PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 3 :
C01B 17/24; D21C 11/12

A1

(11) International Publication Number: **WO 83/ 01437**

(43) International Publication Date: 28 April 1983 (28.04.83)

(21) International Application Number: PCT/US82/01460

(22) International Filing Date: 12 October 1982 (12.10.82)

(31) Priority Application Number: 314,643

(32) Priority Date: 26 October 1981 (26.10.81)

(33) Priority Country: US

(71) Applicant: ROCKWELL INTERNATIONAL CORPORATION [US/US]; 2230 East Imperial Highway, El Segundo, CA 90245 (US).

(72) Inventors: KOHL, Arthur, L. ; 22555 Tiara Street, Woodland Hills, CA 91367 (US). GRANTHAM, LeRoy, F. ; 26117 Hatmor Drive, Calabasas, CA 91302 (US).

(74) Agent: KOLIN, Henry; Patent Department, Rockwell International, Energy Systems Group, 8900 DeSoto Avenue, Canoga Park, CA 91304 (US).

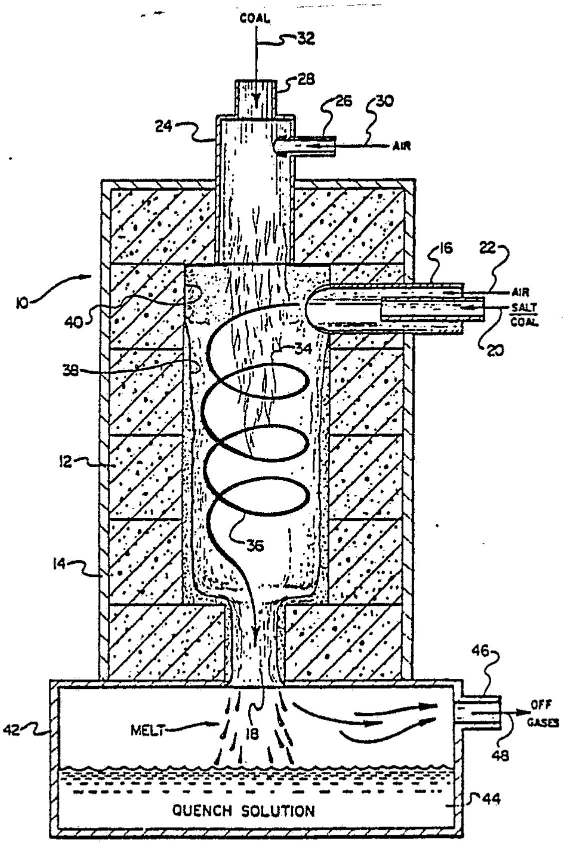
(81) Designated States: AU, BR, DE (European patent), FI, FR (European patent), GB (European patent), JP, NL (European patent), SE (European patent).

Published
With international search report.
With amended claims.

(54) Title: FLOWING MELT LAYER PROCESS FOR PRODUCTION OF SULFIDES

(57) Abstract

An alkali metal oxysulfur compound is converted to a corresponding alkali metal sulfide by reaction with a solid carbonaceous material. Reaction takes place during the heating of an oxysulfur compound and carbonaceous material which results in a melt being formed. The reactants are subjected to centrifugal force and are forced to the periphery of a reaction zone where they form a downwardly flowing melt in which the reduction of the oxysulfur compound to the sulfide continues. Product is recovered from a melt exiting the reaction zone. In a preferred embodiment, one or more of the reactants enter the reaction zone tangentially entrained in a carrier gas.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BE	Belgium
BR	Brazil
CF	Central African Republic
CG	Congo
CH	Switzerland
CM	Cameroon
DE	Germany, Federal Republic of
DK	Denmark
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
HU	Hungary
JP	Japan
KP	Democratic People's Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
RO	Romania
SE	Sweden
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
US	United States of America

FLOWING MELT LAYER PROCESS FOR PRODUCTION OF SULFIDES

Background of the Invention

1. Field of the Invention

The present invention relates to a process for the production of alkali metal sulfides by reduction of the corresponding oxysulfur compounds, that is, compounds containing alkali metal, oxygen and sulfur, such as alkali metal sulfites or sulfates, using a solid carbonaceous reducing agent. In one of its more particular aspects, this invention relates to such a process in which there is formed a melt which is caused to flow in a layer along the periphery of a reaction zone into which the reactants are introduced.

2. Prior Art

The production of alkali metal sulfides has been of significant interest for some time. Alkali metal sulfides as industrial chemicals have a wide variety of end uses. They are also used as intermediates in flue gas desulfurization processes in which sulfur values are recovered from gases produced in burning sulfur-containing fuels and in other industrial processes.

Various processes are known for producing alkali metal sulfides, particularly by the reduction of oxysulfur compounds. U.S. Pat. No. 126,275 describes a process in which molten sodium sulfate is percolated through a heated carbon bed to produce sodium sulfide.

U.S. Pat. No. 1,212,702 describes a process for reducing sodium sulfate or sodium bisulfate to sodium sulfide in a shaft furnace in which a reducing atmosphere is maintained by feeding a controlled amount of air to burn large pieces of carbonaceous matter, such as coal or coke. The sulfate or bisulfate salt is mixed with an excess of coal, charged into the reducing atmosphere of the furnace, and the salt melted and reduced over the heated carbonaceous matter at a temperature of about 1000°C.

U.S. Pat. No. 3,867,251 discloses a process for producing alkali metal carbonates and alkali metal sulfides from evaporated alkaline cooking liquor obtained from pulp production which utilizes a horizontal combustion cyclone to produce turbulence within a reaction chamber. The cooking liquor is pyrolyzed to alkali metal carbonate, carbon and hydrogen sulfide in a first zone, into which a hot oxygen-containing gas is introduced tangentially at a temperature of about 700°C. In a second zone, into which hot flue gases are injected tangentially, alkali metal carbonate in the form of a smelt reacts with hydrogen sulfide to form alkali metal sulfide at a temperature of about 900°C. In a third zone, combustion gases are oxidized by means of tangentially injected oxygen-containing gas at a temperature of about 1100° to 1200°C.

U.S. Pat. No. 4,198,385 discloses a two-stage process for the reduction of sodium sulfate accumulated in spinning baths during viscose fiber manufacture. In the first stage a reducing atmosphere is provided at a temperature greater than the melting point of sodium sulfide, so that molten sodium sulfide plus unreacted sodium sulfate collects in a melt at the bottom of a combustion chamber. In the second stage, a separately applied reducing agent and inert exhaust gases are introduced into the melt to agitate the melt and to produce additional sodium sulfide from unreacted sodium sulfate. The sodium sulfide can then be reacted with zinc oxide to produce sodium hydroxide for use in the spinning baths.

The conversion of oxysulfur compounds to sulfides is particularly important in plants which are designed to remove sulfur oxides from the flue gases of power plants generating electricity by the combustion of fossil fuels.

In the molten carbonate process described in U.S. Pat. No. 3,438,728, sulfur oxide impurities are removed from a hot combustion gas by contacting the gas at a temperature of at least about 350°C. with a molten salt mixture containing alkali metal carbonates as the active absorbent. The molten absorbent solution containing the absorbed sulfur values, principally as alkali metal sulfites, is treated with a reductant gas mixture containing hydrogen, carbon monoxide, or a mixture thereof, at a temperature of at least about

400°C., under reaction conditions favoring formation of sulfides, to convert the absorbed sulfur values to alkali metal sulfides. Thereafter, the molten salt containing the alkali metal sulfides is treated with a gaseous mixture containing steam and carbon dioxide at a temperature below about 450°C., to regenerate the alkali metal carbonates and convert the alkali metal sulfides to hydrogen sulfide gas which can be converted to sulfur or sulfuric acid.

