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METHODS FOR THE REMOVAL OF SULPHUR DIOXIDE FROM WASTE GASES

by

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ABSTRACT

A review is given of methods that have been used, or are currently being developed, for the removal of sulphur dioxide from the waste gases emitted from the combustion of sulphur-containing fuels and from the smelting of sulphide ores. These methods have been classified into ten groups based upon either the removal technique or on the type of absorbent employed in the removal process. An outline of the chemistry of the removal processes is also given together with the current stage of development of the processes.

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LES MÉTHODES POUR L'ENLÈVEMENT DE L'ACIDE SULFUREUX DES GAZ BRÛLÉS

par

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RÉSUMÉ

On présente une revision des méthodes utilisées ou en voie de développement pour l'enlèvement de l'acide sulfureux des gaz brûlés dégagés de la combustion des combustibles sulfurés et de la fusion des minerais sulfurés. On classifie ces méthodes en dix groupes basées soit sur la technique de l'enlèvement soit sur le type de l'absorbant employé dans le procédé de l'enlèvement. On donne aussi un aperçu de la chimie des procédés de l'enlèvement et le point actuel du développement des procédés.

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INTRODUCTION

Sulphur dioxide is present in the effluent gases from a number of industrial processes, and the discharge of these gases into the atmosphere gives rise not only to a serious air pollution problem, but also to the loss of sulphur which is a non-renewable resource. The adverse effects of sulphur dioxide on human health and on plant growth are well established (1-5) and intensive efforts are now underway in most industrialized countries to devise methods to limit the amount of sulphur dioxide discharged into the atmosphere (6-15). In Canada the two main sources of sulphur dioxide as a pollutant are the effluent gases from the industrial combustion of fossil fuels and the off-gases from the pyrometallurgical treatment of sulphide ores (14, 16). The concentration of sulphur dioxide in these waste gases ranges from about 0.1 to 0.3 volume-per cent in power plants and from about 1.0 to over 20 volume-per cent in pyrometallurgical operations. Since the demand for power and minerals is expected to increase steadily in the future (3, 8, 14, 17-19), a similar increase in the quantity of sulphur dioxide discharged into the atmosphere can also be expected, unless appropriate sulphur dioxide removal techniques are introduced.

In principle, the problem of atmospheric pollution by sulphur dioxide could be solved to a large extent by the use of non-pyrometallurgical methods for the treatment of sulphide ores and by the combustion of sulphur-free fuels. However, the demand for low-sulphur fuels far exceeds the available supply (20), and although a variety of methods are available to reduce the sulphur content of fuel oil (21-27) there is no satisfactory method for the removal of organic sulphur from coal (8, 24, 28) without materially altering the physical state of the coal. Thus coal can, in effect, be desulphurized by gasification and considerable research in this area is underway (28-32). Alternative approaches to current smelting practice for sulphide ores, using such techniques as flash smelting, oxygen-enriched air, and hydrometallurgical methods, are being intensively investigated with the object either of increasing the sulphur dioxide content of the off-gases for easier sulphur dioxide removal or of employing other sulphide-reduction techniques that do not yield sulphur dioxide (17,33-47). At the moment these approaches represent essentially long-range solutions to the problem of sulphur dioxide abatement and it may be assumed that existing metallurgical and power plants will be operated for some years to come before being replaced by improved processes that emit significantly smaller amounts of sulphur dioxide.

The most difficult technical problem in sulphur dioxide abatement is the treatment of waste gases containing low concentrations of sulphur dioxide. At the moment no commercially proven method is available that is economically viable for the treatment of weak smelter gases or the flue gases from thermal power stations (10,48).

An appreciation of the technical and economic factors involved in the removal and recovery of sulphur dioxide from the flue gases of thermal power stations may be obtained from the data in Tables 1 and 2. These data

TABLE 1

Some Characteristics of a 1000-MW Thermal Power Station

Property	Quantity
Sulphur dioxide content of flue gas	0.1 - 0.3%
Gas flow	2×10^6 cu ft/min
Dust in gas	800 tons/day
Water in gas	8.6×10^3 tons/day
Gas velocity	35 - 50 mph
Temperature of flue gas leaving stack	~ 150°C (300°F)

TABLE 2

Annual Production of Potential By-Products from a 1000-MW Thermal Power Station (3% Sulphur Coal, 60% Load Factor)

Product	Annual production (tons)
Sulphur	56,000
Sulphur dioxide	112,000
Sulphuric acid	172,000
Ammonium sulphate	230,000
Gypsum	240,000

are based upon a 1000-MW boiler burning pulverized coal containing 3% sulphur (49,50). It was also assumed, for the data in Table 2, that the power station operates at an annual load factor of 60% (51) and that 95% of the sulphur in the coal is converted to sulphur dioxide. It will be seen from these tables that, although a large amount of sulphur dioxide is emitted annually from the power station, the sulphur dioxide is present at a low concentration in a high-velocity gas stream which also contains considerable particulate matter. The compounds listed in Table 2 are the products of various sulphur dioxide removal and recovery processes which will be discussed later. With the exception of gypsum which is normally regarded as a "throw-away" product, all the compounds listed in Table 2 have commercial value. Gypsum may also be used as a source of sulphur for the production of sulphuric acid, but the production process is economically attractive only when the price of sulphur is high (35.52,53). Thus, in an evaluation of any sulphur dioxide removal and recovery method, the credit received for the recovered sulphur or sulphur-containing compound is a significant factor in the overall assessment of the viability of the process (50,54,55). However, under the present conditions of a world-wide over-supply of sulphur, finding a market for the very large quantities of sulphur or sulphur-containing compounds that could be recovered from waste gases poses a serious problem, particularly for the sulphide smelting industry (17,56-58). For example, if the sulphur dioxide emitted from all the thermal power stations in the United States were recovered as sulphuric acid, the amount produced would approximately meet the annual United States requirement for sulphuric acid (50). Similar marketing considerations, together with escalating costs, have recently led to the cancellation (59) of a 700,000-ton-per-year sulphuric acid plant which was to have been built (60) by the International Nickel Company of Canada at Copper Cliff, Ontario to treat the effluent gases from the processing of pyrrhotite. Another potential product of recovered sulphur dioxide is ammonium sulphate which is used as a fertilizer. Here again it has been estimated that the recovery of sulphur dioxide from three coal-burning power stations, each of 500-MW capacity, could supply the total ammonium sulphate requirements of the mid-west of the United States (50).

Elemental sulphur is in many ways the most desirable product of a recovery process for sulphur dioxide, because sulphur has the advantage, over alternative sulphur-containing compounds, of easy storage and handling and of relatively low weight (Table 2). However, a world-wide surplus of sulphur has developed in recent years; a situation that is likely to persist until 1975 (61) and probably for much longer (62) and which is reflected in the dramatic fall in the cost of sulphur from almost $40 per ton in 1968 to less than $6 per ton in 1971. As Canada is the world's leading exporter of sulphur and will shortly become the world's largest producer, the imbalance between world supply and demand has resulted in the stock-piling of large amounts of sulphur by Canadian producers. Canadian inventories of sulphur are expected to reach 24 million tons by 1975 and up to 50 million tons by 1980 (62), and a research and development program has been proposed by Vroom (63) to find new, large-scale uses for sulphur in areas such as building products and highway construction.

In Canada, it is estimated (14, 16) that the quantity of sulphur dioxide emitted from the smelting of sulphide ores and from the combustion of fossil fuels is respectively 4.8 and 1.1 million tons per year out of a total annual emission of sulphur dioxide from all sources of 6.1 million tons. The projected increase in the total emission of sulphur dioxide for 1980 and 2000 is respectively 1.8 and 3.5 times the 1966 emissions.

In the United States, the majority of the sulphur dioxide emitted in waste gases results from the combustion of fossil fuels used in the production of electrical power (48). Forecasts, based upon the expected increase in the demand for electrical power in the United States (8), show that without pollution controls there will be a steady increase in the amount of sulphur dioxide discharged from electrical utility plants in the United States until about the year 2000. The <u>increase</u> in the amount of sulphur dioxide discharged annually from this source alone will be about 2.5 million tons per year (Table 3). By the beginning of the next century, it is expected that, as reserves of fuel oil and cheap coal become depleted, these fossil fuels will be replaced by nuclear energy as the main source of electrical power.

TABLE 3

Estimated Future Amount of Sulphur Dioxide Emitted in the United States without Pollution Controls

Source	Emission of SO_2 in millions of tons				
	1967	1970	1980	1990	2000
Power plant operation (coal and oil)	15.0	20.0	41.1	62.0	94.5
Other combustion of coal and oil	7.9	8.2	7.9	7.4	6.7
Smelting of metallic ores	3.8	4.0	5.3	7.1	9.6
Petroleum refinery operation	2.1	2.4	4.0	6.5	10.5
Miscellaneous sources	2.0	2.0	2.6	3.4	4.5

In Great Britain, a slight decrease is expected during the next few years in the amount of sulphur dioxide emitted from combustion sources (64). This decrease will be a result of the partial replacement of coal as a fuel by natural gas. However, the total annual emission of sulphur dioxide will still be large, viz., 6.3 million tons in 1970 and 5.73 million tons in 1975. In other European countries, however, a steady increase in the amount of sulphur dioxide emitted into the atmosphere, primarily from combustion sources, is anticipated during the next few years (13).

From the statistical viewpoint, this expected steady increase in the amount of sulphur dioxide discharged into the atmosphere by industrialized nations has significant consequences (65). Thus, at the moment, a pollution concentration, ten times greater than the mean daily concentration, could be expected to occur only once every fifty to sixty years. However, if the mean sulphur dioxide concentration in the atmosphere were to double, such an excessive concentration could be expected to occur about twice a year. As the demand for electrical power, for example, is doubling every ten years, and if other factors remain constant, the frequency of serious pollution incidents may be expected to increase much more rapidly than the increase in the mean sulphur dioxide concentration in the atmosphere.

It is the object of this report to provide a review of methods that have been used and that are being developed for the removal of sulphur dioxide from waste gases. Most of these methods involve a separation step that removes sulphur dioxide at a relatively low concentration from the gas phase and concentrates it either in a solid or a liquid phase. Depending upon the particular removal process, the spent absorbent is usually regenerated by physical or chemical means to yield the original absorbent for re-cycling, and to give a relatively concentrated stream of sulphur dioxide for the production of a marketable sulphur-containing product. Although a large number of such methods have been described in the literature, only a few of them have as yet been tested on an industrial scale; the limiting factor with many potential methods being as much of an economic as of a technical nature. For classification purposes, the various removal methods will be considered under the following headings.

Scrubbing with aqueous solutions or slurries.
Scrubbing with ammoniacal solutions.
Additive injection methods.
Adsorption on active carbon.
Absorption on metal oxides.
Catalytic oxidation methods.
Molten salt processes.
Reduction to elemental sulphur.
Applications of organic reagents.
Physical separation methods.

The literature on sulphur dioxide removal methods is very extensive and some of the topics listed above are discussed briefly in a number of general reviews on the prevention of sulphur dioxide pollution (6-13, 20, 48, 49, 51, 66-77). Very detailed surveys of specific removal methods have also been sponsored by the National Air Pollution Control Administration in the United States and these surveys will be referred to in relevant sections.

The costs of the installation and operation of processes for the removal of sulphur dioxide from waste gases are not considered in this report. Economic studies have been made of some sulphur dioxide removal methods (10, 50, 51, 54-56, 78, 79) and indicate that the cost of a given removal process is dependent in a complex manner on a number of interrelated factors including the type and the geographical location of the particular industrial process, the volume of waste gas to be treated, the concentration of sulphur dioxide in the waste gas, and the credit received from the sale of the recovered sulphur or sulphur-containing product. However, it appears likely that in most situations the removal of sulphur dioxide from waste gases could well impose an economic penalty against the industrial operation, particularly during times of low sulphur prices.

SCRUBBING WITH AQUEOUS SOLUTIONS OR SLURRIES

General Considerations

Most processes for the removal of sulphur dioxide from gas streams are based upon scrubbing the gas stream with an aqueous solution or with an aqueous slurry. Both cyclic and non-cyclic scrubbing processes have been described that serve not only for sulphur dioxide removal but also for the recovery of sulphur or a sulphur-containing product that may be sold to offset, in part, the cost of the scrubbing system. In general, methods involving wet scrubbing have several advantages over dry absorption techniques for the removal of sulphur dioxide from waste gases. These advantages include the relative easy circulation and handling of the absorbent, no problems relating to physical attrition and loss of absorption capacity of the absorbent during multiple re-cycling, and good mass transfer between the gaseous phase and the solution phase. There are also some disadvantages associated with wet-scrubbing processes that include the need to cool the incoming gas (usually to $\sim 50°C$), undesirable side reactions that reduce the absorption capacity of the solution or slurry for sulphur dioxide, and the possibility of corrosion of the processing equipment. Some scrubbing processes also require a dust-free gas to avoid the build-up of solids in the absorbent solution.

A detailed study has been published recently by Gressingh et al. of the Aerojet-General Corporation (79) of the application of aqueous scrubbing methods to the removal of sulphur dioxide from gas streams, the main concern of this study being with gases containing low concentrations of sulphur dioxide. The study also includes an extensive bibliography of about seven hundred references on aqueous scrubbing methods. It had been one of the original objectives of this work to screen the known aqueous-scrubbing processes on the basis of chemical-equilibrium calculations in order to eliminate from further study those processes that were incapable of lowering the sulphur dioxide content of the gas stream from 3000 to 150 ppm. However, it was found that all the processes studied did have this capability and, therefore, an internally consistent economic analysis was performed for all published aqueous-scrubbing processes to select those processes that appeared to offer the best prospects for commercial exploitation. On the basis of this economic criterion, the wet scrubbing processes that were recommended as the most suitable for further study were the Mitsubishi lime process, the Cominco exorption process, and the zinc oxide processes developed by Johnstone and by the Aerojet-General Corporation. As the latter process is more closely related to dry oxide absorption than to aqueous scrubbing, it will be considered later in the section dealing with absorption by metal oxides.

A number of aqueous-scrubbing processes are based upon ammonia as an absorbent and these processes will be considered separately from other aqueous scrubbing methods in the next section (page 34).

Scrubbing Methods

(a) Water Scrubbing

Water itself may be used as an absorbent for sulphur dioxide, and, historically, in the Haenisch-Schroeder process, water scrubbing was one of the earliest methods for the removal of sulphur dioxide from dilute gas streams (80).

When sulphur dioxide is dissolved in water, a number of equilibria are established between sulphur dioxide in the gas phase and sulphur dioxide in various forms in the aqueous phase. The principal equilibria and their equilibrium constants are:

$$(SO_2)_g = (SO_2)_{aq.} \qquad \ldots \text{(Eq. 1)}$$

$$H = \frac{(a_{SO_2})_{aq.}}{(a_{SO_2})_g} \qquad \ldots \text{(Eq. 1a)}$$

$$(SO_2)_{aq.} + 2H_2O = HSO_3^- + H_3O^+ \qquad \ldots \text{(Eq. 2)}$$

$$K_1 = \frac{a_{HSO_3^-} \, a_{H_3O^+}}{(a_{SO_2})_{aq.} \cdot (a_{H_2O})^2} \qquad \ldots \text{(Eq. 2a)}$$

$$HSO_3^- + H_2O = SO_3^{--} + H_3O^+ \qquad \ldots \text{(Eq. 3)}$$

$$K_2 = \frac{a_{SO_3^{--}} \, a_{H_3O^+}}{a_{HSO_3^-}} \qquad \ldots \text{(Eq. 3a)}$$

where H is Henry's Law constant, and K_1 and K_2 are the first and second ionization constants of "sulphurous" acid. It should be noted that from spectroscopic studies (81-84) there is no evidence for the presence of undissociated molecules of sulphurous acid (H_2SO_3) in aqueous solutions of sulphur dioxide. The non-ionized sulphur species in water consist almost entirely of uncombined sulphur dioxide molecules. However, the term "sulphurous acid" is well entrenched in the scientific literature and continues to be used. Vapour-liquid equilibria measurements have been made (85) for the binary system sulphur dioxide/water and the experimental data have been found to correlate well with Equation 4 over a temperature range between 0 and 130°C.

$$H = \exp\frac{2851.1}{T} - 9.3795 \qquad \ldots \text{(Eq. 4)}$$

A study of the absorption of sulphur dioxide in water in a packed column is given by Thomas (86).

However, the capacity of water to dissolve sulphur dioxide is very low, the vapour pressure of sulphur dioxide over an aqueous solution being proportional to the square of the hydrogen-ion concentration of the aqueous phase (87). Thus when sulphur dioxide dissolves in water, the pH of the water rapidly falls and solution soon stops. Hence, extremely large quantities of water are needed for the efficient removal of sulphur dioxide from gas streams by water scrubbing, the amount required being between 100 and 200 tons of water per ton of sulphur dioxide absorbed (75, 88). However, sea water and other naturally occurring waters are said to provide an effective scrubbing medium for sulphur dioxide (89) if an improved method of gas-water contact is used (Kanagawa process). A description of the Kanagawa process has been given (90) in which underground water containing calcium ions was used as a scrubbing medium. The influence on sulphur dioxide absorption of a number of variables such as pH, the addition of ammonia, and the rate of gas flow is also discussed. Sea water has also been used as a scrubbing medium in bench-scale experiments at the University of California (91, 92) and it was found that 25 pounds of sea water were needed to scrub one pound of flue gas in a single-stage absorption column. The scrubbing of smelter gases containing 0.8 - 1.2% sulphur dioxide with relatively cold (5°C) river water has been used (93) to remove 95% of the sulphur dioxide from the gas stream. The use of Venturi scrubbers for the water scrubbing of smelter gases has also been proposed (94), and, because calcium oxide was present in the smelter gases, the aqueous solution after scrubbing was alkaline or neutral. Cooling gases containing sulphur dioxide to below their dew point, with the prior injection of water vapour if necessary, has been suggested (95, 96) as a technique for the removal of sulphur dioxide from flue gases.

It is also known that the rate of absorption of sulphur dioxide in water is influenced by the presence in solution of small concentrations of surface-active agents, such as alkyl sulphonates (97-100). In general, the rate of absorption decreases as the concentration of the surface-active agent increases, with minima being observed in the curves of the rate of absorption versus the concentration of the surface-active agent. Both hydrodynamical and chemical factors are believed to be responsible for this type of absorption behaviour. Surface-active agents such as fatty acids that are preferentially adsorbed at the air-liquid interface reduce the rate of gas absorption by reducing the interfacial mass-transfer rate from the gas to the liquid phase (101).

The recovery of sulphur dioxide following absorption in water may be performed by steam-stripping, as in the Haenisch-Schroeder process (80), but the recovery process requires bulky equipment, has high steam-stripping costs, and is uneconomical for the treatment of waste gases. It is claimed that good recovery of sulphur dioxide from water can be obtained by desorption under reduced pressure either by thermal-stripping (102) or by spray desorption in multiple flashing zones, each zone being at a progressively reduced pressure (103).

A novel approach to the absorption of sulphur dioxide in water is based upon the observation that electrically charged droplets of water will dissolve considerably more sulphur dioxide than uncharged water droplets (104). Hence the gas containing sulphur dioxide is passed through a fine spray of water, the latter having been electrically charged by a dc field. The water droplets containing dissolved sulphur dioxide are then carried in the gas stream to a photochemical reaction zone and are subjected to high-intensity ultra-violet light pulsed at 2 to 4 millisecond intervals at a power of 2.4 to 3.64 kJ/pulse. In the photochemical reaction (105) the dissolved sulphur dioxide is reduced to sulphur which may be separated from the water by conventional means.

(b) Manganese Ion Processes

The capacity of water to absorb sulphur dioxide can be greatly increased by trace amounts of certain metal ions, particularly manganous and ferric ions (88, 106-111). These ions have the ability to catalyze the oxidation of dissolved sulphur dioxide to produce sulphuric acid, and such catalytic reactions may be responsible for the formation of sulphuric acid aerosols in a moist, industrial environment (111, 112). In studies of the manganese ion/water system (88, 107, 108), it was found that the pH of the solution had a marked effect on the oxidation reaction which was favoured by neutral or alkaline solutions. However, it was possible to obtain up to a 30% solution of sulphuric acid by bubbling air containing 0.325% sulphur dioxide through water containing 0.03% manganous ions (88). Similarly, the solubility of sulphur dioxide in water was increased sixfold by a concentration of manganous ions in solution as low as 28 ppm (88). A recent study (113) of this catalytic reaction at 25°C over a wide range of manganous ion concentration (0 to 10,000 ppm of $MnSO_4$) showed that the reaction is of zero order with respect to both oxygen and sulphur dioxide and that the rate of the reaction is dependent on the manganous ion concentration. Thus, for a catalyst concentration of between 0 and 100 ppm the reaction rate is proportional to the square of the catalyst concentration but, for a catalyst concentration of 100 to 500 ppm, the rate increases more slowly, and above 500 ppm the reaction rate is only slightly influenced by increases in the catalyst concentration. It has also been observed that the catalytic reaction is easily inhibited by small concentrations of many organic compounds, e.g., phenols (88, 114, 115).

The presence of ozone in combination with a manganous ion catalyst has the effect of increasing the oxidation rate of sulphur dioxide (116). A study of this manganous ion/ozone process (117) showed that excellent sulphur dioxide removal efficiencies were obtained by scrubbing a simulated flue gas containing $\sim$160 ppm of ozone with a 10% sulphuric acid solution which contained 3000 ppm of manganese. However, when an actual flue gas was used much poorer removal efficiences were found. This decrease in removal efficiency was attributed to the inhibition of the catalyst by unidentified poisons in the flue gas. This poor catalytic behaviour, together with the low concentration of sulphuric acid that can be produced, make the process uneconomical for industrial application.

(c) Lime/Limestone Scrubbing Processes

The scrubbing of waste gases with an aqueous slurry of lime or limestone has been demonstrated to offer good removal efficiences for sulphur dioxide and this technique has been the subject of intermittent investigations for many years (118). The limestone may be used to remove sulphur dioxide by the following methods (119).

(i) By direct introduction of powdered limestone into the scrubber.

(ii) By pre-calcining the limestone before introduction into the scrubber.

(iii) In power plant operation, by introduction of the limestone into the boiler where it is calcined and then carried into the scrubber as calcium oxide by the gas stream (page 62).

(iv) In alkaline scrubbing of the gas stream, by regenerating the spent absorbent with limestone in a separate unit.

In the 'thirties, two limestone-based scrubbing processes were developed in England for the removal of sulphur dioxide from the flue gases of thermal power stations.

In the Battersea process (120-122) water from the River Thames is used both as a scrubbing medium and also to carry away the products of the scrubbing reaction. The river water is initially mildly alkaline and has additional chalk or lime added to increase its alkalinity. The reaction of sulphur dioxide with the absorption solution in the scrubbing tower results mainly in the formation of calcium sulphite. The calcium sulphite is oxidized with air, in the presence of a small concentration of manganous ions, to give calcium sulphate which is more suitable than calcium sulphite for disposal in the river. The reaction sequence for sulphur dioxide removal is shown in Equation 5:

$$CaCO_3 + SO_2 \xrightarrow{\text{Scrubbing}} CaSO_3 + CO_2 \xrightarrow[O_2]{Mn^{2+}} CaSO_4 \quad \ldots \text{(Eq. 5)}$$

High efficiences (92 to 97%) of sulphur dioxide removal are obtained with the Battersea process. However, the requirement for large quantities of water and possible water-pollution problems limit its applicability to locations having large supplies of already contaminated water.

The other limestone scrubbing process developed in England, the Howden-ICI process, is a cyclic process in which the flue gas is scrubbed with a re-circulating slurry of 5 to 10% lime or limestone (122-125). Some of the circulating medium is continuously withdrawn, the solids separated, and the clarified liquor returned to the absorption system. The separated solids, consisting mainly of a mixture of calcium sulphite, calcium sulphate,and fly ash, have no commercial value and are discarded. This cyclic process was found to have excellent removal efficiences for sulphur dioxide (98%) but it has been discontinued because it was too expensive to operate.

A cyclic-lime process similar to Howden-ICI process is under development in Japan (the Mitsubishi New Lime process). In this process (126),the flue gases, after cooling and dust removal, are scrubbed with a 10% lime slurry in a series of absorption towers. The calcium sulphite, formed by the reaction of the lime with sulphur dioxide, is oxidized with air to give high-purity gypsum which is recovered by flotation, the mother liquor being returned to the absorption circuit.

In the United States very extensive studies are currently underway of limestone scrubbing for the treatment of waste gases containing low concentrations of sulphur dioxide. This method is now favoured as the short-range solution to sulphur dioxide abatement by both the electrical power industry (12, 119) and the copper smelting industry (127) for the treatment of waste gases from reverberatory furnaces which have too low a concentration of sulphur dioxide for sulphuric acid production by the contact process. The calcium sulphite/calcium sulphate product from the absorption process is discarded. A number of design and process problems have still to be resolved in the lime-limestone scrubbing process and large-scale pilot-plant studies are being undertaken by the Tennessee Valley Authority (119) and by the Smelter Control Research Association in the United States (127) to obtain data on the best mode of limestone addition, the oxidation of calcium sulphite to calcium sulphate, the influence of ionic strength of the scrubbing medium on the absorption of sulphur dioxide, the corrosion and erosion of the scrubber, and the reliability of the scrubbing process.

The application of an aqueous limestone suspension to the removal of sulphur dioxide from flue gases has also been described in a recent German patent (128). In this method, the sludge separated from the used aqueous suspension contacts the incoming flue gas (120°C) in a drying tower in which most of the fly ash is removed before the limestone scrubbing stage.

A method has been described (129) for the preparation of sulphuric acid from the insoluble products that are formed during aqueous-lime scrubbing of the off-gases from a copper smelting furnace. The solids, consisting of calcium sulphite, calcium sulphate, and dust, are separated from the scrubbing liquor in a thickner. The overflow from the thickner is re-cycled to the scrubber while the thickner underflow is filtered and the filter cake returned to the furnace. The reactions given in Equations 6 to 8 take place in the furnace, the silica and alumina being part of the furnace charge:

$$4CaSO_3 = CaS + 3CaSO_4 \quad \ldots \text{(Eq. 6)}$$

$$CaSO_4 + Al_2O_3 = CaAl_2O_4 + SO_3 \quad \ldots \text{(Eq. 7)}$$

$$CaSO_4 + SiO_2 = CaSiO_3 + SO_3 \quad \ldots \text{(Eq. 8)}$$

The sulphur trioxide that is liberated in the furnace from the decomposition of calcium sulphate (Equations 7 and 8) is then recovered from the furnace off-gases by scrubbing with dilute sulphuric acid prior to the aqueous-lime scrubber.

(d) The Basic Aluminum Sulphate Process

The basic aluminum sulphate process was developed by Imperial Chemical Industries Limited in England as a method of recovering sulphur dioxide from gas streams containing relatively large amounts of sulphur dioxide (87, 130). Basic aluminum sulphate is used in this process to provide, in effect, a water-soluble form of alumina. Sulphur dioxide is recovered from the spent absorption solution by thermal stripping, the regenerated scrubber liquor being re-cycled to the absorption tower. The absorption-desorption reaction is shown in Equation 9:

$$\mathrm{Al(OH)SO_4 + SO_2 \rightleftarrows Al(OSO_2H)SO_4}. \qquad \ldots \text{(Eq. 9)}$$

Some sulphur dioxide undergoes oxidation during absorption (Equation 10):

$$\mathrm{Al(OSO_2H)SO_4 + \tfrac{1}{2}O_2 = Al(OSO_3H)SO_4} \qquad \ldots \text{(Eq. 10)}$$

and the sulphate content of the absorption solution is kept at a low level by the treatment of a side-stream of the solution with limestone (Equation 11):

$$\mathrm{Al(OSO_3H)SO_4 + CaCO_3 = CaSO_4 + Al(OH)SO_4 + CO_2} \qquad \ldots \text{(Eq. 11)}$$

Methylene blue was used as an inhibitor to limit oxidation (Equation 10) but excessive losses of the inhibitor were found (87). The basic aluminum sulphate process was used at a copper smelter in Finland (1936-1941) but has not received wide application. The process is most suitable for gases containing at least 1% sulphur dioxide (131).

(e) The Wet Thiogen Process

The wet thiogen process uses water as a scrubbing medium for sulphur dioxide (132). The scrubber effluent is treated with barium sulphide giving sulphur and insoluble barium salts (Equation 12):

$$\mathrm{2BaS + 3(SO_2)_{aq.} = BaSO_3 + BaS_2O_3 + 2S} \qquad \ldots \text{(Eq. 12)}$$

The insoluble salts are removed by filtration, dried, and barium sulphide reformed by heating and reduction (Equations 13 to 15).

$$\mathrm{BaS_2O_3 = BaSO_3 + S} \qquad \ldots \text{(Eq. 13)}$$

$$\mathrm{BaSO_3 + 3C = BaS + 3CO} \qquad \ldots \text{(Eq. 14)}$$

$$\mathrm{BaSO_4 + 4C = BaS + 4CO} \qquad \ldots \text{(Eq. 15)}$$

Some pilot plant runs were made with the wet thiogen process, but the process was abandoned because of its low capacity and poor efficiency in the removal of sulphur dioxide.

(f) Alkaline Sulphite Absorption Processes

Aqueous solutions of alkali sulphites may be used as absorbents for sulphur dioxide (Equation 16):

$$SO_2 + SO_3^{--} + H_2O = 2HSO_3^- \qquad \ldots \text{(Eq. 16)}$$

The spent absorption solution can be regenerated (133) by steam stripping, reflux stripping or by reduction of the separated solid absorbent, methods which yield a relatively concentrated stream of sulphur dioxide or elemental sulphur. Thus in the regeneration technique of the Chevron Research Company (134), sodium bisulphite, formed by sulphur dioxide absorption in a sodium sulphite solution (Equation 16), is converted to sulphur and sodium sulphite for re-cycle by reduction in solution with hydrogen (Equation 17) or with hydrogen sulphide (Equation 18).

$$2NaHSO_3 + 2H_2 = Na_2SO_3 + S + 3H_2O \qquad \ldots \text{(Eq. 17)}$$

$$2NaHSO_3 + 2H_2S = Na_2SO_3 + 3S + 3H_2O \qquad \ldots \text{(Eq. 18)}$$

For these reduction reactions,the pH of the solution is preferably in the range pH3 to pH7 and the temperature is maintained above the melting point of sulphur. Similar reduction reactions also take place with sodium sulphate and sodium bisulphate which are formed as oxidation products during flue-gas scrubbing.

The Wellman-Lord process is the most developed alkaline sulphite absorption process for the removal and recovery of sulphur dioxide from gas streams and is based upon the temperature-dependent absorption-desorption of sulphur dioxide by certain sulphites in aqueous solution (Equation 19):

$$SO_2 + SO_3^{--} + H_2O \underset{T''}{\overset{T'}{\rightleftarrows}} 2HSO_3^- \quad (T'' > T') \qquad \ldots \text{(Eq. 19)}$$

The sulphites of lithium, rubidium, sodium, potassium,and beryllium have been specified in the patent literature (135-138) as being suitable for this reaction, and it is known that the reaction in solution between sulphites and dissolved sulphur dioxide is very fast (139). The Wellman-Lord process is most suitable for gas streams containing between 0.15 and 2 volume per cent of sulphur dioxide. For application of the process to power station or smelter gases, the gas is first scrubbed with water to remove particulate matter and sulphur trioxide (55, 140, 141) while, for application to the tail gases from a sulphuric acid plant, the dry tail gases are first humidified (142). The gas stream is then contacted in an absorption tower with a counter-current flow of a solution containing sodium sulphite and sodium bisulphite. The sulphur dioxide in the gas phase reacts with the sulphite in solution as shown in Equation 19 and 90 to 95% of the sulphur dioxide is absorbed. The spent absorption solution is transferred to a chemical recovery stage where the solution is heated in an evaporator-crystallizer, precipitating crystals of sodium sulphite and releasing sulphur dioxide and water vapour. This sulphur dioxide recovery process, the details of which are confidential, is said to offer significantly lower costs than the direct steam-stripping of the spent absorption solution (55). The gases from the recovery stage are then passed through a condenser for the partial removal of the water vapour, and the concentrated sulphur dioxide that is recovered may be liquified, used to produce sulphuric acid, or reduced to elemental sulphur. The sodium sulphite crystals are separated from the mother liquor in a centrifuge, re-dissolved, and returned to the absorption tower. The mother liquor is returned to the evaporator-crystallizer unit.

Some sodium sulphate is formed in the absorption solution by the reaction of sodium sulphite with either dissolved oxygen or traces of sulphur trioxide (Equations 20 and 21):

$$Na_2SO_3 + \tfrac{1}{2}O_2 = Na_2SO_4 \qquad \text{... (Eq. 20)}$$

$$2Na_2SO_3 + SO_3 + H_2O = Na_2SO_4 + 2NaHSO_3 \qquad \text{... (Eq. 21)}$$

Because sodium sulphate cannot be regenerated by the Wellman-Lord process, the absorption solution is periodically purged of sulphate, the sodium sulphate that is removed being replaced with an equivalent amount of sodium by the addition of a 50% caustic soda solution.

The Wellman-Lord process has been tested on a pilot plant basis at an electrical utility plant in Florida (143) and a full-scale version of the process has been installed recently (July, 1970) to control the sulphur dioxide emission from the tail gases of a sulphuric acid regenerating plant operated by the Olin Corporation at Paulsboro, New Jersey (142). The Paulsboro installation has readily met the design specifications for the amount of sulphur dioxide remaining in the cleaned stack gases (< 500 ppm of SO_2). However, greater than design requirements for caustic soda make-up solution has been found because of the higher than expected oxidation of sulphite during absorption. Modifications of the gas-liquid contact system in the absorption tower are underway to minimize this oxidation.

