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CONTAMINANTS IN SALES GAS PIPELINES – SOURCES, REMOVAL, AND TREATMENT

FINAL REPORT

SwRI® Project No. 18.14226

PR-015-084508

Prepared for:

Pipeline Research Council International, Inc.

Contractor:

Southwest Research Institute

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Number of Pages: 77

Software Included: No

Release Date: September 2010

Abstract:

The objective of this project is to provide information about a problem material found in gas pipelines called “black powder”. It is a mixture or a chemical compound of iron sulfides, iron oxides, dirt, sand, salts, chlorides, water, glycols, hydrocarbons and compressor oils, mill scale, or other materials. The most common constituents, iron compounds of sulfur or oxygen, are corrosion products. In addition to chemical formation, black powder can be formed by microbes normally found in gas pipelines. This material causes machinery, measurement, and pipeline maintenance problems.

This research investigates the forms of iron sulfides, their characteristics, and methods of formation and whether the molecular form can be an indicator of the source of the material. A sampling protocol was developed for proper collection of materials for analysis. Seventeen corrosion samples were collected and analyzed for material constituents and microbial content. The results of this testing were anonymously tabulated in a database. Other tasks in this project include guidelines for removal, handling, and disposal of the material. It discusses symptomatic versus root cause treatments for the prevention and control of black powder, and the corporate culture necessary to manage the problem. It presents recently developed technologies for cleaning or treating a pipeline containing black powder, such as cleaning and anti-microbial agents containing THPS which dissolve iron sulfides, and the use of magnetic filtration. The final task describes concepts for identifying the location of black powder in an operating pipeline and places to look and methods to use to best determine the distribution of the material.



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Catalog No. L5XXXX



Contaminants in Sales Gas Pipelines – Sources, Removal, and Treatment

Contract PR-015-084508

Prepared for the
Operations & Integrity Technical Committee
of
Pipeline Research Council International, Inc.

Prepared by the following Research Contractor:

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Publication Date:
September 2010

PRCI Version Control			
Version	Date of Last Revision	Date of Uploading	Comments
1	14 May, 2010		Draft Report
2	5 October, 2010		Final Report
3			
4			

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Pipeline Research Council International Catalog No. L5XXXX

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EXECUTIVE SUMMARY

The objective of this project has been to provide to the pipeline and related industries information about a problem material found in such pipelines commonly called “black powder”. This material is a mechanical mixture or a chemical combination of a variety of compounds such as iron sulfides, iron oxides, dirt, sand, salts, chlorides, water, glycols, hydrocarbons and compressor oils, mill scale, or other materials. The most common constituents, iron compounds of sulfur or oxygen, are corrosion products as a result of a chemical combination of the iron in the pipe, water in the pipe, and sulfur or oxygen found in the gas. In addition to chemical formation, black powder can be formed by microbes normally found in many gas pipelines. Collections of this material cause machinery, measurement, and pipeline maintenance problems.

This research investigates the seven known forms of iron sulfides, their characteristics, and their methods of formation. It attempts to determine whether the molecular form can be an indicator of the source of the material. Under this project, 17 samples of black powder were collected from voluntary contributors and the various samples were analyzed for material constituents and microbial content. A sampling protocol was developed for careful and proper collection of materials to be analyzed. The results of this testing were anonymously tabulated in a database. Other tasks in this project include “best practices” guidelines for removal, handling, and disposal of the accumulated material. This task further discusses symptomatic versus root cause treatments for the prevention and control of black powder, and the corporate culture necessary to manage the problem. It presents many recently developed technologies for cleaning or treating a pipeline with black powder accumulations. Among these are the use of cleaning and anti-microbial agents containing THPS which dissolves iron sulfides, and the use of magnetic filtration. The final task describes concepts for identifying the location of black powder in an operating pipeline and places to look and methods to use to best determine the distribution of the material. These include sampling methods that prevent sample oxidation, and sidestream and insertion probe material determination and collection methods.

This project was performed over a period of two years.

1. INTRODUCTION

“Black powder” is a term used to describe the appearance of a material that is found in natural gas and other pipelines. The material is always black, sometimes dry, sometimes wet from either water or liquid hydrocarbons, and the solids have been found to consist of a mechanical mixture or a chemical combination of a variety of materials. Among these are iron sulfide, iron oxide, dirt, sand, salts, chlorides, carbonates, glycols, mill scale, welding debris, or sometimes other materials. The most common of these are iron sulfide and iron oxide, which are products of corrosion of the steel pipe because of chemical or biological interactions in the presence of water.

The presence of black powder in natural gas pipelines creates wear and reduced efficiency in compressors, clogs instrumentation, valves, and pipes, and leads to flow losses. It can also compromise the pressure boundary. Several such events in recent years, which had catastrophic results, have increased the visibility of the problem and generated regulatory controls for monitoring and cleaning of piping segments.

PRCI is interested in finding out more about this material because of its significant commercial impact on pipeline operations. The material has not been very well understood by operating companies and so its costs have been considered just a hidden cost of doing business. PRCI’s Operations & Integrity Technical Committee is interested in establishing “best practices” guidelines for controlling, sampling, removing, and as possible, preventing the occurrence of the material. This document provides an attempt to advertise the latest knowledge and methods to address these issues.

This document concludes the second of a two-year research program on the subject of black powder. The first year of this program included a search for information about the types and mechanisms of formation of the various types of iron sulfides. A field sampling protocol was developed and chemical testing of a few submitted samples was initiated. Another task involved identifying best practices for removal, handling, and disposal of the corrosion product.

The second year effort expanded the testing program and in addition to chemical testing, included microbial testing. The results of these tests are added to the industry database initiated in the first year. Another added task in the second year effort was an investigation into how to locate where black powder might accumulate in a pipeline, the methods possible to identify the presence of material, the places to look, and potential means of sampling from a pipeline in operation.

2. TASK 1. A LITERATURE ASSESSMENT OF THE TYPES, PROPERTIES AND CONDITIONS OF FORMATION OF THE IRON-SULFUR MOLECULES AS APPLIES TO NATURAL GAS PIPELINES

2.1 INTRODUCTION

The mix of materials found in a pipeline can consist of a wide variety of components. The materials left in the pipeline during construction or repairs can be easily identified and likely consist of hardware, welding debris, mill scale, sand, dirt, or similar. Some of these should be controlled or eliminated by careful material handling and construction procedures, including temporarily capping unwelded piping sections and cleaning them out as they are placed for welding. A few other components of the black powder may come from the wells such as carbonates, chlorides, sulfur compounds, carbon dioxide, nitrogen, water, or heavy hydrocarbons. It is possible for iron oxides or iron sulfides to come from the well, but this must be rare because few wells have the necessary iron, sulfur, and water constituents. Water, oils, and glycols or their degradation products would be expected to come from processes or machinery on the pipeline. Most of the remaining material is generated in the pipe and consists of corrosion products. After initial operation and clean-out, corrosion products would be expected to be the major components. They increase in quantity with age of the pipeline, increasing sulfur content of the gas, and the presence of water. By far the major corrosion components are iron sulfide and iron oxide. These two components are kin in that the sulfide will form and reside in the pipe in the absence of oxygen, but will convert to iron oxides in the presence of oxygen. The oxygen does not have to be free oxygen, but can come from the breakdown of other compounds containing oxygen atoms. Most commonly, iron sulfides convert to iron oxides immediately upon removal from the pipeline when they are exposed to air. Iron sulfide is black and iron oxide is dark red, but the presence of just a little of either of these will cause all the material in a mixture to turn black. This is the source of the term “black powder” usually applied to the dry version of the material.

Of these components, then, the ones most troublesome to the pipeline industry are the forms of iron sulfide, assuming they are generally the precursors of iron oxides. These iron sulfide compounds are the topic of the following discussion.

The objective of this literature search is to investigate what is known about the different molecular forms of iron and sulfur atom combinations. For each identified molecular form, it is of interest to determine the chemical and physical properties, and the pipeline conditions under which it might be formed.

This is not intended to be a complete chemical or microbiological treatise on the subject, but rather a layman’s description. Please consult the references for more complete details. Most of the material not specifically referenced in this article is attributed to Rickard [Reference 1].

2.2 MOLECULAR FORMS OF IRON AND SULFUR

We find seven combinations of iron and sulfur that have been given names. These are greigite, mackinawite, marcasite, pyrite, pyrrhotite, smythite, and troilite. The molecules are somewhat unique in that they are not always found in stoichiometric ratios, that is, the numbers of atoms and the valences do not always match up; in some structures there are vacancies of one atom or the other or extra metal atoms. This can make for reactive or unstable structures. Each

iron sulfide molecule is formed by a distinctive mechanism. The presence of sulfide or polysulfide ions or elemental sulfur as a reactant can determine the nature of the iron sulfide molecule formed.

First, we will examine the properties of each of these materials.

2.2.1 Mackinawite ($Fe_{(1+x)}S$)

Mackinawite (mack'•i•naw•ite) is a bronze or white gray crystal, but is most commonly found as a granular material with crystal structure visible only under a microscope. It is not magnetic or radioactive. The molecular weight of mackinawite is 85.42 gm. and its density is 4.17 gm/cc. [3, 4]. Difficulties arise in attempting to propose the exact range of mackinawite's composition because it takes up large quantities of nickel and cobalt into its lattice. Mackinawite is sulfur deficient and measurements indicate the "x" in the formula above may range from about 0.04 to about 0.1. There has been reported an amorphous or non-crystalline iron sulfide with a formula very close to mackinawite. [12], [13]

2.2.2 Troilite (FeS)

Troilite (troil•ite) is the stoichiometric version of FeS; it has no vacancies in its crystalline structure like pyrrhotite and mackinawite. It is, therefore, neither magnetic nor radioactive. Its molecular weight is 87.91 gm. and its density is 4.61 gm/cc. This molecule is rare in pipeline deposits. It's most common occurrence and importance is in meteorites. [3, 4]

2.2.3 Greigite (*Cubic* Fe_3S_4)

Greigite (grI'•gite) is sooty black when amorphous and becomes metallic pinkish, tarnishing to metallic blue in crystalline form, which is microscopic in size. It is strongly magnetic, second to magnetite (Fe_3O_4). Its molecular weight is 239.96 gm. and its density is 4.049 gm/cc. It is not radioactive. [3, 4]

2.2.4 Smythite (*Rhombohedral* Fe_3S_4)

Smythite (sMY'•thite) is a brownish-black six-sided crystal that fractures in flat sheets like mica. Smythite is magnetic. Its molecular weight is 861.75 gm. (frequently combined with nickel) and its density is 4.32 gm/cc. It is not radioactive. [3, 4]

2.2.5 Pyrrhotite ($Fe_{(1-x)}S$)

Pyrrhotite (pier'•o•tite) is another of the non-stoichiometric molecules, usually having a different number of iron and sulfur atoms, where the "x" in the formula is about 0 to 0.2. Its color can be bronze, bronze red, or dark brown. The molecule has two symmetries. When pyrrhotite is low in sulfur and the formula is closer to true FeS, then the structure is hexagonal. But when it is high in sulfur, the structure is monoclinic (three unequal length axes in which one is perpendicular to the other two). It is magnetic and not radioactive. Pyrrhotite has a molecular weight of 85.12 gm. and a density of about 4.61 gm/cc. [2, 3, 4, 5]

2.2.6 Pyrite (*Cubic* FeS_2)

Among gemologists, pyrite (pie'•rite) is best known as "Fool's Gold" because of its crystalline color and luster. Pyrite is a polymorph of marcasite, which means it has the same

chemistry, but a different structure and symmetry and crystal shape. They are difficult to distinguish from each other. Pyrite can become magnetic after heating, and it is not radioactive. Pyrite has a brassy yellow color and metallic luster. Its molecular weight is 119.98 gm. and its density is 5.1 gm/cc, heavier than average for metallic minerals. [2, 3, 4]

2.2.7 Marcasite (*Orthorhombic FeS₂*)

Marcasite (mar'•ca•site) is a mineral that is a polymorph of pyrite and the two are often mistaken, even by experts. There is a process that converts from one to the other. The typical crystalline form of marcasite is the distinctive shape of a cock's comb. Marcasite over decades deteriorates, emitting a sulfur smell and corroding susceptible materials near it. Some research has suggested that bacteria may aid and accelerate marcasite deterioration. [5] The reaction is triggered by exposure to air and is mildly exothermic. Marcasite has a molecular weight of 119.98 gm. and a density of approximately 4.8 gm/cc. It can become magnetic after heating and is not radioactive. [2, 3, 4]

2.3 CHEMISTRY OF FORMATION

The mineral sulfides of iron may be formed at low temperatures in water from a variety of distinctive mechanisms. The major controlling factor in the formation of the sulfides is the oxidation state of the sulfur-bearing reactant, since the oxidation state of the iron is ferrous in all these minerals. In particular, the presence of aqueous (dissolved in water) sulfide, or polysulfide (more than one "S" atom) ion, or elemental sulfur, can decide the nature of the final product. The form of the pre-existing iron salt becomes important when it exerts some degree of structural control on the product. For instance, the presence of rhombohedral ferrous carbonate (siderite) produces rhombohedral smythite, and the prior presence of mackinawite controls the formation of greigite.

The absence of air or oxygen is a necessity for the formation of the sulfides. The presence of oxygen, in almost any form, changes the reactions to ferrous oxides. Within the pipeline environment, this is seldom a concern, but it becomes very important when the material is removed from the anaerobic environment in the pipe to the atmosphere, for testing or disposal. Several references [14, 15, 16, 17] have shown that iron oxides in the presence of hydrogen sulfide can produce iron sulfates, also. This is facilitated by the presence of water or humidity.

The following discussion of the conditions under which the sulfides of iron are formed is taken from laboratory tests reported by D.T. Rickard [1]. It can only be assumed that similar chemical processes take place in a gas pipeline.

2.3.1 Formation of Mackinawite

Mackinawite was first formed through the reaction of goethite [FeO(OH)] and hydrogen sulfide (H₂S) at pH values of 4 and 6.5, and through reaction between iron and hydrogen sulfide gas at pH =4. It has also been formed through the reaction between ferrous sulfate (FeS) and sodium sulfide (NaS) at pH of 2 or 3 - 11.7, and goethite and sodium sulfide at pH=7.2-11.4. Heating mackinawite in a vacuum to 70° C produces greigite very rapidly. [3, 4] Sulfur or hydrogen sulfide adsorb very strongly on steel surfaces, thus resulting in mackinawite formation on the surface of steel. In the presence of water, mackinawite is soluble below its saturation limit. Thus, slowly formed mackinawite may be dissolved as fast as it is formed in low

concentrations of H₂S and larger volumes of water. [11] Both Rickard [13] and Berner [12] report finding an amorphous iron sulfide with a formula of FeS., thus not all iron sulfide is identifiable by X-Ray Diffraction.

The stability of mackinawite is temperature dependent; the presence of cobalt, nickel, and copper stabilize it. Mackinawite is the primary product of all reactions between an iron salt and a dissolved sulfide. The reaction from mackinawite to greigite is irreversible.

2.3.2 *Formation of Greigite*

Greigite is most commonly formed as a further reaction of mackinawite. It is formed from the reaction of ferrous sulfate (FeS) and sodium sulfide (NaS), as in mackinawite, but takes place at lower pH of 2-3 to 6.5. Greigite is also formed through the reaction between initial mackinawite and sulfide. In no case was greigite observed to form directly and the initial material is non-magnetic, but becomes so as greigite forms. The rate of conversion from mackinawite to greigite is accelerated at lower pH. Temperature also affects the rate of conversion.

Greigite appears to be unstable with respect to pyrrhotite. Greigite has not been formed through reactions between iron and sulfur at any temperature. Since it depends upon the prior existence of mackinawite for its formation, greigite may be a non-equilibrium phase between mackinawite and pyrrhotite.

2.3.3 *Formation of Smythite*

The only reported synthesis of smythite is by Rickard [1] through the sulphidation of siderite, and thus concluded that siderite was a necessary factor in the formation of smythite. It is partially transformed to pyrrhotite within three hours at 180° C (356° F) in a water suspension.

2.3.4 *Formation of Pyrrhotite*

Pyrrhotite may be synthesized from aqueous solutions but this generally requires high temperatures or very long periods of time. Pyrrhotites were formed in the laboratory through heating greigite and smythite at temperatures as low as 180° C (356° F) in very short periods of time. Troilite has been formed from mackinawite at temperatures as low as 40-45° C (104-113° F).

It appears that the three sulfides, mackinawite, greigite, and smythite are probably unstable with respect to pyrrhotite, and that pyrrhotite will be formed on prolonged aging of these materials, or more rapidly, on heating aqueous suspensions.

2.3.5 *Formation of Marcasite and Pyrite*

Pyrite and marcasite have been synthesized from solution. They can be formed at 25° C (77° F) and 1 atmosphere pressure. Laboratory experiments show that, at temperatures below 150° C (302° F), in aqueous solutions and in the absence of oxidizing agents, pyrite and marcasite will not form through the reaction between dissolved ferrous salt and an aqueous sulfide. However, the addition of a sodium polysulfide solution to a solution of ferrous sulfate yields pyrite and/or marcasite under all conditions. Pyrite was synthesized at pH values between 4.4 and 9.5. Pyrite was minor to marcasite at pH = 4.4. As the pH increased, marcasite decreased, until, at pH=9.5, marcasite was completely absent. The formation of marcasite will

be favored at lower pH values because elemental sulfur is more likely to be a reactant under these conditions. Marcasite can be formed without low pH conditions; the reaction between mackinawite and elemental sulfur is relatively fast at 25° C (77° F) in water, since water can act as a carrier for the elemental sulfur. Crystallized sulfur takes longer to react.

2.3.6 *Water and Sulfides*

Water plays an essential role in the formation of mackinawite. This mineral has not been prepared in the absence of excess water. It is suspected that water acts as the carrier for sulfide ions and that metastable mackinawite is essentially a transition complex intermediate to the formation of pyrrhotite. In very small samples (3 g.), the relative humidity controlled the oxidation rate of mackinawite. Above 50%, humidity oxidation became pyrophoric. For weight samples significantly larger than this, the relative humidity was less significant and oxidation was always pyrophoric. Reactions involving oxidation of iron sulfides are known to be exothermic so that heat is evolved. Therefore, the bulk temperature would be expected to increase, provided that the heat released to the surroundings does not exceed that liberated during oxidation. This is much more probable with larger samples where more heat is produced so that the temperature rises more and leads to pyrophoric activity. [14]

The role of water in the formation of greigite and smythite is less clear. Greigite has been formed from mackinawite with adsorbed sulfide, which was partially dried and only contained about 10 percent water. Smythite was not formed by the passage of gaseous hydrogen sulfide over dry ferrous carbonate. Water may also be a factor in the formation of marcasite and smythite.

Water has also been used to control the auto-ignition of sulfides in air. Wetting the material has the effect of coating the surface and reducing the surface area exposed to oxygen, and it further cools the exothermic oxidation reaction, slowing the progress of heating and drying other adjacent granules. [9] Small quantities of water that do not have the capacity to remove exothermic heat faster than it is produced actually facilitate oxidation. [15]

2.3.7 *Oxygen and Sulfides*

Iron sulfides are very sensitive to free oxygen; they rapidly transform to iron oxide, as indicated by a change in color (reddish). There are two causes of this tendency. (1) The molecule is reactive and prefers the oxide state to the sulfide state. (2) There is the ability of sulfides to form in sub-micron particle sizes, or to shear down to those sizes if it has been previously agglomerated. The large surface area of small particles exposes more material to oxidation and causes oxidation to occur faster. Since the reaction is exothermic, heat can build rapidly, sometimes to combustion, and more rarely, to explosion. [13, 14, 15, 16].

This scenario would support the reported cases of pipeline filters catching fire when removed from the housing and exposed to oxygen.

These processes suggest three methods which have been recommended to use for the control of sulfide combustion in some cases. The oxidation of sulfides can be controlled by exposing the material to a dilute oxygen atmosphere, such as about 8% oxygen in a nitrogen environment. The second is to wet the material with water to slow the rate of reaction and absorb the heat of the exothermic oxidation reaction. The third method is to agglomerate the fine

particles to significantly reduce the surface area exposed to oxygen. These methods allow the transformation from sulfide to oxide to take place slowly.

2.3.8 Rates of Reactions

Throughout the above description of sulfide syntheses, results, and interpretations, it is apparent that the rates of the reactions concerned are of extreme variability. The direct reactions between dissolved ferrous iron and sulfide or polysulfide giving mackinawite or pyrite, are extremely rapid. This is typical of many reactions involving dissolved ions.

Temperature is a factor in reaction rates. In purely chemical reactions, the higher the temperature, the more rapid the reaction takes place. In the case of microbiologically influenced corrosion (MIC); however, a change in temperature could move the environment out of the range of viability of the active microbe and the reaction rate dies rapidly. Most common environmental microorganisms have “optimum” temperatures for growth somewhere in the 20° to 50° C (68° to 122° F) range. [8]

For heterogeneous reactions, particularly those involving one or more solid phases, the reaction is dependent on parameters other than simple concentration, temperature, and pressure. Of particular importance is the surface area of the solid phase. Kinetically, the surface area of a solid phase is proportional to its activity. An increase in surface area increases not only the area for reaction to occur, but also the area for removal of undesirable products. At low temperatures and pressures, and relatively high concentrations of reactants, the rate of precipitation of mackinawite and pyrite is far higher than the rate of crystallization. Therefore, extremely fine-grained products ensue, with enormous surface areas. This is particularly important with regard to mackinawite, which can undergo two further reactions: the equilibration to pyrrhotite and the reaction with more sulfide to form greigite. In a second reference, Rickard states that ferrous sulfide is a second order influence on reaction rate of oxidation. It means that if the surface area doubles the rate increases four times. [13]

As indicated above, water and relative humidity are also strong influences in reaction rate of oxidation of iron sulfides.

This reaction rate information specifically discounts the former belief that only the pyrrhotite form of iron sulfide is responsible for auto-ignition. [9] It appears that any of the iron sulfides, under the right conditions can auto-ignite.

2.4 CHEMICAL INDICATORS

Laboratory tests suggest that the type of iron sulfide minerals may be used as indicators of the physico-chemical conditions prevailing in the environment at the time of their formation. However, since the fundamental requirements for their formation may be satisfied in a variety of ways, the use of these minerals for this purpose is subject to a number of limitations.

The presence of mackinawite, for example, indicates low temperature and neutral to alkaline conditions in the environment at the time of its formation. If mackinawite is exposed to more acid pH values or higher temperatures, it reacts to form greigite or pyrrhotite. However, the presence of mackinawite discloses nothing about the nature of the reactant iron salt, and only indicates that polysulfides, or more oxidized sulfur species, were not available for reaction.

Smythite indicates low temperature conditions at the time of its formation. Its occurrence also implies that, at some stage, siderite (FeCO_3) was present in the system, either as a distinct mineral or as a transitory phase in the replacement of another rhombohedral carbonate.

Since the formation of greigite seems to be dependent upon the prior presence of mackinawite, it can be assumed that before greigite formation, the conditions were favorable for the production of mackinawite. However, since greigite can form from mackinawite at an acid pH at low temperatures or at higher pH values at slightly higher temperatures, its use as an environmental indicator is limited. The magnetic property of greigite is an indicator of its presence.

The formation of marcasite instead of pyrite demonstrates that the system must have contained a pre-existing iron sulfide, and that sulfur was available. It is probable that more acidic conditions prevailed in the environment of marcasite formation since this would encourage the formation and preservation of sulfur. However, since sulfur can exist metastably under a variety of pH conditions, the presence of marcasite is inconclusive proof of the prevalence of acidic conditions.

Pyrite and pyrrhotite form under such a variety of physico-chemical conditions, that little information can be gained from their presence apart from the obvious conclusion that the conditions were not suitable for the formation or preservation of the other sulfide minerals.

