

[54] COAL DESULFURIZATION PROCESS

[75] Inventors: **Arthur F. Diaz**, University City;
Eugene D. Guth, Palos Verdes
 Peninsula, both of Calif.

[73] Assignee: **KVB Engineering, Inc.**, Tustin,
 Calif.

[22] Filed: **Aug. 31, 1973**

[21] Appl. No.: **393,301**

[52] U.S. Cl. **44/1 R**; 201/17; 423/522

[51] Int. Cl. **C10I 9/00**

[58] Field of Search 44/1 R; 201/17; 423/461,
 423/522, 523, 525; 208/8

[56] **References Cited****UNITED STATES PATENTS**

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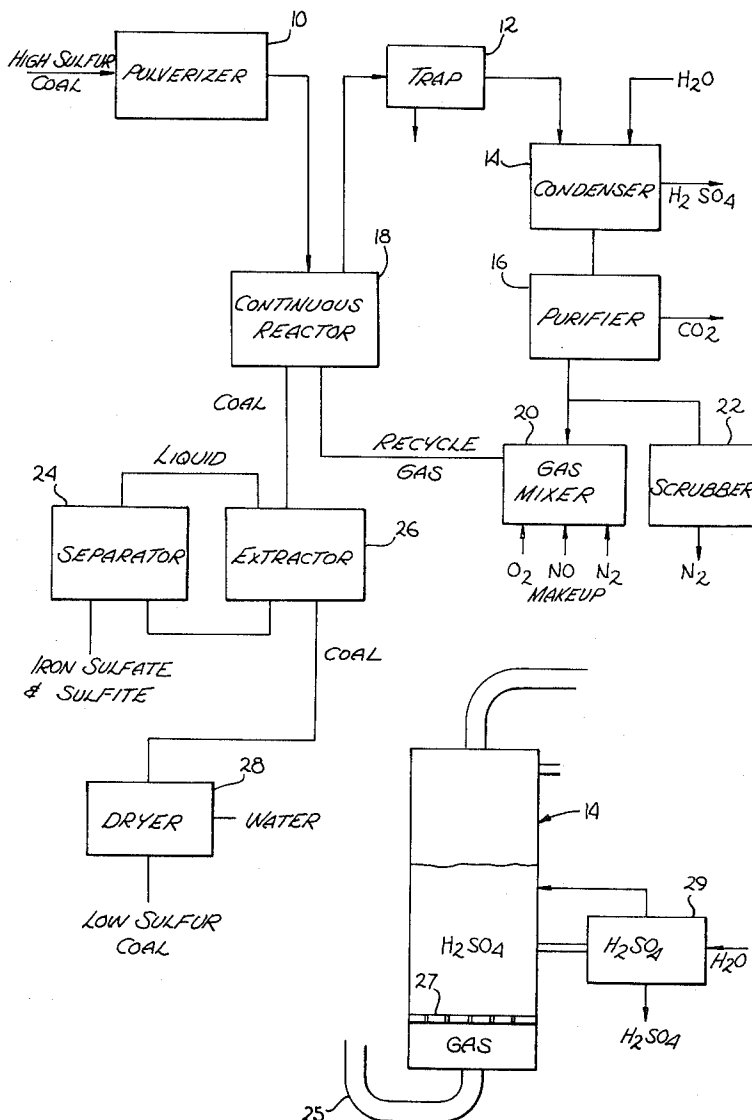
Primary Examiner—Carl F. Dees

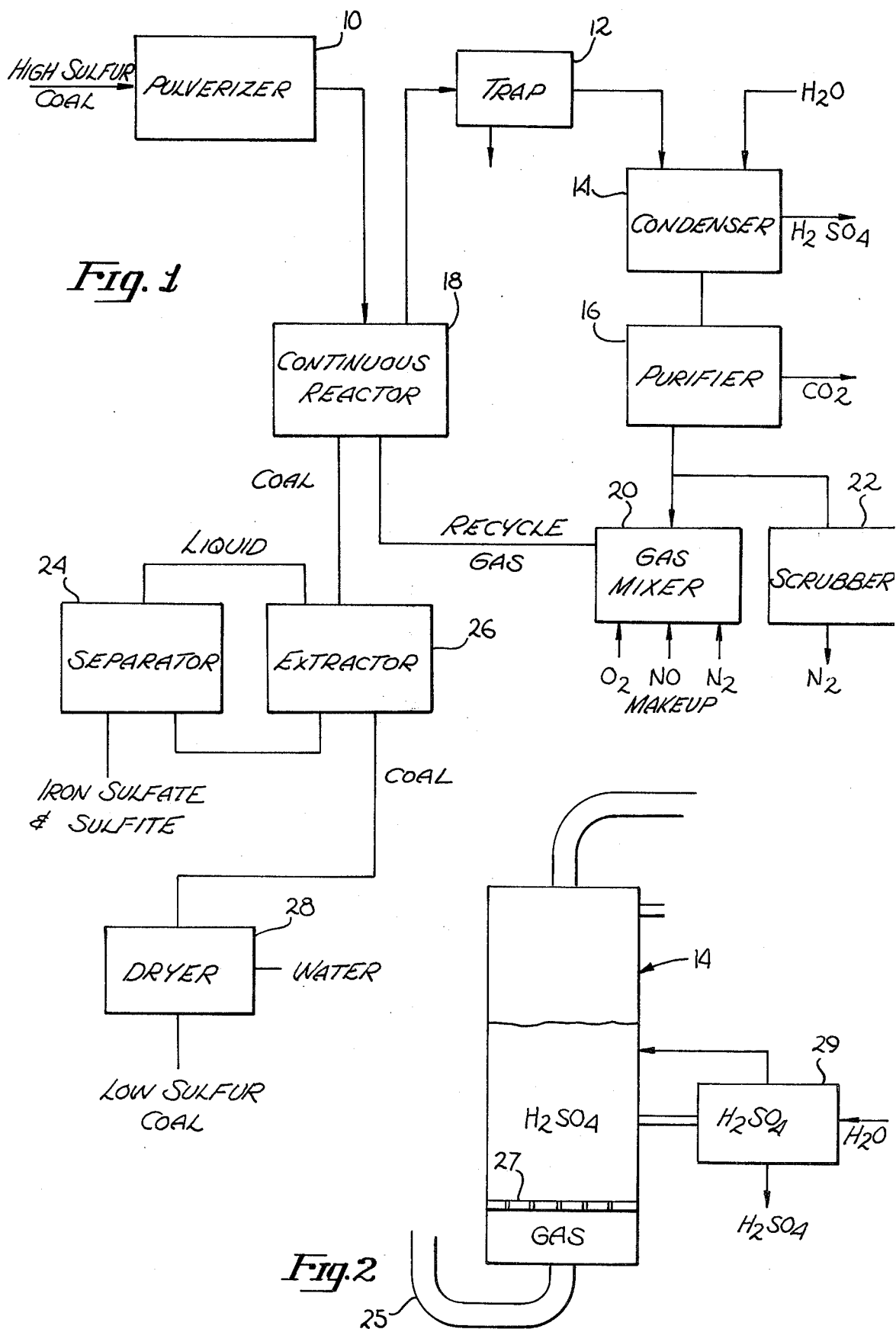
Attorney, Agent, or Firm—Spensley, Horn & Lubitz

