SULPHUR AND SULPHUR DERIVATIVES

(1466G) *Frontispiece*

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SULPHUR
AND SULPHUR
DERIVATIVES

BY

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PREFACE

In addition to furnishing facts connected with the occurrence and production of several sulphur compounds and derivatives, it is hoped that the following pages will stimulate interest in certain problems of large-scale chemical manufacture. The basis of many processes is simple, but the actual apparatus and plant necessary for the manufacture of large quantities of chemical substances which modern conditions demand are somewhat intricate and complicated. The author has endeavoured to describe those portions which are not so intricate that they cannot be appreciated by readers of limited technical knowledge. It has been considered permissible to introduce chemical equations in a few instances, to serve as an introduction to the nomenclature adopted in the science of chemistry. A complete knowledge of all that the equations imply is not necessary for the interpretation of the significant " jargon " of the chemist.

We desire to thank various firms (see list of illustrations) for permission to make use of their blocks.

LIVERPOOL,
June, 1921.

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FOREWORD

"It is to be owned, that many things have been writ of Sulphur ; but the true Foundation of the true Virtues thereof, hath scarcely yet by Man been exactly enough touched or proposed. But those Writers are to be blamed, who describe all things, of which they have no Understanding ; because, in so doing, they did indeed compose and prescribe somewhat ; but nothing fundamentally, or according to its genuine Disposition and Property, as in Writing or Describing is requisite. For in truth, they themselves understood not, yet (through their ambitious Haughtiness) they would compose Books, consisting of letters only, without Soul or Spirit. But I, as one experienced, present you my Experience of Sulphur in all things, viz., what Sulphur is with respect to Medicine, Alchemy, and all other associated Artifices."

"Whosoever shall attempt to describe Sulphur in a most accurate manner (as is fit, though not expedient) will have need of abundance of Paper."—MIRACULUM MUNDI (1656).

INTRODUCTORY

The important rôle played by sulphur products is not much in evidence in everyday life, but there are, in reality, few manufactured articles which have not required at some stage or other of their preparation a compound containing sulphur. It is generally known that brimstone is used in medicine, matches, gunpowder, and for disinfection, but beyond these, few could say for what purposes the quantity of more than one million tons of sulphuric acid is produced every year in this country. In the present book an endeavour will be made to describe the manufacture and uses of the chief products suggested by the general title, and to draw attention to such naturally occurring compounds as are of importance in industry. A brief historical introduction precedes the description of modern methods of manufacture.

It is impossible to name the period when compounds containing sulphur were first used in the arts. Compounds of lead, antimony, and arsenic with sulphur were largely used by the Egyptians in remote ages as pigments and cosmetics, some of these colouring compounds being the earliest chemical preparations produced on a large scale. Egyptian paintings (about 1600 B.C.) have some fifteen different colours in their composition, most of which colours contained sulphur or necessitated a compound of sulphur in their preparation. There is every reason to believe that the manufacture of gunpowder, as of other industrial products, was known to the Chinese many centuries before the Christian era. Gunpowder, first used in Europe about 1200, was prepared in various ways, and introduced into Europe by the Arabs. It is possible that the Chinese knew of the existence of oxygen and the composition of water long before Priestley's discovery in 1784.

The following quotation from Homer is evidence of the primitive use of sulphur in hygiene: "Bring sulphur, old woman, the healer of evils and bring me fire that I may fumigate the hall . . . . thoroughly fumigated the hall, the house-place and chamber." In another passage Achilles, before pouring a libation, cleanses the cup with sulphur. In Pliny's Natural History a similar reference occurs. [Homer, Od. 22, 481–493: Il. 16, 298: Pliny 35, 50.] Dioscorides also was apparently familiar with both crude and melted sulphur (Theion apuron and Theion pepuromenon). A theory which emanated in the first instance from the alchemist Gebir, to the effect that sulphur is one constituent of all matter, was maintained for a considerable period. Probably these early investigators identified sulphur with the principle of "combustibility," failing to recognize it as a distinct element; similarly, with the other constituents of all matter, the principle of "metallicity" was identified with the element mercury, and "fixity" or power of resisting the action of fire, with salt.

Basil Valentine * (1456) records the working of sulphur kilns, and from that date successive research has gradually revealed the chief properties of sulphur and its compounds. The eminent French scientist Lavoisier was the first to establish the fact that sulphur is an element.

In its native state, sulphur occurs in pure crystalline form, and also more commonly intermixed with earthy matter, the latter being the most abundant source of all native sulphur supply. In addition, sulphur is a

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* The existence of this writer has been questioned, and there is considerable evidence (Schlorlemmer) that the works attributed to him were written by Von Tholden in the seventeenth century.

dominant constituent of a large number of minerals of industrial importance, e.g. the main source of our lead supply is the sulphide known as Galena. Zinc blende, another mineral sulphide associated with the sulphur industry, is also mined in Great Britain, though much of the ore is now imported. Of greater importance to the chemical manufacturer than either of these is pyrites, the raw material for producing sulphuric acid. Spain exports pyrites, to the extent of millions of tons annually, to most European chemical works. The ore usually contains 45 to 50 per cent. sulphur. Pyrites from British sources, though of low grade, was of extreme but temporary importance from 1914–18, on account of the impossibility of maintaining importation of sufficient quantities from overseas. Iron pyrites constitutes the metallic-looking substance which is met with in masses of coal. It is also frequently found on some sea beaches, where it occurs in rounded nodules, rusty outside, but having a fine radiating fracture. In geological specimens, especially ammonites, very often the form of the shell is wonderfully preserved by the substitution of pyrites for the original filling.

Sulphates form another group of minerals of industrial importance. Beds or masses of gypsum (calcium sulphate) furnish the cements of the type best known as plaster of Paris. In the form of alabaster, gypsum is used for sculpture and other architectural purposes. Large quantities of waste material containing calcium sulphate are produced in the chemical and pottery industries. Promising results have already been obtained which may lead to the use of this by-product as raw material in other industries. Heavy spar (barium sulphate) is also mined in several districts in England, and is used in the manufacture of paints. Compounds of barium, derived from the sulphate, are used in fireworks and flares where a green light is required. Sulphates of sodium (Glauber salts) and magnesium (Epsom salts) occur as minerals, but more frequently in solution, forming medicinal waters. Sulphur is indispensable to the growth of plants, which derive it from the soil. The proteids of plants, especially peas, beans and lentils, contain 1 to 2 per cent. sulphur, which accounts for the unpleasantly smelling hydrogen sulphide in the products of vegetable decomposition. The presence of sulphur as a constituent of plants was first proved by Deyeur, in 1791. In the vegetable kingdom we find some plants which are particularly rich in sulphur compounds. The characteristic smell of mustard (sinapis alba), onion (allium cepa), and garlic (arena sativa) is due to sulphur compounds; these account also for the pronounced tarnishing effect of certain vegetables on metals. The low orders of plant life represented by bacteria and algae (beggiatoa, oscillaria, ulothrix) contain free sulphur and probably play an important part in plant economy as transmitters of sulphur in an assimilable form to higher orders of plants. An interesting suggestion has recently been made for the practical utilization of the bacterial oxidation of sulphur in soils. Potato growers prefer an acid soil, because acidity, whilst not unfavourable to the potato crop, is entirely unsuited to the "scab" organism, one of the worst potato pests. It is proposed that a dressing of 300–1,000 lbs. per acre of sulphur should be made before planting the potatoes to ensure the requisite degree of acidity. After the removal of the crop, sufficient lime can be added to ensure a neutral soil for the next rotation crop. Sulphur possesses fertilizing properties to a small extent, but in agriculture, or more especially viticulture, it is used as a means of killing the moulds (oidium or uncinula) which attack vines and hops. Flowers of sulphur, or winnowed sulphur, which adheres better to the leaves, is dusted on to the plants. The remedy for the vine disease due to oidium consists of the application of sulphur to the affected vines. Three successive applications are necessary, and these are made with an instrument in the form of a pair of bellows, to which a rose is fixed in order to distribute the sulphur. The first application is made in the spring, the second directly aftre the vine has blossomed, and the third when the grapes begin to ripen. The operation in the spring is the most important, and must be thorough, so as to affect all the hibernating spores. The third application should be made early enough for the sulphur to disappear before the vintage takes place, as its introduction into the wine would give an unpleasant taste. Probably the sulphur acts by slowly setting free sulphurous acid. The sulphur ultimately reaches the soil, where it is transformed into calcium sulphate, which is an excellent dressing for the vine. The "peronospora" disease requires more rigorous measures, such as a mixture of sulphur with powdered lime, or a solution of iron sulphate.

About 100,000 tons of sulphur are used annually in Europe alone for this purpose. For spraying liquids for agricultural purposes sulphur and sulphates are used, but copper sulphate (blue vitriol) is more generally the chief germicidal agent. Sulphates are not regarded as fertilizers in this country, although considerable amounts are applied to crops in the form of ammonium sulphate and superphosphates. It is known, however, that sulphur is essential to crops, and there are cases on record of soils responding markedly to treatment with sulphur and sulphates, larger returns being obtained from gypsum than from lime. Both sulphur and sulphates give increased yields of oats, rape and red clover.

The "curing" of hops is also helped by sulphur, about half a pound for every ten bushels being thrown on the fire in the "oast" or kiln.

In the animal kingdom very many organic bodies contain sulphur, usually in association with nitrogen e.g. albumens, blood, horn, hair, bile (as taurin), urine (as cystin). The human body contains about 1 per cent. of its weight of sulphur. The occurrence of free sulphuric acid in the snail known as aplisia is of interest, and to the writer, at any rate, an unexpected and unusual substance to find in such surroundings.

SULPHUR AND SULPHUR DERIVATIVES

CHAPTER I

SULPHUR

THE most productive deposits of sulphur in the world are those worked in the United States, especially in Louisiana and Texas. These are threatening the economic ruin of the Sicilian producers and the closure of many mines which were formerly the main source of supply. In 1909 eighty of the smaller Sicilian mines were closed, and of the remaining five hundred only six yielded more than a thousand tons per annum. By 1912 the production of Sicilian sulphur had been reduced from 94 per cent. to 50 per cent. of the world's supply. The production in 1914 was 330,000 tons, in 1919 only 180,000.

In any case, the whole sulphur industry of Sicily is menaced with ruin, unless more rational and economic methods of extraction and sale are found. In 1903 nearly 60 per cent. of the ore raised was carried from the galleries at the working face up a steep slippery passage by "carusi," who are frequently deformed as a result of carrying heavy loads. In 1912 the employment of women and girls of seven and eight as "carusi" was forbidden, but owing to the strained economic conditions the government has been implored to relax the regulation. Native sulphur is found, in addition to those regions previously mentioned, in Iceland, Mexico, Japan New Zealand, Greece, Caucasia and in a few other districts. It is always associated with the presence of active or inactive volcanoes. The formation of free sulphur in the volcanic districts is no doubt due in many cases to the action of hydrogen sulphide upon sulphur dioxide, the latter having been produced by the partial burning of a portion of the hydrogen sulphide. This can be represented by the following chemical equations—

$$(1) \qquad \underset{\substack{\text{Hydrogen}\\\text{sulphide}}}{2H_2S} + \underset{\substack{\text{Sulphur}\\\text{dioxide}}}{SO_2} = \underset{\text{Sulphur}}{3S} + \underset{\text{Water.}}{2H_2O}$$

$$(2) \qquad \underset{\substack{\text{Hydrogen}\\\text{sulphide}}}{H_2S} + \underset{\substack{\text{Oxygen}\\\text{(as air)}}}{3O} = \underset{\substack{\text{Sulphur}\\\text{dioxide}}}{SO_2} + \underset{\text{Water.}}{H_2O}$$

Other deposits of sulphur have been formed by the reducing action of bituminous matter, under certain conditions of temperature, on gypsum or other similar mineral sulphates. Some sulphur, but not in quantities of commercial importance, is the result of the activity of bacteria, which also reduce sulphates, and to this cause the presence of hydrogen sulphide in sewers and polluted rivers is mainly due. The formation of sulphurous springs is attributed to the action of bacteria and algae, which transform the sulphates in the waters into sulphur. Some observers have been led to believe that the vast deposits of sulphur found in certain regions are due to the activities of these microscopic plants. In the manufacture of illuminating gas, hydrated oxide of iron is used to remove some of the harmful sulphur compounds (chiefly hydrogen sulphide) present in the crude gas. The oxide can be "revivified" by exposure to air and can again be used in the purifiers. The iron sulphide formed is converted to oxide and free sulphur by the action of air. The oxide can be repeatedly revivified and used until it is "spent" or becomes inactive. The "spent oxide" contains about 50 per cent. of sulphur, and this is utilized by burning, to produce sulphur dioxide, in a similar manner to pyrites "smalls" (*see* p. 40). Until quite recently much sulphur was recovered from "alkali waste," but the process, formerly very extensively used, is now rapidly becoming obsolete, owing to the replacement of the "Leblanc" caustic soda process by electrolytic methods. The mining of sulphur, so far as Europe is concerned, does not require any special detailed account. The masses of rock containing the sulphur, usually mixed with gypsum, are built up into mounds, "calcaroni" (Fig. 1), and covered with the fine material from a previous

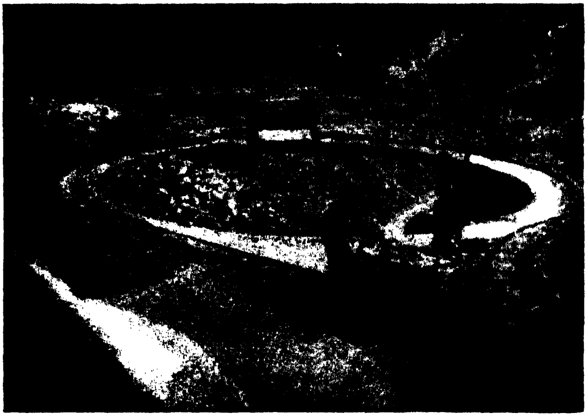

FIG. 1

BUILDING UP A "CALCARONE"

mound. The sulphur is melted, partly by the heat produced by the burning of a portion of the sulphur and partly by the aid of fuel. A recovery of about 60 per cent. is possible, but the escaping sulphurous gases cause destruction to the vegetation in the district. This method has largely been superseded. A marked improvement came with the introduction of a type of furnace in which far better economy of the heat was possible. The Gill furnace, which, with further improvements and modifications is in use under the name of Sanfilippo, has increased the yield of sulphur from the rock (Figs. 2 and 3). By the employment of superheated steam the recovery has been increased in the Romagna (Fig. 4) to 90 per cent:, but the great scarcity of fuel has prevented its extended application in Sicily.

FIG. 2

GENERAL VIEW OF A GILL FURNACE

The sulphur as first obtained by simply melting out from the rock (Fig. 5) is far from pure, and quite useless for many purposes. Most of the impurities, amounting to 3 to 4 per cent. may be removed by distillation or sublimation.

When heated, sulphur melts at about 115°C (239°F) to a pale yellow liquid which darkens in colour and becomes very viscous, as the temperature rises, until at about 180°C it is nearly black, and will hardly flow. On still further heating the pasty mass again becomes liquid at about 260°C, but not so mobile as at 180°C, and finally boils at 444°C (836°F). At the boiling point sulphur is converted into a brownish-red vapour. On the large scale sulphur is distilled or sublimed, and the vapour passed into chambers, usually of

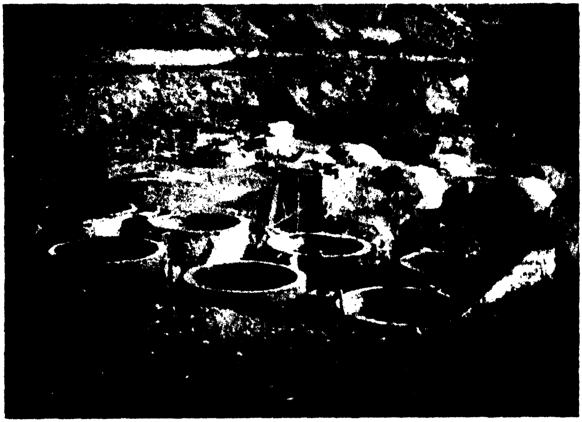

FIG. 3

LOWER PORTION OF GILL FURNACE SHOWING THE COMPARTMENTS

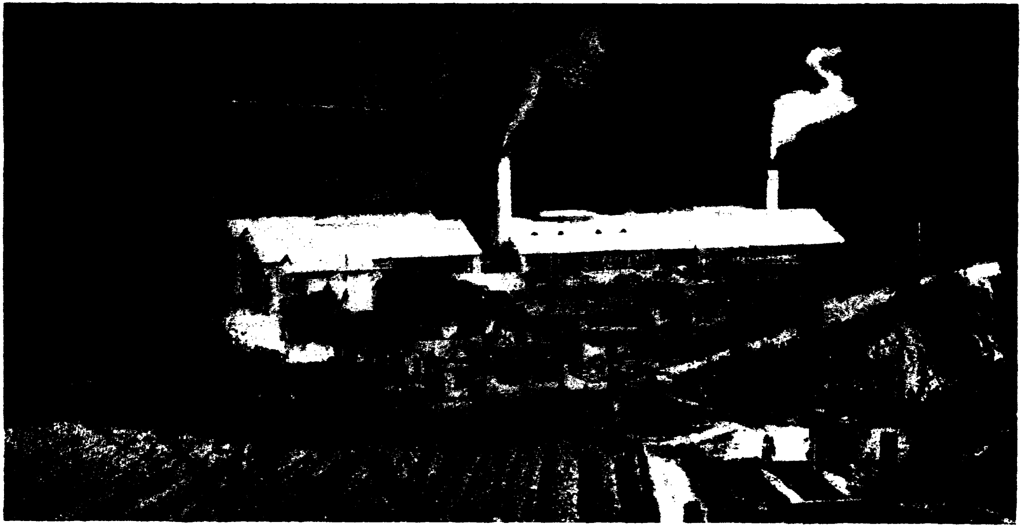

Fig. 4

SULPHUR WORKS, BELLISIO, ROMAGNA

FIG. 5

BLOCKS OF CRUDE SULPHUR, "ZOLFOGREGGIO"

brickwork, upon the sides of which it condenses. So long as the temperature of the chamber is not sufficiently high to cause it to melt, the sulphur is deposited as a pale yellow powder—the so-called flowers of sulphur. The sticks or rolls are made by casting melted sulphur in moulds. Arsenic and the less known element selenium are frequently associated with sulphur, and are not removed in distillation. The use of superheated steam or water has been most skilfully adopted in the mining of sulphur in Louisiana, and by its aid the winning of millions of tons of sulphur has been made possible in situations where usual mining operations were quite impossible.

