

TECHNICAL ASSESSMENT

“BLACK POWDER” IN THE GAS INDUSTRY - SOURCES, CHARACTERISTICS AND TREATMENT

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EXECUTIVE SUMMARY

The original objective of this research was to investigate means of controlling materials ingested into compressors in pipeline, refinery, gathering, and storage services. After an initial industry survey, it was determined that “Black Powder” (various forms of iron sulfide mixed with contaminants) is the least understood and most prominent contamination problem in pipelines and their compression equipment.

The information documented in this report was gathered from technical literature, the Internet, researchers, experts, practitioners in the natural gas industry, field experience, and equipment manufacturers’ publications. This search has determined that there is much expert knowledge in the technical community concerning many aspects of the iron sulfide problem, however, there is only a limited understanding by those in the gas industry that face the problem.

This report discusses information gathered as a part of the research, including a section with references to retrievable literature used.

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1. INTRODUCTION

“Black Powder” is a catch-all term that describes a material that collects in gas piping and creates wear and reduced efficiency in compressors, clogs instrumentation and valves and leads to flow losses in long pipelines. The material may be wet and have a tar-like appearance, or dry and be a very fine powder, sometimes like smoke. Chemical analyses of the material have revealed that it is any of several forms of iron sulfide or iron oxide. Further, it may be mechanically mixed or chemically combined with any number of contaminants such as water, liquid hydrocarbons, salts, chlorides, sand, or dirt.

The original objective of this research was to find a way to control or eliminate materials ingested into compressors in pipeline, refinery, gathering, and storage services. An initial industry survey indicated that the main problem component that was the least understood in the field was iron sulfide. The search was then narrowed to finding an understanding and solution for the iron sulfide problem. It was found that iron sulfide has both a chemical and a microbial source in pipelines. Microbiologically influenced corrosion (MIC) is a form of corrosion that is initiated by microbes that find a habitable environment in natural gas piping. Iron sulfide is not easily filtered out of the flow stream, and it is pyrophoric (can catch fire) under some conditions.

The research has looked into measurement or detection of the material in the pipe flow, filtering it, testing for and limiting the chemicals or conditions that allow it to form, cleaning it out of piping, and safe handling and disposal of the material.

This investigation has also revealed that black powder (iron sulfide) is a known problem in mining and water systems. The same substances are of interest in the investigation of meteorites from space and Martian soil. Some forms of iron sulfide are of interest to geologists and gemologists. Such sources have contributed to the information discussed herein.

The information documented in this report was gathered from technical literature, the Internet, researchers, experts, practitioners in the natural gas industry, field experience, and equipment manufacturers’ information. It is only a representative sample of the information available or that might be identified by testing. This search has determined that there is much expert knowledge in the technical community concerning many aspects of the iron sulfide problem, but it is more concentrated in research, service, and product manufacturing companies than in those faced directly with the problem in the gas industry. In large part, the value of this research is in collecting, collating, and summarizing this information and making it available in concentrated but digestible form for the engineers and other practitioners working in the gas industry. This report aims to provide that summary. Although attempts have been made to gather information from reliable sources and interpret it correctly, this information should only be used as a starting point; refer to the references for more detailed facts.

To date the research has not identified clear solutions or universal fixes to eliminate the iron sulfide problem, but a number of approaches are indicated that should aid in controlling the problem. A few useful solutions are known but not implemented in some companies due to perceived economic limitations or general lack of information.

In the overall picture, some pipelines have black powder problems and others do not. It appears that those lines that do not have the black powder problem belong to smaller companies who do not cover a large area and whose operations are closer to the distribution end than to the gathering end of the pipeline. Black powder is claimed to have occurred in both “dry” and “wet” lines. Even in parallel lines, one can have the problem and the other not. We have not identified any pipeline to date which has been able to eliminate the black powder problem once started.

In discussions with people working in the natural gas industry, it has been observed that sound economic judgment is not always mixed with sound engineering analyses. In many cases, black powder problems are considered a way of life that has no solution and therefore is accepted as one of the problems and expenses of doing business. Very few companies seem to have quantified how much black powder problems are costing them. From this viewpoint, any expenditure that might alleviate or solve the problem is considered additional maintenance or capital expense, and not weighed against the probable reduced cost of maintenance and operation gained by ameliorating the problem. Example situations where economic analyses should be applied include (1) the cost and effort of MIC testing vs. the pipe pitting that results from MIC corrosion and the costs of cleanup of the resulting black powder in the pipeline or compressors; (2) the costs of compressor repairs and cleanout due to fouling from iron sulfide and the resultant loss in performance compared against the cost of a better filter; (3), the costs of testing and enforcing gas tariff limitations on hydrogen sulfide, sulfur, and water content in gas bought/sold compared against the cost of pipe corrosion and black powder removal and disposal and equipment maintenance costs; (4) the economics of paying more for verifiably “cleaner” gas and less for cleanup and maintenance; (5) the false savings associated with reducing routine pigging to remove black powder build-up.

The following sections discuss information gathered as a part of this research, followed by references to retrievable literature used. In a few cases, specific companies are mentioned with technologies or capabilities appropriate to dealing with the black powder problem. This mention is not intended as an endorsement of the company or product nor is it to say that their technology is exclusive. This is documentation of the route the investigation took in gaining information and recognizes their contributions to this body of knowledge.

2. CHARACTERISTICS OF THE MATERIAL

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^0 , 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. General descriptions follow.

2.1 PYRRHOTITE

Pyrrhotite ($Fe_{1-x}S$, where $0 < x < 0.2$) is a very common sulfide. The uncommon formula for pyrrhotite seems to violate the definition of a mineral, that is, a crystal structure with a definite chemical composition. Pyrrhotite is strange, in that it is “non-stoichiometric”. The non-stoichiometry results from cation vacancies which should be occupied but are not. This does not mean that individual crystals have net electrical charges, but rather that pyrrhotite as a mineral can consist of different structural units, such as FeS , Fe_7S_8 , Fe_9S_{10} , and $Fe_{11}S_{12}$.^[2-1]

The structure of pyrrhotite has two symmetries; when it is low in sulfur and the formula is closer to FeS the structure is hexagonal. But when it is high in sulfur, the structure is called monoclinic. Since both phases are present in the same crystal, it is treated as one mineral.

Pyrrhotite is weakly ferrimagnetic, meaning it has its own magnetic field. (Ferromagnetism refers to materials that are attracted by a magnet and can be magnetized, i.e., iron.) It is the most common ferrimagnetic mineral next to magnetite (Fe_3O_4).^[2-2] Magnetism is sometimes the only way to distinguish pyrrhotite from other sulfides.

