CONTROL OF SO_2 IN THE FLUE GASES OF FOSSIL FUEL POWER PLANTS

by

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INTRODUCTION

It is a characteristic of civilization that the progress in the development of human life is always accompanied by various adverse effects. The combustion of fuel for useful heat has been known by human beings since civilization began. More recently, combustion has been used extensively for thermal power generation. "In the next 15 years, as much coal and oil-fired power generating capacity will be built by U. S. power companies as exists today. ..... before the year 2000, fossil fuel fired plant capacity may then double again (1)." Applauding the progress in the prosperity of our civilization, however, we suffer its byproducts at the same time .

There are four major pollutants from fossil fuel burning power plant - sulfur oxides, nitrogen oxides, flyash and submicron particulates. Of these, sulfur dioxide is the most significant noxious material emitted to the atmosphere. Because it has an adverse effect on human health, inhibits the growth of vegetation, causes corrosion of metals and damages the construction of buildings, it is of great public concern. Sulfur dioxide is, according to a survey of Air Pollution Control Office, responsible for 18 percent of the total air pollution in the U. S. A.. The actual sulfur dioxide emission into the air is 21 million tons each year as the result of combustion coal and fuel oil (2). If the emissions continue to be uncontrolled, they are projected to increase by a factor of five in 30 years. If all the work now underway to develop control methods is successful, the increase

can be held to a factor of two or three (3). The need for methods to reduce sulfur dioxide emissions from existing boilers, and those as yet unbuilt, is, therefore, quite pressing. Fig. 1 shows the emission rates as projected by Squires (4).

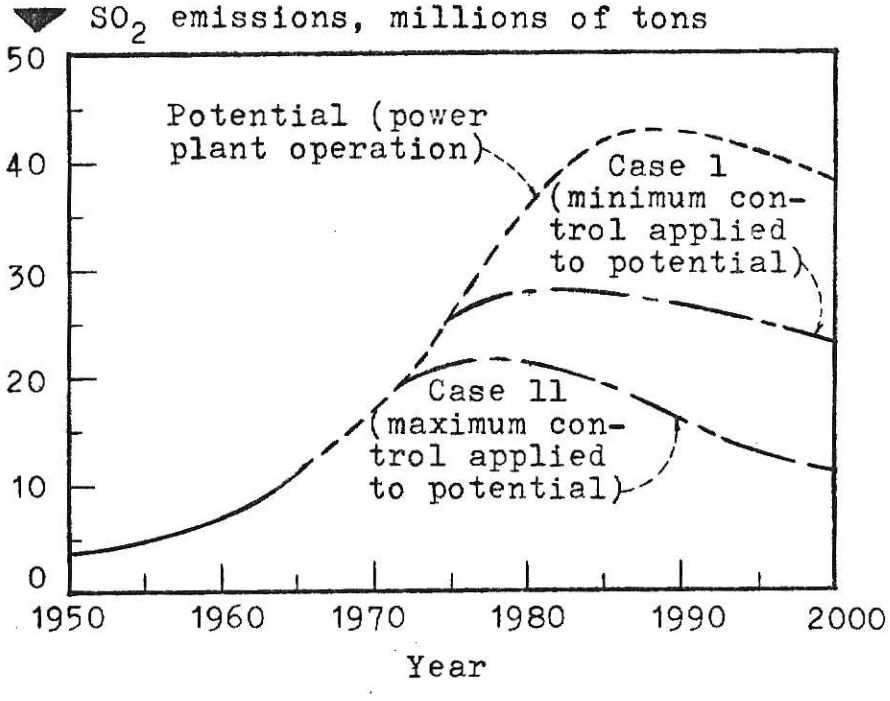

Figure 1. Projected power station SO_2 for U.S. (From M. Squires, Chemical Engineering, Nov. 6, 1967)

PHYSICAL AND CHEMICAL PROPERTIES OF SULFUR DIOXIDE (5)

The oxides of sulfur generally can be divided into six types. These are sulfur monoxide (SO), sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfur sesquioxide (S_2O_3), sulfur heptoxide (S_2O_7) and sulfur tetroxide (SO_4). Except for sulfur dioxide (SO_2) and sulfur trioxide (SO_3), the remainder are unstable and difficult to form in the atmosphere, although it has been suggested that sulfur heptoxide (S_2O_7) can be produced in some atmospheres due to the reaction between sulfur dioxide and ozone. Fossil fuels, such as coal and oil, burnt in the air, will form sulfur dioxide and sulfur trioxide in the ratio of 25 to 30 parts to 1 part.

PHYSICAL PROPERTIES OF SULFUR DIOXIDE

Sulfur dioxide is a non-flammable, non-explosive, colorless gas. The solubility of sulfur dioxide in water is high when it is compared with oxygen, nitric oxide, carbon monoxide and carbon dioxide. For example, at $20^{\circ}C$, the solubility of sulfur dioxide in water is 11.28g/100ml. However, the other gases have solubilities of 0.004 for oxygen, 0.006 for nitric oxide, 0.003 for carbon monoxide and 0.169 for carbon dioxide. Sulfur dioxide also has a pungent, irritating odor in concentrations over 3 ppm. Most people can detect it at concentrations from 0.3 to 1 ppm in air. Some important physical properties of Sulfur dioxide are listed as follows.

Physical Constants of Sulfur Dioxide

Molecular weight	64.06
Density (g/l) (gas)	29.27 at $0^{\circ}C$; 1 atm
Specific gravity (liquid)	1.434 at $10^{\circ}C$
Molecular volume (ml) (liquid)	44
Melting point ($^{\circ}C$)	-75.46
Boiling point ($^{\circ}C$)	-10.02
Critical temperature ($^{\circ}C$)	157.2
Critical pressure (atm)	77.7
Heat of fusion (Kcal/mole)	1.769
Heat of vaporization (Kcal/mole)	5.96
Viscosity (dyne sec/cm^2)	0.0039 at $0^{\circ}C$

CHEMICAL PROPERTIES OF SULFUR DIOXIDE

Sulfur dioxide can act as either a reducing agent or as an oxidizing agent. It is oxidized in the atmosphere by either photochemical or catalytic activation with materials to form sulfur trioxide, sulfuric acid and acid salts, which is our main concern in the problem of air pollution.

At room temperature, sulfur dioxide reacts with hydrogen sulfide (H_2S) to produce elemental sulfur and water, and at higher temperature, it reacts with active metals and amalgams to form oxygen containing anions and sulfides. At $400^{\circ}C$ it is oxidized slowly by oxygen to form sulfur trioxide, but when catalysts are present, the reaction occurs even at room temperature.

In the presence of oxygen and water, ferrous sulfate ($FeSO_4$) catalyzes sulfur dioxide directly to sulfuric acid.

Aluminum oxide (Al_2O_3), magnesium oxide (MgO), ferric oxide (Fe_2O_3), zinc oxide (ZnO), manganic oxide (Mn_2O_3), cerium oxide (Ce_2O_3) and cupric oxide (CuO) can oxidize sulfur dioxide directly to sulfate.

Lead peroxide (PbO_2) and hydrogen peroxide (H_2O_2) are active oxidizing agents. Both of them are used in the analysis of sulfur dioxide in air. Sulfur dioxide also reacts with halogens. Its reaction with iodine is the basis for one of the methods used to measure sulfur dioxide.

Sulfur dioxide reacts with water to form sulfurous acid (H_2SO_3), which is unstable and is oxidized by oxygen from air to form sulfuric acid (H_2SO_4).

FORMATION AND SOURCES OF SULFUR DIOXIDE

FORMATION OF SULFUR DIOXIDE IN THE BOILER (6)

During combustion, almost 90 percent or more of the sulfur present in fuels is converted to sulfur oxides, primary sulfur dioxide. Orning (7) presents data indicating that the average sulfur content of coals used for electric power production in the United States may be taken as 2.5 percent. Residual oil may have a sulfur content from less than 1 percent to more than 4 percent. Many investigators have studied the amount of sulfur dioxide that is converted to sulfur trioxide. Generally, the value is accepted as 1 to 5 percent. The complex process of formation of sulfur trioxide in boilers has not been understood thoroughly as yet. The possible mechanisms suggested are as follows.

(a) The oxidation of SO_2 by molecular O_2

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Increasing the pressure causes a shift in the direction of decreased gas volume, that is, in the direction of SO_3 formation. Increasing the temperature shifts the equilibrium toward greater concentration of SO_2.

(b) Formation of SO_3 in the flame is caused by reaction of atomic oxygen with SO_2 and is given by the following.

$$SO_2 + O \longrightarrow SO_3$$

Atomic oxygen is derived from reactions such as

$$CO + O_2 \longrightarrow CO_2 + O$$

$$H + O_2 \longrightarrow OH + O$$

(c) Catalytic oxidation of SO_2

Many investigators have determined that the iron oxide (Fe_2O_3) on boiler surfaces has a catalytic effect on the oxidation of SO_2, and this effect is significant at a metal temperature of about 1100F. The change in the oxide layer from Fe_2O_3 to Fe_3O_4 may alter the catalytic effect.

SOURCES OF SULFUR DIOXIDE IN THE ATMOSPHERE

Sulfur dioxides found in the atmosphere are emitted from power plants burning fossil fuels, smelters, oil refineries, sulfuric acid plants, furnaces burning fuel oil and other sources. The electric industry accounts for more sulfur dioxide emissions than any other source. In October 1971, Plumley (8) presented in COMBUSTION that "In 1968, approximately 33.2 million tons of sulfur oxide, primarily SO_2, was emitted in the United States. Nearly 76 percent, or 26 million tons, was produced by combustion of fossil fuels. Of this amount, 16.8 million tons was emitted from electric utility boilers, 7.6 million tons by industrial boilers, and the remainder of the emissions from mobile sources." (See Fig. 2)

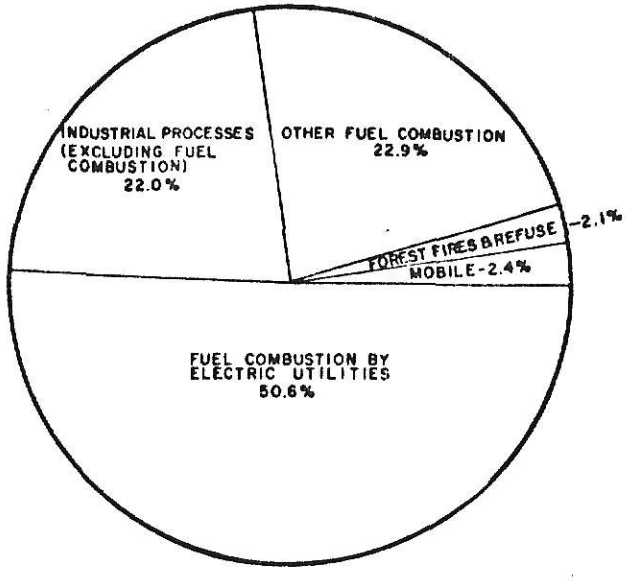

Figure 2. Nationwide sources of SO_2 emissions, 1968. (From A. L. Plumley, COMBUSTION, Oct. 1971)

EFFECTS OF AIR POLLUTED WITH SULFUR DIOXIDE ON PAINTS, METALS, FABRICS AND VEGETATION

EFFECTS ON PAINTS, METALS, AND FABRICS

Atmospheres polluted with sulfur dioxide and its associated acidity, are found to be the most corrosive form of air, even worse than marine atmospheres. Sulfur dioxide in concentrations from 0.1 to 0.2 ppm can destroy certain paint pigments (5). In 1961, Salvin (7) studied color changes on dyed fabric exposed without sunlight in Phoenix, Arizona; Sarasota, Florida; Chicago, Illinois; and Los Angeles, California. The color of the dyed fabric had its greatest change in Chicago where the concentration of sulfur dioxide is high.

The corrosion of metals in the atmosphere is mainly caused by sulfuric acid, which is either formed by sulfur dioxide in the atmosphere or in the droplets on the surface of metals, and this damage is increased with increasing humidity and temperature (5). Gibbons (10) exposed several metals in various sites in Canada. He concluded that "In all cases the Halifax industrial marine site was by far the most corrosive of all the sites. ..... The agressiveness of the Halifax site is attributable in part to the high level of atmospheric sulfur dioxide which influence the rate of corrosion."

Generally, a considerable corrosion of metals would take place even if the annual average concentrations of sulfur dioxide is lower than 0.05 ppm.

