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Production of H₂S from SO₂ obtained from flue gas

This invention is concerned with the economic conversion of sulfur dioxide initially contained in a gas mixture in which the SO₂ was a very minor component to gaseous hydrogen sulfide as a major component in a gas mixture. Although this invention is useful in a variety of circumstances, it is of especial utility in flue gas desulfurization—FGD.

It has long been known that when present in the atmosphere even in small concentrations, sulfur dioxide is detrimental to the well-being of animal, aquatic and plant life. When converted to sulfuric acid by the oxygen and moisture in the air, which conversion takes place readily, sulfur dioxide is responsible for the corrosion of many materials of construction including steel and concrete.

Far seeing people recognized a long time ago that the spewing forth into the atmosphere of large amounts of sulfur dioxide would some day be prohibited in the U.S.A. It has been prohibited in some parts of the world for many years. As long ago as 1930, SO₂ was being scrubbed out of flue gas using limestone slurries. Studies to solve this problem were initiated as long ago as 1935 in the U.S.A. The results of these efforts are described in a paper by Johnstone and Singh which appeared in Industrial and Engineering Chemistry Vol. 32, No. 8 pages 1037—1049. A brief summary of the overall status of FGD in the U.S.A. is contained in an article that appeared in the May 23, 1977 issue of Chemical Engineering pages 101—103. Of the processes mentioned, that closest to the process which constitutes this invention is the so-called Aqueous Carbonate Process (AGP). It is described more fully in Volume II of the Proceedings: Symposium on Flue Gas Desulfurization, New Orleans, March 1976 pages 778—816 (Environmental Protection Technology Series).

A carbonate FGD process is disclosed in French Patent Specification FR—A 2162630 for the removal and its subsequent recovery as hydrogen sulfide, of the bulk of the sulfur dioxide contained in a flue gas, which process includes the steps of

(a) contacting said flue gas with an excess of an aqueous, sodium-carbonate containing reaction medium to react the sulfur dioxide with sodium carbonate and sodium bicarbonate to form a dry mixture of solid sodium sulfite, solid sodium sulfate and unreacted sodium carbonate and/or bicarbonate or an aqueous solution containing sodium sulfite or sulfate, and then separating solid sodium sulfite and sodium sulfate from the solution;

(b) reducing the sodium sulfite and sodium sulfate in the molten state with a carbon-containing reducing agent to molten sodium sulfide;

(c) dissolving the molten sodium sulfide in

water and adding sodium bicarbonate to the sodium sulfide solution to form an aqueous mixture thereof;

(d) reacting the sodium bicarbonate with the sodium sulfide in the mixture to form gaseous hydrogen sulfide and sodium carbonate—sodium bicarbonate containing solution;

(e) recovering the gaseous hydrogen sulfide; and

(f) recycling a part of the aqueous solution of sodium carbonate and sodium bicarbonate to step (a);

(g) recycling the remainder of the sodium bicarbonate containing solution recovered after recovery of the hydrogen sulfide to step (c).

According to the above French Patent Specification the SO₂ absorption step is normally carried out so as to produce a dry mixture of solid particles of sodium sulfite, sodium sulfate and sodium carbonate suspended in the SO₂-denuded gas. These particles have to be substantially completely removed from the flue gas to avoid contaminating the atmosphere with particulate material and excessive consumption of sodium carbonate. This involves the use of complex and expensive procedures such as banks of cyclones followed by an electrostatic precipitator installation.

It will also be noted that in the French Patent Specification the reduction process yields molten sodium sulfide which is dissolved in water. The resulting aqueous solution is then treated with carbon dioxide or as an alternative sodium bicarbonate to form a gas containing hydrogen sulfide.

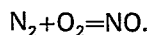
Said French specification also refers briefly to an alternative process in which the SO₂ absorption step produces a solution of alkali metal sulfite and sulfate. Again this results in the need for a relatively complex and expensive separation process such as evaporation. Yet another alternative involving the use of particles of solid sodium carbonate in the absorption step is described in the French specification as requiring a relatively long contact time which in most applications is generally not available.

Many of the absorbents used in previously known processes to scrub SO₂ out of flue gas form slightly soluble compounds. As a result, the equipment used to effect the contact between gas and absorbent becomes covered with scale. The scale formed causes operational difficulties necessitating shut-downs and the incurring of excessive maintenance costs.

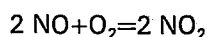
When SO₂ is scrubbed out of flue gas by calcium compounds, either directly or indirectly, the resulting substance becomes a waste disposal problem.

It is an object of the present invention to minimise these disadvantages.

In practice also most fuels, solid and liquid, contain small amounts of nitrogen-containing compounds. When these fuels are burned, the nitrogen appears in the flue gas principally as nitrogen oxide—NO. In addition, at the high temperature reached in many boilers, small amounts of NO are formed from nitrogen and oxygen in accordance with the overall reaction:



It would therefore also be highly desirable to be able to use an FGD process which could if necessary be used or adapted to be used so as to scrub out the oxides of nitrogen as well as the SO₂. It is much easier to scrub NO₂ out of a gas stream with an aqueous scrub liquor than NO. Although the reaction is relatively slow, at moderate temperatures NO and oxygen combine to form NO₂. The reaction is



According to the present invention there is provided a regenerable process for the removal, and its subsequent recovery as hydrogen sulfide, of the bulk of the sulfur dioxide contained in a flue gas containing oxygen, comprising the steps of:

- (a) contacting said flue gas with an aqueous alkaline, sodium-carbonate containing reaction medium substantially saturated with sodium sulfite so as to react the bulk of the sulfur dioxide and a portion of the oxygen with the carbonate to form a slurry of sodium sulfite and sodium sulfate dispersed in the reaction medium, the sodium and alkalinity being supplied to said reaction medium by the addition of recycled solid sodium carbonate from stem (g);
- (b) separating sodium sulfite and sodium sulfate crystals from the reaction medium;
- (c) reducing the separated sodium sulfite and sodium sulfate crystals to solid sodium sulfide;
- (d) forming an intimate blend consisting essentially of said solid sodium sulfide and the separated solid sodium bicarbonate of step (i);
- (e) heating the blend in the substantial absence of air to a temperature sufficient to remove any water present in said blend and to react the sodium bicarbonate with the sodium sulfide in the blend to form gaseous hydrogen sulfide and dry, solid, anhydrous sodium carbonate;
- (f) recovering the gaseous hydrogen sulfide;
- (g) recycling at least part of the sodium carbonate formed in step (e) to step (a);
- (h) adding the remainder of the sodium carbonate formed in step (e) to a sodium bicarbonate saturated solution and carbonating with carbon dioxide to form a slurry composed of solid particles of sodium bicarbonate dispersed in said solution; and

- (i) separating particles of sodium bicarbonate from the slurry formed in step (h) and recycling said separated solid particles of sodium bicarbonate to step (d).

The manner in which the flue gas is contacted by the absorbent for SO₂ is such that the bulk of any particulates suspended in the flue gas will be captured by the scrub slurry. Consequently, nearly all of the pollutants contained in a flue gas will be removed by the scrubbing step of this invention.

In addition it will be apparent that the aqueous slurry containing solid sodium sulfite and sodium sulfate may be very simply and economically separated by mechanical means such as those described hereinbelow from the treated flue gas and so as to provide solid sodium sulfite and sodium sulfate.

