



## Black powder formation by dewing and hygroscopic corrosion processes

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### ABSTRACT

The presence of black powder in natural gas pipelines can lead to equipment erosion, valve failure, instrumentation malfunction, and increased pressure drop. However, despite its impact on downstream and midstream operations, black powder production is poorly understood. In the present work, black powder formation as a result of corrosion was investigated by simulating sales gas conditions in a glass cell. Steel specimens were systematically exposed to a range of CO<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub> partial pressures at differing water condensation rates. The potential for hygroscopic material assisting black powder formation was also investigated. Friable corrosion products found in dewing conditions consisted of siderite (FeCO<sub>3</sub>), mackinawite (FeS), and hematite (Fe<sub>2</sub>O<sub>3</sub>). The expected mass of corrosion products, as determined from experimental corrosion rates, are in line with the high levels of black powder that can be experienced. The presence of hygroscopic NaCl crystals facilitated corrosion at relative humidities as low as 33%.

### 1. Introduction

Black powder, particles which can be entrained by a natural gas stream, is a common problem in natural gas pipelines and if left unchecked can erode equipment, induce greater pressure drops, and clog instrumentation (Baldwin, 1997). Black powder may contain corrosion products, salt, dirt, and other materials such as those trapped in the pipeline during construction. Previous studies examining the composition of black powder have found primarily iron oxides and iron sulfides, but iron oxyhydroxides, iron carbonate, and elemental sulfur were also reported (Bhardwaj et al., 2016; Khan et al., 2015; Sherik et al., 2008; Yamada et al., 2011). The frequent occurrence of the aforementioned species have led researchers to conclude black powder is predominantly a result of corrosion (Baldwin, 1997; Bhardwaj et al., 2016; Khan and Al-Shehhi, 2015; Khan et al., 2015; Sherik et al., 2008; Yamada et al., 2011).

Corrosion in natural gas pipelines is typically caused by the presence of CO<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub> with liquid water. CO<sub>2</sub> and H<sub>2</sub>S are known to be present within natural gas at various concentrations, but O<sub>2</sub> is rarely reported. Exogenous oxygen ingress is attributed to be the primary source of O<sub>2</sub> in natural gas and can lead to concentrations ranging from 0 to 0.03 vol% (Sherik et al., 2008; Sridhar et al., 2001). Liquid water may seldom occur as the gas is dehydrated to 7 lbs H<sub>2</sub>O/MMscf (0.112 mg/l) or lower to reduce the risk of internal corrosion, however, upsets in gas dehydration units may release enough water for condensation to be feasible. Measured dew points of water in the sales gas

network were reported by Sherik et al. (Sherik et al., 2008) The sales gas moisture content consistently exceeded the maximum moisture level of 7 lbs/MMscf (0.112 mg/l) risking dew formation. The measured water dew points were compared to meteorological data to examine the potential for water condensation on the steel pipeline. Winter ambient temperatures were frequently below the water dew point temperatures measured, therefore, water condensation was deemed likely.

Water accumulation at the steel wall may be facilitated if a hygroscopic material such as salt is present on the steel surface. The frequent use in some regions, in particular arid locations, of seawater as an economical hydrotest medium can leave a hygroscopic salt residue on the steel surface once the water is removed unless rinsed properly (Hali et al., 2016; Holden et al., 2010; Zhao et al., 2010). The presence of salts in regions associated with black powder formation has also been attributed to production water carryover in a case study on the mitigation of black powder production in the field (Olabisi et al., 2017). This salt layer can attract and accumulate water potentially deliquescing in the process. In oxic environments, the presence of hygroscopic NaCl particles on mild steel led to corrosion in relative humidities as low as 33%, much lower than the NaCl deliquescence relative humidity of 75% (Schindelholz et al., 2014). Hygroscopic corrosion in CO<sub>2</sub>/H<sub>2</sub>S conditions is even less well studied. Corrosion in non-saturated conditions was observed in CO<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>S (Kolts, 2004; Litke et al., 2013), but neither morphology nor corrosion product composition were analyzed so the potential for black powder production through hygroscopic corrosion processes remains unknown.