The reduction of alkali metal oxysulfur compounds to the corresponding sulfide is also a part of the regenerative sodium-based flue gas desulfurization process described in "A 100-MW Second Generation SO_2 Removal Demonstration Plant for New York State Utilities" by Robert G. Aldrich and Richard D. Oldenkamp, "Proceedings of the American Power Conference, 1977, Vol. 39, p. 319. In this process an aqueous solution of sodium carbonate is used to absorb sulfur dioxide from flue gas. During the absorption step, the solution is converted to a dry spent salt containing unreacted sodium carbonate plus the two oxysulfur compounds, sodium sulfite and sodium sulfate. In order to regenerate the absorbent, it is necessary to reduce the oxysulfur compounds to sodium sulfide, then react the sodium sulfide with water and carbon dioxide to produce hydrogen sulfide gas and sodium carbonate solution.

According to this reference, the reduction step is accomplished in a large pool-type reactor held at about 1000°C. The spent salt is fed into the reactor together with a solid carbonaceous reducing agent such as petroleum coke or coal. Air is also fed into the reactor through feed nozzles located below the surface of the melt. The air serves primarily as a source of oxygen which reacts with a portion of the reducing agent exothermally to provide heat for the system. This reaction generates typical combustion gases such as carbon monoxide, carbon dioxide and water vapor, which bubble through the molten salt pool together with the nitrogen from the air feed. Gases which are produced by the chemical reduction reaction join the combustion product gases, and the mixed gas stream leaves the reactor as product gas. Oxysulfur compounds in the spent salt feed are largely reduced to sulfide by the carbon present in the pool. Molten salt containing the sodium sulfide product, sodium carbonate from the original feed plus small amounts of unreacted carbon and oxysulfur compounds is withdrawn from the molten pool by an overflow system. Gases leave the vessel via a discharge port near the top.

While the process described in this reference provides an effective route to sulfur dioxide removal from flue gases and has many advantages over the prior art cited above, it is not without its disadvantages. The major problem with this reducer design is that it is quite large and therefore expensive. The large size results from the requirement to bubble air and product gases through the pool of liquid without entraining excessive amounts of liquid in the effluent gas or creating a hydraulically unstable pool of melt. For practical purposes, a superficial gas velocity of about 2 feet per second has been found to be the maximum allowable for this type of reducer, and this low velocity establishes the required vessel diameter for a given reducer capacity.

A second problem with this kind of reactor design is the difficulty in maintaining constant melt-discharge rate. For example: A slight increase in air rate will cause the melt level to increase because of the increased number of bubbles within it. This causes a great increase in the instantaneous melt overflow rate which, in turn, can represent a safety as well as operational problem for the melt quench step which follows.

Objects of the Invention

It is an object of the present invention to provide a process for producing alkali metal sulfides in high yields from corresponding oxysulfur compounds.

Another object of this invention is to provide a process in which a mixture of alkali metal sulfites and sulfates produced in a flue gas desulfurization process is reduced to alkali metal sulfides.

Another object of this invention is to provide a process capable of essentially completely reducing alkali metal sulfites to sulfides.

Another object of this invention is to provide a reduction process utilizing molten salts which does not require the molten salt pools of the prior art.

Yet another object of this invention is to provide such a process which can be conducted in a relatively simple apparatus.

Other objects and advantages of the present invention will be apparent in the course of the following detailed description.

Summary of the Invention

In accordance with the broad aspects of the present invention, an alkali metal oxysulfur compound is converted into the corresponding alkali metal sulfide by a process which comprises introducing an alkali metal oxysulfur compound and a solid carbonaceous reducing agent into a reaction zone; subjecting the oxysulfur compound and reducing agent to centrifugal force; heating the reaction zone to melt the oxysulfur compound and to cause the oxysulfur compound and reducing agent to react to produce an alkali metal sulfide; flowing a melt containing the alkali metal sulfide thereby produced, unreacted oxysulfur compound and unreacted reducing agent through the reaction zone and along the periphery thereof, to cause the unreacted oxysulfur compound and the unreacted reducing agent to react to produce additional alkali metal sulfide; and recovering alkali metal sulfide from melt exiting the reaction zone. In a preferred embodiment, the centrifugal force to which the oxysulfur compound and reducing agent are subjected is produced by tangential injection of at least one of the oxysulfur compound and the solid carbonaceous reducing agent entrained in a gaseous stream.

Brief Description of the Drawing

FIG. 1 is a schematic diagram, partly in cross section, of one embodiment of apparatus which can be used in carrying out the process of the present invention, wherein product gas and product melt are discharged together through a single nozzle directly into a quench tank containing an aqueous solution.

FIG. 2 is a schematic diagram, partly in cross section, of another embodiment of apparatus suitable for use in this invention, wherein a major portion of the product gas is withdrawn by way of a centrally located discharge port near the top of the reactor, and product melt is discharged into a quench tank through a nozzle near the bottom of the reactor.

FIG. 3 is a schematic diagram, partly in cross section, of a third embodiment of apparatus which can be used in the present invention, wherein product melt and product gas are discharged into a cooling zone designed to solidify the product melt into a granular product.

FIG. 4 is a section taken along lines 4-4 of FIG. 3.

Description of the Preferred Embodiments

The present invention provides a continuous process for the reduction of oxysulfur compounds which uses a simple reactor of compact design with a low-cost solid carbonaceous material such as coal or petroleum coke as the reducing agent.

The reduction reactions occurring in the process of the present invention may be typified in the following equations:

$$\begin{array}{llllllll}
M_2SO_4 & + & 2C & = & M_2S & + & 2CO_2 & (1) \\
M_2SO_4 & + & 4C & = & M_2S & + & 4CO & (2) \\
2M_2SO_3 & + & 3C & = & 2M_2S & + & 3CO_2 & (3) \\
M_2SO_3 & + & 3C & = & M_2S & + & 3CO & (4) \\
M_2SO_4 & + & 8H & = & M_2S & + & 4H_2O & (5) \\
M_2SO_3 & + & 6H & = & M_2S & + & 3H_2O & (6) \\
4M_2SO_3 & & & = & 3M_2SO_4 & + & M_2S & (7)
\end{array}$$

where M is an alkali metal. Equations 1, 2, 3, and 4 illustrate possible routes to the reduction of some of the most common oxysulfur compounds encountered in practicing the process of the present invention. Equations 5 and 6 depict reduction by the hydrogen combined with carbon in the solid carbonaceous reducing agent. Equation 7 illustrates the disproportionation reaction which results in the formation of additional alkali metal sulfate when the alkali metal sulfite in the reactant stream disproportionates rather than being reduced in accordance with one of Equations 3, 4, or 6 shown above. In the event of disproportionation occurring, the alkali metal sulfate which forms can be reduced to alkali metal sulfide in accordance with Equation 1, 2, or 5.

In order to conduct the desired reduction reactions, use is made of a simple reactor in which the reactions illustrated above are caused to take place at least partly in a melt layer which flows down the inside walls of the reactor. The reactor is heated and the mixture of heated reactants subjected to centrifugal force to cause the formation of a melt layer upon the walls of the reactor. In a preferred embodiment of the invention, the heated reactants are subjected to centrifugal force by injecting at least a part of the reactants tangentially into a reactor of circular cross section. In this manner, the heated oxysulfur compounds are melted and follow a spiral path downwards in the reactor and under the influence of centrifugal force become deposited along the walls of the reactor together with unreacted particles of carbonaceous reducing agent. The resulting melt layer moves downward along the walls during the time that the reaction between the oxysulfur compound and the solid carbonaceous reducing agent is proceeding. The flowing melt layer exits the reactor at the bottom thereof and is cooled by contact with cool gases or by being introduced into an aqueous quench solution. The reduced oxysulfur compounds are soluble in the aqueous quench solution and may be recovered therefrom. For example, the aqueous solution containing the quenched melt may be removed and further processed to recover the desired alkali metal sulfides from the solution. In addition, if desired, the recovered sulfides may be further processed to regenerate alkali metal carbonates or bicarbonates which can be introduced into the reactor along with the oxysulfur compounds to be reduced. Where such salts are used in addition to the oxysulfur compounds, the temperatures utilized in the reactor may be lower than those wherein the salt mixture contains merely sulfates or sulfites.

