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Process for the removal of sulfur dioxide from waste gas.

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MAREE et al.: "Biological sulphate removal in an upflow packed bed reactor"

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Description

The invention relates to a process for the removal of sulfur dioxide from waste gas.
Gaseous effluents from oil-fired or coal-fired power stations and waste incinerators contain various
amounts of sulfur dioxide (SO\textsubscript{2}) which are detrimental to man and the environment (acid rain).

Existing processes for the desulfurization of waste gases can be divided into wet processes, spray-dry
processes and dry processes.

In wet processes, the waste gases are contacted with an aqueous solution or suspension wherein the
sulfur dioxide is dissolved. In order to sufficiently bind the sulfur dioxide in the aqueous solution, the
solution must be alkaline. Known processes use limestone, alkali or ammonia as the source of alkalinity.

Desulfurization of waste gases has often been effected by washing the sulfur dioxide from the gases
using lime. This results in large amounts of gypsum, the utilization of which is becoming increasingly
difficult since the quality requirements of gypsum become more stringent. In a process using ammonia
(often referred to as ammonium sulfate process), sulfur dioxide is washed from the waste gas with an
ammonia solution which eventually leads to the production of ammonium sulfate which may be used as a
chemical fertilizer.

In a spray-dry process, a finely divided lime suspension is blown into an absorber, wherein the sulfur
dioxide reacts with the lime to form a mixture of calcium sulfite and sulfate. The amount of water used is
sufficiently low to avoid the production of waste water. However, the problem of disposing the mixture of
calcium sulfite / calcium sulfate / fly ash has not been solved. Dry processes have not been used in
practice, largely because of the very high costs. Such processes produce a concentrated gaseous flow of
sulfur dioxide.

An important alternative process for the processes mentioned above is the reduction of the sulfur
dioxide by biological processes. Biological reactors have advantages in that they use a relatively simple
technology under moderate pressure and temperature conditions - see for example EP-A-0 326 457.

Summary of the invention

It is an object of the present invention to provide a process for the removal of sulfur dioxide from waste
gases by biological methods.

A further object of the invention is to provide a process for the removal of sulfur dioxide from waste
gases, wherein the sulfur dioxide is converted into a sulfur species that can be easily separated and re-
used.

A further object of the invention is to provide a process for the removal of sulfur dioxide from waste gas
having low energy requirements.

Another object of the invention is to provide a process for the removal of sulfite from waste water
wherein the sulfite is converted into a sulfur species that can be separated and re-used.

These and other objects are achieved by a process for the removal of sulfur dioxide from waste gas,
comprising the steps of:

a) contacting the waste gas with a basic aqueous solution wherein sulfur dioxide is dissolved as sulfite;
b) subjecting the aqueous solution containing sulfite to sulfur reducing bacteria in an anaerobic reactor
wherein sulfite is reduced to sulfide;
c) subjecting the aqueous solutions containing sulfide to sulfur oxidizing bacteria in the presence of a
limiting amount of oxygen in a reactor wherein sulfide is oxidized to elemental sulfur;
d) separating the elemental sulfur from the aqueous solution; and
e) recycling the aqueous solution to step a).

When the sulfur dioxide is present in an aqueous effluent rather than a gaseous effluent, the process
comprises the steps of:

a) optionally adjusting the concentration and the pH in the waste water to obtain an aqueous solution
containing sulfite;
b) subjecting the aqueous solution containing sulfite to sulfur reducing bacteria in an anaerobic reactor
wherein sulfite is reduced to sulfide;
c) subjecting the aqueous solution containing sulfide to sulfur oxidizing bacteria in the presence of a
limiting amount of oxygen in a reactor wherein sulfide is oxidized to elemental sulfur; and
d) separating the elemental sulfur from the aqueous solution.

In the present specification and claims, "sulfite" is to be understood as to comprise any oxygen
compound of tetravalent sulfur, such as sulfite (SO\textsubscript{3}\textsuperscript{2-}), bisulfite (HSO\textsubscript{3}\textsuperscript{-}), metabisulfite (S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}), dissolved
sulfur dioxide (SO\textsubscript{2}), sulfurous acid (H\textsubscript{2}SO\textsubscript{3}) etc.
A "solution containing sulfite" may additionally contain minor amounts of other sulfur components, such as sulfate, thiosulfate etc.

A "waste gas containing sulfur dioxide" is understood to contain sulfur dioxide as the main sulfur pollutant; minor amounts of other sulfur components, such as sulfur trioxide, may also be present and are removed equally well by the process of the present invention.

For the purpose of the present invention, sulfide is understood to comprise all inorganic or non-ionic species of divalent sulfur such as sulfide (S^{2-}), hydrosulfide (HS^{-}), hydrogen sulfide (H_{2}S) and the corresponding polysulfide species. An electron donor is necessary for the biological reduction of sulfur dioxide to sulfide. Suitable electron donors include hydrogen, carbon monoxide, organic substances and mixtures thereof. Examples of organic substances are alcohols, fatty acids, esters, sugars, starches, organic waste, etc. Such electron donors are largely converted into acetate upon anaerobic treatment by sulfur reducing bacteria.

