

## Critical evaluation of Hydrogen Sulfide (H<sub>2</sub>S) when associated with corrosion, worker health and safety



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### ABSTRACT

Hydrogen sulfide (H<sub>2</sub>S) is a colorless gas with a characteristic unpleasant odor (like rotten eggs) that is extremely toxic and corrosive. Due to its toxicity, H<sub>2</sub>S irritates the eyes and/or affects the nervous and respiratory systems. Concentrations on the order of 700 to 1500 ppm can kill a human in a matter of minutes. The media has presented several examples of H<sub>2</sub>S leaks that jeopardize human lives, threaten the integrity of industrial assets, and endanger the environment. This work aims to show the importance of knowledge of the origins and physicochemical properties of hydrogen sulfide in the direct and indirect relations with man, the environment and industrial equipment.

**Keywords:** Hydrogen sulfide, Corrosion, Contaminations, Environment, Leaks.

### 1 INTRODUCTION

The lubricating oil production industry plays a key role in the efficient operation of a wide range of mechanical equipment and vehicles. However, depending on the type of oil, during the manufacturing process, significant risks to the health and safety of workers can occur, especially when it comes to the presence of hazardous chemicals. One such compound of concern is hydrogen sulfide (H<sub>2</sub>S), a toxic, corrosive, and highly flammable gas that can be released during various stages of the lubricating oil production process.

Hydrogen sulfide is a toxic gas that has several adverse effects on human health, as well as can cause significant environmental damage. In this context, the critical evaluation of hydrogen sulfide becomes essential to ensure the quality and safety of the lubricating oils produced, considering the identification of possible sources of contamination, understanding the processes of H<sub>2</sub>S formation, and analyzing its physicochemical properties and the forms of corrosion that, directly or indirectly, can affect industrial processing [1-3].

This chapter aims to present the literature on leaks of this gas that have resulted in deaths or that can cause irreparable injuries to humans and the environment, serving educationally to highlight



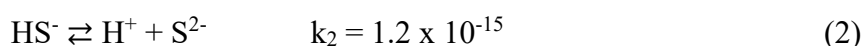
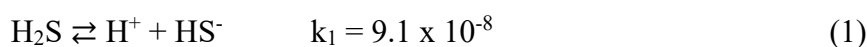
the need for standards and procedures to inhibit and/or prevent such leaks. Present a representative picture of the attack of this toxic gas on humans and identify detection and monitoring systems for this gas in industrial environments. Finally, this work aims to show the importance of knowing the origin and physical-chemical properties of hydrogen sulfide in direct and indirect relationships with man, the environment and industrial equipment.

## 2 MAIN PROPERTIES OF HYDROGEN SULFIDE

H<sub>2</sub>S, whose molecular weight is 34.08 g/mol, is a flammable, toxic gas, has a greater density than atmospheric air and condenses in liquid form at a temperature of -62°C. It is partially soluble in water and organic compounds. The solubility in water at 20°C is 3850 mg/L (0.385%). Generally, the solubility in organic substances is greater than in water. The solubility in ethyl ether is 2.1%, while in hydrocarbons it is around 1.2%. Commonly, solubility decreases by about 2.5% for each degree of increase in temperature.

It has an unpleasant odor, like rotten eggs. The initial perception of its odor varies from individual to individual, however, the concentration of 0.13 ppm (0.18 mg/m<sup>3</sup>) is considered sufficient for the odor to begin to be perceived. It is considered highly toxic acting on the nervous system, eyes, and respiratory tract. H<sub>2</sub>S (34.08 g/mol) is slightly heavier than air (28.8 g/mol).

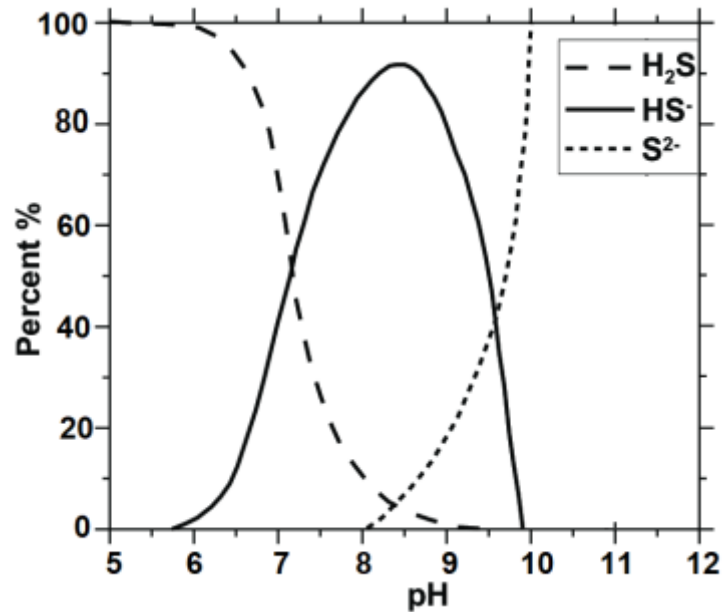
This gas can be found in small concentrations in the human body, as it can be produced by the natural bacteria in the mouth, being a component of bad breath. In the environment, the main sulfur-containing compounds are present in groundwater and are (H<sub>2</sub>S), acid sulfide (HS<sup>-</sup>) and sulfide (S<sup>2-</sup>); and their occurrences are extremely pH-dependent. Regarding the chemical properties of H<sub>2</sub>S, in aqueous solution H<sub>2</sub>S is a weak acid, whose equilibrium in aqueous medium is given by the following reactions, where k<sub>1</sub> and k<sub>2</sub> are the dissociation constants [4].



This reaction is influenced by the pH of the aqueous medium. At pH lower than 7, the non-ionized species (H<sub>2</sub>S) predominates. In the pH range between 7 and 13, the ionized species (HS<sup>-</sup>) is predominant. On the other hand, at pH greater than 14, there is a predominance of the sulfide ion (S<sup>2-</sup>). The distribution of these three species at a temperature of 25 °C is shown in Figure 1 [5].