The product gases may be removed from the reactor and likewise further processed in order to recover valuable byproducts. For instance, the carbon monoxide content may be burned to provide heat and form additional carbon dioxide and the carbon dioxide content may be used to drive hydrogen sulfide from sulfide solutions in accordance with the following reactions:

$$M_2S + 2CO_2 + 2H_2O = 2MHCO_3 + H_2S \quad (8)$$

$$M_2S + CO_2 + H_2O = M_2CO_3 + H_2S \quad (9)$$

Hydrogen sulfide may be separated and converted to sulfur in a Claus plant or utilized in the manufacture of sulfuric acid. The product gases may be removed from the top of the reactor or they may be removed from the bottom of the reactor along with the melt, as desired.

Heat for the reduction reaction may be produced by means of a suitable burner incorporated with the reactor or may be produced by oxidation of a portion of the carbonaceous reducing agent.

The reduction reaction is suitably carried out at an elevated melt temperature, usually in the range of about 900° to 1400°C., and preferably in the range of about 950° to 1150°C.

One of the principal advantages of the present invention is that external heating of the reactor is not required. Rather, heating to produce the required melt temperature is accomplished in situ by the combustion of a fuel by a moving stream of an oxidizing gas. The oxidizing gas serves two purposes, namely, causing combustion of the fuel used to heat the reaction zone and propelling particles of reactants in a spiralling path within the reaction zone in a way such that the particles melt and the resulting melt flows in a layer at the outer periphery of the reaction zone. The thus-produced flowing melt layer enables the reactants to be in contact for a longer period of time than if the reactants reacted only directly in the stream of oxidizing gas without forming such a flowing melt layer.

The process of the instant invention can be used to convert a wide variety of oxysulfur compounds to the corresponding alkali metal sulfides. Some of the more common oxysulfur compounds include lithium sulfite, sodium sulfite, potassium sulfite, lithium sulfate, sodium sulfate, and potassium sulfate as well as other alkali metal sulfites and sulfates. Bisulfates, bisulfites, thiosulfates, and sulfonates can also be converted to sulfides in accordance with the process of this invention.

As reducing agents, any of a wide number of solid carbonaceous materials are satisfactory. Coal or petroleum coke is preferred. Other forms of carbonaceous materials are also suitable. For example, asphalt, peat, lignite, or wood may be used.

In addition to the oxysulfur compound and carbonaceous material, it is sometimes desirable to add another salt in order to lower the melting point of the salt mixture in the reactor, thereby reducing the amount of heat which must be produced in the reactor in order to form the required melt. For this purpose, compounds such as alkali metal halides, for example, sodium chloride or alkali metal carbonates or bicarbonates, such as sodium carbonate and sodium bicarbonate have been found particularly satisfactory. They may be used in an amount of up to about 50% of the oxysulfur compound.

The carrier gas used to introduce reactants into the reactor can be an oxidizing gas, such as oxygen or air, or it may be an inert gas such as nitrogen or flue gas. It is used, in general, in an amount sufficient to entrain the reactants, principally the alkali metal oxysulfur compound and finely divided solid carbonaceous reducing agent. If an oxidizing gas is used, it will function both as an oxidizer and as a carrier and must be added in sufficient quantity to provide both functions. An oxidizer is desirable in order to oxidize a portion of the carbonaceous material which is used as the reducing agent in the reaction. Oxidation of the carbonaceous material results in the release of a large amount of heat, since such a reaction is highly exothermic. Heat is required not only for melting the oxysulfur compound and for keeping the product sulfides in the molten state, but also for the carrying out of the endothermic reduction reactions which are carried out in the reactor. However, it is not desirable to utilize an oxidizing gas in excess of the amount required to provide the requisite heat to the reactor, since an excess of oxidizing gas may result in oxidizing part of the sulfides produced in the reactor, thereby decreasing the overall yield of sulfide.

In some instances it may be desirable to provide the requisite heat by means of a separate burner which may be oriented tangentially or axially with respect to the reactor. However, the use of such an auxiliary burner is not deemed essential, since adequate heat can be furnished by oxidation of a part of the carbonaceous reducing agent in the reactor.

In other instances it may be desirable to use a separate burner to provide part of the heat required and to use an oxidizing gas, such as air or oxygen, as the carrier gas to furnish part of the heat by oxidation of a portion of the carbonaceous material entrained in the oxidizing gas.

The starting materials utilized in this invention containing the oxysulfur compound and which may also contain, for example, alkali metal carbonate and other alkali metal salts as well, can be obtained from various industrial processes. For example, a convenient source of oxysulfur compounds can be the spent absorbent from processes used to desulfurize flue gases from plants burning fossil fuels, spent sulfite "black liquor" from paper mills or spent "seed" from magnetohydrodynamic (MHD) power plants. In the last mentioned case, the principal oxysulfur compound produced is potassium sulfate which is generated when potassium carbonate, added to high temperature combustion gases to increase electrical conductivity, also absorbs sulfur compounds in the gases. Thus, the oxysulfur compound can be derived from a number of process streams. In the case where the oxysulfur compound is formed in the aqueous carbonate process (ACP), it may be desirable to form a premixed oxysulfur compound – carbonaceous material feed for use in the process of the present invention. This is accomplished by mixing the carbonaceous material with the carbonate which is used to absorb sulfur dioxide from the flue gases treated in the aqueous carbonate process. Adding the carbonaceous material to the carbonate while it is in aqueous solution permits a very intimate mixture of dry reducing agent and dry spent absorbent to be obtained. The presence of reducing agent in each droplet of sodium carbonate solution while it is absorbing sulfur dioxide and being dried also acts to inhibit the oxidation of sulfite to sulfate. Adding the reducing agent prior to drying permits use of an aqueous slurry of reducing agent. For example, sewage sludge or a coal slurry may be used. The mixture of sodium carbonate, reducing agent and water is then sprayed into a hot sulfur dioxide-containing gas in the usual manner, whereby efficient contact between liquid droplets and gas is obtained and a dry powder containing both sodium sulfite and reducing agent is obtained as the product of the sulfur dioxide absorption – drying step in the ACP process. This technique obviates the need for mixing reactants in the reactor.

The amounts of solid carbonaceous material, burner fuel, and oxidizing gas required to produce a given amount of alkali metal sulfide will depend upon the nature of the oxysulfur compound feed, the percent conversion desired, the reactor design, and other factors. For example, if the carbonaceous material is carbon and the oxysulfur compound is pure sodium sulfate, at least 2 moles of carbon are required per mole of feed salt for the reduction alone. In addition, fuel and oxidizing gas are required in sufficient amounts that their combustion will provide all of the heat necessary to melt the feed salt, provide the heat for endothermic reduction reactions, raise the temperature of all products to their discharge temperatures, and provide for any heat losses from the system. All or a portion of the required fuel may be in the form of the solid carbonaceous material. The total amount of reactive carbon and hydrogen in both the solid carbonaceous reducing agent and the combusion fuel must be in excess of the stoichiometric amount required to convert all of the oxygen in the oxysulfur compounds and the oxidizing gas to carbon dioxide and water.

