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КЛАСИФІКАЦІЇ МЕТОДІВ ОЧИЩЕННЯ ГАЗІВ ВІД СІРКОВОДНЮ

Описано існуючі класифікації способів очищення газів від сірководню. Показано їх переваги та недоліки. Запропоновано класифікувати методи очищення газів за суттю фізико-хімічних взаємодій сірководню під час його уловлення – конверсійні і неконверсійні. У результаті неконверсійних процесів одержують концентрований сірководеньвмісний газ, який потребує подальшої переробки чи утилізації. Конверсійні методи дають змогу одержати сірку чи інші сульфуровмісні продукти під час окиснення чи розкладу сірководню.

Ключові слова: очищення газів, сірководень, класифікації методів

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CLASSIFICATION OF METHODS OF GASES PURIFICATION FROM HYDROGEN SULFIDE

The existing classifications of methods for purifying gases from hydrogen sulfide is described. Their advantages and disadvantages are shown. It is proposed to classify the methods by nature of physicochemical interactions of hydrogen sulfide during its removal – conversion and non-conversion. As a result of non-conversion processes, concentrated hydrogen sulfide – containing gas is produced, which requires further processing or utilization. Conversion methods allow sulfur or other sulfur-containing products to be produced during the oxidation or decomposition of hydrogen sulfide.

Key words: gases purification, hydrogen sulfide, classifications of methods.

There are many classifications of methods for gases purification from hydrogen sulfide, which combine them according to common features. After all, these methods can be grouped according to the aggregate state of the sorbent (liquid, solid) or the physical and chemical nature of the processes of hydrogen sulfide removal (adsorption, absorption, chemisorption). The subject of classifications is the technological and hardware design of the purification processes, as, for example, technological schemes for cleaning oxygen-containing (ventilation) and non-oxygen (fuel or technological) gases have significant differences. When purifying various sulfur-containing gases (natural, pyrolysis, coke, biological, etc.) there are different requirements for the content of other components of these gases, which causes, for example, the use of additional stages of purification. As a result of purifying gases from hydrogen sulfide, it is possible to obtain sulfur, sulfuric acid or other sulfur-containing products from it. The purification processes can also be continuous or semi-periodic, with and without sorbent regeneration, single- and multi-stage.

Obviously, such a wide range of classifications is present due to the specifics of the processes of sulfur purification, more than an age-old history of the application of some methods, their ageing and the emergence of new methods of purification, as well as the relation to this problem professionals of various specialities. First of all, the specialists in the field of mining and processing of coal, oil and gas. However, as the authors [1] confirmed 40 years ago, “in the near future, the purification of gases from hydrogen sulfide will be converted into a method of obtaining sulfur". Therefore, over time, after the reduction of the role of natural sulfur in the global economy [2, 3] and the emergence of such a term as "gas sulfur", the role of chemists-technologists in the field of inorganic substances has increased significantly in this area.

The aim of the work is to develop the method of classification that fully covers the existing and, in perspective, new methods for the purification of gases from hydrogen sulfide. One of the main existing ways of classifying of methods for purifying gases from hydrogen sulfide is their dividing depending on the aggregate state of sorbents for hydrogen sulfide removal from gases. Such classifications are found in the majority of early publications [1, 4-9]. "Dry" or adsorption methods of purification consist in the removal of hydrogen sulfide using solid sorbents – "cleaning masses". The second group – "wet" or absorption methods – consists in the application of liquid hydrogen sulfide sorbents. Each of these groups is classified depending on the nature of the processes that occur when directly removal the hydrogen sulfide from the gas. So according to [1,6], dry methods are divided into adsorption (physical) and oxidative-adsorption (chemical), and wet – on absorption (physical), chemisorption (physicochemical) and oxidative (chemical).

According to this classification, physical methods are based on cyclic processes of hydrogen sulfide sorption from gases using solid (activated carbon, silica gel, molecular sieves, etc.) or liquid (water or organic solvents) sorbents and subsequent desorption of hydrogen sulfide from sorbents. Desorption is carried out by raising the temperature and/or using an inert carrier (air, natural gas, etc.) or vacuum. The result is obtaining a concentrated hydrogen sulfide-containing gas or a mixture of H_2S with a gas-desorbent.

In wet physical and chemical methods, hydrogen sulfide is absorbed by a solution of alkaline nature (monoethanolamine, sodium or potassium carbonates, ammonia). During the absorbent solution regeneration desorption of H_2S is carried out to obtain a concentrated hydrogen sulfide-containing gas.