The reaction steps occurring in the process according to the invention can be represented in a simplified manner by the following equation, wherein carbon monoxide and hydrogen are used as electron donors:

\[
\begin{align*}
SO_{2} + H_{2}O & \rightarrow H_{2}SO_{3} \quad \text{(gas scrubber)} \\
H_{2}SO_{3} + 3 CO & \rightarrow H_{2}S + 3 CO_{2} \quad \text{(anaerobic reactor)} \\
H_{2}SO_{3} + 3 H_{2} & \rightarrow H_{2}S + 3 H_{2}O \quad \text{(anaerobic reactor)} \\
H_{2}S + 1/2 O_{2} & \rightarrow S + H_{2}O \quad \text{(sulfide reactor)}
\end{align*}
\]

Suitable bacteria for use in the anaerobic reactor to reduce sulfite to sulfide include especially sulfur reducing bacteria, such as species of the genera Desulfovibrio, Desulfitomaculum, Desulfomonas, Desulfofobus, Desulfobacter, Desulfoooccus, Desulfoneua, Desulfobacterium and Desulfomonas. In general, these bacteria are available from various anaerobic cultures and/or grow spontaneously in the anaerobic reactors.

Suitable bacteria for use in the sulfide oxidizing reactor include colorless sulfur bacteria, for example of the genera Thiobacillus, Thiomicrospora, Sulfolobus and Thermothrix.

In order to achieve a partial oxidation in the sulfide oxidizing reactor to essentially produce elemental sulfur rather than higher oxidized sulfur species such as sulfate, the amount of oxygen that is introduced in the sulfide reactor is limited and/or the retention time of the aqueous solution containing sulfide in the sulfide reactor is kept sufficiently short. The amount of oxygen is preferably limited by adding oxygen in an amount of 0.5 to 1.5 moles of oxygen per mole of sulfide. The oxygen supply can be controlled e.g. by controlling the oxygen concentration in the reactor with reference to the sulfide concentration. As an alternative, the oxygen supply can be controlled in relation to the redox potential of the aqueous solution in the reactor or in the reactor effluent. The hydraulic retention time can e.g. be selected as 20 minutes or less. The pH in the sulfide oxidizing reactor is not critical. It may be from slightly basic to neutral to acidic. Preferably, the pH does not exceed about 9. The sulfur oxidizing bacteria may be present as such, or they may be immobilized, for example on a polymeric support. The partial oxidation of sulfide can be carried out for example using the process according to NL-A-8801009.

The elemental sulfur that is produced in the sulfur oxidizing reactor can be separated from the aqueous solution by filtration, centrifugation, flocculation, settling, etc. After separation, the sulfur may be further purified and/or re-used.

The process of the invention is advantageous in that it produces reusable sulfur, and does not require complicated and/or expensive technology. Furthermore it results in considerably reduced costs for waste gas desulfurization.

Another advantage is that fly ash is removed from the waste gas as well and can be separated as a solid, together with the elemental sulfur, or in a separate step. Furthermore, any heavy metals that may be present in the gaseous or aqueous waste flow precipitate as metal sulfite in the anaerobic reactor and are not discharged into the environment.

The essential steps of the present invention, i.e. microbiological reduction of sulfite in an aqueous solution to produce sulfide and partial microbiological oxidation to produce sulfur, may also be used according to the invention in a process for the removal of sulfite from waste water. In case such waste water also contains organic waste, the addition of an electron donor or other nutrients may not be necessary.

The process of the invention is further illustrated with reference to the accompanying figure.

According to the figure, waste gas contaminated with sulfur dioxide is introduced at 1 into a gas scrubber 2. In the gas scrubber, the waste gas is treated in counter-current with a washing liquid that is introduced from 3. The treated waste gas is discharged through 4 or may be purified further. The washing
liquid that has absorbed the sulfite is conducted through 5 and fed to an anaerobic reactor tank 6. An
electron donor such as ethanol, and optional other components such as nutrient elements, buffering agents,
etc. are introduced at 7 into the anaerobic reactor 6. Gases that are produced in the anaerobic reactor,
mainly CO₂ in addition to minor amounts of H₂S, are conducted from the anaerobic tank through conduct 8
to a gas treatment plant (not shown). The anaerobic effluent is conducted through 9 to an aerobic or
partially aerobic reactor 10. Air is introduced into the aerobic reactor 10 through 11 and excess air is
removed through 12. The aerobic effluent containing elemental sulfur is conducted through 13 to a settling
tank 14. The elemental sulfur and optionally other solid components are allowed to settle in tank 14 and
drained off through 15. The clarified solution leaves the separator through 16 and can be re-used as
washing liquid. If necessary, a surplus of the clarified solution is discharged through 17. Additional washing
liquid, optionally containing pH regulators and nutrient elements, can be added through 18 to the recycled
washing liquid in 3.