In Louisiana the sulphur forms a deposit, roughly circular and over half a mile in diameter, beneath some 500 feet of clay, quicksand and rock. The existence of these deposits has been known since 1868, and many unsuccessful attempts had been made previous to the adoption of the method of extraction which is now used. These ineffective attempts had frequently led to disaster and loss of life. The successful method devised by Frasch is one of great ingenuity. A bore hole is made sufficiently wide to permit the introduction of four concentric pipes, deep enough to reach the deposit. Water, super-heated to about 180°C, and consequently, under pressure, is pumped down the two outer pipes which are respectively eight and six inches in diameter. After a time the sulphur, melted by the heat of the water, is raised to the surface by hot compressed air, which is forced down the central pipe. A mixture of air and liquid sulphur flows freely up the adjacent three inch pipe which surrounds the one inch air pipe. The liquid sulphur solidifies in bins, containing as much as 150,000 tons. A well produces about 450 tons per day, until choked by the collapse of the

Fig. 6

LOADING SULPHUR BY GRAB CRANE, LOUISIANA

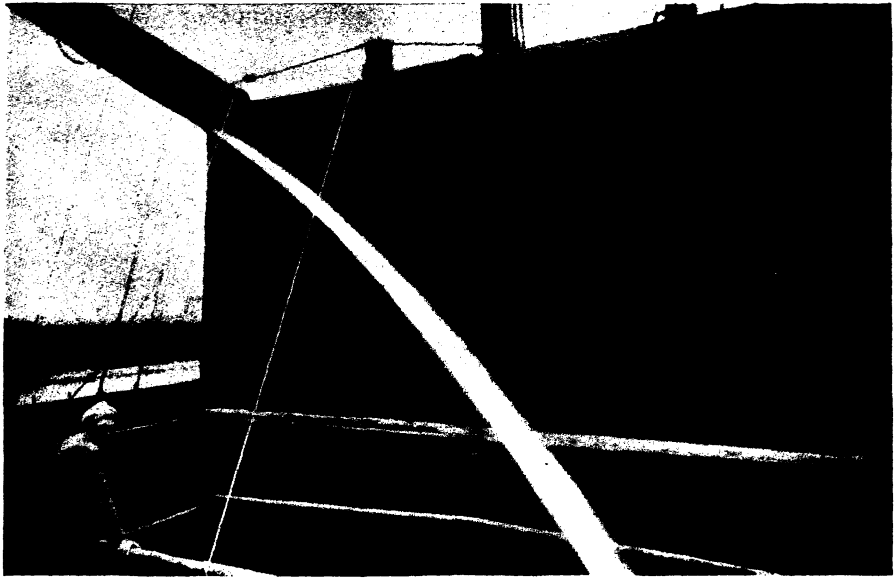

Fig. 7

LOADING A STEAMER WITH SULPHUR AT THE RATE OF ABOUT TEN TONS PER MINUTE rock and quicksands at the bottom. The solid mass of sulphur is blasted and loaded up by " grab " cranes into railway trucks as required (Figs. 6 and 7).

The deposits of Louisiana have been computed to hold 40,000,000 tons. The product contains 99 to 99·6 per cent. of pure sulphur.

CHAPTER II

SULPHUR DIOXIDE AND SULPHUROUS ACID

SULPHUR dioxide, the smell of which is familiar to most people, results from the burning of brimstone or the sulphur in ores such as pyrites already mentioned. It is frequently very abundant in the fumes of locomotives or other fires where coal containing pyrites is burned. The name generally used—sulphurous acid—is not a good one, but may be legitimately used for the solution of sulphur dioxide in water. One volume of water at ordinary temperature and pressure dissolves about fifty volumes of the gas.

The preparation of the gas for the manufacture of sulphuric acid, which industry absorbs a very high percentage of sulphur dioxide made, will be dealt with in another chapter. We shall confine ourselves now to the production of concentrated solutions and of the pure liquefied sulphur dioxide which are employed in many industries. One form of convenient type of furnace made by the Sachsenburg Engineering Co., London (Figs. 8 and 9), in which the sulphur is burned, is shown. It is frequently of importance, as in the manufacture of "hydrosulphites," to produce a gas which shall as far as possible be free from oxygen and, in order that this may be achieved, sulphur burners of this type are used. The sulphur dioxide gas is cooled and absorbed by cold water (Fig. 10). The apparatus is usually designed on the "counter current" principle, i.e. the gas first comes into contact with the solution, which has already been nearly saturated, and the gas, which is now weakened, before leaving the apparatus,

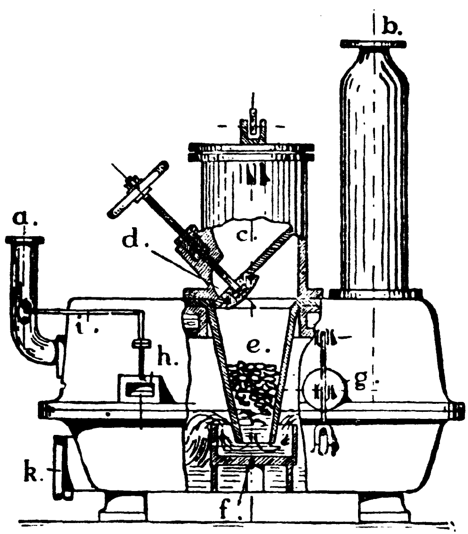

FIG. 8

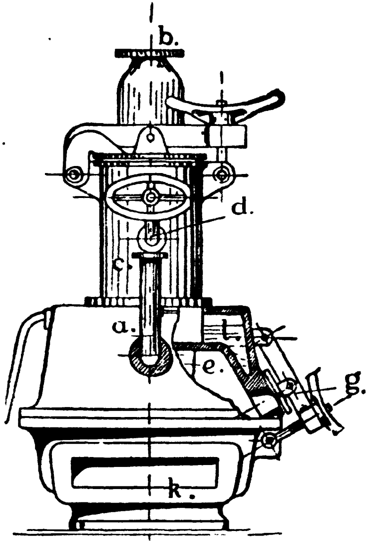

FIG. 9

SULPHUR BURNER

A Air inlet. B Gas outlet. C Charging drum. D Feed valve. E Melting cone. F Overflow. G Fire door locking device. H Inspection hole. I Air pipe. K Cleaning hole. L Cooling vessel.

is brought into contact with the fresh water. By this plan, in which the passage of the gas and water are in opposite directions, strong solutions are produced and loss of gas is avoided.

The decomposition of sulphuric acid by charcoal may be employed to produce sulphur dioxide. The action is represented when the acid is strong by the equation

$$\underset{\text{Sulphuric acid}}{2H_2SO_4} + \underset{\text{Carbon}}{C} = \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Sulphur dioxide}}{2SO_2} + \underset{\text{Water}}{2H_2O}$$

a diluted acid causes the formation of carbon monoxide,

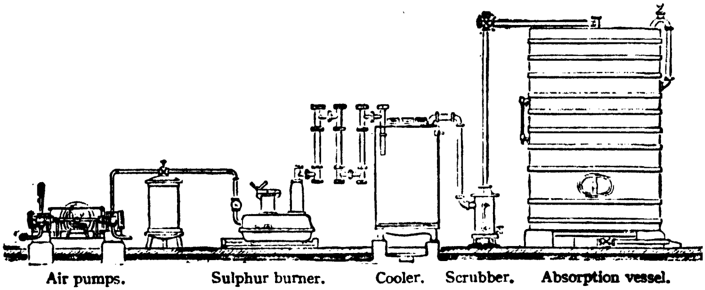

FIG. 10

APPARATUS FOR MANUFACTURE OF SULPHUR DIOXIDE SOLUTION.

and even sulphuretted hydrogen. To utilize the sulphur dioxide obtained from pyrites more complicated and elaborate plant is required. In this case, as we shall see when treating of pyrites kilns later on, the gases do not usually contain more than 6 to 9 per cent. of sulphur dioxide. The gases are absorbed in water, and the dilute solution of sulphurous acid is heated. The mixture of steam and sulphur dioxide passes into a tower of special construction, and the temperatures are very carefully adjusted by the amount of water fed into the top of the tower, so that the steam is condensed and gas containing only a small amount of water vapour passes to the other parts of the plant. The sulphur dioxide is dried by sulphuric acid in a smaller tower and compressed. The finished product—liquid sulphur dioxide—is marketed in iron containers for large consumers or in " syphons," similar to the well-known soda-water syphons, for laboratory purposes or for small scale users. The gas is readily liquefied by cooling with ice and salt, or by a pressure of three atmospheres without cooling. The liquid boils at -8°C and solidifies at -75°C.

Two continental patents of very recent date have some points of interest, and in certain circumstances may prove of technical economic importance. The raw material in both cases is magnesium sulphate. In one patent the process consists in passing hydrogen sulphide over the sulphate at a low red heat. The sulphur dioxide is obtained directly in a sufficiently pure condition for liquefaction, if pure sulphuretted hydrogen is used. In the other process magnesium sulphate, mixed with coke or coal in fine powder, is subjected to a temperature of 600° to 700°C.

Sulphur dioxide is employed for bleaching paper, straw, wood, wool, silk, etc. It is also extensively used for the preservation of fruit, wine, meat, sugar and syrups. The fact that sulphur dioxide has very little "inverting"[1] action on sugar makes it a very suitable preservative of such foods. For the rapid disinfection of ships and for destroying rats and other vermin the portable containers of sulphur dioxide are very convenient.

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[1] " Inversion" is the transformation of cane or beet sugar (Sucrose) into grape sugar and fruit sugar (Fructose)

On evaporation liquid sulphur dioxide absorbs much heat, and is accordingly used in ice-factories.

The solution in water probably contains sulphurous acid, H_2SO_3, but although the acid in the free state can hardly be said to be known, yet the salts, known as sulphites, derived from the acid, are of some importance.

The normal sulphites, such as sodium sulphite Na_2SO_3, are slightly alkaline, and the bisulphites $NaHSO_3$ slightly acid.

Sodium sulphite may be made by passing sulphur dioxide into a solution of caustic soda (sodium hydrate) until saturated, thus producing first the bisulphite, then a further volume of caustic soda solution, equal to that used in the first instance, is added to complete the process. On allowing the solution obtained in the manner described to cool, a crop of crystals of sodium sulphite is obtained. Sodium carbonate is almost invariably used in large scale production; crystals of the carbonate, i.e. "washing soda," are placed in vats and a current of sulphur dioxide passed beneath a false bottom on which the soda rests. The resulting solution of the bisulphite is neutralized with a further quantity of soda. Sodium sulphite is used in industry as an "anti-chlor" to remove chlorine from paper, cotton, etc., which has been bleached by that agent. It is a weak bleaching agent, and is used for delicate fibres, and is also added to sugar juices to prevent them from turning brown during concentration. It is also used in photography. The bisulphite is also an energetic "anti-chlor." Sodium thiosulphate, more usually, though incorrectly, called "hyposulphite," is made by boiling a solution of sodium sulphite with sulphur

$$\underset{\substack{\text{Sodium}\\\text{sulphite}}}{Na_2SO_3} + \underset{\text{sulphur}}{S} = \underset{\text{" Hypo "}}{Na_2S_2O_3}$$

This product is used in photography as a fixing agent —" Hypo "—because it dissolves out the salts of silver on the photographic plate which have not been influenced by light. It is also a valuable " anti-chlor " in dye works, and in the laboratory its marked reducing action is very useful. A still more energetic reducing agent, and one of increasing importance, is sodium hydrosulphite, $Na_2S_2O_4$. This substance is used in indigo dyeing and as a " discharge " for certain colours in the printing of fabrics. Various products containing hydrosulphites are known under trade names such as " Hydros," " Formosul," etc.

CHAPTER III

SULPHIDES AND CHLORINE COMPOUNDS OF SULPHUR.

SODIUM sulphide, Na_2S, is produced by the removal of oxygen from sodium sulphate, Na_2SO_4. "Saltcake," the name under which crude sodium sulphate is known, is reduced by adding carbon, in the form of coal, and heating in a furnace

$$\underset{\text{Saltcake}}{Na_2SO_4} + \underset{\text{Coal}}{C} = \underset{\text{Sodium sulphide}}{Na_2S} + \underset{\text{Carbon dioxide.}}{2CO_2}$$

The sulphide is used in the preparation of a series of dyes, and in the operation of cotton dyeing, but in even larger quantities by tanners for de-hairing hides.

The occurrence of hydrogen sulphide or sulphuretted hydrogen has already been mentioned. This disagreeably smelling gas is produced both in the laboratory and in the chemical works by the action of dilute sulphuric acid on sulphides. It is largely used in chemical analysis for the detection and separation of metals. The sulphides of the metals are mostly characteristically coloured, so much so that zinc sulphide (white), cadmium sulphide (yellow), and mercury sulphide (red) (*see* below) are used for paints. In addition to the colour distinctions of the sulphides, they can be grouped thus—(*a*) insoluble in dilute acid, (*b*) insoluble in alkali, and this forms the basis for the methods of separating either individual metals or groups of metals. Most pyrites used for the production of sulphuric acid contains some arsenic, and for many purposes this must be removed; to this end hydrogen sulphide is used, since the resultant arsenic sulphide is insoluble in sulphuric acid. The gas is poisonous and should not be inhaled.

Iron mono-sulphide is commonly used for making the hydrogen sulphide, and may be made by direct combination, under the action of heat, of iron and sulphur, but as it is a by-product of certain other processes, such as the extraction of antimony from its ore (stibnite) it is usually derived from that source. Where iron pyrites (iron disulphide) is available, it may be heated with material rich in iron to form the mono or ordinary sulphide.

$$\underset{\text{Iron disulphide Pyrites}}{FeS_2} + \underset{\text{Iron}}{Fe} = \underset{\text{Iron monosulphide.}}{2FeS}$$

Zinc sulphide mixed with barium sulphate, known as lithopone, is largely used to replace white lead paints, as it is non-poisonous to handle, and is not blackened by hydrogen sulphide. Lithopone is made by precipitating a hot solution of zinc sulphate with a hot solution of barium sulphide. The resultant heavy white precipitate is washed, dried and strongly heated before it is in a condition ready for the paint manufacturer. Cadmium sulphide is used as a light orange or yellow paint. It is resistant to the action of sunlight, and possesses a good covering power. It is prepared by passing hydrogen sulphide into a solution of a cadmium salt. Mercury sulphide has its value as a colour. Some specimens of native "cinnabar" have a bright red colour, and so only require grinding, but "vermilion" is usually made artificially. There are several modifications of the "wet process" which have largely superseded the "dry" or sublimation process, since the product of the former method is superior. By very thorough mixing of mercury and sulphur a black product results, which is changed into the red sulphide by a strong solution of potash. Mercury sulphide exists in both red and black forms, when prepared by hydrogen sulphide and a mercury salt it is black, but is converted to the red crystalline form by heat. The colour is apt to degenerate in time, but is not blackened so readily as some other red paints by the impurities which contaminate the air of towns.

Carbon bisulphide is made by the direct combination, at a high temperature, of sulphur and carbon. The retorts used are either heated externally or preferably by internal electric heating. The method of internal heating is mainly employed in the United States. The vapour of the sulphur passes up through the charcoal in the upper portion of the vertical shaft furnace, and the gaseous carbon bisulphide passes out from the top into condensing towers. With the older type of plant, in addition to the higher fuel consumption, the retorts require frequent replacement, and in these respects are much inferior to the electrically heated furnaces. The foul-smelling crude liquid carbon bisulphide from the condensers is purified by distillation and by treatment with caustic soda and other agents. The smell of the pure substance is not unpleasant, but that of ordinary qualities is very objectionable. The vapour of carbon bisulphide ignites at a low temperature, and this property as well as the low boiling point (46°C., 115°F), necessitates very great care in storage and transport.

Carbon bisulphide is an excellent solvent for oils, fats, sulphur, etc., and is used principally in this capacity; smaller amounts are used in the rubber industry, and as an insecticide for destroying weevils in grain. Wherever possible, owing to its dangerous inflammability, carbon bisulphide is being superseded by light petroleum or non-inflammable solvents, such as carbon tetra-chloride (CCl_4).

Sulphur combines fairly readily with chlorine, and produces a series of compounds, thus—

S_2Cl_2 Sulphur monochloride.
$S\,Cl_2$ Sulphur di-chloride.
$S\,Cl_4$ Sulphur tetra-chloride.