Pyrrhotite fractures easily and unevenly. It thus subdivides under shearing action to very fine particles. It is described sometimes as being like smoke. Almost any material that can be subdivided so that it has a high surface area to mass ratio is easily combustible. It is reported that pyrrhotite (sometimes referred to as iron sulfide) in the dry state can auto ignite. Auto ignition is unlike auto combustion, which is a much more energetic and rapid reaction. Pyrrhotite most commonly smolders or flames. This research did not identify cases of explosions related to pipeline incidences, but such occasions are found in the mining industry. Even the name pyrrhotite is derived from the Greek root word *pyr* meaning fire.

2.2 TROILITE

The FeS form is called troilite and is also found as nodules in meteorites.^[2-3] It is antiferromagnetic, which means that its magnetic properties depend upon the atomic ordering and whether the specimen is single or polycrystalline.

2.3 MACKINAWITE

There is also a variation of FeS called mackinawite which is Fe_{1+x}S (x is approx. 0.05). This phase is said to be formed by H_2S corrosion of steel.

2.4 PYRITE AND MARCASITE

Another very common sulfide is pyrite (FeS_2). This form is not as commonly found in piping, but is the most widely occurring sulfide found in nature -- the classic "Fool's Gold". Pyrite is a polymorph of marcasite, which means it has the same chemistry, FeS_2 , but a different structure and therefore different symmetry and crystal shapes. They are both diamagnetic, i.e., they are not responsive to a magnetic field. Pyrite and marcasite are difficult to distinguish from each other. Marcasite will more often have a distinctive sulfur smell. Marcasite is less stable and will gradually disintegrate at elevated temperature or over long periods of time (decades).

2.5 FERRIC SULFIDE

There is a ferric sulfide molecule of the form Fe_2S_3 for which no common name or information was found. It is extremely unstable and readily oxidized to hydrated ferric oxide and elemental sulfur. It decomposes at high temperatures to a mixture of FeS and FeS_2 .

2.6 SMYTHITE AND GREIGITE

The sulfide Fe_3S_4 has two forms and names, smythite and greigite and is strongly magnetic.^[2-4]

2.7 HIGHER MULTIPLES OF IRON AND SULFUR

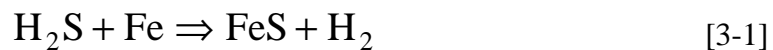
Higher multiples of iron and sulfur exist, such as Fe_7S_8 , Fe_9S_{10} , and $\text{Fe}_{11}\text{S}_{12}$, but they may actually be forms of pyrrhotite (Fe_{1-x}S) or perhaps mackinawite (Fe_{1+x}S).

3. SOURCES OF IRON SULFIDE IN PIPING

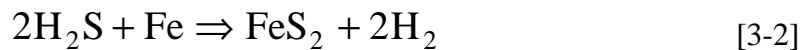
Black powder, at least the iron sulfides and oxides, are known to be created inside natural gas and other similar wells and pipelines. The components and conditions necessary to create the material(s) can be found at some point in many pipelines. Some form of iron sulfide is known to be created by either of two mechanisms: (1) chemical reaction of constituents present in the pipeline, usually hydrogen sulfide, and (2) microbial assimilation of chemical constituents in the pipe and the production of both iron sulfides and pipe wall pitting. The iron oxides are created from subsequent oxidation of the sulfides or by direct oxidation of the iron in piping.

3.1 CHEMICAL PROCESS IN THE PIPE

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



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



In addition to hydrogen sulfide, sulfur can also react to form iron sulfides. Sulfur compounds are present in relative abundance in gas and oil wells. Older fields might have sulfate reducing bacteria that have grown in the formation or have used chemical injection to increase well production.

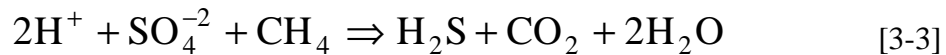
The presence of water in the pipeline can also break loose parts of the iron sulfide coating on the pipe wall and cause it to move down the pipe leaving the pipe wall again exposed for corrosion attack. Iron sulfide, either attached to the wall of a pipe, or collected in the bottom of a pipe, has the 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.

3.2 MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

Microbiologically influenced corrosion (MIC) is a serious form of corrosion that can occur in pipelines and produces black powder or iron sulfide. MIC is pitting of the pipe wall as a result of the activities of microbial communities in areas that provide their required habitat. It can occur on either the inside or outside of the pipe. This report deals only with internal MIC. The extent of MIC and the costs associated with it are only recently being recognized. This has been due

principally to the lack of awareness of MIC by many field personnel, as well as the lack of methods for conducting on-site investigations to identify possible cases of MIC.

The microbes that cause pipe corrosion are basically two families (1) sulfate reducing bacteria (SRB), and (2) 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:



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.^[3-1] Recent GRI research^[3-2], however, has pointed out mackinawite, smythite, and greigite as indicator products of MIC activity.

Whether the presence of hydrogen sulfide is sufficient to indicate microbial activity depends upon whether these two sources of hydrogen sulfide are really one and the same. There is a school of thought that believes hydrogen sulfide that comes from the underground oil formation and the well is actually produced by microbial activity similar to that which produces MIC corrosion in piping. Even if microbes are the source of all hydrogen sulfide, the presence of H₂S in a gas does not mean there are microbes in the pipeline -- the source may also be the producing 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 H₂S, its presence in amounts greater than the maximum allowable is a likely indication of microbes, although it could also mean the failure of a treatment plant has occurred. Similarly, the presence of FeS (or FeS₂) is not necessarily indicative of MIC. Low molecular weight mercaptans may also form iron sulfides, and some natural gases (e.g. West Texas, New Mexico fields) have high mercaptans content, which usually are not removed because they serve as an odorant for distribution (i.e., these gases contain natural odorants, so it is not necessary to add as much mercaptan or other odorants to them before going into distribution lines.) Although the SRB directly produces H₂S 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 waters that are used for secondary recovery (or other sources of water) enter the pipe or well formation, massive activation of these and other microbes can occur, plugging the pores of the deposit, piping mechanisms, and instrumentation with both organisms and metal sulfide precipitates.

APBs consume organic nutrients and produce short chain volatile fatty acids (VFA) such as acetic, formic, lactic, propionic, 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.

Recent research^[3-3 to 3-8] has shown that VFA are key and natural components of reservoir fluids and can be present in very high concentrations (10,000 ppm). It has also been found that VFA concentrations decrease as the SRB action increases, leading to sulfide formation. The VFA are also used by other reservoir microbial species, if conditions can be altered to favor their growth instead of SRB populations. This selective alteration of the reservoir microbial population can be used to produce “biocompetitive” exclusion technology.