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**Table 1**  
Sponsor-provided sales gas conditions.

Parameter	Value
CO <sub>2</sub> Content	1.31 mol%
H <sub>2</sub> S Content	7 ppm
Operating Temperature	33–50 °C
Operating Pressure	40–42 bar
Flow Rate	550 MMscfd (180 sm <sup>3</sup> /s)
Pipeline Diameter	42 (106.7) Inches (cm)

Water availability has been identified as the primary unknown for corrosion in sales gas conditions since the concentrations of CO<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub> are known to be adequate for corrosion to occur. If the water content of the sales gas is high, then water may condense onto the steel surface. However, if the water content is below the thermodynamic dew point temperature, then a hygroscopic material like salt must be present for corrosion to occur. Largely absent from the black powder literature is information relating to corrosion product spallation. A corrosion product layer can grow in a pipeline, but if that corrosion product cannot spall then it cannot become entrained in the gas thus forming black powder. In CO<sub>2</sub>/H<sub>2</sub>S conditions related to sales gas pipelines experiencing dewing corrosion, friable FeS layers were observed (Yaakob et al., 2016). Similar layers may be formed in sales gas conditions which may ultimately lead to black powder formation. H<sub>2</sub>S partial pressure and water condensation rate were critical to the development of the friable layers but were little explored. The effect of CO<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub> concentrations on the development of corrosion product layers due to dewing and hygroscopic corrosion are explored in the present study.

## 2. Experimental procedure

Corrosion in sales gas conditions was examined by exposing X65 steel specimens to CO<sub>2</sub>/H<sub>2</sub>S or CO<sub>2</sub>/O<sub>2</sub> mixtures in dewing or hygroscopic conditions. Gas concentrations were derived from sales gas conditions supplied by the sponsor as shown in Table 1; O<sub>2</sub> and H<sub>2</sub>O concentrations were not supplied.

From the specified gas concentrations and the highest operating pressure, the partial pressures of CO<sub>2</sub> and H<sub>2</sub>S were calculated to be approximately 0.55 bar and 0.3 mbar, respectively. To investigate the effect of H<sub>2</sub>S content, the H<sub>2</sub>S partial pressures tested were 0, 0.1, 0.3, and 1.0 mbar. The H<sub>2</sub>S was diluted with CO<sub>2</sub> for CO<sub>2</sub> partial pressures of 0.96–0.98 bar. Corrosion at 0.1–1 mbar H<sub>2</sub>S is known to be H<sub>2</sub>S dominant, so dilution over the 0.55 bar CO<sub>2</sub> partial pressure should not affect results. Tests with O<sub>2</sub> were conducted at 10 mbar O<sub>2</sub>, the partial pressure expected if the O<sub>2</sub> content was ca. 0.02 mol%. Gas flow rates were kept low so that the specimens experience a largely quiescent gas environment.

Experiments were conducted with API<sup>1</sup> 5L X65 steel specimens. The specimens were machined into two geometries: 1.25-inch-diameter × 0.5-inch-thick (31.7 mm × 12.7 mm) cylindrical specimens for surface and corrosion rate analysis, and 0.5 × 0.5 × 0.08 inch<sup>3</sup> (12.7 × 12.7 × 2 mm<sup>3</sup>) specimens for XRD analyses. Specimens were coated with a fluoropolymer to prevent corrosion on undesired surfaces and eliminate galvanic effects. The composition of the steel is shown in Table 2. As the H<sub>2</sub>S partial pressures used during experimentation fall below the 0.3 kPa guideline for CRAs as noted in NACE MR0175/ISO15156, low-carbon steel usage can be expected under these conditions (NACE MR0175, 2015).

