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Degradation of thermocouple in a temperature programmed sulphidation reactor

Mohan S. Rana *, K. Ravindranath, N. Tanoli

Petroleum Research Center, Kuwait Institute for Scientific Research, P.O. Box 24885, 13109 Safat, Kuwait

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ABSTRACT

Sulphidation due to sulphur bearing gases such as H_2S with refinery materials is a serious problem in the petroleum industry. Measuring instruments such as thermocouples (TCs) used in the refining industry to measure and control temperatures in critical areas are also susceptible to sulphidation when exposed to the sulphur bearing process media. The paper presents an investigation carried out to understand the failure of a TC in a temperature programmed sulphidation (TPS) reactor. The TC was incorrectly installed in the reactor without the external protective sheath. As a result of incorrect installation, the TC was exposed directly to sulphidizing gas of H_2S (5% H_2S in H_2) at a programmed temperature profile (150–1000 °C). The qualitative H_2S consumption with a change in temperature indicated that the H_2S reaction with the TC started at about 400 °C, which corresponds to a physical phenomena on the metal surface. The TPS result indicated that the first H_2S consumption peak in the range 600–780 °C corresponded to the surface phenomena, mostly due to the H_2S chemisorption reaction on the metal surface. However, the bulk phenomena of sulphidation or corrosion require diffusion as a function of further increase in temperature, hence a mass consumption peak in the range of 780–900 °C is recorded. Detailed investigations of corroded TC were carried out using TPS, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The investigation revealed that the failure of the TC was due to catastrophic sulphidation taken place as a result of incorrect installation. The results further suggest that the TPS technique has the potential to study the sulphidation behavior of metals and alloys.

1. Introduction

In recent years, the petroleum refineries have received considerable importance because of the increased demand for fuel oil and supply needs. The demand and supply complement each other. Hence, the petroleum refining industry is demanded continue to operate at near or beyond their refining capacities [1]. Reliable operation of refineries are critical toward ensuring a continued supply of valuable products to meet this energy demand. Operating at or beyond the originally-designed capacity in terms of throughput, temperature and pressure puts the process equipment and piping in the envelope of increased risk in terms of material integrity. Hence, most of the refineries focus on crucial issues of material fitness, risk analysis, and life assessment [2–4]. At the same time, there is a continued need governed by the statutory regulations for the reduction of toxic emissions from the combustion of fossil fuels [5]. The hydrotreating process is used in the petroleum

* Corresponding author.
E-mail address: mrana@kisr.edu.kw (M.S. Rana).

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refinery to reduce toxic emissions by removing S and N from petroleum-derived feedstocks [6,7]. In the hydrotreating process, the S and N in the feedstock gets converted to H_2S and NH_3 through catalytic reactions. The level of H_2S at the end of reactor or the exit may increase up to 4 kg/cm^2 in a typical hydrodesulphurization (HDS) unit. However, the concentration may vary with the processing unit based on factors such as sulphur in the feed, and target for HDS conversion.

H_2S is one of the major corrosive constituents of the hydroprocessing unit. Sulphidation, ammonium bisulphide corrosion and polythionic acid stress corrosion cracking are the major corrosion-related failure modes in hydrotreating units contributed by H_2S [8,9]. H_2S reacts with metals and alloys at high temperatures leading to catastrophic sulphidation and the failure of process equipment and piping [10,11]. Sulphidation mostly results in the general thinning of alloys. Ammonium bisulphide corrosion, on the other hand, is relatively an aggressive form of corrosion leading to equipment failures as well as blockage of heat exchanger tubes, which is a potential cause of pressure drop in refinery units, including hydrotreaters [12–18]. The most troublesome hydrotreating units are those processes for HDS and hydrodenitrogenation (HDN) of heavy petroleum fractions. Polythionic acid stress corrosion cracking is a catastrophic failure of austenitic stainless steels under certain metallurgical conditions [8,19]. In HDS units, polythionic acid is formed by the reaction of metal sulphides generally present on the equipment exposed to sulphur containing hydrocarbons at high temperatures with moisture and air [8,19]. The materials used in refinery process units such as HDS should be resistant to the above forms of corrosion.

