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Catalytic and adsorptive desulphurization of gases

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Abstract

The present paper considers some very important problems: problems which are important in the area of environmental protection, as well as in the technical and technological desulphurization of gases. Here we have selected only those 'dry' technologies in which adsorption and catalytic processes occur. The paper presents the basics of methods for removing sulphur dioxide and hydrogen sulphide from what are called acid gases, as well as equipment for this purpose, together with a discussion of the advantages and disadvantages of particular processes. The introduction to the paper includes the sources of the emission of hydrogen sulphide and sulphur dioxide, their toxicity, and the methods by which atmospheric air can be environmentally protected. The writer realizes that the paper does not include all technologies but only the major directions, which make removal of contamination caused by sulphur compounds from tail gases possible. The typical catalytic dry processes of the conversion of sulphur compounds in tail gases represent a new direction, which is likely to undergo intensive development if we are able to solve the problem of the preparation of appropriate catalysts operating under very difficult and unstable conditions.

1. Section 1

1.1. Introduction

The development of industry and power engineering throughout the world is associated with a number of unfavourable changes in the natural environment. The most serious and harmful environmental results of industrialization are arranged below according to the degree of hazard they represent to natural biological conditions on the planet. They are arranged as follows:

- air pollution
- pollution of inland waters
- noise
- threat of chemicals to living organisms
- radioactivity.

It follows from the above list that air pollution is at present the most serious problem which we face since air is the one indispensable factor which governs human life. Moreover, apart from a few exceptions, air must be assimilated by man from the natural environment in a natural way. It cannot be supplied to human kind, or other organisms, in an artificially prepared form, which is possible in the case of other elements that are a necessary to life, such as water, for instance, or food. In addition, the human organism is very sensitive to changes of the atmospheric composition, and particularly to the concentration of alien, unnatural components in it. Their presence in even incomparably small quantities proportioned to natural components results in a number of disturbances and complications to the human organism. Hence the problem of air purity is, at present, a subject of particular interest.

Air pollution results from the penetration into the atmosphere of different chemical substances in the form of gas, steam, smog or aerosol, such substances being the products of industrial proc-

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esses and power engineering. The substances that are the most dangerous to the natural environment in terms of their quantity and toxicity may be classified as follows: sulphur dioxide, hydrogen sulphide, smog, hydrocarbons, carbon monoxide, lead compounds, and carbon dioxide.

1.2. Sources of sulphur dioxide emission

Table 1 presents the main sources of sulphur dioxide emission to the atmosphere on a global scale [1].

Table 1
Sources of the emission of sulphur dioxide into the atmosphere in the global scale

Sources of emission	Participation percentages
Coal combustion	66.0
Crude oil processing	4.5
Combustion of kerosene products	18.0
Colour metallurgy	10.8
Combustion of waste products	0.3
Combustion of other fuels	0.4

In particular regions of the world these values will be different from those given in Table 1, depending on the state of industrialization as well as on the raw materials of the fuel and the structure of the energy economic system in the given region.

The location of the sources of sulphur dioxide emission and of areas endangered by air pollution is highly irregular; just as irregular as the location of the industrial potential in the world. The greatest air pollution can be observed in the northern hemisphere since 93% of the global quantity of sulphur dioxide is emitted in this area. Estimated values of atmospheric pollution over Poland in the years 1982–93 are presented in Table 2.

Power engineering and metallurgy are situated in close proximity to many branches of industry, particularly those consuming enormous quantities of energy and materials. These branches of industry are engaged in the thermal processing of huge amounts of various raw materials. The concentration of this type of industry in a comparatively small area, as well as the development of the means of environmental protection, which fails to keep pace with industrial advance, have caused and are still causing, the degradation of the natural environment on an unimaginable scale, with all the ensuing consequences.

Table 3 presents the kind and the amount of impurities emitted by power stations, steelworks and ironworks, glassmaking industry and waste material incinerators [2].

The world regions particularly liable to atmospheric contamination by sulphur dioxide are densely populated and highly industrialized areas such as the sea coasts of the USA, the islands of Japan, the Ruhr coal basin, the British Isles, and the Upper Silesian Industrial Area in Poland.

1.3. The toxicity of sulphur compounds emitted into the atmosphere

The pollution of air by industrial smoke, which naturally contains dusts and toxic gases, is the most burdensome to inhabitants of industrialized areas in particular, and to biological life in general. The air pollution not only affects the natural environment directly but, by contaminating surface waters and soil, it degrades their utility values and, at the same time, transfers toxic substances to living organisms and to the whole biological chain.

Sulphur dioxide in the atmosphere partly reacts with oxygen and ammonia to give ammonium sulphate which, in the form of aerosol, settles on the surface of the earth and waters, while the remaining sulphur dioxide is either absorbed by water, reaching the surface of the earth in this form, or is directly absorbed from the air by vegetation and animal organisms.

The action of sulphur dioxide contained in the air causes: acidification of soil, the poisoning of vegetation and living organisms (with high concentrations), and corrosion.

Having penetrated into the soil in the form of ammonium sulphate, or absorbed in meteorological precipitation, sulphur dioxide causes the soil to become acidified, which results in the reduction of crop yields: at high sulphur concentrations, cultivation becomes impossible. Most vegetation,

Table 2
Emission and reduction of industrial air pollution in Poland in 1992 [97]

Kind of industry	Dusts						Gases				
	Emissions				Retained in reduction appliances[a]	Retained in reduction appliances[b]	Emissions			Retained in reduction appliances[a]	Retained in reduction appliances[b]
	Total[a]	Including:					Total[a]	Including:			
		Flue ash[a]	Metallurgical dust[a]	Dust from concrete processing[a]				Sulphur dioxide[a]	Carbon oxide[a]		
Total	684	573	32.9	22.5	20444.0	96.8	3155	1837	675	856.6	21.4
Fuel and power industry	385	375	0.0	–	14852.3	97.5	1951	1443	73	50.6	2.5
including power industry	355	354	0.0	–	14372.8	97.5	1762	1339	38	9.2	0.5
Metallurgical	52	17	28.6	0.1	984.8	95.0	492	77	379	658.4	57.2
including iron and steel industry	43	12	26.4	0.1	680.4	94.0	415	35	348	0.4	0.1
Electro-machine industries	39	30	4.3	–	166.5	81.1	89	38	27	1.4	1.5
Chemical	59	44	0.0	–	1682.2	96.6	189	98	23	139.5	42.5
Mineral	41	8	0.0	22.4	2024.1	98.0	97	21	60	1.0	1.0
including building materials	40	7	0.0	22.4	2019.3	98.1	91	19	59	0.7	0.8
Wood-paper industry	25	20	–	–	370.2	93.5	59	28	17	1.4	2.4
Light industry	12	12	–	–	44.8	78.2	34	17	12	1.7	4.8
Food industry	22	21	–	–	78.1	77.8	81	35	32	1.3	1.5
Remaining industries	48	46	–	0.1	240.9	83.4	163	80	52	1.3	0.8
including non-industrial units	47	46	–	0.1	238.0	84.4	162	80	52	0.9	0.6

[a] Given in thousands of tons.

[b] Given in percentage of pollution produced.

Table 3
Concentration of impurities in tail gases coming from different sources [7]

Specification	Origin of gas				
	From combustion of hard coal in power stations by using LUVO	From combustion of lignite in power stations	From steel works and iron works	From burning rubbish	From glass-making industry
Impurities					
SO_2 (ppm)	350–1700	100–2700	170–4000	290	180–1020
SO_3 (ppm)	0.01	0.01	Lack of data		0.05–0.10
NO_x (ppm)	200–1600	100–500	100–300	200	180–2250
NO_2/NO_x	0.05	0.05			0.03–0.10
HCl (ppm)	30–125	12–60		750	Depending on type of glass
HF (ppm)	5–60	0.3–2.5	Up to 50		
CO (ppm)	300–680		Up to 60000		
Dusts (mg/m^3)	500–35000	1500–25000	Up to 15000	5000	100/for special glasses
Carrier gas					
N_2 vol.-%	60–80	60–78	57–82	71	68–84
CO_2 vol.-%	11–15	11–15	4–10	5	7–15
O_2 vol.-%	4–7	4–7	9–19	11	4–10
H_2O vol.-%	3–8	8–24	Up to 13	13	6–22
Volumetric flow rate (m^3/h)	1000–1500 per 1 MW	1550–2200 per 1 MW	1000–400	4200/t rubbish	1000–500 up to 300 000, depends on type of regenerator
Temperature (K)	393–473 outside LUVO[a]	373–673 outside LUVO			

[a] LUVO = heat exchanger.

especially the conifer, is not resistant to the action of sulphur dioxide. With prolonged emission of sulphur into the atmosphere at a concentration of $0.05 \cdot 10^{-6}$ m^3/m^3, the leaves of trees turn yellow and fall down, leading to the atrophy the trees [3]. There is little resistance to the action of sulphur dioxide for such important cultivated plants as lucerne, clover, barley and rye, particularly in their early vegetation period.

The minimum limiting concentration of sulphur dioxide in air which is capable of damaging crops is $3 \cdot 10^{-5}$% over a one-year period [4]. For man and animal organisms a one-year stay in an atmosphere containing more than $4 \cdot 10^{-6}$% of sulphur dioxide is harmful, whereas at a concentration of 10^{-5}% its toxic action can be observed within 2–3 days [4,5]. Sulphur dioxide also has a corrosive action on metal and concrete constructions, and when a concentration of over 10^{-5}% is maintained unchanged during one year the distinct effects of corrosion can be seen [5].

For the reasons given above the presence of sulphur dioxide in the atmosphere is a cause of considerable damage, particularly to forestry. Of the other sulphur compounds contained in atmospheric air special attention is paid to hydrogen sulphide, carbon disulphide and mercaptans. Hydrogen sulphide (H_2S) in atmospheric air comes mainly from processes of decay and occurs as a waste product of synthetic fibre production and fuel processing (natural gas, crude oil and coal). Its characteristic properties are acidity and toxicity, and its presence in atmospheric air is signalled by its characteristic smell.

The damaging properties of carbon disulphide are generally known. Its concentration in atmospheric air cannot exceed 0.015 mg CS_2/m^3.

In the vicinity of crude oil refinery and cellulose mills the occurrence of sulphur compounds having a characteristic odour (mercaptans, organic sulphides and other sulphur compounds) may be noted.

1.3.1. Toxicity of sulphur compounds to humans

In order to prevent our being poisoned by sulphur compounds a proper knowledge of their toxic properties is of great importance.

Limiting threshold values or maximum permissible concentrations have been established for substances which contaminate atmospheric air. As a rule they ensure safety to man after exposure during an eight-hour day. In general, atmospheric pollution is not a cause of acute illnesses but it does give rise to a distinct increase in people's liability to diseases ending in death. A relation has been pointed out between the growing intensity of air contamination in a given environment and an increase of the death rate. It is believed that air pollution does not result in a specific disease which may lead to death, but that it may cause the hitherto existing illnesses of the respiratory and circulatory systems to become more acute. The illnesses that are most frequently subject to intensification in this way are: chronic bronchitis, chronic diseases that handicap the ventilation of the lungs, bronchial asthma, and coronary diseases.

The sulphur oxides that cause air pollution are the following: sulphur dioxide, sulphur trioxide and their combination with water (steam), sulphuric and sulphurous acids. A concentration of about 1 ppm of SO_2 in air causes the frequency of breathing to accelerate. Persons in good health experience difficulty in breathing at 1.6 ppm concentration, while sick persons suffering from lung diseases experience difficulty at 0.7 ppm. Rats exposed to continuous ppm SO_2 concentrations have a shorter life span and show accelerated ageing as well as injuries to the heart, lung and kidneys.

Sulphuric and sulphurous acids belong to the so-called caustic acids which cause tissue to be destroyed by their direct chemical action. The tissue proteins turn into acidic compounds dissolving in concentrated acid. Haemoglobin turns into dark, acidic haematein and is precipitated, while its intense, irritating action results in the loss of tension of the vascular system.

Hydrogen sulphide, sulphides, mercaptans and carbon disulphide are a great threat to human beings. Hydrogen sulphide causes anoxia and direct damage to the cells of the central vascular system. Carbon disulphide mainly damages the central vascular system, circular nerves and the haemogenous system. Mercaptans display an intensely irritant action. In poisoning induced by these compounds the basic symptoms are connected with their irritating action [6].

1.4. Methods and techniques for the protection of atmospheric air

When the poisoning of the atmosphere by sulphur dioxide and the losses sustained reached crisis proportions, strict measures were taken, aimed at restricting the emission of sulphur dioxide. Research studies were carried out in two directions, aiming at:

- establishing standards and legal regulations for atmospheric protection and the permissible concentration of sulphur dioxide in the air;
- scientific and technological activity developing technical means which would make it possible to reduce the emission of sulphur dioxide.

Methods and techniques for atmospheric air protection may be divided into programming, technological, technical and administrative methods [7].

Programming methods consist in selecting areas which are appropriate in terms of their physiography and developing them in such a way as to make the effect of the newly-built objects on the environment as negligible as possible.

Technological methods are of the greatest importance to atmospheric air protection and consist in developing a production technology which will make it possible to minimize environmental pollution without reducing the output of production and the quality of the product.

Technical methods that are most frequently used are the extraction of waste gases and attempts to neutralize gas pollution.

Administrative methods consist in supervising the compliance with the established standards in the sphere of atmospheric air protection.

The duty of using methods, technologies and technical means to protect atmospheric air from pollution is performed by an institution engaged in establishing admissible concentrations of toxic substances in atmospheric air. The legal determination of their permissible concentrations is one of the principle indices governing site planning which, in turn, constitutes a legal basis for giving a decision on the location of an investment project.

Factories and industrial plants whose gas emissions exceed the established permissible concentration of toxic substances in the air are under an obligation to build, install and operate appliances for the protection of the air against this pollution.

This is the reason why both the overall and detailed location of the given establishment that may cause a permissible concentration of toxic substances in atmospheric air to be exceeded should be agreed upon with the appropriate body set up to protect the air. In an attempt to protect atmospheric air against being polluted, a protection zone should be established, while factories and industrial plants emitting toxic substances into the air are under an obligation to perform measurements of the concentrations of toxic substances; both on site, where they are emitted, and in the air, on the premises of industrial plants, as well as in protection zones [8].

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2. Restricting the emission of sulphur compounds

2.1. The occurrence of sulphur in some raw material

Sulphur compounds occur in almost all natural raw materials used for energy production, i.e. in natural gas, crude oils and coals.

Apart from hydrocarbons, natural gas contains quantities of hydrogen sulphide and organic sulphur compounds. The hydrogen sulphide content in different gas deposits depends on the age of the rock reservoir in which the gas deposit is found. The presence of rocks containing $CaSO_4$ or FeS causes increased amounts of hydrogen sulphide in natural gas. The amount of H_2S in natural gas varies greatly, ranging from trace quantities to as much as about 50 vol.-%. In general the concentrations are below 1 vol.-% [1].

In crude oils sulphur occurs in the form of organic compounds, such as mercaptans, sulphides, or thiophene. Apart from bound sulphur, negligible amounts of elemental sulphur have been detected in certain crude oils. The sulphur content in crude oil ranges from several hundred ppm to 5 wt.-% and sometimes even to 7 wt.-% [2]. The end products coming from the processing of a crude oil that is rich in sulphur require additional cleaning, most frequently in hydrogenation processes. Hydrogen sulphide is obtained as a result of the hydrodesulphurizing process.

Sulphur occurs in coal in both organic and inorganic forms. The inorganic types of sulphur are primarily sulphates and pyrites. The quantity of mineral sulphur is negligible and, in general, does not exceed 0.2% [3].

Organic sulphur occurs in the form of –SH, –S–S– and –S– groups. Thiosteric and dithiosteric groups have also been found in coal. The sulphur content in coals occurs in the range of few tenths of a per cent to several per cent. Some coals even contain as much as 10% of sulphur [4]. When hard coal is burnt, 85–90% sulphur escapes as SO_2, and 1–4% as SO_3. When brown coal is burnt, about 70–90% changes into SO_2.

The iron and steel industry emits considerable quantities of sulphur compounds into the atmosphere. In iron ores sulphur occurs most frequently in the form of pyrites; in the ores of nonferrous metals it is found in the form of sulphides, as well as sulphates of copper, lead and zinc. In the process of roasting nonferrous metals the gases obtained contain sulphur dioxide at high concentration. This may be used as a raw material for producing sulphuric acid.

2.2. *Methods for preventing emission of sulphur compounds*

The methods may be divided into the following groups:

(a) substituting raw materials containing sulphur for similar raw materials which contain minimum quantities of sulphur, or none at all;
(b) removing sulphur compounds from raw materials;
(c) removing sulphur compounds from waste gases.

The implementation of each of these methods requires a different type of technological and technical solution.

The first method can be accomplished if one can find other appropriate power engineering raw materials. This type of solution may be the introduction of nuclear power stations into the power sector, which would substitute for power stations based on coal combustion. This would considerably reduce the emission of sulphur dioxide. There are, however, still other raw materials which, when processed, emit sulphur compounds. The appropriate solution would be either to remove sulphur from the raw material or to remove sulphur compounds from the post-processed products. In the case of gas or liquid raw materials, the removal of sulphur compounds is technically easier that their removal from solid bodies.

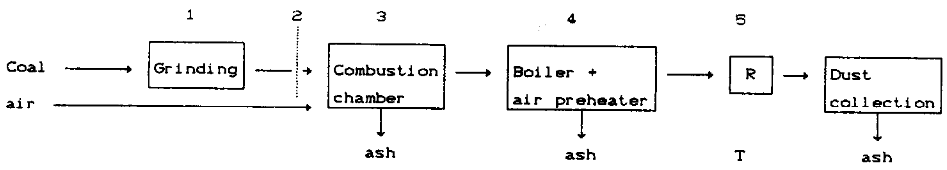
Administrative and legal restrictions as well as the limitation of sulphur content in fuel oils and solid fuels make it necessary for their producers and users to develop and employ ways of limiting the emission of sulphur dioxide into the atmosphere.

The possibilities for substituting high-sulphur fuel oils by making use of low-sulphur crude oils are limited due to their shortage on the world markets. In a convenient position in this respect are the countries of Western Europe, which use low-sulphur North African crude oil. The United States also imports considerable quantities of low-sulphur crude oil from Africa. This type of crude oil gives rise to low-sulphur residues which are put to use as components for producing fuel oils with a reduced sulphur content. However, the amount of low-sulphur crude oil available on a world-wide scale is too small for the production of fuel oils from high-sulphur crude oil to be impeded.

At present the most widespread techniques for reducing the atmospheric emission of sulphur dioxide resulting from the combustion of petrols and oils as well as other products, is the removal of sulphur by catalytic hydrodesulphurization. The basic reaction of the hydrodesulphurization process is the catalytic reaction of hydrogenation of sulphur compounds occurring in the above mentioned products. In general, the hydrodesulphurization of hydrocarbon mixtures containing different sulphur bonds may be written as follows:

$$C_nH_mS_x + 2xH_2 \rightarrow C_nH_{(m+2x)} + xH_2S \qquad (1)$$

The process of removing sulphur from solid fuel is difficult to carry out. Sulphur may partly be removed from pyrites contained in coal. Pyrites are compounds of sulphur with metals, mainly with iron, which is why they display ferromagnetic properties. Owing to this, after being disintegrated they may be separated from coal by electromagnets. Another separation method consists in taking advantage of the difference of specific gravity between pyrites and coal. The disintegrated fine coal is washed. Being lighter,



	T K	Adsorbents
1 - Mixing with brown coal	1370	$CaCO_3$, CaO, $Ca/OH/_2$
2 - Introducing into burner brown and hard coals mixture	1370 - 1570	$CaCO_3$, CaO, $Ca/OH/_2$
1 - 3 - Directly injection to fluized combustion zone	1120	$CaCO_2$
4 - High temperature reaction in gas transfer zone	1370 - 1070	$CaCO_3$, CaO, $Ca/OH/_2$
5 - Low temperature adsorption in movable or fluidized bed	348 - 423	CaO, $Ca/OH/_2$

Fig. 1. The point of the addition of adsorbents in the coal combustion process.

coal is suspended in the wash liquor, while pyrites fall to the bottom.

Most of the sulphur in coal is bonded in the form of organic sulphur, the removal of which is impossible without drastic processes being used. As result of carbonization, gasification or other processes, part of the organic sulphur contained in coal is transformed into gas, and in this state it is removed by means of the commonly known methods.

One apparent solution to the problem of atmospheric pollution is to construct tall chimneys, reaching a height of 300 m or even higher. This is a costly enterprise and, since it is a potential threat to air transport, it cannot be used in every region. In addition, this solution does not remove environmental pollution, but only scatters it over a larger area. There is a possibility of eliminating the emission of sulphur oxides by means of chemical methods. Before waste gases are carried away to the chimney, sulphur oxides are removed by means of a basic substance, e.g. slaked limestone (calcium hydroxide). This process is being used but its wider application is hampered by the high costs involved.

Desulphurization of waste gases is theoretically a solution which enables a considerable reduction of the emission of sulphur dioxide from different sources, including coal combustion. A number of methods have been developed which make it possible to remove 90% of sulphur dioxide from waste gases. The removal of sulphur compounds from waste gases involves an increase of capital outlay by about 25%, and the operating costs by 25%, while 1–6% of the energy generated by the power station is consumed by the desulphurizing systems. The costs associated with the removal of nitrogen oxides give rise to an additional burden, which is 30–50% of the cost of the desulphurization process. These calculations have been made by researchers from the Massachusetts Institute of Technology (USA), who based them on the two-year operating periods of American wet gas desulphurization units [5]. The advantages and disadvantages of dry and wet desulphurisation of gases are controversial. At present, however, dry desulphurization of waste gases is becoming more popular because this process does not produce any liquid wastes; but it may produce dry wastes.

In recent years a number of technologies have been developed in service of the protection of the natural environment, aimed at removing SO_2 and NO_2 from waste gases. The binding of the impurities being emitted may take place at different stages of the processing of the raw material.

Fig. 1 presents a schematic diagram showing at what stage an adsorbent or a reagent binding sulphur compounds may be added (nitrogen or other toxic compounds) [6]. In spite of high costs of the desulphurization process a large number of industrial systems for desulphurizing waste gases are operating all over the world.

2.3. *References*

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3. Processes of adsorption and catalysis

In the process of gas desulphurization two phenomena deserve particular attention: adsorption and catalysis. This process may be dominated by either adsorption or catalysis, or by mixed processes which are difficult to define.

Below we present a brief discussion of adsorption and catalysis processes [1] [1–25].

3.1. *Adsorption*

Adsorption is the process of concentrating a substance on the surface or in the volume of a solid body due to the action of the attracting intermolecular forces. At least two components participate in the adsorption process. The solid body on the surface or in the pore volume of which the concentration of the substance adsorbed takes place is called the adsorbent. The substance being adsorbed which is in the gaseous or liquid phase after passing into the adsorbed state is called the adsorbate. From the thermodynamic viewpoint adsorption is characterized by a reduction in Gibbs free energy. In agreement with all processes with an accompanying reduction in Gibbs free energy, adsorption is a spontaneous process. The transition of a substance from the gaseous state into the adsorbed state is connected with the loss of at least one degree of freedom, which leads to a decrease in the entropy of the ΔS system. But in this case enthalpy, ΔH, decreases, in compliance with the equation given below, and so adsorption is an exothermic process [1].

$$\Delta H = \Delta G + \Delta S \qquad (2)$$

Physical adsorption is caused by intermolecular interaction forces (van der Waals forces, hydrogen bonds, etc). Chemical adsorption, also named chemisorption, is connected with the transition of electrons between a solid body (adsorbent) and an adsorbing substance, the adsorbate. This process is connected with the formation of a chemical compound between the adsorbent and the first layer of the substance adsorbed.

The distinction between physical adsorption from the chemical adsorption of gases on stable adsorbents usually does not present much difficulty. The most important criteria on which the differentiation of both types of adsorption can be based are as follows:

(1) heat of adsorption — inappreciable in the case of physical adsorption; appreciable, of the same order as that of the corresponding chemical reaction, in the case of chemisorption;

(2) reversibility of the process — in the case of physical adsorption, the substance adsorbed may be comparatively easily removed from the surface. The removal of the chemisorbed layer is very difficult and involves severe means;

(3) thickness of adsorption layers — in the case of physical adsorption under appropriate pressure

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[1] Professional publications on adsorption and catalysis are fairly plentiful. The present paper primarily aims to present problems related to desulphurization.

and temperature conditions, adsorption layers are formed with a density corresponding to a few diameters of the molecules of the adsorbate: monomolecular layers are formed in the course of chemisorption.

3.1.1. Activated adsorption

Activated adsorption is, as it were, a transition to the catalytic process, and that is why it is referred to in this paper.

