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### **Prevention and Suppression of Metal Packing Fires**

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#### **Abstract**

Structured packing has been widely used because of large surface area that makes possible columns with high capacity and efficiency. The large surface area also contributes to fire hazards because of hydrocarbon deposits that can easily combust and promote combustion of the thin metal packing materials. Materials of high surface area that can fuel fires include reactive metals, such as titanium, and materials that are not considered combustible, such as stainless steel. Column design and material selection for packing construction is discussed together with employee training and practices for safe column maintenance and operations. Presented also are methods and agents for suppression of metal fires. Guidance for prevention and suppression of metal fires is related to incidents involving packing fires in columns.

## Introduction

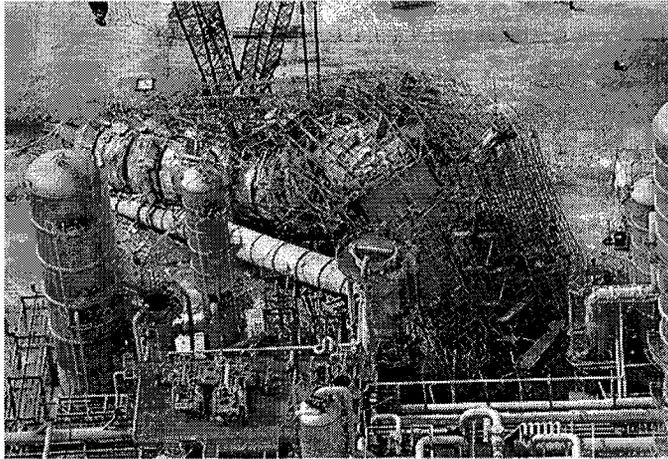
Structured packing was invented in the 1940s as an alternative to random packing and trays for use in industrial distillation columns. It did not find widespread use, however, until the 1970s, after advances helped eliminate problems with structured packing that decreased its efficiency. A photograph of a section of structured packing is shown in Figure 1. Since the 1980s, the popularity of structured packing has increased to the point where it is one of the most popular types of separation column internals today (Kister [3]).



**Figure 1: Koch Flexipac Structured Packing (Reproduced with permission from Koch-Glitsch [4])**

The high surface-to-volume ratio that makes structured packing so efficient can present a fire hazard under the appropriate circumstances. This problem is exacerbated by the fact that pyrophoric (spontaneously combustible) deposits that flow through the process can become lodged in the packing, where they may ignite upon opening the column. Additionally, structured packing is often made from materials such as titanium or zirconium, which are combustible under certain circumstances. Once the packing ignites in the column, it burns at several thousand degrees and is nearly impossible to extinguish, since adding water to a metal fire can cause explosions due to the formation of hydrogen gas when the water contacts the hot metal. Any column internals, including distributors, support plates, and the packing itself will be consumed in the fire, and could ultimately cause the column to collapse due to the intense heat. Figure 2 depicts a column that collapsed due to a metal fire.

Due to the unique hazards associated with metal structured packing, it is necessary to design columns so that the risk of a column fire is reduced and to ensure that the packing inside the column is not ignited during maintenance activities. Finally, proper firefighting measures must be followed in suppressing metal fires in order to ensure that firefighting activities do not actually make the column fire worse.



**Figure 2: Collapsed Distillation Column (Reproduced with permission from Holliday [2])**

### **Hazards Associated with Metal Packing**

Several factors lead to the unusual combustibility behavior of metal packing. Many of these factors are associated with the materials that the packing is made from, but others are a result of the physical design of the packing.

Structured packing is commonly made from titanium and can be made from zirconium. These two metals are classified as reactive metals and form pyrophoric dusts that have a relatively low autoignition temperature and can easily be ignited when maintenance is conducted inside of the column (Schmitt [7]). Hot titanium can also react directly with nitrogen (Pelekh [5]) and can cause explosions when the heated metal comes into contact with water (United States [8]), which can make suppressing titanium fires nearly impossible.

The physical design of structured packing can also increase its combustibility. Metal structured packing consists of thin metal sections with a very high surface to volume ratio (Kister [3]). This high surface to volume ratio is conducive to flame propagation through the packing, which makes metal packing much more likely to combust than large metal sections. Additionally, since the spaces between the metal sheets in a section of packing are rather small, pyrophoric or flammable materials may accumulate in the packing, where they may spontaneously combust or be ignited by maintenance crews working on the column during a shutdown.

### **Packed Column Design Guidelines for Fire Prevention**

Several steps may be taken during column design to reduce the risk of a metal packing fire. Safety should be of the utmost concern in both the design of the vessel and the design of the packing.

Packed distillation columns should be designed so that any fire that occurs in the column can be extinguished quickly. This means that the number of open manways (entrances for workers) on the column should be minimized and that there is adequate firewater access for fire crews trying

to suppress a fire in a packed column. Furthermore, vessel entrances should be large on packed columns that contain structured packing in order to facilitate the removal of the packing from the column.

