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**Process for the chemical-biological desulphurization of coal.**

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## Description

This invention relates to a process for the chemical-biological desulphurization of coal. More particularly, this invention relates to a novel process for reducing the sulfur amount contained in coal, in which process the desulphurizing treatment is carried out exclusively in a chemical way, whereas the regeneration of the leaching solution employed is obtained through a microbiological treatment.

Generally, coal contains a more or less substantial sulfur amount, which represents an undesirable impurity, mainly because of its effect on atmospheric pollution. During combustion of coal, sulfur gives rise to sulfur dioxide and trioxide, which products are considered as two of the most remarkable polluting agents of the atmosphere. These two compounds, in addition to other effects, give rise to the phenomenon of acid rains.

Sulfur can be present in coal both in the form of pyrite ( $\text{FeS}_2$ ) and in the forms of organic sulfur and sulfates. This last form is generally the lowest part of the total sulfur present, whereas the highest part (40-60%) consists of pyrite sulfur.

Sulfur present as organic sulfur is intimately linked to the molecular structure of coal in organic compounds like mercaptans, thiophenes, and so on; as a consequence, its removal is quite difficult and involves the partial destruction of the molecular structure of coal.

On the contrary, pyrite sulfur is present as subdivided into very fine particles dispersed throughout the organic matrix and its removal is easier as a matter of principle.

Many processes are known at present for removing pyrite sulfur from coal, such processes being classifiable into physical, chemical or biological processes.

The exclusively physical processes exploit the fact that pyrite is present in coal as a distinct phase, and they only are efficient as regards pyrite particles of larger sizes, whereas they cannot remove the finest particles, which are a great majority.

In exclusively chemical processes, coal is treated with chemical agents, such as acid or alkaline solutions, that are capable of reacting with sulfur, so giving rise to the formation of soluble compounds. The main problem with such processes consists in that the regeneration of the reacting solution asks for complex and costly chemical treatments.

For instance, in the Meyers process the reactant is made up of water solutions of ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) and ferrous sulfate ( $\text{FeSO}_4$ ), the first of them oxidizing pyrite sulfur so as to reduce itself in turn to give the second one. The exhausted leaching solution is to be regenerated by air oxidation under pressure and at high temperature.

In exclusively biological processes, finely divided coal is mixed with ferric sulfate and ferrous sulfate solutions containing microorganisms of the genus *Thiobacillus*. Such bacteria are known as microorganisms which obtain their energy from sulfur oxidative reactions, so that they have been employed and suggested more than once in processes of interest in the mining field. More particularly, *Thiobacillus ferrooxidans* catalyzes also the oxidation of iron compounds.

Accordingly, biological desulphurization seems to occur both through direct action of microorganisms which adhere to coal particles, so catalysing the oxidation of pyrite, and/or through indirect action, as the microorganisms catalyze the oxidation of ferrous sulfate to ferric sulfate, which in turn oxidizes the pyrite contained in coal.

The main drawback of such kind of processes is due to the fact that the temperature cannot be above  $30^\circ\text{C}$  in order to allow bacteria to live, so that the reaction rate is very slow: coal is to be kept in large basins for a time of the order of 20 days.

A further drawback of biological processes is due to the fact that the microorganisms employed do not stand a pH value much lower than 2, so that they require not too acid an environment during reaction; this condition might cause oxidized iron complex compounds to precipitate, such compounds hindering the reaction course and giving rise to plugging problems in the plant.

Accordingly, the object of the present invention is to provide a process for removing pyrite sulfur from coal, said process being more efficient and advantageous than those adopted up to the present time.

To that aim, chemical-biological treatment is suggested in which the chemical step is kept separate from the biological step, so that the typical optimal conditions can be realized in each one of the two operations.

According to the process of the present invention, coal is treated with an exclusively chemical leaching solution in order to obtain a desulphurization of the type already mentioned in chemical processes, but the exhausted leaching solution is separately re-oxidized biologically by means of the action of bacteria of the genus *Thiobacillus*.

Thus it is possible to realize the optimal physico-chemical conditions for the chemical reaction (high temperatures and low pH values), so as to obtain high reaction rates without the limitations given by the presence of microorganisms. On the other hand, in the biological section it is possible to keep the best conditions for the

microorganism is life, a low temperature being in the first place among such conditions.

