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Contenuti del Brevetto Europeo n. WO/2011/000914, dal titolo “Process of Desulphurization of Low-Medium RankCoal – Procedimento per la Desolforazione di Carbone di Medio e Basso Rango”

(19)



(11)

EP 2 449 066 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

28.12.2016 Bulletin 2016/52

(51) Int Cl.:

C10L 9/02 (2006.01)

(86) International application number:

PCT/EP2010/059367

(21) Application number: **10752533.9**

(22) Date of filing: **01.07.2010**

(87) International publication number:

WO 2011/000914 (06.01.2011 Gazette 2011/01)

(54) PROCESS FOR THE DESULPHURIZATION OF LOW-MEDIUM RANK COAL

VERFAHREN ZUR ENTSCWEFELUNG VON KOHLE MIT NIEDRIGEM BIS MITTLEREM
INKOHLUNGSGRAD

PROCÉDÉ POUR LA DÉSULFURATION DE CHARBON DE RANG BAS-MOYEN

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO SE SI SK SM TR**

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(30) Priority: **01.07.2009 PCT/IT2009/000290**

(56) References cited:

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US-A- 4 488 866 US-A- 4 804 390**

(43) Date of publication of application:
09.05.2012 Bulletin 2012/19

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- **P. Carbini et al: "Desulphurization of European coals using molten caustic mixtures" In: "Processing and Utilization of High-Sulfur Coals III", 1990, Elsevier Science Publishers BV, Amsterdam, XP008120397, pages 361-369, cited in the application * abstract page 367**
- **ALIA ET AL: "Chemical desulphurization of high sulphur coals", FUEL, IPC SCIENCE AND TECHNOLOGY PRESS, GUILDFORD, GB, vol. 71, no. 7, 1 July 1992 (1992-07-01), pages 835-839, XP025455528, ISSN: 0016-2361 [retrieved on 1992-07-01]**

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Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention relates to a selective desulphurization process for low-medium rank coal. In particular the process is highly reproducible and cost-effective, and able to significantly reduce pollutant emissions into the atmosphere.

STATE OF THE ART

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[0002] Coal is the most abundant fossil fuel on earth. In particular, semi-anthracite and anthracite constitute fossil coal in the proper sense of the word and are the only ones exploited on a large scale, by being the richest in carbon and hence being provided with the highest calorific value.

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[0003] There are different types of classification for coals, based on chemical, petrographic, geological or rank criteria. In the past, geological classification was frequently used, with the coals being divided into four basic types: peat, lignite, semi-anthracite and anthracite. The concept of "rank" is currently used, in accordance with the US classification (ASTM D 338), based on physical-chemical characteristics to define its degree of maturity, without taking into account the relative geological age of formation. According to this classification the following can be distinguished, with progressive qualitative characteristics: lignite (low rank), sub-bituminous coal, bituminous coal and anthracite (high rank).

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[0004] The significant environmental impact due to the high sulphur content of some coals, independently of ranking thereof, is one of the major limitations to their use in a thermoelectric power station.

[0005] The sulphur is present in coals in the form of inorganic sulphur, essentially pyrite, and in the form of organic sulphur, i.e. as forming part of the macromolecular structure itself of the carbon.

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[0006] The study carried out on coals having different rank published by Carbini et al.: "Desulphurization of European coals using molten caustic mixtures", Processing and Utilization of High-Sulphur Coals III, 1990, 361-368, is known in the art, wherein molten caustic mixtures were used for the desulphurization.

[0007] In particular, either high rank coal or low-medium rank coal were treated as follows:

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- a caustic mixture of NaOH-KOH in a 9:1 ratio was melted inside a reactor at 350°C;
- the coal was added and the entire mixture was gently stirred mechanically;
- the reaction was allowed to proceed for the necessary duration, stirring the mixture all the time;
- on completion of the reaction, the coal was separated using a steel-wire screen and washed three times, twice with 10% sulphuric acid solution and once with distilled water; and
- the final solid product was dried and analyzed.

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[0008] From the analysis carried out on both coal types tested, it was resulted that the higher the rank, the lower the loss of calorific value in the final solid product.

