SULFURIC ACID PRODUCTION METHODS AND PRODUCTION TECHNOLOGY BY ABSORPTION METHOD

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ABSTRACT

Among mineral acids, sulfuric acid ranks first in terms of production and consumption. Its world production has more than tripled in the last 25 years and now stands at over 160 million tons per year. The fields of application of sulfuric acid and oleum are very diverse. Most of it is in the production of mineral fertilizers (from 30 to 60%), as well as paints (from 2 to 16%), chemical fibers (from 5 to 15%) and metallurgy (from 2 to 15%). is used. 2 to 3%). It is used for various technological purposes in textile, food and other industries.

Keywords: Limited use of raw materials such as mineral acid, sulfuric acid, oleum application areas, sulfur (IV) oxide, oil, coal, natural and associated gases, waste gases of thermal power plants and copper smelting gases contain sulfur(IV) oxide is explained by the low concentration of

INTRODUCTION

In the production of sulfuric acid, raw materials can be elemental sulfur and various sulfur-containing compounds, from which sulfur or directly sulfur (IV) oxide can be obtained[1].

Natural deposits of local sulfur are small, although its concentration is 0.1%. Sulfur is often found in nature in the form of metal sulfides and metal sulfates, and is also a part of oil, coal, natural and associated gases[2]. A large amount of sulfur is present in waste gases and non-ferrous metallurgical gases in the form of sulfur oxides and in the form of hydrogen sulfide released during the treatment of combustion gases[3].

Thus, raw materials for the production of sulfuric acid are very diverse, although elemental sulfur and iron pyrites have been mainly used as raw materials to date[4]. The limited use of raw materials such as waste gases of thermal power plants and copper smelting gases is explained by their low concentration of sulfur (IV) oxides[5].

At the same time, the share of pyrites in the balance of raw materials decreases, and the share of sulfur increases[6].

In the general scheme of sulfuric acid production, the first two stages - preparation of raw materials and burning or roasting them - are important[7]. Their composition and tools depend significantly on the nature of raw materials, which largely determines the complexity of the technological production of sulfuric acid[8].

Brief description of modern industrial ways of obtaining sulfuric acid. Ways to improve production and prospects for development[10].

The production of sulfuric acid from sulfur-containing raw materials involves several chemical processes, in which the degree of oxidation of raw materials and intermediate products changes. This can be shown in the following diagram[9]:

where I is the stage of production of furnace gas (sulfur (IV)oxide)[11],

II is the stage of catalytic oxidation of sulfur (IV) oxide to sulfur (VI) oxide and its absorption (recycling to sulfuric acid)[12].

In actual production, these chemical processes are supplemented by raw material preparation, furnace gas treatment, and other mechanical and physicochemical operations[13]. In the general case, the production of sulfuric acid can be expressed as follows[14]:

Raw materials. Preparation of raw materials. Burning (roasting) of raw materials

The specific technological scheme of production depends on the type of raw materials, the catalytic oxidation properties of sulfur oxide (IV), the presence or absence of a sulfur (VI) oxide absorption stage[15]. Depending on how the oxidation process from SO_2 to SO_3 is carried out, there are two main methods of obtaining sulfuric acid[16].

In the contact method of obtaining sulfuric acid, the oxidation process from SO_2 to SO_3 is carried out in solid catalysts[17].

Sulfur trioxide turns into sulfuric acid at the last stage of the process - the absorption of sulfur trioxide, which can be simplified by the reaction equation[18]:

$$SO_3 + H_2O => H_2SO_4$$

Nitrogen oxides are used as an oxygen carrier when carrying out the process according to the nitrogen (tower) method.

The oxidation of sulfur dioxide is carried out in the liquid phase, and the final product is sulfuric acid:

$$SO_3 + N_2O_3 + H_2O => H_2SO_4 + 2NO$$

At present, the industry mainly uses the contact method to obtain sulfuric acid, which allows the use of more intensive equipment[20].

Consider the process of obtaining sulfuric acid from two types of raw materials: sulfur (iron) pyrites and sulfur by contact method[21].

1) The chemical scheme for obtaining sulfuric acid from pyrites includes three consecutive stages[22]:

Oxidation of iron disulfide of pyrite concentrate with atmospheric oxygen:

Catalytic oxidation of sulfur oxide (IV) with an excess of oxygen in the furnace gas:

$$2SO_2 + O_2 => 2SO_3$$

Absorption of sulfur (VI) oxide with the formation of sulfuric acid:

$$SO_3 + H_2O => H_2SO_4$$

From the point of view of technological design, the production of sulfuric acid from iron pyrites is the most complicated and consists of several successive stages[23].