The adsorption rates of different substances on adsorbents vary over wide limits. The adsorption of gases and vapours may progress very fast, or at a measurable rate. In the course of physical adsorption the quantity of the substance adsorbed under constant pressure decreases with temperature, whereas the physical adsorption rate does not appreciably depend on temperature since, as a rule, it is determined by the diffusion rate. In the case of chemisorption the amount of the substance adsorbed also decreases with increasing temperature. However, the amount of the substance chemisorbed is usually greater than that adsorbed physically and the rate of the process is, to a great extent, dependent on temperature (it increases exponentially with temperature) and is characterized by an appreciable activation energy, of the order of 10 kcal. Chemical adsorption of this type has come to be named activated adsorption. Very often, both types of adsorption at different temperature ranges may be observed for the same substance. At low temperatures physical adsorption takes place, with activated adsorption at high temperatures. Both these processes are, as a rule, separated by a transient area which is characterized by the fact that the increase in the amount of the substance adsorbed takes place as the temperature is increased. The activation energy measured for the activated adsorption area is in many cases of the same order as the energy of the reaction activation between the free radical and the particle. This makes it possible to assume that the activated adsorption process approximates the reaction between the atom and the particle in the gaseous phase since there are always non-saturated valencies on the surface of the sorbent. It is possible that activated adsorption is connected with the physical stretching of the particle on the surface of the adsorbent, often leading to its dissociation. Although the concept of activated adsorption was introduced by Taylor as early as 1931 it cannot be regarded as fully justified experimentally, which is why it continues to be discussed in the professional literature.

Some authors attribute the activation energy calculated from the change of the adsorption rate to the processes of dissolution, diffusion, migration or reaction on the surface rather than to the chemisorption process itself.

In a great number of cases the optimal temperatures for carrying out heterogeneous catalytic reactions correspond to the range of temperatures in which the activated adsorption of reactants can be observed.

Although in some cases activated adsorption is one of the stages of the heterogeneous catalytic process, its role in the process has not been accounted for satisfactorily. It may be assumed that activated adsorption gives rise to the deformation of the particles adsorbed, and that this increases their reactive ability. Moreover, as was stated above, the activation energy of adsorbed particles is lower than that for particles that are found in the gaseous space.

3.2. Catalysis

Catalysis is a change of the rate of a chemical reaction, caused by substances which themselves remain chemically unchanged. The substances which change the rate of chemical reactions are called catalysts. The reaction rate may be increased or decreased as a result of the action of a catalyst. In the former case the catalysis is called a positive catalysis, while in latter case it is negative.

Since the catalyst must necessarily participate in the transient stages of the chemical process, catalysis may thus be defined as a change in the number and nature of the transient stages of the whole chemical process acted on by the catalyst. Every catalyst changes the rate of one reaction only, or of a certain group of definite reactions, i.e. catalysts perform a specific action. The reactions in which output and final products are catalysts have come to be called autocatalytic reactions. All catalytic reactions are commonly divided into homogeneous and heterogeneous reactions. This division is convenient, not because of the essence of the mechanism of the process, but on account of the state of concentration of substances participating in the reaction.

Catalysis plays a significant role, both in nature and technology. The appropriate selection of catalysts means that we are able to carry out processes in the desired direction and with the required speed.

Acceleration of the chemical process with the participation of a catalyst takes place in the majority of cases at the expense of the increase (as a result of the formation of a transient product) in the activation energy as compared with that of the formation of the active complex without the catalyst. In heterogeneous processes the components reacting in the system occur in various phases and the reaction naturally takes place in the boundary layer. In practice, the most frequent case is the combination of a solid body with a liquid or gaseous phase. This is the reason why, in the case of heterogeneous processes, the transport of a substance from the liquid or gas volume to the surface of a solid body is of particular importance.

The practically important feature of a heterogeneous catalyst, as of every catalyst, is the specificity of its action. Different catalysts may direct a chemical process into taking completely different courses. The specificity of the catalytic action makes it possible to carry out a chemical process in the required direction, and this is one of the basic properties which is utilized in the practical application of catalysis in industry. It was found long ago that the presence of some substances in the reacting mixture may reduce or completely damp the activity of the catalyst. Such substances came to be named catalytic poisons, while the phenomenon itself is called the poisoning of the catalyst.

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4. Adsorbents and catalysts

The materials used for H_2S and SO_2 adsorption should possess appropriate physicochemical properties, particularly such surficial properties as specific surface, size and distribution of pores. Particles of H_2S and SO_2 have inappreciable sizes, so the best adsorbents for them should be those with well-developed microporosity (size of pores up to about 1.5 nm). The physicochemical characteristics of H_2S and SO_2 are given in Table 4 and their structure is presented in Fig. 2.

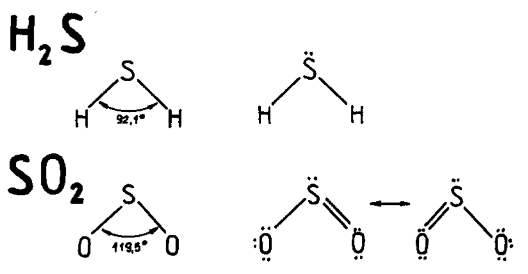

Fig. 2. Structure of H_2S and SO_2 molecules.

Preliminary information on the suitability of a given adsorbent may be obtained on the basis of its thermodynamic properties. The negative formation energy, the so-called high value of log *K*, indicates a high affinity of the adsorbent for the adsorbate.

Information obtained from thermodynamic calculations indicates the possible course of particular reactions in the equilibrium state, which does not necessarily imply that the given adsorbent will be effective in the adsorption process. Another significant feature of the adsorbent is its capacity for regeneration, i.e. the ease with which it can be

Table 4
Characteristic of compounds occurring in tail gases

Gas/steam	Chemical symbol	Molar mass	Density (kg/m^3)	Density with respect to air	Molar volume (kmol/m^3)	Factor of compressibility ($p \cdot 10^3$/Pa)	Melting point (K)	Boiling point (K)	Critical point (K)	Critical pressure (MPa)	Critical density [kg/m^3]
Sulphur dioxide	SO_2	64.06	2.9263	2.2635	21.89	−234	198.0	263.1	420.3	7.8	0.524
Hydrogen sulphide	H_2S	34.08	1.5392	1.1906	22.14	−102.8	187.6	212.8	373.6	9.0	–
Steam	H_2O	18.01	0.768	0.5941	23.45	−344.3	273.16	373.16	647.4	22.0	0.329
Carbon dioxide	CO_2	44.01	1.9768	1.5291	22.26	−69.0	217.2		304	7.4	0.46
Nitrogen	N_2	28.016	1.2505	0.973	22.40	−4.5	63	77.4	126	3.4	0.311
Carbonyl sulphide	COS	60.07	2.72	2.10	22.1	−15.0	135	225	378	6.6	–
Carbon disulphide	CS_2	76.14	1.261				164..6	319.4	546	7.4	–
Ammonia	NH_3	17.03	0.817				195.5	239.8	405.5	11.3	0.235
Sulphur	S	32.066	2.07(r)				385.9^a				
			1.97(j)				392.4	717.7			
			1.92(b)				~393				

r = rhombic, j = monoclinic, b = amorphous, ^{a} other data present value of melting point.

regenerated while still maintaining the same physicochemical properties after many regeneration cycles.

A tremendous number of different adsorbents are used for SO_2 and H_2S removal. They are often specially activated by the addition of an activating agent which does not always make it possible to classify the process occurring as a 'pure' adsorption process or a 'pure' catalytic process. For this reason these two basic factors used for binding sulphur dioxide and hydrogen sulphide will be discussed in a single section.

4.1. Adsorbents

From the viewpoint of their chemical composition, adsorbents may be classified as follows:

- carbonaceous adsorbents
- inorganic adsorbents
- mixed adsorbents.

4.1.1. Carbonaceous adsorbents

The basic carbonaceous adsorbents are active coals obtained during thermal processes in the absence of air (carbonization), followed by activation (steam–gas and chemical processing). Active carbon obtained after the activation process has a well-developed surface area with a large number of micropores. The raw materials for active carbon processes may be: wood, brown coal, hard coal, stems of tropical plants, walnut shells, and other materials available in any particular country [1]. Adsorbents may also be semicoke or coke obtained at low or high coal carbonization temperatures.

The most frequently used adsorbents are specially prepared active coal or other carbonaceous adsorbents.

Active coals prepared with the use of compounds of such metals as Cu, Ag, Hg, Au, Zn, Cd, Al, Co, Ni, Pd, Pt, Ti, V, Cr, Mn, Fe, Sn, Pb, Mo or W may increase the amount of adsorbed hydrogen disulphide or mercaptans [2]. Adsorbents may also consist of active coals prepared with polyalkeneglycol and with a base or inorganic acid. The glycol used may be polyethylene glycol of molecular mass 1000–6000, or polypropylene glycol of molecular mass 1000–3000. As base, one may use the hydroxides of sodium, potassium, magnesium, zinc, nickel or cobalt. As acid, one may use phosphoric, metaphosphoric, sulphuric or nitric acids [3]. Active coal treated with hydrophobic agents such as polytetrafluoroethylene, polyethylene, polypropylene, polystyrene, silicon oil, dimethyldichlorosilane or paraffin is resistant to humidity but it is simultaneously an adsorbent with a great adsorbing power [4]. Active coals containing such oxidizing agents as NaOCl, $NaClO_2$, $KMnO_4$, H_2O_2, Na_2O_2 or impregnated with copper sulphide (15–20 wt.-% w.r.t. coal) are good adsorbents [5].

The patent literature on the adsorption of SO_2 recommends the use of activated carbonaceous adsorbents. These are typical carbonaceous adsorbents such as active coal, semi-coke and coke on which the active phase is deposited, its aim being the increase in the efficiency of the adsorption yield. Thus active coal treated with sulphuric acid [6], iodine, bromide, ammonium chloride [7], nickel and potassium, compounds [8], iodine [9], ammonium sulphate [10], sodium hydroxide [11], a solution containing vanadium and a surface active agent [12], coke impregnated with carbonate of alkali metal or of rare-earth elements [13], brown coal mixed with aluminium oxide gel used as a binder and with ash coming from heavy oil combustion [14] are better adsorbents than the carbonaceous material alone. Brown coals mixed with aluminium oxide ash in sol form as a binder and fly ash (coming from heavy oil combustion) are better adsorbents than brown coal itself. Brown coal (10–20 wt.-% moisture) or hard coal mixed with silica, aluminium oxide or silica–alumina as binders, formed into pellets or tablets and carbonized at a temperature of 870–1270 K displays a high adsorption power which makes it possible to decrease the SO_2 content in flue gas from e.g. 2000 ppm to 50 ppm [15]. When a reactive compound of lime (CaO, $CaCO_3$) is added to active coal, an increase in the adsorption yield is obtained [16]. Several processes can be observed on this adsorbent: SO_2

adsorption on active coal, chemical reaction of SO_2 with the reactive limestone compound and a partial regeneration of the coal.

In this case the active phase reacts with the adsorbent, whereas in other cases the active phase is a factor increasing the yield of the adsorption process.

4.1.2. Inorganic adsorbents

The adsorbents that are most commonly used in industrial practice are aluminium oxides and silicic acid gels [1,17].

Alumina (aluminium oxide) is obtained by calcinating aluminium hydroxides: either the trihydrates (gibbsite, bayerite and nordatrendite) or the dispersed monohydrates (crystalline boehmite and pseudoboehmite). The thermal processing of aluminium hydroxides leads to the production of different types of aluminum oxides. The following are the groups of alumina oxides:

- low temperature (up to 870 K) γ, ρ, ζ and η-Al_2O_3
- high temperature (up to 1270 K) δ, θ-Al_2O_3
- obtained above 1270 K α-Al_2O_3.

The industrial types of alumina usually contain γ-Al_2O_3, and less frequently ζ-Al_2O_3.

In practical applications throughout the world there is a tendency to switch over to the spherical granulation of alumina with different diameters of granules (1–8 mm). Their specific surface area is from 150 to 400 m^2/g and the prevalent pore radius is from 6 to 10 nm. Another very important adsorbent is silicid acid gel which is characterized by well-developed porosity. It is hydrated amorphous silica ($SiO_2 \cdot nH_2O$) capable of being transformed according to the polycondensation mechanism.

The structural characteristics of silica gels usually undergo change within the following limits: surface area 300–750 m^2/g (specific surface), medium radius of pores 1–7 nm, bulk density 0.4–0.9 g/cm^3.

The industrial types of silica gels are divided into:

- broad porous (medium radius of pores, $r = 4.5$–10 nm)
- medium porous ($r = 1.8$–3.5 nm)
- narrow porous ($r = 0.8$–2 nm).

One of the more important and commonly used types of adsorbents comprises the oxides, hydroxyoxides and/or salts of di- or trivalent iron. These adsorb sulphur compounds from gases at both low and high temperatures [18–23]. Mixtures of pyrite and bog iron ore [24], iron oxides in the form of a sponge, containing liquid amine [25] are very good adsorbents of H_2S.

Another inorganic adsorbent which is very often used in industry is titanium oxide. This may react independently as an adsorbent or in a mixture, e.g. with alumina [26,27]. Other titanium compounds such as barium titanate [28], as well as a by-product formed during the production of titanium white, are also used as adsorbents [29].

Natural minerals containing Ca, Mg, Ba, Mn, Fe and Zn are known to be good adsorbents. These metals or their oxides usually have a strong affinity for sulphur. In order to increase the yield of the desulphurization process a variety of activating agents are used, as in the case of carbonaceous adsorbents.

In addition to typical inorganic adsorbents that have been patented there are numerous other adsorbents which may be used in SO_2 or H_2S adsorption. The Japanese patent [30] recommends using a complex of magnesium and alumina, as well as a peroxide of an alkaline earth metal. This substance is very suitable for the selective adsorption of SO_2 and NO_x from flue gases, engine gases, power stations and various industrial plants emitting gases containing sulphur and nitrogen compounds. Another adsorbent is Al_2O_3 granulas covered with a $MnO_x \cdot Al_2O_3$ complex, where the valence of Mn is 2.5+ to 3.5+ and x varies from 1.25 to 1.75 [31]. Another kind of adsorbent is $Mg(OH)_2$ calcined at a temperature of 720–1070 K to a final moisture content of 3–20%. The adsorbent successfully substitutes for active coal. It is suitable for acid gases containing not only sulphur compounds but also NO_x, Cl_2, HCl, HBr, Br_2, HBr, F_2, HF and HCN [32]. Zinc oxide mixed with magnesium oxide and with polyvinyl alcohol or hydroxypropylocellulose (as binders) in the form of granules calcined at a temperature of 650 K is characterized by a high capacity for the adsorption of sulphur compounds (32–34%) [33]. Another adsorbent for adsorbing SO_2, hydrocarbons and organic solvents consists of alumina and slag, obtained from iron refineries and reduction processes by leaching in the electric furnace [34]. The removal of acid pollution from tail gases may take place on cation exchangers containing a metal such as Cu, Ni, Co. A cation exchanger is treated with ammonia solution. The salts formed during the sorption of acid gases are removed by washing the cation exchangers with water [35]. An interesting adsorbent for purifying air and industrial gases is granules obtained by treating magnesium chloride with an ammonia solution. The hydroxide of magnesium obtained is dried and granulated in a special vacuum chamber. The adsorbent obtained in this way displays very high adsorption properties [36].

SO_x is removed from gases by adsorption on an adsorbent containing Na and V in the form of salts or oxides deposited on a porous support containing at least 80% Al_2O_3. The adsorbent may work at adsorption temperatures of 350 to 620 K [37]. The removal of sulphur oxides from flue gases is made possible by an adsorbent containing copper, copper oxide or their mixture dispersed on a support coated with 0.01–1 wt.% Pt or their oxides and 0.01–1 wt.% germanium or rhenium. The flue gases are contacted with the adsorbent at a temperature of 420–720 K. After processing the adsorbent is regenerated with reductive gases [38]. A flue gas containing SO_x is brought into contact in the presence of oxygen with a solid substance like e.g. an alkaline earth metal oxide in the form of particles with a size of 40 microns or smaller, the substance being capable of bonding with gaseous SO_x in an oxidizing atmosphere. This induces the transfer of sulphur oxides from the gas to the solid substance [39]. With the simultaneous removal of SO_2, NO_x and volatile dusts from the flue gas, serpentine and olivine calcined at a temperature of 920 K were used as adsorbents (residues from asbestos production) while the degree of the gas purification from SO_2 was 89%, NO_x 88.9%, and volatile dusts 76.3% [40]. An adsorbent containing lanthanum deposited on aluminium oxide has been patented by standard Oil Company [41]. Sulphur dioxide may be adsorbed on activated volcanic tuff, which is rich in clinoptyllolite [42]. Other unconventional adsorbents are granulated converter and blast-furnace slags [43], metallic-aluminium spinel MAl_2O_4 (where M = Cr, Fe, Co, Ni, Cu, Cd, Hg, Zn) [44] as well as residues from the production of potassium permanganate containing manganese [45].

Table 5
Adsorbing capacity of adsorbent obtained from fly ash

Adsorption temperature (K)	Adsorbing capacity mg SO_2/g adsorbent	Purification degree (%)
298	105	96
323	90	82
373	70	64
473	28	26

4.1.3. Adsorbents and reagents for removing hydrogen sulphide from hot gases

Adsorbents (or reagents) used for H_2S adsorption at high temperatures may be divided into two groups: one containing alkaline earth metals and those containing transition elements. It often happens that adsorbents (or reagents) contain both alkaline earth metals and transition elements, e.g. fly-ash and 'red mud', both of which are industrial waste materials [46].

The basic reactions which play an important role in the process of H_2S removal at high temperature are the following:

$$MeO + H_2S \rightarrow MeS + H_2O \qquad (4.1)$$

$$MeO + H_2(+CO) \rightarrow Me + H_2O(+CO_2) \qquad (4.2)$$

$$Me + H_2S \rightarrow MeS + H_2. \qquad (4.3)$$

The majority of adsorbents (or reagents) occur in the form of oxides, which is why it is mainly reaction (4.1) that occurs.

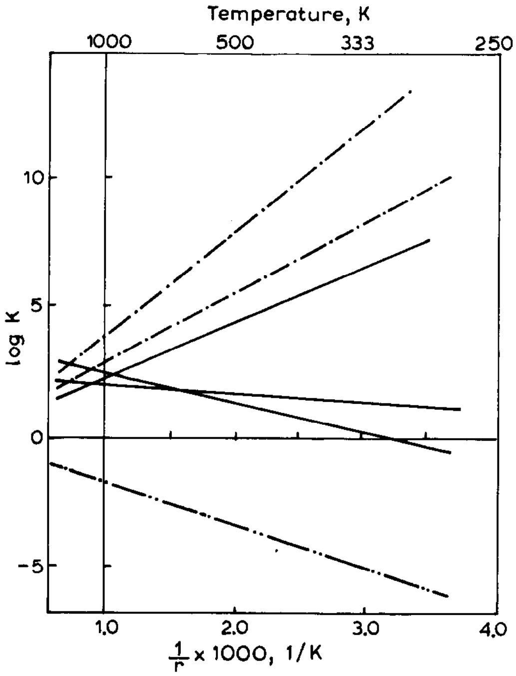

Fig. 3. Dependence of log *K* value on temperature for metal oxide and H_2S reaction.

The presence of H_2 and CO in hot gases implies that reaction (4.2) may also take place and affect the rate of H_2S removal. The effect of temperature on the value of log *K* for reaction (4.1) is presented in Fig. 3, and the log *K* value for 1000 K is given in Table 5.

The positive value of log *K* implies that it is possible and easy to combine metal oxides with H_2S, with the exception of MgO. It follows from Table 6 that Mo oxide should display the best properties, followed by next Ni, Zn, Ca, Co and Mn oxides. In this respect, ferric oxides occupy a decidedly inferior position. However, reaction (4.2) is also important for the process, in which the oxide reaction takes place. It follows from Table 7 that Ca, Mg and Ba oxides as well as Zn and Mn oxides are greatly resistant to the reduction reaction by means of H_2.

Of great importance in the adsorption process (or reaction) are also the products formed as a result of reactions such as H_2O and CO_2, which cause a reduction in the efficiency of H_2S removal. The presence of CO_2 may lead to the formation of carbonates, particularly at high temperatures.

Table 6
Log *K* value for metal oxide or metal and hydrogen sulphide reaction at a temperature of 1000 K [43]

Reactions	log *K*
$CaO + H_2S \rightarrow CaS + H_2$	3.36
$MgO + H_2S \rightarrow MgS + H_2O$	−1.79
$FeO + H_2S \rightarrow FeS + H_2S$	2.29
$FeO + 2H_2S \rightarrow FeS + H_2O + H$	0.58
$1/2Fe_2O_3 + 3/2H_2S \rightarrow FeS + 3/2H_2O + 1/4S$	2.40
$1/2Fe_2O_3 + 2HS \rightarrow FeS + 3/2H_2O + 1/2H$	1.77
$1/3Fe_2O_3 + 4/3H_2S \rightarrow FeS + 4/3H_2O + 1/6S$	1.99
$1/3Fe_2O_3 + 2H_2S \rightarrow FeS + 4/3H_2O + 2/3H$	0.99
$MnO_2 + H_2S \rightarrow MnS + H_2O$	2.80
$ZnO + H_2S \rightarrow ZnS + H_2O$	3.88
$MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O$	5.2[a]
$MoO_3 + 3H_2S \rightarrow MoS_2 + 3HO + 1/2S$	8.7[a]
$CoO + H_2S \rightarrow 1/9Co_9S_8 + H_2O + 1/18S_2$	3.10
$NiO + H_2S \rightarrow NiS + H_2O$	4.1[a]
$NiO + H_2S \rightarrow 1/3Ni_3S_2 + H_2O + 1/6S_2$	2.76
$Ca + H_2S \rightarrow CaS + H_2$	21.08
$Mg + H_2S \rightarrow MgS + H_2$	13.92
$Fe + H_2S \rightarrow FeS + H_2$	3.02
$Fe + 2H_2S \rightarrow FeS_2 + 2H$	1.31
$Mn + H_2S \rightarrow MnS + H_2$	9.07
$Zn + H_2S \rightarrow ZnS + H_2$	6.64
$Mo + 2H_2S \rightarrow MoS_2 + 2H_2$	6.9[a]
$Co + 8/9H_2S \rightarrow 1/9Co_9S_8 + 4/9H$	−1.58
$Ni + H_2S \rightarrow NiS + H_2$	2.4[a]
$Ni + 2/3H_2S \rightarrow 1/3Ni_3S_2 + 2/3H_2$	1.22

[a] Extrapolation values.

Table 7
Log *K* values for metal oxide with hydrogen reaction at a temperature of 1000 K

Reactions	log *K*
$CaO + H_2 \rightarrow Ca + H_2O$	−17.73
$MgO + H_2 \rightarrow Mg + H_2O$	−15.71
$BaO + H_2 \rightarrow Ba + H_2O$	−10.4
$FeO + H_2 \rightarrow Fe + H_2O$	−0.73
$1/2Fe_2O_3 + 3/2H_2 \rightarrow Fe + 3/2H_2O$	0.46
$1/3Fe_3O_4 + 4/Fe + 4/3H_2O$	−0.31
$MnO + H_2 \rightarrow Mn + H_2O$	−6.21
$MnO_2 + 2H_2 \rightarrow Mn + 2H_2O$	2.8[a]
$1/3Mn_3O_4 + 4/3H_2 \rightarrow Mn + 4/3H_2O$	−4.85
$1/2Mn_2O_3 + 3/2H_2 \rightarrow Mn + 3/2H_2O$	−3.12
$ZnO + H_2 \rightarrow Zn + H_2O$	−2.76
$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O$	−1.16
$MoO_3 + 3H_2 \rightarrow Mo + 3H_2O$	4.50
$CoO + H_2 \rightarrow Co + H_2O$	1.53
$NiO + H_2 \rightarrow Ni + H_2O$	2.26

[a] Extrapolation values.

In the group of adsorbents (or reagents) containing alkaline earth metals the most popular reagent is CaO obtained by calcination of calcium carbonate, dolomite and others compounds.

The reaction between CaO and H_2S takes place by way of exchange of an oxygen ion for a sulphur ion. The reaction rate depends to a great extent on the properties of the adsorbent or reagent while the properties of the reagent depend on the method of its formation. The increase in the rate of H_2S removal may be achieved by increasing the temperature and reducing the size of CaO grain. BaO is also used for H_2S removal under appropriate conditions. The best results have been obtained in the temperature range of 1170–1470 K.

When the desulphurized gas contains CO_2, there is a tendency towards the formation of $BaCO_3$. In the range of temperatures given above a decomposition of carbonate takes place and thus the yield of the H_2S removal process increases. H_2S contained in hot gases is treated by calcium carbonate obtained from natural limestone and dolomites. The reaction rate of H_2S with $CaCO_3$ increases in the range of 840–1000 K and then decreases. This may be connected with the changes in the properties of reagent which limit the diffusion process. In the presence of elemental sulphur, $CaCO_3$ may be transformed to CaS. The reaction of H_2S with dolomite is dependent on its calcination. The appropriate calcination of dolomite causes the reaction rate to be greatly increased. Calcium silicates are also used for H_2S removal. Apart from calcium silicate these materials contain Al_2O_3, Fe_2O_3, MgO and negligible amounts of other oxides. The reaction on silicates takes place is as follows:

$$(CaO)_3 \cdot SiO_2 + 3H_2S \rightarrow (CaS)_3SiO_2 + 3H_2O. \quad (4.4)$$

The reaction of H_2S with CaO or $CaCO_3$ may be written as follows:

$$CaCO_3 \underset{4.5a}{\overset{4.5b}{\rightleftarrows}} CaO + CO_2 \quad (4.5)$$

$$CaO + H_2S \rightarrow CaS + H_2O. \quad (4.6)$$

When the above mixture is dominated by CaO the reaction leads to the formation of CaS and H_2O according to reactions of the type (4.6). As a rule the reaction takes place on the external walls of the reagent. This causes a layer of sulphide to be formed outside the molecules. If this layer is permeable, H_2S diffuses into the inside of the molecule of the reagent and water diffuses towards the external layer.

