

# HAZARD IDENTIFICATION

## Pyrophoric Iron Sulfide

### Purpose and Use:

The purpose of this document is to communicate the hazard presented by the formation of pyrophoric iron sulfide inside equipment processing streams that contain hydrogen sulfide and other sulfur compounds. The pyrophoric nature of iron sulfide means that it reacts readily with oxygen. The resulting solid becomes so hot that it serves as a ready point of ignition if the surrounding vapor or other matter is comprised of a flammable mixture or combustible material, including solids, either inside or outside of the process equipment. The possible presence of iron sulfide (FeS) inside process equipment means that the prevention of fires or explosions inside the equipment relies solely on preventing the presence of a flammable mixture, i.e., the ingress of oxygen, or proper cleaning before exposure to air.

The Process Safety Hazard Identification documents serve to help facilities recognize potential risks associated with work practices, safety practices, refinery process equipment, and technology. Hazard Identification documents are meant to:

- Improve process safety awareness with a focus on higher potential risks,
- provide information and ready reference guides for potentially overlooked or under-communicated process safety hazards, and
- share lessons from industry related incidents and near misses.

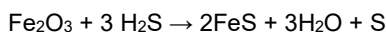
### Category:

Operating Procedures, loss of containment, pyrophorics.

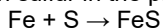
### Scope:

This document covers the formation of FeS on metal surfaces exposed to H<sub>2</sub>S during process operations and the heat generating reactions that occur when FeS is then exposed to an oxygen containing environment. Practices that can help prevent the ingress of oxygen into process equipment are covered as well as steps that may be taken to remove FeS before equipment is opened to the air for maintenance or inspection.

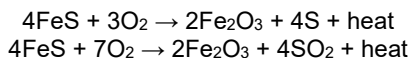
Rust (Fe<sub>2</sub>O<sub>3</sub>) reacts with H<sub>2</sub>S in low oxygen environments, even at ambient temperatures, to form FeS following the reaction below:



At elevated temperatures iron can react directly with sulfur in the process following this reaction.



When later exposed to an atmosphere containing oxygen, even below flammable limits, FeS reacts with the available oxygen in reactions that generate a great deal of heat, leaving the resulting rust particles hot enough to ignite a flammable mixture.



Reactions of FeS with oxygen can occur when the internals of equipment are exposed to air when opening the equipment for maintenance or inspection, resulting in fires that can ignite any flammable or combustible materials that may also be present in the area. This includes the potential ignition of the metals used as structured packing in fractionation towers.

The FeS can also ignite a flammable mixture that occurs inside process equipment due to the unintended presence of oxygen.

Because both iron and sulfur can exist with multiple valencies, iron sulfide can exist in multiple forms, including FeS<sub>2</sub>, Fe<sub>2</sub>S<sub>3</sub>, Fe<sub>3</sub>S<sub>4</sub> and Fe<sub>7</sub>S<sub>8</sub>. All forms can be pyrophoric.

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### **Examples of Potential Consequences and/or Hazards:**

The potential consequences of accumulation of sufficient oxygen inside process equipment where FeS has formed include internal detonation resulting in explosive loss of containment of the material with violent dispersal of vessel parts that can result in domino effects from impact on other process and storage equipment within the considerable range of the flying debris. The potential consequences of opening equipment to the air, typically for maintenance or inspection purposes, which contains FeS, include forming embers of Fe<sub>2</sub>O<sub>3</sub> that are hot enough to burn personnel, but also hot enough to ignite flammable mixtures or combustible liquids and solids that they contact. This has included the ignition of metals used as packing in fractionating towers resulting in the destruction and toppling of those towers. The consequences of the resulting fire, or possible explosion, are largely determined by the quantity of flammable and combustible material nearby when ignition occurs.

