



## **Sulphur Degassing**

Sulphur in the end-products of the oil and gas industries is a natural consequence of its presence in their raw materials. Unless removed, sulphur will cause a myriad of practical and environmental problems. The most common sulphur contaminant is hydrogen sulphide. Others include mercaptans, COS, and CS<sub>2</sub>.

A variety of processes is used to convert and/or remove these compounds. The most common is the modified Claus process, which is almost universally used to convert H<sub>2</sub>S into elemental sulphur. An unintended consequence of the process, however, is the almost inevitable incorporation of unreacted H<sub>2</sub>S into the elemental sulphur being produced.

Air-H<sub>2</sub>S mixtures have two undesirable characteristics: they can be (a) lethally poisonous and (b) explosive. Control of H<sub>2</sub>S is therefore high priority for refineries and gas plants. Extended exposure to air-born H<sub>2</sub>S at concentrations as low as 5 parts per million by volume (ppmv) is likely to cause respiratory irritation. Extended exposure to concentrations as low as 100 ppmv can cause death. Concentrations of 500 ppmv will cause death within minutes. Lethal concentrations are odorless.

H<sub>2</sub>S dissolved in sulphur will be evolved slowly and migrate into the available vapor space. Thus, emission of H<sub>2</sub>S from the sulphur is a health concern for all downstream sulphur storage, handling, and transportation. Furthermore, H<sub>2</sub>S is explosive in air at concentrations above roughly 4 vol%. Accumulation of H<sub>2</sub>S in the vapor space of storage vessels is concerning.

This combination of an explosive poisonous gas leaves sulphur facilities with limited choices for safe handling. Storing the sulphur in air-containing vessels, tanks, or concrete pits creates an explosion hazard. Venting the storage vessels and transfer points to remove the evolved H<sub>2</sub>S creates a hazardous exposure concern. The general industry consensus is (a) to aggressively sweep/vent sulfur storage containers to prevent H<sub>2</sub>S accumulation and (b) to treat the vent gas via incineration or Claus processing to prevent exposure and environmental damage. Nonetheless, personnel exposure remains a concern throughout

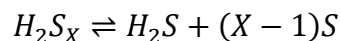
the sulphur handling process. Fresh air breathing apparatus and aggressive venting are commonly used in areas with potential exposure to H<sub>2</sub>S.

Sulphur degassing has long been used at various points throughout the various sulphur industries. In the distant past, degassing was typically performed only as a necessary step while forming and transporting sulphur. But over time, degassing for safety reasons has become more common. Similarly, there is a trend to move the degassing process further upstream so that the safety benefits are provided earlier in the process. For this reason, refineries and gas plants have been adding degassing equipment to their facilities in greater number.

When degassing is used, the typical target for H<sub>2</sub>S in sulphur is 10 ppmw. At this level, the equilibrium concentration limit in the vapor space is less than 4 vol% H<sub>2</sub>S. Thus, it is not physically possible to achieve an explosive H<sub>2</sub>S/air mixture in a storage vessel. It should be noted however, that fires are still possible as the sulphur itself is flammable. Also, the H<sub>2</sub>S concentration in the vapor space can still exceed lethal levels. So while the concentration of H<sub>2</sub>S near and around sulphur handling facilities is greatly reduced, hazards remain.

Liquid sulphur produced from the Claus process typically contains about 200 to 500 ppmw H<sub>2</sub>S, partially dissolved and partially present in the form of polysulfides (H<sub>2</sub>S<sub>x</sub>). The handling of the liquid sulphur produced by a plant using the Claus process can be troublesome. Because of the accumulation of toxic and highly flammable H<sub>2</sub>S gas, fires and explosions have occurred during the storage and transport of liquid sulphur.

H<sub>2</sub>S gas is produced by the gradual decomposition of hydrogen polysulphides present in the liquid sulphur:



where X is at least 5 (see J. Phys. Chem., 70 (1), p. 234–238 (1966)). The dissolved H<sub>2</sub>S then physically desorbs into the gas phase. Consequently, a successful degasification process must remove hydrogen polysulphides as

well as  $\text{H}_2\text{S}$ , to prevent the subsequent generation of additional  $\text{H}_2\text{S}$ .