2.5 MICROBIAL INFLUENCED CORROSION AS SOURCE AND INDICATOR

The activities of microbes found in piping and geologic structures are known to produce iron sulfides and pipe corrosion. Although this mechanism can occur on either the interior or exterior of a buried pipe, this investigation concentrates on the interior corrosion aspect. The most common microbes to be found in gas pipelines that can produce iron sulfides are: (1) sulfate reducing bacteria such as *Desulfovibrio desulfuricans*, and (2) acid producing bacteria such as *Clostridium*. [8, 9] The viability of microbes to corrode piping interior surfaces depends upon the same source materials as sulfide chemical corrosion, that is, water and iron. Furthermore, the microbes depend upon short-chain volatile fatty acids (VFA) as a nutrient source. These are nearly always found where water exists in a closed piping environment.

The products of microbial corrosion are the same components that can be found in a pipeline with no microbial activity; these are hydrogen sulfide and several of the various iron sulfides. Once these compounds are present in a pipeline from any source, it is no longer possible to identify chemically the mechanism from which they may have been derived. Some sources [9, 10] suggest that certain of the sulfides, mackinawite, smythite, or greigite, may be indicators of MIC activity. Other work, however, points out that these same compounds can be generated from purely abiotic processes. [1, 7]

There are, however, some materials and conditions to be found in a gas pipeline that can indicate the presence of MIC. Short-chain volatile fatty acids found in water in piping systems are an indicator that microbes could survive. The very presence of water is another strong contributor to the likelihood of MIC. An unexplained increase in the normal level of hydrogen sulfide could indicate the creation of additional amounts by MIC. These should not normally be measurable because the hydrogen sulfide has the preference to react to become iron sulfides in a very short time frame. Pits in the pipe or the presence of biofilm or corrosion mounds are definite evidence of MIC activity. The presence of sulfides is only an indication of corrosion,

but is none the less a warning that investigation or action is warranted. The presence of iron *oxides* is not counter-indicative of MIC activity or of hydrogen sulfide corrosion. More than likely, they indicate that a sulfide has been exposed to air, either in the pipe environment, or in the sampling or testing processes. [8, 10]

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3. TASK 2. PIPELINE BLACK POWER SAMPLE ANALYSIS

Samples of black powder were accepted from field sites for analysis under this project. Samples 1 through 3 were recycled from the first year project and fourteen new samples were added. The materials were subjected to several procedures including:

1. Radiation Monitoring;
2. Biological Testing;
3. Solvent Extraction;
4. X-Ray Diffraction (XRD); and
5. Energy Dispersive Spectroscopy (EDS).

3.1 RECEIPT OF SAMPLES

The samples, numbered sequentially, can be seen in the as-received condition in Figures 1 and 2. After receipt, the samples were immediately transferred to a glove box under a reduced nitrogen atmosphere to prevent any potential oxidization after opening. All samples visually appeared to be a dark brown to blackish-colored viscous slurry. A strong unpleasant odor, suggestive of hydrogen sulfide or sulfur, was detected during subsequent handling of the samples and packing materials. No evidence of pyrophoric activity was observed during handling.

3.2 RADIATION MONITORING

All of the samples examined were first monitored for residual radiation with a portable radiation meter within 5 cm prior to opening, and again after opening. No indication of intrinsic radiation above background was observed in any of the samples.

3.3 MICROBIOLOGICAL TESTING

Specimens were collected from each sample for microbiological testing using aseptic techniques to minimize the chances of contamination from normal skin flora and from sample collection, manipulation, and airborne sources.

All specimens were examined for the presence of microorganisms using standard laboratory protocols *i.e.*, wet mounts Gram's Stain and culture. Cultures were set up using selective and general purpose media suitable for aerobes, anaerobes, and fungi. While some organisms could be characterized as "rapid growers", many of the organisms are known to be slow growers. For example, certain organisms, such as *Bacillus* species, which are found in soil, may be isolated from culture after only 24 to 72 hours incubation. But Sulfate Reducing Bacteria (SRBs) and many other anaerobes and some fungi require up to 30 days incubation before visible evidence of growth may be detected.

In order to enhance the recovery of microorganisms that may have been present and viable, different nutrient sources (media) were used to encourage the growth and isolation of these suspected organisms. A variety of enriched, selective, and differential media utilized for inoculation for sample aliquots is listed as follows:

- Thiobacillus ferrooxidans broth – to recover Iron-Related Bacteria (IRB);

- Methanobacterium broth – to recover anaerobic, fastidious methanogens;
- Peptone Yeast Glucose broth (PYG) – to recover acid producing bacteria such as clostridia (APB);
- Modified Baar’s broth – to recover sulfate reducing bacteria;
- Anaerobic Brucella blood agar plates – to recover other anaerobic bacteria;
- Tryptic Soy broth (TSB) with 5% sheep blood agar plates – to recover aerobic bacteria; and
- Sabaroud Dextrose Agar – to recover fungi.

All sampling and subsequent culture handling was conducted using aseptic technique in a Class II Biosafety Cabinet. Fluid specimens for examination were thoroughly mixed and sampled from the bottom through the top layers. Solid samples were mixed; clumps were broken up and representative samples were taken using sterile phosphate buffered saline as a diluent. Media inoculation was accomplished using a well vortexed, approximately 1:20 dilution for each sample. All specimens were prepared, stained using Gram’s Stain, and examined under a standard light microscope using 100×, 400×, and 1000× magnifications to aid in the visual detection of microorganisms. In addition, all specimens were subject to wet mount examination using 100× and 400× magnification. All specimens were inoculated into the media specified above and incubated beyond 30 days at 30° C ± 1° C under anaerobic and aerobic conditions, as indicated by media choice.

A *Bacillus* species was recovered from Sample #1. This organism was successfully subcultured in the laboratory. This organism is most likely a contaminant, since *Bacillus* species are ubiquitous and are often found in water sources. Their spores are often airborne. Of note: these bacteria produce organic acids as metabolic byproducts. Some *Bacillus* species use a sulfate reducing pathway for respiration.

A filamentous bacterium resembling an actinomycete was observed from Sample #3. However, the organism was not successfully subcultured despite repeated sampling from Sample #3.

A *Penicillium* species mold was recovered from Sample 17. Because this particular fungal species grew at approximately 22 days incubation, it is most likely a contaminant. Positive indications in methanogen broth cultures were positive for growth. From the selective nature of this broth, the inability to successfully obtain growth on any other media besides the methanogen broth, appear to confirm the presence of Methanogenic species.

3.4 SOLVENT EXTRACTION

During examinations of the first three samples in the first year effort, solvent extraction methods were avoided in an attempt to minimized potential oxidation of the inorganic solids, based upon the assumption that the samples would become less viscous when exposed to oxygen. However, results of the first year efforts were indeterminate, with mostly amorphous results in XRD analyses of the samples. [1] XRD curves were generally amorphous indicating little long range crystallographic order. This amorphous nature is possibly attributed to the high content of organic compounds (estimated to be in the range of 70 – 75%), based upon thermal gravimetric testing results.

In the second year effort, the samples were subjected to solvent extractions. In order to choose appropriate solvents, several samples were examined with Fourier Transform Infrared Spectroscopy (FTIR). In analyses of Samples 2, 4, 5, 6, and 14, hydrocarbons mixed with varying amounts of water were discerned (see Figures 3 through 11) Sample 2 contained a spectrum of a dry hydrocarbon (paraffinic), whereas Samples 4, 5, and 6 appear to be the same paraffinic substance partially diluted in water. Some olefinic (*i.e.*, hydrocarbon with double bonded carbons) character was observed in Sample 6, but it was mostly obscured by water (water possesses three fundamental vibrations at 3300-3400 cm⁻¹ for OH stretching (symmetric and asymmetric) and a bending vibration near 1650 cm⁻¹).

Based on the FTIR testing results, a 0.5 g specimen was collected from each sample and the solvent 1, 2 dichlorobenzene was added to remove any organic constituents in the solid inorganic material. The extraction was performed in a scintillation vial, where mechanical agitation was provided by handshaking and with the use of a vortex mixer. The mixtures then underwent vacuum filtration, leaving the desired solid material on 6 micron filter paper. This process was repeated several times until the extraction of organic contaminants was completed. The remnant inorganic solids were then sealed in glass vials.

3.5 VISUAL AND MAGNETIC EXAMINATIONS OF THE SOLVENT EXTRACTED SOLIDS

The remnant solvent extracted solids were visually examined to determine their coloration, based upon visual judgment. The solvent extracted solids were mostly dark brown to brownish black in color, and the results are summarized in Table 3-1. The solvent extracted solids for each sample can be seen in Figures 3-12 through 3-28.

The remnant inorganic solids were also tested for ferromagnetism with a piece of steel. The ferromagnetic testing results were varied and are summarized in Table 3-1. All of the samples exhibited at least some magnetic properties.

3.6 ENERGY DISPERSIVE SPECTROSCOPY (EDS)

Solvent extracted portions of the samples were examined with EDS, the results of which can be seen in Figures 3-29 through 3-45, and are summarized in Table 3-1. Strong indications of sulfur were observed in Samples 3, 4, 5, 6, 8, 9, 10, 12, 13, 14, 15, and 16. There were strong indications of sulfur and iron in Samples 3, 4, 5, 6, 7, 9, 10, 12, and 13. Stronger indications of iron relative to generally lower levels of sulfur were observed in 2, 11, 14, and 16. Notable indications of silicon were observed in Samples 1, 3, 5, 6, 11, 14, 15, and 16. High levels of carbon, possibly suggestive of an incomplete extraction of organics or of chemical bonding with iron, were observed in Samples 2, 3, 6, 7, 8, 9, 10, 11, 12, and 13. Varying lesser amounts of phosphorous, sodium, calcium, chlorine, and titanium were observed in all of the spectra.

Table 3-1. Summary of Testing Results

Sample Number	Microbiological Testing Results	Visual Appearance of Solvent Extracted Solids	Ferro-magnetic	EDS Analysis Results	XRD Analysis Results
1	A bacillus attributed to contamination	Dark brown	Weakly	Iron, silicon, aluminum, oxygen, potassium, sulfur, chlorine, titanium, manganese	Sulfur, quartz, magnetite, siderite
2	Negative results	Dark brown	Weakly	Iron, oxygen, sulfur, silicon, chlorine, calcium, manganese	Sulfur, siderite, graffonite, sulfur, and noise suggestive of amorphous short range ordering
3	An unknown filamentous bacterium was observed but could not be cultured		Moderately	Sulfur, iron, oxygen, phosphorous, silicon, chlorine, sodium, calcium, manganese	Amorphous, with no apparent long-range order
4	Negative results	Reddish brown	Strongly	Sulfur, iron, oxygen, chlorine, silicon, sodium, calcium, manganese	Sulfur
5	Negative results	Dark brown	Strongly	Iron, sulfur, oxygen, silicon, calcium, chlorine, manganese	Sulfur, magnetite, and noise suggestive of amorphous short-range ordering
6	Negative results	Brownish black	Strongly	Oxygen, sulfur, iron, silicon, chlorine, calcium, manganese	Magnetite, sulfur, and noise suggestive of amorphous short-range ordering
7	Negative results	Dark brown	Insufficient material	Sulfur, iron, oxygen, sodium, silicon, chlorine, calcium	Insufficient material available for analysis
8	Negative results	Dark brown with an oily appearance	Insufficient material	Sulfur, iron, oxygen, sodium, silicon, chlorine, calcium	Sulfur, siderite

Sample Number	Microbiological Testing Results	Visual Appearance of Solvent Extracted Solids	Ferro-magnetic	EDS Analysis Results	XRD Analysis Results
9	Negative results	Dark brown with an oily appearance	Insufficient material	Sulfur, iron, oxygen, chlorine, sodium, silicon, calcium, manganese	Insufficient material available for analysis
10	Negative results	Brownish black with an oily appearance	Weakly	Iron, sulfur, oxygen, chlorine, sodium, silicon, calcium, manganese	Sulfur, siderite, ferroan magnesite
11	Negative results	Brownish black with an oily appearance	Weakly	Iron, oxygen, sulfur, silicon, chlorine, calcium, manganese	Sulfur and noise suggestive of amorphous short-range ordering
12	Negative results	Brownish black	Weakly	Sulfur, iron, oxygen, sodium, chlorine, silicon, phosphorous, calcium, manganese	Sulfur, siderite, magnetite
13	Negative results	Dark brown	Insufficient material	Sulfur, iron, oxygen, sodium, silicon, chlorine, calcium, manganese	Insufficient material available for analysis
14	Negative results	Dark brown	Strongly	Silicon, iron, aluminum, oxygen, potassium, calcium, titanium, manganese, magnesium	Magnetite and noise suggestive of amorphous short-range ordering
15	Negative results	Reddish brown	Strongly	Sulfur, iron, phosphorous, oxygen, silicon, sodium, chlorine, calcium, manganese	Ferrous magnesite, siderite, quartz, crystalline sulfur
16	Negative results	Dark brown	Strongly	Silicon, iron, oxygen aluminum, potassium, calcium, titanium, manganese, magnesium	Quartz, sulfur, magnetite, siderite

Sample Number	Microbiological Testing Results	Visual Appearance of Solvent Extracted Solids	Ferro-magnetic	EDS Analysis Results	XRD Analysis Results
17	Methanogens were successfully cultured, a Penicillium mold was observed as a likely contaminant	Dark brown	Weakly	Iron, oxygen, sulfur, Calcium, Silicon	Siderite, goethite, sulfur

3.7 X-RAY DIFFRACTION ANALYSIS (XRD)

Samples for XRD analyses were ground with a mortar and pestle, placed on a polymer tray under commercially available petroleum jelly, and were examined with a Siemens Kristalloflex 805 X-Ray Diffractometer. The samples were run at a rate of 10 seconds per 2-Theta step from 10° to 60° using a copper gamma source. Attempts at using a chromium source were unsuccessful due to equipment issues. The x-ray diffraction spectral results can be seen in Figures 3-46 through 3- 59, and are summarized in Table 3-1. High background noise, relative to low peak heights, was observed in all of the samples examined and were more noticeable in Samples 2, 3, 5, 6, 8, 11, 12, and 14 (see Figures 3-47, 3-48, 3-50, 3-51, 3-52, 3-54, and 3-56). The background noise was suggestive of short-range ordering of the amorphous structures. The diffraction pattern of Sample 3 was observed to be completely amorphous, with no evidence of any long-range ordering, despite several repeated analysis attempts.

Indications of sulfur were observed in every sample examined except for Samples 3 and 14 (see Figures 48 and 56). Siderite (FeCO₃) and a close analog ferroan magnesite ((Fe, Mg)CO₃) were observed in all samples except 3, 4, 5, 6, 11, and 14. Indications of quartz (SiO₂) were observed in Samples 1, and 16. No evidence of a quartz peak was observed in Sample 14 that would correlate with energy dispersive spectroscopy (EDS) indications of silicon observed in that sample. Magnetite was observed in Samples 1, 5, 6, 12, 14, and 16. Graphtonite ((Fe⁺⁺, Mn, Ca)₃(PO₄)₂) was identified only in Sample 2. Goethite (FeO(OH)), possibly a remnant of steel piping heat treatment, was observed in Sample 17 only.

3.8 DISCUSSION

The objective of this work was to examine black powder slurry samples collected from gas pipelines, for the purpose of characterizing the inorganic portions and potentially verify the presence of iron-sulfur compounds.

During examinations of the first three samples in the first year effort, solvent extraction methods were avoided in an attempt to minimize potential oxidation of the inorganic solids, based upon the assumption that the viscous nature of the samples would minimize through oxidation. However, results of the first year efforts were indeterminate, with mostly amorphous results in XRD analyses of the samples. XRD curves were generally amorphous indicating little

long-range crystallographic order, hypothesized at the time to be due to the high organics content estimated to be in the range of 70 to 75%, based upon thermal gravimetric testing results.

Solvent extraction methods were employed in the second year effort to isolate the inorganic solids in Samples 1 through 3 and in subsequent Samples 4 through 17. In the process of identifying appropriate solvents to use, FTIR analyses were performed on five of the samples. Olefinic and paraffinic compounds associated with water were identified.

After successful solvent extractions, iron and sulfur were observed in EDS results of every sample examined. X-ray diffraction results were again indeterminate in regards to the detection of iron sulfides explored in the literature assessment. In most of the samples, x-ray diffraction results appeared to offer crystallographic correlations of iron and sulfur in the form of elemental sulfur, magnetite, and siderite (FeCO_3 and $(\text{Fe, Mg})\text{CO}_3$). Crystalline forms associated with iron could not be identified in Samples, 3, 4, and 11. Sample 3 was found to be completely amorphous, indicating no long-range crystalline order, though some indications of magnetite were determined in an FTIR analysis of the solvent extracted solids (see Figure 3-60).

Background noise, also suggestive of amorphous phases, was observed in all of the samples examined, but was more noticeable in Samples 8, 10, 12, 15, and 16, in association with siderite and elemental sulfur. The background noise could be the result of variability in the crystalline phases of elemental sulfur or to the presence of iron-sulfur compounds with variable crystalline morphologies. More than 30 allotropes of elemental sulfur have been documented, with the most common allotropes being S_6 , S_7 , and S_8 . [2] A truly amorphous form of sulfur has been documented due to rapid cooling. [3] Several iron-sulfur compounds discussed in the literature search, including mackinawite and pyrrhotite, are non-stoichiometric and lacking long range order will frequently appear amorphous.

Siderite was observed in numerous samples and has been associated with the formation of smythite via sulphidation. Smythite was not observed in any of the samples examined. Magnetite, observed in most samples, could have been the end product of oxidation of prior iron sulphides, and the absence of pyrophoric activity would appear to confirm this. The cause of the oxidation cannot be pinpointed but may include oxidation within the pipe stream or oxidation after sample removal and shipping, despite sampling protocol suggestions. Future sample protocol modifications will likely include suggestions for inert gas purging, as well as larger sample sizes.

Most of the microbiological testing results proved to be negative despite strenuous application of broths to culture likely microbiological species. Apparent false positives, in the form of a bacillus, an unidentified filamentous bacterium, and a penicillin mold, were observed in Samples 1, 3, and 17. However, positive indications of Methanogenic species were noted in Sample 17. Methanogenes are a primitive class of anaerobic bacteria that generate methane as a waste product.

The inability to successfully culture micro biological agents, and sulfate reducing agents in particular, is attributed to several potential causes. Water, a critical ingredient for biological growth was detected in the FTIR results of numerous samples, and was visually observed in many others. It is hypothesized that colonies were likely upstream and otherwise remote from sampling locations, or local conditions at the point of sampling were hostile to life forms (local oxidizing conditions or low pH). MIC testing is also by nature opportunistic, requiring

multiple samplings from the same system in the hope of obtaining positive results. Since active manipulation of black powder samples is already discouraged due to concerns of oxidation of the freshly exposed powders, new and possibly remote sampling techniques will have to be explored.

3.9 REFERENCES

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Figure 3-1. Samples 1 through 6 and 14 in the as-received condition.

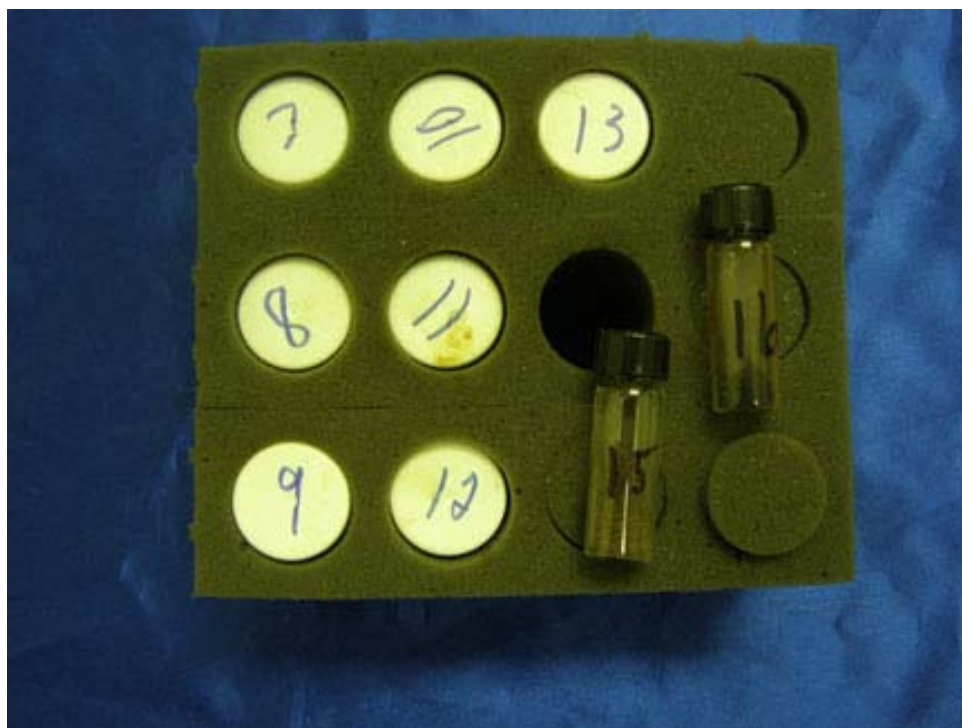


Figure 3-2. Samples 7 through 13 and samples 15 and 16 in the as-received condition.

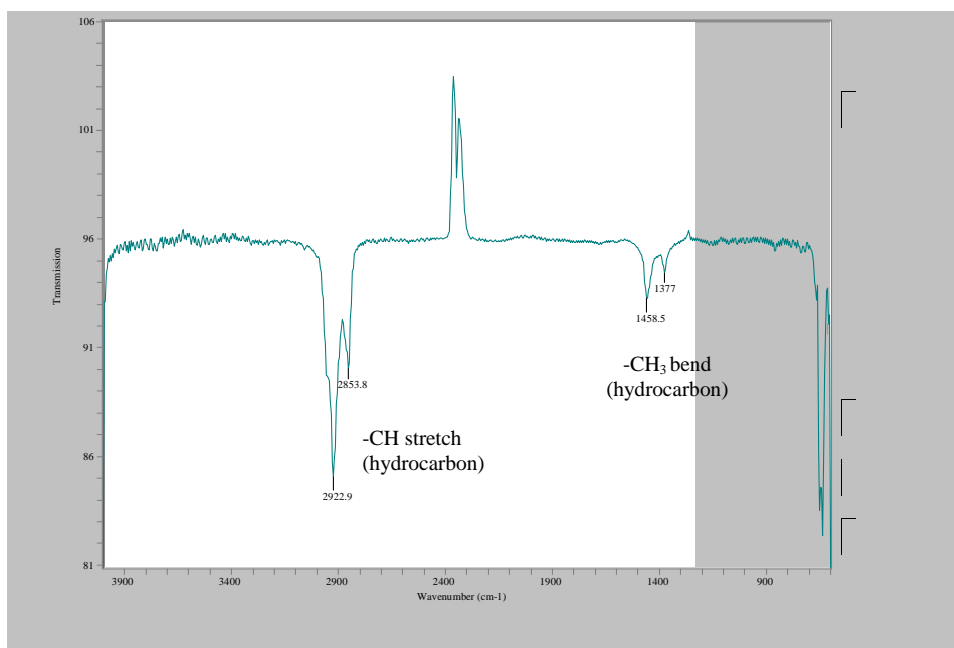


Figure 3-3. FTIR analysis results of Sample 1 showing indications of a paraffinic substance.

