



Pyrophoric Iron Fires

At one time or another, most refineries experience spontaneous ignition of iron sulfide either on the ground or inside equipment. When this occurs inside equipment like columns, vessels, and tanks and exchangers containing residual hydrocarbons and air, the results can be devastating. Most commonly, pyrophoric iron fires occur during shutdowns when equipment and piping are opened for inspection or maintenance. Instances of fires in crude columns during turnarounds, explosions in sulfur, crude or asphalt storage tanks, overpressures in vessels, etc., due to pyrophoric iron ignition are not uncommon.

Often the cause of such accidents is a lack of understanding of the phenomenon of pyrophoric iron fires. This article aims to explain the basics of pyrophoric iron fires and to provide ideas for developing safe practices for handing over equipment for inspection and maintenance.

What is Pyrophoric Iron Oxidation?

The word "pyrophoric" is derived from the Greek for "fire-bearing". According to Webster's dictionary, "pyrophoric material" means "any material igniting spontaneously or burning spontaneously in air when rubbed, scratched, or struck, e.g. finely divided metals".

Iron sulfide is one such pyrophoric material that oxidizes exothermically when exposed to air. It is frequently found in solid iron sulfide scales in refinery units. It makes no difference whether these pyrophoric sulfides exist as pyrite, troilite, marcasite, or pyrrhotite. It is formed by the conversion of iron oxide (rust) into iron sulfide in an oxygen-free atmosphere where hydrogen sulfide gas is present (or where the concentration of hydrogen sulfide (H₂S) exceeds that of oxygen). The individual crystals of pyrophoric iron sulfides are extremely finely divided, the result of which is that they have an enormous surface area-to-volume ratio.

When the iron sulfide crystal is subsequently exposed to air, it is oxidized back to iron oxide and either free sulfur or sulfur dioxide gas is formed. This reaction between iron sulfide and oxygen is accompanied by the generation of a considerable amount of heat. In fact, so much heat is released that individual particles of iron sulfide become incandescent. *This rapid exothermic oxidation with incandescence is known as pyrophoric oxidation* and it can ignite nearby flammable hydrocarbon-air mixtures.

Basic chemical reactions: Iron sulfide is one of the most common substances found in refinery distillation columns, pressure vessels, etc. It is formed by the reaction of rust or corrosion deposits with hydrogen sulfide as shown below:



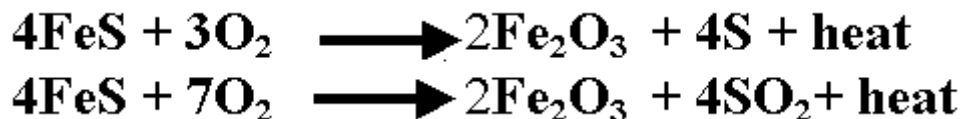
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There is a greater likelihood of this reaction occurring when the process involves a feedstock with high sulfur content. This pyrophoric iron sulfide (PIS) lays dormant in the equipment until the equipment is shutdown and opened for service, exposing the PIS to air, allowing the exothermic process of rapid oxidation of the sulfides to oxides to occur, as shown in the equations below:



The heat usually dissipates quickly unless there is an additional source of combustible material to sustain combustion. The white smoke of SO₂ gas, commonly associated with pyrophoric fires, is often mistaken for steam.

Pyrophoric iron oxidation in Distillation Columns

In petroleum refineries, the equipment most prone to pyrophoric combustion induced fires is the distillation columns in crude and vacuum distillation units. Deposits of iron sulfide are formed from corrosion products that most readily accumulate at the trays, pump around zones, and structured packing. If these pyrophoric iron sulfide (PIS) deposits are not removed properly before the columns are opened up, there is a greater likelihood of PIS spontaneous ignition. The trapped combustible hydrocarbons, coke, etc. that do not get adequately removed during steaming/washing often get ignited, leading to fires and explosions inside the equipment. These fires not only result in equipment damage but can also prove fatal for the personnel who are performing inspection and maintenance work inside the columns.

The accidents due to pyrophoric iron oxidations are entirely avoidable if safe procedures for column handover are followed. The targets of these procedures should be twofold:

- First, to remove all the combustibles
- Second, to remove or neutralize pyrophoric iron sulfide deposits

The basic distillation column oil-cleanup procedure is discussed in steps below.