In a further aspect the present invention provides a system for removing the sulfur dioxide contained in a flue gas, comprising:

(a) a gas contacting device for contacting said flue gas with an aqueous, alkaline, sodium carbonate containing reaction medium saturated with sodium sulfite to react the bulk of the sulfur dioxide and a portion of the oxygen with the carbonate moiety, to form a slurry of sodium sulfite and sodium sulfate dispersed in the reaction medium, and for supplying the sodium and alkalinity to the reaction medium by the addition of recycled solid sodium carbonate, said gas contacting device having an inlet(s) for receiving said flue gas and for receiving said reaction medium, and an outlet(s) for discharging gas and for discharging the reaction product containing sodium sulfite and sodium sulfate;

(b) first conveying means arranged for conveying the reaction medium to first separating means for separating sodium sulfite and sodium sulfate crystals from the reaction medium;

(c) second conveying means arranged for conveying the separated sodium sulfite and sodium sulfate crystals from the outlet of said first separating means to the inlet of a reducing means for reducing the sodium sulfite and sodium sulfate to sodium sulfide;

(d) third conveying means for conveying the sodium sulfide from the outlet of said reducing means to the inlet of a mixing means for forming an intimate blend of said solid sodium sulfide with solid sodium bicarbonate;

(e) fourth conveying means for conveying said blend from the outlet of said mixing means to the inlet of a heating means arranged for heating said blend in the substantial absence of air to a temperature at which sodium bicarbonate would be converted to sodium carbonate and carbon dioxide to form gaseous hydrogen sulfide and dry, solid, anhydrous sodium carbonate;

(f) fifth conveying means for conveying gaseous hydrogen sulfide from the outlet of the heating means to the inlet of a recovering

means for recovering said gaseous hydrogen sulfide;

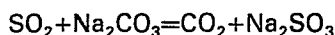
(g) sixth conveying means for conveying said portion of the sodium carbonate from the outlet of said heating means to the inlet of an adding means arranged for adding a portion of the sodium carbonate formed in said heating means to a sodium bicarbonate saturated solution and for carbonating thereof with carbon dioxide to form a slurry composed of solid particles of sodium bicarbonate dispersed in said solution; and

(h) seventh conveying means for conveying the slurry from the outlet of said adding means to the inlet of a second separating means for separating particles of sodium bicarbonate from the slurry formed in said adding means; and

(i) eighth conveying means for conveying the separated particles from the outlet of said second separating means to the inlet of said mixing means.

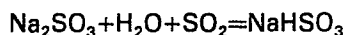
The reactions which are employed in the process consist of:

Absorbing SO_2 in a solution which is saturated with sodium sulfite and preferably also contains dissolved sodium carbonate. The fundamental reaction in the absorption step is:

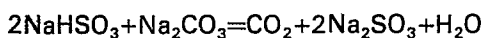


This reaction takes place when the solution in the absorption zone contains some dissolved sodium carbonate.

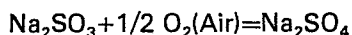
If no sodium carbonate is present, SO_2 is absorbed using dissolved sodium sulfite as the absorbent. The reaction being:



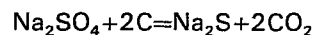
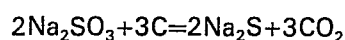
The ability of the absorbent to continue to absorb SO_2 is maintained by the subsequent addition of sodium carbonate. The sodium bisulfite reacts with the carbonate as follows:



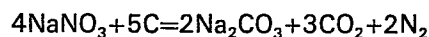
An undesirable reaction but one with which the process can cope is the oxidation of part of the sulfite to sulfate:



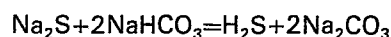
The second series of reactions of the process involve the reduction of the sodium sulfite and sodium sulfate to sodium sulfide by means of a readily available reducing agent. In most instances this will be a carbon-containing reducing agent such as bituminous coal. Other inexpensive carbon-containing reductants such as coke, or wood, or heavy oil also work satisfactorily. The overall reactions, when carbon containing reducing agents which are particularly convenient, are used can be summarized as:



If sodium nitrate is present it is converted to sodium carbonate and nitrogen. The overall reaction is:

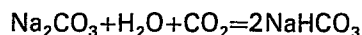


The principal reaction following the reduction reactions is the generation of hydrogen sulfide from sodium sulfide and sodium bicarbonate. The overall reaction is:



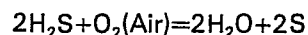
It will be noted that the sequence of the reduction reactions followed by the H_2S generation step results in the regeneration of the sodium carbonate used in the SO_2 absorption step.

The final step of the process in the well-known bicarbonate of soda formation reaction:

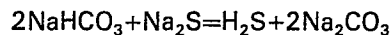
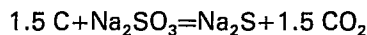
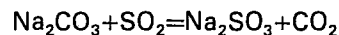
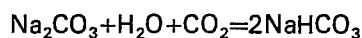


Any convenient, low cost source of CO_2 can be used such as for example the gas resulting from the reducing step where a carbon-containing reducing agent has been used, or the SO_2 -free flue gas.

In most instances the final reaction will be the conversion of the H_2S to sulfur using the classical Claus process; the fundamental overall reaction being:



The relationship of the principal individual reactions to each other may, in the case where a carbon-containing reducing agent is used, be summarized as follows:



The invention will now be described in detail below by way of example with reference to the accompanying drawing which illustrates one embodiment of an apparatus suitable for use in a process according to the present invention.

Figure 1 is a flow diagram depicting the relationship of the various steps to each other when the invention is practised at a site where space is available for all the necessary equipment and the SO_2 -containing flue gas is washed with water to remove particulates prior to the SO_2 removal step. Under less preferable conditions certain steps of the process can be

physically separated. Although not desirable, in some instances it is necessary to carry out certain steps of the process at two different locations. One of the advantages of the invention is that a split operation is technically, feasible. This mode of operation is employed when it provides economic advantages compared with the use of any other process for freeing flue gas from pollutants prior to venting it to the atmosphere.

The invention can be understood by following each step starting with the sulfur compound as it enters the process as sulfur dioxide and finally leaves as gaseous hydrogen sulfide in concentrated form. The SO₂-containing flue gas is scrubbed with water by means not shown to remove the bulk of the particulate solids. By referring to Figure 1 it will be noted that the gas then flows into the lower gas inlet of a first absorption zone or gas-contacting device (1) by means of duct (2). In this zone the gas is contacted by an aqueous slurry, the liquid phase of which is an aqueous solution containing mostly dissolved sodium sulfite and sodium sulfate, minor amounts of other sodium salts, e.g. sodium nitrate, plus a small amount of sodium carbonate. The solid phase is essentially mixed crystals of sodium sulfite and sodium sulfate—the bulk of the solids being composed of sodium sulfite. The temperature of the scrubbing step is controlled so that the anhydrous salt crystallizes i.e. the temperature is maintained at such a temperature that the solid salts which precipitate are free from water of crystallization. A suitable temperature range is between 40°C and 50°C. The purpose of maintaining the scrubbing solution at the indicated temperature is to minimize the fuel cost in a subsequent step of the process. It does not affect the ability of the solution to absorb SO₂ or oxides of nitrogen. The undesirable oxidation of sulfite to sulfate takes place primarily in this first absorption zone.