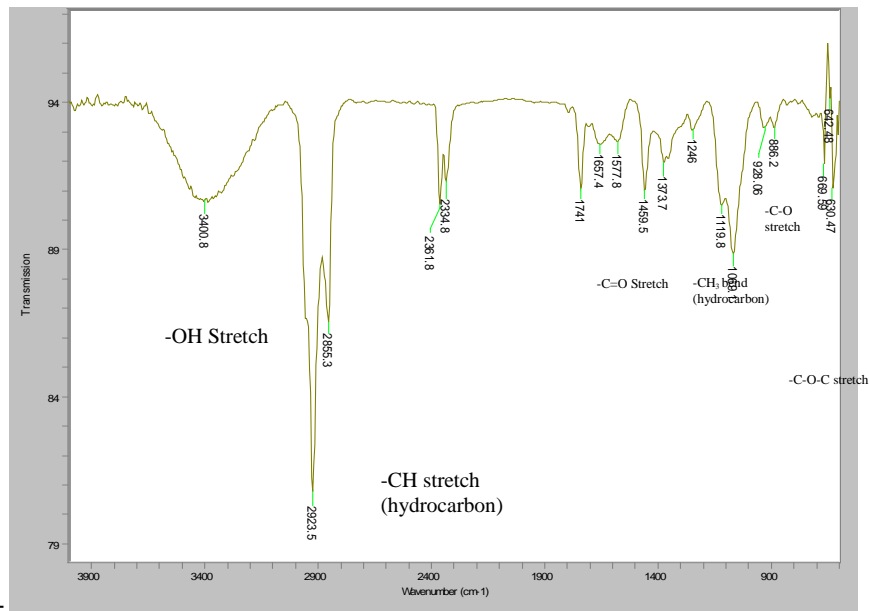


Figure 3-4. FTIR analysis results of Sample 3 showing indications of a paraffinic substance and water.

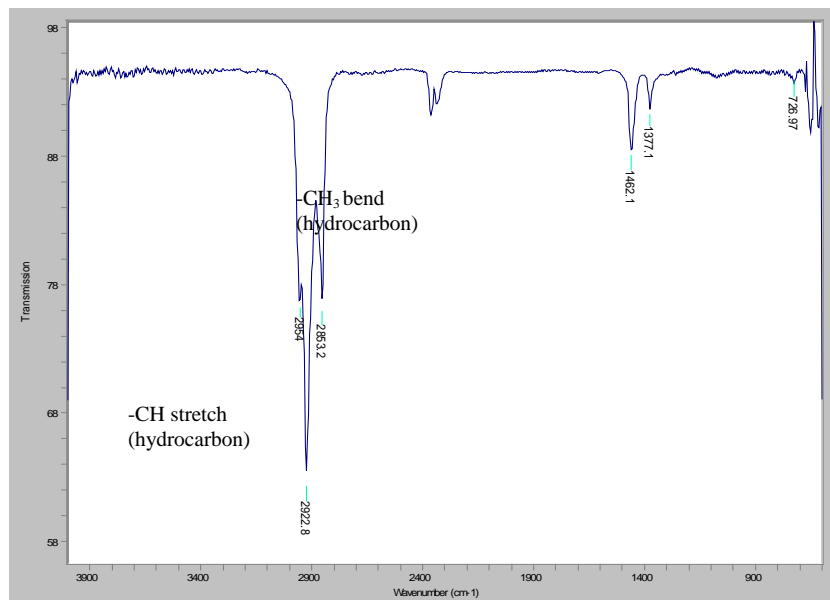


Figure 3-5. FTIR analysis results of Sample 7 showing indications of a paraffinic substance.

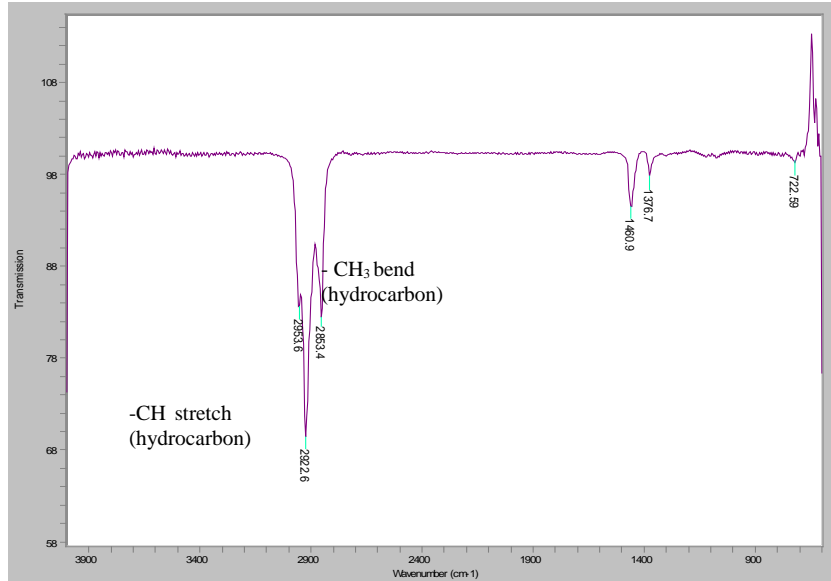


Figure 3-6. FTIR analysis results of Sample 8 showing indications of a paraffinic substance.

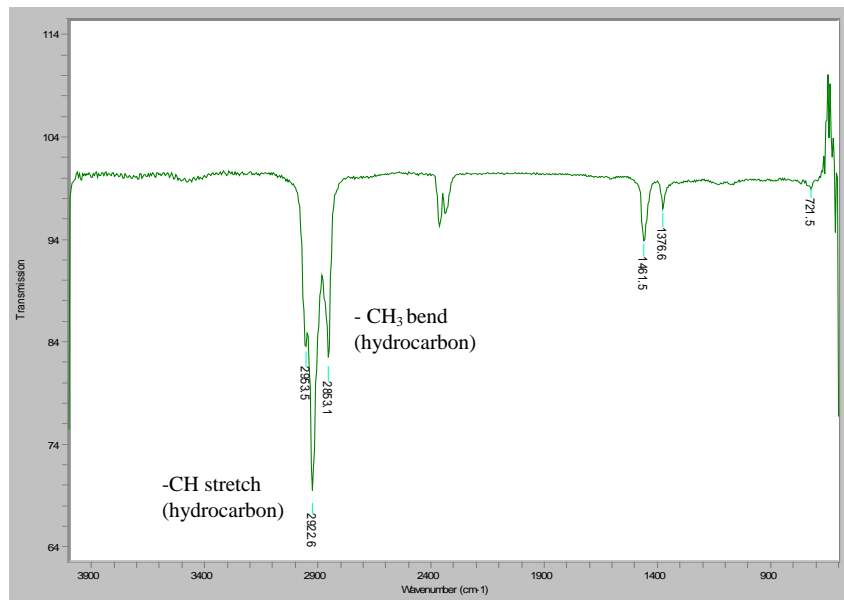


Figure 3-7. FTIR analysis results of Sample 9 showing indications of a paraffinic substance.

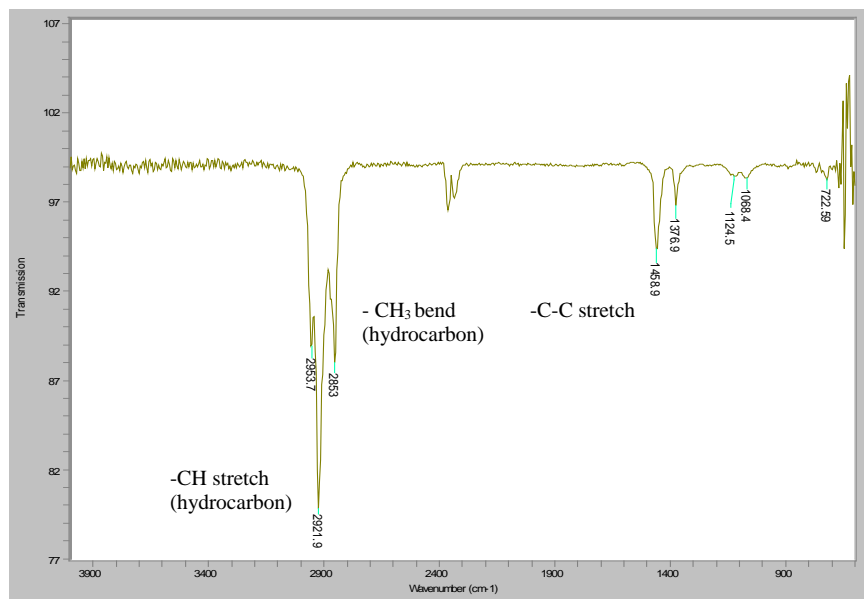


Figure 3-8. FTIR analysis results of Sample 10 showing indications of a paraffinic substance.

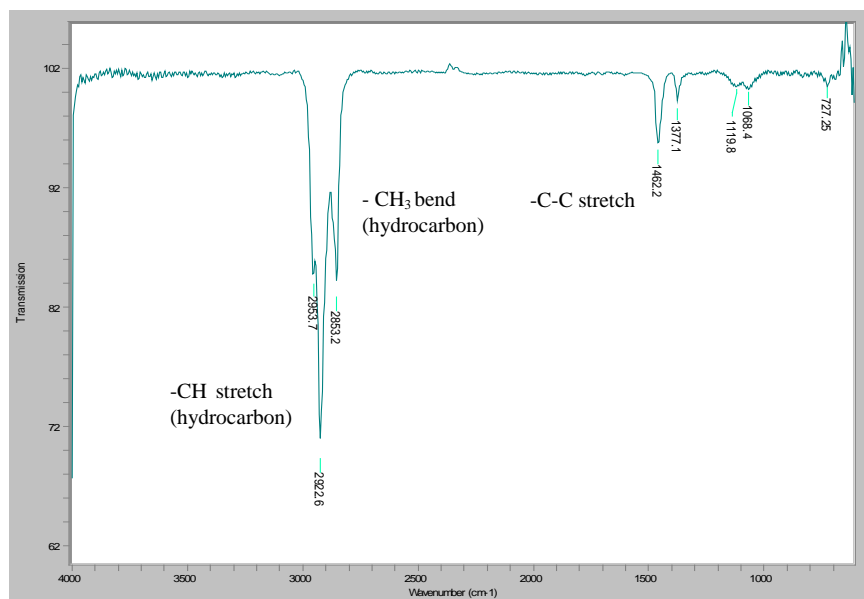


Figure 3-9. FTIR analysis results of Sample 11 showing indications of a paraffinic substance.

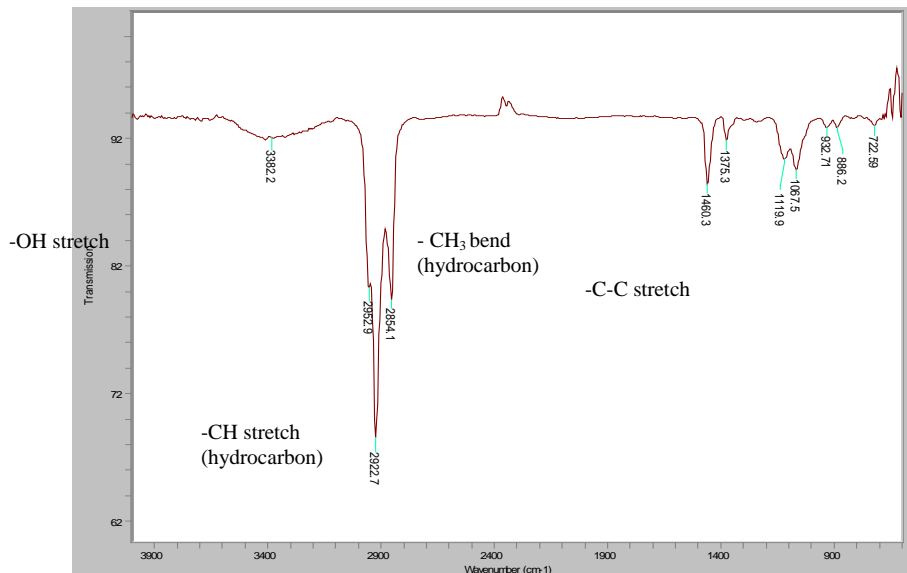


Figure 3-10. FTIR analysis results of Sample 12 showing indications of a paraffinic substance and water.

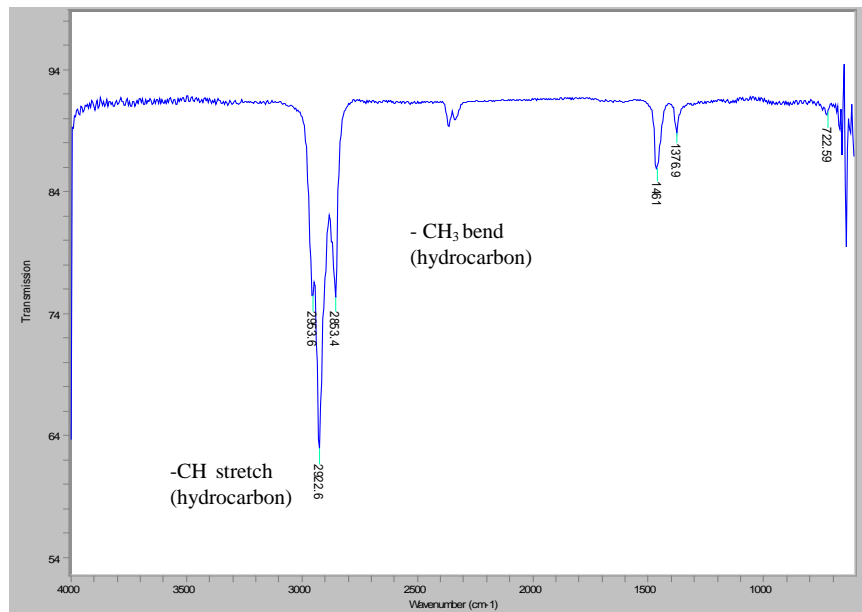


Figure 3-11. FTIR analysis results of Sample 13 showing indications of a paraffinic substance.



Figure 3-12. Photograph showing the collected solids for Sample 1, after solvent extraction and analysis.



Figure 3-13. Photograph showing the collected solids for Sample 2, after solvent extraction and analysis.

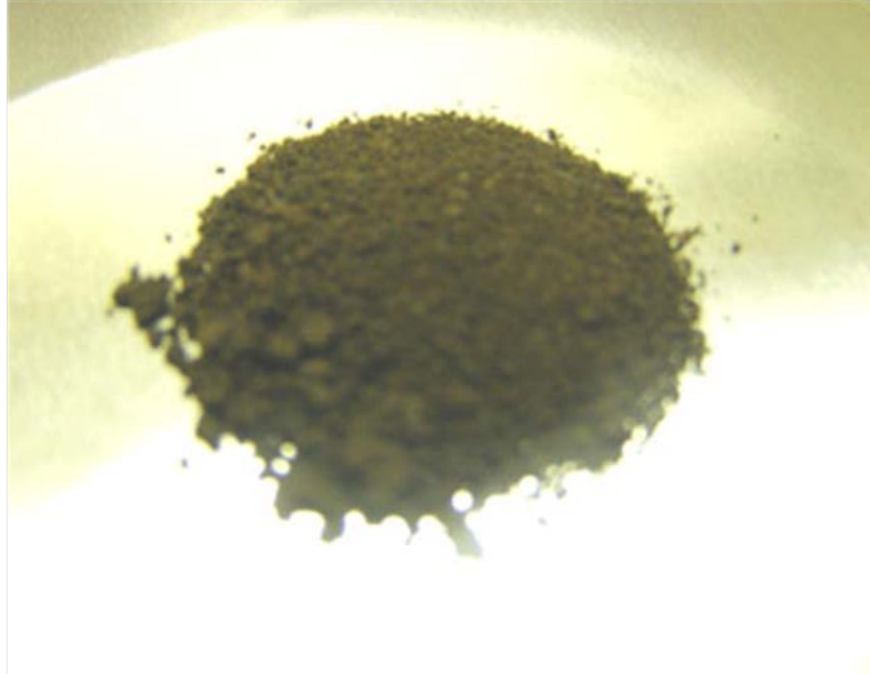


Figure 3-14. Photograph showing the collected solids for Sample 3, after solvent extraction and analysis.



Figure 3-15. Photograph showing the collected solids for Sample 4, after solvent extraction and analysis.



Figure 3-16. Photograph showing the collected solids for Sample 5, after solvent extraction and analysis.



Figure 3-17. Photograph showing the collected solids for Sample 6, after solvent extraction and analysis.



Figure 3-18. Photograph showing the collected solids for Sample 7, after solvent extraction and analysis.



Figure 3-19. Photograph showing the collected solids for Sample 8, after solvent extraction and analysis.



Figure 3-20. Photograph showing the collected solids for Sample 9, after solvent extraction and analysis.



Figure 3-21. Photograph showing the collected solids for Sample 10, after solvent extraction and analysis.

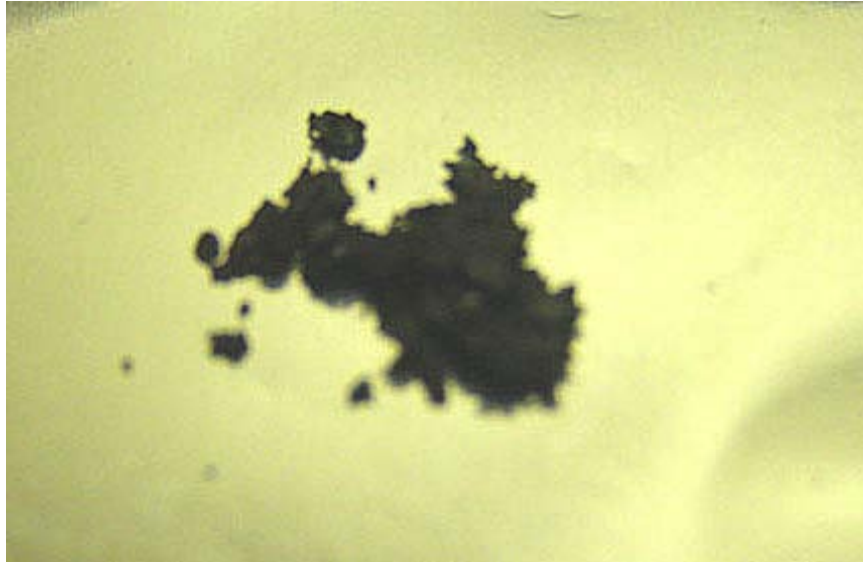


Figure 3-22. Photograph showing the collected solids for Sample 11, after solvent extraction and analysis.

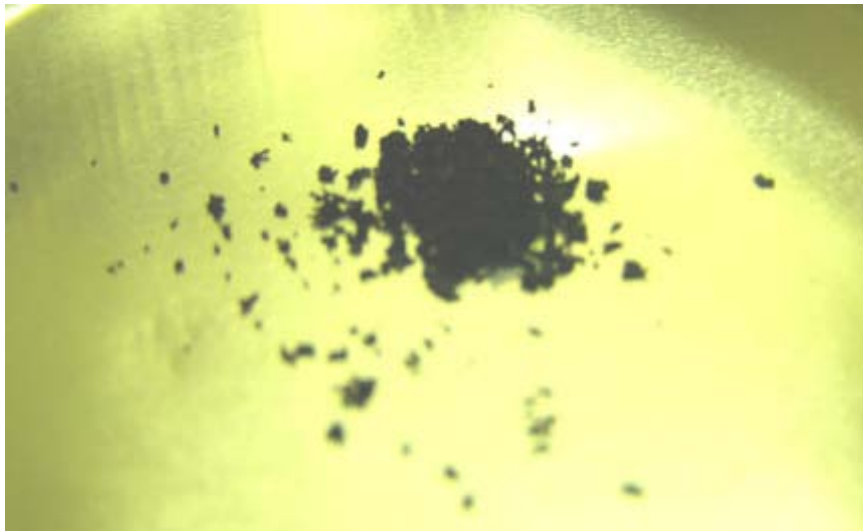


Figure 3-23. Photograph showing the collected solids for Sample 12, after solvent extraction and analysis.



Figure 3-24. Photograph showing the collected solids for Sample 13, after solvent extraction and analysis.



Figure 3-25. Photograph showing the collected solids for Sample 14, after solvent extraction and analysis.



Figure 3-26. Photograph showing the collected solids for Sample 15, after solvent extraction and analysis.

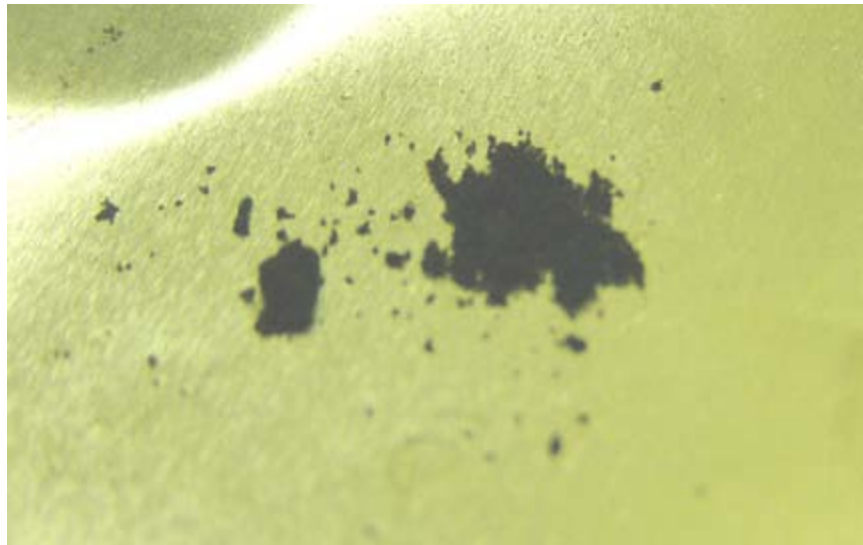


Figure 3-27. Photograph showing the collected solids for Sample 16, after solvent extraction and analysis.



Figure 3-28. Photograph showing the collected solids for Sample 17, after solvent extraction and analysis.

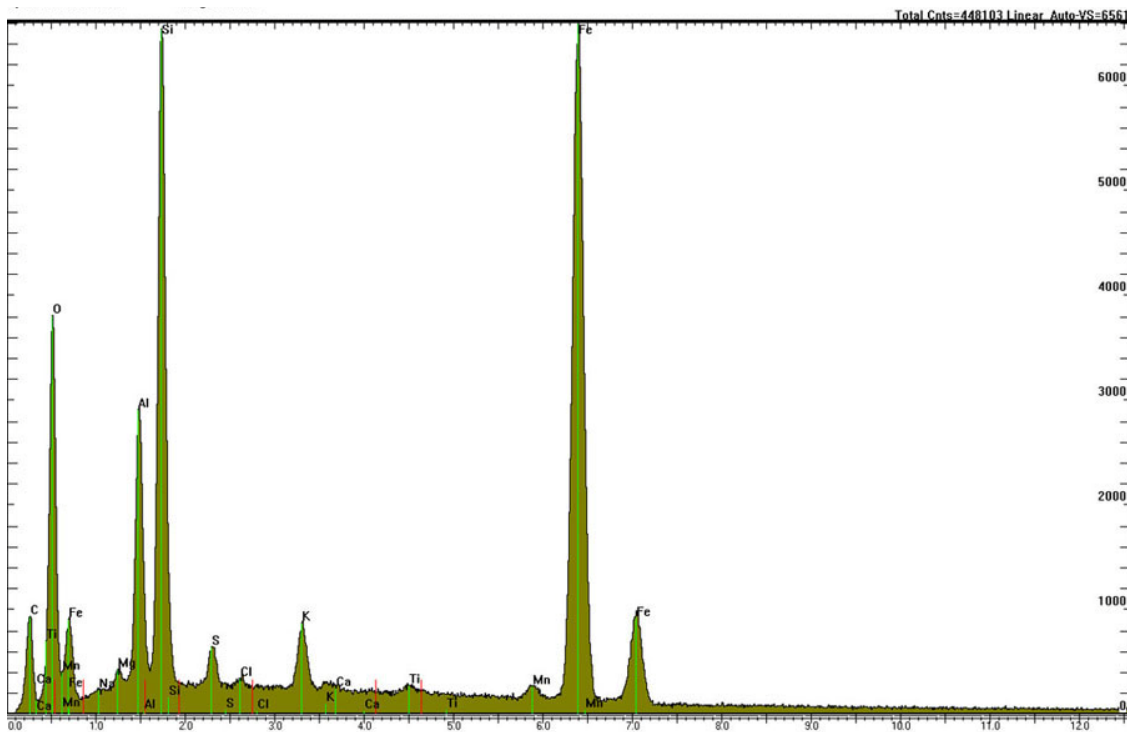


Figure 3-29. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 1.

