

The Management of Black Powder in Crude Oil and Natural Gas Systems

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Content sourced from, and courtesy of, *“Field Guide for Managing Iron Sulfide within Pipelines or Process Equipment.”*

Introduction – What is Black Powder

Black powder is typically a mixture of iron sulfides and iron oxides. Although it may be manifested as a dry, black powder, the black powder can also be in a slurry, accompanied with produced water, lubricating oils, such as from pumps or compressors, and/or glycols, such as from dehydration units.

Iron sulfide can form whenever hydrogen sulfide (H₂S) reacts with iron, such as from steel pipelines. There are numerous forms of iron sulfide.¹ These include

- Pyrrhotite
- Troilite
- Mackinawite
- Pyrite
- Marcasite
- Smythite
- Greigite
- Ferric Sulfide

The reactions between the different forms are complex, and depend on numerous parameters, including temperature, pressure, and concentration of sulfides. Regardless of form, set up programs to monitor and remove those sulfides.

Why is Black Powder a Concern?

First, the existence of black powder within a crude oil or natural gas gathering system or process equipment, suggests the presence of H₂S, which itself poses health hazards. The National Institute of Occupational Safety and Health (NIOSH) recommended exposure limit (10 minute ceiling) is 10 ppm. If the concentration is 100 ppm, coughing, eye irritation, and the loss of smell would occur after 2-15 minutes. Altered breathing and drowsiness would occur after 15-30 minutes, and death may occur after 48 hours. At 500-700 ppm, staggering and collapse would be expected in 5 minutes, and death could occur in 30-60 minutes. At 1000-2000 ppm, near instantaneous death would be expected.²⁻⁴ *Hence, the presence of hydrogen sulfide gas, which is commonly found associated with crude oil and natural gas production, should prompt a rigorous safety program.*

Second, safety concerns are posed by the handling of pyrophoric iron sulfide, such as within the black powder collected on filter cartridges. “Pyrophoric” means that the material can spontaneously burst into flames when dried and exposed to oxygen. *If cartridge filters, which were removed from a process stream, had captured pyrophoric iron sulfide particles and been allowed to dry, then spontaneous combustion could occur, once that pyrophoric iron sulfide is exposed to oxygen.* This safety concern is depicted in Figure 1.⁵ The same safety concern also relates to maintenance pigs removed from pipeline receivers. If patches of pyrophoric iron sulfide deposits remain on a maintenance pig and allowed to dry, spontaneous combustion could result. Figure 2 illustrates a foam maintenance pig, which partially melted as a result of spontaneous combustion.



Figure 1 Cartridges, which collected pyrophoric iron sulfide, were allowed to dry – spontaneous combustion!⁵



Figure 2 Partially melted foam pig.

Best practices call for spraying water onto the pigs as soon as the trap door is opened, and, once removed, flush any black powder off the pig using water. This is depicted in Figure 3. Water serves as a heat sink to remove the heat from the exothermic reaction that occurs when pyrophoric iron sulfide dries. Collect the water and take it to an appropriate disposal site.



Figure 3 Use water to clean pigs removed from receiver whenever pyrophoric iron is suspected.

One of the primary considerations associated with the removal of iron sulfide/black powder from systems relates to the disposal of those corrosion products. Safe handling and disposal of such materials may represent up to 40% of the expense for a cleaning operation.

Third, a health and safety concern may exist if the powder contains any naturally occurring radioactive material (NORM). *The real threat is associated with possible inhalation of fine radioactive material into the lungs, which could pose a long-term health concern.* Always wear the proper personal protective equipment.

Fourth, black powder particulates may pose a risk for possible erosion or abrasion when transported through pipelines. When formed, iron sulfide particles may be as large as 3.9 mils (100 μm). However, that brittle material will shear into fine submicron particles as a result of contacts with the pipe wall. A stream of such particles can damage the impeller of a gas compressor in less than 24 hours, as illustrated in Figure 4. Similarly, such fine particulates can damage ceramic coated gas cooled turbine blades, as illustrated in Figure 5. What makes this figure significant is that the particulates traveled over 75 miles (121 km) downstream to strike the turbine blades.⁶



Figure 4 A damaged impeller.