Its extent depends upon many factors such as the amount of excess air in the flue gas, the presence of trace amounts of dissolved catalytic metals such as iron and copper, temperature, etc. When appreciable concentrations of sodium sulfite and sodium sulfate are in a solution and the solution becomes saturated so that precipitation takes place, the crystals that form are mixed crystals of sodium sulfite and the sulfate. Because the absorption solution is saturated with sodium sulfite, its ability to dissolve oxygen is limited. This diminishes the degree to which the oxidation reaction takes place compared to the degree to which it takes place when less concentrated sulfite scrubbing solutions are employed.

Because of the properties of the absorbent slurry, the solids in the slurry always contain some sodium sulfate mixed with the sodium sulfite. Whenever solid sodium sulfite is mentioned below it must be understood that it

will be mixed with some sodium sulfate. Similarly, it should be understood that the liquid phase of the absorbent slurry will always contain some dissolved sodium sulfate but the predominant solute will be sodium sulfite.

The oxides of nitrogen of the flue gas are also absorbed in this first absorption zone to a greater or less degree depending upon the amount of NO and NO₂ present. If there are equimolar concentrations, most of oxides will be absorbed and form sodium nitrite.

An excess of nitrogen dioxide results in the formation of sodium nitrate as well. As is known, NO in the presence of air is absorbed by aqueous alkaline solutions containing dissolved sulfite, but the absorption takes place more slowly than the absorption of nitrogen dioxide. Since oxides of nitrogen are always present in flue gas containing an appreciable concentration of SO₂, the liquid portion of the absorbent slurry always contains some sodium nitrite and sodium nitrate. As a result of the subsequent steps of the process these oxides of nitrogen are eventually converted to nitrogen and vented to the atmosphere without having to take any special steps to accomplish this objective.

To maintain the solution's ability to absorb SO₂ and to form anhydrous sodium sulfite crystals from the absorbed SO₂, the solution is fortified by the continuous or periodic addition of sodium carbonate the source of which is described below.

The slurry used to contact the SO₂-concentrating gas in the first absorption zone enters it at one end through pipe 3 by means of a pump not shown. The slurry flows through the zone counter-current to the SO₂-containing gas flowing in the opposite direction. The SO₂ is absorbed by the liquid phase of the slurry as the gas leaves the zone through vent pipe 22. As the SO₂ is absorbed additional solid sodium sulfite forms since the solution is maintained in a saturated condition. The slurry leaves the first absorption zone by means of first conveying means in the form of an outlet pipe 4 which conducts it into a settler 5 of a separating means. The larger crystals in the slurry sink to the lower section of the settler and form a more dense magma. The smaller crystals and the bulk of the liquid phase leave the settler through overflow line 6 through which it empties into surge tank 7. The magma formed in the base of the settler leaves through its bottom outlet and flows by means of pipe 8 into centrifuge 9. In centrifuge 9 most of the solids are separated from their accompanying liquid phase. The liquid phase is directed to surge tank 7 by means of pipe 10. Crude sodium carbonate is also fed to surge tank 7 by means of belt 17. The mixture formed in tank 7 is circulated through the absorption zone 1 by means of the pump, not shown, mentioned previously.

The moist solids separated in centrifuge 9 are conveyed by second conveying means including

a belt 11 into a feed hopper 12. By means of screw conveyor 53 from a source not shown, feed hopper 13 is periodically replenished with pulverized bituminous coal. Pulverized coal constituting a carbon-containing reducing agent is removed from hopper 13 by means of screw conveyor 14 and to mixer 15. Crude moist sodium sulfite is withdrawn from feed hopper 12 by means of feeder 16 and also fed to mixer 15. Crude moist sodium sulfite and coal are intimately mixed in mixer 15 and the mixture fed by means of a screw conveyor 18 of second conveying means into the feed end of a reducing means comprising a direct fired rotary kiln 19. By means of screw feeder 20 pulverized coal from hopper 13 and combustion air from line 21 are fed to the kiln's discharge end 19. The coal is burned with essentially the stoichiometric amount of oxygen so that the gaseous atmosphere within the kiln is reducing rather than oxidizing. As the mixture of coal and sodium sulfite moves through the kiln counter-current to the hot products of combustion, the sodium sulfite is reduced to sodium sulfide and the carbon is oxidized to carbon dioxide.

Although not essential it is desirable to use such a ratio of sodium sulfite to coal, approximately 4 to 1, that the bulk of the sodium is converted to the sulfide. It is preferable to control the temperature so that little or none of the mixture within the kiln reaches its melting point. By operating under these conditions, solid particles, mostly sodium sulfide, flow out of the discharge end of the kiln. By having a maximum temperature in the kiln within the range 650°C to 750°C, the salt mixture does not soften. By insuring excess carbon in the mixture leaving the kiln, more than 90% of the sodium sulfite is converted to sodium sulfide.

The solid mixture formed in the rotary kiln is withdrawn through the kiln's discharge outlet by means of a third conveying means comprising a screw conveyor 23 equipped with means, not shown, to prevent air from contacting the hot solid sodium sulfide-containing mixture. Screw conveyor 23 delivers the sodium sulfide-containing mixture to mixing means comprising a continuous mixer-grinder 24 in which it is blended with the stoichiometric quantity of moist sodium bicarbonate the source of which is described below. The mixer-grinder converts the mixture into small particles thoroughly commingled. Mixer-grinder 24 is equipped with seals to prevent the escape of any vapours formed during the blending operation. To ensure that vapours do not escape mixer-grinder 24 is maintained under a slight negative pressure.

The mixture resulting from the blending of the bicarbonate and sodium sulfide-containing solid flows out of the mixer-grinder's outlet into fourth conveying means in the form of a screw conveyor 25 which delivers it to a heating means comprising a steam tube rotary calciner 26. The steam tube calciner is heated by high

pressure steam e.g. steam at a pressure between 27.6 and 31 bars.

In the calciner the bulk of the sodium bicarbonate and the bulk of the sodium sulfide are heated to a temperature of about 200°C. Under these conditions they react to form crude sodium carbonate and gaseous hydrogen sulfide. The water vapour and gaseous hydrogen sulfide leave the calciner's gas outlet and by means of fifth conveying means in the form of a pipe 27 are conveyed to a recovering means including a condenser, not shown, in which the bulk of the water vapour is separated from the H₂S and in a Claus process plant not shown in which the separated H₂S is converted to sulfur.

The crude sodium carbonate-containing solid formed in the calciner leaves the calciner's discharge outlet and by means of a screw conveyor 28 and sixth conveying means in the form of a screw conveyor 29, respective portions of crude sodium carbonate are fed to surge tank 7 via belt 17, and to a dissolver 30 of an adding means. Sodium bicarbonate-containing solution whose source is described below is also fed to the dissolver 30 by means of line 32. The slurry formed in dissolver 30 is piped via a pipe 31 of seventh conveying means to a filter 37. The concentrated filtrate separated from the solids by means of filter 37 is pumped by a pump, not shown, through line 33 into surge tank 34. Wash water is introduced to the washing section of filter 37 by means of water feed line 35. The wash liquor containing the remaining water soluble components of the mixture entering dissolver 30 flows out of filter 37 and by means of line 36 is directed to dissolver 30 via pipe 12. The washed solids, free from water soluble components, leaves filter 37 and by means of screw conveyor 38 is mixed with the fuel fed to the boiler, not shown, in which the sulfur dioxide-containing products of combustion are formed.