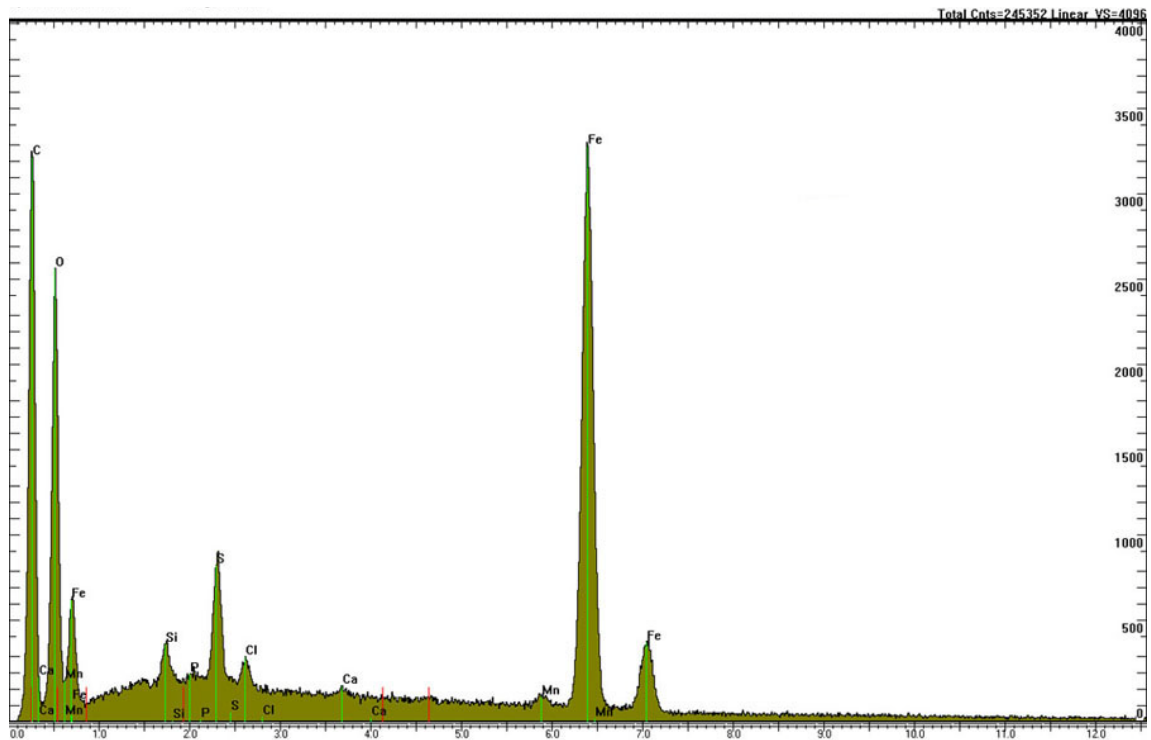


Figure 3-30. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 2.

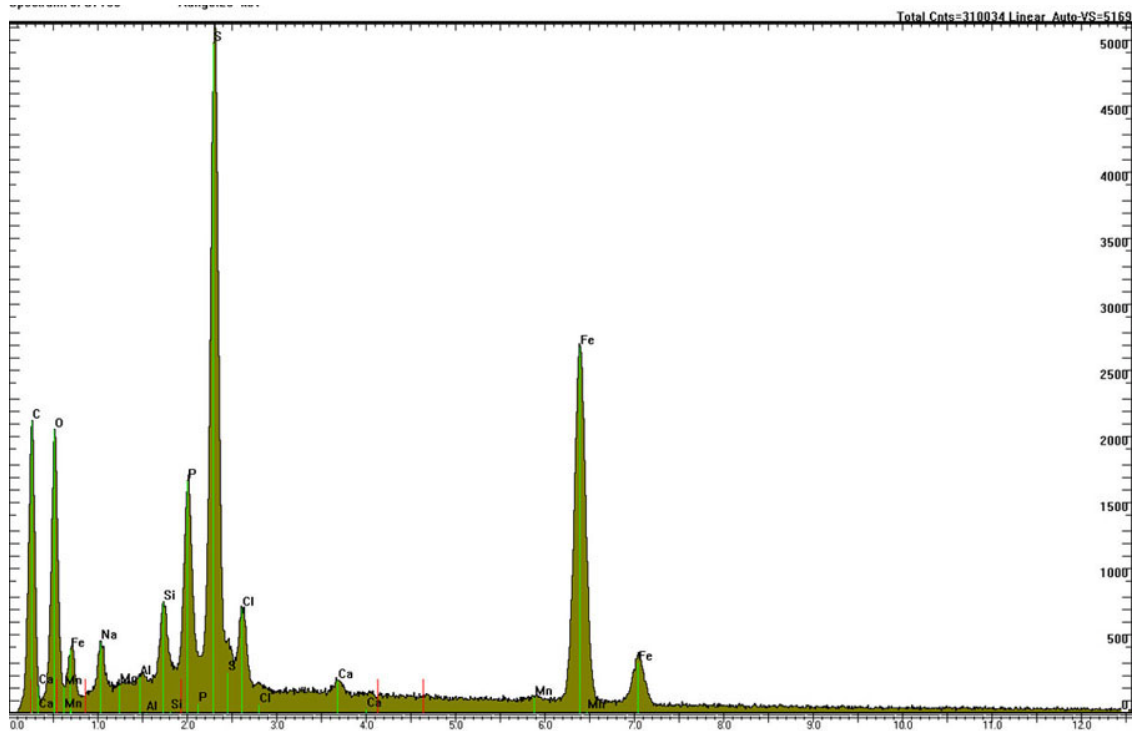


Figure 3-31. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 3.

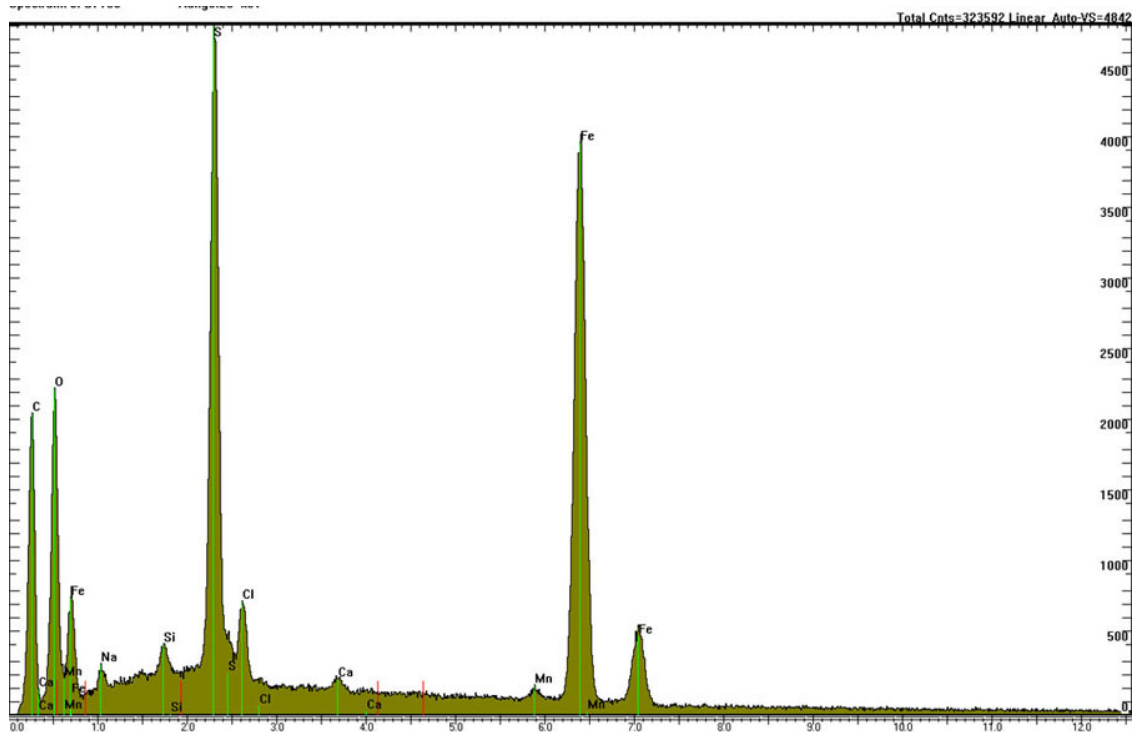


Figure 3-32. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 4.

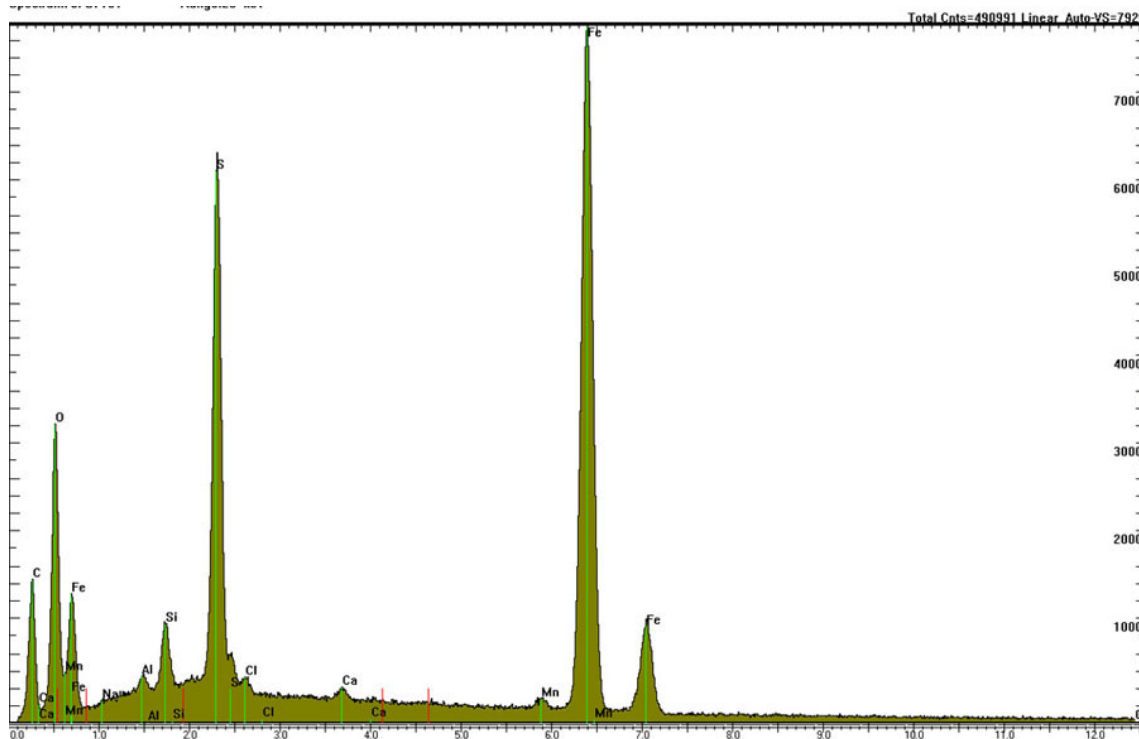


Figure 3-33. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 5.

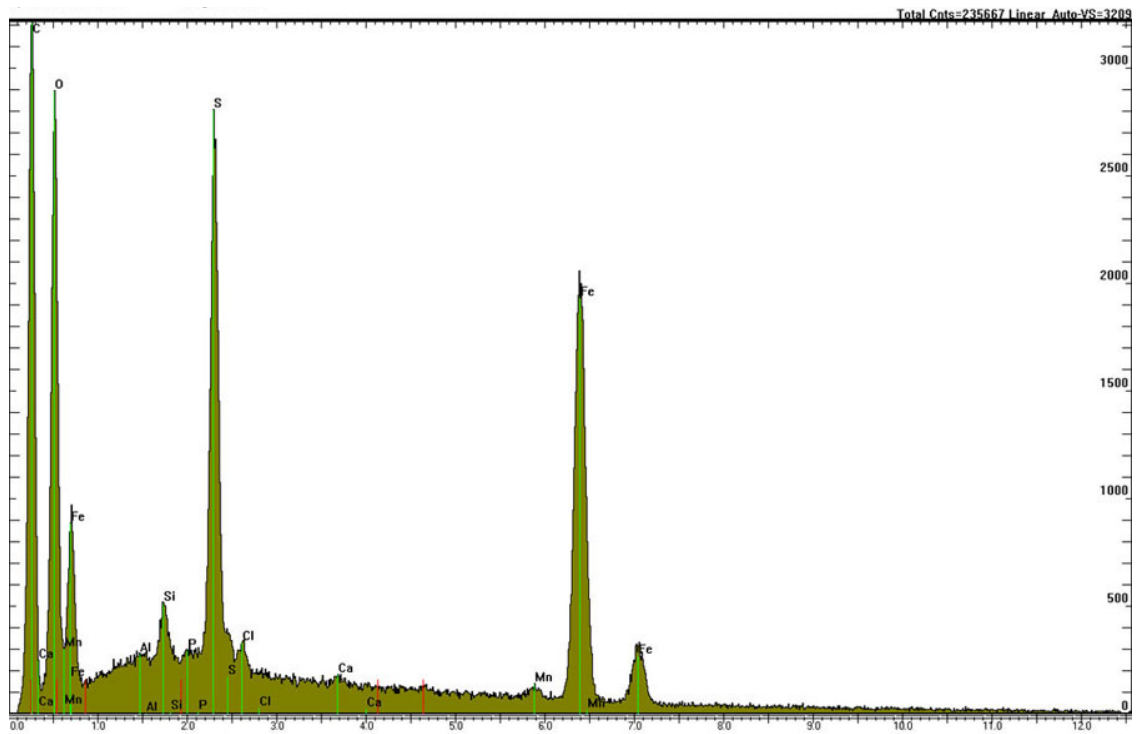


Figure 3-34. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 6.

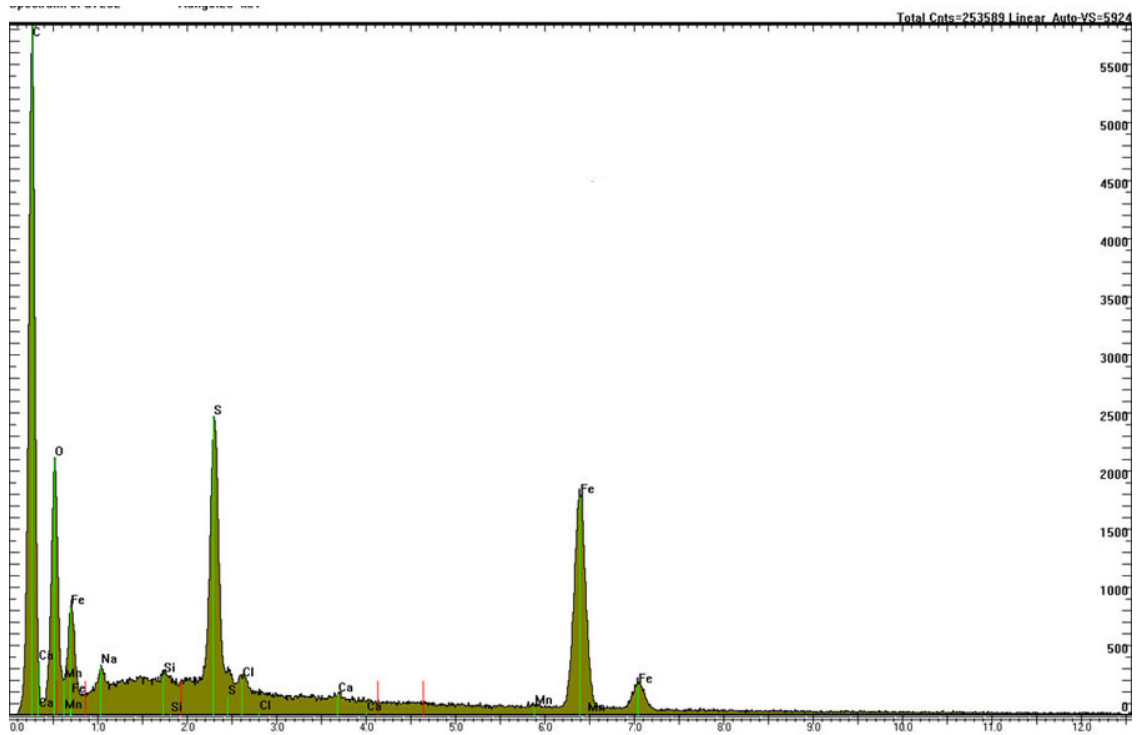


Figure 3-35. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 7.

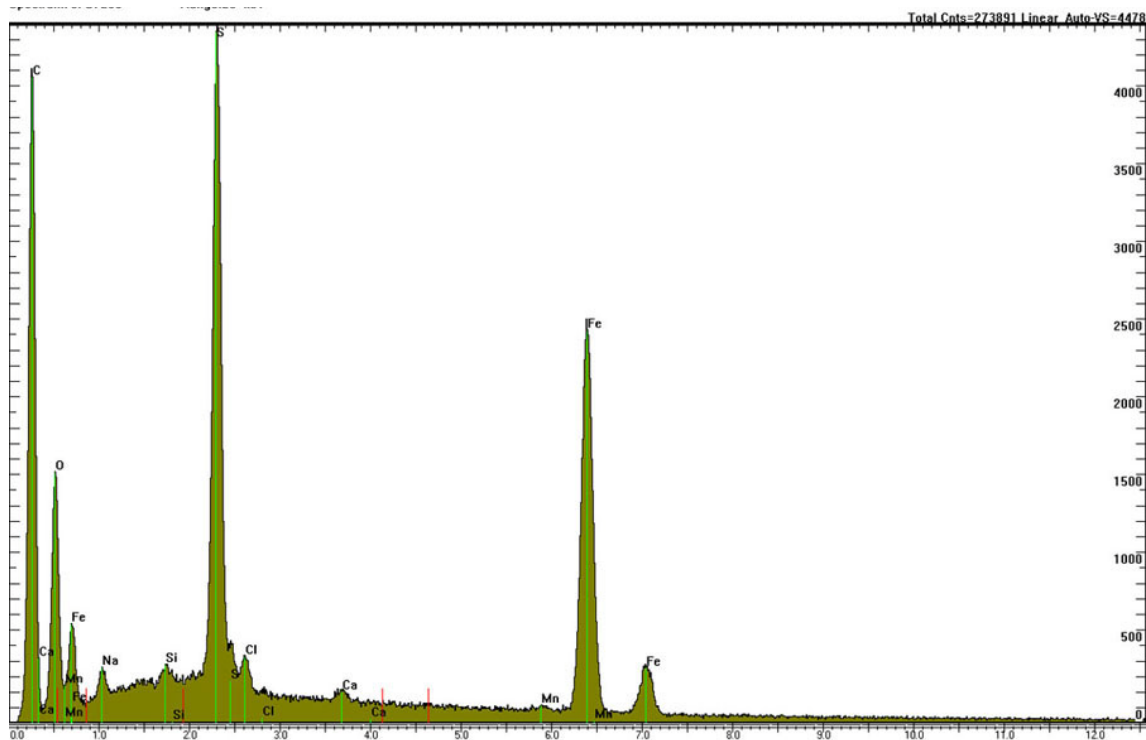


Figure 3-36. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 8.

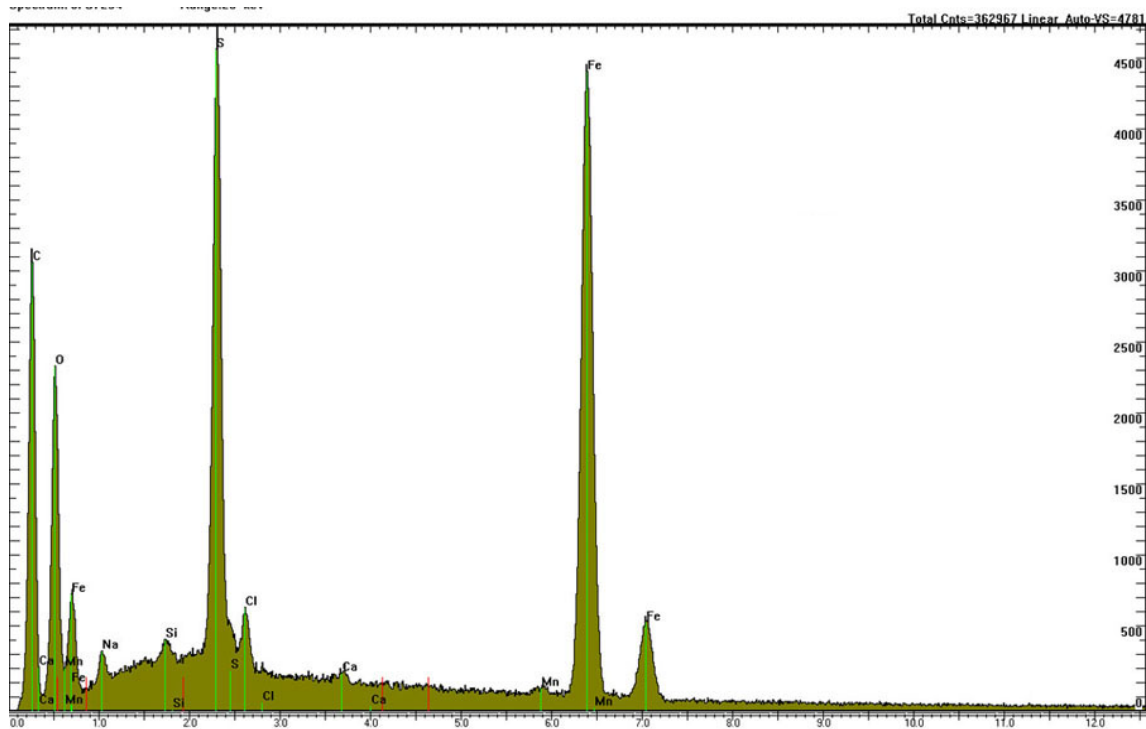


Figure 3-37. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 9.

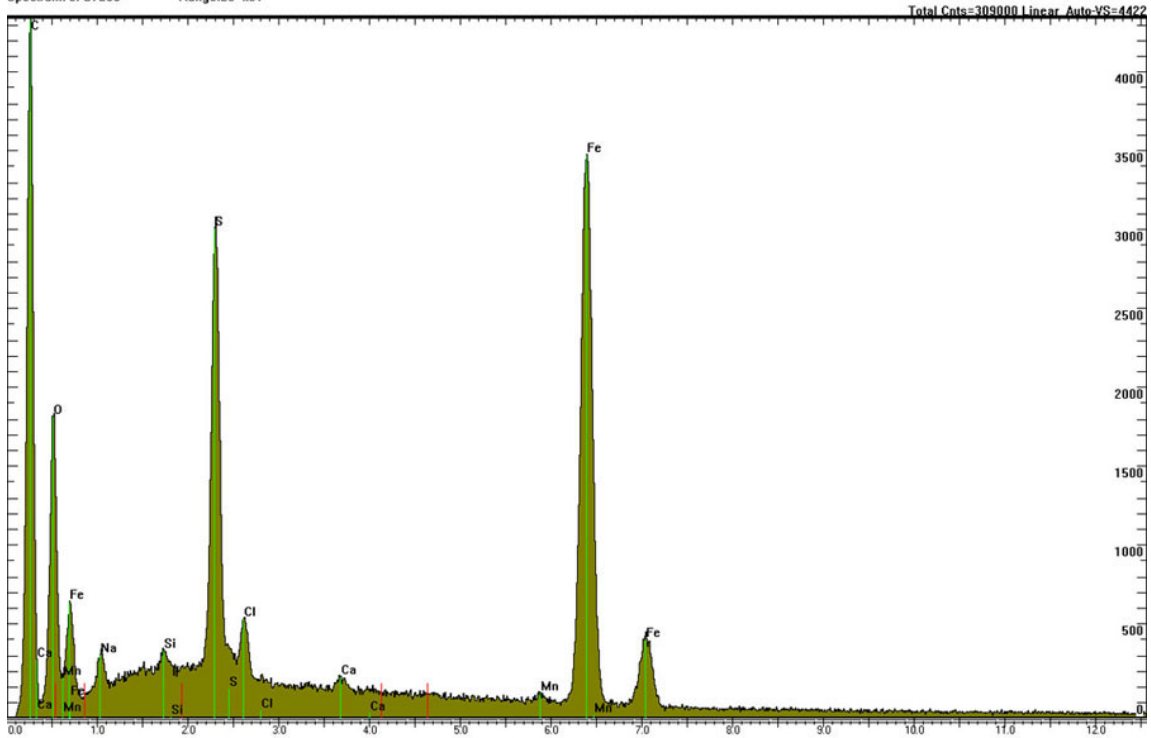


Figure 3-38. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 10.

