ABSTRACT OF THE DISCLOSURE

A process for converting sodium sulfide in the smelt resulted from the burning of black liquor from digesters of semichemical pulp and sulfite pulp to sodium sulfite by oxidation and recovering the latter as pulp digesting chemical, which comprises mixing the spent material with water, adding thereto a minor amount of sodium hydroxide forming the mixture into particles and introducing the particles into a converter packed with dry powder of sodium sulfite, sodium carbonate, etc., containing no sodium sulfide, the process being performed throughout as a wet process.

BACKGROUND OF THE INVENTION

Field of the invention

The invention concerns the conversion of sodium sulfide contained in the ash content of burnt black liquor side-produced of pulp digestion to sodium sulfite by oxidation, and recovery of the converted product for reuse as pulp digesting chemical, the conversion and recovery being performed throughout as a wet process.

The invention is applicable to recovery of the chemical employed in semichemical pulp process using neutral sodium sulfite and sulfite pulp process using acidic sodium sulfite among the various preparation methods of pulp.

Description of the prior art

Disposal of black liquor from digesters in paper and pulp industry has been heretofore considered as a very difficult problem. As well known, in kraft pulp process the spent cooking liquor from the pulp digesters is concentrated, burned and discharged as carbon dioxide gas and steam. The sodium salts contained in the black liquor flows out in molten state during the burning, and it has been proven that the sodium salts can be profitably converted to pulp-digesting chemicals through suitable chemical reaction. However, as to aforesaid semichemical pulp and sulfite pulp process, satisfactory means for the chemical recovery is not yet established. Although the black liquor formed of these processes can be burned, it is commercially unpracticable.

The ash content of the black liquor side-produced of pulp digesting, i.e., smelt, is normally composed of sodium sulfide (Na2S), sodium thiosulfate (Na2S2O3), sodium sulfite (Na2SO3), sodium sulfate (Na2SO4), sodium carbonate (Na2CO3), and a minor amount of insoluble matter, Na2CO3 content being approximately 60% by weight, and that of Na2S being more than 20% by weight. When the black liquor from sodium-based semichemical pulp and sulfite pulp process etc. is concentrated and burned, the sodium salts in the black liquor form a solid solution of sodium carbonate (Na2CO3) and sodium sulfide (Na2S), which flows out from the furnace bottom in molten state.

It is known of old that sodium sulfide (Na2S) is converted to sodium sulfite (Na2SO3) when directly oxidized with air or oxygen, and to sodium sulfate (Na2SO4) if oxidized under severer conditions, through the following chemical reactions:

\[ \text{Na}_2\text{S} + 3/2\text{O}_2 = \text{Na}_2\text{SO}_3 \] (1)

\[ \text{Na}_2\text{S} + 2\text{O}_3 = \text{Na}_2\text{SO}_4 \] (2)

However, no report on the successful preparation of sodium sulfite (Na2SO3) by direct oxidation of sodium sulfide (Na2S) on an industrial scale is made to date.

Because, while it is known that the above reaction (1) takes place at temperatures above 100° C. and the reaction (2), at above 300° C., the reactions being accelerated by the use of air containing steam, the reaction (1) is exothermic, and causes abrupt temperature rise in the reaction system to induce the reaction (2), forming sodium sulfate (Na2SO4) which is useless as a pulp digesting chemical. This is quite unavoidable since 1 kg. of sodium sulfide (Na2S) generates the heat of as much as 2,200 kilocalories through the reaction (1). It is also known that sodium sulfide (Na2S) forms sodium thiosulfate (Na2S2O3) in humid air, at temperatures below 100° C., while presence of large amount of sodium thiosulfate (Na2S2O3) is detrimental to the pulp properties. The sodium thiosulfate-making reaction can be expressed as follows:

\[ \text{Na}_2\text{S} + \text{H}_2\text{O} = \text{NaHS} + \text{NaOH} \] (3)

\[ 2\text{NaHS} + \text{O}_3 = \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \] (4)

Besides the foregoing, there is also the problem of residual sodium sulfide (Na2S), and as a whole it is extremely difficult to convert sodium sulfide (Na2S) to sodium sulfite (Na2SO3) by direct oxidation with air.