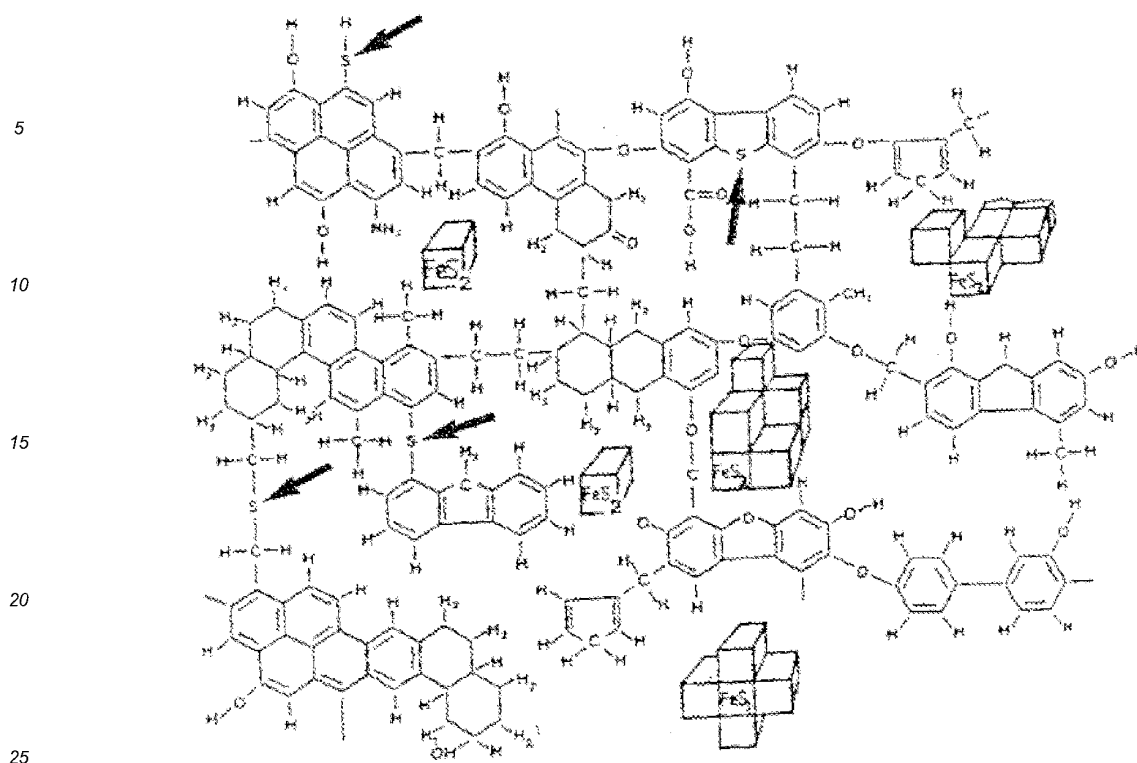
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[0009] It has been hypothesized that such a difference could be ascribable to different structure and surface characteristics, as well as to different degrees of porosity. For sake of greater clarity, a schematic representation of the molecular structure of coal is given below as reported in the publication by Carbini. et al.:

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[0010] Carbini et al. believe that low rank coals show a significant reduction in calorific value most likely because they contain a higher number of carboxylic and phenolic groups than the higher rank coals, said groups increasing the solubilisation of such coals in the caustic mixture. Moreover, the effect of the mechanical disintegration, which follows from the chemical attack, contributes to further increase losses in calorific value. This disintegration, which generates the formation of ultrafine coal particles, is certainly much more remarkable in more porous coals, such as those of lower rank, wherein consequently the loss of calorific value is quite considerable.

[0011] Carbini et al. conclude, therefore, by stating that the process making use of a caustic mixture is not suitable for low rank coals, because the loss of calorific value is so high as to render the process itself economically unacceptable.

[0012] No processes are known up till now, which allow also low-medium rank coals to be treated, so that all the requirements necessary to make their desulphurization effective and economically advantageous are simultaneously satisfied.

[0013] The object of the present invention is, hence, the desulphurization of low-medium rank coal in an efficient and highly reproducible manner, whereas limiting as far as possible the loss of calorific value, in order to upgrade low-medium rank coal and to make economically and environmentally convenient the use thereof.

SUMMARY OF THE INVENTION

[0014] The aforesaid object has been achieved by a process for the desulphurization of low-medium rank coal comprising the steps of:

- a) providing low-medium rank coal;
- b) leaching said coal in an aqueous solution comprising 10 to 20 wt.% of potassium hydroxide, for a period of time of 4 to 8 hours at a temperature less than 100°C;
- c) washing and filtering the so leached coal;
- d) leaching the coal in an aqueous solution comprising 2 to 30 vol.% of hydrogen peroxide, for a period of time of 2 to 6 hours at a temperature of 60 to 90°C; and
- e) washing and filtering the so obtained coal.

[0015] Said process has proved to be particularly suitable for the desulphurization of low-medium rank coals, preferably having a particle size of -5.60 mm.

[0016] In the present invention, with the expression "particle size of -5.60 mm" it is meant to refer to coals having a particle size of less than 5.6 mm.

[0017] Furthermore, the acronym "L.C.V." means Low Calorific Value and the acronym "H.C.V." means High Calorific Value.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The invention, therefore, relates to a process for the desulphurization of low-medium rank coal comprising the steps of:

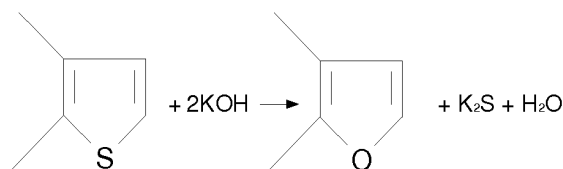
- a) providing low-medium rank coal;
- b) leaching said coal in an aqueous solution comprising 10 to 20 wt.% of potassium hydroxide, for a period of time of 4 to 8 hours at a temperature of less than 100°C;
- c) washing and filtering the so leached coal;
- d) leaching the coal in an aqueous solution comprising 2 to 30 vol.% of hydrogen peroxide, for a period of time of 2 to 6 hours at a temperature of 60 to 90°C; and
- e) washing and filtering the so obtained coal.