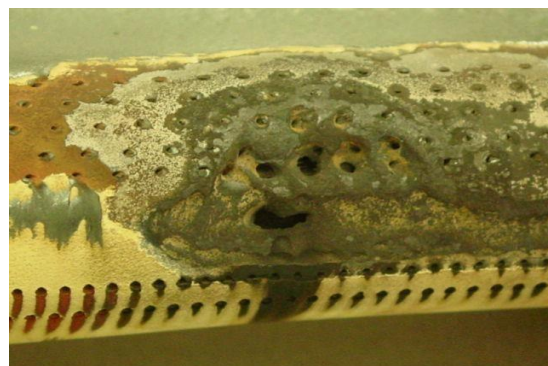


Figure 5 Abrasion to ceramic coated turbine blade.⁶

Besides for concerns related to erosion or abrasion when particles are transported, be aware of the potential for underdeposit corrosion, particularly for wet systems. Bacteria can establish colonies underneath such deposits, which also will reduce the effectiveness of chemical treatments.

Fifth, iron sulfide is electrically conductive, and as such the depositions can form electrical shorts, that may affect instrumentation. Such deposition of conductive material, which is typically called “bridging,” causes electrical shorts and may result in erroneous readings.⁷ Figure 6 illustrates how such deposition can shorten the electrical path for electrical resistance (ER) corrosion probes, resulting in erroneous measurements.



Figure 6 Bridging may shorten electrical paths, and affect accuracy of ER corrosion probes measurements.⁷

(Photograph of probes courtesy of Rohrback Cosasco Systems)

What’s necessary for Black Powder to Form?

Iron sulfide, the predominant component of black powder, can be formed whenever H₂S, water, and iron is present.

H₂S may come from reservoirs or storage caverns, or may be generated by sulfate reducing bacteria. Routine field tests are available to measure the concentrations of H₂S in both the aqueous as well as gaseous phases. Serial dilutions studies are commonly conducted to quantify microbiological populations of sulfate reducing bacteria, commonly called SRBs.

Water is the second key component in forming iron sulfide. It may be produced, such as from production wells, or come from condensation. The water may also be introduced by process upsets. This is the essential electrolyte for the formation of iron sulfides.

Iron is the primary content for steel piping and processing equipment. Iron may also be present within nascent formation waters.

When all three are present, iron sulfide, and hence black powder, may form. Removing H₂S and/or water reduces the likelihood for the formation of any iron sulfide. Periodic sample analysis should be part of comprehensive pipeline integrity management programs.

Field and Lab Analyses

Whenever there are new reports of black powder within a system, conduct field and laboratory tests to verify that iron sulfide is indeed a significant component of that powder. Field tests, such as those to confirm the powder is magnetic and that the powder will release distinctive hydrogen sulfide when wetted by a couple of drops of hydrochloric acid, are excellent screening tools. However, such field tests should also be followed by more precise laboratory tests. Don’t use the appearance alone as the analysis. For example, black powder was reported at one facility, simply based on the color of the product and that the powder clogged in-line filters. Chemical suppliers rushed to offer their products and services, but unfortunately they missed the boat. Subsequent field and laboratory tests demonstrated that that “black powder” was primarily charcoal.⁸

Magnetic Response? The primary components of black powder are iron sulfide and iron oxide, both of which are magnetic. Thus, place a small sample of the dry powder in a clear plastic bag, and run a magnet across the exterior side of the plastic bag. If the material is magnetic, there should be a strong response to the magnet's field. A weak or no response would suggest that neither iron oxide, nor iron sulfide are significant components of that powder.

