United States Patent

St. Pierre

[15] **3,690,808**

[45] **Sept. 12, 1972**

[54] **METHOD AND APPARATUS FOR SULFUR DIOXIDE EMISSION CONTROL IN COMBUSTION SYSTEMS**

[72] Inventor: **George R. St. Pierre**, Worthington, Ohio

[73] Assignee: **The Ohio State University**, Columbus, Ohio

[22] Filed: **Aug. 28, 1970**

[21] Appl. No.: **67,757**

[52] **U.S. Cl.** **431/4**, 23/177

[51] **Int. Cl.** **C01b 17/48**

[58] **Field of Search** ..... 431/4, 10, 2, 3; 110/1 K, 1 J; 23/277 C, 2 C, 167, 177, 178, 135; 48/92, 167, 177; 266/33; 208/246

[56] **References Cited**

UNITED STATES PATENTS

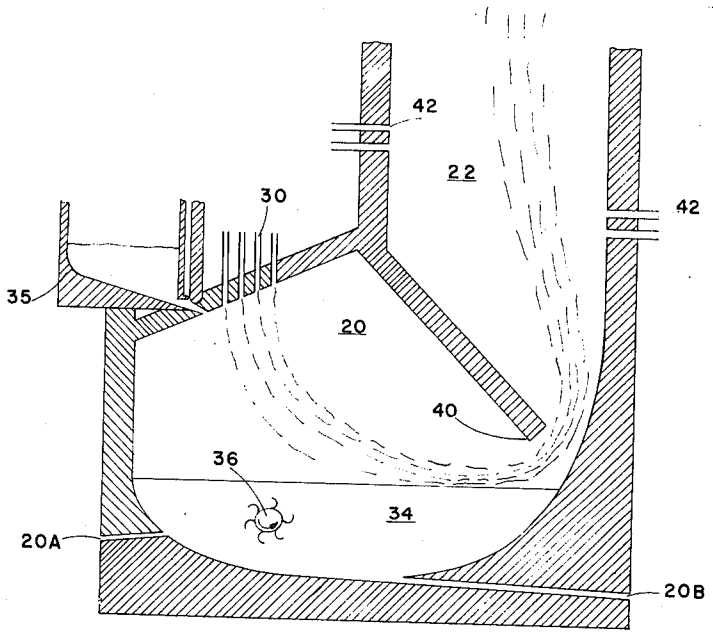
1,886,937	11/1932	Brett	266/37
2,060,134	11/1936	Summey	266/33 R UX
3,004,137	10/1961	Karlovitz	431/2 X
3,567,399	3/1971	Altmann et al.	431/352 X
3,080,855	3/1963	Lewis	122/4 D
3,421,824	1/1969	Herbst	431/10
3,481,289	12/1969	Oda et al.	110/1
3,150,963	9/1964	Kurzinski	266/34 R
3,533,739	10/1970	Pelezarski et al.	48/92 X

Primary Examiner—Frederick L. Matteson
Assistant Examiner—Harry B. Ramey
Attorney—Cennamo, Dunbar & Kremblas

[57] **ABSTRACT**

A method and apparatus for burning fossil fuels containing a significant sulfur content which removes a significant portion of the sulfur oxides released to the atmosphere. The invention is characterized by the dispersal of a molten metal into a combustion chamber for intimate contact with the combustion products to combine with the sulfur compounds produced by the combustion reaction. The metal sulphide may then be collected and refined for recirculation and the sulfur dioxides collected for use or sale.