Figure 1. Equilibrium speciation of aqueous hydrogen sulfide as a function of pH (Modified from House and Weiss[ 5])



Based on Henry's Law, it is possible to state that this gas is soluble in water at room temperature and its solubility is directly proportional to its partial pressure according to equation 3 [6]:

$$C \left( \frac{\text{mol}}{\text{L}} \right) = 0,1013 \frac{\text{mol}}{\text{L atm}} p_{\text{H}_2\text{S}} \text{ atm} \quad (3)$$

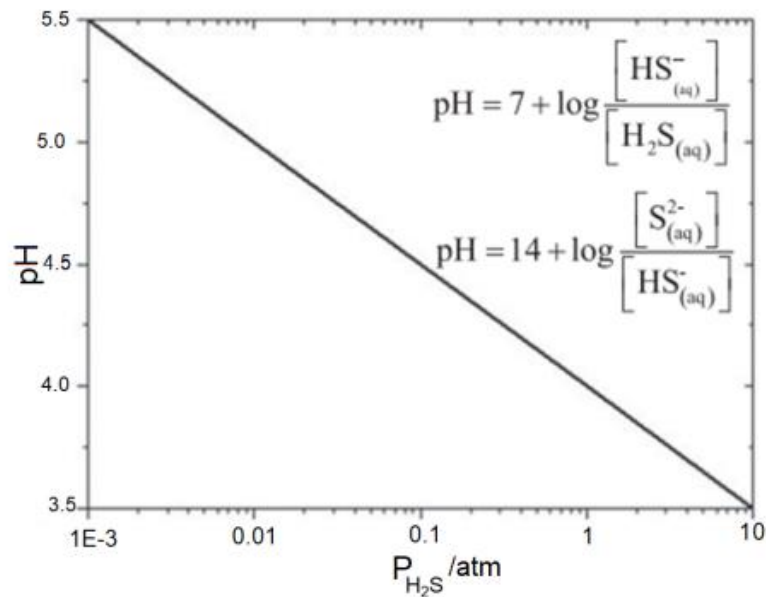
Where

C = solubility;  $p_{\text{H}_2\text{S}}$  = partial pressure and Henry's constant at 25 C° = 0,1013 mol/L<sup>-1</sup>. Atm<sup>-1</sup>

According to Henry's Law, when solubilized in water this gas dissociates and behaves as a weak acid and, consequently, for a given partial pressure of H<sub>2</sub>S ( $p_{\text{H}_2\text{S}}$ ), the actual concentration of H<sub>2</sub>S(aq) becomes less than C, resulting in a more appropriate establishment of an equilibrium condition from the partial pressure. Figure 2 shows two characteristics of the aqueous solutions of this gas. At ordinary pressures saturated solutions are slightly acidic, to change the pH by one unit it is necessary to change the pressure by two orders of magnitude. When the pH of the solution is modified at constant partial pressure and temperature, the equilibrium is disturbed and a new concentration relationship is established [7]. Figure 2 shows the variation of the pH of the solution with the partial pressure of H<sub>2</sub>S.



Figure 2 - Variation of the pH of the solution with the partial pressure of H<sub>2</sub>S(g) at 25 °C (Modified from Oliveira et al.[6])



### 3 ORIGINS OF HYDROGEN SULFIDE

It is considered that hydrogen sulfide can originate in nature and in industrial segments. In nature, it comes from oil fields, natural gas, groundwater, swampy areas, salt deposits, coal, sulphide ores and the emission of volcanoes, that is, it originates from geological processes based on different physical mechanisms -chemical or microbiological.

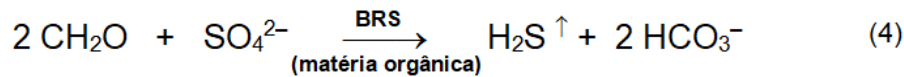
In industrial segments, the origin of H<sub>2</sub>S is known, generally, it comes from chemical removal processes and/or acid gas washing, effluent treatment systems, fermentations, acid pickling, etc.

#### 3.1 SOURCES NATURELS

The natural generation of H<sub>2</sub>S, therefore, is related to diverse geological environments in which the necessary and sufficient components are present to trigger chemical reactions related to geology. Among the mechanisms described in the literature for the generation of H<sub>2</sub>S in oil and natural gas fields, the bacterial mechanism, the thermochemical mechanism associated with the oxidation of hydrocarbons and the thermochemical mechanism that comprises the thermal decomposition of organic matter rich in sulfide compounds stand out [8-10].

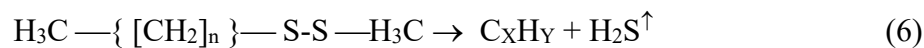
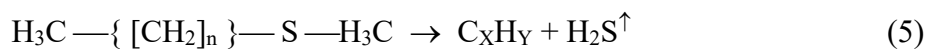
The H<sub>2</sub>S generation mechanisms require a source of sulfur, such as: soluble sulfate (SO<sub>4</sub><sup>2-</sup>) in marine sediments, calcium sulfate (CaSO<sub>4</sub>) or barium sulfate (BaSO<sub>4</sub>); a mediator such as bacteria or high subsurface temperatures and a catalytic agent whose presence will affect the speed of the redox reaction.

In the case of sulfate-reducing bacteria (SRB), other parameters such as pH, organic matter content, salinity, temperature, and absence of oxygen are fundamental in the development of the H<sub>2</sub>S generation process, as shown in the following reaction:

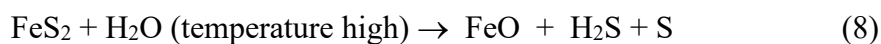
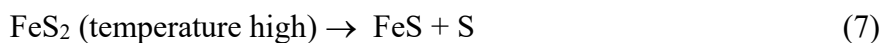


The volumes of H<sub>2</sub>S generated by these mechanisms depend on the availability of the source and the prevailing geological conditions. This indicates that the concentrations of hydrogen sulfide found in nature are random and if there is a geological fault, leaks could possibly occur, the consequences of which are indeterminable. This mechanism can generate H<sub>2</sub>S that can vary from 10 ppm to 100,000 ppm (parts per million) [10].

The thermal decomposition of high-molecular-weight organic sulfide and disulfide molecules inserted in the parent rocks can generate H<sub>2</sub>S, as shown in the following reactions:



Another point that must be added to this work is the formation of sulfur and hydrogen sulfide expelled by a volcano, which can be explained by thermal decomposition and/or vaporization at high temperatures of sulfide minerals (FeS<sub>2</sub>, CuS, NiS, CuFeS<sub>2</sub>, etc.) as shown below by the reactions:



The various eruptions that occurred in the Java volcanic complex, Indonesia, in February 1979, which resulted in 149 deaths, can also be mentioned. Chemical analyzes of these eruptions revealed that they were made up of H<sub>2</sub>S, CO<sub>2</sub> and SO<sub>2</sub> resulting from the thermal decomposition of some minerals existing in the volcanic complex such as: pyrite (FeS<sub>2</sub>), spharelite (ZnS), chalcopyrite (CuFeS<sub>2</sub>), calcite (CaCO<sub>3</sub>) among others [11, 12].