Plans have also been announced recently (144) to install the Wellman-Lord process to remove sulphur dioxide from the tail gases of a new sulphur production facility now under construction at the El Segundo (California) refinery of Standard Oil of California.

(g) Zinc Oxide Processes

When steam stripping is employed to regenerate the spent absorption solution in the alkaline sulphite absorption provess the efficiency of the process for the removal of sulphur dioxide from flue gases is limited by the extent to which the absorbed sulphur dioxide can be recovered from the spent absorption solution without incurring excessive heating costs. For reasonable steam heating costs,not all the sodium bisulphite in solution is decomposed, and a small vapour pressure of sulphur dioxide will exist over the regenerated solution to oppose the absorption of sulphur dioxide from the incoming flue gases. In order to increase the recovery of sulphur dioxide from the spent absorption solution, a chemical regeneration process has been developed by Johnstone and Singh (145, 146). This regeneration process (Figure 1) is based upon the addition of zinc oxide to a well-stirred solution of the effluent liquor to form insoluble zinc sulphite (Equation 22):

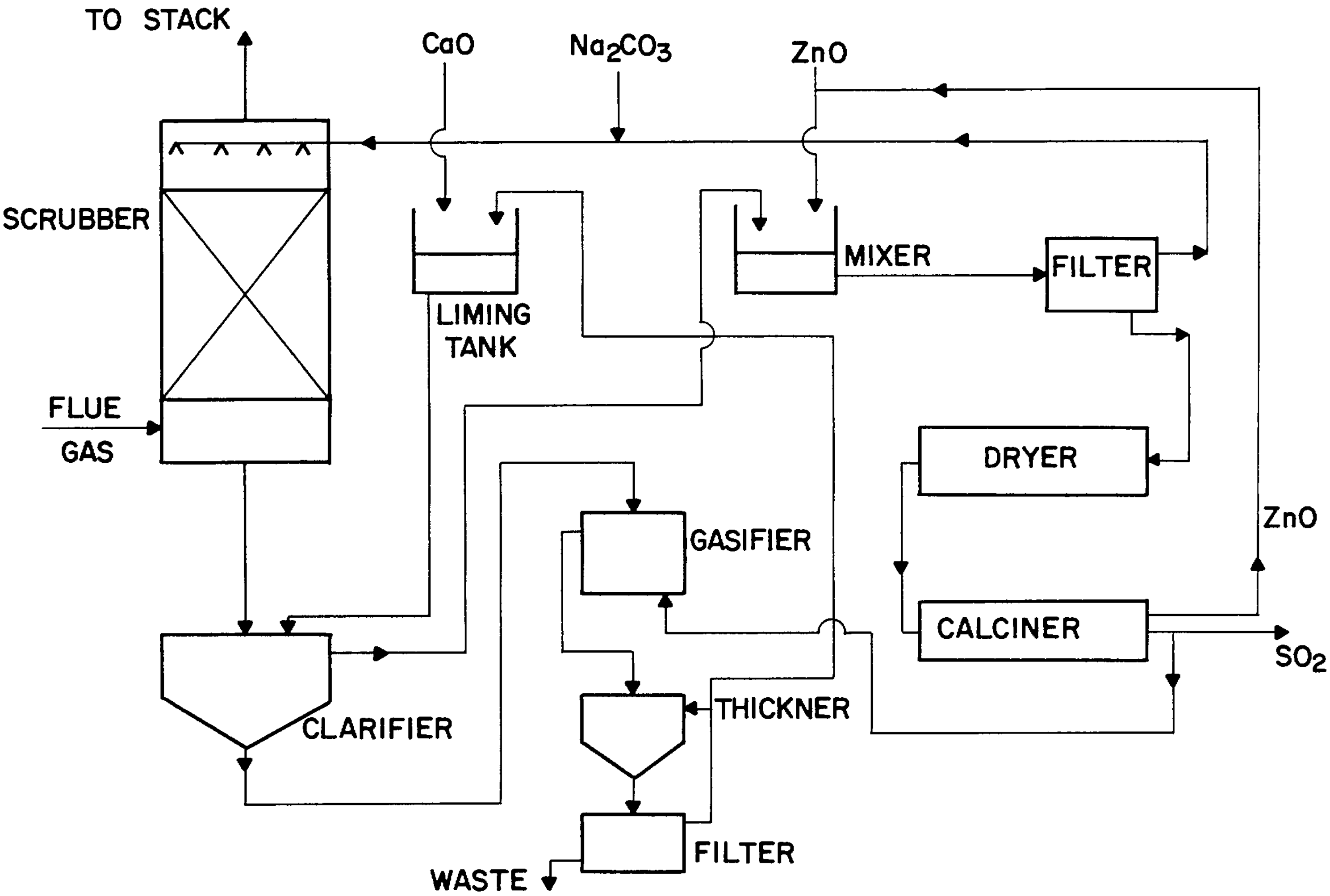

FIGURE I. THE JOHNSTONE AND SINGH ZINC OXIDE PROCESS

$$2NaHSO_3 + ZnO + 1{\cdot}5H_2O = ZnSO_3.2{\cdot}5H_2O + Na_2SO_3 \quad \ldots \text{(Eq. 22)}$$

At a pH somewhat less than 6·5, well-defined crystals of $ZnSO_3 2{\cdot}5H_2O$ are formed. Higher pH's are undesirable because a basic sulphite that has poor settling and filtering properties is formed. The crystals of zinc sulphite are filtered, dried, and calcined to give zinc oxide and a 70/30 mixture of water vapour and sulphur dioxide in the gas phase (Equation 23).

$$ZnSO_3 2{\cdot}5H_2O = ZnO + SO_2 + 2{\cdot}5H_2O \quad \ldots \text{(Eq. 23)}$$

The zinc oxide is recovered for re-cycling.

Any oxide that gives an insoluble sulphite could be used for the reaction in Equation 22. However, zinc sulphite has the advantage that it decomposes at a much lower temperature (300°C) than other sulphites that could be formed in this reaction. As in other absorption processes involving sulphites, some oxidation of the sulphite to the sulphate takes place (Equations 20 and 21), thus decreasing the absorption capacity of the scrubbing solution. Johnstone and Singh (145, 146) found that about 10% of the absorbed sulphur dioxide was converted to the sulphate and they devised the following method for sulphate removal. A slurry of insoluble calcium sulphite is formed in the liming tank (Equation 24):

$$CaO + 2NaHSO_3 = Na_2SO_3 + CaSO_3 + H_2O \quad \ldots \text{(Eq. 24)}$$

The slurry is added to the scrubbing solution in the ash clarifier (Figure 1). The underflow from the clarifier, which contains the insoluble calcium sulphite and fly ash, is acidified in the gasifier with some of the product sulphur dioxide to form soluble calcium bisulphite (Equation 25).

$$CaSO_3 + SO_2 + H_2O = Ca(HSO_3)_2 \quad \ldots \text{(Eq. 25)}$$

Calcium ions are thus made available in solution to precipitate calcium sulphate (Equation 26):

$$Ca(HSO_3)_2 + NaSO_4 = CaSO_4 + 2NaHSO_3 \quad \ldots \text{(Eq. 26)}$$

which is filtered and discarded, the sodium bisulphite being returned to the liming tank.

Processes, involving the direct use of zinc oxide slurries as an absorbent rather than just for the chemical regeneration step as above, have been published in the patent literature (147, 148). In one method (147), the efficiency of removal of sulphur dioxide was 70 to 80% and could be increased to 80 to 90% by the addition of small amounts (0.5 to 50 g/ℓ) of caustic soda, ammonia, or potassium hydroxide (149) to the suspension.

(h) Magnesium Oxide Processes

A magnesium oxide absorption process has been developed recently by the Chemical Construction Company of New York (150-152). In this process an essentially dust-free gas stream containing oxides of sulphur is contacted with a slurry of magnesium oxide in a Venturi scrubber (Figure 2) forming a mixture of hydrated sulphites and sulphates of magnesium (Equations 27 to 30):

$$MgO + SO_2 + 6H_2O = MgSO_3.6H_2O \quad \ldots \text{(Eq. 27)}$$

$$MgO + SO_2 + 3H_2O = MgSO_3.3H_2O \quad \ldots \text{(Eq. 28)}$$

$$MgO + SO_3 + 7H_2O = MgSO_4.7H_2O \quad \ldots \text{(Eq. 29)}$$

$$MgSO_3 + \tfrac{1}{2}O_2 + 7H_2O = MgSO_4.7H_2O \quad \ldots \text{(Eq. 30)}$$

A bleed from the absorption system is taken to a centrifuge where the solids are separated and the clear mother liquor, with added magnesium oxide, is returned to the absorption circuit. The recovered solids are dried to remove adsorbed moisture and water of crystallization and are then calcined to yield sulphur dioxide and magnesium oxide. Some carbon is added in the calcining stage to reduce magnesium sulphate, which is also formed during absorption to magnesium oxide. The regeneration reactions are given in Equations 31 and 32:

$$MgSO_3.7H_2O \xrightarrow{\text{Dry}} MgSO_3 \xrightarrow{\text{calcine}} MgO + SO_2 \quad \ldots \text{(Eq. 31)}$$

$$MgSO_4.7H_2O \xrightarrow{\text{Dry}} MgSO_4 \xrightarrow[\text{C}]{\text{calcine}} MgO + SO_2 + CO_2 \quad .. \text{(Eq. 32)}$$

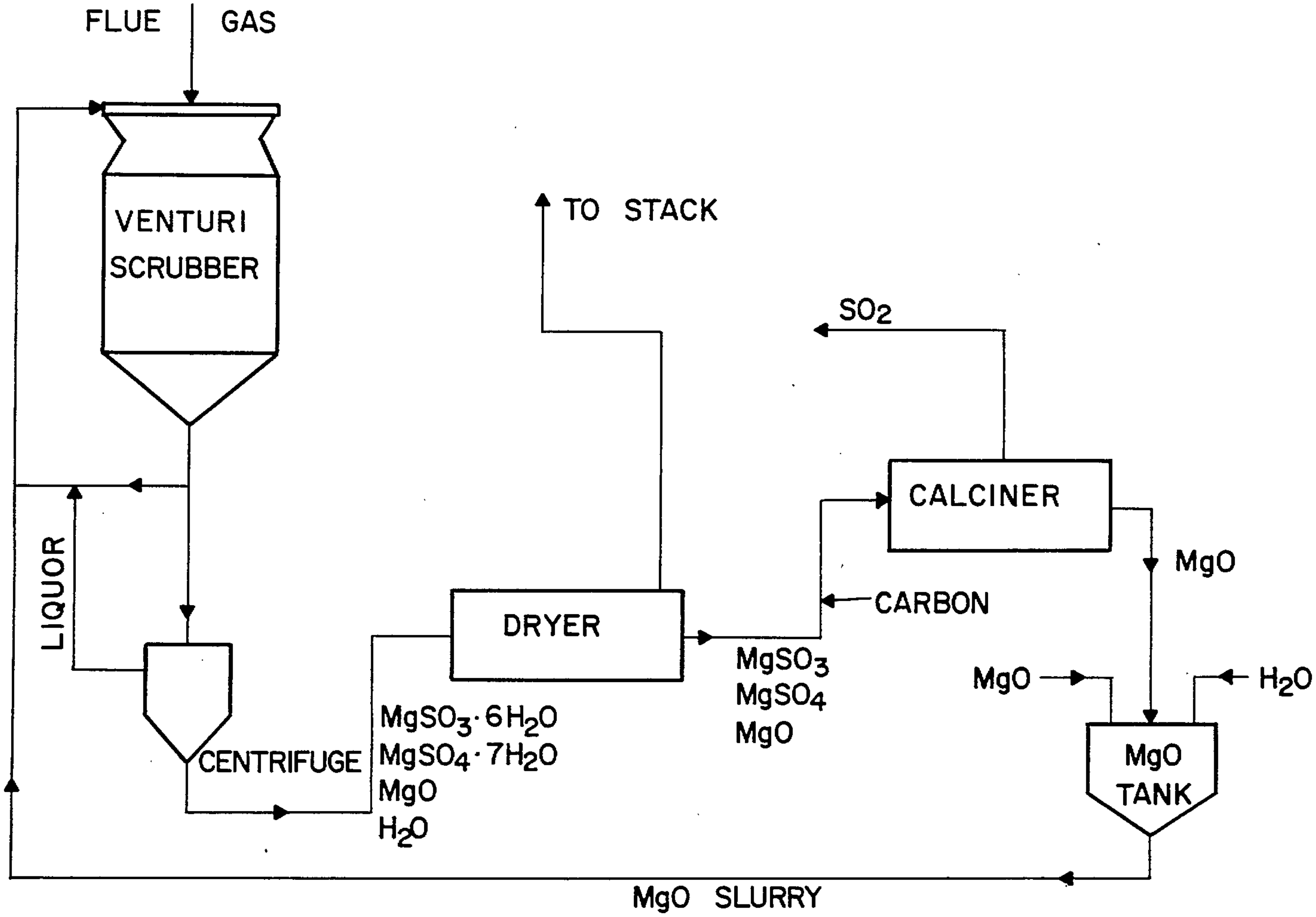

FIGURE 2. THE MAGNESIA - BASE PROCESS

The gas from the calciner contains about 15% sulphur dioxide which, after cleaning, is suitable for the production of sulphur or sulphur compounds.

This magnesium oxide process has been operated on a pilot plant scale, and a full-scale unit is currently being installed at a thermal generating station operated by the Boston-Edison Company (150). The Boston-Edison unit is designed to treat approximately 440,000 cu ft/min of flue gas containing 1400 to 1500 ppm of sulphur dioxide. Start-up is scheduled for late 1971.

Magnesia-based processes have also been employed successfully to remove over 95% of the sulphur dioxide contained in the waste gases emitted from pulp mills (153-155) and from coal fired boilers (156). In the latter study, no regeneration of the spent absorbent was conducted and some problems were encountered from the build-up of fly ash and sulphates in the scrubbing solution.

The regeneration of the spent absorption solution from a magnesia-base scrubbing process may also be performed (157, 158) by first oxidizing the sulphite to sulphate and then adding ammonia to form ammonium sulphate and magnesium hydroxide (Equation 33).

$$MgSO_3 + \tfrac{1}{2}O_2 \rightarrow MgSO_4 \xrightarrow[H_2O]{NH_3} Mg(OH)_2 + (NH_2)_2SO_4 \quad \ldots \quad (Eq. 33)$$

The magnesium hydroxide is then returned to the absorption tower.

(i) The Stone and Webster/Ionics Process

A significant difference between the Stone and Webster/Ionics process (159-161) and other processes for the removal and recovery of sulphur dioxide is that regeneration of the spent absorption solution is performed electrolytically rather than by thermal stripping or by chemical methods. Figure 3 shows the Stone and Webster/Ionics process as applied to an existing electrical utility plant. The flue gases after passing through the electrostatic precipitator are at a temperature of 200 to 300°F, and, as the first step in the sulphur dioxide removal process, the gases are cooled to between 130 and 150°F in a quench tower. In a new utility plant that is designed

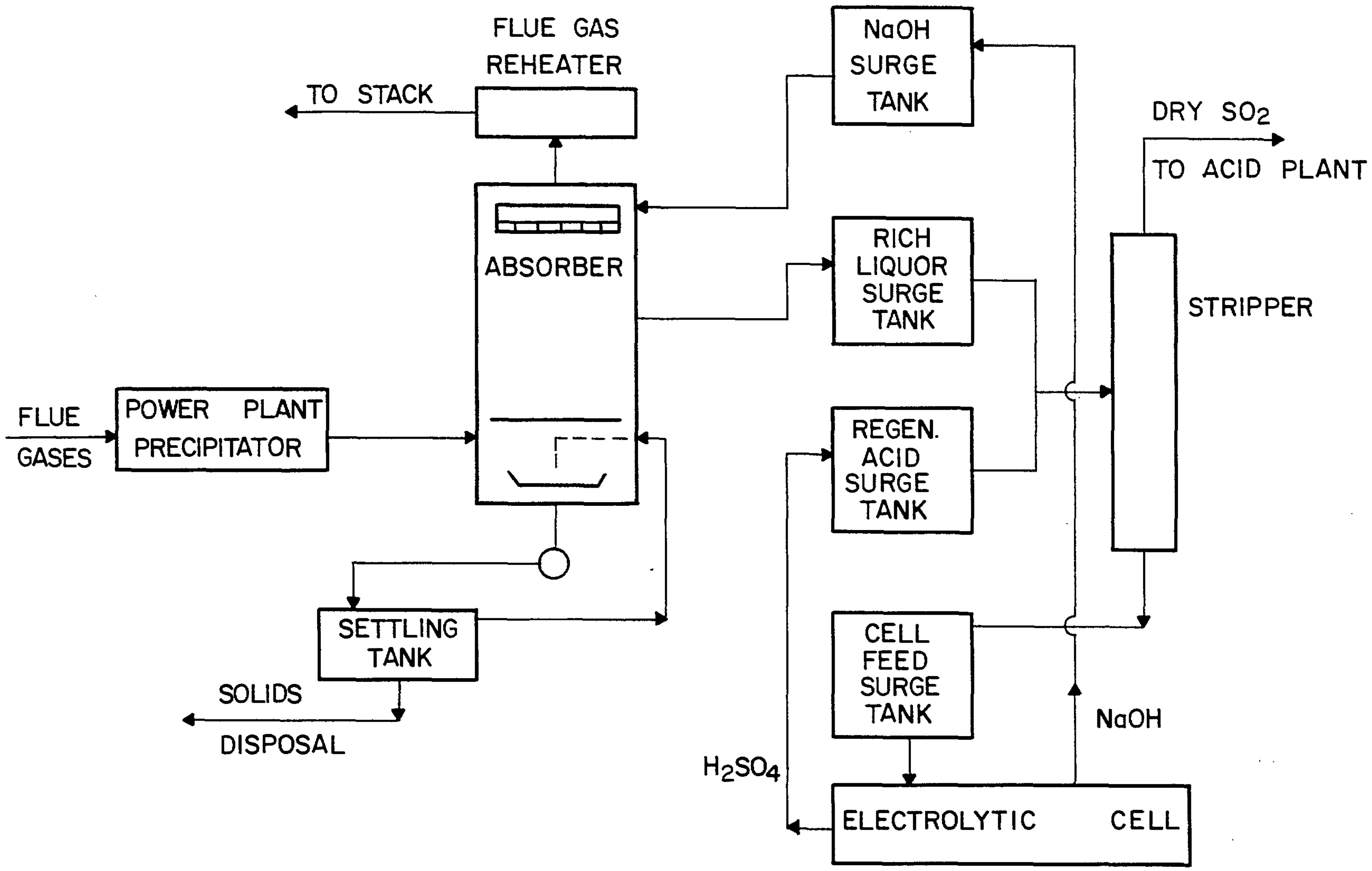

FIGURE 3. THE STONE AND WEBSTER/IONICS PROCESS

to accommodate the Stone and Webster/Ionics process, the electrostatic precipitator and the quench tower may be replaced by a wet scrubber that functions both for particulate removal and for gas cooling (160). The cooled flue gas is then scrubbed by a solution of caustic soda (concentration ~ 4.4 molar per cent) and the sulphur dioxide is converted into sodium sulphite and sodium bisulphite. The principal reactions occurring during absorption are given in Equations 34 to 36.

$$2NaOH + SO_2 = Na_2SO_3 + H_2O \quad \text{... (Eq. 34)}$$

$$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3 \quad \text{... (Eq. 35)}$$

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O \quad \text{... (Eq. 36)}$$

For later electrolytic regeneration of the spent absorption solution it is desirable that a high ratio of HSO_3^-/SO_3^{--} be obtained in the final stage of the absorption system ($pH \simeq 3{\cdot}5$), i.e., in the scrubbing solution the ratio of the absorbed sulphur to the sodium ion content should be close to unity. It is also necessary during the scrubbing operation to minimize the oxidation of the sulphite to sulphate by dissolved oxygen. The amount of oxidation that occurs is known to depend in a complex manner on a number of factors (50, 79, 162, 163) including the design parameters of the scrubber (area of contact, turbulence, and residence time), the presence of catalytic impurities (88, 117, 146, 164-167) and inhibitors (145, 164, 168) in the scrubbing solution, as well as the pH (145, 164, 169, 170), temperature (169), and solute concentration (145, 164, 171) of the scrubbing solution. It has also been observed recently (172) that nitrogen dioxide in the flue gas plays a very important role in sulphite oxidation and that reducing the nitrogen dioxide to nitric oxide, by pre-scrubbing the flue gas with an aqueous ferrous iron solution, significantly reduces the amount of sulphate formed. An overall review of factors influencing oxidation (162), with particular emphasis on the scrubber design, indicated that no definite conclusions could be reached concerning the amount of oxidation to be expected but that with appropriate choice of the scrubber, the amount of oxidation of sulphite to sulphate should not be greater than about 5% of the absorbed sulphur dioxide.

Sulphur dioxide may be recovered from the spent scrubbing solution by the methods listed below.

(1) The scrubbing solution is treated with dilute sulphuric acid (Figure 3) forming sulphur dioxide and sodium sulphate (160, 173). The sulphur dioxide is stripped from the acidified solution, dried, and converted to concentrated sulphuric acid which is the product of the recovery process. The sodium sulphate is then electrolyzed in a three-compartment cell to give caustic soda for re-cycling to the absorption stage and dilute sulphuric acid for the decomposition of the spent scrubbing solution.

(2) The sodium bisulphite in the scrubbing solution is oxidized in the anode compartment of an electrolytic cell (174) to give a solution containing mainly sodium bisulphate (Equation 37):

$$NaHSO_3 + H_2O = NaHSO_4 + 2H^+ + 2e \quad \ldots \text{(Eq. 37)}$$

The mother liquor from the crystallization stage consists of 75% sulphuric acid which is removed as a by-product.

(3) In this method (175) the bisulphite solution from the absorption stage is mixed with sodium bisulphate (produced together with caustic soda and sulphuric acid in the electrolysis of sodium sulphate in a four-compartment cell) and sufficient sulphuric acid to give a neutral solution which is then boiled to expel the sulphur dioxide and to concentrate the dilute sodium sulphate for re-use as feed for the electrolytic cell.

The Stone and Webster/Ionics process is designed to remove 90 to 95% of the sulphur dioxide from power-plant flue gases from the burning of coal containing 3.5% sulphur. Most of the operating cost of this sulphur dioxide removal process (~80%) is related to the electrolytic regeneration system where substantial quantities of electrical power are consumed; a requirement that appears to be a drawback of the process. Under certain conditions of power-station loading, this power could be required for grid distribution. However, the operation of the regeneration cells may be interrupted instantaneously to make this power available, and large surge tanks are incorporated in the system to permit sulphur dioxide removal to be maintained. Regeneration of the spent absorbent solution may then be performed later when power is available.

(j) Manganese Dioxide Processes

The absorption of sulphur dioxide by an aqueous slurry of manganese dioxide has been used for both the removal of sulphur dioxide from gas streams (117, 176-178) and for the hydrometallurgical extraction of manganese from low-grade manganese ore (179, 180). The reaction of sulphur dioxide with manganese dioxide (180) leads to the formation of manganese sulphate, manganese dithionate, and sulphuric acid (Equations 39 to 41):

$$MnO_2 + SO_2 = MnSO_4 \qquad \text{... (Eq. 39)}$$

$$MnO_2 + 2SO_2 = MnS_2O_6 \qquad \text{... (Eq. 40)}$$

$$MnO_2 + \tfrac{1}{2}O_2 + H_2O + 3SO_2 = MnS_2O_6 + H_2SO_4 \qquad \text{... (Eq. 41)}$$

Some other manganese sulphoxy compounds are also formed in undesirable side reactions (9).

In the application of this process to the removal of sulphur dioxide from waste gases, a portion of the absorption solution is continuously removed, and the soluble manganese salts are separated from the unreacted solids. The manganese dithionate may then be separated from the manganese sulphate by evaporation (179), or may be converted into the sulphate by oxidation with air in an autoclave (180). Manganese oxides may be recovered from the manganese sulphate either by calcining at 1000 to 1100°C or by treatment with hydrochloric acid in a cyclic recovery process (178).

Although the manganese dioxide removal process appears to be feasible (117), its development has been limited.

In the Grillo-AGS process (182, 183), a hydrated suspension of mixed oxides of manganese and magnesium at pH 7.5-8.0 is contacted with the flue gas in a spray reactor. About 90% of the sulphur oxides in the gas stream is removed in a contact time of between 0.46 and 1.4 seconds. The spent absorbent contains about 20% sulphur, mainly as sulphites and sulphates, and is separated from the gas stream in a cyclone or lamella separator. Regeneration of the absorbent is performed by reduction with coke at 800 to 1000°C, and the evolved gases are sent to a sulphuric acid plant. The solid residue from the regeneration process is hydrated, classified, thickened to about 30-35% solids, and then returned to the spray reactor.

(k) The Citrate Process

A citrate absorption process has been developed by the United States Bureau of Mines (184, 185) for the removal of sulphur dioxide from waste gases containing 1 to 3 per cent of sulphur dioxide and for the recovery of the sulphur dioxide as elemental sulphur. The reaction,by which the sulphur dioxide which has been absorbed in the citrate solution is reduced to elemental sulphur (Equation 42), is an aqueous-phase analogue of the Claus reaction (186).

$$SO_2 + 2H_2S \quad = \quad 2H_2O + \frac{3}{2}S_2 \qquad \ldots \text{(Eq. 42)}$$

The flow sheet for the citrate process is shown in Figure 4. The hot gases are first washed with water in order to remove traces of sulphuric acid and particulate matter and to cool the gases to about 50°C. The gases then enter an absorption tower and pass against a counter-current flow of a solution containing sodium citrate and citric acid at a pH of about 3·8. At this pH, the solution can absorb between 10 and 20 grams/litre of sulphur dioxide (Equation 43):

$$Na_3Cit + 3SO_2 + 3H_2O = 3NaHSO_3 + H_3Cit \qquad \ldots \text{(Eq. 43)}$$

The absorption capacity of the solution increases from about 5 grams/litre at 65°C to about 32 grams/litre at 25°C. The citrate solution is also a much better absorbent for sulphur dioxide at pH 8 than at pH 3.8. However, large amounts of thiosulphate are formed during the regeneration of an absorbent solution of pH 8, and a pH of about 3.8 is considered optimum for absorption.

The loaded absorbent solution is reacted with the stoichiometric amount of hydrogen sulphide in a well-stirred tank for 10 to 15 minutes giving sulphur (Equation 42). Following thickening and centrifuging, the sulphur is finally separated from residual citrate solution by melting under pressure. In the Bureau of Mines process, it is envisaged that the hydrogen sulphide required for this reduction step would be prepared by reacting a portion of the product sulphur with natural gas and steam over a catalyst at about 700°C (Equation 44):

$$4S + CH_4 + 2H_2O = CO_2 + 4H_2S \qquad \ldots \text{(Eq. 44)}$$

Following the successful operation of the citrate process on a laboratory scale, a pilot plant was installed to treat 400 cu ft/min of reverberatory gas from a copper smelter (Magna Copper Co., San Manuel Arizona). Removal efficiencies for the sulphur dioxide in the reverberatory gas were between 90 and 99%.

Preliminary data indicate that the citrate process also should be applicable to the treatment of flue gases from coal- or oil-burning boilers (185).

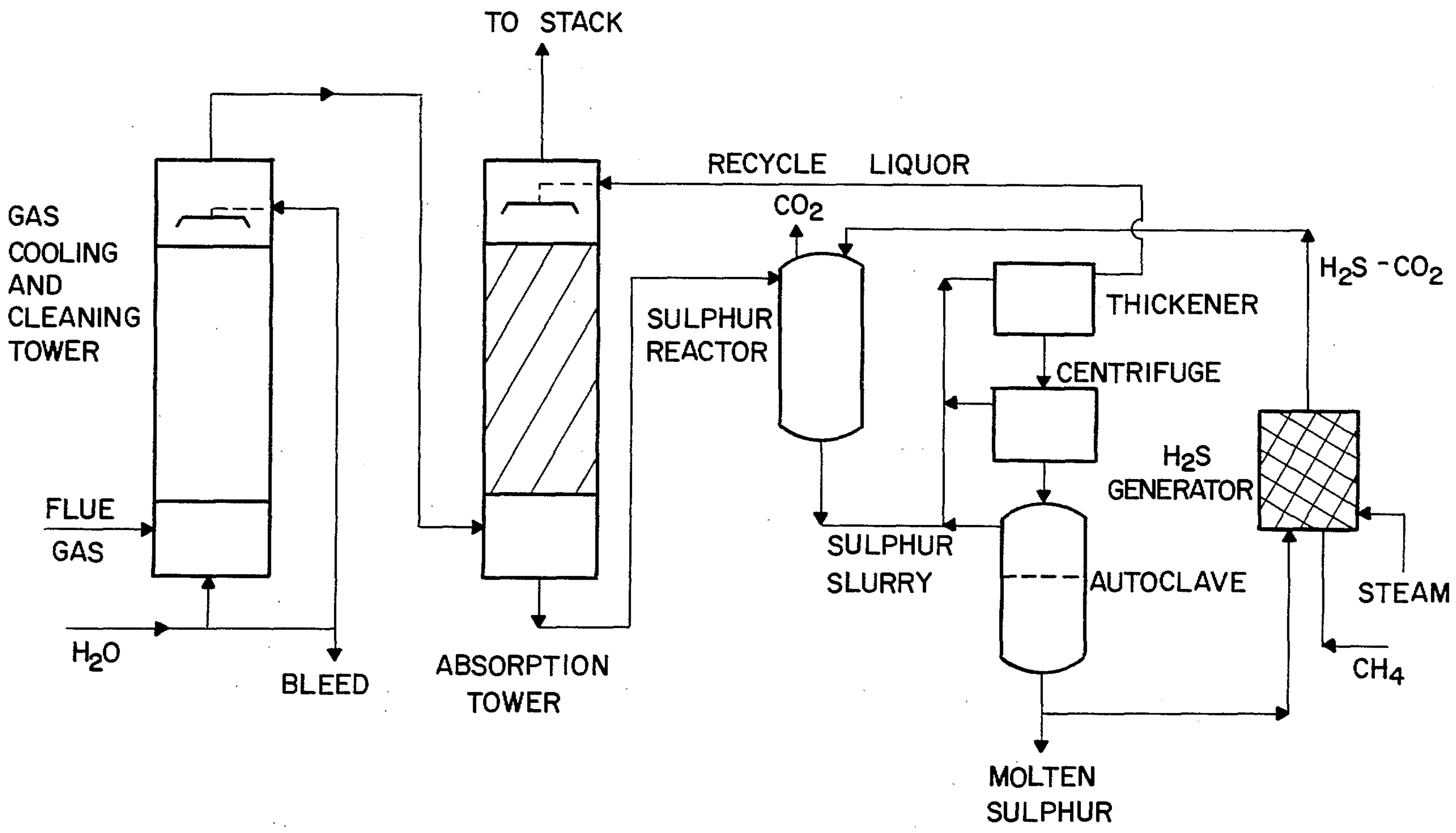

FIGURE 4. THE U.S. BUREAU OF MINES CITRATE PROCESS

(l) The Consolidated Coal Company Formate Processes

A system for sulphur dioxide absorption and sulphur recovery has been developed on a laboratory scale by the Consolidated Coal Company (187, 188). This process is based upon a concentrated solution (85%) of potassium formate as the scrubbing medium. The scrubbing reaction (Equation 45)

$$2KOOCH + 2SO_2 = K_2S_2O_3 + 2CO_2 + H_2O \qquad \ldots \text{(Eq. 45)}$$

is conducted at 200°F, a temperature that is sufficient to give a reasonable plume rise for the cleaned gas. Regeneration of the spent absorption solution is based upon the series of reactions given in Equations 46 to 48:

$$4KOOCH + K_2S_2O_3 \xrightarrow[500\ \text{psig}]{540°F} K_2CO_3 + 2KHS + 2CO_2 + H_2O \qquad \ldots \text{(Eq. 46)}$$

$$2KHS + CO_2 + H_2O \xrightarrow{230\text{-}270°F} K_2CO_3 + 2H_2S \qquad \ldots \text{(Eq. 47)}$$

$$K_2CO_3 + 2CO + H_2O \xrightarrow[1000\ \text{psig}]{540°F} 2KOOCH + CO_2 \qquad \ldots \text{(Eq. 48)}$$

The experimental conditions under which the reactions are conducted are noted with each equation. The overall net reaction for the formate process (Equation 49) is obtained by combining Equations 45 to 48 as:

$$SO_2 + 3CO + H_2O = H_2S + 3CO_2. \qquad \ldots \text{(Eq. 49)}$$

The hydrogen sulphide produced during absorbent regeneration (Equation 47) may be converted to sulphur in a Claus reactor (186). Using a simulated flue gas, containing 0.3% sulphur dioxide, removal efficiences for sulphur dioxide of just under 90% were found for the formate process.

(m) Other Aqueous Scrubbing Processes

In addition to the processes already considered, the patent literature refers to a number of other aqueous processes that are claimed to be effective in the scrubbing of sulphur dioxide from gas streams. The absorbents used in these processes include a 35 to 45% calcium chloride solution (189), a slurry of red mud* (190), a suspension of mixed oxides and and silicates (191), a solution containing selenious acid and sulphuric acid (192), a 40 to 80% sulphuric acid solution containing hydrogen peroxide and peroxydisulphuric acid (193), an aqueous suspension of cupric oxide (194), and a solution containing ferrous and ferric ions (195).