[0019] It was surprisingly found that this process enables not only pyritic sulphur but also organic sulphur to be significantly reduced, since it was observed that whereas the potassium hydroxide can selectively substitute organic sulphur, hydrogen peroxide advantageously selectively acts on pyritic sulphur and on the ash. The sulphur reduction altogether achieved was conveniently associated with a very small reduction in calorific value, thus rendering the process of the present invention particularly convenient not only from the implementing point of view but also from the economic point of view. This can be ascribed to the advantageous selection of the type of reagents used and the mild operating conditions, i.e. relatively short times and low temperatures.

[0020] In fact, it should be noted that the concentrations of said reagents enable the coal matrix to be subjected to a not too aggressive basic attack, hence achieving an economic saving on the reagent, whose cost remarkably affects the process operating costs.

[0021] More specifically, the potassium hydroxide attacks only organic sulphur by an exchange reaction between the sulphur atom contained in the organic molecule and the oxygen atom deriving from the hydroxide. For this reason, the leaching with this reagent alone for times greater than 8 hours has involved a 50% reduction in sulphur levels, though accompanied by a drastic reduction, even exceeding 30%, of the calorific value of the sample, due to a considerable increase in ash (oxidized coal matrix).

[0022] An example of the substitution reaction occurring between the sulphur atom and the oxygen atom in the carbonaceous matrix is the following:



[0023] In order to limit the calorific value decrease, which would result from an exclusively basic attack, hydrogen peroxide (H_2O_2) is used as oxidizing agent at low concentrations and temperatures. It was observed that the use of H_2O_2 enables the calorific value of coal to again increase, due to the decrease of ash (demineralization), and that said increase is directly proportional to the concentration of hydrogen peroxide in the leaching liquor.

[0024] The high efficiency of sulphur reduction, on average about 30%, was found to be of special technical relevance for relatively large particle sizes, i.e. -5.60 mm, said efficiency being obtained through tests carried out on different particle size classes of leached samples. At the same time, the calorific value of the sample thus treated has surprisingly shown an appreciably reduced decrease only of 4 to 10%. It has also been observed that the calorific value of the smaller particle size samples, i.e. -1 mm +0.71 mm, decreases to a less extent than the sample of larger particle size, for the same reduction in sulphur. This presumably takes place because of the greater surface exposed to hydrogen peroxide attack.

[0025] It should be noted that in the present invention, with the expression "particle size - 1 mm +0.71 mm" it is meant to refer to coals having particle sizes smaller than 1 mm but larger than 0.71 mm.

[0026] Another important consideration is that the samples treated with H_2O_2 at high concentrations (20-30 vol.%) and at room temperature have shown a considerable initial increase in calorific value in connection with a reduction in the mineral matter contained therein. In these samples, a small reduction in pyritic sulphur has been also found.

[0027] Preferably, in step b), the leaching is carried out for a period of time of 5.5 to 6.5 hours at a temperature of 65

to 75°C. In this respect, it was observed that said combination of parameters enabled coal desulphurization to be further increased. In accordance with a preferred embodiment, in step d) the aqueous solution comprises 3 to 4 vol.% of hydrogen peroxide. Even more preferred is an embodiment where in step d) the leaching is carried out with an aqueous solution comprising 3 to 4 vol.% of hydrogen peroxide for a period of time of 5.5 to 6.5 hours at a temperature of about 90°C. In this manner, a better balance between a significant desulphurization and a small loss of calorific value can in fact be achieved. Indeed, as will be seen in example 4 to follow, a total reduction in sulphur as percentage by weight of about 30% is observed, with a minimum reduction (about 6%) in calorific value. As this result is obtained with leaching at low reagent concentrations and with temperatures always less than 100°C, the process according to this preferred embodiment is particularly convenient not only from the implementing point of view but also from the economic point of view.

[0028] In the process of the present invention, the order of the two leaching steps can be exchanged, i.e. step d) is carried out in place of step b) and step b) is carried out in place of step d). In this case, in step c) the leaching is conducted until neutral pH is restored.

[0029] Preferably, in step d) the aqueous solution comprises 15 to 25 vol.% of hydrogen peroxide. In this respect, it was observed that at these concentrations a considerable initial increase in calorific value was achieved, for a reduction of the mineral matter contained therein. In these cases, a slight reduction in pyritic sulphur has been also found.

[0030] Moreover, said aqueous hydrogen peroxide solution is preferably at about pH 4.

[0031] Indeed, hydrogen peroxide is most stable at around this pH, especially at concentrations greater than 4 vol.%. Preferably, in order to bring the hydrogen peroxide solution pH to about 4, acids, such as phosphoric acid, sulphuric acid, uric acid and hydrochloric acid, are employed. More preferably, sulphuric acid at a concentration of 0.05 M to 0.3 M is used.