EFFECTS ON VEGETATION (5)

There are two kinds of injuries on plants due to sulfur dioxide, acute and chronic injuries. The maximum concentration that can be tolerated by the cells of different kinds of species is almost the same. Sulfur dioxide is absorbed into the mesophyll through stomata. When the concentration of the gas is over the maximum value, the cells are first inactivated, then killed. When great areas of cells have died, the tissues collapse and dry, leaving marks of interveinal and marginal acute injury.

Chronic injury is due to a slow oxidation of sulfite to sulfate in the cells. When only some cells in an area of a leaf are killed, the area will change its color to brownish red owing to sulfate toxicity. The color change is caused by rupture of some cells. Abscission of leaves often occurs at or before this stage.

Plants may also be injured when the concentration of sulfur dioxide does not reach the amount to cause visible leaf injury. For instance, the growth of a rye grass, Lolium perenne, was definitely retarded in an open atmosphere, or in a greenhouse supplied with ambient air, compared with that in a greenhouse supplied with scrubbed air. There was no evidence of acute leaf injury to be found in a greenhouse with unscrubbed air, yet the rate of senescence of plants was greater than those in washed air, and the rate of tiller formation, number of leaves, and dry weight were reduced by the pollution.

Generally, plants with succulent leaves, such as alfalfa, the grains,

grapes, cotton and endive, are more sensitive to sulfur dioxide than those with heavy waxy leaves, such as pine, citrus and privet.

High light intensity, high relative humidity, moderate temperatures and sufficient moisture supply are factors to cause stomata to open, thus facilitating sulfur dioxide to be absorbed, and plants to be injuried.

The U. S. Public Health Service has presented data to show the effects of sulfur oxides on vegetation. Fig. 3 is plotted from those data. The shaded area represents exposures that are known to cause injury to vegetation. The unshaded area represents exposures that are below those that cause visible injury.

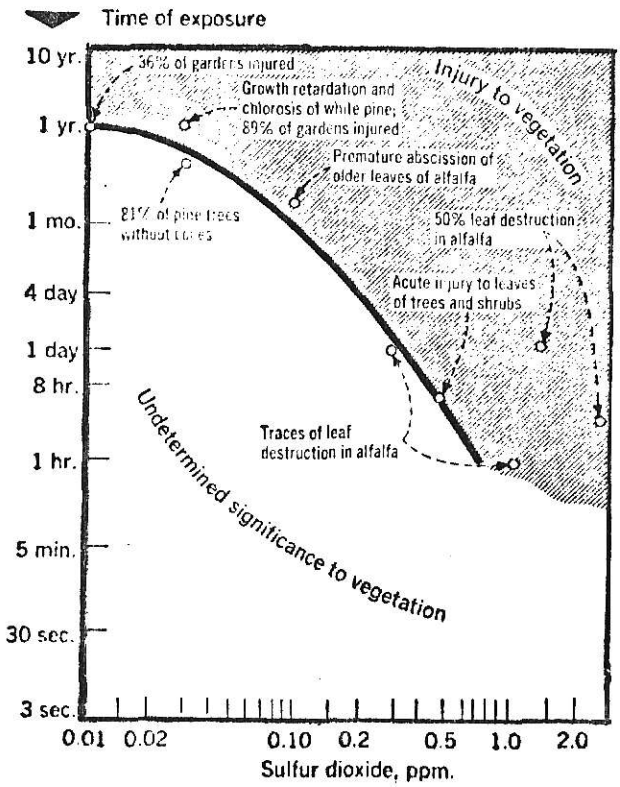

Figure 3. Vegetable destruction from sulfur oxide pollution (From U.S. Public Health Service, Publication No. 1619)

EFFECTS OF AIR POLLUTED WITH SULFUR DIOXIDE ON MAN AND ANIMALS (5)

Reports collected by the U. S. Public Health Service give information on the effects of sulfur dioxide on man and animals.

Detached single cells in tissue cultures were killed at 5 ppm of exposure to sulfur dioxide for eight hours a day for two days. Ciliary movement in isolated trachea ceased after 25 minutes of exposure to 7 ppm. Flow of mucus in all animals was greatly reduced when they were exposed to sulfur dioxide at 10 ppm for tests lasting for 18 or 67 days. There is also a report on the absorption, retention and distribution of sulfur dioxide in the respiratory tracts of animals.

At a concentration of 700 ppm, only 5 percent of the sulfur dioxide reaches the bronchi, however, at 0.05 ppm, 60 percent reaches the bronchi. The percent retention by animals has been shown to decrease with time of exposure and to increase with decreasing concentrations. When humans breathed 16 ppm sulfur dioxide for 30 to 45 minutes, less than two percent reached the pharynx, but 84 percent of this two percent was retained. Absorbed sulfur dioxide is distributed to all parts of the body, and it produces airway resistance via nerve pathways that stimulate receptors to produce reflex bronchoconstriction.

EFFECTS ON PROLONGED EXPOSURES OF ANIMALS TO SULFUR DIOXIDE

Mice and guinea pigs were exposed to sulfur dioxide at concentrations of 33 ppm or below up to 47 days; no significant trouble happened to those

originally healthy. However, the lifespan of rats exposed over their lifetime to concentrations of 1, 2, 4, 8, 16, and 32 ppm of sulfur dioxide would be reduced 0.08 month for each 1 ppm increase in concentration of sulfur dioxide. Rabbits lost their ability to immunize against typhoid either after or during exposure to 7 ppm of sulfur dioxide two hours per day over 5.5 to 8.5 months.

INDUSTRIAL EXPOSURES OF HUMANS TO SULFUR DIOXIDE

One hundred workmen were examined in refrigeration plants where sulfur dioxide concentrations were around 25 ppm; at times concentrations were 80 to 100 ppm, although X-rays showed nothing serious about the lungs or bronchi, symptoms of irritation of the upper respiratory tract were observed. For severe exposure, syptoms were those of coughing, sneezing, eye irritation, sore throat, chest pain and loss of appetite. Most serious cases were tendency to increased fatigue, shortness of breath on exertion, abnormal reflexes and increased duration of colds.

Another example was 53 workers in a German foundry where the concentration of sulfur dioxide had an average value of less than 10 ppm. Most of the workers had worked for ten years. The results of the X-ray examination showed that only seven men had normal lungs whereas in the control group 20 out of 37 had normal lungs.

In determining what levels of sulfur dioxide could be permitted in the atmosphere of cities, the U. S. Public Health Service reviewed the medical evidence and developed the health chart shown Fig. 4. The heavily shaded area represents the duration and concentration of exposures

generally associated with increased mortality. The cross-hatched area represents exposures associated with reports of increased morbidity. The stippled area represents exposures which are expected to be associated with adverse health effects. The unshaded area represents exposures that are not considered to have any immediately apparent significance.

THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPAIRED TO THE REST OF THE INFORMATION ON THE PAGE.

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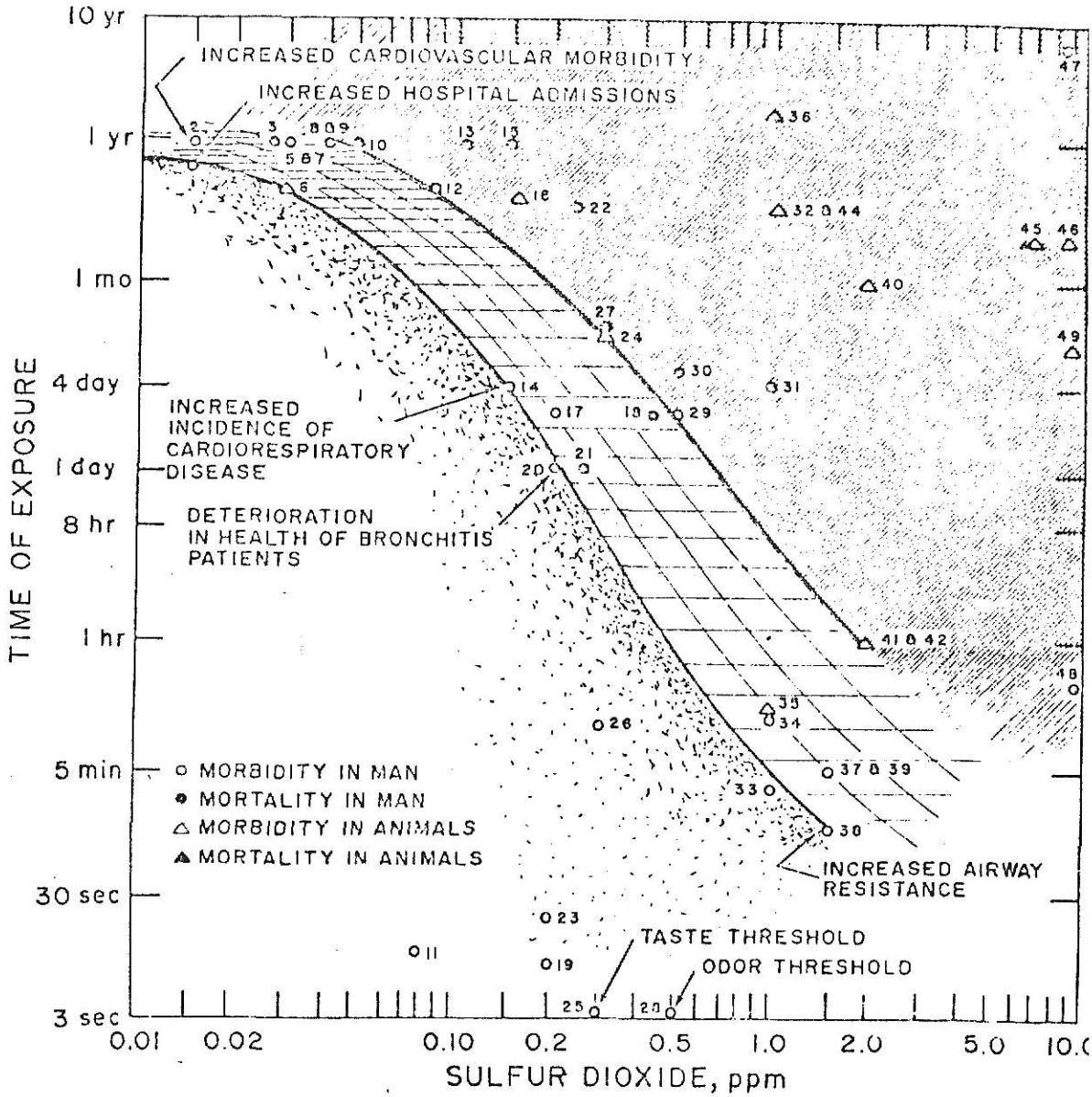

Figure 4. Hazards to health from sulfur oxide pollution (From U.S. Public Health Service, Publication No. 1619)

CONTROL TECHNIQUES FOR SULFUR DIOXIDE

The emission of sulfur dioxide can be controlled in one of three ways.

1. Use of naturally occurring low sulfur oil or coal.
2. Removal of sulfur prior to use.
3. Removal of sulfur dioxide from flue gases.

LOW SULFUR FUELS

The best way of satisfying the demand of control of emission of sulfur dioxide from power plant is to burn low sulfur fuel. Unfortunately, low sulfur fuels generally are not available at a price utilities can pay with their present rate structures. Furthermore, it will not be adequate in the future. Sources of low sulfur fuels (0-1% sulfur) are:

Fuel oil: Lybya, Nigeria, East Texas, Sumatra, Columbia, Argentina, Pennsylvania.

Coal: Southern West Virginia, West Virginia, Western U. S.

DESULFURIZING FUELS

There are problems both in technology and economics to desulfurize fuels before burning. Sulfur in coal can be divided into two parts, organic and inorganic components. Organic components are chemically combined with the coal particles and can not be separated without complete destruction of coal, such as gasification or combustion. Inorganic components are pyites (FeS_2). If existing in large enough particles, they can be liberated by crushing the coal and removing by

float-and-sink method. But in most coal, the particle size is so small that the pyrites can not be effectively removed without carrying away with them a considerable amount of coal. Although we can improve the quality of coal in preparation plants before burning, in most cases the sulfur contents can be decreased less than half of the existing amount. In 1965, 419 million tons of coal were washed, 87 million tons, or nearly 21 percent, were rejected as refuse. The cost is really high (11).

Sulfur in fuel oil can be removed by the process known as hydrodesulfurization, which is to treat the fuel oil with hydrogen and to convert the sulfur contents of the fuel oil to H_2S. Decreasing one third of the sulfur content of a barrel of fuel oil by this method cost 40 cents. In a recent estimation, 60 cents are needed to reduce the sulfur level of one barrel to one percent and 80 cents to 0.5 percent (11).

