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Removing “sulfurcrete” from Claus plant sulfur condensers

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Introduction

Sulfurcrete consists of elemental sulfur, salts formed from sulfur plus CO₂, SO₂, NH₃, 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 H₂S 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. Dry ice blasting for removal of sulfurcrete

1.1 Process description

Dry ice is solid CO₂, i.e. gas cooled to appr –78°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°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 CO₂ to liquefy as ice under the skates of an iceskater. This liquid CO₂ 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.

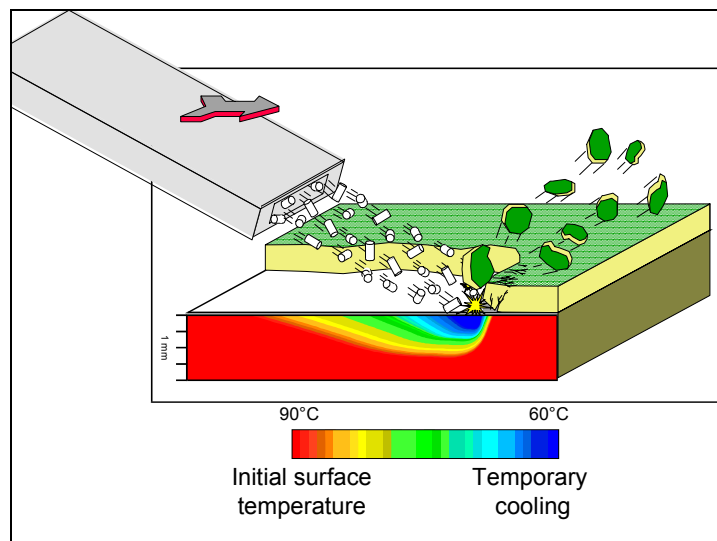
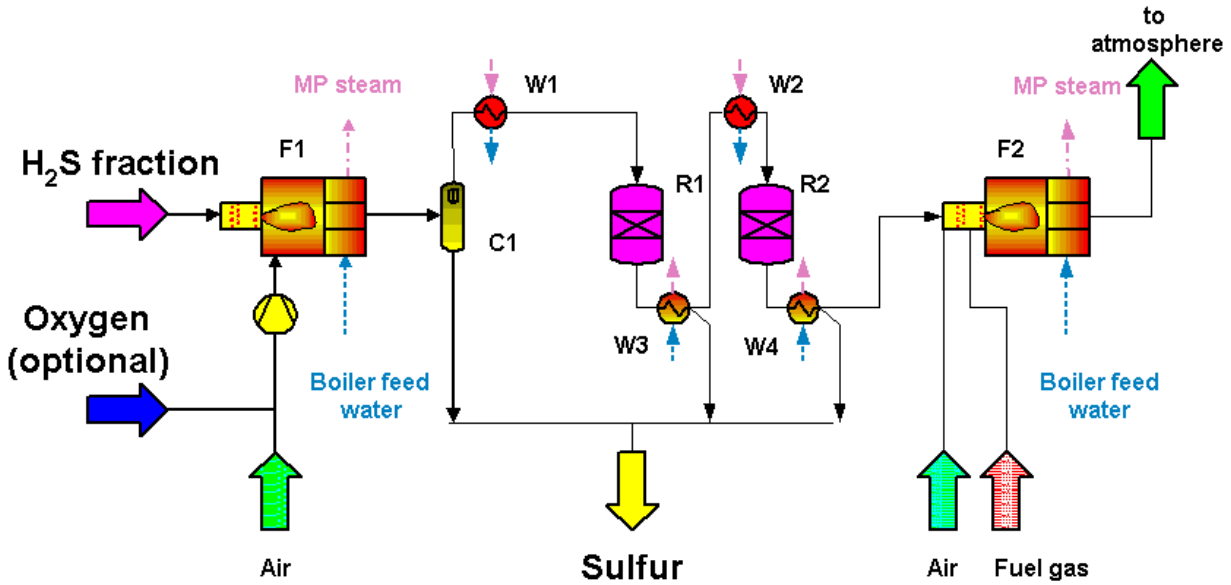


Fig. 1: Process principle of dry ice blasting

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 shear between deposit and carrier surface. The different thermal expansion of deposit and carrier surface enhances to shear off the deposit.

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 2 shows a schematic diagram of a Claus plant, and Figure 3 is a photograph.



F1 Claus furnace with waste-heat boiler
W1, W2 Preheaters
W3, W4 Sulfur condensers

C1 Sulfur separator
R1, R2 Catalytic reactors
F2 Incinerator

Figure 2. Schematic diagram of a Claus plant



Figure 3: A 700 t/d Claus plant at NEAG Voigtei, Germany

Sulfurcrete forms in relatively cool spots of Claus plants, especially in sulfur condensers. 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 condenser. 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 condensers 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 condensers 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 condensers.

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 condensers, all they can achieve is reducing the problem, not really solving it: Sooner or later tubes in the sulfur condensers 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 sensitive to breakage due to the mechanical stress by drilling. And finally many sulfur condensers

^{*} Depending on the modification of sulfur various solidification points exist, ranging from 113°C to 119°C, see e.g. /2/.