The solution and suspended solids contained in surge tank 34 which consists in large part of a mixture of sodium bicarbonate and sodium carbonate is circulated by means of pipe 54 to the liquid inlet of a second absorption zone 40 of the adding means. Carbon dioxide-containing gas is fed to inlet of absorption zone 40 by means of pipe line 41. The source of the carbon dioxide gas is described below. In this absorption zone 40 carbon dioxide is absorbed by the sodium carbonate-containing solution which is maintained saturated with sodium bicarbonate. As a result of the absorption of the carbon dioxide, sodium carbonate is converted to sodium bicarbonate which crystallizes from solution. The slurry leaving absorption zone 40 is directed into a second separating means in the form of a settler 42 by means of line 43 of the seventh conveying means. The larger particles of solid sodium bicarbonate in the slurry settle into the lower section of the settler 42. The

smaller particles and the bulk of the solution leave the settler from its top outlet and by means of pipe 44 is delivered to surge tank 34. The magma formed in the lower section of settler 42 is fed to centrifuge 45 by means of pipe 46. Centrifuge 45 separates the slurry feed into two fractions one of which is the centrifuge cake consisting in large part of moist sodium bicarbonate and the other consisting of the bulk of the solution contained in the slurry. The moist sodium bicarbonate cake is transported by eighth conveying means in the form of a belt conveyor 47 to the mixer-grinder 24. The solution leaving the centrifuge flows by means of pipe 48 into surge tank 34.

The carbon dioxide fed to absorption zone 40 is preferably obtained from the exhaust gas from kiln 19 by means of duct 49 via pipe 41. Should this gas be unavailable as a result of local conditions or should the quantity of CO_2 be insufficient for any reason, then carbon dioxide can be obtained from the gas leaving absorption zone 1. When CO_2 is fed to absorption zone 40 from the gas leaving absorption zone 1, it is piped from vent pipe 22 by means of pipeline 50 into pipe 41 which leads to absorption zone 40. Carbon dioxide-containing gas exiting from absorption zone 1, not needed for absorption in zone 40, is vented to the atmosphere by means of vent pipe 51. No matter the source of the carbon dioxide entering absorption zone 40, the CO_2 will be mixed with a preponderance of nitrogen. The nitrogen plus all of the remaining unabsorbed gas leaves zone 40 by means of vent pipe 52.

Many variations can be employed of each of the steps described above. This process has a large number of unobvious advantages.

Mention has been made of the desirability of removing the particulates from the SO_2 -containing gas prior to its treatment by this process. Although that is desirable, the process of this invention can be carried out successfully even though particulates are present. Most of the particulates that are borne along by the SO_2 containing gas will be scrubbed out by the scrubbing liquid. These solids will leave the scrubbing system eventually along with the solid sodium sulfite.

By using a soluble slurry absorbent, i.e. an aqueous solution saturated with sodium sulfite containing suspended sodium sulfite crystals, there is little tendency for scaling to take place on the interior surfaces of the scrubber. Should scaling occur, the soluble sulfite will quickly redissolve by manipulating the sodium sulfite concentration of the scrub liquor.

If desirable, hydroclones can be used instead of settlers. Similarly, filters can be used instead of centrifuges.

Although it is preferred to reduce the sodium sulfite with coal without allowing the reaction mixture to melt, this is not essential. By carrying out the reduction at a temperature high enough to maintain the bulk of the sodium sulfide in a

molten state, the reduction reaction is speeded up. However, this means a more expensive refractory will be required to line the inner surface of the container in which the reduction is carried out. Moreover, the molten product must be solidified by cooling in an inert atmosphere to minimize reoxidation prior to mixing with the moist sodium bicarbonate.

In carrying out the reduction step, it is desirable to use an excess of reducing agent. The unreacted reducing agent plus the ash from the coal which has reacted plus the ash left as a result of burning the coal will be mixed with the sodium carbonate formed in the steam tube rotary calciner. To rid the system of the ash and to recover the fuel value left in the filter cake, the filter cake is mixed with the fuel fed to the boiler. The weight of filter cake is only a small fraction of the weight of fuel. Because the weight of filter cake is so small compared with the weight of the fuel, adding the filter cake to the fuel does not affect the operation of the burner but it prevents fuel from being wasted.

This process is particularly advantageous when used to control the pollutants in the flue gas of a coal burning large steam raising installation used to generate electricity. Although various sodium salts are formed and then converted to other salts in sequence, other than coal, only utilities are consumed and they are all readily available and relatively inexpensive at such a location.

Prior to this invention, no FGD process was available which was clearly superior to limestone slurry scrubbing. As a result many limestone slurry scrubbing systems have been installed. Many of them were retrofitted to enable units constructed a long time ago to continue to operate and comply with the new regulations. Very often barely enough space was available to install the scrubbers and the auxiliary equipment required to use them.

Among the objects of this invention is the diminution of the cost of flue gas processing in older steam raising units which have already been equipped with limestone scrubbing facilities. When there is only room for the SO_2 scrubbing step, this is accomplished by substituting crude sodium carbonate for the ground limestone. Most of these installations have means for recirculating slurry and for separating a filter cake from a slurry. It may be necessary to install a centrifuge to obtain a centrifuge cake with a low moisture content. This is desirable primarily to save on transportation costs.

The slurry circulated will contain suspended water soluble sodium sulfur salts and the particulates.

The moist filter cake obtained by the centrifugation operation will contain the water insoluble particulates which had been suspended in the flue gas and sodium salts i.e. sodium sulfite, sodium sulfate, along with minor amounts of sodium nitrite and sodium nitrate.

The filter cake is transported by some

convenient means to a location where there is sufficient land to install the rest of the equipment required to carry out the process. Much of the equipment has already been described. Additional facilities will be needed, however. These facilities will consist primarily of a dissolver and filter with means to wash the water soluble sodium salts out of the filter cake using a minimum of water.

By conventional dissolving, evaporating, crystallizing and washing means, the insoluble particulates are separated from the mixed sodium salts. The end results consists of two filter cakes. One is composed of innocuous, water insoluble, solids essentially the ash resulting from the burning of the fuel. The other is a moist filter cake composed principally of sodium sulfite and sodium sulfate.

The sodium salt filter cake is processed as has already been described to recover the sulfur values and to regulate sodium carbonate. Part of the crude sodium carbonate formed in the H_2S formation step is shipped back to the scrubbing operation for additional SO_2 absorption.

It is obvious, too, that it is technically feasible to build and operate a processing facility to service the slurry resulting from two or more FGD scrubbing operations.

The use of an absorbent slurry has been emphasized above because this unobvious method results in capital investment and fuel savings. From the variation described by which particulates are separated from the soluble sodium salts, it will be noted that the invention can be carried out by absorbing SO_2 in an alkaline absorbent liquid whose sodium sulfite concentration is maintained below its saturation value. Sodium carbonate and water are added to the absorbent liquid to keep its composition within a narrow range. Solution containing dissolved sodium sulfite is withdrawn from the scrubbing system. Solid sodium sulfite is recovered by conventional evaporation and crystallization procedures. The recovered moist sodium sulfite filter cake is then processed as described above.