From the preceding discussion, we learned that, due to technical and economical reasons, fossil fuelds had to be burnt which had a high sulfur content and which resulted in stack gases that had a higher content of sulfur dioxide than that required by law. For this reason it was necessary to consider methods of eliminating sulfur dioxide from flue gases before these gases were discharged to the atmosphere.

REMOVAL OF SULFUR DIOXIDE FROM FLUE GASES

There are dozens of processes proposed for removing sulfur dioxide from flue gases. All processes, whether they involve chemical reaction or physical adsorption, generally can be classified into two categories: those operating dry with hot flue gases and those depending on a wet system. For reducing the cost, some processes are intended to recover sulfur dioxide into useful byproducts, such as, dilute sulfuric acid, fertilizer and, best of all, elemental sulfur.

DRY SYSTEMS

Dry systems are those which remove sulfur oxides through contact with solid or molten salts at relatively high temperatures.

DRY LIMESTONE PROCESS (11-13)

This is the simplest process of all the proposed methods to remove sulfur dioxide from flue gases. Pulverized limestone, or dolomite, is injected directly into the hot flue gas stream; sulfur dioxide is captured by forming, with the limestone, calcium or magnesium sulfates ($CaSO_4$ or $MgSO_4$).

The alternative reaction paths in limestone injection are summarized by the series of equations shown as follow:

$CaCO_3 \rightleftharpoons CaO + CO_2$ (above 600°C)

$CaO + SO_2 \rightleftharpoons CaSO_3$ (300-650°C)

Below 650°C:

In O_2: $CaSO_3 + \frac{1}{2} O_2 \rightleftharpoons CaSO_4$

In SO_2: $CaSO_3 + \frac{1}{2} SO_2 \rightleftharpoons CaSO_4 + \frac{1}{2} S_2$

In SO_3: $CaSO_3 + SO_3 \rightleftharpoons CaSO_4 + SO_2$

Above 650°C:

$4CaSO_3 \rightleftharpoons CaS + 3CaSO_4$

$CaS + 2O_2 \rightleftharpoons CaSO_4$

$CaS + 4SO_3 \rightleftharpoons CaSO_4 + 4SO_2$

This method requires no modifications except providing nozzles for blowing the limestone into the gas stream and means to handle the increased dust loadings. Fig. 5 shows the basic arrangement of this process. If the added limestone were all converted into calcium and magnesium sulfates ($CaSO_4$ and $MgSO_4$), some 460 tons of limestone would be required each day for a 500 megawatt boiler burning a 3 percent sulfur fuel.

With only 25 to 35 percent of sulfur oxides removed in the furnace, this method still has a long way to go before reaching the ever increasing stringency of sulfur dioxide emission standards. The optimum temperatures of injection, the best size of pulverized limestone, the necessary time

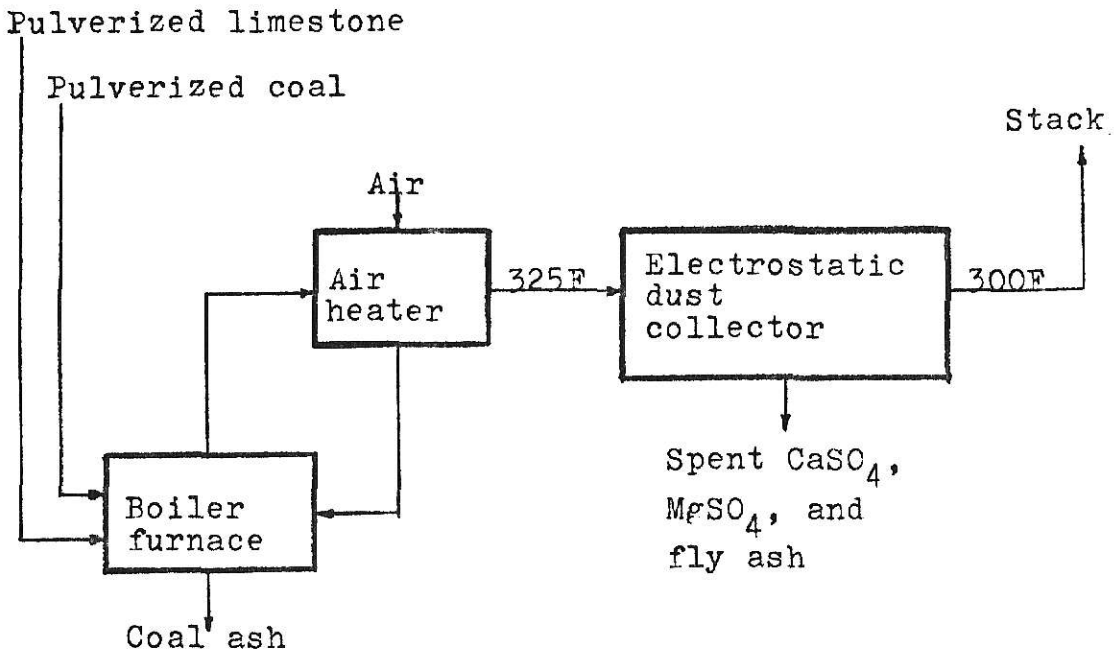

Figure 5. DRY LIMESTONE PROCESS of removing SO_2

to complete the reaction and the required physical and chemical characteristics of limestone are details which are needed before successful designs can be completed. The National Center for Air Pollution Control of the Public Health Service and its supporting laboratories have been investigating these factors for some time.

ALKALIZED ALUMINA PROCESS (11) (13)

This is a dry absorption method, developed by the U. S. Bureau of Mines. Elemental sulfur is recovered as a byproduct. Fig. 6 shows the general arrangement.

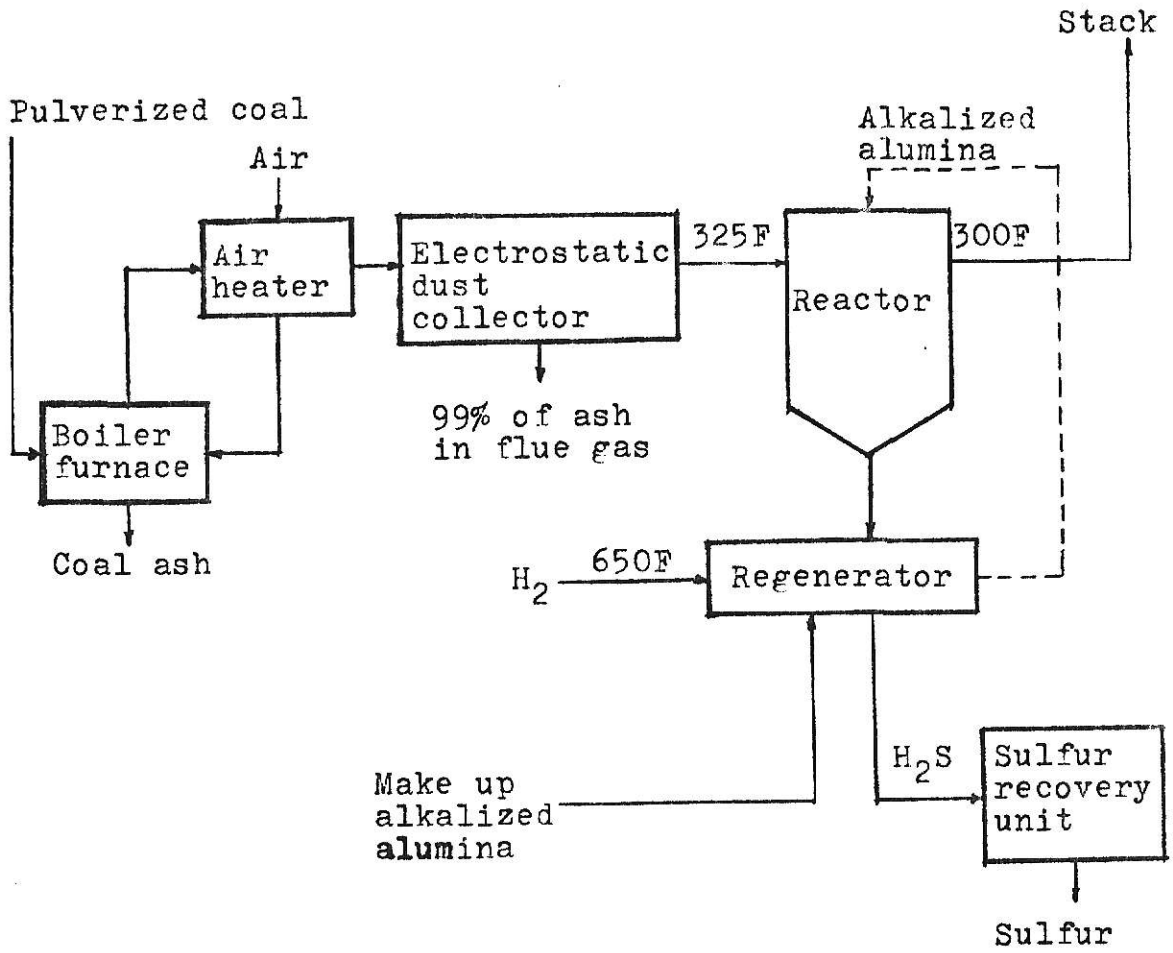

Figure 6. ALKALIZED ALUMINA PROCESS of removing SO_2

Flue gases passing through the dust collector enter the reactor at 325 F. A stream of 1/16-in. diameter pellets of alkalized alumina ($Na_2Al_2O_4$) are dropped from the top of the reactor countercurrent to the gas flow. This material absorbs and reacts chemically with sulfur dioxide and oxygen in the flue gases to form a relatively stable sulfate. The spent alkalized alumina passes into a regenerator where the sulfur is stripped off with added hydrogen, forming hydrogen sulfide (H_2S). The hydrogen sulfide is then moved to a sulfur recovery unit which

produces high quality sulfur. The alkalized alumina after regeneration is sent to the top of the reactor and it dry scrubs the flue gases again.

The ability to recover marketable sulfur to compensate operating cost is the greatest advantage of this process. However, the high attrition of the absorption agent is considered as a serious drawback. Process economics demand a loss of about 0.1 percent, but present losses are seven percent.

It has been reported that this system installed on a small coal-fired plant removed 85 percent of the sulfur dioxide. The Central Electricity Generating Board of Great Britain also has conducted bench scale tests for years.

DAP-Mn PROCESS (12)

This dry absorption system, developed by Japan's Mitsubishi Heavy Industries to remove sulfur oxides, employs absorbent regeneration and recirculation.

The process uses manganese oxide ($MnO_x \cdot iH_2O$) as the absorbent and recovers ammonium sulfate ($(NH_4)_2SO_4$) as a byproduct through the regeneration of the spent absorbent.

Chemical reactions are shown as follow, where x and i vary from 1.5 to 1.8 and 0.1 to 1.0 respectively.

At temperatures of 100°C, manganese oxide has a great affinity for sulfur dioxide.

Absorption:

$$MnO_x \cdot iH_2O + \frac{1}{2} \cdot (2-x)O_2 + SO_2 \longrightarrow MnSO_4 + iH_2O$$

$$MnO_x \cdot iH_2O + SO_3 \longrightarrow MnSO_4 + \frac{1}{2} \cdot (x-1)O_2 + iH_2O$$

Regeneration:

$$MnSO_4 + 2NH_4OH \longrightarrow Mn(OH)_2 + (NH_4)_2SO_4$$

$$Mn(OH)_2 + \frac{1}{2} \cdot (x-1)O_2 + (i-1)H_2O \longrightarrow MnO_x \cdot iH_2O$$

As shown in Fig. 7, the process consists of four steps: absorption, regeneration, soot seperation and crystallization.

Through the disintegrator the powdery absorbent ($MnO_x \cdot iH_2O$) is fed to the absorber where it is dispersed, transported and reacts with the sulfur oxides in the flue gases. The resultant manganese sulfate ($MnSO_4$) and the unreacted absorbent ($MnO_x \cdot iH_2O$) are collected first by mechanical separators and then by electrostatic precipitators. The greater part of the collected absorbent is sent back to the absorber as recycled solids. The remainder is regenerated by the preceding described chemical reactions and then returned to the cycle. To save power and to attain uniform distribution of the absorbent in the gas stream, about 1/4 to 1/6 of the flue gases are bypassed from the main stream before entering into the absorber. Since manganese oxide and sulfur dioxide have a great affinity at temperatures from 100°C to 180°C, absorption takes place at this interval.

