Installation for research of hydrogen sulfide chemisorption from gases by a quinhydrone absorbing solution under pressure

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Abstract - Theoretical bases for the development of an experimental installation of hydrogen sulfide chemisorption from oxygen-free gases by the quinhydrone method under a pressure of up to 10 MPa are described. As a source of hydrogen sulfide-containing gas, it is proposed to use a mixture of industrial compressed nitrogen from cylinders and hydrogen sulfide from its liquefaction installation.

Keywords: hydrogen sulfide, liquefaction, chemisorption, pressure, experimental installation, quinhydrone absorbing solution.

Introduction

Natural and process gases are often under high pressure (0.5…10 MPa). It is advisable to carry out the stage of hydrogen sulfide chemisorption under pressure in the quinhydrone method of gas purification from hydrogen sulfide [1-3]. In the literature, studies of the processes of hydrogen sulfide chemisorption by quinhydrone absorbing solution under pressure are not presented. Therefore, there is a need for such studies.

The main difficulty in creating an experimental installation was to provide a source of hydrogen sulfide. There are methods of obtaining it (in the gaseous state at some excess pressure) from sodium or aluminum sulfide solution by acid decomposition with sulfuric or other acids [4]. The industry does not produce compressed hydrogen sulfide in cylinders. Only the use of hydrogen sulfide in low-volume cylinders compressed to low pressure (~ 3 atm) is known [5]. Therefore, the question arose of obtaining a mixture of hydrogen sulfide in the laboratory under high pressure and ensuring a constant gas pressure for some time with a stable flow rate.

The work aimed to develop the theoretical basis for the creation of an experimental installation for the study of hydrogen sulfide chemisorption from gases by a quinhydrone absorbing solution at a pressure of up to 10 MPa.

Results and discussion

The solution to the problem of obtaining a source of hydrogen sulfide under pressure, we found in the statement about the conditionality of the separation of the substances into gases and liquids. Gases have very low critical temperatures and therefore cannot be in a liquid state at room temperature. Instead, substances classified as liquids have high critical temperatures. Any gas can be converted into a liquid, but it is necessary to pre-cool the gas to a temperature below critical. For example, carbon dioxide can liquefy at room temperature because its critical temperature is 31.1 °C and above room temperature. The same applies to gases such as ammonia (132.25 °C) or chlorine (143.75 °C). But some gases cannot be liquefied at room temperature. These include air (nitrogen, oxygen, and argon), as well as hydrogen and helium, in which critical temperatures are much lower than room temperature. Such gases have wide practical use as refrigerants. To liquefy them, they must be pre-cooled to a temperature below the critical temperature, and then - compressed.

Two methods are usually used in industry for cooling and liquefying gases. The first method of gas liquefaction is associated with the phenomenon of changes in gas temperature during its adiabatic expansion by throttling from one constant pressure to another. The second method of gas liquefaction is carried out by cooling the gas during adiabatic expansion in the expanders and the implementation of external work. The method of adiabatic cooling by throttling is simpler. It does not cause the problem of lubrication of moving parts of devices operating at low temperatures.

Consider the properties of liquid hydrogen sulfide. According to [6], the critical constants of hydrogen sulfide t_{cr} = 100.4 °C; P_{cr} = 88.9 atm. The dependence of the pressure (P, atm) of saturated vapor on the temperature in the range from boiling point to critical (T, K) is described by the equation

$$\lg P = 4.441 - \frac{930.5}{T}. \text{ (1)}$$

The density (ρ, g/cm^3) of liquefied hydrogen sulfide at temperatures (t) from -82 to -63 °C is described by the equation

$$\rho = 0.866 - 1.63 \times 10^{-3}. \text{ (2)}$$

The boiling point or sublimation of hydrogen sulfide at different pressures are presented in table 1 [7].

Table 1

Boiling point or sublimation of hydrogen sulfide at different pressures [7]

P, mm Hg	t_{boil}, °C	P, atm	t_{boil}, °C	P, atm	t_{boil}, °C
0,1	-153,6 (solid)	1	-60,2	20	25,5
1	-134,6 (solid)	2	-45,9	40	55,8
10	-116,5 (solid)	5	-22,3	50	66,7
100	-92,4 (solid)	10	-0,4	60	76,3

As you can see, at a temperature of 25 °C and a pressure of more than 20 atm concentrated (100%) hydrogen sulfide will be in a liquid state. The critical temperature of hydrogen sulfide indicates that its liquefaction can be easily achieved by conventional cooling. At a pressure of 1 atm, it can be liquefied at a temperature of -60.2 °C or less.