The monochloride is used either alone or containing dissolved sulphur for the "cold" vulcanization of rubber. Sulphur chloride is also the starting point in the making of some other products, which in turn are the half-way houses or "intermediates" in the manufacture of medicinal substances and dye-stuffs. The following bodies, which although hardly receiving any mention in most text-books, and which might be considered merely as chemical curiosities, are of considerable and increasing importance—

Thionyl chloride—

$$\underset{\substack{\text{Sulphur}\\\text{chloride}}}{S_2Cl_2} + \underset{\substack{\text{Sulphur}\\\text{trioxide}}}{SO_3} = \underset{\substack{\text{Thionyl}\\\text{chloride}}}{SOCl_2} + \underset{\substack{\text{Sulphur}\\\text{dioxide}}}{SO_2} + \underset{\text{Sulphur.}}{S}$$

Sulphuryl chloride—

$$\underset{\substack{\text{Sulphur}\\\text{dioxide}}}{SO_2} + \underset{\text{Chlorine}}{Cl_2} = \underset{\substack{\text{Sulphuryl}\\\text{chloride.}}}{SO_2Cl_2}$$

Chlor-sulphonic acid—

$$\underset{\substack{\text{Hydrochloric}\\\text{acid}}}{HCl} + \underset{\substack{\text{Sulphur}\\\text{trioxide.}}}{SO_3} = \underset{\substack{\text{Chlor-sulphonic}\\\text{acid.}}}{SO_2(OH)Cl}$$

The last mentioned is extensively used in the manufacture of saccharine, antiseptics and dyes.

CHAPTER IV

SODIUM SULPHATE

SODIUM sulphate is found native in many parts of the world, either in solution or as a deposit left by the drying up of lakes. Crystallized sodium sulphate, known as Glauber salts or Mirabilite (Na_2SO_4, $10H_2O$), occurs in enormous quantities in Siberian lakes, notably those of Marmyshansk. The mineral Thenardite is sodium sulphate without water of crystallization, and if accompanied by gypsum is known as Glauberite.

The mineral waters of many spas contain much sodium sulphate as well as sodium carbonate. The natural waters described as "bitter waters" contain the sulphates of both magnesium and sodium. The saline springs of Cheltenham contain salt (sodium chloride) and sodium sulphate, and those of Epsom are rich in magnesium sulphate.

Until recently the manufacture of sodium sulphate, better known by the trade name of saltcake, was the first stage in the Leblanc process for the production of "alkali," and the group of chemicals included in the "Heavy Chemical Industry." This group includes "caustic soda" sodium carbonate ("alkali"), bleaching powder, hydrochloric acid.

In view of the important part played by saltcake in the chemical industry a chapter is assigned to this sulphate. Since the introduction of the "Ammonia Soda Process" and electrolytic methods, the amount of saltcake produced has very materially decreased, and beyond satisfying the demands for glass works and the requirements of sodium sulphide makers, may be almost regarded as the waste product of hydrochloric acid manufacture. Belgian glassworks require about 80,000 tons annually, and a further 10,000 tons are necessary for sulphide manufacture and other purposes.

The conversion of common salt, which occurs so abundantly in nature, forms the foundation of the soda industry. The history of this enormous industry began with the work of Nicholas Leblanc. A prize was offered in 1775 by the Académie des Sciences for the most practical and profitable process for making soda from salt. The alkali in common use was that obtained from the ashes of seaweed (Kelp) and it was recognized that some method should be devised for obtaining a more plentiful and cheaper supply of alkali from the abundant deposits of salt. Capital was found for building works at St. Denis, but after the execution of the Duke of Orleans, the factory was confiscated. The Emperor Napoleon restored the works to Leblanc, but the gift was of little avail, as he had then no capital. He died by his own hand in extreme poverty. Plate glass made with soda manufactured by the new method was introduced by the famous St. Gobain Company. The high duty on salt, together with political conditions, hindered the progress of the new industry. Two small works were started in England, those of Losh (1770–1861) on the Tyne and Tennant on the Clyde. In 1823 Muspratt erected his alkali works in Liverpool, and in 1828, when there was no further room for extension, the works near St. Helens were started, followed shortly afterwards by those at Newton.

The industry was continually harassed by litigation owing to the escape of noxious gases. The erection of chimneys of great height (400 feet in one instance), did not prevent mischief, but the introduction in 1838 of Gossage's coke-tower condenser was eventually the means of overcoming the difficulties. In 1850 the works at Widnes and Flint were begun, and a period of extraordinary prosperity dawned in the alkali trade. Small as the quantities may seem when compared with the output now, the following figures are of interest—

		1852	1872
Alkali	(Tons)	26,300	93,600
Washing soda		3,500	8,650
Soda bicarb.		1,200	11,700
Bleaching powder		1,250	8,060

In 1880 the alkali production had risen to 430,000 tons and exceeded 800,000 in 1896. In 1909 the export alone amounted to nearly 100,000 tons.

A method of producing sodium sulphate from salt, without the necessity of first making sulphuric acid, was formerly extensively used. This system (Hargreaves-Robinson) has of recent years declined in popularity, but perhaps a modernized and improved plant may again find favour.

The product is particularly suitable for glass manufacture owing to the smallness of the amount of iron (about 0.08 per cent.) which it contains. In this process common salt is exposed to the action of hot gases containing sulphur dioxide, air and steam.

$$\underset{\text{Salt}}{2\mathrm{NaCl}} + \underset{\substack{\text{Sulphur}\\\text{dioxide}}}{\mathrm{SO_2}} + \underset{\substack{\text{Oxygen}\\\text{(air)}}}{\mathrm{O}} + \underset{\substack{\text{Water}\\\text{(steam)}}}{\mathrm{H_2O}} = \underset{\text{Saltcake}}{\mathrm{Na_2SO_4}} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2\mathrm{HCl}}$$

The salt is crushed and shaped into small cakes by a machine, and after drying in a long biscuit oven, these are charged into large (20 ft. diam.) iron cylinders for conversion into saltcake. The object of having the salt in cake form is to enable the gases to pass through the mass more readily. A very pure salt will not react in the way shown, and consequently rock salt is used.

The active agent in the rock salt is probably the small quantity of iron which acts as a "catalyst." (*See* note, p. 27).

Several patents have appeared during the last few years to utilize the same reactions as those used in the Hargreaves process. These seem, however, to involve very great mechanical difficulties. In one of them the vapour of salt is injected into an atmosphere of sulphur dioxide and air, to produce saltcake and chlorine, or, if steam is also present, saltcake and hydrochloric acid.

Saltcake is commonly produced by the action of sulphuric acid on salt, first in the "pot" and then in the furnace. In the old types of furnaces, now obsolete, the hydrochloric acid which is evolved, was not kept separate from the fuel gases, which caused difficulties in the condensation of the acid, and caused wide-spread destruction of vegetation. In those early days, the utilization of the hydrochloric acid was a difficulty, but, as hinted before, the acid made is to-day of almost greater importance than the saltcake. The first stage, carried out in the "pot" (a shallow cast-iron pan about 10 ft. in diameter) results in a mixture consisting mainly of sodium bisulphate,

$$\underset{\text{Salt}}{NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sodium bisulphate}}{NaHSO_4} + \underset{\text{Hydrochloric acid}}{HCl}.$$

but this action is not, in reality so smooth as the equation suggests, since some unchanged salt, and some normal sulphate are found in the mass. The pot is covered in with a dome of brickwork, and the hydrochloric acid gas passes along earthenware pipes either to condensing towers or to other plants where acid in gaseous form is required. The pot is kept hot by the flue gases which have already given up most of their heat to the furnace. As the temperature of the pot is comparatively low, the acid produced is of higher grade in many respects than that made in the second or furnace stage. Attempts have been made to replace the whole of the very arduous hand labour of saltcake furnaces by mechanical means, but unqualified success has not been achieved, although mechanically worked pots and furnaces are in use. The "pot man" introduces a weighed charge of salt into the pot and adds the necessary amount of sulphuric acid from a cistern (heated by waste heat from the pot). A very considerable amount of judgment is necessary in carrying out a satisfactory run, as many factors contribute to the result. The strength of the acid used is varied slightly according to the nature and condition of the salt, and to the desired character of the product.

It is usual to arrange the time-table of the saltcake furnaces so that the stream of hydrochloric acid gas is reasonably constant. This can be done by fixing the time-interval between the successive charging of the pots and arranging for the duration of each stage in the manipulation. By such a plan the stage of very rapid gas production of a particular pot will coincide with the slower gas evolution of the other pots. When the decomposition of the salt is judged to be sufficiently advanced the "pot man" raises the dampers in the short tunnel between the pot and the furnace. The charge is "shoved" by a special long-handled tool into the furnace, where it is received on a paddle by the "furnace man" who spreads the charge over the bed of the furnace. Both "shoving" and spreading are very arduous, but a pair of skilled and experienced men will, by mutual collaboration, carry out this part of the work with apparent ease. It is not difficult to distinguish "old hands" from those new to the work. After spreading the charge, and perhaps raking and turning over the furnace, the doors are closed.

The conversion of unchanged salt and of the bisulphate is completed by this roasting—

$$\underset{\substack{\text{Sodium}\\\text{bisulphate}}}{NaHSO_4} + \underset{\text{Salt}}{NaCl} = \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl.}$$

The roasted charge is raked into iron boxes to cool down a little, as otherwise the clouds of acid vapour are troublesome. With experience the workmen can turn out saltcake of great uniformity, and can control to a large extent the amount of free acid and unchanged salt in the finished product. Good saltcake contains about 95 per cent. of sodium sulphate, but lower grades are quite common.

Note on “Catalysis”

Catalyst is the term applied to a group of substances which speed up chemical reactions and which, after transforming a very large amount of the substances concerned in the reaction, are found unaltered themselves at the finish. It has been long known that the speed of many chemical changes, which take place very slowly under ordinary conditions, is enormously increased by the addition of certain substances which can be recovered, apparently unchanged, after the reaction is completed. For a long time the view was held that catalysts were bodies capable of forming very unstable intermediate compounds with the reacting substances, and that by the splitting up of these the catalyst was re-formed. In such cases, where unstable intermediate compounds have been proved to exist, the name “ pseudo-catalyst ” has been proposed, because the above theory does not suffice to give a general explanation of all catalytic phenomena. Substances may act as “ negative catalysts,” and impede or prevent certain reactions which would otherwise take place easily. Catalytic phenomena have not yet received a general and positive explanation. It is possible that all substances may be specific catalysts for certain reactions, and perhaps all reactions are the result of catalysis.

CHAPTER V

SULPHATES OF CALCIUM, ALUMINIUM, AMMONIUM, COPPER, IRON AND ZINC

CALCIUM sulphate is found abundantly in nature (1) Anhydrite, without water of crystallization, (2) Gypsum, with two molecules of water. In the form of transparent crystals it is known as Selenite, which is frequently present in large well formed crystals in the London clay. Gypsum, when heated to a temperature of about 120°C, loses a portion of the water and is then known as plaster of Paris. On mixing this partially dried gypsum into a paste with water, it rapidly re-combines with the water and sets as a hard mass. If in the first instance gypsum is heated too strongly it loses its power of hardening when mixed with water, and is then known as over-burnt or dead plaster. The burning of crude gypsum requires great care, as the important setting properties of the plaster are very markedly diminished by either insufficient or too prolonged heating. The original gypsum contains about 22 per cent. of water, and the finished product plaster about 7¾ per cent.

Aluminium sulphate is formed by heating the mineral known as Bauxite (Aluminium hydrate) with sulphuric acid of the necessary strength. The hot saturated solution is poured into shallow moulds, where it solidifies. Aluminium sulphate is used in the tanning industry and in paper making as a filler or hardener. It is a useful agent for purifying water, since it clarifies turbid and coloured waters in the following manner. The action of the bicarbonates in the water on the aluminium sulphate results in a very flocculent and voluminous precipitate of aluminium hydrate, which carries down with it both suspended and dissolved organic matter. This type of phenomenon is known as "adsorbtion"; other practical applications are to be seen in the use of charcoal for decolourizing sugar syrups and the treatment of oils with fuller's earth.

The grade of aluminium sulphate used as a mordant[1] in the dyeing industry must not contain free sulphuric acid or iron. The compounds of metals with dyes are known as "lakes," and in the case of iron the lakes are usually violet in colour, which deadens the other shades. Aluminium sulphate unites, as do several other sulphates, with alkali sulphates to form the group of substances known as alums. The alums crystallize in magnificent crystals which contain twenty-four molecules of water. Amongst the best known are potash alum (common alum) $Al_2(SO_4)_3.\ K_2SO_4\ 24H_2O$, iron alum, chrome alum, ammonia alum.

Alum may be prepared from most minerals which are rich in alumina, but alunite or alum stone affords special advantages, since it contains a double sulphate of aluminium and potassium. After roasting the alum stone and extracting the product with sulphuric acid the solution is allowed to crystallize.

Alum and aluminium sulphate are chiefly used by the dyer as mordants, but they are also employed by the paper maker and leather dresser.

Ammonium sulphate is a very valuable compound to the agriculturist, forming an important constituent of many artificial manures. Almost the whole supply of ammonium sulphate is at present derived from the

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[1] Mordants are the substances which are used to combine with dyes in cases where the latter are not fixed on the fibre directly. The compound formed is termed a colour lake. The mordant is usually deposited on the fibre previous to the application of the dye.

distillation of coal, either in gas works or in the manufacture of metallurgical coke. The watery liquid known as ammoniacal liquor or gas water usually contains about 1 per cent. of ammonia. The ammonia is driven off from the liquors by distilling them with lime, and the gaseous ammonia is then absorbed in sulphuric acid and sulphate of ammonia is produced. The commercial product is usually light grey in colour, and may contain traces of free sulphuric acid and other impurities. A very pleasing improvement has taken place recently, and the home-produced article is now frequently as good as the former German product. About 500,000 tons of ammonium sulphate are made annually.

Copper sulphate, or blue vitriol is the most widely used of all salts of copper. It is obtained by dissolving copper in hot dilute sulphuric acid in the presence of air. By the action of air and moisture copper pyrites is slowly oxidized to copper sulphate. This action is utilized to obtain metallic copper from ores and residues containing small amounts of copper. The treatment of the pyrites "cinders," or burnt ore residues, in the manufacture of sulphuric acid, is described later.

The process of making copper sulphate is as follows: Copper in granulated form is repeatedly sprayed with hot dilute sulphuric acid, good contact with air being encouraged. The acid liquor is circulated over the copper until a strong solution is obtained, which is then allowed to crystallize in vats.

Copper sulphate has many practical applications and is, therefore, manufactured on a very large scale. It is used in considerable quantities in vine growing districts as a preventive and remedy for the vine disease known as peronospora; and also alone, or mixed with other materials, for spraying potatoes and other crops, Italy alone requiring about 75,000 tons per annum. Blue vitriol is further largely used in copper plating, for preserving timber, etc., and in pigments.

Iron sulphate (green vitriol or copperas) is used in several industries. It can be readily prepared by dissolving iron in sulphuric acid, but cheaper methods are available. By a partial roasting, iron pyrites (FeS_2) is converted into the lower sulphide (FeS), which is readily oxidized to sulphate ($FeSO_4$) by exposure to the air. The mass of weathered ore is extracted with water, and after clarifying, the solution is run into vats. Green vitriol is frequently obtained as a by-product in other industries, such as the "pickling" of iron plates or rods to remove the "mill scale" before galvanizing or drawing into wire. Iron sulphate is largely used in mordanting wool preparatory to dyeing black with logwood, in the manufacture of black inks and the various types of blue pigment of which Prussian blue is the best known.

The ornamental stone of fine blue colour found native (Lapis Lazuli) can be artificially prepared, the product being known as ultramarine. Ultramarine is made in large quantities by heating a mixture of china clay, sodium sulphate, sulphur and coal. The bright blue form of ultramarine is used in paints, for tinting and printing wall paper; also extensively for correcting the yellowish shade of linen ("blue") paper, starch, etc. Zinc sulphate or white vitriol may be manufactured by leaching roasted zinc sulphide (i.e. zinc blende in which the sulphide has been oxidized to sulphate)

$$\underset{\text{Zinc sulphide}}{ZnS} + \underset{\text{Oxygen}}{2O_2} = \underset{\text{Zinc sulphate}}{ZnSO_4}$$

with water and allowing the solution to crystallize. Zinc sulphate is used in calico printing, dyeing, as a "drier" in oil paints, and in pharmacy.

CHAPTER VI

SULPHURIC ACID OR OIL OF VITRIOL

SULPHURIC acid probably plays a larger part in the world of industry than any other commodity. Nearly every manufactured article requires sulphuric acid at some stage or other of its process, so much so that it has been maintained that a fair criterion of the degree of civilization of any country is its consumption of sulphuric acid. It cannot be stated definitely by whom sulphuric acid or oil of vitriol was first made. Some attribute the discovery to Rhases (born 932). We know that a certain alchemist, known to historians of chemistry as pseudo Geber (fourteenth century) to distinguish him from the real Geber (ninth to tenth century), speaks of a liquid which must have been, almost certainly, sulphuric acid. This alchemist records that when alum is strongly heated a spirit possessing a high degree of solvent power distils over, but he did not apparently make a complete study of its properties. Basil Valentine, a Benedictine monk, who flourished in the fifteenth century, was a truly remarkable man, and his knowledge of practical chemistry excites our wonder. His writings show that both he and his predecessors were aware that oil of vitriol could be produced by (1) distilling a mixture of green vitriol (copperas) and pebbles, (2) by setting fire to a mixture of brimstone and saltpetre.

There was, no doubt, some confusion between sulphurous and sulphuric acids.

Libavius, at the end of the sixteenth century, showed how the various methods then in use for preparing sulphuric acid might be simplified.

