Pyrophoric hazards

Smoldering fire in vacuum column during shutdown

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Summary

1. Accidentology
2. Pyrophoric products and their risks
3. REX- Smoldering fire in vacuum column during shutdown
4. Recommendations

Accidentology

- **2004** Explosion on the manhole of DHT drum at distillation unit in refinery
- **2005** Explosion in sour water tank in refinery
- **2008** Flash when opening an isolated line for blind removal
- **2009** Rupture of an unfluxed vacuum residue storage by overpressure
- **2013** Auto ignited fire in filters waste drum
- **2015** Ejection of flange under nitrogen pressure
- **2016** Fire during maintenance works on flare system
- **2017** Vacuum column fire during shutdown
- **2023** Column collapse during maintenance works
- **2024** Molten sulphur fire in rail tank car

Common keyword in root causes analysis : PYROPHORIC

- Lack of identification of pyrophoric risk-

Pyrophoric products and their risks

- **WHAT IS A PYROPHORIC PRODUCT ?**

- Substance that spontaneously ignites upon contact with air, without an external ignition source. This can occur at ambient temperature for solids, liquids, or gases.
- They maybe used to create self-igniting devices such as fireworks and flares

Examples of pyrophoric substances

- Phosphorus
- Sulfur Selenium
- Arsenic
- Antimony
- Bismuth

Pyrophoric products and their risks

Some metals may be pyrophoric

- Sodium, potassium, cesium…
- Raney nickel
- Zinc dust
- Organometallics compounds or metal alkyls in refineries and petrochemicals, ie organometallic compounds used in the catalysis of olefin polymerization are often pyrophoric.
- Iron sulphides FeS that are formed through rust sulfidation in absence of O2 and presence of H2S (common in refineries) :

$$Fe_2O_3(rust)+3\ H_2S \rightarrow 2FeS+S+3H_2O$$

Pyrophoric materials are dangerous because they can cause fires and explosions when exposed to air.

Indeed, they have caused several severe industrial accidents

Smoldering fire in vacuum column

May 2017– Germany –Vacuum column in a refinery

Smoldering fire in vacuum column

Chronology of the incident

May 12th- May 14th **Execution of shutdown procedure**

→ Feed out, cooling, emptying-Flushing, blinding for chemical cleaning

May 14th **Performing of chemical cleaning**

→ Injection of decontamination chemical via steam and water at specified points

→ Continuous analytical follow-up of chemical reactant (DecoShield ™) in condensate streams

→ Cleaning stop criteria reached & final water flushing

→ Blinding for column entry

May 16th -21:40 **Blinding for entry ready & opening of top and bottom manholes**

May 17th 3:00-5:00

→ First positive gas testing result for column atmosphere

→ Remaining manholes open

→ Atmosphere checks every 2 hours (all OK)

07:30

→ Column bottom entry of 11 contractors

Smoldering fire in vacuum column

Chronology of the incident

May 17th

11:38 ----- Sharp increase of temperatures noticed by panel operator (DCS alarm specifically set at 40˚C to monitor the column, +200 ˚C in 20 min)
Within less than 10 minutes strong smoke fumes exiting the top manholes

11:41 ----- Evacuation of people inside the column (below the concerned beds)
----- Water injection into column via recycle line on top of the column

11:44 ----- Emergency Response Plan activated and evacuation of all refinery units

11:58 ----- External column cooling (sprinkler system and fire brigade)