The main (structural) diagram of this production is shown in Fig. 1:

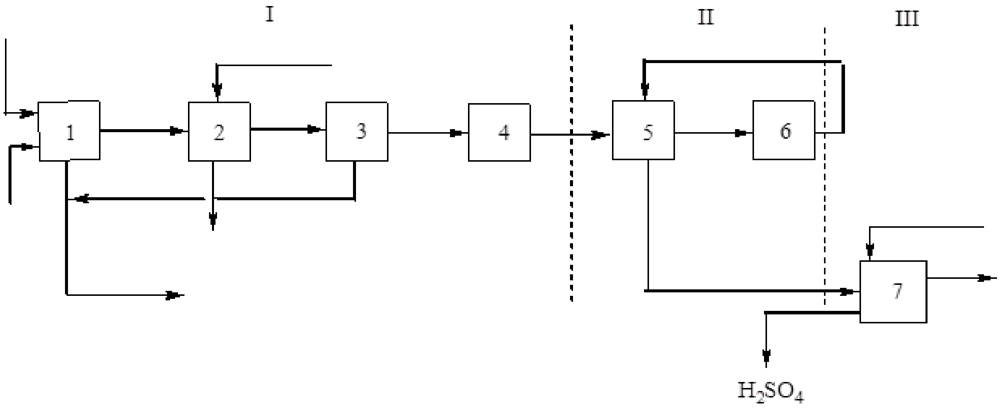

Fig. 1. Block diagram of one-contact production of sulfuric acid from flotation pyrite.

I - obtaining roasting gas: 1 - roasting pyrites; 2 – gas cooling in the waste heat boiler; 3 - general gas purification, 4 - special gas purification; II - communication: 5 - gas heating in a heat exchanger; 6 - communication; III - absorption: 7 - absorption of sulfur oxide (IV) and formation of sulfuric acid.

Roasting of pyrite in air flow is an irreversible non-catalytic heterogeneous process that proceeds with heat release during thermal dissociation stages of iron disulfide[24].

FeS_2 \u003d 2FeS + S2

An increase in the driving force of the combustion process is achieved by pyrite flotation, which increases the amount of iron disulfide in the raw material, by enriching the air with oxygen and using excess air during combustion up to 30% of the stoichiometric amount. In practice, baking is carried out at a temperature not higher than 1000 ° C, because beyond this limit, the particles of the baked raw material begin to sinter, which causes their surface to decrease and makes it difficult to wash the particles. air flow.

Furnaces of various designs can be used as reactors for roasting pyrites: mechanical, powder-like roasting, fluidized bed (CF). Fluidized bed furnaces are high intensity (up to 10,000 kg / m 2 per day), ensures complete combustion of iron disulfide (the sulfur content in the slag does not exceed 0.005 by weight) and controls the temperature, which facilitates the process of its use. heat of combustion reaction. Among the disadvantages of KS furnaces, the amount of dust in the combustion gas increases, which makes cleaning difficult. Currently, KS furnaces have completely replaced other types of furnaces in the production of sulfuric acid from pyrites.

The technological process of production of sulfuric acid from elemental sulfur by contact method differs from the production process from pyrite by a number of features. These include:

- special design of furnaces for the production of furnace gas;
- increase of sulfur (IV) oxide in furnace gas;
- there is no furnace gas pretreatment step.

Further operations of contact with sulfur (IV) oxide in terms of physical and chemical principles and devices do not differ from the process based on pyrites and are usually carried out according to the DKDA scheme. In this method, the temperature of the gas in the communication apparatus is controlled by introducing cold air between the catalyst layers.

A schematic diagram of the production of sulfuric acid from sulfur is shown in fig.2

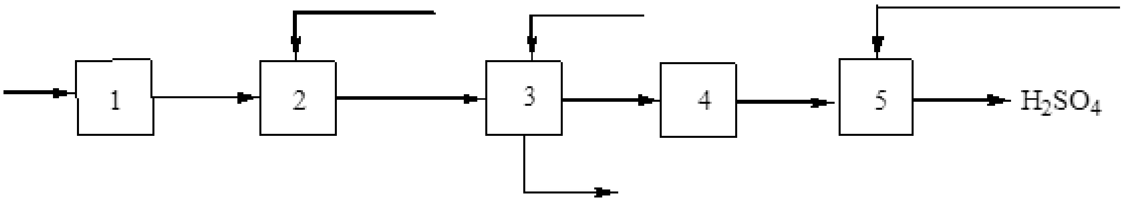

fig.2 Block diagram of the production of sulfuric acid from sulfur.

1 - air drying; 2 - burn sulfur; 3 – gas cooling, 4 – contact; 5 - absorption of sulfur oxide (IV) and formation of sulfuric acid.

There is also a method of obtaining sulfuric acid from hydrogen sulfide called "wet" catalysis, which consists of a mixture of sulfur (IV) oxide and water vapor obtained by burning hydrogen sulfide in an air stream. Sulfur (IV)oxide is oxidized to sulfur (VI) oxide in a solid vanadium catalyst. The gas mixture is then cooled in a condenser, where the vapors of the sulfuric acid formed turn into a liquid product.