### 2.1. Dewing corrosion apparatus and experimental procedure

Dewing conditions were examined by exposing steel specimens to water-saturated CO<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub>S or CO<sub>2</sub>/O<sub>2</sub> mixtures in the apparatus shown in Fig. 1. The apparatus and procedures for testing in dewing conditions are based largely on those used by Yaakob et al. (Yaakob et al., 2016), to test marginally sour TLC conditions, though modifications were made to better control the steel temperature and therefore the water condensation rate. Experiment selection was guided by the test matrix shown in Table 3.

Gas, metered by a rotameter, at the desired CO<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub> concentrations, was bubbled through 1 L of heated deionized (DI) water located in the bottom of the glass cell to heat and saturate the gas with water. The temperature of the water, which is controlled by the hot-plate, is set such that the gas above the solution near the specimens is held at the desired temperature of 30 °C. Gas was bubbled through the glass cell for a minimum of 3 h before the steel specimens were inserted.

One large cylindrical specimen and one XRD specimen were included in each test. The specimens were then ground with silicon carbide abrasive papers to a 600 grit finish with water as the coolant. The water was rinsed from the surface with isopropanol immediately after grinding to minimize unwanted corrosion. The specimens were cleaned in isopropanol in an ultrasonic bath, dried with cool air, and then the initial mass was recorded. Specimens were stored in nitrogen until insertion, which was ordinarily less than an hour after polishing. The cylindrical specimens were inserted directly into PEEK specimen holders designed to provide a gas-tight seal to the lid. The smaller XRD specimens were suspended from the lid with a specially designed holder where the steel specimen was held by a magnet within an aluminum body which aids heat transfer to the temperature control system. Peltiers and heatsinks were placed over the specimens, and the resultant stack was fastened to the lid. Temperature control was then initiated to cool the specimens to 25 or 15 °C to achieve the low water condensation rate (WCR) of 0.015 ml/m<sup>2</sup>/s or high WCR of 0.05 ml/m<sup>2</sup>/s, respectively. The WCRs were calculated with an in-house water condensation model.

Specimen temperature control was performed with a PID controller. Steel temperature was measured with 10 kΩ thermistors mounted to the side of the cylindrical specimens or within the aluminum body of the XRD specimen holder. Peltiers held in thermal contact with the specimen facilitates cooling by acting as a heat pump when electrical power is applied. By controlling the amount of power supplied to the Peltier, the amount of heat transferred can be controlled. Power to the Peltiers is supplied by an external AC to 12 V DC power supply controlled with pulse width modulation to the duty cycle determined with the PID algorithm. During operation, a significant amount of heat is generated, so a water-cooled heatsink is placed over the Peltier to prevent overheating. Additionally, a double-pole-double-throw mechanical relay was installed between the controller and the Peltier to more easily switch the polarity of the Peltier, if necessary.

After specimen insertion, the glass cell was allowed to purge for an additional 30 min with CO<sub>2</sub> before H<sub>2</sub>S was then added into the system, when required. The H<sub>2</sub>S concentration was set by mixing a CO<sub>2</sub> and a premixed CO<sub>2</sub>/H<sub>2</sub>S stream metered by a rotameter upstream of the glass cell. The H<sub>2</sub>S concentration was measured with colorimetric gas detector tubes and adjusted as necessary. The desired oxygen concentration was achieved by mixing CO<sub>2</sub> and air in the same manner as CO<sub>2</sub>/H<sub>2</sub>S. The O<sub>2</sub> partial pressure was measured with an O<sub>2</sub> analyzer throughout the experiment and adjusted as needed. Gas was continuously passed through the glass cell throughout the experiments. Effluent gas containing H<sub>2</sub>S was vented through a sodium hydroxide solution then an activated carbon scrubber. Test conditions were monitored and adjusted as needed to maintain experimental parameters.

After the allotted exposure time, the specimens were removed and immediately rinsed with isopropanol to remove water and prevent

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