[0032] According to a preferred embodiment, in step d) the leaching is carried out at room temperature. In this respect, it has been observed that high desulphurization and contextually a reduced loss in calorific value without heating the solution can be achieved, with evident advantages from both the economic and implementing points of view.

[0033] Preferably in step b) of the process of the present invention, the leaching is carried out for a period of time of 5.5 to 6.5 hours at a temperature of 65 to 75°C. Indeed, it has been observed that these conditions allow a high desulphurization and a further reduced loss of calorific value to be attained.

[0034] With regard to step a), the coal which has proved to be most suitable for treatment according to the process of the present invention has been coal with a particle size of -5.60 mm. As will be seen from the following examples, the desulphurization process of the invention of low and medium rank coals allows a 95-100% recovery of the treated sample, differently from the process described by Carbin et al. However, the greatest cost-effectiveness is observed when the process of the invention is applied to low and medium rank coals with relatively large particle size (-5.60 mm).

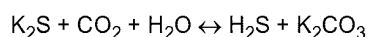
[0035] Preferably, said low-medium rank coal has a particle size of -1 mm +0.71 mm, since as previously stated the calorific value of the samples with smaller particle size decreases to a less extent than the sample with larger particle size, for the same reduction in sulphur.

[0036] According to a preferred embodiment, the process of the present invention further comprises a step of sodium hydroxide restoration wherein:

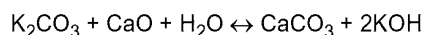
i) the leaching solution resulting at the end of step b) containing potassium sulphide is reacted with carbon dioxide to obtain potassium carbonate; and

ii) said potassium carbonate is reacted with calcium oxide to obtain calcium carbonate and potassium hydroxide.

[0037] The leaching solution derived from step b) is actually rich in potassium sulphide. By treating the same with carbon dioxide, potassium carbonate is obtained according to the following reaction:



[0038] Subsequently, by reacting K_2CO_3 with calcium oxide, potassium hydroxide is regenerated according to the following reaction:



[0039] Potassium hydroxide is thus conveniently obtained, having been regenerated for use in step b) of the process of the invention, with evident economical advantages. Alternatively, according to a further preferred embodiment, humic acids and/or humates are extracted from the leaching solution resulting at the end of step b). In fact, after the step b) of leaching the coal with the KOH solution, a slight darkening of the solution appeared, due to the presence of humic acids and/or humates. It has been reported (Saimir A. Lolja, 1999) that the extraction of humic acids by alkaline-air oxidation out of low rank coals slightly increases after 4 hours at low temperature.

[0040] Thus, this preferred embodiment allows to obtain an alkaline humic and fulvic extract from Sulcis coal. Surpris-

ingly, a by-product, such as the leaching solution coming from step b), indeed finds a convenient direct or indirect application to commercial agriculture, as fluid extract with a high content of humic/fulvic substances present therein.

[0041] In fact, organic matter, compost, humus, humates, humic acid and fulvic acid are all related to, and are parts of, decaying plant materials. These organic materials are food for soil life and a storehouse for minerals, energy and water. They also serve as mediums on which certain organisms can grow. Humic substances are known to stimulate plant roots and soil life (mostly fungal populations), chelate minerals (holding them for future use by plants), improve absorption of minerals for root and plant use, and improve the effectiveness of herbicides. Particularly, humic and fulvic extract obtained from this process can be advantageously used as soil amendment or physiological plants' activator.

[0042] An example of a plant for the implementation of said process, is a plant comprising:

- i) a first tank, wherein the coal is leached in an aqueous solution comprising 10 to 20 wt.% of potassium hydroxide;
- ii) a first washing unit, wherein the coal outletting from said first tank is washed;
- iii) a second tank, wherein the washed coal is leached in an aqueous solution comprising 2 to 30 vol.% of hydrogen peroxide;
- iv) a second washing unit, wherein the coal outletting from said second tank is washed.

[0043] The plant further comprises a unit for restoring potassium hydroxide present in the leaching solution outletting from the first tank.

[0044] Alternatively, the plant further comprises a unit for extracting humic acids and/or humates present in the leaching (alkaline) solution outletting from the first tank. The plant further comprises a unit for mixing humic and fulvic acids and/or humates present in the leaching solution outletting from the first tank with the said aqueous solution of hydrogen peroxide outletting from the second tank. This advantageously allow to decrease the pH of the humic and fulvic acids and/or humates solution outletting from the first tank.

[0045] Working Examples of the present invention are given herein below by way of nonlimiting examples, wherein low-medium rank coal is desulphurized according to the aforescribed process. In particular, Sulcis coal has been used, thus named because it is extracted from the geographical area of Sulcis in south-west Sardinia (Italy), and defined as "sub-bituminous long-flame coal" according to the US classification ASTM D 338.

[0046] Furthermore, it should be noted that in order to be considered economically acceptable, the coal preferably exhibits a L.C.V not less than 4000 kcal/kg. Therefore, in the following examples, the L.C.V. was measured in the first instance followed by evaluation of relative percent loss, even if the corresponding H.C.V for completion of information have been also reported.