The packing inside of a distillation column should be constructed from the materials that will provide safe operations in the intended application. Various alloys, such as Hastelloy C, are available that provide an alternative to titanium and zirconium in some corrosive services and may not be as combustible. Table 1 lists some of these materials and their price in comparison to 316L stainless steel.

**Table 1: Costs of Metal Packing Materials Relative to 316L Stainless Steel**

| <b>Material</b>       | <b>Cost Relative to 316L SS</b> |
|-----------------------|---------------------------------|
| <b>410S</b>           | 0.81                            |
| <b>304L</b>           | 0.88                            |
| <b>316L</b>           | 1.00                            |
| <b>317L</b>           | 1.08                            |
| <b>Monel</b>          | 6.64                            |
| <b>Titanium</b>       | 11.73                           |
| <b>Hastelloy C276</b> | 18.74                           |

In order to ensure that the safest and most economical material is chosen for the packing in a distillation column, a materials expert and company operating experience should be consulted during the column design phase.

Finally, increasing the surface-to-volume ratio of structured packing increases its combustibility (Dubobbin [1]). Two factors that affect the packing surface-to-volume ratio are the thickness of the individual metal sheets that make up the packing and the size of the spaces between the sheets. While decreasing the packing combustibility (Yeh [10]), increasing the packing thickness also increases the weight per given section of packing. Additionally, decreasing the space between the metal sheets in the packing decreases flammability (Dunbobbin [1]), but also sacrifices capacity and makes the packing more prone to solids fouling (Kister [3]). Therefore, it may be necessary to make some trade-offs between efficient packing design and safe packing design, particularly when there is a known fire risk associated with the process into which a column is to be installed.

## Maintenance Guidelines

Most column fires start when maintenance is going on inside of the column due to the fact that the column is open to ambient air and the fact that maintenance in a distillation column often involves hot work (grinding, welding, or other activities that generate sparks). Because of this, care must be taken when preparing distillation columns for maintenance, opening columns to the atmosphere, and performing actual work on distillation columns.

A fire in a packed distillation column can be ignited during maintenance by any of the following:

- Ignition of flammable organic or reactive metal deposits due to hot work.
- Spontaneous combustion of pyrophoric deposits inside of the column when they are exposed to oxygen after the column is opened.
- Static electricity (Wagner [9]).
- Temperatures inside of the open column above the ignition temperature of material lodged in or stuck to the packing.

Steps to avoid any of the above conditions are suggested in order for maintenance to be conducted safely inside of the column.

When preparing a distillation column for maintenance, it is recommended that a work plan be developed that includes provisions for proper cleaning of the column, proper procedures for opening and entering the vessel, and the installation of physical barriers inside of the column to prevent hot work from igniting the packing. The primary consideration in planning a column shutdown is determining whether or not the packing can be removed from the column, since this is the best way to prevent a metal packing fire. Additionally, all work crews should be informed of the hazards associated with working inside of a packed column, and should be informed of their role in preventing or suppressing metal fires. Finally, proper cleaning should take place in order to remove pyrophoric deposits from inside of the column and make sure the column is free of flammable organics to the extent possible.

The following steps can be taken to help ensure packed columns containing metal structured packing are cleaned prior to opening the column:

1. Follow normal shutdown procedures for cleaning the column. Dry (superheated) steam should be used to keep the packing from blowing out.
2. Allow the column to cool below 212°F. Compensate for any volume contraction during cooling by adding nitrogen to prevent a vacuum from forming in the column.
3. Continue cooling of the column, ensuring that all sections of the column are adequately supplied with water. Monitor the column temperature and continue cooling the column for at least 24 hours and until the temperature inside of the column is less than 100°F.

Additionally, chemicals such as potassium permanganate can be used to remove pyrophoric deposits from the packing, if this can be done safely and effectively (Sahdev [6]).

In opening a column to the atmosphere, the following practices should be considered:

- Work crews should open as few manways as possible, and ensure that all of the feeds to the distillation column are properly blinded.
- One to two hours should be allowed between opening of manways, and the temperature and carbon monoxide levels should be verified to be safe inside of the column between manway openings.
- The packing should be kept wet to the extent possible during and after the initial opening of the column.
- Once the column is opened, physical barriers, such as fire blankets, should be put into place inside of the column to prevent ignition of the packing inside of the column due to hot work.
- Finally, the temperature and the carbon monoxide level inside of the column should be monitored as long as the column is open to the atmosphere.

When performing maintenance inside of the column, physical and procedural barriers can be put into place to reduce the probability of a large-scale column fire. Physical barriers to packing ignition include:

- Placing fire blankets below welders or grinders.
- Flooding the packed column with water up to a point just below work crews if the column is structurally sound enough to resist the high pressures generated by filling it.
- Placing a protective water barrier between the work crews and the packing below.

A water barrier involves a piece of sheet metal that is fitted to the inner diameter of the column and covered with a plastic tarp. Water is added onto the barrier to create a pool inside of the column to catch sparks.