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 dry ice blasting all these problems can be overcome. However, in order to be successful against the very hard sulfurcrete some patented features (see /3/) have to be observed with respect to the blasting nozzle. As described above the high velocity of the dry ice pellets is necessary to achieve the liquefaction of the pellets' edges. To ensure that a deflector is applied which forces the pellets under an almost constant angle to the deposits' surface. The deflector is designed and shaped in a way that the carrier gas reaches almost the speed of sound between the deflector and the inner wall of the tube.

The deflector is moved at approx 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.

To increase the efficiency in some cases addition of a slightly abrasive blasting material is advantageous, especially when treating very hard surfaces. The abrasive material then creates scratches in the deposits where then the dry ice pellets can act better. Also for polishing the metallic surface after cleaning slightly abrasive blasting materials can help.

This process has been applied in a Claus plant of NEAG at Voigtei/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 approx. 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 oversize so that it worked satisfactorily despite the plugging.

Dry ice blasting was applied even though the sulfurcrete layers were very hard. Cleaning could be carried out at speeds of approx 4 to 6 m/min so that cleaning took approx one minute per tube. Overall cleaning could be finished within 28 working hours. It was done with pure dry ice without any additives for increased abrasion. Cleaning was complete, i.e. 100% of the surface were metallic again. Cleaning of totally plugged tubes takes longer, but is possible to do.

When applying dry ice blasting one has to expect electrostatic charging of the equipment cleaned. To avoid that the sulfur condensers were earthed while dry ice blasting took place.

2. Comparison to other cleaning methods

Dry ice is more expensive per m² than e.g. high pressure water for cleaning surfaces or sand for sandblasting. But it has a number of advantages that often far outweigh its higher price. These advantages are:

- no cleaning agent residues remain in the equipment, there is neither waste nor solvent left after cleaning
- no waste water is generated
- the blasting material is not abrasive so that the surface remains unscathed. Rather the surface after cleaning shows lower roughness so that future deposits stick less and therefore extended operation intervals are experienced between cleaning steps.
- Downtime can be reduced.

- Restart requires less time since drying of equipment becomes superfluous which is necessary after high pressure water cleaning. Similarly no sand needs to be removed as is mandatory after sandblasting.

Especially the non-abrasive nature of dry ice proved time and again to be important. High pressure cleaning washes out some of the pipe surface, preferably already slightly corroded material. This led to markedly reduced service life of sulfur condensors in a number of plants. Dry ice blasting by contrast leaves the pipe surface intact. As described above the combined effects of cooling, thermal contraction and kinetic energy shear off the deposits. In some cases where frequent routine cleaning has to take place even after 50 treatments with dry ice no reduction of the wall thickness of the pipes could be detected. This is in sharp contrast indeed to high pressure water treatment.

Furthermore the lower downtime and the faster restart can earn so much money that overall dry ice blasting in a fast growing number of cases proved more economic compared to options which are cheaper when considering the cleaning process alone. Examples will be discussed below.

3. Other refinery applications

Refineries face a number of new trends these days due to increasingly stringent environmental protection regulations. An example case is the Auto-Oil Program of the European Union which requires reduction of sulfur and other noxious substances in refinery products, as in gasoline and in diesel fuel.

To achieve that oils are hydrogenated in various processes in the refinery converting sulfur species into H_2S . However, while hydrogenating sulfur compounds also nitrogen compounds are hydrogenated forming ammonia in the process. This additionally formed ammonia usually ends up via a sour water stripper in the Claus plant. As described above ammonia salts lead to plugging in Claus plants creating a case for dry ice blasting. But this is certainly not the only process affected.



Fig. 4: Cleaning a heat exchanger using the CryoClean® process

One can clearly see the small diameter of the tubes which are cleaned. Usually cleaning-in-place of equipment is possible. This specific exchanger was cleaned with the tube bundle withdrawn from the shell.

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 dry ice 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 dry ice with slightly abrasive additive. 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.

As dry ice blasting leaves no residue of blasting agent, it is often possible to clean components in place. That saves time for disassembly and re-assembly. Cleaning in place often allows that components need not be cooled down. Please remember that cooling by the dry ice takes place only locally and need not pertain to the complete component. If there is no cooling also the heat-up phase can be omitted. This again saves time so that the re-start to full production can occur earlier, and it saves utilities.

The non-abrasive action of the dry ice 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.

The dry ice process 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. As an example the cleaning of a platformer reactor may be cited which was carried out in an Austrian refinery. There the catalyst and the process must not see water. Applying dry ice helped to save a lot of time and effort which would have been necessary to dry out the reactor after cleaning. With dry ice blasting simply no water entered the vessel.

4. Summary

Dry ice blasting using the dry ice process allows to clean surfaces in reactors and in tubes down to a diameter of 6 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. Dry ice 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. Finally dry ice blasting creates no waste water nor other waste beyond the deposits which are removed. Therefore no cleaning of the equipment after treatment is necessary, especially no drying, as is necessary after high pressure

water cleaning. All these features make dry ice efficient and economical which led to an exponential growth rate for its application in recent years.

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.