Regeneration of the spent absorbent ($MnSO_4$) is accomplished in the oxidizer by pumping manganese sulfate ($MnSO_4$) and ammonium hydroxide (NH_4OH) solutions into the oxidizer and mixing them with the compressed

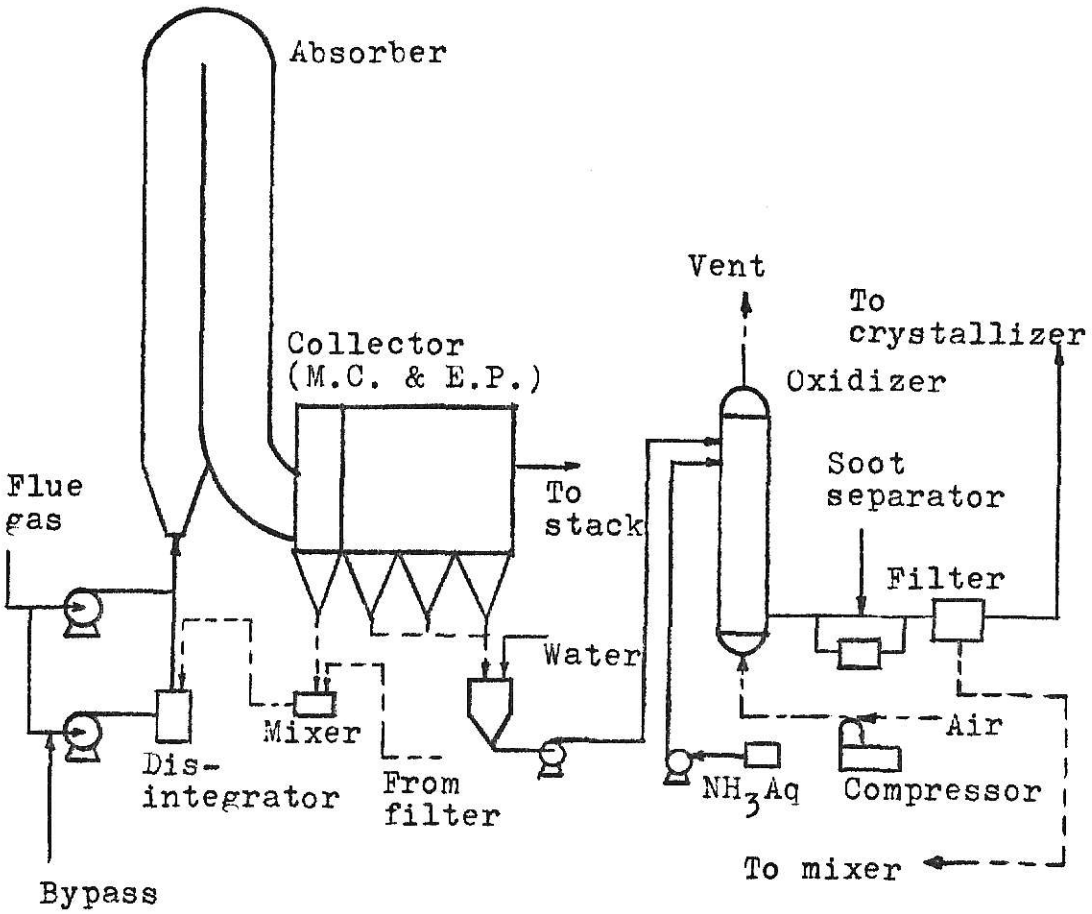

Figure 7. THE DAP-Mn PROCESS

air inside. The resultant fresh absorbent ($MnO_x \cdot iHO$) is filtered out of the ammonium sulfate ($(NH_4)_2SO_4$) solution when the solution passes through the filter. Then the ammonium sulfate solution is fed to the crystallizer and collected as a byproduct.

There is no dust collector before the absorber. Soot is seperated from the absorbent by the flotation method. Kerosene is used as an additive. Tests showed that an excellent quality of ammonium sulfate could be recovered without contamination of soot.

A 90-percent efficiency of removal of sulfur dioxide has been proved in a pilot plant of a 1000 KW. unit. Chubu Electric Power Co. also has started another test on a 222,000 KW. oil-fired power plant at its Yokkachi station. It is said that same result has been achieved.

MOLTEN CARBONATE PROCESS (13) (16)

This is another dry absorption system employing abosrbent regeneration and recirculation. Fig. 8 shows the basic flow diagram.

Flue gases from the boiler are treated in a scrubber with a molten mixture of alkalimetal carbonate salts (a mixture of 32 wt. percent Li_2CO_3, 33 wt. percent Na_2CO_3 and 35 wt. percent K_2CO_3). The molten carbonates react with sulfur oxides to form sulfites and sulfates which remain dissolved in unreacted carbonate. The salt mixture is then

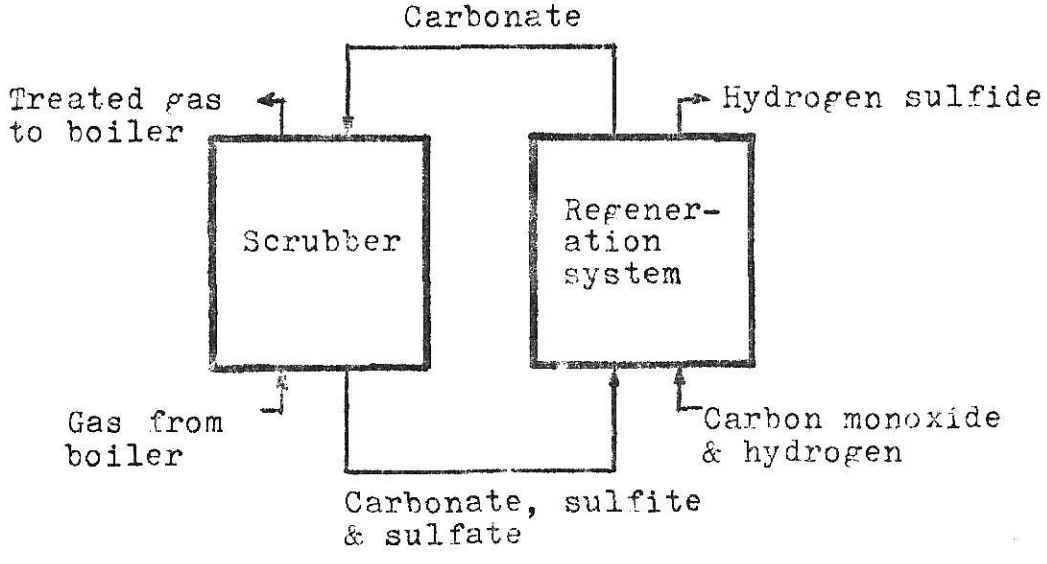

Figure 8. Basic MOLTEN CARBONATE PROCESS flow diagram

circulated to the regeneration system where a mixture of carbon monoxide and hydrogen reacts with sulfite and sulfate, converts them to hydrogen sulfide and thus regenerats the carbonate. The regenerated carbonate is then recirculated to the scrubber to continue the process and the hydrogen sulfide is converted into elemental sulfur or sulfuric acid.

A process which is now being developed change the regeneration system of Fig. 8 to a two-step arrangement (see Fig. 9). By using hydrogen, or carbon monoxide, or mixtures of the two at 1100 F or above, the alkalimetal sulfates and sulfites from the scrubber are reduced to alkalimetal sulfides. Then by reaction with steam and carbon dioxide at 800 F, the alkalimetal sulfides are converted to hydrogen sulfides and the alkalimetal carbonates.

To avoid building up fly ash in the circulating carbonate melt, most of the fly ash is removed before it enters the scrubber and the remainder is filtered out after it leaves the scrubber.

Chemical reaction formulas for the scrubbing step, the reduction step and the regeneration step are shown as follow.

The scrubbing step:

Flue gases are treated with the alkalimetal carbonate melt in the scrubber at 800 F or above.

$$SO_2 + M_2CO_3 \longrightarrow M_2SO_3 + CO_2 \qquad (a)$$

$$SO_3 + M_2CO_3 \longrightarrow M_2SO_4 + CO_2 \qquad (b)$$

where M stands for lithium (Li), sodium (Na) and potassium (K) cations.

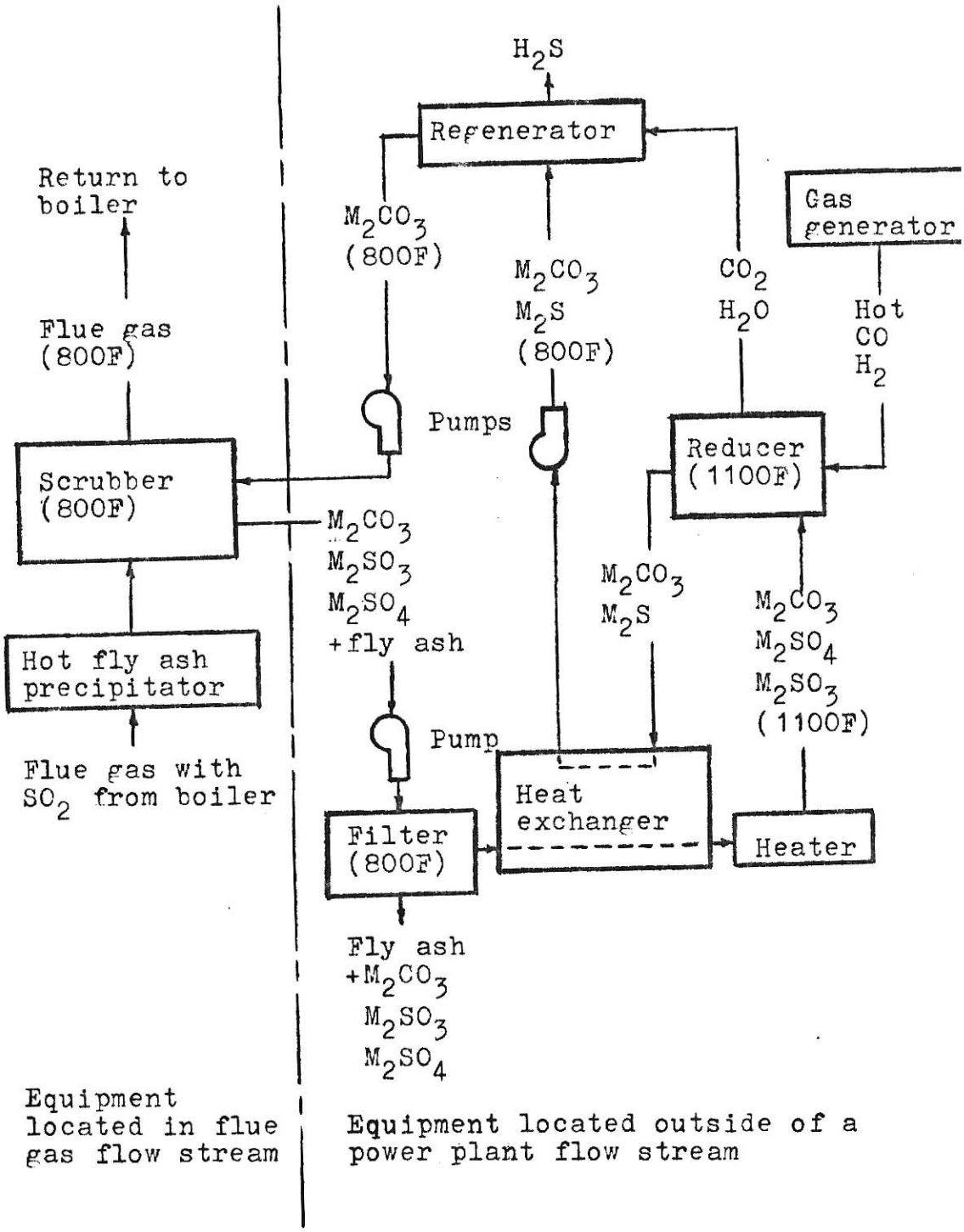

Figure 9. SO_2 removal system flow diagram

The rates of absorption are very rapid and limited only by mass transfer processes. There is also a possibility for M_2SO_3 to be oxidized to M_2SO_4 by oxygen, but the rate of reaction is much slower than that of (a) and (b) and the amount of sulfite oxidized is, as determined by tests, only 10 percent.

$$M_2SO_3 + \frac{1}{2} O_2 \longrightarrow M_2SO_4 \qquad (c)$$

Chemical studies show that the carbonate melt has a high affinity with sulfur oxides. In the scrubbing step, it is important to bring about good contact between the liquid and gas phases without increasing a large pressure drop in the gas stream.