The reduction of reagent action with time depends on these processes. $CaCO_3$ decomposes at a temperature of about 1100 K according to reaction (4.5), and the CaO formed reacts according to reaction (4.6). The CO_2 produced diffuses outside the adsorbent. When the layer of CaS formed outside the adsorbent is sufficiently compact, the CO_2 diffusion discontinues and so does the reaction. An increase in temperature causes the layer to be destroyed and so the reaction may continue.

4.1.4. Adsorbents (or reagents) containing transition elements

In this group the greatest attention is given to adsorbents containing Fe, Zn and Mn. These metals or their oxides display the strongest affinity for sulphur compound (Table 6), but oxides are less resistant to the reaction by means of H_2 or CO as compared with alkaline earth oxides.

The removal of H_2S by means of Fe_2O_3 or Fe_3O_4 may be described as follows:

$$Fe_3O_4 + H_2S \rightarrow FeS + Fe_2O_3 + H_2O \quad (4.7)$$

$$2Fe_2O_3 + H_2S + 2H_2 \rightarrow FeS + Fe_3O_4 + 2H_2O \quad (4.8)$$

$$2Fe_2O_3 + H_2S + 2CO \rightarrow FeS + Fe_3O_4 + 2CO_2. \quad (4.9)$$

The above cycle may be repeated until all the iron oxides are consumed. The presence of steam and CO_2 in hot gases affects the increase in the efficiency of gas purification. The following reaction may also take place:

$$FeS + H_2S \rightarrow FeS_2 + H_2. \quad (4.10)$$

Table 8
Chemical composition of manganese ores and 'red mud' [43]

Component	Ocean manganese ore	Lake manganese ore	'Red mud'
SiO_2	15.0	35.2	12.0
Al_2O_3	4.8	3.0	22.6
Fe_2O_3	19.5	50.5	29.7
Mn_3O_4	31.8	3.3	–
CaO	25.9	1.2	4.5

The decomposition of iron oxides may also be accompanied by the formation of elemental sulphur and in this case FeS acts as a catalyst.

'Red mud', which comes from the production of aluminium, appears to be a better for H_2S removal than Fe_2O_3 itself (Table 8).

Zinc oxide is used for H_2S removal from hot gases. The reaction with zinc oxide is less complex than that with iron oxide as oxygen ion is replaced by sulphide ion. In order to increase the contact surface of zinc oxide, it is coated onto the well-developed surface of a typical catalyst carrier, e.g. Al_2O_3. Zinc oxide is characterized by a low regeneration capacity. This can be increased by the addition of Fe_2O_3. The zinc ferrite produced, i.e. $ZnFe_2O_4$, does not display similar properties to ZnO, which volatilizes at high temperature.

Manganese oxides may occur in several oxidation states. In a reducing atmosphere such as H_2S the following transitions may occur:

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO.$$

According to Westmoreland, MnO is the most active oxide in the reaction with H_2S,

$$MnO + H_2S \rightarrow MnS + H_2O. \qquad (4.11)$$

This reaction occurs violently at a temperature of 1270 K. Good adsorptive properties are also displayed by natural adsorbents such as manganese ores extracted from oceans or lakes. The chemical compositions of these adsorbents are given in Table 8. Manganese ore is a mixture of several metal oxides, and it sometimes contains appreciable amounts of $CaCO_3$, Al_2O_3 and SiO_2. The presence of aluminium and silicon oxides causes these ores to have a well-developed internal surface (100–300 m^2/g). The regeneration of these adsorbents is performed by means of air at a temperature of about 1600 K. The oxidizing agent may also be O_2, CO_2 or H_2O.

For the removal of H_2S from hot gases use is also made of V_2O_5, WO_3, CuO and MoO_3. In order to be active in H_2S removal, all these oxides should have a well-developed internal surface which facilitates good contact between the reactants. In the course of the regeneration process all the adsorbents presented above suffer a reduction in their internal surface after each regeneration cycle. This lowers their activity in the H_2S adsorption process.

4.1.5. Adsorbents or reagents for removing SO_2 from hot gases

The above mentioned inorganic adsorbents used for H_2S removal are also put to use for SO_2 adsorption from flue gases. The most widely used for SO_2 removal from hot gases are quicklime (CaO), hydrated lime ($Ca(OH)_2$), fly-ash, various kinds of limestone such as dolomite, iron ores, magnesium hydroxide appropriately prepared [36], and ferric sulphate [47]. Sulphur oxides may be removed from gas at a temperature of up to 1200 K on an yttrium oxide combined with one of the oxides of the following elements: Al, Mg, Zn, Ti or Ca [48].

4.1.6. Zeolite adsorbents

The zeolites represent a separate group of adsorbents. Both synthetic and natural zeolites are used to adsorb both SO_2 and H_2S. Zeolites are very good adsorbents and are characterized by a strong affinity for sulphur.

Crystalline zeolites, commonly known as zeolite molecular sieves, possess strong adsorptive properties. A molecular sieve, appropriately selected to correspond to the composition of a liquid or gas mixture, favours the adsorption of one component of the mixture. The selectivity of the molecular zeolite sieve depends on the following factors: size of molecules of the components of a liquid or gas mixture as compared with the effective diameter of the regular pores of zeolite, and the polar character of the molecules being adsorbed. A great amount of research into the use of zeolites in H_2S and SO_2 adsorption has been performed by Dudzik and Ziółek [49–54].

4.1.7. *Mixed adsorbents*

The compositions of these adsorbents represent mixtures, frequently with equal weight of the components of a typical carbonaceous adsorbent as well as of another adsorbent or inorganic compound. Examples of mixed adsorbents are given below. A porous adsorbent for the desulphurizing of gases is produced by mixing zinc oxide with graphite or aluminium oxide with the use of a pore-forming agent, which may be azodicarbamide [55]. Sodium carbonate mixed with a coal material, e.g. lignite, and subjected to heat above 1150 K in a reducing medium is used for binding SO_2 coming from flue gases [56]. For dry gases use is made of a macroporous anion exchanger subjected to reaction with ethylenediamine, propylenediamine or hexamelthylenediamine [57]. The adsorbent of sulphur oxides is produced by mixing a hydrophilic binding material, such as a gel of aluminium oxide, silica gel or aluminosilicate with powdered iron ore and then with brown coal [58].

4.2. *Catalysts for converting sulphur compounds from flue gases*

In the process of extracting sulphur from gases containing sulphur compounds, so-called multiphase contact catalysis takes place. The mechanism of the contact with the catalyst is complex, and different for different catalysts acting in the same reaction [59,60]. At present there is no theoretical basis which would make it possible, without carrying out experimental studies, to select the appropriate catalyst for the reaction being studied. The catalyst is thus selected as a result of testing and elimination. The mechanism of its action can sometimes be established for particular cases, but concepts and ideas cannot be generalized. In contact processes an important role is performed by adsorption and diffusion. It is necessary for the particles of substrates to flow to reach the surface of the contact as a result of diffusion, which also carries away particles from the reaction surface. The process on the contact surface starts with the adsorption of the substrate particle. It is assumed that only those particles of substrates are adsorbed which have active centres of a dimension which fits onto the surface. It is desirable that the contact surface should be as extensive as possible. The process of obtaining sulphur [61] from flue gases containing sulphur may take place on:

- catalysts with an aluminium oxide carrier, as well as aluminium oxide usually activated and promoted by means of metals of Group 6, 8, 9 and 10;
- active carbons, cokes, and semi-cokes, as well as cokes and semi-cokes activated and promoted mostly with metals of Group 6, 8, 9 and 10;
- synthetic and natural zeolites (zeolites may be activated with various metals);
- titanium and zirconium oxides.

The type and number of the products obtained depend on the properties of the catalyst, its activity and selectivity. The catalysts used in industry for the conversion of ($H_2S + SO_2$) to sulphur are, first and foremost, aluminium oxides, bauxite, and activated aluminium oxides, as well as aluminium oxides modified with the compounds of metals of Group 6, 8, 9 and 10. The most frequently used elements are: Co, Mo, Ni, Cr, W, V [62–65].

Obtaining active aluminium oxides with a developed internal surface is the subject of a great number of patents, the most essential particulars of which are as a rule not revealed.

Effective catalysts of the Claus reaction are obtained by saturating aluminium oxide with an aqueous solution of yttrium or lanthanum compounds with the addition of 1 to 25% Ti, Pb, Mn, Mo, Ni, Co, Fe compounds or of uranium [66]. $Ni–Mo/Al_2O_3$ or $Cr–Mo/Al_2O_3$ catalysts were used as catalysts for desulphurizing flue gases from a Claus system [67]. The catalyst used for the Claus process can also be obtained by treating a mixture of bauxite and boehmite with an acidic water solution and drying [68].

Catalysts based on titanium and zirconium oxides represent the most effective and selective catalysts in the oxidizing of hydrogen sulphide to obtain elemental sulphur. Despite the fact that the specific surface area of titanium and zirconium oxides is not large, the catalysts display a high activity.

A catalyst used for purifying waste gases containing sulphur compounds may consist of platinum metals, i.e. platinum, ruthenium or rhodium, on a TiO_2–Al_2O_3 carrier [69]. Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Mo or W metals deposited on active carbon represent active catalysts for the conversion of sulphur oxides. These catalysts operate at a temperature of 340 K. Another catalyst is a mixture of a powdered Mg compound or compounds of oxide carbonate or hydroxide type with a powdered aluminium powdered compound or compounds of oxide or hydroxide type. In order to increase the catalytic properties, ceric oxide is added to this mixture [70].

Krupp–Koppers GMBH uses Mo, W, Co and/or Ni sulphides for SO_2 and NO_x removal. A mixture of sulphides, e.g. of Mo and Co deposited on an Al_2O_3 carrier, is used for removing both H_2S and SO_2. This process takes place at a temperature of 340–400 K under a pressure of 1–100 MPa [71]. For purifying gas Mitsubishi Heavy Industries proposes tungsten, titanium or aluminium as catalysts [72], while Union Oil Co. of California proposes a catalyst containing vanadium and/or bismuth as well as their compounds [73].

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5. Gas desulphurization processes

5.1. General

The methods of gas desulphurization may be classified according to: (1) the degree of sulphur oxidation in the compounds produced, and (2) the state of concentration in which reactions take place. Depending on demand, desulphurization processes are carried out in order to obtain such commercial products as sulphur, sulphuric acid, ammonium sulphate, copper sulphate or other sulphur compounds.

In view of the concentration state the desulphurization methods may be divided into dry, semi-dry and wet methods.

'Dry' gas purification consists in adding a dry adsorbing agent while the adsorbent used does not change its concentration state. The processes of 'semi-dry' purification depend on the adsorbent (or reagent) being added in the form of a solution or liquid; the chemical reaction takes place in the liquid phase while the temperature is selected in such a way that the adsorbent (or reagent) consumed can be removed in its solid state from the flowing tail gases.

In the 'wet' processes the reagent is added in the form of a liquid in which the impurities react with the solution. This results in wastes which are subjected to further treatment.

Each of these methods has its advantages and disadvantages. Current methods tend to make use of dry or semi-dry methods. Preference is given to methods whose final product is pure sulphur.

Presented below are dry desulphurization methods based on the adsorption and catalytic processes.

A comparison of capital and operating costs as well as of the degree of the purification of tail gases by particular methods is presented in Table 9 [1]. The gases subjected to desulphurization processes may be divided, according to their composition and suitability, into two basic groups:

- gases containing as their basic components hydrocarbons and other non-hydrocarbon combustible compounds, e.g. coke-oven gas, synthesis gas etc.;
- tail gases, post-processed gases containing hydrogen sulphide, sulphur dioxide, mercaptans, carbon disulphide and other sulphur compounds diluted with nitrogen and carbon dioxide.

The methods for removing sulphur compounds from these basic groups of gases are completely different.

When the first group of gases is desulphurized, it is necessary to use methods which do not disturb

Table 9
Comparison of dry, semi-dry and wet purification processes of tail gases [1]

Emitted component after process (mg/Nm^3)	Raw gas	Process		
		Dry	Semi-dry	Wet
SO_2	800	400–600	200–300	100 (two stages)
HCl	1500	50–100	30–60	10–30
HF	20	3–5	0.5–3	0.5–2
Σ total residue (kg/t waste)		60–70	55–60	45–50
Capital costs (DM/m^3·h gas)		20–40	30–60	80–100
Operating costs (DM/t)		17–24	20–23	22–30

their basic gaseous components. These should be sensitive, selective methods which will make it possible to obtain a product completely freed of sulphur compounds.

The second group of gases are technological wastes which should be subjected to treatment in such a way as to obtain a commercial product or an inactive one that does not pollute the environment. The problem of desulphurization is of prime importance not only on account of the protection of the environment but also in respect of the rational recovery of sulphur as a costly raw material for industrial use.

5.2. *Purification of gases containing hydrogen sulphide*

5.2.1. *Oxidation of hydrogen sulphide to obtain sulphur*

5.2.1.1. Desulphurization by iron compounds. In the production of coke-oven gas, desulphurization by means of natural iron oxides has been carried out since 1860. Since then, according to Howitz's proposal, increasingly frequent use has been made of bog iron ore for gas purification. In Europe this method is used practically exclusively for desulphurizing coke-oven gas. Its low capital costs, industrial simplicity, as well as a high efficiency of desulphurization down to only traces of hydrogen sulphide in the final product, mean that this method is preferred. Iron oxides perform their desulphurizing function only when they occur in their hydrated form as $Fe_2O_3 \cdot H_2O$ or as ferric hydroxide $Fe(OH)_3$ [2]. In principle, without taking the occurrence of intermediate compounds into account, the reaction of hydrogen sulphide with ferric oxide runs according to the equations:

$$2Fe(OH)_3 + 3H_2S \rightarrow 2FeS + S + 6H_2O \quad (5.1)$$

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O. \quad (5.2)$$

The first reaction takes place when the purification medium is alkaline, whereas the second reaction occurs when the medium is inert.

The transition of iron from the oxide or hydroxide forms to the sulphur form causes the binding power of the purifying material to decrease and finally to become completely exhausted. The purifying material is regenerated by the action of oxygen according to the following equations:

$$2FeS + 3H_2O + 3/2O_2 \rightarrow 2Fe(OH)_3 + 3S \quad (5.3)$$

$$Fe_2S_3 + 3H_2O + 3/2O_2 \rightarrow 2Fe(OH)_3 + 3S \quad (5.4)$$

$$Fe_2S_3 + 3/2O_2 \rightarrow Fe_2O_3 + 3S. \quad (5.5)$$

The bonding reactions and the regeneration are represented in the total equation:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \ -443.1 \text{ kJ} \quad (5.6)$$

The sulphur bonding and the regeneration of sulphide are exothermic processes. For the purifying material to be regenerated a certain amount of water is needed in order to generate ferric hydroxide or hydrated ferric oxide [2]. Moreover, the required concentration of oxygen (or air) must be outside the explosive limit of the gas–oxygen mixture. This is of special importance when synthesis gas is being desulphurized since $CO + H_2$ mixtures display the widest explosive range of all gases. The explosive limits for CO are 16.6–74.8%, and for hydrogen 9.5–66.3%, which implies that in the presence of 5–7% oxygen in the gas–air mixture the explosive limit is exceeded. Thus the required amount of oxygen should not be higher than its theoretical demand, according to the regeneration equations, in an attempt to avoid the action of oxygen upon the catalysts used for the synthesis. The amount of oxygen needed for oxidizing 1 vol.-% of H_2S (16 g/m^3 of gas) is 0.5% of O_2 or 2.5% of air. Despite careful regeneration of the purifying material, and a sufficient amount of water, the adsorbing capacity of the mass gradually decreases.

With the use of well-constructed purifiers, the application of high activity material, and a correct and well-operated process, the operation period in industry comes to an end when 45–60% of elemental sulphur in dry material is achieved. In addition to the increase in the sulphur content some other reactions cause the activity to decrease. Sulphide and ferric oxide are capable of binding HCN contained in gas to obtain Berlin blue or Berlin white according to the equations.

$$3FeS + 6HCN + 3O_2 \rightarrow Fe_2(Fe(CN)_6) + 3H_2O + 3S \quad (5.7)$$

$$3Fe(OOH)_2 + 6HCN \rightarrow Fe_2(Fe(CN)_6) + 6H_2O \quad (5.8)$$

$$Fe_2(Fe(CN)_6) + 4Fe(OH)_3 + 12HCN \rightarrow Fe_4(Fe(CN)_6)_3 + 12H_2O \quad (5.9)$$

$$4Fe(OH)_3 + 3Fe(OH)_2 + 18HCN \rightarrow Fe_4(Fe(CN)_6)_3 + 18H_2O. \quad (5.10)$$

The reduction of $Fe(OH)_3$ is caused by hydrogen sulphide

$$2Fe(OH)_3 + 3H_2S \rightarrow 2Fe(OH)_2 + S + 2H_2O. \quad (5.11)$$

Part of hydrogen cyanide changes into rhodanates, primarily in the presence of ammonia and carbon disulphide:

$$HCN + H_2S + O + NH_3 \rightarrow NH_4CNS + H_2O \quad (5.12)$$

$$CS_2 + NH_3 + FeO \rightarrow HCNS + FeS + H_2O \quad (5.13)$$

$$2HCNS + FeO \rightarrow Fe(CNS)_2 + H_2O. \quad (5.14)$$

The concentration of rhodanates, water-soluble hydrogen cyanide compounds, etc., may amount to 1–4%. Moreover, ferric sulphate binds NO in the form of Roussin's salt $Me^IFe_4(NO)_7S_3$. In the presence of oxygen these salts are unstable and disintegrate to form NO_2. Due to side reactions and the local overheating of the material during the regeneration process the formation of sulphites and ferric sulphates can be observed and their concentration in the dry material may rise to 3 per cent.

The binding rate of hydrogen sulphide is dependent on temperature and shows a maximum at a temperature of 308–313 K. Exceeding of this temperature is followed by a slow drop in the activity of the material. The course of the regeneration process is most advantageous at a temperature of 313–323 K. When this temperature is exceeded a large amount of SO_2 and SO_3 is formed. In practice the process of binding H_2S and regenerating the material is carried out at 303–308 K, in both continuous and periodic processes. Hydrogen sulphide binding is hindered when the purifying material is used in an acid reaction. The reaction medium should be at least neutral, and preferably alkaline. In the course of the operation the neutral reaction medium may turn into an acid one. In gasworks the material reaction is adjusted by maintaining the ammonia concentration in the input gas within 2–8 m^3 NH_3 per 100 m^3 of gas.

Sulphur can be produced from gases containing H_2S by oxidizing them with air at a temperature of 500–570 K over ferro-oxide as a catalyst at a volume rate that does not exceed 15 000 m^3/h and with a 1:6 oxygen/H_2S ratio. The conversion of hydrogen sulphide is 97–100% with 95% selectivity. The catalyst should have a 1–2 m^2/g specific surface area, 44–45% porosity, a 250–290 nm pore diameter and 1.0–2.0 mm grain size. This procedure is suitable for producing sulphur from hydrogen sulphide raw materials or for purifying tail gases [3].

H_2S may be removed from a gas stream by mixing it with a substance containing $FeCl_3$. The mixture is passed through a bed of inert granular material by means of which H_2S becomes oxidized while elemental sulphur becomes deposited on the granular material.

The $FeCl_3$ catalyst may also contain ions of one or more metals of V, Mn, Cu, Mg and Ti. The appropriate material making up the bed may be haematite granules with a bed temperature of 295–388 K. The deposited sulphur is removed from the bed through periodic abrasion [4].

Desulphurization of synthesis gas, free of NH_3 and containing 1–20 g of H_2S per Nm^3 is carried out in the following way: 0.05–1.5 vol.-% of oxygen and 0.01–0.1 ton of steam per 1000 Nm^3 of purified gas are added. The gas, with additions, is brought into contact with an adsorbent containing 40–60 wt.-% of roasted pyrite and 40–60 wt.-% of bog iron ore. The contact takes place in adsorption plate-type columns at a temperature of 288–313 K with a 1000–5000 mm pressure of H_2O [5].

Sumitomo Heavy Industries [6] proposes a procedure consisting in introducing the gas containing H_2S and oxygen into the reactor with a mobile the catalyst bed (iron oxide or active carbon) at a temperature not higher than 370 K. On the catalyst in the reactor the oxidation of H_2S takes place to obtain elemental sulphur which deposits on the catalyst. The catalyst with the deposited sulphur passes to the regeneration column, which has a mobile bed where it is brought into contact with an inert gas at 520–720 K in order that the sulphur may be removed and the catalyst regenerated. After being regenerated the catalyst is passed back to the reactor.

5.2.1.2. Desulphurization by post-etched deposits. When metal plates or iron objects are etched with sulphuric acid a large amount of solution is obtained. Post-etched metallized solutions, and particularly the so-called post-etched deposits have found wide applications as purifying material. The iron content in post-etched deposits is about 30–37% [7,8]. It has been found that the period during which hydrogen sulphide can be adsorbed by post-etched deposits is longer than when bog iron ore is used. At the same time the adsorption of hydrogen sulphide and its regeneration are more uniform than when use is made of bog iron ore [7]. Post-etched deposits can be saturated by means of sulphur to a degree far exceeding 45%. Still higher sulphur contents (51–55%) in the purifying material have been obtained by using physical mixtures of bog iron ore (60–40%) with post-etched deposits (40–60%) [8].

5.2.1.3. Desulphurization by post-aniline sludges. Post-aniline sludges are waste materials containing active iron compounds. They are obtained after the organic nitro-compounds have been transformed into amines according to Becharup's method. The reaction according to which active iron hydroxide is formed with the use of this method is as follows:

$$RNO_2 + 3Fe + 6HCl \rightarrow RNH_2 + 3FeCl_2 + H_2O \quad (5.15)$$

$$RNO_2 + 2FeCl_2 + 2Fe + 4H_2O \rightarrow RNH_2 + 2FeCl_2 + 2Fe(OH)_3 \quad (5.16)$$

$$2FeCl_2 + 4H_2O \rightarrow 2Fe(OH)_2 + 4HCl. \quad (5.17)$$

The amount of total iron in the dry mass of post-aniline sludge ranges from 60–63%, whereas that of active iron [2] is 43–45%.

5.2.1.4. Desulphurization by other compounds (with 'Laut' or 'Lux' masses). Owing to the development of the production of aluminium the alkaline residues have been used after the treatment of bauxite as a mass for binding H_2S since about 1900. The composition of these residues is as follows: about 50% Fe_2O_3, 2–7% Na_2CO_3, 5–15% CaO and MgO as well as up to 100% SiO_2 and Al_2O_3 as a complement.

Such masses ('Lauts' and 'Luxes', as they are called) display a better purifying efficiency than that of the best bog iron ores. For purifying synthesis gases the most frequent use has been made of 100% Laut or Lux masses or a mixture containing 2/3 Lux mass and 1/3 bog iron ore. The activity of different masses with the same amount of water and iron oxide usually displays certain differences connected with the amount of water and active iron oxide. Lux masses possess a higher bulk density (750–850 kg/m^3) than bog iron ores (700–800 kg/m^3), and their pH oscillates between 7 and 8.

Installations for purifying gases by removing H_2S by means of Lux mass are identical with those in which bog iron ores have been used.

The purifying material (bog iron ore, Laut's mass enriched in sulphur) is roasted in order to

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[2] The concentration of active iron in the dry mass of post-aniline sludge determined on the basis of calculation from the first saturation with hydrogen sulphide.

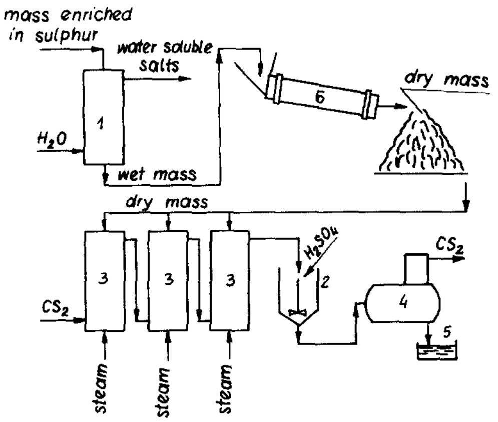


Fig. 4. Diagram of the sulphur extraction process from masses enriched with sulphur: 1,3 — extractors, 2 — mixer, 4 — catalytic and adsorptive desulphurization of gases distiller, 5 — pit of sulphur, 6 — rotary drier.

obtain SO_2, e.g. in cellulose mills, sulphur acid plants etc., or elemental sulphur is extracted. The latter process makes it possible to reuse the regenerated mass for desulphurizing gas (twice in case when only sulphur is extracted and 3–4 times when other components are also removed, such as iron sulphates, rhodanates, sodium cyanide etc., which impede the desulphurization processes). For extraction purposes a proposal was made to use carbon disulphide, dichlorobenzene, ethyl trichloride, phenol and ammonium sulphide.