The reactants can be introduced into the reactor in a number of different ways depending upon the result sought and the type of starting materials which are used. The most desirable configurations are those in which the combustion mixture and the mixture of oxysulfur compounds, reducing agent, and carrier gas are introduced through separate ports. In particular, it is desired to introduce a mixture of, for example, oxysulfur compound, carbonaceous material and a carrier gas tangentially while at the same time introducing fuel, which may be the same carbonaceous material, and oxidizing gas through a specially designed burner port, such as a "vortex" burner located at the center top of the reactor. This combination of gas streams results in producing the desired spiral path for the reactants and also realizing optimal heating conditions for the reactant stream.

In an especially preferred embodiment of the present invention, air is used as both the carrier gas and the oxidant, coal is used as the carbonaceous material functioning as both the reducing agent and the oxidizable fuel and a mixture of sodium sulfite, sodium sulfate and sodium carbonate is the salt mixture. In this embodiment, coal and approximately one-half of the air is introduced axially to the reactor through a burner which imparts a swirling flow to the combustion products, while a mixture of salts, coal and the remainder of the air is introduced tangentially. This arrangement results in producing the desired cyclone action in the reactor so that the reactants are propelled through the reactor in a spiral path, the desired melt formation takes place in the traversal of the spiral path through the reactor and the melt is deposited upon the wall of the reactor and flows down the wall as the reaction proceeds.

In the process of the present invention the oxysulfur compounds fed to the reactor are reduced to the corresponding sulfides. For example, where the feed consists of sodium sulfite and sodium sulfate, sodium sulfide is produced. Since the reaction takes place in a flowing layer of melt, the product sulfide is recovered as a melt.

Melt residence time within the reactor may vary within a wide range depending upon the velocity of the reactant stream within the reactor, the temperature and pressure of the reactor and the length of the reaction zone within the reactor. In general, melt residence times less than about 2 minutes and preferably about 5 to 60 seconds are used. The residence time is adjusted to be long enough to insure that at least about 80% of the oxysulfur compound introduced into the reactor is reduced to sulfide.

The product melt exiting the reactor must be cooled in order to enable recovery of the sulfide for its use in further processing. For this purpose it is convenient to contact it with water or cool gas, although other methods may be used if desired. In the case of the water contact, the melt flows into a water bath or is contacted by a spray of liquid water. Alternatively, an aqueous solution containing previously dissolved melt or other process salts may be used. Provision is made for the removal of the gaseous products of the reaction as well as the products present in the melt. The aqueous solution containing the quenched melt may be drawn off from the quench tank and subjected to further processing including recovering relatively pure alkali metal sulfide from the solution, in accordance with known procedures.

If it is desired to recover the alkali metal sulfide in solid form, instead of an aqueous quench, a gas-contacting device such as a prilling tower is utilized. The melt containing the sulfide product is blown through a discharge nozzle at the bottom of the reactor by the gases formed during the reactions taking place within the reactor and is formed into small droplets. These droplets harden into fine shot-like beads or prills as a result of contacting relatively cool gas in the prilling tower. Gas is continuously removed from the prilling tower, cooled and reinjected to provide the means for cooling and solidifying the prills. The prills, containing alkali metal sulfide, fall to the bottom of the prilling tower and are collected in a bed either in the tower or in a separate vessel as desired. Gas containing carbon dioxide and water vapor is passed through the bed at a temperature below the melting point of the salts and preferably in the range of about 250° to 650°C. The alkali metal sulfide is thereby converted to alkali metal bicarbonate or carbonate in accordance with Equations 8 or 9.

Preferably all or a portion of the gas produced in the reduction is used as the source of carbon dioxide for these reactions. This gas, as pointed out above, contains an adequate supply of carbon dioxide and can be enriched in water vapor, if necessary, by the injection of liquid water or steam. Because of their special shape, the prills form a porous high surface area packed bed which is permeable to the flow of gas and does not hang up or plug in the contact zone.

The use of the prilling tower for recovering solid alkali metal sulfide from the reduction reactor can also be taken advantage of in MHD feed regeneration and the regenerated prills recycled directly to the MHD combustor. Ash compounds which were in the original seed or were added with coal in the reducer will be decomposed by the high temperature in the MHD combustor and redistributed downstream of the MHD channel so that only a small portion reappears in the spent seed. In this way the ash in the seed can be recycled to extinction with all of this eventually leaving via the main discharge point for coal ash which passes through the channel.

When used for the regeneration of spent salt for flue gas desulfurization, it is desirable to remove ash and produce the regenerated carbonate in the form of an aqueous solution. To accomplish this, the prills are dissolved in water which is filtered or otherwise separated to produce a solution of sodium carbonate and an insoluble ash cake.

The prilling tower recovery process described above is given as one example of a gas/particle contact process. Similar results can be obtained by use of a fluidized bed rotary kiln or other gas/solids contactor.

The products of the process of this invention include not only the melt referred to above, which is a source of the alkali metal sulfide, but also gases which are produced in the various reactions occurring in the reactor. These gases include carbon monoxide, carbon dioxide and water vapor. The production of a gaseous product having a CO_2:CO ratio of at least about 1:1 is desirable. With this ratio being realized, the carbonaceous material is substantially used up in the reactor. The appreciable quantity of carbon dioxide present in the gaseous product can be used for carbonate regeneration if desired.

Among the principal advantages of the present invention, in addition to those already mentioned, is the fact that, since the carbonaceous material is used up in the reactor, there is very little carbon contaminating the product sulfide. Another advantage lies in the realization of very much higher gas velocities than in conventional molten pool reducers, which permits the use of smaller vessels and results in major cost savings. Further, the elimination of the need to inject air and feed materials beneath the surface of a high temperature pool of melt obviates the problem of plugging of nozzles. Another advantage is the reduction of ash-melt interaction. That is, the ash-melt interaction to form insoluble silicates does not have sufficient time to reach equilibrium because of the short residence time in the reactor. Sodium loss and processing problems downstream of the reducer attributable to silicate contamination are therefore virtually eliminated. Another advantage is that liquid level control of very hot corrosive highly agitated pools of molten salt is unnecessary.

Referring now to FIG. 1 of the drawings, a reactor 10 is a vessel of circular cross section lined with a corrosion resistant refractory 12, such as fusion cast alumina blocks within a metal containment 14. Reactor 10 has a tangential entry nozzle 16 located near the top of the reactor and a discharge nozzle 18 located at the bottom of the reactor. A mixture of salts containing oxysulfur compounds and pulverized solid carbonaceous reducing agent, such as coal, is introduced into reactor 10 through tangential entry nozzle 16 via a line 20. Air is supplied via a line 22 to entrain the salt-coal mixture. The top of reactor 10 is provided with a burner 24, which includes a tangential entry nozzle 26 and an axial entry nozzle 28. Air is supplied through tangential entry nozzle 26 via a line 30, and combustion coal is supplied to axial entry nozzle 28 via a line 32. A flame 34 is shown exiting burner 24 and occupying the top part of reactor 10. A spiral path 36 represents the course followed by the mixture of salt and reductant coal, which is introduced together with a carrier air stream through tangential entry nozzle 16. A melt 38, shown along an inside wall 40 of reactor 10, is formed as molten salt particles and associated particles of reducing agent are thrown to wall 40 by the action of centrifugal force. Melt 38 proceeds downwardly in a moving layer along the inside wall 40 of reactor 10 and exits reactor 10 through discharge nozzle 18, together with product gases. The mixture of melt and product gases enters a quench tank 42, containing an aqueous quench solution 44. Quench tank 42 is equipped with an exit nozzle 46, through which the off-gases are removed via a line 48. The product salts can be recovered from quench solution 44 and further processed as desired.