In the above description of the invention mention is made of the flue gas and absorbent slurry flowing counter-currently to each other. One aspect of this invention is the devising of an absorbent, all of whose components are substantially soluble in water which has a constant high level of SO_2 absorption capability. As a result the absorption medium can be used effectively in cocurrent contactors such as a venturi scrubber or in cross flow contactors.

Principal items of expense of all scrubber operations are the initial expense of the scrubbing equipment and the energy expended to achieve the necessary gas-liquid contact so that the SO_2 is absorbed. This energy expenditure is measured by the pressure drop required to cause the gas to flow through the scrubbing system. Anything that results in

adequate SO_2 removal while reducing pressure drop as well as capital investment provides material economic benefits. Unlike most SO_2 scrubbing processes, this process can be operated at a relatively high pH, at a pH of 8 or higher without any appreciable penalty. This means inexpensive materials of construction can be used. In addition, it is possible to employ a well-known device to improve the absorption of a volatile acidic gas by an alkaline solution—that device is to maintain a very small concentration of ammonia in the system. This device is useful when absorbing CO_2 as well as SO_2 . The NH_3 enters the vapor phase, reacts with the acidic gas to form a salt particle that quickly absorbs water vapor so that it is enlarged and easily wetted. The moist particle is rapidly dissolved by the scrub liquor. On dissolution, at the high pH, ammonia vaporizes and the cycle is repeated. By this means the need is eliminated for the acidic gas to diffuse through the gas-liquid interface, usually the rate controlling step in gas absorption operations. The savings in pressure drop resulting from the maintenance of a small concentration of ammonia in the scrubbing system is larger than the cost of the ammonia that has to be continuously supplied.

When sodium carbonate is substituted for limestone in a scrubber already installed, the SO_2 absorption capacity of the system is increased. If a small ammonia concentration is maintained in the system, 1% or less, the SO_2 absorption capacity is further increased. By increasing the desulfurization capacity of the already installed equipment, it becomes possible to burn fuel with an increased sulfur content and still limit the SO_2 leaving the system to allowable quantities. Since the cost of fuel varies inversely with its sulfur content, less expensive fuel can be burned thereby providing additional substantial saving in the steam raising operation.

No part of this invention is dependent upon the particular type of equipment which has been mentioned in the above description. Any suitable slurry-gas contacting equipment can be used in the SO_2 and CO_2 absorption steps. Similarly various types of centrifuges, filter or settlers can be used to separate solids from slurries. In fact, the process has the advantage that nothing is lost when some of the solids in the slurry accompany the filtrate. This means emphasis can be placed on obtaining low water content filter cakes. It has already been pointed out that the reduction step can be carried out so that the reactants and products remain solid or at a temperature so high they melt.

When the reactants stay solid, the reduction can be carried out in a direct fired rotary kiln or a multiple hearth furnace. When the reaction is carried out at a temperature at which the sodium sulfide-containing mixture is molten, the reactor can be a refractory lined pot with means for adding the sodium salts to be reduced and

the reductant. Air can be blown into the mixture to burn some of the reductant to provide the necessary heat. By providing a product outlet the whole operation can be made continuous. The reaction between sodium sulfide and sodium bicarbonate to evolve H_2S and sodium carbonate is carried out conveniently at a temperature between about $180^\circ C$ and $220^\circ C$. Even lower temperatures can be used by increasing the amount of water in the initial mixture. The rotary steam tube calciner is a particularly useful piece of equipment in which to carry out this reaction when high pressure steam is available. In its absence, a high boiling liquid heat transfer fluid such as the well-known Dowtherms can be used in place of high pressure steam. Other equipment can also be employed provided the intimate mixture of Na_2S and $NaHCO_3$ is heated to the reaction temperature under substantially muffle conditions. A multiple hearth muffle furnace can be used as well as an indirectly heated rotary kiln.

One of the factors which influences the economics of this invention is the amount of energy required to recover a pound of H_2S . This item is strongly influenced by the moisture content of the mixture of Na_2S and $NaHCO_3$ which is heated to evolve H_2S . The higher the moisture content, the lower the temperature to which the mixture has to be heated. In most instances the moisture content is controlled so that two to three pounds of water are vaporized per pound of H_2S evolved although under some circumstances it is advantageous to vaporize three times this quantity. If it is convenient to heat the mixture above $200^\circ C$, good conversions are obtained when somewhat less water is present in the initial mixture.

In summary, then, this invention provides an improved process for the recovery of the sulfur values from an SO_2 -containing flue gas while simultaneously purifying it so that it may be exhausted to the atmosphere as a substantially clean and harmless effluent. Variations can be employed with respect to procedures and proportions without changing the scope of the invention as defined by the following claims.

Claims

1. A regenerable process for the removal, and its subsequent recovery as hydrogen sulfide, of the bulk of the sulfur dioxide contained in a flue gas containing oxygen, comprising the steps of:

- (a) contacting said flue gas with an aqueous alkaline, sodium-carbonate containing reaction medium substantially saturated with sodium sulfite so as to react the bulk of the sulfur dioxide and a portion of the oxygen with the carbonate to form a slurry of sodium sulfite and sodium sulfate dispersed in the reaction medium, the sodium and alkalinity being supplied to said reaction medium by

the addition of recycled solid sodium carbonate from stem (g);

- (b) separating sodium sulfite and sodium sulfate crystals from the reaction medium;
- (c) reducing the separated sodium sulfite and sodium sulfate crystals to solid sodium sulfide;
- (d) forming an intimate blend consisting essentially of said solid sodium sulfide and the separated solid sodium bicarbonate of step (i);
- (e) heating the blend in the substantial absence of air to a temperature sufficient to remove any water present in said blend and to react the sodium bicarbonate with the sodium sulfide in the blend to form gaseous hydrogen sulfide and dry, solid, anhydrous sodium carbonate;
- (f) recovering the gaseous hydrogen sulfide;
- (g) recycling at least part of the sodium carbonate formed in step (e) to step (a);
- (h) adding the remainder of the sodium carbonate formed in step (e) to a sodium bicarbonate saturated solution and carbonating with carbon dioxide to form a slurry composed of solid particles of sodium bicarbonate dispersed in said solution; and
- (i) separating particles of sodium bicarbonate from the slurry formed in step (h) and recycling said separated solid particles of sodium bicarbonate to step (d).

2. A process as claimed in Claim 1 in which process a substantial amount of insoluble solid particulate material is present in the separated crystals of step (b), wherein, prior to the reducing step (c), said separated crystals of step (b) are contacted with water to dissolve the sodium sulfite and sodium sulfate crystals to form a solution of sodium sulfite and sodium sulfate, the solution is separated from the remaining solid particulate material, and the separated solution is then evaporated to recover sodium sulfite and sodium sulfate crystals.

3. A process as claimed in Claim 1 or Claim 2 in which process said reaction medium is a slurry, whose solid phase is substantially sodium sulfite and sodium sulfate crystals.

4. A process as claimed in Claim 3 characterized in that the absorptive capacity of the slurry for sulfur dioxide is maintained by the addition of solid, dry, sodium carbonate, the amount of solid sodium carbonate added to the slurry being substantially equivalent to the amount of solid sodium sulfite and sodium sulfate crystals separated from the reaction medium.

