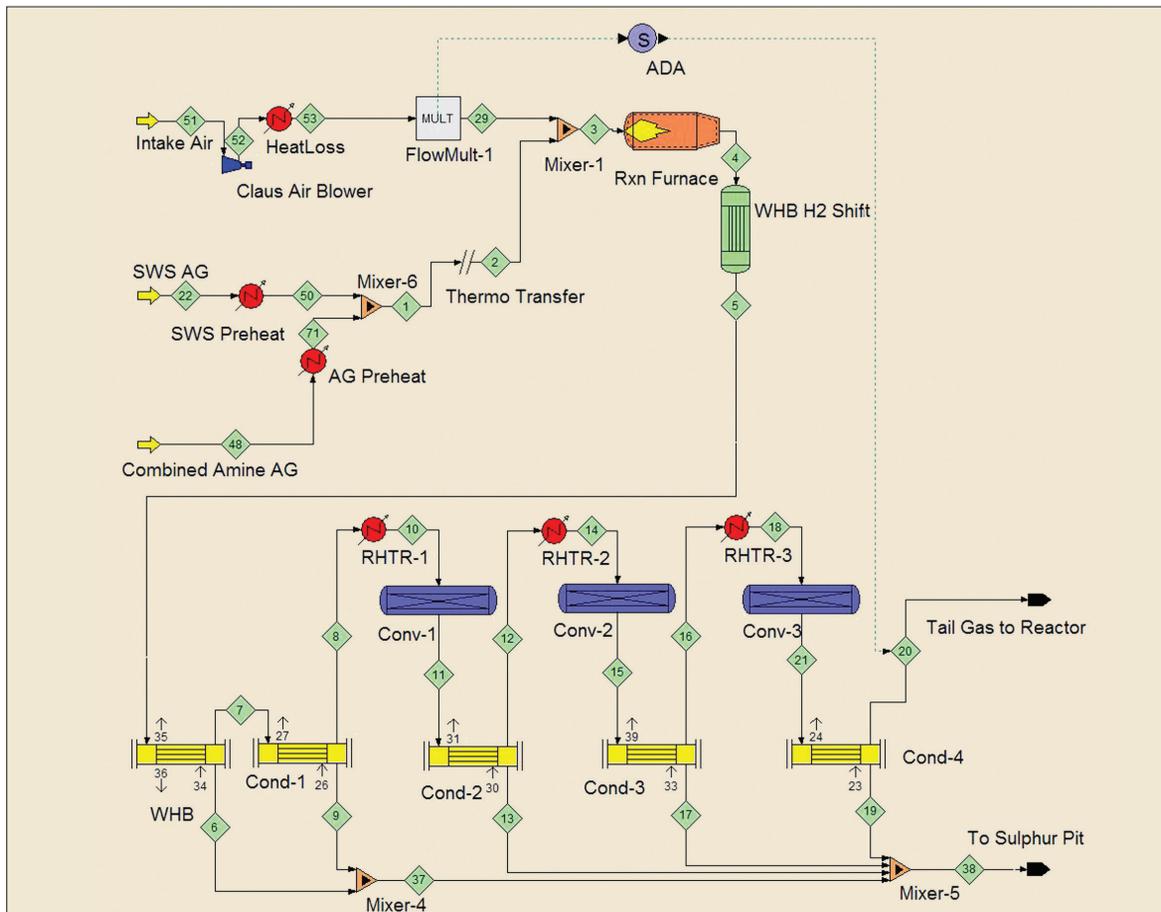


Figure 3 Flowsheet for straight-through reaction furnace with preheat of SWAG and AAG

hydrocarbons on the basis of fundamental reaction rate data measured by ASRL.⁵

Because the ProTreat kinetic model is based on the correct fundamentals, it is a predictive tool that can be used to anticipate accurately the effect of process changes. This is a capability that an empirically fitted model simply does not have because such models are based on empiricism, not physico-chemical fundamentals, so extrapolation can be quite uncertain.