Accordingly, the present invention specifically provides a process for the chemical-biological desulphurization of coal, said process comprising the following separate operations:

- 5 a) chemical treatment of coal, previously ground, with a leaching water solution containing ferric sulfate, ferrous sulfate and sulfuric acid;
- b) biological regeneration of the exhausted leaching solution, through oxidation of ferrous sulfate to ferric sulfate, by the action of a microorganism of the genus *Thiobacillus*.

10 Preferably, the coal to be treated is previously ground and sieved so as to obtain a fine and homogeneous granulometry, thus favouring to the utmost degree the reaction rate; the preferred grain size is lower than 1 mm.

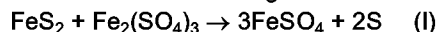
Next, coal is treated with an acid water solution so as to neutralize and solubilize the gangue fraction consisting of basic compounds like calcium oxide (CaO) and magnesium oxide (MgO). To that aim it is convenient to employ a portion of the acid solution that is obtained from the leaching reaction of pyrite, after separation of coal treated.

15 After neutralization, coal is separated from the solution and conveyed to the section where it undergoes the treatment a) according to this invention.

The solution fed to the chemical treatment contains  $\text{Fe}^{3+}$  ions at concentrations higher than 30 g/l, and  $\text{Fe}^{2+}$  ions at concentrations lower than 1 g/l, and it has a pH value lower than 1.5.

Ground coal is mixed with the leaching solution at a proportion between 10% and 50% by weight.

20 The main reaction of the chemical desulphurization process is the oxidation of pyrite by means of ferric sulfate which is in turn reduced to ferrous sulfate according to the reaction scheme:



The pyrite iron is dissolved as ferrous sulfate and sulfur is oxidized to elemental sulfur.

25 The leaching process is carried out in a common mixing chemical reactor of the discontinuous or the continuous type, or in any other suitable apparatus, or also in a number of series- or parallel-connected apparatuses. The reaction environment is heated for instance by means of steam or electric power, and it is kept at a temperature between 120°C and 140°C. The pressure is preferably kept between  $2.03 \cdot 10^5$  Pa and 6.08 Pa ( $\approx$  between 2 and 6 atm).

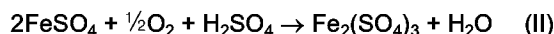
30 When the whole or almost the whole amount of pyrite has been converted, the mixture is unloaded and the coal is separated from the solution, for example by sedimentation or centrifugation. Then, it is washed with water so as to remove all soluble sulfates.

Elemental sulfur produced by such reaction is separated from coal for instance by means of steam or with a solvent, and then it is recovered.

35 Alternatively, a conversion process can be devised, for instance a biological process, for converting elemental sulfur to sulfate directly in the solution coming out of the treatment a), before separating the same from the solid.

40 The exhausted leaching solution is conveyed according to the present invention to the biological regeneration treatment b), in a fermentation vessel or a chemostat (or more than one of the same) or in any other container in which microorganisms of the genus *Thiobacillus*, preferably *Thiobacillus ferrooxidans*, capable of oxidizing ferrous to ferric ions, are introduced.

The regeneration of the solution is performed by means of the catalytic action of the above microorganisms according to the following general scheme:



45 Ferrous sulfate produced by the leaching reaction of pyrite in the chemical section of the process is re-oxidized to ferric sulfate; in the reaction course,  $\text{H}_2\text{SO}_4$  is to be continuously introduced so as to keep the pH at the fixed level.

50 According to a preferred embodiment of the present invention, a mutant strain of *Thiobacillus ferrooxidans* (according to the classification given in Bergey's Manual of Determinative Bacteriology) is employed for the biological reaction, said strain being purposely selected for the process of this invention. Such strain, which has been called KA2/27, has been deposited with the Deutsche Sammlung von Mikroorganismen, German Federal Republic, on October 29, 1987, with the accession number DSM 4298.

The microorganism selected is able to stand very high concentrations of ferric ions, higher than 35 g/l, as well as very low pH values, even lower than 1.5.

55 The reaction temperature of the biological treatment b) according to the present invention is kept at 25-35°C, and preferably between 28 and 30°C, whereas the pH value can advantageously be lower than 1.5; the best results are obtained at pH's between 1.2 and 1.5.