3.3 BIOCOMPETITIVE EXCLUSION

There are recent discoveries and field experiments that have identified a means of combating SRB growth with the competitive growth of more favorable microbes.^[3-3 to 3-8] By introducing nitrates into a reservoir, the environment can be changed to favor indigenous denitrifying bacteria (DNB) such as *Thiobacillus denitrificans*. The DNB are more voracious competitors for the VFA and thereby inhibit the detrimental SRB growth, which cause the generation of hydrogen sulfide and subsequently iron sulfide. This process results in biocompetitive exclusion of SRB.

This alternate DNB population produces nitrogen instead of hydrogen sulfide. In the reservoir, the transformed nitrogen has the benefit of increasing well pressure while the reduction of the SRB population prevents reservoir plugging, both factors aid in the well’s production. It is usually not necessary to add microbial cultures to the reservoir since the beneficial species of organism are either indigenous to the formation, or they arrive at the same time and means as the SRB. By the selective alteration of the composition of water with very low concentrations of inorganic nutrient formulations, which include nitrate and nitrite, the deleterious activity of SRB can be retarded.

The nutrients required to promote DNB growth and retard SRB production consist of sodium or ammonium salts of nitrate and nitrite. Molybdates have also proven to aid the process if provided in the right proportions with nitrates and/or nitrites. The process of biocompetitive exclusion as applied to SRB is described and protected under U.S. patent 5,405,531 and is assigned to Geo-Microbial Technologies, Inc. doing business as The LATA Group in Ochelata, OK.

Papers published by the discoverers of the biocompetitive exclusion process^[3-4 to 3-6] describe testing the system in active wells which have become sour since initial production. Although batch injections of nutrients are described, the later work identifies that continuous injection at low rates

is necessary to maintain positive effects. They also describe well monitoring in which it is determined that a week to a month is necessary for the reduction of hydrogen sulfide to take effect. Similarly, the effects last for about that same period of time after injection is discontinued.

This treatment program is applicable to reservoirs and formations where the residence time of chemicals and microbes can be long enough to have effect. It is unlikely to be applied directly in gas piping where gas velocities allow short residence times. The referenced articles did not state whether there were undesirable effects such as DNB wastes, new corrosion concerns, or ill affects on other treatment programs.

4. FILTERING

The most common and historical means of dealing with black powder is to filter it just before it enters a compressor, station, or processing plant. Filters of various technologies and names are usually specified and supplied as a part of the compressor design package when the unit or piping is installed. Sometimes purchasers specify filter performance requirements in their bid request. Sometimes the design requirements given are accurate and sometimes they are hardly known. At other times the conditions change after the initial installation. The net result is that regardless of what is requested or promised, it is usually impossible to get field measurements to accurately determine the performance of filters and separators at any one condition. The only identifiable measure of filter performance is an increase in pressure drop measured across a particle removal device, this indicates that it is collecting material and starting to clog up. It is difficult to identify the quantity and description of what gets through the filter. Ideally, filters are cleaned out or backflushed at optimum points indicated by ΔP , to minimize flow resistance, penetration, or overflow.

A brief review of the industry indicated that there are a number of designs for removing solid or liquid material from a gas pipeline. Many are designed to trap particular materials; not all are good for every type of material or service.

The following are some general comments which should be considered in the design or selection of a filter for iron sulfide. Along with the filtration of iron sulfide, filters nearly always need to be able to handle liquids because they are present either as water or hydrocarbons in many systems. Note that not all filtration systems are designed with these two components in mind.

1. In order to trap iron sulfide, a filter must be designed to remove sub-micron sized particles.
2. To trap any significant volume of liquids, the filter must have a volume for catching liquid slugs, as well as a means of dropping out mist.
3. A backflushing method of cleaning filters will make the filter last longer between filter replacements. Although a manual system can have some value, an automatic sensing and actuating system is the best way to prevent the powder from caking so heavily that it cannot be backflushed. An automatic system, however, is a maintenance item in itself.
4. A filter should have a means of sensing pressure drop or another indication of filter effectiveness and fullness.
5. A self-cleaning system needs to be fitted with a means for removal of the black powder and liquids. In view of the pyrophoric nature of the powder, the depositories for the powder and the filters should either be fire-proof or they should treat the material to remove its auto ignition characteristic. (See *Section 7.0.*)

6. Simplicity of filter replacement must be designed into the system. Considerations should be given to ease of access into the vessel without compromising the pressure boundary during normal operation, minimum time required for removal and replacement of filters, and crew safety during work while the vessel is open.

The latter point could be implemented by using a design that includes a removable filter holder. A second filter holder could be fitted with new filters outside the unit and once the filter vessel is opened, the whole holder could be changed out quickly with a minimum of tool work.

From an overview perspective of the black powder problem, it is our opinion that filtering is needed as a near-term solution to the problem. However, under the scrutiny of a root-cause analysis and a permanent solution, filtering is a superficial or local spot solution. Filtering would be less demanding and less expensive if the source of the gas were to be properly treated to eliminate iron sulfide formation. For this reason, the direction of our investigation did not dwell at length on filtering solutions.

5. SENSING THE PRESENCE OF PARTICLES IN THE GAS FLOW

As discussed in *Section 4.0*, filtering could be performed better if it were possible to detect the presence of liquid or solid particles in the gas flow stream. A portion of the effort under this research task was directed toward determining the availability of existing instrumentation or technologies possible for the development of sensors for particles flowing in a gas pipeline. The need to know the presence and characteristics of particles flowing in a pipeline is predicated on several possible scenarios.

1. The need to know the “normal” flow condition of the system in terms of particles is not determined from gas composition sampling and testing. It would be helpful to know the type of particles (solid or liquid), the typical number of particles as a function of volume, the size distribution of solid particles, the flow velocity of the particles separate from the gas flow velocity, and the differences in these statistics before and after filtration equipment.^[5-1] This information would be used to adjust designs and capacities of filtration and compression equipment and to time maintenance of that equipment for known capacities or limitations. This type of measurement could be done for a very few select points in a pipeline. Although this mode of operation may not require ownership of the measurement instrument, it would require installation of special spool piece(s) or piping loops to accommodate measurement.
2. The value of knowing the changes that occur in the above particle parameters over time would improve maintenance. Measuring particle counts and sizes would aid in determining changes in gas sources, changes in atmospheric or environmental conditions, development of information on MIC or chemical sources of iron sulfide, and maturity of field conditions. This type of information would allow adjustment of gas treatment facilities, provide information for more preferential selection of gas suppliers, determine the effects of changes in gas composition, and signal timing for gas composition or particle analysis testing. These measurements should be taken at strategic points at regular time intervals of a week to a year. Depending upon the frequency, this mode of testing could be performed as an in-plant task or as a service.
3. The ability to monitor for and detect upset conditions in the pipeline as applies to the movement of larger than normal quantities of solids or liquids in the pipe would reduce damage. Knowledge about the presence or movement of such slugs in the pipe before they arrive at compression or filtration locations would allow the adjustment of valves, filters, and machines to handle the condition or to minimize the deleterious effects. Comparing these occurrences with process variables would allow the determination and control of con-

ditions that produce such undesirable situations. This measurement scheme would best be done by continuous monitoring simultaneously at a number of places in a pipeline.