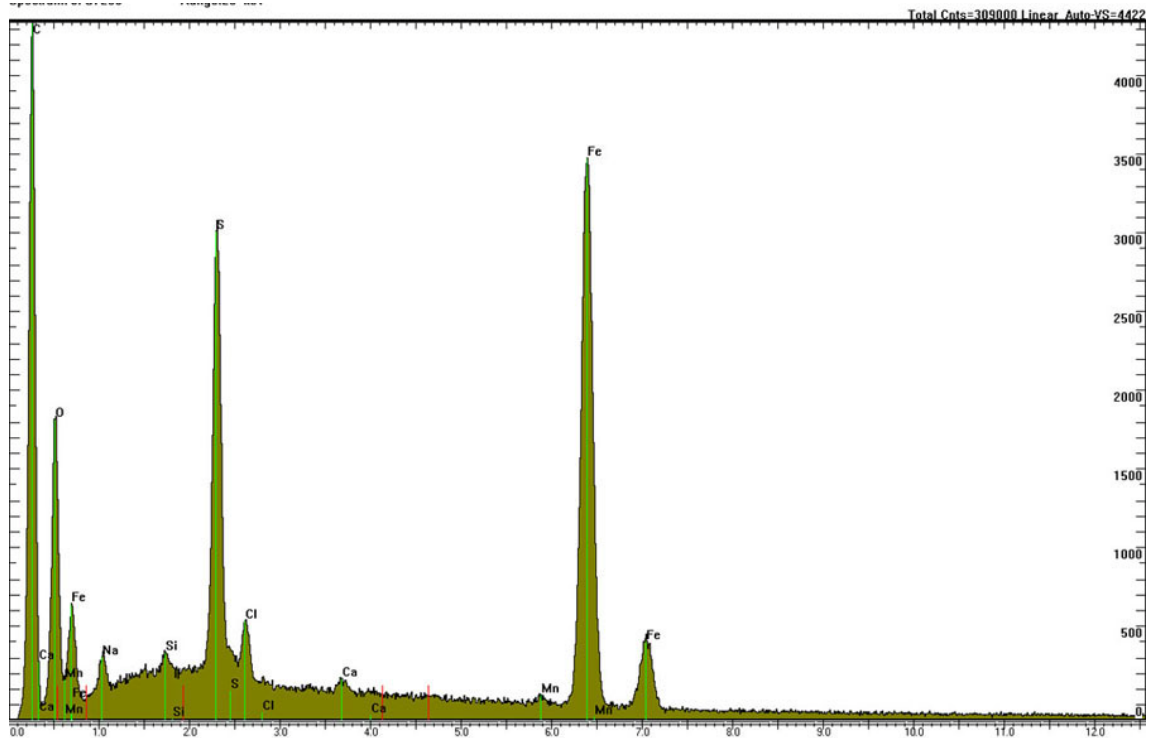


Figure 3-39. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 11.

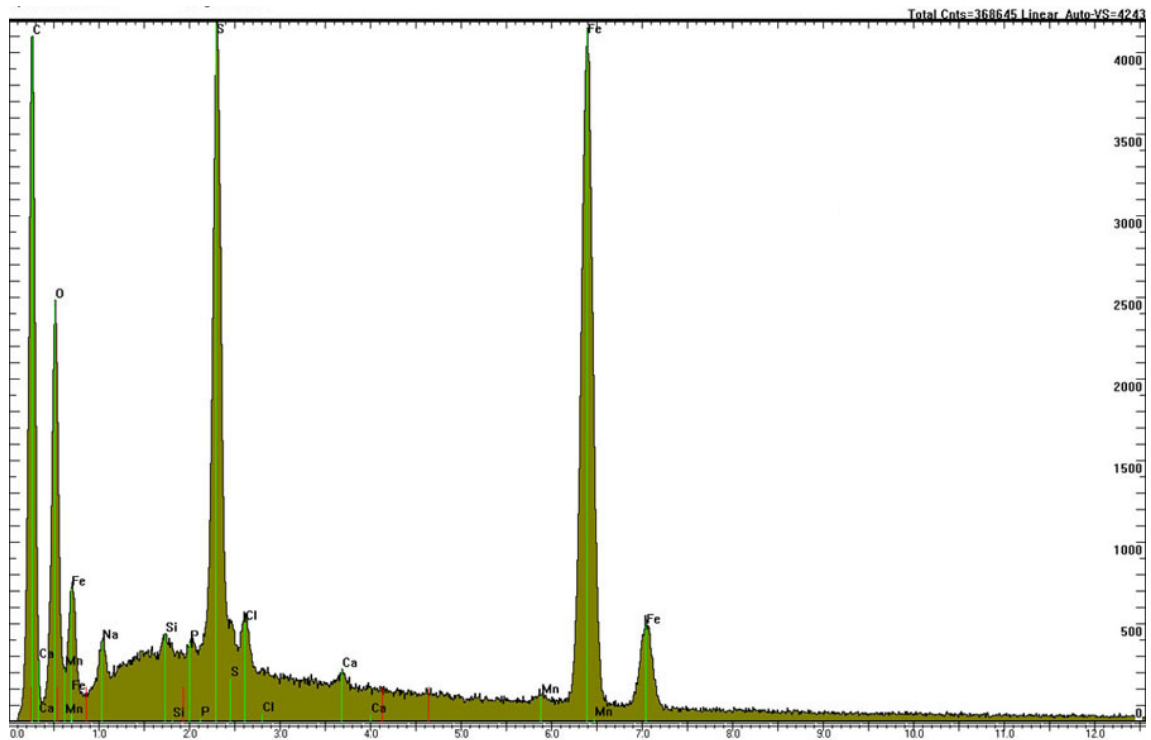


Figure 3-40. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 12.

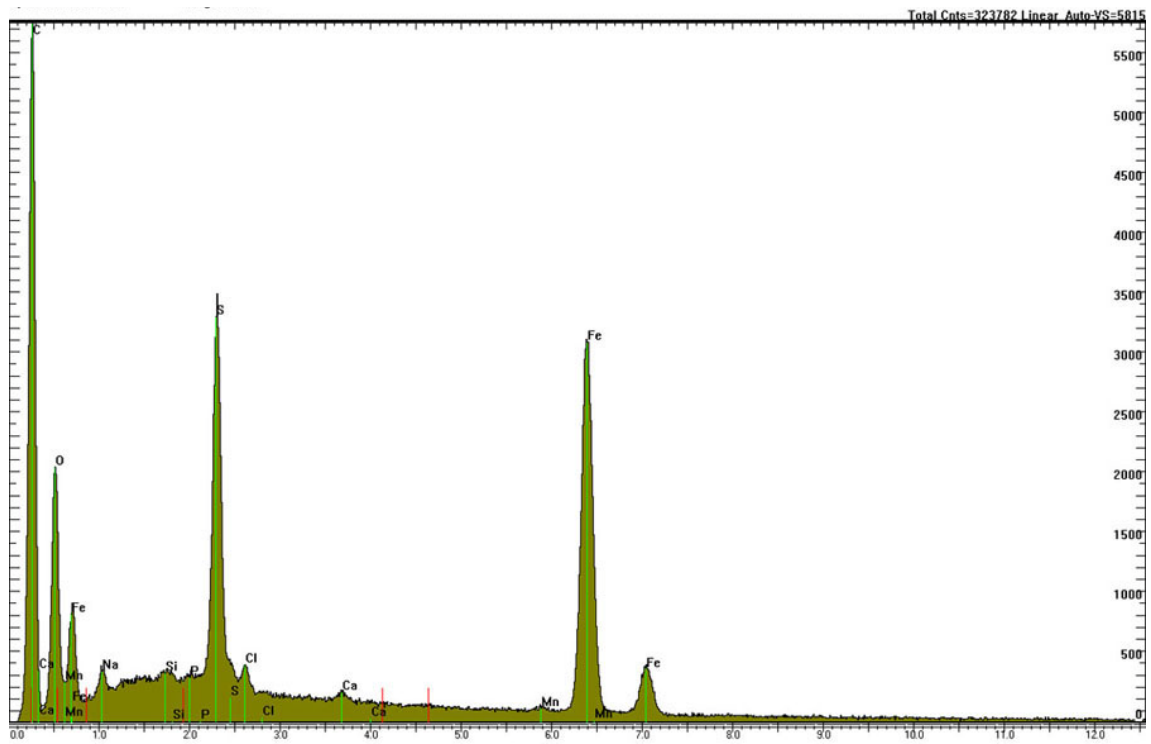


Figure 3-41. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 13.

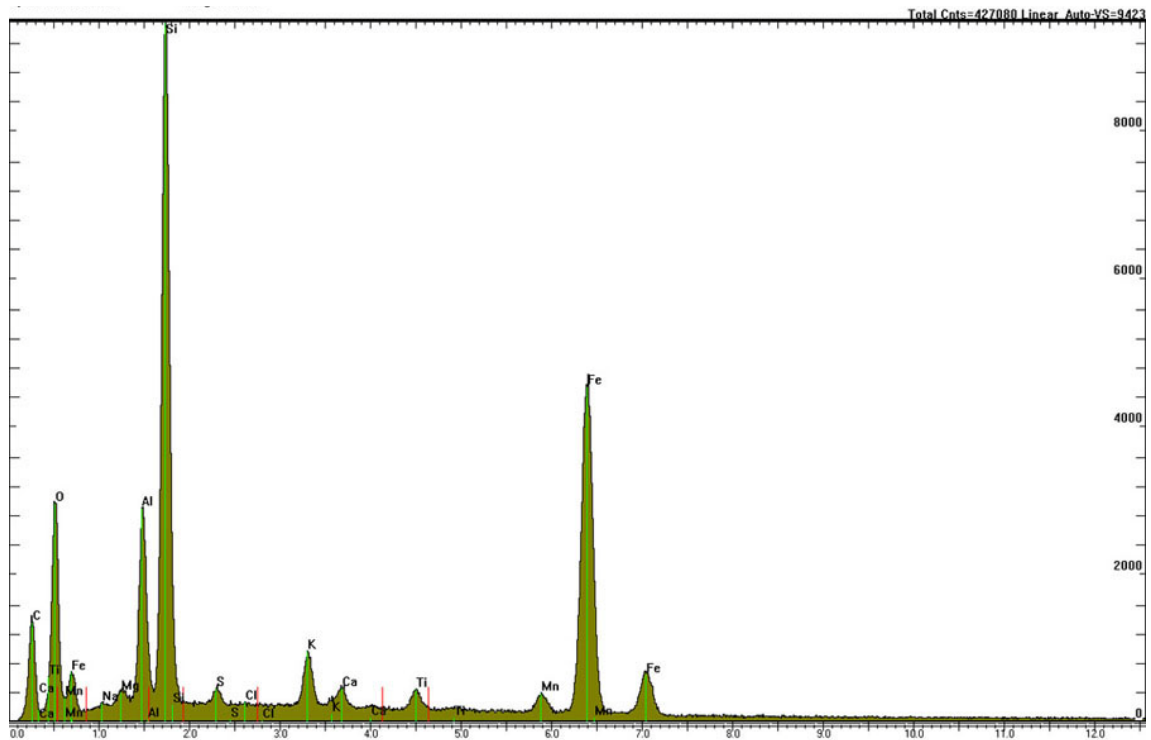


Figure 3-42. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 14.

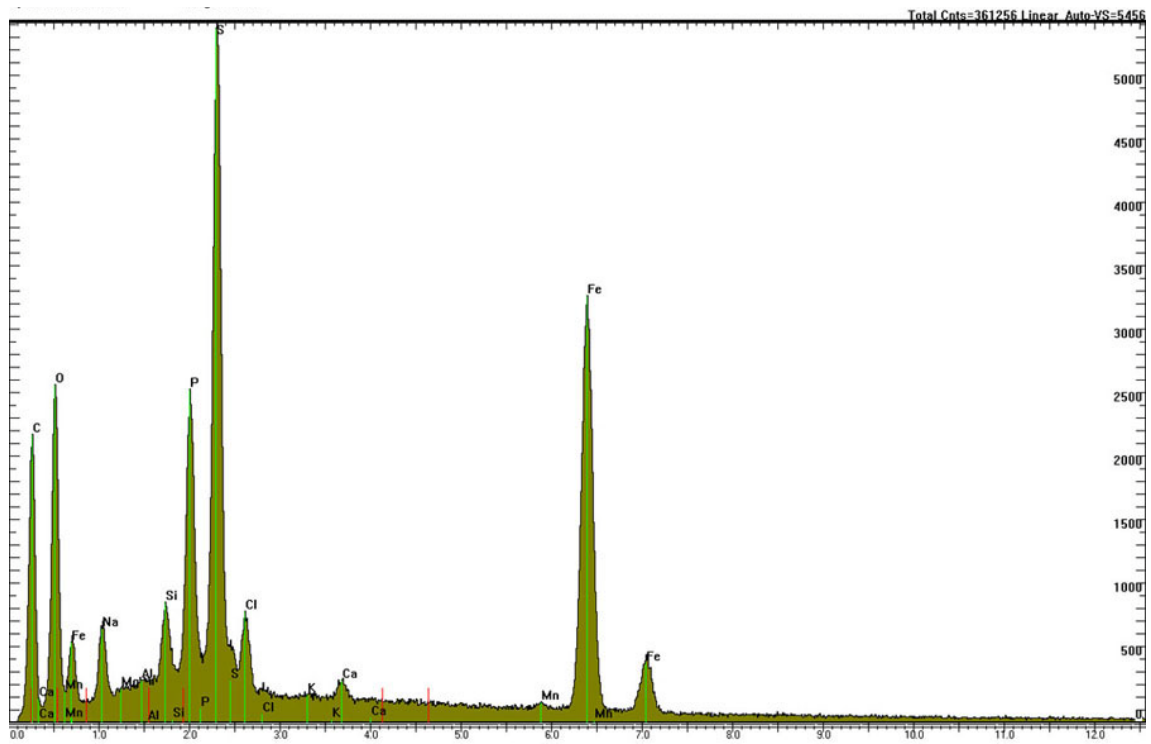


Figure 3-43. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 15.

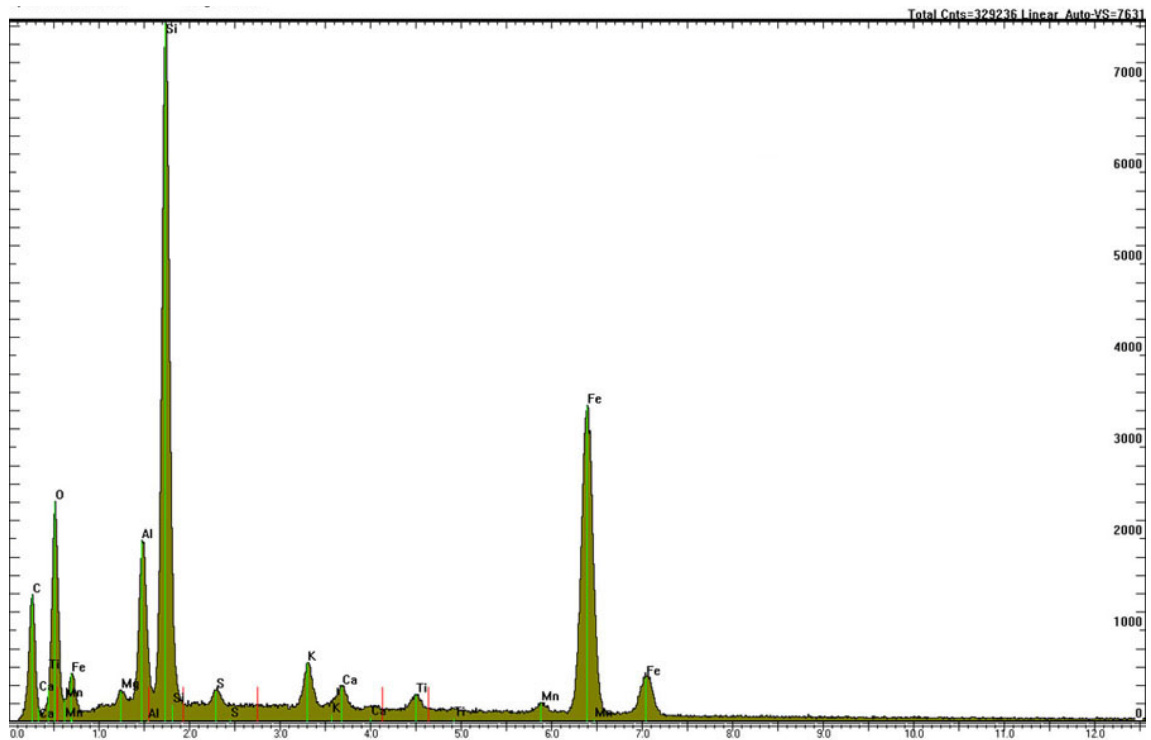


Figure 3-44. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 16.

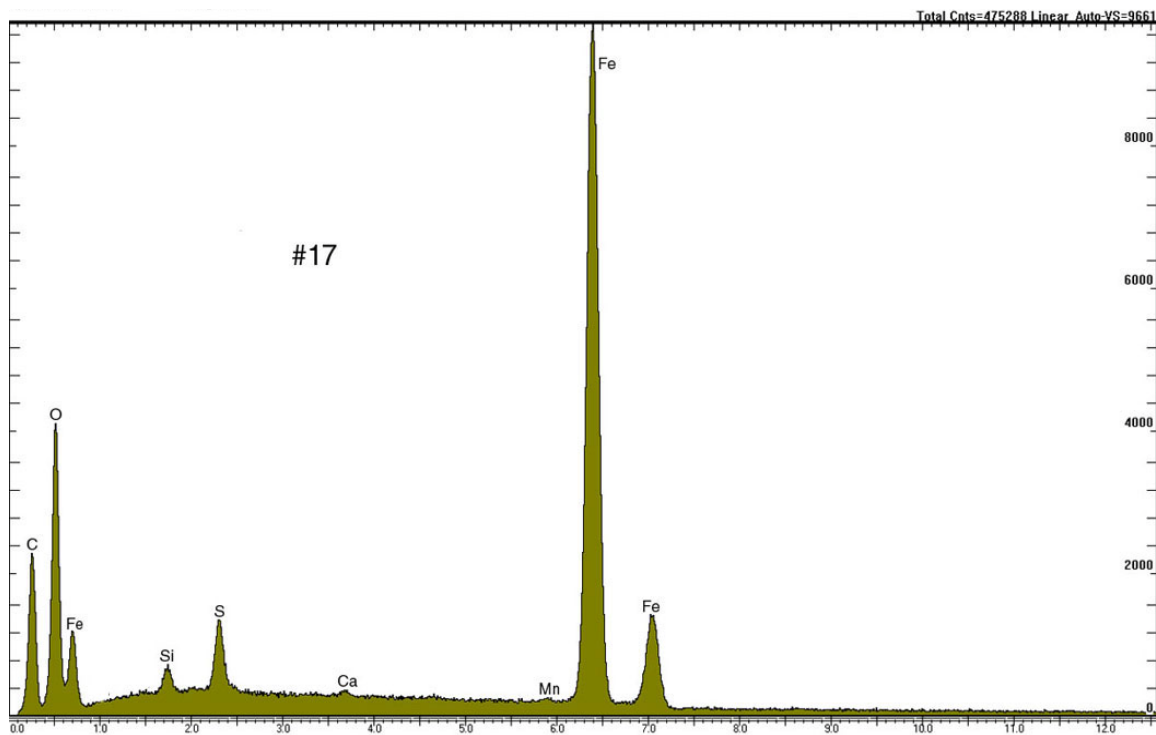


Figure 3-45. Energy dispersive x-ray spectroscopy spectrum of the solvent extracted solids from Sample 17.

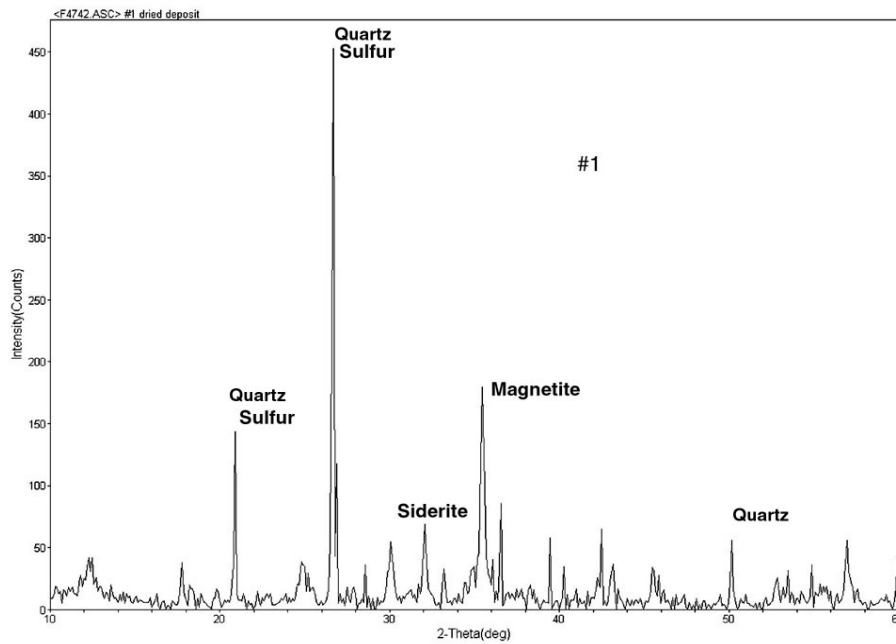


Figure 3-46. X-ray diffraction curve for Sample 1. Peaks for sulfur, quartz, and magnetite were identified.

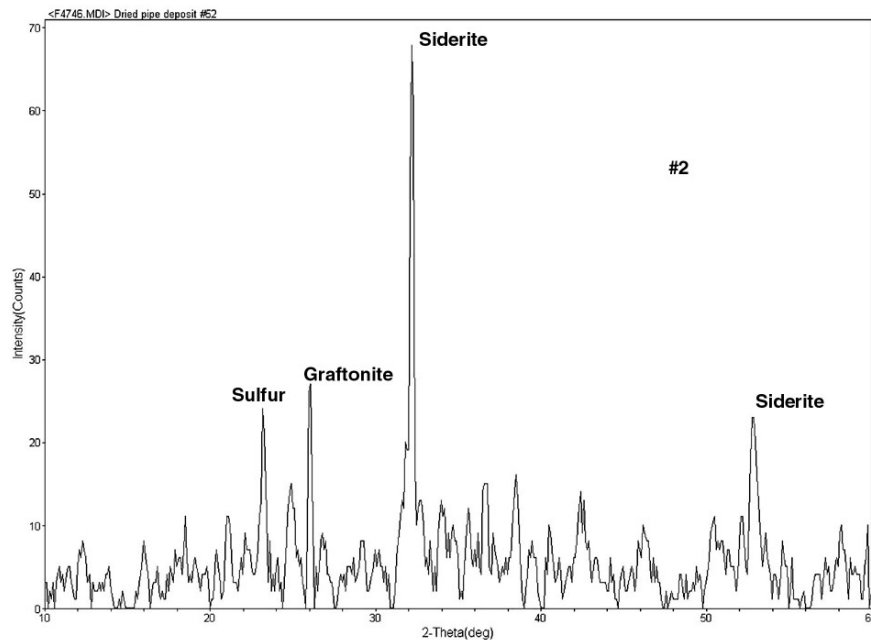


Figure 3-47. X-ray diffraction curve for Sample 2. Peaks for siderite, graftonite, and sulfur were identified. Considerable noise was observed suggestive of amorphous phases.