16 Claims, 7 Drawing Figures



Patented Sept. 12, 1972 3,690,808

6 Sheets-Sheet 1

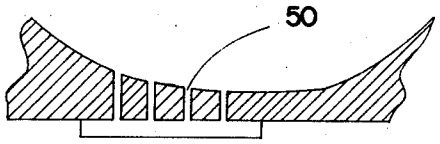


FIG. IA

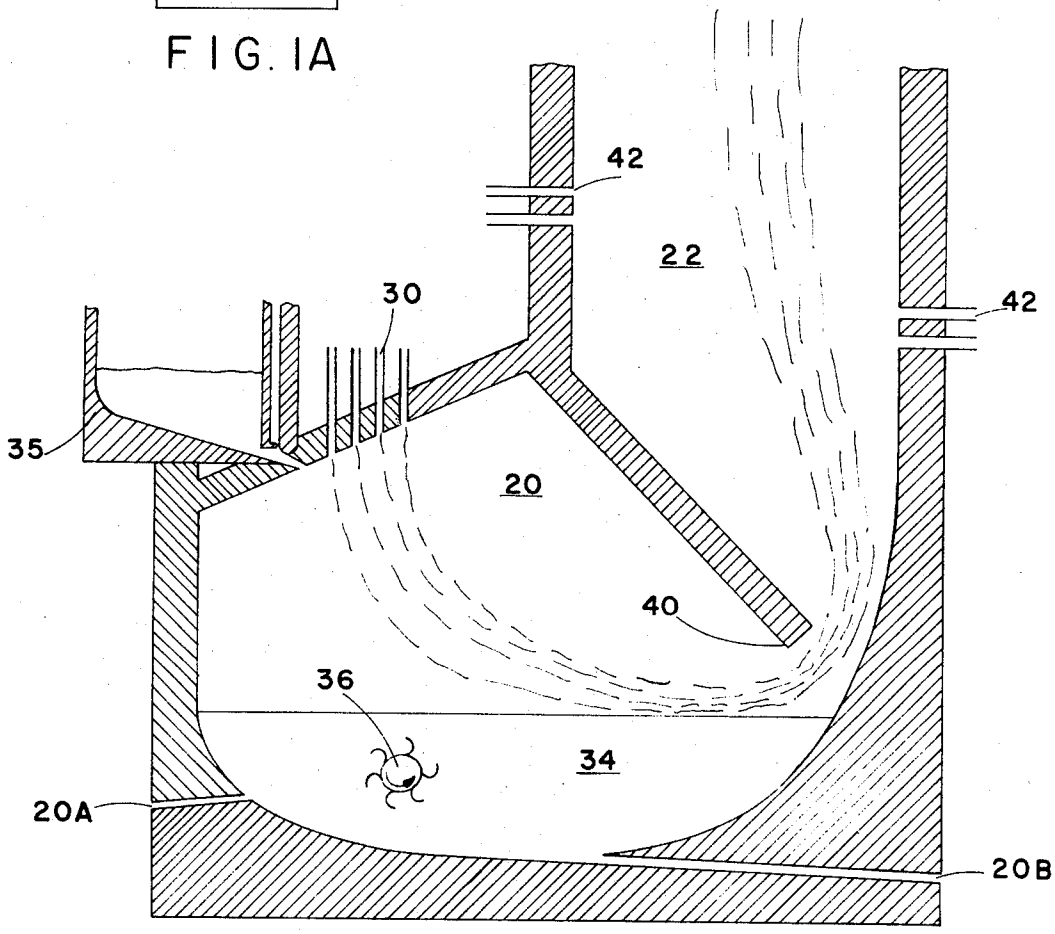


FIG. I

INVENTOR
GEORGE R. ST. PIERRE

BY:
Cennamo, Dunbar & Kremblas
ATTORNEYS

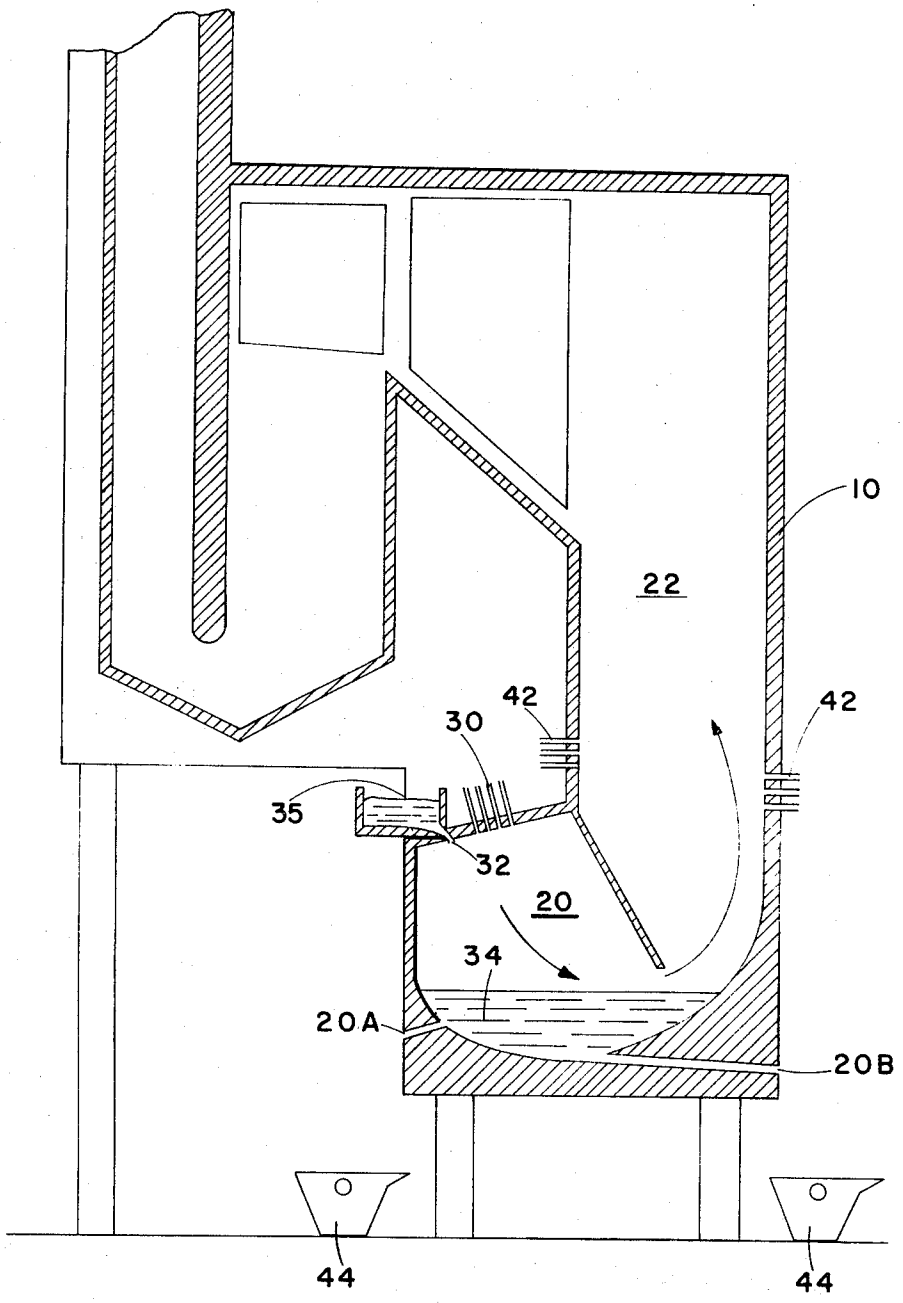


FIG. 2

INVENTOR
GEORGE R ST. PIERRE

BY Cennamo, Dunbar & Kremblas
ATTORNEY

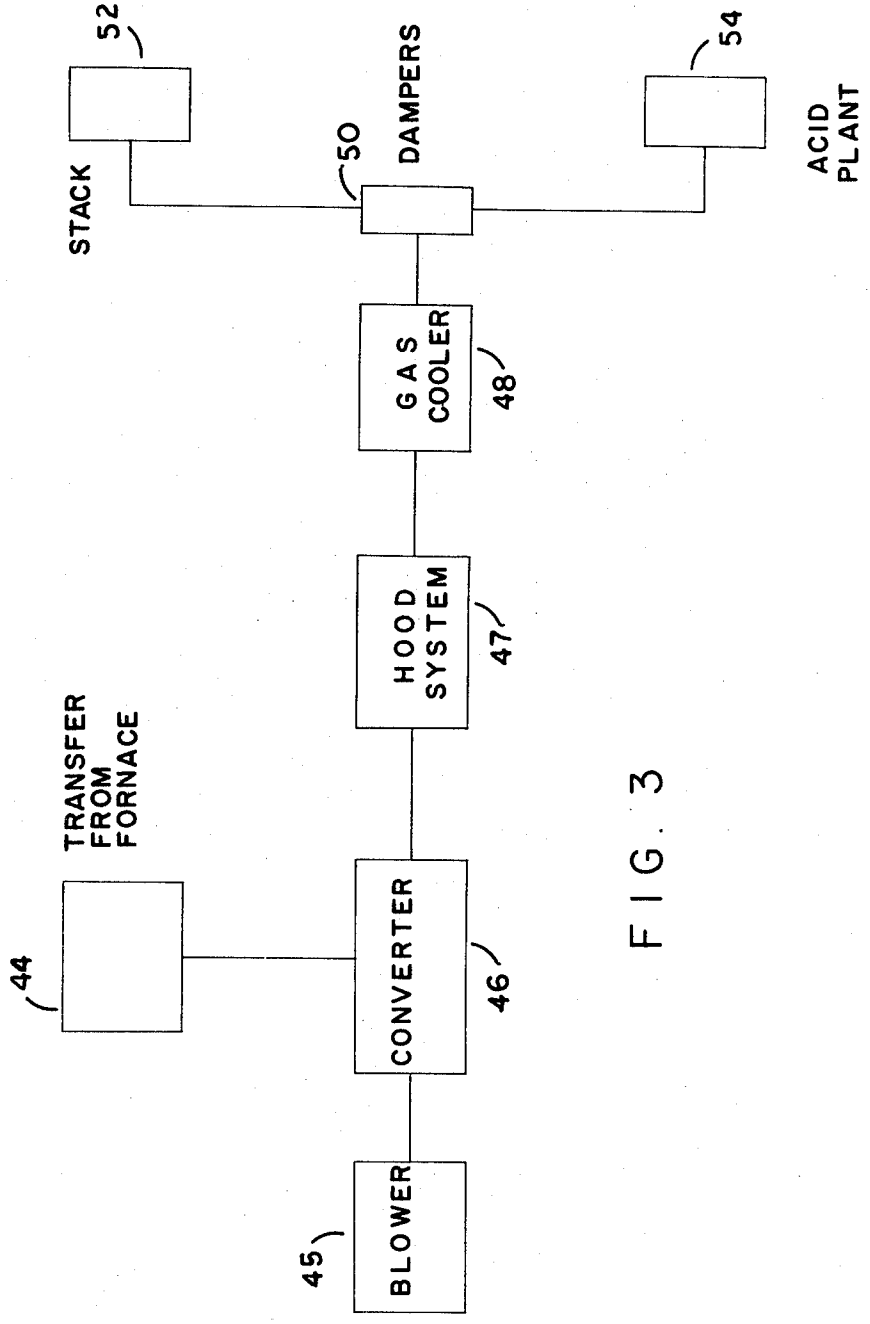


FIG. 3

INVENTOR
GEORGE R. ST. PIERRE

BY:

Cennamo, Dunbar & Kremblas

ATTORNEY

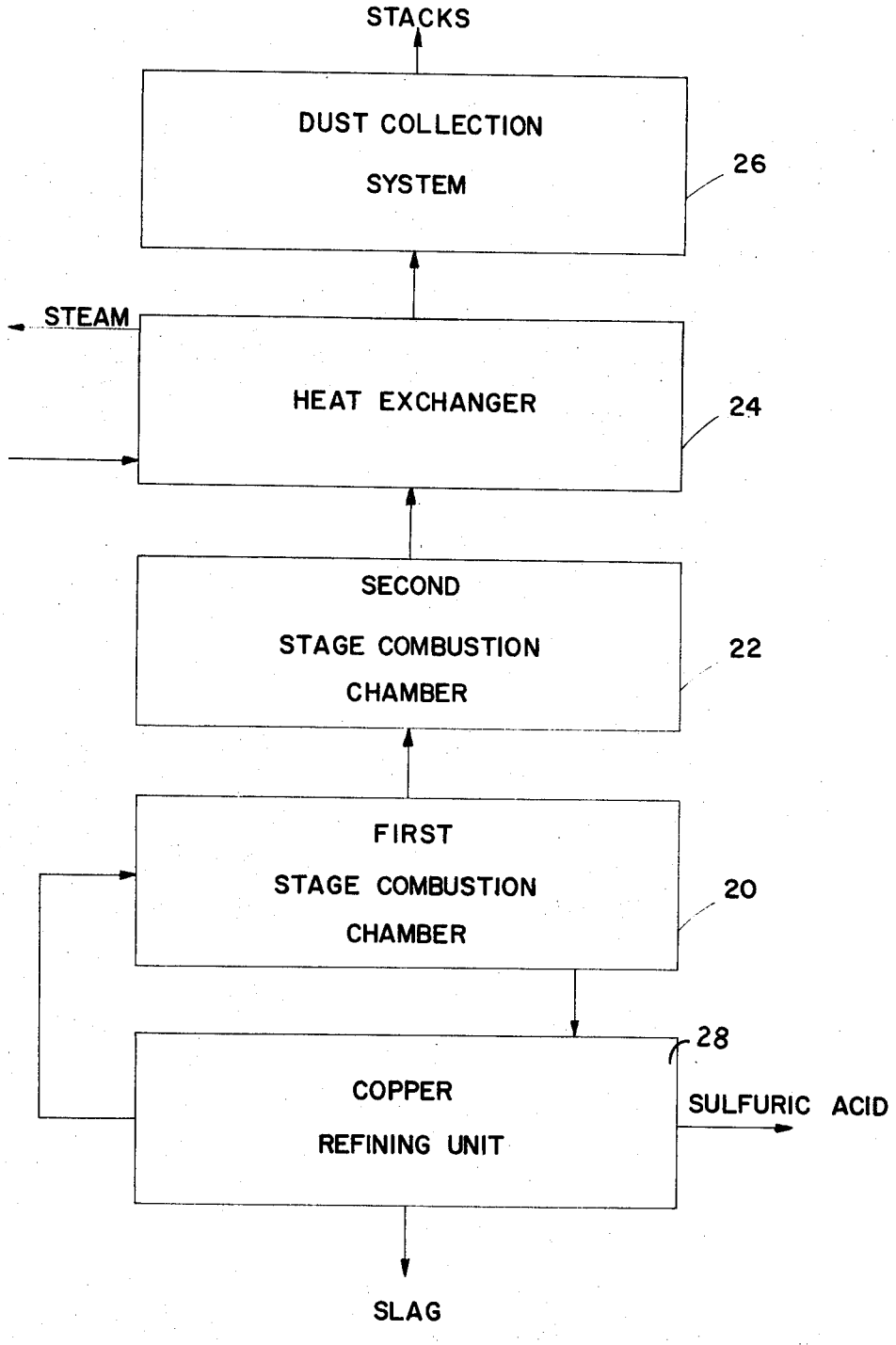
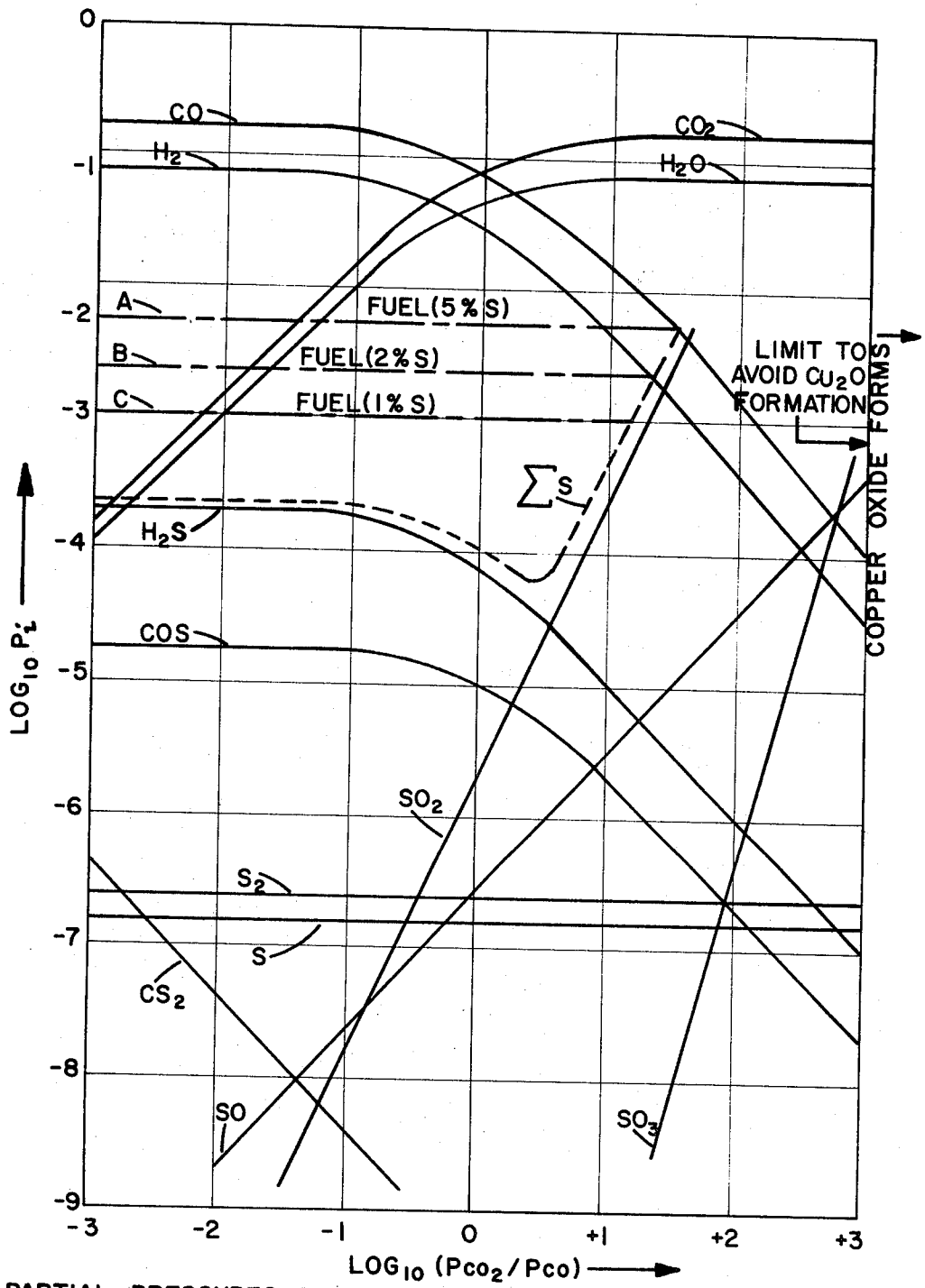