Necessary criteria for in-situ particle measurement are that the unit work in an industrial environment and that it not be “expensive”. To work in an industrial environment implies that it accommodate gas pipeline temperatures and pressures inside the pipe as well as varied environmental temperatures and moisture levels outside the pipe. Optical systems need to be either self-cleaning or designed to handle/avoid the dirty conditions produced by black powder in the pipe. “Expensive” is relative, but a \$100,000 laboratory grade instrument will not be risked in the field environment. As in many things, cheaper is more desirable, but an instrument that gives good information reliably and is easy to operate will raise the level at which return on investment can still be achieved. Instruments under the \$20,000 to \$30,000 range fall into the realm of “normal analytical instruments” and will likely be accepted.

One of the concerns in measuring particle size and counts is using a sensor and method that does not affect the accuracy of the sensing process. To some extent, by-pass flow and sample withdrawal methods may reduce the number or size range of the particles that reach the sensing head. A second concern is the range of particle sizes that may need to be sensed. A range of several orders of magnitude is necessary to detect particles that may be from sub-micron size up to 1000 micrometers. The sensing of solid particles versus liquids provides another level of challenge to instrumentation.

Research sponsored by the AGA has investigated sensing technology for particle measurement as applied to scrubbers.^[5-1] This work suggests that there are a number of technologies that could be applied to advancing a solution to the sensor problem. The AGA work recommended the laser phase Doppler particle measurement system as the best potential for particle measurement, but no system was known to be commercialized for in-plant measurements.

A laser applied in a forward scatter counter method is built and sold by Insitec Measurement Systems of San Ramon, CA, a division of Malvern Instruments of Southborough, MA. Referred to as the PCSV (Particle Counting, Sizing, and Velocimetry), it is advertised that the instrument can be applied to systems with particle size of 0.2 to 200 micron, concentrations of up to 10^7 particles per cm^3 for submicron and up to 100 ppm by volume for supermicron particles, and with velocities of 0.1 to 400 m/sec (0.33 to 1320 ft/sec).^[5-2 to 5-5] It is not ruggedized or otherwise adapted to harsh industrial environments.

The Peerless Mfg. Co., which designs and manufactures scrubbers, has an instrument for counting and sizing particles in a pressurized gas stream in industrial environments. Applied to an isokinetic sampling line rather than in the main flow pipe, it works under full pipeline pressure and temperature conditions. An isokinetic sampling probe is a tube curved at a right angle directly into the flow path from the tube entering the side of a pipe. Compared to a hypodermic-tipped probe,

this configuration provides a sample that is not leaned of the larger particles or drops. The Laser Isokinetic Sampling Probe (LISPSM) can be applied to systems with particle size from 0.3 to 50 microns in diameter, concentrations of up to 10^7 particles per cm^3 for submicron and up to 10 grams per m^3 for the supermicron range. Velocities of 0.1 to 400 m/sec (0.33 to 1320 ft/sec) can be measured with accuracies of +/- five percent of indicated size. The system has to be setup to detect either liquids or solids, but it does not distinguish between the two.^[5-6] An important application of this system is to measure the size and concentration of particles entering and leaving a scrubber or filter to define its efficiency. Peerless uses their laser system as a service to industry and customers of its products. It has been used in five service jobs since development in 1994.

6. QUALITY AND TESTING

6.1 GAS QUALITY

Natural gas, by definition, is a mixture of hydrocarbons, sometimes with noncombustible material components which are in a gaseous state. The amount of each of the components in the gas stream can significantly affect measurement, operation, pipeline efficiency, and customer use. Therefore, an acceptable quality specification is assigned in transactions of natural gas. Gas companies use many different quality specifications; a typical gas quality specification is given below.

Oxygen: The oxygen content shall not exceed 0.1 percent by volume, and the parties shall make reasonable efforts to maintain the gas free from oxygen.

Hydrogen sulfide: The hydrogen sulfide content shall not exceed 0.25 grains per 100 cubic feet of gas.

Mercaptans: The gas shall not contain more than 0.25 grains of mercaptans per 100 cubic feet of gas.

Total sulfur: The total sulfur content, including mercaptans and hydrogen sulfide, shall not exceed 2 grains per 100 cubic feet of gas.

Carbon dioxide: The carbon dioxide content shall not exceed 2 percent by volume.

Liquids: The gas shall be free of water and other objectionable liquids at the temperature and pressure at which the gas is delivered, and the gas shall not contain any hydrocarbons which might condense to free liquids in the pipeline under normal pipeline conditions and shall, in no event, contain water vapor in excess of 7 pounds per 1 million ft³.

Dust/gums/solid matter: The gas shall be commercially free of dust, gums, gum-forming constituents, and other solid matter.

Heating value: The gas delivered shall contain a daily, monthly or yearly average heating content of not less than 975 nor more than 1175 Btu per cubic foot on a dry basis.

Temperature: The gas shall not be delivered at a temperature of less than 40 °F, and not more than 120 °F.

Nitrogen: The nitrogen content shall not exceed 3 percent by volume.

Hydrogen: The gas shall contain no carbon monoxide, halogens, or unsaturated hydrocarbons, and no more than 400 ppm of hydrogen.

Isopentane⁺: The gas shall not contain more than 0.20 gallons of isopentane or heavier hydrocarbons per thousand cubic feet.

6.2 EFFECTS OF COMPONENTS

There are a variety of components of natural gas which are: normal, abnormal, corrosive, inert, dangerous, or useless. Classically, the objective has been to maximize the heating value, but it is also necessary to minimize the detrimental effects, such as corrosion and damage to pipeline equipment. In many instances, the trace components that have negligible influence on heating value cause the formation of iron sulfide (black powder) and the resulting equipment problems.

Of the generally desirable hydrocarbon components, isopentane and heavier components can drop out as free liquids at some point in the range of normal operating conditions. Liquids of any source are not desirable because they cause equipment problems.

Other naturally occurring or frequently found components are hydrogen sulfide, sulfur, carbon dioxide, water, and nitrogen. All of these components occupy space and absorb energy to be moved, thus reducing pipeline efficiency; they either do not support combustion or they absorb energy when the natural gas is burned. All of these players except nitrogen can form acidic compounds contributing to corrosion.