The reduction step:

This step is mainly used to reduce the mixture of sulfites and sulfates, which came from the scrubber, to sulfides. For a more rapid reaction rate, the molten mixture of alkali metal sulfites, sulfates and carbonates are heated to 1100F before entering the reducer. Sulfites in the mixture are caused to react rapidly to form sulfate and sulfide according to the reaction:

$$4M_2SO_3 \longrightarrow 3M_2SO_4 + M_2S \qquad (d)$$

Sulfates are reduced by hydrogen and carbon monoxide from the gas generator to sulfides in the following manner:

$$M_2SO_4 + 4H_2 \longrightarrow M_2S + 4H_2O \qquad (e)$$

$$M_2SO_4 + 4CO \longrightarrow M_2S + 4CO_2 \qquad (f)$$

The reaction rates are slow but can be increased by raising the temperature. However, in order to save on equipment wear it is preferable to have the reaction take place at a temperature as low as possible. Considerable effort has been spent in optimizing the reduction at about 1100F.

The regeneration step:

This step is to convert the alkali metal sulfides to hydrogen sulfides, and meanwhile to regenerate the carbonates. The stream of alkali metal sulfides and carbonates coming from the reducer are brought in contact with a mixture of carbon dioxide and water in the regenerator. The following reaction occurs.

$$M_2S + CO_2 + H_2O \longrightarrow M_2CO_3 + H_2S \qquad (g)$$

The equilibrium conditions of equation (g) are favorable for the production of hydrogen sulfide at temperature below $1100^{o}F$, and the reaction is accomplished at 800 F. The resulting melt (M_2CO_3) is circulated directly to the scrubber and the hydrogen sulfide can be received by a Claus plant for conversion to sulfur.

This molten carbonate process has been proposed by the Atomics Internation Div. of North American Rockwell and supported by the National Air Pollution Control Administration. According to the estimation of North American Rockwell the sulfur dioxide removed is over 95 percent.

STILL PROCESS (13) (15) (20)

The last dry absorption process to be discussed here is a German process which uses lignite ash as the absorbent.

Lignite ash has a high lime content. Passing through a mechanical dust collector, flue gases contact the absorbent in a series of three counterflow reactors. Sulfur dioxides in the flue gases are converted to calcium sulfites ($CaSO_3$) and sulfates ($CaSO_4$) by the lime content. After a final removal of particulate matter in an electrostatic precipitator the clean gas stream is directed to the stack. Heating the spent ash, which contains calcium sulfites and sulfates ($CaSO_3$ and $CaSO_4$), sulfur dioxide and the regenerated absorbent are produced.

The difficulties of sulfate fouling the absorbent causes relative high material consumption and thus increases the operating cost. Tests showed that 80 percent sulfur dioxide removal on a 10,000 KW. coal-fired unit was achieved.

WET SYSTEMS

Wet systems are those which bring the flue gases into contact with an aqueous solution.

BATTERSEA WASHING PROCESS (2) (11)

This is the earliest full scale sulfur dioxide removal system which was made in 1934 at the Battersea Station in London. The basic arrangement is shown as Fig. 10.

Water from the River Thames (which is highly alkaline) is passed through the condenser; some of it is pumped to two counterflow towers packed with wooden slates. Flue gases, passing through the wooden slats, flow upward while the river water falls over from the top. In the second tower, chalk ($CaCO_3$) is added to the water to insure more complete absorption of sulfur dioxide.

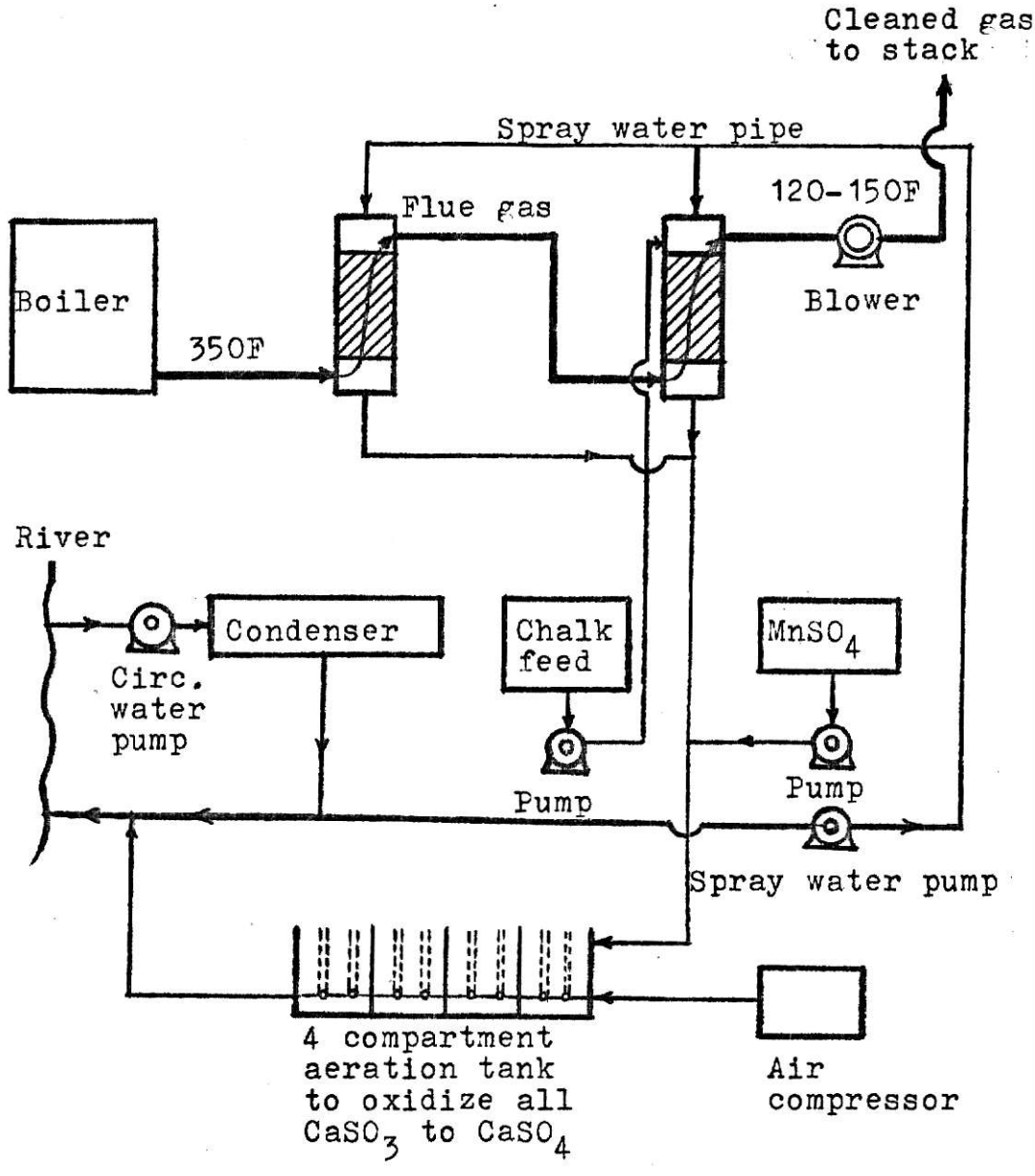

Figure 10. BATTERSEA WASHING PROCESS

In this process, about 90 to 95 percent of sulfur dioxide in the flue gases is absorbed and formed to calcium sulfite and sulfate ($CaSO_3$ and $CaSO_4$) in the washing water. For complete oxidation of the sulfite to sulfate, the washing water is fed to an aeration tank after it leaves the second tower. To promote oxidation, small amounts of a catalyst ($MnSO_4$) is added ahead of the aeration tank. Water overflowing from the aeration tank joins the condenser discharge water to return the river.

The main disadvantage of this process is that flue gases enters the stack at only 125 F. The buoyancy of the stack plume is destroyed, therefore the flue gases settle rapidly to the ground, especially on cool days. Although free of sulfur dioxide, the cloud is much objectionable, visually. In 1963, another similar scrubbing system was put in service in Bankside Station nearer the center of London.

COMBUSTION ENGINEERING WET SCRUBBER PROCESS (13) (17)

Initiating a research program from 1963, Combustion Engineering finally developed this dry limestone injection-wet scrubber-nonrecovery process as its means to air pollution control for power plants burning fossil fuels. Fig. 11 shows the basic flow diagram of this process.

This process employs mainly two steps to remove sulfur oxides in the flue gases. First, by injecting an alkaline earth additive to the furnace, then by wet scrubbing.

Calcium and magnesium oxides formed after liberation of carbon dioxide are found to be much more active with sulfur dioxide and sulfur trioxide in the flue gases and with the scrubber water than the uncalcined alkaline-earths. The followings are chemical reactions in the furnace.

$$CaCO_3 \cdot MgCO_3 \xrightarrow[\Delta]{1500\ F} CaO + MgO + 2CO_2$$

$$CaO + SO_3 \longrightarrow CaSO_4$$

$$MgO + SO_3 \longrightarrow MgSO_4$$

$$CaO + SO_2 \xrightarrow{O_2} CaSO_4$$

$$MgO + SO_2 \xrightarrow{O_2} MgSO_4$$

In the above reactions, sulfur trioxide is completely neutralized, whereas only 20 to 30 percent of sulfur dioxide is neutralized. The quantity of additive added to the furnace usually is 105 to 110 percent of the stoichiometric amount.

In the wet scrubber, calcium and magnessium oxides that have not yet combined with sulfur dioxide or sulfur trioxide have the following chemical reactions.

$$2CaO + H_2O + 2SO_2 \longrightarrow CaSO_3 + CaSO_4 + H_2O$$

$$2MgO + H_2O + 2SO_2 \longrightarrow MgSO_3 + MgSO_4 + H_2O$$

In addition to the removal of sulfur oxides, over 99 percent of the fly ash is removed from the flue gases during the scrubbing action.

The calcium sulfate ($CaSO_4$), calcium sulfite ($CaSO_3$) and magnesium sulfite ($MgSO_3$) are stable and are mostly precipitated. However, magnesium sulfate ($MgSO_4$) is quite soluble. Because of this the recycling water becomes highly concentrated with magnesium sulfate. If there is a clarifier installed in the system, the precipitated solids are carried

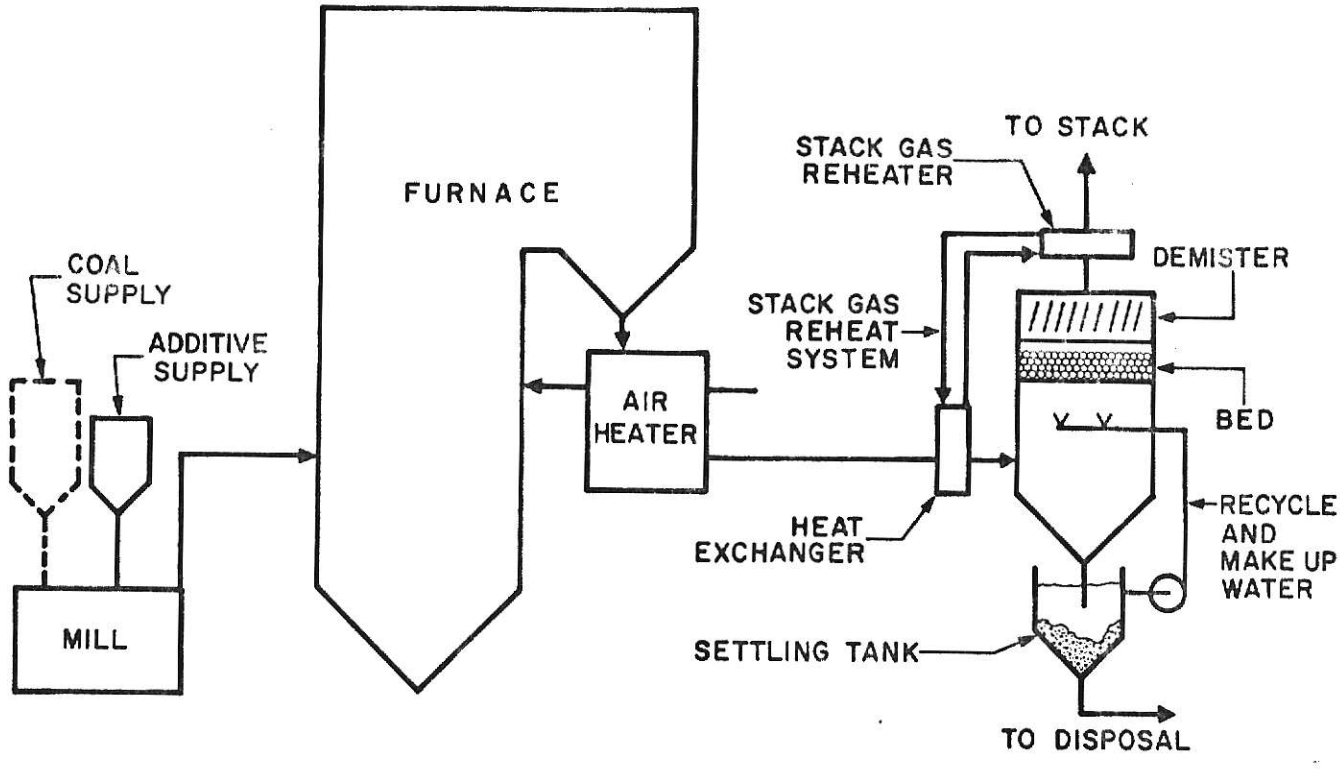

Figure 11. COMBUSTION ENGINEERING WET SCRUBBER PROCESS

to it and they settle with the fly ash and are then removed to a disposal area.