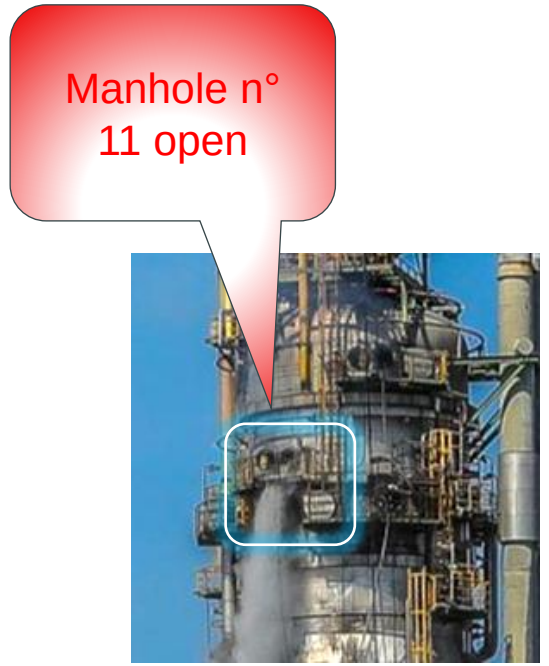
12:37 ----- Steam from the bottom commissioned (up to 17t/h), after deblinding

12:45 ----- Lower manholes closed (N°1-9) by fire brigade

12:55 ----- Rescue of 3 Unit contractors trapped outside of the column at top level

14:38 ----- All temperature indications below 500°C (end of measuring range)

14:55 ----- Emergency Response Plan deactivated
----- Column left under water flushing from top, closing of manhole N°11



Smoldering fire in vacuum column
**** Consequences ***

Actual consequences

- **Human** : no injuries- 11 persons checked (suspicion of smoke inhalation). High psychological stress

- **Environmental**: smoke/steam cloud widely visible, limited odor nuisance . No immediately dangerous concentrations of toxic gases offsite (CO or SO_2)

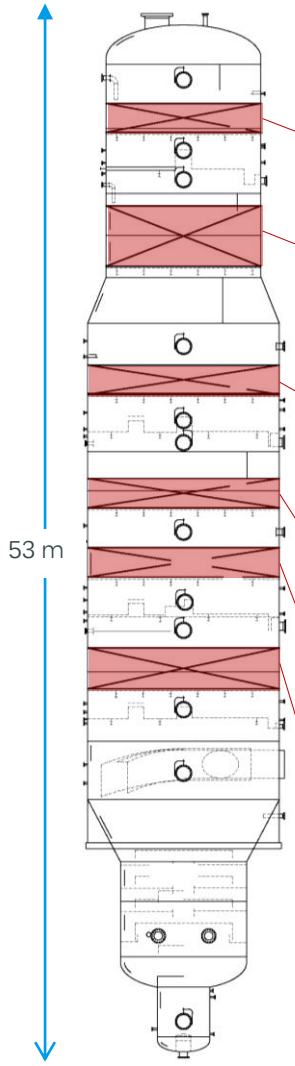
- **Material/ production** :

- Overall margin loss about 100M$ of VDU unavailability
- 11 M$ Repair costs and significant mechanical damage of column internals

- **Media** : local media response, quite objective communication

Smoldering fire in vacuum column

**** Damage extent ***



Column internals severely damaged; shell can be reused showing limited damage

Bed 1

- OK

Bed 2

- Bed collapsed
- Beams slightly deformed

Bed 3

- Bed destroyed
- Beams bent out of shape
- Chimney tray broken down

Bed 4

- Beams partially damaged
- Packing partially ok

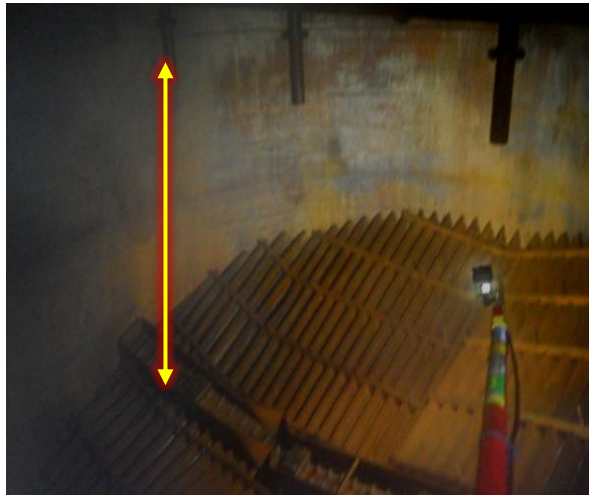
Bed 5

- Packing partially damaged
- Beams OK

Bed 6

- Bed 6 intact (but anyway SD scope)