[57] **ABSTRACT**

Coal is desulfurized by heating it in comminuted form in the presence of NO_2 and other gases to remove part of the sulfur in the coal. Sulfur still remaining in the coal will be in the form of an inorganic sulfate or sulfite or included in an organic radical, assuming coal has a condensed aromatic ring structure, with two double bonded oxygen atoms attached. This sulfur is for the most part removed by a subsequent additional step of exposing the pre-treated coal to water or to a heated alkali metal hydroxide solution.

50 Claims, 4 Drawing Figures





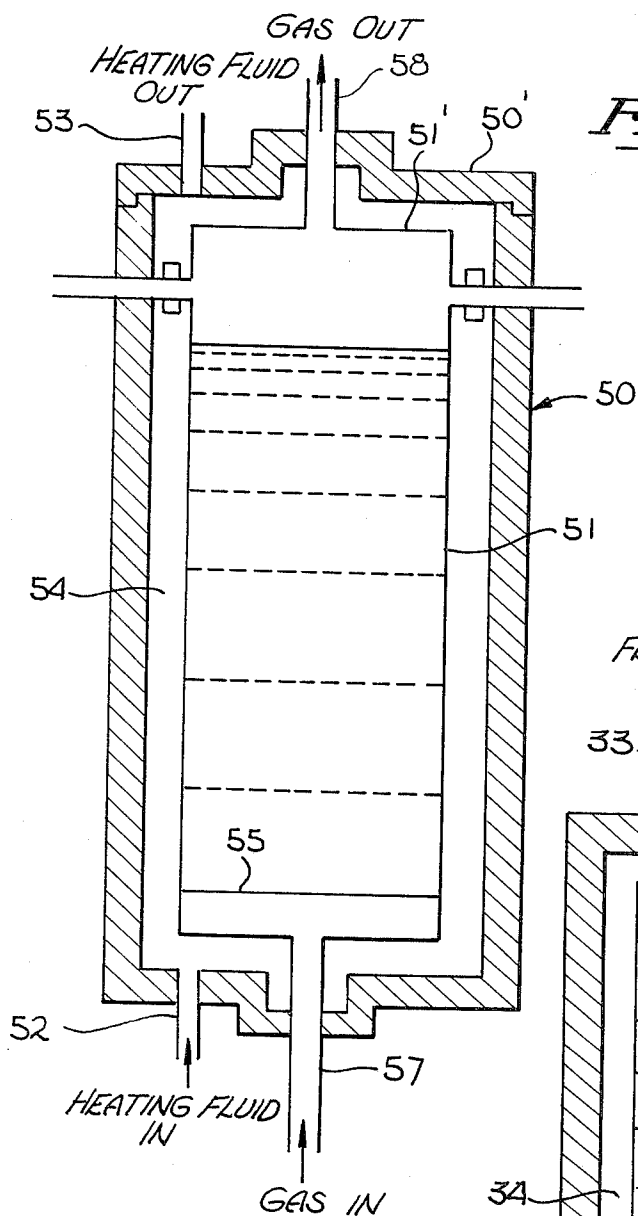


Fig. 4

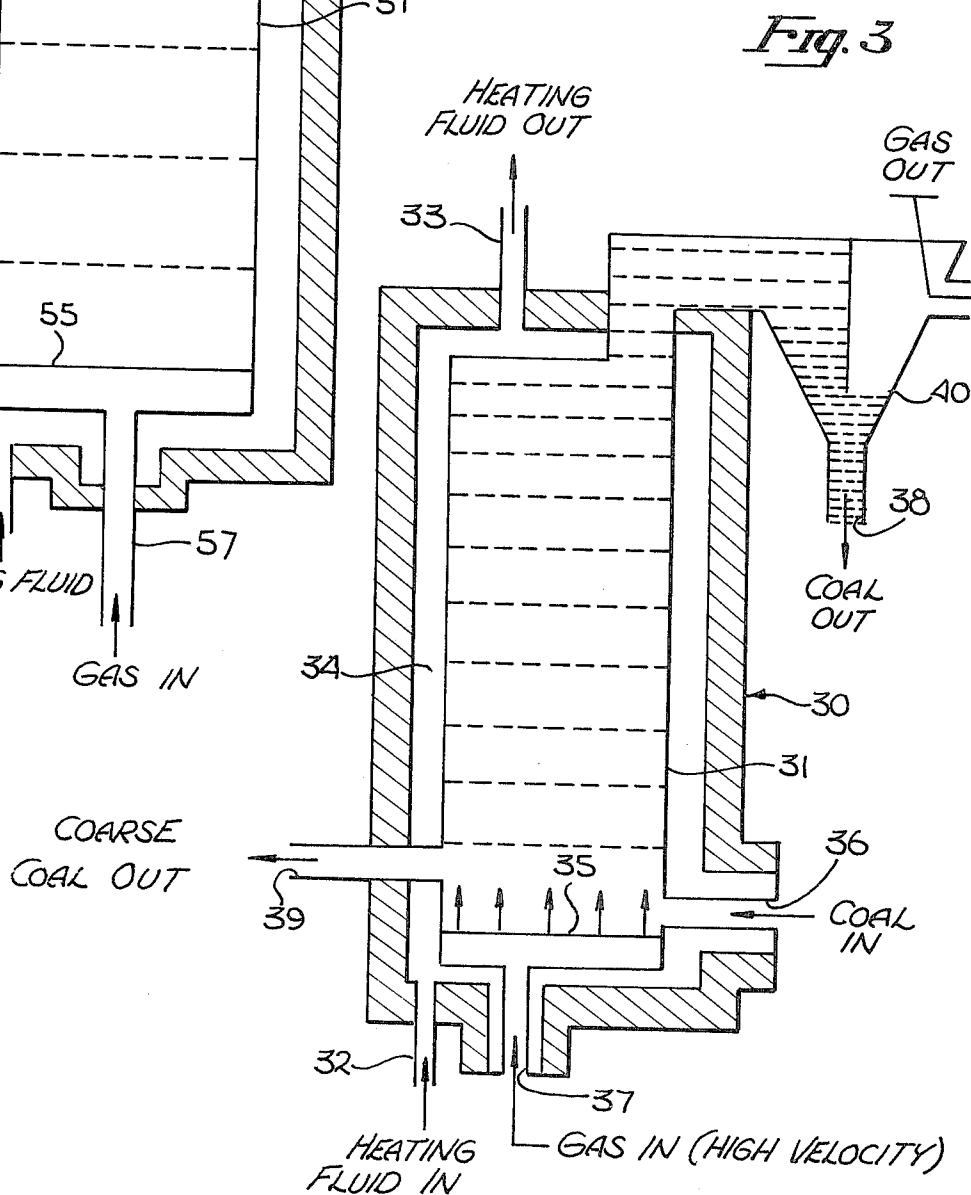


Fig. 3

COAL DESULFURIZATION PROCESS

BACKGROUND OF THE INVENTION

1. Prior Art

Among the prior art known to the inventors is U.S. Pat. No. 3,451,769 issued June 24, 1969, to Kishitaka, et al., which is not concerned with desulfurizing coal, but is nevertheless considered of some pertinency. This patent teaches the concept of oxidation of ferrous ions to ferric ions by employment of NO_2 as a catalyst in the presence of oxygen. The invention thereafter achieves a simplification of processing by mixing the oxidized solution with a concentrated amount of unoxidized solution and subsequently neutralizes the mixture with ammonia. This entire process involves the treating of waste pickling liquors. The present invention, on the other hand, involves the use of NO_2 to selectively oxidize the sulfur in coal in the presence of both carbon and hydrocarbon. Unlike Kishitaka, in the present invention the sulfur is in a solid (not liquid) phase. Kishitaka has water present and depends upon the solution of NO_2 to form nitric acid which is the oxidizing agent. The use of an alkali metal hydroxide in the present invention method is an added step to remove sulfur not previously removed, while Kishitaka uses ammonia as an integral reagent.

U.S. Pat. No. 3,387,941 issued June 11, 1968 to Murphy, involves desulfurizing coal with steam and alkali metal hydroxides at $500^\circ\text{--}850^\circ\text{C}$. The present invention, on the other hand, operates at lower temperatures of $100^\circ\text{--}500^\circ\text{F}$ and hydroxides are used only to hydrolyze and dissolve previously oxidized organic sulfur compounds. Water is only used to mechanically extract previously oxidized iron-sulfur compounds in the coal (iron and sulfites and sulfates).

U.S. Pat. No. 3,607,718 issued Sept. 21, 1971 to Leaders, also teaches a sulfur removing method for coal—involving the dissolution and hydrogenation of the coal to remove ash and inorganic and organic sulfur by the use of a partially hydrogenated hydrocarbon solvent. This is a process clearly totally different from that of this invention.

U.S. Pat. No. 3,375,188 issued Mar. 26, 1968 to Bloomer, teaches a method for deashing coal by dissolving pulverized coal at $600^\circ\text{--}850^\circ\text{F}$ in a boiling aromatic hydrocarbon mixture. The present invention method is carried out at a lower temperature without hydrocarbons being present, and the coal itself is not dissolved but the sulfur bearing components are oxidized and subsequently leached out.

