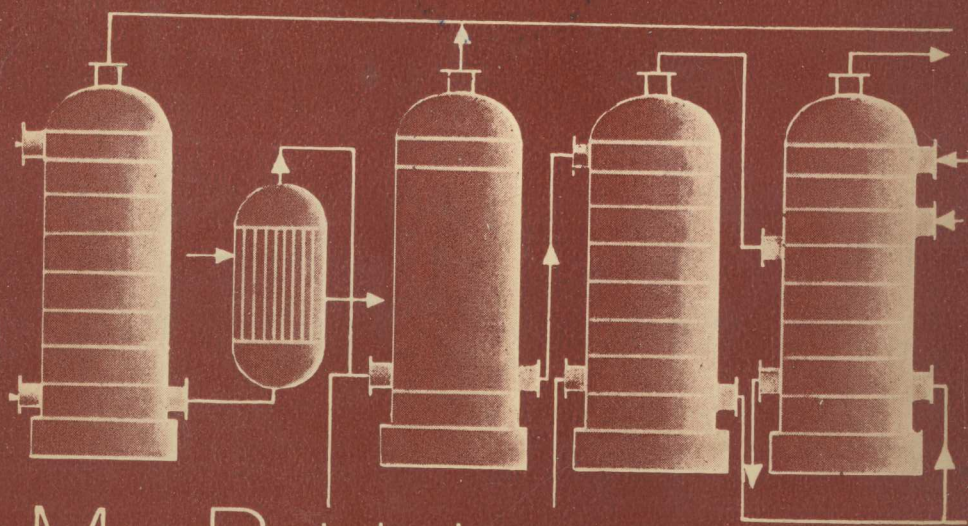# Chemical Technology

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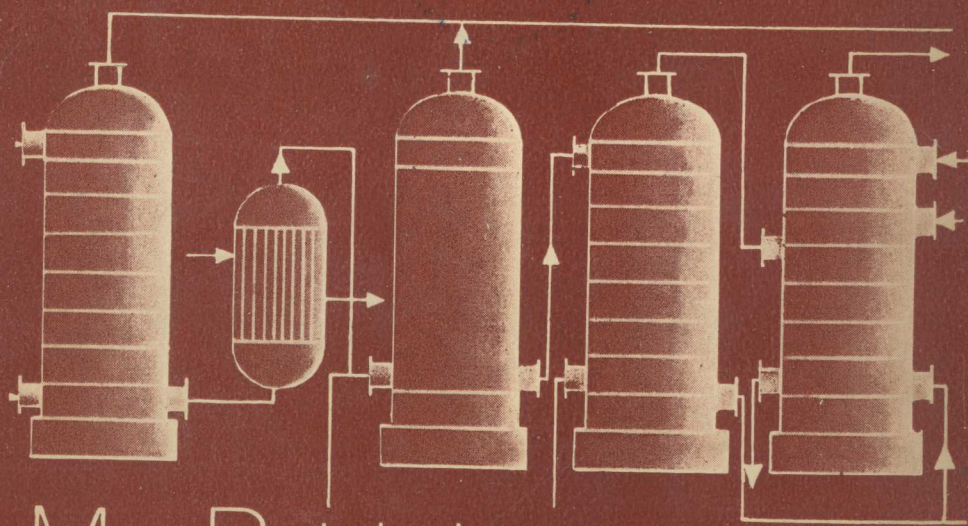Edited
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IN TWO PARTS

EDITED
BY I. P. MUKHLYONOV, D.SC.

The Most Important Industrial Chemical Processes

Chemical Processes

PART 2

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Preface

There are at present more than 50 000 known inorganic chemical compounds and about three million organic ones*. Although only a relatively small part of them are produced commercially the number of chemical products manufactured is still tremendous. The chemical industry, in the narrow sense, encompasses the manufacture of inorganic acids, alkalis, salts and oxides, products of organic synthesis, high-molecular compounds (synthetic resins, plastics, chemical fibres, rubber, varnishes, and glues)—more than 50 000 various products. Chemical technology also embraces the manufacture of building materials, metallurgy, pulp-and-paper, petroleum-refining and coal-carbonization industries, and chemical processing of shale, peat, wood, and other naturally-occurring organic materials. Tens of thousands of other products are made in these branches of industry.