Distillation Column Oil Cleanup Procedure

1. **Steaming:** The steaming is done after all liquid hydrocarbons have been drained from the column and associated piping. The objective of steaming is to make the column and associated piping free of residual hydrocarbons. The column vent and pump strainers in the side draw piping are de-blinded and steaming is started from utility connections at the bottom of the column. Generally, steaming is continued for about 20 to 24 hrs, ensuring the column top temperature remains more than 100 °C throughout the operation.

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2. **Hot Water Washing:** When clear steam is observed exiting the column vents, water washing of the column should be started. With steam still in commission, water is sent to the column, usually via reflux lines, and it is drained from the column bottom, associated pump strainers, etc. The water flow rate should be adjusted so that steam still comes from the vent (i.e. water should not result in condensing of all steam before it reaches the column top). Water flow should be stopped for 2-3 hrs and then resumed. This cycle of steaming and washing should be repeated several times for a total of about 15 to 20 hours. Injection of a turpene-based detergent into the steam can also be considered. The condensate-soap solution can be collected and circulated through the various side cuts.

3. **Blinding:** When clear water is observed at side draw pump strainers, etc., associated piping should be isolated by installing blinds wherever isolation is possible.

4. **Cold Water Washing:** The hot water wash should be followed by a cold water wash (i.e. steam should be fully closed). The cold water washing is done for about 20-24 hrs.

5. **Chemical Injection for Removal and Neutralization of PIS Deposits:** During the cold-water wash or after washing is over, chemical injection for removal of pyrophoric sulfides should be considered. The various options for chemical treatment are discussed below:

- Acid cleaning - This procedure involves pumping in an acid with some corrosion inhibitor. The acid dissolves sulfide scale and releases hydrogen sulfide gas. It is effective and inexpensive, however, disposal of hydrogen sulfide gas can be a problem, as can corrosion (when the system contains more than one alloy). Dilute hydrochloric acid solutions may also be used. The resulting iron chloride turns bright yellow, acting as an indicator for removal of the iron sulfide.
- Acid plus hydrogen sulfide suppressant - Additional chemicals can be added to the acid solution to convert or scrub the hydrogen sulfide gas.
- Chelating solutions - Specially formulated, high pH, chelating solutions are quite effective in dissolving the sulfide deposits without emitting hydrogen sulfide, but this is an expensive application.
- Oxidizing chemicals - Oxidizing chemicals convert sulfide to oxide. Potassium permanganate (KMnO_4) has been used commonly in the past to oxidize pyrophoric sulfide. Generally the potassium permanganate is added to the tower during the cold water washing as a 1% solution. At various intervals, samples are taken and checked for color. The colors of the fresh KMnO_4 and the spent MnO_2 are purple and brown respectively. If the color of the solution becomes brown, additional KMnO_4 is needed. The reaction is judged complete when the solution color remains purple. It takes approximately 12 hours to complete the job.

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The cost of potassium permanganate treatment is more expensive than acid cleaning and traditional oxidizing agents such as sodium hypochlorite or hydrogen peroxide. Nevertheless, it is less corrosive to equipment than acid cleaning and used properly can be safer than other oxidizing agents.

The following conditions should be avoided when using potassium permanganate:

- Do not add KMnO_4 to acids or use in a low pH environment
- Combustible materials should not be allowed to contaminate KMnO_4 stocks
- Residual MnO_2 may remain in vessels after treatment and cause combustion or flammability issues in equipment with large surface areas such as packed towers
- KMnO_4 cannot be used in conjunction with most detergents
- KMnO_4 may have a “bad reputation” in some processing plants, but this is often times the result of misuse by contractors or plant personnel.

If you're considering the use of KMnO_4 in a cleaning services and would like to consult with an expert its safe application procedures, please contact Dr. Phil Vella of Carus Corporation via phone at (815) 224-6869.

