WINNING THE WAR AGAINST BLACK POWDER

Preventative measures and improved technology can minimize costly damage from iron sulfide, iron oxide contamination

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Abstract
Black Powder is formed due to a chemical reaction of H\textsubscript{2}S, water, and iron. Black Powder is a pernicious challenge to all pipeline operators. This paper analyzes the problem plus proven methods to minimize its production as well as improved technology for its removal and remediation.

Black Powder
The formation of black powder -- a chemical reaction of H\textsubscript{2}S, water and iron -- is a problem for compressors that can escalate if preventative and removal actions are not taken.

Black powder is a common challenge that spans all phases of the natural gas industry from the wellhead to the burner tip. Its removal is necessary to improve or maintain operational efficiency and safety. This paper assimilates information from several sources and provides experiences from operator’s perspective on the difficulties that foreign materials in the gas stream pose for production, gathering, processing and pipeline transportation. Typical contaminants in the gas stream are water, glycol, amine, methanol, compressor lubricating oils, salts, chlorides, liquid hydrocarbons, sand, dirt, production stimulators and black powder.

Of those, black powder is the most troublesome. Black powder contamination manifests itself through reduced pipeline efficiency, clogged instrumentation, fouled measurement equipment, valves that cannot operate due to an accumulation of debris. It can clog compressor valves, compressor cylinders, compressor pistons, and filter/separators.

Additionally, black powder can affect pipeline integrity programs that rely on magnetic flux leakage inspection and geometry tools due to debris-induced lift-off of sensors. Sometimes the contamination is dry and powdery. At other times it is wet or has a tar-like appearance. Black powder is not just a corrosion issue; it is produced in the gas stream from chemical reactions or from microbial activity.
Black power can be an expensive problem. One pipeline has stated that it spends US $5.2 million a year in direct costs associated with black powder removal. A single compressor station that has had a filter/separator compromised due to filter collapse can have remediation costs of more than US $400,000.

Other expenses would include filter element replacement, solid waste volume disposal of filter elements, increased horsepower to pump the same throughput, compressor valve replacements and substitution or repair of fouled instrumentation.

**Chemistry**

As stated earlier, black powder is formed through the chemical reaction of H₂S, water and iron in pipe. The major components of these reactions are iron sulfide (Fe + S) and iron oxide (Fe + O). The resulting compounds are black in appearance, therefore the term black powder.

\[ \text{H}_2\text{S} + \text{Fe} \rightarrow \text{FeS} + \text{H}_2 \]

Iron sulfide

\[ 2\text{H} + \text{Fe} \rightarrow \text{Fe}^{2+} + \text{H}_2 \]

Iron oxide

Iron sulfide and iron oxide particles, whether wet or dry, are extremely small. Laboratory analysis of both wet and dry samples indicates a range 0.2 < particle diameter < 4 µ, with more than 81.6% of the particle sample being less than 1 µ with the greatest concentration of that particle range being 0.2 < particle diameter < 0.4 µ. Subsequently, dry black powder has a smoke-like appearance.

Wet black powder may exhibit as clumps, but when it is subjected to high velocity or impinges upon hard surfaces, it may shear into smaller sub-micron particles. When black powder is in suspension as a liquid, it presents the same characteristics as when dry. Typical density for iron sulfide and iron oxide are 151 lb./ft.³ and 355 lb./ft.³ respectively.

The common chemical forms of iron sulfide include pyrrhotite, troilite, mackinawite, pyrite and marcasite, ferric sulfide, smythite and greigite. Of these forms of iron sulfide, pyrrhotite exhibits pyrophoric tendencies.

Pyrophoric iron sulfide oxidizes exothermally when exposed to air. It is formed in the gas stream where H₂S exceeds the concentration of oxygen. As previously stated, due to the sub-micron particle size of iron sulfide, it has an enormous surface area-to-volume ratio.

Subsequently, when exposed to air, it is oxidized back to iron oxide and either free sulfur or SO₂ gas is formed. This reaction between iron sulfide and oxygen is accompanied by the generation of 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 flammable hydrocarbon-air mixtures.
Iron sulfide in the chemical forms of mackinawite, smithite and greigite are typical indicators of microbial activity in the gas pipeline. Additionally the confirmation of sulfate-reducing bacteria (SRB) and acid producing bacteria (APB) in the pipeline is a positive indication that microbial corrosion exists.