The embodiment of FIG. 2 differs from that of FIG. 1 primarily in the manner of removing product gas. In this embodiment, a reactor 100 is of circular cross section and lined with a corrosion-resistant refractory 102 within a metal containment 104. Tangential entry nozzles 106 are positioned near the top of reactor 100. At the top of reactor 100 and centrally located is a gas discharge nozzle 108, coated with a refractory 110. Gas discharge nozzle 108 is configured to minimize the discharge of particulate matter with the gas. This embodiment permits the product gases to be removed at a high temperature, so that heat recovery can be realized, thereby improving the overall thermal efficiency of the process. The melt is discharged through a discharge nozzle 112 at the bottom of reactor 100 into a quench tank 114, containing an aqueous quench solution 116 and an agitator 118. High pressure water or steam is injected through nozzles 120 to break up the stream of melt falling from discharge nozzle 112 before it contacts quench solution 116. Quench tank 114 is equipped with an aqueous solution feed nozzle 122, through which the aqueous quench solution is fed to quench tank 114 via a line 124; a quenched melt discharge nozzle 126, through which aqueous solution containing the quenched melt is discharged via a line 128; and gas discharge nozzle 130, through which product gases from quench tank 114 are discharged via a line 132.

Referring to FIG. 3 and FIG. 4, reactor 200 is a circular cross-section reactor lined with a corrosion-resistant refractory 202, such as fusion-cast alumina blocks, surrounded by a thermally insulating castable refractory 204 within a metal containment 206. Reactor 200 is equipped with two tangential feed nozzles 208 in the upper portion of reactor 200 and a discharge nozzle 210 at the bottom thereof. A feed hopper 212 is adapted for controlled feeding of a feed mixture 214 of salts containing oxysulfur compounds and pulverized solid carbonaceous reducing agent into a line 216 through which it is conveyed to at least one of the feed nozzles 208 by a carrier gas such as air. The carrier gas enters via a feed line 218 and a blower 220. A separate burner 222 is shown with its own fuel line 224 and air supply line 226. Discharge nozzle 210 is designed to increase the velocity of the discharge gas sufficiently to cause it to produce breakup of the melt formed in reactor 200. Melt flows downwardly along an inside wall 228 of reactor 200 and with product gas is discharged through nozzle 210 into a melt solidification chamber 230. Gas is continuously removed from this chamber via a line 232, cooled in a heat exchanger 234 by means of a heat recovery fluid and returned to chamber 230 via a line 236. Gas circulation is forced by a blower 238 and an amount of product gas equal to the net amount of gas produced in the reactor is continuously removed from the system via a line 240. The solid granular product is removed through a valve 242. Cooling in chamber 230 is accomplished by simple contact of falling droplets with a rising stream of cool gas. Alternative cooling techniques such as fluidized beds or rotary granulators may be employed within the scope of this invention.

The invention will be better understood by reference to the following examples which illustrate embodiments of the process of this invention and should not be construed as limiting the scope of the invention.

EXAMPLE 1

A unit was constructed having the general configuration of the reactor and fuel system of FIG. 3. The upper portion of the reactor was a cylinder 5 in. ID by 7.3 in. in height. Below this was a conical section 6 in. in height with a 2 in. ID discharge port at the bottom. The unit was equipped with two tangential feed nozzles near the top of the cylindrical section. A feed salt having a nominal composition: Na_2CO_3-30%, Na_2SO_3-50%, Na_2SO_4-20% was fed through one of the nozzles mixed with powdered petroleum coke. A natural gas/air burner was fired through the second nozzle. Product melt and gas were discharged through the bottom nozzle. Typical results are given in Table I.

TABLE I

	Test A	Test B
Salt Feed	13.2 lb/hr	5.2 lb/hr
Coke Feed	2.8 lb/hr	2.2 lb/hr
Natural Gas to Burner	42.00 scfm	43.00 scfm
Total Air Feed	9.39 scfm	9.83 scfm
Product Gas Composition		
CO_2	16.3 vol.%	12.7 vol.%
CO	0.8 vol.%	3.3 vol.%
O_2	0	0
Internal Reactor Temp.	972°C.	1021°C.
Reduction to Sulfide	85%	95%

EXAMPLE 2

A test reactor was constructed of simple cylindrical design in the general shape and configuration of the unit shown in FIG. 1. The inside diameter was 1 ft. and the inside height 6 ft. The unit had one tangential feed inlet and a central burner port at the top. Coal was fed as fuel with air through the central burner. Salt was fed through the tangential feed nozzle together with pulverized coal, using air as the transport gas. The nominal composition of the salt was varied in the two runs as shown in Table II. Typical test results were as follows:

TABLE II

	Test C	Test D
Salt Composition		
NaCl	0	3.4%
Na_2CO_3	15.0%	13.5%
Na_2SO_3	20.0%	0
Na_2SO_4	65.0%	83.1%
Coal/Salt Ratio in Feed	0.25 lb/lb	0.38 lb/lb
Feed Rates		
Coal-Salt Mixture	250 lb/hr	414 lb/hr
Coal to Burner	80 lb/hr	105 lb/hr
Total Air	150 scfm	214 scfm
Product Gas		
CO_2	11 vol.%	14 vol.%
CO	12 vol.%	14 vol.%
Temperature at Exit	1186°C.	1100°C.
Conversion to Sulfide	85%	87%

It will, of course, be realized that many variations in the configuration of reaction zones and other reaction conditions may be used in the practice of this invention within the limits of the critical parameters set forth herein. Thus, while the examples illustrating this invention have been described with respect to specific concentrations, feed rates, temperatures, and other reaction conditions, and what is now considered to represent its best embodiment has been illustrated and described, the invention may be otherwise practiced within the scope of the teaching set forth, as will be readily apparent to those skilled in this art. Accordingly, this invention is not to be limited by the illustrative and specific embodiments thereof, but its scope should be determined in accordance with the claims thereof.

Claims:

1. A process for converting an alkali metal oxysulfur compound into the corresponding alkali metal sulfide which comprises:

introducing an alkali metal oxysulfur compound and a solid carbonaceous reducing agent into a reaction zone;

subjecting said oxysulfur compound and said reducing agent to centrifugal force;

heating said reaction zone to melt said oxysulfur compound and to cause said oxysulfur compound and said reducing agent to react to produce an alkali metal sulfide,

flowing a melt containing said alkali metal sulfide, unreacted oxysulfur compound and unreacted reducing agent through said reaction zone and along the periphery thereof to cause said unreacted oxysulfur compound and said unreacted reducing agent to react to produce additional alkali metal sulfide; and

recovering alkali metal sulfide from melt exiting said reaction zone.

2. A process according to Claim 1 wherein said oxysulfur compound and said reducing agent are subjected to centrifugal force by means of a gas stream acting upon said oxysulfur compound and said reducing agent.

3. A process according to Claim 2 wherein said gas stream comprises a carrier gas for at least one of said oxysulfur compound and said reducing agent.

4. A process according to Claim 3 wherein said carrier gas comprises an oxygen-containing gas.

5. A process according to Claim 4 wherein said oxygen-containing gas comprises a carrier for said reducing agent and at least part of the heat for heating said reaction zone is produced by reaction between said reducing agent and said oxygen-containing gas.

6. A process according to Claim 1 wherein said reaction zone is of substantially circular cross section.

7. A process according to Claim 3 wherein said carrier gas enters said reaction zone tangentially.

8. A process according to Claim 2 wherein said gas stream is produced by means of a vortex burner.

9. A process for converting an alkali metal oxysulfur compound into the corresponding alkali metal sulfide which comprises:

introducing near the top of a reaction zone of substantially circular cross-section a mixture of an alkali metal oxysulfur compound and a finely divided solid carbonaceous material entrained in a gas stream in a manner to cause said mixture to traverse said reaction zone in a downwardly spiralling path and to be thrown to the periphery of said reaction zone;

heating said reaction zone to melt said oxysulfur compound and to cause said oxysulfur compound and said carbonaceous material to react to produce an alkali metal sulfide and a gaseous product;

forming a downwardly flowing melt layer comprising unreacted oxysulfur compound, carbonaceous material and product alkali metal sulfide at the periphery of said reaction zone, whereby said unreacted oxysulfur compound and carbonaceous material react to produce alkali metal sulfide and a gaseous product while flowing downwardly along the periphery of said reaction zone; and

discharging said gaseous product and a melt containing alkali metal sulfide from said reaction zone.