This invention successfully solved those problems inherent in the direct oxidation which is one of the recovery means of pulp-digesting chemicals from smelt obtained by concentrating and burning the semi-chemical pulp and sulfite pulp originated black liquor, in which the above reactions (2), (3), and (4) are effectively inhibited, whereby enabling recovery of high purity pulp-digesting chemicals at high yields throughout by wet process, concurrently effecting prevention of public nuisance.

SUMMARY OF THE INVENTION

According to the invention during the recovery of burnt smelt in semichemical pulp and sulfite pulp process, sodium sulfide (Na2S) is very efficiently converted to sodium sulfite (Na2SO3) while preventing formation of sodium thiosulfate. This is accomplished by the following process.

The smelt flowing from the furnace bottom upon burning of black liquor from pulp digesters is dropped into saturated solution of the smelt to be instantaneously cooled and solidified. It is a preferred practice to subject the flowing smelt to a steam or water jet on the quenching solution surface so as to convert it into fine particles immediately before dropping into the solution, similarly to the known practice in kraft pulp process. This has the same effect as of grinding. The subject method however is different from kraft pulp process in that the solution in the smelt-receiving tank has the composition quite close to the saturated solution of smelt. Therefore, the solid
of the quenched smelt in the receiving tank are not dissolved, but precipitate or float in the receiving tank. The particles are separated from the solution by filtration or settling. If sodium hydroxide is added to the slurry without the particle sizes, pulverized with a wet-type grinder. The ash particles, i.e., solidified smelt, are formed into a slurry as mixed with water at suitable ratio. The optimum slurry concentration differs depending on sodium sulfide (Na₂S) content of the smelt, but generally that of not lower than 50% is preferred. In order to improve the fluidity of the slurry, it may be heated at suitable places with steam or other suitable means, so as to maintain a temperature not lower than 80°C. Then the slurry is sent to the direct oxidation zone. The construction of direct oxidation zone is variable, the matter of prime importance being that the zone must be capable of thoroughly mixing finely divided hydrous particles to allow their sufficient contact with air.

That is, a converter capable of such perfect mixing of the wet particles is packed with finely divided particles containing no sodium sulfide (Na₂S) in advance, and maintains the temperature of approximately 110°C to 120°C, and into which aforesaid wet ash particles are fed at a slow rate. Thus fed wet ash particles are first dried, and then oxidized. Although the oxidation reaction is exothermic, since the heat is used for evaporating the water content in the subsequently fed ash particles, objectionable temperature rise in the converter does not take place. Thus the temperature within the converter can be optionally controlled by regulating the quantities of sodium sulfide (Na₂S) content and water content of the slurry being fed. The optimum ratio between the ash and water for suitable temperature control in the converter is, if sodium sulfide (Na₂S) content of the dry ash is 25%, 1 kg. of ash per 1 kg. of water. In practice, however, it is the easiest way of temperature control to supply more than 1 kg. of ash per 1 kg. of water and if the temperature in the converter rose above the predetermined level, to feed water into the converter, since sodium sulfide (Na₂S) content of the ash varies incessantly.

Thus the evaporation of water content from the ash particles supplied into the converter and subsequent oxidation are repeated while the temperature of direct oxidation zone is maintained constant. Also since the air contacting with the ash particles contains the steam formed by the evaporation of water content in the particles, formation of sodium sulfite is remarkably accelerated.

