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Comparison of different processes for preventing deposition of elemental sulfur in natural gas pipelines: A review

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ABSTRACT

The presence of S_8 in natural gas streams has caused many problems at the delivery points and measuring equipment. There are many treatment processes, including absorption, adsorption, membranes and conversion processes. In this work, a literature review was carried out on the main methods available for removal of sulfur compounds from gas streams as well as an analysis of the feasibility of its application in pipelines. The results showed that, due to the complexity of the processes and to the costs involved in implementation and maintenance, the mechanisms of control by adsorption are the most attractive for use in pipelines.

1. Introduction

Natural gas is a fossil fuel that is gaining an increasingly significant portion of the global energy matrix. This change is due to the technical and economic benefits provided by the use of this energy source. Natural gas is cheaper than other sources of fossil fuels and reduces the costs associated with maintenance. As for the environmental aspects, the use of natural gas as a form of energy brings benefits such as reductions in sulfur dioxide (SO_2), nitrogen oxides (NO_x), particulate matter and carbon dioxide (CO_2).

Natural gas consists of a mixture of light hydrocarbons that, under normal pressure and temperature conditions, is in gaseous state. According to Lopes (2003) natural gas is composed predominantly of methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and, in smaller proportions, other higher molecular weight hydrocarbons. It may also have low levels of contaminants such as nitrogen (N_2), carbon dioxide (CO_2), water (H_2O) and sulfur compounds such as hydrogen sulfide (H_2S), mercaptans (RSH), carbonyl sulfide (COS), carbon disulfide (CS_2) and elemental sulfur (S_8).

In the production and transportation of natural gas, several problems may occur, among which the formation and deposition of elemental sulfur is one of the most widely observed. Santos et al. (2013) stated that the formation and deposition of S_8 in pipelines can lead to various problems that affect safe transport from the production in the wells to the processing of the natural gas. According to Zhou et al. (2013), the pipe blockage caused by sulfur deposition and the corrosion caused by perforated pipes and damaged equipment can seriously affect the normal operation in the field, resulting in low production or even shutdowns.

Pack et al. (2013) concluded that the presence of traces of sulfur vapor in the gas stream could lead to the formation of elemental sulfur deposits by desublimation in the metering devices during the depressurization process. Chesnoy and Pack (1997) and Pack et al. (2012) have shown that elemental sulfur deposition onto measurement instruments may cause errors of up to 2%, or even higher in some cases, in the readings of transported gas volumes.

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Menezes et al. (2014) showed in his research that an error of 2% in the measurement of the volume traded can cause losses of extremely significant revenues for the company when large volumes of natural gas are transported, and the company may suffer financial penalties from the regulatory agency, depending on the country where the gas transporter carries out its activities.

Taylor and Kimtantas (2014) reported that solid elemental sulfur deposits can accumulate and cause flow constriction, thereby reducing the separation capacity of the equipment. They can plug instrumentation connections, cause poor process control, and require additional maintenance costs.

Several studies have been conducted to investigate the mechanisms of formation and deposition of elemental sulfur in natural gas pipelines. According to Pack (2005) and Cézac et al. (2008), nucleation is the most probable mechanism promoting sulfur deposition in natural gas pipelines. According to these authors, the processes of sulfur formation and deposition essentially comprise three nucleation steps, namely particle formation, coagulation and/or condensation (particle growth), and deposition.

Santos et al. (2013) reported that the formation of yellow powder, also known as elemental sulfur, can be influenced by changes in operating conditions such as pressure and temperature drops, as well as the gas composition and additives used during transport in pipelines. These authors constructed phase diagrams for various compositions of natural gas using the HYSYS® process simulator, and they showed that the phase equilibria is best represented by the state Peng-Robinson equation. Moreover, the results showed that nucleation and desublimation are the most likely mechanisms that lead to the formation and deposition of elemental sulfur.

Serin et al. (2005) studied the process of expansion of natural gas by means of a flash to study the sulfur desublimation process. The authors modeled the phenomenon and conducted an experimental procedure that allowed the determination of the mass of sulfur deposited depending on the gas flow rate. Thus, the results obtained by the modeling and the experimental values for the deposited sulfur helped confirm the hypothesis of desublimation.