Alternative oxidation technologies are being developed with a focus on

- increasing safety in application
- saving water
- eliminating odor problems
- minimizing wastewater problems
- reducing wastes

One such alternative is Zyme-Flow®. Zyme-Flow® offers unique chemistry which is patented and offered by license from United Laboratories International, LLC as Zyme-Flow® and related products. The Zyme-Flow® chemical applications are administered by a highly trained staff of technicians provided by United and sold only by license from United Laboratories International, LLC.

The Zyme-Flow® generic Vapour Phase® method is apparently unique in that the de-oiling and oxidizer composition that is being dispersed actually may be vaporized in the steam (instead of being just atomized). This allows the Zyme-Flow® composition to

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travel (in easily measurable concentrations) extensive distances and throughout equipment with high efficiency for contacting and condensing on internal surfaces. The composition may expend quickly, but the application technicians can measure its progress. This prevents over-dosing.

A very generic Vapour Phase® procedure may include:

1. Stop feed and de-inventory the unit per normal procedures.
2. Perform initial isolation per the pre-established plan with the Zyme-Flow® specialists.
3. Establish a thorough steam path throughout the equipment.
4. Add Zyme-Flow® to the incoming steam (commonly only 1-3 points are needed even for very large units).
5. Continue the injection and steaming for 8-12 hours.
6. Perform isolation per pre-established plan with the Zyme-Flow® specialists.
7. Possibly perform a final rinse with cold water to cool the columns quickly.
8. The unit is then ready for opening, ventilation, and hot work.

One major advantage for oxidizing pyrophoric iron sulfide is that the distribution dynamics of the Vapour Phase® applications are often more efficient than atomized distribution methods. This is why Zyme-Flow® is often used for decontamination of flare lines and overhead systems where few injection points can be utilized. The same dynamics allows for full treatment of most tight packing structures in refinery columns.

In some situations, Zyme-Flow® applications may be combined simultaneously or in sequence with compatible solvent and oxidizer products to target specific challenges such as monomer / polymer coatings and other challenges. These applications require specialty design consideration from the Zyme-Flow® specialists. This is especially important in structured packing situations where polymerization tends to coat and protect the pyrophoric deposits from contact with oxidizers until cooling promotes cracking of the polymer.

Solvent/Surfactant Steam Dispersion Methods

There are alternatives to the steam, wash, blind, and wash again technologies. These include steam dispersion technologies which are sometimes combined with oxidizer washing technologies. These alternatives may include steam dispersion of organic solvent products and can be very good to excellent de-oiling and degassing compositions (which expose pyrophoric iron sulfide to subsequent oxidizer treatments).

For critical path process units in a turnaround, a very generic procedure may include:

1. Stop feed and de-inventory the process equipment per normal procedures.
Sometimes this involves steaming and sometimes water displacement.
2. Establish a steam flow throughout the equipment. The design of the flow path is critical.

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3. Add chemicals to the incoming steam to promote de-oiling and degassing of the equipment (this may involve numerous injection points).
4. When the outflow vapors are within safety and environmental specifications, blow down the equipment to the atmosphere for a short time (or continue to flare or condenser as needed).
5. Perform isolation as needed prior to final washing for oxidation (per pre-designed isolation plan).
6. Perform a thorough water wash with oxidizer until the oxidation requirement of the fluid path is complete. Sometimes this must involve total fluid fill of the equipment to obtain positive contact of pyrophoric surfaces.
7. The unit is then ready for opening, ventilation, and hot work (unless other chemical treatments are required).

This generic procedure may allow for 24-48 hours of savings over the extended steaming, isolation, and washing approaches, and may be safer to perform. There are several products currently offering this type of service. Many of them are strong encapsulators and require secondary treatment to break the emulsions.

The oxidizers Zyme-Flow and Zyme-Ox are proprietary products from United Laboratories International, LLC for most refinery and petrochemical decontamination applications. For more information on Zyme-FlowSM Process Technology, the readers can visit www.zymeflow.com or contact Mr. Bevan Collins at tankzyme@aol.com.

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Case Studies: Pyrophoric Iron Fires

The history of refining is replete with cases of fires and explosions due to pyrophoric iron ignitions. A few of these cases are discussed below (details like the location and date of the incidents are not included), to give the reader an idea of the nature of pyrophoric iron fires and the lessons learned.