Hydrogen sulfide and sulfur are major subjects of this document. Some pipelines reportedly allow as high as 1 grain of hydrogen sulfide per 100 cubic feet of gas.

Carbon dioxide is a strong acid former and can cause significant pipeline corrosion where water dropout occurs. Allowable levels for this component may be as high as 3 percent by volume.

The effects of water are pointed out in the discussion of MIC. Water also causes corrosion and equipment damage, and, in fact, corrosion cannot occur in the absence of liquid water.

Oxygen is not naturally occurring in natural gas, but can intrude through leaks in low pressure systems. It can cause significant corrosion in very small concentrations and combustion in larger portions. Some companies reportedly allow as much as 1 percent oxygen. Even when oxygen is not in the free, gaseous state, it can contribute to reactions if it is present in sulfates, nitrates, water, or other oxygen containing molecules.

The interaction of oxygen, carbon dioxide, hydrogen sulfide, and water in combinations in natural gas pipelines is discussed in detail by Lyle.^[6-1] This *PRCI* research concludes that in the presence of stagnant water inside pipelines transporting natural gases with oxygen concentrations on the order of 10 ppmv there is little effect on steel corrosion, while 100 ppmv produces fairly high corrosion rates. It recommends that transmission pipeline companies consider limiting maximum oxygen concentrations to 10 ppmv. With regard to carbon dioxide content in natural gas pipelines, oil and gas industry experience indicates that significant corrosion of steels can occur at carbon dioxide partial pressures as low as 7 psi, or about 1.4% by volume. No minimum below which pitting will not occur has been established. Normal carbon dioxide gas quality levels are about 2 to 3 percent. The research indicates that in the presence of oxygen, water, and carbon dioxide, high

concentrations of hydrogen sulfide in excess of all gas quality specifications (maximum of 1 grain per 100 SCF) can retard corrosion, but this is not a practical consideration. In these tests, carbon dioxide seems to be a corrosion accelerator. Other combinations of these components were investigated.

6.3 TESTING

There are several types of testing that can be conducted on a gas pipeline to provide useful information on black powder formation. Among these are gas composition, water content testing, powder composition, and location or origin testing.

Sulfate reducing bacteria produce short chain fatty acids, as well as carbon dioxide, hydrogen, methane, and hydrogen sulfide. Since the gases in this list are also components in natural gas, testing for their presence can only provide supportive evidence of microbial activity. Testing for short chain fatty acids is indicative of current biological activity. These acids can be detected using a variety of methods which include ion and gas chromatography and high pressure liquid chromatography, but these are expensive tests which must be performed by an experienced person, and not likely in the field.

6.4 Gas Composition Testing

Gas composition testing involves collecting a sample of the gas from a specific location in the pipe and testing for its constituent gases. Normally, liquids and particularly solids are not collected, even avoided. Many gas composition tests look only for hydrocarbons and a few other common constituents to verify compliance with heating value specifications. An example analysis includes the following:

Methane	Iso-pentane
Ethane	Normal-pentane
Propane	Hexanes
Iso-butane	Nitrogen
Normal-butane	Carbon dioxide

These components normally do make up 100 percent of the sample at levels down to hundredths of a percent. Historically, gas composition analyses have been performed for the purpose of calculating the heating value of the gas and its average molecular weight. These parameters are useful in determining the horsepower needed to pump the gas and the amount of energy that can be obtained from burning it -- important economic factors in selling and using the gas.

It is well-known in technical circles, however, that sulfur, hydrogen sulfide, oxygen, and water vapor, some in parts per million, can be important in the formation of iron sulfide and other corrosion products. As discussed earlier, the presence of these components in very small quantities can provide:

- the constituents for chemical formation of iron sulfide;
- the environment for growth of sulfate reducing bacteria and acid producing bacteria whose metabolic processes result in the production of iron sulfide; and
- direct corrosion of steel by oxygen, carbon dioxide, or combinations of the two.

Therefore, it is important to test gas composition samples for these lesser components, to monitor the likelihood of iron sulfide formation. To the extent possible their presence, particularly water, hydrogen sulfide, carbon dioxide, and oxygen, should be controlled within the limits discussed (see *Section 6.2*) and within the rationale for limits that are being sought by continuing research. Where such limits are specified in tariff restrictions they of course should be enforced at custody transfer points. Apparently this is not widely done at this time. This effort to identify and remove the small quantities of these iron sulfide producing chemicals may be the most effective approach to preventing the formation of iron sulfide and prevent the damage it causes. Again, the economics of this effort should be weighed against the total impact of the presence of iron sulfide and microbiologically influenced corrosion in an entire piping system.

Even within the limits of these reasonable restrictions on trace components, consider the following mass balance: Hydrogen sulfide at 1 part per million (ppm) (0.25 grains per 100 cubic feet is 4 ppm) in a continuous gas stream of 10 MMCFD, if all converted to iron sulfide (FeS), will produce over 800 pounds of iron sulfide in a year. Thus even gas meeting many H₂S specifications can produce large amounts of FeS_x and higher quantities can make the situation much worse.

Sampling of natural gas from active pipelines for composition testing is a straight forward and conventional procedure which will not be described here.

6.5 Water Testing

Water is an important factor in the support of environmental conditions necessary for microbes to thrive and multiply. It is also a factor in direct oxidation of the walls of carbon steel pipe and MIC cannot occur in the absence of liquid water. As discussed earlier, most pipelines have some water content, and changing atmospheric temperature or other pipeline environmental temperatures can cause water vapor to quickly condense in the pipe and gravitate to the lowest point. For this reason, Canadian gas transmission companies reportedly have lower allowances for water content than companies in other countries, particularly in the more temperate zones. This investigation did not have the opportunity to determine whether they also have lower incidence of iron sulfide. If water is not drained off frequently, it can cause the microbial spores which may be dormant in the pipe, to bloom grossly and rapidly and cause MIC.

SRB and APB prefer to exist at the interface between a water puddle and a drier area. They create what is referred to as a biofilm. Thus, the most likely locations to find MIC evidence is at low

places in piping where water is likely to exist and to collect. Avoidance or frequent elimination of these sites is desirable to avoid pipe damage and iron sulfide creation.

Since the biofilm is the best site for microbial growth, it is also the best medium for identification of their existence. Ideally, the water should be sampled from a pipeline without exposing it to air and it should be tested before the microbe count has a chance to change significantly. This implies a sample tube or pipe that is small, to expose the water to as little air as possible coming out of the valve. The tube should fill the collection vessel from the bottom to overflowing so that there is no air space and then capped or valved off immediately. This nearly air-free sample should then be tested within the hour for SRB or APB; more practically, the test is usually performed within 24 hours. Five to 10 milliliters of water is sufficient for testing for both aerobic and anaerobic bacteria. A good sample vessel might be designed somewhat like a gas sample bottle with inlet and outlet valves on opposite ends and sanitized and then purged with nitrogen or natural gas prior to being filled with the water sample.