5. A process as claimed in Claim 3 or Claim 4 characterized in that step (a) is carried out at a temperature of above $35^\circ C$.

6. A process as claimed in any one of claims 3 to 5 characterized in that step (a) is carried out at a pH in excess of 8.

7. A process as claimed in Claim 6 characterized in that ammonia is maintained in the step (a) at a concentration of from 0.1% to 1%.

8. A process as claimed in any one of claims 3 to 7 characterized in that in step (b) the crystals of sodium sulfite and sodium sulfate are separated from the reaction medium by filtering a portion of the slurry to obtain a moist filter cake, the solid portion of which is substantially sodium sulfite and sodium sulfate crystals, and a filtrate which is returned to step (a).

9. A process as claimed in any one of Claims 1 to 8 characterized in that the sodium sulfite and sodium sulfate crystals are reduced with a carbon-containing reducing agent to form sodium sulfide and a carbon dioxide-containing gas.

10. A process as claimed in Claim 9 characterized in that carbon dioxide formed in the reduction of the crystals of sodium sulfite and sodium sulfate with a carbon-containing reducing agent is used as the source of carbon dioxide in step (h).

11. A process as claimed in any one of Claims 1 to 10 characterized in that step (e) is carried out at a temperature in the range of from 180°C to 220°C.

12. A system for removing the sulfur dioxide contained in a flue gas containing oxygen, comprising:

- (a) a gas contacting device (1) for contacting said flue gas with an aqueous, alkaline, sodium carbonate containing reaction medium saturated with sodium sulfite to react the bulk of the sulfur dioxide and a portion of the oxygen with the carbonate moiety, to form a slurry of sodium sulfite and sodium sulfate dispersed in the reaction medium, and for supplying the sodium and alkalinity to the reaction medium by the addition of recycled solid sodium carbonate, said gas contacting device having an inlet(s) for receiving said flue gas and for receiving said reaction medium, and an outlet(s) for discharging gas and for discharging the reaction product containing sodium sulfite and sodium sulfate;
- (b) first conveying means (4) arranged for conveying the reaction medium to first separating means (5,9) for separating sodium sulfite and sodium sulfate crystals from the reaction medium;
- (c) second conveying means (18) arranged for conveying the separated sodium sulfite and sodium sulfate crystals from the outlet of said first separating means (5,9) to the inlet of a reducing means (19) for reducing the sodium sulfite and sodium sulfate to sodium sulfide;
- (d) third conveying means for conveying the sodium sulfide from the outlet of said reducing means (19) to the inlet of a mixing means (24) for forming an intimate blend of said solid sodium sulfide with solid sodium bicarbonate;
- (e) fourth conveying means (25) for conveying said blend from the outlet of said mixing means (24) to the inlet of a heating means (26) arranged for heating said blend in the substantial absence of air to a temperature at

which sodium bicarbonate would be converted to sodium carbonate and carbon dioxide to form gaseous hydrogen sulfide and dry, solid, anhydrous sodium carbonate;

- (f) fifth conveying means (27) for conveying gaseous hydrogen sulfide from the outlet of the heating means (26) to the inlet of a recovering means for recovering said gaseous hydrogen sulfide;
- (g) sixth conveying means (29,31,33,54) for conveying said portion of the sodium carbonate from the outlet of said heating means (26) to the inlet of an adding means (30,40) arranged for adding a portion of the sodium carbonate formed in said heating means (26) to a sodium bicarbonate saturated solution and for carbonating thereof with carbon dioxide to form a slurry composed of solid particles of sodium bicarbonate dispersed in said solution; and
- (h) seventh conveying means (43) for conveying the slurry from the outlet of said adding means (30,40) to the inlet of a second separating means (42,45) for separating particles of sodium bicarbonate from the slurry formed in said adding means (30,40), and
- (i) eighth conveying means (47) for conveying the separated particles from the outlet of said second separating means (47,45) to the inlet of said mixing means (24).

Patentansprüche

1. Regenerativverfahren zur Entfernung der Hauptmenge des in einem sauerstoffhaltigen Rauchgas enthaltenen Schwefeldioxyds und zu dessen nachfolgender Rückgewinnung als Schwefelwasserstoff, umfassend die folgenden Stufen:

(a) Kontaktieren dieses Rauchgases mit einem wässrig-alkalischen, Natriumcarbonat enthaltenden, weitgehend mit Natriumsulfit gesättigten Reaktionsmedium, um die Hauptmenge des Schwefeldioxyds und einen Teil des Sauerstoffs mit dem Carbonat unter Bildung einer Aufschlämmung von im Reaktionsmedium dispergiertem Natriumsulfit und Natriumsulfat umzusetzen, wobei das Natrium und die Alkalinität dem Reaktionsmedium durch Zugabe von rückgeführtem festem Natriumcarbonat aus Stufe (g) zugeführt werden,

(b) Abtrennung der Natriumsulfit- und Natriumsulfatkristalle aus dem Reaktionsmedium,

(c) Reduktion der abgetrennten Natriumsulfit- und Natriumsulfatkristalle zu festem Natriumsulfid,

(d) Bildung eines innigen Gemischs, das im wesentlichen aus dem besagten festen Natriumsulfid und dem abgetrennten festen Natriumcarbonat aus Stufe (i) besteht,

(e) Erhitzung des Gemischs unter weitgehendem Luftausschluss auf eine genügend hohe Temperatur, um alles in diesem Gemisch vor-

händige Wasser zu entfernen und das Natriumbicarbonat mit dem Natriumsulfid im Gemisch unter Bildung von gasförmigem Schwefelwasserstoff und trockenem, festem, wasserfreiem Natriumcarbonat umzusetzen,

(f) Gewinnung des gasförmigen Schwefelwasserstoffs,

(g) mindestens teilweise Rückführung des in Stufe (e) gebildeten Natriumcarbonats in Stufe (a),

(h) Zugabe des Rests des in Stufe (e) gebildeten Natriumcarbonats zu einer gesättigten Natriumbicarbonatlösung und Carbonisierung mit Kohlendioxyd, um eine aus festen, in dieser Lösung dispergierten Natriumbicarbonatteilchen zusammengesetzte Aufschlammung zu bilden, und

(i) Abtrennung der Natriumbicarbonatteilchen von der in Stufe (h) gebildeten Aufschlammung und Rückführung der besagten abgetrennten festen Natriumbicarbonatteilchen in Stufe (d).

2. Verfahren nach Anspruch 1, bei dem eine erhebliche Menge unlösliches Festteilchenmaterial in den abgetrennten Kristallen aus Stufe (b) vorliegt, worin vor der Reduktionsstufe (c) diese abgetrennten Kristalle aus Stufe (b) mit Wasser in Berührung gebracht werden, um die Natriumsulfit- und Natriumsulfatkristalle unter Bildung einer Lösung aus Natriumsulfit und Natriumsulfat aufzulösen, die Lösung vom restlichen Festteilchenmaterial abgetrennt und die abgetrennte Lösung dann zur Gewinnung von Natriumsulfit- und Natriumsulfatkristallen eingedampft wird.