Case studies

Using the ProTreat Sulphur Plant Model allows one to look at a comparative case study involving both the one-zone and the two-zone designs in the context of ammonia destruction. The case studies use a typical

combined AAG feed stream, consisting of bulk amine acid gas and tail gas unit (TGU) recycle gas streams, and a typical SWAG composition. In a one-zone design, all of the AAG is combined with the SWAG prior to entering the reaction furnace. However, in a two-zone design, all of the SWAG is combined with only a portion of the AAG. In actual practice, the portion of AAG that is combined with the SWAG is determined through a feed-back control loop based on the effluent temperature of the first zone. The combined gas is then fed through the burner and passes through the front reaction chamber. The front zone effluent combines with the bypassed AAG and enters the back zone of the reaction furnace. In the back zone, the hot gas from the

Acid gas feed compositions		
Component	Amine acid gas (AAG), mol%	Sour water acid gas (SWAG), mol%
H ₂ O	1.4	25
H ₂ S	92.1	33.5
CO ₂	5	0
NH ₃	0	41.5
CH ₄	0.5	0
H ₂	0.0012	0
N ₂	0.9988	0
Total flow rate, lbmol/h	462	200

Table 1

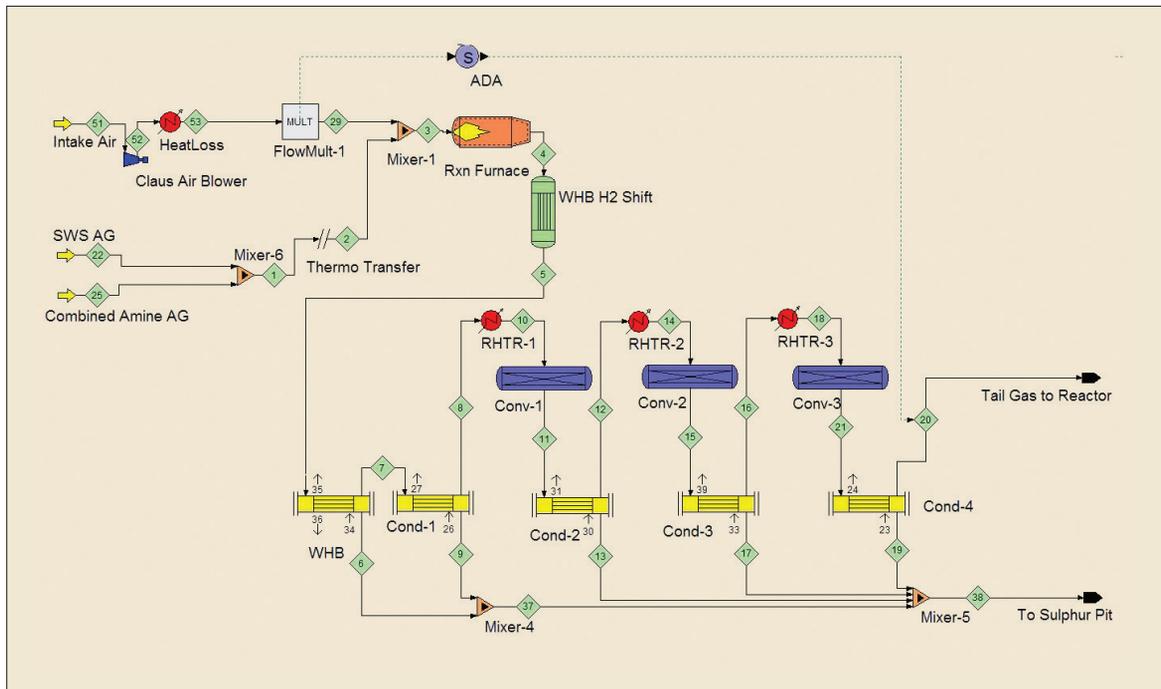


Figure 4 Flowsheet for straight-through reaction furnace without preheat of acid gas feeds

front zone (not a burner) provides the heat required by the reactions. All cases use the feed compositions given in **Table 1**.

There are two case studies:

- Case study 1: ammonia destruction in a one-zone reaction furnace design is assessed by varying the amount of preheat provided to the AAG and SWAG feeds. **Figures 3** and **4** both show one-zone designs. **Figure 3** shows SWAG and AAG feed preheaters. **Figure 4** shows no preheating.
- Case study 2: ammonia destruction in a two-zone reaction furnace design is assessed by varying the percentage of clean acid gas that is bypassed to the back zone of the two-zone furnace. **Figure 5** shows the two-zone design.