Fig. 4 is a schematic diagram of the extraction process. The sulphur rich mass is subjected to a preliminary extraction with water in an attempt to remove water soluble salts. Next, the mass is dried in a rotary cylinder drier until the amount of water needed for extraction (about 20–25%) is obtained. The dried mass is extracted in countercurrent by means of CS_2 (or another solvent), while the extraction efficiency is about 95% in terms of sulphur. The extract, containing, apart from sulphur, tar and resin substances, is refined with sulphur acid (oleum), and then CS_2 is distilled off. The degree of purity of sulphur obtained in this way is 99.8–99.9%. The mass contained in the extractors, after being extracted, is freed from CS_2 residues by blowing it through with steam. After being mixed with a certain amount of fresh mass and water, and after adjusting the water content, the mass is suitable for use in the desulphurization process. After being subjected to three extractions the mass contains about 15–20% of Berlin blue and is not fit for use again. In order to isolate cyanide compounds from the extracted mass, it is necessary to turn insoluble ferrocyanide into soluble salts. For this purpose the dried mass is mixed with lime, and according to the equation given below:

$$Fe_4(Fe(CN)_6)_3+6Ca(OH)_2 \rightarrow 3Ca_2(Fe(CN)_6)+4Fe(OH)_3 \quad (5.18)$$

a grey–blue mixture, which is easily extracted with water, is obtained.

5.2.1.5. Sulferox process. The Sulferox process [9] has been developed for removing sulphur compounds from natural gas by the Shell Development Company. In this process the ligands of iron compounds are used for binding H_2S; the following reactions take place:

$$2Fe(III)L+H_2S \rightarrow 2Fe(II)L+S+2H^+ \text{ (adsorption)} \quad (5.19)$$

$$2Fe(II)L+1/2O+2H^+ \rightarrow 2Fe(III)L+H_2O \text{ (regeneration)} \quad (5.20)$$

where L = ligand of the chelating iron.

The decomposition of the ligands is a complex process. Knowledge of the mechanism of the ligand decomposition has enabled the inventors of this method to control the decomposition, which has become a key to using it in practice.

According to the inventors, the mechanism of the decomposition of ligands is as follows:

$$2Fe(II)L+O_2+2H^+ \rightarrow 2Fe(III)L+H_2O_2 \quad (5.21)$$

$$Fe(II)L+H_2O_2 \rightarrow Fe(III)L+\cdot OH+\cdot OH \quad (5.22)$$

$$Fe(II)L+\cdot OH \rightarrow Fe(III)L+OH^- \quad (5.23)$$

$$L+\cdot OH \rightarrow \text{degradation products.}$$

The total reaction is as follows:

$$H_2S + 1/2O_2 + L \rightarrow S + H_2O + \text{degradation products.} \quad (5.24)$$

Research on this method was started in the 1970s, and in 1986 an installation with a production capacity of 1.5 million $m^3/24$ h acid gas was built in White Castle La., USA.

5.2.1.6. Desulphurization with the use of catalysts. Leng Lensovet Tech. recommends the procedure of oxidizing H_2S to obtain S by means of air at a temperature of 540–820 K over a catalyst consisting of silicon dioxide, copper or copper oxide [10].

Mobil Oil Corp [11] uses the following process: the gas containing hydrogen sulphide and other sulphur compounds is subjected to prior catalytic hydrogenation in an attempt to turn all the sulphur compounds into hydrogen sulphide. Next, the gas is oxidized with oxygen over a catalyst containing titanium dioxide as an active component as well as metallic sulphate of alkaline earths at a temperature of 430–490 K. The volume rate of the gas flow is 500–3000 h^{-1}. After being oxidized, the sulphur becomes liquified and separated from the waste gas. The oxidation conditions are adjusted by the change of temperature and of the $H_2S:O_2$ ratio. The waste gas containing no free sulphur is passed into a Claus reactor. The purification efficiency is 99.5%.

The Institute of Gas Technology (USA) [12] recommends a technique for desulphurizing gas streams containing reduced sulphur compounds, particularly H_2S, by bringing them into contact with a stable compound which removes sulphur, such as Cr_2O_3, $ZnCr_2O_9$ and/or $ZnAl_2O_4$ at a temperature of 478–1140 K. As a result, a reaction takes place between the reduced sulphur compounds and the metal compound, with the formation of sulphide bonds as well as the removal from the gas of over 65 mole-% of the reduced sulphur compounds. The reagent retains its efficiency through many cycles, operates at a high temperature, and does not consume H_2 and other serviceable gas components. The regeneration of the above mentioned compounds is carried out at a temperature of 1258–1420 K with the use of air or SO_2 and O_2 mixtures. H_2S is removed selectively [13] from the hot gas by bringing the gas into contact with the packing, which is Ni or NiO at a temperature of above 1000 K, as well as with the formation of a liquid phase containing Ni and S, which flows away continuously to expose a fresh surface for a further reaction to take place. In this method, continuous reception and removal of the liquid from the reaction-zone occurs.

Hydrogen sulphide can be removed from a gas by oxidizing it to obtain elementary sulphur with air in the presence of potassium iodide as a catalyst in acidified aqueous solution. This procedure is suitable for purifying natural gas, generator gas and gases produced when crude oil and bituminous shales are processed [14].

Union Oil Co. of California has patented a technique of oxidizing H_2S to obtain elemental sulphur over a V_2O_5 catalyst on a carrier consisting of Al_2O_3 and SiO_2 [15].

The oxidation process takes place at a temperature of 390–500 K. The gas being purified may contain from 100 ppm to 10 mole-% of H_2S. The partial pressure of sulphur stays below the quantity that makes its condensation possible, and that is why sulphur is not deposited on the catalyst, while the catalyst itself maintains its activity, according to the authors, during a period of over 30 days.

5.2.1.7. Desulphurization by activated carbon. One of the first methods of removing H_2S from gas was Engelhardt's [2]. It consists in the catalytic oxidation of H_2S on the active surface of carbon in the presence of small amounts of oxygen, and sulphur adsorption on the carbon.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S. \quad (5.25)$$

In the course of this process heat is evolved, which causes the temperature of active carbon to rise, the increase in temperature being about 5°C per g H_2S per 1 m^3. Due to this rise in temperature and the difficulty in carrying away heat from the

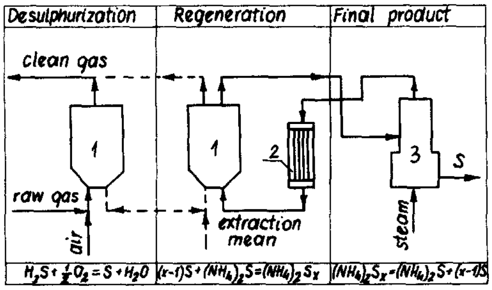


Fig. 5. Diagram of gas desulphurization process by means of active carbon (according to Engelhardt's method): 1 — adsorber, 2 — heat exchanger, 3 — distiller.

adsorbers the use of the method is limited to a maximum H_2S content of about 5 g/m^3.

Above a temperature of 313 K there is a rapid increase in the oxidation of the adsorbed sulphur to SO_2 and SO_3, and the carbon itself oxidizes to CO_2 and CO. If tar components occurring in even very small amounts they contaminate active carbon at a relatively rapid rate. With sulphur adsorption the space velocity of gas is about 300. This velocity is considerably higher than when the method with iron oxide is used. In general, adsorbers of 19–20 m^3 capacity are used, so they are sufficient for desulphurizing about 600 m^3 of gas during a period of 1 h. The height of the carbon layer is usually 1–2.2 m. Each adsorber contains about 6.6–6.7 m^3 of carbon with 2–4 mm grain size. Depending on its quality carbon can adsorb 30–150 wt.-% of sulphur. Small quantities of ammonium ion in the gas act as a catalyst and accelerate the oxidation of hydrogen sulphide. A negligible water content (10–25 g/m^3) in the gas does not hinder the course of the desulphurization process and even accelerates it, but water fog which may occur in appreciable amounts should be removed. The active carbon is regenerated by extraction with ammonium sulphide.

Fig. 5 is a schematic diagram of the desulphurization system. In the course of sulphur extraction from ammonium sulphide, ammonium polysulphide is formed; while being heated this decomposes to produce sulphur. Upon condensation, distillation vapours containing ammonium, hydrogen sulphide and steam display the repeated formation of ammonium sulphide.

In the course of desulphurization by means of active carbon a partial removal of organic sulphur and the so-called gas condensate takes place (high molecular-mass organic compounds). The profitability of the desulphurization method with active carbon is mostly dependent on the current price of carbon. H_2S is more effectively removed from gas mixtures of hydrocarbons containing heavy hydrocarbons by oxidizing hydrogen sulphide to obtain elemental sulphur. The oxidation process is carried out with the use of air at a temperature of 333–373 K in the presence of the adsorbent, which is activated carbon. The sulphur separated on carbon is removed by extracting it with a liquid hydrocarbon fraction separated from the hydrocarbon mixture being purified. The regeneration of the adsorbent is carried out at a temperature of 333–393 K, while the hydrocarbon fraction hydrated with sulphur is subjected to distillation to separate the sulphur. The rise in the temperature of the oxidation stage from 283 to 333 and 373 K increases the percentage removal of H_2S from 31.7 to 61.6 and 100%, respectively.

5.2.1.8. Systems for gas desulphurization.

5.2.1.8.1. Systems with periodic action under atmospheric pressure. In order to purify gas to free it of H_2S the so-called purifiers filled with bog iron ore are used. In principle the construction of purifiers is identical in small and even the largest systems. It is only their dimensions and the number of the layers of purifying material that are different. These purifiers are cylindrical tanks containing wooden grates. The thickness of the layer of purifying material on these grates is from 400 to 500 mm. The gas, divided into several streams, passes through the layers of the purifying material at a speed of 3–9 mm/s. A schematic diagram of the construction of purifiers is presented in Fig. 6. As a rule the gas is passed successively through four purifiers. In an attempt to achieve safety the purifiers are connected by means of connector boxes with a water lock.

The purifiers are made of thick steel sheets. Their diameter may be 11 m and their height comes up to 10 m. Their number may vary from

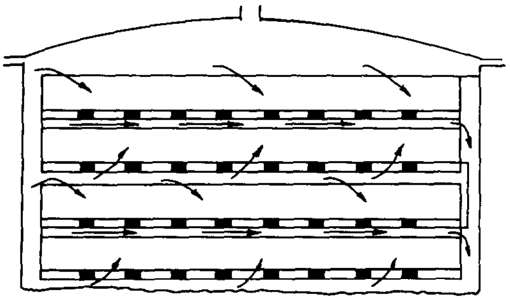


Fig. 6. Diagram of purifier.

several grates to a dozen or so. The packing between the convex cover, made of a metal plate, and the cylindrical jacket of the purifier is attained by means of rubber gaskets. Each cover is provided with a vent valve and is insulated. The bottom of the purifiers is lined with concrete and the walls have a lining covered with acid-proof mortar. All the iron elements that are not protected in this way are covered with a layer of acid-proof varnish. Each purifier has two inlet and outlet holes for gas. The flow of gas from one side to the other is switched over by means of water locks. In the connecting box placed at the gas input and output, gap locks are built in and these make it possible for changes of gas division to be made in the layers of the purifying material. The natural bog iron ores frequently display a considerable heterogeneity which is connected with their different efficiency in purifying gas from hydrogen sulphide. The concentration of components having a colloidal structure like, for instance, humic acids or plant residues in ores, may result in the formation of low temperature carbonization products due to the overheating of purifying material during operation.

Natural bog iron ores almost always contain bacteria (ferric and/or sulphuric ones), which makes it possible for uncontrolled or even hazardous processes to occur.

5.2.1.8.2. Systems with continuous operation. In an attempt to reduce the overall dimensions of gas desulphurization systems, a continuous desulphurization process has been used [16]. The system described in current publications [17] consists of two 0.6-m-diameter towers (Fig. 7). A granular adsorbent (iron oxide) is supplied to the upper part of the tower. The saturated adsorbent is received in the bottom part of the tower. Other systems of this type operating in Germany and Great Britain are installations consisting of several columns filled with specially activated granular iron oxide [18,19].

The grains of the adsorbent with a 13–19 mm diameter pass down the column under the influence of their own weight. The supply and removal of the adsorbent takes place continuously without switching off the supply of gas by means of appropriate locks and valves. A typical desulphurization system consists of three columns. The diameter of the columns is about 3 m, their height being over 12 m. In the system a gas containing 10–17 g H_2S/m^3 is purified. The purification process takes place under atmospheric pressure until an H_2S content ranging from 1.3 to 5.7 g/m^3 is obtained. The gas flow in the columns may be in parallel or countercurrent to the movement of the grains of the adsorbent.

5.2.1.8.3. High pressure systems for purification of hydrogen sulphide. Systems of this type generally operate under a pressure of about 0.7–1.4 MPa. They are capable of purifying about 425 000 m^3 of gas per 24 h, the gas containing 230 mg H_2S/m^3. The system consists of two sec-

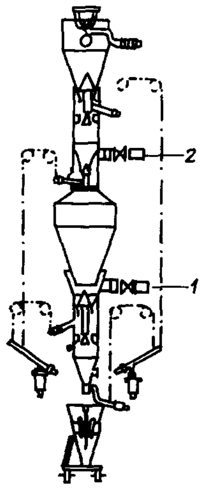


Fig. 7. Diagram of system for continuous purification of gas from hydrogen sulphide by means of iron oxides: 1 — gas inlet, 2 — gas outlet.

tions, and in each of them there are four cylindrical columns containing iron oxide. The height of the iron oxide layer in the column is 3.05 m. The deactivated iron ore is activated with air outside the column [20].

5.2.2. Oxidation of hydrogen sulphide to obtain sulphur dioxide

The simplest technique of removing H_2S from waste gases is to oxidize it to SO_2. The above process may take place in a furnace or, according to the recommendation of Philips Petroleum Co., in a gas burner. The burner is supplied with a mixture of waste gases and of fuel gas, e.g. high-methane natural gas [21]. The process is applied to waste gases obtained from the Claus process. In the case of gases containing other compounds, e.g. hydrocarbons, the removal of H_2S is principally carried out by using adsorption processes with different kinds of adsorbents. Adsorbents can be used to obtain SO_2 by blowing them through with gas containing oxidizing components. The technique of removing H_2S from gas may take place, according to Mitsubishi Heavy Industries Company [22] in a reactor packed with metal (wire or steel network) at a temperature of 620–770 K. The regeneration of the packing takes place at a 870–1070 K temperature by means of an air purge.

The reactions taking place are as follows: — initiating reaction:

$$H_2S + Fe + O_2(\text{air}) \rightarrow FeO(\text{or } Fe_2O_3) + SO_2 \quad (5.26)$$

— adsorption reaction:

$$FeO(\text{or } Fe_2O_3) + H_2S \rightarrow FeS(\text{or } Fe_2S_3) + H_2O \quad (5.27)$$

— regeneration reaction:

$$FeS(\text{or } Fe_2S_3) + 3/2O_2(\text{air}) \rightarrow FeO(\text{or } Fe_2O_3) + SO_2. \quad (5.28)$$

The method developed by Union Oil Co. of California makes use of steam and air for oxidizing hydrogen sulphide [23]. This process is also used for treating gas streams containing from 10 ppm to 2 vol.-% H_2S in the presence of a catalyst containing bismuth and vanadium. The catalyst selectively oxidizes H_2S without generating sulphur trioxide and without oxidizing other components contained in the gas. The oxidation process takes place at a temperature below 500 K (on the inlet), under 0.1–0.5 MPa pressure and at 100–5000 h^{-1} volume rate. According to the information given by the company, at least 90% H_2S becomes oxidized to form SO_2.

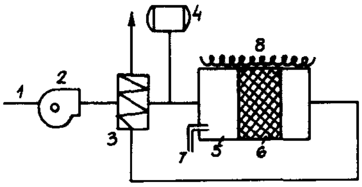


Fig. 8. Removal of sulphides from gases with the use of ozone: 1 — gas inlet, 2 — blower, 3 — heat exchanger, 4 — ozone generator, 5 — column, 6 — catalyst bed, 7 — burner, 8 — heating of column.

Another technique for removing sulphides from gas consists in bringing it into contact with ozone in the presence of a catalyst containing at least one of the following metals: Pt, Rd, Rh, Cu, Fe, Co or Ti [24]. The gases containing sulphides are blown into the heat exchanger and heated up to 360–390 K. The heated gas is mixed with ozone supplied from a generator and is introduced into the oxiding bed of the catalyst. The spent catalyst bed is heated at a temperature of 520–720 K for regeneration. A diagram of the appliance is presented in Fig. 8.

The presence of hydrogen in the gas also prevents the formation of SO_3 during the oxidation of hydrogen sulphide to SO_2 [25]. The selectively acting catalyst, the selection of temperature (520–730 K) as well as gas streams cause no generation of excess heat in this process. The catalyst recommended is V_2O_5 on a carrier (mordenite).

Chevron Research Co. [26] makes use of zinc oxide for removing H_2S from post-reforming gas. The speed of the gas flow through the sorbent bed is 1000–10000 volumes per sorbent volume. The CRC also removes HCl on a molecular sieve (zeolite 4A).

For H_2S oxidation Mitsubishi Electric Corp. uses ozone. The process consists in bringing gas containing foul components such as H_2S, methyl sulphide, or mercaptan, into contact with a fluidized bed made of silica gel in a tower in an attempt to adsorb water from the gas, bringing the dry gas into contact with a bed made of silica gel (containing a high concentration of adsorbed ozone) in a tower applied interchangeably, with an additional tower for the foul components to be oxidized with ozone and removed from the gas. The ozone is brought from the ozone generator into the tower for regenerating the silica gel by means of ozone as well as bringing the gas after being acted upon by ozone into the tower filled with active carbon for removing the excess of ozone and the residues of foul components [27]. The removal of hydrogen sulphide as well as of sulphur oxides may be carried out in the apparatus presented diagrammatically in Fig. 9 [28].

The apparatus consists of a washing system placed in the upper part of the contacting device. The adsorptive iron hydroxide, the adsorptive bed made up of Cu–Mn oxides, and the adsorptive bed of active carbon saturated with base are arranged in series in the washing system. SO_2 becomes adsorbed on the bed of metal oxides and NO_2 and residual SO_2 become adsorbed on the active carbon bed without generating NO.

In particular, the air containing H_2S, SO_2 and NO_2 is brought in through a filter placed in the washing system and is washed with water. The air that has been washed is brought in through the heat exchanger onto the bed of iron hydroxide for H_2S to be removed, and then it is brought in onto the bed made up of metal oxides for SO_2 to be removed. Next the gas from this bed is brought in onto the bed of active carbon for NO_2 to be removed without generating NO_2. The purified gas is let out of the blower through the filter into the atmosphere.

The technique of purifying the gas containing H_2S consists in bringing it into contact with a mass containing metallic copper at a temperature of 520–820 K: in cutting off the flow, bringing the mass containing copper sulphide into contact with a mass containing O_2 at 520–618 K for $CuSO_4$ to be generated, cutting off the flow, bringing the mass into contact with a reducer, preferably H_2, at a temperature of 570–720 K in an attempt to regenerate the mass, cutting off the flow of the reducer and restarting the flow of the gas containing H_2S. In the course of the regeneration process the emission of SO_2 and steam takes place. The above method has been developed by the Institute Français du Petrole [29].

5.3. Gas desulphurization by the Claus process

When a gas does not contain hydrocarbon compounds then the Claus method is used to purify it from H_2S. This is one of the most widely used methods for the dry removal of H_2S. Developed almost 100 years ago, the method was at first used reluctantly, but in the 1940s it began to be put to use in industry as one of the most universal, simple methods for dry desulphurization of gas. Currently a number of modifications of the Claus process are being used, and the most typical of these are presented below.

5.3.1. Mechanism of the reaction

The methods of removing hydrogen sulphide from gases by oxidizing consist in turning H_2S into sulphur or sulphur dioxide. The oxidation process progresses in the gaseous phase according to the following reactions:

$$H_2S + 1/2O_2 \rightleftharpoons S + H_2O \qquad (5.29)$$

$$2H_2S + O_2 \rightleftharpoons S_2 + 2H_2O \qquad (5.30)$$

$$\Delta H = -443.1 \text{ kJ/mol}$$

$$H_2S + O_2 \rightleftharpoons SO + H_2O \qquad (5.31)$$

$$SO + 1/2O_2 \rightleftharpoons SO_2 \qquad (5.32)$$

$$\Delta H = -518.3 \text{ kJ/mol}$$

$$2H_2S + SO_2 \rightleftharpoons 3S + 2H_2O \qquad (5.33)$$

$$\Delta H = -146.3 \text{ kJ/mol.}$$

The course of the reaction (5.33) is slow.

Porous substances with an intensively developed surface significantly reduce the energy of

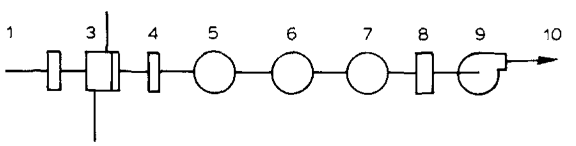


Fig. 9. Apparatus for removing H_2S, SO_2 and NO_x from air: 1 — air inlet, 2 — filter, 3 — scrubber, 4 —heat exchanger, 5 — adsorbent bed (iron hydroxide), 6 — adsorbent bed (metal oxide), 7 — adsorbent bed (active carbon), 8 — filter, 9 — blower, 10 — purified air.

activation of the hydrogen sulphide oxidation reaction. In practice, every porous solid body displays a catalytic activity in this reaction.

The catalytic dry oxidation of hydrogen sulphide is a process running in the heterophase system: purified gas with a solid body as catalyst. In the course of the H_2S oxidation process carried out on porous solid bodies it is assumed that the adsorption phase is followed by the action of the microcrystalline structure of the catalyst towards the generation of radicals and ion radicals.

The theoretical conversion of H_2S under standard conditions and at temperatures below 520 K attains a value of 100%. The conversion drops steeply as the temperature increases, reaching its minimum at a temperature of about 820 K and then increasing again at higher temperatures. At a given H_2S/O_2 ratio the conversion to obtain sulphur is higher at a lower temperature whereas the conversion to obtain SO_2 is a maximum at a temperature of 820 K.

Acid gases containing over 50% hydrogen sulphide are subjected to the so-called Claus process. A typical schematic diagram of the Claus process is presented in Fig. 10 [30].

In the Claus furnace the gas containing hydrogen sulphide becomes oxidized according to the following reaction:

$$H_2S+3/2O_2 \rightarrow H_2O+SO_2. \qquad (5.34)$$

By means of the appropriate control of the air inflow for combustion, the $H_2S{:}SO_2=2{:}1$ ratio must be accurately maintained. This is when maximum conversion is obtained.

The gases from the furnace are cooled in the cooler system and enter the converter filled with the appropriate catalyst.

Reaction (5.33) takes place in the converter.

Since the reaction is exothermic, a rise in temperature in the converter follows. The gases entering from the first converter pass through the cooler to the second converter, and then to the third one. In the cooler a reflux of the sulphur stream takes place, the sulphur being collected in special pit collectors. The sulphur obtained from the installation is characterized by its high purity and makes a commercial product.

5.3.2. *An analysis of the basic parameters of the desulphurization of gases by means of Claus method*

The Claus process takes place with more than 95% efficiency when a number of conditions are satisfied, and these will be discussed below. In our analysis of the process we shall make use of a list of hypothetical partial reactions that may proceed under the following conditions:

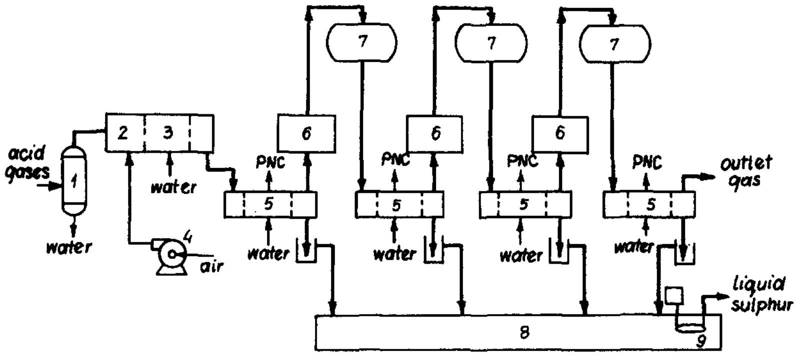


Fig. 10. Diagram of a typical Claus system: 1 — condenser, 2 — reaction furnace, 3 — colder, 4 — blower of air, 5 — condensers, 6 — heat exchangers, 7 — reactors, 8 — sulphur pit, 9 — pump for liquid sulphur. PNC — low pressure steam, PWC — high pressure steam.

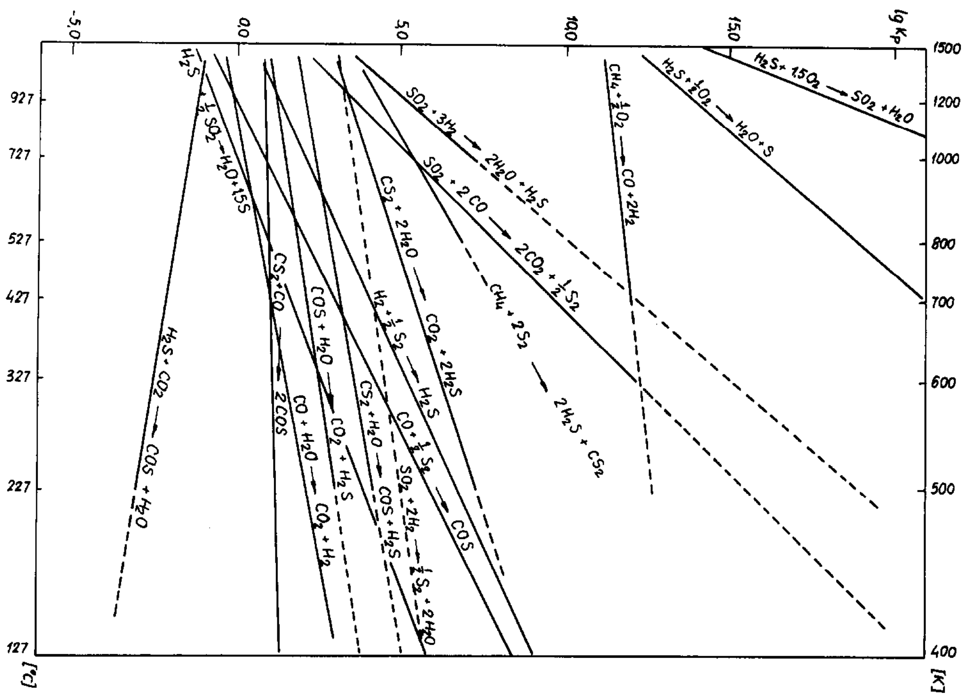


Fig. 11. Dependence of chemical equilibrium (K_p) on temperature for the hypothetical Claus reaction process.