EXAMPLES

Example 1

[0047] A 20 g sample of Sulcis coal (particle size -5.60 mm) was subjected to leaching with a 10 vol.% aqueous hydrogen peroxide solution stabilized with a 0.1 M aqueous sulphuric acid solution. The test was carried out in batch mode using a 50 ml volume of leaching liquor and placing the flask, containing the coal and leaching solution, in a temperature controlled shaking bath at room temperature for a period of time of about 2 hours.

[0048] The sample, after being washed and filtered, was subjected to a second leaching step with a 10 wt.% aqueous potassium hydroxide solution, for a bath residence time of 6 hours at a temperature of 70°C.

[0049] The sample, which was subsequently washed, neutralized and filtered, was then analyzed.

[0050] The results obtained are presented in the following table:

	%S	L.C.V. [kcal/kg]	H.C.V. [kcal/kg]
Starting coal	7.48	5081	5429
Coal obtained from example 1	5.36	4744	5070
% S reduction = 28.34%			
Percentage decrease in L.C.V. = -6.63%			

[0051] As can be seen from the data reported above, the process of the present invention wherein step d) is carried out before step b) enables the sulphur quantity present in low-medium rank coal to be significantly reduced, whereas at the same time achieving a lower and conveniently contained reduction in calorific value.

Example 2

[0052] A 20 g sample of Sulcis coal (particle size -5.60 mm) was subjected to leaching with a 20 vol.% aqueous hydrogen peroxide solution stabilized with a 0.2 M aqueous sulphuric acid solution. The test was carried out in batch mode using a 50 ml volume of leaching liquor and placing the flask, containing the coal and leaching solution, in a temperature controlled shaking bath at room temperature for a period of time of about 2 hours.

[0053] The sample, after being washed and filtered, was subjected to a second leaching step, with a 10 wt.% aqueous potassium hydroxide solution for a bath residence time of 6 hours at a temperature of 70°C.

[0054] The sample, which was subsequently washed, neutralized and filtered, was then analyzed.

[0055] The results obtained are presented in the following table:

	% S	L.C.V. [kcal/kg]	H.C.V. [kcal/kg]
Starting coal	7.48	5081	5429
Coal obtained from example 2	5.21	4882	5634
% S reduction = 30.38%			
Percentage decrease in L.C.V. = -3.91%			

[0056] As can be seen from the data reported above, the increase of the concentration of hydrogen peroxide in solution improves both desulphurization and above all the preservation of calorific value, which is far less reduced than in the previous example 1.

Example 3

[0057] A 20 g sample of Sulcis coal (particle size -5.60 mm) was subjected to leaching with a 16 wt.% potassium hydroxide solution at a temperature of 70°C. The test was carried out in batch mode using a 50 ml volume of leaching liquor and placing the flask, containing the coal and leaching solution, in a temperature controlled shaking bath for a time of about 6 hours.

[0058] The sample, after being washed, filtered and returned to neutral pH, was subjected to a second leaching step, with a 3.5 vol.% aqueous hydrogen peroxide solution for a bath residence time of 6 hours at 90°C. The sample, which was subsequently washed and filtered, was then analyzed.

[0059] The results obtained are presented in the following table:

	%S	L.C.V. [kcal/kg]	H.C.V. [kcal/kg]
Starting coal	5.97	5196	5526
Coal obtained from example 3	4.15	4715	5414
% S reduction = 30.49%			
Percentage decrease in L.C.V. = -9.26%			

[0060] In the present example, step b) precedes step d). In this case, it was observed that the percent reduction of sulphur is comparable to that one of the previous examples 1 and 2, whereas the loss in calorific value is a little higher, but nevertheless again conveniently less than 10%.

Example 4

[0061] A 20 g sample of Sulcis coal (particle size -5.60 mm) was subjected to leaching with a 10 wt.% potassium hydroxide solution at a temperature of 70°C. The test was carried out in batch mode using a 50 ml volume of leaching liquor and placing the flask, containing the coal and leaching solution, in a temperature controlled shaking bath at room temperature for a time of about 6 hours.

[0062] The sample, after being washed, filtered and returned to neutral pH, was subjected to a second leaching step, with a 3.5 vol.% aqueous hydrogen peroxide solution for a bath residence time of 6 hours at 90°C. The sample, which was subsequently washed and filtered, was then analyzed.

[0063] The results obtained are presented in the following table:

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	% S	L.C.V. [kcal/kg]	H.C.V. [kcal/kg]
Starting coal	5.97	5196	5526
Coal obtained from example 4	4.23	4836	5196
% S reduction = 29.16%			
Percentage decrease in L.C.V. = -6.92%			

[0064] As can be seen from the data reported above, by reducing the concentration of potassium hydroxide in solution, desulphurization is maintained close to that one obtained in the preceding example 3, whereas the calorific value is found to be advantageously less reduced.