Zhu et al. (2011) concluded that temperature is the dominant parameter affecting condensate formation, whereas pressure is the dominant parameter for desublimation. In general, natural gas transportation systems operate under conditions of high flow rates, low temperature drops (due to thermal insulation) and high pressure drops (because of turbulent flow). Unless there is a sudden local temperature drop in the system, pressure variation seems to be an important parameter for describing the deposition mechanism. Thus, the mechanism of elemental sulfur deposition via nucleation and desublimation seems to be more probable. Cézac et al. (2008) stated that the desublimation occurs due to temperature reduction at pressure drop points where the final temperature is below the temperature of the triple point of sulfur (368.5 K). Therefore, the sulfur present in the gas stream is converted directly from the gaseous phase to the solid phase, and it deposited downstream of pressure reduction equipment.

The solubility of sulfur in the gas stream is directly influenced by temperature, pressure and gas composition. Sun and Chen (2003) evaluated the influence of pressure and temperature on the solubility of sulfur with different gas compositions, and they concluded that the temperature has greater influence on the solubility than the pressure. Cézac et al. (2008) found that, in the processed gas under the conditions of transport, the solubility of sulfur in the gas is very low, less than 0.005 mg/m^3. This justifies the fact S_8 deposits occur even when the concentration of sulfur in the gas stream is very low.

Santos et al. (2015) studied the influence of the amount of sulfur present in the vapor phase in the gas stream using the gas equilibrium diagrams. Four simulations were performed using the HYSYS® process simulator and the Peng-Robinson Equation of State. Simulations were performed with added sulfur contents of 0.01, 0.5, 1 and 5 ppm in the current natural gas of the Field-School Project of the Fazenda Mamoeiro field in the state of Bahia, Brazil. The results showed that, even at low concentrations, the presence of sulfur modifies the equilibrium diagrams, requiring higher temperatures for maintaining equilibrium when the concentration of S_8 in the gas stream increases.

In Brazil, for delivering natural gas to the customer, it is necessary that existing contaminants are within an acceptable level determined by the National Agency of Petroleum, Natural Gas and Biofuels (ANP). According to Santana and Machado (2014), the maximum level of sulfur compounds allowed by the ANP in the natural gas delivered to the customer is 70 mg/m^3. In other countries, this maximum level is also stipulated in their legislation. According to Lopes (2003) in the United States, the H_2S content is often limited to 4 ppmv. There are levels specified as low as 1 ppmv in some European countries. The maximum total sulfur content, including carbonic sulfides, disulfides, etc., usually has contents ranging from 10 to 20 ppmv.

The aforementioned studies show that the mechanism of formation of elemental sulfur, as well as the problems caused due to deposition, are well documented in the literature. Thus, it is evident that studies are needed with the goal of searching for alternatives that can eliminate and/or reduce the presence of this compound. Worldwide, there are a number of studies and patents that have been developed for use in removing sulfur compounds in natural gas streams. The vast majority of these processes have been developed for use in Natural Gas Processing Units (NGPU's). The goals of this study are to carry out a literature review on the desulfurization processes of gaseous streams and to analyze the feasibility of their application in pipelines as an alternative to preventing the formation and deposition of S_8 in transmission lines, control equipment and measurement devices.

2. Materials and methods

The methodology used in this work was to conduct a literature review using the main portals and patent search banks on methods of gas stream desulfurization. The research portals used included Science Direct, Periodic Capes, Scopus and Google Scholar for scientific articles and the National Institute for Industrial Property (INPI) and World Intellectual Property Organization (WIPO) for the patent search. The keywords used in searches were as follows: desulfurization methods, removal of sulfur, natural gas, absorption, adsorption, membrane, and sulfur compounds conversion processes.

Silva Filho (2013) stated that the most important processes for removing H_2S from gas streams were proposed by Kohl and Nielsen (1997) and can be grouped into liquid absorption, adsorption on solids, permeation through membranes, and conversion. Szarblewski et al. (2012) grouped the sulfide removal processes of hydrogen into in three principle approaches: chemical, physical and biological.

3. Literature review

From the literature, the main processes that were found consist of technology to be employed in NGPUs, the so-called desulfurization units. These technologies most often are employed to remove H_2S and recover elemental sulfur from gas streams. According to Tagliabue et al. (2009), gas treating technologies can be roughly divided into two main categories: (i) separation, with contaminant concentrations of 10 wt% or higher in the feed; and (ii)