Bed 3



Smoldering fire in vacuum column
***Explanation ***

- **Presence of large quantity of pyrophoric iron-sulfide after chemical cleaning**
  - Increased iron sulfide (pyrophoric FeS generated ignition) build-up during last run (higher corrosion rate ?)

$$Fe_2O_3(rust)+3\ H_2S \rightarrow 2FeS+S+3H_2O$$

  - Inefficiency of chemical cleaning related to:
    - Misinterpretation of analytical data by cleaning company leading to premature stop of chemical cleaning
    - Maldistribution of chemical within the column

- **Incomplete application of HSE procedure „confined space entry“**
  - Pyrophoric risk after chemical cleaning (identified as a safety measure) is not explicitly reminded in the specific risk analysis
  - Prescribed measures in specific risk assessment and work permits have been fully implemented, BUT continuous moistening of all beds not prescribed in risk assessment/ work permit as per above mentioned procedures

- **Aggravating circumstances**

  1- Opening of all manholes by contractors (not in line with work peremit)

  2- Degraded mitigation measure efficiency (man hole 11 open→ injected water did not reach the bottom of the column)

  3- Kinetics of accident did not allow to activate mitigation measures in place (fire hoses ready to use at each manhole)

  4- Lack of supervision

Column collapse during maintenance works ***Explanation ***

Ignition of pyrophoric materials and temperature increase when air entered inside the column after manhole removal

Oxidation Reaction

$$4\ FeS + 3\ O_2 \rightarrow 2\ Fe_2O_3 + 4\ S\ (+\ \textit{generation of heat})$$

$$2\ FeS + 3{,}5\ O_2 \rightarrow Fe_2O_3 + 2\ SO_2$$

• Identified Root Causes

- Unefficency of the chemical decontamination
- Weakness in the risk identification and assessment
- Lack of washing of tower internals , water injection on the top of the column not immediately efficient

Recommendations

- Contractor technical offer for chemical decontamination must be reviewed and challenged . **Adequate expertise** must be available

- **Risk analysis** must be conducted, involving a multidisciplinary team with relevant expertise

- On any opening of column with packing always **ASSESS** POTENTIAL PRESENCE OF PYROPHORIC PRODUCTS.

  If confirmed or in case of doubt, consider that the opening of a column with packing is a **safety critical operation** that requires application of a specific procedure

- Temperature and gas **monitoring** necessary

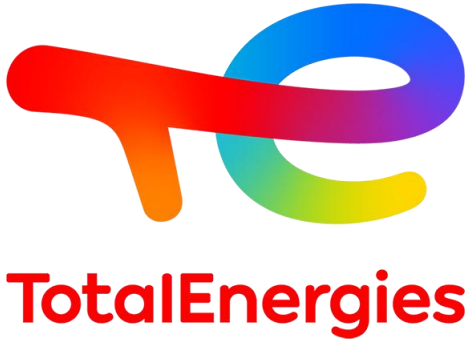
- Implement a more **gradual** tower **opening** and aeration process to avoid chimney effect when the packing is still dry.

Recommendations

- Include tower internal **wetting** at the opening of the manholes. Tower internals should be periodically water washed to prevent dry out. The water wash frequency will be typically once a day (even once a shift) once the tower is open.

- **Manholes** must be ready to be closed, and the column must be equipped with a system allowing watering with fire water of the whole interior of the column which can be activated quickly from the ground.

- Reinforce processes to ensure that **lessons learnt** from previous decontaminations are adequately incorporated into procedures and on-site expertise and prepare adequately technical aspects of decontamination of capacities when pyrophoric risk is possible. Indeed, knowledge of personnel about the chemical decontamination needs to be reinforced



Thank you for your attention