- in the presence of an excess or deficiency of the oxidizing agents;
- in the presence of an excess or deficiency of the reducing agents.

We shall also use the relationships between the change of thermodynamic potential of the isothermal–isobaric reaction

$$\Delta G^{\circ} = \Delta H - T\Delta S^{\circ} \tag{5.35}$$

with the equation of chemical equilibrium

$$\Delta G = -RT\ln K_p. \tag{5.36}$$

Here, G = thermodynamic potential, H = enthalpy, S = entropy, R = gas constant and T = absolute temperature.

This will make it possible to determine the constant chemical equilibria of K_p (or $\log K_p$) of these partial reactions in the range of temperatures characteristic of the gas desulphurization process by means of the Claus method [31–34]. The dependence of $\log K_p$ on temperature for 16 partial reactions of the gas desulphurization process is presented in Fig. 11.

The summary diagram presented in Fig. 11:

- illustrates the complexity of the Claus process;
- facilitates the comparison of tendencies to a spontaneous course of particular reactions;
- discloses the significance of undesirable reactions supported by the excess or deficiency of certain reagents;
- indicates the reagents that should immediately be removed from the reaction system;
- makes it possible to determine the most advantageous ranges of temperatures and pressures in which the course of the desirable reaction will be adequately fast if the appropriate catalyst is used.

In the case when air is used as an oxidizing agent in the typical Claus process, the reaction furnace is also charged, besides oxygen, with non-reactive nitrogen which, on the one hand, causes the dimensions of the system to be enlarged and, on the other hand, the efficiency of the process to be reduced [30].

The presence of inert gas in the reaction mixture acts analogically to the increase of pressure, and thus according to the rule of perversity, it displaces the equilibrium towards the substrates, which is disadvantageous from the viewpoint of the efficiency of the Claus reaction.

The basic reaction that should take place in a Claus furnace is the oxidation hydrogen sulphide to give sulphur dioxide (5.34). This is a reaction which progresses with great efficiency at high temperatures, up to over 1000 K. With a deficiency of oxygen, reaction (5.29) takes place, in which hydrogen sulphide is oxidized to sulphur. As the temperature increases up to 1500 K, the equilibrium constant of the chemical reaction (5.34) decreases over the temperature range considered (Fig. 11).

When other gases, such as hydrocarbons, are present, part of the oxygen is consumed by these gases. When there is a deficiency of oxygen the formation of carbon monoxide and hydrogen can be observed:

$$CH_4+1/2O_2 \rightleftharpoons CO+2H_2. \qquad (5.37)$$

With an excess of oxygen, carbon dioxide and water are formed

$$CH_4+2O_2 \rightleftharpoons CO_2+2H_2O. \qquad (5.38)$$

The presence of hydrogen and carbon monoxide results in the occurrence of disadvantageous reactions, i.e. sulphur dioxide produced in the reaction (5.35) reacts according to the following equations:

$$SO_2+3H_2 \rightleftharpoons 2H_2O+H_2S \qquad (5.39)$$

$$SO_2+2CO \rightleftharpoons 2CO_2+1/2S_2 \qquad (5.40)$$

$$SO_2+2H_2 \rightleftharpoons 2H_2O+1/2S_2. \qquad (5.41)$$

The reactions (5.39)–(5.41) take place at rather high temperatures. The sulphur that has been produced may react with hydrocarbons, hydrogen and carbon oxide:

$$CH_4+2S_2 \rightleftharpoons 2H_2S+CS_2 \qquad (5.42)$$

$$H_2+1/2S_2 \rightleftharpoons H_2S \qquad (5.43)$$

$$CO+1/2S_2 \rightleftharpoons COS. \qquad (5.44)$$

At lower temperatures the equilibrium of these reactions is displaced to the right. The compounds, i.e. oxysulphide and carbon disulphide, formed in the reactions (5.42) and (5.44) undergo hydrolysis in the presence of water or steam:

$$CS_2+2H_2O \rightleftharpoons CO_2+2H_2S \qquad (5.45)$$

$$COS+H_2O \rightleftharpoons CO_2+H_2S. \qquad (5.46)$$

In the case of a deficiency of H_2O a reaction of the following type may take place:

$$CS_2+H_2O \rightleftharpoons COS+H_2S. \qquad (5.47)$$

In addition, carbon dioxide may react with disulphide according to the reaction:

$$CO_2+CS_2 \rightleftharpoons 2COS. \qquad (5.48)$$

As can be seen from the diagram (Fig. 11), reaction (5.34) would take place if, in the course of the oxidation of hydrogen sulphide to obtain sulphur dioxide, the temperature in the whole combustion chamber were equalized at a level of about 1100 K. Equally level, stable and conforming to stoichiometry should be the concentration of oxygen in each point of the combustion chamber. The gases should be thoroughly mixed, and the reaction products immediately carried away in order that no secondary reactions take place. In the presence of other gases such as hydrocarbons, the amount of air supplied should make allowance for this fact.

Reduction of the temperature below 1000 K and in a deficiency of oxygen cause sulphur to be able to generate as early as in the furnace according to reaction (5.34), as well as in the reaction (5.33) which should take place in the converters.

The second important stage of the Claus process is the conversion of hydrogen sulphide and sulphur dioxide to obtain elemental sulphur (reaction (5.33)). As can be seen from Fig. 11, the conversion takes place with greater efficiency in the range of lower temperatures. The most essential thing is to retain, at the same time, a stoichiometric relation of H_2S to SO_2, such as 2:1, which in the case of variable flows of H_2S as well as in the presence of hydrocarbons is practically possible only with the aid of a computer since only this type of system ensures a sufficiently rapid control. Fig. 12 presents a computer control diagram of

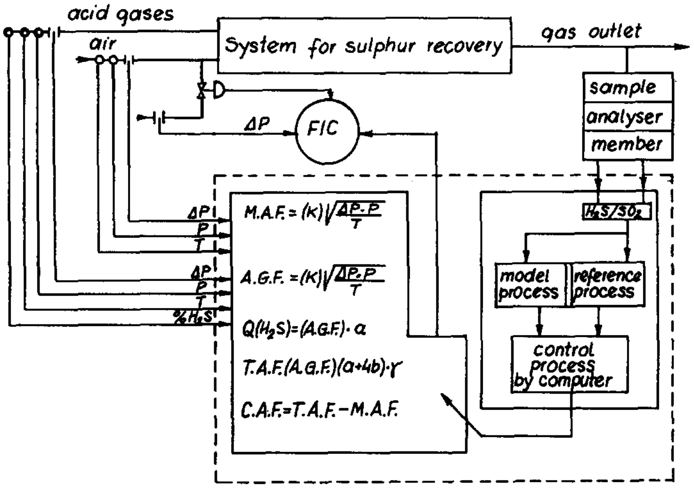


Fig. 12. Diagram of computer control for gas desulphurization process: FIC — inlet air adjustment, MAF — measurement of air flow velocity, AGF — flow velocity of acid gas, TAF — theoretical air flow velocity, CAF — specific air flow velocity. a — % H_2S, b — % hydrocarbons, γ — correction factor, Q (H_2S) — H_2S flow velocity.

the process proposed by EM Aquitaine [35].

In general it may be said that an increase in the efficiency of Claus process and thus the reduction of the quantity of H_2S and SO_2 in waste gases may be achieved as follows:

— increasing the efficiency of gas combustion with the use of appropriate burners;
— establishing optimal reaction temperatures both in the Claus furnace and the converters;
— applying a perfect mixture of gases;
— in the case of the presence of ammonium in the gases, additional combustion should be applied;
— allowance should be made for an additional demand for oxygen in the case of the presence of hydrocarbons;
— the quantity of air should be continuously controlled with the changing composition of the gas stream;
— strict adherence to the H_2S/SO_2 ratio = 2:1;
— strict adherence to the uniform distribution of gas in the converters;
— applying appropriate highly efficient catalysts for H_2S and SO_2 conversion as well as by-products of the CS_2 and COS type;
— eliminating oxygen in reaction products since it causes sulphates to form and these deactivate the catalyst.

5.3.3. Catalysts used in the Claus process

The gases leaving a Claus furnace with the H_2S/SO_2 ratio 2:1 pass through the converters, and in systems of this type there are at least two of them. The converters are filled with a catalyst on which the basic conversion takes place. Catalysts used in the Claus process have to exhibit a high activity, mechanical strength and long lifetime. The problem which is of great importance in the process of removing sulphur compounds from gases is the use of such a catalyst which would cause all the sulphur compounds present, and those forming in the particular stages of the process, to undergo conversion. In the process of oxidizing H_2S to obtain sulphur, various materials having a well-developed inner surface and an appropriate chemical composition are being used.

Among the materials that are used most frequently are aluminium oxides of the bauxite type and specially activated aluminium oxides. Activated aluminium oxides are also often modified with metal compounds of Groups 6, 8, 9 and 10. The most frequently used are metal oxides such as Co, Mo, Ni, Cr, W, V. At present, ever increasing use is made of Ti/Al_2O_3 or TiO_2. These are highly active catalysts. As catalysts (or adsorbents) in this process one can use active carbons, activated cokes and semi-cokes, zeolites and iron

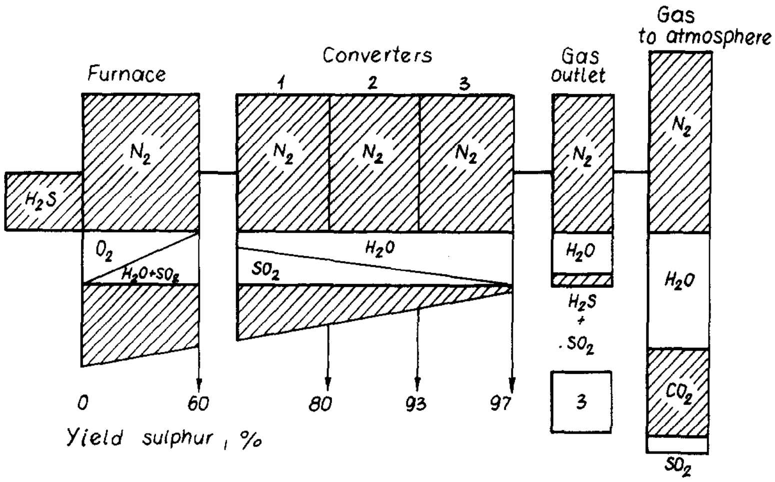


Fig. 13. Change of gas concentration for particular stages of the Claus process.

oxides. Both the chemical composition and porosity, and particularly the diameter of pores play a basic role in the usability of a given material as a catalyst in Claus convertors. Activated semi-cokes are characterized by a high activity but a moderate selectivity. The presence of water or steam in the stream of gases causes their activity to decrease. For this reason coal materials are used to a decidedly lesser degree in Claus converters.

Investigations have also been conducted on the use of zeolites in the Claus reaction. Zeolites are characterized by high activity and selectivity. However the presence of water causes Lewis acidity to be reduced and the zeolite becomes deactivated [30]. As many authors point out [36] the porosity of catalysts for the Claus process plays an essential role and is one of the most important factors. When the size of the catalyst (adsorbent) pores is of the same order as that of the molecule of the sulphur adsorbed (0.5–1 nm), then the sulphur is strongly adsorbed. Apart from micropores a significant role is played by the system of inner bonds of meso- and macropores with micropores.

5.3.4. Advantages and disadvantages of Claus method, and techniques for increasing efficiency of reaction

The Claus method is used in industry as one of the main conventional methods for removing H_2S from gas. However, the efficiency of the reaction is closely connected with the H_2S content of the gases. With high concentrations of H_2S in gas (above 50%), the Claus method for H_2S removal gives good results. When the H_2S content is low (below 5%) its conversion is reduced to a minimum.

The problem of concentration is closely connected with the economics of the process [37]. In the conventional Claus process with air as the oxidizing agent, 1.5 oxygen molecules are needed for 1 H_2S molecule, according to reaction (5.34). In addition to oxygen, nonreactive nitrogen is supplied to the reaction which creates a need to enlarge the size of the system, as well as reducing the efficiency of the process. Fig. 13 presents the changes of gas concentration in the particular stages of the Claus process. The second factor inhibiting the reaction is the formation of water. Apart from increasing the appropriate size of the system, water causes the reaction temperature to be reduced. Control of the reaction temperature occurs by increasing the gas temperature, which results in a disadvantageous direction of the reaction and in the formation of noxious products.

A reduction in the efficiency of the gas desulphurization process may also be caused by a variable (in time) content of hydrocarbons in the gas being desulphurized. This is closely connected with the demand for oxygen which is used to oxidize the hydrocarbons to carbon oxides and water.

Table 10
Air demand in Claus reaction depending on the content of hydrocarbons in gas

Hydrocarbons in acid gas (%)			Air demand for oxidation of hydrocarbons as a percentage of the total amount of air H_2S content in acid gas (%)				
C_1	C_2	C_3	5	10	20	40	90
1	0.6	0.4	44	29	17	9	4
2	1.1	0.8	62	44	29	17	8
4	2.3	1.6	76	62	44	29	15
8	4.6	3.2	86	78	62	44	26

Table 10 presents the effect of the content of some hydrocarbons in gas on the demand for air [30].

The dependence of the size of the system on the H_2S concentration in gases is presented in Table 11.

Some side reaction occur in the Claus reaction. The reaction conditions create the formation of such products as COS and CS_2 in quantities ranging from 600 to 1500 ppm [37].

An increase in the efficiency of the Claus reaction and thus the decrease of H_2S and SO_2 quantity in waste gases may achieved by: increasing the dwell time of gas in the combustion chamber; and/or increasing the efficiency of gas combustion. These techniques may be implemented by using different burners, i.e. a contact burner giving a long flame or one with a diffuser giving a short flame of high turbulence.

Further efficiency increases may be achieved by: applying combustion (auxiliary in the case of ammonium in the gas); appropriate distribution of gas in converters for each molecule of H_2S and SO_2 to be brought into contact with the catalyst; applying appropriate high-efficiency catalysts for the conversion of H_2S as well as by-products of CS_2 and COS type; adhering to a strict control of the $H_2S/SO_2 = 2{:}1$ ratio; establishing the optimum reaction temperature; and eliminating oxygen from the reaction products.

Table 11
Dependence of the size of the system on H_2S concentration in tail gases

H_2S content in gas (%)	Dimension factor
95	1.0
30	2.0
20	3.0
15	4.0
5	7.0

5.3.5. Claus process applied to gases with lower H_2S concentration

When the hydrogen sulphide concentration in acid gases is from 30% to 50% it is necessary to use a bypass of part of the acid gases, whereas the remaining part of gases enters the reaction furnace. A typical system with the use of a bypass is presented in Fig. 14. The reactions taking place are identical to those in a typical Claus system except that the gas streams are separated into two directions: 1/2 of the stream becomes oxidized in the furnace to form sulphur dioxide, while the remaining part containing hydrogen sulphide is joined with the stream coming out of the furnace so as to make both streams enter the converter. When the concentration of hydrogen sulphide in the gases is lower than 30% and often reaches only 5%, it is necessary to burn part of the sulphur in the reaction in order for the reactions typical of this process to take place. The schematic diagram of such a system is presented in Fig. 15. The sulphur from the tank is pumped into the reaction furnace in which the following reaction takes place.

$$S + O_2 \rightarrow SO_2. \qquad (5.49)$$

The quantity of air supplied is such as to cause only sulphur dioxide to form. Part of the acid gases is supplied directly to the converter by means of the heat exchanger. One of the great advantages

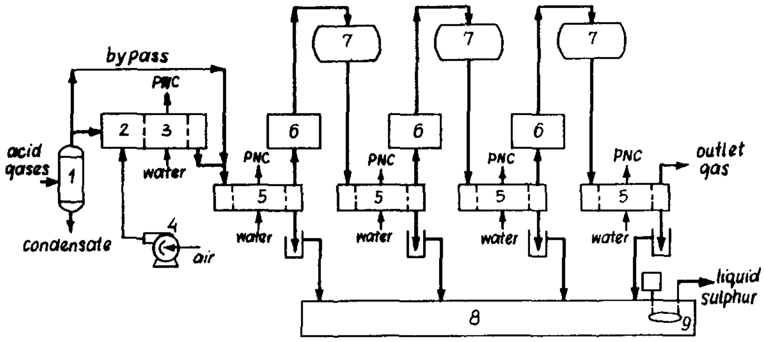


Fig. 14. Claus process with 30–50% H_2S with the use of an additional bypass: 1,5 — condensers, 2 — reaction furnace, 3 — cooler, 4 — air blower, 6 — heat exchanger, 7 — reactors, 8 — pit of sulphur, 9 — pump for liquid sulphur. PNC — low pressure steam.

of this process is that it gives sulphur of high purity. If however, the sulphur from the first converter contains impurities it is subjected to oxidation or evaporation. Despite the variable flows of acid gases, the circulating sulphur is a factor which maintains the stability of Claus process. This process is being used in the industries of USA, Canada, Iran and Saudi Arabia.

Although the process presented above may be applied to gases containing even 5% H_2S, the authors [30] are of the opinion that the Selectox process possesses far more profitable features than that in which sulphur is burnt, and particularly with still lower H_2S quantities in the gas, and for small systems. In this process (Fig. 16) hydrogen sulphide, during its catalytic oxidation to sulphur, to one or more stages. In the Selectox converter the appropriate temperature is maintained by introducing part of the circulating gas. Apart from the Selectox converter the remaining systems are identical to those used in the standard Claus process. Depending on the concentration of hydrogen sulphide in inlet gas the process proceeds with an efficiency of 90 to 97%. Apart from having no restrictions as to the hydrogen sulphide content, the Selectox process possesses a very stable catalyst of high selectivity. While passing through the catalyst, the hydrocarbons contained in the gas do not undergo any conversions, and less air is used than in a conventional Claus system. The closed cycle of part of the gas creates good conditions for thermal stability of the process. Since there is no open flame, the process is easy to control, and after being stopped it is easy to restart. The first industrial application of this process took place towards the end of 1981. Very good results with gas containing 13–17% H_2S were obtained. When H_2S concentration in the gas was below 5%, no recirculation was used. This process may also be used for purifying waste gases containing small

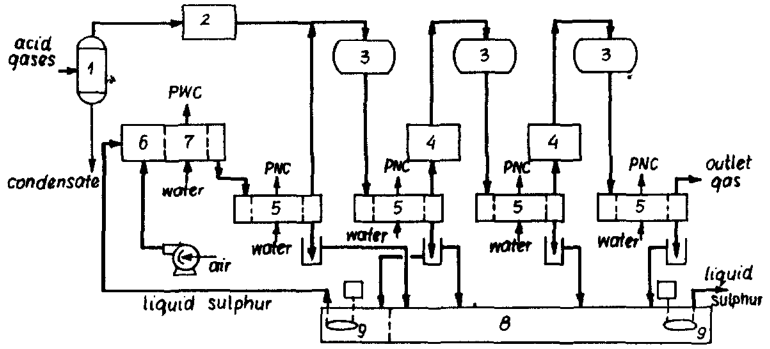


Fig. 15. Claus process with sulphur oxidation: 1,5 — condensers, 2 — preheater, 3 — reactors, 4 — heat exchanger, 6 — reaction furnace, 7 — cooler, 8 — pit of sulphur, 9 — pump for liquid sulphur. PNC — low pressure steam, PWC — high pressure steam.

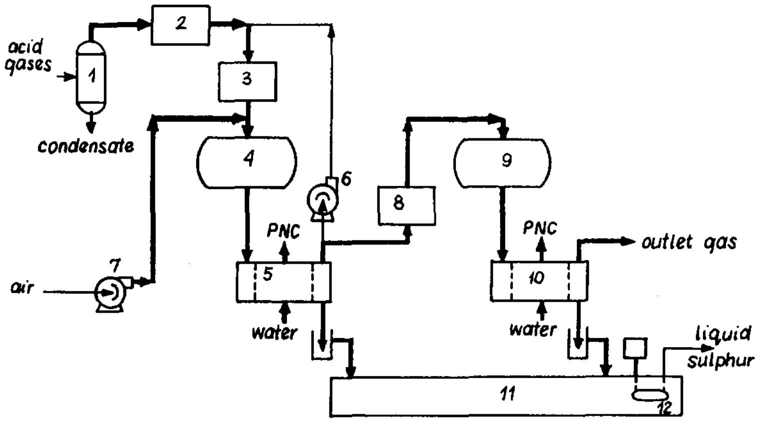


Fig. 16. Diagram of the Selectox process: 1 — condenser, 2 — preheater, 3 — heat exchanger No. 1, 4 — Selectox reactor, 5 — condenser No. 1, 6 — circulating pump, 7 — air blower, 8 — heat exchanger No. 2, 9 — Claus reactor, 10 — condenser No. 2, 11 — pit of sulphur, 12 — pump for liquid sulphur. PNC — low pressure steam.

quantities of acid gases. The efficiency of this process is about 99%.

5.4. Superclaus process

The 'Comprimo' firm and the Gas Institute (Holland) have jointly developed a new process — called Superclaus [39] — based on the Claus process by using modifications of the control system and a newly developed, selective oxidation catalyst. The sulphur yield in this process rises to 99.5%. The major purpose of the Superclaus process is to overcome the defects and imperfections of the Claus process, the most serious of them being the formation of water in the reactors and the increase of its concentration in technological gas. This has a negative effect on H_2S and SO_2 conversion to sulphur in the Claus equilibrium reaction by decreasing their concentration. In the Claus process the required $H_2S:SO_2$ ratio in the gas is 2:1. The essential difference between the new process and the Claus process consists in rejecting this critical ratio and substituting it for the gas containing an excess of hydrogen sulphide. This excess causes a SO_2 concentration in the gas leaving the second reactor. The unreacted H_2S becomes oxidized with air to obtain sulphur in the presence of the new, selective catalyst. The air consumed in oxidizing H_2S is the same in both the Claus and Superclaus processes, but in the latter the air is divided into two parts: the greater part is directed to Claus burners, while the remaining part of the air is brought into the third reactor filled with the new catalyst. In this way a flexible control of the air quantity and gaseous sulphur compounds ratio is obtained. The new catalyst ensures a complete conversion of H_2S to sulphur with the negligible formation of SO_2 even in the presence of excess air (Fig. 17).

The catalyst is insensitive to a high water concentration in technological gas. Moreover, it does not catalyze CO, H_2, or CH_4 oxidation reactions, nor the formation of COS and CS_2. It displays chemical and thermal stability as well as a satisfactory mechanical strength. The catalyst contains a carrier on which the oxide of an active metal is precipitated.

There are two variants of the Superclaus process, and these are Superclaus 99 and Superclaus 99.5.

The Superclaus process 99 includes the thermal stage and three stages of catalytic reactors. The first and the second reactors are loaded with the standard Claus catalyst, while the third one is loaded with the new catalyst which ensures the efficient oxidation of H_2S to elemental sulphur.

Superclaus 99.5 is a variant of the process used in situations when the required recovery of sulphur contained in the waste gas is greater than 99.5%.

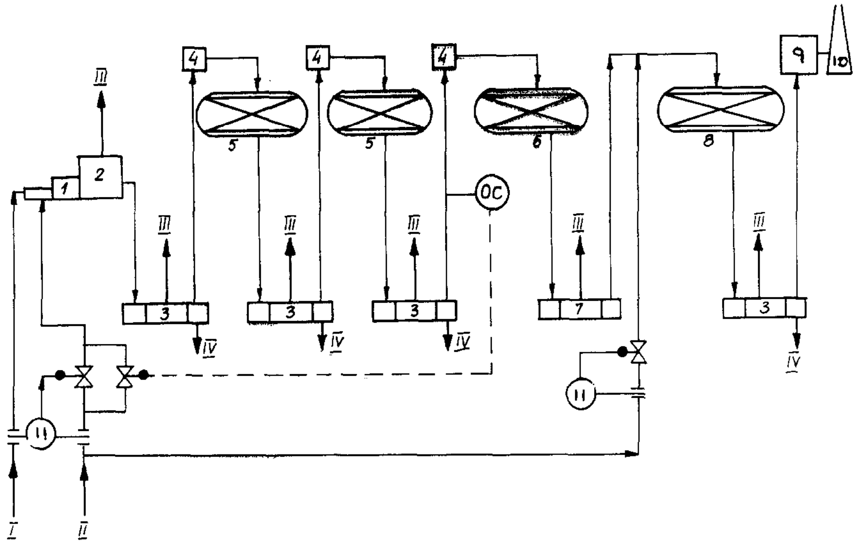


Fig. 17. Conceptual diagram of Superclaus 99.5 process: 1 — combustion chamber, 2 — steam boiler, 3 — condenser, 4 — preheater, 5 — reactor, 6 — hydrogenation reactor, 7 — gas cooler, 8 — selective oxidation reactor, 9 — reheat furnace, 10 — chimney, 11 — gas meter. Conduits: I — raw gas, II — air, III — steam, IV — sulphur.