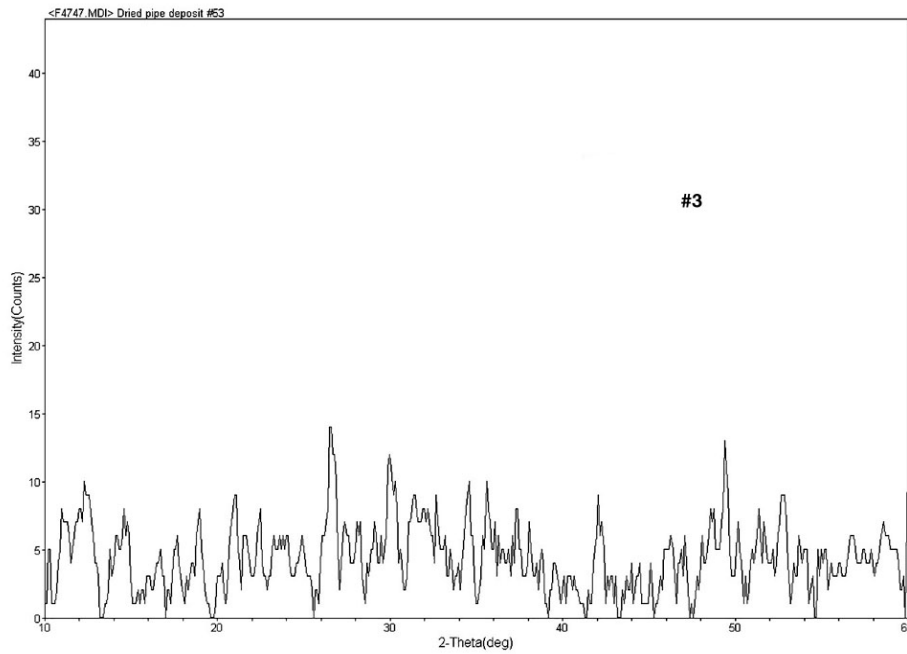


Figure 3-48. X-ray diffraction curve for Sample 3. No long-range ordering could be ascertained. The results were essentially amorphous.

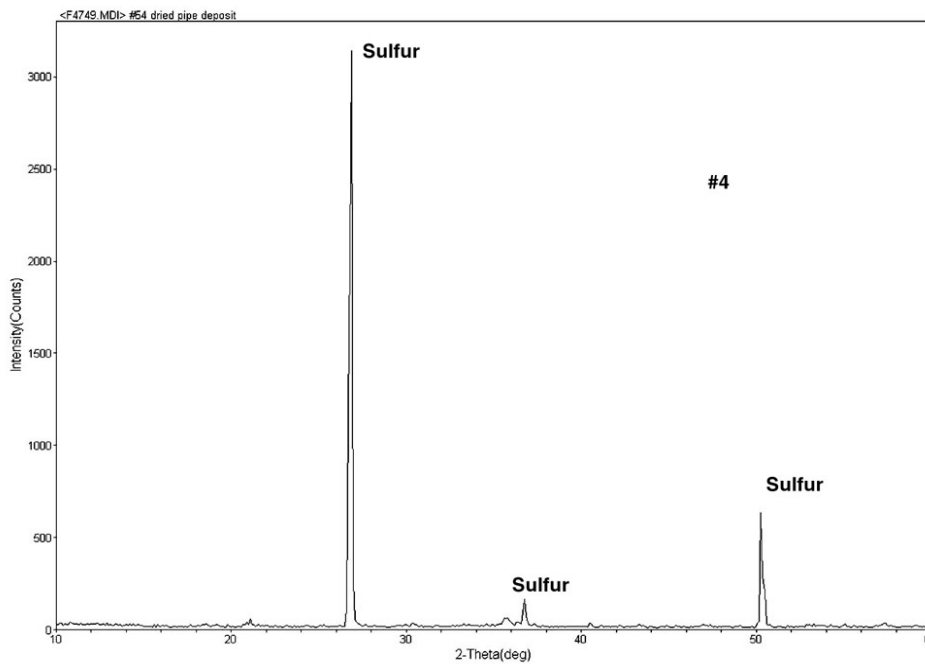


Figure 3-49. X-ray diffraction curve for Sample 4. Several peaks for sulfur were identified.

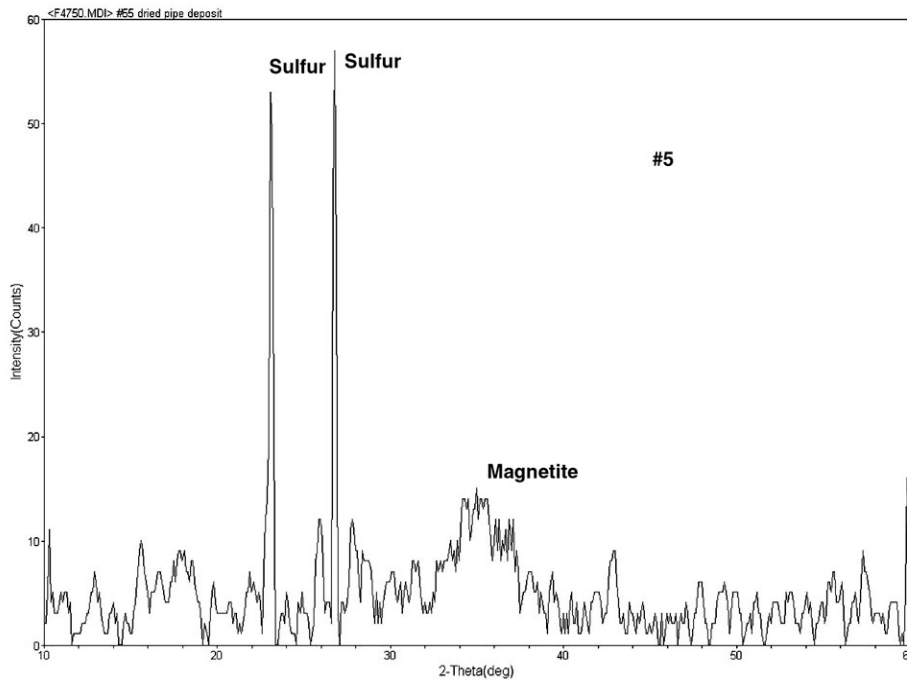


Figure 3-50. X-ray diffraction curve for Sample 5. Peaks for sulfur and magnetite were identified. Noise, suggestive of amorphous phases, was also observed.

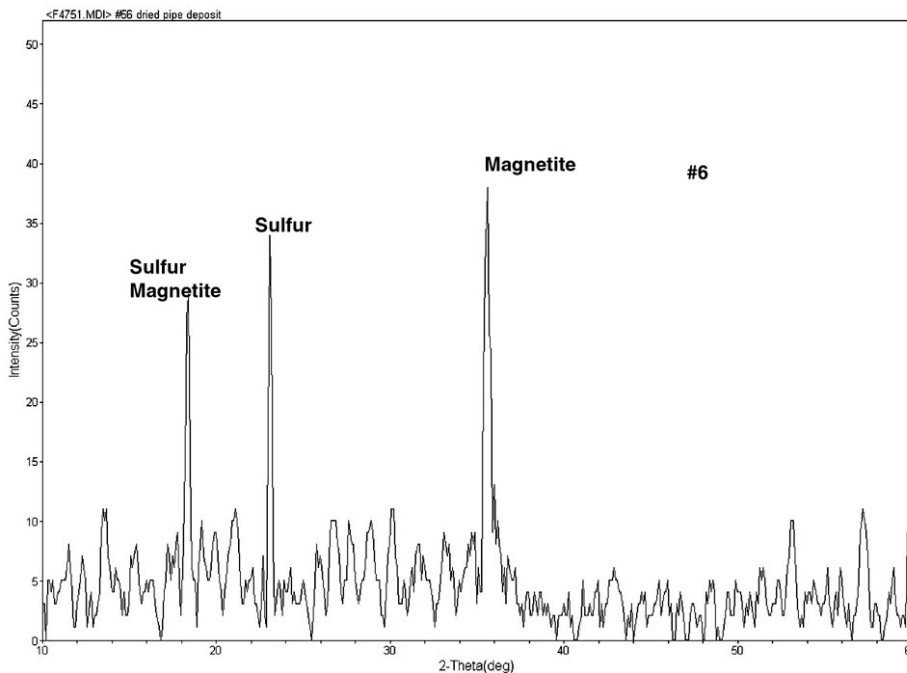


Figure 3-51. X-ray diffraction curve for Sample 6. Peaks for sulfur and magnetite were identified. Noise, suggestive of amorphous phases, was also observed.

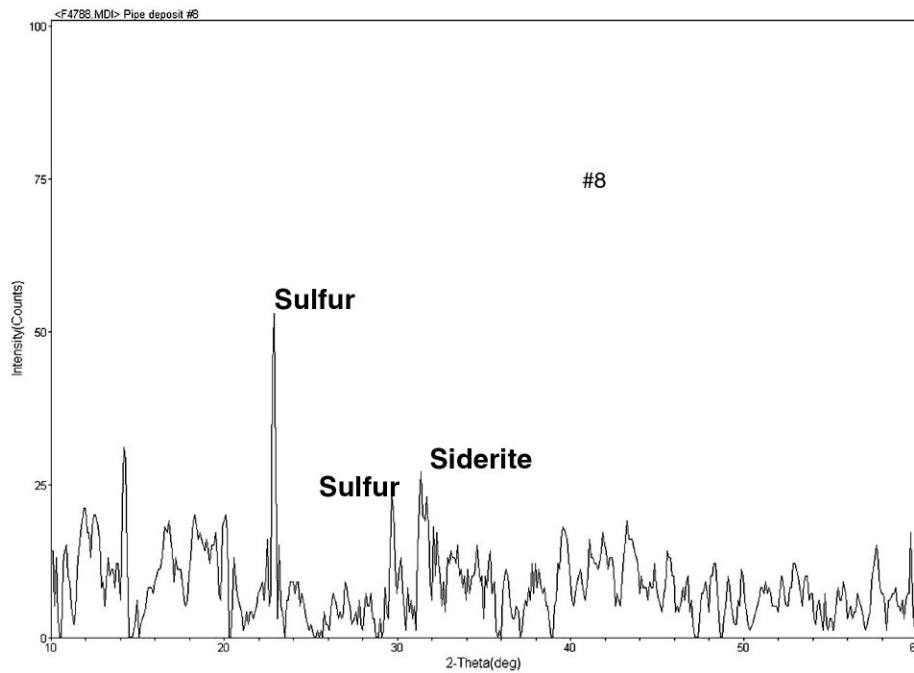


Figure 3-52. X-ray diffraction curve for Sample 8. Peaks for sulfur and siderite were identified. Noise, suggestive of amorphous phases, was also observed.

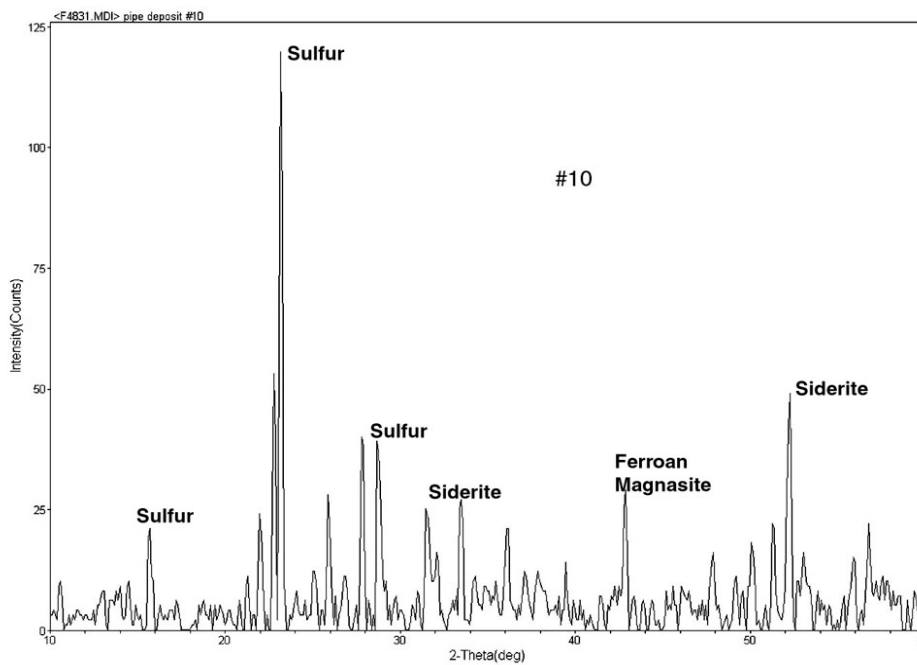


Figure 3-53. X-ray diffraction curve for Sample 10. Peaks for sulfur, siderite, and ferroan magnesite were identified.

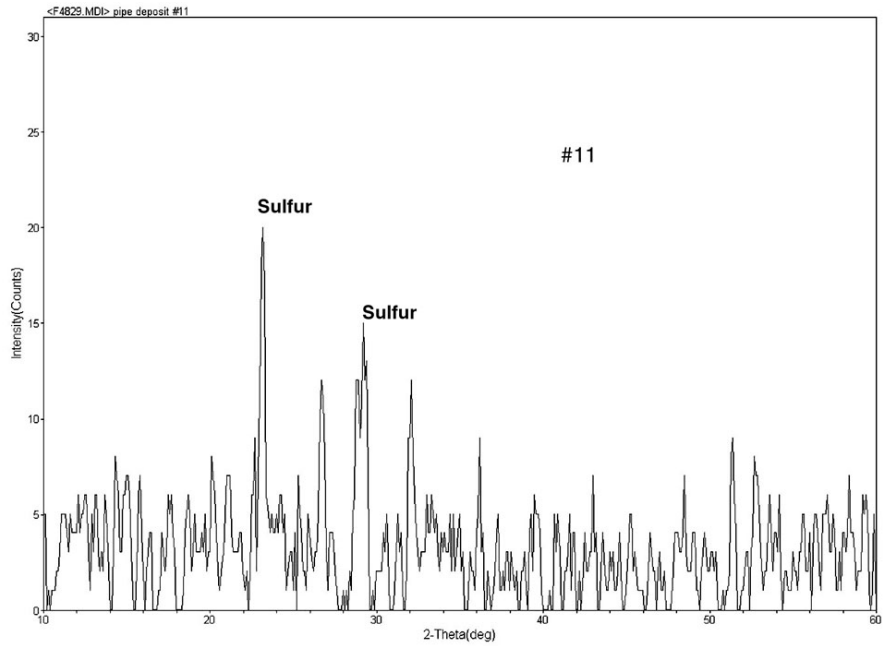


Figure 3-54. X-ray diffraction curve for Sample 11. Several peaks for sulfur were identified in a noisy background suggestive of amorphous phases.

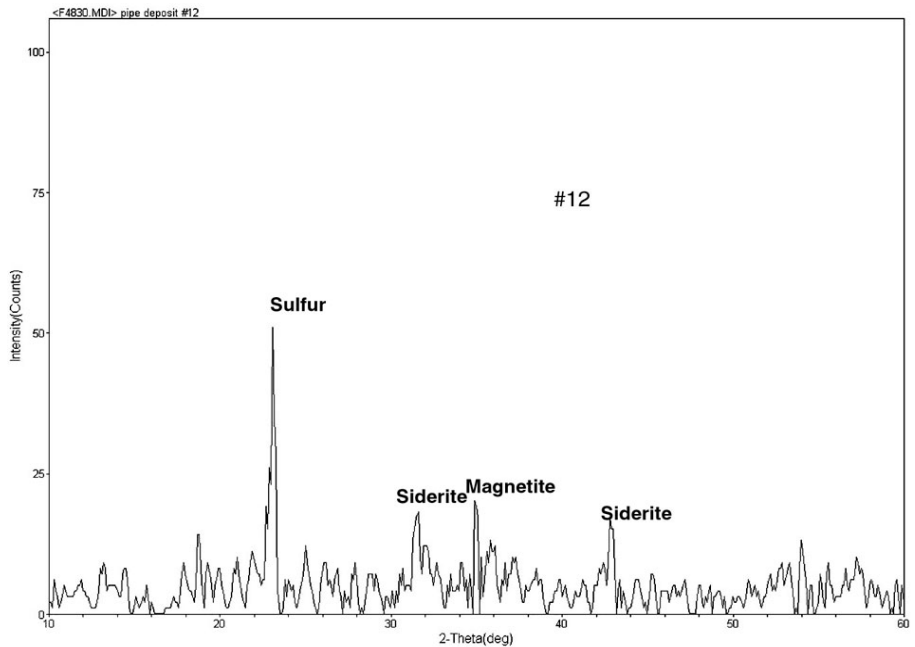


Figure 3-55. X-ray diffraction curve for Sample 12. Peaks for magnetite, siderite, and sulfur were identified. Noise, suggestive of amorphous phases, was also observed.

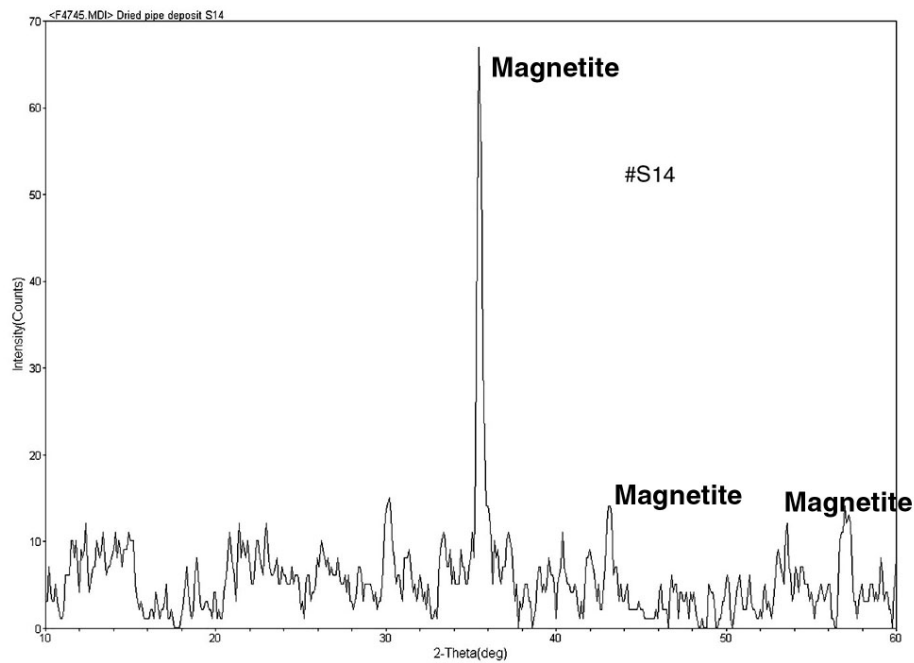


Figure 3-56. X-ray diffraction curve for Sample 14. Peaks for magnetite were identified in a noise filled background suggestive of amorphous phases.

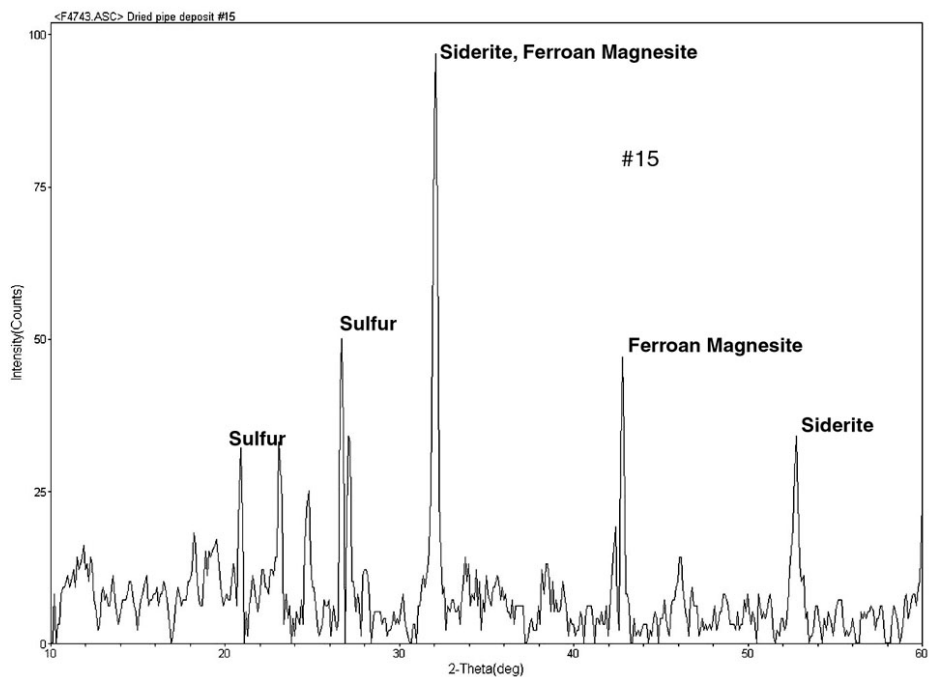


Figure 3-57. X-ray diffraction curve for Sample 15. Peaks for siderite, ferroan magnesite, and sulfur were identified.

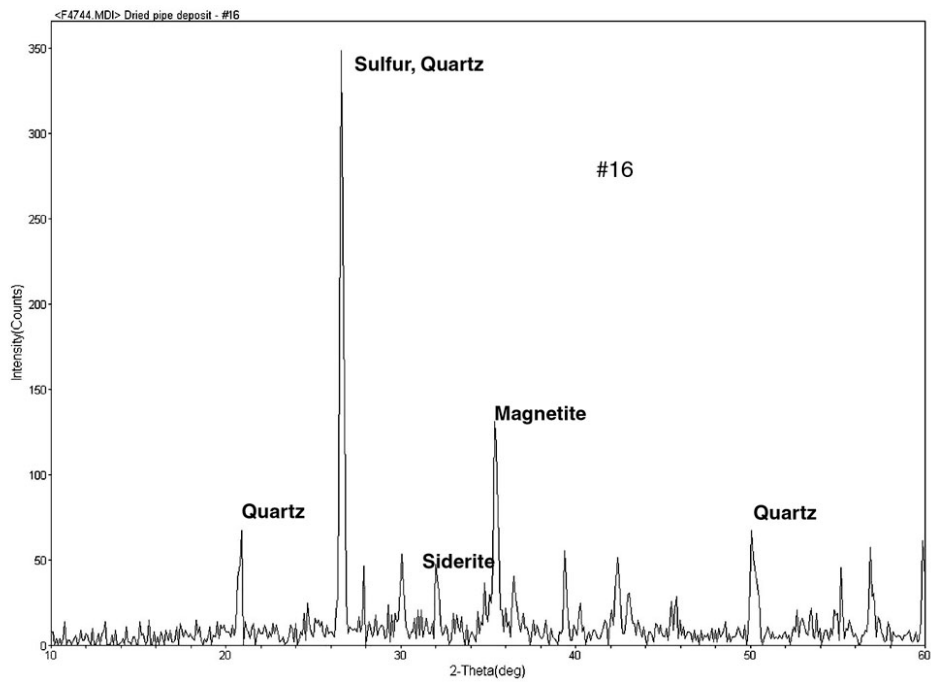


Figure 3-58. X-ray diffraction curve for Sample 16. Peaks for sulfur, quartz, magnetite, and siderite were identified.

