Removing “sulfurcrete” from Claus plant sulfur condensers with TubeMaster, the tube cleaning system of mycon

Introduction

Sulfurcrete consists of elemental sulfur, salts formed from sulfur plus CO\(_2\), SO\(_2\), NH\(_3\), and dust from abrasion of Claus catalysts. The hardness of this material matches that of granite (see e.g. /1/). Almost any Claus plant operator knows the nasty problems sulfurcrete creates. Primarily it sooner or later plugs the tubes in sulfur condensers. Under the surface of the sulfurcrete layer traces of sulfuric acid are formed and lead to corrosion. Both effects of course are highly unfavorable and therefore sulfurcrete has to be removed.

However, that is a very difficult task indeed. Sulfur recovery plants convert toxic H\(_2\)S to harmless elemental sulfur. That is a very important task and therefore sulfur recovery plants must have a very high onstream factor. Cleaning sulfur condensers, however necessitates down-time which has to be as short as possible. But sulfurcrete is extremely hard and therefore its mechanical removal is possible only by very massive means, as drilling. That in turn causes substantial mechanical stress on the equipment to be cleaned and often leads to damages. Washing sulfurcrete out is not an option as it is insoluble in most common solvents, especially those which are easy to handle, as water.

Though this problem is common to many of the roughly 1 000 Claus plants worldwide there was no satisfactory answer available. But recently a surprisingly simple method for the removal of sulfurcrete was introduced.
1. **Blasting for removal of sulfurcrete**

1.1 **Process description**

For slight soiling dry ice can be used as an abrasive. Dry ice is solid CO$_2$, i.e. gas cooled to appr $-78^\circ$C where it solidifies. The rice-grain size pellets of dry ice in the unit’s hopper (see Fig. 2) are metered into a stream of compressed air or inert gas. In the blasting nozzle the carrier gas reaches almost the speed of sound which accelerates the pellets to speeds of 180 to 330 m/s. The pellets hitting the deposits have three effects:

- The low temperature of $-78^\circ$C cools the deposit down locally. That makes the deposits on the surface brittle and leads to a slight contraction of the deposits. Due to the local thermal shock cracks form in the deposit.
- Where the pellets hit the surface high pressure is generated at the edges. This causes the CO$_2$ to liquefy as ice under the skates of an iceskater. This liquid CO$_2$ is a good solvent for many substances which helps to break the integrity of the deposits’ surface. Dry ice migrates into these cracks and evaporate there very fast, almost explosively. That multiplies the dry ice volume and in the process breaks off the deposits.
- Kinetic energy of the dry ice particles which impact on the deposits’ surface mechanically remove it and the carrier gas conveys them to the outlet.

![Fig. 1: Process principle of dry ice blasting](image)

Schematically these effects are shown in Fig. 1. It highlights the very narrowly confined local cooling due to the dry ice impact (blue section in Fig. 1) which is the cause for thermal stress within the layer to be removed. It also demonstrates that the underlying carrier surface is only very little affected by temperature reduction. Therefore the thermal stress remains primarily confined to the deposit which effects the thermal sheer between deposit and carrier surface. The different thermal expansion of deposit and carrier surface enhances to sheer off the deposit.

There no additional waste is created since the dry ice evaporates and leaves the site as gaseous CO$_2$. The surface, now cleaned may be further treated with the dry ice. The pellets are not hard enough to cause abrasion. Rather this treatment just reduces the roughness of the surface and actually polishes it.
The blasting pressure is adjustable from typically 2 to 16 bar. Specific nozzles are to be applied depending on the geometry of the surface to be cleaned.

The use of dry ice pellets as a blasting medium is not sufficient for heavy and hard sulphur deposits or for removing rust. An abrasive blasting agent is used here. The blasting agent to be used is selected according to the condition of the surface. The special nozzles from Mycon and her sister company Kipp Umwelttechnik are accurately set according to the requirements. This accurate selection means the interior surface of the pipe is not only cleaned but also milled or polished. This results in substantial improvements in surface quality and significantly reduces energy costs. It also facilitates future cleaning, as deposits may be less likely to settle. Mycon and Kipp Umwelttechnik have many years' experience of cleaning and surface improvement of all kinds of pipes. It has successfully cleaned steel, stainless steel, bronze, red bronze, copper, brass, titanium (there are special requirement characteristics for the blasting procedure here) and graphite pipes. For curved pipes, specific criteria need to be considered for the blasting procedure.

1.2 Sulfurcrete removal

The task of Claus plants is to convert toxic hydrogen sulfide to elemental sulfur. They can also remove pollutants, particularly by converting ammonia to nitrogen and water. There are many publications about Claus plants which describe the details (see, for instance, /2/). Figure 4 shows a schematic diagram of a Claus plant, and Figure 5 is a photograph.

![Figure 2. Schematic diagram of a Claus plant](image-url)
Figure 3: A 700 t/d Claus plant at NEAG Voigtei, Germany

Sulfurcrete forms in relatively cool spots of Claus plants, especially in sulfur condensors. In Claus plants they are operated typically in the temperature range 125°C to 160°C. At higher temperature the sulfur becomes highly viscous and therefore does not flow freely from the condensor. At lower temperature than 125°C the temperature difference to the sulfur solidification point at appr 119°C becomes too small. The lower the temperature the lower the vapor pressure of sulfur becomes and therefore sulfur condensors in principle are more efficient at low temperature. However, the salts forming during sulfur condensation in the heat exchanger are then more stable which makes higher temperature preferable. The optimum therefore usually is to operate the sulfur condensors at the higher end of the feasible range. Especially the formation of CO₂ salts of ammonia can be avoided by operation at higher than 150°C. But what still remains are stable SO₂ and SO₃ salts of ammonia, dust from catalyst abrasion plus sulfur droplets which tend to plug the condensors.