The SRB microbes Clostridium and Desulfovibrio deulfuricans consume sulfates and produce H$_2$S. While APB microbes do not produce H$_2$S, they supply nutrients and provide hospitable environments for SRB to grow.

**Reducing Black Powder**

Regardless of the origin of H$_2$S in the gas stream, a concentration of 1 ppm and a throughput of 500 MMscfd (14 x $10^6$ m$^3$/d) potentially could produce as much as 3600 lb. (1630 kg) of black powder in a month.

Operators who can minimize the introduction of water and reduce the H$_2$S content in their gas stream will see a resulting reduction in black powder formation.

Microbiologically influenced corrosion cannot exist without water, so water should be removed wherever it is known to accumulate.

The best barrier to black powder production is tariff enforcement. Unfortunately, even when some constituents in the gas stream (such as CO$_2$, H$_2$S, oxygen, water, and sulfur compounds) meet the existing tariff requirements of a few percent to a few parts per million, they still can allow significant corrosion.

The greatest impediment to black powder formation is a conservative tariff that limits H$_2$S to 1 ppm, total sulfur content of 5 grains per 100 scf, 5 lb. of water per MMscf, 1.4% by volume of CO$_2$ and 10 PPM of oxygen.

**Removal methods**

Under current technology, black powder can be removed from gas pipelines through chemical or physical means.

In the chemical process, water or an oil-soluble chemical agent is injected into the gas stream. The chemical agent should be compatible with the solids to be removed and is based on pipeline operating parameters. The important operating parameters include the type of compressor, dew point, and waste disposal plans.

In addition to operating parameters, the nature of the deposit is critical. Hydrocarbon deposits comprised of
waxes and paraffin are easier to remove with an oil-soluble chemical while salts are easier to clean with an aqueous cleaning solution. It is important to remember that when using a water soluble chemical agent, the pipeline must be thoroughly dried after debris is removed.

Another important aspect of injecting a chemical agent into the gas stream is solvent compatibility. Solvents include water and methanol for water-soluble cleaners or diesel and hydrocarbon condensate for oil-soluble cleaners.

An effective cleaning agent must form either a stable dispersion or a complete solution. A solution is clear or translucent in appearance with no distinct phases. A stable dispersion for pipeline injection applications must remain in a homogenous single phase for a minimum of 72 hours to be effective. Should the cleaning solvent separate from the cleaning agent, its performance will be significantly reduced.

Physical removal of black powder is accomplished through pigging and filtration/separation. In the pigging process, a tool is inserted and pushed through the pipeline using compression. There are two methods of pigging: dry and chemical. The cleaning action of the pig is a function of brushes or cups that scrape the pipe wall. The scraping action loosens black powder on the metal and pushes loose debris ahead of it.

Four aspects of chemical pigging are important for optimal cleaning results: solids penetration, solids suspension, mixture flowability and mixture separability.

Solids penetration is the ability of the chemicals to break the surface contact of debris and loosen it from the pipe sidewall. After the debris is loosened, it must be carried down the pipe in suspension in large quantities.

The carrying capacity of the chemical agent and solvent is much greater than the original density. Therefore, the mixture flowability is extremely important; it must not increase greatly in viscosity or surface tension.

The final aspect, mixture separability, is the tendency of the debris to separate into distinct phases in order to facilitate disposal. Should an emulsion present, the entire quantity of material will require disposal. Optimally, three phases will present — oil, aqueous, and solids. This will enable the capture of the cleaning agent for a subsequent chemical pigging project and the removal of solid debris for reduced volume of hazardous waste material.

Physical removal of black powder also involves a filtration or separation function that typically is installed upstream of a compressor station or gas processing facility.

**Traditional Filter Systems**

In traditional filtration systems, multiple filters in parallel are typically placed in the gas stream to capture and retain solid particles. They must be suitable for sub-micron particle retention and they must be able to coalesce and pass liquids for capture by the mist extraction section of the filter/separator.

Most filter element designs are unable to perform both processes. A primary problem with a filter element that is designed to remove sub-micron particles is that it can become plugged rapidly and require frequent changing. This progressive pressure drop also compromises throughput, decreasing pipeline revenues.
If operating conditions do not allow by-passing or shut downs, the filter element pressure differential may become so great that the elements collapse, compromising the filter/separator completely. Hazardous waste handling and disposal issues are an additional concern with contaminated filters, especially where high levels of pyrophoric iron sulfides are present raising the likelihood of spontaneous combustion during the removal and transport processes.