In Alaska, in March 1995, the Akutan volcano expelled extremely toxic fumes consisting of the following gases into the atmosphere: SO<sub>2</sub>, H<sub>2</sub>S, HCl, HF and CO<sub>2</sub>, causing panic and environmental pollution [13].

In September 1997, the Kusatsu-Shirane volcano located near Chiba (Japan) expelled a large amount of toxic fumes into the atmosphere. Analyzes carried out inside the crater in the southwest region showed the following composition: 0.5% SO<sub>2</sub>; 60-65% H<sub>2</sub>S and 33-37% CO<sub>2</sub> (dry basis). The tragic record reveals that four people who were on an excursion there died from hydrogen sulfide contamination [12, 14].



### 3.2 EMISSIONS FROM INDUSTRIAL SOURCES

In industrial segments, the origin of H<sub>2</sub>S is known, generally, it comes from chemical removal processes and/or acid gas washing, effluent treatment systems, fermentations, acid pickling, etc.

Depending on the levels of H<sub>2</sub>S present in a gas stream, it is possible to remove it, while enabling environmental preservation and a source of high-purity sulfur raw material. The Claus process [15,16] to produce sulphur consists essentially of two reactions as follows:

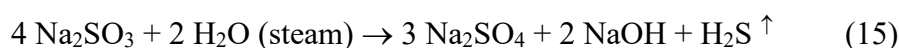
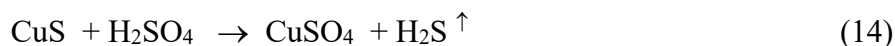
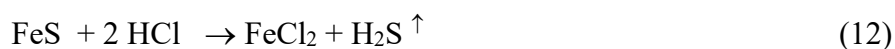


Carbon disulfide (CS<sub>2</sub>) is employed as a solvent for oils, fats, and greases and is also used as a chemical intermediate in other chemical processes. The process of obtaining carbon disulfide takes place in a reactor where the molten sulfur reacts at high temperature, with a carbon source, preferably with natural gas (CH<sub>4</sub>). The preheated natural gas and sulfur pass through a fixed bed of silica gel, in a temperature range of 500 to 700°C, forming carbon disulfide and releasing hydrogen sulfide (H<sub>2</sub>S) as shown in the reaction:



Part of the H<sub>2</sub>S is burned to provide sulfur dioxide (SO<sub>2</sub>) and react with hydrogen sulfide in the presence of catalysts, aiming to use the sulfur to be used again in the process.

The reactions presented, also represent of the following are some generation processes H<sub>2</sub>S in various industrial segments:



Knowing these particularities and the physical-chemical characteristics of H<sub>2</sub>S, the work in question seeks interdisciplinary, to bring together all the vectors that, directly or indirectly, are related to H<sub>2</sub>S and in this way establish a management aimed at identifying the relationships between the harmful effects of sulfide of hydrogen to man, the environment and industrial equipment [17].



## 4 HYDROGEN SULFIDE TOXICITY

According to Souza *et al.* [7] when inhaled, H<sub>2</sub>S penetrates the lungs into the bloodstream, where it is oxidized or reacts with essential enzymes that contain metallic elements, such as copper, zinc, and iron, forming metal sulfides, which can cause vital metabolic dysfunctions. With the increase in the concentration of H<sub>2</sub>S in the body, it is no longer possible to fully oxidize it, so the excess of H<sub>2</sub>S acts on the central nervous system and can cause dizziness, suffocation and even paralysis of the respiratory system. At concentrations above 250 ppm, H<sub>2</sub>S can cause pulmonary edema and, with exposure to concentrations above 1000 ppm, coma and death can occur, as shown in Table 1 [2,17,18].

Table 1 - Effect of Hydrogen Sulfide on the human body [2]

Concentration H <sub>2</sub> S, ppm	Exposure time	Effects on Human Beings
0.05 - 5	1 min	Detection of characteristic odor
10 - 30	6 - 8 h	Eye irritation
50 - 100	30 min - 1h	Conjunctivitis, breathing difficulties
150 - 200	2 - 15 min	Loss of sense of smell
250 - 350	2 - 15 min	Eye irritation
350 - 450	2 - 15 min	Loss of consciousness, convulsions
500 - 600	2 - 15 min	Respiratory and circulatory disturbances
700 - 1500	0 - 2 min	Collapse, death.

The three routes of incorporation of hydrogen sulfide into the human body can be classified into:

Inhalation – gases are absorbed by the respiratory system (lungs);

Ingestion – absorption usually occurs in the intestines, liver, spleen and kidneys by ingestion of food and water contaminated by H<sub>2</sub>S;

Skin absorption – skin absorption occurs by direct contact with the toxic gas.

The toxic effects of H<sub>2</sub>S on the human body are related to the concentration of inhaled gas. Low concentrations of this gas can cause symptoms such as dizziness, fatigue, nausea, cough, diarrhea, loss of appetite, skin irritation, feeling dry and painful in the nose and chest, gastritis, and headache. At higher concentrations, they can cause neurological damage, respiratory paralysis and death by asphyxiation. It is not yet fully clear whether the effects of exposure to low concentrations of H<sub>2</sub>S are cumulative or whether the effects are completely reversible [7].

Some evidence suggests that exposures to H<sub>2</sub>S may be associated with the risk of miscarriages. H<sub>2</sub>S exposure in rats was observed to increase the length of pregnancy and calving difficulties [19, 20].

The study by Fiorucci *et al.*[18] demonstrated that H<sub>2</sub>S in addition to being known as a toxic pollutant, has also come to be recognized as a regulator of various physiological processes, acting as a mediator of various aspects of gastrointestinal and hepatic function. According to the aforementioned



authors, the role of H<sub>2</sub>S in the gastrointestinal tract, liver, and other organs may open up news paths for developing therapies for a variety of pathological disorders.

## 5 INDUSTRIAL HYDROGEN SULFIDE LEAKS

It is important to show that the presence of hydrogen sulfide in this segment can cause impacts that affect humans, the environment and industrial facilities, as shown below in the examples presented.

According to the U.S. Chemical Safety and Hazard Investigation Board (CSB) [21] a reactive chemical incident is a sudden event involving an uncontrolled chemical reaction with significant increases in temperature, pressure, or gas that has caused, or has the potential to cause, serious harm to people, property, or the environment.