In dry chemical methods, hydrogen sulfide, absorbed by a solid cleaning mass, interacts with the active component of this mass to form a sulfide compound which is further oxidized. An example of such a process is a classic method of gases purification from hydrogen sulfide by sorbent with an active $Fe(OH)_3$ to form Fe_2S_3 (2FeS+S) [1,8,10]. In addition to the Iron compounds for these processes, adsorbents based on Zinc, Manganese, Copper, Calcium and the like can be used. During the regeneration of the sorbent with air oxygen from the hydrogen sulfide produces sulfur or sulfur dioxide. It means that these compounds act as catalysts of the oxidation process of hydrogen sulfide with oxygen.

Wet chemical methods, unlike wet physical and physicochemical methods, allow sulfur or other sulfur-containing products to be produced during the oxidation of hydrogen sulfide with an oxidizer contained in an alkaline solution. Reduction-oxidation systems Fe^{3+}/Fe^{2+}, V^{+5}/V^{+4}, As^{+5}/As^{+3}, quinone/hydroquinone etc. are used in these methods as the oxidizing agents [1,8,12]. During the purification of gases, chemosorbed hydrogen sulfide interacts in an absorbent solution with an oxidizing form of oxidant causing the sulfur obtaining. The regeneration of the solution is carried out mainly by aerating. During this, the oxidant is converted again from the reducing form into oxidative. After separation of the obtained sulfur, the regenerated solution is returned to the hydrogen sulfide chemisorption.

However, even then some difficulties occur in such classifications. Thus, the purification of gases from hydrogen sulfide by a solution of sodium hydroxide is essentially a wet chemisorption process, but desorption methods for regeneration of the solution are not used, but the neutralization of hydrogen sulfide is carried out by oxidation of it to sulfates. But then, by the sum of the transformations of hydrogen sulfide, this method can be described as wet chemical.

Expansion of hydrogen sulfide-containing gas sources, application and development of technics of desulfurization processes and, consequently, the emergence of new processes led to the need for applying other classifications. Thus, in numerous catalytic processes of the production of synthetic fuels, ammonia, alcohols, etc., there was a need to clean technological gases not only from hydrogen sulfide, but also from other sulfur-containing compounds, which often are poisons for catalysts. This stimulated the development of new purification methods, in which hydrogen sulfide and organic sulfurous compounds catalytically oxidize or recover. These methods have not started to be included in the group of dry methods, but in the separate group – catalytic [7], catalytic-adsorption methods [8], methods of treating hydrogen sulfide into sulfur [9–11]. Tendencies in the treating of gases from low-yield sources, the rapid increase in the share of energy from renewable sources [15–17], also contribute to the development of new purification processes.

Thus, there were developed processes that, with only a certain assumption or not at all, can be attributed to any of the groups described above. The membrane process, which consists of separating the gas mixture into selective membranes through which H_2S, CO_2 or H_2O pass faster than, for example, CH_4, could possibly be attributed (with a certain assumption) to dry adsorption methods. The biological method, which consists in usage of thiobacillus for purification of gases, for which hydrogen sulfide and other compounds of sulfur are nutritious, can be attributed to a new (biological) subgroup of wet methods. Electrochemical methods that allow to decompose hydrogen sulfide in an absorbing solution under the action of a direct current into sulfur and hydrogen can be attributed (also with a certain assumption) to a group of wet chemical methods. But the plasmochemical method, which consists in the decomposition of hydrogen sulfide into sulfur and hydrogen in plasma, is difficult to attribute to a group of methods, neither by aggregate state, nor by the nature of processes. There is known the classification [10], in which, alongside with dry and wet, a new group is introduced – non-traditional or modern methods (membrane, biological, plasmochemical, etc.). However, such a grouping of the above methods is artificial and has no common feature that combines them.

In addition to the wide range of processes used to purify gases, each of them can be used at various stages of sulfur purification processes. In industrial methods for purifying gases from hydrogen sulfide, the following main and auxiliary processes can be distinguished: preliminary preparation of gases for cleaning; direct removal of hydrogen sulfide from gases; treatment of hydrogen sulfide to sulfur, sulfuric acid or other sulfur-containing products; waste utilization.

The processes of preliminary preparation of gases are carried out before the stage of dry or wet removal of hydrogen sulfide from the gas, which makes it possible to improve the purification of various components of gases, to reduce the negative impacts of impurities, etc. For this purpose, catalytic oxidation or reduction of sulfur-containing and other compounds present in the gas is used, as well as condensation of hydrocarbons, chemical purification from some components of gases, etc. [6, 7].

Since removed hydrogen sulfide is not a commercial product, and its storage is difficult, then after the stage of hydrogen sulfide removing from the gases it is necessary to utilize or neutralize it. Processes of hydrogen sulfide transformation into sulfur, sulfuric acid or other sulfur-containing products are carried out by catalytic, plasmochemical, thermal and other methods [8,9,13]. Thus, the world-known method of Claus is a separate process and allows converting concentrated hydrogen sulfide into sulfur, and, for example, H_2S is obtained by wet cleaning with aqueous solutions of ethanolamines. According to [9,11-13], the method of Claus is isolated in a separate group – the methods of treating hydrogen sulfide into sulfur, although the essence of processes is the catalytic process of oxidation of hydrogen sulfide to sulfur. In addition, concentrated hydrogen sulfide after monoethanolamine cleaning can also be converted to sulfuric acid by “wet” catalysis or to sulfur and hydrogen – by the plasmochemical method.