He also established the fact that the acid produced by various methods—from alum, green vitriol, or sulphur, was one and the same substance.

The introduction of sulphuric acid into England is ascribed to Cornelius Drebbel. Drebbel (born in Holland, 1572), came to England in 1604, probably with his friend Huygens. He built a submarine boat and navigated it from Westminster to Greenwich. He died in London, 1634, " very fair and handsome and of very gentle manners, altogether different from such like characters"! He also invented incubators for chickens and contributed largely to the introduction of the microscope into England.

Dossie furnishes evidence (" Elaboratory Laid Open," 1758) that Ward's patent was being worked. He was an English Pharmacist and the principal founder of the Society for the Encouragement of Arts, Manufactures and Commerce. The use of a mixture of sulphur and saltpetre is believed to have been begun by Lefevre and Lemery, but " Dr." Ward (1685-1761) had the monopoly in England, as he best knew how to manage the process (*Eng. Pat.* 1749, No. 664). Ward built the first sulphuric acid works at Twickenham, but the stench causing much annoyance to the residents, he removed in 1740 to Richmond. He heated a mixture of sulphur and saltpetre in iron pots and collected the acid produced in glass vessels, which contained a little water. The very dilute acid obtained in this way was laboriously concentrated in glass retorts heated on a sand bath. Roebuck erected the first lead chambers to replace the glass vessels as used by Ward, at Birmingham, in 1746, and three years later at Preston Pans. The first chambers were very small, and for a long period a size of about 10 square feet was not exceeded The mixture of sulphur and saltpetre in the vessel was set alight and the door closed. As soon as the acid vapours were absorbed by the water present, air was admitted, a further quantity of the mixture introduced, and the same procedure followed.

The acid made in this manner was not only used in England, but was exported, and it is to this fact that the name "English sulphuric acid" was adopted, and is still in use in some countries. Kingscote and Walker built a works for the manufacture of sulphuric acid in Battersea, in 1772, and one in Eccles ten years later. The Eccles factory had four square chambers, each 12 ft., and four 10 square ft. in section, and 40 ft. in length. A further step forward in the history of the chamber process was the adoption, at the suggestion of Chaptal, of a method of burning the sulphur in a separate vessel outside the chamber, and causing the gases to pass into the chamber after mixing with nitrous gases and steam. This procedure had the effect of speeding up the reaction and largely increasing the output of acid.

Previous to 1788 the consumption of sulphuric acid was small, but at that date the use of chlorine for bleaching purposes began, and the methods of that day required large quantities of sulphuric acid in the manufacture of bleaching compounds.

The production of sulphuric acid centres in the oxidation of sulphur, first to the dioxide (SO_2) by burning, and then by other means to trioxide (SO_3), followed by the solution of the latter in water.

$$\underset{\text{Sulphur}}{S} + \underset{\text{Oxygen}}{O_2} = \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2}$$

$$\underset{\substack{\text{Sulphur}\\\text{dioxide}}}{SO_2} + \underset{\text{Oxygen}}{O} = \underset{\substack{\text{Sulphur}\\\text{trioxide}}}{SO_3}$$

$$\underset{\substack{\text{Sulphur}\\\text{trioxide}}}{SO_3} + \underset{\text{Water}}{H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

The mere mixing of the dioxide with air or oxygen is insufficient, as combination does not take place sufficiently rapidly without the intervention of a third substance. This oxidation is effected, in the method most usually employed, by an oxide of nitrogen. The theories and opinions as to the exact events in the chamber process are very numerous. No attempt will be made to discuss the pros and cons of the various equations which have been put forward from time to time. When it is appreciated that the composition of the gases entering the chamber system is undergoing continuous changes both of composition and of physical condition, it will be readily grasped that a long list of possible reactions can be made out, and many of these may be taking place at the same time in different parts of the system. The following equations may be taken as a guide, but the formation of intermediate compounds, although such have been proved to occur, will not be discussed in detail.

$$\underset{\substack{\text{Sulphuric}\\\text{dioxide}}}{SO_2} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Nitrogen}\\\text{peroxide}}}{NO_2} = \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{oxide}}}{NO}$$

$$\underset{\substack{\text{Nitric}\\\text{oxide}}}{NO} + \underset{\text{Oxygen}}{O} = \underset{\substack{\text{Nitrogen}\\\text{peroxide.}}}{NO_2}$$

In this simple form it appears that quite a small quantity of nitrogen peroxide (NO_2) should suffice, as with more oxygen it is re-formed, and so is again available for oxidizing a further quantity of sulphur dioxide. In actual practice, however, air must be used as the source of oxygen. Since air contains only one-fifth of its volume of oxygen, a large quantity is necessary, and this means that the active gases are much diluted by the useless nitrogen in the chambers. The process would accordingly be very slow, if a high percentage of nitrogen oxides were not present. The valuable oxides of nitrogen, previous to about 1860, were largely lost, in spite of the proposals of Gay Lussac, in 1827, to recover them by means of towers, packed with coke, and sprinkled with strong sulphuric acid, by which they might be absorbed. The Gay Lussac towers have perpetuated the memory of that masterly investigator, whose work is encountered in almost every branch of chemical investigation, and who thus helped materially to advance chemical industries.

The first recovery towers were erected in 1842, but did not come into general use until the invention of the "Glover Tower" overcame difficulties connected with the concentration of sulphuric acid. A strong sulphuric acid is necessary for the absorption of the nitrous gases, but dilution with water to a weaker acid is further necessary to release the absorbed oxides, and this involved a re-concentration—a costly and by no means easy thing in those days. Before 1838 native sulphur from Sicily was used as the source of sulphur dioxide for conversion into sulphuric acid.

In that year a monopoly was granted for export to a Marseilles firm, who raised the price from £5 to £14 per ton. The immediate answer of England was to turn her attention to the replacement of sulphur by pyrites, as proposed by Dr. Thomson (1773–1852). The firm of Hill, of Deptford, were the first to use pyrites in their works.

The first large installation for using the gases given off in the roasting of pyrites, to replace those of burning brimstone, was that erected in the works of Thomas Farmer, of London.

CHAPTER VII

SULPHURIC ACID MANUFACTURE

In England sulphur is now almost entirely replaced by pyrites as the raw material for sulphuric acid manufacture, but where sulphur is relatively abundant, as in certain localities in America, much is used in the place of pyrites.

It is not easy in burning sulphur to avoid some of it distilling off unburnt, and thus causing trouble. In some brimstone furnaces air is admitted in such quantity as to ensure combustion sufficient to maintain the heat of the furnace. The sulphur partly sublimes into a second compartment into which a further supply of air is admitted to complete the combustion. Recently rotary furnaces have been introduced.

The pyrites ore is first broken up into lumps about the size of road metal. Formerly the breaking was largely done by hand, in order to avoid the production of much fine material or " smalls." Previous to the introduction of the various types of furnaces for using smalls the latter constituted a source of trouble and loss. Many attempts have been made to form the fine pyrites into balls or cakes, which could then be worked up with the lumps. The introduction of mechanically worked " burners " has largely done away with the necessity of such expedients. If judiciously spread in the kilns a certain amount of small ore may be worked off with the lump, but there is always a chance of the air supply being checked or the fine ore passing through the grate unburned, thus causing an objectionably high percentage of sulphur to remain in the " cinders."

A type of kiln for burning lump ore is shown (Fig. 11) which embodies most of the important features which must be taken into consideration in the design of pyrites kilns.

It is usual to build the kilns in sets of about thirty, arranged in a double row, back to back, so as to assist in conserving heat.

To start a set of " burners " they are first partially filled with burnt ore (" cinders ") and heated to a dull red by firing with old timber and coke. Pyrites is then charged in and the sulphur ignites. The kiln is coaxed into action by regulating the supply of air and ore, and gradually brought into satisfactory working, producing in a couple of days an even flow of sulphur dioxide. The kilns are charged in a definite order and each " burner-man " has a fixed number of charges per shift. The actual amount of ore charged depends on the size of the kilns and the richness and character of the pyrites employed.

The sulphur in the ore may vary from 30 to 50 per cent., but about 45 per cent. is usual.

The pyrites kilns or burners are protected from loss of heat by covering the exposed end with non-conducting material, and by a bed of sand above the top arches. In sulphuric acid manufacture the sulphur in the pyrites is not only the raw material, but in large measure the fuel also, and consequently loss of kiln heat must be obviated as much as possible. The bottom of the kiln consists of a grate fitted with square bars, which can be turned round as required by a large key which fits on to the end of the bar. The bars in the normal position are ⟐ ⟐, but when turned to the position ⊡ ⊡ the spaces between the bars are increased from about 1¼ inches to 2 inches. The rotation of the bars breaks up and loosens the burnt pyrites, which then falls into

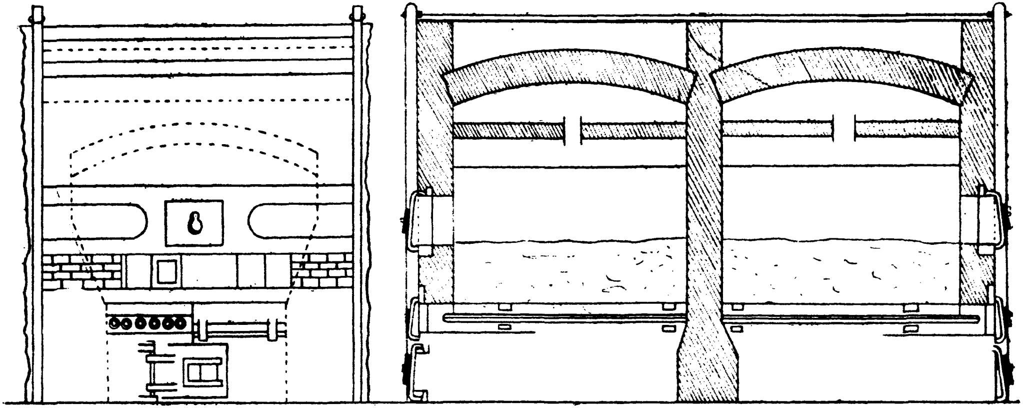

FIG. 11

PYRITES KILNS

the compartment below the grate to cool. Badly or partially burnt ore may jamb between the bars and cause difficulties.

The air necessary for the combustion of the sulphur in the ore is very carefully regulated by small sliding doors. If the air supply is too small, large lumps of partially burnt ore, cemented together by the fusible mono-sulphide of iron (FeS) may form, and sulphur, instead of its oxide, pass into the gas flues. These lumps, if formed, must be broken up and perhaps pulled out of the kiln—a laborious and disagreeable task. If on the other hand too much air is admitted, the kiln may be chilled and not sufficiently hot to ignite the next charge ; further, of course, an excess of air will dilute the gases unnecessarily. The labour of working lump kilns is considerable and suggestions have been made to mitigate this by mechanical means. A few years ago a patent was granted for a mechanically worked pyrites burner with a revolving conical grate to obviate the "screwing" of the grate bars by hand labour. The writer is not aware if satisfactory results have been achieved.

The roasting of "smalls" is carried out almost entirely in mechanically driven furnaces, which have replaced, in most works, the hand-worked types. These hand-worked furnaces were usually built with a series of shelves, one above the other, from which the ore was raked from time to time until, in the course of many hours, it had traversed the whole of the shelves.

In modern practice the ore is mechanically fed on to the top of a large cylindrical furnace, and is gradually passed over a series of shelves or hearths. The first shelf frequently serves merely as a drying bed, and the actual roasting takes place on the succeeding hearths. The combustion of the sulphur in the ore is so controlled that the heat is never so great as to cause the ore to sinter into lumps or as to prevent the delivery of the roasted product at a reasonably low temperature from the lowest hearth. The ore on the hearths is turned over and moved forward by iron rakes with the teeth set at such an angle that the ore is conveyed alternately from the centre to the circumference of the furnace and *vice versa*. The raking arms are kept cool by the circulation of either air or water, according to the type of furnace employed. The arms are driven round by a hollow shaft passing up through the centre of the furnace (Fig. 12). In some designs of mechanical roasting furnaces the arms are so fitted into the central shaft that, in case of an obstruction, they are lifted out of

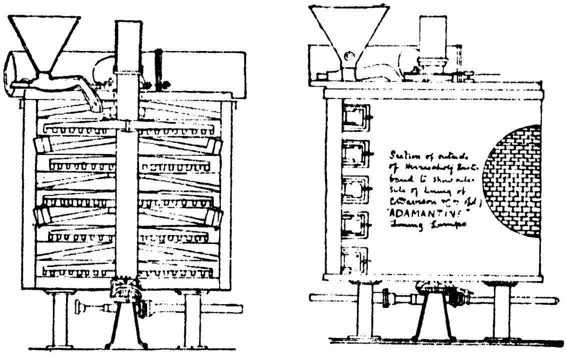

FIG. 12

PLAN SHOWING HERRESCHOFF FURNACE OR KILN FOR ROASTING PYRITES SMALLS, SPENT OXIDES, ETC.

Showing lining shelves, floor and gas pipes, made of Charles Davison & Co.'s (Ltd.) "Adamantine" Blue Fireclay Blocks and Pipes (Buckley, Chester).

the shaft; in others a "shearing pin" is introduced in the driving gear, which serves as a safety device and prevents extensive damage to the mechanism.

In some cases where the ore (e.g. zinc blendes) does not contain sufficient sulphur to maintain the temperature necessary for efficient roasting, extra heat is supplied to certain hearths, which are practically "muffles" or closed roasting hearths. In the majority of cases where an average quality of pyrites smalls is roasted, the temperatures of the various shelves are controlled by the regulation of the ore-feed and by the admission of air.

Some varieties of pyrites possess the disadvantage of splitting up on being charged into the hot kiln, and thus causing trouble, either by preventing the air permeating the charge or by causing much dust which is carried forward with the gases. In the case of some ores—the type of non-freeburning ores—the splitting takes place with explosive violence to such a degree that they are a source of danger to the burner men. The true cause of this explosive splitting is not known, in fact it is likely that the cause is not identical in every case. The presence of flinty material certainly does not account for this behaviour in many cases—the writer having experienced a very quiet and satisfactory burning of pyrites containing over 20 per cent. of silica!

The absence of free-burning properties in some ores is supposed to be due to the presence of combined or included water, or even to liquefied carbon dioxide, but a physical condition of strain seems the most acceptable explanation of such troublesome properties.

An important point which is intimately connected with the utilization of pyrites smalls for acid manufacture is that it provides an outlet for quantities of ore, amounting to millions of tons, which otherwise would be regarded as practically of no value. Most varieties of pyrites contain copper, but this may be present in such small amount that a metallurgical method of extraction is out of the question as a commercial proposition. These low-grade ores are treated at the mines as follows—The copper sulphide which they contain is converted by exposure to air and water into the soluble copper sulphate from which the metallic copper is precipitated by iron, the product being known as "cascara" or "copper precipitate." The ores, after being denuded of copper in this way, are usually in the condition of smalls, and may be roasted in mechanical furnaces for the production of sulphuric acid. In the case of pyrites containing a higher percentage of copper than those referred to above, but still of too low a grade to be described as copper ore, the sulphur is first roasted out for making sulphuric acid, and the pyrites cinders or burnt ore are afterwards treated by a roasting and lixiviation process for the extraction of copper and other metals which they may contain.

In some countries, notably America, enormous quantities of sulphuric acid are extracted from the gases of the copper smelting furnaces, and the acid may thus be regarded as a by-product. It is possible that in the future English copper smelters will also in some cases erect acid works to utilize the waste sulphurous gases which have hitherto been allowed to escape mainly into the atmosphere. A limit to the amount of acid allowed to escape into the air from chemical works is fixed by law, but at present copper smelters are not restrained by the same regulations.

CHAPTER VIII

SULPHURIC ACID MANUFACTURE (*Contd.*)

FROM the pyrites kilns the gases, which should contain about 9 per cent. of sulphur dioxide and the same amount of oxgyen, pass the " nitre oven " containing the " nitre pot." The latter is usually a cast iron trough about 2 feet in width and 4 feet in length. The pot is provided with a pipe at the bottom, which projects through the front of the kilns to allow the contents to be run out when required. The object of the nitre pot is to maintain the necessary amount of nitrous gases in the chambers, and to replace any loss of this valuable agent in the system (*see* p. 35).

The hot gases from the kilns keep the temperature of the pot up to a barely visible red heat. At definite intervals, usually once an hour, a few pounds of sodium nitrate (chili saltpetre, or shortly, " nitre ") is charged in with a scoop through a small opening which is provided with a close-fitting door. A measured quantity of sulphuric acid is run into the pot, regulated according to the strength of the acid and the quantity of nitre in the pot. The whole process is known as " potting," and the frequency and amount of nitre " potted " is determined by the composition, as shown by the colour of the gases in the vitriol chambers (*see* p. 52). The acid decomposes the nitre producing nitric acid, but at the high temperature of the oven this may be regarded as water and nitrous gas.

$$\underset{\substack{\text{Sodium}\\\text{nitrate}}}{NaNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{bisulphate}}}{NaHSO_4} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{HNO_3}$$

The sodium bisulphate thus produced is known as sal enixum, usually contracted into "sally." The "sally" is run off, by removing the plug which closes the run-off pipe into a cast iron tray, where it solidifies on cooling into cakes, which are often worked up in the saltcake pots (*see* p. 25). Care is required in emptying the pots as the hot liquid bisulphate may splash and cause severe burns which are difficult to heal.