Downstream of the furnace(s) the flowsheets are all identical and are typical of a three-bed Claus unit. Reaction furnace parameters are set to typical values: the residence time in the reaction chamber is arbitrarily set to 1.1 seconds. The length-to-diameter (L/D) ratio is 3.5 for the one-zone furnace and for each zone in the two-zone reaction furnace.

The typical residence time for a reaction furnace is nominally one second; however, it should be pointed out that regardless of whether the design is one-zone or two-zone, the resi-

dence time required to destroy ammonia depends on both temperature and ammonia concentration in the feed gas. When using the two-zone design, the front zone often has a longer residence time than the back to ensure fairly complete destruction of ammonia.

A one-zone design is modelled in ProTreat using a single reaction furnace block consisting of burner plus reaction chamber where the AAG, SWAG, and combustion air are all mixed together before entering the furnace itself. The two-zone design is modelled using two reaction furnace blocks in series. The front zone (Zone 1) contains a burner and all the SWAG, part of the AAG, and the combustion air are mixed together as Zone-1 feed. The back zone (Zone 2) does not contain a burner. It is fed with effluent from Zone 1 combined with the bypassed portion of the AAG.

Results and discussion: one-zone furnace

The ammonia concentration for the combined SWAG and AAG stream is about 12.5 mol%. This is well above the typical maximum ammonia concentration for a one-zone design and the results show why this is the case. The informal industry standard for the maximum acceptable ammonia concentration in any reaction furnace effluent is 100–150 ppmv (wet basis). This is to

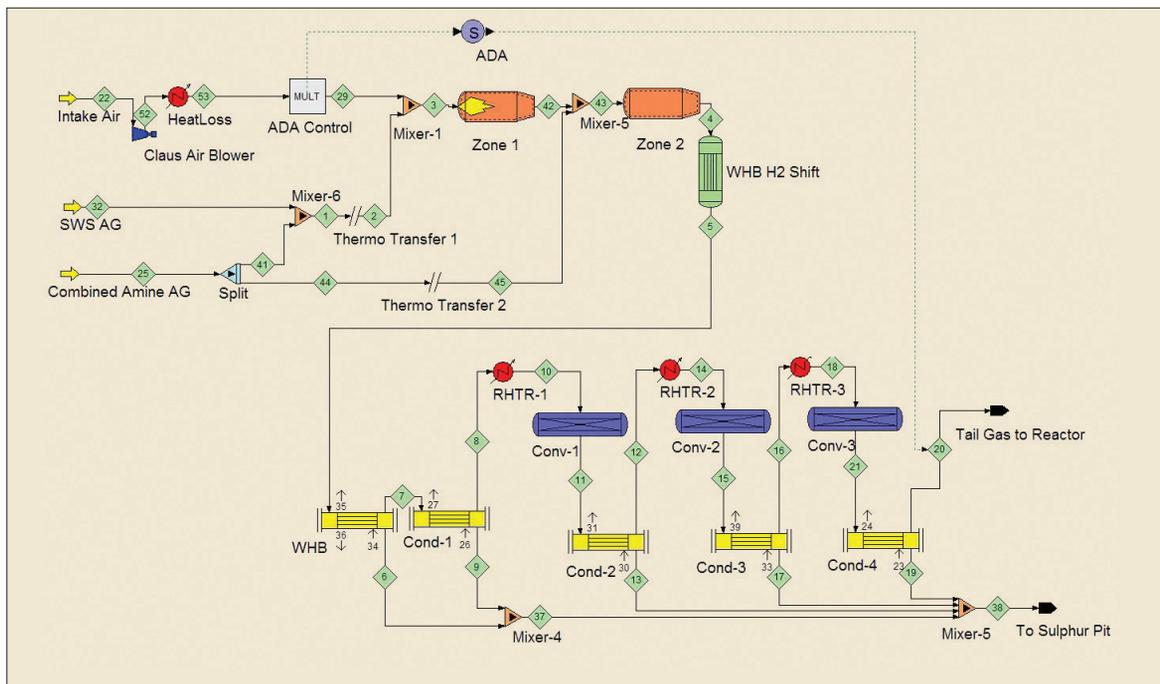


Figure 5 Flowsheet for the two-zone (front-side split) reaction furnace

prevent the precipitation of ammonium salts in the downstream sulphur condensers. After running the simulation in **Figure 4** using the ProTreat kinetic model, it was found for the one-zone furnace without preheat that the ammonia concentration in the calculated effluent was approximately 343 ppmv. This is two to three times the advised limit. If this same simulation were run using a simple equilibrium based