3. Verfahren nach Anspruch 1 oder 2, bei dem das besagte Reaktionsmedium eine Aufschlammung ist, deren feste Phase im wesentlichen aus Natriumsulfit- und Natriumsulfatkristallen besteht.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, dass das Absorptionsvermögen der Aufschlammung für Schwefeldioxyd durch Zugabe von festem, trockenem Natriumcarbonat aufrechterhalten wird, wobei die Menge festes, der Aufschlammung zugesetztes Natriumcarbonat im wesentlichen der Menge fester, aus dem Reaktionsmedium abgetrennter Natriumsulfit- und Natriumsulfatkristalle äquivalent ist.

5. Verfahren nach Anspruch 3 oder 4, dadurch gekennzeichnet, dass Stufe (a) bei einer Temperatur oberhalb 35°C durchgeführt wird.

6. Verfahren nach einem der Ansprüche 3 bis 5, dadurch gekennzeichnet, dass Stufe (a) bei einem pH über 8 durchgeführt wird.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, dass man in Stufe (a) eine Ammoniakkonzentration von 0,1% bis 1% aufrechterhält.

8. Verfahren nach einem der Ansprüche 3 bis 7, dadurch gekennzeichnet, dass in Stufe (b) die Natriumsulfit- und Natriumsulfatkristalle durch Filtrieren eines Teils der Aufschlammung von Reaktionsmedium abgetrennt werden, um einen

feuchten Filterkuchen, dessen fester Anteil im wesentlichen aus Natriumsulfit- und Natriumsulfatkristallen besteht, und ein Filtrat, das in Stufe (a) zurückgeführt wird, zu erhalten.

9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, dass die Natriumsulfit- und Natriumsulfatkristalle mit einem kohlenstoffhaltigen Reduktionsmittel reduziert werden, wobei sich Natriumsulfit und ein kohlendioxydhaltiges Gas bildet.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, dass man das bei der Reduktion der Natriumsulfit- und Natriumsulfatkristalle mit einem kohlenstoffhaltigen Reduktionsmittel gebildete Kohlendioxyd als Kohlendioxydquelle in Stufe (h) verwendet.

11. Verfahren nach einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, dass Stufe (e) bei einer Temperatur im Bereich von 180°C bis 220°C durchgeführt wird.

12. Anlage zum Entfernen des in einem sauerstoffhaltigen Rauchgas enthaltenen Schwefeldioxyds, umfassend:

(a) eine Gaskontaktierungsvorrichtung (1) zum Kontaktieren dieses Rauchgases mit einem wässrig-alkalischen, Natriumcarbonat enthaltenden, mit Natriumsulfit gesättigten Reaktionsmedium, um die Hauptmenge des Schwefeldioxyds und einen Teil des Sauerstoffs mit dem Carbonatanteil unter Bildung einer Aufschlammung von im Reaktionsmedium dispergiertem Natriumsulfit und Natriumsulfat umzusetzen, und zur Zuführung des Natriums und der Alkalinität zum Reaktionsmedium durch Zugabe von rückgeführtem festem Natriumcarbonat, wobei die besagte Gaskontaktierungsvorrichtung einen oder mehrere Einlässe zur Aufnahme dieses Rauchgases bzw. dieses Reaktionsmediums und einen oder mehrere Auslässe zur Gasabgabe und zum Austrag des Natriumsulfit und Natriumsulfat enthaltenden Reaktionsprodukts aufweist,

(b) erste, zur Förderung des Reaktionsmediums zu einer ersten Trennvorrichtung (5, 9) zur Abtrennung von Natriumsulfit- und Natriumsulfatkristallen aus dem Reaktionsmedium vorgesehene Fördermittel (4),

(c) zweite zur Förderung der abgetrennten Natriumsulfit- und Natriumsulfatkristalle vom Auslass der besagten ersten Trennvorrichtung (5, 9) zum Einlass einer Reduktionsvorrichtung (19) zur Reduktion des Natriumsulfits und Natriumsulfats zu Natriumsulfid vorgesehene Fördermittel (18),

(d) dritte Fördermittel zur Förderung des Natriumsulfids vom Auslass der besagten Reduktionsvorrichtung (19) zum Einlass einer Mischvorrichtung (24) zwecks Bildung eines in-nigen Gemischs des besagten festen Natriumsulfids mit festem Natriumcarbonat,

(e) vierte Fördermittel (25) zur Förderung des besagten Gemischs vom Auslass dieser Mischvorrichtung (24) zum Einlass einer zum Erhitzen dieses Gemischs unter weitgehendem Luftausschluss auf eine Temperatur, bei der sich

Natriumbicarbonat in Natriumcarbonat und Kohlendioxyd umwandeln würde, unter Bildung von gasförmigem Schwefelwasserstoff und trockenem, festem, wasserfreiem Natriumcarbonat vorgesehenen Erhitzungsvorrichtung (26),

(f) fünfte Fördermittel (27) zur Förderung gasförmigen Schwefelwasserstoffs vom Auslass der Erhitzungsvorrichtung (26) zum Einlass einer Aufbereitungsvorrichtung zur Rückgewinnung dieses gasförmigen Schwefelwasserstoffs,

(g) sechste Fördermittel (29, 31, 33, 54) zur Förderung des besagten Natriumcarbonatanteils vom Auslass dieser Erhitzungsvorrichtung (26) zum Einlass einer für die Zugabe eines Anteils des in dieser Erhitzungsvorrichtung (26) gebildeten Natriumcarbonats zu einer gesättigten Natriumbicarbonatlösung und deren Carbonisierung mit Kohlendioxyd unter Bildung einer aus festen, in dieser Lösung dispergierten Natriumbicarbonatteilchen zusammengesetzten Aufschlammung vorgesehenen Zuführvorrichtung (30, 40),

(h) siebente Fördermittel (43) zur Förderung der Aufschlammung vom Auslass dieser Zuführvorrichtung (30, 40) zum Einlass einer zweiten Trennvorrichtung (42, 45) zur Abtrennung der Natriumbicarbonatteilchen von der in dieser Zuführvorrichtung (30, 40) gebildeten Aufschlammung und (i) achte Fördermittel (47) zur Förderung der abgetrennten Teilchen vom Auslass der besagten zweiten Trennvorrichtung (42, 45) zum Einlass jener Mischvorrichtung (24).