From the nitre oven the gases pass into the bottom of the Glover tower. This tower does two things, (1) it accomplishes the concentration of acid that has already been made in the chambers, and (2) it "denitrates" or removes the nitrous compounds in the acid used in the Gay Lussac towers, thus returning the nitrous gases to the process. If this return of nitrous gases from the end to the beginning of the system is efficient, the amount of nitre required for the pot will be small. It must be remembered that the object of the nitre pot is to make up any deficiency in the nitrous gases necessary for the reaction. The Glover tower is made of stout lead sheet, and is lined with acid-resisting bricks. The tower is surrounded at the base by a dish of very thick lead, from which the hot and concentrated acid flows. Samples of the flow are taken from time to time, and the volumes of the weak acid from the chambers and the nitrous acid from the recovery towers respectively, introduced at the top of the tower, are regulated according to the strength and temperature of the outflowing acid (Fig. 13).

The acid flowing from the base of the Glover tower is the usual commercial "vitriol," and is generally about 75 per cent. true sulphuric acid. It is not pure, and contains impurities taken up from the gases from the pyrites kilns.

Glover towers are packed with some acid resisting

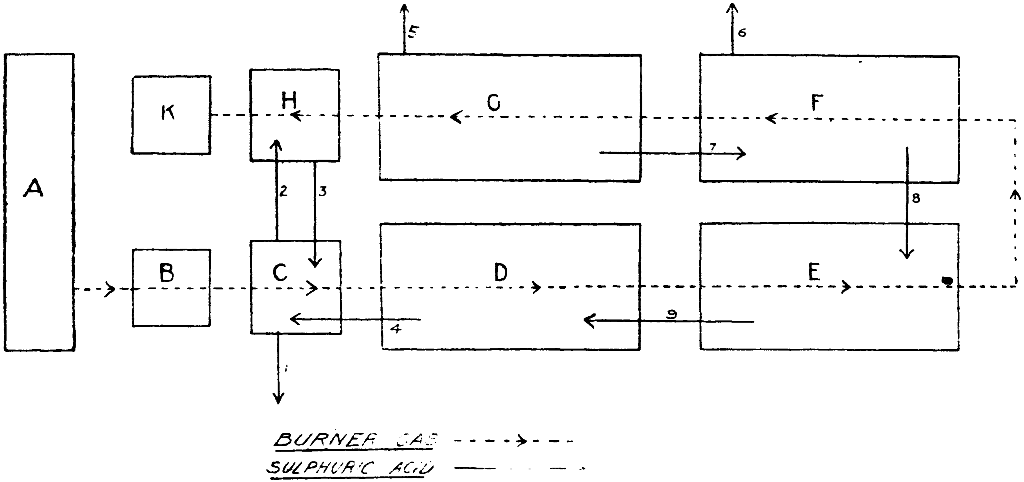

FIG. 13

DIAGRAM OF CHAMBER PROCESS

A Pyrites kilns. B Nitre oven. C Glover tower (burner gas enters at the bottom). D, E, F, G, 1st, 2nd, 3rd, 4th chambers. H Gay Lussac tower. K Chimney. 1. Acid for sale (flowing from the bottom of C). 2. Strong acid for absorbing nitrous gases, pumped up after cooling, from bottom of C to top of H. 3. Strong acid for de-nitration, pumped up from bottom of H to top of C, 2 and 3 are "circulation acid." 4. Chamber acid pumped to top of C. 5, 6. Weak acid for de-arsenication, etc. 7, 8, 9. Weak acid for concentration in Glover tower.

material, specially shaped bricks or rings are often used. Flint stones, particularly the irregularly shaped ones, make a satisfactory filling. The choice of a suitable filling material is not easy, as it is not possible to combine all the desirable qualities of packing in any one

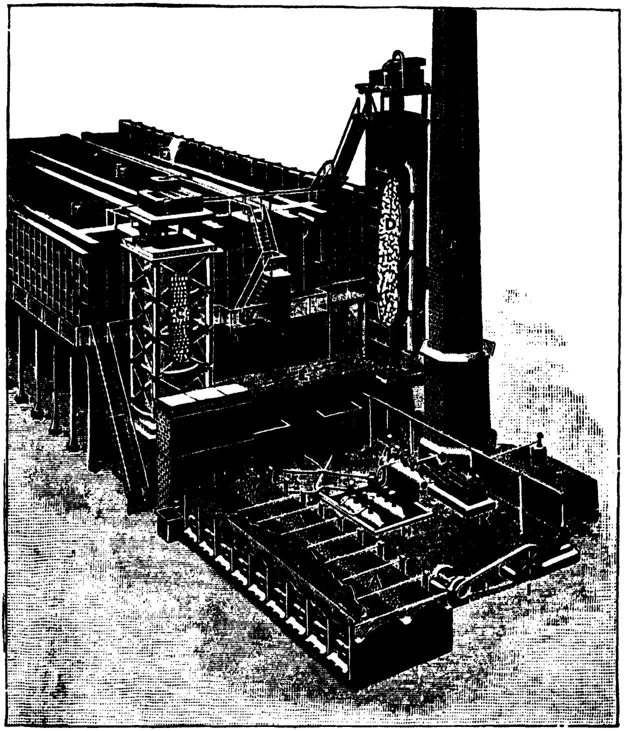

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FIG. 14

GENERAL VIEW OF SULPHURIC ACID WORKS

material or shape of material. It is obvious that the filling must be capable of resisting hot and concentrated acid without cracking or being seriously attacked; it must also provide space enough between the pieces to allow the sulphurous gases to pass through, and at the same time offer as large a surface as possible, so as to produce a thin but extensive film of acid for concentration by the hot gases (Fig. 15). For structural considerations it is desirable to use a filling which is as light as possible, but in any case the 30 feet Glover tower is a very costly item to construct.

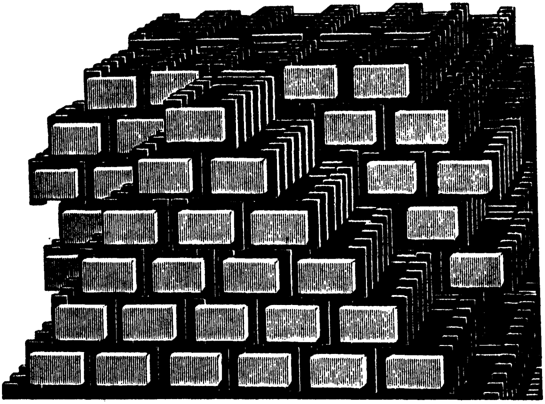

FIG. 15

"OBSIDIANITE" PACKERS.

Showing method of filling for Gay Lussac, Catch, or Contact Towers, Scrubbers, Denitrators, etc. For Glover Towers they are put in the same way, but with very dusty acid may be put in hollow down.

The feed of acid to the top of the tower is maintained from two cisterns, which are kept supplied by means of automatic pumps, known as "acid eggs" (*see* p. 78), or in some cases by centrifugal pumps. One of the stock cisterns is supplied with weak acid from the chambers, and the other with acid from the bottom of the Gay Lussac or recovery towers. The combined effect of the high temperature and the dilution with the weak acid is to remove the nitrous compounds in the Gay Lussac acid and return them to the system, together with the sulphurous gases from the kilns.

In some works liquid nitric acid is fed into the top of the Glover tower to serve the same purpose as the nitre pot, in other cases this plan is only adopted in starting up the system or as a rapid expedient for restoring a plant which is working badly owing to a deficiency of nitre. A method has recently been adopted which is likely in the course of a few years to supersede both the potting of nitre and the direct use of nitric acid in sulphuric acid manufacture by the chamber system (*see* p. 74). There is no doubt that a certain amount of the sulphur dioxide from the kilns is actually converted into sulphuric acid in the Glover tower, but authorities differ very materially as to the percentage "make" of acid in the tower. The gases leaving the top of the tower and entering the first chamber are a complex mixture, and frequently it is difficult to sample and not easy to interpret the results of analysis in a wholly satisfactory manner.

The ordinary form of vitriol chamber is an oblong rectangular construction of sheet lead, usually of greater breadth than height, but modern practice favours a high form of chamber. The size of these chambers is variable, but the following dimensions are customary—100 feet long, 25 feet wide, 20 feet high. Four such chambers form a set, being connected by lead tunnels which enter and leave the ends of the respective chambers.

The bottom of the chambers consists of a large shallow dish, into which the sides of the chamber hang down from the supporting framework. Before starting operations the sides are sealed with water or weak acid, so that no gases can escape.

Many varieties and devices for the suspension of the chamber walls and roof are in use to-day. The framework may be of iron or wood, and although of the greatest interest to the designer of chamber plant, details need not be given here. Other shapes of chamber than the rectangular are employed (*see* frontispiece). We shall have occasion to observe later that the whole manufacture can be carried out in towers (*see* p. 54), but this is not the process with which we are now dealing.

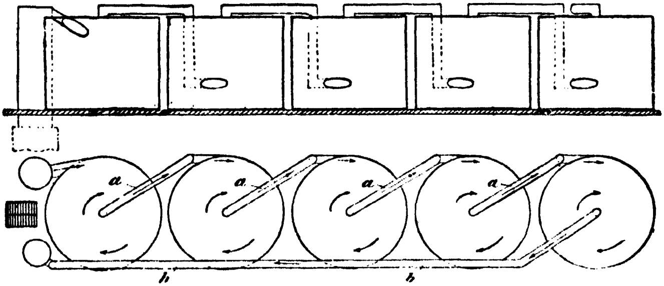

Fig. 16

TANGENTIAL CHAMBERS

The thorough mixing of the various gases in the chambers is imperative, and to enhance this circular or polygonal chambers have been designed. The best known is the tangential system (Fig. 16). Another design which, in addition to other advantages, aims at increased temperature control, employs tower-like chambers of conical shape, which can be cooled by water trickling down the outsides. The ordinary oblong chamber is usually protected from high winds and from abrupt changes of temperature by scantlings, or is even completely housed. In many situations it is an advantage to have the chambers at a good height above the ground level, as the space below can be used for pyrites stores or other purposes, and the chutes which convey acid from the various parts of the plant can be more conveniently arranged to deliver into the particular cisterns.

Most works have their own ideas, learnt from experience, of the best conditions of temperature and composition of the gases in each chamber. It must be clearly understood that chamber plants are worked in such a manner as to produce the type of acid required. As an illustration of this we may mention that the acid required for the manufacture of super-phosphates for fertilisers will obviously not require the same freedom from impurities as an acid which may ultimately be used in the preparation of a food product, or for the filling of electric accumulators. The manufacturer of superphosphate manures requires a large volume of relatively weak acid, and so there is no reason to aim at producing acid of high strength beyond that required in the working of the acid plant itself. A demand for a purer acid is met by taking advantage of the fact that the purer but weaker acid made in the last chambers of a set can be worked up separately for certain specific purposes (*see* p. 70). The acid formed in the first chamber contains 60 to 65 per cent. of true sulphuric acid, that formed in the end chambers being weaker. A temperature varying from 60°C to 100°C prevails in the first chamber, and about 35°C in the last of the set. At the higher temperatures the lead of which the chambers are made is liable to corrosion, but the output is decreased if the system is not warm enough.

Steam is introduced into the chambers to maintain the required temperature, or water sprays, specially designed for the purpose, to help in the heat control. The steam or water thus introduced is a necessary agent in the chemical changes taking place to form the sulphuric acid (*see* p. 34).

The colour of the mixture of gases in the various parts of the chamber system affords a very good guide to the acid maker. In the first parts of the plant (i.e. that nearest to the pyrites kilns) the gases are whitish, and gradually change, as the end of the system is reached, to a yellow-brown colour, and red-brown as they enter the Gay Lussac tower.

The Gay Lussac tower, or towers, as two " in tandem " are conducive to good working, are similar in general structure to the Glover towers. The lead sheets forming the tower are not so thick as in Glover towers, as both the gases passing up and the acid trickling down are cold. The packing may be of coke or, preferably, of acid-proof blocks or rings, which present a large surface and thus bring the gases passing up the tower into intimate contact with the stream of strong acid. The Gay Lussac tower is of large size, the capacity at least 1 per cent. of that of the chambers, and with tandem towers it may reach almost 4 per cent. The object of the Gay Lussac tower is to retain the valuable nitrous compounds for further use in the chambers, and allow the inert nitrogen to pass away. The gases leaving the Gay-Lussac pass away to the chimney ; these should be quite colourless, any brown colour signifying a serious loss of the valuable nitrous gases.

The acid used for absorbing the useful contents of the gases leaving the last chamber is strong acid from the Glover tower after it has been well cooled.

Most sulphuric acid is made in the first chamber, amounting to about 70 to 75 per cent. of the whole output; the second chamber contributes a further 15 to 20 per cent., and the remainder is furnished by other portions of the plant, including the Glover tower.

CHAPTER IX

TOWER SYSTEMS FOR MAKING SULPHURIC ACID

THE fact that some sulphuric acid is produced in the Glover tower has induced many investigators and inventors to substitute towers for chambers.

There are many varieties of the tower system of production, differing mainly in variety of devices to effect control. These systems must not be confused with the tower-like designs of chambers already mentioned (p. 50), in which the reacting bodies are mainly in gaseous form.

About twenty years ago reaction and mixing towers were introduced to increase output of acid. These auxiliary towers were usually placed between the chambers. An early form of reaction tower contained a large number of perforated earthenware plates, so arranged that the openings in consecutive layers are not in the same line. By this means a very intimate contact between the incoming gas and the liquid acid is obtained. A so-called chamber regulator, or additional tower, between the last chamber and the Gay Lussac towers has been found useful in the working control of the process. The tendency to increase the size of these auxiliary towers led to the proposal to employ a system of towers only, without chambers, relying mainly on the reactions taking place in the liquids.

The systems associated with the names Opl and the Griesheim Company are perhaps the best known. It cannot be stated that the tower systems have proved themselves in all respects superior to other designs of plant, but it must be acknowledged that the number of tower plants recently erected, or in the course of erection, is increasing fairly rapidly. Owing to the very recent date of the majority of the patents relating to the tower systems for making sulphuric acid, we will devote some space to this subject.

A point which may be of importance arises in connection with the difficulties encounted in the purification from dust of the sulphur dioxide produced in mechanical furnaces, without undue cooling of the gases. We shall have occasion to refer to the difficulty of cleaning the gas, and at the same time conserve the heat necessary for the successful working of the Glover towers. In one patent relating to the working of a tower system it is pointed out that the gases may be introduced at a much lower temperature than has hitherto been considered necessary. A series of six or eight towers is recommended, with arrangements for the circulation and distribution between the towers of the acid produced (Fig. 17). The regulation of the action is mainly controlled by the correct mixing of the acid produced in the various towers and by delivering the correct proportion into the appropriate towers. The chemical control required is very considerable, and the continuous presence of skilled technical chemists is necessary. The older systems are not so sensitive to rapid changes, and the wider working margin of conditions is an advantage, as less skilled attention is required.

The burner gases from the pyrites kilns, which may have been cooled, are passed through a series of towers in which they are treated with nitric acid.

In the first stage, requiring about 15 per cent. of the total tower-space, the sulphur dioxide is oxidized, and it is of the highest importance that the gas should be brought into intimate contact with an excess of nitric acid, so as to bring about a very rapid oxidation. For

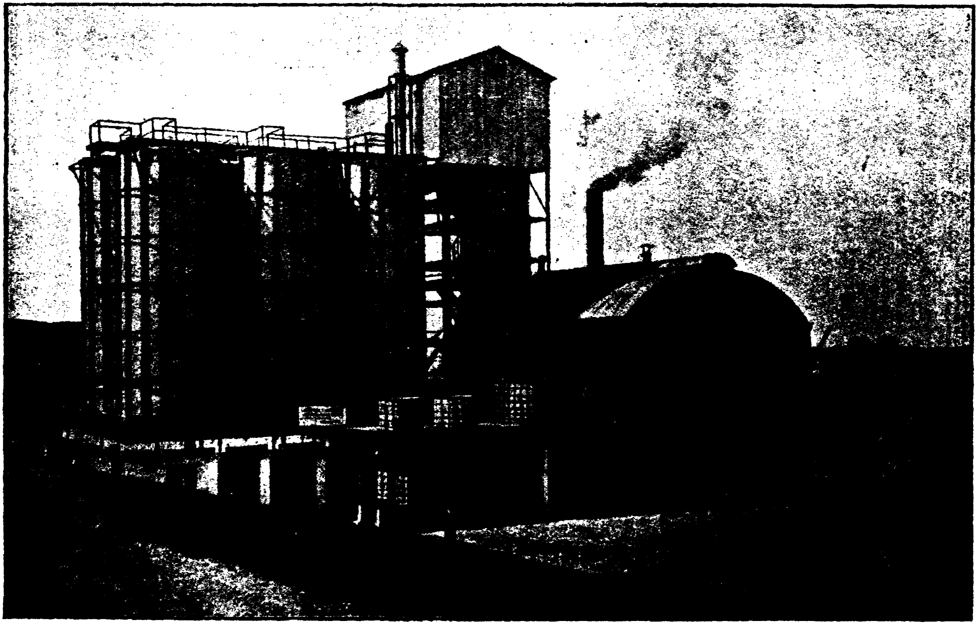

FIG. 17

the second stage, that of the regeneration of the nitric acid, the remaining portion of the system must be of adequate size to allow the much slower actions to be completed. It is quite impossible to give details of the working of the towers, but the accompanying diagram (Fig. 18), taken from a patent specification, will indicate the complexity of the acid circulation. Mention is also made here of a method of control by returning a portion of the gaseous products to preceding towers. In some designs the burner gases are passed in succession through the towers, in others simultaneously into some of them.