furnace calculation, the ammonia level in the effluent would be only about 0.5 ppmv ammonia. The cause of the huge discrepancy is the equilibrium model's failure to account for the actual kinetic rates for each of the important reactions. An equilibrium model assumes all reactions come to equilibrium – nothing could be further from the truth, especially for ammonia destruction.

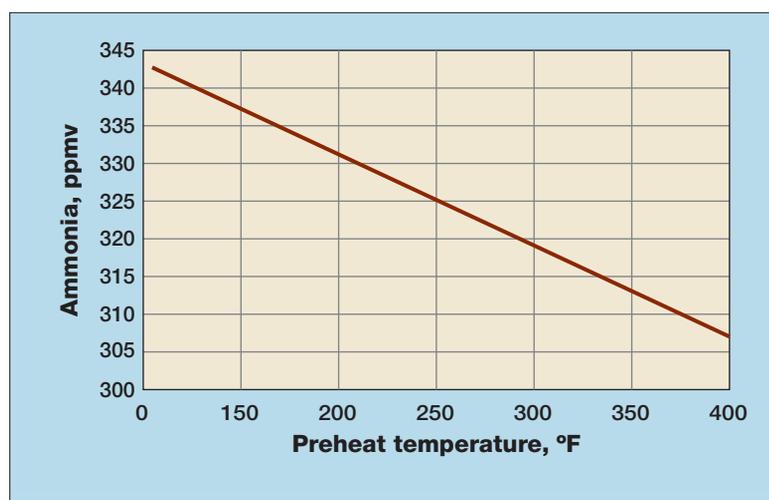


Figure 6 Effect of gas preheat temperature on ammonia from one-zone furnace

When preheating was used on both the AAG and SWAG feed streams (but not on the combustion air stream) to the one-zone furnace (see **Figure 3**), to provide a combined acid gas stream temperature of around 380°F (193°C), the ammonia level in the effluent dropped from 343 ppmv (no preheat) to 309 ppmv. (**Figure 6** summarises the results from various levels of preheat.) Preheating of just the combustion air alone to 450°F (232°C) was also studied. (There is nothing to corrode the steel with hot air and there are no hydrocarbons to crack, so air preheat can be used to provide higher

temperatures.) This amount of air preheat produced 287 ppmv ammonia. This was better performance than with acid gas preheat alone because the mass flow of the combustion air was considerably larger than the mass flow of acid gas, hence the preheat effect was greater. Both cases left ammonia in the furnace effluent well above the advised limit; however, the results indicated some ability to mitigate ammonia levels by preheating in a one-zone furnace design. With preheat alone, in some cases the ammonia levels may be sufficiently reduced to meet the advised limits when using a one-zone reaction furnace.

Another simulation study was done for the one-zone design with the acid gas preheated to 380°F (193°C), by holding all variables fixed and varying the residence time in the furnace. To meet the 100-150 ppmv industry guideline with a one-zone furnace, more residence time would be required for this particular case. An ammonia level of 95 ppmv could be achieved by increasing the residence time to 1.4 seconds.

It is quite possible to destroy ammonia adequately in a one-zone furnace to acceptable levels and lower. However, this may require the one-zone furnace to be outfitted with adequate preheaters as well as to have enough volume to provide the necessary residence time.