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	Potential Concerns	Potential Consequences and/or Hazards
1.0	Transmission of air from an FCC regenerator to the reactor	<p>1.1 Because malfunction/erosion of a regen slide valve results in losing the level in the reactor and makes it difficult to keep reactor pressure higher than the regenerator and main fractionator, the performance of these slide valves is monitored with maintenance scheduled and performed regularly.</p> <p>1.2 The pressure balance between the reactor and the regenerator is rigorously maintained to prevent a driving force that would push flow of air from the regenerator to the reactor.</p> <p>1.3 Excess air pressure is relieved at the blower discharge in the event of a loss of pressure balance control.</p>
2.0	Compressor or eductor operation with a sub-atmospheric suction pressure	<p>2.1 Compressor and eductor controls are established with a suction pressure above atmospheric pressure to ensure that if leakage occurs it will be process contents leaking to the atmosphere instead of air leaking into the process equipment.</p> <p>2.2 The suction side of compressors and eductors that have the potential to draw inlet pressures below atmospheric pressure are provided with alarms to alert operations of the need to take corrective action.</p> <p>2.3 The suction side of compressors and eductors that have the potential to draw inlet pressures below atmospheric pressure can be provided with safety instrumented shutdown systems that trip the compressor or eductor before a suction pressure below atmospheric is reached.</p>
3.0	Introduction of air / oxygen streams into flare systems where FeS might be present	<p>3.1 Operating procedures prohibit the introduction of oxygen or air into flare systems where pyrophoric FeS might be present based on the presence of H<sub>2</sub>S in other relief streams.</p> <p>3.2 Flare headers include a liquid seal drum with sufficient seal height to ensure that the flare header operates under a slightly positive pressure to ensure that inadvertent leakage would be from inside the flare header outward where the leak would be detected rather than into the header where it likely would not be quickly detected.</p> <p>3.3 On flares without a liquid seal drum, and for some flares with a liquid seal drum, sweep gas, normally methane or natural gas, is introduced into the flare header to purge air that has inadvertently leaked into the flare header toward the flare.</p>
4.0	Pyrophoric FeS remains inside equipment opened for maintenance or inspection	<p>4.1 The entire internals of the equipment are wetted and maintained constantly wet while sludge or other solid contents are removed from the equipment. The solids removed are constantly maintained under a layer of water when removed from the vessel as they are packaged for disposal.</p> <p>4.2 Cleaning residual FeS present in sludge that remains inside process equipment before removal from the vessel is typically performed in a</p>

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multi-step process that consists of:

- 4.2.1 Steaming – removes residual hydrocarbons
- 4.2.2 Hot water washing – this step could include the addition of terpene-based detergent to help remove residual sludge
- 4.2.3 Blinding the equipment away from the rest of the process
- 4.2.4 Cold water washing
- 4.2.5 Chemical injection to react with remaining FeS. Injected chemicals may include:
  - 4.2.5.1 Acid – dissolves sulfide scale but releases H<sub>2</sub>S
  - 4.2.5.2 Chelating solutions – High pH, effective, but at a higher cost
  - 4.2.5.3 Oxidizing chemicals, most commonly KMnO<sub>4</sub>, which is less corrosive than most acidic washes
  - 4.2.5.4 Other proprietary chemical cleaning materials are available that are effective on FeS.

*However:*

- 4.2.5.5 Avoid adding KMnO<sub>4</sub> to acidic solutions
  - 4.2.5.6 Avoid adding KMnO<sub>4</sub> to combustible materials
  - 4.2.5.7 Residual MnO<sub>2</sub> can create flammability problems in high-surface vessels, e.g., with internal packing
- Avoid using KMnO<sub>4</sub> in combination with detergents

5.0 Rust (Fe<sub>2</sub>O<sub>3</sub>) remains on vessel surfaces when it is returned to service that will be converted to FeS during operation at higher temperature and H<sub>2</sub>S concentration

5.1 The surface of vessels may be pickled/passivated after closing and air freeing to convert rust to iron that is more resistive to conversion through contact with H<sub>2</sub>S under pressure at higher temperatures.

5.1.1 Pickling is typically performed with weak acidic solutions that react with rust remaining on the steel surface to form iron and iron compounds less subject to reaction with H<sub>2</sub>S.

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### References and Resources:

C. Ender and D. Laird, "Minimize the Risk of Fire During Column Maintenance," *Chemical Engineering Progress*, pp 54 – 56, September 2003.

D. E. Powell, R. H. Winters, and M. A. Mercer, *Field Guide to Managing Iron Sulfide (Black Powder) Within Pipelines or Processing Equipment*, Houston TX: NACE International, 2019

AFPM Safety Bulletin, *Hazards of purged tanks – Formation of Pyrophoric Iron Sulfide in Low Oxygen Environments*, available on the Safety Portal at <https://safetyportal.afpm.org/File/142/1>

### Industry Incidents:

On April 26, 2018, an explosion occurred at the Husky refinery in Superior, Wisconsin as the refinery was shutting down its FCC unit in preparation for a turnaround. The explosion occurred inside two-unit vessels, the primary absorber, and the sponge absorber. Oxygen that migrated from the FCC Regeneration vessel to the Reactor vessel accumulated in these gas concentration unit vessels. The resulting explosion hurled debris into an asphalt tank 200 ft. away, resulting in the domino effect of a large release of asphalt, some of which spilled outside the tank dike wall and ultimately caught fire. Other pieces of debris were found up to 1,200 ft. away from the primary and sponge absorber vessels. See U.S. Chemical Safety Board *FCC Unit Explosion and Asphalt Fire at Husky Superior Refinery* available at <https://www.csb.gov/husky-energy-superior-refinery-explosion-and-fire/>

In 2003, an investigation by Koch-Glitsch into 56 incidents of fires inside distillation columns during maintenance activities found that most of them involved pyrophoric ignition.

Revision	Date	Summary of Changes
Initial	August 2024	First Draft
Revision	September 2024	HIPS
Revision	October 2024	PSW
Legal	December 2024	AFPM, PSW
Final	February 2025	Published

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