Revendications

1. Procédé à régénération pour éliminer et récupérer ultérieurement sous forme de sulfure d'hydrogène, la majeure partie du dioxyde de soufre contenu dans un gaz de carneau contenant de l'oxygène, qui comprend les stades:

(a) de mettre ce gaz de carneau en contact avec un milieu de réaction aqueux alcalin contenant du carbonate de sodium et sensiblement saturé en sulfite de sodium de manière à faire réagir la majeure partie du dioxyde de soufre et une fraction de l'oxygène avec le carbonate pour former une suspension de sulfite de sodium et de sulfate de sodium en dispersion dans le milieu de réaction, le sodium et l'alcalinité étant apportés au milieu de réaction par addition de carbonate de sodium solide recyclé du stade (g);

(b) de séparer les cristaux de sulfite de sodium et de sulfate de sodium de milieu de réaction;

(c) de réduire les cristaux de sulfite de sodium et de sulfate de sodium séparés en sulfure de sodium solide;

(d) de former un mélange intime consistant essentiellement en ce sulfure de sodium solide

et en le bicarbonate de sodium solide séparé au stade (i);

(e) de chauffer le mélange en l'absence sensible d'air jusqu'à une température suffisante pour chasser l'eau éventuellement en présence dans le mélange et faire réagir le bicarbonate de sodium avec le sulfure de sodium de mélange afin de former du sulfure d'hydrogène gazeux et du carbonate de sodium anhydre, solide, sec;

(f) de recueillir le sulfure d'hydrogène gazeux;

(g) de recycler au stade (a) au moins une partie du carbonate de sodium solide formé au stade (e);

(h) d'ajouter le reste du carbonate de sodium formé au stade (e) à une solution saturée de bicarbonate de sodium et à la carbonater au moyen de dioxyde de carbone pour former une suspension de particules solides de bicarbonate de sodium en dispersion dans la solution, et

(i) de séparer les particules de bicarbonate de sodium de la suspension formée au stade (h) et de recycler au stade (d) ces particules de bicarbonate de sodium solide séparées.

2. Procédé suivant la revendication 1, dans lequel une quantité sensible de matière particulaire solide insoluble est présente dans les cristaux séparés du stade (b) où, avant le stade de réduction (c), ces cristaux séparés du stade (b) sont mis en contact avec de l'eau pour dissoudre les cristaux de sulfite de sodium et de sulfate de sodium et former une solution de sulfite de sodium et de sulfate de sodium, la solution est séparée de la matière particulaire solide restante et la solution séparée est alors évaporée pour la collecte des cristaux de sulfite de sodium et de sulfate de sodium.

3. Procédé suivant la revendication 1 ou 2, dans lequel le milieu de réaction est une suspension dont la phase solide est formée sensiblement de cristaux de sulfite de sodium et de sulfate de sodium.

4. Procédé suivant la revendication 3, caractérisé en ce que la capacité d'absorption de la suspension pour le dioxyde de soufre est maintenue par addition de carbonate de sodium solide sec, la quantité de carbonate de sodium ajoutée à la suspension étant sensiblement équivalente à la quantité de cristaux de sulfite de sodium et de sulfate de sodium solides séparée de milieu de réaction.

5. Procédé suivant la revendication 3 ou 4, caractérisé en ce que le stade (a) est exécuté à une température supérieure à 35°C.

6. Procédé suivant l'une quelconque des revendications 3 à 5, caractérisé en ce que le stade (a) est exécuté à un pH supérieur à 8.

7. Procédé suivant la revendication 6, caractérisé en ce que de l'ammoniac est maintenu au stade (a) en une concentration de 0,1 à 1%.

8. Procédé suivant l'une quelconque des revendications 3 à 7, caractérisé en ce qu'au stade (b), les cristaux de sulfite de sodium et de sulfate de sodium sont séparés du milieu de

réaction par filtration d'une fraction de la suspension pour donner un gâteau de filtration humide dont la fraction solide est formée sensiblement de cristaux de sulfite de sodium et de sulfate de sodium, outre un filtrat qui est renvoyé au stade (a).

9. Procédé suivant l'une quelconque des revendications 1 à 8, caractérisé en ce que les cristaux de sulfite de sodium et de sulfate de sodium sont réduits à l'aide d'un réducteur contenant du carbone pour donner du sulfure de sodium et un gaz contenant du dioxyde de carbone.

10. Procédé suivant la revendication 9, caractérisé en ce que le dioxyde de carbone formé lors de la réduction des cristaux de sulfite de sodium et de sulfate de sodium par un réducteur contenant du carbone est utilisé comme source de dioxyde de carbone au stade (h).

11. Procédé suivant l'une quelconque des revendications 1 à 10, caractérisé en ce que le stade (f) est exécuté à une température dans l'intervalle de 180°C à 220°C.

12. Système pour séparer le dioxyde de soufre contenu dans un gaz de carneau contenant de l'oxygène, qui comprend:

(a) un dispositif de mise en contact de gaz (1) pour mettre ce gaz de carneau en contact avec un milieu de réaction aqueux alcalin contenant du carbonate de sodium et saturé en sulfite de sodium pour faire réagir la majeure partie du dioxyde de soufre et une fraction de l'oxygène avec le carbonate et former une suspension de sulfite de sodium et de sulfate de sodium en dispersion dans le milieu de réaction, du même que pour apporter le sodium l'alcalinité au milieu de réaction par addition de carbonate de sodium solide recyclé, lequel dispositif de mise en contact de gaz comporte une ou des admissions pour recevoir le gaz de carneau et recevoir le milieu de réaction et une ou des sorties pour évacuer le gaz et évacuer le produit de réaction contenant du sulfite de sodium et du sulfate de sodium;

(b) un premier dispositif transporteur (4) agencé pour transporter le milieu de réaction à un premier dispositif séparateur (5, 9) pour séparer les cristaux de sulfite de sodium et de sulfate de sodium de milieu de réaction;

(c) un second dispositif transporteur (18)

agencé pour transporter les cristaux de sulfite de sodium et de sulfate de sodium séparés depuis la sortie du premier dispositif séparateur (5, 9) jusqu'à l'entrée d'un dispositif de réduction (19) pour réduire le sulfite de sodium et le sulfate de sodium en sulfure de sodium;

(d) un troisième dispositif transporteur pour transporter le sulfure de sodium de la sortie du dispositif de réduction (19) à l'entrée d'un dispositif mélangeur (24) pour former un mélange intime de ce sulfure de sodium solide avec du bicarbonate de sodium solide;

(e) un quatrième dispositif transporteur (25) pour transporter le mélange depuis la sortie du dispositif mélangeur (24) jusqu'à l'entrée d'un dispositif de chauffage (26) agencé pour chauffer ce mélange en l'absence sensible d'air jusqu'à une température à laquelle le bicarbonate de sodium serait converti en carbonate de sodium et dioxyde de carbone pour former du sulfure d'hydrogène gazeux et du carbonate de sodium anhydre, solide, sec.

(f) un cinquième dispositif transporteur (27) pour transporter le sulfure d'hydrogène gazeux de la sortie du dispositif de chauffage (26) jusqu'à l'entrée d'un dispositif collecteur pour collecter ce sulfure d'hydrogène gazeux;

(g) un sixième dispositif transporteur (29, 31, 33, 54) pour transporter la fraction de carbonate de sodium depuis la sortie du dispositif de chauffage (26) jusqu'à l'entrée d'un dispositif d'alimentation (30, 40) agencé pour admettre une fraction du carbonate de sodium formé dans le dispositif de chauffage (26) dans une solution saturée de bicarbonate de sodium et pour carbonater celle-ci au moyen de dioxyde de carbone et former une suspension composée de particules solides de bicarbonate de sodium en dispersion dans la solution;

(h) un septième dispositif transporteur (43) pour transporter la dispersion depuis la sortie du dispositif d'alimentation (30, 40) jusqu'à l'entrée d'un second dispositif séparateur (42, 44) pour séparer les particules de bicarbonate de sodium de la suspension formée dans le dispositif d'alimentation (30, 40), et

(i) un huitième dispositif transporteur (47) pour transporter les particules séparées depuis la sortie du second dispositif séparateur (47, 45) jusqu'à l'entrée du dispositif mélangeur (24).

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