# Black Powder Problem Will Yield To Understanding, Planning

## Part 1: Research finds it comes from producing wells, storage fields and corrosion in the pipe

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Black powder is the least under stood component of ingestion problems confronting natunal gas compressors and pipe lines, but it will yield to several control actions, based on the findings of a preliminary research study.

As used here, "black powder" means various iron sulfide forms, mixed with contaminants, that are found in some pipe lines. Based on information gathered from technical literature, researchers in other industries, experts, gas industry engineers and other sources, it needs to be understood better by pipe line managers.

The good news is, once management resolves to conquer the problem, knowledge in other industries is available, along with various methods and equipment, to start helping reduce black powder's impact on operations, maintenance and pipe line economics. Diligent managers should consider the following:

• Review contract and tariff agreements concerning acceptable amounts of water, carbon dioxide, hydrogen sulfide and all other sulfur components, and oxygen. Acceptable quantities should be set as low as can be measured, tolerated, and enforced in light of recent research and technology. Content enforcement should be aggressive.

• Train employees and contractors regarding microbiologically influenced corrosion's (MIC) impact on the pipe line system. Field and supervisory personnel should be taught monitoring and sampling procedures, as well as handling and treatment.

• Avoid water in the pipe line. Remove it, purify it, or drain it at every opportunity when it is encountered in plant and pipe systems. This procedure should be followed when water is injected into wells and used in hydro testing and cleaning operations. Whenever water is introduced, the affected area should be cleaned of moisture and microbes. Without water, MIC cannot exist.

• Review operating and construction practices to avoid, eliminate or chemically treat areas that will trap and hold water and microbes. This includes dead legs, low flow areas and storage. Low points should have drains.

• Review and sharpen practices relating to selecting and applying biocides and using pigs and filters.

• Evaluate the economic impacts of corrosion and black powder and factor them into technical and operational decisions. Costs of new powder-control equipment, testing and procedures should be balanced against the avoided costs of current black-powder maintenance activities. Improvements should be evaluated in terms of net expected value, in other words, benefit versus cost.

• Seek creative methods of testing, filtering, measuring and chemically treating to deal with black-powder problems. There are no accepted tried-and-true methods. Everything should be carefully scrutinized.

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**What is it?** Black powder is a catch-all term that describes material that collects in gas pipe lines and creates wear and reduced compressor efficiency, clogged instrumentation and valves, and flow losses in long pipe lines. The material can be wet, with a tar-like appearance, or dry and be a fine powder, sometimes like smoke. Chemical analyses reveal it is any of several forms of iron sulfide and iron oxide. Further, it can be mechanically mixed or chemically combined with any number of contaminants, such as water, liquid hydrocarbons, salts, chlorides, sand or dirt.

Some pipe lines have black-powder problems and others do not. It appears those lines closer to the gas gathering end of the system have problems, while those at the distribution end, with relatively small systems, do not. Black powder is claimed in both "dry" and "wet" lines. One parallel line can have a problem while the other does not. No pipe line has been identified to date that has been able to eliminate the problem once it starts.

Few companies seem to have quantified what their black-powder problem is costing. From this viewpoint, any spending to alleviate or solve the problem is seen as an additional maintenance or capital expense and not weighed against the probable reduced maintenance and operating cost gained by the solution. Examples where economic analyses should be applied include:

• Cost and effort of MIC testing versus the pipe pitting that results from such corrosion, and the costs of cleaning up powder in pipe line and compressors

• Compressor repair and cleanup costs due to iron sulfide fouling and the resulting performance loss as compared to the cost of a better filter

• Costs of testing and enforcing stricter gas-tariff limitations on hydrogen sulfide, sulfur and water in gas brought into the pipe line, compared to the cost of pipe corrosion and black powder removal and disposal, as well as increased equipment maintenance costs

• Economics of paying more for verifiably "clean" gas and paying less for powder cleanup and pipe line maintenance

• The savings gained from reduced pigging compared with the eventual cost of significant black powder cleanup and corrosion repair. Black powder is primarily iron and sulfur in molecular combination, but there are a number of chemical forms. Although some are well understood, others have characteristics that are not fully understood.

The fact that there are several molecular and crystalline structures of iron and sulfur is attributable to the chemical properties of sulfur. It can exist as neutral S , as an anion ($S^{-2}$) and as a cation ($S^{+6}$). Numerous possibilities exist for hybridization with unpaired electrons in the d orbitals. The end result is a large number of structures and ratios of metals to sulfur. Furthermore, sulfur can exhibit covalent or metallic bonding, or both. Sulfides are brittle, which can result in shearing of the particles to sub-micron size.

**Iron Sulfide Sources.** Black powder, at least the iron sulfides and oxides, is known to be created inside natural gas wells and pipe lines. The components and conditions necessary to create the material(s) can be found at some point in many pipe lines. Some form of iron sulfide is known to be created by either of two mechanisms:

• Chemical reaction of constituents present in the pipe line, usually hydrogen sulfide

• Microbial assimilation of chemical constituents in the gas and the production of both iron sulfides and pipe wall pitting.