FIG. 4

INVENTOR.
GEORGE R. ST. PIERRE
BY
Cannamo, Dunbar & Kremblas
ATTORNEYS



PARTIAL PRESSURES OF SPECIES IN EQUILIBRIUM WITH COPPER/COPPER SULPHIDE AT 1127°C AND ONE ATMOSPHERE TOTAL PRESSURE

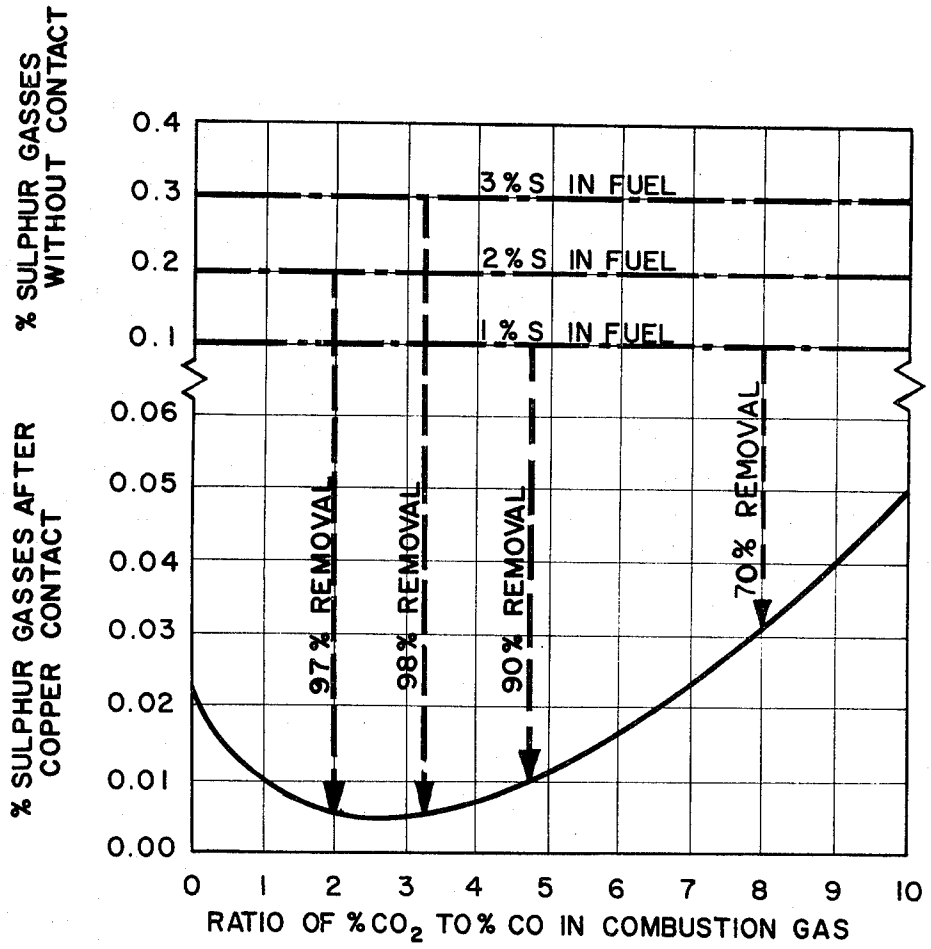
FIG. 5

INVENTOR.
GEORGE R. ST. PIERRE

BY

Cennamo, Dunbar & Kremblas

ATTORNEYS



SULPHUR REMOVAL FROM COMBUSTION GASES CONTACTED WITH COPPER (Cu/Cu_2S) AT 1127°C (2061°F) AND ATMOSPHERIC PRESSURE $\%CO + \%CO_2 = 17.0$ $\%H_2 + \%H_2O = 7.0$

FIG. 6

INVENTOR.
GEORGE R. ST. PIERRE

BY

Cennamo, Dunbar & Kremblas
ATTORNEYS

METHOD AND APPARATUS FOR SULFUR DIOXIDE EMISSION CONTROL IN COMBUSTION SYSTEMS

BACKGROUND OF THE INVENTION

Air pollution in general and particularly pollution by sulfur-oxides has come under increasing scrutiny. Most air pollution control officials believe that sulfur-oxides are the most damaging, corrosive, and irritating to human beings of all common air pollutants.

By far the major source of air pollution by sulfur-oxides is the fossil-fueled power plants which are, at this point in time and for some time to come, necessary to meet present demands for electricity. The power industry and the general public is faced with the problem of rapidly increasing air pollution and already intolerable levels while attempting to meet ever-increasing demands for electrical power. An estimated **28** million tons of sulfur dioxide is emitted into the atmosphere annually. Sufficient nuclear power plants cannot be constructed in the near future; therefore, no immediate relief from this source is foreseen.

The increasing demand for low sulfur content fuel would quickly drain these reserves and therefore a solution to this problem must come from another direction. Desulfurization of residual fuel oil shows some promise but appears to be prohibitively expensive. The outlook for desulfurization of coal is even less promising according to pollution control experts. The remaining alternatives are emissions control and coal gasification.

Attempts to control emissions from power plant combustion systems have been directed along two approaches. One approach has attempted to remove sulfur-oxides from the combustion gases leaving the combustion chamber. Such systems include a variety of scrubbing processes, methods of passing the gases through aqueous solutions of chemicals which react with sulfur dioxide, and other methods involving contacting the stack gases with fluidized absorbent beds.

A typical wet scrubbing system is represented by the lime-scrubbing process utilized in conjunction with the injection of powdered limestone blown into the combustion chamber. The gas is cooled after leaving the chamber and scrubbed with an aqueous solution of lime or limestone to remove the solid particles of sulfite and sulfate, fly ash, and most of the remaining sulfur oxides. It is then necessary to reheat the gas to maintain plume buoyancy leaving the stack. The commercial developments of this process have experienced start-up troubles.

The several processes employing aqueous solutions of substances which react chemically with sulfur dioxide usually require high efficiency electrostatic fly-ash eliminators, an absorber in which the gas comes into contact with the solution, a mist eliminator, and in most, provision for reheating the gas going to the stack. The efficiency of the heat generated suffers in this type of system.

The absorption processes using various dry solids including several metal oxides involve contacting the gas in a packed or fluidized bed or in some form of a "raining solid" device. However, some of the most promising solid reactive agents have been found to be insufficiently stable, physically and chemically, to last through the large number of cycles of absorption and regeneration to make the process economically feasible.

Inexpensive, untreated carbon and activated carbon have been used to attempt to remove sulfur dioxide from stack gases. The beds of activated carbon act as a catalyst to produce sulfuric acid which is held by the carbon. However, the carbon must be removed to chemically recover the acid and then be recycled.

None of the stack-gas cleaning processes has been operated in large power plants for more than a few weeks and costs therefore are highly speculative and relatively high.

The other approach to this problem is represented by the limestone injection process such as disclosed in U. S. Pat. No. 3,481,289. This process involves injecting into a combustion chamber hydroxide converted from oxide in calcined limestone or dolomite, together with newly prepared powder of limestone or dolomite. However, reports from attempts to develop an installation in a practical size plant have not been encouraging. Further, the total solids to be disposed of amount to nearly three times the normal fly ash from a coal containing 10 per cent ash. The disposal problem is staggering, for example, 160,000 tons per year for a 200-MW power plant. In addition, wet scrubbing has been necessitated since the injection of powdered limestone alone removed insufficient quantities of sulfur oxides.