In the laboratory, cooling mixtures and refrigerants are used to cool and liquefy gases. These are usually various liquefied gases that are boiling. One of the effective and available refrigerants is nitrogen, the boiling point of which is -195.75 °C.

Analysis of the above dependences made it possible to propose hydrogen sulfide in the liquefied state to create a hydrogen sulfide-containing gas mixture under pressure. As a carrier of hydrogen sulfide, which will ensure the flow of gas under pressure, we proposed to use industrial gas nitrogen from cylinders. Mixing nitrogen with hydrogen sulfide vapors will make it possible to obtain a hydrogen sulfide-containing gas mixture of a certain composition with a stable flow rate and pressure. An additional parameter for regulating the composition of the gas mixture may be a change in the temperature of the liquefied hydrogen sulfide.

To implement this method, we have developed a special design of a container (cylinder) for obtaining and storing liquefied hydrogen sulfide and a method of its filling, and also proposed the design of a bubble-type absorber for studies of hydrogen sulfide chemisorption under pressure by quinhydrone absorbing solution. Assistance in the design and manufacture of equipment was provided by specialists of Karpatnaftochim LTD (Kalush, Ivano-Frankivsk region).

Particular attention in the design of the installation for research was paid to the selection of materials for the manufacture of both the apparatus for storing hydrogen sulfide (cylinder) and other components of the installation. Hydrogen sulfide-containing gases under pressure in the presence of moisture are extremely corrosive. The problem of sulfide cracking of welded pipelines and equipment is especially acute in the gas industry due to the development of fields with significant impurities of hydrogen sulfide and other harmful substances [5]. The destruction of the metal in some cases can be very intense, which causes a great danger of production. As the partial pressure of hydrogen sulfide increases, the flooding of steel and the rate of its corrosion increase.

The initial data for the selection of structural material for the capacity of liquefied hydrogen sulfide (cylinder) were: operating temperature limits -190…+ 70 °C, the design pressure of 16 MPa. The construction material - steel 10X17H13M2T was chosen, the corresponding calculations were carried out and the cylindrical vertical device with the welded hemispherical bottom and a flat cover with two unions on a special carving is made. Fastening of a cover to the case - flange on 8 hairpins of M30×170, a face type of "tongue-groove" with a paronite gasket. The main dimensions of the device: inner diameter D = 0.1020 m, thickness of the shell and bottom $S = S_b = 14$ mm, flat cover $S_c = 32$ mm. Volume $V = 2$ dm^3.

Initially, the cylinder was filled with hydrogen sulfide. The scheme of installation for filling is presented in figure 1.