It is, of course, impossible to describe all these manufacturing processes in a textbook on chemical technology. Therefore, the textbook is devoted only to typical chemical engineering processes and the equipment in which they are carried out, using as examples those branches of the chemical industry which are of the most importance.

A distinction is made between the technology of organic products and the technology of inorganic products. However the border line between them is not very definite since both organic and inorganic compounds are used jointly as raw materials in many industrial processes, and reactions between organic components yield both organic and inorganic products. There are industrial processes in which organic compounds are produced from inorganic substances, for example the manufacture of urea from ammonia and carbon dioxide. The processes of manufacturing organic and inorganic products are often interrelated and can rationally be combined at one and the same chemical factory. Thus, for carrying out hydrogenation, chlorination, hydrochlorination, nitration, sulfonation and saponification of organic compounds corresponding inorganic substances are employed and they are manufactured at the same factory as the organic compounds.

Synthesis gas ($n\mathrm{CO} + m\mathrm{H_2}$) which is produced from methane with steam is a raw material for the manufacture of hydrogen, employed in synthesis of ammonia, and, at other ratios of CO to $\mathrm{H_2}$,

* Organic chemicals include all carbon compounds except carbon dioxide, its salts and the metal carbides, which are considered to be inorganic in nature.

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of saturated and unsaturated hydrocarbons; synthetic alcohols are also made from it.

Chapter 1 of Part II was written by I. Mukhlyonov and A. Amelin, Chapters 2 and 3 were rewritten for the third edition by L. Kuznetsov, Chapters 4 and 5 were written by E. Tumarkina, Chapter 6 by A. Averbukh, Chapter 7 by I. Furmer, Chapter 8 by I. Furmer and A. Amelin, Chapters 9 and 10 by A. Averbukh and Chapter 11 by E. Tumarkina.

Contents

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1. Properties, Uses and Methods of Production

Properties. Anhydrous sulphuric acid (monohydrate), H_2SO_4, is a heavy, oily liquid which mixes with water in all proportions with liberation of large quantities of heat. The density of H_2SO_4 at 0 °C is 1.85 g/cm³. It boils at a temperature of 296 °C and freezes at —10 °C.

Commercially not only the monohydrate is known as sulphuric acid, but this name is also applied to its aqueous solutions ($H_2SO_4 + nH_2O$) and also to solutions of sulphur trioxide in monohydrate
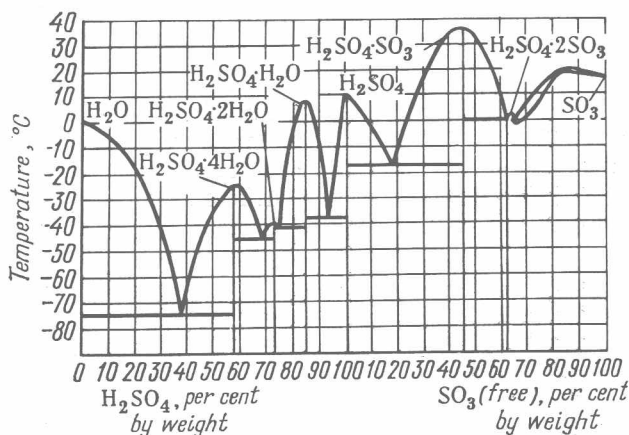
Fig. 1. Phase diagram of crystallization in the H_2O-SO_3 system

($H_2SO_4 + nSO_3$), also described as oleum. Oleum "fumes" when exposed to air due to desorption of SO_3. Pure sulphuric acid is a colourless liquid, but the technical product has a dark colour due to impurities present in it.

In manufacturing, transporting and using sulphuric acid the relation between its melting and boiling points, and the concentration are very important. As shown in Fig. 1, when the concentration of sulphuric acid is increased from 0 to 64. 35% free SO_3, six hydrates are consecutively formed; these are individual chemical compounds