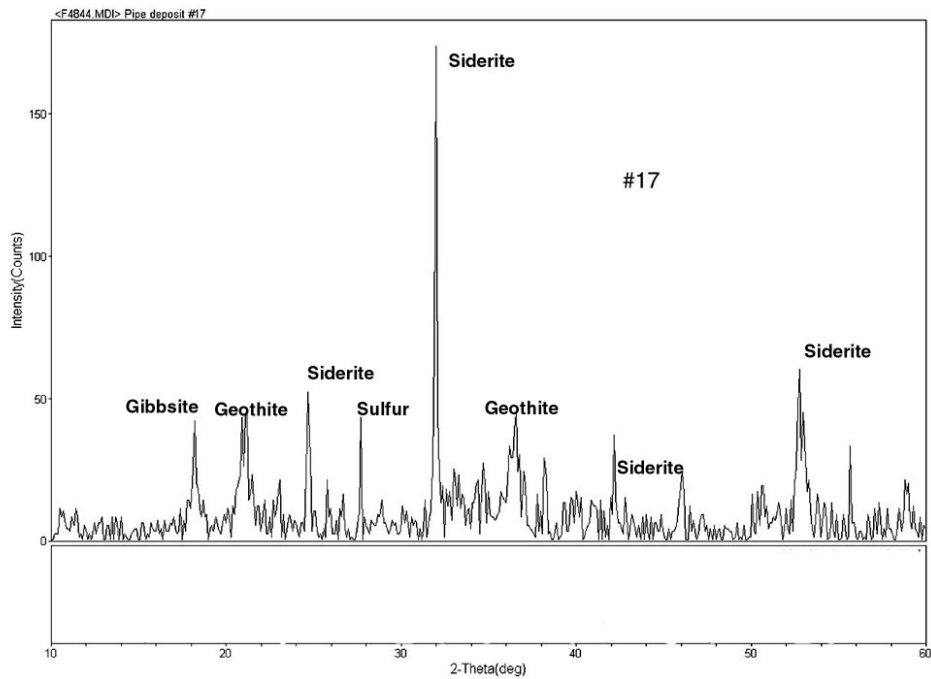


Figure 3-59. X-ray diffraction curve for Sample 17.

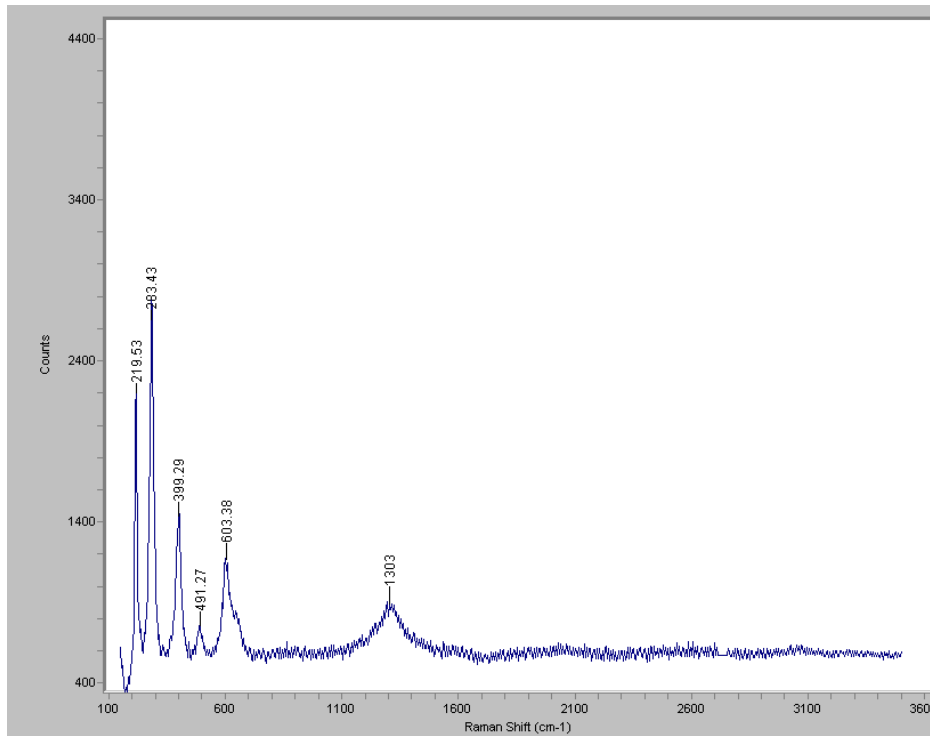


Figure 3-60. FTIR analysis results of the solvent extracted solids from Sample 3, in which some indications of magnetite were determined.

4. TASK 3. BLACK POWDER REMOVAL, HANDLING AND DISPOSAL FROM NATURAL GAS PIPELINES AND PLANT PIPING SYSTEMS: ROOT CAUSE AND SYMPTOMATIC TREATMENTS

The reality of black powder is that once it infests a gas pipeline, there are no known examples where a company has eliminated it. Another perspective is probably true: every pipeline is subject to black powder eventually. The brighter side is that there are things that can be done to control the problem and there is optimism that better methods can be discovered and applied in the future; they are improving. Also, understanding of the problem and the methods to deal with it are becoming more widespread. There are two methods to approach controlling black powder: (1) treating the root causes, and (2) treating the symptoms; the latter is most common.

4.1 WHAT CAN A COMPANY DO TO CONTROL BLACK POWDER? [2]

The *root cause* steps to controlling black powder involve controlling the components that cause or support internal pipe corrosion. These are water, reactive sulfur, sulfur reducing bacteria, and to a lesser extent oxygen and carbon dioxide. Controlling these components in the pipeline gas is needed to eradicate iron corrosion components at the source – before or soon after the gas first enters the pipeline.

- Liquid water should be prevented or eliminated and cleaned out when it is known or expected to have accumulated. Without water, no corrosion is possible. Conditions that allow condensation of water vapor should be avoided.
- Hydrogen sulfide should be eliminated, avoided, or kept to one to two parts per million.
- Other sulfur compounds should be controlled.
- Carbon dioxide and oxygen should be minimized (CO_2 partial pressure < 7 psi; O_2 < 10 ppm).
- Tests for microbiologically influenced corrosion (MIC) should be performed, and infestations treated when found.
- Solids should be filtered to sub-micron size, at most one micron, before custody transfer points and compression machinery.

The pipeline from well to user's burner tip must be treated as a single system when trying to control corrosion. It cannot be divided into company sections unless each is doing its part to control the corrosive components entering and leaving their section. The chemistry does not recognize changing ownership along the pipeline. Obviously, the greatest burden falls upon the well and gathering sections of the pipeline. Ignoring the problem by sending material downstream is also counter-productive. Instead of finger-pointing to the responsibilities of others, the costs of corrosion prevention should be shared among all owners of a pipeline from gathering to distribution. Certainly, the distribution company benefits as much from clean gas as the transmission company and both should assist the gathering company(ies) with the costs of making the gas clean for all. Obviously, this is a culture change from present practice.

4.2 CORPORATE RESPONSIBILITY FOR CONTROLLING BLACK POWDER

“We have corrosion control personnel. Shouldn’t it be their responsibility to control black powder and all pipe corrosion?” The truth is they can’t do it alone: almost everyone in a pipeline or gas company needs to understand about black powder and the part his job plays to control it. It is a system problem from the well to the end-user. Within companies, control requires a corporate culture, and among interconnected pipelines, control requires cooperation among companies. Here is a look at where responsibilities lie.

4.2.1 *Corrosion Control*

Most of these people have a job defined around cathodic protection; but we must remember that cathodic protection is mainly for external corrosion of the pipe. The corrosion control staff has other jobs that make them responsible for internal corrosion, including identification of the problem and locations, and testing and treating for MIC. They may also be responsible for remediation, such as pigging, if that is not a contracted service. However, there are many activities within a company that can influence corrosion that the corrosion control staff has no control over, as we see in the following sections.

4.2.2 *Engineering*

Engineering has control or influence over how the pipe is designed. This includes whether it can be pigged, whether it has low places to trap liquid water, what facilities there are for draining or removing water that may form or be deposited, the types and locations of filtration, the tolerance of machinery and controls to contamination and corrosion, and what kind of materials are used to build the pipeline that may have corrosion resistant properties. What they build determines susceptibility of the pipeline to corrosion and the ability to clean it or keep it clean.

4.2.3 *Process Engineering or Chemists*

Process Engineering or Chemists have to deal with the type of gas and the contaminants in it. They design the processes to remove undesirable solids or liquids by filtering, dehydrating, and more sophisticated processes. They should address the removal of compounds such as sulfur or carbon dioxide. The composition of the gas may actually change over the life of the pipeline as gas becomes sourer, or different gathering fields are brought into the delivery system. What they do to clean up the gas has a large impact on corrosion.

4.2.4 *Management*

Management has to recognize and understand the problem in order to support all who are active participants in the control of black powder. Management largely controls where budgets will be spent and should be the drivers for cost analyses. Pressure on them to produce continuous profits usually is the driver for decisions that produce short-term savings (such as flowing corrosive gas) instead of long-term savings (reduced maintenance costs as a result of clean piping). Management’s understanding of black powder and its cost effects will determine how the corporate culture is defined. Management must be the leaders in establishing cooperation with companies upstream and downstream on the pipeline and other pipelines to which the same gatherers may sell gas if they reject it.

4.2.5 Finance

Finance has control over budgets and the tradeoffs between money for capital equipment to prevent black powder versus money for maintenance to repair its consequences. They should have the data to determine when certain types of maintenance are driven by excessive corrosion problems and what return on investment is possible from preventive measures. The cost of downtime should be a factor in their analyses. Purchasing agents should be mindful of quality in the purchase of filters, pigging services, MIC remediation, and materials used in piping and components. Financial decisions with regard to construction and preservation of plant infrastructure, operations, and maintenance should be made based on longer-term return than the immediate quarter.

4.2.6 Gas Quality Tariff Negotiators

It is unusual to think of lawyers as having concern about corrosion and black powder formation, but those who negotiate and set long-term agreements for the constituents in the natural gas that will be bought and sold may actually have more influence than any others. The corrosion constituents in the gas bought is the starting point for the black powder that can form in the piping system and the damage to the pipe that results from corrosion. Conservative tariff limitations should be set for the corrosion components of the gas, as well as the heat content. Trade-offs should be evaluated with attention to the long-term corrosion damage to the infrastructure and the resultant costs. It may be economically preferable to pay more for cleaner gas rather than accept short-term bargains for gas containing components that will cause corrosion, reduce safety and reliability, and compromise the capital assets.

4.2.7 Gas Control

Their decisions amount to compliance with and enforcement of the tariff agreements. They are usually the ones who decide to mix “dirty” gas with “cleaner” gas to meet tariff requirements. From the corrosion perspective, this is not productive since all of the corrosive components (e.g., hydrogen sulfide) in the “dirty” gas still go through the pipe and can react to form black powder and similar corrosive compounds and damage. Again, short-term expediency accepted without regard to eventual loss. Once the black powder “disease” has been contracted, it has never been eliminated.

4.2.8 Operations

All aspects of corrosion in the pipeline influence Operations eventually. Initially, they will be impacted by the rate at which filters are filled and instrument lines are plugged. Soon the impact is seen in compressor valves and other component wear, such as blades or piston rings. This results in more downtime, reduced reliability, greater risk, compromised safety, and more maintenance costs. System upsets such as dehydrator overflow, filter plugging or penetration, water slugging, and the like cannot be ignored when they cause liquid water, solids, or more than normal sulfur to be released into the pipeline. These events should trigger a remedial action. Later, the buildup of solids or liquids in the piping reduces performance and efficiency. All of these have dollar impacts somewhere in the company.

4.2.9 Maintenance

Maintenance is tied closely to Operations, but the impacts are somewhat different. Maintenance personnel are sometimes the first to see the impact of black powder formation or corrosion. They need to be knowledgeable to identify where and when and in what quantity the material is found in the system and have a means of reporting the time, frequency, parts or materials, and other costs of repairs. Most importantly, maintenance persons required to handle the black powder in removing it from the machinery, filters, and piping need to be aware of its capacity for auto-ignition and treat it accordingly. In some cases, the material must be handled as a hazardous waste for disposal.

4.2.10 Safety

All companies in industry have a growing concern for safety. The impacts of black powder and other corrosion should be a part of that attention in every company. All employees, through operator qualification training, should be made aware of the material, the hazards, and implications it has on their specific job tasks. New employees and contractors should be introduced to the problem and instructed on how to deal with or report it for their job. Safety meetings and posters should give the problem regular attention. There should be a corporate system for reporting black powder problems or occurrences.

There are some other specific tasks dealing with black powder and corrosion that, depending upon company organization, may be independent functions, or fall under one or the other of the functions above.

4.2.11 Flow Measurement

The accurate measurement of the flow of gas through the pipeline is the “cash register” of the business. The accuracy and reliability of the devices that are used to do this, orifice meters, turbine meters, and the like, can be strongly influenced by the presence of solids or liquids in the pipe. It should be the responsibility of measurement personnel to monitor, police, and report out-of-specification upset occurrences that affect pipeline facilities.

4.2.12 Hydrotesting

Whenever water is put into a pipeline that is to be used for natural gas service, the water should be examined for corrosive content, but most importantly, after the hydrotest, the water must be completely removed and the system then cleaned to kill the ingested bacteria. Consideration should be given to using liquids other than water, or follow the water treatment with a liquid such as diesel fuel, hydrocarbon condensate, or alcohol that will scavenge the water, evaporate itself, and not support corrosion. A biocide should also be used.

4.2.13 Pipeline Integrity and Cleaning

Those responsible for pigging the pipelines to first clean them and then determine their integrity have the best and most comprehensive gauges to determine the severity of corrosion and the amount of black powder accumulation. They should be aware of: (1) the cumulative amounts of corrosive chemicals transported in the pipe, (2) MIC identification and treatments, (3) time intervals between cleanings, (4) best cleaning methods, (5) potential weak areas in the pipe identified from gauging and smart pig runs, (6) failures due to corrosion, and (7) process

upsets that need remediation. Their pipe cleaning program should use innovative methods and should continually evaluate the latest technologies.

Some gas companies may have only a few clerical personnel remaining at a location who have no significant need to know about black powder. Consequently, black powder and other corrosion concerns need to be revealed to everyone in the company and it should be recognized as a disease that saps profits.

In order to control pipeline corrosion and black powder formation, a corporate culture is required that includes:

Education of employees,

Active engagement by management and financial staff,

Engineering and rehabilitation of the infrastructure and the process to minimize corrosion and limit its impact,

Conservative setting and aggressive enforcement of tariff limits on the corrosive components of gas in order to preserve infrastructure and minimize maintenance and operating costs,

Responsibility appropriate to their job taken by all who encounter black powder,

A reporting and analysis mechanism to spread awareness and provide data for analysis of the impact of black powder,

Financial evaluation to determine risk, return on investment, maintenance cost, and capital infrastructure preservation,

A safety program to deal with the material properly for personnel, the environment, the public, and the plant infrastructure, and

Co-operation with other companies involved with receiving or passing the corrosive components or the resulting solids through the pipelines.

4.3 SYMPTOMATIC METHODS TO DEAL WITH CLEANING, HANDLING, AND DISPOSING OF BLACK POWDER

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The present industry practice appears to concentrate more on dealing with the symptoms of black powder than with the root causes. There is much more emphasis on remediating the results of corrosion than preventing it from happening. Although it appears that the prevailing opinion is that it is too expensive to treat gas and control the corrosive components, the actual cost analysis of that comparison is not evident. Another reason for a dearth of root cause action may be lack of information by management concerning the cause of the problem or the root cause solutions. Until root cause methods are strongly invoked and proven to be effective, the need will continue for remediation by symptomatic methods. Methods are improving and the search for better ones should continue. The keys are communication and co-operation.

Several brand name commercial pipe cleaning methods and products are mentioned in the following discussion. The intention of the author was to deal with these methods using scientific or generic names, but the reality is that many of these companies have protected the composition

of their cleaning compounds and other methods, preventing identification of the base constituents or methods to duplicate their products. It would not do the industry a service to avoid discussion of these commercial brands since they provide significant new progress in pipe cleaning. Referring to them without using their commercial names or manufacturers would confuse proper identification. Our greatest fears are that this research has not found other unique or significant products, and the perceptions by other manufacturers that their product should have been discussed.

4.3.1 Construction Precautions

During pipeline construction, cautionary measures can be taken to reduce iron dust in a pipeline. It is recommended that, prior to, and during field installation, joints of pipe should have the ends capped to minimize the entrance of oxygen and moisture that could corrode or rust the pipe inside walls. In addition, before field welding, each joint of pipe should have rust particles and wheelabrator steel shot blown out of the pipe by the contractor using a high pressure air hose. Any efforts that can remove mill scale from the pipe walls would be advantageously performed at this time. These construction practices should reduce the amount of solids left inside of the pipeline after construction that impact ensuing operations and budgets.

4.3.2 Material Identification

The nature of the material built up in the pipeline determines the remedial actions to be taken to clean up the pipe. The first action should be to try to sample and analyze the material at various points in the pipe and vessels. One of the most critical actions occurs at this point. Since iron sulfides are easily and quickly oxidized because they are pyrophoric and frequently of very small particle size (large surface area to volume ratio), it is imperative to protect the sample from oxidation all the way from inside the pipeline to the completion of the analyses. The sampling and testing protocols must prevent exposure of the sample to oxygen for more than very brief moments.

The location in which pipeline black powder is sampled is important because of the possibility of oxidizing the sample before it is tested. The most common location to sample black powder is from a pig trap when the pig is removed. This location is very susceptible to sample oxidation because of the large opening. Removing sample material from filters is also common. Depending upon the size and design of the filter, oxidation is also a potential problem if the filter opening is large. In the case of pig trap or filter case sampling, the sample should be collected rapidly and immediately purged with an inert gas or liquid that does not contain oxygen. Remember that water does trap oxygen. The container should be completely filled to avoid the presence of oxygen. One of the best sample locations when it is available is drainage out of the bottom of a vessel or liquid trap. The difficulty of this method is that the material must be in a medium that allows it to flow through a valve. One advantage of drawing samples from vessels or filters instead of pig traps is that the samples may better represent the chemistry in the pipe in the immediate vicinity. The product of pigging is obviously a homogeneous collection from the entire length of the pigged section.

When brief oxygen exposure occurs, remediation should follow by enclosing the material in an inert gas or liquid for removal of the oxygen and preservation until testing. In the laboratory, preparation of the sample and processing must be done in a glove box with an inert atmosphere, or otherwise protected by a hydrocarbon or inert liquid or gas. Ignorance of this fact

in the past, or inattention to it going forward, is the reason many samples are misidentified as iron *oxides* instead of *sulfides* because the conversion from sulfides to oxides has already taken place in the sampling process; the sulfur has been released as sulfur dioxide, usually.

All that is in the matrix of materials in any pipeline is a mixture of compounds, frequently in layers. Some come from the upstream wells, some may be from construction, some lubricants from the machinery, some glycols and similar from plant processes the gas has been exposed to, and some is from corrosion. Hydrocarbons and water usually serve as binders to hold the mass of material together and adhere it to the pipe. This material should be identified, and if possible, its layering defined, in order to plan an effective cleaning schedule.

Moisture due to the presence of any liquid – water, hydrocarbon, lubricant, glycol, surfactants, biocides, etc. – can serve as a binder to draw and hold together the solid materials in the pipe. These liquids also serve as an adhesive to cause the material to adhere more easily and longer to the pipe walls. Once this happens, it may not be evident that liquid is even present. It only becomes evident when, after cleaning, the matrix is broken up and all components are separated once again. But once trapped in this matrix of solids, water can still act as a catalyst to corrosion.

4.3.3 *Cleaning*

The objective of chemical cleaning agents are to cost effectively break down the organic-matrix bonds that firmly secure the particles to themselves and to the pipeline so that the iron and other solid particles can be carried out of the pipelines by pigging, sweeping, or other means of agitation. The major question in pipeline cleaning is determining whether, and when, the pipeline has been cleaned sufficiently.

Progressive and advanced cleaning technologies, involving innovative pig improvements and pioneering chemistries, are reducing the number of pig cleaning runs needed to effectively clean a pipeline, thus, reducing internal corrosion tendencies and the amount of time a line is out of service, while increasing profitability, reliability, and pipeline life.

There are a number of effective cleaning fluids and pigging configurations that can remove significant amounts of pipeline deposits. They should be chosen in type and order of use according to the findings of the material identification performed above. Initial pig runs can be useful in determining the amount of buildup and the moisture content of the material.

Among the number of liquids used to clean pipelines, some are more effective than others, and some have detrimental qualities along with their benefits. The liquids can be oil soluble, water soluble, or amphoteric (able to react as either an acid or a base). Some pipeline companies will not allow water or water-based cleaning products in their pipelines, so an oil soluble cleaner and diluent should be recommended. Most pipeline cleaners are introduced into pipelines at concentrations of 10-15%.

Here is a brief discussion of some of the more common cleaning liquids. Most chemical manufacturers that produce specialty chemicals for the oil and gas industry have product lines that include pipeline cleaning chemicals under trade names, and many have proprietary contents. This makes it very difficult to talk about them generically, but to ignore them or be otherwise vague in describing them would also be a disservice to their useful applications. In addition, there may be other products not discovered in this investigation that are valid pipeline cleaning agents; our apologies to those suppliers.

4.3.4 Diesel Fuel

Red diesel is commonly used because it is relatively cheap and available. Diesel's biggest advantage is that it is not water; it is a hydrocarbon. It is a diluent for oils and thus can loosen *some* deposits. It does *not* dissolve iron sulfides, iron oxides, or many other solids. It is a carrier for solids and does wash out free water.

4.3.5 Gels

Gels have been in the pigging market for over a decade. They are usually polymer-based, but can be composed with many different chemicals to meet the need of removing the deposits and binders found in the debris. They can dilute or loosen some deposits and are a good carrier for removing loose material. The gel reduces the wall friction experienced by cleaning pigs and wets the debris particles for dispersion. This allows a pig to run longer distances in the pipe without getting stuck.

One of the negatives of gels is that they get into joints, gaps, instruments, and other available pockets that are not swept clean by the flow, and they stay there, along with whatever material was carried by that portion of the gel flow. The volume of gel that goes in is increased by the material removed from the pipe walls, but a portion of the gel, and particles suspended in it, do not come out of the pipe. The gel tends to stick in crevices, branches and other pockets along the pipe. Gel pigs are particularly suited to large lines where turbulent flow rates are not possible, and where large quantities of debris are anticipated. [8]

4.3.6 Tetrakis (Hydroxymethyl)Pphosphonium Sulfate [THPS]

THPS was developed as a fire retardant and is used as a biocide. Besides those uses, THPS is largely applied as an anti-foulant pipe cleaning agent. The residuals from this cleaning process serve as a biocide. THPS is sold for pipe cleaning under many brand names, and many of the actual compositions are proprietary. A number of the brands surely have other chemicals added into their mix including surfactants, emollients, or detergents.

THPS is well known as a highly effective biocide for a variety of water treatment applications, including oil fields. However, while using THPS for this application in oil wells, it was discovered that it is also able to dissolve a range of iron sulfides. This led, in some instances, to the use of THPS solely for this purpose, although the dual functionality (as a biocide and iron sulfide dissolver) significantly increased the economic effectiveness of this form of treatment, as two chemical products could now be replaced by one. Testing determined that the best results were obtained with THPS combined with ammonium chloride or phosphonate. Because THPS combines with iron sulfides by chelation, no sulfur dioxide is released as when sulfides are oxidized. [10] As a biocide it is used in parts per million; as a cleaning agent the ratio is approximately 20% THPS.[12] Since THPS is effective over a pH range of 3 to 10, the natural pH of a pipe is not important. If the pH needs to be adjusted after use of THPS, it is recommended to deactivate it with peroxide. [11] It is also rapidly deactivated in the presence of free oxygen or in the presence of high pH products, such as corrosion inhibitors. This property also makes it useful in scavenging oxygen from a pipeline environment.[12]

THPS is an advance in pipe cleaning technology because it is a fast acting, non-corrosive, high performance, biodegradable, low aquatic toxicity microbiocide. THPS can be denatured with a solution of 3% hydrogen peroxide for acceptable discharge into the environment and is

one of the most environmentally accepted biocides used by the global marine oil and gas industry.

THPS is a non-foaming, saltwater soluble phosphonium salt that has a compact molecular structure important for rapid biocidal performance, corrosion control, anti-fouling (black powder dispersion), and oxygen scavenging. It combines with trace amounts of oxygen in pipeline facilities and forms THPO, a denatured, non-hazardous by-product.

