

Study on Elemental Sulfur Formation from Black Powder Deposits

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The Black Powder in gas and associated processing equipment is a global phenomenon that many operating companies had and still suffering from. The composition of Black Powder has been found to vary significantly in chemical composition. However, the constituents mainly consist of iron sulfides (FeS) and iron oxides.

Black Powder is known to cause serious problems to pipelines, such as flow inefficiency, product contamination, wear, plugging, and under deposit corrosion. Another major concern is the possible formation of elemental sulfur, which could be produced as a by-product of oxidation of iron sulfides. It also can be produced from H₂S dissociation at elevated temperatures or by microbiological reactions involving the reduction of sulfate.

Black powder also presents another problem for the collected deposit samples (in equipment, piping, or cleaning pigging of pipelines) as they are sometimes left exposed to the environment for prolonged periods, and analysis of the deposits shows the presence of elemental sulfur. In these situations, it is not clear whether the elemental sulfur is present due to process contamination or due to exposure to the environment.

To investigate this, a study of Black Powder deposits was carried out to determine the effect of exposure to air at different lengths of time (6 hours, one day, one week, two weeks and three weeks) for atmospheric conditions, and at higher temperature (50°C) for the same samples at the same lengths of time. This will enable better understanding of the formation of elemental sulfur for black powder deposits. The results of this study are presented in this paper.

Keywords: Black Powder, Deposits, Iron Sulfide (FeS), 50°C, Sulfur (S₈)

INTRODUCTION

Black Powder is a phenomenon that all oil and gas companies are facing and presenting a variety of problems in associated processing equipment and pipelines, such as flow inefficiency, product contamination, wear, plugging and under deposit corrosion, among others.

Another major concern is the possible formation of elemental Sulfur (S_8), which could be produced as a by-product of oxidation of iron sulfides. It also can be produced from H_2S dissociation at elevated temperatures or by microbiological reactions, involving the reduction of sulfate.

Black powder also presents a “dilemma” for the collected deposit samples (in equipment, piping, or cleaning pigging of pipelines) as they are sometimes left exposed to the environment for prolonged periods, and analysis of the deposits shows the presence of elemental sulfur. In these situations, it is not clear whether the elemental sulfur is present due to process contamination or due to the exposure to the environment. This has been raised in Kuwait oil company (KOC)TM while investigating the formation of elemental sulfur in one of the fuel gas pipelines, when the asset owner questioned the analysis results for black powder deposit samples collected during pigging operations since they were collected two days after opening the pig receiver.

The literature on this specific subject is limited. As a result, this experimental study was initiated to determine the actual effects for environmental exposure of black powder deposits containing iron sulfides and the formation of elemental sulfur, which can be shared on a wider platform. The details of the study, findings and results are discussed in this paper.

BACKGROUND

Pipeline FG-098, which carries fuel gas from the refinery to the gathering centers for equipment and for blanketing purposes, suddenly exhibited high amounts of black powder accumulation during cleaning pigging operations. The asset owner did not have the sample bottles to collect the deposits immediately from the pig receiver and; therefore, planned to contact the inspection and corrosion team for deposit collection the next day. However, due to shift changes and gaps in communication, the actual deposits collection was delayed for a few days. As a result, the deposits were left exposed to the environment for that period (Figure 1 and Figure 2).



Figure 1: Black Powder Accumulation in Fuel Gas Pipeline FG-098

After the deposits collection, wet chemistry and X-ray diffraction (XRD) analysis confirmed the presence of iron sulfides (FeS), Iron oxides and elemental sulfur (S₈), being the common factor in the deposits. This was concerning, since it suggests the involvement of H₂S and oxygen in the process and the incoming fuel gas from the refinery, which as per the specification, should be free of acid gases.

Subsequently, the asset owner was informed on the findings and concerns. A decision to form a task force team was made to investigate the reasons for the formation of elemental Sulfur and to provide mitigation actions to ensure integrity of the downstream assets.



Figure 2: Black Powder Accumulation in Fuel Gas Pipeline FG-098

The investigation results showed the presence of contaminants (CO₂ and H₂S) in the fuel, and mitigation actions were put in place, such as increasing cleaning pigging operations, explore utilizing gas sweetening facilities and H₂S scavenging. However, the elemental sulfur formation was in question since the deposits were left exposed to the environment for a few days.

Therefore, the environmental effects on the deposits had to be determined, especially for the formation of elemental sulfur (S₈) from black powder deposits containing iron sulfides, which in this instance was exposed to air for a prolonged period.