In drilling and onshore oil and natural gas production, when drill rods are removed too quickly from wells it can cause the release of H<sub>2</sub>S-containing fluids into the drilling area itself. This release can also occur at sampling points and during testing on drilling wells. Even with oil drilling on platforms, there is a risk that the drilling mud will have a high H<sub>2</sub>S content. Storage and processing areas are also considered high-risk locations [22-24].

During the refining process, crude oil with a high H<sub>2</sub>S content is desulphurized, with extremely high risks at the transfer points. Generally, H<sub>2</sub>S accidents in oil refineries are associated, directly and indirectly, with corrosion of industrial equipment. H<sub>2</sub>S-associated corrosion can be defined as the total, partial, superficial or structural deterioration of materials, causing the breakdown of industrial equipment, resulting in leaks [25, 26].

In Brazil, an event that marked the H<sub>2</sub>S generation and deaths in news in the media occurred in 1996, in Rio Grande do Sul, in a corn storage silo caused the death of three workers. The deterioration/fermentation of corn generated high levels of H<sub>2</sub>S, causing poisoning of the workers, as shown in Figure 3 [27].





Figure 3 – Gas poisoning and killing three workers in Rio Grande do Sul (Brazil) [27]



Another accident mentioned occurred a leak of natural gas contaminated with  $H_2S$  on Petrobras' P-37 offshore platform, in the Campos Basin, causing the death of two workers who worked for a contractor that provided services to Petrobras [28].

Another hydrogen sulfide ( $H_2S$ ) leak that should be reported occurred at a waste lubricating oil recycling plant located in Ohio, Columbus, United States, resulting in the evacuation of 4,000 people who worked at the plant, as well as people who were in business establishments in the areas surrounding the waste oil treatment plant. According to a statement given by the company's chief financial officer, the hydrogen sulfide leak occurred due to a power outage that indirectly caused a gasket to rupture on a pump. The leak issues occurred when the process was restarted. Some aspects of this leak are presented in Figure 4 [29].

Figure 4 - 4,000 workers are evacuated in Columbus, United States, after a toxic gas ( $H_2S$ ) leak [29].



This reported leak occurred on January 16, 2002, where two workers died and eight were hospitalized when they were exposed to the hydrogen sulfide leak at the Georgia-Pacific Naheola Mill facility, located in Pennington, Alabama, United States. The sodium acid sulfide ( $NaSH$ ) solution was delivered daily by tanker trucks. In the previous twenty-four hours, 15 trucks had unloaded the product



and it was later found that about 20 liters of each truck had leaked into the industrial sewerage. Due to an operational error, sulfuric acid was released into the NaSH retained in the sewage, which resulted in the change in pH and the rapid evolution of hydrogen sulfide (H<sub>2</sub>S). Three workers fainted from the evolution of the gas while the others tried to pull out the victims, unfortunately, the workers near the tanker truck died instantly. Figure 5 below shows the tanker trucks near the hydrogen sulfide leak. The reaction of sulfuric acid to sodium acid sulfide resulted in the release of hydrogen sulfide as shown below:

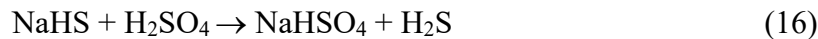


Figure 5 - View of tank trucks near hydrogen sulfide leak [30]



Thus, for the proper detection of H<sub>2</sub>S, it is essential to plan and locate continuous detectors, coupled to alarm devices that can identify concentrations that are dangerous to workers' health.

Facilities must have a basic emergency plan in place, which can minimize, restrict, or eliminate the toxic effect of H<sub>2</sub>S. In the event of a fire with gases containing H<sub>2</sub>S, the combat teams must use special respiratory protection equipment and the nearby equipment must be cooled with water until the gas source is blocked and extinguished, as there is both a risk of poisoning and explosions due to the flammability of the gas [1,17].

Studies by Jianwen *et al.* [31] state that the release of hydrogen sulfide from natural gas poses serious threats to the lives and property near the leak. This study developed a risk analysis method for H<sub>2</sub>S poisoning, taking into account the probability of risk, the scope of harm, and the dose-response model. This study adopts the Gaussian plume model to estimate the extent of diffusion of the explosion of a natural gas well containing H<sub>2</sub>S. This proposed method can provide support for pipeline safety and maintenance management, as well as evacuation after accidents occur.

In another study reported by Jianwen *et al.* [32] quantitative risk analysis has been found to be an effective method for safety management of the transportation of natural gas containing H<sub>2</sub>S. This study evaluates the important parameters such as fatal length and cumulative fatal length in the

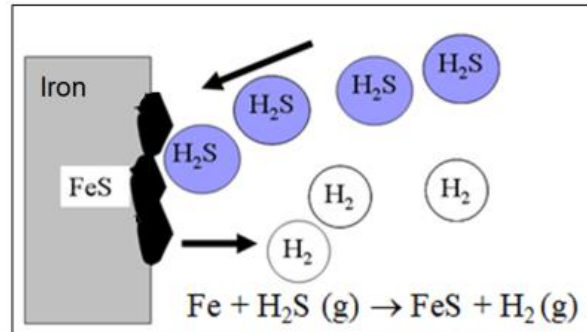


establishment of a Geographic Information System for pipelines. Statistical data are also used to estimate the frequency of failure along the sample pipeline. Thus, this study estimated that H<sub>2</sub>S releases can generate different threats to public safety. This risk would be related to different factors such as hole dimensions in the pipeline, exposure time, pipe diameter, operational condition and population density. In assessing exposure time, this study describes a method for assessing the safe exit time available under acceptable risk criteria. Thus, the method proposed in this study is useful with regard to the planning and construction of new pipelines, adjusting existing pipelines, and supporting pipeline safety management.

## 6 CORROSIVENESS OF HYDROGEN SULFIDE

According to Gentil [33], corrosion can be defined as the total, partial, superficial or structural deterioration of materials by chemical or electrochemical attack, associated or not with mechanical effects, and can be classified as chemical corrosion and electrochemical corrosion. Figure 6 below demonstrates how an iron plate can react with H<sub>2</sub>S in the absence of moisture. In the initial step, the adsorption of the H<sub>2</sub>S gas on the surface of the iron occurs, and then the attack, forming a film of ferrous sulfide (FeS) [34].

