Ammonia Destruction in SRUs — 1. Furnace Types and Mechanism

With the release of our new Sulphur Recovery Unit (SRU) model a few weeks ago, it's our intent that future issues of The Contactor™ will alternate focus between gas treating and SRUs, with an occasional foray into COM interfaces and how they can enhance your simulation experience. This is the first issue to deal with sulphur recovery, and in its own right, it's also the first of a three-part series dealing with ammonia destruction in furnaces.

Ammonia is associated with nitrogen-containing components in crude oil. Processing sour gas and sour water that contains ammonia in an environmentally acceptable manner has always been a challenge in refineries. This note focuses on destroying ammonia in the reaction furnace of an SRU. Nearly complete destruction of ammonia is needed to prevent plugging downstream units in the SRU with ammonium salts.

The effectiveness of ammonia destruction is strongly affected by the configuration and operation of the reaction furnace. We begin with a brief introduction to two of the most common reaction furnace configurations and end with a discussion of ammonia destruction chemistry.

One-zone 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) premixed and fed to the furnace via a single burner. This design is used when the feed gas contains no ammonia, but it can also be used successfully when ammonia is present in small concentrations.
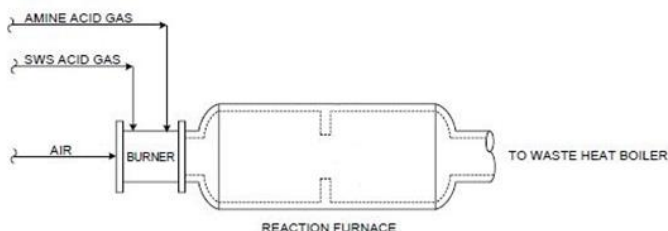

Figure 1   Sketch of One-zone Furnace

A benefit of the one-zone furnace is that all the acid gas passes through the burner flame and is exposed to the highest possible temperature for the destruction of contaminants. Insufficient destruction of hydrocarbons in the reaction furnace can have disastrous effects on the converter beds downstream, especially if they contain aromatics. Another benefit is the relatively straightforward nature of the control scheme because controls do not have to address splitting gas between zones.

However, one-zone furnaces may experience problems with flame stability, particularly if the gas is lean in H_2S, and the furnace may be more susceptible to flame out. This can be mitigated by preheating feeds (including combustion air), and spiking with natural gas or fuel gas.

Two-zone Furnace

An alternative furnace design is the two-zone one-burner furnace, 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.
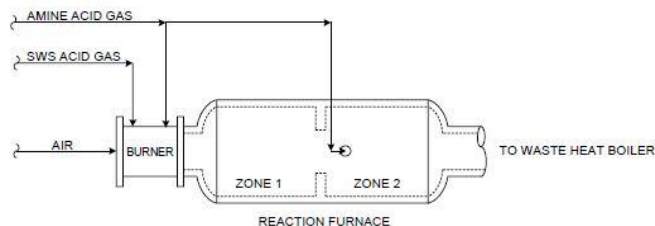

Figure 2   Sketch of Two-zone Furnace

All the ammonia-bearing SWAG enters the burner in the front zone. The higher temperature there encourages adequate ammonia and contaminant destruction. The AAG is rich in H_2S but contains relatively little ammonia. 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 uses enough air (O_2) flow to convert one-third of the total H_2S to SO_2. If fed to the flame, this would leave the remaining two-thirds unreacted, so it would act merely as a heat sink and lower the flame temperature. Flame cooling is prevented by short circuiting a portion of the AAG around the front-zone burner flame.
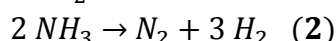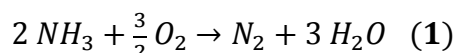
Controlling the percentage AAG bypassed controls the flame temperature which must be high enough to ensure adequate ammonia destruction —generally 2,300–2,700°F, but capped by the refractory material's thermal limits. Generally, no more than 60% of the total H_2S in the SRU feed is bypassed. This ensures the front zone does not operate in the oxidizing region which would produce substantial amounts of NO_X and SO_X, possibly forming hot, very corrosive, aqua regia. Controls for acid gas bypass are generally based on the flame temperature in the front zone and the concentration of H_2S in the AAG feed.