When used in a conventional coal-fired power plant having the production characteristics as shown in
table A, the main gaseous and aqueous flows and the content of the relevant components according to the
process of the invention are approximately as follows (the numbers refer to the figure):

1. Untreated waste gas: 1.7*10⁶ m³/h
5. Washing liquid containing sulfite (1 g S/l): 2000 m³/h
7. Ethanol: 1,500 tons/h
6. Anaerobic reactor: 21,000 m³
8. Anaerobic gas: ± 80 % CO₂, ± 20 % H₂S
9. Anaerobic effluent: ca. 800 mg S²⁻/l
10. Sulfide reactor: 4000 m³
11. Aeration: 50,000 m³/h
13. Sulfide reactor effluent: ca. 800 mg S⁰/l
14. Sulfur settling tank: 2000 settling plates, 1 m³/plate
15. Sulfur slurry: 1.6 ton S⁰/h

Estimated capital outlay for the introduction of a waste gas desulfurization system according to the
invention in a power plant as described above is about Dfl 80,000,000, compared with about Dfl.
160,000,000 for a corresponding conventional desulfurization system (Meetprogramma voor Rookgasonz-
waveling: Measuring Programm for Waste Gas Desulfurization, NOVEM, EPON, Zwolle, The Netherlands,
December 12, 1988); running costs of the system of the invention are estimated at Dfl. 20,000,000 a year,
compared with Dfl. 38,000,000 a year for a conventional system.

TABLE A.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>plant power</td>
<td>600 MW</td>
</tr>
<tr>
<td>waste gas production</td>
<td>1,668,300 Nm³/h</td>
</tr>
<tr>
<td>sulfur content of coal</td>
<td>0.7%</td>
</tr>
<tr>
<td>SO₂</td>
<td>2000 kg/h</td>
</tr>
<tr>
<td>CO₂</td>
<td>415 tons/h</td>
</tr>
</tbody>
</table>
Claims

1. A process for the removal of sulfur dioxide from waste gas, comprising the steps of:
   a) contacting the waste gas with a basic aqueous solution wherein sulfur dioxide is dissolved as sulfite;
   b) subjecting the aqueous solution containing sulfite to sulfur reducing bacteria in an anaerobic reactor wherein sulfite is reduced to sulfide; and characterised by the steps of
   c) subjecting the aqueous solution containing sulfide to sulfur oxidizing bacteria in the presence of a limiting amount of oxygen in a reactor wherein sulfide is oxidized to elemental sulfur;
   d) separating the elemental sulfur from the aqueous solution; and
   e) recycling the aqueous solution to step a).

2. The process of Claim 1, wherein an electron donor selected from the group consisting of hydrogen, carbon monoxide, organic substances and mixtures thereof, is added to the aqueous solution before step b).

3. The process of Claim 2, wherein the electron donor comprises ethanol.

Patentansprüche

1. Verfahren für die Beseitigung von Schwefeldioxid aus Abgas, bei dem
   a) das Abgas mit einer basischen wässrigen Lösung in Kontakt gebracht wird, wobei Schwefeldioxid als Sulfit gelöst wird;
   b) die Sulfit enthaltende wässrige Lösung Schwefel reduzierenden Bakterien in einem anaeroben Reaktor ausgesetzt wird, wobei Sulfit zu Sulfit reduziert wird;
   c) die Sulfit enthaltende wässrige Lösung Schwefel oxidierenden Bakterien in Gegenwart einer begrenzten Menge von Sauerstoff in einem Reaktor ausgesetzt wird, wobei Sulfit zu elementarem Schwefel oxidiert wird;
   d) der elementare Schwefel von der wässrigen Lösung abgetrennt wird; und
   e) die wässrige Lösung zu dem Verfahrensschritt a) zurückgeleitet wird.

2. Verfahren nach Anspruch 1, bei dem der wässrigen Lösung vor dem Verfahrensschritt b) ein Elektronendonator zugefügt wird, der aus der aus Wasserstoff, Kohlenmonoxid, organischen Substanzen und Gemischen derselben bestehenden Gruppe ausgewählt wird.


Revendications

1. Procédé destiné à éliminer le dioxyde de soufre d’un gaz d’échappement, comprenant les étapes de :
   a) mise en contact du gaz d’échappement avec une solution aqueuse basique dans laquelle est dissous le dioxyde de soufre sous forme de sulfite;
   b) soumission de la solution aqueuse contenant le sulfite à des bactéries réduisant le soufre dans un réacteur anaérobie dans lequel le sulfite est réduit en sulfure; et caractérisé par les étapes de :
   c) soumission de la solution aqueuse contenant le sulfure à des bactéries oxydant le soufre en présence d’une quantité limitante d’oxygène dans un réacteur dans lequel le sulfure est oxydé en soufre élémentaire;
   d) séparation du soufre élémentaire de la solution aqueuse; et
   e) recyclage de la solution aqueuse vers l’étape a).

2. Procédé selon la revendication 1, dans lequel un donneur d’électron(s) choisi dans le groupe consistant en hydrogène, monoxyde de carbone, substances organiques et mélanges de ceux-ci, est ajouté à la solution aqueuse avant l’étape b).

3. Procédé selon la revendication 2, dans lequel le donneur d’électron(s) comprend l’éthanol.