EXPERIMENTAL PROCEDURE

Since black powder deposit in pipelines is typically a mixture of iron sulfides, iron oxides and other contaminants, Iron sulfides (FeS) found in the pigging deposits was the focus of this investigation while exposed to the environment, since oxygen / oxidation process, will break the iron-sulfur bond, and form elemental sulfur.

For this study, high pressure gas pipelines HP-116 (leaving booster station to export) was chosen, since black powder with iron sulfides were always found in every cleaning pigging run, but without any elemental sulfur presence in the analysis.

Five set of samples were collected from HP-116 and kept for analysis at different durations for 6 hours, one day, one week, two week and three weeks at room temperature (Figure 3). The same samples were kept at the same length of time, but under constant temperature-controlled oven at 50°C, to simulate the environmental condition for exposed deposits in Kuwait.



Figure 3: Experiment Samples in Petri Dish for Oxidation of Iron Sulfides (FeS) from Black Powder Deposits

The samples were homogenized and subjected to the following analysis:

- **XRD analysis:** Washing samples with toluene and acetone to remove organic compounds and then subject the samples to XRD analysis. The results are presented in Table 1 and Figure 4 to Figure-7.
- **Gravimetric analysis:** For loss on drying at 100°C, 500°C and 900°C. The results are presented in Table 2.
- **Water soluble analysis:** Using boiled distilled water to analyze pH, Chloride, Hardness, Calcium, Magnesium content, total dissolved solids, Soluble sulfide, Sulfate, dissolved Manganese and dissolved Iron. The results are presented in Table 3.
- **Acid soluble analysis:** Digested with concentrated Hydrochloric Acid (HCl) to extract the acid soluble minerals. The acid extract analyzed for Iron, Manganese, Calcium, Magnesium content and the amount of acid insoluble minerals was calculated. The results are presented in Table 4.
- **Microbial analysis:** To determine bacterial growth, using Most Probable Number (MPN) Serial Dilution technique in accordance with NACE TM0194¹ and results are tabulated in Table 5.

RESULTS

Initial Sample (Analysis Immediately Carried Out):

The XRD for the initial sample collected showed different forms of iron sulfides and iron oxide (such as Mackinawite, Greigite, Troilite, Pyrite and Pyrrhotite, without elemental sulfur). This was the desired finding for the samples.

The different types of iron sulfides observed inform on the stability and reactivity² in the process. They will not be discussed in detail; however, the following should be noted for the reader for better understanding of these FeS types:

- **Mackinawite:** The first FeS type to form in the reactions occurring in the system, with higher iron than sulfur ratio and can form in temperatures below 140°C.
- **Greigite:** Forms from Mackinawite and additional Sulfide at lower pH (2.3 - 6.5).
- **Troilite:** is rare form of FeS, rarely found in the earth crust, with an even ratio of iron to sulfur and is non-magnetic. They can transform into Pyrrhotite type at temperatures up to 120°C.
- **Pyrite:** A stable form of FeS and usually called “fool’s gold”. The form at temperature of 150°C. They can provide protective scale to the pipelines; however, it easily can be broken and therefore, significant corrosion would be expected.

Pyrites used to be mined as a source for sulfur many years ago, since then, it is obtained through the petrochemical industry.

- **Pyrrhotite:** Another stable form of FeS. Dry pyrrhotite are pyrophoric and is subjected to spontaneous combustion with exposure to oxygen, due to the heat generated by the thermal reaction. Wetting for the deposits is suggested, as was done for sample collection for this experiment.

From the initial sample XRD analysis, it is evident that the reactions are active and continuous in the process stream, leading to the formation of different types of FeS, based on temperature and pH (Mackinawite forms initially as FeS at low temperatures, reacts with H₂S to form Pyrite (FeS₂), Greigite, also, forms from Mackinawite at low pH environments, Pyrrhotite (FeS) forms at higher temperature...etc.).

The wet chemistry analysis results showed low pH of 5.5, which is acidic. Chloride content was found at 250 ppm, suggesting water accumulation. These conditions are known to promote corrosion confirmed by the Fe to Mn ratio and the iron content of 44% observed in the acid soluble analysis. Positive identification (Qualitative) for sulfide presence, confirms that H₂S exists in the process, leading to sour corrosion and the formation of FeS in the black powder deposits.

**Bacterial analysis showed zero counts for SRB, GAB and GAnB.*

Sample Exposed for 6 hours at Room Temperature and 50°C:

No major changes were observed, apart from changes to the FeS percentages and types, due to exposure to oxygen or higher temperatures.