Procedural barriers for fire prevention include wetting sparks as they fly off of grinding equipment, ensuring that there is a fire watch on every level of a packed column so that fires can be extinguished quickly, and ensuring that adequate extinguishing materials are available at each hot work location so that small fires can be extinguished before they become large ones. Additionally, the work area around the job site should be kept clean so that fire crews are able to access the column quickly in the event of an emergency. Finally, all work crews involved in a column shutdown should be informed of the procedures necessary for safe work, and plant personnel should ensure that work crews follow these procedures.

The best way to prevent fires from occurring inside of a packed distillation column during maintenance is to remove all of the packing before maintenance is conducted inside of the column. While this procedure may be time consuming, it limits the amount of time that the packing is exposed to the atmosphere in the confines of the column to the amount of time it takes to open the column and remove the packing. Removing the packing from the column eliminates the possibility that it will be ignited by hot work, which is perhaps the most hazardous activity that can lead to a column fire.

## **Suppressing Metal Fires**

Suppression of metal fires is particularly difficult due to the resultant high temperatures, the potential for steam explosions, and the potential for hydrogen explosions when water contacts the hot metal (United States [8]). The key to successfully extinguishing metal fires is early detection and suppression with extremely large quantities of water. While burning metals can cause water to split into hydrogen and oxygen and explode, water is very effective in extinguishing metal fires if the metal is completely drenched, since it cools and suffocates the fire (United States [8]). The use of water in small quantities or on large metal fires, may present an explosion hazard as the intense heat produced by the metal fire may produce hydrogen gas from the water.

In industrial practice, it is common to use nitrogen to suppress fires inside of distillation columns. This practice may be effective for small fires involving stainless steel, but it is not very effective for large fires involving any metal and is entirely ineffective for titanium fires, as hot titanium can react exothermically with nitrogen (Pelekh [5]). Additionally, if a column is flooded with nitrogen or any other inert gas, personnel should be kept away from any open manways and should be kept out of the column until the atmosphere in the column is verified to be breathable.

Several fire extinguishers other than water exist that can suppress metal fires. These extinguishing agents, called Class D extinguishers include liquids, such as trimethylboroxane, solid powders, such as Pyrene powder and Met-L-X powder, and gases such as argon, are usually in powder form (United States [8]). Table 2 lists several of these agents. Since most of these agents are only available in powder form, they are probably not useful in suppressing a large-scale column fire due to the difficulty in transporting the materials to the fire on a large scale. They may, however, be useful on small fires. More research in this area could produce fire-extinguishing agents that would be easily deliverable to a column fire, allowing firefighters to easily extinguish fully developed metal fires.

## **Conclusions**

In conclusion, the high temperatures experienced in metal structured packing fires along with the extreme difficulty in extinguishing a large-scale metal fire present a unique process hazard. In order to prevent combustion of packed internals, packed columns should be designed first and foremost with safety in mind and maintenance activities should be conducted in as safe a manner as possible, with special attention to preventing ignition of the packing due to hot work. The key to controlling a metal fire once it starts is early detection and suppression with copious amounts of water.

Further opportunities for research in the area of metal fires include research into the flammability characteristics of metal packing, the development of affordable and effective substitutes to reactive metal packing, and the development of better metal fire extinguishing agents. Research into these areas will, undoubtedly, prevent further loss of property and possible loss of life.

**Table 2: Class D Extinguishing Agents (8)**

| <b>Agent</b>  | <b>Description</b>  | <b>Known Uses</b>  |
|---|---|--|
| <b>G-1 Powder<br/>(also called<br/>Pyrene or<br/>MetalGuard</b> | Composed of graphitized foundry coke powder with an organic phosphate additive. Graphite conducts heat away from the fire, lowering the temperature of the metal below its ignition point.  | Titanium, zirconium, aluminum, and iron fires                      |
| <b>Met-L-X<br/>Powder</b>                                       | Composed of a sodium chloride base with additives. Clings to surfaces and cakes up, smothering the fire.  | Has been used successfully with zirconium, titanium, and aluminum  |
| <b>Lith-X Powder</b>  | Composed of graphite based with additives. The powder smothers the fire and draws heat away from it.  | Titanium and zirconium use have been reported                      |
| <b>TMB Liquid</b>   | Trimethylboroxine liquid. Agent is applied using a specialized extinguisher. Contact with a metal fire causes the trimethylboraxne to react and breakdown into boric oxide and methanol, which forms a molten boric oxide coating on the surface of the metal to suppress the fire. | Has been used on zirconium and titanium fires                      |
| <b>Pyromet<br/>Powder</b>                                       | Pyromet powder consists of sodium chloride, diammonium phosphate, protein, and a waterproofing agent. It is available in 25 lb extinguishers.   | Has been used in fires involving titanium, zirconium, and aluminum |
| <b>Inert Gases<br/>(argon and<br/>helium)</b>                   | Smothers the fire by displacing oxygen from the atmosphere.   | Has been used successfully on zirconium fires                      |

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