Improved Black Powder Removal from Gas Pipelines using Innovative Gelled Fluids, Traditional Cleaning Methods and Careful Candidate Selection.

Abstract

This paper outlines the principles required to achieve effective black powder removal from pipelines, which is a widespread problem in operational gas pipelines. It discusses the economics and effectiveness of debris removal using different methods. It is shown that the gel-pig fluid method can produce very effective results in a single pass on long lines. Such lines may be impossible to effectively clean using other methods, even when the line is broken into smaller sections. The problem of effective transport of the powder out of the pipeline, rather than just its removal off the pipewall, is given particular attention. In the past there has often been a blanket approach to black powder removal but this paper highlights the importance of careful treatment selection for specific applications. Some recent case histories are reviewed with a range of pipeline diameters and lengths in a variety of areas.

Introduction

"Black Powder" is a very common phenomenon in gas pipelines all over the world, which causes widespread problems in equipment fouling and flow reduction (Fig 1). Despite its common occurrence, it is not a problem that is necessarily well understood across the industry, in terms of its formation, removal, inhibition, prevention or lost money. In order to understand how the material is formed and, more particularly for this paper, how it is removed, it is helpful to have knowledge of the physical and chemical properties of the material. This is also important when considering some of the more extravagant claims for black powder removal processes which may be difficult to scientifically justify.

There is an excellent technical assessment on black powder in the gas industry by the Gas Machinery Research Council (Ref 1), which gives a very good background on the subject. Black powder is produced in a gas pipeline by direct chemical reaction or following biological production of H_2S , and is usually accompanied by the presence of water (even in only minute quantities). The most common major component in black powder is iron sulphide, although iron oxides may also be present, these materials give the black coloration. Iron Sulphide is found in many chemical forms, with different concentrations of iron and sulphur. The most common forms or iron sulphide include pyrrhotite, troilite, mackinawite, pyrite and marcasite. In addition, there may be variable quantities of other materials that may serve as binders for this otherwise dry & powdery material. Common binders include compressor oil, glycol and its breakdown products, condensates, other hydrocarbons and water. Consequently black powder may come in any form: talc-like powder, molasses, grease or wax-like materials, so no one single approach can necessarily be used in all cases.

Chemistry of Black Powder

Iron sulphide, the major component in black powder, is usually formed from hydrogen sulphide (H_2S) in the hydrocarbon gas reacting directly with the steel wall of the pipeline.

 $H_2S + Fe \Longrightarrow FeS + H_2$

(Eq.1)

Alternatively, the H_2S may be produced by sulphate reducing bacteria (SRBs) on the pipewall; this tends to have a more localised effect on the pipewall leading to pitting. Pitting is a self-perpetuating process that can severely accelerate localised corrosion, to the point of failure of the pipeline integrity. The presence of water helps promote the chemical reaction, and a small percentage +/- 5% will greatly accelerate the process.

The presence of 1ppm of hydrogen sulphide in a gas stream flowing at 10 MMCFD will potentially produce over 800 lbm (363 kg) of iron sulphide "black powder" in a year. 1 ppm is a common industry limit for H_2S in lines, in many cases it could be substantially higher. This shows how quickly a large quantity of black powder can form with "in-spec" gas. (Iron sulphide can also react in the presence of moist air to form iron oxides and sulphur. Sulphur is also a troublesome material, causing further corrosion.)

Iron oxides may also be formed by chemical reaction between the steel wall of the pipeline and components present in the gas product, or by acid producing bacteria (APBs) in aerobic conditions. Once again, the presence of water increases the reaction rate by both stabilising the dissociated Fe^{2+} ion in solution, as well as providing a conductive path for electron flow, as corrosion is an electrochemical process.

 $2\mathrm{H}^{+} + \mathrm{Fe} \Longrightarrow \mathrm{Fe}^{2+} + \mathrm{H}_{2} \tag{Eq.2}$

Reasons to Remove Black Powder

The reasons to remove black powder from a pipeline are well established. During the operation of the pipeline a loss of efficiency may be noticed over time with changes in internal diameter and surface roughness causing increased pressure drop requiring greater horsepower to move the product. Gas quality may be negatively impacted by unacceptably high concentrations of solids in the product with the accompanying problems of over-frequent filter changes, erosion, etc. Black powder presence may also increase the corrosion rate in a line by offering a suitable environment for SRBs to thrive in, or by preventing the corrosion inhibitors that are dosed into the gas stream from reaching the surface of the metal surface in order to protect it. Pipeline inspection tools require a clean pipeline in order to successfully inspect the condition of the line. The weight of these tools, combined with the small clearances and strong magnetic fields produced by MFL (Magnetic Flux Leakage) techniques, make these tools particularly prone to getting clogged up with black powder, causing an expensive misrun.