Example 5

[0065] A 20 g sample of Sulcis coal (particle size -5.60 mm) was subjected to leaching with a 20 vol.% aqueous hydrogen peroxide solution stabilized with a 0.2 M aqueous solution of sulphuric acid. The test was carried out in batch mode using a 50 ml volume of leaching liquor and placing the flask, containing the coal and leaching solution, in a temperature controlled shaking bath at room temperature for a time of about 6 hours.

[0066] The sample, after being washed and filtered, was subjected to a second leaching step with a 10 wt.% of aqueous potassium hydroxide solution, for a bath residence time of 6 hours at a temperature of 70°C. The sample which was subsequently washed, neutralized and filtered, was then analyzed.

[0067] The results obtained are presented in the following table:

	% S	L.C.V. [kcal/kg]	H.C.V. [kcal/kg]
Starting coal	5.97	5196	5526
Coal obtained from example 5	4.52	5084	5413
% S reduction = 24.29%			
Percentage decrease in L.C.V. = -2.15%			

[0068] In the present example, analogously to examples 1 and 2, step b) precedes step d). In this case, the percent reduction of sulphur is observed to be a little lower than in the preceding examples, whereas the loss of calorific value is greatly reduced.

[0069] A comparison of example 2, in particular, with the current example 5, whereby step d) in both examples is performed at room temperature with a concentrated 20 vol.% hydrogen peroxide solution, shows that the increase of the residence time (from 2 to 6 hours) improves the preservation of L.C.V but decreases percent desulphurization of the coal.

Example 6

[0070] A 20 g sample of Sulcis coal (particle size -1 mm +0.71 mm) was subjected to leaching with a 16 wt.% aqueous potassium hydroxide solution at a temperature of 95°C. The test was carried out in batch mode using a 50 ml volume of leaching liquor and placing the flask, containing the coal and leaching solution, in a temperature controlled shaking bath at room temperature for a time of about 6 hours.

[0071] The sample, which was subsequently washed, neutralized and filtered, was then analyzed.

[0072] The results obtained are presented in the following table:

	% S	L.C.V. [kcal/kg]	H.C.V. [kcal/kg]
Starting coal	5.97	5196	5526
Coal obtained from example 6	3.04	3663	3993
% S reduction = 49.08%			
Percentage decrease in L.C.V. = -29.50%			

[0073] The present example was conducted using coal of smaller particle size i.e. -1 mm + 0.71 mm and by carrying out only steps a)-c), i.e. without using hydrogen peroxide. In this case, desulphurization is very high, but there is an approximate 30% loss of L.C.V. and so therefore the process results to excessively negatively affect the price of coal which depends on its calorific value.

Example 7

[0074] A 20 g sample of Sulcis coal (particle size -5.6 mm) was subjected to leaching with a 16 wt.% aqueous potassium hydroxide solution at a temperature of 90°C. The test was carried out in batch mode using a 50 ml volume of leaching liquor and placing the flask, containing the coal and leaching solution, in a temperature controlled shaking bath for a time of about 12 hours.

[0075] The sample, which was subsequently washed, neutralized and filtered, was then analyzed.

[0076] The results obtained are presented in the following table:

	% S	L.C.V. [kcal/kg]	H.C.V. [kcal/kg]
Starting coal	5.97	5196	5526
Coal obtained from example 7	4.81	4904	5233
% S reduction = 19.40%			
Percentage decrease in L.C.V. = -5.62%			

[0077] The present example was conducted using coal of particle size -5.60 mm, by carrying out only steps a)-c), i.e. without using hydrogen peroxide. In this case, the loss of calorific value is less than 10% but the desulphurization is too low.

Example 8

[0078] This example refers to the extraction of humic and fulvic substances from the leaching solution resulting at the end of step b).

[0079] A 20 g sample of Sulcis coal (particle size -2mm) was subjected to leaching with a 10 wt% aqueous potassium hydroxide solution at a temperature of 95°C.

[0080] The test was carried out in batch mode by means of a 50 ml volume of leaching liquor and placing the flask, containing the coal and the leaching solution, in a temperature controlled shaking bath for a time of about 6 hours. The sample was filtered and the reacted leaching solution, which was dried, was then analyzed.

[0081] The results obtained are presented in the following table:

Parameter	[wt%] dry basis
C	52.61
H	4.75
N	1.80
O	32.67
Ash	4.22
S	3.95
HA + HF	67

[0082] The results of this example are consistent with the elemental analyses provided in US4,788,360 and US5,391,534, thus confirming that humic and fulvic substances have been effectively extracted.

[0083] This example clearly shows that the present invention allow to obtain humic and fulvic acids and/or humates by means of a simplified and cheap process.

[0084] In fact, it should be noted that, according to this preferred embodiment, the said leaching solutions can be considered by-products of this process, instead of wastes.

[0085] From the detailed description and the aforementioned examples, the advantages achieved by the process of the present invention are evident. In particular, said process enables low-medium rank coals to be treated such as to simultaneously satisfy all the requirements necessary to make their desulphurization effective and economically advantageous.