Often, it is difficult or impossible to sample and test in the field with a high degree of detail. In this case as much care as possible should be taken to minimize oxidation or contamination of the sample and to reduce the time before it is tested. Some useful results may still be achieved from samples collected and tested somewhat outside of these parameters.

The water sample should be tested for microbial content and the type determined by culture. Such tests should be done by a qualified laboratory. However, on-site test kits are commercially available. They permit testing to be performed by trained gas company personnel. A reduced pH of the water can indicate APB activity. (See *Section 6.4 Testing Equipment and Services.*)

If there were no water in a pipe, it would not be necessary to test water for evidence of the problems it causes. Therefore, if there is a low place in the pipe that collects water and there is a way to get the water out there, it should be removed frequently to reduce the chances for corrosion, microbial blooming, and biofilm growth. Testing for microbial content should be a secondary effort. Therefore, all water should be removed whenever samples are taken for testing.

6.6 Powder Composition Testing

When black powder is found in piping, instrumentation, or compression equipment, it is sometimes helpful to verify its composition by chemical testing to identify or verify its likely origin. The origin could be chemical combination or microbial corrosion. There are dark materials that can occur from other materials or chemical reactions that may not be iron sulfide.

Certain forms of iron sulfide are pointers to MIC presence in a pipeline. As discussed (see *Section 3.0 Sources Of Iron Sulfide In Piping*), mackinawite, smythite and greigite are considered to be indicators of microbial activity in piping. The most positive indication of MIC is the presence of pits in the pipe wall. Another is testing to confirm the presence of SRB or APB. Normally a

larger pit will have smaller individual pits inside of it. In more developed cases, the pits may overlap each other. Striations and tunneling parallel to the pipe axis are also pointers to MIC, but it can also occur without these signs. Sometimes the pits are covered by a nodule of material composed of the microbes and the material they consume and deposit. As pits deepen and become more numerous, individual pitting becomes less obvious.

The activity of acid producing bacteria (APB) can be identified from the presence of short chain fatty acids such as acetic, formic, lactic, butyric, and valeric acids. Due to the symbiotic coexistence of APB and SRB, if these short chain fatty acids are found, there is good reason to expect the presence of SRB.

Purely chemical formation of the iron sulfide is indicated by presence of iron sulfide and hydrogen sulfide without the identification of short chain fatty acids or smythite, greigite, or mackinawite.

An easy test of black powder to confirm it is a form of iron sulfide is to acidify it by placing a portion of the powder in a tube of hydrochloric acid (HCl). The hydrogen sulfide smell (rotten eggs) is proof of the presence of sulfide. Caution should be taken when performing this test since hydrogen sulfide (H₂S) and hydrogen chloride (HCl) are very toxic and should not be inhaled! There are commercial test kits available to perform more quantitative determinations of sulfides.

Powder that is red or partly red rather than completely black most likely contains iron oxides. These should not exist in the anaerobic conditions in gas pipelines, but iron sulfide can easily oxidize after being removed from piping. Sulfides typically oxidize to sulfates or elemental sulfur. The latter is positive evidence of oxidation. Iron sulfide samples stored in flexible plastic containers with air space in them will in a short time partially collapse the container due to the conversion from sulfides to oxides causing a partial vacuum. Exposure of dry black powder to sufficient oxygen may result in auto ignition as discussed in *Section 4.0* of this report.

Once MIC is identified as a source of the iron sulfide, biocide treatment can be an aid. It is wise at that point to select the best biocide by confirming its effectiveness against the specific sets of microbes found in the pipe environment. Seek aid from the biocide supplier or certain qualified independent testing labs for appropriate tests. These tests usually involve sampling the pipeline water as described in *Section 6.3.2*. It should be kept in mind that there is usually not just one type of microbe present when corrosion is taking place.

6.7 Location or Origin Testing

The above testing methods may be used creatively to aid in vectoring the source of MIC or sulfide entry into the pipeline.

In cases where hydrogen sulfide or other sulfides enter a pipeline, direct chemical conversion to iron sulfide will likely take place. This problem occurs most commonly in gathering pipelines

where gas comes directly from wells and numerous wells are added together before becoming or being added to a major long run transmission line. Once sulfide enters the pipeline at any point, conversion to iron sulfide is prompt. The material can progress down the pipeline from that point.

In the case of MIC generated iron sulfide, a similar phenomenon occurs. When the components that promote microbial growth get together, a colony and a biofilm are created. Black powder can migrate from such points to locations downstream in the pipeline.

When black powder is found at any point in the pipeline, such as a filter or compressor, it is helpful to be able to identify the source of the material in order to be able to minimize or eliminate it. Performing the above gas, water, or powder testing at accessible ports in the pipe may provide clues to the source by identifying where the powder is or is not and whether it has MIC signatures or not. If the ability exists to inspect inside the pipe wall, the existence of wall pitting is a positive indication of a MIC source. If gas testing shows sulfides, it is likely that black powder exists or will be formed soon downstream from that point in the pipe. Water testing should indicate either a positive indication of MIC presence or the likelihood of near future formation at that point. Finding iron sulfide powder at a location in a pipe, without other indicators, is not definitive as to whether the powder is forming locally or has moved from upstream. Identifying an upstream location without black powder would help to vector to the source. It does not aid the vectoring process if the powder is being formed at a number of sites near the gathering portion of the pipeline. Appropriate sites for performing gas collection, water draining, or powder inspection and removal are not always conducive to effective powder source vectoring. (See discussion on pigging under *Section 7.0 Powder Removal, Handling, and Disposal.*)

If an operator should be fortunate enough to locate the/a source of black powder formation, it should be possible to determine whether it was formed by MIC or chemistry and treated appropriately. MIC should be physically cleaned, treated with biocide, and consideration given to whether the pitting damage warrants repair or replacement. If possible, it would also be wise to look at modifying the pipe design to prevent the collection of water and the formation of biofilms. Chemical formation of iron sulfide can be eliminated by removal or reduction of hydrogen sulfide or other gaseous sulfides from the gas. Although the resulting pipe wall thinning could be damaging over the long run, it is more generally distributed than MIC damage.