To reduce the possibility of pluming, and also to restore the buoyant effect of the cleansed flue gases, a closed-cycle heat transfer circuit is used to extract heat from the flue gases before they enter the wet scrubber and to return heat to them after they leave the wet scrubber.

To save make up water the clear water decanted from the top of the settling tank is recycled as spray water to the scrubber.

Following successful pilot plant work, commercial size Combustion Engineering systems have been installed successively at the Meramec No. 2

unit of Union Electric Co., St. Louis, Mo. (140,000KW.; Sept. 1968), at the Lawrence No. 4 unit of Kansas Power and Light Co., (125,000KW.; Nov. 1968) and, also, a second unit on a 430,000KW. boiler (early 1971). A recent report in the magazine "aware" (January, 1972) revealed that the world's largest sulfur dioxide removal facility, with a similar process, was scheduled to be in operation by mid 1973 in the coal-fired La Cygne, Kansas, Power Plant.

Operations showed that the sulfur dioxide removal efficiency of burning 3.4 percent coal was equivalent to firing coal with less than 0.5 percent sulfur. In addition, over 99 percent of particulate matter and 30 percent of nitrogen oxide were removed at the same time.

WELLMAN-LORD PROCESS (13) (18) (19)

The Wellman-Lord process is a wet absorption method which depends on byproduct recovery. The process consists of three important steps: reaction with an absorbent; special treatment to remove sulfur dioxide from the absorbent; and stripping and concentration of sulfur dioxide into the purified anhydrous liquid (see Fig. 12).

Initial wet scrubbing in the reactor is done mainly to discard fly ash and sulfur trioxide. It is believed that sulfur trioxide is absorbed on the fly ash and removed with it. Chemical solution from the reactor is fed to a special treatment area, where sulfur dioxide removal begins. The cleansed flue gases leaving the reactor area through a booster fan discharge to the stack at 140 F. The Wellman-Lord engineers guaranteed no visible plumes until the outside temperature fell below 45 F.

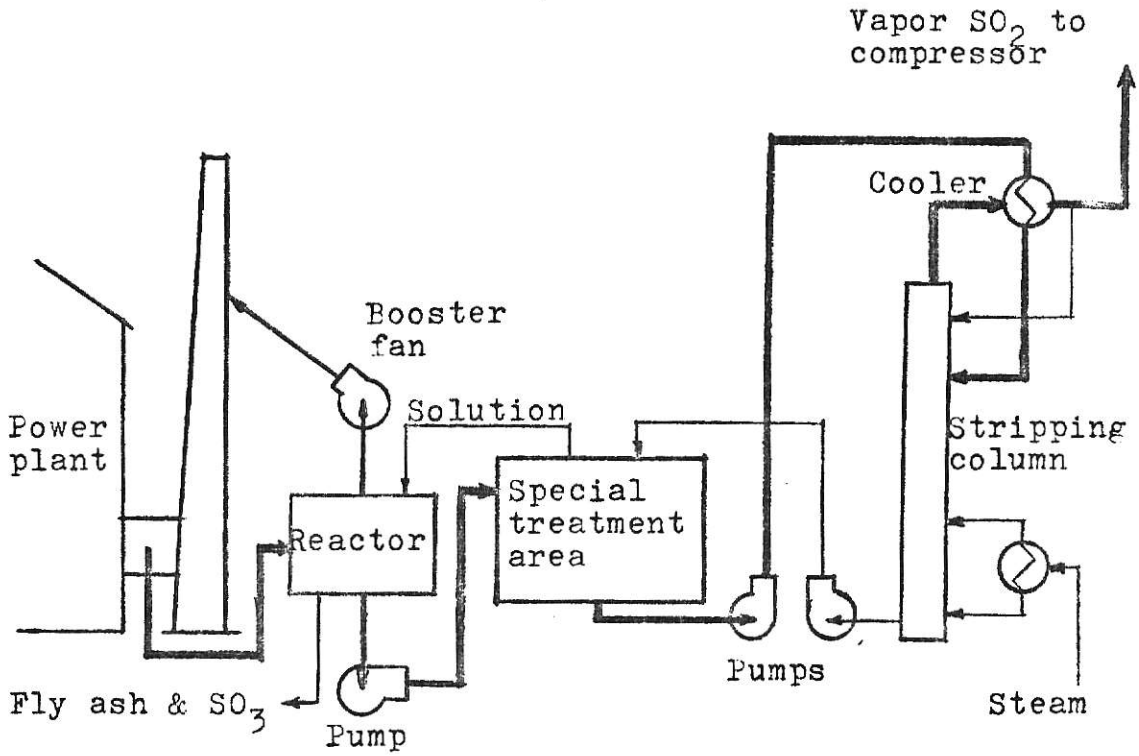

Figure 12. WELLMAN-LORD PROCESS for sulfur removal

With a potassium sulfite (K_2SO_3) solution, the special treatment area takes out the sulfur dioxide by converting the K_2SO_3 to $KHSO_3$.

$$K_2SO_3 + H_2O + SO_2 \longrightarrow 2KHSO_3$$

For high efficiency in the removal of sulfur dioxide, the temperature must be controlled within narrow limits.

The product from the special treatment area is pumped through a cooler to the recovery area, where potassium bisulfite ($KHSO_3$) precipitates out of solution as potassium pyrosulfite ($K_2S_2O_5$).

$$2KHSO_3 \xrightarrow{\text{cooled}} K_2S_2O_5 + H_2O$$

The pyrosulfite ($K_2S_2O_5$) is then heated by steam to convert it back to potassium sulfite (K_2SO_3) for recycling and for the recovery of sulfur dioxide (SO_2).

$$K_2S_2O_5 \xrightarrow{\text{steam stripping}} K_2SO_3 + SO_2$$

Steam is injected directly into the bottom of the stripper, and the sulfur dioxide is separated by gas-liquid countercurrent contact and is carried out through the top of the unit. The steam consumption rate is 4-4.5 lbs. per pound of sulfur dioxide produced.

Steam coming from the top of the stripping column is condensed and is separated from the sulfur dioxide vapor. Then the sulfur dioxide vapor is compressed and sent to a distillation column as a condensed liquid product. The product can be converted to either elemental sulfur or sulfuric acid as desired.

This process removes 90 percent or more of the sulfur dioxide in addition to removing 99 percent of the fly ash. System economics requires a high sulfur dioxide removal in the K_2SO_3 scrubbing step. The loss of sulfur dioxide in the initial wet scrubbing is an economic loss and the oxidation of K_2SO_3 to K_2SO_4 causes a corresponding economic loss.

AMMONIA AND NEW LIME PROCESSES (13)

Both of these two wet absorption processes were developed by Japanese Mitsubisi Heavy Industries.

Flue gases passing through the air heater and the dust collector enter a cross-flow scrubber where ammonia reacts with sulfur dioxide and water to form ammonium sulfite ($(NH_4)_2SO_3$), which is subsequently converted to ammonium bisulfite (NH_4HSO_3). (see Fig. 13)

$$2NH_3 + H_2O + SO_2 \longrightarrow (NH_4)_2SO_3$$

$$(NH_4)_2SO_3 \longrightarrow NH_4HSO_3 + NH_3$$

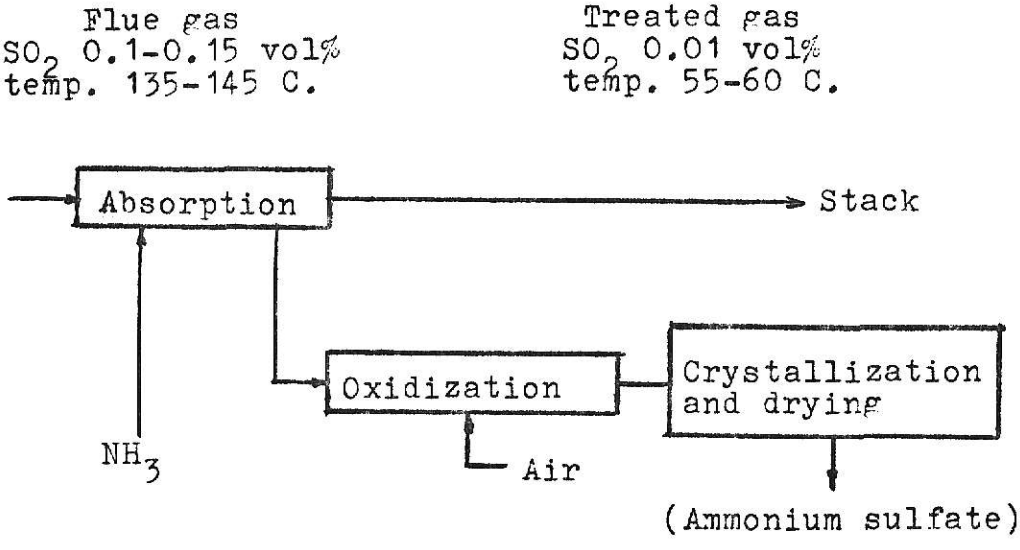

Figure 13. MITSUBISHI AMMONNIA PROCESS

The cleansed flue gases flow to the stack and the absorbent goes to an oxidation unit where ammonia further reats with bisulfite (NH_4HSO_3) to reform sulfite ($(NH_4)_2SO_3$). The sulfite is oxidized to sulfate ($(NH_4)_2SO_4$) to complete the reaction.

$$NH_4HSO_3 + NH_3 \longrightarrow (NH_4)_2SO_3$$

$$2(NH_4)_2SO_3 + O_2 \longrightarrow 2(NH_4)_2SO_4$$

Crystallization and drying of the sulfate flow, completes the process.

In the New Lime process, flue gases passing through the air heater and the dust collector enter a series of absorbers where sulfur dioxide in the gas stream reacts with a lime and calcium sulfite slurry.

The cleansed gases discharge to the atmosphere while the slurry is oxidized to yield gypsum ($CaSO_4 \cdot 2H_2O$).

$$Ca(OH)_2 + CaSO_3 + SO_2 + 3H_2O + O_2 \longrightarrow 2(CaSO_4 \cdot 2H_2O)$$

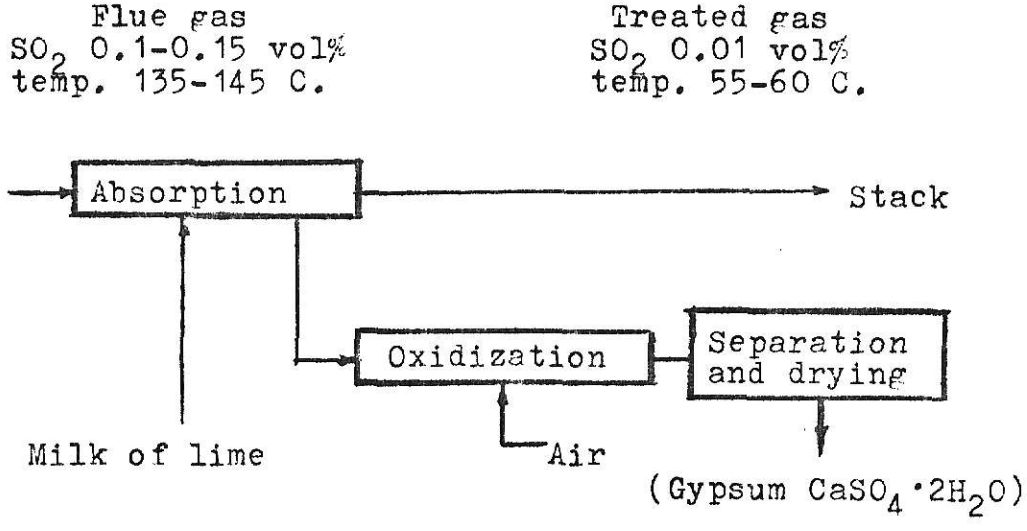

Figure 14. NEW LIME PROCESS developed in Japan

The gypsum is filtered and dried to a crystalline form, and the filtrate is recycled.