U.S. Pat. No. 3,723,291 issued to Thakker on Mar. 27, 1973 involves adding an alkali metal carbonate to the coker feed stack prior to coking and then after coking, treating the coke with hydrogen at a temperature of from $1,000^\circ\text{F}$ to $2,000^\circ\text{F}$. This is a totally different and much higher temperature process than that of the present invention.

SUMMARY OF THE INVENTION

The present invention method provides an improved method for desulfurizing coal while producing concentrated sulfuric acid as a commercially useful by-product.

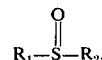
The preferred embodiment of the present invention involves the following steps: Coal is first converted into particulates. We prefer to use pulverized coal in which no particulate is larger than approximately one fourth

inch in diameter. Although the process can be made to work on larger particles the sulfur removal efficiency is reduced. The pulverized coal is placed into a reaction chamber into which is passed a combination of four gases with the interior of the chamber being maintained at a temperature in the range from 100° to 500°F , for from 1 to 30 minutes, for continuous reaction or for from 0.5 to 5 hours for batch reaction, at a pressure in the range from 1 to 20 atmosphere. The process can be either on a batch or continuous basis as desired.

The gases used are preferably O_2 (0.5 to 20 volume %), NO (0.25 to 10 volume %), NO_2 (0.25 to 10 volume %) and N_2 the remainder. The resulting sulfur containing products from this step will typically be FeSO_4 , SO_3 or SO_2 gas and



and



FeSO_4 is removed by water extraction as this salt is soluble in water. The SO_3 is converted into concentrated H_2SO_4 by being passed into a condenser containing a solution of H_2SO_4 . The SO_2 is recycled to the reactor where it is subsequently oxidized to SO_3 . It is within the scope of our invention to convert the SO_2 or other sulfur containing compounds to SO_3 by exposure of the SO_2 to oxygen within the reactor by further reacting the reactor effluent gas before contacting the gas with sulfuric acid. It is also within the scope of our invention to react the SO_3 gas with compounds such as calcium oxide or sodium hydroxide to form calcium sulfate or sodium sulfate instead of sulfuric acid. These latter two variations are not discussed in detail herein. In addition to calcium oxide or sodium hydroxide, any other alkali metal or alkaline earth oxide or hydroxide may be employed. If it is desired to remove the sulfur from the above two indicated hydrocarbon sulfur containing radicals, a subsequent exposure thereof to sodium hydroxide heated to a temperature of from $200^\circ\text{--}220^\circ\text{F}$ at a pressure of from 1 to 20 atmospheres for 1 to 30 minutes is required.