One benefit of a two-zone furnace is greater ammonia destruction from the higher flame temperatures that result from controlling bypass rate. The benefit of a high flame temperature derives from improved kinetics for the complex, and somewhat counterintuitive, ammonia destruction mechanism described below.

A negative aspect of two-zone furnaces is a direct result of the very AAG bypassing that is central to their operation. The AAG bypassed carries with it any contaminants that are in the original gas and these are harder to destroy in the cooler environment of the second zone with its inherently shorter residence time. Additional negatives are that two-zone furnace controls are more complex, and the second zone must have a large side nozzle which complicates the mechanics of installing and maintaining the refractory lining.
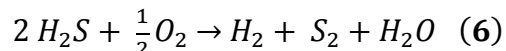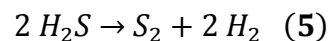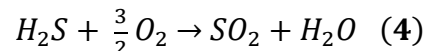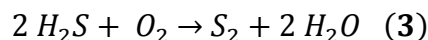
Ammonia Destruction Pathways

Adequate destruction of ammonia is extremely important for reliable SRU operation because excessive ammonia can lead to precipitation of ammonium salts (sulfide, bisulfide, sulfate, sulfite, and bicarbonate). This can occur 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:

$$2\,NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3\,H_2O \quad (\mathbf{1})$$
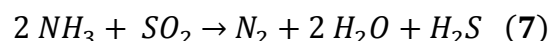$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \quad (\mathbf{2})$$

Both the direct oxidation and cracking pathways shown here are well documented, and both occur; however, there is another pathway reported by ASRL[†], and this reaction pathway, represented by Reaction (7) below, dominates in operating plants:

_H_2S Oxidation (Very Fast Reactions)_

$$2\,H_2S + O_2 \rightarrow S_2 + 2\,H_2O \quad (\mathbf{3})$$
$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O \quad (\mathbf{4})$$
$$2\,H_2S \rightarrow S_2 + 2\,H_2 \quad (\mathbf{5})$$
$$2\,H_2S + \tfrac{1}{2}O_2 \rightarrow H_2 + S_2 + H_2O \quad (\mathbf{6})$$

_NH_3 Oxidation (Fast Reaction)_

$$2\,NH_3 + SO_2 \rightarrow N_2 + 2\,H_2O + H_2S \quad (\mathbf{7})$$

This mechanism proposes that because the reaction rate of H_2S with O_2 is so much faster than between ammonia and O_2, the H_2S consumes O_2 first, producing SO_2 according to Reaction (4). The SO_2 then oxidizes ammonia according to Reaction (7). In the ProTreat® SRU 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 addresses the extent of destruction of aliphatic and aromatic hydrocarbons on the basis of fundamental data, also measured by ASRL[‡].

Because the ProTreat® simulator's 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 physicochemical fundamentals. Extrapolation can be quite uncertain with a purely empirical model.

Parts 2 and 3 in this series are case studies of one-zone and two-zone furnaces, respectively and will appear in the February, 2017 and April, 2017 issues of The Contactor™.

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To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. Visit www.protreat.com/seminars for details.

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[†] Clark, P.D., Dowling, N.I., Huang, M., _Mechanisms of Ammonia Destruction in the Claus Front-End Furnace_, ASRL Quarterly Bulletin Vol XXXIV, No. 4, pp. 1–50, Jan–Mar 1997.
[‡] Clark, P.D., Dowling, N.I., Huang, M., _Chemistry of the Claus Front-End Reaction Furnace: Hydrocarbon Reactions and the Formation and Destruction of CS_2, ASRL Quarterly Bulletin, Vol XXXIII, No. 4, pp. 1–49, Jan–Mar 1997.