**Filterless Separation Technology**

In the past two decades, filterless separators have emerged as a leading method for contaminant removal and have proven effective in eliminating black powder solids and liquids in hundreds applications throughout the natural gas transmission stream. Utilizing technology patented by Mueller Environmental Designs, filterless helical coil separators combine inertial and impingement processes. In concept, the Mueller KLS Helical Coil is similar to a straight-through swirl tube separator. It is important to make this distinction because most inertial type separators are considered to be cyclones. Cyclones consist of separators with tangential inlets and/or cylinder-on-cone designs, whereas swirl tubes are cylindrical in shape with an axial inlet.

Swirl tube separators typically have vanes or blades which force the gas stream to rotate causing a region of swirl between the vanes and the gas outlet tube. Swirling flow plays a central role in process intensification and is the basis for the operation of foam breaking or ‘defoaming’ separators. Other advantages of swirl tubes are that they operate at lower pressure drops, higher capacities, are less prone to clogging, very forgiving for changes in operating conditions and offer a more stable flow compared to cyclones. Unlike a traditional swirl tube, which uses vanes to force the gas stream to turn and create swirl, the Helical Coil Separator uses helical gas passages. The helical gas passages aerodynamically prevent flow separation within the helical gas passage. The passage cross-section, turning angle, and axial pitch generate swirl without loss of aerodynamic efficiency.

In addition to being an inertial type separator the KLS Helical Coil is also an impingement type. As liquids enter the helical gas passages, the liquid aerosols impinge and coalesce on the walls of the passages. The aerodynamically efficient flow through the channels allows the impinged liquids to stay on the walls of the channels forming a film that helps to improve the separation efficiency. The axial and radial positions of the helical gas passage outlets preserve aerodynamic efficiency while enhancing aerosol separation. Upon entering the helical gas passage, contaminant aerosols are forced to turn about the axis. The high velocities and forced turning of the gas impart inertial and centrifugal forces on the aerosols. These forces cause the aerosols to impinge and coalesce on the outer wall of the helical gas passage forming a film boundary. The film boundary acts like a secondary separation mechanism, aiding in the collection of sub-micron particles in the gas stream.
Significant regions of swirl velocity are found within the KLS Helical Coil Separator. These areas include the helical gas passage outlet, the area between the helical element and the clean gas tube inlet, and the annulus region between the helical housing tube and the clean gas tube.

As the gas flow exits the helical gas passage, it develops a high degree of swirl throughout the entire region between the helical gas passage outlet and the clean gas tube, producing centripetal acceleration in excess of 10,000 G. The aerosols are pushed radially outward by the centrifugal forces caused by the swirling flow. The aerosols eventually arrive at the surface of the helical housing tube where the axial component of the torroidal vortex separates them from the gas and pushes them into the contaminant collection chamber.

Research shows that unlike cyclonic technology, turndown is not an issue with the KLS Helical Coil Separator. CFD analysis reveals that the velocity patterns throughout the Helical Coil are unchanged due to the flow rate. This means that the inertial fields and the separation mechanism exist independently of the gas flow rate.

**Sampling is Essential**

Testing of black powder in pipelines and compressors is essential to determine the chemical pigging and/or cleaning process that will be required.

Analysis of the chemical constituents and particulate sizes of pipeline debris is needed for the selection of new filtration/separation equipment.

When samples are taken for testing, they must be sealed immediately. As soon as the debris sample is exposed to atmosphere, it begins oxidizing and potentially forming Magnetite (Fe₃O₄). If that occurs, when the pipeline debris is sampled and analyzed, it is often presumed that sulfides do not exist and only pipeline corrosion by-products are present.

Type of analysis performed on the debris should include full particle identification, bulk density, and particle size and distribution. Minimum capabilities of the laboratory should include:

- Polarized light microscopy
- Epi-reflected light microscopy
- Scanning electron microscopy
- Energy-dispersive X-ray spectrometry
- X-ray diffraction
- Attenuated total reflection-Fourier infrared spectroscopy
- IMIX image processing software
- ASTM D 854-98 standard test methods for specific gravity of soils

![Dry Black Powder](image1)

![Wet Black Powder](image2)
Conclusion
With an aggressive two-pronged approach pipeline and compressor operators can effectively battle black powder.

They should minimize the content of water and H₂S in the pipeline, preferably through effective tariffs that restrict the foreign constituents of the gas of the gas stream.

Operators should also proactively remove black powder by integrating modern separation technology in their systems and when necessary use chemical processes and pigging methods to remove black powder buildup from their pipelines.

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