In order to achieve such a high degree of recovery, the Superclaus system contains additionally a hydrogenation stage. A schematic diagram of the Superclaus 99.5 process (Fig. 17) includes:

- thermal stage;
- two Claus reactors;
- hydrogenation reactor;
- reactor for selective H_2S oxidation.

Since the new selective catalyst is insensitive to water, there is no need for water condensation behind the hydrogenation reactor, which is typical of almost all variants of the Claus process. The gas from the hydrogenation reactor becomes cooled up to the optimum temperature on the inlet to the selective oxidation reactor. The indispensability of the thermal stage no longer comes into consideration since all sulphur compounds and sulphur steam undergo conversion to H_2S in the hydrogenation reactor, and the reactors 1 and 2 may operate with H_2S in excess as well as with the H_2S:$SO_2 = 2$:1 ratio. The required flexibility in this variant of the process is achieved by introducing the excess of air into the reactor of selective hydrogen sulphide oxidation. The Superclaus process may be used both in the newly built developed and the hitherto existing Claus systems.

Owing to the simplicity of the process and of the equipment, some additional investments are negligible as compared with those needed for a conventional Claus system. The investment needed for reconstruction of the existing three-stage Claus system makes up barely 5% of the general initial investment. In the case of a two-stage Claus system the additional investment outlays make up 17% of the general initial expenses. If the recovery of 99.5% sulphur is needed, then an additional, supplementary hydrogenation stage is indispensable, and in this case additional investment outlays, in comparison with those for a two-stage Claus system, reach 30%.

5.5. Desulphurization of tail gases from Claus process

5.5.1. The BSR/Selectox I process

The first industrial unit based on the above method was built in Lingen (Germany) in 1978. The assumption on which the process was built was a 99.5% recovery of sulphur from the gases leaving a Claus system. The BSR/Selectox I process (Beavon Sulfur Removal Selective Oxidation [38]) is made up of two sections: hydrogenation,

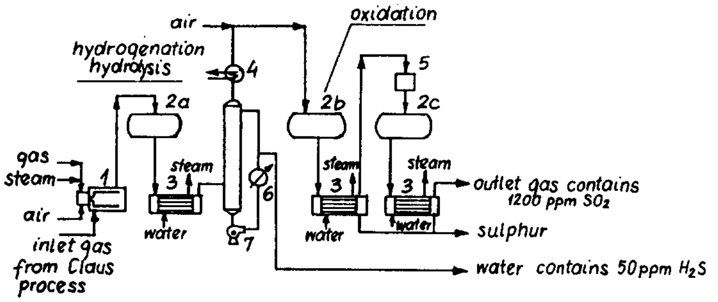


Fig. 18. Diagram of BSR/Selectox I process: 1 — furnace, 2a — hydrogenation reactor, 2b — oxidation reactor, 2c — Claus reactor, 3 — cooler, 4 — heat exchanger, 5 — preheater, 6 — flow meter, 7 — pump.

hydrolysis and oxidation. Fig. 18 presents a diagram of this process. A mixture of gases leaving the Claus system is heated up to 600–700 K. Steam is added to the stream of gases so that the amount of coke formed is reduced. A hot mixture of gases is introduced into the reactor in which hydrogenation and hydrolysis take place over the cobalt–molybdenum catalyst according to reactions (5.39), (5.43), (5.45) and (5.46).

The hot gases from the reactor pass through the heat exchanger so that the water formed boils under reflux. This reduces the gas volume by about 30%. The removal of water makes it possible to increase the efficiency of the process. The condensed water contains negligible quantities of dissolved CO_2 and H_2S. It may be used for precooling the gas in the scrubber. Next the gas containing H_2S passes to the reactor filled with the Selectox-32 catalyst in which H_2S is oxidized with air to sulphur. The amount of air is strictly selected to correspond to the quantity of H_2S contained in the gas. An excess of air may lead to reactions which cause the catalyst to overheat and sulphate. The gas leaving the reactor is cooled down in order to precipitate the sulphur formed. The recovery of sulphur may be increased by combining the Selectox-32 reactor with a reactor containing a typical Claus catalyst. The gas stream reaching the latter reactor contains negligible amounts of water and so the effectiveness of the process is considerably improved. Table 12 shows the concentrations of compounds in gases at particular stages of the process.

5.5.2. The SCOT process

The SCOT process (Shell Claus off-gas treatment) has been developed by the Shell company. It consists in the reduction of all the sulphur compounds contained in the gas, together with the sulphur mist, by hydrogen or a mixture of hydro-

Table 12
Gas composition in BSR/Selectox I process [38]

Component	Measurement unit	Tail gases from Claus	After hydrogenation	After cooling	After BSR Selectox I	After final Claus reactor	After burning
H_2S	ppmv	4000–10000	10000–15000	12000–20000	2000–3000	400–600	1
SO_2	ppmv	3000–6000	0	0	1000–1500	200–300	1000–1500
COS	ppmv	300–5000	10–30	15–40	15–40	15–40	1
CS_2	ppmv	300–5000	0	0	0	0	0
S_x	ppmv	7000–1000	0	0	700–800	700–800	1
H_2	vol.-%	1–3	2–3	3–4	2–3	2–3	0
CO	vol.-%	0.5–1	0	0	0	0	0
CO_2	vol.-%	1–15	1–15	1–20	1–20	1–20	1–15
H_2O	vol.-%	30–35	30–35	1.5–4	3–6	3–6	8–12
N_2	vol.-%	60–70	80–90	80–90	80–90	80–90	80–90
Recovery sulphur	wt.-%	93–96	93–96	93–96	98.5–99	98.4–99.6	99.4–99.6

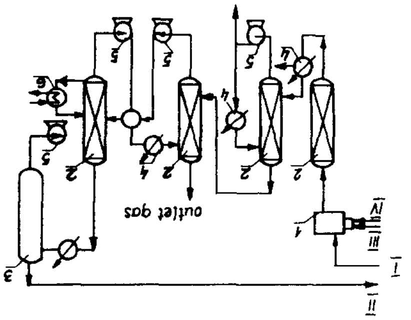


Fig. 19. Diagram of SCOT process: 1 — mixing chamber, 2 — reduction reactor, 3 — adsorbers, 4 — heat exchanger, 5 — pumps, 6 — steam generator. I — tail gas from Claus process, II — gas for Claus system, III — fuel, IV — air.

gen or carbon monoxide over a cobalt–molybdenum catalyst at a temperature of 570 K, leading to hydrogen sulphide. Hydrogen sulphide is selectively removed by absorption in amine. Amine containing absorbed H_2S reclaimed, and H_2S is transferred to a Claus system. A diagram of the system is presented in Fig. 19. The total recovery of sulphur from the gases (Claus + SCOT) is 99.9%.

5.5.3. *Sulfreen process*

The Sulfreen process, developed by the SNEA and Lurgi companies, makes use of the adsorptive and catalytic properties of the catalyst and maintains a stable $H_2S{:}SO_2 = 2{:}1$ ratio, similarly to the process in typical Claus systems. The Sulfreen process consists of the stages of adsorption and reclamation. The adsorption process takes place at a temperature of 410 K, and then the catalyst–adsorbent is gradually heated up to 550 K. Sulphur in the form of vapour is removed from the catalyst and then cooled in the cooler. The catalyst is then cooled down to the adsorption temperature. In order to prolong the service life of the catalyst, it is blown through with gas rich in H_2S. The sulphates that have been formed on the catalyst are reduced and do not poison it. A diagram of the system is presented in Fig. 20. The overall efficiency of the process (Claus + Sulfreen) is 98–98.5%.

5.5.4. *The Modop process*

The Modop process (Mobil Oil direct oxidation process) [40] allows a recovery of 99.5% sulphur from the gases leaving a Claus system. This depends on the water content, temperature and the feed of raw materials in stoichiometric quantities. Such a unit has been developed in Germany, where three systems are desulphurizing 7.7 million m^3 gas per 24 h, thus 'producing' 1050 tons of sulphur/24 h. The gases leaving the two-stage Claus system are heated up to a temperature of 530–600 K and introduced into the reactor in which sulphur compounds are hydrogenated. The hydrogenation process is carried out in the presence of a nickel–cobalt–molybdenum catalyst. Next the gas is cooled down in three stages: in the boiler (with a supply of steam at 0.6 MPa pressure), in the heat exchanger and finally in the tower with circulating water. After that the cooled gas is heated (two-stage heating), mixed with air and fed to the reactor which contains the CRS-31 catalyst (80% titanium oxide).

The oxidation process takes place at a temperature of 440–470 K. The temperature of waste gases from the reactor is 520–540 K. The gas is cooled down to precipitate the sulphur. Fig. 21 presents a schematic diagram of the Modop system.

5.5.5. *The ELSE process*

A process of waste gas desulphurization from Claus system has been developed by the Amoco company in the USA. It is called the ELSE process

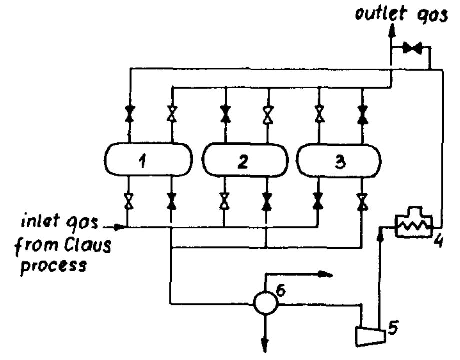


Fig. 20. Diagram of Sulfreen process: 1,2,3 — reactors, 4 — heat exchanger, 5 — blower, 6 — cooler.

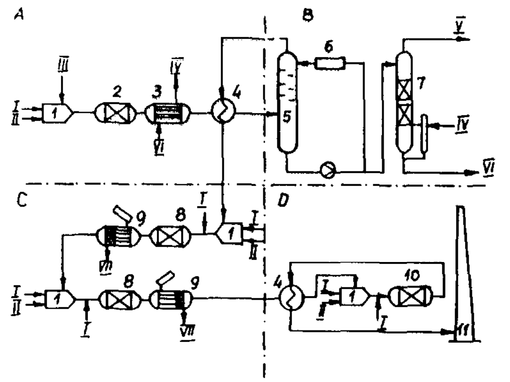


Fig. 21. Diagram of Modop process: 1 — furnace, 2 — hydrogenation reactor, 3 — boiler, 4 — heat exchanger, 5 — cooling column, 6 — air cooler, 7 — condensation column, 8 — oxidation reactor, 9 — cooler, 10 — additional reactor for oxidation of gas, 11 — chimney. I — air, II — fuel, III — tail gases from Claus system, IV — steam, V — vapour phase, VI — water treated for boiler, VII — sulphur.

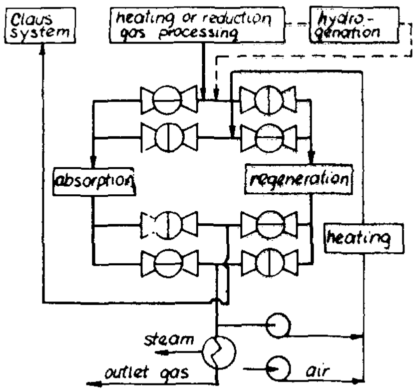


Fig. 22. Diagram of ELSE process.

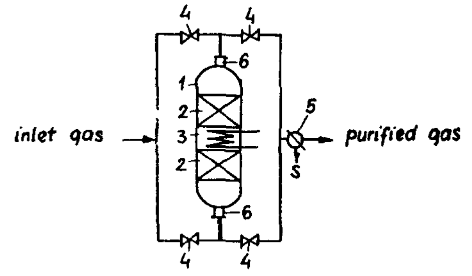


Fig. 23. System for desulphurization of gas: 1 — reactor, 2 — catalyst bed, 3 — heat exchanger, 4 — control valves, 5 — sulphur condenser, 6 — pipe flange.

(extremely low sulfur emission) [41], and its efficiency is over 99.98%. Zinc oxide is used as a sorbent in the ELSE process. The concentration of sulphur compounds over this sorbent is very low: in waste gases it is 10 to 50 ppm. In laboratory tests of the cyclic operation of the adsorbent (adsorption–regeneration), the service life of reacted sorbent was over 1000 h (Fig. 22).

Two variants of the ELSE process were developed: type 1 is marked in the Figure with a full line. The waste gases from a Claus system, heated up to a temperature of 313–923 K, are introduced into the absorber. H_2S reacts with ZnO to form ZnS and H_2, while COS and CS_2 form CO_2 and ZnS. At a temperature of over 813 K, SO_2 reacts with H_2 to form H_2S which is adsorbed. After being adsorbed, part of the gas mixes with air in order that the oxygen concentration is reduced to several per cent in order to control the regeneration temperature. The heat contained in the waste gas is recovered to produce steam. The spent zinc oxide is regenerated by means of diluted air at a temperature of about 923 K. Zinc sulphide becomes oxidized and decomposes with the emission of SO_2, which is passed back to the Claus system.

Variant 2 of the ELSE process is marked in the Figure with a broken line. The tail gases from Claus system, heated to 588–728 K, are introduced into the hydrogenation reactor containing a Co–Mo catalyst.

5.5.6. Other methods for reducing the emission of H_2S+SO_2 gases

Apparatus and technology for increasing the effectiveness of the Claus process are described in Ref. [42]. The solution consists of passing the gas containing SO_2+H_2S through several stable catalyst beds on which part of the sulphur formed is retained. During the first phase of loading the gas at the outlet from the first bed is heated above the sulphur condensation point, after which it is passed through the second bed in an attempt to recover sulphur. During the second loading phase the gas is passed, without further heating, through the second bed in order to cool it down and to separate sulphur in the cooled bed. After one of the beds has been subjected to full loading, the direction of the gas flow through both the beds is changed. Fig. 23 presents a diagram of this process. The solution given above has been described in a patent [43].

The removal of hydrogen sulphide and sulphur dioxide from the tail gas formed in a Claus reaction is done by passing the gas through the first catalyst bed containing sulphur at a temperature above the dew point, condensing the sulphur vapour by reducing the temperature, passing the gas through the second catalyst bed without the previously removed sulphur at a temperature below the dew point, and then in reversing the direction of the flow after the sulphur has previously been removed from the first bed and loaded onto the second bed. The improvement lies in separating the gas into two flows. One is passed through the first bed and the sulphur is removed, and then it is joined with the second stream and passed through the second bed. The method does not require the use of gas for regenerating the catalyst. The cost of the equipment for regenerating the catalyst is relatively low.

The Babcock–Hitachi firm has patented a method [44] in which the gas containing H_2S and SO_2 is introduced onto a movable catalyst bed. The sulphur produced on the catalyst grains is removed by steam. In this way the catalyst itself is regenerated. The regenerated catalyst (e.g. aluminium oxide) is passed back to the movable bed through the heater or cooler.

Sumitomo Heavy Industries [45] has patented a technique in which the catalyst in the Claus reactor is in the form of plates having a honeycomb or multi-pipe structures, on which metal oxide is precipitated over titanium oxide as a carrier. The raw gas flows along the vertical plates of the catalyst and there is no settling of sulphur on the catalyst plates.

It is possible to increase the effectiveness of the Claus process by using catalysts with increased activity. A catalyst proposed for the conversion of $H_2S + SO_2$ to sulphur is one with the composition Na_2O, Fe_2O_3, SiO_2, TiO_2, K_2O on Al_2O_3 as a carrier [46]. Exxon Research and Engineering Co. [47] has patented a technique which uses cerous oxide precipitated on an inert carrier (Al_2O_3) with thermal resistance for binding gases containing H_2S and SO_2 obtained from the Claus system. The gases are brought into contact with the catalyst at a temperature of 620 K with the access of O_2. As a result, cerium oxysulphate is formed and this is changed into CrO_2 in the presence of regenerative gases containing H_2 or H_2S. A regenerative gas may be one being fed to the Claus system.

Table 13
Action of SO_2 upon people [49]

Specification	Dose	
	(mg/l)	(ppm)
According to Lemon–Hess		
Lethal dose within 0.5–1 h	1.4–1.7	525–650
Danger dose within 0.5–h	0.4–0.5	150–190
Effect perceptible during many hours action	0.02–0.03	8–12
Dose sustained during 6 h without consequence	0.06–0.1	25–40
According to Zeechuisen		
Dose can be sustained during 3 min	0.12	50
Dose can be sustained during 1 min	0.3	120
According to Henderson–Haggard		
Small but still perceptible	0.008–0.013	3–5
Irritation of eyes	0.05	20
Irritation of mucous membrane	0.02–0.03	8–12
Induction of cough	0.05	20

The Aluminum Co. of America has patented [48] a catalyst which is resistant to sulphate poisoning. This is a catalyst of activated Al_2O_3/Na_2O type, characterized by the following properties: specific surface = over 100 m^2/g, Na_2O content = over 0.5%.

5.6. *Desulphurization of gases poor in SO_2*

The final waste product of the Claus process is SO_2 which is obtained as a result of oxidation of the mixture ($SO_2 + H_2S$) leaving the last Claus converter. The combustion products of coal, crude oil, fuel oil and of other energy raw materials (as presented earlier) also contain SO_2 in addition to other compounds. Sulphur dioxide is known to be very dangerous to living organisms. Table 13 presents data on its action on humans [49,50].

Desulphurization of tail gases containing SO_2 continues to be a major problem in the protection of the atmosphere. The problem lies in the diffi-

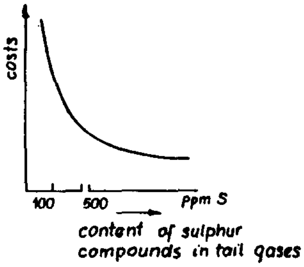


Fig. 24. Dependence of costs on sulphur content of tail gases.

culty of finding simple and economic desulphurization methods which would be suitable for hot gases. An additional difficulty is that gases are highly diluted, and the more a gas is diluted, the lower is the effectiveness of the process, and the higher are the costs of desulphurization (Fig. 24).

The wet methods in use require, in most cases, dedusting and precooling of the gases as well as a high consumption of raw materials. The use of the wet method results in a product which does not always sell readily. By making use of dry methods (adsorptive and catalytic ones) it is possible to obtain a product of commercial value. The product that is obtained most frequently and most readily is elemental sulphur. Fig. 25 presents the prospects for recovering sulphur from tail gases containing SO_2.

The basic stages of dry methods for desulphurizing tail gases are as follows:

(1) detecting and concentrating sulphur compounds;
(2) transforming these compounds to a chosen product;
(3) separating a given product from the adsorbent or catalyst.

The above three processes may take place in one or many appliances. The temperatures of the adsorption or desorption processes are different, as are the end products obtained.

Ad (1). A number of adsorbents are used for detecting sulphur compounds and their concentration.

Ad (2). In order to obtain the product, e.g. sulphur, a reduction process is used.

One of the most widely used methods for reducing SO_2 emission is to oxidize it to SO_3 and then to bind it by means of water or ammonia. The end products in this case are sulphuric acid and ammonium sulphate. Table 14 presents the most significant methods for removing SO_2 from tail gases.

Ad (3). Separation of sulphur formed on the adsorbent or catalyst is connected with desorption or refining processes.

Below we discuss some desulphurization methods for tail gases containing sulphur dioxide.

5.6.1. *Dry LIFAC method for tail gas desulphurization*

In recent years intense research has been carried out in Finland for developing an effective and economic method for tail gas desulphurization. Towards the end of 1984 Tampella Boiler Division started research into an effective, simple and economic desulphurization method which could be used in the power industry. They assumed the development of a dry method which would not produce sewage and would not involve the treatment of solutions and sludges. The LIFAC method [51] that has been developed is an improved method of dry desulphurization which consists in injecting limestone and activating non-reacted lime with water in a separate reactor. The system consists of a device for injecting limestone, an activation reactor, and a dust collector (electrostatic precipitator or cloth filter). The reaction product is a dry powder which is removed from

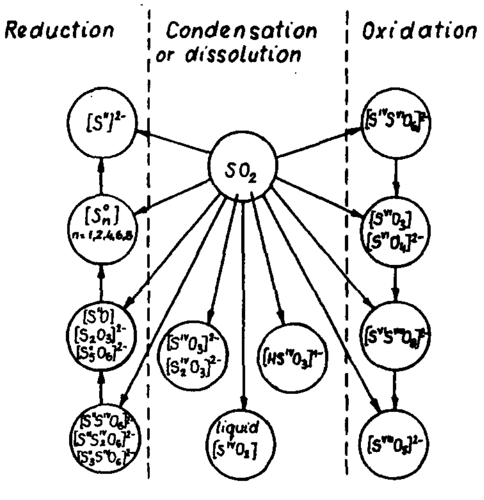
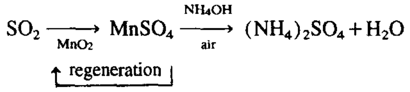
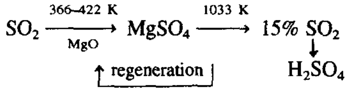
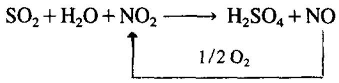
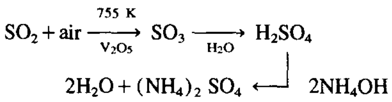
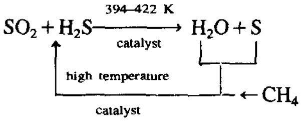
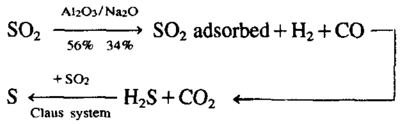


Fig. 25. Diagram of possible SO_2 conversion.

Table 14
A review of tail gas desulphurization processes taking place in the gaseous phase [37]. Processes carried out to obtain products containing S^{6+}

Type of adsorbent (method)	Annotation	Chemistry of the process
Dry lime or hydrated lime (T V A)	Reaction with lime in the presence of air, leading to the formation of sulphate or sulphite. Swedish Bahco process uses hydrated lime. FRG procedure according to Carl Still makes use of ash from brown coal	$CaCO_3 \rightarrow CaO \xrightarrow{SO_2,\ SO_3,\ air} CaSO_4 + CO_2$
Manganese dioxide (Mitsubishi)	Oxidation of SO_2 to sulphate by means of air, regeneration of MnO_2. Production of ammonium sulphate	 $SO_2 \xrightarrow[MnO_2]{} MnSO_4 \xrightarrow[air]{NH_4OH} (NH_4)_2SO_4 + H_2O$ regeneration
Magnesium active oxide (Chemical)	MgO is 'the collector' for concentrating SO_2, MgO is then regenerated. Concentrated gas containing SO_2 is oxidized to obtain sulphuric acid	 $SO_2 \xrightarrow[MgO]{366–422\ K} MgSO_4 \xrightarrow{1033\ K} 15\%\ SO_2 \downarrow H_2SO_4$ regeneration
Chamber of special construction (Tyco Labs., MA)	Special construction of chamber for gases desolved in water. NO?NO$_2$ are used as oxygen carriers.	 $SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$ $1/2\ O_2$
Modified contact process (Monsanto/Penelec) (Tokyo Tech.)	Typical contact process carried out to obtain sulphuric acid (Monsanto) or process performed to obtain ammonium sulphate. The above process has been developed, first and foremost, for diluted gases	 $SO_2 + air \xrightarrow[V_2O_5]{755\ K} SO_3 \xrightarrow[H_2O]{} H_2SO_4$ $2H_2O + (NH_4)_2\ SO_4 \longleftarrow 2NH_4OH$
Active carbon (Sulfacid Lurgi) (Hitachi, Tokyo) (Reinluft, Germany) (Westvaco Corp, USA)	All methods make use of different active carbons. Concentrated gases are oxidized catalytically to SO_3. Different forms of beds (fluidized, movable, stable) are used	$SO_2 \xrightarrow[active\ carbon]{air,\ H_2S} H_2SO_4$
Processes aimed at obtaining sulphur		
Sulfreen (SNPA Lurgi)	Catalytic action of active carbon. Gas flux contains H_2S and SO_2 (from Claus process)	$2H_2S + SO_2 \xrightarrow[active\ carbon]{} 2H_2O + 3/2\ S_2$
Catalytic process redox (Princeton Chem. Res., USA)	Modified Claus process consisting in using a highly active catalyst. In the case of H_2S deficiency it is obtained from a product	 $SO_2 + H_2S \xrightarrow[catalyst]{394–422\ K} H_2O + S$ high temperature $\leftarrow CH_4$ catalyst
CO/SO_2 redox (Chevron Research) (Univ. Mass.)	The process is also tested in respect of the presence of nitric oxides. At lower temperatures COS is formed	$SO_2 + 2CO \xrightarrow[811\ K\ Cu/Al_2O_3]{}, 2CO_2 + S$
Alcaline aluminium oxide (US Bureau Mines) (UK Central Elect Board)	Concentration of diluted SO_2 on alkaline aluminium oxide as well as catalytic reduction 'in situ' to obtain H_2S with the use of reforming gases containing H_2. H_2S passes into Claus system	 $SO_2 \xrightarrow[56\%\ \ 34\%]{Al_2O_3/Na_2O} SO_2\ adsorbed + H_2 + CO$ $S \xleftarrow[Claus\ system]{+SO_2} H_2S + CO_2 \longleftarrow$

the tail gas. The injection of limestone itself into the gas results in the secondary emission of dusts. This was counteracted by moistening the tail gases, which increased the effectiveness of the

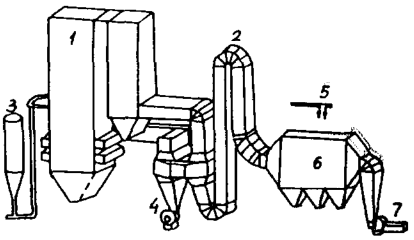


Fig. 26. Diagram of LIFAC system: 1 — boiler, 2 — activation reactor, 3 — limestone injection, 4 — air preheater, 5 — water injection, 6 — electrofilter, 7 — tail gas to chimney.

electrostatic precipitator and reduced emissions. The waste product of the LIFAC method may be utilized as landfill as it does not contain heavy metals which are harmful to health. The LIFAC method was tested in the Pohjolan Voima power station in Kristina on a 220 MW capacity boiler fired with coal dust. The first full-scale system of this type was put into operation in the Imatran Voima power station in In. The system was assembled on one of four power units. A diagram of the system is presented in Fig. 26.