Conventionally, direct oxidation of smelt is performed by the steps of collecting the smelt by dry system, solidifying the same by cooling, following dissolving the comminuted solid with mixture of air and steam. In such a method the dry solidifier often causes troubles, and during the grinding noxious dust scatters about to make the operation hazardous. Furthermore, throughout the procedures of grinding, transfer, and direct oxidation, there is always the danger of dust explosion. The conventional process is again subject to the serious defect that due to the difficulties for controlling direct oxidation temperature, the product comes to contain objectionably large amounts of impurities such as unreacted Na₂S (residual sodium sulfide), sodium thiosulfate (Na₂S₂O₃), and sodium sulfate (Na₂SO₄), etc. Whereas, in accordance with the present invention, the dry solidifier which is apt to cause troubles is dispensed with, and because wet system is employed, scattering about of dust never takes place. Obviously, there is neither a danger of any dust explosion. Also because the temperature can be easily and accurately controlled, the product contains little impurities. There is no need of mixing steam with air as the oxidizing agent, as an extra step.

In the process of this invention, however, still a very minor amount of sodium thiosulfate (Na₂S₂O₃) is formed, and the products value as a digesting chemical may be somewhat reduced for the pulp-making where the presence of sodium thiosulfate is strictly prohibited. Therefore, still another unique step is incorporated in the invention to overcome this objection. That is, a minor amount of NaOH is fed into the converter, if the concentration of the slurry formed by mixing the ash particles separated from the receiving tank with water, before the slurry is reacted in the converter. Normally desirable amount of NaOH ranges from 2 to 20% by weight of dry, solid particles. The ash particles as separated from the receiving tank are naturally containing water, and consequently are undergoing the aforesaid reaction (3), whereas, since the ash particles concurrently contain considerable amount of sodium carbonate (Na₂CO₃), the amount of sodium hydrosulfide (NaHS) formed of the reaction (3) is at most several percents of that of sodium sulfide (Na₂S), as can be understood from the concept of chemical equilibrium. When sodium hydroxide (NaOH) is added to the ash particles containing water, the reaction (3) is inhibited following the law of mass action, and the amount of sodium hydrosulfide (NaHS) is further reduced, consequently minimizing the formation of sodium thiosulfate (Na₂S₂O₃) through the reaction (4).

**BRIEF DESCRIPTION OF THE DRAWING**

The drawing shows a process diagram illustrating one embodiment of the present invention.

**DESCRIPTION OF THE PREFERRED EMBODIMENT**

One preferred embodiment of the invention will be explained, referring to the attached drawing.

The drawing shows a process diagram of a pilot plant in which 10 kg./hr. of smelt flows out from the furnace bottom. Referring to the drawing, the smelt flowing from a black liquor incinerator (not shown) flew down through the spout 1 into saturated solution of the smelt in a receiving tank 2. Before dropping into water, the smelt was formed into fine particles by the steam jet 3. The smelt solidified as dropped into the solution was carried to the vibrating screen 5 by a slurry pump 4, where the particles were separated from the solution and flew down into the dish grinder 6, to be further comminuted into finer particles of less than 100 mesh in size. The filtrate was returned to the receiving tank 2. At the exit from the vibrating screen 5, approximately 8 kg./hr. of an aqueous liquid 7 for temperature control was added, which also served as a transporting medium to assist smooth flowing down of the particles into the disk grinder 6 and discharging of particles from the same grinder. This transporting medium was supplied from the solution in the receiving tank 2, and water was separately supplied to the receiving tank 2. As the converter 8, a kneader of 25 liters in capacity with two rotating blades was used in this particular example.

No special supply of air or oxygen from external source was required in this embodiment. At the initiating stage of the operation, the converter 8 was packed with approximately 25 liters of a powdery mixture of sodium carbonate (Na₂CO₃) and sodium sulfide (Na₂S₂O₃) at the ratio of 1:1, and heated to 120°C. with hot air current. Into such a converter 8 the mixture of fine particles and water from the grinder 6 was caused to flow. Once the reaction started, no further heat was supplied to the converter. The product discharged from the converter 8 was an ashen white powder. The compositions of the starting smelt and the product were as given below:

<table>
<thead>
<tr>
<th>Na₂S</th>
<th>Na₂S₂O₃</th>
<th>Na₂S₂O₅</th>
<th>Na₂S₂O₄</th>
<th>Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Smelt</th>
<th>20.0</th>
<th>0.3</th>
<th>2.0</th>
<th>3.5</th>
<th>60.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>0.5</td>
<td>3.0</td>
<td>3.0</td>
<td>4.4</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Note:** The numerical values in the above table are average of 5 runs, expressed by percent by weight.