Physically dissolved  $\text{H}_2\text{S}$  is easy to remove—chemically-bound  $\text{H}_2\text{S}$  is more challenging. Above  $159^\circ\text{C}$  ( $318^\circ\text{F}$ ) sulphur rings will open due to homolytic bond scission to form a chain of sulphur atoms with a radical at each end. During the Claus process, these radicals react with the available  $\text{H}_2\text{S}$  to form hydrogen polysulphide ( $\text{H}_2\text{S}_x$ ). These polysulphides likely exist in a variety of sulphur chain lengths and quite possibly as  $\text{HS}_x\cdot$  radicals. Below  $159^\circ\text{C}$ , the chains are unstable and will slowly form elemental sulphur and  $\text{H}_2\text{S}$ . But the process is very slow and is equilibrium-limited by the surrounding dissolved  $\text{H}_2\text{S}$ .

A number of solid and liquid catalysts can be used to accelerate the breakdown of the hydrogen polysulphides and, because decomposition of the hydrogen polysulphides is limited by the presence of dissolved  $\text{H}_2\text{S}$  in the sulphur, a sparge vapor (usually air) is also used. Without a catalyst the degassing time is typically measured in hours but this drops to 15–30 minutes depending on the catalyst and the sparge gas used. The catalyst accelerates the decomposition of the hydrogen polysulphides while the sparge vapor removes dissolved  $\text{H}_2\text{S}$ .

Continual removal of dissolved  $\text{H}_2\text{S}$  facilitates degassing. It has been estimated that sending the degasser off-gases to the incinerator causes an overall loss of plant sulphur recovery efficiency of 0.1 % so it may be important to mix off-gas with tail-gas and route it to a TGTU, especially if the sulphur plant is operating close to environmental limits. However, capturing degassed  $\text{H}_2\text{S}$  can be problematic with air sparging because air also produces  $\text{SO}_2$ . Note that  $\text{O}_2$  is not required for polysulphide decomposition using either amines or solids as catalysts, so an inert sparge gas (e.g.,  $\text{N}_2$ ) would prevent  $\text{SO}_2$  formation, albeit at the cost of much slower degassing. See Clark et al. (ASRL Quarterly Bulletin No.157 Vol. XLVIII No.1, April – June, 2011 pp. 61–80) for an excellent up-to-date review of current knowledge on sulphur degassing.

OGT | SulphurPro®'s sulphur degassing model is based on the research results and findings recently developed by the Alberta Sulphur Research Institute (ASRL). Their work relates degassing rates to sparge and sweep gas flow rates, whether the sparge is air (contains  $\text{O}_2$ ) or inert ( $\text{O}_2$  free), as well as to the specific catalyst used. Catalyst data measured by ASRL are for liquids, not solids. As already mentioned, degassing rates are profoundly accelerated by the presence of oxygen but it must be remembered that oxygen also causes  $\text{SO}_2$

formation. This makes further treatment of the evolved gas in an amine system problematic because of irreversible neutralization of the amine by  $\text{SO}_2$ .

SulphurPro's degassing model has been developed via an empirical fit to laboratory data so it does not take the same rigorously fundamental approach characteristic of other ProTreat® and SulphurPro® models, based on bubble size, and flows around and within bubbles, for example. Mass transfer rates of  $\text{O}_2$  into the liquid sulphur and rates of  $\text{H}_2\text{S}$  transfer into sparge gas are calculated empirically rather than from first principles. The model invokes catalyst effects on the kinetics of polysulphide decomposition empirically for the simple reason that the actual reaction kinetics are as yet unmeasured so they're unknown. Reaction rate data on catalysts are available at the 10 ppmw level of morpholine, ammonium sulfite, aromatic amine and urea. Should the user have other information on reaction kinetics, however, the decomposition kinetics can be dialled up or down using a kinetic factor.

Given the sparge gas flow rate and composition (especially the oxygen content) as well as the temperature, pressure and feed composition of the liquid sulphur flowing to the degassing unit, OGT | SulphurPro's calculations will predict either (a) the residual  $\text{H}_2\text{S}$  content in the degassed sulphur for a given volume of degassing vessel containing a specific catalyst (or without a catalyst), or (b) the sulphur residence time (vessel size) to achieve a given  $\text{H}_2\text{S}$  residual in the treated sulphur. SulphurPro's capabilities in these regards certainly far exceed those of competitive simulation software.

~~~~~  
To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. For details visit [www.ogtrt.com/seminars](http://www.ogtrt.com/seminars).

**ProTreat®**, **SulphurPro®**, **ProBot™**, and **The Contactor™** are trademarks of Optimized Gas Treating, Inc. Other trademarks are the property of their owner.