which are mutually insoluble in the solid state and form eutectic mixtures (see Part I, Fig. 61). In the zone of SO_3-concentration from 64.35% to 100% crystallization produces solid solutions, i.e. this part of the diagram may be considered to be composed of two separate diagrams (see Part I, Fig. 61). Fig. 1 shows that acids of concentrations close to pure SO_3, $2SO_3 \cdot H_2O$, $SO_3 \cdot H_2O$ and $SO_3 \cdot 2H_2O_2$ cannot be manufactured and used in the winter at low temperatures since this might result in crystallization of the solutions which would plug acid lines between shops, storage tanks, pumps, and other unheated apparatus. All commercial grades of sulphuric acid have concentrations close to eutectic compositions.
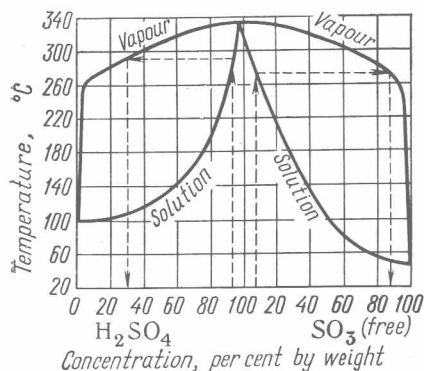
Fig. 2. Boiling diagram of the H_2O-SO_3 system at 1 atm

The vapour-liquid phase equilibrium for H_2O-SO_3 mixtures at atmospheric pressure is shown in Fig. 2. The mixture with a concentration of 98.3% H_2SO_4 is azeotropic, i.e. the temperatures at which the vapour condenses and the liquid boils, 336.6 °C, coincide. At a small change in composition in either direction from the azeotropic point the temperature at which vapour condensation begins, called the dew point, differs sharply from the temperature at which the solution boils. Correspondingly, the composition of the liquid phase and that of the vapours above it (or vice versa) also differ sharply.

The vapour-liquid phase diagram of the H_2O-SO_3 system (Fig. 2) is used in determining sulphuric-acid concentrations when water is being evaporated from it. The diagram shows that if acid with a concentration below 80% H_2SO_4 is heated, it will boil at a temperature lower than 200 °C and that almost exclusively water will pass over into the vapour phase; only if the concentration of the acid lies above 93% (the dotted line on the diagram) does the H_2SO_4 content of the vapour phase increase significantly.

The vapours of sulphuric acid dissociate at high temperatures:

$$H_2SO_4 \rightleftarrows H_2O + SO_3$$

and at temperatures above 400 °C there are already more SO_3 molecules in the vapours than those of H_2SO_4. Further heating leads to the dissociation of SO_3

$$2SO_3 \rightleftarrows 2SO_2 + O_2$$

At temperatures above 700 °C SO_2 is the predominant component of the vapours and above 1000 °C SO_3 is almost completely dissociated. The degree of dissociation changes with the pressure. This type of thermal dissociation is quite typical for complex chemical compounds. The heat of the reactions which participate in producing sulphuric acid and the intermediate compounds at 298 °K (25 °C) are:

Reaction	kJ/mole	kcal/mole
$S(gas) \rightarrow S(rhombic)$	64.8	15.5
$S(rhombic) + O_2(gas) \rightarrow$		
$\rightarrow SO_2(gas)$	289	71.0
$SO_2(gas) + \frac{1}{2}O_2(gas) \rightarrow$		
$\rightarrow SO_3(gas)$	96.1	22.91
$SO_3(gas) \rightarrow SO_3(liquid)$	39.8	9.50
$SO_3(gas) + H_2O(gas) \rightarrow$		
$\rightarrow H_2SO_4(gas)$	125.0	29.83
$H_2SO_4(gas) \rightarrow H_2SO_4(liquid)$	50.2	11.98
$H_2O(gas) \rightarrow H_2O(liquid)$	44.1	10.52

Sulphuric acid is an extremely active chemical compound. It dissolves the oxides of metals, also most pure metals, and displaces all other acids from their salts at high temperatures. Especially strong is the tendency to combine with water, which results from its capacity to form hydrates. It removes water from other acids, from crystal hydrates of salts, and even from oxygen derivatives of hydrocarbons, which do not contain water as such but contain hydrogen and oxygen in the ratio $H : O = 2$. Wood and other plant and animal tissues containing cellulose $(C_6H_{10}O_5)_n$, starch and sugar decompose in concentrated sulphuric acid; water combines with the acid and only finely-divided carbon remains. In dilute acid cellulose and starch decompose to form sugars. Concentrated sulphuric acid produces acid-burns upon contact with the skin.