Recent reports for most systems suggested at this time offer much to be desired relative to a practical solution to the sulfur removal problem.

Prior art in combustion systems in general range from those discussed above to systems in which some type of solid was introduced in relatively small quantities to attempt to reduce corrosive effects of the sulfur-oxides in the boiler system. However, none of these systems made any attempt to remove sufficient quantities of sulfur-oxides to noticeably reduce air pollution. Such systems include, for example, the system disclosed in U.S. Pat. No. 3,080,855. Iron oxides are used here to adjust flue gas composition by fixing sulfur dioxide levels by the reduction of sulfur trioxide.

Another rather typical anti-pollution approach in the prior art is disclosed in U.S. Pat. No. 3,421,824, which relates to a two-stage burning process in which atomized fuel is burned to produce impurity-containing intermediate solid products which are removed and thereafter burning any remaining gases so as to accomplish complete combustion of the fuel. The removal of the intermediate solid formed in this manner relates to physically separating the solids from the gases by cyclones, settling chambers, filtering beds or the like. There is no provision for specifically dealing with sulfur oxides.

SUMMARY OF THE INVENTION

In general, the present invention provides a method of removing sulfur compounds produced by the combustion of fossil fuels in the combustion chamber. According to the present invention, a metal in the liquid state is introduced into the combustion chamber and dispersed to intimately contact the combustion gases. The metal chemically combines and/or dissolves with the sulfur constituents in the combustion gases and is, therefore, prevented from passing through the stacks to the atmosphere.

In the most efficient form, the air-fuel mixture is controlled upon introduction to a first stage combustion chamber to establish a reducing condition nonfavorable to the oxidation of the molten metal introduced to capture the sulfur products. The combustion gases after contact with the metal pass into a second stage combustion chamber wherein additional air is injected to drive the combustion of the gases toward completion. In a typical power plant application the hot combustion gases are then passed in heat transfer relationship with water for steam generation.

In order to operate within practical economic limits, the metal sulfide formed in the first combustion chamber is delivered to a refining system which produces refined metal for recirculation through the first chamber and sulfur dioxide which is collected and may be used for sulfuric acid production, for example.

Copper is the preferred metal for circulating through the system because of its significant solubility for sulfur and its ability to combine chemical therewith. In addition to the favorable economics in the use of copper, technology exists for the refining of copper matte and the collection of sulfur dioxide produced by the process.

Further, the reactions of copper in the liquid state with sulfur compounds occurs at rates which are favorable in view of the short residence time of the combustion gases in the combustion chamber. Prior art systems such as limestone injection have encountered problems in sufficient removal of sulfur-oxides because the chemical reaction between the solid powder form employed and the sulfur oxides apparently progresses at slower rates than are desirable for truly efficient results.

OBJECTS OF THE INVENTION

Accordingly it is a principal object of the present invention to provide a method for removing the sulfur oxides in the combustion chamber which are produced by the combustion of fossil fuels.

It is another object of the present invention to provide a method of the type described wherein a molten metal may be employed to remove sulfur oxides formed by the combustion reaction from the combustion chamber and wherein existing technology may be used to regenerate the metal for recirculation and to collect the sulfur dioxide so produced for economic benefit.

It is another object of the present invention to provide a method and apparatus for emission control of sulfur oxides produced in combustion chambers which removes substantially most of the sulfur oxides produced by fossil fuel combustion in an economically feasible manner.

It is a further object of the present invention to provide a method and apparatus of the type described which may be adapted for use in existing steam generating facilities.

Other objects and features of the invention will become apparent when taken in conjunction with the drawings, in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially schematic view in section of a combustion chamber constructed in accordance with the present invention illustrating the introduction of a liquid metal into the first chamber for intimate contact with the combustion gases;

FIG. 1*a* is a partial view illustrating a modified means for agitating a molten pool of metal in accordance with the present invention;

FIG. 2 is a schematic view similar to the view shown in FIG. 1 illustrating a combustion system as adapted for use in a typical power plant boiler system;

FIG. 3 is a block diagram illustrating a typical refining system which may be incorporated in the present invention;

FIG. 4 is a block diagram illustrating the method of the present invention as adapted for use in a typical steam generation system;

FIG. 5 is a graph of calculated partial pressures of the significant gas species formed by the combustion of fossil fuels containing sulfur based on the Standard Gibbs free energy of formation and corresponds to the equilibrium values for coexistence of said species with copper saturated with copper sulfide; and

FIG. 6 is a graph representing the potential sulfur removal from the combustion products of fossil fuels by contact with molten sulfur in the combustion chamber as related to the ratio of carbon dioxide to carbon monoxide present in the combustion reaction products.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring in detail to the drawings, a block diagram of a combustion system constructed in accordance with the present invention is illustrated in FIG. 4. For purposes of illustration, the embodiment shown is described in relation to a typical power plant operation; however, other applications are possible without departing from the spirit of the present invention.

As seen in FIG. 4, the combustion system includes first and second stage combustion chambers **20** and **22** respectively. Second stage chamber **22** is operatively connected to a conventional heat exchange system **24**, wherein the heat from the hot combustion gases is used to generate steam. The combustion gases leave heat exchange system **24** and preferably pass through a dust collection system **26** before leaving the stacks and entering the atmosphere.

First stage combustion chamber **20** includes a recirculation system for the entry of liquid metal and the outlet of a mixture of the liquid metal, matte and slag. This mixture is transferred to a refining unit **28** wherein sulfur and sulfur compounds are removed and the slag is separated. The refined metal is then returned to a reservoir communicating with the first stage combustion chamber for recirculation. Preferably, the refining unit is in the form of a convertor wherein the sulfur is preferentially oxidized and converted to sulfur dioxide and utilized, for example, in the manufacture of sulfuric acid.

Referring specifically now to FIGS. 1 and 2, a typical example of the present invention is schematically illustrated as adapted to a furnace for a steam generator. A furnace housing **10** is provided with first and second stage combustion chambers **20** and **22**. The first stage chamber **20** includes an array of burners **30** for the ingress of the fuel-air mixture.

Reservoir **35** stores a supply of liquid metal which is preferably continuously fed into chamber **20**. The

liquid metal in reservoir **35** may be replenished on a batch basis or continuously dependent upon the design of the closed loop recirculation system.

Essential to the present invention is that the liquid metal introduced into chamber **20** be brought into sufficient intimate contact with the combustion gases passing through chamber **20** to permit the sulfur to combine with the liquid metal by either absorption and/or chemical combination. In the embodiment shown, the liquid metal is introduced from reservoir **35** via a port **32** and falls to the bottom of chamber **20** to form a pool **34**. The molten pool is agitated by an impeller **36** which is designed to throw a dense shower of fine droplets upwards into the combustion gases in chamber **20**. Port **32** is preferably arranged with burners **30** to direct the stream of liquid metal directly into the flow of combustion gases from the burners. This tends to provide a more intimate contact between the combustion gases and the liquid metal which complements the desired contact obtained by the dense shower of liquid metal droplets created by impeller **36**. The efficiency of the removal of sulfur from the combustion gases is dependent upon obtaining sufficient contact between the combustion gases and the liquid metal to permit sulfur to be combined with the liquid metal in the short time available for reactions. Periodically, the bath **34** is partially tapped through outlets **20** A and **20B**.

It is important to point out that the liquid metal or alloy used in connection with the present invention possesses certain characteristics. First, it must have a significant solubility for sulfur and/or a capability of forming one or more stable compounds with sulfur. Second, it must not be readily oxidized in combustion gas mixtures under conditions which can be readily controlled. Third, it must have a melting point below temperature ranges normally occurring in the conventional furnace systems employing organic fuels. And lastly, the metal used should possess a relatively low solubility for carbon.