Iron oxides are created from subsequent oxidation of the sulfides or by direct oxidation of the iron in pipe lines.

Iron sulfide and, apparently, many of its variations can be quickly and efficiently created in a gas pipe line from the chemicals naturally available. Hydrogen sulfide ($H_2S$) easily reacts with the iron in pipe to form iron sulfide as in the formula:

$$H_2S + Fe \Rightarrow FeS + H_2 \qquad (1)$$

The presence of a small percentage of water (approximately 3 to 9%) aids this reaction. Under more oxidizing conditions, pyrite ($FeS_2$) may form in accordance with the formula

$$2H_2S + Fe \Rightarrow FeS_2 + 2H_2 \qquad (2)$$

In addition to hydrogen sulfide, sulfur also can react to form iron sulfides. Sulfur compounds are relatively abundant in gas and oil wells.

Water in the pipe line also can break loose parts of the iron sulfide coating on the pipe wall and cause it to move down the pipe and accumulate at a lower or more stagnant flow area. Iron sulfide, either attached to the pipe wall, or collected in the pipe bottom, has the negative effects of increasing roughness, decreasing flow area and increasing pressure drop. Furthermore, over time, its formation thins the pipe wall and reduces the margin of safety against compromise of the pressure boundary.

**Microbial-Influenced Corrosion.** MIC, or pitting of the pipe wall, is a serious form of corrosion that can occur in pipe lines and produces black powder or iron sulfide. It can occur either on the pipe's inside or outside. The focus here is on internal MIC.

The extent of MIC and the costs associated with it have only recently been recognized. This has been due principally to the lack of concern by many field personnel, as well as the lack of methods for conducting investigations to identify possible cases without shutting down and opening the pipe. Microbes that cause pipe corrosion are basically two families:

Sulfate-reducing bacteria (SRB)

Acid-producing bacteria (APB).

It has been shown that SRB microbes, such as *Clostridium* and *Desulfovibrio desulfuricans*, consume sulfates and produce hydrogen sulfide. These anaerobic bacteria use the reduction of sulfate as a source of energy and oxygen, in accordance with reactions such as:

$$2H^+ + S0_4^{-2} + CH_4 \Rightarrow$$
$$H_2S + CO_2 + 2H_20 \qquad (3)$$

Methane is used here as an illustration only. The bacteria can consume more complicated organic compounds. These bacteria sometimes have been associated with the formation of pyrite in geological formations. Hydrogen sulfide can react to form a number of metal sulfides, suggesting that there may not be any unique iron sulfide that forms as a result of bacterial activity. Recent GRI research, however, has pointed to the iron-sulfide forms mackinawite, smythite and greigite as indicator products of MIC activity.

The presence of H2S in a gas does not mean there are microbes in the pipe line. The source may be the pro ducing wells, and probably is, particularly for gathering lines.

In the case of transmission and distribution lines in which the gas has been treated to remove $H_2S$, its presence in amounts greater than the maximum allowable is a likely indication of microbes, although it could also mean the failure of an upstream treatment plant.

Similarly, the presence of FeS, or $FeS_2$, is not necessarily indicative of MIC. Low-molecular-weight mercaptans may also form iron sulfides, and some natural gases, for example in West Texas and New Mexico fields, have high mercaptans content. These usually are not removed because they serve as a natural odorant for distribution. Although SRB directly produce $H_2S$ instead of FeS, the conversion of the first to the second is direct and prompt at the site of the microbial activity where iron is present.

In a dry or otherwise inhospitable environment, SRB can become largely dormant. When injection water that is used for secondary recovery, or other water, enters the pipe or well formation, massive activation of these and other microbes can occur, plugging the pores of the producing formation, pipe mechanisms and instrumentation with both organisms and metal sulfide precipitates.

APB consume organic nutrients and produce short-chain, volatile fatty acids (VFA) such as acetic, formic, lactic, propioic, butyric and valeric acids. Carbon dioxide and hydrogen are produced by organic fermentation. SRB consume VFA as a carbon source and produce acetic acid and carbon dioxide, in addition to hydrogen sulfide; therefore, the two microbial communities support each other and frequently co-exist at favorable sites. Although APB do not produce the black powder components, they are a good indicator of the likelihood of SRB which do produce iron sulfide. APB may form oxides, depending upon the pH of the liquids present.

**Editor's note:** This is the end of Part 1. In Part 2, the author describes black-powder preventive measures-such as filtering, pigging and washing-and steps that operators can use to drive an aggressive iron-sulfide monitoring and prevention program.

**ACKNOWLEDGMENT**

Based on Report No. TA 97-4, "Technical Assessment: Black Powder in the Gas Industry - Sources, Characteristics and Treatment," prepared by the author for the Gas Machinery Research Council (GMRC).

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