[0086] Specifically, the process of the invention allows low-medium rank coal to be significantly desulphurized in an efficient and highly reproducible manner, to conveniently limit to less than 10% the loss of calorific value so as to upgrade low-medium rank coal and render its use both economically and environmentally advantageous.

[0087] This can be ascribed to the advantageous selection of the type of reagents used and the mild operating conditions, i.e. relatively short times and low temperatures. In fact, it should be noted that the concentrations of said reagents enable a not too aggressive basic attack on the coal matrix, with consequently a significant energy saving, as well as a considerable simplification in terms of the implementation and equipment required. These advantages are even more evident considering that a regeneration and restoration step is provided for the potassium hydroxide used.

[0088] It should also be noted that the present invention has overcome the technical prejudice raised by Carbini et al., who sustained that the process with a NaOH and KOH mixture is not suited to low rank coal because the loss of calorific value is so high as to make said process economically unacceptable.

Claims

1. A process for the desulphurization of low-medium rank coal comprising the steps of:
 - a) providing low-medium rank coal;
 - b) leaching said coal in an aqueous solution comprising 10 to 20 wt.% of potassium hydroxide, for a period of time of 4 to 8 hours at a temperature of less than 100°C;
 - c) washing and filtering the so leached coal;
 - d) leaching the coal in an aqueous solution comprising 2 to 30 vol.% of hydrogen peroxide, for a period of time of 2 to 6 hours at a temperature of 60 to 90°C; and
 - e) washing and filtering the so obtained coal.
2. The process according to claim 1 wherein in step b) the leaching is carried out for a period of time of 5.5 to 6.5 hours at a temperature of 65 to 75°C.
3. The process according to claim 1 or 2 wherein in step d) the aqueous solution comprises 3 to 4 vol.% of hydrogen peroxide.
4. The process according to claim 3 wherein in step d) the leaching is carried out for a period of time of 5.5 to 6.5 hours at a temperature of about 90°C.
5. The process according to claim 1 wherein step d) is carried out in place of step b) and step b) is carried out in place of step d), and wherein in step c) the washing is conducted until neutral pH is restored.
6. The process according to claim 5 wherein in step d) the aqueous solution comprises 15 to 25 vol.% of hydrogen peroxide.
7. The process according to claim 5 or 6 wherein in step d) the leaching is carried out at room temperature.
8. The process according to any one of claims 5-7 wherein in step b) the leaching is carried out for a period of time of 5.5 to 6.5 hours at a temperature of 65 to 75°C.
9. The process according to any one of claims 1-8 wherein in step a) said low-medium rank coal has a particle size of -5.60 mm.
10. The process according to claim 9 wherein in step a) said low-medium rank coal has a particle size of -1 mm +0.71 mm.
11. The process according to any one of claims 1-10, further comprising a step of sodium hydroxide restoration wherein:
 - i) the leaching solution resulting at the end of step b) and containing potassium sulphide is reacted with carbon dioxide to obtain potassium carbonate; and
 - ii) said potassium carbonate is reacted with calcium oxide to obtain calcium carbonate and potassium hydroxide.
12. The process according to any one of claims 1-10, wherein humic acids and/or humates are extracted from the leaching solution resulting at the end of step b).

Patentansprüche

1. Verfahren zur Entschwefelung von Kohle mit niedrigem bis mittlerem Inkohlungsgrad, das folgende Schritte aufweist:

- a) Bereitstellen von Kohle mit niedrigem bis mittlerem Inkohlungsgrad;
- b) Herauslösen der Kohle in einer wässrigen Lösung, die 10 bis 20 Gew.-% Kaliumhydroxid aufweist, für 4 bis 8 Stunden, bei einer Temperatur unter 100°C;
- c) Waschen und Filtern der so ausgelaugten Kohle;
- d) Herauslösen der Kohle in einer wässrigen Lösung, die 2 bis 30 Vol.-% Wasserstoffperoxid aufweist, für 2 bis 6 Stunden, bei einer Temperatur zwischen 60 und 90°C; und
- e) Waschen und Filtern der so gewonnenen Kohle.

2. Verfahren gemäß Anspruch 1, wobei in Schritt b) das Herauslösen über 5,5 bis 6,5 Stunden bei einer Temperatur zwischen 65 und 75°C durchgeführt wird.

3. Verfahren gemäß Anspruch 1 oder 2, wobei in Schritt d) die wässrige Lösung 3 bis 4 Vol.-% Wasserstoffperoxid aufweist.

4. Verfahren gemäß Anspruch 3, wobei in Schritt d) das Herauslösen über 5,5 bis 6,5 Stunden bei einer Temperatur von etwa 90°C durchgeführt wird.

5. Verfahren gemäß Anspruch 1, wobei Schritt d) anstatt von Schritt b) durchgeführt wird und Schritt b) anstatt von Schritt d) durchgeführt wird und wobei in Schritt c) das Waschen durchgeführt wird, bis ein neutraler pH-Wert wiederhergestellt ist.