H₂S Release when wetted by HCl? Another field test consists of placing a small sample of the powder on a glass plate, and wetting it with a drop or two of hydrochloric acid. If the sample is predominantly iron oxide and iron sulfide, there should be a rigorous bubbling associated with the hydrogen gas that is released when the oxides or sulfides are wetted by the acid. The presence of sulfides would be confirmed by the distinct aroma of hydrogen sulfide gas that would be released. That's why a small sample size and only a couple of drops of hydrochloric acid are used in this test - personal safety.

Follow up with laboratory analyses. More rigorous laboratory analysis frequently starts by using a scanning electron microscope (SEM) equipped with an energy dispersive spectrophotometry (EDS) capability. This analytical technique is commonly used to identify the elements that constitute the sample. The EDS technique is comparable to X-Ray Fluorescence techniques in identifying the elements present. Other techniques may include atomic absorption analysis of liquid samples or wet chemistry techniques, such as CHNS for quantifying the presence of carbon, hydrogen, nitrogen, and sulfur. There are, of course, numerous other analytical techniques that are available, such as Gas Chromatography-Mass Spectroscopy, which can detect concentrations of elements as low as parts per billion (ppb). As appropriate, consult specialists to select the proper analytical techniques, based in part on results from field tests and knowledge of individual systems.

Before leaving this point, know the strengths and limitations of individual analytical techniques or even instruments. One sample was analyzed using SEM/EDS, and it was reported that that sample contained 83.6% iron. However, the sample had virtually no response to the presence of a magnet during field testing. Accordingly that sample was reanalyzed using a different SEM/EDS instrument – this one having the capability to detect elements as light as carbon. Those results indicated the sample contained 31.4% iron, and 64.3% carbon. (Wet chemistry tests for carbon, part of the CHNS tests, confirmed the latter SEM/EDS analysis.) This example illustrates the need for use of multiple techniques, and the data should be reviewed to confirm the results are consistent.⁸

The Movement of Particles and Modeling

Another consideration in determining whether the presence of black powder could potentially pose an operational challenge relates to the potential transportation of those particulates through a pipeline system. Just like flow modeling can be used to assess flow regimes in liquid systems, the transportation of fine dry particulates has also been studied. Figure 7 illustrates results from one mathematical modeling study of particulate size versus the required velocities required for transportation through five common pipe sizes.^{9, 10} The obvious question is how the size of the particulates within any particular pipeline is determined. Figure 8 illustrates one approach for collecting samples from the middle of an operating pipeline and capturing those particulates on filter paper.

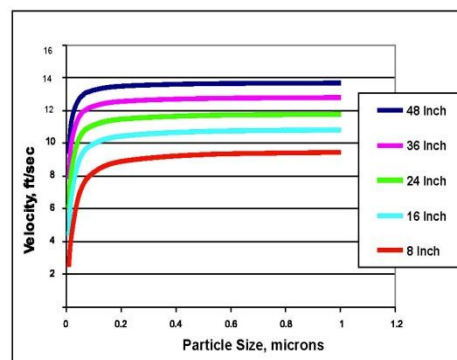


Figure 7 Velocities required to transport particles.^{9, 10}

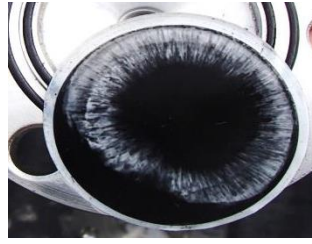


Figure 8 Collect samples to measure particle size.

This would be a rather quick test – Only a single layer of particles would be needed for determining size.