Technological schemes of various methods of purifying gases from hydrogen sulfide supplement the stages of disposal or utilization of waste. For example, after wet chemical purification of gases, waste solutions are utilized, for example, by electrochemical or biological methods [8]. These methods can be classified as separate waste recycling methods and can be used for the recycling of waste absorbing solutions from different methods of gas purification, but can be considered as an integral part of the gas-cleaning process. Catalytic processes of oxidation or reductions of sulfur-containing compounds in gases are often used to purify gas emissions after the application of basic purification methods. These processes are also isolated in a separate group, although it is often an integral part of the gas-cleaning process. That is, the whole gas-cleaning process at various stages can use different physicochemical essence processes, which creates complexity during their classification.

An overview of modern classifications of methods often does not cover all existing methods, but only the main industrial for those or other industries [14–17].

In our opinion, for the full coverage of the existing methods, as well as, if they emerge, of new industrial methods of gases purification from hydrogen sulfide, it is necessary to apply a classification based on the essence of physicochemical INTERACTIONS with hydrogen sulfide, which is accompanied or not accompanied by a change in THE DEGREE OF OXIDATION OF SULFUR. Thus, according to this classification, **non-conversion** processes that occur without the chemical interaction of hydrogen sulfide can be distinguished, as well as **conversion** processes – with its interaction and transformation.

According to the proposed classification, for non-conversion methods, we must include adsorption, absorption, chemisorption and membrane processes. As a result of these processes, concentrated hydrogen sulfide -containing gas is produced, which requires further processing or utilization. It is implemented by one of the conversion methods.

Based on the chemical properties of hydrogen sulfide, three types of conversion processes can be identified with its participation: neutralization (binding), oxidation and decomposition reactions [13]. Neutralization processes correspond to chemisorption processes, when hydrogen sulfide is removed by the absorbent solution and interacts with its alkaline component. But since this interaction is a reversible process, during the regeneration of the absorbent solution there is desorption of hydrogen sulfide to obtain a concentrated hydrogen sulfide-containing gas. In the case of monoethanolamine, these processes can be described by the following equation

$$2RNH_2 + H_2S \Leftrightarrow (RNH_3)_2S. \qquad (1)$$

Although in this process, however, there is an interaction of hydrogen sulfide, the hydrogen sulfide as a result of the purification remains unchanged and sulfur does not change its degree of oxidation. Therefore, methods of this group are classified as non-conversion.

Conversion methods, accompanied by the oxidation of hydrogen sulfide, make it possible to obtain sulfur, sulfuric acid or other sulfur-containing products from it. Reactions of oxidation of hydrogen sulfide with the production of sulfur or other sulfur-containing products occur under the influence of catalytic (adsorption-catalytic), biological or liquid-oxidation (chemical) processes. These processes can be described, for example, by the following general equations:

$$H_2S + 1/2O_2 = S + H_2O, \qquad (2)$$

$$H_2S + 3/2O_2 = SO_2 + H_2O. \qquad (3)$$

Consequently, in the conversion methods, due to the interaction of hydrogen sulfide, the degree of oxidation of sulfur increases.

For more than half a century, hydrogen sulfide, obtained during the conversion gas purification, is the main raw material for the production of sulfur and sulfuric acid in the world [2,3,13]. However, during the desulfurization processes, such an element of hydrogen sulfide as hydrogen is often not used and is most often bounded into the water (equations 2 or 3). Given the importance of hydrogen energy for society, it is relevant to obtain from hydrogen sulfide, not only sulfur but also hydrogen. Hence, hydrogen sulfide becomes a complex raw material for obtaining these two valuable products.

It is possible to decompose hydrogen sulfide on sulfur and hydrogen using methods of radiolysis, electrolysis, photolysis, thermolysis and plasmolysis. In industry, for the decomposition of hydrogen sulfide, mainly plasmochemical and electrochemical processes are used.

Conclusions. The classification of methods for purifying gases from hydrogen sulfide by the physical and chemical nature of the interaction of hydrogen sulfide, accompanied or not accompanied by a change in the degree of oxidation of sulfur, enables to fully cover the existing and (in perspective) new desulfurization processes. In non-conversion methods, hydrogen sulfide does not enter into chemical interactions, which is accompanied by a change in the degree of oxidation of sulfur, and in the conversion ones – it occurs the interaction of hydrogen sulfide with an oxidizer (preferably oxygen) or its decomposition, during which the degree of oxidation of sulfur increases.

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