10. A process according to Claim 9 wherein the alkali metal oxysulfur compound comprises a member selected from the group consisting of sodium sulfite, sodium sulfate, and potassium sulfate.

11. A process according to Claim 9 wherein said mixture of an alkali metal oxysulfur compound and a finely divided solid carbonaceous material is in the form of solid particles individually containing both alkali metal oxysulfur compound and carbonaceous material, said solid particles resulting from evaporation of water from an aqueous slurry containing an alkali metal oxysulfur compound and a carbonaceous material.

12. A process according to Claim 9 wherein said melt is discharged from one end of said reaction zone and said gaseous product is discharged from the opposite end thereof.

13. A process according to Claim 9 wherein said melt and said gaseous product are discharged from the bottom of said reaction zone, said gaseous product causing said molten alkali metal sulfide to break up into individual droplets.

14. A process according to Claim 9 wherein said melt is cooled after discharging from said reaction zone.

15. A process according to Claim 9 wherein said melt is quenched in an aqueous solution after discharging from said reaction zone.

16. A process according to Claim 9 wherein said melt is converted into solid particles and collected into a bed through which carbon dioxide and water vapor are passed to convert the alkali metal sulfide present in the melt to alkali metal carbonate.

17. A process according to Claim 9 wherein said gas stream comprises an oxidizing gas.

18. A process according to Claim 9 wherein said gas stream comprises an inert gas.

19. A process according to Claim 9 wherein heating of said reaction zone is accomplished by introducing a mixture comprising a fuel and an oxidizing gas axially into said reaction zone.

20. A process according to Claim 9 wherein heating of said reaction zone is accomplished by introducing a mixture comprising a fuel and an oxidizing gas tangentially into said reaction zone.

21. A process according to Claim 19 or Claim 20 wherein said fue comprises a portion of said carbonaceous material.

22. A process according to Claim 9 wherein said gas stream comprises air and heating of said reaction zone is accomplished partly by oxidizing a portion of said carbonaceous material and partly by introducing a mixture comprising a fuel and air into said reaction zone.

23. A process according to Claim 22 wherein the amounts of air introduced into said reaction zone with said carbonaceous material and with said fuel are approximately equal.

AMENDED CLAIMS

(received by the International Bureau on 21 March 1983 (21.03.83))

(amended) 1. A process for converting an alkali metal oxysulfur compound into the corresponding alkali metal sulfide which comprises:

introducing an alkali metal oxysulfur compound and a solid carbonaceous reducing agent into a reaction zone;

subjecting said oxysulfur compound and said reducing agent to centrifugal force, causing said oxysulfur compound and said reducing agent to traverse said reaction zone in a downwardly spiralling path and to be thrown to the periphery of said reaction zone;

heating said reaction zone to melt said oxysulfur compound and to cause said oxysulfur compound and said reducing agent to react to produce an alkali metal sulfide;

flowing a melt containing said alkali metal sulfide, unreacted oxysulfur compound and unreacted reducing agent through said reaction zone and along the periphery thereof to cause said unreacted oxysulfur compound and said unreacted reducing agent to react to produce additional alkali metal sulfide, said melt being flowed through said reaction zone at a rate such that at least about 80% of the alkali metal oxysulfur compound introduced into said reaction zone is reduced to alkali metal sulfide; and

recovering alkali metal sulfide from melt exiting said reaction zone.

2. A process according to Claim 1 wherein said oxysulfur compound and said reducing agent are subjected to centrifugal force by means of a gas stream acting upon said oxysulfur compound and said reducing agent.

3. A process according to Claim 2 wherein said gas stream comprises a carrier gas for at least one of said oxysulfur compound and said reducing agent.

4. A process according to Claim 3 wherein said carrier gas comprises an oxygen-containing gas.

5. A process according to Claim 4 wherein said oxygen-containing gas comprises a carrier for said reducing agent and at least part of the heat for heating said reaction zone is produced by reaction between said reducing agent and said oxygen-containing gas.

6. A process according to Claim 1 wherein said reaction zone is of substantially circular cross section.

7. A process according to Claim 3 wherein said carrier gas enters said reaction zone tangentially.

8. A process according to Claim 2 wherein said gas stream is produced by means of a vortex burner.

(amended) 9. A process for converting an alkali metal oxysulfur compound into the corresponding alkali metal sulfide which comprises:

introducing near the top of a reaction zone of substantially circular cross-section a mixture of an alkali metal oxysulfur compound and a finely divided solid carbonaceous material entrained in a gas stream in a manner to cause said mixture to traverse said reaction zone in a downwardly spiralling path and to be thrown to the periphery of said reaction zone;

heating said reaction zone to melt said oxysulfur compound and to cause said oxysulfur compound and said carbonaceous material to react to produce an alkali metal sulfide and a gaseous product;

forming a downwardly flowing melt layer comprising unreacted oxysulfur compound, carbonaceous material and product alkali metal sulfide at the periphery of said reaction zone, whereby said unreacted oxysulfur compound and carbonaceous material react to produce alkali metal sulfide and a gaseous product while flowing downwardly along the periphery of said reaction zone, at a rate such that at least about 80% of the alkali metal oxysulfur compound introduced into said reaction zone is reduced to alkali metal sulfide; and

discharging said gaseous product and a melt containing alkali metal sulfide from said reaction zone.

10. A process according to Claim 9 wherein the alkali metal oxysulfur compound comprises a member selected from the group consisting of sodium sulfite, sodium sulfate, and potassium sulfate.

11. A process according to Claim 9 wherein said mixture of an alkali metal oxysulfur compound and a finely divided solid carbonaceous material is in the form of solid particles individually containing both alkali metal oxysulfur compound and carbonaceous material, said solid particles resulting from evaporation of water from an aqueous slurry containing an alkali metal oxysulfur compound and a carbonaceous material.

12. A process according to Claim 9 wherein said melt is discharged from one end of said reaction zone and said gaseous product is discharged from the opposite end thereof.

13. A process according to Claim 9 wherein said melt and said gaseous product are discharged from the bottom of said reaction zone, said gaseous product causing said molten alkali metal sulfide to break up into individual droplets.

14. A process according to Claim 9 wherein said melt is cooled after discharging from said reaction zone.

15. A process according to Claim 9 wherein said melt is quenched in an aqueous solution after discharging from said reaction zone.

16. A process according to Claim 9 wherein said melt is converted into solid particles and collected into a bed through which carbon dioxide and water vapor are passed to convert the alkali metal sulfide present in the melt to alkali metal carbonate.

17. A process according to Claim 9 wherein said gas stream comprises an oxidizing gas.

18. A process according to Claim 9 wherein said gas stream comprises an inert gas.

19. A process according to Claim 9 wherein heating of said reaction zone is accomplished by introducing a mixture comprising a fuel and an oxidizing gas axially into said reaction zone.

20. A process according to Claim 9 wherein heating of said reaction zone is accomplished by introducing a mixture comprising a fuel and an oxidizing gas tangentially into said reaction zone.

21. A process according to Claim 19 or Claim 20 wherein said fuel comprises a portion of said carbonaceous material.

22. A process according to Claim 9 wherein said gas stream comprises air and heating of said reaction zone is accomplished partly by oxidizing a portion of said carbonaceous material and partly by introducing a mixture comprising a fuel and air into said reaction zone.

23. A process according to Claim 22 wherein the amounts of air introduced into said reaction zone with said carbonaceous material and with said fuel are approximately equal.

(new) 24. A process according to Claim 1 wherein said melt is flowed through said reaction zone at a rate such that the residence time of said melt in said reaction zone is about 5 to 60 seconds.