Consequently the decision is taken to clean the line of black powder, and the focus is then changed to which method should be utilised. An initial impression would be that current practices appear to be split into two main areas: Chemical Removal, and Physical Removal. The following discussion, will explain that, in effect, true chemical removal is not performed and current techniques are based on physical removal methods.

Chemical Reactions for Chemical Cleaning of Black Powder

Iron sulphide is practically insoluble in water, but soluble in acids with the liberation of toxic H_2S , at much higher concentrations than in the product gas. This could go on to further corrode the pipe, as well as constitute a significant health hazard. Therefore, acid is not generally considered a safe & suitable treatment.

$$FeS + 2HCl \Rightarrow FeCl_2 + H_2S$$
 (Eq.3)

There are a number of non-acid solvents for iron sulphide and iron oxides which are based on chelants such as the aminocarboxylates, and other sequestering agents, however, at neutral or alkaline pH they generally require significant temperatures (over 160°F, 71°C) and exposure times of more than one hour. This is generally not possible in pipeline applications. Some low ph (<5 pH) chelating agents may function at more realistic ambient temperatures (80°F, 26°C), but contact times would be in excess of one hour. This is again impractical for pipeline applications, as an extended chemical slug length would be required, leading to extravagant cost. At lower ambient temperatures, the reaction rate would be too slow to be practical. Even when using chelating agents at acid pH, there is still the problem of H₂S generation. The same problems of slow reaction rate at ambient temperatures would also apply to iron oxide removal, although H₂S would not be an issue.

Chemical cleaning methods would have to be water-based, with the additional cost of drying the line to an acceptable specification, in addition to the cost of lost production during shutting in the line to execute the cleaning and drying stages of treatment.

In addition to impracticably slow reaction kinetics, the amount of cleaning products is going to make the process of true dissolution very expensive. The amount of cleaning agent to dissolve the black powder is dependent on the type of chemistry used and the amount of black powder to be removed. In any event the amount of cleaning agent will be several times the quantity of the debris itself. There have been pipelines that have been cleaned using physical methods that produced 500,000 lbm (226,796 kg) of black powder. To truly dissolve that quantity of debris (which is most unlikely due to reaction time and temperature limitations) would require millions of pounds of cleaning chemicals, which would cost millions of dollars. There would also significant costs of chemical disposal. Typical black powder chemical removal treatments reported in the literature add 10-20% of an already diluted cleaning product to water in a slug volume of perhaps 50-200 barrels (8-32 m³). However, in such cases, there cannot be enough active ingredient available to dissolve significant quantities of black powder, without even taking into account the most unfavourable reaction kinetics.

Consequently, it is not believed to be chemically practical nor economically viable to truly dissolve or chemically clean black powder in gas pipeline applications. Methods which claim to chemically remove black powder should be treated with careful scrutiny. Competent laboratories can readily measure the dissolved iron content of the discharge fluid following such cleaning methods, it is quite likely to be insignificant.

Physical Removal of Black Powder

It is believed that all of the current pipeline cleaning processes used to remove black powder are based on physical removal. It is true that many of the removal techniques also involve the use of chemicals, such as dispersants, solvents (which are only solvents for the binders) or gelling agents, but the black powder is still conveyed out of the pipeline without actually taking part in any chemical reaction. It still comes out of the pipe as black powder. This is perfectly acceptable. In almost all cases brush pigs are used to remove the black powder from the pipe wall. Therefore, the key issue is which technique provides the most efficient and cost effective method for physical transportation of the black powder out of the system. Examples of physical removal processes are given in the following paragraphs.

Dry Pigging.

This traditional form of mechanical removal can be done routinely on piggable lines and relies on the use of mechanical pigs (commonly brush pigs) run through the pipeline (Fig 2). It does not involve taking the line off-stream, or introducing water to the system. On the other hand very little black powder is removed on each run, so multiple runs are required, and it is impossible to assess the amount removed compared to the amount left behind. (That is usually found clogging up the MFL tool when it is run!) On longer lines, pig wear and the build up of dry debris in front of the pig add to the risk of sticking the pig, whilst the presence of binding contaminants may make the deposits too difficult to remove, and may result in them being smeared back onto the pipe wall.