5.6.2. Alkaline system for desulphurizing tail gases

The system of alkaline desulphurization of tail gases uses a dry method which has been developed especially for small boiler systems with a heating capacity of 1–10 MW, which are used for a short period during the year, while the installation costs are a greater consideration than the operating costs. The system is based on a simple concept in which the use of acid carbonate sodium ($NaHCO_3$) as an additive agent allows effective desulphurization at the 95% level. Owing to the very high reactivity of sodium bicarbonate, achieved by thermal decomposition in the air being supplied at a temperature of 423 to 523 K, the system can be effectively operated without a separate reactor and an end dust cleaner. The additive is blown by means of hot tail gases or hot air into the raw gas channel before being passed to the filter and mixing device. The mixer causes a uniform gas distribution in the whole cross-section of the channel. The residence time of the additive agent is determined, first and foremost, by the formation of a filter cake on filter sacks. It is taken for granted that the cloth filter is appropriate. A diagram of the alkaline method for desulphurization of tail gases is presented in Fig. 27. The principal reaction and the final separation take place in the ECOPULSE type cloth filter. When constructing the filter, particular attention was paid to an optimum gas distribution. The system is equipped with a compact, automatic bypass system which protects filtration materials from temperature fluctuations. The encased electric heating of the filtering funnel makes it possible for the separated dust to be removed without difficulty. This is sufficient for a minimum temperature to be maintained in the filter above the dew point during a short standstill. The regeneration of the filtration material in the ECOPULSE type filter is performed by an injection of compressed air. This makes it possible to maintain an approximately stable difference of pressures, depending on the loading of its surface.

The readily soluble salt formed in the above method for desulphurizing tail gases must be stored in special stacking yards. The course of reaction in the alkaline method is as follows:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \qquad (5.50)$$

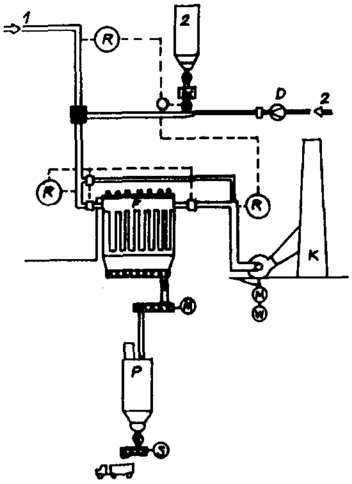


Fig. 27. Technological diagram of alkaline desulphurization of tail gases by the Flakt Company method for boilers of 1–10 MW: 1 — inlet of tail gases from boiler, 2 — inlet of hot air or tail gases (transportation agent). D — blower, F — cloth filter, K — chimney, M — engine, P — product tank, R — control system, S — feeding screw, W — fan, Z — additive agent tank.

(thermal decomposition of the additive agent)

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

(chemisorption) (5.51)

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

(oxidation to obtain the basic component of the final product). (5.52)

Among the advantages of the alkaline method for desulphurizing tail gases, one should also mention the a high effectiveness of desulphurization, optimum dedusting (20 mg/m^3), low capital costs, a dry final product, simple construction, absence of sewage, and low supervision costs.

5.6.3. System for desulphurizing tail gases on the basis of the CDAS method

The CDAS method (conditioned dry adsorption system) [52] is also a dry desulphurizing method but one including the pretreatment of waste combustion gases. It was developed for a boiler house with 3 to 50 MW heating capacity and with a high mean utilization time during the year. The boiler house operates on the basis of $Ca(OH)_2$ as an additive agent. The construction of the system is relatively simple but in comparison with the alkaline method, it is more expensive due to the use of an additive having a lower reaction efficiency. Depending on the type of slaked lime (powdered) and the final temperature in the cloth filter, the purifying effectiveness may attain 90%. The system (Fig. 28) consists of a complex reactor which contains a cooling section and a reactive part. The cooling of tail gases is advisable since reaction at a temperature of above 373 K is ineffective. Cooling in the vicinity of the dew point is the most reasonable in terms of stoichiometric ratios and effectiveness. The cooling section is built in the form of a cyclone through which tail gases pass, which results in the predusting of ash. Through the internal part the tail gases reach the upper part of the reactor and are subjected to the action of very small water drops, thus cooling them. In turn, this is followed by the reactive section, where the circulating material is blown in continuously. Fresh lime is blown in, depending on the sulphur dioxide concentration in the purified gas behind the filter. Added to the reactor is the original reactive zone to which waste gases are supplied which have been prereacted in the cloth filter. The secondary reaction is attained due to the formation of the filter cake and owing to this the full effectiveness of the desulphurizing process reaches 90%.

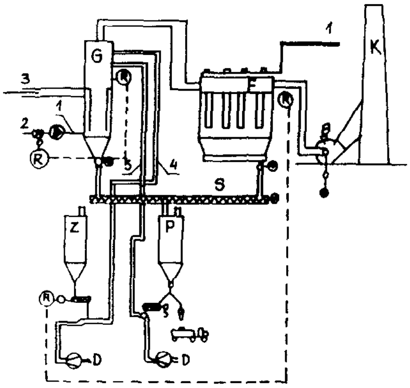


Fig. 28. Technological scheme of CDAS desulphurization of tail gases by the Flakt Company method for boilers of 1–50 MW: 1 — compressed air, 2 — water, 3 — inlet of gases from boiler, 4 — fresh lime, 5 — continuous recirculation. D — blower, F — cloth filter, G — reactor, K — chimney, M — engine, P — product tank, R — control system, S — feeding screw, W — fan, Z — fresh lime tank.

The systems of Flakt Industrialagen GmbH, producing final dry products, are being used in power stations, boiler houses, waste incineration, the ceramic industry and aluminium metallurgy. Unlike the wet methods, dry sorption methods have met with increasing approval for several years now and are increasingly wider found. The CDAS method is typical of these gas purification technologies, i.e. high desulphurizing effectiveness (up to 95%), optimum dust removal (<20 mg/m^3), low operating costs (Fig. 29), dry final product, low storage costs, low costs of the additive agent, recirculation potentiality, as well as fully automated operation.

5.6.4. The NIRO-atomizer method

This method is a modification of the well-known method for desulphurizing tail gases with milk of lime. It consists of using additives (sodium sulphate) having a catalytic effect and

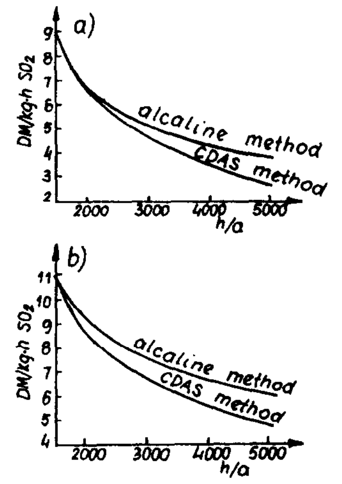


Fig. 29. Total operating costs for 1 kg/h SO_2: a — concerns the desulphurization process only; b — concerns the whole system.

making it possible to remove nitrogen oxides from gases in the presence of SO_2 and oxygen [53]. Tail gases (Fig. 30) are brought into the atomizing absorber, supplied with milk of lime suspension with the addition of NaOH or sodium versenate and of sodium sulphate. The dry product formed at 358–383 K is removed in an electrostatic filter or in sack filters. The binding of NO in the strictly determined temperature interval runs according to the reaction:

$$4NO + 3O_2 + 2Ca(OH)_2 \rightarrow \text{Catal. } 2Ca(NO_3)_2 + 2H_2O \quad (5.53)$$

on stable particles activated with sulphate. The method is characterized by the capital costs being the lowest among the dry methods. The product, however, has no commercial value. The effectiveness of NO removal ranges from 20 to 60%.

5.6.5. Desonox method

This method simultaneously removes sulphur and nitrogen oxides. The Deguss AG firm of Frankfurt am Main has carried out comprehensive research into the improvement of a method for removing SO_x and NO_x from tail gases. In one of the two sections of the system being tested the joint action of zeolite catalysts made it possible to transform nitrogen oxide (with ammonia added) into nitrogen and steam, while the use of an oxidizing catalyst permitted the optimum conversion of sulphur dioxide [54]. The pilot system operated for about 7000 h. The average effectiveness of tail gas purification achieved a 90% level. The favourable test results provided a confirmation of the correct choice made by Stadtwerke Munster (Department of Public Works, City of Munster) when they resolved to build a Desonox system, the cost of which will amount to 24 million DM.

Below we describe processes making use of coal-derived adsorbents for removing SO_2 from tail gases. Japanese firms have made great achievements in this field. Earlier technologies used the adsorption of sulphur compounds, e.g. SO_2, on coal material, i.e. coal, semi-coke, coke, active carbon, followed by SO_2 desorption at increased temperature. The desorption process was effected by means of tail gases or inert gas. The final product was SO_2 having a higher concentration than that in the inlet gases.

The group of sorptive–catalytic methods includes technologies making use of stationary beds of carbon sorbents in the simultaneous removal of nitrogen and sulphur oxides, the earliest among them being the Unitika method and Sumitomo Heavy Industries method developed in Japan in the 1970s. Tail gases with added ammonia are introduced onto the stationary bed of active carbon or coke at a temperature of 390 to 420 K, when sulphur dioxide is oxidized to the trioxide and is retained in sorbent pores in the form of sulphuric acid or ammonium salt. In parallel NO is reduced by steam and ammonia to obtain nitrogen and steam.

In connection with the decrease in its ability to catalyze NO reduction by the adsorbed sulphuric acid or its salts, the sorbent was subjected to regen-

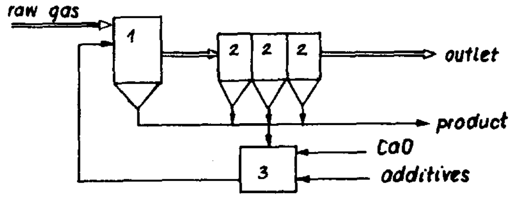


Fig. 30. Diagram of NIRO-atomizer process: 1 — reactor, 2 — separators, 3 — mixer.

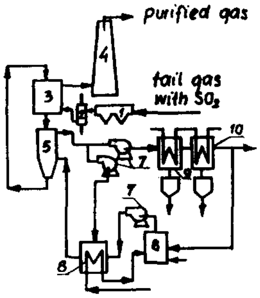


Fig. 31. Takeda process: 1 — dedusting device, 2 — heat exchanger, 3 — adsorber, 4 — chimney, 5 — desorber, 6 — generator of regeneration gas, 7 — blower, 8 — preheater, 9,10 — condensers.

eration at 620–870 K with the emission of gases containing up to 30% SO_2, which were processed to sulphuric acid, liquid SO_2 or elemental sulphur. The single-stage SUMITOMO process developed on an industrial scale of 300 000 m^3/h in Matshima in 1983 was characterized by a relatively low efficiency of nitrogen oxide reduction (50%) [53].

5.6.6. The Takeda process

In 1972 the Japanese firm Takeda Chemical Industries patented a new technology for desulphurizing industrial gases based on SO_2 adsorption on active carbon. The regeneration of the adsorbent is carried out by blowing it through with gas containing carbon monoxide and/or hydrogen at a concentration of at least 40% [55].

Fig. 31 presents a diagram of a system proposed by the Takeda company. After passing through the dedusting device 1, the gas contaminated with sulphur dioxide becomes cooled down in the exchanger 2 to a temperature ranging between the dew point and 650 K. In the adsorber 3, which is an apparatus with a movable bed of any type, a practically complete binding of SO_2 takes place: the purified gas is expelled into the atmosphere through the channel 4. In the desorber 5 the regeneration of active carbon takes place and after that the adsorbent is conveyed to the apparatus 3 where it is used again. After leaving the desorber, a large part of the gas is recycled through the heater B, while the remaining gas is directed to the SO_3 recovery section. In the condenser 9 the gas is cooled down to about 274 K in an attempt to separate inappreciable quantities of dilute H_2SO_4. The precipitation of liquid SO_2 takes place in the condenser 10 at a temperature of 230 K, while the remaining gas containing carbon monoxide and/or hydrogen is carried away to the utilization centre.

5.6.7. The Sulfacid process

The process of SO_2 adsorption on active carbon, referred to as the Sulfacid process, has been developed by Lurgi Apparate-Technik GmbH, Bergbau-Forschung and Babcock and Wilcox. Although it is used mainly in chemical plants producing H_2SO_4 by the contact method it may successfully be used for desulphurizing any gas containing 0.1–1% SO_2 and at least 5% free oxygen, e.g. for reducing the SO_2 content in the tail gases from liquid fuel-fired power stations. Considering the fact that the gas flux cannot contain more than 20 mg of dust/m^3, the Sulfacid process is unfortunately unsuitable for use in coal-fired power stations. It is desirable in the Sulfacid process that the gas introduced into the adsorber should be sufficiently cool. In this process sulphuric acid is obtained [55].

5.6.8. The Bergbau-Forschung/Uhde

The Sumitomo method became a starting point for the Bergbau-Forschung/UHDE (BF) process which has been developed in Germany. The process has been put into operation in a two-stage reactor (Fig. 32) with a movable bed of active coke at a temperature of 350–420 K. The dedusted

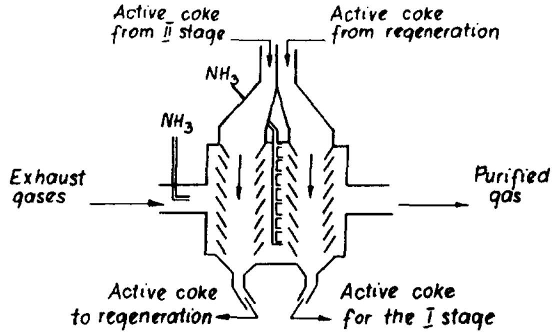


Fig. 32. Two-stage adsorber.

waste gases are introduced into the first stage of the reactor in which SO_2 adsorption and its conversion into sulphuric acid generally proceed with the use of oxygen and steam contained in gases. At the same time other gas components, such as HCl and HF as well as heavy metals and the remaining dust, are adsorbed.

The gases, from which about 80% sulphur dioxide has been removed, are supplied with additional ammonia and introduced into the second stage, supplied with the sorbent from the regeneration. Here the oxide is reduced to nitrogen and the remaining quantity of SO_2 is bound. The sorbent from the second stage, containing negligible quantities of sulphuric acid and ammonium sulphate, is utilized in the first stage and then passed back to the regeneration stage, running at 823–873 K. After regeneration the gases are converted into sulphuric acid, liquid SO_2 and elemental sulphur.

During 1979–1985 the process was tested, first in a prototype system in Lünen (Germany) and then in four pilot systems, each having a capacity of 12 000 m^3/h. The information obtained was utilized to design an industrial plant with a capacity of 1200 m^3/h, which was put into operation in 1987 in a brown coal-fired power station in Arzberg (Germany).

5.6.9. The Westvaco process

Fig. 33 presents a diagram of the system developed by the American Westvaco Corporation, consisting of five basic parts in which the following processes are performed: adsorption of SO_2 (I), cooling of the adsorbent (II), formation of elemental sulphur (V), recovery and processing of sulphur (IV), and generation of reducing gas (III) [55].

In the first adsorption stage only sulphur trioxide is in practice removed from the hot inlet gas, after which the gas leaves the apparatus and is cooled down. On the four successive shelves of the adsorber over 90% of SO_2 becomes bound. After that, active carbon is conveyed by means of an elevator to the top of the column where its regeneration begins. The adsorbent is first subjected to the action of hydrogen sulphide which reduces H_2SO_4 to sulphur, and in the succeeding section this is followed by a high-temperature recovery of about a quarter of the adsorbed sulphur through direct evaporation in a jet of the recirculating steam.

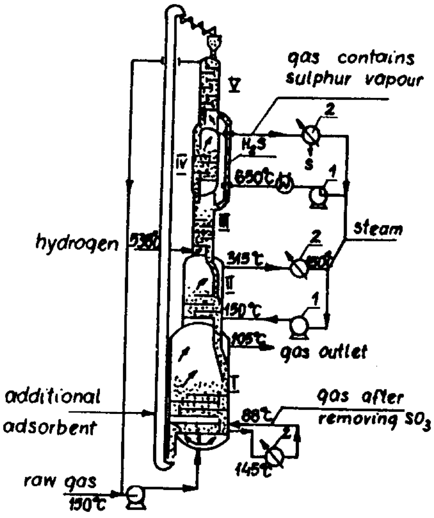


Fig. 33. Westvaco process: I — adsorption section, II — adsorber cooling block, III — H_2S generator, IV recovery and sulphur processing, V — elementary sulphur processing. 1 — blower, 2 — heat exchanger

The remaining part of the sulphur reacts with hydrogen to form hydrogen sulphide, which is used in the first regeneration stage. The hydrogen necessary for this reaction is supplied from outside the system. After being cooled to 423 K the carbon may be re-used for SO_2 adsorption.

In broad outline, the Westvaco process consists in desulphurizing gases at the cost of the use of a certain amount of hydrogen with the simultaneous production of sulphur as a by-product. Owing to the use of a fluidized system the dustiness of the inlet gas does not cause the operation of the system to be disturbed.

5.6.10. Other solutions to dry desulphurization of gases containing SO_2

Numerous companies are working on the problem of increasing the effectiveness of dry desulphurization methods by using different new solutions or well-known modification techniques.

Modifications consist of introducing appropriate adsorbents or catalysts that make it possible to obtain the required final product, to reduce the energy-consumption of the process, to increase the effectiveness of the process by using special appliances permitting the reagents to be brought into almost perfect mutual contact, as well as to introduce some additional substances to increase the conversion of sulphur compounds.

Babcock–Hitachi KK proposes the following solutions [56]: the tail gas containing SO_2 is brought from the adsorption tower into contact with an adsorbent containing carbon on which SO_2 is adsorbed in such a way that the purified gas that does not contain SO_2 is carried away from the column. The adsorbent containing SO_2 is heated to 620–720 K in the desorption column to obtain desorbed gas containing SO_2, CO_2, H_2 and N_2. In the reduction column the gas is brought into contact with a reducing agent containing carbon at a temperature of 958–988 K. SO_2 is reduced to sulphur and after it is precooled in the cooler, liquid sulphur is obtained. The tail gas from the cooler, containing H_2S and carbonyl sulphide, is supplied to a Claus reactor and cooled in the cooler, collecting liquid sulphur from it. Consumed reducing agent is burned down in the furnace. The hot combustion gases form a heating medium.

An increase in the effectiveness of the desulphurization process can be achieved by using ammonia. The Babcock–Hitachi, Sumitomo Heavy Industries, and Bergwerkeverband GmbH companies recommend adding ammonia to the tail gas [57–59]. In the case of the presence of nitrogen oxides in the gas this acts as a reducing agent. Nitrogen is obtained as a result of the reaction. In the presence of SO_2, ammonia forms NH_4HSO_4 and $(NH_4)_2SO_4$, which are adsorbed on coke or another coal material. As a result of desorption, SO_2 is obtained again, but in a concentrated form, as well as steam and NH_3. This mixture is brought into contact with semi-coke in order to obtain elemental sulphur [60].

The Bergwerkeverband GmbH recommends introducing NH_3 into tail gases at a temperature of 380–450 K [57,61,62]. The tail gases are passed through two movable beds of granular adsorptive material, arranged perpendicularly to the gas flow in the downward direction, containing carbon and a catalyst. In the first bed the majority of sulphur oxides are removed, whereas in the second bed, in the presence of gaseous ammonia there follows a catalytic reduction of nitrogen oxides to free nitrogen as well as a separation of further quantities of sulphur oxides. The introduction of NH_3 into the space between the two layers causes it to become well mixed with the flowing gases, which significantly increases the effectiveness of the process. A large number of companies are now using catalysts instead of carbon, on which SO_2 undergoes a reduction to elemental sulphur in the presence of a reducing gas such as H_2 or CO [63,64]. The catalysts may be Ca, Mg, Fe, or Cu oxides precipitated on a carrier (bauxite, aluminium oxide, silica, titanium oxide), Ni, Co, Mo [63], iron and manganium oxides [65], copper oxide precipitated on tungsten, titanium or aluminium oxides [66,67].

Mitsubishi Heavy Industries [67] has solved the problem of removing nitrogen and sulphur oxides in the following process: the tail gas is brought into contact in a reactor containing a catalyst (copper precipitated on tungsten, titanium and aluminium) in order to remove NO_x and SO_x from the gas. Part of the catalyst is introduced into the regenerator in an attempt to regenerate it under the action of the gas containing H_2 and/or CO and to produce gas with a significant SO_x concentration. The regenerated catalyst is passed back to the reactor. The gas with a high SO_x concentration is brought into contact with carbon in the reducing device for reducing SO_x to sulphur, which undergoes condensation in the condenser. The carbon that has been consumed is partly burned with the air in a furnace designed for generating H_2 and/or CO. The gas is returned to the regenerator for regenerating the catalyst (Fig. 34).

Exxon Research and Engineering Co. [47] proposes the removal of SO_x and NO_x from gases by bringing them into contact with CrO_2 at 770–970 K in an attempt to remove SO_2 to generate cerium oxysulphate and next by bringing the gas that has

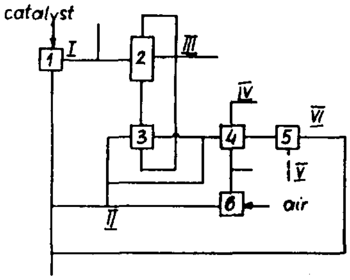


Fig. 34. Purification of flue gases according to Mitsubishi Heavy Ind.: 1 — catalyst tank, 2 — reactor, 3 — regenerator, 4 — reduction device, 5 — sulphur cooler, 6 — furnace for H and/or CO processing. I — flue gas, II — reduction gas, III — regenerated catalyst, IV — carbon, V — sulphur, VI — purified gas.

been formed with cerium oxysulphate in the presence of ammonia at 770–970 K under oxidizing conditions to removing NO_x. The above process may be carried out in one or more reaction zones. CrO_2 may be regenerated through the reaction of cerium oxysulphate with a reducing gas, e.g. H_2. The advantage of the process is that the contamination of both gases is removed in one process and at the same temperature.

The Standard Oil Co. [68] carries out the removal of sulphur oxides from gas by means of SO_x adsorption at a temperature of 370–1170 K on an adsorbent containing MgO and at least one free or bounded rare-earth element metal chosen from La, Le, Ir, Sm, or Dy, followed by the removal of adsorbed SO_x by means of hydrocarbon in the presence of a cracking catalyst. At a temperature of 650–1170 K a gas containing hydrogen sulphide is obtained. This process is particularly suitable for reducing SO_x from the exhaust gas from the regenerator in equipment designed for catalytic cracking. A similar process is presented in the patent [69], the difference being that the catalyst used is Al_2O_3 with lanthanum precipitated on it.

Mitsubishi Heavy Industries [70] recommends the following process for tail gas desulphurization with sulphur recovery. The tail gas containing SO_x is brought into contact with an adsorption agent for adsorbing SO_x. The adsorbent with the adsorbed SO_x is acted upon by steam to desorb gas rich in SO_x. Part of this gas is turned back by the heat exchanger, while the remaining gas is passed, through the heat exchanger, to the reduction furnace from where the reduced gas is obtained. Next it is introduced into the furnace where elemental sulphur is obtained. The tail gas contains H_2S and COS. The improvement lies in the gas being directed to the combustion furnace from which tail gases containing SO_2 are obtained and these, after being passed through heat exchangers and the preheater, are joined with the tail gas at the inlet to the system.

The desulphurization of gases with the use of the hydrogenation, dehydration and then oxidation processes is proposed by the Union Oil Co. of California [71]. Raw gas is brought into contact with a hydrorefining catalyst in the presence of steam, H_2, CO or a mixture of it at 420–695 K, which results in at least 80% of sulphur compounds undergoing conversion to H_2S through hydrolysis and hydrogenation. The gas is dried until the amount of steam falls below 15 vol.-%. A mixture of the hydrorefined, dehydrated gas and gas containing O_2 is brought into contact with the oxidation catalyst at 390–500 K, which results in at least 80% of H_2S being oxidized to sulphur. The free sulphur is separated from the gas. The recommended hydrorefining catalyst is a mixture of oxide and/or metal sulphide of Cr, Mo, W with oxides or sulphides of Fe, Co, Ni, whereas the recommended oxidation catalyst is the same oxide or vanadium sulphide precipitated on porous oxide. The firm claims that this procedure is inexpensive, economic, and suitable for the treatment of raw natural gas, raw refinery gases, gases obtained from coal gasification, and tail gases from the Claus process, after their hydrogenation.