SCRUBBING WITH AMMONIACAL SOLUTIONS

General Considerations

The removal of sulphur dioxide from gas streams by scrubbing with aqueous solutions of ammonia has been widely investigated (50), and a number of ammonia-based processes have been used industrially for the treatment of effluent gases from thermal power stations (197, 198), smelter operations (199-201), and sulphuric acid plants (202). The main products of the absorption of sulphur dioxide in an aqueous ammonia solution are ammonium bisulphite and ammonium sulphite (Equations 50 and 51):

$$NH_3 + H_2O + SO_2 = NH_4HSO_3 \qquad \ldots \text{(Eq.50)}$$

$$2NH_3 + H_2O + SO_2 = (NH_4)_2SO_3 \qquad \ldots \text{(Eq.51)}$$

A small amount of ammonium sulphate is also formed in the absorption solution from the oxidation of ammonium sulphite by oxygen (Equation 52):

$$(NH_4)_2SO_3 + \tfrac{1}{2}O_2 = (NH_4)_2SO_4 \qquad \ldots \text{(Eq.52)}$$

A detailed account of the chemistry and the kinetics of the absorption of sulphur dioxide in ammoniacal solutions is given in a recent report by

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*"Red mud" is a waste product of the aluminum industry and consists mainly of the oxides of Fe, Al, Ti Ca and Si (196).

the Tennessee Valley Authority (50), and some of the more important parameters are briefly reviewed below.

(1) In the system water/sulphur dioxide/ammonia, the partial pressures of sulphur dioxide and ammonia over the aqueous phase are given (203), for the pH range of 4.71-5.96, by the relationships in Equations 53 and 54:

$$P_{SO_2} = \frac{M(2S-C)^2}{(C-S)} \qquad \text{... (Eq. 53)}$$

$$P_{NH_3} = \frac{NC(C-S)}{2S-C} \qquad \text{... (Eq. 54)}$$

where S and C are the molar concentrations of sulphur dioxide and ammonia in the aqueous phase. The constants M and N are temperature dependent and have the values 0.038 and 0.023 at 50°C. For a practical scrubbing system, in which some ammonium sulphate is present, the partial pressure relationships in Equations 53 and 54 are modified to Equations 55 and 56:

$$P_{SO_2} = \frac{M(2S-C+2A)^2}{C-S-2A} \qquad \text{... (Eq. 55)}$$

$$P_{NH_3} = \frac{NC(C-S-2A)}{2S-C+2A} \qquad \text{... (Eq. 56)}$$

where A is the molar concentration of ammonium sulphate. The effect of ammonium sulphate in the absorption solution is to decrease the amount of ammonia available for absorption and thus to increase the partial pressure of sulphur dioxide in the gas phase.

(2) Over a limited range of the ratio of S:C (0.7-0.9) the pH of an ammonium sulphite-bisulphite solution is given by Johnson (203) as the relationship in Equation 57:

$$pH = -4.62\frac{(S)}{(C)} + 9.2 \qquad \text{... (Eq. 57)}$$

and by Chertkov(204) for the ratio of S:C from 0.5 to 0.95, by the relationship in Equation 58:

$$\mathrm{pH} = 8.88 - 4\frac{(S)}{(C)} \qquad \ldots \text{(Eq.58)}$$

(3) The equilibrium concentrations of ammonium sulphite and ammonium bisulphite in solution are related approximately to the hydrogen-ion concentration (205) as shown in Equation 59:

$$\frac{[HSO_3^-]}{[SO_3^{--}]} \simeq 1.59 \times 10^7 [H^+]. \qquad \ldots \text{(Eq.59)}$$

(4) For the application of ammoniacal solutions to the treatment of flue gases from power stations, although the concentration of carbon dioxide in a flue gas is much greater than the concentration of sulphur dioxide, free-energy calculations indicate that carbon dioxide will not displace sulphur dioxide from the absorption solution (50).

(5) The degree of oxidation of sulphite to sulphate during scrubbing (Equation 52) depends upon a number of variables, which were discussed under the Stone and Webster/Ionics process (see page 25).

Scrubbing Methods

(a) Cominco Absorption Process

Probably the best known ammonia-based process for the removal of sulphur dioxide from waste gases is the Cominco absorption process (10, 199-201, 206). This process was developed by the Consolidated Mining and Smelting Company of Canada, Limited, at Trail, British Columbia, in the nineteen thirties to treat the waste gases from sulphide smelting operations. At Trail, 96% of the sulphur dioxide produced is recovered and the ambient air quality is maintained well within the limits prescribed by the International Joint Commission and the Provincial Government (207).

The Cominco process, which produces sulphuric acid and ammonium sulphate, is shown in schematic form in Figure 5. The hot smelter gases are first cooled with dilute sulphuric acid in a spray tower; a step that also removes dust and sulphur trioxide. The cooled gas then passes to two scrubbing towers where the gas is contacted with a solution containing ammonium sulphite and ammonium bisulphite. The principal reactions occurring during absorption are given in Equations 50-52. Careful control of pH is necessary in the scrubbing steps to ensure maximum removal of sulphur dioxide.

For sulphur dioxide recovery, part of the scrubbing solution is diverted to a stripper where it is acidified with sulphuric acid and stripped with air to give a gas stream containing sulphur dioxide (Equations 60 and 61) which is used as feed for a sulphuric acid plant:

$$2NH_4HSO_3 + H_2SO_4 = 2(NH_4)_2SO_4 + 2SO_2 + 2H_2O \quad \ldots \text{(Eq. 60)}$$

$$(NH_4)_2SO_3 + H_2SO_4 = (NH_4)_2SO_4 + SO_2 + H_2O \quad \ldots \text{(Eq. 61)}$$

The solution leaving the stripper contains ammonium sulphate which is crystallized in a two-stage evaporator, centrifuged and dried.

In the patent literature (208-213) a number of other processes are described that are similar to the Cominco absorption process.

(b) Exorption Processes

An exorption process (200) was operated by Cominco during part of the second world war when ammonia was in short supply. The process is based upon the absorption of sulphur dioxide in an ammonium sulphite solution, followed by thermal decomposition (130°C) of the ammonium bisulphite solution to yield sulphur dioxide and ammonium sulphite for further absorption (Equation 62):

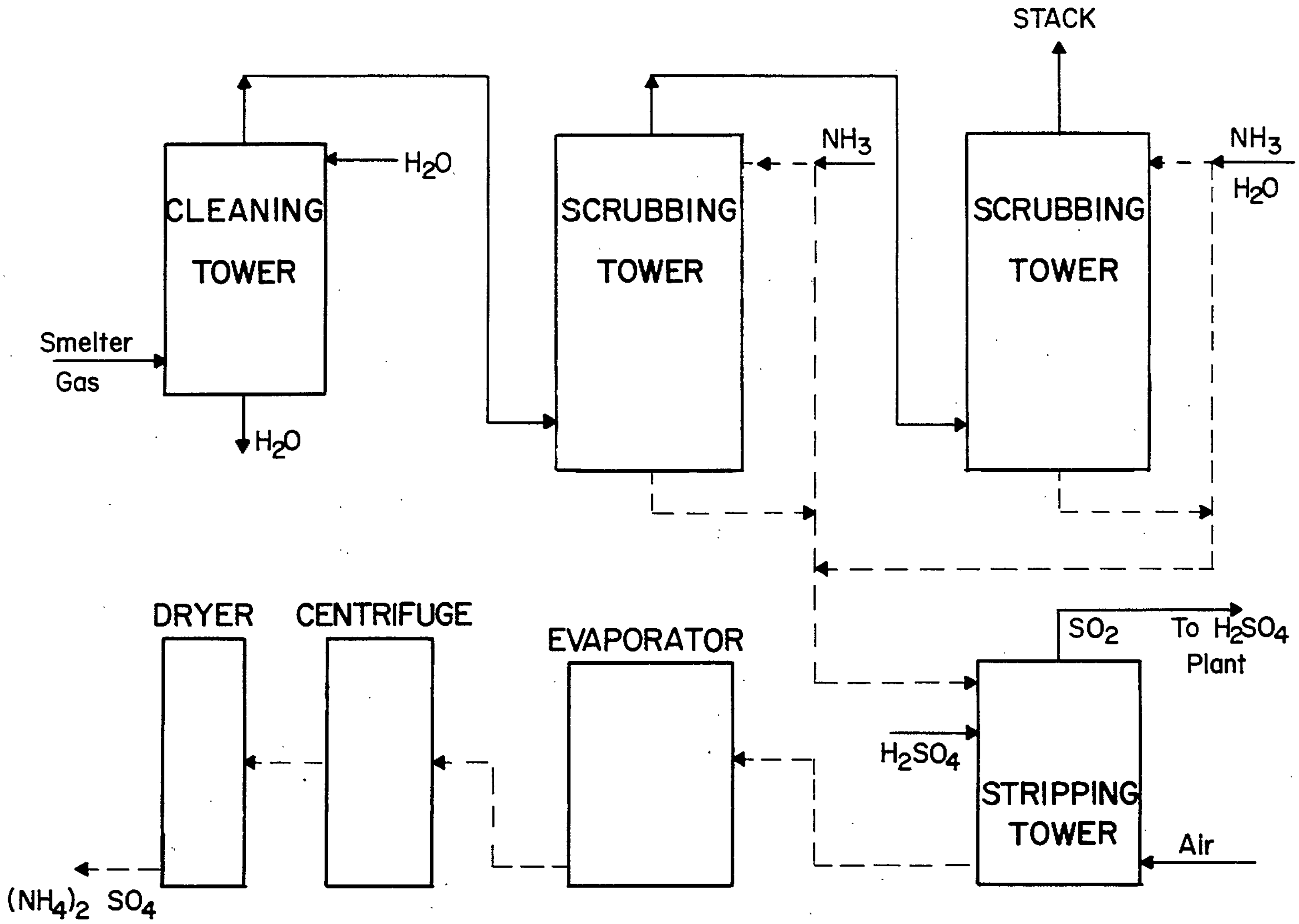

FIGURE 5. THE COMINCO ABSORPTION PROCESS

$$2NH_4HSO_3 \underset{heat}{\overset{absorption}{\rightleftarrows}} (NH_4)_2SO_3 + SO_2 + H_2O \quad \ldots \quad (Eq. 62)$$

When this process is operated in a closed cycle, ammonia theoretically is not consumed, whereas one mole of ammonia is fixed for each mole of sulphur dioxide released in the Cominco absorption process (200). However, in practice, some build-up of ammonium sulphate was found to occur in the absorption solution and a portion of the absorption solution had to be processed for sulphate removal.

The Guggenheim process (214) was developed about thirty years ago and is similar to the Cominco exorption process (Equation 62), except that the recovered sulphur dioxide is reduced to sulphur over heated carbon. Ammonium sulphate formed in the absorbent solution by oxidation of ammonium sulphite was treated with lime to regenerate ammonia for re-use; the by-product calcium sulphate was discarded. After some pilot-plant runs the process was abandoned (75).

(c) The Showa-Denko and Other Ammonia-Injection Processes

The Showa-Denko process (197, 198) was developed in Japan for the removal of sulphur dioxide from the flue gases of thermal power stations. The process (Figure 6) involves injecting ammonia and steam into the flue gas ahead of the scrubber, at a point where the temperature of the gas stream is less than the decomposition temperature of ammonium sulphite and ammonium bisulphite. This injection technique was adopted to reduce corrosion of the scrubber. The gas stream, following ammonia injection, is scrubbed with additional ammonia to convert the ammonium bisulphite formed in the gas-phase reaction to ammonium sulphite (Equation 63):

$$NH_4HSO_3 + NH_3 = (NH_4)_2SO_3 \quad \ldots \quad (Eq. 63)$$

A portion of the circulating scrubbing solution is continuously withdrawn and is filtered to remove fly ash. The ammonium sulphite is then oxidized

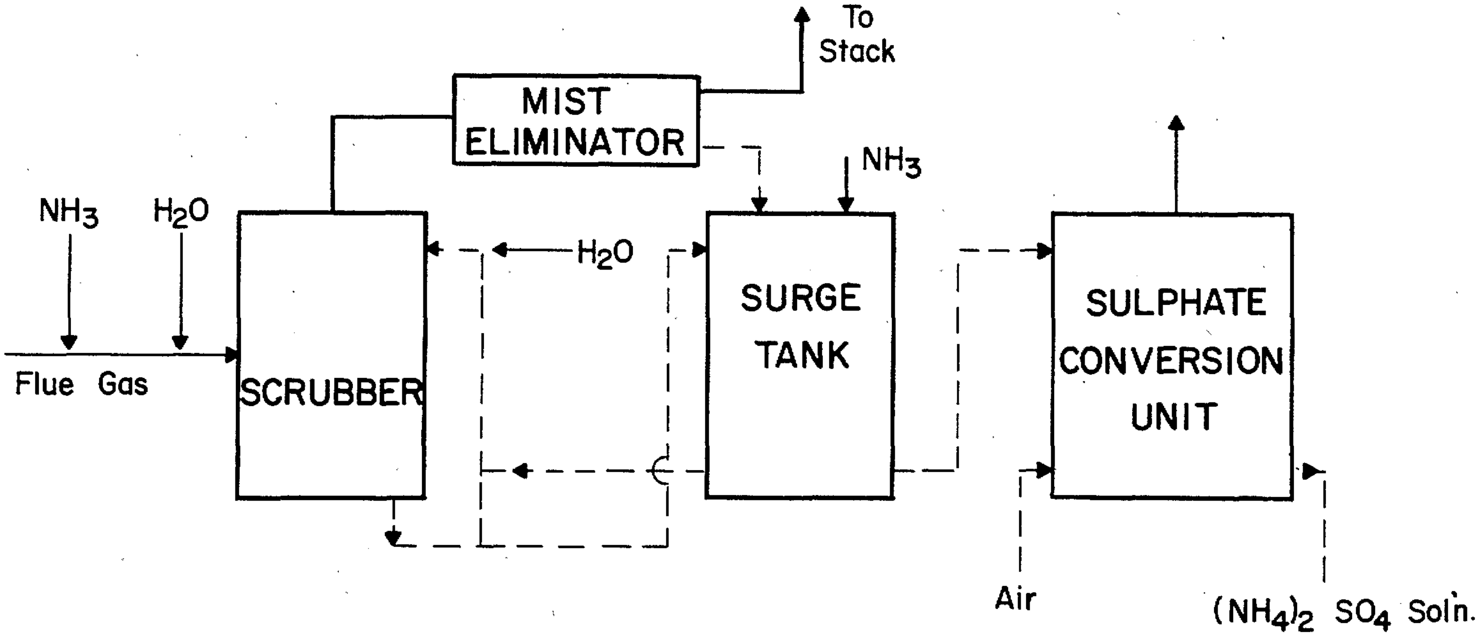

FIGURE 6. THE SHOWA - DENKO PROCESS

with air to form ammonium sulphate which is recovered in an evaporator-crystallizer. Very high efficiences for the removal of sulphur dioxide (>98%) and utilization of ammonia (>99%) are claimed for this process. The ammonium sulphate product is sold as a fertilizer.

Two other processes that are very similar to the Showa-Denko process and involve the injection of ammonia have been described (215, 216). In the Petersen process (216), however, sulphur dioxide is recovered and not ammonium sulphate as in the Showa-Denko process.

A laboratory study (217) of the gas-phase reaction of ammonia with sulphur dioxide in a simulated flue gas employed somewhat different conditions to the ammonia-injection techniques mentioned above. In this study, approximately the stoichiometric amount of ammonia was added to the flue gas at a point where the temperature of the flue gas was above the decomposition temperature of the principal ammonium salts which are formed from various ammonia/sulphur dioxide gas-phase reactions. The approximate decomposition temperature of these salts are $(NH_4)_2SO_3$, 140°F; NH_4HSO_3 and NH_4HSO_4, 300°F; and $(NH_4)_2SO_4$, 455°F. This method of ammonia addition resulted in a well dispersed mixture of reactants that gave essentially quantitative removal of sulphur dioxide when the gas stream was cooled to less than 140°F. About 75% of the nitrogen dioxide in the flue gas was also removed at the same time. The large excess of carbon dioxide in the flue gas had no effect on these reactions. On further cooling of the gas to below its dew point, the ammonium salts were dissolved in the aqueous condensate. The bulk of the condensate was then evaporated, and the ammonium sulphite and ammonium bisulphite in the evaporator residue were decomposed thermally to yield ammonia and sulphur dioxide. The sulphur dioxide was separated from the ammonia by reaction with zinc oxide to form zinc sulphite (145) and the ammonia was returned to the vapour-phase reactor. The zinc sulphite was then decomposed at 430°F to form zinc oxide and sulphur dioxide, the zinc oxide being recirculated and the sulphur dioxide liquified as the product of the removal process.

(d) The Ugine Kuhlman/Weiritam Process

This process was developed in France (218) and is similar to the Showa-Denko process in that ammonia is injected into the flue-gas ahead of an aqueous scrubber (Figure 7). However in the initial, pilot plant tests of this process using the flue gas from an oil-fired furnace, no recovery of sulphur dioxide was made. Instead, a portion of the re-circulating scrubbing solution (containing ammonium sulphite, ammonium bisulphite and ammonium sulphate) was withdrawn and treated with a lime slurry at ~100°C, liberating ammonia for re-cycle and insoluble calcium salts that were separated and discarded. In a later development of the process, a thermal stripping method is said to be available (50) for the recovery of sulphur dioxide that has very low steam requirements.

Removal efficiencies for sulphur dioxide of between 93 and 97% have been obtained with the Ugine Kuhlman/Weiritam process.

(e) The Fulham-Simon-Carves Process

The Fulham-Simon-Carves process (219) was developed in England by the Fulham Power Station and Simon-Carves, Limited, as a method to reduce the emission of sulphur dioxide from thermal-power stations. The initial work was begun in 1938, but was interrupted by the war (220). A further large scale pilot-plant program was undertaken in 1954 in order to study the operating parameters of the process for the treatment of 56,000 cu ft/min of flue gas from a coal-fired boiler (221,222). A schematic drawing of the process is given in Figure 8. The flue gases are first passed through an electrostatic precipitator and are then scrubbed with a re-circulating solution of ammonia. In these development tests by-product ammonia containing hydrogen sulphide was used as the absorbent, and in some of the earlier tests manganous ions were also added to the scrubbing solution to enhance the oxidation of ammonium sulphite to ammonium sulphate (220). The reactions occurring during scrubbing are given in Equations 64 to 67:

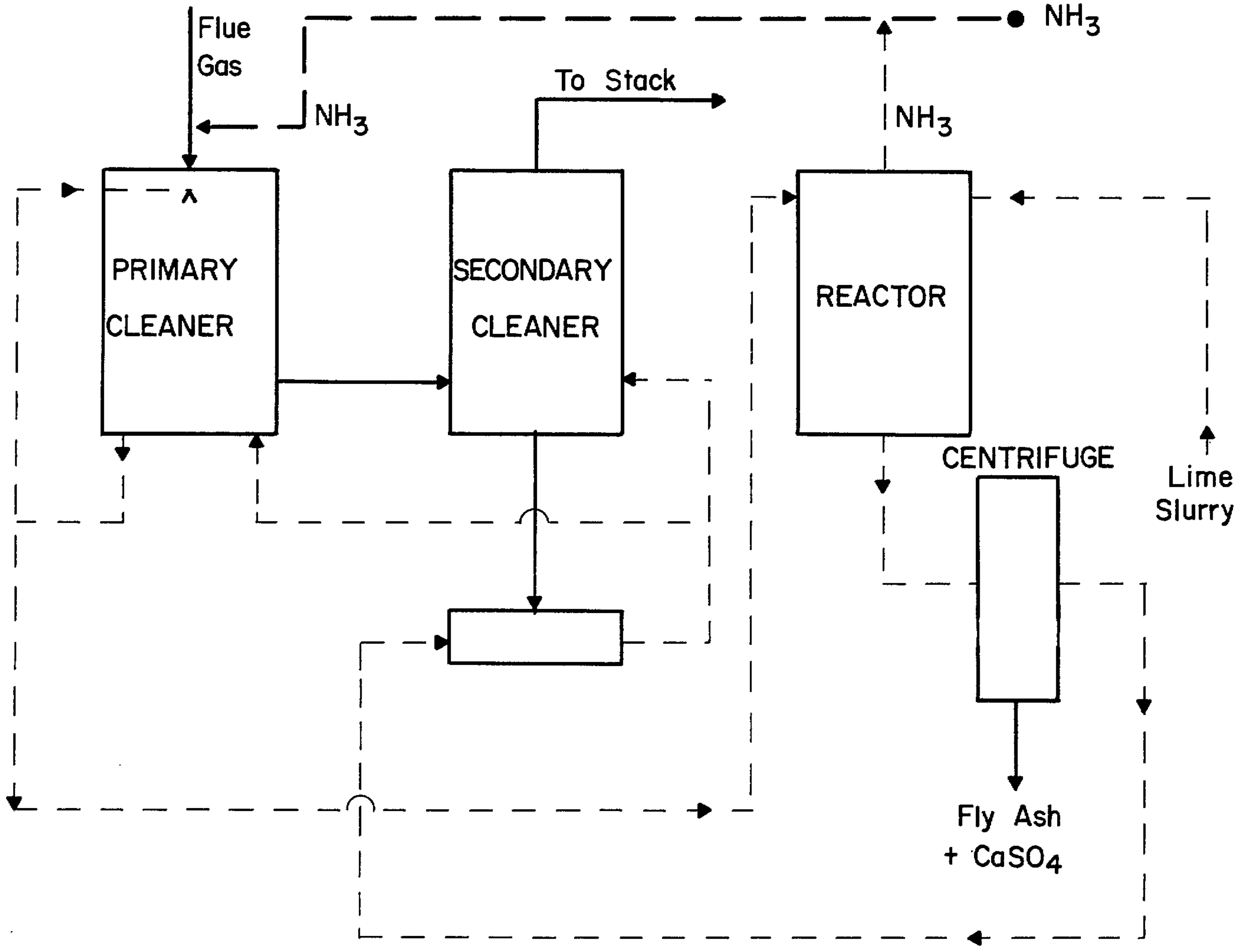

FIGURE 7. THE UGINE KUHLMANN / WEIRITAM PROCESS

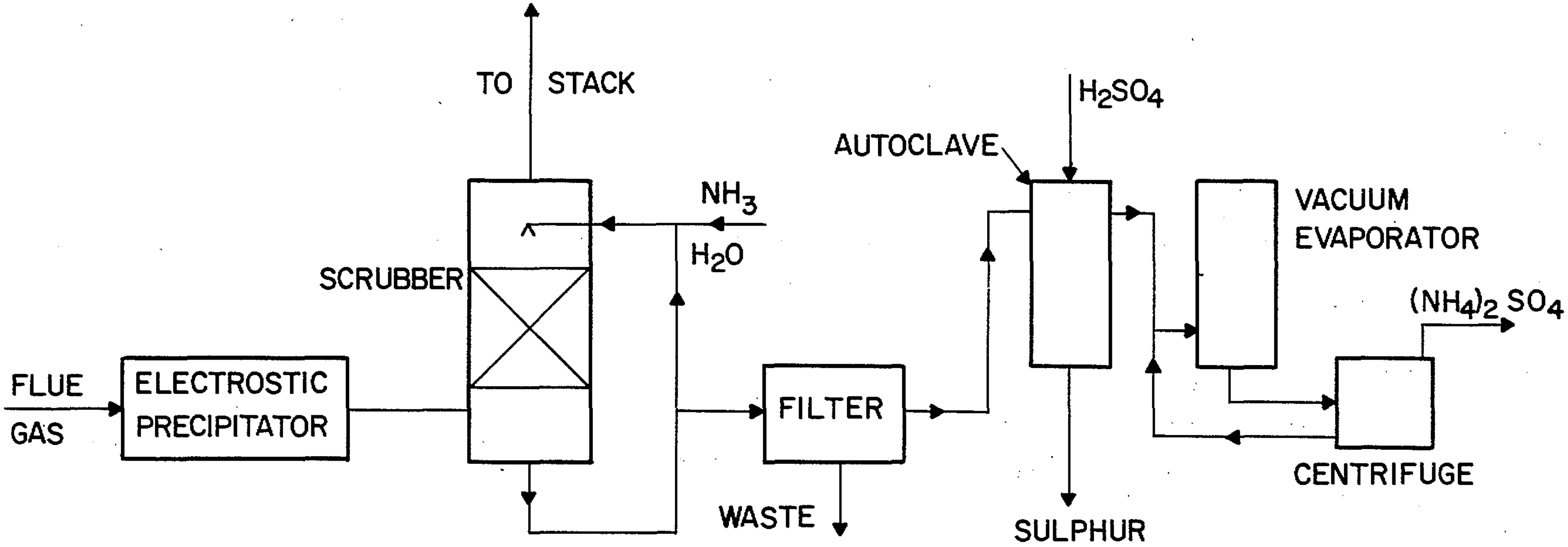

FIGURE 8. THE FULHAM - SIMON - CARVES PROCESS

$$NH_3 + H_2O + SO_2 = NH_4HSO_3 \quad \ldots \text{(Eq. 64)}$$

$$2NH_3 + H_2O + SO_2 = (NH_4)_2SO_3 \quad \ldots \text{(Eq. 65)}$$

$$(NH_4)_2SO_3 + \tfrac{1}{2}O_2 = (NH_4)_2SO_4 \quad \ldots \text{(Eq. 66)}$$

$$2H_2S + NH_4HSO_3 + 2(NH_4)_2SO_3 = 3(NH_4)_2S_2O_3 + 3H_2O \quad \ldots \text{(Eq. 67)}$$

If synthetic ammonia is used as the absorbent the reaction leading to the formation of thiosulphate (Equation 67) does not occur, although it may be noted that thiosulphate acts as a catalyst (50) for the oxidation of sulphite to sulphate (Equation 66). A portion of the re-circulating scrubbing solution is withdrawn, filtered to remove residual fly ash, and then treated in an autoclave with a small amount of sulphuric acid to give sulphur and ammonium sulphate (Equations 68 to 70):

$$3(NH_4)_2SO_3 + H_2SO_4 = 3(NH_4)_2SO_4 + H_2O + S \ldots \text{(Eq. 68)}$$

$$6NH_4HSO_3 = 3(NH_4)_2SO_4 + 2H_2O + 2S + H_2SO_4 \quad \ldots \text{(Eq. 69)}$$

$$3(NH_4)_2S_2O_3 + H_2SO_4 = 3(NH_4)_2SO_4 + H_2O + 4S \ldots \text{(Eq. 70)}$$

This autoclave or "Katasulf" sulphur-recovery process (9, 75, 223) may be conducted either batch-wise or on a continuous basis, and is performed at 150°C - the temperature of the minimum viscosity of sulphur. The ammonium sulphate in the mother liquor of the autoclave is crystallized, dried, and sold as a fertilizer.

These pilot plant studies indicated that the Fulham-Simon-Carves process is capable of achieving very high removal efficiences of sulphur dioxide but the process has not been developed on a production scale.

(f) Other Ammonia-Based Removal Methods

In addition to the ammonia-based processes already considered, the following methods involving ammonia have been suggested for the removal and/or recovery of sulphur dioxide from waste-gas streams.

(1) The catalytic oxidation of sulphur dioxide to sulphuric acid in the gas stream before ammonia injection (224,225), which yields ammonium sulphate and is similar to the Kiyoura process (page 103).

(2) The formation of ammonium sulphate, without the loss of ammonia, by scrubbing waste gases with a solution containing a slight stoichiometric deficiency of ammonia in the presence of an active-carbon catalyst (226).

(3) The decomposition of an ammonium bisulphite solution into ammonia and sulphur dioxide by heating a mixture of the bisulphite solution and an organic base such as triethylamine (227,228) or triethanolamine (229); the ammonia and sulphur dioxide are evolved successively on heating the mixture.

(4) Treatment of an ammonium sulphite-bisulphite solution with phosphoric acid (230) to give sulphur dioxide, and ammonium phosphate for use as a fertilizer.

ADDITIVE INJECTION METHODS

General Considerations

In the last few years considerable effort has been devoted to the study of additive-injection methods for the removal of sulphur dioxide from the flue gases of power stations (196,231-241). In principle, this technique is very simple. It involves the injection of the powdered additive at a point in the flue gas stream where good solid-gas mixing can occur and where the temperature of the flue gas is sufficient to bring about the desired chemical reaction between the additive and sulphur dioxide. The products of this reaction, together with any unreacted additive and fly ash, are removed from the flue gas by electrostatic precipitators before the flue gas is discharged to the atmosphere. From the viewpoint of power-station operation, additive injection is a relatively straightforward technique for the removal of sulphur dioxide because it requires the installation of only a limited amount of conventional equipment such as conveyors and injectors for additive handling and the method also has the advantage of being readily adaptable to existing power plants (235). In contrast to alternative and technologically more complex, chemical-scrubbing techniques for the removal of sulphur dioxide from flue gases, additive injection does not require the addition of chemical processing units to the power plant because the boiler itself acts as a chemical reactor. In a number of wet-scrubbing techniques, it is also necessary to re-heat the flue gas before discharge to the atmosphere. This re-heating step is not necessary in additive-injection methods because the flue gas is discharged from the stack at a sufficiently high temperature to ensure a good plume buoyancy. Chemical recovery of sulphur is not normally performed in additive-injection methods and it is therefore important that the additive should be cheap and readily available. A corollary to discarding the additive after use is that the cost of the additive-injection process can be assessed more accurately than the cost of those sulphur dioxide removal and recovery processes that credit part of the cost of removing sulphur dioxide against the (fluctuating) price of the sulphur or the sulphur-containing compound recovered (54).

Although four additives have been used on a trial basis in power stations (234), viz., limestone, dolomite, nahcolite and "red mud" (see footnote page 34), the most extensive studies of additive-injection methods have been made with limestone and dolomite. Thus, taking limestone as an example, the overall reaction between limestone and sulphur dioxide is generally considered to consist of the calcination of the limestone to give calcium oxide, followed by the reaction of the calcium oxide with sulphur dioxide and oxygen in the flue gas to form calcium sulphate (Equations 71 and 72).

$$CaCO_3 = CaO + CO_2 \qquad \ldots \text{(Eq. 71)}$$

$$CaO + SO_2 + \tfrac{1}{2}O_2 = CaSO_4 \qquad \ldots \text{(Eq. 72)}$$

However, this reaction sequence of carbonate → oxide → sulphate is known from both isothermal (242,243) and non-isothermal (244,245) studies of the $CaCO_3$-CaO-$CaSO_4$ system to provide a much simplified representation of the reactions that occur in limestone injection.

Because of the very high velocity of air in a power station (Table 1) the residence time for the calcination and sulphation reactions is very short (2 to 6 seconds). During this residence time the temperature also varies from 3000°F to 300°F and the cooling rates for the additive may thus be as high as 1350°F/second (246). Obviously a greater residence time could be achieved by mixing the powdered limestone with the fuel, rather than by injection of the limestone after combustion. However, such an additive technique has been found to be unsatisfactory (196,235,247,248) because a serious loss of absorption capacity of the limestone results from the high-temperature calcination in the boiler; an effect known as "dead burning".

Although only limited kinetic data are available on the calcium carbonate-sulphur dioxide reaction under simulated power-station operation (242, 244), equilibrium thermodynamic considerations can be used to provide boundary conditions for the maximum attainable performance that can be expected in the reaction sequence, carbonate → oxide → sulphate. Although the results obtained from such equilibrium studies represent a limiting situation that will not be achieved in actual practice, the thermodynamic data do indicate the optimum temperature conditions for various phases of the reaction and the appropriate temperatures for additive injection. Both dolomite and limestone have been examined from this thermodynamic viewpoint (246). Thus in the calcination reactions for limestone (Equation 71) and dolomite (Equation 73),

$$CaCO_3 \cdot MgCO_3 \quad = \quad CaCO_3MgO + CO_2 \qquad \ldots \text{ (Eq. 73)}$$

the carbon dioxide present in the flue gas will tend to limit the dissociation of the carbonates, and for flue gases containing 14.5% carbon dioxide the calcination temperature must exceed 1400°F for calcium carbonate and 730°F for dolomite. At temperatures lower than these, the oxides will tend to revert to the carbonates in the presence of the flue gas.

The equilibrium constant (K) for the reaction of calcium oxide, or magnesium oxide, with sulphur dioxide in the presence of oxygen (Equation 74) is given by Equation 75,

$$MO + SO_2 + \tfrac{1}{2}O_2 \quad = \quad MSO_4 \qquad \ldots \text{ (Eq. 74)}$$

$$K = \frac{[MSO_4]}{[MO]} \cdot \frac{1}{X_{SO_2}(X_{O_2})^{\frac{1}{2}} P^{3/2}} \qquad \ldots \text{ (Eq. 75)}$$

where M represents Ca or Mg, the terms in square brackets are the activities of the solid reactants, X_{SO_2} and X_{O_2} are the mole fractions of sulphur dioxide and oxygen in the gas phase, and P is the pressure in atmospheres. At one atmosphere pressure and assuming the solids to have unit activities, Equations 75 reduces to Equation 76.

$$X_{SO_2} = \frac{1}{K(X_{O_2})^{\frac{1}{2}}} \qquad \ldots \text{ (Eq. 76)}$$

Table 4 shows the effect of temperature on the equilibrium concentration of sulphur dioxide in contact with calcium oxide or magnesium oxide in a flue gas containing 2.7% oxygen (246). It will be seen from this table that there is only a relatively narrow range of temperature in which these oxides are effective in reducing the sulphur dioxide content of the flue gas, i.e., the temperature range for calcium oxide is from 1770 to 2250°F and for MgO is from 1200 to 1550°F.