It is therefore an object of the present invention to provide an improved and simplified method for the desulfurization of coal.

Another object of the present invention is to provide an improved coal desulfurizing method which provides H_2SO_4 acid as a by-product at a cost which renders the same commercially saleable.

These and other objects of this invention may be had by referring to the following description taken in conjunction with the accompanying drawings.

DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a block diagram representing the process for removing sulfur from coal in accordance with the presently preferred embodiment of the invention;

FIG. 2 is a diagrammatical illustration in section of the condenser of FIG. 1;

FIG. 3 is a diagrammatical illustration, in section, of the reactor of FIG. 1, suitable for continuous processing; and

FIG. 4 is a diagrammatical view in section of a reactor for the present invention suited for batch processing.

DETAILED DESCRIPTION OF THE INVENTION

Referring now to the drawings and more particularly to FIG. 1, there is shown a representative continuous process arrangement for carrying out the present invention. A batch processing arrangement is also understood to be within the scope of this invention.

Coal in crushed or raw form is initially fed into a pulverizer 10 which serves to convert the raw coal into particles to be processed, the size of which will range from 200 mesh to as large as one fourth inch in diameter. Pulverizers for accomplishing this commutation are well known and are commercially available, and thus pulverizer 10 will not be described in detail.

The converted coal is then fed into a reactor 18. Reactor 18 will be more fully described hereinafter in combination with FIG. 2. Reactor 18 receives the coal particles from pulverizer 10, together with a predetermined quantity of a combination of the following four gases in the below listed relative quantities:

O ₂	— 0.5 to 20 volume %
NO	— 0.25 to 10 volume %
NO ₂	— 0.25 to 10 volume %
N ₂	— balance

The chemical reaction which occurs both in reactor 18 and in subsequent steps in accordance with this invention will be described hereinafter. The physical steps only will first be considered. Upon being heated for a period of time of from 1 to 30 minutes at a pressure in the range from 1 to 20 atmospheres at a temperature of from 100° to 500°F in reactor 18, the output from reactor 18 will typically be a combination of materials, some solid, some gaseous, including Fe SO₄, desulfurized coal and some additional hydrocarbons containing some sulfur. The solid portion of the output from the reactor 18 is directed to an extractor 26.

Water is added to the reactor products in extractor 26 and the inorganic sulfur present as sulfates or sulfites dissolves and passes to separator 24 with the liquid stream. This soluble portion includes the sulfur initially present as iron pyrites which is converted to sulfates and sulfites in the reactor. To aid in the removal of the sulfates and sulfites in the extractor, a soluble caustic such as sodium hydroxide may be added to the water in extractor 26. The water may also be kept warm to facilitate solubility.

The liquid phase, as mentioned above, passes to separator 24 where it is cooled to precipitate the inorganic sulfates and sulfites, which are then removed by filtration. The water is then heated and recycled through extractor 26.

The solid phase product of extractor 26 is then passed to dryer 28 where it is dried. The drier is a standard commercial product, known to the art, and need not be described in detail. The dried output of drier 28 is coal having a substantially lower sulfur content than that entering the process.

The gaseous products from reactor 18 flow through trap 12 which removes volatile fuels and entrained coal particles which are carried in the gas stream. Suitable

traps are commercially available and commonly known.

The clean gas from trap 12 which contains sulfur dioxide and sulfur trioxide given up by the coal in reactor 18 is bubbled through a sulfuric acid solution in condenser 14 dissolving sulfur trioxide in the acid solution. As previously mentioned, it is also within the scope of our invention to react with the SO₃ to form other compounds instead of sulfuric acid (i.e., with ammonium hydroxide to form ammonium sulfate, with sodium hydroxide to form sodium sulfate, with calcium oxide to make calcium sulfate). These compounds could also be made by reacting the sulfuric acid with the appropriate basic compound.

A cross-sectional representation of the condenser 14 is shown in greater detail in FIG. 2. Fed into inlet pipe 25 are the outlet gases from reactor 18, including O₂, N₂, NO, NO₂, SO₂ and SO₃. It should be noted that two other gases may also be generated in reactor 18; these are CO and CO₂. The latter two gases will be produced, if at all, from an unavoidable minimal oxidation of some of the coal particles in the reactor in the presence of oxygen. Any CO produced will merely pass on through the system without affecting the present invention process as CO is basically inert. Any generated CO₂ on the other hand, should be removed, and this is accomplished at a later stage in the present invention method in a manner hereafter to be explained.

The incoming gases to condenser 14 are treated as follows: The gases containing SO₃ are bubbled up under some pressure through a porous disk 27 situated within and near the lower end of the condenser. This disk 27 permits the gases to pass up therethrough while preventing liquid H₂SO₄ previously included within the condenser 14 from leaking through. Any sulfur trioxide in the gas will dissolve in the acid covering porous disk 27. The acid with dissolved sulfur trioxide is passed into tank 29 where water is added to make more sulfuric acid. The withdrawal of concentrated acid from the vessel and its replacement by water keeps the acid concentration in the tank approximately constant during operation.

The gas passing through condenser 14, having its acid soluble sulfur compounds removed, consists primarily of O₂, NO, NO₂, CO, and CO₂, N₂, and acid insoluble sulfur compounds. This gas is passed through purifier 16 where the CO₂ is removed. A fraction of the gas leaving purifier 16 (about 0.1 to 1%) is vented through scrubber 22 (which removes the noxious components). This is necessary since the reactant gases are consumed by the process, causing a buildup in the inert gas in the gas stream. By venting a portion of the gas and providing makeup gas, as indicated by gas mixer 20, the active gas proportions can be maintained.