Pyrophoric fire/explosion inside a Vacuum column in a Crude Unit

During a turnaround in the Crude Unit the vacuum column was being prepared for handover to maintenance. The oil was removed from the column and the column was steam purged. A water washing connection was made in the light vacuum gas oil (LVGO) reflux pump suction. Meanwhile, instruction was given for removal of a 40-inch spool piece in the column overhead line to facilitate overhead exchanger blinding. Air ingress occurred from this open flange, leading to auto-ignition of pyrophoric iron sulfide inside. An explosion took place causing damage to the internals. White smoke (SO_2) was also observed at the open end. Nitrogen injection and water washing were immediately begun to quench the heat and halt the oxidation reaction inside the column.

Lessons learned:

Before carrying out any maintenance activity on overhead exchangers, proper water washing and blinding must be completed. Full-face blinds should be provided wherever spool pieces are dropped.

Pyrophoric Fire inside the floating head cover of a Naphtha Stabilizer Reboiler

During a maintenance and inspection (M&I) shutdown, after steaming of the reboiler loop, the floating head cover of the naphtha stabilizer reboiler (S&T exchanger) was opened so the bundle could be pulled for cleaning. The head cover was left in the open position. After about 2 days, fire and smoke was observed from the head cover. It was determined that the fire occurred because of the PIS ignition of residual hydrocarbons. The fire was immediately extinguished with water. The cover was thoroughly flushed with water and kept wet.

Lesson learned: Whenever exchangers in naphtha service (containing sulfur) are opened for maintenance, the exchanger areas must be properly water washed for PIS removal. No amount of steaming can ensure full removal of PIS or residual hydrocarbons.

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Pyrophoric Fire inside a Naphtha Tank

A naphtha tank (floating head type) was emptied out for maintenance. It was left unattended for one month. One day, flames and smoke were observed coming from the tank. Upon investigation, it was found that PIS had ignited leading to combustion of residual naphtha in the tank.

Lessons learned: Tanks in high-sulfur hydrocarbon service, such as naphtha, crude, etc., must be properly emptied and washed before allowing them to remain idle for maintenance. Also, such tanks should be kept under adequate nitrogen blanketing.

Pyrophoric Fire inside a Hydrotreater Reactor

During a maintenance shutdown, a naphtha Hydrotreater reactor feed/effluent heat exchanger was to be opened. The reactor gas loop was thoroughly nitrogen purged. During deblinding of the exchanger air ingress occurred to the reactor causing excessive heat build up in the reactor due to a pyrophoric iron fire. The temperatures went as high as 500 °C. Heavy smoke was observed from the open flanges and the reactor platform area became hot. The heat was immediately quenched by purging with nitrogen.

Lessons learned: Whenever piping associated with a naphtha Hydrotreater reactor has to be opened, purging N₂ must be kept opened during blinding and deblinding of the upstream and downstream flanges in exchangers.

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General Precautions to Avoid Pyrophoric Iron Fires

1. The scraps and debris collected from cleaning of filters in naphtha / crude service must be kept wet and disposed of underground.
2. Tanks, reactors, columns, and exchangers in high-sulfur feed service must be kept properly blanketed with N₂ during idle periods.
3. All equipment and structured packing must be properly water washed and kept wet when exposed to the atmosphere.
4. In processes where catalyst handling is required (such as in Hydrotreating and fluid catalytic cracking) caution must be taken during catalyst recharge or disposal. When unloading any spent coked catalyst, the possibility exists for iron sulfide fires. If the spent catalyst is warm and contacts oxygen, iron sulfide will ignite spontaneously and the ensuing reaction may generate enough heat to ignite carbon deposited on the catalyst. Therefore catalyst must be stripped of all hydrocarbons, cooled to about 50 °C and wetted with water to prevent it from igniting vapors. Once cooled, the used catalyst may be emptied into drums for later shipment to a regenerator or a disposal site. As the catalyst may be highly pyrophoric (containing iron sulfide, etc.), it should be dumped into drums containing an internal liner for shipment. The drum and liner should first be filled with inert gas, which is then displaced by the catalyst. The liner should be tied off and a small chunk of dry ice placed inside the drum before sealing. These precautions should protect against catalyst auto ignition.

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