TABLE 4

Equilibrium Concentration of SO_2 in Contact with CaO or MgO in a Flue Gas Containing 2.7% Oxygen

CaO		MgO	
Temperature (°F)	SO_2 Concentration (ppm)	Temperature (°F)	SO_2 Concentration (ppm)
1600	0.02	1100	0.05
1700	0.24	1200	1.0
1800	2.0	1300	16.0
1900	13.0	1400	180.0
2000	75.0	1500	1,600.0
2500	65,000.	1600	11,000.0

The lower temperature in these temperature ranges corresponds to an equilibrium concentration of ~ 1 ppm sulphur dioxide, and the upper temperature to an equilibrium concentration of 3000 ppm sulphur dioxide. It may be noted from Equation 76 that the equilibrium partial pressure of sulphur dioxide is inversely dependent on the partial pressure of oxygen. Hence, as the oxygen content of the gas phases decreases, so also does the effectiveness of calcium oxide or magnesium oxide for the removal of sulphur dioxide from the gas phase.

Absorbent Reactivity

It is known from experimental tests that some limestones exhibit greater reactivity than others for the absorption of sulphur dioxide, and limestones from various sources have been examined in an attempt to delineate the factors that are responsible for these differences in reactivity (249-252).

Thus Potter (250) in a study of the absorption efficiency (at 980°C) for sulphur dioxide of eighty-six previously calcined samples of limestones showed that, with the possible exception of iron, differences in the chemical composition of the samples were of only secondary importance in predicting their absorption capacity. This result is somewhat in disagreement with other work (231, 252) where the presence of iron oxide in the limestone was considered to catalyze the calcium oxide/sulphur dioxide reaction, hence it has been suggested that any impurity in the limestone which promotes the oxidation of sulphur dioxide will enhance the absorption capacity of the limestone (252).

The surface areas of calcined samples, as measured by a nitrogen-adsorption method (B.E.T.), are also unrelated to the sulphur dioxide capacity of the limestone (250). However the absorption capacity does appear to be related to the pore size of the calcined samples (250, 251) and those samples which have the largest number of pores above 0.3 μm act as the best absorbents. In general, Potter (250) found no difference in the amount of sulphur dioxide absorbed between samples which had been pre-calcined and samples that were calcined in-situ during sulphur dioxide absorption. Of the eighty-six limestones he tested, chalk and oolitic samples had the best absorption properties. The average utilization of calcium oxide for the eighty-six samples corresponded to only a 45% reaction of the absorbent with sulphur dioxide, suggesting a reaction rate that that was diffusion limited by the surface layer of calcium sulphate on the absorbent. As calcium sulphate has a somewhat larger molar volume than calcium oxide, blocking of the pores of calcined limestone may be expected as the sulphation reaction proceeds.

Half-calcined dolomite ($CaCO_3 . MgO$) has been shown to possess a higher absorbent utilization for sulphur dioxide than calcined limestone (253). Thus at 600°C, a temperature at which calcined limestone has a very low absorption capacity for sulphur dioxide, half-calcined dolomite gave a 50% absorbent utilization for sulphur dioxide and the use of coarse particles of half-calcined dolomite on a panel bed filter has been suggested as a means of removing both sulphur dioxide and fly ash from flue gases (253,254).

In general, limestone calcined at high temperatures (~1300°C) has been found to give a lower B.E.T. surface area, less pores above 0.3 μm in the sample (250), as well as lower absorption capacity for sulphur dioxide (242,250,255,256) than limestones calcined at about 1000°C. The presence of silica in the fly ash of coal-fired power stations may also be anticipated to decrease the absorption capacity of limestone additives (246) because of the slagging reactions shown in Equations 77 and 78.

$$2CaO + SiO_2 = Ca_2SiO_4 \qquad \ldots \text{(Eq. 77)}$$

$$CaO + SiO_2 = CaSiO_3 \qquad \ldots \text{(Eq. 78)}$$

The combustion of coal results not only in the formation of sulphur dioxide but also of small amounts of sulphur trioxide. The amount of sulphur trioxide formed is related to the sulphur content of the coal, with about 6 ppm of sulphur trioxide emitted in the flue gas for each one per cent of sulphur in the coal (257). Because sulphur trioxide reacts much more readily than sulphur dioxide with calcined limestone, virtually all the sulphur trioxide in a flue gas may be removed by the limestone injection process (246). Hence, limestone, in sub-stoichiometric amounts with respect to the sulphur content of the coal, has been injected into boilers to limit the formation of sulphuric acid in the flue gas and thus prevent cold-end corrosion (258). However, the ready removal of sulphur trioxide from flue gases by limestone injection has important consequences with regard to the efficiency of operation of electrostatic precipitators which are very widely used for the removal of particulate matter from flue gases before they are discharged into the atmosphere. At normal flue gas temperatures (240-350°F), trace quantities of sulphur trioxide play a critical role in precipitator operation by fixing moisture on the particle surface, thus providing surface conductivity which is necessary for efficient precipitator operation in this temperature range (12, 237, 257, 259). Hence, a decrease in the removal efficiency of electrostatic precipitators has been observed in studies of the removal of sulphur dioxide from flue gases by dolomite injection (237), and normally a concentration of 15 to 18 ppm of sulphur trioxide in the flue gas is considered desirable for efficient precipitator operation (257). At temperatures above 450°F, the volume conductivity of the particulate matter in the gas stream becomes the controlling factor governing the efficiency of operation of electrostatic precipitators, and studies indicate that when a limestone injection technique is used the precipitator should be operated at about 600°F for the most economical removal of solids (257).

Reaction Mechanism

The mechanism of the reaction between sulphur dioxide and limestone has been studied in a temperature range relevant to power-station operation under both isothermal and non-isothermal conditions (241-245). The results of these studies show that the generally accepted mechanism for the reaction between sulphur dioxide and limestone (Equations 71 and 72) is a considerable simplification of the actual steps involved in the reaction and that the final products of the reaction depend upon both the temperature and the residence times employed in the measurements.

Chan et al. (243) have studied the absorption of sulphur dioxide from a 5% SO_2/95% N_2 gas mixture by limestones and dolomites which were pre-calcined under standard conditions (260). The absorption characteristics of the calcined samples were measured by thermogravimetric analysis from room temperature to 745 °C. Three distinct absorption regions were found; a unimolecular chemisorption region at room temperature, an intermediate region (200 to 450°C) where absorption was due to a temperature-enhanced but diffusion-limited process, and a fast absorption region between 500 and 700°C. In this latter high-temperature region, calcium sulphite, which is the initial product of the reaction between calcium oxide and sulphur dioxide, disproportionates to form calcium sulphate and calcium sulphide (Equation 79):

$$4CaSO_3 = 3CaSO_4 + CaS \qquad \ldots \text{(Eq. 79)}$$

A small amount of elemental sulphur was also formed at high temperatures and Chan et al. suggested that the sulphur was produced from the reactions given in Equations 80 and 81:

$$CaS + 2SO_2 = CaSO_4 + S_2 \qquad \ldots \text{(Eq. 80)}$$

$$4CaSO_3 + 2SO_2 = 4CaSO_4 + S_2 \qquad \ldots \text{(Eq. 81)}$$

The relative amounts of the sulphur-containing species formed was also dependent on the absorption temperature, as may be seen from Table 5.

TABLE 5

Distribution of Sulphur in Compounds Formed at 565°C and 745°C by Reaction Between SO_2 and CaO

Temperature (°C)	S^{--}	SO_3^{--}	SO_4^{--}
565	11%	55%	34%
745	24%	7%	69%

Borgwardt (242) has studied the kinetics of the isothermal absorption of sulphur dioxide on pre-calcined (980°C) limestones from four different sources using a flue gas obtained from burning a sulphur-rich fuel oil as a controlled source of sulphur dioxide. For absorption between 540 and 1100°C, it was found that the activation energy for the absorption reaction depended on the particular limestone and varied from 8.1 to 18.1 kcal/g mole. After about 20% utilization of the calcium oxide, diffusion resistance from the gas phase became the rate-limiting step in the absorption reaction, and the absorption rate decreased rapidly with increasing conversion of the oxide to the sulphate.

In a laboratory study, Coutant et al. (244) have examined the absorption of sulphur dioxide by limestones and dolomites in a dispersed-phase reactor, an experimental arrangement which simulates the non-isothermal conditions found in a boiler environment. By this technique, the influence of particle residence-time, particle size, temperature, sulphur dioxide concentration, and the chemical state of the additive on the absorption of sulphur dioxide was investigated. The following conclusions were reached from this study.

(1) The time taken by the additive particle to reach the ambient gas temperature depends upon the chemical and physical properties of the particle, and this time may represent a significant fraction of the residence time of the particle.

(2) While the particle is still at a relatively low temperature, sulphite formation is the main mode of sulphur dioxide absorption. However, as the temperature of the particle increases, the sulphite either disproportionates (Equation 79) or oxidizes to give the sulphate (Equation 82).

$$CaSO_3 + \tfrac{1}{2}O_2 = CaSO_4 \qquad \ldots \text{(Eq. 82)}$$

When the particle temperature approaches the ambient-gas temperature, which is higher than the sulphite decomposition temperature, the absorption reaction proceeds at a different rate to give the sulphate.

(3) Initially, as the particle size decreases the reactivity of the particle increases but smaller particles (<50 μm) show no dependence of reactivity on size. Except for very low concentrations of sulphur dioxide, the reactivity of the particles is not significantly influenced by changes in the concentration of sulphur dioxide.

(4) The order of reactivity for limestone-based additives was limestone > hydrated limestone > calcined limestone but for dolomites, the reactivity order was somewhat different viz., dihydrate > raw stone > monohydrate > calcined dolomite.

The greater reactivity of the uncalcined additive as compared to the calcined additive is in agreement with other studies (261) where unsuccessful attempts were made to increase the absorption capacity of limestones for sulphur dioxide by pre-calcining the additive before injection into the furnace. It is worth noting that calcined or hydrated additives would have to offer significant improvements over the untreated additive for the absorption of sulphur dioxide, in order to offset the extra costs involved in their preparation before injection (235).

Industrial Applications

The limestone-injection technique has been tested on a semi-industrial scale in Germany (7, 231, 236), Japan (239), and the United States (196, 234, 235, 237) for the removal of sulphur dioxide from the flue gases of power stations. In these tests, finely ground limestone was injected into the furnace in amounts up to twice the stoichiometric requirements for the formation of calcium sulphate. In all these tests the degree of absorbent utilization has been found to be disappointing (12), generally with only a 10 to 15% limestone utilization achieved per stoichiometric equivalent of limestone added. The limestone utilization has also been found to decrease with an increase in particle size and, on a unit weight basis, calcites and aragonites have been found to be better absorbents than dolomites (196). In principle, higher limestone loadings than twice stoichiometric amounts can be used, and tests have shown that such loadings do result in improved efficiences of sulphur dioxide removal (237). However, such large additions of limestones significantly increase the problem of the removal of solids from the flue gas and may also interfere with boiler operation. Thus for coal containing 4% sulphur, the amount of limestone needed for the stoichiometric reaction with the sulphur in the coal is 270 lb of limestone per ton of coal.

In general, although the injection of limestone or of a limestone derivative into a flue gas following combustion has the advantages of simplicity and cheapness, the efficiency of absorbent utilization is insufficient for routine use of the method with sulphur-rich fuels. The main application of limestone-type absorbents would appear to be for either intermittent use under those metereological conditions where local concentrations of sulphur dioxide exceed legislative limits or to maintain the operation of small, essentially out-dated power plants (12).

Nahcolite is the only compound that has been found to give significant removal efficiences (~70%) for sulphur dioxide when added in amounts that were roughly stoichiometric with respect to the sulphur dioxide content of the flue gas (234). The nahcolite was injected into the flue gas just before the electrostatic precipitators of a power plant where the gas temperature is about 300°F. Nahcolite is a naturally occurring form of sodium bicarbonate which is found in large deposits in the Piceance Basin in Colorado (262). The chief problem with the use of nahcolite as an additive for sulphur dioxide removal is in the disposal of the highly soluble sodium salts formed in the sulphation reactions.

A French patent (263) describes the injection of sodium carbonate or sodium hydroxide into the combustion zone of the furnace and the recovery of the original sodium salts from the flue gases by water washing and an ion-exchange process. The injection of an aqueous manganous salt, or manganese dioxide, into the flue gases just before they enter the stack has also been suggested as a removal method for sulphur dioxide (264). This latter process depends upon the catalytic action of manganous salts discussed earlier (page 12). Red mud is another compound which has been tested as an absorbent on a semi-industrial scale but was found to give similar or poorer absorbent loadings than limestone (196, 234).

In an alternative dry-limestone absorption technique (265), flue gas at 700°F was passed through a tower packed with limestone that had been activated with 0.25 wt % cupric chloride. When the sulphur dioxide in the flue gas had reacted with about 60% of the limestone in the absorption tower, the flue gas was diverted to a second absorption tower and the absorbent in the first tower was regenerated by reduction of the calcium sulphate with carbon monoxide. The removal of 95% of the sulphur dioxide from a flue gas which contained 0.37% sulphur dioxide was achieved by this method.

Fluidized-Bed Combustion

In fluidized-bed combustion, relatively coarse particles of coal are pneumatically transported to the combustion zone of the furnace where an upward flow of air, suitably distributed by a grid, maintains a dense suspension of solids in the bed. The temperature in the combustion zone is between 1400 and 1800°F. The controlled addition of limestone or dolomite to the combustor (Figure 9) has been shown to reduce significantly the amount of sulphur dioxide evolved during combustion (266-270). With absorbent additions corresponding to about twice the stoichiometric requirements for the sulphur content of the coal, sulphur dioxide removal efficiences of between 70 and 99% have been achieved(266). This range of removal efficiences as found in various tests, is related to the types of

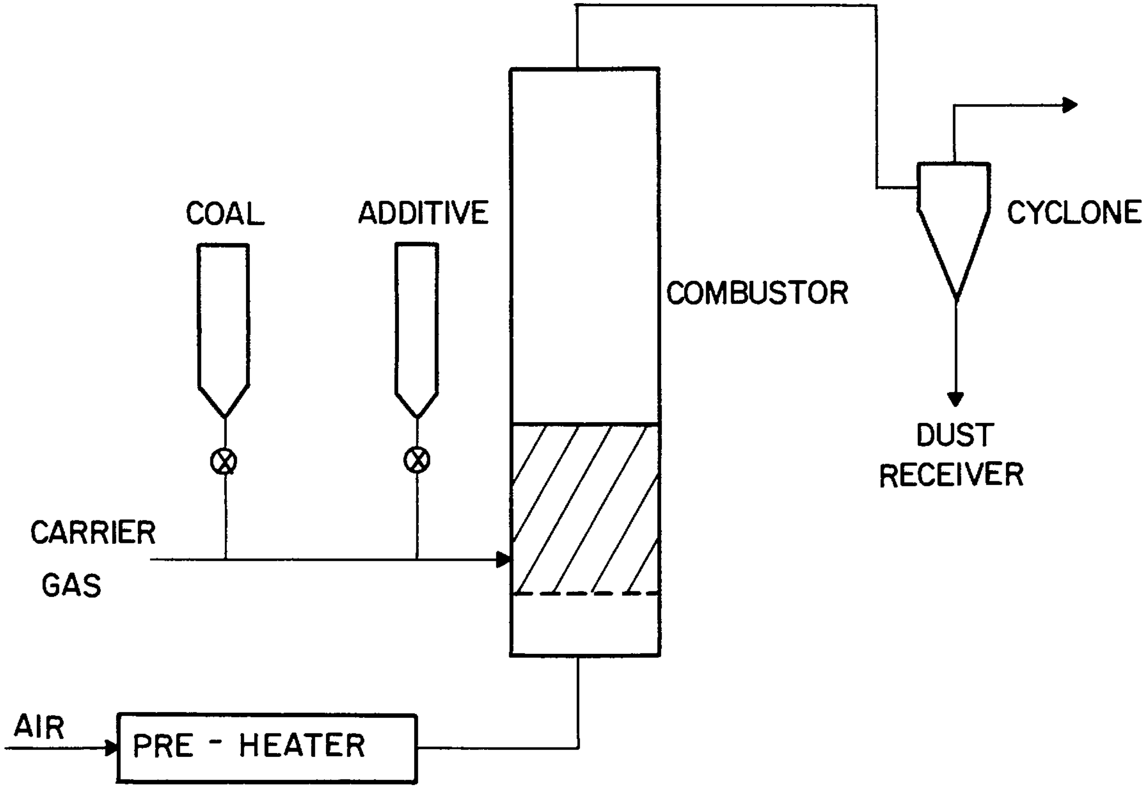

FIGURE 9. SIMPLIFIED SCHEMATIC OF FLUIDIZED BED COMBUSTION UNIT

absorbent and coal used; also, for a given coal and limestone, the removal efficiency is dependent on the type of baffling used in the combustor (267). However in general, for limestone additions of similar stoichiometry to the sulphur content of the coal, the removal efficiency for sulphur dioxide in fluidized-bed combustion is much higher than in the limestone injection-process. These high removal efficiences for sulphur dioxide during fluidized-bed combustion may be attributed to certain special characteristics of the fluidized-bed combustion process, viz., the temperature of the fluidized bed is about optimum for the limestone/ sulphur dioxide reaction, good gas-solid contact is obtained in a fluidized bed, and improved residence times as compared to additive-injection methods are obtained in the fluidized-bed process. Another advantage of fluidized-bed combustion is that much coarser absorbent particles (18 to 26 mesh) can be used than in additive-injection methods which employ minus 200-mesh particles.

During combustion in a fluidized bed, some attrition of the absorbent particles takes place, the attrition being greatest for the least sulphated particles (267). The fines produced by attrition are elutriated by the gas stream and are collected in cyclones with fly ash and fine coal. The used absorbent is about 50% sulphated when it is withdrawn from the combustor and may be discarded in a "once-through" process or, alternatively, the used absorbent may be regenerated (266, 267, 271). Regeneration by the direct thermal decomposition of calcium sulphate is impractical, but may be accomplished by the reduction of the calcium sulphate with carbon monoxide or hydrogen (Equations 83 and 84) at elevated temperatures (52, 53, 272).

$$CaSO_4 + CO = CaO + SO_2 + CO_2 \qquad \ldots \text{(Eq. 83}$$

$$CaSO_4 + H_2 = CaO + SO_2 + H_2O \qquad \ldots \text{(Eq. 84)}$$

Although bench-scale absorption-regeneration studies of the reactivity of a limestone absorbent used in fluidized-bed combustion indicated some loss of absorbent reactivity with re-cycling, the useful life of the absorbent was increased more than four times over that for a once-through process (267). However, the viability of absorbent re-cycling depends upon how the cost of regeneration may be offset by the decrease in the requirements for fresh absorbent and by the sale of the recovered sulphur dioxide.

Limestone Injection - Wet Scrubbing Process

The limestone injection - wet scrubbing process has been developed in the United States (119, 273-277) and is employed for the removal of sulphur dioxide and dust from flue gases. In this process (Figure 10), a slight stoichiometric excess of limestone (or dolomite) is fed into the furnace where it calcines and partly reacts with the combustion gases, removing all of the sulphur trioxide and about 20% of the sulphur dioxide in the flue gas (273). The flue gas from the furnace carries the unreacted additive, the reaction products of the additive and sulphur oxides, and the fly ash to a wet scrubber. In the wet scrubber, the calcined additive (CaO or MgO) dissolves in the aqueous phase and reacts with the sulphur dioxide remaining in the flue gas to form mainly sulphites and sulphates which are either precipitated or dissolved in the scrubbing medium (278). Following the scrubbing stage, the flue gas is de-misted, re-heated, and then discharged to the atmosphere. Particulate matter in the flue gas is also entrained in the scrubber. The waste solids in the scrubbing solution are collected in a settling tank and the clarified solution is re-circulated to the scrubber for further absorption.

The Combustion Engineering, Incorporated version of the limestone injection-wet scrubbing process has been tested at several power stations in the United States and further installations are planned (273, 274). From these tests, it was found that, with a flue gas obtained by burning coal containing 3.4% sulphur, the removal efficiences for sulphur dioxide, particulate matter, and oxides of nitrogen were 85%, 99%, and 30% respectively. Recovery of sulphur is not undertaken in this process, although part of the cost of the sulphur dioxide removal equipment is offset by the replacement of electrostatic precipitators by wet scrubbers.

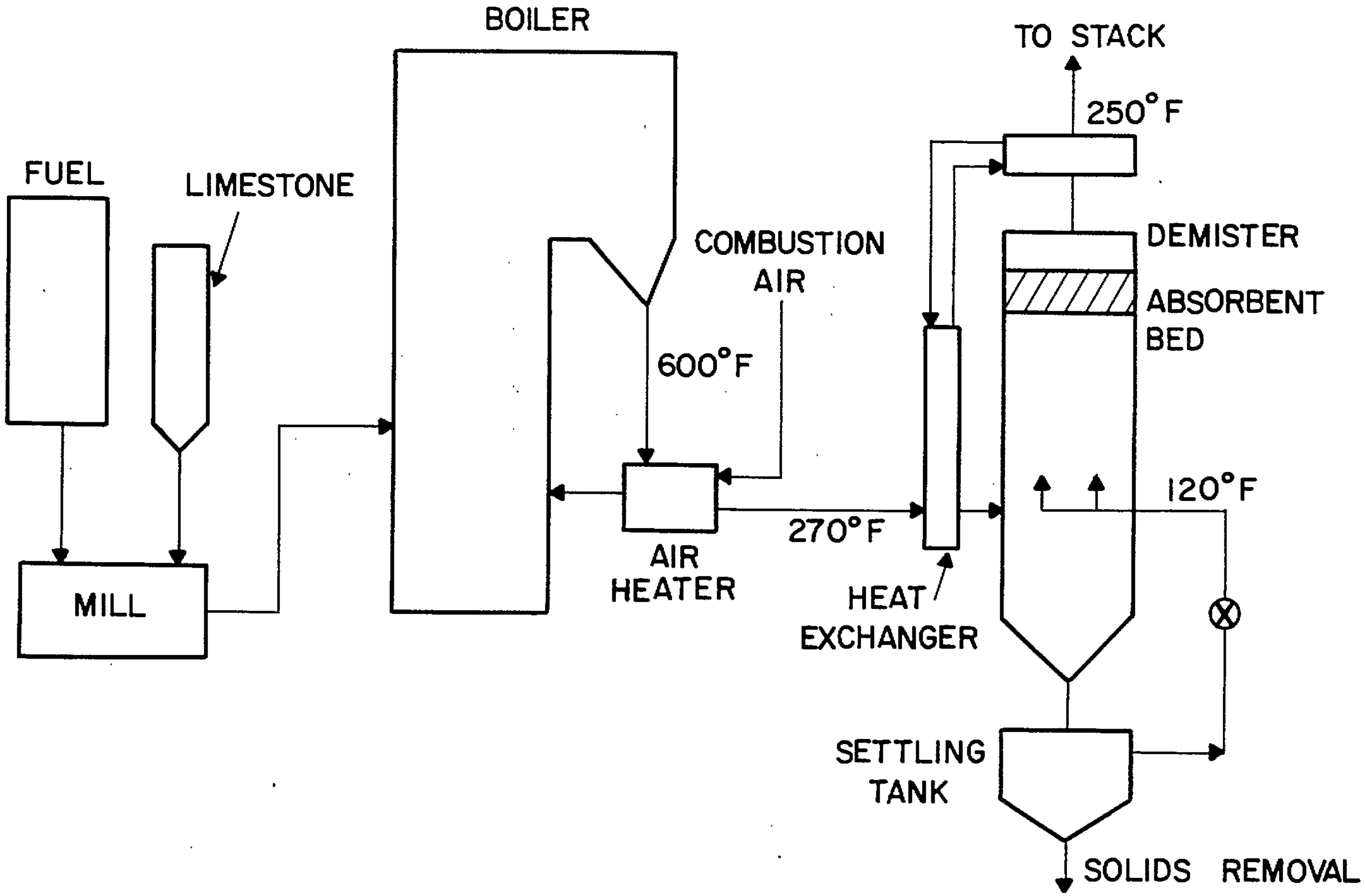

FIGURE 10. THE LIMESTONE INJECTION - WET SCRUBBING PROCESS

From a theoretical study of the wet-scrubbing stage of the limestone injection-wet scrubbing process (279), it appears that the ionic strength of the scrubbing solution could have an important influence on the solubility of the basic species responsible for sulphur dioxide absorption and also that an optimum ionic strength of the scrubbing solution may be desirable. Hence, when a dolomitic, as distinct from a high-calcium limestone is used as an additive, a build-up of highly soluble magnesium sulphate occurs in the scrubbing solution that may adversely influence sulphur dioxide absorption. Such an ionic-strength effect on the absorption of sulphur dioxide during limestone scrubbing has been observed in pilot-plant studies conducted recently by the Tennessee Valley Authority (119), in which it was found that a scrubbing solution of ionic strength between 0.8 and 1.0 had the best absorption capacity for sulphur dioxide. It has also been shown that the rate-limiting step in the scrubbing process using slurries (i.e., in the gas → liquid → solid reaction chain) is the step involving the solid phase (279). In pilot plant studies of limestone scrubbing by the Tennessee Valley Authority, problems were encountered from the build-up of fine platelets of calcium sulphite which did not settle-out of the slurry solution in a satisfactory manner. An oxidizing unit has recently been installed in the slurry circuit to oxidize the calcium sulphite to calcium sulphate; the calcium sulphate is more easily separated from solution for waste disposal (119) than is calcium sulphite.

ADSORPTION ON ACTIVE CARBON

General Considerations

The adsorption of sulphur dioxide on the surface of active carbon forms the basis of several industrial methods for the removal of sulphur dioxide from flue gases. To provide a background to these industrial methods, an account will first be given of laboratory studies on the adsorption of sulphur dioxide on active carbon, and, in particular, of the influence of oxygen and water vapour on the amount of sulphur dioxide that is adsorbed. Thus, a study of the adsorption of sulphur dioxide on carbon black at 0°C (280) showed that the amount of sulphur dioxide adsorbed was strongly dependent on the amount of oxygen on the carbon surface, and that the amount of sulphur dioxide adsorbed decreased considerably following removal of surface carbon-oxygen complexes by heat treatment at 2700°C. Similarly, the differential heat of adsorption of sulphur dioxide on carbon at low surface coverage (280) was less for the heat-treated carbon than for the untreated carbon (6 kcal/mole and 15 kcal/mole respectively). In a series of studies, Davtyan and co-workers (281-283) found that the low temperature (20°C) catalytic oxidation of sulphur dioxide on active carbon gave sulphur trioxide which was fixed on active sites on the carbon surface and did not pass into the gas phase. The presence of water vapour in the gas phase, however, led to the formation of sulphuric acid (Equation 85) and to the freeing of the active sites on the carbon surface for further adsorption.

$$SO_2 + H_2O + \tfrac{1}{2}O_2 \quad = \quad H_2SO_4 \qquad \ldots \text{(Eq. 85)}$$

It was found that the sulphuric acid formed on the carbon surface could be removed by thermal decomposition at 270°C with no change in the subsequent catalytic activity of the carbon (282).

Billinge (284) obtained results similar to those of Davtyan and co-workers in a study of the adsorption of sulphur dioxide, from a simulated flue gas, on lignite coke at 70°C and 100°C. His general conclusions were:

(1) The adsorption of sulphur dioxide on carbon is enhanced by the presence of oxygen and water vapour and adsorption takes place under these conditions to give sulphuric acid.

(2) The adsorption capacity of lignite coke increases to a maximum with successive adsorption/desorption cycles and the increase in adsorption capacity is accompanied by an increase in the surface area of the coke.

(3) The number of active sites available on the carbon surface is proportional to the specific surface area of the carbon.

Stacy et al. (285) found that the amount of sulphur dioxide adsorbed on active carbon was small over the temperature range 50 to 300°C and amounted to less than 1% of the total surface area of the carbon. In this temperature range, the amount of chemi-sorbed sulphur dioxide was not significantly affected by the temperature, but physical adsorption was found to decrease with increasing temperature and to become negligible above 250°C. The carbon could be regenerated by heating at 950°C in a stream of helium.

Laboratory studies have also been made (286) of the possible use of coal (previously heated to 400°F) as a cheaper, alternative adsorbent for sulphur dioxide than active carbon. Although active carbon was found to have a much higher adsorption capacity for sulphur dioxide than coal (forty-eight times), the relative cheapness of coal makes it about twice as attractive economically as an adsorbent. In these measurements, adsorption was performed at 250°F and desorption at 400°F in a stream of helium. The adsorption capacity of the coal was found to remain virtually unchanged after forty adsorption-desorption cycles.

A high-temperature laboratory study (287) of the removal of sulphur dioxide from a simulated flue gas by active carbon has shown that, between 600 and 800°C, the main products of the reaction are hydrogen sulphide, carbonyl sulphide, and a carbon-sulphur complex of high stability. Between 100 and 140°C, the gaseous products of this high-temperature reaction could be reacted with oxygen over an active-carbon catalyst to produce sulphur, which was deposited on the carbon surface.

Industrial Processes Using Active Carbon

(a) Adsorbents

All the industrial processes employing active carbon for the adsorption of sulphur dioxide employ cheap carbon adsorbents that may be prepared from a variety of carbonaceous materials. Thus charcoal, and semi-cokes prepared from coal, lignite, or peat are suitable adsorbents (288-293). The adsorption capacity of carbon is also improved by pretreatment, before carbonization, with iodides (294), soluble salts of copper, nickel, cobalt, iron and manganese (295), alkaline salts (296), or silica (297).

In general, the regeneration of carbon is simpler than the regeneration of chemical absorbents. However, because adsorption is a surface phenomenon, relatively large quantities of carbon are required for the efficient removal of sulphur dioxide from gas streams, the adsorption capacity of carbon for sulphur dioxide being considerably less than that of chemical absorbents.

(b) The Hitachi Process

The Hitachi process is essentially a low-temperature gas-adsorption technique in which sulphur dioxide is removed from flue gases by adsorption on carbon. Preliminary laboratory studies by Hitachi (298) indicated that both oxygen and water vapour were necessary in order to obtain significant adsorption of sulphur dioxide on carbon. The nominal composition of a flue gas from a thermal power station is: water, 10-13%, carbon dioxide, 10-13%; sulphur dioxide, 0.1-0.3%; the balance being mainly nitrogen. As would be expected from the laboratory studies, adsorption of sulphur dioxide on carbon occurs readily from a flue gas at 150°C, and sulphuric acid forms on the carbon surface. Following adsorption, the carbon may be regenerated by washing with water or with dilute sulphuric acid. The rate of desorption of the adsorbed sulphuric acid depends on the raw material used for the preparation of the carbon and can be increased by preliminary activation of the carbon with steam at 800°C; the effect of steam treatment is to enlarge the pores in the carbon structure (299).

Two pilot plant runs have been made using the Hitachi process for the treatment of the flue gases from heavy-oil-fired boilers and the process is now being installed in Japan to treat the flue gases from a 100-MW boiler (12). The process uses three adsorption towers, each containing active carbon (298,300,301). The flow of the flue gas to the towers is controlled by dampers at the inlet and outlet of each tower (Figure 11) so that, while two towers are being used for adsorption, the third may be regenerated by washing. Several washing tanks are used, the wash water being re-cycled. As may be seen from Figure 11, part of the flue gas enters the drying tower, the remainder going to the adsorption tower. The gas from the drying tower, which has a decreased sulphur dioxide content, also enters the adsorption tower where the majority of the remaining sulphur dioxide in the gas is removed. When the adsorption capacity of the adsorption tower has been reached, the gas is switched to the other two towers.

The standard operating conditions used in one of the pilot plant runs with the Hitachi process (298) is given in Table 6.