Since NO, O₂ and NO₂ exist in an equilibrium at any temperature, only NO and O₂ need be supplied, the required NO₂ being formed from the mixture.

As shown in FIG. 1, the reconstituted gas mixture is then recycled through reactor 18.

While most of the processing equipment required to practice the invented process is standard equipment, the reactor itself is not and therefore detailed descriptions of suitable reactors for both continuous and batch processing follows:

Referring now to FIG. 3 which illustrates a continuous process reactor utilizing a so-called fluidized bed for the handling of the coal.

The reactor comprises an outer casing 30 and an inner shell 31 spaced therefrom. The inner shell must be capable of withstanding the process pressure and temperature contemplated, and the outer casing is preferably thermally insulated. Heating fluid, for example steam or hot oil, is introduced into the space between casing 30 and shell 31 through inlet pipe 32. After passing through the annular space 34 between the casing 30 and shell 31, thereby heating shell 31 and its contents, the heating fluid flows out of outlet 33. An inlet 37 is provided at the bottom of shell 31 for the purpose of introducing the oxidizing gas into the reactor. As will be presently discussed, the oxidizing gas is blown through the reactor at high velocity. It will therefore be desirable that the gas be preheated to prevent the gas from cooling the contents of the reactor.

Coal is conveniently introduced into the reactor at the bottom of the reactor and from the side at inlet 36. A porous disk 35 below the coal inlet spreads the inlet gas across the area of the reactor so that its vertical velocity is relatively uniform over the entire area.

The gas stream flowing upward through the particles of coal causes the particles to be agitated and thus the coal in the reactor acts as a fluid. Coal entering at inlet 36 flows upward through the reactor and eventually out of the top of the reactor through outlet 38. Coarse pieces of coal which are too large to flow upward under the influence of the oxidizing gas and other particles of coal flow out of the coarse coal outlet 39.

Oxidized coal flowing out of outlet 38 is separated from the oxidizing gas by a cyclone separator 40, a standard item, well known in the art.

As previously described, the coal output is fed to the extractor while the gas is fed to a condenser through a trap.

The batch type reactor illustrated in FIG. 4 includes an outer casing 50 and inner shell 51 similar to the casing 30 and shell 31 of FIG. 3, except that in the case of casing 50 and shell 51, removable tops 50' and 51' are provided to allow charging of the shell with coal. Alternatively, hatches could be provided for this purpose.

The heating jacket 54 is supplied with heating fluid through inlet 52, the outlet being indicated as 53.

A porous disk 55 spreads the flow of gas entering through inlet 57 in a manner identical to that previously described for the continuous process reactor. Gas outlet 58 directs the spent oxidizing gas to the trap and condenser.

In operation, the batch reactor is disassembled, removing casing cover 50' and shell cover 51', and a charge of pulverized coal is loaded into the reactor. The reactor is then covered, heating fluid is started heating up the vessel and oxidizing gas is blown through the charge. After sufficient time to oxidize the sulfur compounds in the coal has passed, the fluid and gas flows are stopped, the reactor disassembled, and the charge removed and placed in the extractor for the next step in the process.

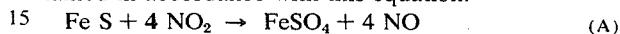
A representative empirical formula for coal is $C_{100}H_{80}NS$ which also includes FeS and $FeSO_4$. This coal may, when including these typical sulfur compounds, be depicted by the formula $C_{100}H_{80}NS \cdot FeS \cdot FeSO_4$. Of the three S's in this highly empirical and generalized formula, the sulfur content will typically divide as follows:

$FeSO_4$	—	5%
FeS	—	47 ½%
R_1-S-R_2	—	47 ½%

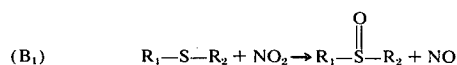
The S in the R_1-S-R_2 formula is considered as the organic sulfur included in the coal while FeS (Pyrites) and $FeSO_4$ is the inorganic iron bearing sulfur. The R would in turn reference the $C_{100}H_{80}$ of the above noted general formula.

The chemical reaction steps of the presently invented method may generally be explained as follows:

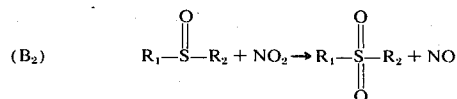
NO_2 gas reacts in the coal reactor 18 with FeS contained in accordance with this equation.



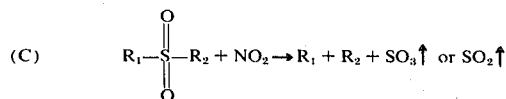
The organic sulfur on the other hand reacts as follows with the NO_2 gas, also within reactor 18 in accordance with the following equation:



The partially oxidized organic sulfur compound again reacts with the NO_2 gas in the reactor, thusly:



The organic sulfur compound which now contains two doubled bonded oxygen atoms further reacts with NO_2 gas within the reactor 18 as follows:



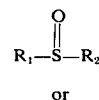
The reactions represented by equations (A), (B₁) and (B₂) all result in the production of NO gas. This NO combines with oxygen as indicated by equation (D) to produce NO_2 ; this NO_2 is used again in equations (A), (B₁), (B₂) and (C).



Thus without water, without hydrogen, without a hydrogenated organic solvent and without an alkali soak, most of the organic sulfur is freed from the coal.

The reactor products produced by the reactor as depicted in equation (B₁) and (B₂) to the extent that they do not react further with NO_2 to totally free the organic sulfur, may further be treated in accordance with an additional process as follows:

Each of these reaction products may be exposed in the extractor 26 to NaOH or some other alkali metal hydroxide, thus the following will occur:



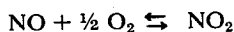


+ H_2^- + $\text{NaOH} \rightarrow \text{R}_1 + \text{R}_2 + \text{Na}_2\text{SO}_3$ in solution or Na_2SO_4 in solution.

The above-described reaction which is intended to remove additional organic sulfur not totally removed in reactor 18 is carried out in the extractor 26.