Both processes have a 90 percent sulfur removal efficiency.

ADSORPTION METHODS

In the adsorption method the flue gases are brought into contect with a solid which removes sulfur dioxide with the sulfur dioxide condensed on the solid. The sulfur dioxide is recoverable from the solid.

The loading capability of chemical absorbents is enormous, yet its regeneration process is complex, whereas adsorbents have a less loading capability but a simpler regeneration process. Two wet and one dry adsorption methods are illustrated below. All use carbon as the adsorbent.

LURGI (SULFACID) PROCESS (13) (15) (20)

This wet adsorption process was developed by Lurgi Company of Germany (see Fig. 15).

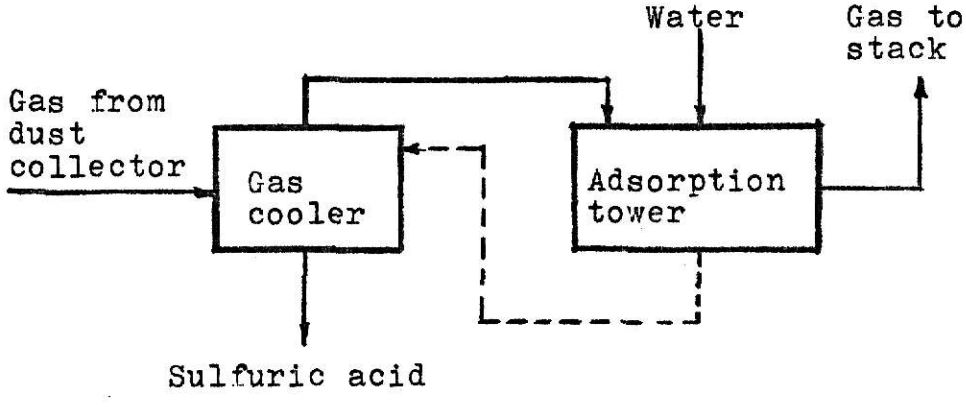

Figure 15. LURGI PROCESS gives sulfuric acid

Flue gases from the dust collector contact weak sulfuric acid (from the adsorption step) in the gas cooler. Then the cooled gas stream passes through the carbon bed of the adsorber, where, in the pores of the carbon, sulfuric acid is being formed from the sulfur dioxide. Water is intermittently sprayed into the adsorption tower in order to remove the acid.

The acid concentration increases as a result of recycling the dilute acid which is used to cool the flue gases in the gas cooler. The final strength depends on the incoming gas temperature.

This process has been tested on a sulfuric acid plant and a 2000 KW. coal-fired power plant. Though its operation is simple, the temperature drop of the exiting flue gases, the pressure drop through the carbon bed and the need for acid-resistant materials are important factors which must be considered in the design.

HITACHI PROCESS (11) (13) (18)

The Hitachi process of Japan is similar to the Lurgi process. Both processes remove low-concentration sulfuric acid from carbon by washing with water. But the gas-carbon contacting arrangement is different. In the Hitachi process, six carbon towers operate in a cyclic manner. Dampers are used to divert gases. A single tower goes through a 60-hour cycle of 30 hours for adsorption, 10 hours for washing and 20 hours for drying.

This process has a smaller temperature drop for the flue gases than the Lurgi process. However the capital cost is high due to its large number of towers and dampers.

A 2000 KW. oil-fired pilot plant was operated at the Goi station of Tokyo Electric Power Co. in 1967. A 90 percent removal of sulfur dioxide was reported.

REINLUET PROCESS (13) (15) (20) (21)

Reinluft's is a German dry-adsorption process. Coke is used as the adsorbent. Fig. 16 shows the basic arrangement of this process.

Flue gases between 250 and 320 F enter the lower section of the two-stage adsorber, where all sulfur trioxide and sulfuric acid mist

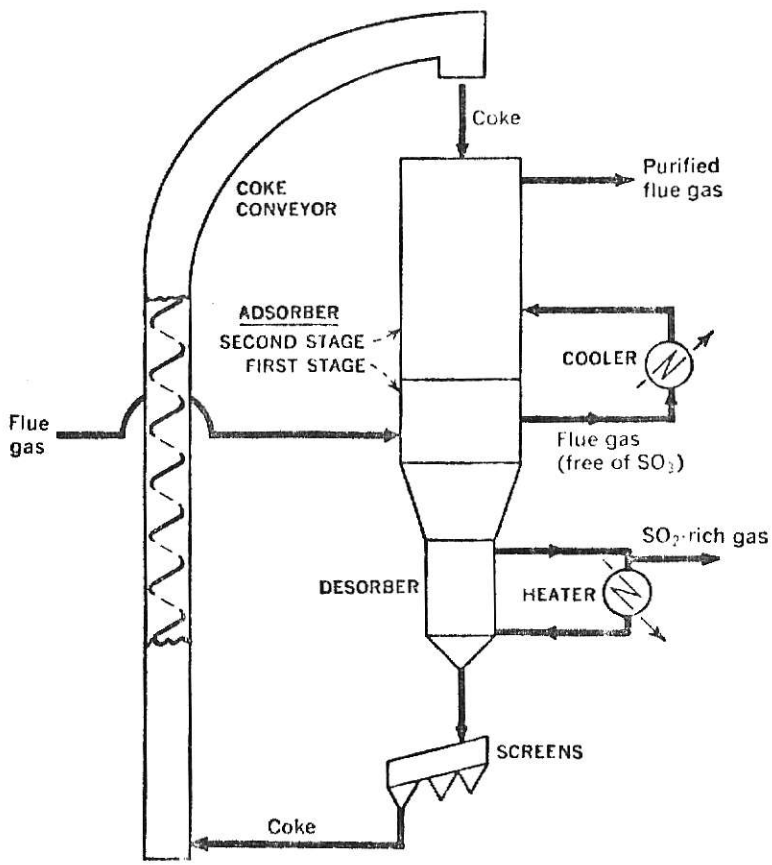

Figure 16. REINLUFT PROCESS uses coke to remove SO_2

are removed by activated coke. This removal is due to the characteristic of activited coke which catalyzes the formation of, and then adsorbs, sulfur trioxide and sulfuric acid at elevated temperatures. Then the gas stream, which is free of sulfur trioxide, is cooled before it enters the second stage, since oxidation of sulfur dioxide is more easily accomplished at lower temperatures. Adsorption continues in the second stage. Treated flue gases, having lost up to 99.9 percent of their original sulfur dioxide, leave at the top.

The regeneration process of the Reinluft design is accomplished by employing another characteristic of coke, which is that the adsorbed acidic materials in the coke can be easily scavenged by a small gas stream at temperatures which are higher than those in the adsorber.

By circulating the gas stream through a heater, the regeneration process is maintained around 750 F. The sulfuric acid in the coke evaporates to sulfur trioxide and water. Sulfur trioxide is then reduced to sulfur dioxide.

$$2SO_3 + C \longrightarrow 2SO_2 + CO_2$$

$$2SO_3 + S \longrightarrow 3SO_2$$

The chemical bond between sulfur dioxide and activated coke is so weak that sulfur dioxide is easily flushed away by a small amount of scavenging gas.

The gas stream from the desorber contains 40 to 55 percent sulfur dioxide by volume. It is high enough so that sulfur is recovered as elemental sulfur, sulfuric acid or liquefield sulfur dioxide.

Drawbacks of the method include self-ignition at high temperatures in the presence of oxygen, space needed to recirculate the large amount of coke, the cost of the electrostatic precipitator and the heating of the reducing gas.

CATALYTIC OXIDATION (13) (20) (22)

Catalytic oxidation is a method where sulfur dioxide, by means of a catalyst, is converted to sulfur trioxide which reacts with water to form sulfuric acid.

Monsanto's Cat-Ox process (see Fig. 17) is the most famous catalytic oxidation method for sulfuric acid recovery.

Since the catalyst (vanadium pentoxide V_2O_5) requires a high temperature (850 F) for its action, and since the dust must be removed before the gases contact the catalyst, the catalytic converter has to be installed in front of the economizer and at the rear of the electrostatic precipitator. This requires a fairly large precipitator and limits its application to new plants.

Hot flue gases at 850 F, passing through an electrostatic precipitator, enter the catalytic converter where as much as 90 percent of the sulfur dioxide is oxidized to sulfur trioxide. Then the sulfur-trioxide-rich flue gases pass through the economizer and air preheater. Formed by sulfur trioxide and moisture in the gas stream, the sulfuric acid begins condensing in the air preheater. The remainder is an acid mist which is removed in the mist eliminator. The venting of the cleansed flue gases to the stack and the sending of the collected acid to storage complete the process.

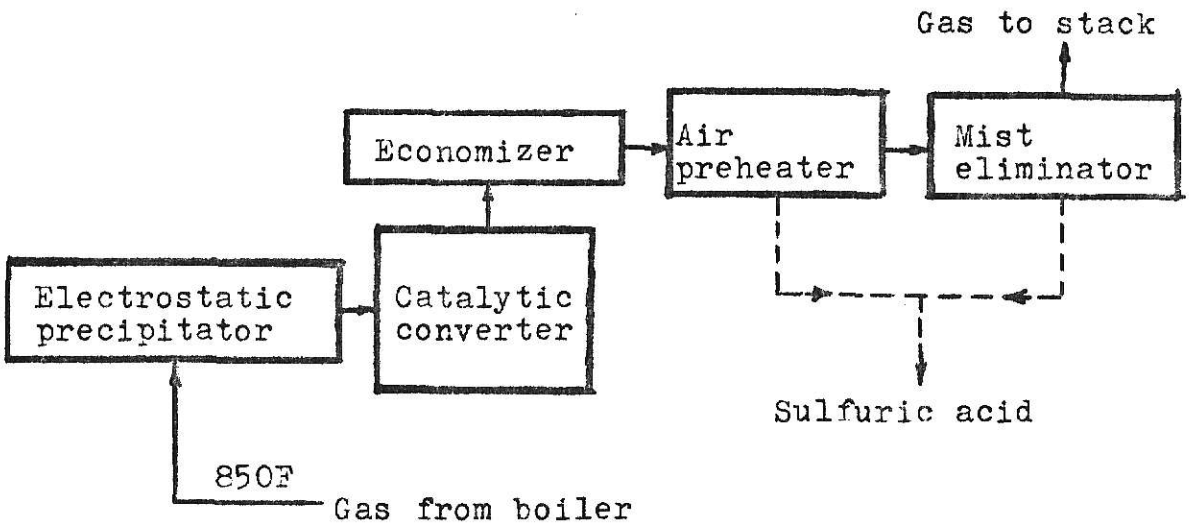

Figure 17. Monsanto's CAT-OX PROCESS

This process removes 90 percent sulfur dioxide and 99 percent plus fly ash from the flue gases. Its outstanding advantages are that no moving parts are required and no recycling absorbent is needed. Its main drawbacks include the large size of the precipitator, the limiting application of the process and the need of corrossion-resistant steel for the air preheater and mist eliminator.

CONCLUSION

A technical review of the problem of air pollution due to SO_2 from power stacks, discussed in the foregoing pages, gives the impressions that: (a) to burn naturally occurring low-sulfur fuels will not be adequate in the future, (b) removal of the sulfur from fuel before it is burned appears difficult and costly in the case of coal, (for oil, desulfurization is technically simpler but economically expensive), and (c) the only way left to solve this problem is to remove SO_2 from the flue gases.

However, the installation and maintenance of equipment for the removal of SO_2 from flue gases is still costly. Some processes, therefore, are based on the recovery of sulfur, or its compounds, to compensate for some of these high costs. All these processes have one difficulty; the treatment of enormous gas volumes that contain very low concentrations of sulfur dioxide. Flue gas passing to the stack generally contains 2000 to 3000 ppm of SO_2. If it is decided to recover the sulfur economically, concentrations of SO_2 which are 300 to 500 times as great are required (2). It is the leanness of the input gas which makes the selective absorption difficult and it is this leanness which raises the size of the gas-handling equipment out of all proportion to the amount of sulfur recovered.

In the end of this report, a basic engineering idea is introduced here by the author to solve this problem. The idea is an old art in the turbine-power generation field, and whether or not it works well, both

technically and economically, is still unknown. For a better environment to live in, it deserves a try.

