Introduction

Recent events have increased the awareness of the potential for internal fires in distillation equipment, especially in columns equipped with structured packing. Following these incidents, Koch-Glitsch performed an investigation on previous events with structured packing in the industry. Our search was not limited to only columns with Koch-Glitsch products, but we intended to obtain a complete picture on all incidents. In total we were able to track 56 incidents, but we assume the estimated number of unreported or undocumented cases is higher. Based on our findings, it is clear, that the large majority of the incidents were related to columns packed with structured packing (Wire Gauze and Sheet Metal, see Fig. 1).

Fig. 1 Incidents by Equipment Type
**History**

Wire Gauze structured packing was introduced in 1964. Initially the application was very limited to the Fine Chemical and Pharmaceutical Industry. In the first 10 years only a few hundred columns were equipped with structured packing. With the introduction of sheet metal structured packing in 1977, the product was extended to the Chemical and Petrochemical Industry as well as in Refineries (since 1983). The installed base of structured packing has increased significantly. Currently there are a few thousand columns in operation using structured packing in a wide variety of materials of construction. Figure 2 shows an increase of incidents over the past 10 years, likely the result of the significant increase in the number of columns operating with structured packing.

Fig. 2 Incidents over Time (in 5 years interval)

![Incidents over Time](chart.png)

* 3 incidents without detailed information

**Known Causes of Fire**

Structured packing is very popular because of its high efficiency created from the high specific surface area and its low pressure drop. For the separation of temperature sensitive products, the small liquid hold up is also an advantage. All of these benefits are the source for possible problems during shut down and maintenance.

Any hydrocarbon product residues remaining in the column after shut down may coat the packing with a very thin film with a surface area similar to the packing. It is very difficult to remove 100% of the residue. At elevated temperatures, with exposure to the atmosphere, small quantities of hydrocarbons have the potential for self-ignition.
Increased pressure drop is usually the first indication of the formation of coke or polymers inside the packing. However, by the time this increase is measurable the coke already occupies a large portion of the packed bed. Cooling such a lump of coke may create various problems:

- Due to the low liquid (or cooling water) hold up in the packing a limited amount of heat can be removed.
- Cooling water can not penetrate the coke formation and will only act upon the upper surface, therefore leaving the center and the bottom of the coke at elevated temperatures.
- The temperature gauge of the column measures the temperature in the vapor phase close to the vessel wall and most probably not the temperature inside the coke formation. One may be fooled that ambient temperature is reached inside the column even though the majority of the coke may remain at elevated temperature.

Pyrophoric substances - like iron sulfide (FeS) – formed by sulfur corrosion of carbon steel components can settle on the packing during operation. Conventional cleaning methods cannot remove the iron sulfide from the packing. Once exposed to the atmosphere, iron sulfide will auto ignite at ambient temperature.

New packing is coated with a thin film of lubricating oil from the manufacturing process. In one incident, new packing caught fire after hot work was performed above the packing.

**Fig. 3  Cause of Incident**

Once ignited by a hydrocarbon or pyrophoric fire, the thin sheet of the packing (0.1 to 0.2 mm) can support a metal fire. In some columns, temperatures up to 1500 °C (2700 °F) have been reported.
Some metals are highly reactive and more susceptible to ignition than others and require special caution e.g. titanium, aluminum, zirconium, etc. Replacement with a less sensitive material of construction should be considered.

Ignition sources typically follow one of two patterns:

1. Spontaneous ignition –
   This can be either by pyrophoric material or if the column temperature is above hydrocarbon auto-ignition temperatures
2. Hot work inside the column –
   This work is generally performed in close proximity of the structured packing and caused by welding, cutting, grinding, or any heat or sparks generating type of operation.

Hereafter, due to most incidents being caused by pyrophoric ignition, we would like to elaborate in more detail on these cases.

**Pyrophoric Ignition of Structured Packing in Crude Vacuum Column**

*Case 1:*
An Eastern European Refinery installed Gempak® Structured Packing in August 1993 in the Crude Vacuum Column # 3. All column internals were made of 410 S material. Structured packing was used in all sections to reduce pressure drop and minimize flash zone pressure to maximize Vacuum Gas Oil Yield. The column was designed for a crude with a sulfur content of 1.5 – 1.7%. However, due to problems with crude supply in 1994, the refinery switched to a higher sulfur content crude (2.8 – 3.0 %). The unit was shut down in April 1995 for the first time after being in continuous service for 19 months.

The shut down was performed in the following order:
After 2 days of steaming and cooling down the column, the manways were opened starting from the bottom. After opening the manway second from the top, the maintenance crew recorded smoke coming out of the manway and monitored glowing inside the packed bed. The manways were closed again and the steaming process continued. The top pump-around return was used to feed water into the column after the steaming was concluded. The next day, the column was again opened. The inspection revealed that the packing in bed 2 was destroyed by fire. The packing was removed from the column and the column was put back into operation without any packing in bed 2.

Although the packing was completely destroyed, major damage to the structure of the column vessel and casualties was avoided by the fast reaction of the maintenance crew to close the manways.