It will be understood that in lieu of sodium hydroxide, there may be used potassium hydroxide or any other alkali metal hydroxide for the indicated purpose. This step when employed is preferably carried out at from 1 to 10 atmospheres, at a temperature in the range of from 180°F to 230°F.

It will be observed that in the above reactions, the active gas which reacts with the sulfur compounds present in the coal is NO_2 . Neither NO nor O_2 is directly involved in the reaction, however, both NO and O_2 are unavoidably present since NO , O_2 and NO_2 react in an equilibrium reaction as follows:



Thus as NO_2 is consumed by the reaction with sulfur, additional NO_2 is formed by the equilibrium reaction. Similarly, NO_2 is formed as NO and O_2 are supplied in the make-up gas.

Any FeSO_4 contained within the coal in the reactor 18 (or produced as a result of reaction (A)), will not further react therein as it is already fully oxidized. It will later be precipitated out in the extractor 26 where water is added to the coal. Thus, the FeSO_4 is removed basically by mechanical as opposed to chemical means.

It will, of course, be apparent from an examination of the chemical reactions occurring in reactor 18 that the oxidized sulfur compounds there formed, if they are further to be reduced are soluble in caustic and not in water — thus encouraging use of the additional but not necessary step previously described.

A further note regarding the oxidation step in reactor 18 for the removal of sulfur in the organic form is considered significant. The oxidation reaction product



in equation (B₁) combined with additional NO_2 at step (B₂) resulting in a further oxidized state of the sulfur in the organic radical, permitting the substantial removal of the organic sulfur at step (C) by the still further exposure of the radical



to NO_2 gas freeing the R_1 and R_2 (coal) radicals from the organic sulfur without the employment of the caustic step previously described.

While both of the reactor products of the organic sulfur containing radicals will react with caustic as employed above, it should further be noted that only the reaction product produced by equation (B₂) will react with NO_2 to free the sulfur [equation (C)].

A further study of equations (A), (B₁), and (B₂) indicate the formation of NO which is required for equation D to go forward and the reaction product of equation D is NO_2 which is required for the reaction of (A), (B₁), (B₂) and (C) to occur.

The gases which are introduced into reactor 18 are as follows:

NO	— ¼ to 10% by volume
O_2	— ¼ to 20% by volume
NO_2	— ¼ to 10% by volume
N_2	— remainder.

While N_2 is preferred, another inert gas or gases may be substituted in whole or in part thereof. The inert N_2 gas is required primarily for safety purposes (i.e., to prevent an explosion) in the otherwise highly volatile atmosphere which would be present in reactor 18, especially under conditions of elevated temperature and pressure. The inert N_2 is also present in the selective reaction of the sulfur in the coal as opposed to the combustion thereof.

Of course some of the O_2 and NO is consumed during the reactions which occur as above described in the reactor 18, which must be replenished. NO_2 exists in equilibrium with NO and O_2 at any temperature, and thus is spontaneously formed from a mixture of NO and O_2 and need not be individually supplied.

The following are examples of the sulfur reduction which has been obtained by utilizing the process of this invention in accordance with the batch process which takes place in a period from 1 to 4 hours. The continuous process on the other hand, will typically occur in from 1 to 30 minutes.

EXAMPLES

EXAMPLE 1.

Using the batch reactor process a sample of Lower Kittanning coal previously pulverized and segregated as to size was treated. Coal of -14 +28 mesh particle size was loaded into the reactor, the reactor assembled and heated to 200°F. For 3 hours a gas mixture consisting of air with 9 per cent nitrogen oxide added was passed through the reactor and the bed of coal at one atmosphere pressure. The flow rate was such that about 10 times the stoichiometric quantity of oxygen required to oxidize the sulfur to sulfate forms was passed through the reactor.

The coal had an initial sulfur content of 4.3 per cent (3.6% pyritic, 0.7% organic, a trace of sulfate). After treatment, the coal was removed from the reactor, washed with water and dried. The total sulfur content was 1.58 percent (i.e., 63% of the sulfur was removed). The coal was then washed with 10 per cent aqueous sodium hydroxide followed by water and then dried. The total sulfur content was 0.47 per cent (i.e., 87% of the sulfur was removed).

EXAMPLE 2.

Using the batch reactor process a sample of Lower Kittanning coal previously pulverized and segregated as to size was treated. Coal of -14 +28 mesh size was loaded into the reactor, the reactor assembled and heated to 200°F. For 3 hours a gas mixture consisting of air with 4.5 per cent nitrogen oxide added was passed through the reactor and the bed of coal at 1 atmosphere pressure. The flow rate was such that about

10 times the stoichiometric quantity of oxygen required to oxidize the sulfur to sulfate form was passed through the reactor.

The coal had an initial sulfur content of 4.3 per cent. After treatment, the coal was removed from the reactor, washed with water and dried. The total sulfur content was 2.5 per cent (i.e., 43 per cent of the sulfur was removed). The coal was then washed with 10 per cent aqueous sodium hydroxide followed by water and then dried. The total sulfur was 2.1 per cent (i.e., 50 per cent of the sulfur was removed). Approximately 95 per cent of the initial coal sample was recovered after treatment and before extraction.

EXAMPLE 3.

Using the batch reactor process a sample of Illinois NO.5 coal previously pulverized and segregated as to size was treated. Coal of -14 +28 mesh size was loaded into the reactor, the reactor assembled and heated to 200°F. For 3 hours a gas mixture consisting of air with 4.5 per cent nitrogen oxide added was passed through the reactor and the bed of coal. The flow rate was such that about 12 times the stoichiometric quantity of oxygen required to oxidize the sulfur to sulfate forms was passed through the reactor.

The coal had an initial sulfur content of 3.5 per cent (1.6% pyritic, 1.9% organic, a trace of sulfate). After treatment, the coal was removed from the reactor, washed with water and dried. The total sulfur content was 1.9 per cent (i.e., 37% of the sulfur was removed). The coal was then washed with 10 per cent aqueous sodium hydroxide followed by water and then dried. The total sulfur content was 1.2 per cent (i.e., 60 per cent of the sulfur was removed).

EXAMPLE 4.