Results and discussion: two-zone furnace

For the two-zone furnace, an acceptable ammonia level was achieved with acid gas bypass of around 30%. The ammonia concentration in the effluent from Zone 2 was approximately 90 ppmv on a wet basis at this percentage bypass. In **Figure 7**, the concentration of ammonia in the effluent from the back zone is shown as a function of the percentage bypass. As the bypass percentage

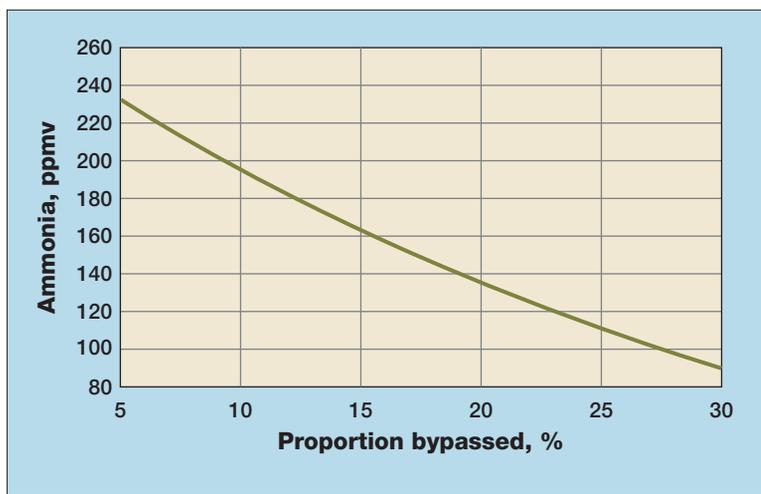


Figure 7 Effect of acid gas bypass on ammonia in Zone 2 effluent

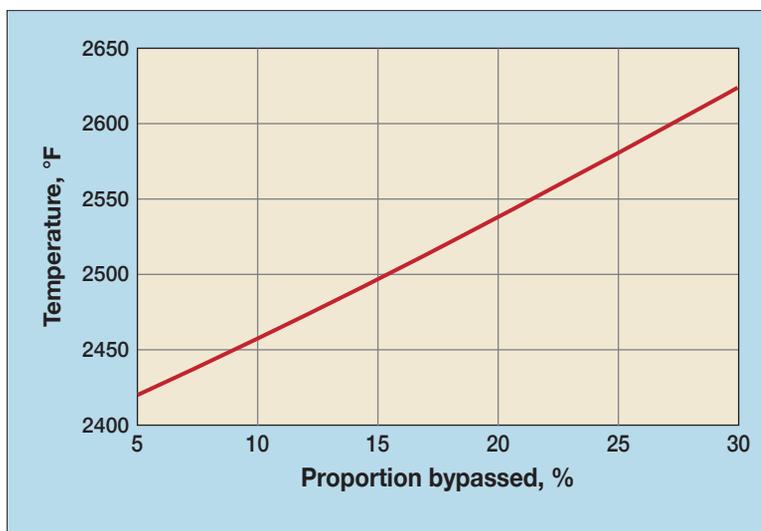


Figure 8 Effect of acid gas bypass on temperature in Zone 1

approaches zero, ammonia from the back zone approaches 275 ppmv. As already seen with the one-zone furnace, the outlet without preheat was approximately 343 ppmv ammonia. The difference in this zero-bypass case results from the mixing characteristics that are assumed in the front and back zones of the two-zone furnace. In the front zone, the burner mixing characteristics are set equivalent to a high intensity burner by selecting this option in ProTreat. This selection accounts for mixing imperfections in the chamber of a commercial size unit but with burners having good mixing characteristics. The back zone is set to the perfectly mixed option because there is no burner located in that zone.