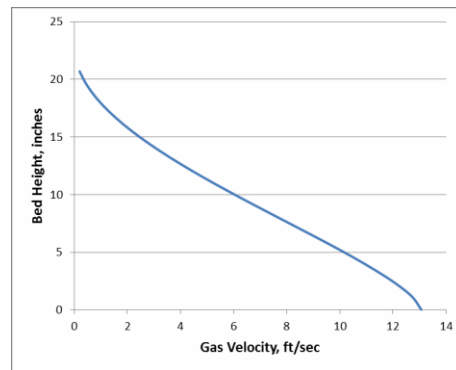
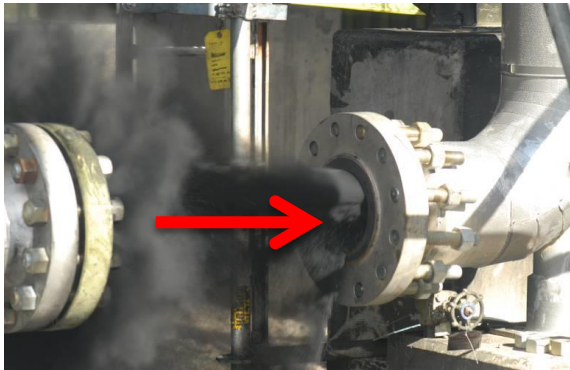


Figure 9 Powder being blown out of a pipeline⁸, bed height, and velocities to displace that powder.^{9,10}

The modeling of particulates can also be used to determine how high a bed of particulates can grow (develop), depending on gas velocities.^{9,10} The photo on the left of Figure 9 illustrates a blowdown of dry black particulates from one particular pipeline within a processing facility. Note the arrow at the midpoint in the pipe's internal diameter. Essentially all flow of particulates is above that point, which represents the bed height. Thus, the entire flow is directed through a reduced cross-sectional area, increasing the localized velocities, and transporting the particles.

Chemicals, such as diethylene Glycol (DEG), Triethylene Glycol (TEG), commonly used in gas dehydration, are found in black powder. Field studies suggest oily black powder requires 2 -2 ½ times the velocities required to transport dry black powder.⁹

How to Remove Black Powder

There are two approaches to removing accumulations of black powder from pipelines or process equipment. The first is maintenance pigging of pipelines, and the second approach is through chemical treatments. Chemical treatments often accompany maintenance pigging runs, as will be described in the case study below.

Maintenance Pigging

There are numerous different styles of maintenance pigs. Foam pigs, such as those depicted in Figure 10 illustrate foam pigs, which are designed to remove liquids or slurries from pipelines. The pig on the right was used to dehydrate a pipeline.



Figure 10 Maintenance pigs used to displace liquids (left) or scrape/clean multi-diameter pipelines (right).

Adjust the frequency of maintenance pig runs to control the volumes of solids or liquids removed from individual pipelines. The goal is to keep those volumes “manageable.” Also, a regular maintenance pigging program will help reduce the roughness of the interior surface of the pipe caused by depositions, which will enhance flow efficiency and reduce expenses, such as the fuel for compressors.

Chemical Treatments

Chemicals are commonly employed to treat or clean pipelines. They may be in the form of corrosion inhibitors, biocides, or other products, such as chelants, which are used to chemically clean pipelines. One of the first products considered for chemically cleaning pipelines and removing black powder is a chemical known as Tetrakis (Hydroxymethyl) Phosphonium Sulfate, commonly called THPS. This chemical has a unique ability to control microbiological populations, and has been applied in systems throughout the world. The applications are typically at 200-500 ppm (active) for low flow portions of a system, such as tanks or vessels, or 1000 ppm (active) for quick eradication of microbiological populations within pipelines. However, THPS also serves as a chemical chelant for removing black powders, i.e., iron sulfide and iron oxide corrosion products, from pipelines when applied at the 200,000 ppm concentrations typical for chemical cleaning operations. The structure is illustrated in Figure 11.¹¹

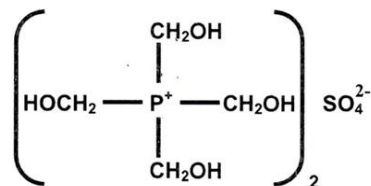


Figure 11 Chemical structure of Tetrakis (Hydroxymethyl) Phosphonium Sulfate (THPS).¹¹

A new NACE publication provides several case studies related to the use of chemical products to remove black powder depositions.¹² These include the application of THPS, a chemical widely used in crude oil and natural gas gathering systems. An example below provides a synopsis of such an application of THPS on an offshore pipeline, which had limited treatment options. The net effect was that the THPS functioned not only as an effective biocide, but also functioned as a chelant.