The technology introduced here is to burn fuels at high pressure by the use of a supercharged boiler (23). Such systems would have the advantage that smaller volumes of gas would require treatment for SO_2 removal.

Then any gas cleaning process discussed in the foregoing pages which had added to it the supercharged boiler design, (Fig. 18), would have the advantage of handling a far smaller gas volume than those systems having combustion at atmospheric pressure. Furthermore, if a national fuel policy were implemented, low-sulfur fuels could be reserved for the small user who could not afford sulfur-recovery apparatus.

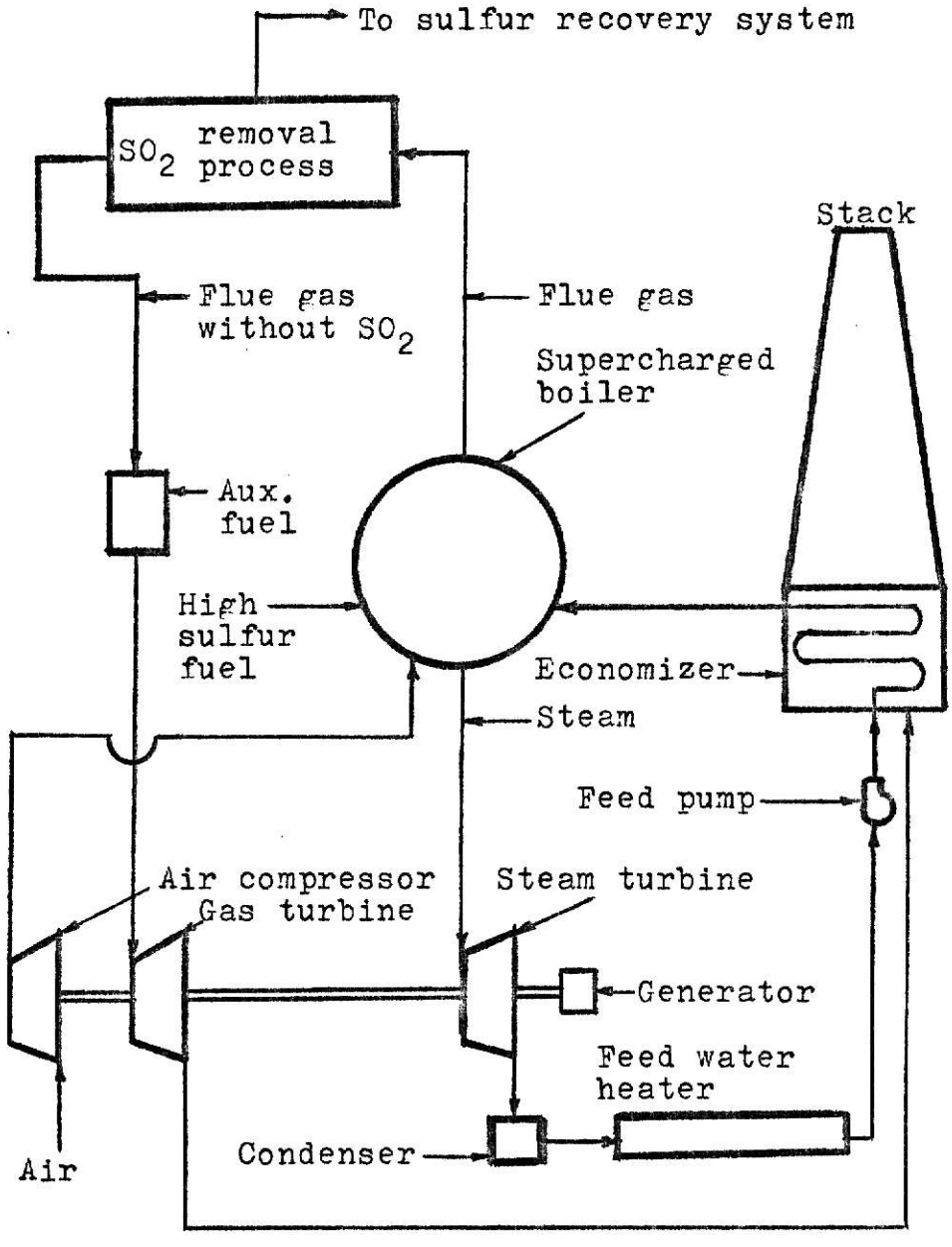

Figure 18. SO_2 removal unit using the supercharged-boiler design[2] to concentrate the SO_2 in the flue gas in order to reduce the gas volume to be treated.

ACKNOWLEDGEMENT

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REFERENCES

1. Ehrlich, S., "Air pollution control through new combustion processes," Combustion, Aug. 1971, Vol. 43, pp. 36-39.
2. Frankenberg, T. T., "Sulfur removal: For air pollution control," Mechanical Engineering, Aug. 1965, Vol. 87, pp. 34-41.
3. Olds, F. C., "Progress and programs in air pollution abatement," Power Engineering, June 1971, Vol. 75, pp. 54-56.
4. Squires, M., "Air pollution: The control of SO_2 from power stacks," Chemical Engineering, Nov. 6, 1967, pp. 260-268.
5. "Air quality criteria for sulfur oxides," U.S. Department of Health, Education, and Welfare Public Health Service, Publication No. 1619, Washington: Government Printing Office, March 1967.
6. Coykendall, L. H., "Formation and control of sulfur oxides in boilers," J. APCA, Dec. 1962, Vol. 12, pp. 567-569.
7. Orning, A. A., Proceeding National Conference on Air Pollution, Washington, D. C. Nov. 1958, pp. 155-161.
8. Plumley, A. L., "Fossil fuel and the environment - Present systems and their emission," Combustion, Oct. 1971, Vol. 43, pp. 36-43.
9. Salvin, V. S., "Effect of air pollution on dyed fabrics," J. APCA, Sep. 1963, Vol. 13, pp. 416-422.
10. Gibbons, E. V., "Atmospheric corrossion testing of metals in Canada," Corrossion, June 1961, Vol. 17, pp. 144-146.
11. Reid, W. T., "Sulfur oxides control in central station power plants," HPAC Conference Proceedings 1967.

12. Ingraham, T. R., and Marier, P., "Note on the mechanism of the absorption of SO_2 by limestone," Mechanical Engineering, June 1971, Vol. 21, p. 347.

13. Maurin, P. G., and Jonakin J., "Removing sulfur oxides from stacks," Chemical Engineering, Apr. 27, 1970, pp. 173-180.

14. Uno, T. et al "Scale-up of SO_2 control process," Chemical Engineering Progress, Jan. 1970, Vol. 66, pp. 61-65.

15. Zentgraf, K. M., "The present state of flue gas desulfurization," Combustion, Nov. 1969, Vol. 41, pp. 6-11.

16. Oldenkamp, R. D., and Margolin, E. D., "The molten carbonate process for sulfur oxide emission," Chemical Engineering Progress, Nov. 1969, Vol. 65, pp. 73-76.

17. Plumley, A. L. et al "Removal of SO_2 and dust from stack gases," Combustion Engineering Inc., Windsor, Connecticut.

18. "Profit in stack gas," Chemical Week, Jan. 20, 1968.

19. Wright, W. L., "SO_2 removal technology and economics," Westinghouse Electric Cooperation, East Pittsburgh, Pennsylvania.

20. Slack, A. V., "Air pollution: The control of SO_2 from power stacks," Chemical Engineering, Dec. 4, 1971, pp. 188-196.

21. "Coke cleans flue gas in German process," Chemical Engineering, Oct. 23, 1967, pp. 94-98.

22. "SO_2 control processes for stack gases reach commercial status," Environmental Science and Technology, Nov. 1968, Vol. 2, pp. 994-997.

23. Gaffert, G. A., "Steam power station," McGRAW-HILL book Company, Inc., New York and London, Second edition, pp. 228-229.

APPENDIX

STATE AND LOCAL SO_2 CONTROL REGULATIONS-CONDENSED

"Table 1 A-D is a condensed listing of state and regional limits as of April 1970. These limits and their effective dates are given for large power plants. Different limits sometimes apply to industrial and small power plant users and are not shown." (17)

TABLE 1A

STATE AND LOCAL SO_2 CONTROL REGULATION - CONDENSED

As of October 1970

STATE	AREA	COAL		OIL	
		MAXIMUM SULFUR%	EFFECTIVE DATE	MAXIMUM SULFUR%	EFFECTIVE DATE
California	L. A. Co Monterey	0.5 0.5	5-59 7-69	0.5 0.5	5-59 7-69
Conn.	Statewide	1.0	9-71	1.0	9-71
District of Columbia		1.0	7-69	1.0	7-69
Florida	Jacksonville Manatee Co	2.0 1.5 1.0 ---	10-68 1-69 1-70 ----	2.0 1.5 1.0 2.0	10-68 1-69 1-70 12-68
Illinois	Chicago	1.8 1.0	7-70 1-72	1.8 1.0	7-70 1-72

TABLE 1B

STATE AND LOCAL SO_2 CONTROL REGULATION - CONDENSED

As of October 1970

STATE	AREA	COAL		OIL	
		MAXIMUM SULFUR%	EFFECTIVE DATE	MAXIMUM SULFUR%	EFFECTIVE DATE
Maryland	Baltimore	1.0	7-70	1.0	7-70
Mass.	Boston	1.5 0.7	10-70 10-71	2.0 1.0	10-70 10-71
Minnosota	Minn-St. Paul	1.5	4-72	2.0	4-72
Missouri	St. Louis	2.0 1.5	12-68 3-70	2.0 2.0	12-68 3-70
Montana	Statewide	2.6 2.0 1.3	7-70 7-71 7-72	3.6 2.7 1.8	7-70 7-71 7-72

TABLE 1C

STATE AND LOCAL SO_2 CONTROL REGULATION - CONDENSED

As of October 1970

STATE	AREA	COAL		OIL	
		MAXIMUM SULFUR%	EFFECTIVE DATE	MAXIMUM SULFUR%	EFFECTIVE DATE
Nevada	Reno	-	-	1.2	7-70
New Hampshire	Existing New	2.6 1.3	10-70 10-70	2.0 1.5 1.25 1.0	10-70 10-71 10-72 10-73
New Jersey	Statewide Except 7 Rural Counties	1.0 0.2	5-68 10-71	1.0 0.5 0.3	5-68 10-70 10-71
New York	Statewide Metro NYC	2.1 1.0 0.26	6-70 10-69 4-71	3.0 1.0 0.37	6-70 10-69 4-71
North Dakota	Statewide	2.0	7-70	2.7	7-70

TABLE 1D

STATE AND LOCAL SO_2 CONTROL REGULATION - CONDENSED

As of October 1970

STATE	AREA	COAL		OIL	
		MAXIMUM SULFUR%	EFFECTIVE DATE	MAXIMUM SULFUR%	EFFECTIVE DATE
Ohio	Cincinnati	1.25	1-69	1.25	1-69
	Cleveland				
	Existing	2.0	12-71	2.0	12-71
	New	1.0	10-69	2.0	10-69
Penn.	Allegheny Co	1.7	12-69	2.3	12-69
	Philadelphia	2.0	5-70	1.0	5-70
		1.0	7-71	0.5	10-72
		0.3	10-72	0.3	10-73
Tennessee	Chatanooga	2.0	3-69	2.0	3-69
	Nashville	2.0	3-70	2.0	3-70
Virginia	Wash DC area	1.0	7-69	1.0	7-69

CONTROL OF SO_2 IN THE FLUE GASES OF FOSSIL FUEL POWER PLANTS

by

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B. S., Taiwan Cheng Kung University, 1966

AN ABSTRACT OF A MASTER'S REPORT

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ABSTRACT

Sulfur dioxide from the stacks of fossil fuel power plants is one of the most noxious materials emitted to the atmosphere. It has an adverse effect on human health. It inhibits the growth of vegetation, causes corrosion of metals and damages the construction of buildings.

To control this harmful pollution we can use one of the following three methods:

(a) burn naturally occurring low-sulfur oil or coal,

(b) remove the sulfur prior to burning the fuel,

(c) remove the sulfur dioxide from the flue gases.

Due to technical or economical difficulties, the first two ways were discarded from consideration as a means to solve the problem. The best solution of the problem is to remove SO_2 from the flue gases.

However, the installation and maintenance of equipment for the removal of SO_2 from flue gases is still costly. Some processes, therefore, compensate their high costs by the recovery of sulfur or its compounds.

To avoid the treatment of enormous gas volumes that contain very low concentrations of sulfur dioxide, and to reduce the size of the gas-handling equipment, supercharged boiler design is recommended in this report.