Copper or copper based alloys are the preferred choices for use in the present invention.

For example, copper will dissolve about 1.8 percent by weight of sulfur at 1,200° C and the solubility of carbon in liquid copper is less than 0.002 percent. In addition, copper will not readily oxidize in combustion gas mixtures unless the ratio of carbon dioxide to carbon monoxide is approximately 1,000 to 1 or greater at 1,200° C. Copper also has a melting point in the preferred range noted above and can be refined by well known methods to remove sulfur for conversion to sulfuric acid. Silver and silver based alloys would also be suitable; however, the cost of silver represents such an economic disadvantage that it is an impractical choice under most conditions.

It is very desirable to prevent the oxidation of the liquid metal being introduced to remove the sulfur pollutants for at least two reasons. Firstly, the oxide would tend to coat various portions of the chamber and present a maintenance problem and secondly, the efficiency of the removal of sulfur from the combustion gases would be significantly decreased.

The range of satisfactory operating conditions for any particular combination of fuel, oxidant and liquid metal has been determined by thermodynamic and stoichiometric calculations. For example, using copper as the liquid metal circulated through chamber **20**, the theoretical ratio of carbon dioxide to carbon monoxide in the fully reacted fuel/oxidant mixture should be less that 1,000 to 1 and preferably less than 10 to 1.

It is important to recognize that combustible mixtures do not react completely within most combustion systems. Therefore, the actual mixture leaving the first stage combustion chamber may have a carbon dioxide to carbon monoxide ratio less than the theoretical ratio calculated from the input materials because of the incompleteness of the combustion reactions. Therefore, a nonequilibrium condition exists wherein some uncombined oxygen is still present.

The important consideration then, is to control the oxidant/fuel ratio to prevent the oxidation of the liquid metal introduced to remove sulfur. The desired value of the oxidant/fuel ratio to accomplish this objective can be determined by calculations based upon the assumption of complete reactions. For example, the following calculations are for a system burning pulverized coal having the following compositions:

TABLE I

Proximate Analysis (% by wt)		Ultimate Analysis (% by wt)	
Volatile Matter	14.0	Sulfur	2.0
Fixed Carbon	75.0	Hydrogen	4.0
Ash	9.0	Carbon	80.0
Moisture	2.0	Nitrogen	1.0
Total:	100.0	Oxygen	4.0
		Ash	9.0
		Total:	100.0

The theoretical requirement for complete combustion of such a coal is 130.0 standard cubic feet of air per pound of coal. Assuming complete combustion reactions, the combustion products have the following approximate analysis by volume percent:

TABLE II

	VOLUME %
Sulfur Dioxide	0.167
Water Vapor	5.350
Carbon Dioxide	17.880
Nitrogen	76.600

The combustion products would also contain equilibrium traces of other species such as oxygen, carbon monoxide, methane and other molecules depending upon the temperature and pressure conditions. As previously noted, however, combustion reactions do not go completely to equilibrium in most actual combustion systems, therefore a significant amount of uncombined oxygen is still present in the reacted mixture.

However, the thermodynamic oxidizing potential of the gas mixture is determined by its theoretical composition based on the assumption of all reactions proceeding to equilibrium.

Therefore, to prevent oxidation of the copper, it is necessary to adjust the fuel/oxidant ratio so that the theoretical composition of the combustion products yield a thermodynamic oxidizing potential less than that required to form the metal oxide. As previously

mentioned, this condition exists where the carbon dioxide to carbon monoxide ratio is less than about 1000 in the case of liquid copper in the temperature ranges normally encountered.

To illustrate conditions which are favorable for the prevention of copper oxidation and for the absorption of sulfur by the copper, the following calculations are based upon burning coal, having the same analysis as the previously mentioned example, with air in proportions of 113.8 standard cubic feet per pound of coal or **87.6** per cent of the theoretical requirement for complete combustion. The approximate composition of the reacted gas mixture assuming complete reactions is then the following:

TABLE III

	VOLUME %
Sulfur Dioxide	0.185
Water Vapor	5.010
Hydrogen	0.912
Carbon Dioxide	15.040
Carbon Monoxide	4.700
Nitrogen	74.150

The above composition includes all of the sulfur, that is, the sulfur is not considered as removed in accordance with the present invention. However, the carbon dioxide to carbon monoxide ratio is 3.2 and the water vapor to hydrogen ratio is 5.5.

By way of example, if 95 percent of the sulfur is removed in accordance with the present invention, the above gas composition of Table III becomes the following:

TABLE IV

	VOLUME %
Sulfur dioxide	0.0094
Water vapor	5.050
Hydrogen	0.885
Carbon dioxide	15.220
Carbon Monoxide	4.570
Nitrogen	74.270

Now by adding 32.3 standard cubic feet of air per pound of fuel to the gas composition given in Table IV, which represents the gases leaving chamber **20** and entering the second stage chamber **22**, it brings the total air in the second chamber to 146.1 standard cubic feet per pound of fuel. This represents 112.4 per cent of the theoretical requirement for complete combustion and the gas compositions that result are approximately as given in Table VI, as follows:

TABLE VI

	VOLUME %
Sulfur Dioxide	0.0075
Water Vapor	4.78
Carbon Dioxide	15.94
Nitrogen	76.97
Oxygen	2.30

Table VI then represents the theoretical gas composition leaving second stage chambers **22** and eventually passing through the stacks into the surrounding environment.

Of course, in the actual combustion system, the technical design factors relative to practical costs will determine the efficiency of the system. However, in a well designed system, a very significant portion of the sulfur can be removed. The significant factors controlling the efficiency will be described in detail later herein.

Again equilibrium traces of other species would be present in the combustion products. The major portion of the sulfur is removed from the combustion products by reaction with the liquid copper. The calculations given herein are for a combustion gas temperature of 1,227° C.

As indicated above, the carbon dioxide to carbon monoxide ratio is in the preferred range and this reducing condition is achieved by using approximately 87.6 percent of the theoretical requirement for complete combustion.

To generalize, a favorable reducing condition is established in accordance with the present invention in the first stage chamber **20** by using a fuel/oxidant ratio which is theoretically insufficient for complete combustion and which maintains a condition which prevents the oxidation of the liquid copper and promotes the removal of the sulfur. The optimum fuel to oxidant ratio will vary somewhat according the specific application and depend upon the requirements of the specific combustion system.

The liquid copper, matte (and slag) mixture (which forms in pool **34**) must be prevented from passing into the second chamber by a suitable chamber design, such as for example, by a baffled outlet **40** or the like in the chamber wall separating chambers **20** and **22**. Another method to accomplish the same result would be to design the gas flow pattern such that the reacted gaseous mixture could not entrain an appreciable amount of the fine liquid copper droplets as the gases flow out of chamber **20** and into chamber **22**.

Since reducing conditions are maintained in chamber **20**, additional air is introduced into second stage chamber **22** through ports **42** to drive the combustion reactions toward completion. The design of the second stage chamber **22**, or additional stages if desired, may vary somewhat depending upon how the hot combustion gases are to be utilized and the requirements for each power plant. For example, in steam generation applications, temperature and composition controls may be imposed and achieved through the use of preheated air and/or the adjustment of the amount of excess air used and the specific design of the system.