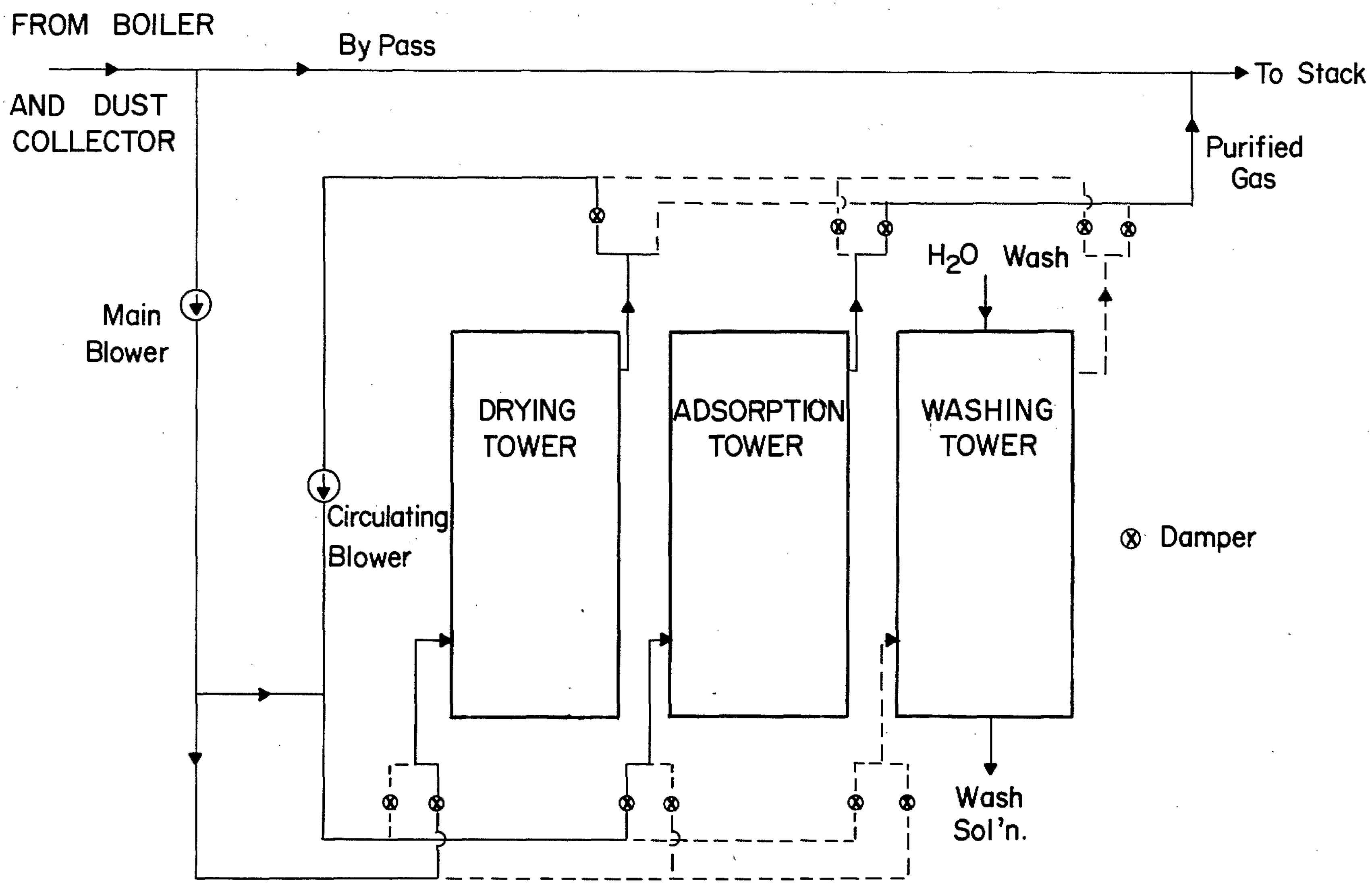

FIGURE II. THE HITACHI ACTIVE CARBON PROCESS
(Water Wash Circuit Not Shown)

TABLE 6

Operating Conditions for Hitachi Adsorption Process

Item	Test Condition
Volume of treated gas	6,000 Nm^3/hr *
Dried gas temperature	130°C
Adsorbed gas temperature	100°C
Cycle time	60 hr
Drying time	20 hr
Adsorption time	30 hr
Washing time	10 hr

It was found in the pilot plant runs that the efficiency of removal of sulphur dioxide decreased somewhat with increase in the number of operating cycles of the adsorbent but that the removal efficiency became effectively constant after about 1500 hours of operation. Overall desulphurization efficiencies in excess of 90% were achieved.

The following advantages are claimed for the Hitachi process.

(1) A high desulphurization capacity.

(2) Easy desorption of sulphuric acid from the carbon adsorbent by small amounts of water.

(3) Carbon regeneration does not require a high temperature.

(4) Safe operation because the ignition point of the carbon is ~400°C, a temperature which is much higher than the temperature of the adsorption/desorption cycle.

(5) Flue gas temperatures, following sulphur dioxide adsorption, are greater than 100°C, implying good plume buoyancy.

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*Nm^3 throughout this report means normal cubic metre (at 0°C and a pressure of 760 mm Hg).

(6) No modifications are necessary to the existing boiler structure of the power plant.

(7) The dilute sulphuric acid (20%) produced during the regeneration of the adsorbent may be concentrated and used in a variety of industrial processes, e.g., fertilizer manufacture.

(c) The Reinluft Process

This process has been developed in Germany (302-305) and is based upon the same principle as the Hitachi process, viz., that the low-temperature adsorption of sulphur dioxide on active carbon is greatly enhanced by the presence of oxygen and water vapour -- both of which are constituents of flue gases. The significant difference between the Reinluft and Hitachi processes is in the method of adsorbent regeneration; the Reinluft process depends upon the reduction of the adsorbed sulphuric acid by the active carbon adsorbent as shown in Equation 86,

$$2H_2SO_4 + C \xrightarrow{750°F} 2H_2O + 2SO_2 + CO_2 \quad . (Eq. 86)$$

while in the Hitachi process dilute sulphuric acid is recovered from the adsorbent by washing with water.

The Reinluft process has been operated on a trial basis at a number of industrial power plants in Germany over the last decade. Various modifications have been made to the process as a result of the operating experience gained in these trials, including a lowering of the gas temperature to overcome carbon ignition problems in the adsorber tower (306). A diagram of a Chemiebau design for a current Reinluft plant (304) is given in Figure 12. There are two sections to the plant; an adsorption unit in which sulphur dioxide is stripped from the flue gas, and a desorber unit in which the active carbon is regenerated and sulphur dioxide recovered. The carbon adsorbent is transferred between the two sections by a conveyor system. Fresh carbon is added to the adsorbent circulation system to replace the carbon that is consumed by the regeneration reaction (Equation 86). The

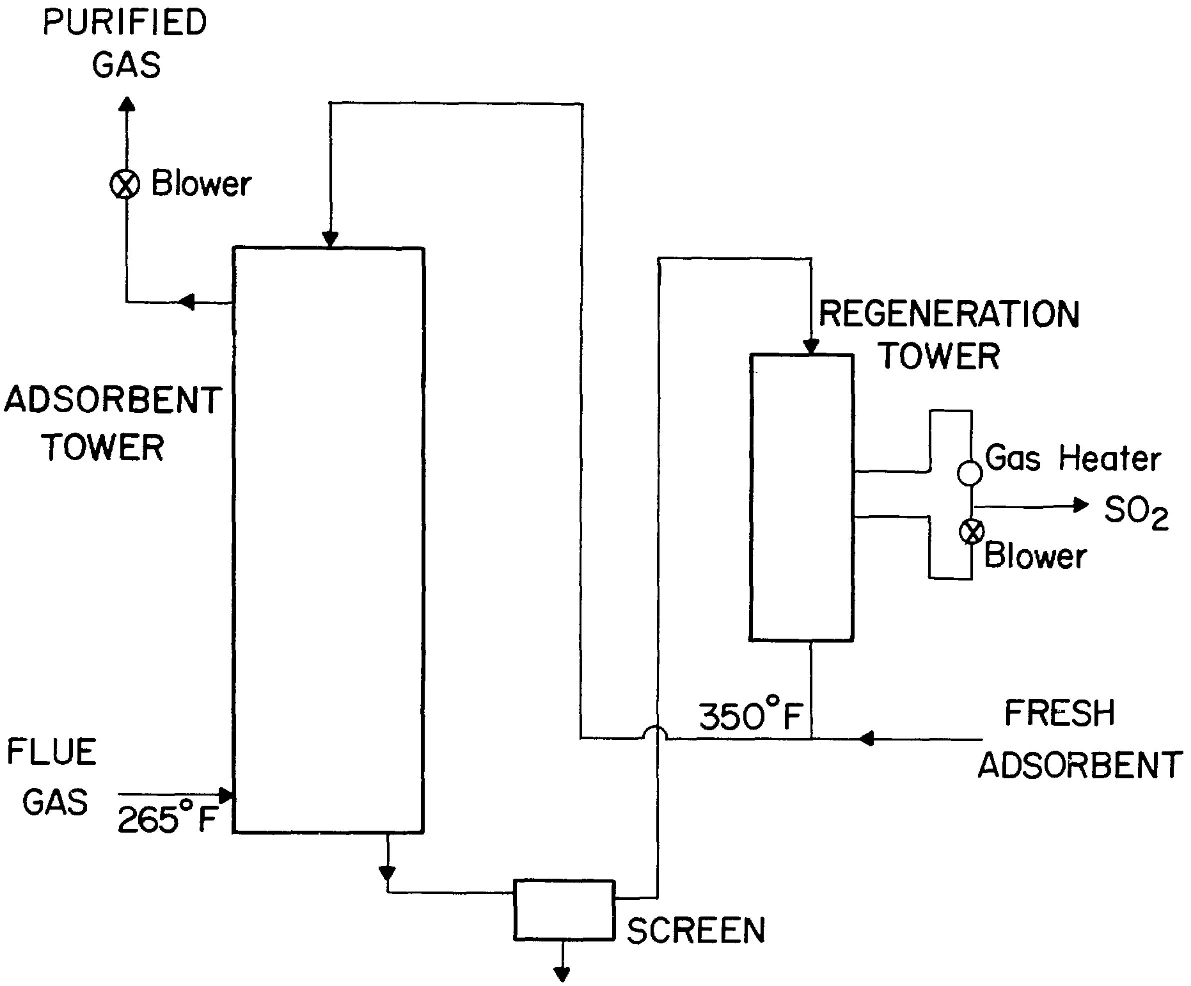

FIGURE 12. CHEMIEBAU DESIGN OF THE REINLUFT PROCESS

adsorption capacity of the active-carbon adsorbent has been found to increase following regeneration as a result of an increase in the surface area and the pore volume of the carbon. The gas from the regeneration step contains about 40% sulphur dioxide.

The advantages claimed for the Reinluft process include a good efficiency for sulphur dioxide removal (70 to 85%), simultaneous removal of fly ash, a high-temperature stack-gas, and a readily available, cheap adsorbent.

(d) The Sulfacid Process

This carbon-adsorption process has been developed by the Lurgi Apparatebau Company in Germany (7, 13, 306). and, like the Hitachi process, produces dilute sulphuric acid as a by-product. The method is recommended for gas streams containing between 0.1 and 1.5% sulphur dioxide. For gas streams of higher sulphur dioxide content, dilution of the gas stream with air is required making the process unsuitable for sulphur dioxide-rich smelter gases (307).

In the Sulfacid process (Figure 13) the flue gas is first cooled to between 60 and 70°C with dilute sulphuric acid in an absorption column. The cooled and washed gas then passes downwards through a stationary bed of a porous, carbonaceous catalyst. Without interrupting the gas flow, water is sprayed intermittently into the catalyst bed to remove the dilute sulphuric acid formed in the pores of the carbon adsorbent. It is this dilute (10 to 15%) sulphuric acid that is used to cool the incoming flue gas. When the dust concentration in the flue gas exceeds 100 to 150 mg/Nm^3, it is recommended that a Venturi washer should be used to clean and cool the flue gas. The sulphuric acid produced using a Venturi washer has a concentration between 25 and 30%.

The cleaned flue gas is saturated with water vapour at about 60°C and requires re-heating before being discharged into the atmosphere.

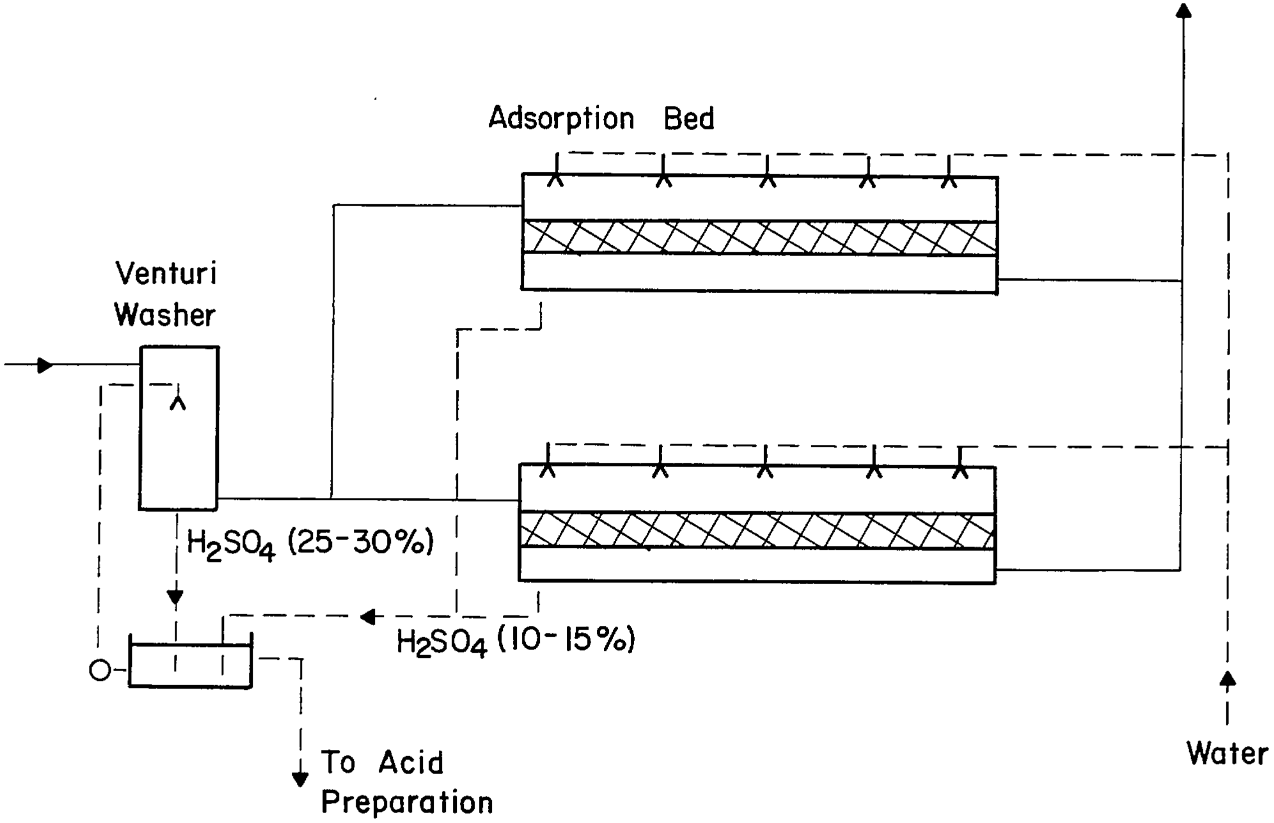

FIGURE 13. THE LURGI SULFACID PROCESS

(e) The Westvaco Process

The Westvaco process has been described recently in the patent literature (308,309). As with the other processes described above, an active-carbon adsorbent is used to catalyse the formation of sulphuric acid from the sulphur dioxide, oxygen, and water vapour present in flue gases (Equation 85). Following sulphur dioxide adsorption, the spent adsorbent is transferred to a regenerator stage (Figure 14) where the adsorbed sulphuric acid is reduced by hydrogen sulphide to form sulphur dioxide and/or sulphur (Equations 87 and 88).

$$H_2SO_4 + H_2S = SO_2 + S + 2H_2O \qquad \ldots \text{(Eq. 87)}$$

$$H_2SO_4 + 3H_2S = 4S + 4H_2O \qquad \ldots \text{(Eq. 88)}$$

The relative amounts of sulphur dioxide and sulphur formed during regeneration are a function of the temperature which may be varied between ambient temperatures and 570°F. The reaction in Equation 87 is favoured at temperatures above 250°F.

The adsorbent, following hydrogen sulphide regeneration, is transferred to a second reducing stage to remove adsorbed sulphur. A variety of reducing agents may be used for this purpose but hydrogen is preferred. Between 800-1300°F, hydrogen sulphide is formed by the reaction of the adsorbed sulphur with hydrogen (Equation 89).

$$S + H_2 = H_2S \qquad \ldots \text{(Eq. 89)}$$

Some of the recovered hydrogen sulphide is then used for the initial reduction of the adsorbed sulphuric acid (Equations 87 and 88). The remainder of the hydrogen sulphide may be reacted with sulphur dioxide from the initial reduction stage (Equation 87) to produce sulphur by the Claus reaction.

The advantages of the Westvaco process are that very little carbon is lost during the process, elemental sulphur is recovered as a product, and the process operates at flue gas temperatures (200 to 450°F).

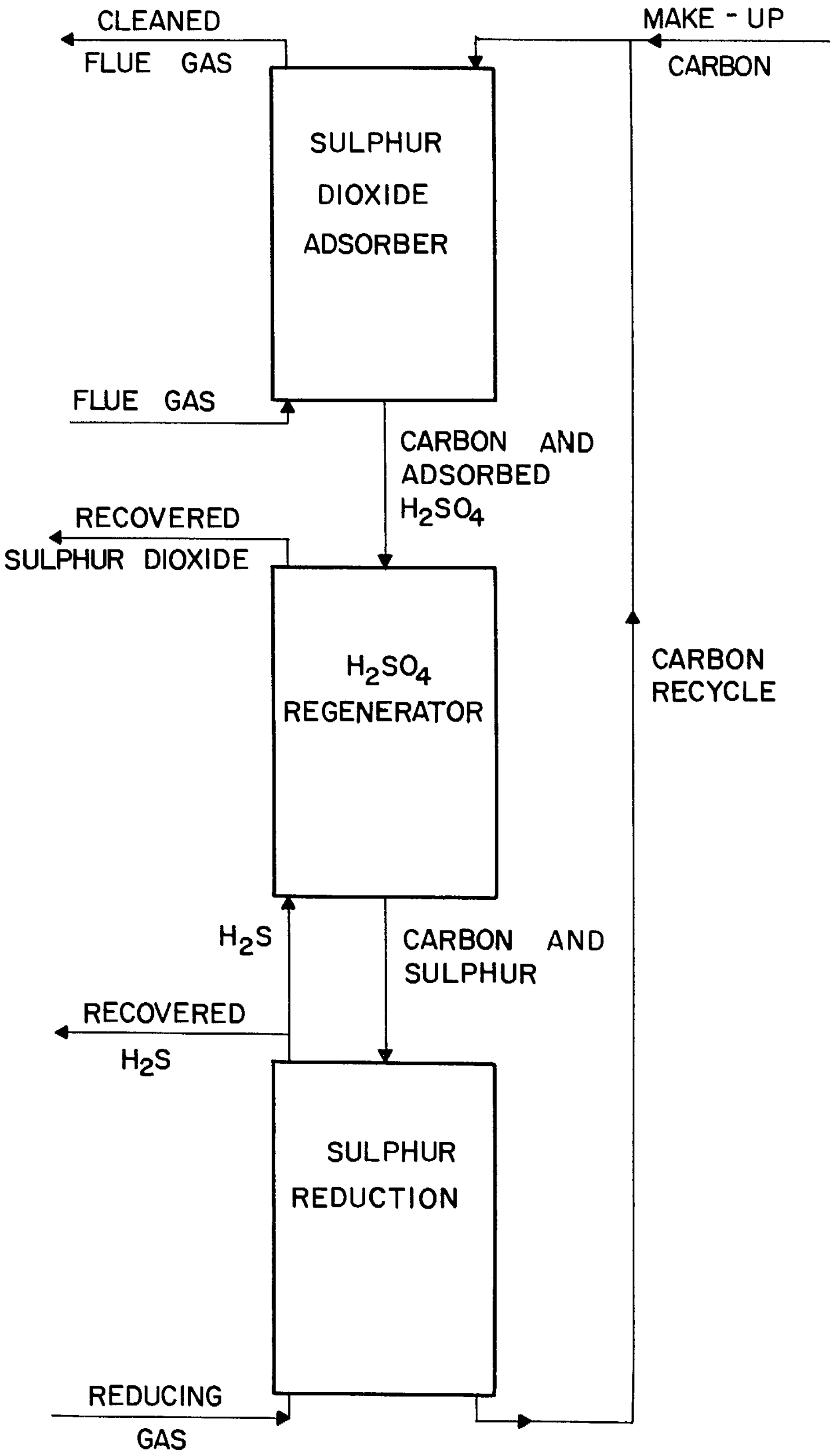

FIGURE 14. THE WESTVACO PROCESS

ABSORPTION ON METAL OXIDES

General Considerations

The application of dry-oxide absorbents to the removal of sulphur dioxide from gas streams has been extensively investigated. Particular emphasis has been given in these investigations to the use of dry oxides for the removal of sulphur dioxide at low concentrations, such as occur in the flue gases from thermal power stations. For power-station applications, one advantage of a dry-absorption technique is the ability to operate the absorbent at flue-gas temperatures and thus assure a high-temperature plume at the stack. In most wet-scrubbing processes on the other hand, it is necessary to re-heat the cleaned gas before discharge from the stack in order to obtain good plume buoyancy. A high loading capacity for sulphur dioxide is also often achieved with dry-oxide absorbents. The main disadvantages that are associated with dry-oxide absorbents are:

(1) the regeneration of the spent absorbent for re-cycling may involve transferring the absorbent to a separate regeneration system that is operated at a higher temperature than the absorption stage of the process;

(2) the physical loss of the absorbent by attrition during all phases of the sulphur dioxide removal and recovery process;

(3) the loss of the absorption capacity of the absorbent following multiple absorption-regeneration cycles.

If the absorbent is a readily available, cheap material, disposal of the spent absorbent as a non-marketable waste product may be considered. However, the disposal of very large tonnages of spent absorbent can present significant problems, particularly in an urban area.

A detailed study has been made by the Tracor Corporation (Austin, Texas) of the potential application of the oxides of forty-eight metals to the absorption of sulphur dioxide from flue gases (310,311). Based upon either published or estimated thermodynamic data, an initial screening of the oxides was made to determine which of the oxides had the equilibrium-thermodynamic capability of reducing the sulphur dioxide concentration in the flue gas to a prescribed level, and also which of the oxides gave a sulphur dioxide absorption-product that could be thermally regenerated to yield the original oxide for further absorption. The thermodynamic criteria adopted for this study were that the logarithm of the equilibrium constant, K, for the absorption step should be less than -3.8 at the absorption temperature (corresponding to an equilibrium concentration of 150 ppm of sulphur dioxide), and that log K for the thermal desorption step should be greater than -2.0 at the desorption temperature. The oxide had to meet both of these criteria in order to be considered potentially useful as an absorbent for sulphur dioxide. Oxide regeneration methods other than thermal treatment were not considered. Figure 15 illustrates the difference, based upon these criteria, between two good absorbents (CuO and SnO) and a poor absorbent (BaO) for sulphur dioxide. The horizontal dashed lines in Figure 15 are the values of log K specified above. Absorbents prepared from mixed-metal oxides may also have good absorption-desorption characteristics for sulphur dioxide but they were not considered in the Tracor study because of the lack of relevant thermodynamic data and the large number of compositional variations possible with mixed-metal oxides.

This thermodynamic screening procedure reduced the number of potential absorbents to the oxides of sixteen metals, viz., Ce_2O_3, CeO, TiO_2, ZrO_2, V_2O_5, Cr_2O_3, FeO, Fe_2O_3, CoO, ZnO, NiO, Al_2O_3, SnO_2, HfO_2, Bi_2O_3, VO_2,and ThO_2. Samples of these oxides were then prepared in a kinetically active form, and the rate of reaction of the oxide with sulphur dioxide in a simulated flue gas was determined experimentally using

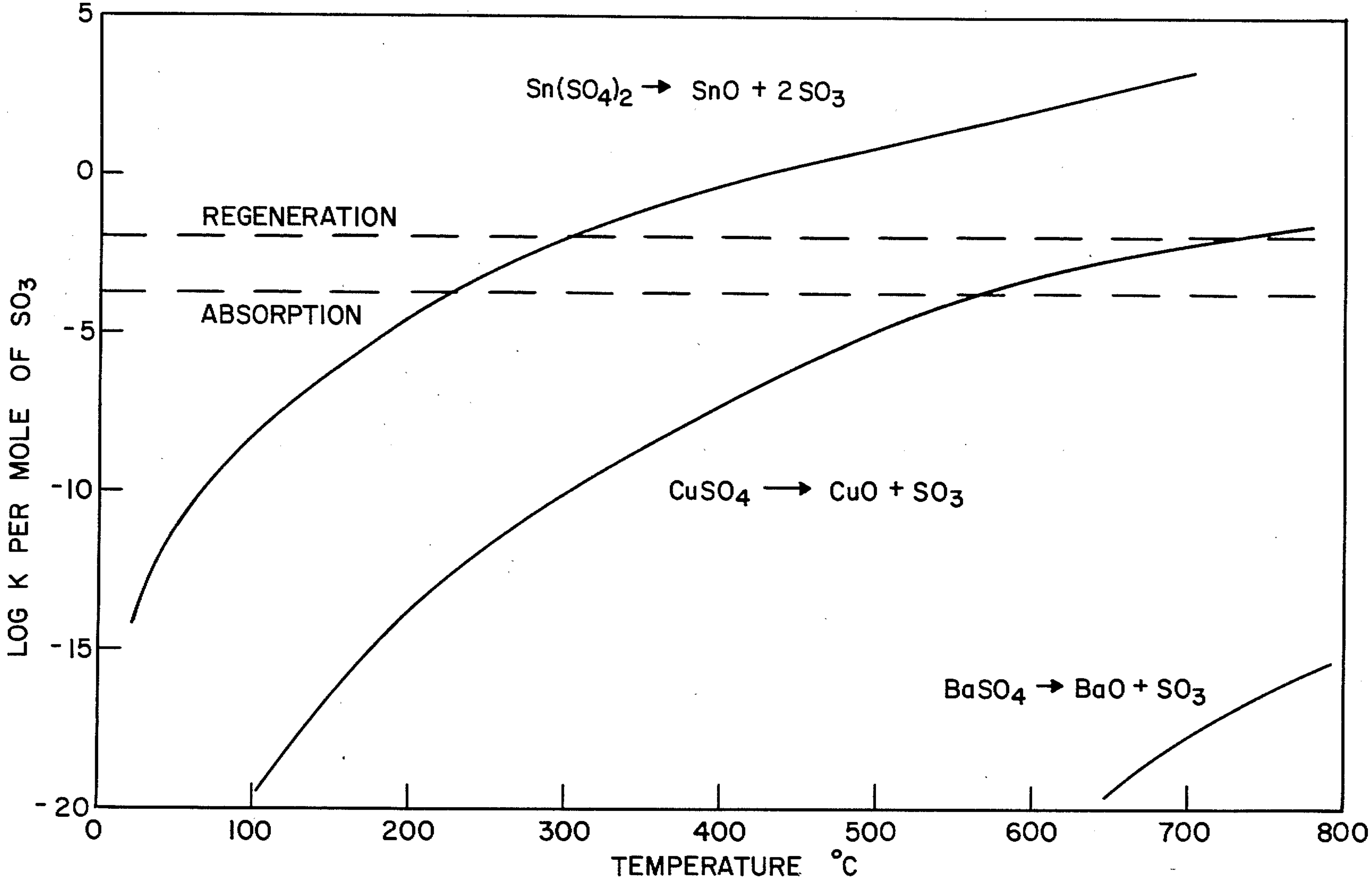

FIGURE 15. VALUES OF LOG K FOR THE DECOMPOSITION REACTIONS FOR TIN, COPPER, AND BARIUM SULPHATES

an isothermal gravimetric technique. By this method it was possible to reduce the number of potentially useful absorbents to the following oxides: Cr_2O_3, CuO, Fe_2O_3, and Co_3O_4. From considerations based upon cost, reaction stoichiometry, and other factors, CuO and Fe_2O_3 were recommended as being the most suitable of these remaining four oxides for further study.

A critical review has been made (312) of the thermodynamic-screening methods and of the recommendations of the Tracor study. This review criticizes some of the estimated thermodynamic data and the neglect of the possible formation of metal carbonates from carbon dioxide in the flue gas; nevertheless, the review concluded that the overall approach adopted in the Tracor study is valid and basically sound.

The conslusions reached in the Tracor study are similar to those reached by Bienstock et al. (313) in an earlier experimental study of the absorption of sulphur dioxide on a number of oxides. These authors recommended that alkalized alumina and the oxides of manganese, cobalt, and copper, merited further investigation as absorbents for sulphur dioxide.

Results of a further experimental study of the sulphur dioxide/ absorption-regeneration characteristics of seventeen metal-oxides are given in a report (314) by the Avco Corporation (Lowell, Massachusetts). The oxides were mainly prepared by calcining the co-precipitated hydro-oxides of the metal to be investigated (Cu, Co, Cr, Fe, Mn, Na, Ni, Zn, K or Li) and a supporting element -- usually aluminum. The absorption characteristics of the active oxides for sulphur dioxide were measured at 300°C, 450°C and 550°C. All the absorbents could be regenerated thermally at 650°C. Of the oxides examined, cupric oxide was found to have the best overall absorption-regeneration characteristics, and further study of the oxides of manganese and iron was recommended. Cupric oxide had the additional advantage that it could be regenerated with hydrogen at 450°C, suggesting the possibility of an absorption-regeneration cycle at the same temperature.

A number of individual, dry-oxide absorption processes that have received attention will now be considered.

Oxide Absorption Processes

(a) The Alkalized Alumina Process

The absorption of sulphur dioxide from flue gases by alkalized alumina ($NaAlO_2$) has been the subject of detailed studies since about 1960, particularly by the United States Bureau of Mines (313, 315-329). The results of initial laboratory tests showed that alkalized alumina was an effective absorbent for sulphur dioxide at elevated temperatures (130 to 350°C), had a relatively high capacity for sulphur dioxide (15 to 20 g SO_2/100 g absorbent), could be regenerated in cyclic operations without loss of absorption capacity, and regeneration of the absorbent produced hydrogen sulphide that could be converted into sulphur by the Claus method. In the light of these promising results, a study of the use of alkalized alumina for the removal of sulphur dioxide from the stack gases of thermal power stations has been undertaken recently by the Central Electricity Research Laboratories in England (11, 330).

The reactions that take place on the absorption of sulphur dioxide by alkalized alumina (Equations 90 and 91),

$$2NaAlO_2 + SO_2 = Na_2SO_3 + Al_2O_3 \quad (T<230°C) \quad \ldots \text{(Eq. 90)}$$

$$2NaAlO_2 + SO_2 + \tfrac{1}{2}O_2 = Na_2SO_4 + Al_2O_3 \quad (T>230°C) \quad \ldots \text{(Eq. 91)}$$

depend both on the temperature and the presence of oxides of nitrogen in the gas phase. Thus the reaction in Equation 91 occurs at all temperatures in the presence of oxides of nitrogen which act as a catalyst for this reaction. The spent absorbent is regenerated by reduction with hydrogen (Equations 92 and 93),

$$Na_2SO_3 + Al_2O_3 + 3H_2 = 2NaAlO_2 + 2H_2O + H_2S \quad \ldots \text{(Eq. 92)}$$

$$Na_2SO_4 + Al_2O_3 + 4H_2 \quad = \quad 2NaAlO_2 + 3H_2O + H_2S \qquad \ldots \text{ (Eq. 93)}$$

and following regeneration, the absorbent is in its active form and suitable for re-cycling. The hydrogen sulphide produced during regeneration is of a suitable concentration for the direct production of sulphur by the Claus method.

Alkalized alumina may be prepared by a number of methods (316, 320, 324,331,332). In the Bienstock process (316), a basic sodium aluminum carbonate is first precipitated by the addition of sodium carbonate to a solution of aluminum sulphate. The precipitate is dried at about 130°C, crushed, and then activated by heat treatment at 600 to 700°C, in an atmosphere of hydrogen, nitrogen, or air, to give a non-stoichiometric compound of approximate composition $NaAlO_2$. The basic sodium aluminum carbonate may also be mixed with other metal salts before drying (324). For high rates of sulphur dioxide absorption and high sulphur loading, the alkalized alumina should contain over 30% Na_2O (320).

Detailed laboratory studies have been made both of the absorption of sulphur dioxide on alkalized alumina in fixed-bed (313), free-falling (318, 321) and fluidized-bed reactors (322,323,325), and of the subsequent regeneration of the spent absorbent (323,325,326).

Several conclusions were reached from these studies.

(1) The amount of sulphur dioxide absorbed on alkalized alumina is strongly dependent on the initial activation temperature of the basic sodium aluminum carbonate, and maximum loading of the absorbent is achieved by activation between 600 and 700°C. Activation at lower temperatures leads to incomplete decomposition of the basic sodium aluminum carbonate and activation at higher temperatures results in sintering of the absorbent surface.

(2) For a given temperature, the rate of absorption of sulphur dioxide on alkalized alumina is a linear function of the sulphur dioxide concentration in the concentration range from 0.03 to 0.3% sulphur dioxide.

(3) The rate of sulphur dioxide absorption decreases with increase in temperature from 100°C to 400°C. Thus, a 10% loading of the absorbent (a proposed loading for the regeneration step) was obtained in 38 minutes at 100°C and in 116 minutes at 400°C.

(4) The absorption rate is increased significantly (two to threefold) at 300°C by the presence of small amounts of nitrogen oxides in the flue gas.

(5) The presence of moisture in the gas stream is necessary to obtain significant absorption of sulphur dioxide.

(6) Significant attrition of the absorbent occurs during absorption and regeneration, the attrition rate depending to some extent on the size and the crushing strength of the alkalized-alumina pellets.

(7) With reformed propane, the regeneration rate is negligible below 600°C, but by 700°C, it is satisfactory.

(8) At 700°C, the regeneration rate using dry hydrogen or dry carbon monoxide increases with the reductant concentration up to a concentration of about 5%, and the rate of reduction with hydrogen is greater than with carbon monoxide (0.09 min^{-1} and 0.06^{-1} respectively).

(9) At 700°C, the presence of water vapour increases the rate of reduction by carbon monoxide but decreases the rate of reduction by hydrogen.

(10) Mathematical equations were developed that are useful in predicting the efficiency of absorption and regeneration of sulphur dioxide in fluidized beds of alkalized alumina.

The alkalized alumina process was operated on a pilot plant basis for two years (1967 to 1969) to treat the flue gases from a small, coal-fired furnace (319). In this pilot plant study, absorption was performed with the flue gases rising against a free-falling stream of alkalized-alumina spheres (Figure 16). The process was shown to be capable of removing 90% of the sulphur dioxide from the gas stream (920 cu ft/min) and of producing a regenerator gas suitable for sulphur production.