Moreover, it is necessary that air, or oxygen-enriched air or pure oxygen are bubbled through the vessel in which the reaction occurs, such gases being bubbled in amounts sufficient to the life of the microorganism,

and to the full development of the reaction (II).

Further, carbon dioxide may be bubbled as a source of carbon for microorganisms.

In order to supply other nutritive substances to the microorganisms, it is useful to continuously introduce into the reservoir also nitrogen and phosphorus sources, such as for instance ammonium salts, nitrates, phosphates. A suitable nutritive composition can be that of the 9K medium of M. Silverman and D. Lundgreen, which

contains  $(\text{NH}_4)_2\text{SO}_4$ , KCl,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , distilled water and sulfuric acid. In order to allow the biomass to be easily separated from the solution processed, the reaction vessel is to be so constructed so as to allow only the clear solution to flow out, whereas microorganisms are kept inside the vessel, for instance by means of suitable filtering aids.

The regenerated leaching solution having the composition characteristics already given above is continuously extracted from the fermentor and conveyed again to the reactor in which the chemical desulphurization process is carried out, so as to start the cycle again.

As can be observed, the process according to the present invention takes advantage of both kinds of processes, i.e., of the chemical as well as of the biological process, without undergoing their drawbacks. The process can be advantageously employed for treating different kinds of coal containing any sulfur amounts; in particular, it is very efficient for processing bituminous and sub-bituminous coals having very high sulfur concentrations.

Desulphurized coal so produced has optimal characteristics for employment as non-polluting fuel or for any other uses.

## Claims

1. Process for the chemical-biological desulphurization of coal, comprising the following separate operations:
  - a) chemically treating the previously ground coal with a leaching water solution containing ferric sulfate, ferrous sulfate and sulfuric acid;
  - b) biologically regenerating the exhausted leaching solution, through oxidation of ferrous sulfate to ferric sulfate by the action of a microorganism of the genus Thiobacillus.
2. Process according to claim 1, wherein said leaching solution conveyed to said chemical treatment a) of coal contains  $\text{Fe}^{3+}$  ions at a concentration higher than 30 g/l and  $\text{Fe}^{2+}$  at a concentration lower than 1 g/l.
3. Process according to claims 1 or 2, wherein said leaching solution has a pH value lower than 1.5.
4. Process according to each one of the preceding claims 1-3, wherein the ground coal is mixed with said leaching solution at a proportion between 10% and 50% by weight.
5. Process according to each one of the preceding claims 1-4, wherein said chemical treatment a) of coal occurs at a temperature between 120 and 140°C.
6. Process according to each one of the preceding claims 1-5, wherein said chemical treatment a) of coal occurs at a pressure between  $2.03 \cdot 10^5$  Pa and  $6.08 \cdot 10^5$  Pa ( $\approx$  between 2 and 6 atm).
7. Process according to claim 1, wherein coal is previously ground down to a granulometry lower than 1 mm.
8. Process according to claim 1, wherein the ground coal is contracted, before said chemical treatment a), with a water solution acidified with  $\text{H}_2\text{SO}_4$  for neutralizing the alkaline components contained in the gangue.
9. Process according to claim 8, wherein said  $\text{H}_2\text{SO}_4$ -acidified water solution is made up of a portion of said exhausted leaching solution.
10. Process according to each one of the preceding claims 1-9, wherein, after said chemical treatment a), the coal so treated is separated from said exhausted leaching solution, said solution being fed to said biological regeneration step b).
11. Process according to claim 1, wherein said biological regeneration b) of the exhausted leaching solution is obtained employing microorganisms of the species Thiobacillus ferrooxidans.

12. Process according to claim 11, wherein said microorganisms belong to the mutant strain KA2/27 of Thiobacillus ferrooxidans deposited with the Deutsche Sammlung Von Microorganismen under the accession number DSM 4298.
- 5 13. Process according to claim 12, wherein said operation b) is carried out at a temperature between 25 and 35°C.
14. Process according to claim 12 or 13, wherein during said biological regeneration b) the pH value is kept below 1.5 by adding sulfuric acid.
- 10 15. Process according to each one of the preceding claims 12-14, wherein during said biological regeneration b) air, or oxygen-enriched air, or pure oxygen are bubbled through the fermentation broth.
16. Process according to each one of the preceding claims 12-15, wherein during said biological regeneration b), carbon dioxide is also bubbled through the fermentation broth.
- 15 17. Process according to each one of the preceding claims 12-16, wherein during said biological regeneration b), nitrogen and phosphorus sources are also added to the fermentation broth.