(new) 25. A process according to Claim 9 wherein said melt layer flows downwardly along the periphery of said reaction zone at a rate such that the residence time of said melt in said reaction zone is about 5 to 60 seconds.

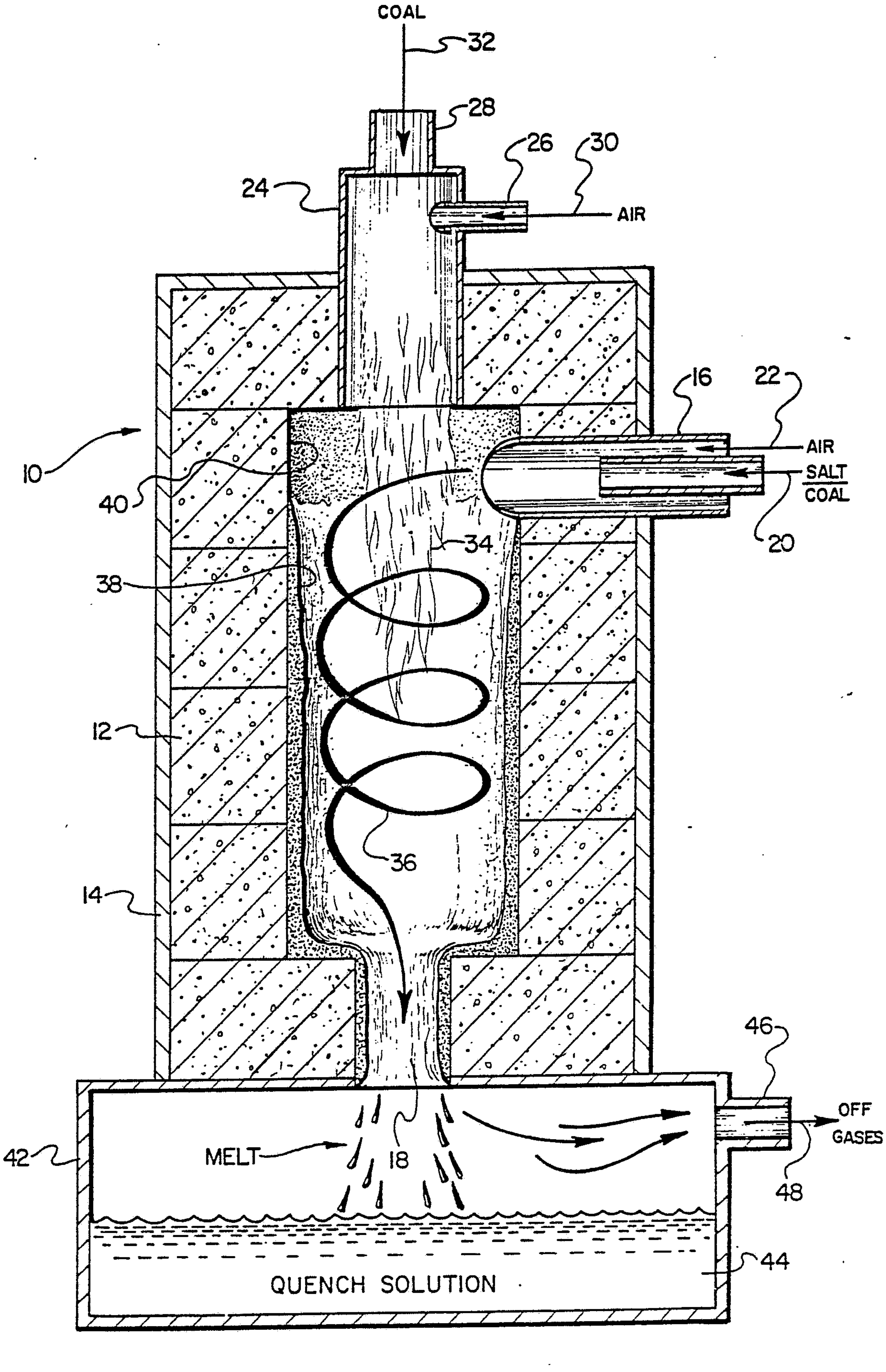

COAL
32
28
26
30
24
AIR
16
22
AIR
SALT
COAL
10
40
20
34
38
12
36
14
46
42
MELT
18
OFF GASES
48
QUENCH SOLUTION
44

Fig.1.

Fig.2.

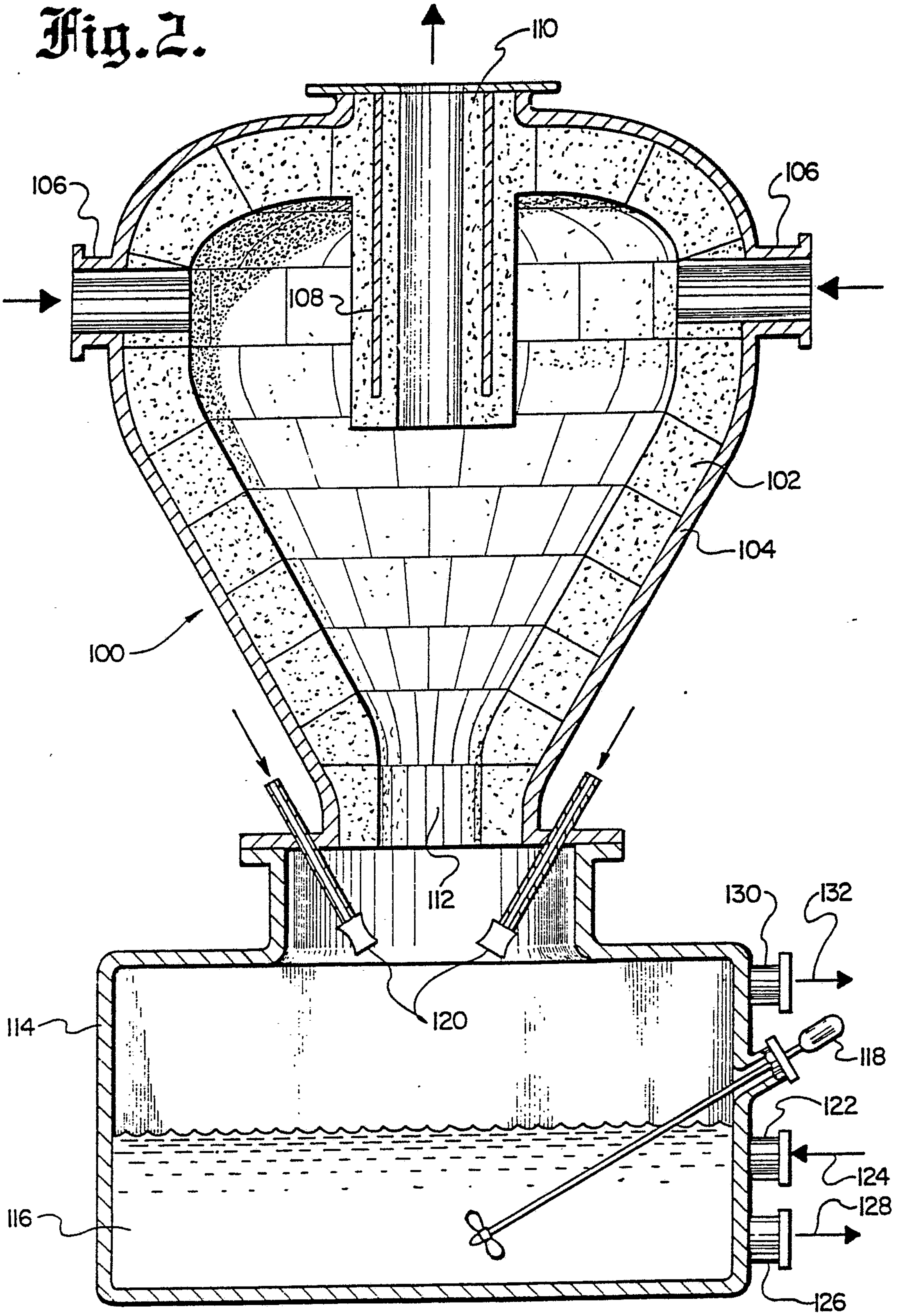

110
106
106
108
102
104
100
112
130
132
120
114
118
122
124
116
128
126

Fig.3.