Figure 6 – Mechanism of chemical corrosion of H<sub>2</sub>S with Iron



The chemical corrosion associated with H<sub>2</sub>S corresponds to the attack of anhydrous hydrogen sulfide directly on the metallic material, without the presence of water and without the transfer of electrons from one area to another. In this process, the adsorption of H<sub>2</sub>S occurs on the surface of the metal or metal alloy, forming a sulfide film. The increase in the rate of corrosion is related to factors such as temperature, pressure and H<sub>2</sub>S concentration. In this way, the increase in temperature, pressure and concentration of this gas accelerates the rate of corrosion.

As an example of the increase in temperature (150 to 200°C), Figure 7 shows the attack of H<sub>2</sub>S on the cadmium coating with the formation of yellowish cadmium sulfide based on the reaction;





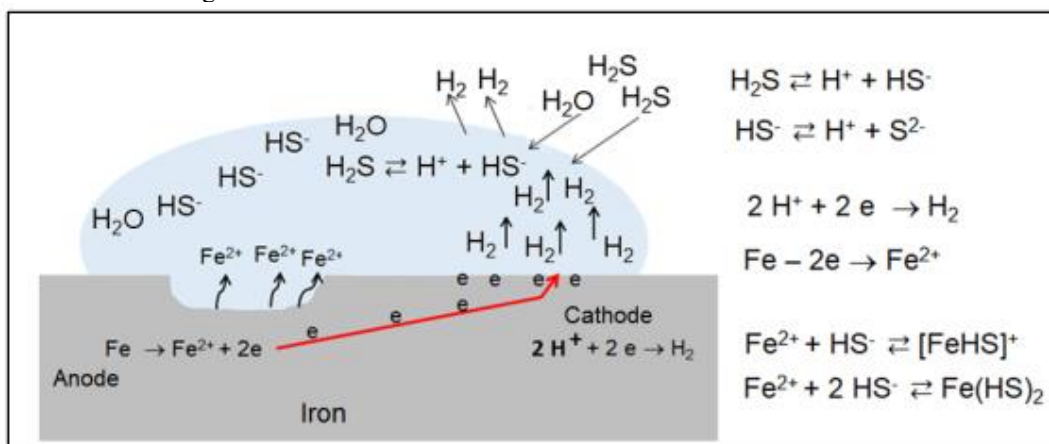
Figure 6 - H<sub>2</sub>S attack on cadmiated screws from 150 to 200°C



In order to reduce the corrosion of these materials, metal alloys are used to form a protective film that acts as a barrier against weathering, making the material more resistant to corrosion.

Electrochemical corrosion, on the other hand, [35,36] is a spontaneous process that can occur when a metal or metal alloy comes into contact with an electrolyte, occurring simultaneously anodic and cathodic reactions. The transfer of electrons from the anodic to the cathode region is done by means of a metallic conductor, and a diffusion of anions and cations in the solution closes the electrical circuit. The intensity of the corrosion process is measured by the number of ion charges that discharge at the cathode or by the number of electrons that migrate from the anode to the cathode, as shown in the diagram shown in Figure 7.

Figure 7 - Electrochemical mechanism of H<sub>2</sub>S reactions with iron



Electrochemical corrosion associated with hydrogen sulfide can be classified as pitting corrosion in the presence of H<sub>2</sub>S; graphitic corrosion of cast iron in the presence of H<sub>2</sub>S; microbiological corrosion due to the action of sulfate-reducing bacteria; corrosion under stress and corrosion under fatigue.

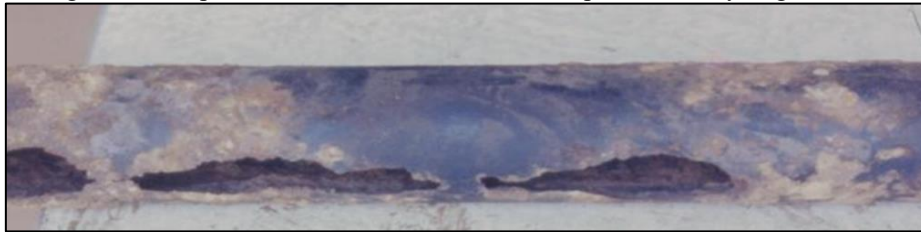
The associated graphitic corrosion in cast iron with carbon contents ranging from 2.7 to 4 % carbon [2, 33]. The electrochemical mechanism refers to the localized attack on the ferrite matrix ( $\alpha$ -





Fe), which serves as the anode, while the graphite remains intact as it functions as a cathode. These localized reactions leave the material porous and very fragile, as shown in Figure 8 below.

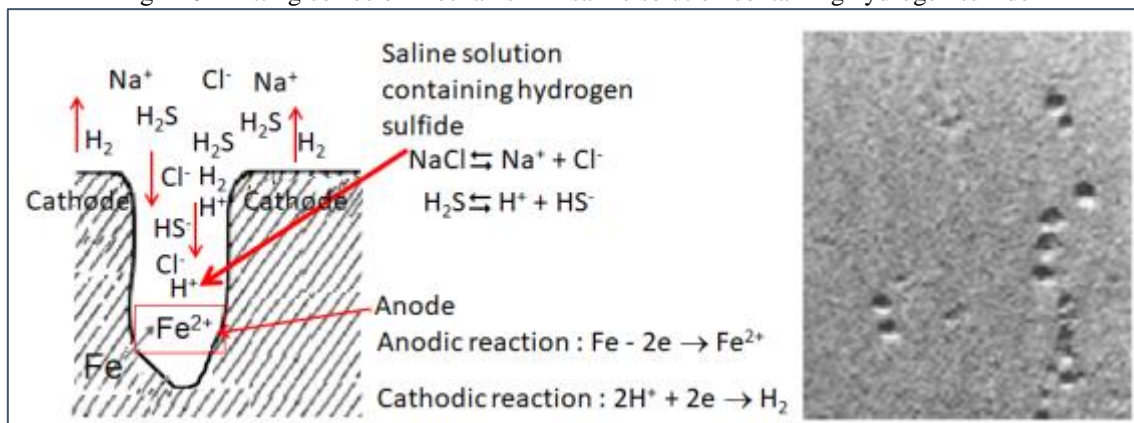
Figure 8 – Graphitic corrosion associated with the presence of hydrogen sulfide



Pitting corrosion in carbon steel associated with H<sub>2</sub>S usually occurs in points or in small areas located on the surface of carbon steel, forming small angular cavities whose depths are greater than their diameters. The electrochemical cell starts with small anodic areas and large cathode areas, thus constituting a system that allows and/or promotes the vertical penetration of the material at the site. The mechanism with anodic and cathodic reactions represented by the corrosion of carbon steel (Fe) in aqueous solutions of sodium chloride containing hydrogen sulfide at acidic pH is shown in Figure 9 below.