Thus, in contrast to the methods of production of sulfuric acid from pyrite and sulfur, in the process of wet catalysis there is no special stage of absorption of sulfur (VI) oxide, and the whole process includes only three consecutive stages:

1. Combustion of hydrogen sulfide:

H_2S + 1.5O 2 \u003d SO_2 + H_2O - DH 1, where DH 1 \u003d 519 kJ

with the formation of a mixture of sulfur (IV) oxide and water vapor of equimolecular composition (1: 1).

2. Oxidation of sulfur (IV) oxide to sulfur (VI) oxide:

$SO_2 + 0.5O_2$<=>SO_3 - DN_2, where $DN_2 = 96$ kJ,

while maintaining the equimolecular composition of a mixture of sulfur oxide (IV) and water vapor.

3. Condensation of steam and formation of sulfuric acid:

$SO_3 + H_2O$<=>H_2SO_4 - DH_3, where DH_3 \u003d 92 kJ

Thus, the process of wet catalysis is described by the general equation:

$H_2S + 2O_2$ \u003d H_2SO_4 - DH, where DH \u003d 707 kJ.

The wide scale of production of sulfuric acid creates a particularly acute problem of its improvement. The following main directions can be distinguished here:

Thus, the rate of oxidation of sulfur (IV) oxide depends on two quantities that change in opposite directions with increasing temperature. As a result, the temperature dependence of the oxidation rate should exceed the maximum. It also follows from equation (4) that the greater the oxidation rate of sulfur (IV) oxide, the lower the rate of conversion of sulfur (IV) oxide to sulfur (VI)oxide. As a result, the temperature dependence of the reaction rate for each degree of conversion is represented by an individual curve with a maximum. In the form. 7 shows a series of similar curves corresponding to different degrees of conversion for a gas of constant composition. It follows that the rate of the oxidation reaction reaches its maximum at certain temperatures, the higher it is, the lower the conversion rate and represents the exact optimum temperature.

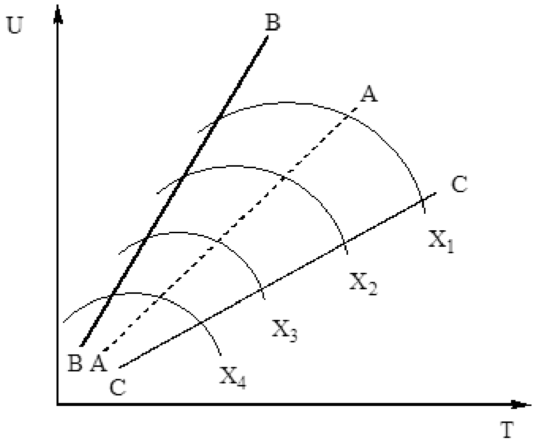

Fig. 3. The temperature dependence of the oxidation rate of sulfur oxide (IV) at different levels of conversion X 1.< X 2 < X 3 < X 4

The AA line connecting the optimal temperature points is called the optimal temperature sequence line (OTS) and indicates that for best results the contact process should be started at a high temperature, which ensures a high speed of the process (practice in , about 600°C), and then transformations to reduce the temperature to reach a higher level, maintaining the temperature regime on the LOT. Lines BB and CC in the figure indicate the range of temperatures accepted in the actual technological process of communication

Thus, the contradiction between the kinetics and thermodynamics of the sulfur (IV) oxide oxidation process is very successfully overcome by the design of the communication apparatus and the temperature regime. This is achieved by dividing the process into stages, each of which corresponds to the optimal conditions for the contact process. Thus, the initial parameters of the contact mode are determined: temperature 400 - 440°C, pressure 0.1 MPa, amount of sulfur (IV) oxide in the gas 0.07 vol. shares, the amount of oxygen in the gas is 0.11 vol. shares.

Apparatus-technological scheme of fine purification of sulfur dioxide and oxidation of sulfur dioxide in a four-layer contact apparatus with filter catalyst layers.

Reactors or contact devices for catalytic oxidation of sulfur (IV) oxide are divided into devices with a solid catalyst layer (shelf or filter), in which the contact mass is located in 4-5 layers, and with a liquid layer. devices. After the gas passes through each layer of the catalyst, the heat is removed by introducing cold air or gas into the apparatus or by using heat exchangers installed in the apparatus or separately removed.

At present, the most common in contact production of sulfuric acid and oleum is the technological scheme using the double contact "DKDA" (double contact - double absorption) principle. A part of such a scheme is shown in the figure, except for the furnace part and the general gas cleaning section, which are technologically the same for all schemes. nine.

Plant capacity up to 1500 t/day for monohydrate. Consumption coefficients (per 1 ton of monohydrate): pyrite 0.82 t, water 50 m 3, electricity 82 kW h.

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