When the foregoing operation was repeated except that 4.8% to the dry solid of sodium hydroxide 9 was added simultaneously with the temperature-controlling water 7,
the resulting composition of the product and that of the starting smelt were as follows:

<table>
<thead>
<tr>
<th></th>
<th>Na$_2$S</th>
<th>Na$_2$SO$_3$</th>
<th>Na$_2$SO$_4$</th>
<th>Na$_2$CO$_3$</th>
<th>NaOH</th>
<th>Insoluble matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelt</td>
<td>23.4</td>
<td>0.2</td>
<td>2.9</td>
<td>7.8</td>
<td>67.3</td>
<td>14.8</td>
</tr>
<tr>
<td>Product</td>
<td>0.2</td>
<td>35.6</td>
<td>6.0</td>
<td>50.2</td>
<td>4.1</td>
<td>8.1</td>
</tr>
</tbody>
</table>

1 Sign denotes that NaOH was added to the smelt.

As above-demonstrated, addition of sodium hydroxide (NaOH) is markedly effective for prevention of sodium thiosulfate (Na$_2$S$_2$O$_3$) from forming.

Incidentally, the product of the invention has higher sodium carbonate (Na$_2$CO$_3$) and sodium hydroxide (NaOH) contents and lower sodium sulfite (Na$_2$SO$_3$) content, compared with normally used digesting liquor in pulp industry. However, upon dissolving the product in water and causing the aqueous solution to absorb sulfur dioxide (SO$_2$), the liquid can serve as the perfectly good digesting or cooking liquor.

The apparatus shown in the above embodiment is no more than one suitable example, which may very well be replaced by other equally effective apparatuses. For instance, as the converter, fluidized bed, rotary kiln, or cement mixer can be used with equivalent results.

What is claimed is:

1. A process for converting the sodium sulfide contained in the smelt obtained from semi-chemical pulp and sulfite pulp processes to sodium sulfite comprising:
   1. subjecting the flowing smelt to a steam or water jet to convert the smelt into fine particles immediately before dropping into a quenching solution having a composition which is saturated with the smelt so that the solid particles are instantaneously cooled and solidified but do not dissolve in the quenching solution but wherein they float on top of the quenching solution or precipitate from the quenching solution from which they are subsequently separated,
   2. forming a slurry of the separated solid fine smelt particles into a concentrated slurry of at least 50%;
   3. passing the slurry at a slow rate into a reactor vessel packed with finely divided particles of sodium carbonate and sodium sulfite but containing no sodium sulfide, and which reactor vessel is maintained above 100° C. and below 300° C.,
   4. contacting the smelt particles in the reactor vessel with air, whereby the reaction occurring which is exothermic evaporates the water content of the slurry, and oxidizes the sodium sulfide in the smelt to sodium sulfite, and whereby the temperature in the reactor vessel is maintained and controlled to a temperature below 300° C.,
   5. removing and recovering the sodium sulfite from said reactor vessel.

2. A process according to claim 1 wherein any smelt particles which are still of an excessively large particle size after they are separated from the quenching solution are pulverized with a wet type grinder.

3. The process of claim 1, in which no air or oxygen is supplied into the converter from any external source, but the air present in the converter is used as the source of oxygen.

4. The process of claim 1, in which the oxidation reaction is performed at the temperatures ranging from 110 to 120° C.

5. The process of claim 1, in which the liquid separated from the particles in step (2) is returned to the quenching solution.

6. The process of claim 1, in which about 1 to 20 percent by weight sodium hydroxide based on the weight of the dry solids of the slurry is added to the slurry to minimize the formation of sodium thiosulfate.

7. The process of claim 1, wherein the slurry is ground before it reaches the reactor so that the solids in the slurry are in particulate form.

8. The process of claim 1, wherein the slurry is ground before it reaches the reactor so that the solids in the slurry are in particulate form.

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