6.8 TESTING EQUIPMENT AND SERVICES

There are a large number of companies that can perform various aspects of the testing needed for black powder characterization, water microbial testing, and gas composition analysis. A few tests can be performed in the field, but many yield best results when properly sampled in the field and expeditiously tested by laboratory experts. This is particularly true for microbial testing since the sample may either increase or decrease in population between sampling and testing. A certain

degree of biochemical knowledge is needed to effectively perform field sampling or testing. This is not to rule out the average gas plant personnel, but is a caution that appropriate skills, training, methods, and materials must be acquired and used.

Test sample kits were determined to be available from at least two companies. Bioindustrial Technologies, Inc. of Georgetown, Texas, participated in a series of projects funded by the Gas Research Institute (GRI) in the late 80s and early 90s concerning the identification of microbial influenced corrosion (MIC) in gas piping. As a part of those research projects, a number of technical reports were issued that are available for purchase.^[6-2 to 6-4] Besides the technical information on MIC formation and treatment, they outlined testing procedures for field identification of MIC sources. The results of these investigations are MIKITs for testing and analysis and Field Guides for procedural instructions on sampling and testing. (See *Section 6.0 References*.) The kits allow either field analysis, or the samples may be sent to their labs for analysis.

The following companies provide testing services and were interviewed for information: Dixie Testing & Products, Inc. of Houston, TX and Geo-Microbial Technologies, Inc. of Ochelata, OK.

7. POWDER REMOVAL, HANDLING, AND DISPOSAL

Once black powder is generated in a pipeline, removing, handling, and disposing of it is a necessary evil which must be dealt with until the material is prevented from forming. There are reasons to have concerns about how this should be done. The black powder can be loose or adhered in the pipe, large or small quantities, dry like smoke or wet and tar-like, possibly pyrophoric, and a nuisance or a hazard. It is very common for iron sulfide to form in a pipe and adhere to the surface in thin layers. The presence or amount of coating on the pipe may not be known in many cases and is only revealed when the line is repeatedly pigged or washed. The presence of black powder in a pipe has the effect of increasing surface friction and roughness and increasing the horsepower required to move an amount of gas through the pipe. Obviously these factors have negative economic implications.

7.1 REMOVAL

The most common method for the removal of black powder from a pipeline is filtration at a compressor station. The purpose at this point, however, has more to do with protection of the compressor than purely collection and removal of black powder. This subject is discussed in *Section 4.0 Filtration*.

Most iron sulfide tends to adhere to the metal (pipe wall) where it forms. In some cases it is held in place by an encrustation of salt. Another factor that aids in holding the powder in place is liquids. The powder adheres to wetted surfaces or collects in pools of water or hydrocarbon.

Factors that affect the movement of iron sulfide are dryness, changes in flow rate induced by pressure changes, and abrasive actions that shear the powder off of pipe walls. This cleaning action is accomplished by (1) abrasives moving through the pipe, (2) water or other liquids, particularly in slugs, and (3) pigging. Although all of these mechanisms can happen incidentally as natural consequences of pipeline operation, they are also created intentionally to remove black powder buildup from a piping section. (Inspection pigging may be considered “incidental cleaning”.)

In some cases, mild abrasives such as nut shells are induced into a pipe section and retrieved downstream with the black powder they break loose. Such materials are most common in centrifugal compressor sites which can tolerate the materials passing through and cleaning blades and stators.

More commonly liquids are used to wash down piping and remove iron sulfide. Although water is common and inexpensive, it is not good if any is left in the pipe to support MIC growth and oxidation. Diesel fuel or alcohol have been used as cleaning agents that will not promote microbial growth and are relatively inexpensive and disposable. Other cleaning agents are formulated by

commercial suppliers specifically for cleaning piping of black powder. Typically these are more expensive than water, diesel fuel, or alcohol, but have fewer side effects. In most cases the liquid is trapped as a slug between two pigs. This causes it to fill the pipe more completely, control the liquid distribution, and provide better retrieval.

Pigging involves moving an object with scraping action through the pipe by gas pressure. The cleaning action of the pig is to push loose material ahead of it out of the pipe as well as to scrape the walls of the pipe to remove more adhered material.

The subject of pigging to remove black powder was discussed at the 1996 SGA Black Powder Summit. One of the more experienced companies indicated that using a heavy pig was more effective in breaking loose and moving black powder. Some indicated scraper pigs were effective, while others had less faith in their capabilities. It was noted that after a number of pigs were sent through a line, an intelligent pig passed through would then pick up much black powder. This is apparently due to the fact that many iron sulfides are magnetic, and after being broken loose from the pipe wall into small pieces, the fine iron sulfide particles are attracted to the magnetic field which exists around a smart pig.

Pigs are also helpful in removing water and other liquids collected in piping. The pig pushes the liquid down the pipe, sometimes causing it to combine with powder to form a sludge. This water removal is advantageous in preventing the growth of microbes.

Sections of piping that are constructed in such a manner that they cannot be pigged or otherwise opened for cleaning and inspection are candidates for MIC growth to the extent of pipe penetration. Collection of water in such a section or deadleg is an even greater inducement to MIC and oxidation corrosion.

One difficulty with inserting anything, solid or liquid, into the pipe for cleaning is that it must have a means of getting in and likewise for being retrieved. Such means and location strongly limit the ability to clean piping where that intent was not designed in. This applies to pigging and liquid washing. Construction of deadlegs, side branches, and unpiggable piping should be avoided from the standpoint of black powder formation. Even design of instrumentation lines should include a means of isolating and cleaning out the line to prevent clogging and loss of signal.

None of the above methods should be construed as effective in the total removal of iron sulfides from pipewalls. It is true that large amounts of material can be scooped from the bottom of the pipe, scraped from the walls, or washed loose, but corrosion engineers verify that it is very difficult to clean iron sulfides down to bare metal, even on steel pipe corrosion coupons. To do this requires a hydrochloric acid wash and subsequent neutralization with ammonia or bicarbonate and then water wash to a neutral pH. This method would require a means to capture and dispose of hydrogen sulfide released. Such a process has been used in plant systems. To apply this

method to a corroded transmission pipe is surely more difficult, and practically the number of steps must continue, to include removing any residual water as well.

7.2 HANDLING

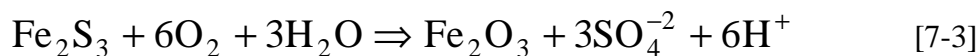
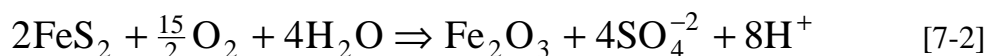
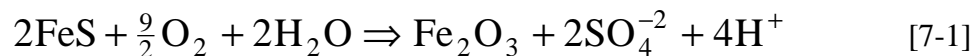
Once black powder is removed from piping, whether by filter cleanout, pigging, or other access to piping, compressor, or instrumentation internals, some attention must be given to the safe handling of the black powder. The main hazard is associated with the pyrophoric nature of the material.