Uses. The high chemical activity of sulphuric acid combined with the comparatively low cost of manufacturing it has resulted in its use on a tremendous scale and in a great variety of applications. It is hard to find any important branch of the economy in which either sulphuric acid or products made from it are not used. The largest consumption of sulphuric acid is in manufacturing inorganic fertilizers: superphosphate, ammonium sulphate, etc. Many acids (for example, phosphoric, acetic, and hydrochloric acids) and salts are manufactured from sulphuric acid. It is used extensively in manufacturing various non-ferrous and rare metals. In metal processing sulphuric acid or its salts are used for pickling steel items prior to painting, tinning, nickel plating, chrome plating, etc. Large quantities of sulphuric acid are consumed in purifying petroleum products. Processes for manufacturing a number of dyes,

paints and varnishes, pharmaceuticals and some plastics are also based on sulphuric acid. It is used in making ethyl alcohol, some ethers, detergents, a number of insecticides and herbicides. Dilute solutions of sulphuric acid and its salts are used in manufacturing artificial silk and for treating fibres or cloths before dyeing in the textile industry and in other branches of the light industry. In the food industry sulphuric acid is used in manufacturing starch, syrup and a number of other products. Sulphuric-acid lead batteries are used in transportation. It is used for drying gases and in concentrating acids. Finally, sulphuric acid is used in nitrating operations and in manufacturing a large number of explosives.

For nitrating operations, manufacturing ethyl alcohol from ethylene, concentrating nitric acid and in many other cases 92 to 98% H_2SO_4 is used and diluted 50-80% H_2SO_4 is formed. Such acid is reconcentrated by evaporating water according to the diagram of Fig. 2.

Manufacturing methods. Sulphuric acid was manufactured as early as the 13th century, in very small amounts of course, by thermal decomposition of iron vitriol ($FeSO_4$), and because of this one of the grades of sulphuric acid is still called vitriol oil, although manufacture of sulphuric acid from ferrous sulphate was discontinued many years ago.

Sulphuric acid is now manufactured in two ways: by the nitrous process, which has been in use for more than 200 years, and by the contact process, developed at the end of the 19th and beginning of the 20th centuries. The contact process is replacing the nitrous (tower) one.

The first stage in manufacturing sulphuric acid by any method is the production of a sulphurous gas by burning a sulphur-containing material. After the sulphurous gas has been purified (especially carefully in the contact method) it is oxidized to sulphur trioxide, which combines with water to form sulphuric acid. Oxidation of SO_2 to SO_3 in usual conditions takes place at a very low rate and catalysts are used to accelerate the process.

In the *contact process* for manufacturing sulphuric acid the sulphur dioxide is oxidized to the trioxide over a solid catalyst. Improvements in manufacturing acid by this method have brought the cost of the pure and more concentrated contact sulphuric acid down to just slightly above that of tower acid. Because of this in the USSR only plants using the contact process are now built. At present approximately 80% of all the acid produced is made by the contact method.

In the *nitrous process* nitrogen oxides are the catalysts. The SO_2 is oxidized mainly in the liquid phase and the operation is carried out in packed towers. The nitrous process, in accordance with the type of apparatus used, is also known as the *tower process*. In the

tower process after the dust particles (pyrite cinders) are removed from the sulphurous gas obtained by burning a sulphur-containing raw material and with a content of 9% SO_2 and 9-10% O_2, it enters into a system of several (from 4 to 7) packed towers. The temperature at the inlet to the first tower is about 350 °C. In the towers a number of absorption-desorption processes in which chemical conversions are involved take place. A nitrous vitriol solution is fed to the top of the first two or three packed towers; the solution contains dissolved nitrogen oxides which are chemically combined as nitrosyl sulphuric acid, $NOHSO_4$.

At a high temperature the nitrosyl sulphuric acid is hydrolyzed in the reaction

$$2NOHSO_4 + H_2O \rightleftarrows 2H_2SO_4 + N_2O_3 - Q \tag{a}$$
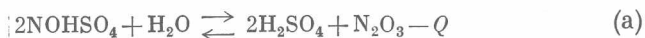
The sulphur dioxide is absorbed by the water and forms sulphurous acid:

$$SO_2 + H_2O \rightleftarrows H_2SO_3 + Q \tag{b}$$

the latter reacts with the nitrogen oxides in the liquid phase

$$H_2SO_3 + N_2O_3 \rightleftarrows H_2SO_4 + 2NO + Q \tag{c}$$

The SO_2 is partially oxidized in the gas phase

$$SO_2 + N_2O_3 \longrightarrow SO_3 + 2NO + Q \tag{d}$$

The SO_3 is absorbed by the water and also forms sulphuric acid

$$SO_3 + H_2O \longrightarrow H_2SO_4 + Q \tag{e}$$

The nitrogen oxide is desorbed into the gas phase and is oxidized to nitrogen dioxide by the oxygen from the air