High Velocity Flushing.

This depends on pumping a low-viscosity fluid through the line at a high velocity, and has the advantage of not necessarily requiring a piggable line. The fluid may be water (which then requires the line to be subsequently dried) or a hydrocarbon like diesel (which has cost and environmental implications). These fluids have little or no particle suspension properties and a very high level of fluid turbulence is relied upon to convey the solid particles out of the line. Although black powder is a variable commodity, a typical value for its specific gravity is around 4.7, so it will have a tendency to settle rapidly in a stationary low-viscosity fluid.

Solid particle movement through fluid flow in horizontal lines occurs in one of two basic types of movement. The solid particle can slide along the bottom of the inner wall of the line. This is often referred to as sliding-bed flow and is a very poor method of particle transport. The other type of particle transport is where the degree of fluid turbulence is great enough to lift the particle from the pipe wall and keep it suspended in the fluid. This is the principle behind velocity flushing. The primary parameters influencing which type of particle flow occurs are the fluid velocity, fluid viscosity, particle size and the difference in density between the particle and the fluid. J.T.Davies (Ref 2). proposed a theoretical model (Equation below) that can be used to determine the fluid velocity required to just suspend a particle in fluid flowing through a horizontal line. This model shows close correlation with published experimental data.

$$V_{sus} = 1.08 * (1 + \alpha * c)^{1.09} * (1 - c)^{0.55*n} * v^{-0.09} * d^{0.18} * [2 * \Delta \rho / \rho_{f}]^{0.54} * D^{0.46}$$
(Eq.4)

where, V _{sus}	=	Minimum fluid velocity to keep particles in suspension (m/sec)
d	=	diameter of the debris particle (m)
D	=	Line ID (m)
$ ho_F$	=	fluid density (kg/m ³)
Δρ	=	fluid density minus particle density (kg/m ³)
ν	=	kinematic viscosity of the fluid (m^2/sec)
α	=	constant estimated by Davies to be 3.64
С	=	volume fraction of solids in the fluid (volume of solids / total volume)
n	=	hindered settling term, which is dependent on the particle terminal
		settling velocity and varies between 3 and 4

The fluids may have difficulty removing organic binders which may hold the black powder deposit together. In larger diameter lines the necessary flow rates required may require an expensive pumping spread (See Table 1), or the flow rate will be insufficient and particles will be left behind. On longer lines, the consequent friction pressure may be over the burst limits of the pipe. In addition, the amount of flush fluid may make the technique impractical or too expensive. Consequently this approach is not generally a good one for gas lines, unless they are of the smaller and shorter type.

Dry Air & Pig Process.

Lightweight foam swabs and foam/brush pigs are run through the pipeline driven by superdry air (dewpoint = -90° F, (-68°C) and can remove a significant quantity of debris whilst keeping the line dry. With the use of large filter socks to catch the debris, it is possible to obtain a reasonable estimate of the amount of debris removed, whilst helping prevent a dust nuisance. Of course the line must be purged of hydrocarbon first and it must be established that no pyrophoric deposits are in the line. Black powders that consist of iron sulphides are commonly pyrophoric, and are not suitable candidates, whereas iron oxide deposits make good candidates. Organic binders that are co-deposited with the debris will make cleaning difficult, as this technique relies on removing the debris in the pores of the foam swabs as fine powder. Once again a technique best suited to smaller, shorter lines, or where the line requires to be dried at the same time.

Pigging with "Solvent" or Chemicals

In this application a solvent, which has been selected to help dissolve binders that consolidate the black powder, is pumped between conventional mechanical pigs. The solvent is not intended to dissolve the black powder itself. Like high velocity flushing, the fluids have poor suspension properties and rely on turbulence to transport the black powder, so similar limitations of pumping spread cost and friction pressure exist. It is difficult to obtain reliable information on the cleanliness of the line, as the debris exiting the line tends to be concentrated around the pigs. Consequently it may be difficult to predict the cleanliness endpoint and cost, as multiple runs may be required whilst the pipeline is off-line. The process is ineffective when inorganic binders are present, and requires the line to be dried if water based fluids are used. Once again a technique best suited to smaller, shorter lines.