Using the batch reactor process, a sample of Illinois No.5 coal previously pulverized and segregated as to size was treated. Coal of -14 +28 mesh particle size was loaded into the reactor, the reactor assembled and heated to 200°F. For 3 hours a gas mixture consisting of air with 10% nitrogen oxide added was passed through the reactor and the bed of coal at one atmosphere pressure. The flow rate was such that about 12 times the stoichiometric quantity of oxygen required to oxidize the sulfur to sulfate forms was passed through the reactor.

The coal had an initial sulfur content of 3.5% (1.6% pyritic, 1.9% organic, a trace of sulfate). After treatment, the coal was removed from the reactor, washed with water and dried. The total sulfur content was 1.9% (i.e., 46% of the sulfur was removed). The coal was then washed with 10% aqueous sodium hydroxide followed by water and then dried. The total sulfur content was 1.0 per cent (i.e., 71% of the sulfur was removed).

EXAMPLE 5.

Using the batch reactor process, a sample of Lower Kittanning coal previously pulverized and segregated as to size was treated. Coal of -80 +100 mesh particle size was loaded into the reactor, the reactor assembled and heated to 200°F. For 3 hours a gas mixture consisting of air with 5% nitrogen oxide added was passed through the reactor and the bed of coal at one atmosphere pressure. The flow rate was such that about 10 times the stoichiometric quantity of oxygen required to oxidize

the sulfur to sulfate forms was passed through the reactor.

The coal had an initial sulfur content of 4.3% (3.6% pyritic, 0.7% organic, a trace of sulfate). After treatment, the coal was removed from the reactor, washed with water, and dried. The total sulfur content was 2.9% (i.e., 33% of the sulfur was removed). The coal was then washed with 10% aqueous sodium hydroxide followed by water and then dried. The total sulfur content was 1.9% (i.e., 56% of the sulfur was removed).

EXAMPLE 6.

Using the batch reactor process, a sample of Lower Kittanning coal previously pulverized and segregated as to size was treated. Coal of -14 +28 mesh particle size was loaded into the reactor, the reactor assembled and heated to 200°F. For 1.5 hours a gas mixture consisting of air with 10% nitrogen oxide added was passed through the reactor and the bed of coal at one atmosphere pressure. The flow rate was such that about 5 times the stoichiometric quantity of oxygen required to oxidize the sulfur to sulfate forms was passed through the reactor.

The coal had an initial sulfur content of 4.3% (3.6% pyritic, 0.7% organic, a trace of sulfate). The coal was then washed with 10% aqueous sodium hydroxide followed by water and then dried. The total sulfur content was 1.4% (i.e., 67% of the sulfur was removed).

EXAMPLE 7.

Using the batch reaction process, a sample of Lower Kittanning coal was treated as described above. The coal was -14 +28 mesh size reacted for 5 hours at 200°F using air with 5 per cent nitrogen added. An excess of oxygen of 16 times was passed through the reactor.

The coal had an initial sulfur content of 4.3%. After oxidizing and without any extraction (washing), the coal had a sulfur content of 3.3% (i.e., 23% of the sulfur was removed by the oxidation treatment).

There thus has been described a new and improved process for desulfurizing coal and producing sulfuric acid in commercial quantities as a valuable by-product.

What is claimed is:

1. A method for desulfurizing coal which includes the steps of:

- a. heating coal particles to a temperature of from 100° to 500°F; and
- b. subjecting said heated coal particles to an oxidizing gas having NO₂ as one of its constituents, said NO₂ selectively oxidizing sulfur-containing compounds in said coal particles, said other constituents of said oxidizing gas being substantially non-reactive with said coal, whereby oxidized sulfur-containing compounds and gaseous sulfur compounds are formed which are readily separable from said coal particles.

2. The method of claim 1 wherein said particles of coal have a diameter of no more than one-fourth inch.

3. The method of claim 1 wherein said reaction takes place at a temperature of 100° to 500°F and a pressure of 1 to 20 atmospheres over a period of 1 to 30 minutes.

4. The method of claim 1 wherein said oxidizing gas includes an inert gas in addition to said NO₂, said oxidizing gas being at least 0.25% by volume NO₂.

5. The method of claim 4 wherein said oxidizing gas further includes O₂ and NO, said O₂ being less than 20% by volume of said oxidizing gas and said NO being less than 10% by volume of said oxidizing gas.

6. The method of claim 5 wherein said O₂, said NO and said NO₂ exist in approximately equilibrium proportions.

7. The method of claim 4 wherein said inert gas is nitrogen.

8. The method of claim 6 wherein said oxidizing gas further includes O₂ and NO, said O₂ being less than 20% by volume of said oxidizing gas and said NO being less than 10% by volume of said oxidizing gas.

9. The method of claim 8 wherein said O₂, said NO, and said NO₂ exist in approximately equilibrium proportions.

10. The method of claim 1 wherein said particles are oxidized and thereafter further including the step of leaching oxidized sulfur compounds from said particles of coal after said reacting step.

11. The method of claim 10 wherein said leaching is done by water.

12. The method of claim 10 wherein said leaching is done by a solution of water and caustic.

13. The method of claim 10 wherein said oxidizing gas is comprised of an inert gas.

14. The method of claim 10 wherein said oxidizing reaction takes place at a temperature of 100° to 500°F, at a pressure of 1 to 20 atmospheres, over a period of 1 to 30 minutes.

15. The method of desulfurizing coal containing sulfur in the form of iron pyrites which includes the steps of:

a. oxidizing said iron pyrites by reaction with NO₂ gas, said coal being in the form of particles no larger than about one-fourth inch in diameter, said oxidation step being of 1 to 30 minutes duration at a temperature of 100° to 500°F and at a pressure of 1 to 20 atmospheres, whereby said iron pyrites are oxidized to form sulfates and sulfites; and

b. leaching said sulfates and sulfites out of said particles of coal.

16. The method of claim 15 wherein the leaching is done by water.

17. The method of desulfurizing coal containing sulfur in the form of an organic compound which includes the steps of:

a. oxidizing said organic sulfur compound by reaction with NO₂ gas, said coal being in the form of particles no larger than about one-fourth inch in diameter, said oxidation step being of 1 to 30 minutes in duration, at a temperature of 100° to 500°F and at a pressure of 1 to 20 atmospheres, whereby said organic compounds are oxidized to form sulfates and sulfites; and

b. leaching said sulfates and sulfites out of said particles of coal.