The produced waters from oil production have a high chloride content, where the occurrences of carbon steel pitting end up generating leaks and environmental contamination [37].

Figure 9 - Pitting corrosion mechanism in saline solution containing hydrogen sulfide



Petroleum formation waters can be contaminated by sulfate-reducing bacteria (SRB) that can generate electrochemical corrosion with anodic and cathodic reactions. The formation of a biofilm on the metal surface by means of sessile bacteria that, through the elaboration of extracellular polymers, surround and agglutinate the cells, protecting them against the adverse conditions of the corrosive environment. After the fixation of these bacteria on the metal surface and the corrosive medium containing nutrients, there is consequently the growth and multiplication of the bacteria. The corrosive



process and the process of evaluating the development of sulfate-reducing bacteria are shown in Figures 10 and 11 below.

The conditions for the development of this procedure are laid down under the following conditions:

- the absence of oxygen in the reaction medium facilitates the development of sulfate-reducing bacteria;
- the temperature in the order of 30 to 40°C promotes the growth of the microbiological process;
- levels above 100 mg/L of soluble sulphate may be considered as a source of sulphur necessary for the process;
- pH in the range of 5.5 to 8.5 promotes the development of the corrosive process, although the ideal pH value is 7.2. However, at pH higher than 11 there is no development of the microbiological process;
- The presence of nutrients, organic matter, and soluble chlorides increase the likelihood of microbiological development [38-39].

Figure 10 – Mechanism of corrosion by sulfate-reducing bacteria

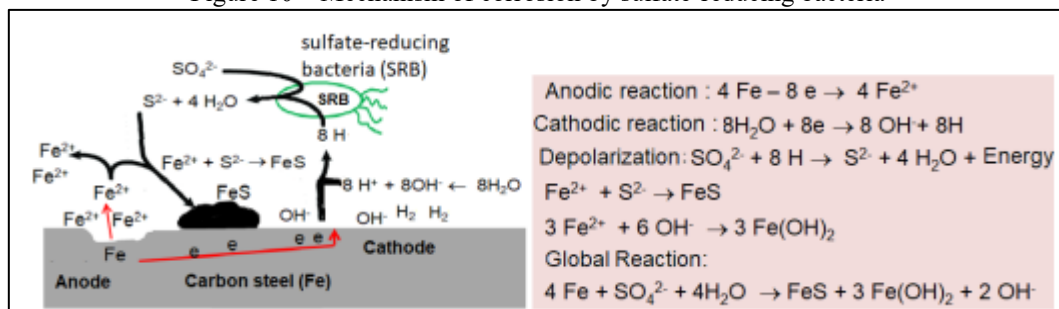


Figure 11 – Corrosion development in media containing sulfate-reducing bacteria

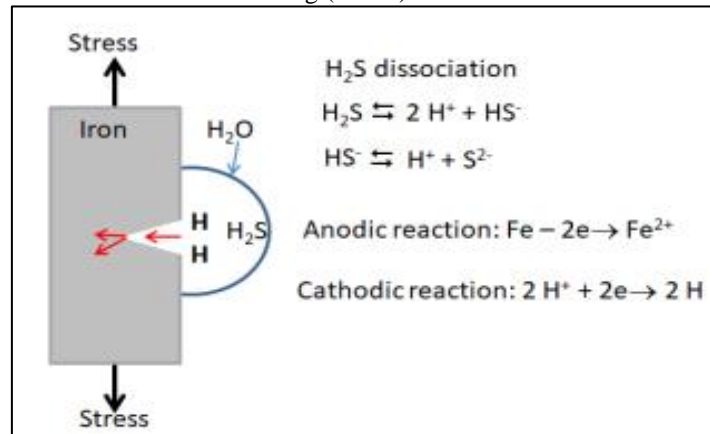


Understress corrosion in the presence of  $H_2S$  can be defined as the cracking of a metal or alloy under the joint action of tensile stress applied to the presence of an aqueous solution of hydrogen sulfide ( $H_2S$ ). This type of corrosion is mainly found where the metal meets its surroundings, causing



localized modifications to its mechanical properties and resulting in brittle fractures. Research shows that even small amounts of H<sub>2</sub>S (>0.0003 Mpa) in the gas phase are enough for corrosion to begin. One of the accepted mechanisms to explain this process consists of the generation of atomic hydrogen (H) from H<sub>2</sub>S and produced around the regions of pitting and/or formation of atomic hydrogen (H) by the cathodic reduction of H<sup>+</sup> ions, as shown in the diagram presented in Figure 12. It can generally occur in medium and/or high mechanical strength carbon steels [2, 40-42].

Figure 12 - Sulfite Stress Corrosion Cracking (SSCC) corrosion mechanisms in the presence of H<sub>2</sub>S



When considering compliance with design standards during the fabrication and/or assembly stages, it is worth considering the possibility of very high site-specific stresses, mainly due to residual stresses that normally occur during the welding process. On the other hand, site-specific deformations, geometric flaws, and impurities or imperfections in the material must also be considered. Due to the possibility of high stresses, it is recommended that welded areas be subjected to heat treatments in order to mitigate stresses, with effective control of weld hardness and weld heat affected regions. Thus, it is vital to avoid or minimize these problems based on guidelines drawn up in compliance with specific H<sub>2</sub>S-related standards such as the MR 0175-2000 standard [2].

Currently, with the presence of high CO<sub>2</sub> and H<sub>2</sub>S content in petroleum industrial equipment, the use of special steels [43-44] and Ni-P coatings [45] has stood out in the prevention of pitting and under-stress corrosion.

The mechanism of fatigue corrosion in the presence of H<sub>2</sub>S is the process of fatigue accentuated by corrosion that depends on the value of the frequency, the corrosive conditions (medium) and the time of exposure of the material to the corrosive medium. It does not have any defined limit, as occurs in resistance only to the fatigue process. Cracks perpendicular to the direction of the stress are observed and follow a more or less straight and regular path, so that it is possible to recognize the part where it started and which is often related to the corrosion pitting initially formed on the surface of the metal.



Cracks are usually transgranular. Increasing the concentration of H<sub>2</sub>S reduces fatigue resistance [2, 46].

## 7 METHODS OF DETECTION AND MEASUREMENT OF H<sub>2</sub>S

Considering the occurrence of H<sub>2</sub>S in the environment, the most used methods for measuring the concentration of H<sub>2</sub>S in ambient air samples are gas chromatography, volumetric spectrometry, among others. With the increased interest in monitoring atmospheric air quality, the need for more accurate, reliable and sensitive techniques to perform this monitoring also increases [17].