$$2NO + O_2 \longrightarrow 2NO_2 + Q'' \tag{f}$$

The nitrogen oxides, $NO + NO_2 \rightleftarrows N_2O_3$, are absorbed by sulphuric acid in the following three or four towers by the reverse reaction of equation (a). To accomplish this, the cooled sulphuric acid with a low nitrosyl content which flows out of the first towers is fed to these last towers. When the oxides are absorbed the nitrosyl sulphuric acid which participates in the process is formed. In this way the nitrogen oxides circulate in the system and, theoretically, they are not consumed. Practically, however, due to incomplete absorption some of the nitrogen oxide is lost. The nitrogen oxides consumption, expressed in terms of HNO_3, is 10-20 kg per ton monohydrate H_2SO_4 produced. The sulphuric acid made by the nitrous method is contaminated with impurities and dilute, with a concentration of 75-77%, and it is mainly employed in making inorganic fertilizers.

2. Producing the Roaster Gas

Sulphurous anhydride, SO_2, is a colourless gas, 2.3 times heavier than air, with an acrid odour. Pure SO_2 is liquefied at atmospheric pressure at a temperature of -10 °C. When dissolved in water it forms the weak, unstable sulphurous acid:

$$SO_2 + H_2O \rightleftarrows H_2SO_3$$
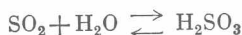
Any substance containing sulphur, either found in nature or a waste product of another manufacturing process, may be used for producing sulphur dioxide (and, consequently, sulphuric acid). In nature sulphur is usually found in one of three forms: (1) elementary native sulphur in a mixture with other minerals; (2) sulphides of metals, for instance iron pyrite, FeS_2, copper pyrite, $FeCuS_2$, copper glance, Cu_2S, zinc blende, ZnS, and also PbS, CoS, NiS, etc.; (3) sulphates: gypsum, $CaSO_4 \cdot 2H_2O$, anhydrite, $CaSO_4$, and also Na_2SO_4, $MgSO_4$, etc.

More than 40% of the sulphuric acid made in the USSR is produced from gases obtained by burning pyrite, consisting of the mineral and admixtures to it. Pure iron pyrite, FeS_2, contains 53.5% S and 46.5% Fe. In pyrite the sulphur content usually varies from 35 to 50%, and the iron content from 30 to 40%; the remainder is composed of sulphides of the non-ferrous metals, carbonates, sand, clay, etc. In the USSR there are important pyrite fields in the Ural mountains area, in the Caucasus and in the Central Asia Republics. There are also rich pyrite fields in Spain, Norway, Portugal, Italy and Canada. Pyrite is often found together with the sulphides of non-ferrous metals which are the raw material for manufacturing copper, zinc, lead, nickel, silver, etc. To separate the sulphides of the non-ferrous metals the ore is size-reduced and divided by flotation into concentrates containing the sulphides of the non-ferrous metals and the so-called flotation tails; the latter consist mainly of iron pyrite. Pyrite containing only small amounts of non-ferrous metals is delivered to the plants directly as mined in lumps of various sizes. At the sulphuric-acid manufacturing plants pyrite is crushed in jaw- and roll crushers and then roasted to produce roaster gas.

When sulphides of copper, zinc and other non-ferrous metals are roasted at metallurgical plants gases containing sulphur dioxide are formed which are utilized for manufacturing sulphuric acid. It follows that together with the non-ferrous metals, sulphur dioxide is also produced from the sulphurous ores. More than 25% of the sulphuric acid produced is made from waste gases of non-ferrous metallurgy. A large part of the gases produced in non-ferrous metallurgy have an SO_2-content lower than 3%. For making sulphuric acid the gas must first be concentrated. However, at some plants

the gases are not subjected to concentration but are discharged to the atmosphere. At present fuller utilization of the SO_2-containing gases of non-ferrous metallurgical plants is planned.

The best raw material for manufacturing sulphur dioxide is sulphur, which is obtained by melting it out of sulphur-containing rock and also as a by-product in manufacturing copper, in purifying industrial gases, etc. Sulphur has a melting point of 113 °C, it ignites easily and can be burned in furnaces of simple design. If sulphur is burned in air the SO_2 concentration of the gas is higher than of that obtained in roasting pyrite, and the content of undesirable impurities in it is lower.