18. The method of claim 17 wherein said leaching is done by water.

19. The method of claim 17 wherein said leaching is done by a solution of water and caustic.

20. The method of claim 17 wherein said oxidation step does not convert all of said organic sulfur compounds to sulfates and sulfites and wherein said leaching is done by a solution of water and caustic, said caustic converting said organic sulfur compounds to sulfates soluble in said caustic solution.

21. The method of desulfurizing coal containing sulfur in the form of an organic compound which includes the steps of:

a. oxidizing said organic sulfur compound by reaction with NO₂ gas, said coal being in the form of particles no larger than about one-fourth inch in diameter, said oxidation step being of 1 to 30 minutes in duration, at a temperature of 100° to 500°F and at a pressure of 1 to 20 atmospheres; and

b. hydrolyzing said oxidized organic sulfur compounds and leaching the products of said hydrolyzation reaction by contacting said coal containing said oxidized organic compounds with a caustic solution, whereby said oxidized organic compounds are converted to sulfates and said sulfates are dissolved in said caustic solution.

22. The method of desulfurizing coal and producing sulfuric acid which includes the steps of:

a. placing particles of coal having a diameter of no more than one-fourth inch in a reactor vessel, said vessel being maintained at a temperature of 100° to 500°F and a pressure between 1 and 20 atmospheres;

b. circulating oxidizing gas through said reactor, said oxidizing gas having NO₂ as one of its constituents, said NO₂ selectively oxidizing sulfur-containing compounds in said coal particles, said other constituents of said oxidizing gas being substantially non-reactive with said coal; and

c. removing gaseous sulfur compounds from said oxidizing gas after it has passed through said reactor by contacting said gas with water whereby said gaseous sulfur compounds are dissolved in said water and sulfuric acid is formed.

23. The method of claim 22 wherein said oxidizing gas comprises an inert gas.

24. The method of claim 22 and further including the step of leaching oxidized sulfur compounds in said coal with a leaching agent after said coal has been reacted with said oxidizing gas.

25. The method of claim 24 wherein said leaching is done by water.

26. The method of claim 24 wherein said leaching is done by a solution of water and caustic.

27. The method of claim 26 wherein said caustic is NaOH.

28. The method of claim 12 wherein said caustic is NaOH.

29. The method of claim 19 wherein said caustic is NaOH.

30. The method of claim 23 and further including the step of leaching oxidized sulfur from said coal with a leaching agent after said coal has been reacted with said oxidizing gas.

31. The method of claim 30 wherein said leaching is done by water.

32. The method of claim 30 and further including the step of removing said leached sulfur compounds from said leaching agent by reducing the temperature of said leaching agent whereby the solubility of said sulfur compounds in said leaching agent is reduced.

33. The method of claim 32 wherein said oxidizing gas comprises the following gases:

NO	— 0.25 to 10% by volume
NO ₂	— 0.25 to 10% by volume
O ₂	— 0.5 to 20 % by volume
N ₂	— balance.

34. The method of desulfurizing coal which includes the steps of:

- a. heating particles of coal between -14 and $+28$ mesh size to 200°F ;
- b. flowing a gas mixture comprised of air with 10% NO by volume, thus forming NO_2 in situ; said mixture being added through said coal particles at one atmosphere for a period of 3 hours,
- c. washing said coal particles with water;
- d. washing said coal particles with a 10% aqueous solution of NaOH; and
- e. washing said coal particles with water, whereby said sulfur is extracted from said coal particles.

35. The method of claim 34 with the amount of NO added to said air in the range from 0.25 to 10% by volume.

36. The method of claim 34 with the usual amount of NO added to said air increased to 10% and the time said gas is passed through said coal particles is reduced to 1.5 hours.

37. The method of claim 1 wherein said particles of coal has a particle size of from -14 to 28 mesh.

38. The method of claim 1 wherein said coal particles are contacted with said oxidizing gas for 1 to 4 hours in a batch operation.

39. The method of claim 38 wherein said oxidizing gas is at least 0.25% by volume NO_2 .

40. The method of claim 38 and further including the step of leaching oxidized sulfur compounds from said particles of coal after said oxidizing step.

41. The method of desulfurizing coal and producing salts of sulfuric acid which includes the steps of:

- a. placing particles of coal having a diameter of no more than one-fourth inch in a reactor vessel, said vessel being maintained at a temperature of 100° to 500°F and a pressure between 1 and 20 atmospheres;

b. circulating oxidizing gas through said reactor, said oxidizing gas having NO_2 as one of its constituents, said NO_2 selectively oxidizing sulfur-containing compounds in said coal particles, said other constituents of said oxidizing gas being substantially non-reactive with said coal; and

c. removing gaseous sulfur compounds from said oxidizing gas after it has passed through said reactor by contacting said gas with a compound selected from the group consisting of: NH_4OH , alkali metal oxides, alkali metal hydroxides, alkaline metal oxides, and alkaline metal hydroxides, whereby said gaseous sulfur compounds form salts of sulfuric acid.

42. The method of claim 41, wherein said oxidizing gas comprises an inert gas.

43. The method of claim 41 and further including the step of leaching oxidized sulfur compounds in said coal after said coal has been reacted with said oxidizing gas.

44. The method of claim 43, wherein said leaching is done by water.

45. The method of claim 43, wherein said leaching is done by a solution of water and caustic.

46. The method of claim 45, wherein said caustic is NaOH.

47. The method of claim 41, wherein said oxidizing gas is contacted with NH_4OH , and said salt of sulfuric acid formed is ammonium sulfate.

48. The method of claim 41, wherein said oxidizing gas is contacted with calcium oxide, and said salt of sulfuric acid formed is calcium sulfate.

49. The method of claim 44, wherein said oxidizing gas is contacted with sodium hydroxide, and said salt of sulfuric acid formed is sodium sulfate.

50. The method of claim 42 and further including the steps of leaching oxidized sulfur compounds from said particles of coal after said reacting step.

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