In addition to water or hydrocarbon-based solvents, liquids consisting of water containing dispersing agents, mutual solvents and emulsions have also been introduced in recent years, but require the line to be dried if water based fluids or emulsions are used. These offer some advantages with dispersing chemicals helping wetability and break up of particle

agglomerations thus reducing the effective particle size. However compared with gel pigging, these chemicals have little or no suspension properties, with solid particles falling rapidly when insufficient fluid turbulence exits (Fig 3). Although now often referred to as "Chemical Pigging", this is a deceptive terminology as there is little or no chemical reactions taking place; the principle effect is still attempting to mechanically flush the solids out of the line. Many chemical vendors clearly state that the chemicals they use only facilitate the removal of black powder and do not dissolve it; some are not so clear.

Once again it is useful to remember the specific gravity of black powder particles is around 4.7. This is heavy, and typical of the materials selected for weighting agents in heavy oilwell drilling muds. Such fluids would be carefully designed, with gelling agents essential to keep such heavy particles in suspension; dispersing agents do not provide significant suspension properties. The principles for solids transport out of the line are the same as with High Velocity Flushing, with the inclusion of mechanical pigs to increase the speed & quantity of debris disturbed. However, in large diameter gas lines it is not possible to reach these high velocities (see Table 1) and the particles will not be transported, and will build up in front of the pig, causing debris to be left behind, or risking sticking the pig. As such it is generally not possible to attempt to clean the line in a single pass, as the chemical pigging systems do not have the suspension capacity to carry the black powder out of the line, or distribute them throughout their volume, and this results in many runs being required. It is normal to split the line into sections in order to cope with the quantity of debris. Unless a multi-pass, nonaggressive approach to pigging is utilised, there is the distinct chance of sticking a pig. There is also the chance of this happening if the job has to be stopped prematurely as the debris will rapidly fall out of suspension and be concentrated in front of the pig.

Gel Pigging

In this process gels that can hold heavy deposits in suspension for days are pumped between mechanical pigs, which scrape off the debris from the pipe wall, distribute it through the volume of the gelled fluid, and contain the gel to give 360-degree coverage. The gels may be based on water or hydrocarbon fluids and can be selected to suit the deposits and binders, and. appropriate binder solvents may also be included in the pig train if required. A range of highly developed gel products is required to suit stringent pipeline cleaning requirements; a selection of gel pig fluids supplied by BJ Process and Pipeline Services is shown in Figure 4. Depending on the fluid chosen, it may not be necessary to dry the line after the treatment, and in some instances the cleaning may be done on-line and in a single pass without splitting the line into sections. It is also possible to obtain high quality information on the quantity of debris removed, as well as the cleanliness of the line.

The gel pig fluids are carefully selected to have suitable properties of debris suspension without excessive friction pressure, whilst being able to effectively wet the debris particles and disperse them in the entire volume of the fluid. This prevents a heavy concentration of solids in front of the mechanical pigs that can lead to pig damage, by-pass, or ultimately a stuck pig. This allows mechanical pigs to be effective over far longer distances than with dry pigging or pigging with solvents or chemicals. The gel pig system is particularly suited to large lines where turbulent flow rates are not possible, and where large quantities of debris are anticipated.

Typically a separator gel is used to sweep away pipeline fluids, condensate, or water and improve separation from the drive fluid. A number of debris removal gel slugs are run between mechanical pigs; the number & volume of stages is designed around the quantity of debris expected. A number of treatment modifications can be made, such as the inclusion of a drying stage or corrosion inhibitor stage at the end of the pig train. Advanced gel pig fluids are as safe and as environmentally friendly as the fluids they are based on; water-based fluids are extremely environmentally friendly.

Gel pigging techniques may at times appear to be more expensive than other techniques, however all aspects of the cost of treatment must be taken into account, and balanced against the considerable benefits. Such benefits include the ability to clean the line in one pass, whilst quantifying debris removal. In some cases cleaning is performed on-line, at times without the need for drying and with less risk – all important factors leading to reduced loss of production. When these factors are taken into account, gel pigging may often offer the most cost-effective solution to black powder problems.

Choice of Black Powder Removal Method

Before a removal method can be chosen, it is essential to gather comprehensive information about the nature of the problem. A sample, or a number of samples, should be taken and carefully analysed. It is possible that the black powder may not have a homogeneous composition & distribution along the length of the line. Close to a compressor station the deposit may be more widespread, and may contain compressor oil or glycol residues that bind & coat the deposit, making it more difficult to remove. At places like river crossings or elevation changes pipeline geometry changes serve to trap both moisture and black powder being carried along by the gas flow, leading to a localised concentration.