All the steps in the alkalized alumina process, as developed by the United States Bureau of Mines, have been shown to be technically feasible. The process has the advantages of not lowering the temperature of the flue gas, as occurs in aqueous scrubbing processes, and also of producing a potentially marketable, or easily stored product - sulphur. However, during the development program on this process, certain disadvantages have appeared, the chief of which is the apparently intractable problem of physical attrition of the alkalized alumina. Although the reasons for this poor resistance to attrition are not known, the hygroscopic nature of alkalized alumina and the presence of large cracks and voids in the fabricated absorbent have been suggested as possible causes for the physical breakdown of the absorbent (333). This loss of the alkalized alumina absorbent which costs about 25 cents/pound, the large temperature difference between the absorption and regeneration stages, and the excessive consumption of reducing gas make the alkalized alumina process expensive to operate and the process development has now been discontinued in the United States (8).

(b) The United States Bureau of Mines Copper Oxide Process

A recent laboratory study has been made by the United States Bureau of Mines (334) of the removal of sulphur dioxide from flue gases using a copper oxide absorbent (Equation 94).

$$CuO + SO_2 + \tfrac{1}{2}O_2 = CuSO_4 \qquad \ldots \text{(Eq. 94)}$$

This study arose from efforts to develop an absorbent for sulphur dioxide that had better properties than alkalized alumina; in particular, the

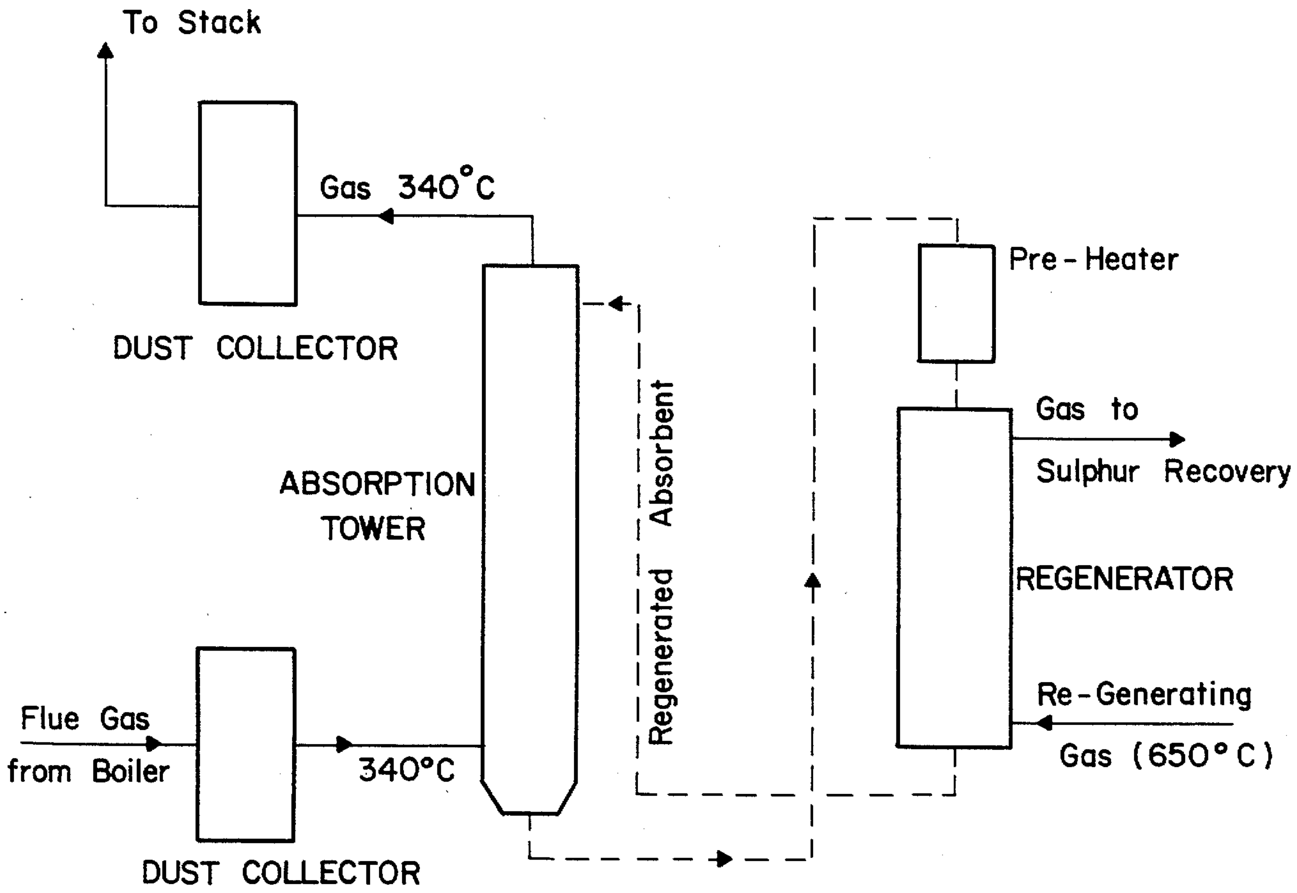

FIGURE 16. ALKALIZED ALUMINA ABSORPTION PROCESS

properties that were required were improved attrition resistance and the ability to regenerate the absorbent at a lower temperature, either thermally or with a lower consumption of reducing gas than was required for alkalized alumina.

Cupric oxide absorbents were prepared by the thermal decomposition of cupric salts that had been absorbed from solution on an alumina or silica support, and it was found that absorbents prepared on an alumina-catalyst support possessed excellent attrition resistance. The rate of sulphur dioxide absorption on copper oxide was dependent on the copper content of the absorbent and on the second power of the temperature. At 300°C, the optimum copper content was 4 to 5 wt % of the alumina support. At higher copper concentrations some of the copper oxide was relatively inaccessible to sulphur dioxide; the result was poor utilization of absorbent

Thermal regeneration of the absorbent was possible by heating to 700°C in air or in nitrogen. However, the rate of regeneration was low, and the absorption capacity of the regenerated absorbent was reduced significantly by this treatment, making thermal regeneration unsuitable for a cyclic process. It was found that reductive regeneration of the absorbent could be accomplished readily at about 425°C with hydrogen or methane (Equations 95 and 96).

$$CuSO_4 + 2H_2 = Cu + SO_2 + 2H_2O \quad \ldots \text{(Eq. 95)}$$

$$2CuSO_4 + CH_4 = Cu + 2SO_2 + CO_2 + 2H_2O \quad \ldots \text{(Eq. 96)}$$

Methane was the preferred reducing agent because the gas requirements were about stoichiometric. With hydrogen as a reductant, four to five moles of hydrogen were required per mole of sulphur dioxide evolved; a discrepancy that was attributed to multiple reactions involving sulphides. Also, with methane regeneration, the physical and chemical properties of the absorbent remained constant after 200 absorption-regeneration cycles.

The main disadvantage that was noted with the copper oxide process was the relatively low absorption rate of sulphur dioxide at 300°C.

Thus the large-scale application of this process to the absorption of sulphur dioxide from flue gases at 300°C would require a large absorption reactor that would present considerable resistance to the flow of flue gas. However, if the inlet gas temperature to the absorber could be increased to the regeneration temperature (~425°C) a significant improvement in the rate of sulphur dioxide absorption would result and a much smaller absorption tower would be required. The economics of sulphur dioxide removal by this process would then be significantly improved.

(c) The Shell Flue Gas Desulphurization Process

The Shell process (335) has been developed successfully to the pilot plant stage for the removal of sulphur dioxide from the flue gases emitted from the combustion of sulphur-rich fuel oil; this process is now considered viable for application to a commercial-scale unit (336). The process employs cupric oxide on an alumina support (337) as an absorbent for sulphur dioxide (Equation 94). The absorbent is held in a number of thin, flat layers in a specially designed "parallel passage reactor" (338), and the sulphur dioxide in the flue gas reaches the absorbent by diffusion. Two identical reactors are used in this process. After a satisfactory degree of absorption has been achieved in one reactor, the flue gas is diverted to the second reactor and the spent absorbent in the first reactor is regenerated. Both absorption and regeneration are conducted at the same temperature (about 400°C) and the absorbent itself is not moved. Various gaseous reducing agents can be employed for the conversion of the spent absorbent to copper such as hydrogen, light paraffinic hydrocarbons, or a hydrogen/carbon monoxide mixture produced by steam reforming of natural gas. The oxidation of copper to cupric oxide in the regenerated absorbent occurs rapidly at 400°C by reaction of the copper with oxygen in the flue gas. Usually only a certain fraction "α" of this cupric oxide is converted to copper sulphate in the absorption reaction, α typically having a value between 0.5 to 0.6. With hydrogen as a reducing gas, the reactions in the absorption-regeneration process are given in Equations 97 to 99.

$$Cu + \tfrac{1}{2}O_2 = CuO \qquad \ldots \quad (Eq. 97)$$

$$CuO + \alpha SO_2 + \frac{\alpha}{2} O_2 = \alpha CuSO_4 + (1-\alpha)CuO \qquad \ldots \quad (Eq. 98)$$

$$\alpha CuSO_4 + (1-\alpha)CuO + (\alpha+1)H_2 = Cu + \alpha SO_2 + (1+\alpha)H_2O \quad \ldots \quad (Eq. 99)$$

It will be seen from these equations that when α is 0.5, three moles of hydrogen are required per mole of sulphur dioxide produced. Under certain regeneration conditions, incomplete reduction of cupric sulphate takes place, resulting in the formation of cuprous sulphide rather than copper (Equations 100 to 102).

$$\alpha CuSO_4 + (1-\alpha)CuO + (\frac{4}{3}+\alpha)H_2 = \frac{2}{3}Cu + \frac{1}{6}Cu_2S + (\alpha-\frac{1}{6})SO_2 + (\frac{4}{3}+\alpha)H_2O \quad \ldots \quad (Eq. 100)$$

$$\frac{2}{3}Cu + \frac{1}{6}Cu_2S + \frac{3}{4}O_2 = \frac{5}{6}CuO + \frac{1}{6}CuSO_4 \qquad \ldots \quad (Eq. 101)$$

$$\frac{5}{6}CuO + \frac{1}{6}CuSO_4 + (\alpha-\frac{1}{6})SO_2 + \tfrac{1}{2}(\alpha-\frac{1}{6})O_2 = \alpha CuSO_4 + (1-\alpha)CuO \ldots \quad (Eq. 102)$$

The presence of cuprous sulphide in the regenerated absorbent gives a decrease in absorption capacity and inefficient utilization of hydrogen. However methods are now available to limit the amount of cuprous sulphide formed during regeneration to an insignificant level (336).

The sulphur dioxide recovered in the Shell process is converted to sulphur. This sulphur-conversion step is performed by first concentrating the recovered sulphur dioxide by an aqueous absorption-stripping process to give pure sulphur dioxide which is then either (a) reacted with hydrogen sulphide from the refinery to give sulphur in a Claus reactor or, (b) when hydrogen sulphide is not available as would be the case with flue gases from a power plant, two thirds of the recovered sulphur dioxide is reduced to hydrogen sulphide (339) which is then reacted with the remaining one-third of the sulphur dioxide in a Claus reactor. The off-gases from the Claus process are re-cycled to the sulphur dioxide absorption reactor.

Until now the Shell process has only been used to treat the flue gases from the combustion of fuel oil. To apply the process to treat the flue gases from the combustion of coal it would probably be necessary first to remove particulate matter from the flue gas before it enters the absorption reactor. The maximum sulphur dioxide concentration in a flue gas that can be handled by the Shell process has been established as 0.5% (336). This upper concentration limit is specified in order to avoid an excessive temperature build-up during the absorption reaction. Under normal operating conditions it is expected that the absorbent will have an absorption-regeneration lifetime of at least 8,000 cycles.

The overall efficiency of the Shell process for the removal of sulphur dioxide from flue gases and its later recovery as elemental sulphur is 88% (336).

(d) The DAP-Mn Process

In the DAP-Mn process (Mitsubishi Heavy Industries Ltd., Japan), sulphur dioxide is removed from flue gases by reaction with activated manganese dioxide and ammonium sulphate is recovered as a by-product of the oxide-regeneration step (340-345).

The activated manganese dioxide absorbent is a hydrated, non-stoichiometric form of manganese dioxide (MnO_2) having the general formula $MnO_x.YH_2O$, where x = 1.5 to 1.8 and Y = 0.1 to 1.0. The absorption reactions (Equations 103 and 104) occur readily between 100 and 180°C.

$$MnO_x.YH_2O + SO_2 + \tfrac{1}{2}(2-x)O_2 = MnSO_4 + YH_2O \quad \ldots \text{(Eq. 103)}$$

$$MnO_x.YH_2O + SO_3 = MnSO_4 + \tfrac{1}{2}(x-1)O_2 + YH_2O \quad \ldots \text{(Eq. 104)}$$

The regeneration reactions for the spent absorbent are given in Equations 105 and 106.

$$MnSO_4 + 2NH_4OH = Mn(OH)_2 + (NH_4)_2SO_4 \quad \ldots \text{(Eq. 105)}$$

$$Mn(OH)_2 + (x-1)O_2 + (Y-1)H_2O = MnO_x \cdot YH_2O \quad \ldots \text{(Eq. 106)}$$

In the operation of the DAP-Mn process (Figure 17), activated manganese dioxide (mean particle size 40 μm) in excess of stoichiometric requirements is injected into the flue gas and reacts with the sulphur oxides (Equations 103 and 104) in a dilute fluidized-bed reactor. The absorbent is carried in the flue gas to a solids separator, where about 90% of the absorbent is recovered for re-injection. The remaining 10% of the absorbent is leached with water to give a solution of manganese sulphate. This solution is then treated with ammonia under compressed-air agitation to give ammonium sulphate and manganese dioxide (Equations 105 and 106). The manganese dioxide is filtered, dried, and returned to the absorption reactor while the ammonium sulphate is recovered by crystallization. A small amount of soot is deposited on the absorbent and is removed by flotation with kerosene.

The DAP-Mn process has been successfully developed from laboratory-scale experiments to a semi-commercial scale for the treatment of the flue gases from a 55 MW oil-fired power station (343). In these latter tests, sulphur dioxide removal efficiences of better than 90% were achieved with a flue gas containing 0.11% sulphur dioxide. It was also found that the overall reaction rate of sulphur dioxide, and the rate of regeneration of the absorbent, could be expressed satisfactorily by equations that were independent of the plant scale. The trials of the DAP-Mn process have all been conducted with oil-fired boilers. For satisfactory operation of this process with coal-burning utilities, the flue gas must be cleaned prior to absorbent injection (12). Some manganese oxide is lost from the process to the stack gases and may present a health hazard (20).

A DAP-Mn unit is currently under construction in Japan to treat the flue gases from a 110-MW oil-fired boiler; the unit is expected to be operational early in 1972 (12).

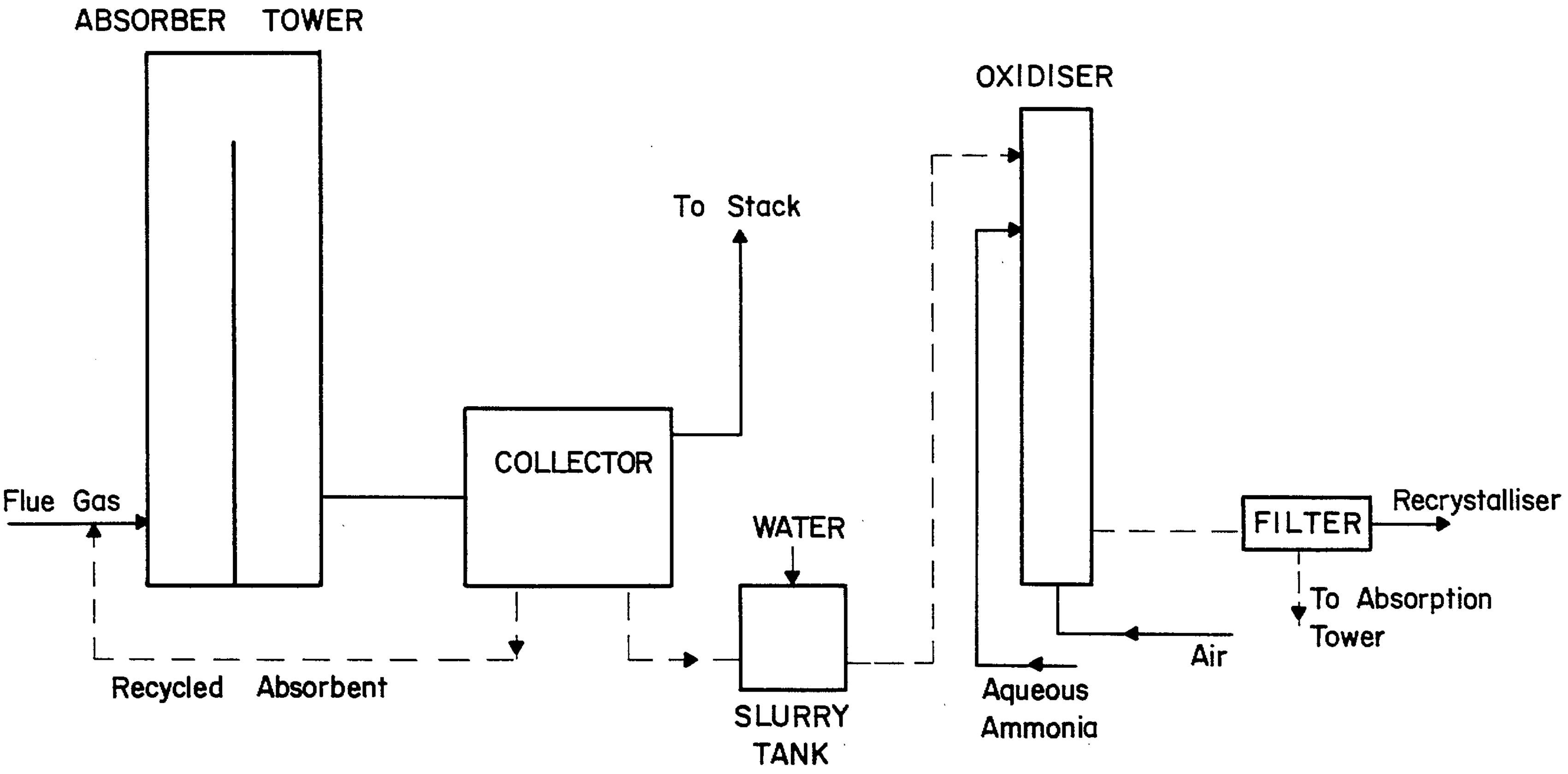

FIGURE 17. THE MITSUBISHI DAP - Mn PROCESS

(e) Zinc Oxide Absorption Processes

Several studies have been made of the absorption of sulphur dioxide by zinc oxide (172, 346-348). One of the more significant of these studies is the recent laboratory investigation by Graefe et al. (172) who have examined the low-temperature absorption of sulphur dioxide by a fluidized bed of zinc oxide. The simulated flue gas used in their studies was almost saturated with water vapour at the absorption temperature (55°C) by pre-scrubbing the gas with water at 50°C; the pre-scrubbing step is also used to remove fly ash and sulphur trioxide from the flue gas. Their study leads to three main conclusions.

(1) In the presence of water vapour the absorption of sulphur dioxide on zinc oxide is rapid and leads primarily to the formation of hydrated zinc sulphite (Equation 107).

$$ZnO + SO_2 + 2{\cdot}5H_2O = ZnSO_3.2{\cdot}5H_2O \quad \ldots \text{(Eq. 107)}$$

In experimental tests about 50 g of sulphur dioxide were absorbed per 100 g of zinc oxide before sulphur dioxide breakthrough occurred.

(2) The presence of liquid water in the fluidized bed results in defluidization of the bed and promotes extensive oxidation of the hydrated zinc sulphite (Equation 108).

$$2ZnSO_3.2{\cdot}5H_2O + O_2 = 2ZnSO_4.H_2O + 3H_2O \quad \ldots \text{(Eq. 108)}$$

(3) The presence of nitrogen dioxide in the gas stream also promotes the oxidation of zinc sulphite; however, nitrogen dioxide may be removed from the gas stream by pre-scrubbing with an acidified ferrous iron solution (Equation 109).

$$2FeSO_4 + H_2SO_4 + NO_2 = Fe_2(SO_4)_3 + H_2O + NO \quad \ldots \text{(Eq. 109)}$$

A tentative scheme has been proposed by Graefe et al. (172) both for the removal of sulphur dioxide by absorption in a fluidized bed of zinc oxide (Equation 107), and also for the regeneration of zinc oxide and the recovery of sulphur dioxide by heating the spent absorbent in steam at 275°C. The amount of zinc sulphate formed during absorption is uncertain. If significant amounts of the sulphate were formed, high-temperature treatment (1000°C) would be required to regenerate zinc oxide for re-cycling (349) and to recover sulphur dioxide (Equations 110 and 111).

$$ZnSO_4 = ZnO + SO_3 \qquad \ldots \text{(Eq. 110)}$$

$$SO_3 = SO_2 + \tfrac{1}{2}O_2 \qquad \ldots \text{(Eq. 111)}$$

Because zinc sulphate is highly soluble in water, it could be easily separated from insoluble zinc oxide and zinc sulphite before this high-temperature decomposition step.

(f) The Grillo Process

The Grillo process (350) was developed in Germany and uses a mixture of metal oxides and alkaline-earth hydroxides as an absorbent for sulphur dioxide. The absorbent is deposited on a porous carrier such as coke and contacts the flue gas in a stirred-bed reactor at temperatures above the dew point of the flue gas (preferably between 100 and 300°C). The spent absorbent is separated from the carrier by shaking and screening. It is then regenerated by heating with coke at 900°C to reduce the sulphites and sulphates to sulphur, hydrogen sulphide, and carbonyl sulphide. These gaseous products are burned to form a gas containing 10 to 15% of sulphur dioxide which is cooled and converted to sulphuric acid. The calcined absorbent is slaked with water, deposited on coke, and re-cycled.

Removal efficiences for sulphur dioxide of 90% have been achieved with the Grillo process (7).

(g) The Still Process

The Still process (7,351) was also developed in Germany and uses ash from the combustion of lignite coal as an absorbent. Lignite ash has a high lime content and is hydrated before use to form calcium hydroxide. Following preliminary dust removal the flue gases are passed through the absorbent to form calcium sulphite and some calcium sulphate. Heating the sulphite releases sulphur dioxide and regenerates the absorbent for re-use. The calcium sulphate cannot be regenerated by heating so some sulphate build-up occurs in the absorbent. The Still process, on a pilot plant scale, has removed about 80% of the sulphur dioxide from the flue gases of a coal-fired boiler.

(h) Other Oxide Absorption Methods

A laboratory study has been made (352) of the absorption of sulphur dioxide, from a sulphur dioxide-air mixture, by a uranium dioxide absorbent (Equation 112).

$$UO_2 + SO_2 + O_2 = UO_2SO_4 \qquad \text{... (Eq. 112)}$$

Oxygen is necessary for this reaction and the absorption product is represented as UO_2SO_4, although its exact composition is not known. Commercially available uranium dioxide does not react with sulphur dioxide and an active form of uranium dioxide was used in these studies. Its preparation is based upon the rather unique reaction of uranyl compounds with sulphur vapour (353) in which uranium oxide is formed (Equation 113), rather than a sulphide as is usual with other metals.

$$UO_2SO_4 + S = UO_2 + 2SO_2 \qquad \text{... (Eq. 113)}$$

Equation 113 also represents the reaction used for the regeneration of the spent absorbent, regeneration being performed at 500°C with a mixture of 80% nitrogen - 20% sulphur vapour. During a series of absorption regeneration cycles, it was found that the reactivity of the absorbent increased and, although the initial absorption runs were conducted at 500°C, towards the end of the series good absorption rates were found at 300°C. Much of the chemistry of this process has not as yet been examined. Some erratic results were obtained for material balance during absorption-regeneration cycles, and the sulphur dioxide capacity of the absorbent was found to vary from run-to-run; thus these results indicate that a more detailed investigation is required to obtain a better understanding of the process.

Developments have been reported (354) in the design of high-temperature glass-fabric filters for use in sulphur dioxide removal. The concept involved here is to use the filter to either trap the products of the gas-phase reaction between sulphur dioxide and an oxide absorbent, e.g. MnO_2, CaO, MgO, or alkalized alumina, or alternatively to coat the filter with a suitable absorbent and thus provide a large surface area for the sulphur dioxide-absorbent reaction. A filter was designed that was able to resist degradation at temperatures up to 1200°F and the feasibility of its use was demonstrated as a collector for the products of the reaction between sulphur dioxide and the dispersed oxide additives. However, much work remains to be done in the application of this technique to sulphur dioxide removal, particularly in the area of absorbent regeneration.

Several oxides of manganese, either prepared chemically (313, 355-358) or in their naturally occurring form (359, 360), have also been studied as absorbents for sulphur dioxide. Although these oxides have good absorption characteristics and loading capacities for sulphur dioxide, particularly in the presence of water vapour (355), the manganese sulphate formed on absorption (Equations 114 to 116) is difficult or uneconomical to regenerate (313).

$$MnO_2 + SO_2 = MnSO_4 \qquad \ldots \text{(Eq. 114)}$$

$$2Mn_2O_3 + 4SO_2 + O_2 = 4MnSO_4 \qquad \ldots \text{(Eq. 115)}$$

$$Mn_3O_4 + 3SO_2 + O_2 = 3MnSO_4 \qquad \ldots \text{(Eq. 116)}$$

Red mud (361) and finely divided magnesium oxide and/or calcium oxide (362) have also been proposed as reversible absorbents for sulphur oxides.

CATALYTIC OXIDATION METHODS

General Considerations

The catalytic conversion of sulphur dioxide to sulphur trioxide (Equation 117) is the basis of the contact process for the commercial production of sulphuric acid (363,364).

$$2SO_2 + O_2 = 2SO_3 \qquad \ldots \text{(Eq. 117)}$$

Platinum-based catalysts, formerly used in the contact process, were very expensive and susceptible to poisoning and have been replaced by catalysts based upon vanadium pentoxide (365,366) which give a tenfold better cost:performance ratio than platinum (367). The oxidation of sulphur dioxide (Equation 117) is a typical heterogeneous, exothermic reaction whose equilibrium is strongly dependent on temperature and is also influenced by the amount of excess oxygen present in the gas phase (Equation 118).

$$\frac{[SO_3]}{[SO_2]} = K\,[O_2]^{\frac{1}{2}} \qquad \ldots \text{(Eq. 118)}$$

The effect of temperature on the theoretical conversion efficiency of sulphur dioxide to sulphur trioxide in the presence of various amounts of sulphur dioxide and oxygen (365) is given in Table 7.

TABLE 7

Theoretical Conversion Efficiency of Sulphur Dioxide to Sulphur Trioxide Under Various Conditions

Temp. (°C)	Theoretical Conversion Efficiency					
	Vol. % SO_2	0.47	1.20	8.0	10.0	12.0
	Vol. % O_2	7.25	4.20	13.0	11.0	9.0
350		99.8	99.7	99.8	99.8	99.7
400		99.2	98.9	99.3	99.2	98.9
450		97.6	96.6	97.9	97.5	96.5
500		93.7	91.3	94.5	93.4	91.4
550		-	-	87.6	85.7	82.3
600		-	-	76.8	74.0	69.8
650		-	-	62.2	59.1	55.5

When a new acid plant is operated at its rated capacity, conversion efficiences of 95 to 98% are achieved. However, many acid plants are operated at a higher than rated capacity and the conversion efficiency is reduced to 90 to 95% (365). The main source of sulphur dioxide for sulphuric acid production is from the burning of sulphur with smaller amounts of sulphur dioxide obtained from the roasting of sulphide ores (368). In general, as the amount of sulphur dioxide in the feed-gas increases, the amount of oxygen decreases so that sulphur dioxide-rich gas streams have to be diluted with air.

In conventional contact-acid plants the optimum concentration of sulphur dioxide in the feed gas is 7.0 to 7.5% and, for satisfactory plant operation, the sulphur dioxide concentration should be maintained reasonably constant. Normally, contact-acid plants can accommodate fluctuations in the rate of gas flow much more readily than changes in the concentration of sulphur dioxide. This requirement for a uniform concentration of sulphur dioxide in the feed gas is important in the production of sulphuric acid by the contact process,from the off-gases from a copper converter, because the converting process is cyclic and the sulphur dioxide concentration in the off-gases varies from zero to over twenty per cent (369-371).

In the operation of a conventional contact plant, the purified dry gas, containing sulphur dioxide,is initially heated to 420 to 430°C. This is the minimum temperature range in which the vanadium pentoxide catalyst will function satisfactorily. The heated gas is then passed through a fixed bed of catalyst pellets in the "converter". The reactant gases are heated to about 600°C by the exothermal reaction in the converter and the reaction stops at about 70% conversion. In order to obtain acceptable yields of sulphur trioxide, the gas leaving the converter is cooled in a heat exchanger, which serves to partly heat the incoming gas to the converter, and is then passed through a second converter. This process may be repeated for a third, or even a fourth, conversion pass. The sulphur trioxide produced in the converter stages cannot be dissolved in water because a dense mist of droplets of sulphuric acid is formed. Instead, the sulphur trioxide is absorbed in a 97 to 99% sulphuric acid solution which is converted to sulphuric acid by the addition of either water or a more dilute solution of sulphuric acid. If the concentration of sulphur dioxide in the feed gas is decreased, less heat is evolved from the oxidation reaction and consequently, less heat is available to heat the gas entering the converter. The minimum concentration of sulphur dioxide for "autothermal" operation of the converter is from 3.5 to 4%. For concentrations of sulphur dioxide below this autothermal range, the pre-heater used on plant start-up can be employed on a continuous basis to heat the incoming gas. However, the operation of the pre-heater significantly increases the cost of sulphuric acid production, as does the larger-scale of heat-exchange equipment required to handle the dilute gas stream.

Because the conversion efficiency of sulphur dioxide in the contact process is somewhat less than 100%, significant amounts of sulphur dioxide (>1,000 ppm) are emitted from the stacks of sulphuric acid plants (365, 372). To improve the conversion efficiency of sulphur dioxide and, thus, to reduce the amount of sulphur dioxide wasted in the contact process, a "double contact" process has been developed recently in Germany (373, 374). In this process, sulphur trioxide is removed from the gas phase,by absorption in sulphuric acid,after about 90% conversion of the sulphur dioxide has taken place. The composition of the remaining gas is now well-removed from equilibrium conditions and a further catalytic oxidation stage increases the theoretical overall conversion efficiency of sulphur dioxide to 99.5% or better. Under normal load conditions,this very high conversion efficiency reduces the concentration of sulphur dioxide in the stack gases to 100 to 120 ppm. The optimum concentration of sulphur dioxide in the feed gas to the double-contact process is approximately 9.9%, with the minimum sulphur dioxide concentration for autothermal operation being about 7%. The relative costs of a double-contact plant and a conventional contact plant with a sulphur dioxide removal and recovery system, are discussed by Kronseder (372) who suggests that the later combination may be more economical under certain circumstances.

Popovici et al. (375) have found that the removal of sulphur dioxide from the off-gases of a conventional contact plant, by absorption in an ammoniacal solution, gives a waste gas which has a lower concentration of sulphur dioxide than the off-gases from the double-contact process. Following absorption of sulphur dioxide, the scrubbing solution is neutralized with hot phosphoric acid to form ammonium phosphate (for fertilizer use) and a gas stream containing 18% sulphur dioxide which is re-cycled for the production of sulphuric acid.

The Contact Process Applied to Smelter Gases

As was discussed earlier, large quantities of sulphur dioxide are emitted annually in the stack gases of plants using pyrometallurgical methods for the treatment of sulphide ores. When the sulphur dioxide concentration in the smelter gas is greater than the autothermal minimum (3.5-4.0% SO_2) the contact process is frequently used to recover the sulphur dioxide as sulphuric acid (58, 376). The contact process has not been used to treat smelter gases containing less sulphur dioxide than this autothermal minimum (55). However, a modified version of the contact process (the Cat - Ox process) has been used successfully to recover sulphur dioxide from the flue gases of thermal power stations and will be described later in this context. For the production of sulphuric acid from smelter gases by the contact process, it is important that the gases be thoroughly cleaned in order to prevent both the de-activation of the catalyst and the blocking of the catalyst bed by entrained solids (77). The estimated upper impurity limits for some elements in a cleaned smelter gas (366) that is to be used in the contact process are given in Table 8.

TABLE 8

Estimated Maximum Impurity Limits in a Cleaned 7% SO_2 Smelter Gas for Use in the Contact Process

Substance	Approximate Limit, Dry Basis (mg/Nm^3)
Chlorides, as Cl	1.2
Fluorides, as F	0.25
Arsenic	0.9
Lead	1.2
Mercury	0.25
Selenium	50.0
Total Solids	1.2

The general cleaning procedure adopted for smelter gases is as follows (366). Coarse dust is first removed from the hot gas by a cyclone or by an electrostatic precipitator. The gas is then further cleaned by scrubbing with water or with dilute sulphuric acid to remove fine dust and sulphur trioxide. The gas leaving the scrubber is usually at a temperature of between 55 to 75°C and is saturated with water vapour. The moisture content of the gas is reduced by further scrubbing with cold water or with dilute sulphuric acid and, after passage through a mist eliminator, the gas is dried in a counter-current flow of 93% sulphuric acid. This cleaned and dried gas is then sent to the first converter stage of the contact process. The sulphuric acid used to dry the smelter gas is later used as a source of water in the final sulphur trioxide absorption stage.

The cleaning of gases from the roasting of lead ores can present problems because lead fume, carried in the sulphur dioxide stream, is difficult to remove in the gas purification system and can cause blocking in scrubbing towers and similar equipment through the build-up of deposits of insoluble lead sulphates and oxides (377).