Because of its fire retardant properties, the application of THPS in pipelines can assist in controlling the auto-ignition of black powder at pig receivers, once the material is exposed to sunlight and oxygen.

4.3.7 *EnerFlow 780*

EnerFlow 780 is a concentrated liquid pipeline treating product capable of removing iron sulfide (black powder) from within gas pipeline systems. It works to totally remove iron sulfide over a period of time, which will vary depending upon the concentration and nature of the type of iron sulfide present. The product is designed for continuous injection or intermittent batch methods. When continuously injected into the gas pipeline, Enerflow 780 is reported to remove iron sulfide. Enerflow 780 is available through Rapid Energy Services. They also provide a variety of inhibitors, dispersants, surfactants, and cleaners. [6]

4.3.8 *PowderSolv™ and “FeSx™”*

PowderSolv™ and “FeSx™” are environmentally friendly pipe cleaning products, which are capable of dissolving iron sulfides and iron oxides at a neutral pH. Unlike acids, there is no hydrogen sulfide liberated in the process, thus increasing operational safety. These properties suggest it may contain THPS. By penetrating the debris matrix, the products dissolve the iron compounds that bind the matrix together. The process allows cleaning programs that produce significantly less waste in a shorter time. Corrosion tests have shown that reacted products remaining in a pipe actually provide a level of corrosion inhibition. The magnetic problems associated with black powder are negated by the dissolution of the iron in the black powder debris matrix. Thus, these products are beneficial for pipeline integrity measurements since wall thickness gauging and pit detection (ILI) accuracy is improved. From economy and efficiency standpoints, these products have proven successful in cleaning black powder from meter runs, fouled vessels, filter separators, and compressors. “PowderSolv™ and “FeSx™,” are products of Synergy Services, Inc. (SSI). SSI has proprietary technology that allows them to determine the cleanliness of the pipe, thus assuring the removal of essentially all black powder deposits in the system. [3]

4.3.9 *Solids Removal*

There are many available methods of filtration for black powder type solids in piping systems. Some have been available for many years while others, such as cyclone separators, are relatively recent. These devices are useful for the removal of particles, especially near the inlet to a plant with compression machinery or flow measurement instrumentation. The following is a brief outline of the general types.

1. Gas-liquid separators (most familiar type)
 - a. Vertical (most efficient)

- b. Horizontal (greater capacity per unit cross-sectional shell area)
 - c. Spherical (least efficient but most compact and cheapest)
- 2. Oil-bath scrubbers (environmental concerns – PCB's, spillage)
- 3. Dry scrubbers (removes black powder greater than four microns)
- 4. Cartridge-type coalesce scrubbers (best for dry gas service – removes black powder particles down to two to four microns)
- 5. Dust filters (removes course particulates)
- 6. Cyclone separators
- 7. Magnetic separators

4.3.10 Magnetic Separation

The use of strong magnets for the removal of iron sulfides is a new and unique application that has merit. Since some of the iron sulfides are magnets, others are attracted to magnets, and several other pipeline solids containing iron (oxides) are attracted to magnets, this method is useful in removing many of the solids of a wide variety of particle sizes. Unlike filters, particles of all sizes that are attracted to a magnet can be captured. The limitations of magnetic separators are a temperature limit of about 150 degrees C, less effectiveness in large diameter pipe, and inability to capture non-magnetic or amorphous solids. The magnets have a 10+ year life. Advantages are low pressure drop across them, and they are easy to clean. Magnetic separators can be used in series with paper media filters to increase the life of the paper filters, or to catch what passes through them. The magnets also can collect pipe surface slag (mill scale), construction debris, and other materials made to be magnetic by the strong fields of ILI pigs. The magnets work equally effectively in gases or liquids. One Eye Industries Inc. is the supplier of these devices. Their magnet type and geometry is unique. [4, 5]

4.3.11 Black Powder Disposal

Since the components of generic black powder vary widely, the nature of the material removed from a pipeline is unique; that is, the debris from every pipeline is different, and the debris from a given pipeline can be expected to change over time. Thus, the characteristics of black powder removed from a pipeline cannot be generically described; each event must be sampled and tested for hazardous material content.

Another factor that strongly influences the nature of the debris removed is the type of material used to clean out the pipe. Hydrocarbons probably make the material combustible. The hydrocarbons may occur in the material removed, or be the removing solvent. Any cleaning agent that oxidizes the sulfides likely creates gaseous sulfur dioxide. The presence of carbon dioxide and water can create acids. Cleaning agents such as potassium permanganate, PowderSolv, THPS, or perhaps other proprietary products may be successful in neutralizing the material to harmless substance, depending upon the other constituents that may be in the pipe debris. Thus, it is important to plan the pipe cleaning process to treat the material in the pipe to the best advantage to make it safely segregated and disposable when removed, if that is possible. Some cleaning agents may move the materials out of the pipe, but produce a hazardous clean-up, while other agents may actually make a hazardous material in the pipe into a benign material for disposal. One negative aspect of the ability to dissolve iron sulfides is that the residual material may be allowed to move down the pipeline to the next operator, rather than be removed where the sulfides are dissolved.

When debris is removed from a pipeline, there needs to be a plan in place for disposal of the material. This action is dependent upon the results of tests performed on the material to identify its contents and characteristics. Tests such as Toxic Characteristic Leaching Procedure (TCLP), Resource Conservation and Recovery Act (RCRA) metals, pH, polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs), flash point, and reactivity may be necessary. These results must then be compared with jurisdictional laws for disposal of materials.

Sometimes the company contracted to remove the black powder from a pipeline is also responsible for disposal of the material. In other cases, that responsibility is left to the owner of the pipeline. Frequently in this case an Environmental Services Company is employed to develop a waste disposal plan for temporary storage, packaging, shipping identification and paperwork (MSDS), transportation, and final deposit. The final process depends heavily on whether the debris is determined to have hazardous contents or is classified as a non-hazardous industrial waste. The costs for transportation and disposal need to be factored into the clean-up plan. [7]

One commonly reported practice is to store black powder, especially smaller quantities, such as found in filter elements in metal containers, until it oxidizes and no longer has the potential to auto-ignite. Even though this action makes the remaining material safer to handle, the fallacy in this method is that oxidation of iron sulfides releases sulfur dioxide, a highly hazardous gas, which is the major component of "acid rain". Since the gas is not usually visible in small quantities, it may not be noticed. Release of large quantities of sulfur dioxide in this manner can be hazardous to personnel and the public, in addition to the undesirable environmental consequences.

Water can be helpful in safely removing black powder from a pipeline or plant. Wetting the material delays the tendency to auto-ignite through oxidation. This can be particularly helpful when the environment where the removal is taking place may be an explosive atmosphere. However, there are also difficulties with this process. Applying water to the powder while it is still in the piping system is introducing the ingredients for corrosion, unless the system is valved in such a manner that the water cannot make its way into inaccessible places in the piping or vessels, and it can be cleaned out thoroughly before re-closing the system. It should be pointed out, however, that wetting is a temporary solution because once the powder dries out again, the combustibility returns; it has not changed the material chemically. There are a host of stories of black powder being stored or hauled and it igniting during the process. The handling and disposal plan needs to be carried to the next step where final disposal is accomplished in a safe, if not environmentally friendly way.

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5. CONCEPTS FOR THE LOCATION AND CAPTURE OF BLACK POWDER SAMPLES FROM NATURAL GAS PIPELINES

In the management of corrosion products in a natural gas pipeline, there are several needs. One is to determine the simple presence of the corrosion products, primarily iron oxides or iron sulfides. Once the presence of the material is known, it becomes important to capture samples and submit them to testing to determine the exact chemical composition and structure of the material and whether it contains corrosion-causing microbes. This knowledge is helpful in determining the source(s) of the corrosion and the areas in which the material may be deposited. It is also necessary knowledge for determining a course of treatment, and methods for handling the materials removed from a pipeline. Another piece of information helpful in determining the source of the corrosion products is locating where it resides in the pipeline, or where it is found now that it did not exist previously. Some of the methods to do this may be intuitive or obvious, but others require some planning, preparation, and perhaps engineering.

This document attempts to present concepts for (1) where in a pipeline it is reasonable to attempt to locate black powder, and (2) methods to use to capture samples for testing. In the process of sampling, it is also important to maintain the integrity of the material so that it does not change composition through oxidation.

5.1 LOCATION

There may be several needs for locating black powder in an extensive pipeline. The fundamental question to answer is “does this pipeline have corrosion and black powder buildup?” Beyond that basic question, others arise. “Since we have black powder, where does it exist or where is it coming from?” Where the material is found may be useful in determining the source(s). Another need is to capture some of the material, perhaps from different locations or times, and determine its chemical content. This information helps to establish the process by which the material may have formed, and the components in the pipeline that allowed it to form. Further, it may be helpful to determine whether the material is wet or dry, and its state of adhesion or looseness; particle size may also be useful in planning pigging operations, filter design, or other particle capture plans.

The first concern is determining the locations from which corrosion product material may be found. Once black powder is formed in a pipeline, it may move downstream to some or all parts of the line. So, in one respect, anywhere you find it is a good place to capture it. But, there are sites where it may be more expected to be found, or where it may be easier to capture a sample for testing. Determining quantity of material accumulated is also helpful information in scheduling or planning cleanup operations. So it makes some difference whether the need to locate black powder is for test sample capture, or for knowledge of where it does exist. On the other hand, there may be strategic locations in a pipeline where it is necessary to determine if it exists “here”, and so methods may need to vary on how to locate material inside the pipeline. In some places, it may be easy and natural to be able to open the pipe to search for corrosion products, while in more remote locations, particular engineering may be necessary to provide that capability. Obviously, methods that do not require the compromise of the pressure boundary would be preferential to those that can only occur during shutdown.

The obvious first points of interest are those that are normally opened for other reasons from time to time and can be used to look for or collect black powder samples. Among these

points are filters, pig traps, and any drains in components of the pipeline such as vessels or the pipe itself. Filters are among the natural places to find black powder because their purpose is to remove it from the system and the filtration elements need to be cleaned out or replaced periodically. There are several types of filtration, including paper element, coalescing, cyclone, and the newer magnetic filters. Paper element filters need to be removed and sometimes it is possible to extract material samples from the media. Cyclone and coalescing filters usually have some means of extracting the collected material while the process is operating. This may also be possible with appropriately designed magnetic filters. The caution is to avoid exposing the material to oxygen for more than seconds or a minute. (See instructions on sampling.) This may take some planning before the pressure boundary is opened.

Pigging is also a normal means of removing black powder and can be used for collecting samples, again taking caution to avoid oxidation by being ready to sample as soon as the pressure boundary is opened. Pig traps are somewhat less desirable as sampling locations than filters, because a pig collects material from the full length of the pipe that it traverses and homogenizes the sample before extraction from the pipe. This compromises the ability to say what form of material came from what section of the pipe. The sample is an average of the entire pigged section. This may not be a major issue if the pipe section is relatively short and has few or no side entry points.

Vessel drains are a good source for black powder, especially if the material is in liquid suspension, so that it will flow out of a valve from the vessel. This ability to control material extraction has the best ability to limit oxygen exposure and control sample size. Drains in the pipeline, especially if they are located at low places in the pipe, can be just as effective as in vessels, although perhaps not as accessible.

In addition to low places in the pipe, black powder may naturally collect at locations where the diameter increases and the velocity decreases. It is at these locations that the particulate matter would have a tendency to drop out of the flow and collect. This is another reason for collecting from drains in vessels.

Since water or liquid traps are naturally at low places in the pipeline and have a valve or other means for removing the collected liquid, they may also be good locations for the removal of corrosion product samples.

Another natural location for finding black powder is in equipment such as compressors and their associated hardware, and in flow measurement devices. This equipment is from time to time opened for inspection or maintenance. Although the purpose is usually not to find black powder, the presence of same should be noted and it may even be valuable to be prepared to collect a sample in the event the material is found, expected or not. In some systems where black powder is heavily present, the sole purpose of opening equipment may be to remove the undesirable material to improve operations. When samples are needed, this may be a good time and place to be prepared to collect a sample for testing as soon as the pressure boundary is opened.

Besides locating the presence of solids in a pipeline, the determination of the presence of water is also instructive in the control of the formation of many corrosion products. It must be kept in mind that without water, no corrosion is possible, and the presence of water catalyzes many corrosive mechanisms. Water should be eliminated and its future accumulation prevented wherever and whenever it is found in a pipeline.

5.2 METHODS OF COLLECTING BLACK POWDER FROM AN OPERATING PIPELINE

In addition to the above natural reasons for opening a pipeline, there are other means that do not require opening the pressure boundary. Some of these can be considered continuous monitoring, while others are still of a batch nature.

There are systems in service which use a side stream off of the main pipeline to capture or detect material in the pipe, either liquid or solids. Among these are adaptations of commercial analyzers for particle detection, particle sizers, and particle traps. These devices usually need to be set to detect either liquid droplets or solid particles, but not both. How they divert flow from the main pipe into a side stream is a matter of careful design so that the particles are not diverted around a stagnant zone at the entrance to the side stream. Some flow rate must be maintained into the sampling tube so that particles are attracted into the trap. In order to maintain such flow, the flow must be vented to a lower pressure area, either downstream of a pressure drop in the same pipe, or into a separate system at lower pressure. The detection, sampling or sizing device is then placed in the side stream line. Since non-trivial hardware is required for this process, it should be viewed as a rather permanent installation, although the device might be portable and moved to different side stream locations on the same or different pipelines.

Similar to the side stream particle detector is the laser particle detector. The laser, however, requires a “window” through which to view the interior of a pipe. This could be either a clear section inserted in the pipe, or insertion of the laser through a valve into the pipe. The biggest obstacle to this method must be maintaining the pressure boundary without leakage while allowing the laser beam or laser body and beam penetration into the pipe.

At pipe locations where there is a valve into the pipe of sufficient size and type, insertion devices can be placed into the pipe to look for, catch, pickup, or otherwise detect the presence of solids in the pipe at that point. The most direct method is to place a borescope through the valve from the top of the pipe and insert it far enough to view the bottom of the pipe and any deposits that may be located there. The insertion may have to be performed by an insertion device as discussed in the following. Detection of the presence of material is the first step in identification of black powder. Subsequent methods include techniques to capture material and extract it from the pipe, or identify it in place. The use of an insertion probe with specially designed tip devices may provide this capability.

Pipe insertion devices are used for several purposes, mainly to inject pressure sensors into the flowstream of the pipe. The insertion device makes it possible to force a shaft and end device into the pipe through a ball-type valve pushing against the static pressure in the pipe, while preventing leakage out of the pipe. Usually it involves a pair of movable seals to alternately hold the pressure and a lead screw to perform the force-amplified insertion.

It is not known whether this technique has progressed beyond the conceptual stage to practical application, but it has possibilities. End effectors for the insertion tip could include a 2, 3, or 4 fingered device that could be caused to open and close to capture a small sample of solid material. Another concept is a “sticky finger” substance, somewhat like modeling clay or an adhesive, on the end of the effector that would attach to loose material and bring it out of the pipe. Since some iron sulfide and iron oxide compounds are attracted to a magnet or are magnets, the tip might simply be a magnet, perhaps with a sleeve to enclose and try to capture the attracted material for extraction. This method may somewhat filter the material captured. Yet another method similar to the sidestream tube might be using a hollow tube inserted into the

material and a small valve opened on its exterior end to allow the pressure inside the pipe to push small loose particles through the pipe to the outside. A capture vessel would be attached to the outside end of the transport tube. This method depends upon finding or making the encountered material small and granular or powdery without it blowing downstream. It may also depend upon the pressure level in the pipe and whether there is a need to capture the transporting gas.

APPENDIX A: PIPELINE “BLACK POWDER” CORROSION SAMPLING PROTOCOL

This Sampling Protocol is a part of a project between PRCI and Southwest Research Institute® (SwRI®). The object of the testing is to identify the characteristics of the variety of “black powder” materials found in gas pipelines and accompanying hardware throughout the world. The information collected will be included in a database that will be made available (at least) to PRCI member companies.

This protocol is presented as a method for collecting a pipeline corrosion product known commonly as “black powder” for the purpose of testing to determine its chemical components. “Black Powder” is a descriptive name that should not be a suggestion that the material is or contains gunpowder. “Black powder” is a corrosion product that occurs in natural gas pipelines and other places naturally. The name describes its most common color, but the chemical contents are not universal or uniform, thus the reason for testing to determine the chemical constituents.

Hazards. Within the variety of black powder components are some chemicals that can present some hazards to handling the material. A partial list of the most common findings is provided below. Further cautionary information can be obtained from MSDS sheets for the individual chemicals.

Pyrrhotite. A form of iron and sulfur that reacts easily and can slowly smolder and burn when it is dry and exposed to oxygen. Wetting with water will stop or delay the oxidation reaction.

Liquid Hydrocarbons. Hydrocarbon chains above about 6 carbon atoms become liquid. The first, hexane, is often used as a solvent. Pentane (boiling point 36 degrees C) may be either a gas or a liquid. Liquid hydrocarbons do not occur often in gas pipelines, but well gathering systems, and upsets in process systems can release such components into a pipeline. These liquids may be mixed with water or glycols used in dehydrators. Other than being volatile and the vapors flammable, they are not harmful in small quantities.

Natural Gas. It is almost obvious that at least a small portion of natural gas will be released or captured in the material sample when black powder is collected. The released quantity should be minimized and the captured quantity should be sealed from release. Spark potential must be prevented.

Radioactivity. Pipeline corrosion products from some parts of the world are known to be radioactive. At least one of the sources of such contamination is the presence of radon in pipeline gas. The radon gas can transfer electrons with lead (Pb). Although the distribution of radioactive materials within a pipeline are low levels, mechanical cleaning actions such as pigging can concentrate levels at the point of human exposure.

Heavy Metals Such as Mercury. This is a rare but possible problem. Mercury can take liquid or vapor forms in the feed gas.

Protection of the Sample. It is anticipated that many black powder samples oxidize very easily and quickly upon exposure to air. To prevent this, the samples should be handled according to these directions at all stages of sampling and packaging to avoid oxidation.

The sample collected should be representative of the bulk material present. Form is not important (lumps, fines, liquids, etc), but the sample should not be collected to omit material that looks different. If the sample is liquid with solids in it, enough solids should be collected to constitute the 30 gram sample. The liquid is not of value to this testing, but is useful in protecting the sample from oxidation.

Protection of the Sampler. The main caution to the person collecting the sample is to take care to be clean and quick. Protective clothing and equipment will prevent contamination of hydrocarbons, radioactivity, natural gas, or possible heavy metals. If the opening for sample collection is large, exposure to air can create flammable hazard. Although skin exposure to iron-sulfides is not harmful, it should be avoided if possible; fine material is difficult to wash off and can be inhaled; wet material is also messy. Inhalation of natural gas should also be avoided.

Locations to Collect Samples. Preparation for taking black powder samples should be made before the opening of the pressure boundary is done. If the opening is made and black powder is found, and *then* the decision to sample is made, the sample may already be contaminated with air before the material is collected and protected.

There are a number of likely locations to collect or find black powder samples. It can be drained from the bottom of vessels or filters, or collected when the filters are opened for replacement. Any time maintenance is performed on a pipeline or its machinery, which involves opening the machine or pipe, the opportunity exists to be exposed to black powder. Another common exposure is the material removed during pigging. The latter may be mixed with cleaning fluids, gels, or other materials, but if identified with the sample, they may not compromise the sample, if they do not chemically react with the black powder. Sometimes it may be possible to obtain samples adequate for testing through drains; these usually must have water in them if they are to flow. If the exposed residue has enough loose volume, the sample should be collected by plunging the collection container deep within the sample and sealing it before bringing it to the surface of the material. Places where water may collect and be drained are likely places for black powder to form.

Specimen Container. Chemical testing requires only 30 to 50 grams (1-2 ounces) of material. *Samples larger than 50 grams or 2 ounces should not be collected.* Thus, the container should be sized to collect only the appropriate amount of material and not more. It is best if the container is non-breakable (non-brittle plastic), and it should have an air-tight seal. If the sample has no liquid, it can be collected in a plastic bag with the air purged. Place this plastic bag inside another plastic bag and seal again. A steel vessel is not desirable because it may allow corrosion to continue. The vessel and seal should be able to resist a certain amount of expansion or collapse of the volume within it as temperatures or altitudes change.

Samples for chemical testing should be collected as promptly as possible after the black powder is exposed. During the collection process, the sample material should be exposed to as little air (oxygen) as possible. This includes the time from first opening the pressure boundary until the sample is collected and sealed in its container.

The proper sample should completely fill the collection container. If the appropriate sample quantity does not completely fill the container, the air in the container should be displaced with a corrosion-neutral gas such as nitrogen or argon. Alternate filling fluids of more questionable value could be carbon dioxide, or natural gas. Water from within the pipe could be a last resort. Other water, even distilled, contains absorbed oxygen.

It is recommended to protect the sample vessel from potential damage or leakage during shipping or other transportation by wrapping it with tape or other cushioning material or packaging. Place the sample package in a larger, also sealable container or bag.

Labeling and Shipping. Labeling and documentation information needed is given below. This information should be enclosed in the box, or e-mailed to SwRI (address below). The sample should be packaged and labeled as follows:

The residue, sealed in double plastic bags with air purged out if dry, or an unbreakable plastic container if it contains liquid, will need to be packaged in strong outer fiberboard box. An MSDS sheet for a flammable material (See Hazards paragraphs above) should be attached on the outside. Nothing needs to be written on the outside of the box, just the label attached to this document and an MSDS sheet in a packing list pouch. (Iron sulfide MSDS sheet to accompany this document.)

These are regulations from CFR49 for transportation. FedEx ground is a suggested carrier to use. The proper shipping name under CFR49 is: Flammable solid, corrosive, inorganic, n.o.s., class 4.1, UN3180, packing group II. Any further questions should be directed to the U.S. Department of Transportation at 1-800-467-4922. The SwRI shipping department can be reached at 210-522-5615, and ask for Alex.

The sample, packaged as described and accompanied by the requested database information above, and a payment of US\$2,500 to cover testing and database development, should be sent to:

Richard Baldwin
Division 18/Bldg. 77
Southwest Research Institute
9503 West Commerce
San Antonio, Texas 78227
United States

Questions and database information may be directed to rbaldwin@swri.org

Samples that do not meet these requirements of sample size and packaging, collection method, documentation, and payment will not be accepted, or will not be processed.

Labeling and Documentation. In addition to collecting a sample for testing, the sample has much more value if it has documentation defining its source and pedigree and a contact for follow-up information. The following list is information that is desirable to have accompanying the sample. For PRCI testing, the items with (*) are required and all entries are requested, if known.

Revision 1, 11/3/2008

“Black Powder” Sample and Data Base Information

Testing sponsored by PRCI International and performed at Southwest Research Institute[®], San Antonio, Texas, U.S.A.

Contact information:

Company:

*Address, City, State/Province, Country:

*Pipeline name or designation:

*Knowledgeable person:

*Phone no.: _____ and/or E-mail address: _____

Sample information:

*How long (time) between opening the pressure boundary exposing the sample to air, and it being sealed in this container? _____ (hours, minutes)

*What gas or liquid was used to purge this sample?

Hardware from which the sample was removed: _____

How long since this pipe line was cleaned or pigged? _____(months)

*Average or typical Hydrogen Sulfide (H₂S) content of the gas in this pipe line? _____ parts per million, or _____ grains per 100 cubic feet of gas.

Average or typical total Sulfur content of the gas in this pipe line? _____grains per 100 cubic feet of gas.

*Average or typical flow rate through this pipe? _____ mmscfd, or specify units.

Pipeline gas temperature and pressure at this site (give units) T _____,
P _____

Acceptable moisture content? _____ lbs per 100 cubic feet of gas. Is this often exceeded? _____

Digital photographs of the collection would be of interest.

This information, with the results of the test, will be included in a database owned by PRCI.

E-mail to rbaldwin@swri.org