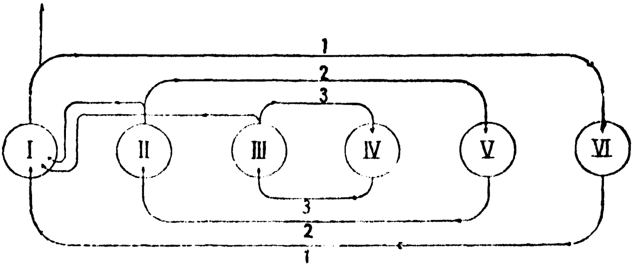

FIG. 18

CIRCULATION DIAGRAM. "OPL" SYSTEM

Almost the whole of the literature relating to these new systems is to be found in the patent specifications of various countries, and very little information is to be found outside this source. It is at present impossible to forecast the future of the rival systems, but it is obvious that a very large number of conditions of locality, raw materials, etc., must be considered in each case. A somewhat similar prospect will be found in any attempts to decide the pros and cons of contact systems, to be considered in another chapter, as contrasted with chamber or tower systems.

CHAPTER IX

FUMING SULPHURIC ACID OR OLEUM

THE manufacture of fuming oil of vitriol or " Nordhausen " sulphuric acid, was worked in Bohemia from about 1790, but the process adopted was given up about 1900, when it could no longer compete with the " contact " or catalytic process. The consumption of fuming sulphuric acid was comparatively small in England until the year 1914, when the demand for the explosives industry became enormous, and now, with the establishment of the dye industry, large quantities will still be required.

Fuming sulphuric acid, or oleum, as it is almost universally known in chemical industries, may be defined as sulphuric acid (H_2SO_4) mixed or combined with sulphur trioxide (SO_3). We can conveniently regard sulphuric acids to be a series of products resulting from the combination of sulphur trioxide with water, in a general formula thus—$mSO_3\ nH_2O$. Some of these, in which " m " and " n " have quite simple values, are usually regarded as definite compounds. Thus $SO_3 . H_2O$ is sulphuric acid, $2SO_3 . H_2O$ is known as pyro sulphuric acid, $SO_3 . 2H_2O$ and $SO_3 . 3H_2O$ have also been isolated. In the non-fuming class " m " is less than " n," but if "m" be the greater then the acid will belong to the class of fuming acids.

The old methods of manufacturing oleum were based upon the action of heat on certain sulphates. Iron sulphate, known also as copperas or green vitriol, was most largely employed (*see* p. 31). The crystals of copperas ($FeSO_4 7H_2O$) were submitted to a roasting process to remove the water and partially to convert them into a different iron sulphate [$Fe_2(SO_4)_2$].

The roasted mass was heated in clay retorts, and the sulphur trioxide driven off with some sulphuric acid.

The residual oxide of iron was used as a red paint, and was almost as important a product as the fuming acid itself.

From about 1900 the decomposition of sulphates to form sulphur trioxide had fallen into disuse, but in Germany, perhaps owing to the very abnormal conditions of pyrites importation prevailing in 1914–1918, the question of utilizing other materials, in order to supplement the sulphuric acid supply, seems to have been re-investigated. In addition to the scarcity of pyrites, the production of calcium sulphate in large quantities as a waste product in other branches of chemical industry probably served as a further stimulus. Calcium sulphate is decomposed by heating, and the resulting sulphur trioxide is then available for making sulphuric acid.

The sulphate is strongly heated in a tubular revolving furnace similar to those used in the manufacture of cement.

The manufacture of sulphuric acid might be undertaken in conjunction with cement production, and, in fact, this suggestion is incorporated in several patents. In the majority of the latter the decomposition of the sulphate is effected not by heat only, but by the addition of such material as clay. In these processes the gaseous products are rich in sulphur dioxide, which is oxidized to the trioxide by passing over a contact body, while the solid products are suitable for cement manufacture.[1]

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[1] Various waste products, rich in calcium sulphate, might be used in the manufacture of sulphuric acid, e.g. gypsum of too low a grade for profitable plaster making, and, quite possibly, the old or broken moulds which are an expense and inconvenience in the pottery industry might be turned to account in the same way.

One of the earliest of these patents is Cumming's, who proposed, in 1886, to heat bricks made of gypsum and clay in a kiln, but by far the greater number were taken out in the period 1914–1917.

The first man to make use of the fact that, when a mixture of sulphur dioxide and oxygen is passed through a tube containing heated platinum, combination takes place with the formation of sulphur trioxide, was Peregrine Phillips, a Bristol vinegar maker. The patent is dated 1831, but the process could not compete with the chamber process, and there was no considerable demand for fuming acid at that time. Although Phillips was the inventor of the " contact " process, the working out of practical methods of adapting it to the manufacture of oleum may be dated from the investigations of Winkler and of Squire and Messel, about 1875. The sulphur dioxide and oxygen were made by causing ordinary concentrated sulphuric acid to fall on to a heated surface. The steam was removed from the decomposition products, and the resulting mixture of gases made to re-combine by passing them over heated platinized pumice (the " contact mass " or " catalyst," *see* p. 27).

$$\underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Steam}}{H_2O} + \underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Oxygen}}{O}$$

$$\underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Oxygen}}{O} = \underset{\text{Sulphur trioxide.}}{SO_3}$$

In the same year Winkler suggested a very similar process, in fact nearly identical, but employing platinized asbestos in the place of pumice as the contact body.

The platinizing of the contact carrier is done by dipping it into a solution of platinum chloride.

The mechanical difficulties were very considerable, but the process was worked at Silvertown for a number of years. On the Continent, notably at Mannheim, Kreuznach, and Höchst, oleum was manufactured in a similar manner.

The use of gases from brimstone burners and the method of absorbing the sulphur trioxide produced in strong sulphuric acid, effected a considerable advance.

A number of agents to replace platinum have been suggested from time to time, oxides of iron, chromium and copper being amongst the earliest proposals. The number of suggested catalysts is now very large, and many patents have been granted for them, or for suitable mixtures, and also for methods of preparing the catalytic masses in markedly active condition.

About 1882 the idea of using the gases from ordinary pyrites burners began to receive attention as a practical proposition. The purification of these gases from dust and other impurities was studied, and it was found at a very early stage in the development of the contact processes that the activity of the catalytic agent was very soon diminished or even extinguished by the poisonous effect of impurities. The complete removal of the so-called catalytic poisons is very far from easy, and large plant is required. Arsenic, phosphorus and mercury have generally been considered as the most harmful poisons, but other impurities such as iron, lead, copper, the halogen gases, especially fluorine and chlorine, are very deleterious.

The purification plant aims at effecting such a thorough removal of harmful substances that the gases are optically and chemically pure. The presence of acid mist is injurious, mainly owing to the fact that it acts as a carrier of other impurities.

The gases are cleaned by repeated washing with sulphuric acid in towers, cooling, subsequent drying, and re-heating.

One form of the contact apparatus consists of a number of vertical iron pipes containing the catalytic agent. The temperature is controlled and adjusted with the greatest care, as also the composition and speed of the gases. To maintain the correct temperature, the gas stream is frequently divided in such a manner that a portion of incoming gas enters the outer casing of the apparatus containing the contact tubes, near the bottom; in so doing it cools the contact mass and is itself warmed ; at the top the stream passing up the outer casing meets with the other stream of gas. This mixture of the two streams flows in a downward direction through the contact tubes. The heat developed in the contact tubes is very considerable, and so by regulating the proportions of cool and hot gas streams respectively, it is possible to control the action and maintain the temperature very nearly at the optimum point. The most suitable temperature for a maximum conversion depends mainly on the quantity of gas passing through the apparatus, the composition of the gas, and the efficiency of the contact material.

As much as 96 per cent. of the sulphur dioxide may be converted, but it is not usual to aim at such a high conversion in one contact apparatus. By employing two convertors 80 to 90 per cent. is transformed in the first unit, and the action completed in a second unit, after removing the sulphur trioxide formed in the first. Many modifications have been introduced from time to time, especially in the direction of more efficient utilization of the heat of the reaction. Heat interchangers serve to cool the gases passing to the absorbers, and transfer the heat taken up to other gases passing to parts of the system where it may be utilized (auxiliary contact units, etc.) (*See* note below). So far we have only mentioned asbestos and pumice as supports or carriers for the platinum necessary as contact agent, but we shall have opportunity later of indicating other substances which are employed for this purpose. Almost any material which is not affected by any of the constituents of the gases, and which is not likely to break up at a high temperature, may be used.

It is almost inevitable that in the course of time the contact material becomes poisoned or inert, and, therefore, it is generally necessary to choose a support for the very costly platinum of such a nature as not to interfere with the valuable part of the mass. Another type of process, which is known as the Mannheim, makes use of the "burnt ore" or "pyrites cinders" (mainly oxide of iron) as a catalytic agent. The advantages of this material are its cheapness and the fact that it acts itself as a purifier of the burner gases from arsenic and some other impurities. From the fact that pyrites cinders are available at a very low cost in the majority of chemical works, the question of poisoning of the material hardly matters. The arsenicated cinders can readily be replaced by fresh material. In this Mannheim process the air supplied to the pyrites furnaces is carefully dried, and the pyrites are also

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NOTE.—The theory underlying the consideration of the best conditions for maximum output of contact plant is very complicated. The chemical equation showing the oxidation of sulphur dioxide to the trioxide is one of the class known as reversible, and may be represented thus—

$$SO_2 + O \rightleftarrows SO_3.$$

Under usual conditions of pressure, in the case of a mechanical burner gas, the conversion to the trioxide begins about 200°C and is nearly completed at about 430°C. Above this temperature the trioxide "dissociates," and at about 1,000°C is reduced again to the dioxide.

freed from all moisture before charging into the kilns. The heated and dry gases from the pyrites burners pass directly into the reaction chamber containing the burnt ore. The kilns and reaction chamber are carefully cased in to prevent the entry of any moisture. The quantity of sulphur dioxide converted in this system falls short, as a rule, by a considerable amount, of that which is usual in the platinum contact process. After the complete removal of the sulphur trioxide the remaining unconverted gases are re-heated to the necessary temperature and passed through a converter containing platinum, in which the oxidation of the sulphur dioxide is completed. Frequently the converting chamber contains nets of platinized asbestos, arranged in removable frames. The popularity of the Mannheim process has waned to some extent recently, the maintenance costs in many cases being rather high. It seems quite feasible that under some conditions a combination of the chamber systems with an iron oxide (pyrites cinders) contact process might possess considerable advantages.

A third contact process is known as the Schroeder-Grillo, or frequently by the latter name only. The same considerations of purification of the gases and every possible attention to economic heat exchange must be noted as in the other types.

The contact material is platinum, but the support is magnesium sulphate. The platinum is very finely divided, and a far smaller amount is required, also the platinum is readily recovered by dissolving out the magnesium sulphate. The contact mass is spread on perforated trays in the converter chamber, and arrangements are made for a very thorough mixing of the gases when passing from one tray to the next. The purification of the gases, a matter of the greatest importance in the working of the contact processes, has been the subject of a very large number of patent specifications. In one of these the removal of traces of hydrochloric acid from the burner gases is accomplished by the use of sodium sulphite. In another patent, associated with the Tentelew Co., of Petrograd, hydrochloric acid and silicon fluoride are removed by washing the gases with solutions of alkalis. In both these processes other variations in the practice of cooling, scrubbing, and heating are employed. Whatever contact system is adopted the methods employed for absorption of the resultant sulphur trioxide are similar. It is a practical impossibility to absorb sulphur trioxide completely in water or in weak sulphuric acid; even if a large number of absorption vessels is used a considerable amount of fume will escape absorption. Almost perfect absorption may be obtained by using sulphuric acid of about 98 per cent. Since concentrated sulphuric acid does not attack iron seriously, the absorbers used in making oleum are constructed of wrought iron. Cast iron is also used for absorbers when sulphuric acid is being made.

Oleum cannot with safety be stored in cast iron vessels, because, although they resist the action of sulphuric acid so well, the fuming acid apparently penetrates into the pores of the metal, and causes cracking or even violent explosions, perhaps due to the generation of gas. What method the future will regard as the best for sulphuric acid production is a question that cannot be answered. Many controversial views have been published, and each method has its advocates and its antagonists. Many writers adopt the view that the end of the chamber system is even now in sight. This view is not shared by the writer. The chamber plant has been considerably improved during the last few years, the stimulus being, without doubt, due largely to the competition of the contact systems.

If the demands of the future are confined to strong acid only (i.e. above 70 per cent.), then the outlook would be very dark for the chamber system, but it is highly probable that the older system will hold its own for many years to come as the cheapest plant for the production of sulphuric acid up to the strength mentioned.

The maintenance and running costs of tower systems compared with chamber plants of similar capacity are not readily ascertained, and their life-history, as far as England is concerned, is too short to warrant an expression of opinion as to their place in the future of sulphuric acid manufacture.

CHAPTER XI

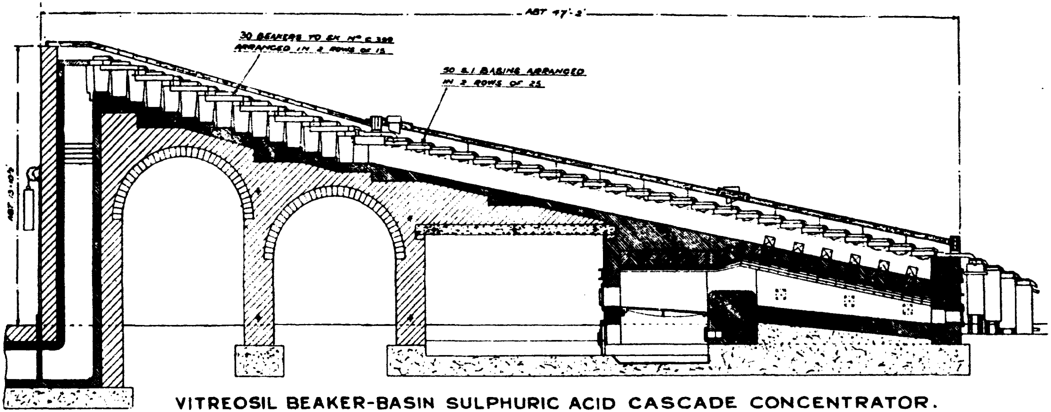
CONCENTRATION AND DE-ARSENICATION OF SULPHURIC ACID. ACCESSORY PLANTS

We mentioned (p. 45) that the sulphuric acid flowing from the bottom of the Glover tower was the usual commercial oil of vitriol. For some purposes this acid is too impure, for others it is not sufficiently concentrated.

Leaden pans, heated by waste heat in many cases, may be used for removing some of the water from a weak acid, cast iron pans if the acid is not very weak; some of the alloys of iron and silicon are so very resistant to the corrosion of hot acid that apparatus made of these alloys is preferably employed.

One form of concentrator may be described as a staircase of basins, which are heated by the hot gases of a furnace beneath, and are so arranged that the lip of each basin overhangs the next basin below (Fig. 19). The acid to be concentrated is run in at the top and flows through the series of basins until at the lower end the strength is about 95 per cent. true acid. Basins made of pure fused silica (Fig. 20) give a cleaner acid than the alloy basins, but greater care in handling is required. Formerly retorts of glass or platinum were much used but, except in cases where exceptional purity is required, the use of such brittle or costly apparatus has been abandoned.

Hot fuel gases, provided that a good contact with the acid can be made, afford an excellent method of removing the water from sulphuric acid. In the Kessler system, which is largely used, the hot gases from



VITREOSIL BEAKER-BASIN SULPHURIC ACID CASCADE CONCENTRATOR.

FIG. 19

a furnace burning coke are made to pass along the surface of the acid from which they take up much of the water with only a little acid vapour. Before they leave the apparatus the gases pass up through a small tower-like structure down which incoming weak acid is trickling, and then into a scrubbing box which removes the final traces of acid carried over from the concentrator. Another system also depending on the use of hot gases is known as the Gaillard tower. The acid to be concentrated is forced into the top of the high tower as a fine spray, and meets the hot gases which enter the bottom of the tower. The necessary draught to keep the gases moving is provided by fans made of "Regulus" metal (antimony-lead alloy) Fig. 21. The strong acid flows from the base of the tower, and the water vapour containing a little acid is recovered in scrubbing towers. Other systems based on similar principles have also been devised.

FIG. 20

The presence of arsenic in sulphuric acid and its removal by hydrogen sulphide have been previously referred to (*see* p. 18).

Arsenic, even in small amounts, is objectionable for many purposes, and consequently steps must be taken either to obtain an acid free from this impurity, or, at any rate, to reduce the amount to a few parts per million.

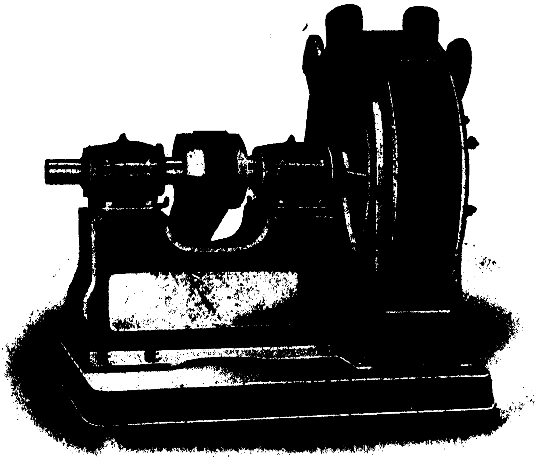


FIG. 21

KESTNER "REGULUS METAL" FAN

The crude acid from which the arsenic is to be removed is generally selected from that made in the last chambers, as the acid from that source contains less impurities, and is about the most convenient strength for the treatment with hydrogen sulphide. The acid and the gas are brought into intimate contact, and the solid arsenic sulphide is then separated from the acid.