The Contact Process Applied to Power Stations (Cat - Ox Process)

The contact process has been successfully adapted by the Monsanto Company for the removal of sulphur dioxide from the flue gases of coal-burning power stations in which the sulphur dioxide concentration is well below the autothermal minimum required for the conventional contact process. In this Cat - Ox process, the flue gases are cleaned to remove particulate matter but are not dried; the moisture in the flue gas is used as the source of water for the formation of sulphuric acid.

After the technical feasibility of the "Cat - Ox" process for the treatment of flue gases had been demonstrated with a 400-cu ft/min pilot plant (378), a prototype study was performed with a 24,000-cu ft/min plant at a base-load electrical generating station of the Metropolitan Edison Company (Portland, Pennsylvania). This prototype unit (379, 380) removed ~90% of the sulphur dioxide and virtually all the fly ash from the flue gas and recovered the sulphur dioxide as 80% sulphuric acid.

The main steps in the process are shown in Figure 18. Hot flue gases (950°F) from the boiler are first passed through a high-efficiency dust removal system that is a combination of an electrostatic precipitator and a mechanical separator. The efficient removal of particulate matter from the gas stream is very important and is performed to prevent fouling of the catalyst in the converter stage of the process. Because some build-up

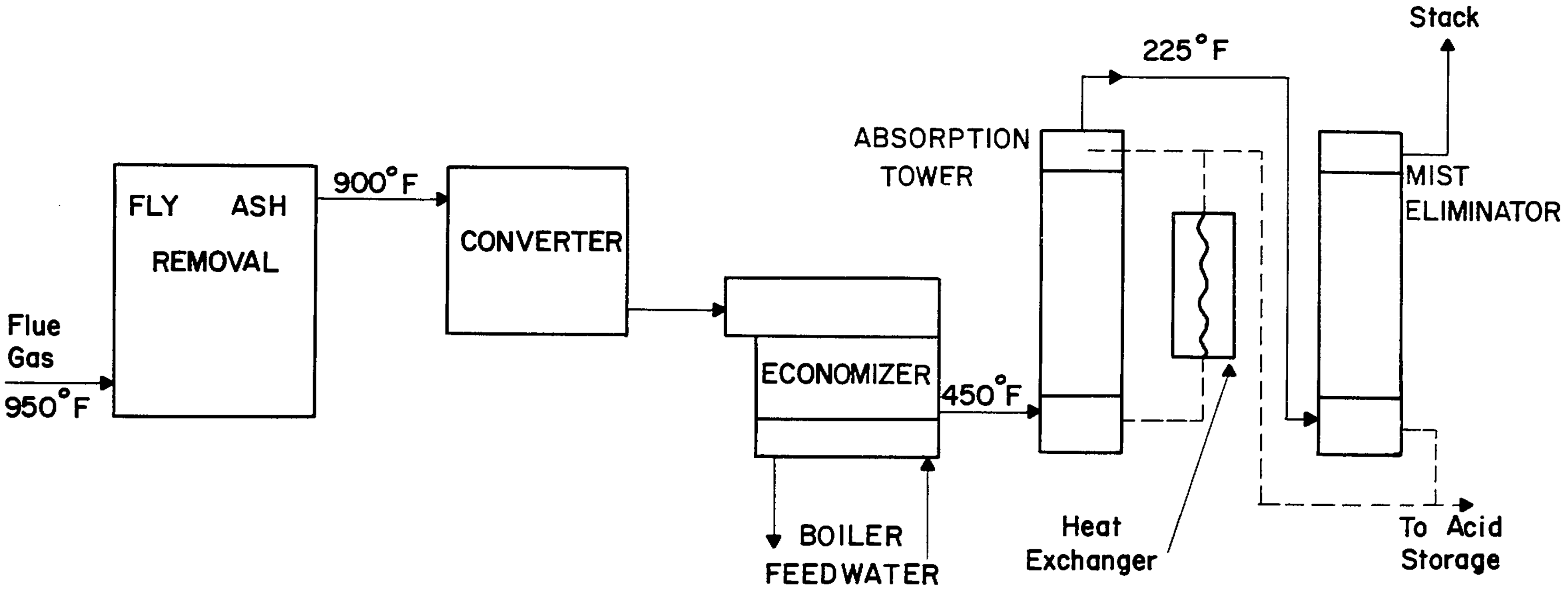

FIGURE 18 THE MONSANTO (CAT-OX) PROCESS

of fly ash does occur on the catalyst surface and causes an undesirable pressure drop in the converter, the catalyst beds were removed for cleaning every two months. Although no loss of catalytic activity was found after cleaning, there was some mechanical loss (2.5%) of the catalyst. With the converter operating at design temperatures, about 90% of the sulphur dioxide in the gas stream was oxidized to sulphur trioxide. At a flue gas temperature of 750°F, corresponding to a 50% boiler load, the sulphur dioxide conversion efficiency fell to 80%.

Following the converter stage, the gas is cooled to just above the dew point in an economizer. The gas is then passed through an absorption tower counter-current to a stream of cool sulphuric acid. The gas leaves the absorption tower at 225°F, passes through a mist eliminator to remove fine droplets of sulphuric acid, and is then discharged to the atmosphere. The discharged gas contains less than 10 ppm of 100% sulphuric acid.

As the Cat - Ox process is essentially the sulphuric acid contact process modified for low concentrations of sulphur dioxide, the process favours the use of a sulphur-rich fuel that will increase the sulphur dioxide content of the flue gas. Thus in one economic evaluation (380), the operating costs of the Cat - Ox process are met at $13.50/ton of 100% H_2SO_4 for a boiler burning 3% sulphur-coal and at $8.00/ton of 100% H_2SO_4 for the same boiler burning 5% sulphur-coal. It is worth noting that large tonnages of sulphuric acid can be produced by this process. As a general guide, one ton of 100% sulphuric acid is produced per day per megawatt of capacity when burning coal containing 3.5% sulphur.

The Cat - Ox process is best suited to a base-load power station where a steady stream of sulphur dioxide-containing flue gas can be obtained. The method has the advantage that all the components in the process, other than pumps, are found in conventional power stations. The Cat - Ox process is to undergo full-scale commercial testing shortly at a 100-MW power station at Wood River, Illinois and should be on-line early in 1972 (12,381).

The Kiyoura Process

In the Kiyoura process (382-384), an essentially dust-free flue gas is passed through a catalytic converter (V_2O_5) to oxidize the sulphur dioxide to sulphur trioxide. Small amounts of residual fly ash in the flue gas have a negligible effect on the efficiency of the converter (385). After the converter stage, ammonia is injected into the flue gas where it reacts with the sulphur trioxide and available moisture to form ammonium sulphate. The ammonium sulphate is recovered from the gas stream in cyclones or by electrostatic precipitation. The Kiyoura process has been used on a 200-kW boiler and gave a 93% removal-efficiency for sulphur dioxide. The ammonium sulphate produced is better than 98.5% pure and has a reasonable market potential in the far east as a fertilizer. Alternatively, ammonium phosphate can be produced by reacting the ammonium sulphate with phosphate rock (386).

Other Oxidation Methods

A catalytic-oxidation/dry-absorption technique for sulphur dioxide removal has been investigated (387). It is based upon the oxidation of sulphur dioxide to sulphur trioxide, followed by the reaction of the sulphur trioxide with sodium sulphate absorbed on an inert carrier (Equations 117 and 119).

$$Na_2SO_4 + SO_3 = Na_2S_2O_7 \qquad \ldots \text{(Eq. 119)}$$

The absorption of sulphur trioxide on sodium sulphate was found to be rapid between 545 and 600°F and the absorption rate was constant up to about 70% of the capacity of the absorbent. At 545°F, the vapour pressure of sulphur trioxide over the absorbent was also low enough for the removal of 95% of the sulphur trioxide in the gas stream. The vapour pressure of sulphur trioxide over sodium pyrosulphate increases sharply with temperature and at 1020°F essentially quantitative decomposition of sodium pyrosulphate occurs, giving a gas, rich in sulphur trioxide, and sodium sulphate for recycling. Oxides of nitrogen and water vapour have a negligible effect on the sulphur trioxide absorption rate.

MOLTEN SALT PROCESSES

The Atomics International Molten Carbonate Process

A molten carbonate absorption process is under development by the Atomics International Division, North American Rockwell Corporation, California, for the removal of sulphur dioxide from power-plant flue gases and for the subsequent recovery of the sulphur dioxide as hydrogen sulphide (388-391). The process involves the high-temperature scrubbing of the stack gas by a eutectic mixture of lithium, sodium, and potassium carbonates (eutectic composition: Li_2CO_3, 32 wt %; Na_2CO_3, 33 wt %; K_2CO_3, 35 wt %). The physical properties of the eutectic are given in Table 9 and a simplified schematic of the process is given in Figure 19.

TABLE 9

Physical Properties of the Carbonate Eutectic

Property	Value
Melting Point	747°F
Viscosity (800°F)	12 cp
Specific Gravity (800°F)	2.0
Specific Heat (800°F)	0.4
Thermal Conductivity (800°F)	0.24 Btu/hr ft °F

The molten carbonate process may be divided into three stages; a scrubbing stage and two absorbent-regeneration stages. In the scrubbing stage, the eutectic is maintained at about 50°F above its melting point and at this temperature (800°F) it is a clear, mobile liquid. As much as possible of the fly ash is removed from the flue gas by high-efficiency electrostatic

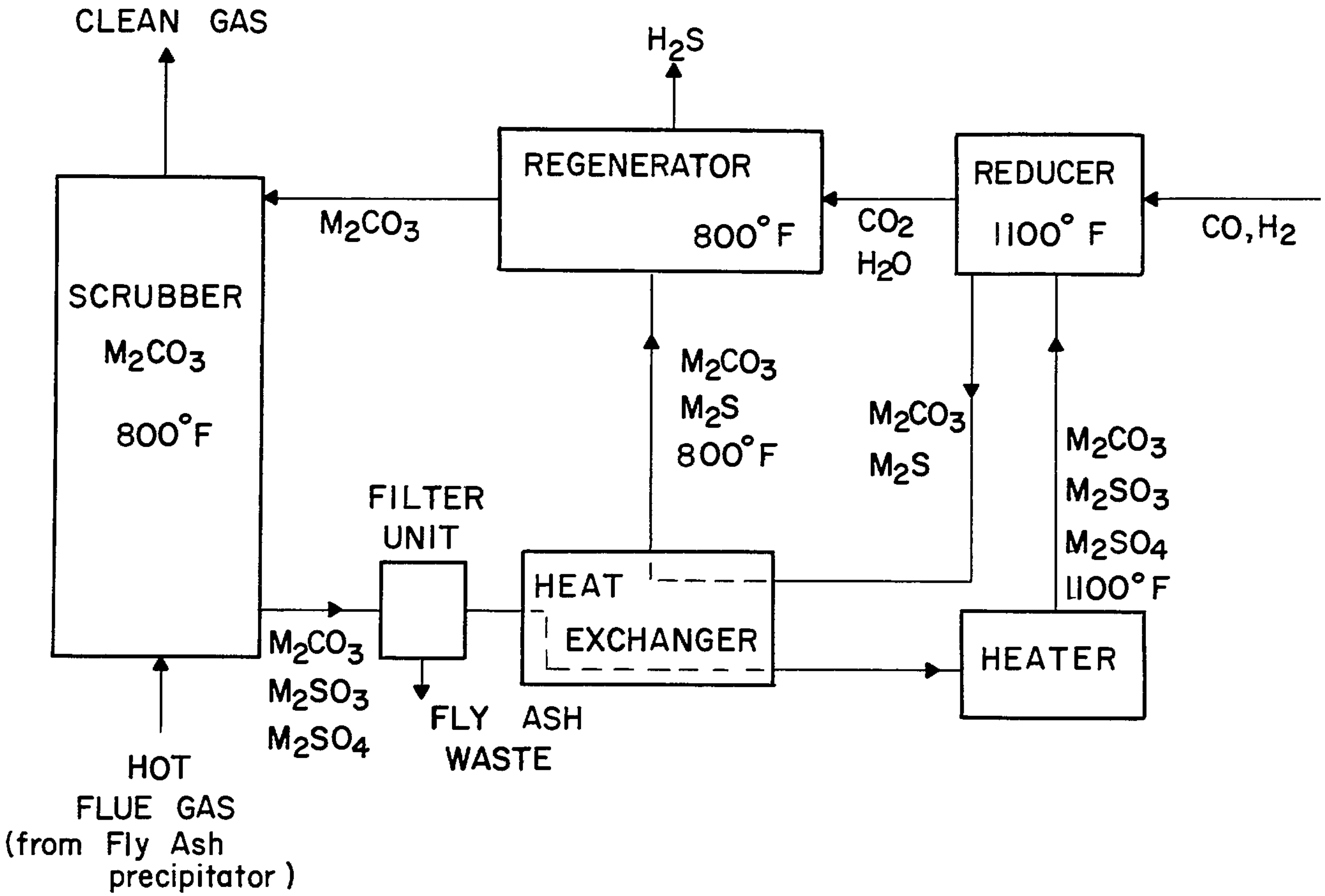

FIGURE 19. THE MOLTEN CARBONATE PROCESS

precipitators before the gas enters the scrubber. The sulphur oxides in the flue gas then react with the molten carbonates in the scrubbing unit to give sulphites and sulphates. These reactions are given in Equations 120 and 121, where M represents the alkali metal cation.

$$M_2CO_3 + SO_2 = M_2SO_3 + CO_2 \qquad \text{... (Eq. 120)}$$

$$M_2CO_3 + SO_3 = M_2SO_4 + CO_2 \qquad \text{... (Eq. 121)}$$

Some oxidation of the alkali-metal sulphites to sulphates also takes place during scrubbing (Equation 122).

$$M_2SO_3 + \tfrac{1}{2}O_2 = M_2SO_4 \qquad \text{... (Eq. 122)}$$

At 800°F, the equilibrium constants for the primary absorption reactions (Equations 120 and 121) greatly favour the formation of sulphite and sulphate and the conversion of up to 40% of the carbonate is achieved before the sulphur dioxide concentration over the melt exceeds 200 ppm. The reactions in Equations 120 and 121 are also very rapid and the rate-limiting step in the absorption of sulphur dioxide by the eutectic appears to be in the mass-transfer processes in the scrubber (389). The absorption process is also slightly exothermic, and the heat evolved during absorption partly compensates for heat losses from the scrubber.

The regeneration of the spent absorbent involves the conversion of the alkali-metal sulphites and sulphates, formed during absorption (Equations 120-122), first to the sulphides, and then to the carbonates. Following filtration of the spent absorbent to remove residual fly ash, the absorbent is heated to 1100°F. At this temperature, the disproportionation reaction in Equation 123 occurs rapidly.

$$4M_2SO_3 = 3M_2SO_4 + M_2S \qquad \text{... (Eq. 123)}$$

The disproportionation reaction will also take place at temperatures lower than 1100°F but its rate is too low for practical purposes. The sulphates formed by disproportionation are then reduced, also at 1100°F, by a hydrogen-rich reformer gas (75% H_2, 21% CO) at a pressure of 10 atmospheres in the reducer (Figure 19) to give the alkali-metal sulphides (Equations 124 and 125):

$$M_2SO_4 + 4H_2 = M_2S + 4H_2O \qquad \text{... (Eq. 124)}$$

$$M_2SO_4 + 4CO = M_2S + 4CO_2 \qquad \text{... (Eq. 125)}$$

A hydrogen-rich reducing gas is preferred as a reductant because the rate of reduction with hydrogen is about three times the rate of reduction with carbon monoxide. Batch tests indicate that 40 to 60 minutes are required for this step.

The sulphide-carbonate mixture from the reducer is then pumped, via a heat exchanger, to the regenerator where the overall reaction in Equation 126 takes place:

$$M_2S + CO_2 + H_2O = M_2CO_3 + H_2S \qquad \text{... (Eq. 126)}$$

This highly exothermic reaction occurs rapidly at 800°F and utilizes carbon dioxide and water recovered from the reducer stage (Equations 124 and 125). The regenerated carbonate is transferred directly to the scrubber. The exit gas from the regenerator contains about 30% hydrogen sulphide and may be fed directly to a Claus reactor for the production of sulphur. The sulphur dioxide removal efficiency of the molten carbonate process is about 95%.

It has recently been announced (392) that the Consolidated Edison Company of New York City plans to build a $4-million pilot plant, at its 350-MW Staten Island power plant, to test the molten carbonate process on a commercial scale.

Other Molten Salt Processes

A molten salt process has been described (393) that employs a salt melt of potassium phosphate, potassium sulphate, and potassium pyrosulphate as an absorbent for sulphur dioxide. The sulphur dioxide reacts with the melt at 370°C giving an increase in the potassium pyrosulphate content of the melt. The melt, enriched in potassium pyrosulphate, is regenerated at 650°C in an inert-gas stream to form sulphur trioxide that is recovered by washing with water.

A slurry of potassium carbonate in molten potassium thiocyanate, at 180°C, has also been reported (394) to be an effective scrubbing medium for sulphur dioxide. Insoluble potassium sulphite is recovered from the spent scrubbing medium by filtration and is then reduced by coal to give potassium sulphide. The sulphide melt is next leached with water and the hydrogen sulphide evolved is recovered and can be converted to elemental sulphur by the Claus reaction. The aqueous liquor is carbonated to produce potassium bicarbonate, which is then calcined to form the carbonate for re-cycle to the scrubber.

REDUCTION TO ELEMENTAL SULPHUR

General Considerations

Sulphur dioxide may be reduced to elemental sulphur by a number of solid or gaseous reducing agents, and several reduction processes have been operated commercially during periods of high sulphur prices (10, 35, 75, 77, 395). As has been noted earlier, elemental sulphur has certain advantages over sulphur-containing compounds as an end product of a sulphur dioxide recovery scheme. Sulphur can be stored indefinitely, and, because of its low weight (Table 2), freight costs are lower than for sulphur-containing compounds.

The Allied Chemical Corporation has conducted a critical review (396) of the large number of sulphur dioxide reduction methods described in the literature and, on the basis of technical and economic considerations, has concluded that only the following reducing agents are suitable for industrial applications:

solid carbon, particularly coke;

gaseous hydrocarbons, such as methane;

reformer gas (a mixture of carbon monoxide and hydrogen); and

hydrogen sulphide.

In the Allied Chemical Corporation review, pure hydrogen and pure carbon monoxide were rejected as reducing agents for sulphur dioxide because of cost and because they offered no technical advantages over cheaper, reformed natural gas, and coal and petroleum coke were rejected because their use could lead to contamination of the recovered sulphur with ash, coal tar, or carbon.

For a given feed gas,the cost of a particular reducing agent will vary directly as the sum of the concentrations of sulphur dioxide and oxygen in the gas stream. One mole of oxygen will consume the same quantity of reducing agent as one mole of sulphur dioxide; therefore,it is important in any reduction process to avoid dilution of the feed gas with air.

In the past, coke has been used successfully to produce sulphur on an industrial scale from the off-gases of smelters and from other gas streams containing high concentrations of sulphur dioxide (75, 87, 200, 397). Therefore, methods using coke as a reducing agent have the advantage of a well-proven technology, as well as the ability to handle dust-laden gases. However, where a choice of reducing agents is available,current practice favours natural gas rather than coke because natural gas is generally cheaper than coke and is also often more readily available than coke at many industrial locations (10, 398).

Most of the sulphur dioxide reduction schemes described in the literature are multi-stage processes that use the Claus reaction (186) for the final stage of sulphur recovery. Because the waste gases from the Claus reactor are normally discharged into the atmosphere, the sulphur dioxide pollution arising from the reduction process is governed by the efficiency of the Claus process. In order to provide data for the optimum design of Claus reactors, the kinetic factors governing the efficiency of the Claus reaction have been investigated in detail (399).

A description will now be given of some reduction processes that have been developed for the production of sulphur from sulphur dioxide.

Coke Reduction Methods

(a) The Trail Process

This reduction process for sulphur dioxide (75,200,400,401) was operated by the Consolidated Mining and Smelting Company of Canada Limited, at Trail, British Columbia between 1935 and 1943. In the Trail process, essentially pure sulphur dioxide, produced from the Cominco absorption process (page 36), was blown together with some oxygen through a bed of incandescent coke. The oxygen was added to maintain the temperature in the coke bed by reaction with some of the coke because the reduction reactions are not sufficiently exothermic to be self-supporting. According to Lepsoe (401), the main reactions occurring in the coke bed are given by Equations 127 to 129.

$$SO_2 + C = CO_2 + \tfrac{1}{2}S_2 \qquad \ldots \text{(Eq. 127)}$$

$$CO_2 + C = 2CO \qquad \ldots \text{(Eq. 128)}$$

$$SO_2 + 2CO = 2CO_2 + \tfrac{1}{2}S_2 \qquad \ldots \text{(Eq. 129)}$$

The reducing reactions do not go to completion. Considerable quantities of carbonyl sulphide were formed by the reaction of carbon monoxide with sulphur above the hot zone of the furnace ($T \geq 1300°C$). The appropriate quantity of sulphur dioxide was added to the exit gases from the furnace to bring the ratio of SO_2:(COS + CO) to 1:2; the gas mixture was then cleaned in a cyclone to remove coke dust. The gas next passed through a pre-catalyst chamber packed with firebrick where the reactions in Equations 129 and 130 take place.

$$2COS + SO_2 = 2CO_2 + 3/2\,S_2 \qquad \ldots \text{(Eq. 130)}$$

After cooling to about 500°C the gas was passed through a chamber containing an alumina catalyst for further reaction, and the sulphur was then condensed from the gas phase. When Cominco discontinued operation of the Trail process in 1943, about 150 tons per day of sulphur were being produced (200). However, the Trail process is still in use at a smelter in Spain (77).

(b) The Boliden Process

The Boliden process (9, 87) was developed in Sweden for the recovery of sulphur from sulphur dioxide in smelter gases. In the first stage of this process, a portion of the smelter gas was diluted with air to bring its oxygen content to a pre-determined level. A typical analysis of the diluted gas would be, sulphur dioxide, 5%; oxygen, 12%; and nitrogen, 83%. This gas was then blown through a bed of red-hot coke to form a reducing gas which contained mainly carbon monoxide, carbon dioxide and sulphur vapour, together with some carbonyl sulphide, hydrogen sulphide and carbon disulphide. In the second stage of the process, the reducing gas was added to the remainder of the feed gas and the mixture was passed through two catalyst chambers, the catalyst being a mixture of ferric oxide and aluminum oxide. In the catalyst chambers, a number of sulphur-producing reactions occur (Equations 129 to 132), and sulphur was finally recovered from the cooled gas stream in specially designed precipitators.

$$SO_2 + 2H_2S = 2H_2O + 3/2S_2 \qquad \text{... (Eq. 131)}$$

$$SO_2 + CS_2 = CO_2 + 3/2S_2 \qquad \text{... (Eq. 132)}$$

Because there is a relatively large amount of oxygen, compared to sulphur dioxide, in the feed gas, consumption of coke by this process is much greater than in the Trail process.

The Boliden process was operated successfully for several years in Sweden but was discontinued in 1943 because of the high cost of coke.

(c) The ICI Process

A small pilot plant, operated in the nineteen thirties by Imperial Chemical Industries Limited, produced 5 to 6 tons per day of sulphur (75, 397). In this process, pure sulphur dioxide was diluted by about 50% with air and then passed through a bed of coke that was operated at a temperature of 800 to 900°C. Some unreduced sulphur dioxide was maintained in the exit gases from the reducer in order to react with carbon monoxide, carbonyl sulphide and hydrogen sulphide, formed during the reduction process, in a catalyst tower, to give sulphur. Coke consumption was found to be high, at about 1.7 times the stoichiometric requirements, so that cheap coke is necessary for the economic recovery of sulphur by this process.

Methane Reduction Methods

(a) The Asarco Process

The lack of an adequate local market for liquified sulphur dioxide, and for sulphuric acid led the American Smelting and Refining Company (Asarco) at Garfield, Utah to develop a methane reduction process for the recovery of sulphur from smelter gases (402, 403). The process was operated on a semi-commercial scale between 1940 and 1944 and produced high-purity sulphur from smelter gases containing about 7% sulphur dioxide. About 95% of the sulphur in the off-gases was recovered.

The Asarco process consisted essentially of three stages. In the first stage, sufficient natural gas was added to the smelter gas to convert all the residual oxygen to carbon dioxide and to react with the sulphur dioxide to form sulphur (Equation 133).

$$CH_4 + 2SO_2 = 2H_2O + CO_2 + S_2 \qquad \ldots \text{(Eq. 133)}$$

This non-catalytic reduction process was conducted at a minimum temperature of 1250°C in a steel chamber lined with refractory brick. As with other carbon reduction processes side reactions produce significant quantities of carbonyl sulphide and hydrogen sulphide (Equation 134).

$$3CH_4 + 4SO_2 = 4H_2S + 3CO_2 + 2H_2O \quad \ldots \text{(Eq. 134)}$$

In the second stage of the process the carbonyl sulphide was reduced to sulphur by reaction with residual sulphur dioxide (Equation 130) over a bauxite catalyst at 425 to 450°C. Sulphur was removed at this stage of the process and the gas temperature was adjusted to 210°C. Hydrogen sulphide was then removed in a Claus reactor in the final stage of the process. The development of the Asarco process has been described in detail by Fleming and Fitt (403).

Interest in the Asarco process has recently been revived and a pilot plant is currently under construction at El Paso, Texas, as a joint venture between Asarco and the Phelps Dodge Corporation, to treat sulphur dioxide resulting from copper smelting operations (58).

(b) The Texas Gulf Sulfur Process

The Texas Gulf Sulfur process (404) is similar to the direct-reduction Asarco process above, except that the initial reduction stage is performed in the presence of a catalyst which permits the reduction to be performed at 850 to 1000°C instead of at about 1250°C as in the Asarco process. Activated alumina, bauxite, or quartz may be used as catalysts for this reaction. The reduction reaction is followed by two reaction stages, as in the Asarco process, to convert carbonyl sulphide and hydrogen sulphide to sulphur.

Pilot plant operations were carried out in 1958 and 1959 at the INCO iron ore reduction plant at Copper Cliff, Ontario (405) to treat gases containing about 10% sulphur dioxide. Although the pilot plant runs were successful, this method was too expensive for commercial development.

(c) The Allied Chemical Process

At Falconbridge, Ontario, Allied Chemical Canada Limited has recently installed a high-capacity plant (~150, 000 tons/year) to recover sulphur from the gases from the direct reduction of pyrrhotite to sponge iron by the SL/RN process (406). Almost no details of the Allied Chemical process at Falconbridge have been disclosed except that natural gas is used as a reducing agent (405,407). However, the reduction method may well be similar to an Allied Chemical process described in recent German patents (408-410). In this process, some of the sulphur dioxide in the gas stream is catalytically reduced by methane at 815 to 1095°C to give sulphur and hydrogen sulphide. The hydrogen sulphide is then converted to sulphur by reaction with the remaining sulphur dioxide in a Claus plant.

Hydrogen Sulphide Reduction Methods

The catalytic reduction of sulphur dioxide by hydrogen sulphide (Equation 131) forms the basis of the well-established Claus process (186, 411), and a low-temperature version of this reduction method (the modified Claus process) has been proposed for the removal of sulphur dioxide from waste gases (412-416). Although the reduction method has the advantage of producing elemental sulphur, considerable care would have to be exercised in any large-scale use of hydrogen sulphide, because it is a considerably more undesirable pollutant than sulphur dioxide.

In a recent laboratory study of the modified Claus process (412), the stoichiometric amount of hydrogen sulphide required for the reaction in Equation 131 was added to a simulated flue gas. The gas was then passed through an alumina catalyst bed which was at a temperature of 100°C. The sulphur dioxide was reduced quantitatively to sulphur which condensed on the catalyst surface. In order to achieve a nearly complete consumption of both reactant gases it was found that their concentrations should be maintained as close as possible to the stoichiometric requirements. Catalyst loadings of about 20 grams of sulphur per 100 grams of catalyst were obtained before sulphur dioxide breakthrough occurred. The catalyst was successfully regenerated for re-cycling by a two-stage process that consisted of heating the catalyst to 510°C to evaporate the condensed sulphur, followed by washing the cooled catalyst with a dilute solution of ammonia to desorb traces of sulphates that poison the catalyst. At about 100°C, neither oxygen nor water vapour had any effect on the sulphur-loading capacity of the catalyst. However, the presence of oxides of nitrogen, in the concentration range from 200 to 2000 ppm, resulted in an approximately twofold decrease in the sulphur-loading capacity of the catalyst.

The Ontario Research Foundation has conducted small-scale tests of the modified Claus process for the treatment of waste gases emitted from an electrical generating station and from a copper-nickel smelter (416). It was found that this process was unsuitable for the treatment of the flue gases from the generating station because of very poor removal efficiences for sulphur dioxide and very low sulphur loadings of the activated alumina catalyst. These poor results were attributed to the poisoning of the catalyst surface for the Claus reaction by adsorbed sulphuric acid and it was suggested that the sulphuric acid was formed on the catalyst surface by the oxidation of sulphur dioxide, in the presence of moisture, by nitrogen dioxide in the flue gas (Equation 135).

$$SO_2 + NO_2 + H_2O \quad = \quad H_2SO_4 + NO \qquad \ldots \text{(Eq. 135)}$$

Subsequent laboratory experiments confirmed the deleterious effects of oxides of nitrogen on the efficiency of alumina catalysts in the modified Claus process. Smelter gases have a much lower concentration of oxides of nitrogen than boiler flue gases and it was found that the modified Claus process operated satisfactorily while treating smelter gases containing ~1% sulphur dioxide. For commercial application of this process, it was envisaged that two thirds of the sulphur produced would be converted to hydrogen sulphide for re-cycle to the Claus reactor, the remaining sulphur being sold.

A reduction method similar to those above is also under development by Princeton Chemical Research, Incorporated, in the United States (417,418). In this process, elemental sulphur is reacted catalytically with methane to form hydrogen sulphide. The hydrogen sulphide is then added to the flue gas where it reacts with sulphur dioxide in the presence of a catalyst to yield sulphur. As in other studies of the modified Claus process (412,416), activated alumina catalysts were found to undergo a steady decline in catalytic activity during the reduction process, an effect which was traced to the presence of oxides of nitrogen in the reactant gases. The catalytic activity of molecular-sieve catalysts (e.g. Linde Type 13X), however, was found to be unaffected by oxides of nitrogen. In the conceptual design of this process, a part of the recovered sulphur is employed for the preparation of hydrogen sulphide for use in the sulphur dioxide reduction step (Equation 131).

Welty et al. (419) have also proposed a method to recover sulphur from flue gases based upon the Claus reaction. In their approach the sulphur dioxide in a major portion (60 to 75%) of the flue gas is catalytically reduced to hydrogen sulphide at a high temperature with natural gas. The unreacted minor portion of the flue gas is then mixed with the cooled flue gas containing hydrogen sulphide and the combined gas stream is reacted in a countercurrent flow of a freely falling Claus catalyst at 200 to 400°C. Sulphur condenses on the catalyst surface and is recovered by heating, a step which also serves to regenerate the catalyst.

Carbon Monoxide Reduction Methods

The reduction of sulphur dioxide by carbon monoxide (Equation 129) is one of the gas-phase reactions that occur when coke is used as a reducing agent for gas streams rich in sulphur dioxide. This reaction takes place readily at 500°C in the presence of a bauxite catalyst, and, between 250-500°C, slightly hydrated alumina is an effective catalyst (401). Studies have been made by the Chevron Research Company of the application of carbon monoxide to the catalytic reduction of sulphur dioxide at the low concentration levels of sulphur dioxide found in flue gases from combustion processes (420,421). In this context, carbon monoxide has the advantage that it will also reduce oxides of nitrogen to nitrogen (421). However, carbon monoxide is readily oxidized to give carbon dioxide, so it is therefore necessary that there be sufficient carbon monoxide in the flue gas to react with both the oxygen and the sulphur dioxide present (421,422). This requirement for a low oxygen concentration in the flue gas means that, before a carbon monoxide reduction process could be economically applied to flue gases, changes in combustion practice would be required with the furnace operating at a near stoichiometric fuel-air mixture. It has been found that the reaction rate between carbon monoxide and sulphur dioxide is effectively independent of the carbon dioxide concentration in the concentration range found in flue gases, but that the reaction rate decreases drastically at oxygen concentrations above 0.5% oxygen (423).

Carbonyl sulphide is also produced during the reduction of sulphur dioxide by carbon monoxide (Equation 136).

$$CO + \tfrac{1}{2}S_2 = COS \qquad \text{... (Eq. 136)}$$

The amount of carbonyl sulphide formed is dependent on the temperature and on the carbon monoxide concentration (421,423) and may be minimized by maintaining the carbon monoxide concentration at the stoichiometric requirements for the reaction given in Equation 129. However, the formation of carbonyl sulphide remains a major difficulty in using carbon monoxide to reduce sulphur dioxide.

APPLICATIONS OF ORGANIC REAGENTS

Organic Liquids

Many organic liquids, including amines, amides, imides, ketones, alcohols, and esters, can absorb significant quantities of sulphur dioxide (424, 425), and their application to the removal of sulphur dioxide from gas streams has been the subject of numerous patents (424, 426-431). However, in spite of the large number of potential organic absorbents for sulphur dioxide, only two, dimethylaniline and xylidene, have been used routinely on an industrial scale and both have been used on smelter gases containing 4 to 6% sulphur dioxide. There are no known applications of organic liquids for the treatment of the flue gases from the combustion of sulphur-containing fuels, whose content of sulphur dioxide would not exceed about 0.3%.