Thus, a highly efficient sampling method should be used, as errors occurred in this step cannot be corrected later during the analysis. Thus, during the planning of the sampling, the objectives of the work, the expected concentrations of the analyte, the availability of meteorological data, the transport and storage of the samples, and the conditions of analysis must be correctly established [47].

According to Cruz and Campos [47], an ideal air sampling system should be representative of the matrix; Made simple so that it can be used in any region; The sample size shall be compatible with the sensitivity of the analytical method and no sample losses and/or degradation shall occur during the sampling period, or during the time between sampling and analysis. The incorrect choice of method can lead to the formation of precipitates or dissociations during sampling and in the period prior to chemical analysis, generating false results.

Sampling methods for H<sub>2</sub>S in atmospheric air can be divided into passive sampling, active sampling, and remote sensing. In active sampling, a vacuum pump is used to transport the air into the sampling device, and the use of air flow meters is required to determine the air volume or sampling rate. This method is considered difficult to perform in remote areas due to the need to use batteries or an electric power line [48].

Active sampling is divided into continuous and discontinuous sampling. Continuous sampling is based on the association of the sampling and analysis systems through an instrument called a monitor, analyzer or continuous sampler, placed at the sampling site for a period suitable for the desired measurements. The advantage of this method is the measurement of variations in pollutant concentrations over a short period of time, being useful in identifying concentration peaks, warning situations and accidents, in assessing the conformity of air quality with short-term standards, in providing data for modeling and calibration, and in assessing the temporal distribution of atmospheric levels of a given pollutant [47, 49-51].

In discontinuous sampling, samples are collected for an established time for later analysis in the laboratory. Its disadvantage is the need for laboratory analysis. Discontinuous sampling uses discontinuous methods without preconcentration that involve collecting samples over a short time





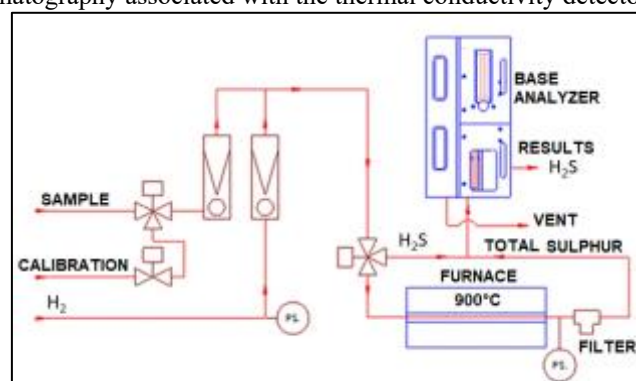
interval using evacuated containers called canisters, or plastic bags, and sampling methods that pre-concentrate the species of interest by passing air through a sorbent medium or a cryogenic system [52].

Passive sampling uses devices capable of fixing gases or vapours from the atmosphere, at a rate controlled by physical processes such as diffusion or permeation, not involving the active movement of air through the sampler. This method is considered an interesting alternative due to the advantages it presents when compared to active techniques, such as ease of performance, low cost, easy transportation to remote regions not requiring electricity, periodic calibrations, measurements of the volume of air sampled and technical staff permanently at the sampling site. One of the disadvantages is the absence of the ability to provide instantaneous concentrations, it only provides weekly and/or monthly average concentrations, it also does not allow the alteration of the sampling rate, it does not differentiate transient episodes of high and low concentrations in a given period [48].

Regarding the analytical methods, gas chromatography is the most used method for the determination of low levels of  $H_2S$ , due to the volatility of these compounds, the adequate separation capacity associated with the ease of detection. Another widely used method is molecular spectrophotometry, one of the most widely used being the methylene blue method. This method is based on the oxidative coupling of two molecules of *N,N*-dimethylphenylene-1,4-diamine (DMPD) with sulfide, in the presence of small amounts of ferric ion, producing the methylene blue dye [6].

In gas chromatography associated with the thermal conductivity detector, the different eluted gases have different thermal conductivities. When the thermal conductivity is lower, the amount of heat transferred reduces and causes an increase in temperature, which is detected by a metal filament in contact with the analysis system. This temperature increase causes an increase in the electrical resistance of the metallic conductor, which is compared to the resistance observed in another compartment, containing the same metallic filament in contact only with the carrier gas. The difference in resistance between the two metal wires, caused by the different thermal conductivities of the gases, is converted into a potential difference (mV) which is proportional to the analyte concentration [53]. The simplified scheme of this technique is shown in Figure 13.

Figure 13 - Gas chromatography associated with the thermal conductivity detector for  $H_2S$  determination

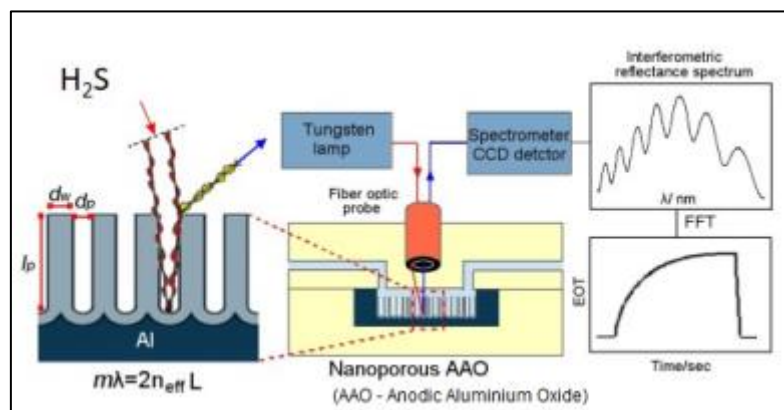




Kumeria & Losic [54] developed a sensor for the detection of volatile sulfur compounds, capable of detecting H<sub>2</sub>S at concentrations up to 2% (v/v). The sensor was developed based on the Reflectometric interference spectroscopy. One nanoporous anodic aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) was compressed and covered with a thin layer of gold backed on a microchip. A small optical fiber has been connected to this that measures the differences in the refractive index of light. The construction scheme of this micro-sensor is shown in Figure 14 below.

In this detection method, white light is reflected at the bottom and top of the nanopores, generating an interference pattern. Compounds that have sulfhydryl (-SH) groups such as H<sub>2</sub>S and mercaptans have an affinity for gold. The binding of molecular species such as H<sub>2</sub>S on the surface of the pores induces modifications in the Fabry-Perot interference pattern, causing changes in the refractive index of light and its wavelength. These changes in wavelength have been identified, quantified and associated with H<sub>2</sub>S concentration[54].