The sulfur and sulfur compounds in the combustion gas mixture are absorbed by or chemically combined with the liquid copper upon contact. Most of the contact between the copper and sulfur compounds is provided by the spray of droplets created by impeller **36**, however, additional sources of contact are provided by the incoming stream of liquid copper as it falls downward to pool **34** as previous described, and further by the contact between the combustion gases and the surface of pool **34** which is continuously agitated by the action of impeller **36**. The latter two

sources of contact may be increased in efficiency by appropriate design. For example, the incoming stream could be introduced initially into chamber **20** in a fine spray of droplets that fall through the combustion gas stream or the gas stream could be directed to impinge more directly into the pool of liquid copper. Further, tuyers, such as shown in FIG. **1***a* at **50**, could be employed to inject an inert gas into pool **34** to cause agitation and promote contact of the liquid metal with the combustion gases.

The term droplets or droplet form as used herein is intended to include any liquid particles from the size range of a finely divided mist to large drops and is not intended to be limited to only liquid particles of uniform size within a defined pattern.

Now referring specifically to the chemistry and metallurgy involved in the removal of sulfur in first stage chamber **20**, the following list represents the primary chemical reactions which can occur upon the contact between liquid copper and the combustion gas mixture. The intermediate reactions and many other species which may be present are ignored in this description for the purposes of clarity since they are not significant relative to the purposes of the present invention.

$$2\,Cu + \tfrac{1}{2}\,S_2 = Cu_2S \quad (1)$$
$$2\,Cu + SO + CO = Cu_2S + CO_2 \quad (2)$$
$$2\,Cu + SO + H_2 = Cu_2S + H_2O \quad (3)$$
$$2\,Cu + SO_2 + 2\,CO = Cu_2S + 2\,CO_2 \quad (4)$$
$$2\,Cu + SO_2 + 2\,H_2 = Cu_2S + 2\,H_2O \quad (5)$$
$$2\,Cu + SO_3 + 3\,CO = Cu_2S + 3\,CO_2 \quad (6)$$
$$2\,Cu + SO_3 + 3\,H_2 = Cu_2S + 3\,H_2O \quad (7)$$
$$2\,Cu + COS = Cu_2S + CO \quad (8)$$
$$2\,Cu + \tfrac{1}{2}\,CS_2 + \tfrac{1}{2}\,CO_2 = Cu_2S + CO \quad (9)$$
$$2\,Cu + H_2S = Cu_2S + H_2 \quad (10)$$
$$2\,Cu + CO_2 = Cu_2O + H_2 \quad (11)$$
$$2\,Cu + H_2O = Cu_2O + H_2 \quad (12)$$
$$2\,Cu + \tfrac{1}{2}\,O_2 = Cu_2O \quad (13)$$

Reactions (1) through (10) lead to the removal of the sulfur gases from the combustion products by the formation of a copper sulphide phase or by the solution of Cu_2S into copper. Liquid copper will dissolve about 8.9 percent by weight of Cu_2S at 1,100° C which corresponds to 1.8 percent by weight of monatomic sulfur in solution. The melting point of pure copper is 1,084° C and the solution of sulfur into copper lowers the melting point. The temperatures attained during the combustion of fossil fuels with air or oxygen-enriched air (with or without preheating) are generally well in excess of the monotectic temperature of 1,102° C so that the condensed phases, copper and copper sulphide, remain liquid.

To determine the proper conditions for transferring sulfur from the gas phase to the copper phase, the standard Gibbs free energies of formation of the compounds were applied to give the free energy changes for Reactions (1) through (12).

These calculations permit the prediction of conditions favorable for sulfur removal from the combustion gases and unfavorable for the formation of copper oxide. FIGS. **5** and **6** are graphs illustrating representative results of such calculations.

The calculated partial pressures of the gas species are based on the Standard Gibbs free energy of formation and correspond to equilibrium values for coexistence with copper saturated with copper sulphide, that is, a mixture of Cu and Cu_2S. Representative calculations are placed on a decadic logarithmic basis in FIG. **5** to show all of the species on a single graph. As can be seen H_2 and H_2O are included and the H_2O/H_2 ratio is in equilibrium with the CO_2/CO ratio at each point through the water-gas reaction. The absolute values of the partial pressures are based on a total pressure of one atmosphere and a combustion gas composition established by partial burning with air of a fossil fuel having a ratio of H to C of about 1 to 15 on a weight basis. Therefore, nitrogen represents about 75 percent of the gas. Included in FIG. **5** are the maximum values of CO_2/CO for operation without the formation of copper oxide. Also included are lines A, B, and C, which are representative levels of the total of the partial pressures of the sulfur species generated by fuels containing 1, 2, and 5 percent sulfur by weight when no removal of sulfur occurs. As can be seen the total of the partial pressures of the sulfur species in equilibrium with Cu/Cu_2S (the ΣS line) lies well below these lines for values of P_{CO}/P_{CO} less than about **10** ($\log P_{CO}/P_{CO} = +1$) at 1,127° C (2061° F). The separation of the ΣS line below the fuel lines indicates the potential effectiveness of copper (saturated with Cu_2S) to remove sulfur from hot combustion gases. This is shown more clearly in FIG. **6** where the calculated results are replotted on a linear expanded scale. In FIG. **6** some illustrative percentages for the removal of sulfur are indicated. For example, at a CO_2/CO ratio of 3.2, 98 percent of the sulfur in a fuel containing 3 percent S can be removed by contact with copper.

FIGS. **5** and **6**, therefore, represent typical calculations for the potential removal of sulfur from combustion gases by contact with copper saturated with copper sulphide. Similar results are obtained for other fuel compositions and operating temperatures.

The liquid pool **34** formed in the lower portion of chamber **20** includes liquid copper, copper sulphide or matte, slag and some ash which would also be trapped by the liquid metal droplets thrown upwards by impeller **36**. Preferably, in the embodiment shown, a portion of pool **34** is tapped on a batch basis through outlet **20B**. The portion removed through outlet **20B** is transferred to refining unit **28**. The amount of liquid in pool **34** which is tapped depends upon the circulation rate of the liquid copper through the combustion chamber **20** and refining unit **28**. The circulation rate should be in the range of 0.001 to 10 pounds of metal per pound of fuel burned. The preferred range, however, is 0.05 to 0.50 pounds of copper per pound of fuel based upon copper entering and leaving the combustion chamber and takes into consideration both the efficiency and the economics of operating the system. The optimum rate within the above noted preferred range might vary depending upon the design characteristics of each individual system.

It should be noted that outlet **20A** is disposed at a higher position relative to outlet **20B**. Periodically, slag may be conveniently tapped through outlet **20A** because the slag, being the less dense component of the mixture tends to rise to the upper portion of pool **34**. Therefore, an excessive accumulation of slag is prevented and very little liquid copper or matte is lost when the slag is tapped.

It should be pointed out that the pool **34** could also be tapped continuously and transferred by conven-

tional means, such as ladles or by a pumping system, to the refining unit and then to the reservoir **34**. Whatever the method and means used in the recirculation system, however, the important factor is that sufficient metal be circulated through chamber **20** to effect the efficient removal of sulfur from the combustion gas mixture.

The circulation rate required to achieve the percentages of sulfur removal indicated as the upper limit under the conditions specified in the calculated results represented in FIG. **6** can be approximately determined by the following equation:

$$\frac{M_{Cu}}{M_{fuel}} = \frac{W}{100} \times \frac{100-(\%S)_{Cu}}{(\%S)_{Cu}} \times \frac{(\%S)_{fuel}}{100} \qquad (14)$$

Where M_{Cu}/M_{fuel} is the pounds of copper recirculated into the combustion system per pound of fuel burned, W is the percentage removal of the sulfur from the fuel by the copper, $(\%S)_{Cu}$ is the percentage by weight of sulfur in the Cu/Cu_2S mixture leaving the combustion system, and $(\%S)_{fuel}$ is the percentage by weight of sulfur in the fuel.