The greatest hazard seems to exist when the material is dry and in a fine powder form. Collecting the material in aggregates or chunks causes less risk of combustion because the surface to mass ratio is much smaller. Wet black powder, whether from water or hydrocarbons, is less likely to combust because the liquid serves as a heat sink. General practice has been to wet down the powder with water as it is removed from piping or filters to retard combustion. The drawback to this method, however, is that it is not permanent. At such time as the material dries out, the risk of combustion returns. This may occur in the first depository after removal from the pipe, during transportation where it may be exposed to forced draft which induces drying and oxygen exposure, or it may not occur until the material is deposited into a landfill or other “permanent” site. There are several reports of black powder smoldering or catching fire in the back of a truck transporting it to a landfill. Others report that they store removed filters in a steel box and keep them there until they have smoldered and stopped, thus converting to iron oxide instead of iron sulfide, before taking them to a landfill.

7.3 NEUTRALIZING BLACK POWDER FOR SAFE HANDLING

There are several methods available for the neutralization of iron sulfide. This investigation was able to identify a few of them. These methods involve actual chemical transformation of the material. The concern at this point is the nature of the chemical components produced by the reaction(s). It is possible to produce components less desirable than the iron sulfide.

The first method to neutralize iron sulfide is natural oxidation. The oxidation of iron sulfides is somewhat complicated. The reaction equations for the complete oxidation of FeS, FeS₂, and Fe₂S₃ by oxygen are given in Equations 7-1 to 7-3.



Complete oxidation of iron sulfides in ambient conditions may only occur for FeS₂ (both pyrite and marcasite). Ferrous sulfide (FeS) is readily oxidized by moist air to form elemental sulfur and Fe₃O₄. At high temperatures, Fe₂O₃ is formed.^[7-1] Ferric sulfide (Fe₂S₃) is readily oxidized to a hydrated ferric oxide and elemental sulfur. It decomposes at high temperatures to a mixture of FeS and FeS₂.^[7-1] We also know that sulfur dioxide (SO₂) was found after dust fires in pyrite mines.^[7-2] Oxidation of SO₂ continues in the atmosphere to produce sulfuric acid, resulting in acid rain.

A great number of reactions are possible in the black powder mixture of iron sulfides found in gas pipelines, and the composition of products is going to depend highly on the material found in the black powder and on the reaction conditions. It is possible for a chemist to determine the equilibrium reaction products of iron sulfide compounds under different conditions. Sulfide compounds generally are stable only under very reducing conditions. This means that sulfide materials are usually only found in environments where there is a lot of organic material, such as in coal beds. This also explains their stability in natural gas pipelines and their flammability in air. Reacting iron sulfide-containing black powder with an acid under reducing conditions will form hydrogen sulfide. Alternatively, a basic solution of a strong oxidizer may encourage rapid formation of sulfate before gas can evolve.

Potassium permanganate (KMnO₄) is reportedly unique among oxidants that could be used to treat iron sulfide. It is safe to use and easy to apply and usually disposable. When applied as a less than 4 percent solution, it is relatively harmless if it contacts the skin, requires no special materials of construction, and does not form harmful or potentially explosive by-products.

The reaction of potassium permanganate (purple colored) and iron sulfide produces a brown liquid. When the iron sulfide is completely consumed, the excess permanganate solution again turns purple giving a positive visual indication when the reaction is complete. The by product of the reaction is manganese dioxide, which is biologically inert and can be discharged directly to a waste water facility. Depending upon the original contaminants, the solution may also contain oxidized organics or iron oxides. Reducing agents such as sodium thiosulfate or citric acid can be used if it is necessary to remove the manganese dioxide.^[7-3]

Another advantage of the potassium permanganate cleaning method is that it is faster than the multiple (more hazardous) steps of acidizing, thus reducing downtime. A unit or pipe can be filled with the solution and either circulated with pumps or agitated with air, nitrogen, or steam. If the color of the solution turns brown, more permanganate should be added. If the color is purple, the reaction is complete and the unit can be drained and opened.

Potassium permanganate is more expensive than other potential oxidizing agents such as sodium hypochlorite, or hydrogen peroxide, or temporary treatment methods such as water saturation.

Current permanganate costs are \$1.50 to \$1.80 per pound, while the alternative chemicals are about 30 percent less and water is considerably less. The cost advantage comes when compared against longer treatment times (downtime), waste handling and treatment, disposal problems and equipment, lack of undesirable side reactions, and worker safety.^[7-3]

7.4 DISPOSAL

Almost all iron sulfide forms appear in nature, but in a pipeline it may mix with other liquid hydrocarbons to make the material a hazardous waste, or a material that must be deposited in a secure landfill. Since there are varieties of formulas for iron and sulfur combinations and a large number of other materials that could be combined with it, the classification of a hazardous material most likely must come from a test. The Toxic Characteristics Leaching Procedure (TCLP) test is designed to determine whether materials in the powder or sludge will leach into the soil to cause problems. This test must be performed on typical samples to determine whether any component has a hazardous flash point, is acidic or corrosive, flammable, etc. The pyrophoric nature of some forms of iron sulfide may make it a substance that requires controlled disposal.

8. SUMMARY

Although this report is not complete in dealing with black powder, several important actions it discusses can go a long way toward reducing the operational, maintenance, and economic impacts of the black powder on well, pipeline, storage, and process plant equipment. The following actions should be considered:

- Companies should review contract and tariff agreements with regard to acceptable amounts of water, carbon dioxide, hydrogen sulfide, 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. Enforcement should be aggressive.
- Companies should raise the awareness and train employees and contractors regarding MIC and its impact on their system. Field and supervisory personnel should be taught about monitoring and sampling procedures, as well as handling and treatment.
- Water should be avoided, removed, purified, or drained at every opportunity or when encountered in plant and piping systems. This should be considered in water injection into wells, hydrotesting, and cleaning operations. Whenever water is introduced, the affected area should be cleaned of moisture and microbes. Without water, microbiologically influenced corrosion cannot exist.
- Review operation 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 volumes; low points should have drains.
- Continuously review company practices with respect to use and application of biocides, pigging, and filtering technology.
- The economic impacts of corrosion and black powder should be evaluated and weighed into technical and operational decisions. Estimated costs of new equipment, testing, or procedures should be balanced against avoided costs of present black powder maintenance costs. Improvements should be evaluated in terms of net expected value (benefit vs. cost).
- Creative methods of testing, filtering, measuring, and chemical treating should be sought to deal with the black powder problems. There are no accepted or tried and true methods; everything should be subjected to careful scrutiny.

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