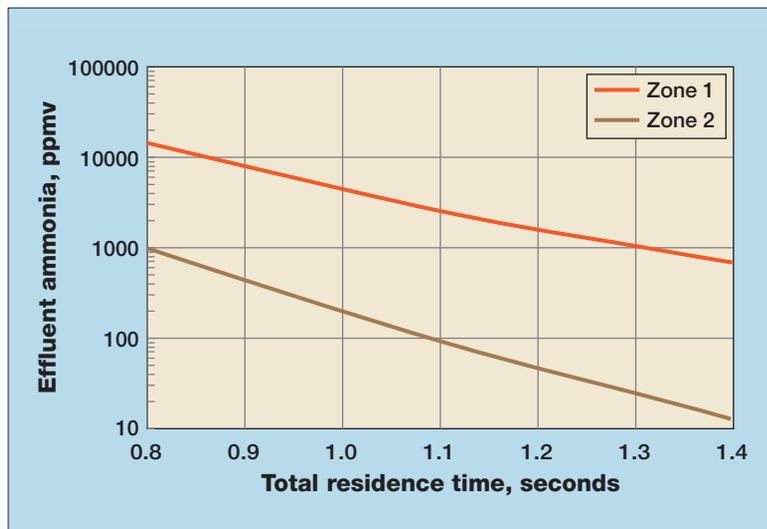


Figure 9 Effect of total residence time in the two-zone furnace on ammonia in effluent from each zone with 30% bypass

As the bypass percentage is increased, the concentration of ammonia from the back zone decreases almost linearly. This is due in part to the increasing temperatures in the front zone, as seen in **Figure 8**. Additionally, the concentration of SO_2 is increasing in the front zone. At a bypass of around 30%, the temperature approaches the upper end of the minimum acceptable temperature range (2300–2700°F, 1260–1480°C). As discussed earlier, higher temperature is achieved through bypassing the portion of H_2S that does not need to be converted to SO_2 and which would have acted as a heat sink had it been allowed to enter the first zone. Front zone temperature increases with increasing bypass. Ammonia destruction kinetics, of course, respond exponentially to higher temperature, providing greater extent of reaction.

Another interesting aspect of two-zone furnaces is the effect of residence time on the ammonia concentrations in the effluent from the two furnace elements. As shown in **Figure 9** for a two-zone furnace, ammonia concentrations from each zone decrease as the total residence time in the two combined zones increases. Over the range of practical residence times (0.8–1.4 seconds), ammonia destruction trends exponentially with residence time.

Three important factors play a large role in the adequate destruction of ammonia in the reaction furnace, namely, residence time, temperature in

the furnace, and proper mixing of combustion air with the acid gas entering the burner. It is important to ensure an almost completely homogeneous mixture of combustion air and acid gas to ensure complete and even combustion of the acid gas and complete ammonia destruction.

Conclusions

There are many considerations pertinent to each reaction furnace design. The one-zone furnace is usually able to relieve the rest of the SRU adequately from hydrocarbon contaminants by ensuring all the acid gas passes through the high temperatures of the burner. Compared to the two-zone reaction furnace, the acid gas controls are simpler. One-zone furnaces generally require more equipment upstream of the furnace to ensure the acid gas is adequately preheated to ensure a stable flame. Conversely the two-zone furnace has some further mechanical and maintenance challenges associated with the additional nozzle in the reaction furnace vessel.

The two-zone furnace will generally achieve higher ammonia destruction compared to a single zone. This results from the ability to bypass clean AAG around the burner into the second zone, which raises the flame temperature in the first zone. However, to achieve the higher level of ammonia destruction, a more complicated control scheme is needed to control the bypass, primary acid gas, and the flow rate of combustion air. This is not to say a single-zone furnace is unable to achieve adequate ammonia destruction because with the addition of preheaters and increased residence time, a one-zone furnace is able to achieve the desired destruction levels. This might be a trade-off against the operating complexity and bypass cost of a two-zone system.

A two-zone furnace increases the likelihood of subjecting the SRU to contaminants that are present in the otherwise clean (ammonia free) amine acid gas being bypassed around the burner unit. Bypassing aliphatic and aromatic hydrocarbons around the flame can have devas-

tating effects on downstream catalyst beds.

Besides the temperatures in the furnace, another key parameter in ammonia destruction is the residence time in the reaction chamber. As shown in **Figure 9**, increasing the total residence time, whether in a single- or two-zone furnace, has a significant effect on the ammonia concentrations in the effluent gas – of course, the impact of residence time will only be seen in a furnace model that includes chemical reaction kinetics. By using the ProTreat SRU model, highly realistic simulations that take into account deep-seated chemistry and reaction kinetics vs just equilibrium can be used to investigate different reaction furnace designs quantitatively. Using a fundamentals basis greatly improves model reliability and realism, and it results in a model that is truly a virtual plant capable of revealing new insights into complex processes.

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