20 **Patentansprüche**

1. Verfahren zur chemisch-biologischen Entschwefelung von Kohle, das auf folgenden Verfahrensschritte besteht:
- 25 a) chemische Behandlung der vorher vermahlten Kohle mit einer Ferrisulfat, Ferrosulfat und Schwefelsäure enthaltenden Laugewasserlösung;
- b) biologische Regenerierung der erschöpften Laugewasserlösung durch Oxydierung von Ferrosulfat in Ferrisulfat über die Wirkung eines Mikroorganismus des Thiobacillus Genus.
2. Verfahren nach Anspruch 1, bei dem die vorgenannte Laugewasserlösung zur vorgenannten chemischen Behandlung a) von Kohle,  $Fe^{3+}$  Ionen in einer Konzentration höher als 30 g/l und  $Fe^{2+}$  Ionen in einer Konzentration niedriger als 1 g/l enthält.
- 30 3. Verfahren nach Anspruch 1 oder 2 bei dem die vorgenannte Laugewasserlösung einen pH- Wert niedriger als 1,5 hat.
- 35 4. Verfahren nach je einem der vorhergehenden Ansprüche 1 bis 3, bei dem die vermahlte Kohle mit der vorgenannten Laugewasserlösung in einem Verhältnis zwischen 10 und 50 Gew. % vermischt wird.
5. Verfahren nach je einem der vorhergehenden Ansprüche 1 bis 4, bei dem die vorgenannte chemische Behandlung a) von Kohle bei einer Temperatur zwischen 120 und 140°C stattfindet.
- 40 6. Verfahren nach je einem der vorhergehenden Ansprüche 1 bis 5, bei dem die vorgenannte chemische Behandlung a) von Kohle bei einem Druck zwischen  $2,03 \cdot 10^5$  und  $6,08 \cdot 10^5$  Pa ( $\approx$  zwischen 2 und 6 Atm) stattfindet.
- 45 7. Verfahren nach Anspruch 1, bei dem die Kohle zu einer Korngröße kleiner als 1 mm vermahlt wird.
8. Verfahren nach Anspruch 1, bei dem die vermahlte Kohle, vor der genannten chemischen Behandlung a), mit einer Wasserlösung von  $H_2SO_4$  zur Neutralisierung von im Gang enthaltenen Alkali-Bestandteilen in Berührung gebracht wird.
- 50 9. Verfahren nach Anspruch 8, bei dem die mit  $H_2SO_4$  versäuerte Wasserlösung aus einem Teil der vorgenannten erschöpften Laugewasserlösung besteht.
- 55 10. Verfahren nach je einem der vorhergehenden Ansprüche 1 bis 9, bei dem, nach der chemischen Behandlung a), die so behandelte Kohle von der vorgenannten erschöpften Laugewasserlösung getrennt wird, wobei die genannte Lösung zur vorgenannten biologischen Regenerierung b) zugeführt wird.
11. Verfahren nach Anspruch 1, bei dem die vorgenannte biologische Regenerierung b) der erschöpften Lau-

geloesung durch Mikroorganismen der Art von Thiobacillus ferrooxidans erhalten wird.

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12. Verfahren nach Anspruch 11, bei dem die vorgenannten Mikroorganismen des-Stammutants KA2/27 von Thiobacillus ferrooxidans zugehoert, der bei der Deutschen Sammlung von Mikroorganismen unter der Eingangnummer DSM 4298 hinterlegt ist.
13. Verfahren nach Anspruch 12, bei dem die vorgenannte Behandlung b) bei einer Temperatur zwischen 25 und 35°C durchgefuehrt wird.
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14. Verfahren nach Anspruch 12 oder 13, bei dem waehrend der vorgenannten biologischen Regeneration b) der pH-Wert unter 1,5 durch die zugabe von Schwefelsaeure gehalten wird.
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15. Verfahren nach je einem der vorhergehenden Anspruechen 12 bis 14, bei dem waehrend der vorgenannten biologischen Regeneration b) durch die Fermentationsbruehe Luft oder mit Sauerstoff eingereichte Luft oder auch seiner Sauerstoff geblasen wird.
16. Verfahren nach je einem der vorhergehenden Anspruechen 12 bis 15, bei dem waehrend der vorgenannten biologischen Regeneration b) auch Kohlendioxyd durch die Fermentationsbruehe geblasen wird.
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17. Verfahren nach je einem der vorhergehenden Anspruechen 12 bis 16, bei dem waehrend der vorgenannten biologischen Regeneration b) zur Fermentationsbruehe auch Stickstoff- und Phosphor-Quellen zugegeben werden.