An offshore trunkline and lateral was breached with the passage of Hurricane Ike. Once the pipeline was repaired, it was pigged to remove the seawater. Significant concentrations of H₂S were measured during the dewatering operations, evidencing the activity of sulfate reducing bacteria within the seawater. Thus, one of the top priorities was to apply a strong biocide treatment, such that threats of any microbiologically influenced corrosion could be quickly minimized. The target was a treatment rate of 1000 ppm active THPS, at the terminus (end) of the gathering system, as it enters the processing facility. Thus, the application of THPS at the upstream end of the trunkline had to

be based in part on (a) the estimated volume of seawater still remaining within the pipeline, coupled with (b) the volume of produced water from other the offshore platforms that also fed this gathering system.^{13, 14}

The net result was that THPS had to be applied at essentially concentrate form, or approximately 200,000 ppm to achieve the target 1000 ppm treatment rate (after dilution), as the wet gas and liquids arrived at the onshore processing facility. That enabled the THPS to also function as a chelant.¹²

Shortly thereafter, a new connection was made to the subsea trunkline, and the “hot tap” coupon, i.e., a metal sample of the trunkline, was obtained and metallurgically analyzed. Although the presence of iron sulfide was anticipated, none was found, despite the initial observation of H₂S during the dewatering operation.¹⁴ The reanalysis of the data evidences the effectiveness of THPS in not only eradicating the microbiological population of SRBs, but also in chemically cleaning any sulfides from the subsea piping, as evidenced from the metallurgical examination of the sample from the pipe, after the breach, dewatering, and chemical treatments.¹²

Synopsis

The book “Field Guide for Managing Iron Sulfide within Pipelines or Process Equipment” provides extensive resources to assist the reader in managing the integrity of their systems, as well as guidance for managing the detection and removal of black powder and, in particular iron sulfide from within their pipelines or processing facilities.

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About the Authors

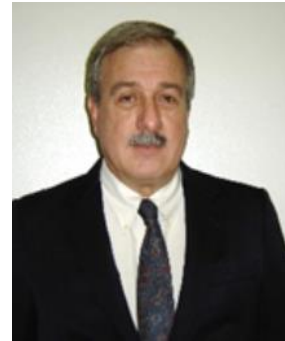
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Daniel Powell is a professional engineer and NACE Fellow. Before retiring, Daniel focused his 40-year career in managing internal corrosion. He started by testing corrosion inhibitor packages for chemical cleaning of nuclear power steam generators, and later transitioned to providing internal corrosion control for the crude oil and natural gas production at ARCO Alaska. Later, he joined Williams Companies, Inc., focusing on corrosion control and providing integrity management for their production, processing, and transmission pipelines. Dan has authored over 30 publications, and is presently serving as an instructor for the NACE Internal Corrosion course.



Robert H. Winters, Sr. Pipeline Consultant

Robert H. Winters is a microbiologist and chemist, who has worked for El Paso Corporation, Tenneco, Inc., Tennessee Gas Pipeline Company, as well as Williams Companies, Inc. He also provided technical service consultancy for the crude oil and natural gas industry through Champion Technologies and is now providing those services through Clariant Corporation. The combination of operations experience, coupled with technical service consultancy, provides a diverse background for driving practical solutions to the challenges the industry faces. He has been a member of NACE for 40 years, has authored over 14 publications, and serves on numerous NACE committees for internal corrosion control.



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Mark Mercer is a Petroleum Engineering Technologist and Power Engineer with over 40-years in the oil and gas industry. He has had significant workings in complex gathering, processing, and transmission operations throughout the countries of Canada and the United States. He has been a member of NACE since 1981, working in cathodic protection, coating, and chemical treating with various service companies. He is a NACE certified Senior Internal Corrosion Tech, and is a Staff Technical Specialist, internal corrosion SME with Williams Companies, Inc.





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