The cost of the sulphur is several times that of pyrite and therefore only 20% of the sulphuric acid produced in the USSR is made from it, mainly at plants far from sources of pyrite.

Coal always contains sulphur in amounts from 1 to 3 per cent. During combustion of the coal the sulphur is burned and discharged to the atmosphere in the form of SO_2. Absorption-desorption methods have been developed for purifying combustion products, in which the SO_2 is recovered and utilized in manufacturing sulphuric acid.

However the cost of sulphuric acid obtained from such combustion-product gases is several times that of acid made from pyrite, and the amount made in this way is very small. Worldwide the amount of sulphur dioxide discharged to the atmosphere exceeds by more than two times the amount converted into sulphuric acid.

When coal is carbonized or petroleum refined the sulphur contained is partially converted to hydrogen sulphide in the gas phase. When the gas is purified either elementary sulphur or gaseous hydrogen sulphide is obtained; the latter is burned to produce SO_2-gas and from it—sulphuric acid.

In the Soviet Union there are enormous deposits of calcium sulphate and sodium sulphate which are not yet utilized in the production of sulphuric acid, i.e. they are potential raw material.

When steel is pickled the sulphuric acid used is converted to iron sulphate. When petroleum products are refined there is a residual asphalt, the so-called acid sludge, which contains sulphuric acid. In a number of organic-chemical processes waste-liquor dilute sulphuric acid containing large amounts of organic chemical impurities is produced. These and other similar industrial waste products containing sulphuric acid or its salts, when heated in the presence of reducing agents, yield a sulphurous gas which can be converted to sulphuric acid.

Methods for producing sulphurous gas by roasting the principal raw materials—pyrites, and then by burning sulphur, are discussed in the following paragraphs.

Iron pyrite is roasted in air in furnaces of various types at atmospheric pressure. Pyrite oxidation is described by the following overall

equation

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2 + 3400 \text{ kJ} \qquad \text{(a)}$$

which is used in drawing up material and heat balances. Actually, this irreversible process is comprised of a number of successive and parallel chemical reactions and of diffusion processes which determine the overall process rate at the high temperature.
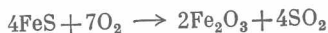
When pyrite is heated to temperatures above 500 °C in the furnace the first process that occurs is pyrite dissociation:[1]

$$2FeS_2 \longrightarrow 2FeS + S_2$$
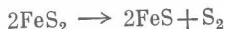
The sulphur quickly burns in the gas phase:

$$S_2 + 2O_2 \longrightarrow 2SO_2$$
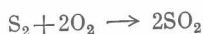
The iron sulphide is oxidized according to the following reaction equation:

$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$$

Actually below 600 °C oxidation proceeds through formation of sulphates of iron which are intermediate compounds, and at higher temperatures FeO is first formed and then Fe_3O_4 or Fe_2O_3. In all cases when a sulphide is oxidized a thin layer of iron oxides is formed, and further combustion is usually limited by the rate of diffusion of the oxygen of the air into the unoxidized FeS core and the rate of the diffusion of SO_2 from the depth of the grain outward in the opposite direction. It is this inner-diffusion process which limits the overall rate of pyrite roasting.

From 5 to 10% of the sulphur in the pyrite passes into the gas phase as SO_3. This sulphuric anhydride is produced by oxidation of SO_2, resulting from the catalytic properties of the cinder, and also by decomposition of sulphates which may have been present in the pyrite or have been formed during its oxidation.

When the pyrite cinder leaves the furnace at high temperatures and when the excess of oxygen in the gas is small, for instance in fluidized-bed roasters, the overall roasting process is described by the following reaction equation:

$$3FeS_2 + 8O_2 \longrightarrow Fe_3O_4 + 6SO_2 + Q \qquad \text{(b)}$$

During the roasting process the sulphides of other metals present in the pyrite are also oxidized, carbonates present decompose, and As_2O_3, SeO_2 and all the water contained in the pyrites are transferred to the gas phase. The pyrite cinder consists of oxides of iron, and sulphates and oxides of other metals, quartz, alumosilicates, and unoxidized FeS. From 0.5 to 2% of the sulphur remains in the cinder.

Experimental data picturing the conversion of the sulphur when pyrite is burned in a stationary-bed furnace are given in Fig. 3.