A very usual form of de-arsenicator consists of a tower, built of sheet lead, containing a large number of triangular bars which serve to bring the gas and liquid into contact, without allowing the precipitated arsenic sulphide to lodge in the tower. In another form, known as the "Trepex" de-arsenicator, the impure acid is sprayed into the hydrogen sulphide by rapidly revolving paddles, enclosed in a cylindrical casing (Fig. 22). A third method is to force the hydrogen sulphide into the acid contained in vertical vessels. When the strength of the acid does not exceed about 60 per cent. little difficulty is experienced, provided also that the acid contains only traces of nitrous compounds, and that the hydrogen sulphide is present in excess of that required to precipitate the whole of the arsenic.

The yellow arsenic sulphide may be allowed to settle out in cisterns, and any remaining suspended in the acid may be removed by filtration.

In the presence of paraffin oil the arsenic sulphide is readily removed as a scum. The removal of the arsenic from strong sulphuric acid is not so readily carried out but by using a large excess of hydrogen sulphide, with or without paraffin oil, it is possible to do so.

The resulting arsenic sulphide is troublesome to dispose of, since it is not usually of a high grade of purity, even after prolonged washing and drying. Although this arsenic sulphide is frequently described as arsenic penta-sulphide (As_2S_5) the writer, as a result of many analyses, is of the opinion that the precipitated sulphide is a mixture of arsenic tri-sulphide (As_2S_3) and free sulphur, and seldom, if ever, contains the true penta-sulphide. In another method of removing a considerable portion of the arsenic present in sulphuric acid, advantage is taken of the volatility of arsenic tri-chloride. Hydrochloric acid is added to the arsenical acid and the

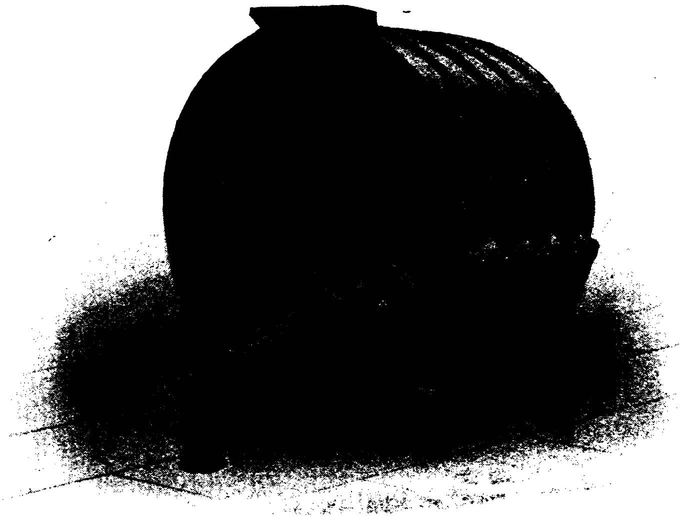


Fig. 22

" TREPEX " DE-ARSENICATOR (DAVIS BROS.)

resulting tri-chloride ($AsCl_3$) is expelled by blowing air through the liquid. The arsenic tri-chloride, on treatment with water, reforms hydrochloric acid, and arsenic trioxide (As_2O_3) is precipitated. The " white arsenic " thus produced, after washing and drying, is ready for sale.

Arsenic is used to harden copper employed in the construction of boiler fire-boxes, but the glass industry, in which it serves as a decolouriser, is the chief outlet for the product. Many sheep dips and weed-killers contain compounds of arsenic. Much of the common sulphuric acid has a reddish colour, due to selenium. This element bears a strong resemblance to sulphur, and has at present little commercial importance.[1]

Though rightly described as a rare element, the presence of selenium has been proved in many minerals, especially in association with sulphur, as in pyrites. During the process of de-arsenication, most of the selenium is also removed. Its presence is objectionable in acid which may be used in the preparation of products which are to be utilized in articles of food. We call attention to this because of the importance of never regarding "traces" of anything as always negligible. In a case which came under the writer's cognizance, the few parts per million of selenium in pyrites were the cause of considerable inconvenience in a prepared product which contained only a few tenths of a part per million, but which was, in consequence, considered impure.

In 1786, Cavendish showed experimentally that, by passing electric sparks through a vessel containing air,

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[1] Selenium is most readily obtained in the refining of copper by the electrolytic method. The probably unique property of changing its electric conductivity when illuminated is taken advantage of in certain instruments.

the oxygen and nitrogen would combine, and rather more than a century later attempts were made to translate the almost forgotten experiments into practice, and now millions of horse-power are used to produce nitrates and nitric acid from the air.

Germany obtained the nitric acid, indispensable in the manufacture of explosives, almost exclusively from this source.

For practical purposes at the present time, a more convenient and adaptable method of obtaining nitrous gas for sulphuric acid plant, is by the oxidation of ammonia. The apparatus required is small and readily controlled. The nitrous gases from the " catalysor " usually pass directly into the first chamber of the sulphuric acid plant (Fig. 23).

Ammonia, in the form of gas, with air, is passed over a " catalyst " (*see* p. 27), and under correct conditions is converted to nitric oxide as shown by the equation.

$$\underset{\text{Ammonia}}{4NH_3} + \underset{\text{Oxygen}}{5O_2} = \underset{\text{Nitric oxide}}{4NO} + \underset{\text{Water.}}{6H_2O}$$

Fine nets of thin platinum wire form a good catalyst, but other materials may also be used. The ammonia must be very pure, as the platinum net is easily "poisoned" by some impurities which may occur in commercial ammonia. The conditions must be favourable to the action taking place as represented above, since, if adverse, the action may go too far, and useless nitrogen take the place of the oxide as

$$\underset{\text{Ammonia}}{4NH_3} + \underset{\text{Oxygen}}{3O_2} = \underset{\text{Nitrogen}}{2N_2} + \underset{\text{Water.}}{6H_2O}$$

One of the chief difficulties, more or less inevitable in all mechanical furnaces, is the formation of an exceedingly fine dust which, unless removed, will contaminate

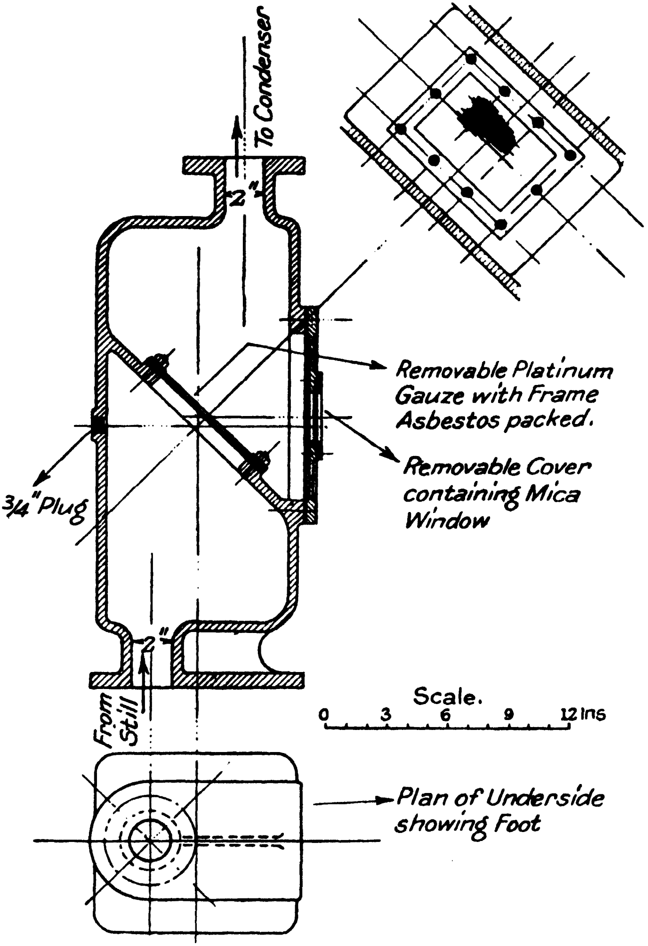


FIG. 23

OXIDATION OF AMMONIA

the sulphuric acid produced. In most systems it is to the advantage of the sulphuric acid maker to produce the sulphur dioxide as free from dust as possible, but at the same time at a high temperature. The hot gases are useful in effecting the concentration of the acid, and are almost an essential to the restoration of the valuable nitrous gases to the system (*see* p. 36).

The most usual method of removing dust from the roaster gases is by filtration through some material, such as broken brick, but it is evident that steps have to be taken to prevent the filters becoming choked. If the high speed of the gases, containing the suspended dust, can be abruptly changed to a much lower speed then much dust, at any rate the coarser particles, will settle out. In order to secure this settling of the dust the gases are passed into chambers of much larger area than the inlet pipe. A series of abrupt changes of speed of the gases are further effected by baffle plates in the chambers. It is obvious that the larger the area of the dust-catching chambers so much the greater will be the amount of heat lost and, therefore, the number and size of the chambers must be limited, and an average struck between the extremes of either a dusty and hot gas or a clean and cooler gas.

A suggestion has been made, and it appears a reasonable one, to scrub the dusty sulphurous gases with sulphuric acid—in so doing a small percentage of the output is contaminated, but the bulk is preserved from dust. This method is only advantageous in localities where there is an outlet for the strongly contaminated acid.

An electrical method of separating solid and liquid substances from gases holding them in suspension, has been applied by Cottrell. The Cottrell process is destined to hold a leading place in a variety of chemical and metallurgical industries. Lodge, in 1885, carried out a number of experiments on the dispersion of fog by electrical discharges. Cottrell, in 1906, repeated the older trials, and was convinced that the method could be developed into a sound commercial process.

The problem of removing the very troublesome acid mist from the gases of a Mannheim contact plant (*see* p. 63) was first attacked. The experiments have resulted in a very extensive field of application. The general principle of electrical precipitation of solid or liquid particles is based on the fact that such particles become electrically charged themselves when floating in the space between two highly-charged conductors, and will in consequence be attracted by one or other of the conductors.

Two forms of apparatus are in use, known respectively as (1) the vertical or "chain and tube" type, (2) the horizontal or "plate and chain" type (Figs. 24, 25, 26). In one large installation, capable of dealing with 3,000000 cubic feet of gas per minute, no less than 240 tons of dust are removed every twenty-four hours. In another case, where the nuisance caused by the fumes escaping from a battery of Gaillard towers (*see* p. 69) was very considerable, the amount of acid recovered averaged 25 tons of 50 per cent. acid per twenty-four hours.

The installations of "Cottrell Precipitators" put up, in the first instance, to remedy a nuisance, have proved, in most cases, an excellent investment, as the loss of valuable material—copper, lead, arsenic, potash (from cement kiln dust), sulphuric and nitric acids—has been prevented.

Sulphuric acid, as we have noted previously, when fairly strong (70 per cent. and upwards) has very little corrosive action on iron. This fortunate fact enables the chemical engineer to convey and store sulphuric acid in iron vessels. At a lower strength than 70 per cent., while the acid attacks iron, lead is comparatively immune; the latter material is therefore used when it is necessary to handle weak acids.

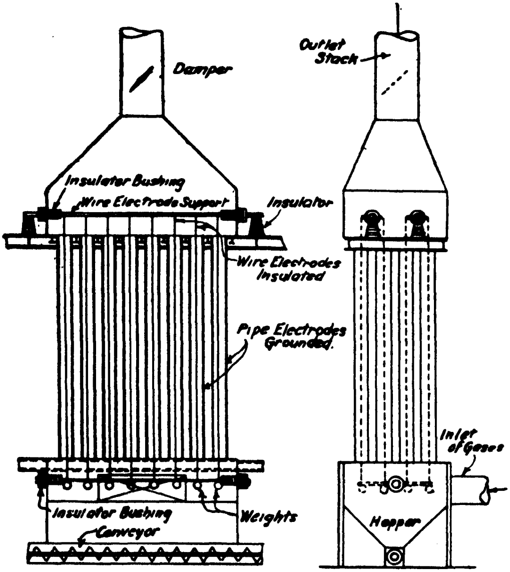


FIG. 24

For raising acid, as, for instance, elevating the Gay Lussac tower acid to the top of the Glover tower (*see* p. 46) compressed air is generally used, though the employment of mechanically driven centrifugal pumps has replaced this method in some factories. These pumps are of iron or special alloys which resist the corrosive action of the acid. A device known as an "acid egg" has been found very satisfactory as an acid elevator, the more so because the " life " of these eggs is usually a long one. The egg, which is made of cast iron of considerable thickness, is placed at a lower level than the tank from which it is supplied. A common design consists of a cylindrical vessel about 6 feet long and 3 feet in diameter, with three flanged openings.

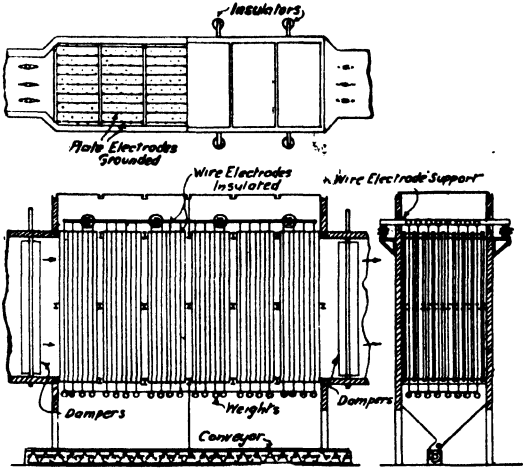


FIG. 25

It is supported on blocks in a horizontal position, with the inlets and outlets on the top. The acid to be raised flows by gravity through a "back-pressure" valve, which is so constructed that it shuts off communication with the supply tank when the supply of compressed air is turned on. The outlet pipe for the acid passes through another of the openings, its foot extending to a small cavity at the bottom of the egg. The compressed air inlet is furnished with an automatic valve, actuated by a float, which admits the air only when the egg is full (Fig. 27).

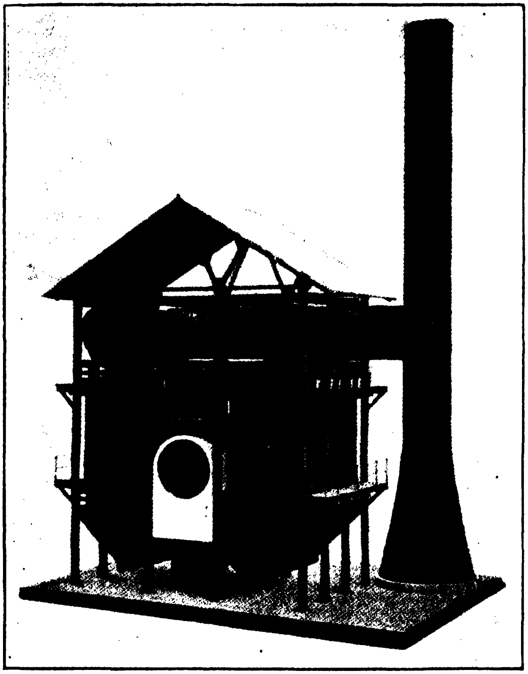


FIG. 26

MODEL OF "COTTRELL PRECIPITATOR"

Apparatus so designed requires practically no attention, acting quite automatically. Where continuous pumping is not required, of course, hand-controlled valves may be used. The valves are usually cast in

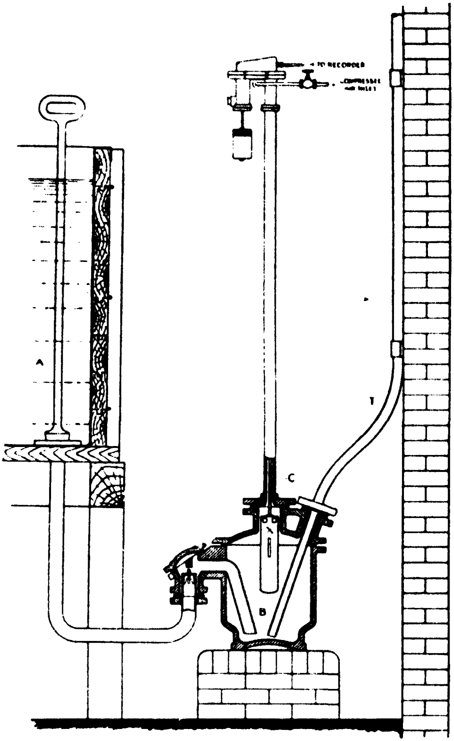


FIG. 27

KESTNER ACID ELEVATOR

The acid from the feed tank A flows by gravity into the body B of the acid elevator. As soon as B is full the liquid operates the part X of the float which, by means of the rod C, closes the air exhaust valve and opens the compressed air valve. The acid is discharged through the pipe T and the air, after delivering the liquid, exhausts through the same pipe, the consequent fall of pressure operates the valves in the opposite direction.

moulds and machined, a hard lead, containing much antimony, being the alloy most frequently employed. Other designs of acid eggs are also used.

Acid is raised in some cases by " air lifts," in which the acid is raised in the pipe by cushions of air between short lengths or plugs of acid, or the air and acid are so thoroughly mixed that a froth or emulsion is produced. In both methods the pressure or " head " is much less than is the case where the whole pipe is full of acid, consequently there is considerable saving both of structural material owing to reduced strain, and of expenditure of power. The usual package for sulphuric acid is a large glass bottle or " carboy " of about ten gallons capacity. The carboy is inserted into a " skip " or basket constructed of iron bands, with straw packing. Wherever feasible, cylindrical tanks mounted on railway trucks are infinitely preferable to the relatively fragile carboys. The tank waggons contain from ten to twelve tons, or roughly the equivalent of 250 carboys. For emptying the tanks a tap is provided at the bottom, but a less troublesome method is to employ compressed air to force the acid along a distributing pipe. Plain wrought iron is used for the strong acid, and lead-lined tanks for the weaker qualities. Wrought iron drums, holding 5 to 15 cwt., can also be used.