It should be pointed out that some loss of copper will occur and of course such losses must be minimized to achieve economical operation. However, depending upon the design of each system, fresh copper will from time to time have to be added to the recirculation system. To be economically efficient, the percentage of nonrecoverable loss of copper should not, for example, exceed about 3 percent for a system having a recirculation rate of 0.2 pounds of copper per pound of fuel burned. For higher or lower recirculation rates than the example given, the percentage of copper loss permissible for practical economic operation will vary accordingly. To summarize, the recirculation rate of copper through the system should be at least 100 pounds of copper per ton of fuel burned. In general, the efficiency of sulfur removal will be increased as the circulation rates increase; however, nonrecoverable losses of copper and operating costs increase also. Therefore, the optimum circulation rate will depend upon the specific design and individual requirements of each system and will represent a compromise between the sulfur removal and the cost of operating the system.

In the embodiment shown, the liquid tapped from pool **34** falls into a conventional ladle **44** which is then transferred by any conventional liquid metal handling system, not shown, to converting unit **28**.

A typical conventional central refining unit **28** is shown in FIG. **4** and described briefly herein and illustrates a preferred refining system for use in the closed-loop recirculation system of the present invention. However, it should be emphasized that other types of units could be employed which will achieve the desired results.

Referring now to FIG. **4**, the refining unit, commonly referred to as a Hoboken type, receives the liquid copper, matte, and slag mixture from chamber **20** from a transfer system **44**. Although a greater capital outlay is required, the Siphon convertor is preferred because its design reduces the escape of the sulfur dioxide gases and other pollutants to the atmosphere and also increases sulfuric acid production.

A typical Siphon convertor plant consists of a convertor shell **46**, with its refractory lining, tuyeres and rotating mechanism, motor drive, flue, etc., a hood system **47** and a tubular gas cooler **48** which allows rapid cooling of the gases to keep formation of sulfur trioxide down to a minimum and to secure satisfactory temperature conditions for the dampers **50**.

The bottom of the cooler is fitted with hoppers for dust collection. A suction fan blower **45**, with a variable-speed drive, makes it possible to adjust the draught to an almost negligible value at the mouth of the convertor. Two motor driven dampers **50** allow clear separation between the gases containing SO_2 and the other gases free of SO_2. Each gate-type damper **50** can be secured in one of seven positions between the fully open and closed positions.

One damper communicates with the gas cleaning unit for sulfur dioxide delivered to the acid plant **54** and the other damper communicates with a cleaning unit and stack **52** for the other gases.

The dampers are also electrically interconnected and controlled; thus the damper **50** leading to the stack **52** is locked in the closed position while the convertor is blowing. This damper must be in the fully closed position before the other damper **50** for SO_2 gases can be turned open in this type of unit.

If the sulfuric acid plant is located at some distance from the convertor aisle, and if the flues are not corrosion-proof, a small pulverized lime injector may be provided for blowing fine lime into the flues. This lime will absorb the small quantities of SO_3 which could have been formed and which have not been neutralized by zinc or lead oxides. Flues connect directly to the stack for removal of gases during periods when SO_2-free gases are produced, i.e., slag skimming and preheating.

In addition to the usual materials handling facilities, such as travelling cranes, equipment for copper casting, etc., the necessary gas-cleaning equipment before entry of the gases into the sulfuric acid plant must be provided.

What is claimed is:

1. A method for removing sulfur from fossil fuel combustion products formed in a combustion chamber including the steps of introducing a metal in a liquid state into said combustion chamber, collecting the metal sulfide formed for removal from the combustion chamber; processing said metal sulfide to refine the metal and produce sulfur dioxide; recirculating the refined metal through said combustion chamber; and collecting the sulfur dioxide produced in the refining process.

2. The method defined in claim **1** wherein said metal is one taken from a group comprising copper, silver, a copper-based alloy or a silver-based alloy.

3. The method defined in claim **2** wherein said metal has a melting point below approximately 1,600° C, a significant solubility for sulfur and the ability to chemically combine with sulfur.

4. The method defined in claim **1** wherein said metal is copper.

5. The method defined in claim **4** wherein said copper is continuously dispersed in said combustion chamber in droplet form during the combustion reaction in intimate contact with combustion reaction products.

6. The method defined in claim **1** wherein said metal is a copper-based alloy.

7. The method defined in claim 1 wherein the fuel and oxidant is introduced into a first combustion chamber in an oxidant to fuel ratio less than the theoretical requirement for complete combustion; maintaining said oxidant to fuel ratio at a value required to maintain the carbon dioxide to carbon monoxide ratio in the combustion reaction products at a value of less than 100 to 1.

8. The method for removing sulfur from fossil fuel combustion products comprising the steps of contacting the combustion products in a combustion chamber with molten copper droplets to combine with the sulfur constituents of said products to form copper sulfide collecting the copper sulfide removed from said combustion chamber; processing said copper sulfide to produce refined copper and sulfur dioxide; recirculating the refined copper through said combustion chamber; and collecting the sulfur dioxide produced in the refining process.

9. The method defined in claim 8 wherein the fuel and oxidant is introduced into the combustion chamber in a predetermined quantity to establish a reducing condition in said chamber defined by the theoretical composition of the combustion products yielding a thermodynamic oxidizing potential less than required for oxidation of said metal.

10. A method for removing sulfur from the combustion products of a fossil fuel comprising the steps of introducing fuel and oxidant into a first combustion chamber, the oxidant to fuel ratio being predetermined to control the ratio of carbon dioxide to carbon monoxide formed by the combustion reaction at a value less than approximately 10 to 1; continuously dispersing a molten metal into said first combustion chamber for intimate contact with the gaseous combustion products formed, said metal having a melting point below approximately 1,600° C, and/or a significant solubility for sulfur, and/or the ability of chemically reacting with sulfur and sulfur containing compounds; communicating the combustion products formed in said first combustion chamber with a second combustion chamber; introducing excess oxidant into said second chamber to drive the combustion reaction therein toward completion; removing the mixture of metal and metal sulfide formed in the first combustion chamber for collection; processing said mixture of metal and metal sulfide to obtain refined metal and sulfur oxides; recirculating the refined metal through the first combustion chamber; and collecting the sulfur oxides.

11. The method defined in claim 10 wherein said metal is one taken from a group comprising copper, copper-based alloys, silver or silver-based alloys.

12. The method defined in claim 10 wherein said metal is dispersed in said chamber in droplet form.

13. In a combustion system for burning fossil fuels containing a significant sulfur content the combination of a combustion chamber; means for introducing an oxidant-fuel mixture into said chamber; means for continuously dispersing a molten metal into said combustion chamber in intimate contact with the combustion products formed in said chamber; a metal refining system; means for delivering the metal sulfide formed in said chamber to said metal refining system; and means for collecting the refined metal from said refining system and the sulfur oxides formed in the refining process; and means for recirculating said refined metal through said combustion chamber.

14. The system defined in claim 13 including control means associated with said means for introducing said oxidant-fuel mixture to maintain a predetermined oxidant to fuel ratio less than the theoretical requirement for complete combustion of the input fuel materials.

15. The system defined in claim 13 including a reservoir containing a supply of molten metal received from said refining system and communicating with said combustion chamber; and means for controlling the flow of metal from said reservoir to said chamber.

16. The system defined in claim 13 wherein said combustion chamber includes a pool of molten metal formed in the bottom portion thereof and is provided with a first and second tap outlet communicating with said pool for removal of the metal from said chamber, one of said outlets being disposed at a higher level in said chamber relative to the other of said outlets.

* * * * *