Measurement and control of temperature is one of the most common requirements of refinery instrumentation and the thermocouples (TCs) are by far the most widely used temperature sensors. TC elements are normally not exposed to the process, but are inserted through thermowells to avoid corrosion reactions and damage. The continuous exposure of thermocouple elements (−Ve and +Ve, KN and KP respectively) to reducing/sulphiding atmospheres at high temperatures can lead to the destruction of thermoelements, resulting in thermocouple failure.

To study the sulphidation of HDS catalysts, a temperature programmed sulphidation (TPS) equipment was procured. During the commissioning and test run of the equipment, certain abnormal behavior related to H_2S consumption and temperature profile were noticed. The equipment was shutdown to study the observed abnormal behavior. The paper presents the results of an investigation carried out to understand the root causes of the abnormal behavior in the consumption pattern of H_2S during the test run and to relate the H_2S consumption as a function of temperature. XRD and SEM-EDS analyses were carried out on the damaged TC to correlate with the TPS data.

2. The temperature programmed sulphidation (TPS) experiment

The TPS measurements were carried out in a flow apparatus which consists of U-tube type quartz reactor, operating at atmospheric pressure and temperatures of up to 1250 °C. A 5 vol% H_2S in H_2 mixture was used as the sulphiding gas with a flow rate of 50 cm^3 min^{-1}. A thermal conductivity detector (TCD) cell was used to determine the adsorption and/or consumption of H_2S. The quartz reactor was pretreated in Ar at 150 °C for 15 min, then it was cooled to room temperature. Ar was used as a TCD carrier gas while H_2S/H_2 sulphiding gas flowed into the system at 50 cm^3 min^{-1}. After the baseline TC signal was stabilized, the heating of the catalyst sample was carried out at 15 °C/min. A liquid nitrogen trap at −78 °C was used to the reactor effluent line just before TCD to remove water vapour or contaminant gas produced during the sulphiding process.

A K-type sheathed TC was used in the quartz reactor to control the reactor bed temperature accurately in the TPS equipment. The primary alloys of K type TC are chromel, the positive leg (KP: 90% Ni, 10% Cr) and alumel, the negative leg (KN: 95% Ni, 2% Mn, 2% Al, 1% Si). The chromel–alumel TC used in the reactor was 1.6 mm in diameter, was magnesium oxide insulated, and sheathed in alloy 600 (chemical composition in weight%, Cr: 14.8; Fe: 9.1; C: 0.15; Ni: 75.3).

During the sulphidation test run, unusual consumption of H_2S, along with abnormal rise in bed temperature were noticed. In view of the abnormal behavior, the test run was discontinued and an investigation was conducted.

3. Visual examination

The TPS equipment was dissembled, the reactor tube was removed and subjected to visual examination. The TC was found installed in the reactor without its protective sheathing which exposes the TC directly to the H_2S flow. Upon conducting a visual examination, the thermocouple was found to be discolored and disintegrated. Small sections from the tip were found separated from the thermocouple (Fig. 1). The separated sections could be easily crushed into powders with fingers. The powders appeared grayish-black in color with a characteristic smell of sulphur compounds.

4. Characterization

The affected location of the thermocouple was examined using scanning electron microscope (SEM, TESCAN TS5135 MM Vega). The energy dispersive spectroscopy (EDS, OXFORD Instruments) was used to characterize the chemical constituents of the affected sections of the TC. The SEM and EDS investigations were also carried out on an undamaged part of the TC which was situated outside the furnace for the purpose of comparison. The X-ray diffraction (XRD) patterns were recorded (PANalytical PW3040 X'pert PRO) for the affected samples to identify the crystalline phases.