CHAPTER XII

RESIDUAL PRODUCTS

THE mineral designated pyrites usually contains, in addition to iron and sulphur, a number of other elements in small amounts. The following can be regarded as typical of a class of mineral of frequent occurrence—

Iron. Fe	40·30
Sulphur. S.	45·46
Copper. Cu.	1·42
Zinc. Zn.	3·40
Lead. Pb.	1·25
Tin. Sn.	0·03
Arsenic. As.	1·00
Antimony. Sb.	0·03
Cobalt. Co.	0·06
Nickel. Ni.	
Manganese. Mn.	0·06
Bismuth. Bi.	0·01
Calcium oxide. CaO.	0·17
Barium oxide. BaO.	0·24
Magnesium oxide. Mg.O.	0·29
Silica. SiO_2	2·88
Phosphorus pentoxide. P_2O_5	0·02
Alumina. Al_2O_3	1·22
Carbon dioxide. CO_2	0·60
Silver. Ag..	16 dwt. 8 grains.
Gold. Au.	16 grains.
Selenium. Se	50 parts per million.

(*See* note at end of chapter re analysis of solid matter in sulphuric acid made from the above pyrites.)

From the small amounts present in many instances in the list, it might be considered that the majority were negligible. As a matter of experience in large scale working, many of these impurities are by no means negligible, and may cause irregularities in the working of plant as well as difficulties in the purification and utilization of the products in which sulphuric acid made from such a pyrites is employed.

An attempt is made here to outline the distribution and destiny of some of the elements given in the list. Of the sulphur present in the ore the greater part is burned off in the kilns—which should yield cinders containing from 1 to 2 per cent. of " sulphide sulphur," and slightly higher figures for " total sulphur."

At the temperature prevailing in the pyrites kilns the calcium sulphate and barium sulphate are not split up, and consequently both will be found in the cinders.

The arsenic, antimony and selenium are mostly volatilized and found again in the sulphuric acid produced. In general the other bodies present in the pyrites are carried forward mechanically with the inevitable dust, and consequently Glover tower acid will be found to contain traces of every element found in the original ore. A certain amount of arsenic is always retained by the burnt ore, probably fixed as calcium arsenate or a more complex compound. We will consider, further, only those metals present in the cinders which are or may be extracted.

The copper, silver, gold, lead and zinc are rendered soluble by roasting with salt. The "chloridized ore" is washed with weak acid (a mixture of sulphuric and hydrochloric acids recovered by washing the fumes from the roasting furnace), and the resulting liquor containing the elements enumerated is separated from the insoluble portion. Silver and gold can be to a large extent precipitated by the addition of zinc iodide; the resulting precipitate, silver iodide, is treated with scrap zinc to produce metallic silver and to reform the zinc iodide. The precipitated silver contains most of the gold present in the pyrites; a certain proportion of zinc and lead is also precipitated in the process.

The copper is recovered in a further series of vats, in which the solution is kept in contact with scrap iron, which results in the precipitation of nearly the whole of the copper, a corresponding part of the iron passing into solution.

One method of separating lead is based on the solubility of lead chloride in a hot solution of calcium chloride, from which it can be readily recovered as spongy lead.

The zinc can be obtained from the liquors, after the removal of the copper, by the action of hydrogen sulphide or other available soluble sulphide.

The flue dusts from the chloridizing roasters contain an appreciable quantity of bismuth which is not difficult to recover. The final liquors from the "wet" copper process outlined above are rich in iron salts from which pigments are prepared by precipitation and the requisite roasting of the resulting hydrate of iron.

The washed burnt ore is compressed into blocks or briquettes which, after being strongly heated in a kiln to harden, are sold for use in the place of iron ore in blast furnaces. For the iron smelting industry it is important that the impurities in the briquettes should be kept down to a low figure, as otherwise the metal produced from them will be of inferior quality.

Note.—For purposes of comparison we include an analysis of the solid matter in a Glover tower acid made from ore of almost identical composition with that given above.

	Ordinary kilns	Mechanical burners.
Selenium	0·130	0·185
Lead	0·085	0·106
Copper	0·090	0·210
Arsenic	8·475	7·125
Antimony	0·027	0·032
Bismuth	Trace	Trace
Iron	0·487	0·812
Aluminium	0·275	0·266
Zinc	0·125	0·140

The above existed in solution in the acid. The suspended matter was also examined with the following results—

Total	0·412	1·532
Insoluble in acids	0·040	0·255
(i.e. Silica	0·023	0·218
Iron and Alumina	0·007	0·037)

The suspended matter which was soluble in acids was found to be made up of—

Selenium	0·143	Nil
Lead	0·108	0·206
Copper Bismuth	Traces	Traces
Arsenic	0·009	0·003
Antimony	0·053	0·026
Iron	0·031	0·700
Aluminium	0·012	0·127
Zinc	Nil	0·010

CHAPTER XIII

USES OF SULPHURIC ACID

WE have given in the previous chapters an outline of the industrial methods of manufacture of sulphuric acid and several related compounds. The uses of sulphuric acid are so numerous that it is probably quite beyond any single technological chemist to enumerate them all.

Previous to the year 1914, the yearly consumption of sulphuric acid was about 1,040,000 tons, calculated as 100 per cent. acid. In addition to this, 22,000 tons of oleum, also calculated to 100 per cent. acid, for purposes of comparison, were used. During the years 1914–18 the production of superphosphate was curtailed owing to the enormous quantities of acid required for munitions. The possible production on the return of more normal conditions is computed to be 1,265,000 tons, and 450,000 tons respectively.

In the manufacture of artificial manures of the "superphosphate" group many thousand tons are used annually.

Probably more than two-thirds of the sulphuric acid produced is now used for fertilizers, including the superphosphates and ammonium sulphate.

Under good agricultural conditions soils may contain as much as 0.3 per cent. of phosphoric acid, but usually very much less than this amount. Different crops remove from the soil varying but very considerable quantities of this extremely necessary compound every year. If a corresponding quantity is not replaced and returned to the soil, the latter becomes sterile in a short time. This has actually happened in the past, and in many countries, formerly large grain producers, the food production is very greatly diminished. The tri-calcium phosphate [$Ca_3(PO_4)_2$] which occurs in soils and rocks is insoluble in water, and even when very finely ground, is only very slowly assimilated. If an immediate result is not required, or if the soils are acid or marshy, this phosphate may be used, but in the majority of cases it is advantageous to convert it into a more soluble compound.

By treating the tri-calcium salt with sulphuric acid it is converted into the mono-calcium salt [$CaH_4(PO_4)_2$] which is the chief constituent of superphosphate fertilizers. The mono salt is soluble in water and so permeates the soil and reaches the roots of the plants.

The crude or naturally occurring phosphate (phosphorite) is found in very large quantities in Florida, Tennessee and Carolina, Algeria and Tunis, France (Somme), and Belgium. The material from these sources differs very considerably in composition, the calcium carbonate and fluoride varying within rather wide limits.

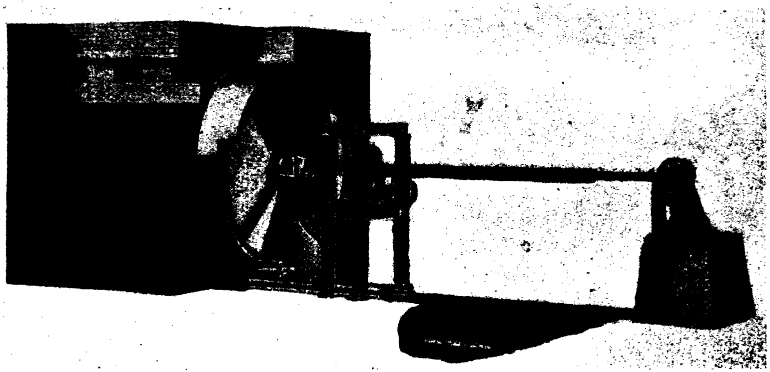
The phosphatic rock is finely ground and treated with an amount of sulphuric acid of certain strength, determined by a previous analysis of the rock. The acid and the ground rock are put into a mixer fitted with agitating ploughs. The hot pasty mass is then allowed to fall into large chambers or " dens," in which the chemical changes are completed. After some time the contents of the den are removed either by hand or preferably mechanically (Fig. 28). The resulting superphosphate is generally crushed to break up any lumps, and is then ready for sale. It is obvious that the manufacture must be conducted with care, as the finished product must not be damp, nor should it contain free sulphuric acid which would be harmful to the soil and would also cause rapid destruction of the bags in which it is stored.

There are chemical as well as economic reasons which render any drying of the superphosphate, after making, a difficult matter, and one to be avoided, if possible.

The next important market for sulphuric acid is ammonium sulphate manufacture, the latter also an extremely valuable fertilizer. The quantities of sulphuric acid used for this purpose approximate to that used in the superphosphate industry. Actual figures are not given here, as the periods of manufacture are seasonal, and to some extent fertilizer plants are used as outlets for surplus acid. The factors mentioned lead to very fluctuating outputs, and a further cause of variation is the seasonal variations in the amount of ammoniacal liquor produced in gas works, which hitherto have been the chief sources of ammonia.

In the manufacture of ammonium sulphate, gaseous ammonia is passed into a "saturator" containing sulphuric acid of correct strength; the crystals of the sulphate thus produced are separated from the "mother liquor" by draining and drying in a centifugal machine. It is important that the amount of free acid left in the product should be very small, or even better, entirely absent. The crude ammonium sulphate is usually grey in colour, this being probably due mainly to traces of metallic impurities in the sulphuric acid used, a yellow colour indicating usually the use of an arsenical acid.

The third highest demand for sulphuric acid formerly came from the manufacturers of sodium sulphate, which has already been described (*see* p. 22). The introduction of other methods for the production of caustic soda and chlorine has displaced "saltcake" and



Simon Carves, Ltd.

FIG. 28

THE "ALLIBON GOULDING" HORIZONTAL SUPERPHOSPHATE DEN AND MECHANICAL EXCAVATOR

Fig. 28 shows the horizontal type of "Allibon-Goulding" den and the mechanical excavating device. The den is a circular horizontal chamber of brickwork or concrete (about 11 ft. in diameter and 14 ft. long). A slot in the bottom of the den forms the discharge opening for the excavated superphosphate, allowing it to fall on a tray conveyor in a tunnel beneath. The excavator consists of a hollow cast-iron shaft carrying a hub upon which cutting arms or blades are mounted. A shield, slightly smaller in diameter than the den, prevents the gases, given off from the mass, causing inconvenience to the attendants. The excavator gradually advances into the den as the superphosphate is removed. A headstock, supporting the hub, is mounted on a travelling bogey which passes through the discharging slot at the bottom of the den. This type of den can deal with about 30 tons in a few hours, the actual excavating only occupying about one and a half hours, with the expenditure of very little energy which is supplied by a 3 horse-power motor. In some situations the vertical type of den is more convenient. The fact that the mass of superphosphate can be mechanically excavated whilst still hot is a favourable feature, as a fine, dry, friable product is obtained. Excavation by hand is slow and not unaccompanied by risk of accident through falls of the superphosphate.

hydrochloric acid as intermediates in the manufacture of both caustic soda and bleaching powder, but saltcake is still required for making sodium sulphide and in glass works, and hydrochloric acid is an important commodity in the chemical industry.

Considerable quantities of sulphuric acid are required in the iron and steel industries, where it is used to prepare iron sheets and other articles before tinning or galvanizing. This "pickling," as it is known in practice, may also be carried out by the use of hydrochloric acid, which is frequently preferable, but as sulphuric acid is largely used in making the hydrochloric acid, the consumption of sulphuric acid is not much altered by the use of the alternative pickling medium.

In wire drawing it is of great importance to remove the " mill scale " from the rods before drawing, and also to induce the formation of an even film or rust. The thin layer of rust forms very quickly when the rods or wire are removed from the pickling trough and rinsed with water ; the function of the rust is probably that of a lubricant in the dies through which the wire is drawn.

Large quantities of sulphuric acid are used in the various operations that come under the categories of dyeing and bleaching.

Compounds produced by the action of sulphuric acid on many products separated from coal tar, form the starting points in the manufacture of dye stuffs. The process known as " sulphonation " is one of the commonest in the production of either intermediates or the dyes themselves. A good illustration of this use is seen in the manufacture of phenol (carbolic acid) from benzol. A considerable amount of phenol is separated directly from coal tar, and need not be considered here, but the product from benzol is also of importance.

$$\underset{\text{Benzol}}{C_6H_6} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Benzol sulphonate}}{C_6H_5HSO_3} + \underset{\text{Water.}}{H_2O}$$

$$C_6H_5HSO_3 + \underset{\text{Caustic soda}}{NaOH} = \underset{\text{Phenol.}}{C_6H_5OH} + NaHSO_3$$

In many cases ordinary sulphuric acid is not " strong " enough to work satisfactorily, and in such cases oleum is used for the purpose. On considering the equation of sulphonation illustrated above, it will be noted that water is one of the products of the action, and this will, of course, weaken the acid as it is being used. Weak acid will not sulphonate as a rule, and by using oleum the weakening effect of the water is checked by the formation of further quantities of sulphuric acid from the sulphur trioxide present in the oleum—$SO_3 + H_2O = H_2SO_4$.

Concentrated sulphuric acid has itself a strong affinity for water, and this property is very largely made use of in another operation in technical organic work. The process of nitration is the starting point of an important group of dyes and explosives. We will illustrate this case in the same manner as above—

$$\underset{\text{Benzol}}{C_6H_6} + \underset{\text{Nitric acid}}{HNO_3} = \underset{\text{Nitro-benzol}}{C_6H_5NO_2} + \underset{\text{Water.}}{H_2O}$$

Here we may again note the formation of water in the nitration of benzol by means of nitric acid.

If strong nitric acid is used the action is easily accomplished, but in some cases it is not the once-nitrated product but the twice—or thrice—nitrated product that is required. In these cases the water which is formed must be taken up as it is formed, and for this purpose a mixture of nitric and sulphuric acid is used

$$C_6H_6 + 2HNO_3 = \underset{\text{Di-nitro-benzol}}{C_6H_4(NO_2)_2} + 2H_2O \text{ or}$$

$$C_6H_6 + 3HNO_3 = \underset{\text{Tri-nitro-benzol.}}{C_6H_3(NO_2)_3} + 3H_2O$$

These illustrations will serve our present purpose, but the reader must be willing to extend the application of the processes of sulphonation and nitration to many hundreds of similar cases occurring in the production of dyes, explosives, photographic and pharmaceutical chemicals.

The manufacture of saccharine, a powerful sweetening agent, involves a modified form of sulphonation.

Mention was made (*see* p. 21) of the derivative of sulphuric acid known as chlorsulphonic acid; the action of the latter on toluol is the first step in the production of saccharine.

$$\underset{\text{Toluol}}{C_6H_5CH_3} + \underset{\text{Chlorsulphonic acid}}{SO_2(OH)(Cl)} = \underset{\text{Toluol chloro-sulphonate}}{C_6H_4.CH_3.SO_2Cl} + \underset{\text{Water.}}{H_2O}$$

This saccharine, which is not related in any way to the sugars, must not be confounded with the glucose, obtained from starch, which is also sometimes spoken of as saccharine, and which is a member of the sugar group. Starch is converted, by the action of acids, into gum-like substances, such as dextrin, or into sweetish sugar-like bodies such as glucose, which are used in the brewing and confectionery industries.

The textile trades consume large quantities of sulphuric acid in the recovery of grease from the waste wash-waters.

Many thousands of tons of sulphuric acid are used in connection with the refining of oils, advantage being taken of the variations in the susceptibility to attack by sulphuric acid of some of the constituents of the crude oils.

In the preparation of acids from their salts sulphuric acid is the most frequently used acid, partly on account of its relative cheapness and partly because it affords a means of readily separating the products formed.

A few examples must suffice as illustrations of the general applicability of the reaction, taken from actual practice.

$$\underset{\substack{\text{Calcium}\\ \text{acetate}}}{\left.\begin{matrix}CH_3COO\\ CH_3COO\end{matrix}\right\rangle} Ca + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4} = \underset{\substack{\text{Calcium}\\ \text{sulphate}}}{CaSO_4} + \underset{\text{Acetic acid.}}{2CH_3COOH}$$

Similarly with formic, oxalic, citric, salicylic acids and many others.

Sulphuric acid is also used for the process of "esterification" in the preparation of the group of substances known as "esters," many of which find a place in artificial fruit essences. The following represents the course of the action usually employed—

$$(a)\ \underset{\substack{\text{Sodium}\\ \text{formate}}}{HCOONa} + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\ \text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{Formic}\\ \text{acid.}}}{HCOOH_3}$$

$$(b)\ HCOOH + \underset{\substack{\text{Methyl}\\ \text{alcohol}}}{CH_3OH} \rightleftharpoons \underset{\substack{\text{Methyl}\\ \text{formate}}}{HCOOCH_3} + \underset{\text{Water}}{H_2O}$$

The two actions are simultaneous, but are given in the form above for clearness. The action of the water in (*b*) especially in the presence of acid will tend to cause the action to take place in the reverse way (i.e. "hydrolysis" of the ester). The yield of ester depends upon the adherence to strict conditions which can be calculated beforehand when the "equilibrium constants" of the reacting substances are known.

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