6. Verfahren gemäß Anspruch 5, wobei in Schritt d) die wässrige Lösung 15 bis 25 Vol.-% Wasserstoffperoxid aufweist.

7. Verfahren gemäß Anspruch 5 oder 6, wobei in Schritt d) das Herauslösen bei Raumtemperatur durchgeführt wird.

8. Verfahren gemäß einem der Ansprüche 5 bis 7, wobei in Schritt b) das Herauslösen über 5,5 bis 6,5 Stunden bei einer Temperatur zwischen 65 und 75°C durchgeführt wird.

9. Verfahren gemäß einem der Ansprüche 1 bis 8, wobei in Schritt a) die Kohle mit niedrigem bis mittlerem Inkohlungsgrad eine Partikelgröße -5,60 mm aufweist.

10. Verfahren gemäß Anspruch 9, wobei in Schritt a) die Kohle mit niedrigem bis mittlerem Inkohlungsgrad eine Partikelgröße von -1 mm +0,71 mm aufweist.

11. Verfahren gemäß einem der Ansprüche 1 bis 10, welches zudem einen Schritt der Wiederherstellung von Natriumhydroxid aufweist, wobei:

- i) die Herauslöse-Lösung, die am Ende von Schritt b) entsteht und Kaliumsulfid enthält mit Kohlenstoffdioxid in Reaktion gebracht wird, um Kaliumkarbonat zu erhalten, und
- ii) das Kaliumkarbonat mit Kalziumoxid in Reaktion gebracht wird, um Kalziumkarbonat und Kaliumhydroxid zu erhalten.

12. Verfahren gemäß einem der Ansprüche 1 bis 10, wobei Huminsäuren und / oder Humate aus der Herauslöse-Lösung extrahiert werden, die am Ende von Schritt b) entsteht.

Revendications

1. Procédé de désulfuration d'un charbon de rang bas-moyen comprenant les étapes suivantes :

- a) la fourniture d'un charbon de rang bas-moyen ;
- b) la lixiviation dudit charbon dans une solution aqueuse comprenant 10 à 20 % en poids d'hydroxyde de potassium, pendant une période de temps de 4 à 8 heures à une température inférieure à 100 °C ;
- c) le lavage et la filtration du charbon ainsi lixivié ;

d) la lixiviation du charbon dans une solution aqueuse comprenant 2 à 30 % en volume de peroxyde d'hydrogène, pendant une période de temps de 2 à 6 heures à une température de 60 à 90 °C ; et
e) le lavage et la filtration du charbon ainsi obtenu.

- 5 2. Procédé selon la revendication 1, dans lequel, dans l'étape b), la lixiviation est réalisée pendant une période de temps de 5,5 à 6,5 heures à une température de 65 à 75 °C.
- 10 3. Procédé selon la revendication 1 ou 2, dans lequel, dans l'étape d), la solution aqueuse comprend 3 à 4 % en volume de peroxyde d'hydrogène.
- 15 4. Procédé selon la revendication 3, dans lequel, dans l'étape d), la lixiviation est réalisée pendant une période de temps de 5,5 à 6,5 heures à une température d'environ 90 °C.
- 20 5. Procédé selon la revendication 1, dans lequel l'étape d) est réalisée à la place de l'étape b) et l'étape b) est réalisée à la place de l'étape d), et dans lequel, dans l'étape c), le lavage est réalisé jusqu'à ce qu'un pH neutre soit restauré.
- 25 6. Procédé selon la revendication 5, dans lequel, dans l'étape d), la solution aqueuse comprend 15 à 25 % en volume de peroxyde d'hydrogène.
- 30 7. Procédé selon la revendication 5 ou 6, dans lequel, dans l'étape d), la lixiviation est réalisée à température ambiante.
- 35 8. Procédé selon l'une quelconque des revendications 5 à 7, dans lequel, dans l'étape b), la lixiviation est réalisée pendant une période de temps de 5,5 à 6,5 heures à une température de 65 à 75 °C.
- 40 9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel, dans l'étape a), ledit charbon de rang bas-moyen présente une taille de particule de -5,60 mm.
- 45 10. Procédé selon la revendication 9, dans lequel, dans l'étape a), ledit charbon de rang bas-moyen présente une taille de particule -1 mm +0,71 mm.
- 50 11. Procédé selon l'une quelconque des revendications 1 à 10, comprenant en outre une étape de restauration de l'hydroxyde de sodium dans laquelle :
- 55 i) la solution de lixiviation obtenue à la fin de l'étape b) et contenant du sulfure de potassium est mise à réagir avec du dioxyde de carbone pour obtenir du carbonate de potassium ; et
 ii) ledit carbonate de potassium est mis à réagir avec de l'oxyde de calcium pour obtenir du carbonate de calcium et de l'hydroxyde de potassium.
- 60 12. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel des acides humiques et/ou des humates sont extraits de la solution de lixiviation obtenue à la fin de l'étape b).

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- **CARBINI et al.** Desulphurization of European coals using molten caustic mixtures. *Processing and Utilization of High-Sulphur Coals*, 1990, vol. III, 361-368 [0006]