One problem common to the use of any organic liquid for the scrubbing of gas streams is the critical dependence of the process on the loss of the scrubbing liquid in the stream of purified gas. Although the vapour pressure of the organic compound may be low, significant loss of the compound can occur if a large volume of gas is treated. This loss of the organic reagent represents not only a serious economic penalty against the process but poses a potential atmospheric pollution threat. Therefore, it is likely that any process using organic liquids for sulphur dioxide removal will require additional processing steps to recover the volatilized absorbent from the cleaned gas stream; steps which will add significantly to the cost of the process. A further potential disadvantage of organic liquids for sulphur dioxide removal from waste gases is the possibility of decomposition of the liquid due to side reactions, during the scrubbing process, which could lead to irreversible losses of the absorbent.

From a study of a number of organic amines, tetraethylenepentamine has been selected (425) as a potentially useful compound for the removal of sulphur dioxide from flue gases at temperatures between 200 and 350°C. However, experimental studies have shown (425,432) that, during sulphur dioxide absorption in tetraethylenepentamine, a variety of solid di- and polythionates are formed through disproportionation of the amine-sulphur dioxide adduct. It has also been shown that attempts to recover sulphur dioxide, from the amine-sulphur dioxide absorption product, by thermal stripping lead to the formation of sulphur, hydrogen sulphide, as well as sulphur dioxide. These side reactions infer that a chemical recovery step would have to be developed for the efficient regeneration of the spent absorbent before tetraethylenepentamine could be used for the scrubbing of flue gases (425).

The use of organic liquids to absorb sulphur dioxide from flue gases does not look promising because of the disadvantages noted above, and also because of the lack of adequate equilibrium and kinetic data for sulphur dioxide absorption in organic liquids and the lack of knowledge of the influence of gaseous impurities on the stability and the absorption capacity of organic liquids. The cost, and even the commercial availability, of very large quantities of the selected organic compound also pose serious questions as to the feasibility of processes based on the large-scale use of organic liquids.

Processes Using Organic Liquids

(a) The Asarco DMA Process

In the Asarco (American Smelting and Refining Company) process dimethylaniline (DMA), which is anhydrous, is used to remove sulphur dioxide from smelter gases containing about 5% sulphur dioxide (433,434). The smelter gases are first cleaned to remove particulate matter and moisture and are then contacted counter-currently with dimethylaniline in an absorption tower (Figure 20). During absorption considerable heat of solution is evolved which is removed by intercoolers in the absorption tower. It is important to maintain the dimethylaniline absorbent at a reasonably low temperature because, with increase in temperature, the vapour pressure of dimethylaniline increases and the solubility of sulphur dioxide in dimethylaniline decreases. The purified gases leaving the absorption tower are first scrubbed with a solution of sodium carbonate, to remove residual sulphur dioxide and entrained dimethylaniline, and are then contacted with dilute sulphuric acid which reacts with any remaining dimethylaniline vapour to give dimethylaniline sulphate.

Sulphur dioxide is removed from the sulphur dioxide-enriched absorption solution by steam stripping. The recovered sulphur dioxide is cooled to remove water vapour and dimethylaniline vapour and is then dried in a dehydrating tower. The lean dimethylaniline solution is separated from entrained water and is then re-cycled to the absorption tower. The recovery of dimethylaniline, from the gases leaving the absorption tower and from the residue from the steam-stripping process, is necessary to render the process economical.

The Asarco DMA process was developed about twenty-five years ago and achieved a 99% removal of sulphur dioxide from gas streams containing 5% sulphur dioxide (434). Two small plants using this process are still in operation in the United States for the treatment of smelter gases containing over 4% sulphur dioxide (10).

(b) The Lurgi Sulphidine Process

In the sulphidine process (274, 434, 435), which has been used industrially in Germany, an approximately 1 to 1 suspension of xylidene ($C_6H_3(CH_3)_2NH_2$) or toluidene ($C_6H_4CH_3NH_2$) in water is used as an absorbent for sulphur dioxide (Equations 137 and 138).

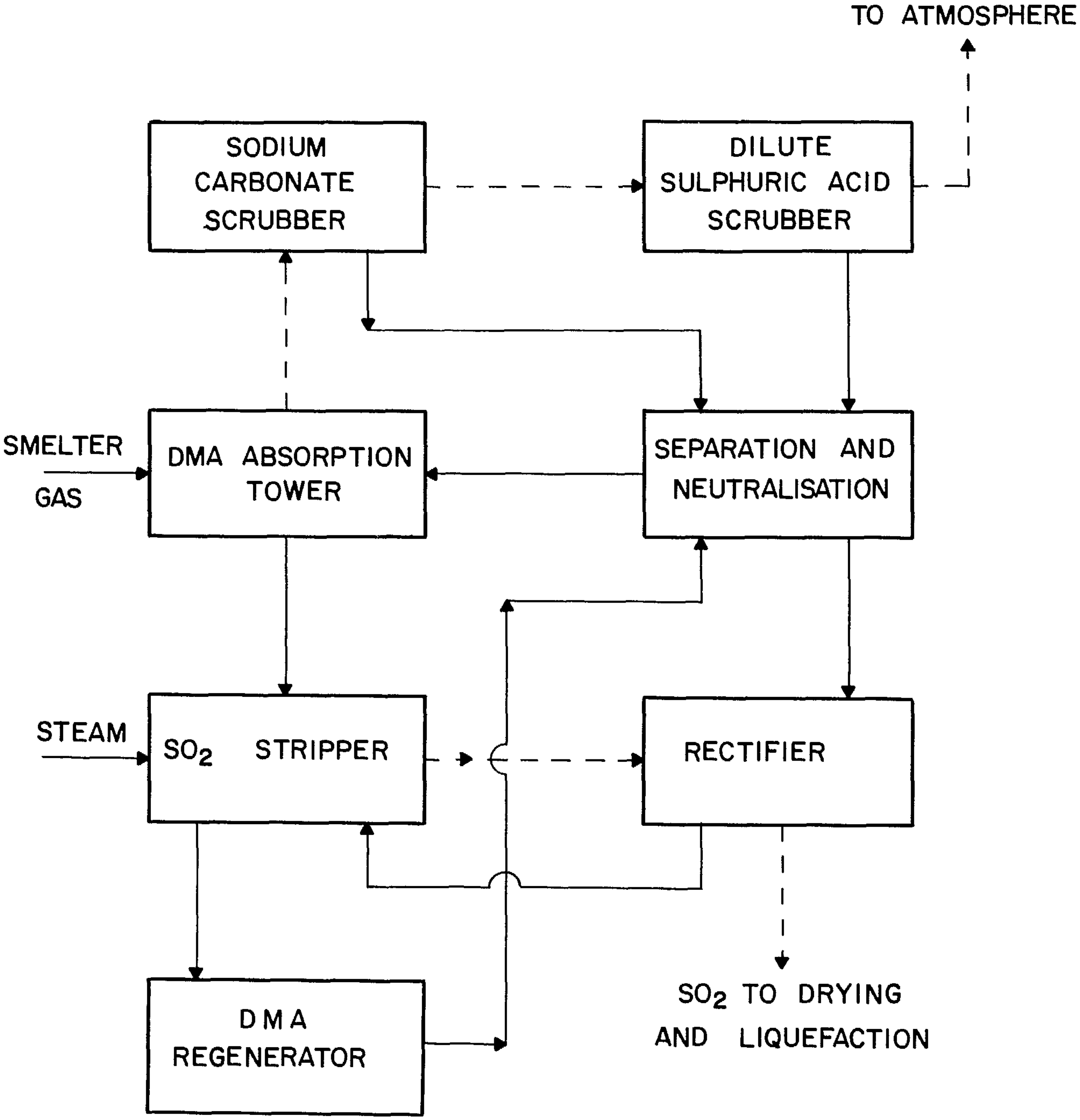

FIGURE 20. THE ASARCO DMA PROCESS

$$C_6H_3(CH_3)_2NH_2 + SO_2 + H_2O = C_6H_3(CH_3)_2NH_3HSO_3 \quad \ldots \text{(Eq. 137)}$$

$$2C_6H_3(CH_3)_2NH_2 + SO_2 + H_2O = [C_6H_3(CH_3)_2NH_3]_2SO_3 \quad \ldots \text{(Eq. 138)}$$

The absorbed sulphur dioxide is recovered from the spent absorption solution by thermal stripping. Although the absorption solution has a high capacity for sulphur dioxide (~220 g/l), the process is complicated by the need to recover xylidene vapour from the purified gases and is economical only for gases high in sulphur dioxide. A small amount of sulphate is also formed during absorption (Equation 139).

$$[C_6H_3(CH_3)_2NH_3]_2SO_3 + \tfrac{1}{2}O_2 = [C_6H_3(CH_3)_2NH_3]_2SO_4 \quad \ldots \text{(Eq. 139)}$$

The concentration of sulphate in the absorbent solution is controlled by the addition of sodium carbonate (Equation 140), and the sodium sulphate that is formed is removed in the waste water.

$$[C_6H_3(CH_3)_2NH_3]_2SO_4 + Na_2CO_3 = 2[C_6H_3(CH_3)_2NH_2] + Na_2SO_4 + CO_2 + H_2O \quad \ldots \text{(Eq. 140)}$$

The high losses of xylidene, both in the purified gas and as soluble xylidene sulphate, make the sulphidine process uneconomical and development of it has been discontinued.

Organic Solids

The application of organic solids to the removal of sulphur dioxide from gas streams has received relatively little attention as compared to other sulphur removal methods (436). This lack of attention is no doubt due in part to certain inherent properties of most organic solids, viz., high cost, poor thermal stability, and optimum adsorption capacity at low temperatures. Several laboratory studies have been made of the suitability of organic ion-exchange resins for sulphur dioxide adsorption and both thermal and chemical regeneration techniques have been employed to regenerate the loaded resins. Thus, Cole and Shulman (437) showed that the equilibrium uptake of sulphur dioxide on several commercial ion-exchange resins depended on the functional group and on the porosity of the resin, also that the resins had adsorption capacities similar to typical inorganic adsorbents such as charcoal and silica gel. However, the rates of approach to adsorption equilibrium with the resins were slow and, when the concentration of sulphur dioxide was low, molecular sieves were much better adsorbents.

Layton and Youngquist (438) studied the adsorption capacity for sulphur dioxide of the weak-base, macroreticular ion-exchange resin Amberlyst A-21 (Rohm and Haas Company). It was found that a large fraction of the sulphur dioxide adsorbed on the fresh resin could not be removed by thermal treatment or by low-pressure regeneration. However, the residual capacity of the regenerated resin for sulphur dioxide remained higher than either charcoal or silica gel but was somewhat less than the capacity of molecular-sieve adsorbents. The resin also had a large heat of adsorption, which means that the adsorption capacity of the resin decreases rapidly with increase in temperature; this property is useful for thermal regeneration but limits the upper temperature at which adsorption may be conducted.

For some other types of weakly basic ion-exchange resins, it has been found that successive adsorption-regeneration cycles lead to a decrease in the adsorption capacity of the resin (439). A study of a series of resins of the R-OH type of different basicities indicated that the more basic resins gave the best retention of sulphur dioxide (440). In this and other studies of ion-exchange resins (441-443), chemical regeneration of the resin was employed, and in some cases oxidation of the adsorbed sulphur dioxide to sulphate was observed (441, 442).

No studies have been noted in which organic ion-exchange resins have been used for the removal of sulphur dioxide from the waste gases emitted from industrial operations.

A study has been made of several nitrogen-containing polymers as adsorbents for sulphur dioxide (444, 445). These polymers were incorporated into melt-spun fibres and were examined on the basis of sulphur dioxide capacity, regeneration ability, and resistance to degradation in a simulated flue gas. On the basis of these criteria the compound selected as the most suitable adsorbent for sulphur dioxide from a flue gas was a styrene-dimethylpropylmaleimide copolymer. A fibre was prepared containing 60% of this copolymer, with polypropylene as the fibre-forming constituent. It was found that the adsorption capacity of this fibre for sulphur dioxide decreased with increasing temperature, and that its useful upper temperature limit was about 95°C. During successive adsorption-regeneration cycles, using a simulated flue gas as a source of sulphur dioxide, a build-up of sulphate occurred on the fibre. Since the sulphate could not be regenerated thermally, the adsorption capacity of the fibre decreased with re-cycling. At the moment this process shows promise only for the treatment of relatively cool flue gases ($T < 95°C$).

Materials containing cellulose, such as cotton, paper, and sawdust, also offer some promise as inexpensive adsorbents for sulphur dioxide (438). A preliminary investigation has shown that waste newsprint can adsorb up to 10% of its weight of sulphur dioxide from a simulated flue gas at 215°F and that the adsorbed sulphur dioxide may be recovered by heating between 350 to 450°F (445).

PHYSICAL SEPARATION METHODS

Ham et al. of the Westinghouse Electric Corporation in the United States have made an extensive study of a number of physical techniques that could, in principle, be used for the removal of sulphur dioxide from the flue gases of power stations (447). The following criteria were specified for this study.

(i) The flue gas was at a temperature of 300-400°F and one atmosphere pressure, and contained 3000 ppm of sulphur dioxide.

(ii) The removal efficiency of the process for sulphur dioxide should be not less than 90%.

All of the physical techniques examined in this study were rejected as unsuitable for further more detailed investigation either because of uncertain technical feasibility or because of unfavourable costs. A brief summary of the methods examined and of the reasons for rejection are given below.

(a) Gaseous Diffusion

The best-known application of this method is for the separation of uranium isotopes as performed in a number of national atomic energy programs. The diffusion process is also technically feasible for the removal of sulphur dioxide from flue gases. However, preliminary design and cost calculations for a cascade separation system, based on Oak Ridge National Laboratory experience with uranium enrichment, indicated that for a 500-MW power plant the capital cost alone of the separation system would be $650/ kW, making the process uneconomical.

(b) Membrane Separation

The membrane separation process depends upon the ability of one component of a gaseous mixture to diffuse more quickly than the other components through certain polymeric materials. Silicone rubber is one of the best membrane materials for the separation of sulphur dioxide from a flue gas, and, for a membrane 0.002 inches-thick, sulphur dioxide has an eight-times greater diffusion rate than carbon dioxide. A cost analysis of a seven-stage diffusion system, coupled to a 600-MW power plant. indicated a capital cost of $133/ kW, making the process uneconomical.

A brief examination was also made of the application of immobilised liquid membranes for the separation of sulphur dioxide from flue gases. Although these membranes have been used successfully to separate carbon dioxide from a carbon dioxide-oxygen mixture (448), it was shown that they offered no advantages over wet scrubbing for the removal of sulphur dioxide from flue gases.

(c) Centrifuge Separation

It was found that the use of a series of centrifuges in cascade would be technically feasible for the separation of sulphur dioxide from a flue gas and that the cost of separation would be somewhat dependent on the material of construction of the centrifuge, e.g., titanium, maraging steel, or filament-wound glass resin. However, regardless of the constructional material, the minimum cost for the separation of the sulphur dioxide from the flue gas would be greater than $100/kW which renders the process uneconomical for application to power stations.

(d) Condensation Separation

The passage of flue gases over a cryogenically cooled surface (-194°F) to condense sulphur dioxide from the gas phase was found to be technically unattractive because the fiftyfold excess of carbon dioxide over sulphur dioxide in the gas phase would lead to blocking of the condenser tubes with solid carbon dioxide. An alternative condensation technique that was perhaps technically feasible but which was totally uneconomical involved the use of the Joules-Thomson effect,to form solid carbon dioxide and liquid sulphur dioxide from the flue gas, and cyclone separation of the two phases.

(e) Other Physical Techniques

Two other physical techniques that were rejected were a mass spectrometer separation -- a method that is technically feasible but which operates at a low gas pressure and possesses a small throughput -- and the use of high-intensity magnetic fields to modify the transport properties of the components of the gas phase. The latter method would require very large magnetic fields (10^5-10^7 gauss) and possesses doubtful technical feasibility.

Three techniques that involve the oxidation of sulphur dioxide were also examined in the Westinghouse study.

(i) An electrical discharge process that has been proposed for the oxidation of relatively high concentrations of sulphur dioxide (449).

(ii) The application of high-intensity electromagnetic radiation from a continuously operated laser.

(iii) The application of electron irradiation either from an electron accelerator or from an isotopic source.

Although these three methods were considered to be technically feasible, they possess a low efficiency for the conversion of sulphur dioxide to sulphur trioxide and were felt to offer no advantages over the well-established catalytic oxidation methods used in the production of sulphuric acid. However, a preliminary investigation by Palumbo and Fraas (451) indicates that the application of a pulsed, high-frequency current may have applications to the removal of sulphur dioxide from gaseous mixtures. The concept involved in this study was that, since the ionization energy of sulphur dioxide is less than the ionization energy of the other major constituents in a flue gas, the sulphur dioxide may preferentially take part in reactions induced by the high-frequency current and be removed from the flue gas as a low vapour-pressure product. Strong evidence for such an effect was found for a 0.979% sulphur dioxide-nitrogen mixture containing 4% of humidified air. About 96% of the sulphur dioxide was removed as sulphur and sulphuric acid, indicating that this technique may have possibilities for sulphur dioxide removal.

SUMMARY

The outstanding technical and economic problem in the control of sulphur dioxide emissions is the treatment of waste gases containing low concentrations of sulphur dioxide. In recent years there has been intensive research and development on methods for the removal of sulphur dioxide from such gases and some of the more promising methods are undergoing, or about to undergo, large-scale testing to assess their costs and operating reliability. These removal methods include carbon adsorption processes, several aqueous scrubbing processes, the catalytic oxidation process, and the molten carbonate process. In the next few years, sufficient experience should have been gained with these removal methods to allow a meaningful comparison of the different processes to be made. It appears likely, however, that no single removal method will be appropriate for all situations and that the selection of a given removal method will depend on the complex inter-relationship of a number of technical and economic factors that will be specific to the particular industrial operation. Currently, in North America, under the impetus of impending pollution control legislation, the lime/limestone scrubbing process is favoured as the short-range solution for the treatment of waste gases containing low concentrations of sulphur dioxide. This method possesses some unresolved technical problems, which are being actively investigated, and removes sulphur dioxide as gypsum which is discarded as a waste product. With the present depressed international market for sulphur, the disposal of gypsum avoids the difficulty of selling large quantities of sulphur, or a sulphur-containing product. Thus, if the economic penalty of a "throw-away" process is no greater than the additional costs involved in a process for recovering and selling sulphur dioxide of low market value, there is no economic incentive to incur the process complications and expense of a sulphur dioxide removal and recovery method.

For waste smelter gases containing more than 3.5 to 4% sulphur dioxide, the sulphuric acid contact process is widely used for the control of sulphur dioxide emissions. However, unless the smelter has an assured market for concentrated sulphuric acid, the sale of large quantities of sulphuric acid can present a difficult marketing problem. In some cases, where the smelter is a long distance from potential markets, serious consideration is being given to the neutralization of excess sulphuric acid with limestone, the resulting calcium sulphate being discarded as a waste product. It may be expected that modifications to current smelting practice will result in waste gases having higher concentrations of sulphur dioxide than at present. The direct reduction of sulphur dioxide to sulphur should then be performed readily without the need for a preliminary sulphur dioxide concentration step. The recovered sulphur could then be stored until a favourable market situation develops.

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APPENDIX A

SUMMARY OF PROCESSES FOR THE REMOVAL OF SULPHUR DIOXIDE FROM WASTE GASES

Table 10 contains an alphabetical listing of sulphur dioxide removal methods that have been developed or are currently under active investigation. Included in this table are a very brief description of the removal process, the type of gas stream to which it is applicable, the end product of the removal process, and the page in the main body of this report where further details and literature references to the process may be found.

TABLE 10

Summary of Processes for the Removal of Sulphur Dioxide from Waste Gases

Process (Main developer, where relevant)	Brief Process Description	End Product of Process	Type of Gas Treated	Current Stage of Process Development	Page Process Noted in this Report
Alkalized Alumina Process (U.S. Bureau of Mines, CEGB, England)	SO_2 is absorbed on alkalized alumina at 290 to 360°C. The spent absorbent is removed from the gas stream and regenerated by reduction with reformed natural gas at 650 to 700°C.	H_2S	Flue gas	Extensive laboratory and pilot plant studies in the U.S.A. Process development discontinued recently in the U.S.A. because of high requirements for reducing gas and high absorbent losses through attrition.	80
Allied Chemical Process	Methane reduction process. Details not published.	S	Smelter gas	A 150,000-tons/year sulphur recovery plant, installed recently at Falconbridge, Ontario, is undergoing operational testing.	114
Asarco Process	Non-catalytic methane reduction process, followed by a two-stage process for the treatment of COS and H_2S formed during reduction.	S	Smelter gas	Pilot plant operation in the 1940's. Large pilot plant now under construction at El Paso, Texas, to treat copper smelter gases.	112
Basic Aluminum Sulphate Process (ICI, Ltd.)	Gas stream scrubbed with solution of $Al(OH)SO_4$ to give $Al(OSO_2H)SO_4$ and $Al(OSO_3H)SO_4$. $Al(OSO_2H)SO_4$ regenerated by heating. Oxidized sulphate removed by precipitation with $CaCO_3$	SO_2, $CaSO_4$	Smelter gas	Operated commercially in Finland, 1936-1941. Process not in current use.	16
Battersea Process	Thames river water with added lime used as a scrubbing medium, giving $CaSO_3$ and $CaSO_4$. Mn^{2+} added to effluent solution to convert $CaSO_3$ to $CaSO_4$ for disposal in the Thames.	$CaSO_4$	Flue gas	In use with several British power plants.	14

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Process (Main developer, where relevant)	Brief Process Description	End Product of Process	Type of Gas Treated	Current Stage of Process Development	Page Process Noted in this Report
Boliden Process	Coke reduction of part of the gas stream to give primarily S, COS, CO, CO_2 and H_2S which are reacted with the remainder of the feed gas in two catalyst chambers.	S	Smelter gas	Plant with 20,000-25,000 tons/year capacity operated in Sweden between 1933 and 1943. Process not in current use.	111
Catalytic Oxidation Process	Oxidation of SO_2 to SO_3 over a V_2O_5 catalyst. Minimum concentration of $SO_2 \simeq 4\%$.	H_2SO_4	Smelter gas	Widely used commercially in the treatment of smelter gases.	98
Cat-Ox Process (Monsanto)	Modification of contact process to treat gases with a low concentration of SO_2.	H_2SO_4	Flue gas	Feasibility studies on thermal power plants, full-scale commercial installation underway on 100-MW power plant.	100
Chevron Research Process	CO is introduced into gas stream to reduce SO_2 to sulphur over a catalyst at ~540°C.	S	Flue gas	Laboratory studies.	116
Citrate Process (U.S. Bureau of Mines)	SO_2 is absorbed in an aqueous citrate solution at 50°C. Spent absorbent is regenerated with H_2S at 130°C. Overall process is a liquid-phase analogue of Claus reaction.	S	Flue or smelter gas	Pilot-plant operation with reverberatory furnace gas (400 cu ft/min).	30
Combustion Engineering Process	Limestone injection into a boiler removing all the SO_3 and some SO_2. Most of the remaining SO_2 is removed by wet scrubbing using calcined additive as the absorbent.	$CaSO_3$/ $CaSO_4$	Flue gas	Tested at a number of power utilities in the U.S.A.	61
Cominco Absorption Process	SO_2 absorbed in an ammonia-based solution, and recovered from the scrubber side stream by acidification with sulphuric acid.	SO_2, $(NH_4)_2SO_4$	Smelter gases, particularly in the 1% SO_2 concentration range	In full-scale use at Trail, British Columbia for over thirty years.	36

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Process (Main developer, where relevant)	Brief Process Description	End Product of Process	Type of Gas Treated	Current Stage of Process Development	Page Process Noted in this Report
Cominco Exorption Process	SO_2 absorbed in an $(NH_4)SO_3$ solution and recovered by heat treatment of side stream of scrubbing solution, $(NH_4)_2SO_3$ returned to scrubber.	SO_2, $(NH_4)_2SO_4$	Smelter gas	Operated for a limited time in the early 'forties at Trail, British Columbia.	37
DMA Process (American Smelting and Refining Co.)	Dimethylaniline used as absorbent, SO_2 recovered by steam stripping.	SO_2	Smelter gas	Two small plants in operation in the U.S.A.	119
DAP-Mn Process (Mitsubishi Heavy Industries)	SO_2 is absorbed on activated manganese dioxide, which is regenerated by treatment with NH_3 and O_2.	$(NH_4)_2SO_4$	Flue gas	Operated on a 55-MW power plant, a 110-MW unit scheduled for start-up in 1972.	88
Formate Process (Consolidated Coal Co.)	Absorption of SO_2 in an 85% solution of KO_2CH at 200°F. Absorbent regenerated by reduction with CO at elevated temperatures and pressures.	H_2S	Flue gas	Laboratory studies.	33
Fulham-Simon-Carves	SO_2 is absorbed in an ammoniacal solution. H_2SO_4 added to scrubber effluent and autoclaved.	$(NH_4)_2SO_4$, S	Flue gas	Extensively studied on pilot plant scale. Not in current use.	42
Grillo Process	Absorbent of mixed metal oxides and alkaline-earth hydroxides on a coke carrier. Spent absorbent is separated mechanically from the coke carrier and the sulphites are reduced by carbon, off-gases burned to give SO_2.	SO_2	Flue gas	Pilot plant studies.	92
Guggenheim Process	SO_2 is recovered by steam stripping, following absorption in $(NH_4)_2SO_3$ solution, and is reduced by carbon to give S. $(NH_4)_2SO_4$ is also formed during absorption and is reacted with lime to regenerate NH_3 for re-cycle to absorber.	S, $(NH_4)_2SO_4$	Smelter gas	Pilot plant studies. Process not in current use.	39

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Process (Main developer, where relevant)	Brief Process Description	End Product of Process	Type of Gas Treated	Current Stage of Process Development	Page Process Noted in this Report
Haenisch-Schroeder Process	SO_2 absorbed in water is recovered by thermal treatment. Oxidized sulphur species removed by precipitation with lime.	SO_2, $CaSO_4$	Flue gas	Process developed at the end of the last century. Not in current use.	9
Hitachi Process	Low-temperature adsorption of SO_2 on active carbon. Carbon regenerated by water washing.	H_2SO_4 (dil.)	Flue gas	Tested on number of power plants in Japan, 100-MW unit under construction.	66
Howden - ICI Process	Effluent gases scrubbed with a suspension of CaO, $Ca(OH)_2$ or $CaCO_3$. Mixture of $CaSO_3$ and $CaSO_4$ separated from scrubber side-stream for disposal.	$CaSO_3$, $CaSO_4$	Flue gas	Commercial plants operated in Britain in 'thirties and 'forties. Not in current use.	14
ICI Reduction Process	Carbon reduction of SO_2 to give S, CO, COS and H_2S, followed by catalytic stage to treat sulphur-containing gases to yield sulphur.	S	50% SO_2	Small pilot plant in the 'thirties, Not in current use.	112
Kanagawa Process	Process uses various naturally occurring water supplies (sea water, underground water or alkaline water) as absorbent. Efficiency of process said to depend on intimate gas-liquid contact.	-	Flue gas	Pilot plant studies in Japan.	11
Kiyoura Process	NH_3 injection into the gas stream in the presence of a V_2O_5 catalyst. $(NH_4)_2SO_4$ recovered from gas stream.	$(NH_4)_2SO_4$	Flue gas	Pilot plant studies in Japan.	103
Limestone Injection (Numerous organizations)	Powdered limestone (or dolomite) injected into the boiler. Reaction products removed from the gas stream by electrostatic precipitators.	$CaSO_4$, $CaSO_3$	Flue gas	Method employed on an experimental basis in several power plants. Absorbent utilization has been found to be disappointing.	56

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Process (Main developer, where relevant)	Brief Process Description	End Product of Process	Type of Gas Treated	Current Stage of Process Development	Page Process Noted in this Report
Lime/limestone scrubbing (Numerous organizations)	Gas stream scrubbed with a lime/limestone slurry giving $CaSO_3$ and $CaSO_4$; $CaSO_3$ may be oxidized to $CaSO_4$ with air.	$CaSO_3$/ $CaSO_4$	Flue gas, smelter gas	Numerous pilot-plant studies, and full-scale trials planned for 1972 in the U.S.A.	13
Magnesium Oxide (Chemical Construction Co., Babcock and Wilcox Co.)	$MgSO_3$ is formed in a scrubber by the reaction of SO_2 with a suspension of MgO. The $MgSO_3$ is calcined to release SO_2 and MgO for re-cycling.	SO_2	Flue gas, tail gas from H_2SO_4 plant, off-gases from pulping process	Full-scale industrial application with a sulphuric acid plant. Unit for 120-MW power plant under construction.	23
Molten Carbonate Process (North American Rockwell)	A molten eutectic of Li, K, and Na carbonates used as absorbent for SO_2. Regeneration of spent absorbent by reduction with reformer gas.	H_2S	Flue gas	Extensive laboratory studies. Process to be tested on a commercial pilot plant basis by Consolidated Edison Power Co.	104
Princeton Chemical Research Process	Elemental sulphur is reacted catalytically with CH_4 to give H_2S which is then added to the gas stream to react with SO_2 to form S. Some of the S recovered is used to produce H_2S.	S	Flue gas	Laboratory studies underway.	116
Reinluft Process	Low temperature adsorption of SO_2 on active carbon giving H_2SO_4. The H_2SO_4 is reduced by thermal treatment using the adsorbent as the reducing agent.	SO_2	Flue gas	Several industrial trials of the process in Germany.	70
Shell Desulphurization Process (Shell Oil Co.)	SO_2 is absorbed on CuO at ~400°C forming $CuSO_4$. The $CuSO_4$ is reduced with hydrogen giving Cu and SO_2, also at ~400°C.	SO_2, for in-plant conversion to S	SO_2 concentration $\ngtr 0.5\%$	Pilot plant development completed. Process ready for full-scale commercial application.	86

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Process (Main developer, where relevant)	Brief Process Description	End Product of Process	Type of Gas Treated	Current Stage of Process Development	Page Process Noted in this Report
Showa-Denko Process	NH_3 is injected into the gas stream ahead of an aqueous scrubber. Scrubbing with additional NH_3 gives $(NH_4)_2SO_3$ which is oxidized with air to $(NH_4)_2SO_4$.	$(NH_4)_2SO_4$	Flue gas	Tested on a semi-commercial scale since 1966.	39
Still Process	Lignite ash, containing a high concentration of Ca, is hydrated and used as an absorbent for SO_2. The $CaSO_3$ produced is decomposed thermally giving SO_2 and CaO for re-cycle.	SO_2	Flue gas	Pilot plant studies.	93
Stone and Webster/ Ionics Process	SO_2 is absorbed in an aqueous NaOH solution, which is then regenerated electrolytically.	H_2SO_4	Flue gas	Extensive pilot plant studies.	25
Sulfacid Process (Lurgi)	SO_2 adsorbed on beds of active carbon, which are periodically washed with water to desorb H_2SO_4.	H_2SO_4 (dil.)	0.1-1.5% SO_2	Pilot plant studies.	72
Sulphidine Process	SO_2 is absorbed in 1/1 mixture of xylidene and water, forming xylidene sulphite which is decomposed by heat giving xylidene and SO_2.	SO_2	Smelter gas	Used in Germany up to 1946. Not in current use.	120
Texas Gulf Sulfur Process	The catalytic reduction of SO_2 by CH_4 followed by a two-stage catalytic recovery process for various sulphur-containing gases produced during reduction.	S	Smelter gas	Successful pilot plant studies in the late 'fifties at Copper Cliff, Ontario. Process apparently uneconomical for full-scale operation.	113
Trail Process (Cominco)	High-temperature reduction of a concentrated stream of SO_2 by coke. Additional recovery stages for other sulphur-containing compounds are also used.	S	SO_2 + some oxygen	Commercial unit operated at Trail, British Columbia between 1935 and 1943. Process currently used at a Spanish smelter.	110

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Process (Main developer, where relevant)	Brief Process Description	End Product of Process	Type of Gas Treated	Current Stage of Process Development	Page Process Noted in this Report
Ugine Kuhlman-Weiritam Process	NH_3 is injected into the gas stream ahead of an aqueous scrubber. A sidestream of the scrubbing liquid is withdrawn and treated with a lime slurry, liberating NH_3 for re-cycle and precipitating calcium salts.	$CaSO_4$, $CaSO_3$	Flue gas	Pilot plant studies in France.	42
Wellman-Lord Process	SO_2 is absorbed in an aqueous sulphite solution, from which it is recovered by thermal stripping.	SO_2	0.15-2% SO_2	Several commercial units installed or under construction.	18
Westvaco Process	SO_2 is adsorbed on active carbon giving H_2SO_4 which is reacted with H_2S to yield sulphur and/or SO_2. Some of the recovered S is reacted with H_2 to give H_2S for use in the reduction stage.	S	Flue gas	Process under development.	74
Wet Thiogen Process	SO_2 is absorbed in H_2O. Scrubber solution reacted with BaS to give S and insoluble barium salts. These salts are heated and then reacted with carbon to give BaS for re-cycle.	S	Smelter gas	Process studied in early 1900's. Development discontinued after pilot plant investigations.	17
Zinc Oxide Process	SO_2 is absorbed in an Na_2SO_3 solution forming $NaHSO_3$. A sidestream of the absorption solution is reacted with ZnO yielding hydrated $ZnSO_3$ and Na_2SO_3 for re-cycle. The $ZnSO_3$ is calcined to give ZnO for re-use and SO_2.	SO_2	Flue gas	Pilot plant studies in the U.S.A. in the 1940's. Process not in current use.	20

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