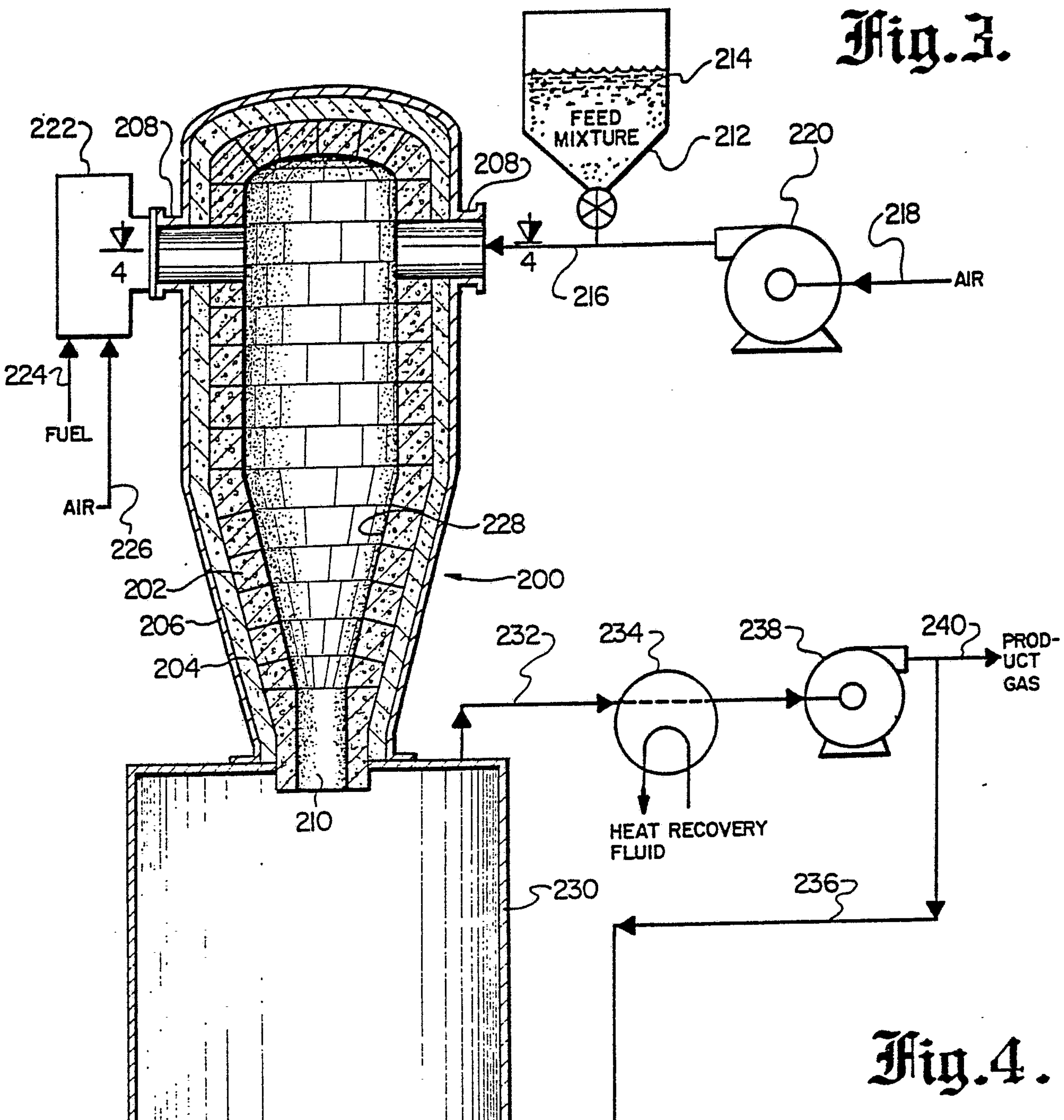
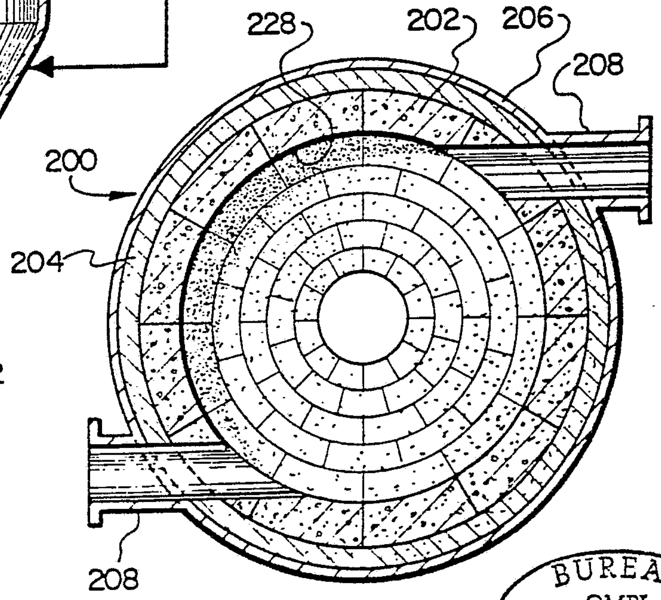

214
FEED MIXTURE
212
220
218
AIR
222
208
208
4
4
216
224
FUEL
AIR
226
228
200
202
206
204
210
232
234
238
240
PRODUCT GAS
HEAT RECOVERY FLUID
230
236
242
SOLID PRODUCT

Fig.4.


228
202
206
208
200
204
208

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 82/01460

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.^{3} C01B 17/24, D21C 11/12
US. CL. 423/561A, 566, 206R, Digest 3; 162/30.1

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	423/201, 206R, 207, 561A, 566, Digest 3 422/184, 185 162/30,1, 30.11, 31

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	GB, A, 159,202, (Basset), 19 February 1921	
A	US, A, 2,678,615, (Soderlund), 18 May 1954	
X	US, A, 2,261,995, (Greenwalt), 11 November 1941	1,6
X	US, A, 3,867,251, (Holme), 18 February 1975	1-8, 9-23
Y	US, A, 3,083,077, (Bjorkman et al), 26 March 1963	1-8
Y	US, A, 3,333,917, (Bergholm), 01 August 1967	1-23
~~Y P~~	~~US, A, 4,351,252, (Shindome et al), 28~~ September1982	~~1-23~~
Y	US, A, 4,280,982, (Shindome et al), 28 July 1981	1-23
Y	US, A, 2,590,905, (Tomlinson et al), 01 April 1952	1-23
*		

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 13 JANUARY 1983	Date of Mailing of this International Search Report [2] 19 JAN 1983
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] GARY P. STRAUB

Form PCT/ISA/210 (second sheet) (October 1981)

International Application No. PCT/US 82/01460

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
Y	US, a, 2,535,730, (Gadert), 26 December 1950	1-11, 13-23
Y	US, A, 4,241,041, (Farin), 23 December 1980	16
Y	US, A, 4,243,645, (Lahoda), 06 January 1981	16
Y	SU, A, 349,049, (Brekson VG Kholostykh VI) 11 Sept 1972	1-23
A	Pulp & Paper Canada, 83:8, 1982, (B. Warnqvist), NSP-A New "Soda"/Kraft Recovery Process Based On A Cyclone Furnace, Pages T230-T231	1-23