During the next shutdown in April 1996, new packing was installed in bed 2.

*Case 2:*
The same refinery installed structured packing in the # 4 Vacuum Unit in July 1994 made of 316L SS because of the high sulfur content of the processed crude oil.

Pyrophoric substances formed by corrosion when the highly sulphurous feed was processed. The pyrophoric compounds were a result of corrosion of external equipment (heat-exchanger, coolers etc.) which was reintroduced into the column by the reflux and pump-around return. The liquid distributed
over the cross section of the column carried the pyrophoric components into the packed bed, where it coated the packing (Fig. 4). The large surface area of the packing provided the surface area for the iron sulfide, which ignited when the column was open during the 1995 shut down.

**Fig. 4** Material Selection Promoting Formation of FeS in Auxiliary Equipment

![Diagram showing material selection and FeS formation](Image)

*Learnings:*
The fractionation bed below the top pump-around is more sensitive to FeS deposits because of the smaller specific liquid load.

Steaming of the column and water wash is not sufficient to remove the FeS deposits from the packing surface.

Consider material selection not only for packing and vessel, but also for piping and heat-exchanger. FeS formed in Carbon steel heat-exchangers and piping is re-introduced into the column via reflux.
Prevention

Constantly review the shut-down and maintenance procedures. Consult the procedures before any shut-down and make sure they include the latest safety considerations. It is especially important to revise the procedures when revamping a trayed column with structured or random packing. In addition to many other plant specific issues, the following points should be addressed in the procedures:

**Consideration for Shut-down Procedures:**

- Cool column to ambient temperature before opening
- Wash column extensively and remove any residue as well as other deposits
- Execute chemical neutralization to remove pyrophoric material
  - E.g. permanganate or percarbonate wash
- Purge column with inert gases is recommended
  - Make sure you follow confined spaces entry procedures to ensure the safety of the personnel entering the column!
- Open column carefully and continuously monitor packing as well as column temperature
- Minimize the number of open manways
  - to reduce air circulation
  - to be able to seal the column fast

**Consideration for Maintenance Procedures:**

- Monitor air quality and temperature inside the column and the packed bed continuously during shut down. Install additional temperature gages and utilize continuous air monitoring with multiple gas analyzers to detect combustion products.
- Be careful when working above or in close proximity of structured packing
  - Do not cut, grind or weld the packing
  - Remove the packing before hot work
  - If hot work is absolutely required above the packing, take extensive measures to protect it
- Do not force air circulation inside column
- Watch out for smoke, fire and temperature increases inside the column
- Utilize knowledgeable, experienced and trained contractor

**Safety Consideration:**

- Be careful using water to extinguish packing fire
  - Temperatures may be very high and water can evaporate instantly
  - Possible formation of hydrogen in case of metal fire (extremely high temperatures), may result in an explosion
- Liquid hold up in packing is very low, so the use of water may not be as effective as expected
- Cutoff the supply of oxygen by:
  - Seal the column (do not obstruct entry to column – manway - during shut down)
  - Purge column with inert gases
  - Fill the column with steam
- Prepare staff and equipment to extinguish fire at any time during shut down
Chemical Wash to remove Pyrophoric Substances from Distillation Columns

Several vendors offer chemical neutralization of pyrophoric compounds prior to vessel entry. This typically consists of rinsing the tower with a potassium permanganate solution, either in vapor or liquid phase. The permanganate chemically oxidizes the FeS. A final water rinse is then conducted prior to vessel entry. Unfortunately, permanganate leaves a manganese dioxide (MnO₂) residue on the packing and vessel surfaces, which is virtually impossible to completely rinse. This residue is an oxidizer that may initiate or support combustion in the right circumstances. Potassium permanganate also interferes with the degreasers typically used for chemical cleaning procedures. It must therefore be used in a two step process extending the time required for cleaning the vessel. Finally, the MnO₂ sludge generated by the permanganate must be disposed of.

Sodium percarbonate (sodium carbonate peroxyhydrate) is an alternative to permanganate washes that has none of the major disadvantages. It can be used in a single step process, leaves no residue, and has no special disposal requirements. As with permanganate, it can be applied in either vapor or liquid phase. Unfortunately, few vendors have experience with its use. Due to the nature of the oxidizer, it is imperative that it be applied by experienced personnel.

Chemical neutralization procedures should always be used if there is reason to suspect the presence of pyrophoric substances in a packed tower. However, no neutralization procedure is perfect. This is especially true in a heavily fouled tower. We are aware of at least one incident where a packed bed ignited after vapor phase neutralization with potassium permanganate. The FeS was not completely neutralized and ignited the packing during tower ventilation. The vessel was closed and the fire was extinguished without significant damage to the internals or the vessel shell due to proper monitoring during ventilation and quick response by operations and maintenance personnel.

There can be no substitute for careful evaluation of ventilation, entry, and emergency response procedures. Operations and maintenance people must be properly trained and ready to respond at the first sign of problems to prevent major equipment damage or potential injury to plant personnel.

References:
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