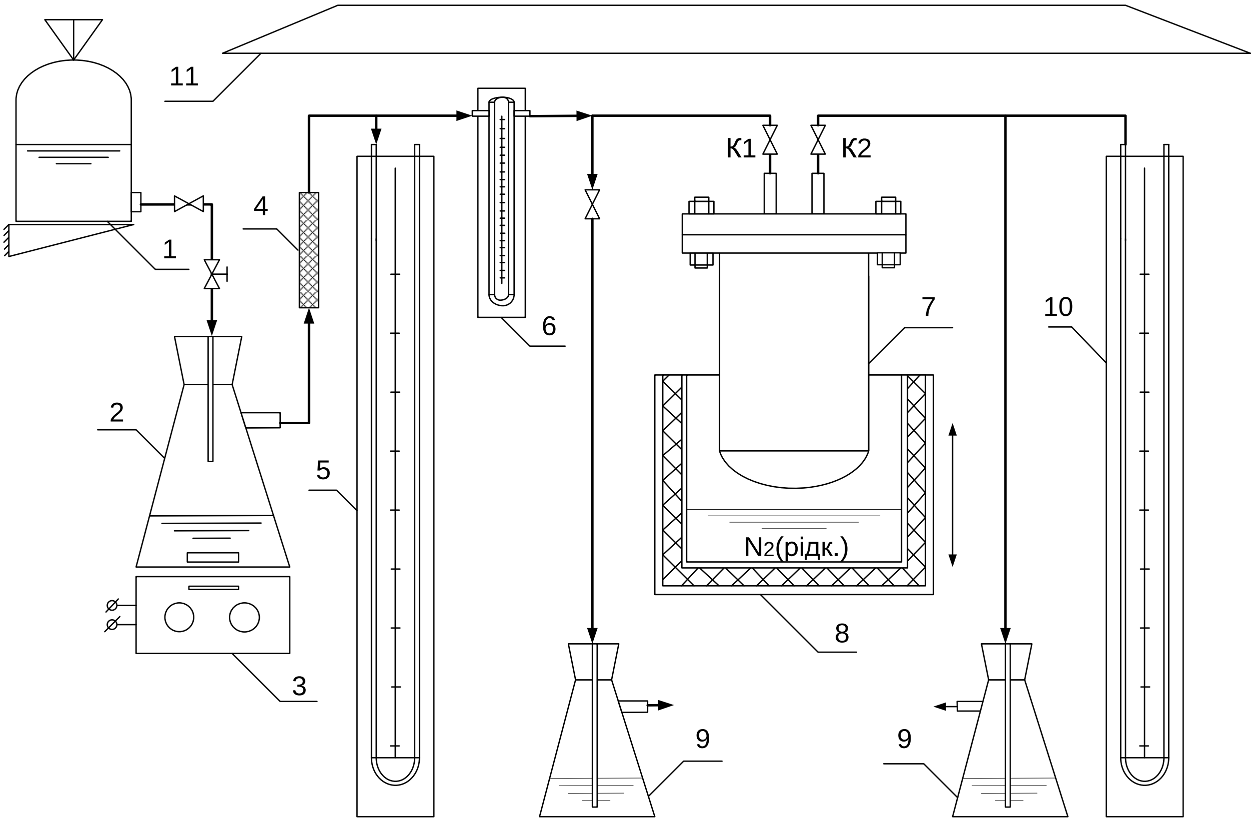

Fig.1 The scheme of installation of a cylinder filling with hydrogen sulfide.

The production of liquefied hydrogen sulfide is due to its production in the gaseous state. To do this, a solution of sodium sulfide was decomposed with a solution of sulfuric acid (1:4 wt.) in tank 2. Sulfuric acid was fed from vessel 1 under hydraulic pressure. Mixing of the reagents was performed using a magnetic stirrer 3. The resulting hydrogen sulfide gas was purified in an absorber 4. The pressure and gas flow were controlled by a manometer 5 and a rheometer 6. First, all the hydrogen sulfide (unstable flow rate) was sent for sanitation in absorber 9, filled with an acidified solution of potassium permanganate. Gas with a stable flow rate has already flowed into cylinder 7. Liquid nitrogen (from JSC "Lviv Chemical Plant") was poured into a thermostated tank 8 from the Dewar tank. Due to the decrease in temperature, the gas liquefied and a vacuum was formed in cylinder 7. The pressure stability in the system is ensured by regulating the acid supply to tank 2 and regulating the liquid nitrogen level in tank 8. The pressure was monitored using U-shaped manometers 5 and 10 filled with mineral oil. Uncondensed gases were supplied for sanitation to tank 9.

Due to such repetitive operations (7-10), it was possible to obtain 0.5… 0.6 dm^3 of liquefied hydrogen sulfide. With the help of taps K1 and K2 carried out the overlap of gas flows into and out of cylinder 7.

The research of hydrogen sulfide chemisorption under pressure was carried out on the installation, the scheme of which is shown in Figure 2. This experimental installation was mounted at LLC “Lviv Experimental Mechanical Plant” (Lviv).