## Revendications

- 25
1. Procédé pour la désulfuration chimique-biologique de la houille, comprenant les opérations suivantes:
- a) traitement chimique de la houille précédemment moulue, avec une solution lixivante aqueuse contenant du sulfate ferrique, du sulfate ferreux et de l'acide sulfurique;
- 30
- b) régénération biologique de la solution lixivante épuisée au moyen de l'oxidation du sulfat ferreux à sulfate ferrique par action d'un micro-organisme du genre Thiobacillus.
2. Procédé selon la revendication 1, dans lequel ladite solution lixivante dirigée vers le traitement chimique a) de la houille contient de ions  $Fe^{3+}$  à une concentration au-dessus de 30 g/l et de ions  $Fe^{2+}$  à une concentration au-dessous de 1 g/l.
- 35
3. Procédé selon les revendications 1 ou 2, dans lequel ladite solution lixivante a une valeur du pH au-dessous de 1,5.
4. Procédé selon une des revendications précédentes 1-3, dans lequel la houille moulue est mixée avec ladite solution lixivante en proportion du 10 au 50% en poids.
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5. Procédé selon chacune des revendications précédentes 1-4, dans lequel ledit traitement chimique a) de la houille a lieu à une temperature entre 120 et 140°C.
6. Procédé selon chacune des revendications précédentes 1-5, dans lequel ledit traitement chimique a) de la houille a lieu entre  $2,03 \cdot 10^5$  Pa et  $6,08 \cdot 10^5$  Pa ( $\approx$  entre 2 et 6 atm.)
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7. Procédé selon la revendication 1, dans lequel la houille est précédemment moulue à une granulométrie au-dessous de 1 mm.
8. Procédé selon la revendication 1, dans lequel la houille est contactée, avant ledit traitement chimique a), avec une solution aqueuse acidifiée par  $H_2SO_4$  pour neutraliser les composants alcalins contenus dans la gangue.
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9. Procédé selon la revendication 8, dans lequel ladite solution acidifiée est formée par une portion de ladite solution lixivante épuisée.
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10. Procédé selon chacune des revendications précédentes 1-9, dans lequel, après ledit traitement chimique a), la houille traitée est séparée de ladite solution lixivante épuisée, ladite solution étant dirigée vers ladite

phase de régénération biologique b).

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11. Procédé selon la revendication 1, dans lequel ladite régénération biologique b) de la solution lixivante épuisée est obtenue en utilisant des micro-organismes de l'espèce Thiobacillus ferroxidans.
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12. Procédé selon la revendication 1, dans lequel lesdits micro-organismes appartiennent au genre mutant KA2/27 de Thiobacillus ferroxidans déposé pres le Deutsche Sammlung von Microorganismen sous le numero d'accès DSM 4298.
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13. Procédé selon la revendication 1, dans lequel ladite opération b) est réalisée à une temperature entre 25 et 35°C.
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14. Procédé selon la revendication 1, dans lequel pendant ladite régénération biologique b) la valeur du pH est maintenue au-dessous de 1,5 par addition d'acide sulfurique.
- 25
15. Procédé selon chacune des revendications 12-14, dans lequel pendant ladite régénération biologique b) l'air ou l'air enriché d'oxygène ou bien l'oxygène pur est barboté à travers le bouillon de fermentation.
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16. Procédé selon chacune des revendications précédentes 12-15, dans lequel pendant ladite régénération biologique b) le bioxide de carbone est barboté aussi à travers le bouillon de fermentation.
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- 40
17. Procédé selon chacune des revendications précédentes 12-16, dans lequel pendant ladite régénération biologique b) les sources d'azote et de phosphore sont ajoutées aussi au bouillon de fermentation.
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