Operation at higher temperature may enhance ease of operation, however comes at the cost of reduced sulfur recovery as some sulfur vapor passes through the condenser unrecovered. In view of current stringent regulations with respect to sulfur recovery that often is not an acceptable option. So whatever operators try to overcome the problem of plugging in sulfur condensors, all they can achieve is reducing the problem, not really solving it: Sooner or later tubes in the sulfur condensors contain sulfurcrete deposits and may eventually even be plugged. Compounding the problem is the hardness of sulfurcrete which matches that of granite.

The conventional method of removing sulfurcrete is drilling the layer out of the tubes. That leads necessarily to minor or major scratches on the surface of the tubes which then serve as preferred spots of a new deposit formation. Also major damage may occur when drills deviate into the steel rather than removing the deposits. Since sulfur condenser tubes are usually made of carbon steel there always is some corrosion after an extended operating period. Corroded areas are especially

Depending on the modification of sulfur various solidification points exist, ranging from 113°C to 119°C, see e.g. [2].
sensitive to breakage due to the mechanical stress by drilling. And finally many sulfur condensors use U-tubes and the bended part of the tubes cannot be reached by drilling. That means that part of the tubes remains uncleaned reducing the useful service life of that heat exchanger. With “TubeMaster” all these problems can be overcome.

The deflector is moved at appr 3 to 12 m/min through the tube driven by the carrier gas. The speed is controlled depending on the cleaning effect and has to be adapted for each application individually. It depends on many parameters, as the material of the deposits, the thickness of the deposit layer and its hardness.

This process has been applied in a Claus plant of NEAG at Voigтеi/Germany. There gas from natural gas fields is treated. The concentrated H2S fraction is recovered from three different absorption processes. NEAG has three Claus plants in parallel, equipped with MODOP as the tail gas treatment. The plants have a total sulfur capacity of 1000 t/d. The sulfur condenser of the 700 t/d unit contains 1882 tubes of appr. 50 mm diameter and is 6400 mm long. More than 70% of the tubes contained deposits. In the lower section of the heat exchanger tubes were even totally blocked by sulfurcrete. Cleaning of the tubes has not been necessary for many years because the exchanger had sufficient overdesign so that it worked satisfactorily despite the plugging.

Cleaning with dry ice blasting could be carried out at speeds of appr 4 to 6 m/min so that cleaning took appr one minute per tube. Overall cleaning could be finished within 28 working hours. Cleaning was complete, i.e. 100% of the surface were metallic again. Cleaning of totally plugged tubes takes longer, but is possible to do.

2. Comparison to other cleaning methods

TubeMaster is more expensive e.g. high pressure water for cleaning surfaces. But it has a number of advantages that often far outweigh its higher price. These advantages are:

- Dry cleaning
- Excellent cleaning results
- Improves surface quality within the pipe
- Significant energy savings
- Extends operating times
In parallel the market for the sulfur rich heavy residues is shrinking forcing refineries to upgrade them by hydrogenation and/or treat them in a visbreaker or converting them in a coker. The heat exchangers upstream of the visbreaker or coker get regularly plugged by soot and highly viscous organic material. They have to be cleaned routinely to avoid total blockage. Up to now that is done mostly by high pressure water with detrimental effects, as is demonstrated by an example case described here in more detail:

A visbreaker heat exchanger had to be cleaned from the typical deposits of soot, heavy hydrocarbons and undefinable polymers. The tubes were 25 x 2.6 mm, 7 600 mm long. The client up to now had used high pressure water of 2 500 bar pressure. Despite this high pressure the cleaning effect was only 90%. Furthermore the huge energy input through the water added to the corrosive effect and increased the unevenness of the tube inner surface. This undesirable situation led the client to try dry ice blasting.

The deposit layer before cleaning was appr 2 mm. That required forceful cleaning. Therefore, as the blasting medium dry ice plus slightly abrasive material was applied. With CryoClean® the heat exchanger could be cleaned within 22 hours. After that treatment the inner tube surface was 100% metallic and clean, while with high pressure water only 90% cleaning could be realized.

Due to the already progressed corrosion of the tubes the inner walls of the tubes were polished after cleaning again using TubeMaster. The result was very good smoothness of less than 0.6 µ. This corresponds to the quality of a honed surface.

Such smooth surface offers little nuclei for new deposits. Therefore the interval between cleanings of the heat exchanger could be prolonged by about 50% compared to high pressure water cleaning.

The non-abrasive action of TubeMaster also increases the lifetimes of the components. Cleaning can take place more often without detrimental effect on the component.

Because the process is easily controlled, even complex units can be cleaned easily.

TubeMaster is of particular interest for turn-arounds. It is finding rapidly growing interest in refineries especially where it is important to keep equipment dry during and after cleaning and where a speedy re-start pays.

3. Summary

TubeMaster allows to clean in tubes down to a diameter of 3 mm. Deposits to be removed may be as weak as oils and fats, or as hard as sulfurcrete. The cleaning process is non-abrasive so that in one case studied even after 50 routine cleaning cycles the original wall thickness of the pipe was still intact. TubeMaster allows to clean most equipment items in place, i.e. no disassembly and later re-assembly is required. In addition the cleaned surface mostly is of better smoothness after treatment than before. This reduces adhesion and thus increases the service intervals between cleanings.

There is a lot of experience available which makes it possible to optimize additives and the blasting process to the specific application.
Dry ice blasting can help increase the on-stream time and thus this process and especially the patented cleaning of tubes can ensure better economy.

4. **Literature**


3. M. Heisel, A. Buinger, J. Kipp “Sulfur” 2004