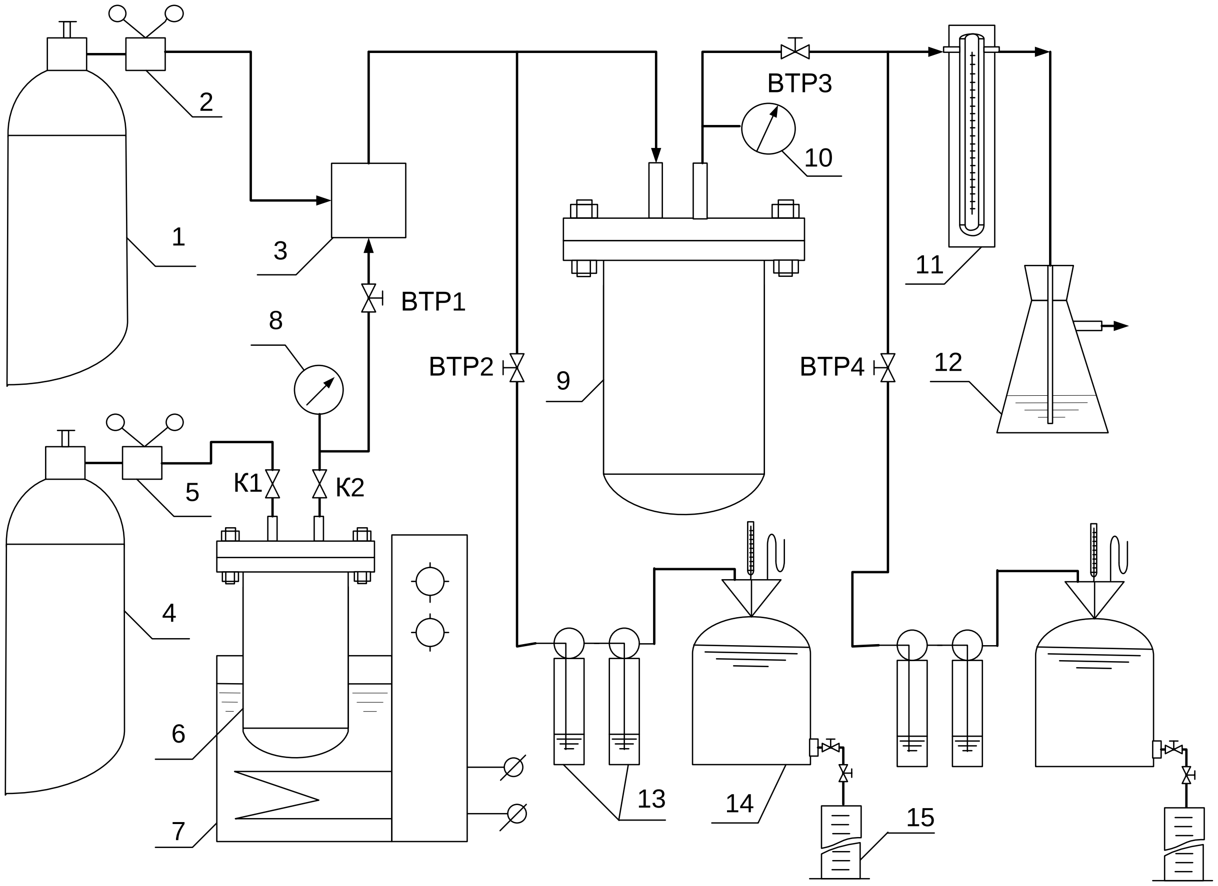

Fig.2 Scheme of installation for research of hydrogen sulfide chemisorption under pressure

Industrial nitrogen for the production of nitrogen-hydrogen sulfide mixture was used from cylinder 1 (from JSC "Lviv Chemical Plant"). The gas was fed into the gas mixer 3. The H_2S supply to the gas mixture was regulated by the BTP-1 valve (fine control valve). To compress ("blow out") H_2S from cylinder 6, nitrogen supply was provided under slightly higher pressure from cylinder 4. The pressure and nitrogen supply were regulated using a reducer 5. The use of thermostat 7 also made it possible (by heating and increasing pressure) to increase the partial pressure of hydrogen sulfide in the gas mixture.

After mixer 3, the gas mixture was sent to absorber 9 for chemisorption of H_2S with quinhydrone absorbing solution in bubbling mode. The pressure in absorber 9 was monitored by a manometer 10.

The initial data for the selection of structural material for the absorber were as follows: operating temperatures + 15…+ 45 °C, design pressure 16 MPa. The construction material was chosen - steel 20, the appropriate calculations were performed and a cylindrical vertical device with a welded hemispherical bottom and a flat cover with two fittings for special threads was made. Fastening of a cover to the case - flange on 8 hairpins of M30×170, a face type of "tongue-groove" with a paronite gasket. The main dimensions of the absorber: inner diameter D = 0.105 m; the height of the inner cylindrical part H = 0.5 m, the thickness of the shell and bottom $S = S_b$ = 14 mm, the thickness of the flat cover S_c = 34.0 mm, the volume of the apparatus V = 4.5 dm^3.

Valves BTP-2 and BTP-4 (before and after the absorber, respectively) in the installation were provided for gas sampling for hydrogen sulfide content. After hydrogen sulfide chemisorption in the absorber, the gas through the valve BTP-3 was fed for sanitation in a container 12, and released into the atmosphere.

After each series of studies, the pressure in the absorber was vented by releasing gas through the neutralization system 12. To regenerate the absorption solution after a series of studies, the air was supplied to the absorber using a compressor (not shown in figure 2).

The developed installation allows studying the influence of gas pressure and initial concentration of sodium carbonate in quinhydrone absorption solution on the degree of hydrogen sulfide chemisorption from a gas mixture.

Conclusion

1. Theoretical principles of obtaining a nitrogen - hydrogen sulfide gas mixture under pressure have been developed. The source of hydrogen sulfide is liquefied gas.
2. An experimental setup for the study of H_2S chemisorption from gases under pressure up to 10 MPa by a quinhydrone absorbing solution was developed and fabricated.

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