Past history of treatment success should be evaluated and a clear understanding of what the targets are for a successful job. Is a 20% increase in flow efficiency considered a success, or does the line have to be returned to "as-new" condition? If this is not established at the start, it will be impossible to evaluate the treatment at the end.

Case Histories

1 130 miles 24-inch Natural Gas Pipeline.

This line required cleaning to remove black powder prior to inspection. The line was purged and broken into sections. A number of sections were cleaned using mechanical pigs propelled by air. After several hundred pig runs, over a period of 2 months, the inspection pig was launched. No data was recovered.

2 130 miles 24-inch Natural Gas Pipeline.

This is the same line as described above, but cleaned the following year. After obtaining sample analysis and carefully designing a gel-cleaning job, over 30,000 lbm (136,000 kg) of debris was removed in 5 days (<2 weeks total job time) and the intelligent pig was run. It was recovered clean, and full data was recorded.

3 10" field Transmission Line

10" line with launcher and receiver on both sides of river crossing with gas coming direct from producing wells. Pipeline about 3,000 ft in length with accumulated black power at low points in pipeline restricting flow. Client judged line was over 50% full with black powder deposits.

Water based gel was pumped between pigs, & pushed with customers gas. Train came in with black powder up front, but clean gel in the rear. Job completed in one day. Customer placed pipeline back in service, with design flow achieved again with minimal pressure drop.

4 700 miles<, various diameters up to 24 inch, Gas Distribution Line.

Unacceptably large amount of debris being caught in filters following initial conversion from crude oil services to gas service with water based cleaning fluids followed by hydrotest water, producing large amount of black powder (mostly iron oxide). It appeared line had not been dried properly. Operational pigging did not cure problem.

Pipeline system problems were re-evaluated and hydrocarbon-based gel pig trains were then used to clean the lines, leaving them dry. Approx 30 days were required, with the pig train propelled by product gas in order to reduce downtime. Over 1,000,000 lbm (453,600 kg) of black powder was removed, along with quantities of water. Cleanliness of over 98% was confirmed by debris analysis. No operational problems have been reported since the gel cleaning.

Conclusions

- 1 There is no "one size fits all" solution to black powder problems.
- 2 Each cleaning job has to be designed to suit the type of deposit and the properties of the pipeline itself. To facilitate this representative samples are required.
- 3 Purely chemical removal of black powder from gas pipeline is not currently believed to be a viable removal process due to production of H2S with acid fluids, or very slow reaction rates, very large treatment volumes, and high costs of non-acid fluids. In any case, costs would be extremely high.

(Such purely chemical processes may, however, be viable in other applications, such as the chemical or pharmaceutical industry where a "polished" pipeline is required, and the treatment times & costs can be borne.)

- 4 Current black powder removal processes are based on the physical removal of the black powder without chemical reaction with it. Pigging with chemical solutions may help to break-up & disperse the deposits, but their removal is still a physical process.
- 5 Other methods such as velocity flushing and gel pigging are also physical methods.
- 6 Gel pigging has been used to remove the largest quantities of black powder from gas pipelines with the minimum risk.
- 7 Once black powder is removed from a system, it would be prudent to consider its future prevention either by use of inhibitors, or by a change in the gas treatment process

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References

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- 2 J.T.Davies, Calculation of Critical Velocities to Maintain Solids in Suspension in Horizontal Pipes, Chemical Engineering Science, Vol. 42, No. 7, 1987

Table 1. Typical Flow Rates Required to Maintain Particle Transport in Horizontal Pipes. Particle of Sand, 100 micron diameter, Fresh Water, 60 °F (15.5°C)

Pipeline ID (inches/m)	Fluid Velocity (ft/s, m/s)	Flow Rate (USgpm, m3/hr)
4/0.1	3.2/0.972	121/27
8/0.2	3.6/1.1	545/124
12/0.3	3.8/1.17	1318/298
24/0.6	4.1/1.25	5600/1,272
36/0.9	4.2//1.29	13,006/2,954
48/1.2	4.3/1.31	23,480/5,333





Figure 2 Mechanical Pigs



Figure 3 Suspension properties Comparison: Chemical Cleaning Product on Left after seconds, Gel Pig Fluid on Right after 24 hours



Figure 4 Selection of water-based and hydrocarbon based gel pig fluids, before use.



Figure 5 Sidestream sample from passing gel pig fluid, with a considerable quantity of black powder in suspension.