Figure 14 - Schematic diagram of the nanoporous AAO (Anodic Aluminium Oxide) reflective interferometric sensor [54] modified.



Infrared spectrometry is a simple, fast technique, requires a small amount of sample, is non-destructive and has high selectivity. However, quantitative applications differ from those for ultraviolet or visible radiation because of the great complexity of the spectrum, the narrow absorption bands, and the capabilities of the instruments in the spectral region. Infrared spectra can be obtained through methods that include transmission and reflection, currently reflection techniques have been more widely used mainly because they do not involve sample preparation processes that are often time-consuming and laborious. This technique can be used for most liquid and solid substances and can be by: specular reflection; diffuse reflection; and attenuated total reflection. Bearing in mind that in the present study the attenuated total reflection accessory was used, some characteristics of this technique will be discussed below [55, 56]. Figure 15 shows a view of the infrared spectrometer.



Figure 15 – Infrared spectrophotometry [56]



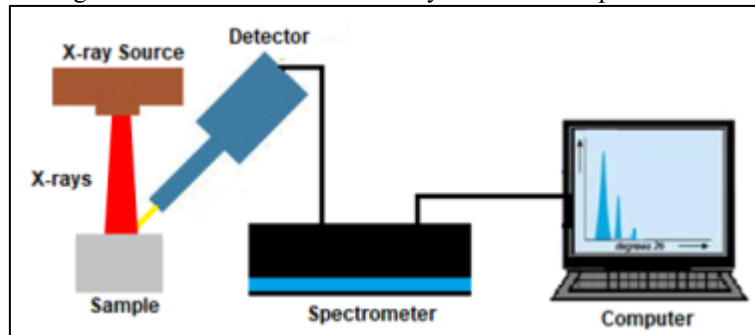
In X-ray Fluorescence Spectroscopy sample it is placed in a cylinder which is then irradiated by an X-ray tube. The characteristic excited X-radiation is measured and the cumulative count of this is compared with the scores previously obtained for the calibration standards. In X-ray fluorescence spectroscopy, the X-ray fluorescence spectrometer is used as analysis equipment. In this technique, the ejection of the innermost electron from the X atom to produce the X ion<sup>+</sup> it can be caused by an electron beam of appropriate energy or by X-rays [56].

In the X-ray source, electrons are generated from a heated tungsten filament (cathode) and accelerated toward the anode, which consists of a target of certain metals such as W, Mo, Cr, Cu, Ag, Ni, Co, or Fe, depending on the range of wavelengths required. The tube has a wave ray of up to 10 Å, beyond which the intensity of the X-rays reach the sample causing the emission of rays in a region of 0.2-20 Å. The fluorescence is scattered by a flat crystal, usually lithium fluoride, which acts as a diffraction grating. The fluorescence can then be detected by a photon counter, a semiconductor detector, or a gas flow detector [56]. The schematic of the X-ray fluorescence spectrometer is shown in Figure 16.

The presence of this crystal makes it possible to select a specific wavelength or range of wavelengths according to the energy range of interest and characterizes a specific type of spectrometer, the Dispersive Wavelength Spectrometer (WDXRF). Another type of spectrometer is the energy dispersive spectrometer (EDXRF)). To do this, it must receive the non-scattered fluorescent X-rays and convert them into a series of pulses of different voltages that correspond to the different wavelengths it has received. These energies where the electronic pulses generated by the radiation are converted into pulses per second. These pulses are accumulated in channels that correspond with the energies required by the multichannel analyzer wavelengths [55, 57,58].



Figure 16 - The schematic of the ray fluorescence spectrometer



The continuous monitoring of H<sub>2</sub>S presented in the examples in Figure 17 and the mandatory use of portable gas detectors by workers in industrial environments are widely used as shown in Figure 18, in order to preserve the life, safety and integrity of the equipment. These devices operate based on different principles such as electrochemistry, photoionization, gas chromatography, infrared, and catalytic detection. Portable detectors are easy to use, often have audible and visual alarms to indicate hazardous concentrations, and can be easily transported to different locations. The sensors send electrical signals to a central control panel, which displays the readings and triggers alarms when the H<sub>2</sub>S concentration exceeds the permissible limits [47].

Figure 17 – Examples of equipment for H<sub>2</sub>S monitoring in industrial systems



Figure 18 – Examples of portable detectors for use by workers to control and prevent H<sub>2</sub>S leaks



Portable H<sub>2</sub>S leak detectors are crucial devices for ensuring safety in industrial, laboratory, and petroleum environments. Equipped with highly sensitive sensors, these detectors can quickly monitor H<sub>2</sub>S concentrations in ambient air and issue audible and visual alerts if levels exceed safe limits. The



portability of these devices allows them to be easily transported and used in a variety of situations, providing professionals with a valuable tool for mitigating potential hazards and preventing serious H<sub>2</sub>S-related accidents. In addition, as a safety tool, it is essential to use personal protective equipment such as masks with special filters for H<sub>2</sub>S and/or with a portable supply of air or oxygen.

## 8 CONCLUSIONS

The various technological routes that, directly or indirectly, have been dealing with the high human losses and the deterioration of equipment resulting from the corrosive and toxic action of hydrogen sulfide (H<sub>2</sub>S) must be established parameters based, among others, on the following points:

- On the criteria and physical-chemical properties of hydrogen sulfide;
- Knowledge of corrosive processes at all levels, that is, from the project to the industrial operations involved such as hydrogen sulfide;
- In the careful selection of anti-corrosion protection materials and techniques, notably coatings and corrosion inhibitors specific to hydrogen sulfide;
- In the research and development of products or specific formulations for hydrogen sulfide sequestering action;
- In research and development of processes and/or recoveries aimed at optimizing traditional processes and encouraging research into new alternative processes aimed at reducing costs and greater operational safety in processes for removing soluble sulfides and hydrogen sulfide with recovery sulfur and/or sulfuric acid;
- In the development of hydrogen sulfide monitoring programs based on online equipment already available on the market;
- Increasing the technical staff's awareness of the importance of developing clean technologies aimed at environmental decontamination and the transformation of a pollutant existing in the gas stream into a high purity raw material for use in other industrial processes;
- In the formation of public awareness in society and civil defense bodies in order to be aware of the harmful effects of hydrogen sulfide and take the necessary measures for clarification, rescue, evacuation and removal of contaminated people.



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