UOP Inc. recommends [72] a process for separating inorganic sulphur oxides from gaseous mixtures. It consists of bringing a flux of gases into contact with a stable sorbent of sulphur oxides. The sorbent contains copper, copper oxide or a mixture of copper and oxide dispersed on a carrier together with 0.01–1 wt.-% of the platinum metal or platinum oxide (in relation to the total mass of the sorbent) and 0.01–1 wt.-% of germanium, rhenium, tin or oxides of these metals.

The gas is brought into contact with the sorbent at 420–720 K. After use the sorbent is regenerated with the reducing gas. The sorbent ensures the appropriate removal of sulphur oxides from tail gases and makes it possible to release gases into the atmosphere. The presence of the platinum metal (particularly palladium or Pt + Pd) and Ge, Re or Sm accelerates the regeneration of the sorbent and reduces a tendency to the formation of copper sulphide in the course of regeneration. In this connection regenerated sorbent with the optimum ability to adsorb SO_2 is obtained.

Mitsubishi Heavy Industries [73] recommends the following process: the tail gas containing SO_2 is supplied to the desorption zone of the gas containing SO_2 and to the regenerating zone. The cooling gas is brought into the regenerating zone. One part of the gas containing SO_2 is returned to the desorption zone and the remaining part is brought into the furnace where SO_2 is reduced to sulphur by hydrogen. A small amount of gas containing SO_2 is supplied to a flowmeter and a concentration sensitive detector, and the values obtained are processed by a computer which gives the quantities of SO_2 in the gas. An increase in the effectiveness of the desulphurization process is also achieved by passing the tail gas through a catalyst of special construction, e.g. a honeycomb [74]. The catalyst elements arranged in a series parallel to the flow of gases maintain a stable velocity distribution. This ensures the effective utilization of the catalyst.

An interesting solution is the process recommended by Combustion Engineering [75]. The reactor packing of sodium carbonate and carbon material is maintained at a temperature of above 1150 K in a reducing environment, which causes vapours of elemental Na to be liberated. The rising vapours react with oxygen supplied over the surface of the packing in order to produce Na_2O vapours which are introduced into the tail gas. The Na_2SO_4 produced then undergoes precipitation. This method is profitable when the tail gas comes from a glass-furnace into which sulphate returned as part of the furnace charge. The reactor packing can be made of salts, soda, or organic acids, particularly of spent paper liquor. The process is presented diagrammatically in Fig. 35.

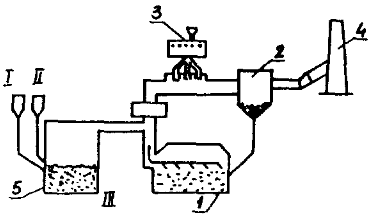


Fig. 35. Removal of sulphur oxides from flue gases of glass furnace: 1 — glass furnace, 2 — sediment tank, 3 — sprinkler, 4 — chimney, 5 — tank of raw materials. I — sodium carbonate, II — carbonaceous material, III — air.

In power stations fuelled by fine coal, where current is provided by steam turbine sets, the desulphurization process is carried out in a fluidized bed outside the furnace [76]. The fluidized bed operates at 1070–1170 K with the addition of substances to bind sulphur, such as dolomite and limestone. The gases are reduced in temperature, depending on the temperature of the furnace, when heat is given up by gases in the boiler. After leaving the fluidized bed the tail gases are subjected to a dedusting treatment. This technique is useful for fine-coal fired steam electric power stations where the coal is burned in combustion chambers. Since the optimum desulphurization temperature is maintained in the fluidized bed, the bed and boiler may be of moderate size. The waste heat is utilized to the highest degree.

Foster Wheeler Energy intends to patent a process in which sulphur dioxide is removed from tail gases by passing them through a movable bed consisting of particles of hot carbon in an attempt to reduce sulphur dioxide to elemental sulphur which is removed from the bed [77].

SO_x is removed from tail gases in a ‘dry’ desulphurizing appliance by feeding a granular adsorbent to an adsorption tank, where it is brought into contact with the tail gas flowing horizontally through the tank. The improvement of the process lies in the fact that the adsorbent feed rate is higher from the side of the tank supplied with the tail gas than on the opposite side of the tank, i.e. where the purified gas is removed. In this way a higher

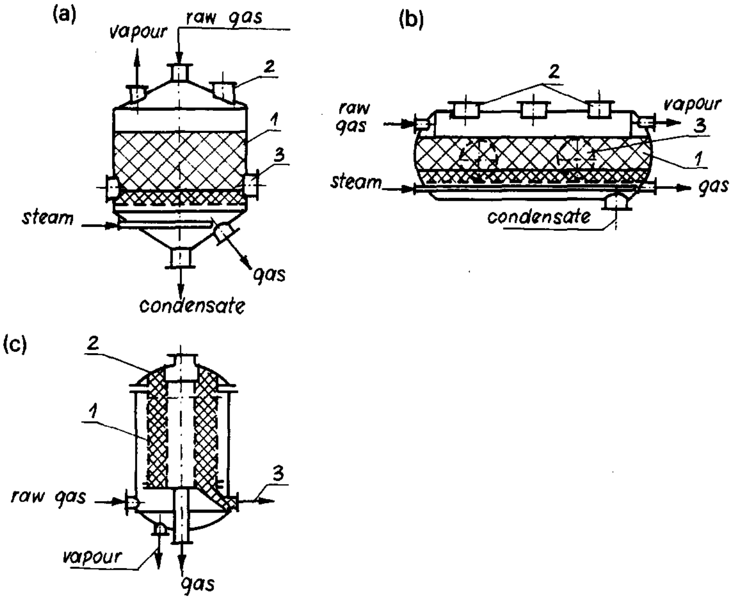


Fig. 36. Adsorbers with stationary bed: a — vertical, b — horizontal, c — with ring layer. 1 — adsorbent layer, 2 — load hatch, 3 — unload hatch.

adsorption efficiency is achieved and the blockage of conduits with the adsorbent is avoided [78].

5.7. Equipment used in gas desulphurization processes

5.7.1. Adsorbers with a stationary layer

If the gas flow is negligible and, furthermore, periodic, containing a variable type of impurities, then with a low concentration of impurities in the flow it may be economical to use adsorbents in the form of layers with an appropriate shape that do not undergo regeneration. The carriers of the adsorbing substance are usually cellulose layers or fibres with an appropriately high carbon content. The layer is changed when its capacity starts to approach saturation. In an attempt to avoid transferring impurities to the environment, one of the most frequently used methods for dealing with the layers is their combustion, or regeneration of the adsorbent in the case when the loads are accumulated in such amounts that this becomes a remunerative business.

When the gas flux is so strong that the cost of a new adsorbent would be too high in relation to the cost of regeneration, then the adsorption process is carried out in adsorbers with a stationary regenerated layer. Such an adsorber (Fig. 36) operates until a state corresponding to the breakdown point is achieved. The inflow of the contaminated gas is then cut off and the layer regeneration cycle is started [79].

Depending on the height of the adsorbent layer, a distinction is made between adsorbers with thin or thick layers. Thin layers are placed between barriers, the preferred partitions often taking the form of nets. On account of the sorption ability of such a layer, a large number of layers are usually placed in the adsorber. The gas flow is most frequently directed from the top, which makes it possible to use greater linear gas velocities without tending to destroy the structure of the layer. The advantage of this type of layer is the relatively negligible drop in gas pressure which it confers.

Adsorbers with layers of thickness 0.25–1.0 m usually take the form of long, horizontal tanks in which the layer rests on a sieve partition. The greater height of the layer makes it possible to carry out the process without regeneration for a longer time, but the drop in the gas pressure is higher. Complications may also be caused by the adsorption heat carried away, and therefore the

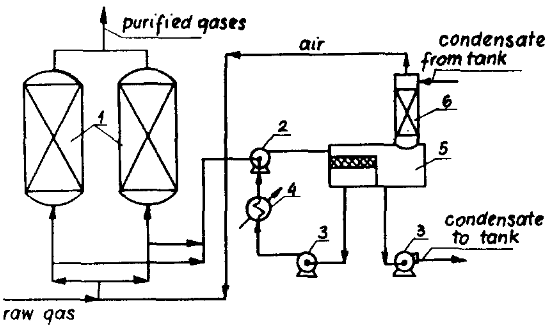


Fig. 37. Adsorption system with carbon vacuum regeneration: 1 — adsorbers, 2 — vacuum pump with liquid ring, 3 — liquid pumps, 4 — coolers, 5 — separator, 6 — scrubber.

use of thick layers is not recommended when the concentration of impurities exceeds 100 ppm.

If the gas flux is not periodic, it is necessary to use at least two adsorbers to carry out adsorption continuously. If the process of adsorption is carried out in one apparatus, the regeneration of the adsorbent takes place in the other one.

One of the most commonly used regeneration techniques is heating the layer, which results in the desorption of adsorbed impurities. Common steam or hot air are used in this process. Heat regeneration is used when the concentration of impurities is comparatively negligible and the required effectiveness of adsorption is high. After regeneration, the adsorbent should usually be dry and cooled down to ambient temperature. Heat regeneration is also carried out by unloading the saturated adsorbent, which is usually active carbon, and then by drying, sintering and activating it. This process is performed in vertical-rake ovens or drum-rotary ones at 1150–1250 K.

In the course of vacuum regeneration, which is usually carried out after adsorption under atmospheric pressure, impurities are adsorbed as a result of the formation of a vacuum in the adsorber (30–60 kPa pressure). The build-up of pressure as well as the sucking in of steam is most frequently accomplished by means of a water-ring pump (Fig. 37).

5.7.2. *Adsorbers with a movable layer*

In adsorbers with a movable layer the adsorption process runs continuously without switching off the apparatus while the layer is regenerated. As a result the gas purification process becomes intensified. The basic element of the adsorber with a movable layer is a vertical, cylindrical column, either with or without shelves (Fig. 38). The flow of the adsorbent being regenerated is passed to the top of the column from where, under the influence of gravity, it is shifted downwards, or poured by weirs when the column is equipped with shelves. Flowing in from the bottom of the apparatus the contaminated gas flows upwards through the empty channels where the adsorption of impurities takes place. The purified gas leaves the apparatus through its upper part. In the shelf adsorber the gas flows through the holes of the shelf and causes the adsorbent grains to move towards the weirs and to fall from shelf to shelf (Fig. 39). When leaving the adsorption section the saturated adsorbent is directed to regeneration, which takes place in the bottom part of the column, referred to as a desorption column. The heating agent is steam transmitting heat to the grains of the saturated layer falling down in the pipes of the exchanger.

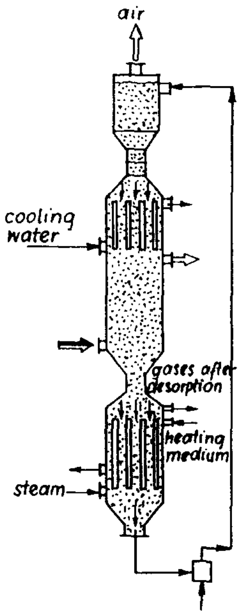


Fig. 38. Diagram of continuous adsorption with movable (dropping) adsorbent layer: 1 — adsorption column, 2 — adsorber (heat exchanger), 3 — adsorbent cooler, 4 — separator.

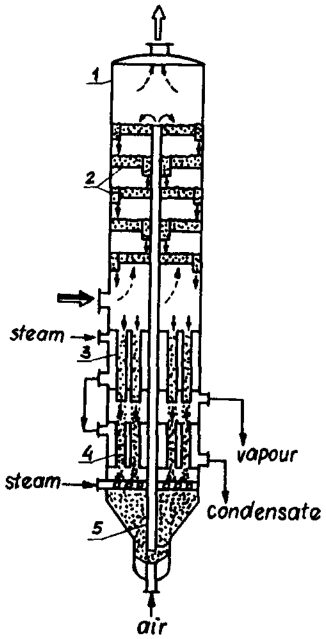


Fig. 39. Diagram of shelf adsorber: 1 — column, 2 — shelves, 3 — preheater, 4 — desorber, 5 — circulation pipe.

The continuous desorption of impurities takes place in the upper zone of the desorber from where steam is usually directed to undergo condensation. The hot and wet adsorbent leaving the bottom zone of the desorber is transported by means of a cool and dry air jet to the upper part of the adsorber, the grains of the adsorbent being dried and cooled.

5.7.3. *Fluidized bed adsorbers*

The adsorption process in a fluidized adsorbent layer may be carried periodically or continuously.

The drop in the effectiveness of the adsorption process, the low degree of saturation of the adsorbent and the unsatisfactory efficiency of gas purification connected with the heterogeneity of the grains are reasons why adsorption in a single fluidized bed has not found practical application. These defects are to a great extent eliminated in multistage adsorbers in which, in an attempt to approach the countercurrent flow of phases and thus to improve the efficiency of adsorption, the adsorbent bed is divided into stages.

In such a system the advantages of the fluid bed are put to use, e.g. the possibility of collecting the adsorption heat by placing in the bed elements to carrying away the heat (coils), the drop in the gas pressure being an approximation to a stable gas pressure, and the increased flow of the purified gas.

A multistage system is also preferred when there is a need for frequent regeneration of the bed. In the system shown in Fig. 40 the adsorbent undergoes circulation through the adsorption and regeneration zones. The saturated adsorbent is transported to the upper transitory tank and is continuously supplied to the downward shifting layer, which is regenerated in countercurrent by a steam jet. The regenerated adsorbent, flowing onto the first shelf of the adsorber, is subjected to fluidization by means of the flow of gas being purified and is poured with overflows onto the successive shelves lying at a lower level. Under stationary conditions a mean gain in mass of the adsorbed substance takes place on each shelf. This basic appliance for adsorbing impurities from tail gases often makes use of patented improvements.

5.7.4. *Different solutions to systems for adsorbing SO_2 or other sulphur compounds from gases*

Mitsubishi Heavy Industries [80–83] uses a cylindrical apparatus for adsorbing sulphur oxide contained in tail gas. In this equipment the rotary

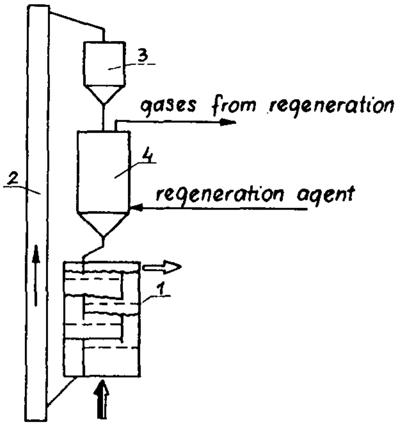


Fig. 40. Diagram of fluidized bed adsorber: 1 — multi-shelf fluidized bed adsorber, 2 — conveyor, 3 — intermediate tank, 4 — adsorber regenerator.

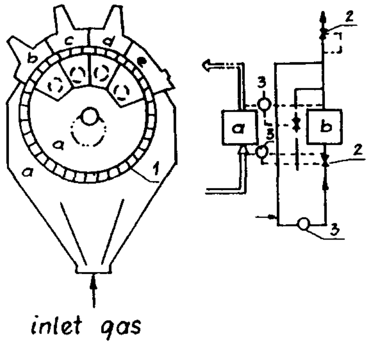


Fig. 41. Device for adsorbing sulphur oxides according to Mitsubishi Heavy Ind.: 1 — rotary cage element, 2 — control valves, 3 — heat exchangers. a — adsorption zone, b — preheating zone, c — desorption zone, d — cooling zone.

cage element filled with active carbon passes through adsorption, heating, desorption and cooling zones (Fig. 41). In such a system the precise sealing of particular zones is difficult on account of thermal stresses as well as poor workmanship. In this connection the gas flow for each of the zones is automatically controlled so that pressures in the adjoining zones are different. A movable bed of the coal adsorbent is also used by the Mitsui Mining Co Ltd. [84]. Berkwerksverband GmbH [85] removes sulphur oxides from tail gas by passing it crosswise through the reactor in which the layer of the granular adsorbent moves slowly downwards (Fig. 42). The reactor is equipped with a heat exchanger consisting of a number of vertical pipes through which the cooling water flows upwards between the horizontal branching pipes. The gas flows between the cooling pipes of the exchanger, which are arranged at appropriate distances, and the side walls through which the gas enters and leaves the reactor have inclined, parallel gaps. The reactor may have a cylindrical or a flat shape. As the adsorber one may use active carbon or molecular sieves. This technique is particularly suitable for purifying gases emitted by power stations. By way of example, cooling improves the desulphurization effects from 62 to 97%, and the example quoted processes 120 000 m^3/h tail gas at a temperature of 420 K, desulphurizing and cooling it to 360 K in the reactor in which the cooling water with a flow intensity of 520 m^3/h is heated from 330 to 370 K. The adsorbent remains in the reactor for 60 h.

Foster Wheeler Ener [86] has presented a rotary sieve separator for separating tablets of active carbon from the mixture being a heat exchange agent, i.e. from sand. The above device is provided with a sieve with holes, having an inlet for supplying a mixture. The sieve rotates, which causes the medium exchanging the heat to pass through the sieve holes and to fall into the first basket placed directly under the sieve. The carbon tablets pass trough the outlet holes and fall into the second basket placed near the first basket.

Energy Pollution presents a device for desulphurizing the tail gas from boiler furnaces [87] making use of dry reactive sorbents for removing impurities. Impurities in the form of gases or stable particles are removed from tail gases by means of sorption or reaction with a sorbent disintegrated into particles or with a reagent containing no liquid. From the place where it is formed, the tail gas is transferred downwards through a vertical conduit to the emission point, while the sorbent or reagent particles are uniformly introduced into the gas flux which carries them away. The gas with the particles carried away starts a countercurrent circulation so as to lengthen the contact time with impurities. Next the direction of the gas flow changes to separate the stable particles, and the pure gas is directed to the emission point. This is a dry process which makes it possible to remove 95% impurities from gas. The apparatus is char-

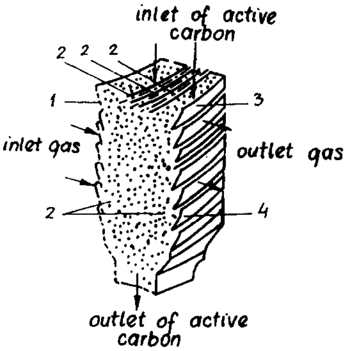


Fig. 42. Adsorber with special construction according to Berkwerksverband GmbH: 1 — reactor, 2 — cooling pipes, 3 — shelves, 4 — gaps.

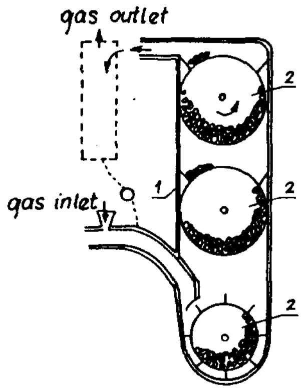


Fig. 43. Fluidized bed column for removing damaging gas components: 1 — column, 2 — drums filled with balls.

acterized by a low drop in pressure and need not be made of corrosion resistant material since no aggressive solutions are formed. The vertical fluidized column for carrying out the gas reaction with stable particles which adsorb damaging components from the gas has a rectangular cross-section and appropriately spaced rotary sieve drums occupying the whole cross-section of the column. The drums are filled with balls or other elements. The gas together with the stable adsorption particles is introduced at the base of the column. The drum situated at the lowest level has a reduced diameter and radial protrusions on the blade circumference, which prevents the stable particles from accumulating at the bottom of the column. The remaining drums are equipped with external plucking elements protecting them from the effect of stable particles getting between the drums and the walls of the column. This technique is particularly suitable for removing HCl, HF, SO_3, and SO_2 from tail gases. The fluid bed in the column, having the structure described above, is characterized by uniformity, i.e. no gas channels or fissures are formed in it, which may cause the efficiency of the gas reaction with the stable particles to be reduced. The gas issuing from the column may be separated from the stable particles and returned to undergo the adsorption process. Fig. 43 is a diagram of the above appliance.

Mitsubishi Heavy Industries [88] presents a solution in which the adsorbent collector has a cylindrical shape. The cylinder rotates on the horizontal axis. The appliance aims collecting the adsorbent with the gas tightness of the collector being maintained. The charging hopper is equipped with a tilted closing plate moved by means of a slide block. The entry of the inlet funnel for tilting closure is sealed with a bellow which ensures tightness.

An increase in the desulphurizing efficiency of tail gases may be obtained by using an appliance with corrugated plates arranged in front of the gas inlet to each of the adsorption chambers parallel to the direction of the gas flow [89] or with the use of an appliance (Mitsubishi Heavy Industries) [90] provided with internal or external pipes mounted on the rotary base. Between the pipes there are partition walls, each of them being filled with an adsorbent. In order that the gas is treated without leakage from the chambers, both pipes are equipped with supports to form a rotary element. The upper and bottom gas channels are fixed to the upper and bottom ends of each chamber. The gas in the chambers flows from the bottom to the top. There are water seals between the gas channels and the chambers.

A very simple adsorption system for desulphurizing tail gases, with a perforated box containing gas-permeable cylinders filled with a granular adsorbent, e.g. active carbon, is recommended by Babcock–Hitachi [91]. The tail gases coming from coal-fired boilers contain a large amount of dust. The appliance for removing dust and SO_2 from tail gases is presented in Fig. 44. The way the appliance operates is very simple. The box 1 has round openings 3 in two opposite walls 2. Cylinders 4 made of gas-permeable material, e.g. wire net, are in the box 1. They are placed in such a way that each cylinder connects two

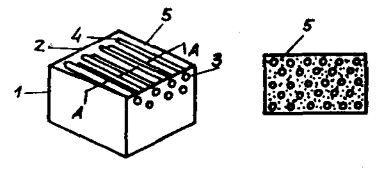


Fig. 44. Adsorption device for desulphurizing flue gases, produced by Babcock—Hitachi Company: 1 — box, 2 — perforated walls, 3 — openings, 4 — cylinders, 5 — active carbon.

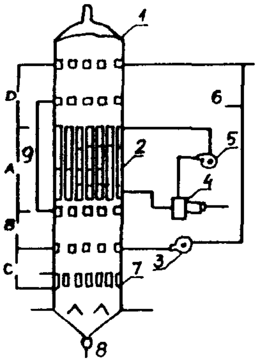


Fig. 45. System for gas desulphurization according to Sumitomo Heavy Ind.

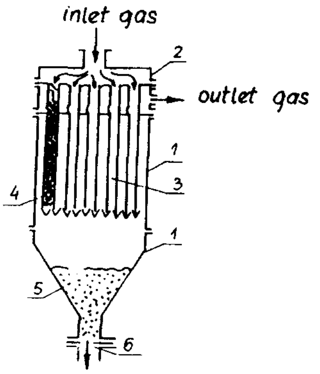


Fig. 46. Catalytic reactor for flue gases: 1 — jacket, 2 — perforated plate, 3 — contact pipes, 4 — spiral channel, 5 — conical bottom, 6 — pipe for removing ash, / — connector.

opposite openings 3. The granular adsorbent 5, e.g. active carbon, fills the box outside the cylinders 4. The tail gases containing SO_2 and fly-ash flow into the box 1 through the openings 3, while SO_2 present in the gases diffuses to the adsorbent 5 through the cylinders 4.

Another solution to the adsorber is a shutter-like construction [92]. This type of construction keeps the charge of comminuted material in a vessel provided with axially arranged inlet and outlet connector pipes in the perpendicular as well as axially arranged inlet and outlet connector pipes in the horizontal. As a supplement to the normal set of shutters the construction is provided with additional sets of midshutters. All of them are inclined downwards and to one another, while midshutters are placed between the main shutters.

The flue gases (at 570–670 K) are transmitted from the steam producer to the main heat exchanger where they are cooled down to 470 K. The gases are then passed through equipment to remove ash and then directed to the adsorber where SO_2 is removed. After SO_2 is adsorbed the purified gases are released to the atmosphere [93]. Noteworthy in this process is the interesting solution for the adsorber. It consists of a body with inlet and outlet conduits for the gas subjected to purification and for the gas being tested.

In order to carry out adsorption and desorption processes continuously, the adsorber has the shape of a pipe. Inside the adsorber, placed coaxially a certain distance from the walls, is a heating pipe. Moreover, the adsorber is provided with a pipe for removing impurities, the pipe being connected to circular channels between the heating and adsorbing pipes.

A system for dry sulphur removal [94] with the prospects of a considerable reduction in the amount of energy for preheating and cooling is presented in Fig. 45. The desulphurization system includes preheating and cooling zones in the vertical system, constructed in such a way that the carrier gas flows from bottom to top. In the preheating zone the adsorbent with adsorbed SO_x is heated.

Ishikawajuma–Harima Heavy Industries [95] gives a description of an appliance for separating sulphur from gas containing SO_2 by bringing the gas into contact with powdered carbon. The appliance is equipped with a conveyor for supplying powdered carbon to the reaction zone. The gas feed is at the start of the reaction zone so that the gas is supplied to the carbon spread uniformly on the conveyor moving along at a steady speed. The reaction zone is on the flat, upper surface of the conveyor belt.

In order to increase the efficiency of SO_2 catalytic oxidation, a technique has been patented in which the reactor is provided with perforated plates (2) with contact pipes [96]. The inside surfaces of the pipes form a spiral channel, and the catalyst is deposited on the surfaces of the pipes (Fig. 46). The reacted gases escape through the connector pipe, while the ash gathers at the conical bottom. It is removed at fixed periods of time. A reactor designed in this way ensures an increase in the efficiency of receiving heat from the catalyst and the maintenance of optimum temperature conditions.

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