(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 010 289**
**A1**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: **79103981.1**

(22) Date of filing: **16.10.79**

(51) Int. Cl.$^3$: **C 10 L 9/02**

(30) Priority: **17.10.78 US 952108**

(43) Date of publication of application:
**30.04.80 Bulletin 80/9**

(84) Designated Contracting States:
**DE FR GB**

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(54) **Mild oxidative coal desulfurization.**

(57) A process for the removal of pyrite from coal which comprises preparing an aqueous slurry containing finely-divided coal particles; adding to the slurry an hydroxide or carbonate of an alkali or alkaline earth metal selected from the group consisting of sodium, lithium, potassium and magnesium, as well as mixtures of these hydroxides and carbonates, in amounts sufficient to continuously maintain the pH of the slurry between about 8 and 12; and then agitating the slurry while treating the slurry with oxygen or an oxygen-containing gas.

**EP 0 010 289 A1**

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The present invention relates to a process for the removal of pyritic sulfur from coal.

The present energy crisis has produced both economic and governmental incentives to use more coal as fuel to replace oil and gas imported in ever increasing amounts. Counterbalancing these incentives are governmental regulations which establish a permissable level of pollutants from the combustion of these fuels. One of the major pollutants is sulfur dioxide. Unfortunately, most of the coal reserves in this country contain sulfur in amounts which are too excessive to burn in compliance with existing law. Major consumers of coal, such as electric utilities, have two alternatives to follow, namely they can buy low sulfur content coal or use flue gas desulfurization to remove sulfur dioxide after combustion. The first alternative would be most feasible if sulfur could be removed from the coal using methods which are both practical and economical.

Most coals which are available for use in this country contain sulfur in several different forms, i.e., sulfate sulfur, organic sulfur and pyritic sulfur. The organic sulfur is chemically bonded within the organic molecular framework of the coal while the pyritic sulfur consists of sulfur in the form of iron pyrite, which is disseminated as a separate mineral phase throughout the body of the coal. In general, sulfate sulfur constitutes a minor fraction of the sulfur content in coals, i.e. less than about 0.2 weight % of the coal. The organic sulfur and pyritic sulfur constitute a major fraction of sulfur in the coal and together they constitute up to about 5 - 8 weight % of the coal. The pyritic sulfur constitutes between about 40-60% of the total sulfur content in the coal. Therefore, the removal of the pyritic sulfur alone can significantly reduce the sulfur content and, therefore, the sulfur emissions which occur upon combustion of coal.

The pyritic sulfur exists as a distinct phase within the body of the coal. It is therefore possible to liberate the pyrite from the coal physically and by means of chemical techniques to remove the liberated pyrite from the coal, without altering in any significant way the properties of the coal.

It is generally known that pyritic sulfur can be removed from coal by chemical oxidation to a species which is soluble in water. Such processes are preferably carried out by employing a basic solution as the reaction medium. For example, in U.S. Pat. No. 3,960,513 to J. C. Agarwal et al, an aqueous slurry containing crushed coal is treated with ammonium hydroxide in the presence of oxygen. The pyritic sulfur in the coal is converted to a soluble species, e.g. ferric or ferrous sulfate, along with ammonium sulfate as a by-product. The soluble sulfate may be removed by a conventional solids-liquid separation. Ammonium sulfate may then be recycled to generate additional ammonium hydroxide. Despite this advantage, however, the process is best carried out by employing both elevated temperatures and pressures, (e.g. about 300 psig). This of course necessitates the use of expensive equipment which increases the cost of desulfurization process.

The present invention is directed to a process for the removal of pyritic sulfur from coal by chemical oxidation utilizing a basic solution as the reaction medium under mild conditions, i.e. temperatures only slightly above ambient and atmospheric pressure. Briefly, this process comprises preparing an aqueous slurry containing finely-divided coal particles, adding to the slurry an hydroxide or carbonate of an alkali or alkaline earth metal selected from the group consisting of sodium, lithium, potassium and magnesium, as well as mixtures of these hydroxides and carbonates, in an amount sufficient to continuously maintain the pH of the slurry between about 8 and 12 and then agitating the slurry while treating the slurry with oxygen or an oxygen containing gas such as air. The process may be advantageously carried out at temperatures of between about 40 and 70°C and at atmospheric pressure. The treated slurry may be subjected to a conventional solids-liquid separation to recover the desulfurized solid coal.

The process of the present invention is broadly applicable to the treatment of various types of coal. In particular, the process is directed to the desulfurization of bituminous coals which are combusted to generate steam in electric utility plants or industrial boilers. Coals that may be treated in accordance with the present invention are the medium and high volatile bituminous coals such as for example Ohio No. 6 coal. It will be understood of course that the present invention is not limited to the treatment of the above-mentioned coals alone and that coals other than bituminous coals such as anthracite and lignite coal may be treated as well. In general, the coals that are treated in accordance with the present invention will contain a pyritic sulfur concentration in the range of from about 0.5 to about 4% by weight of the coal.

The raw coal which is obtained from mines in chunk size, for example, is first reduced to a finely-divided particle size. The particle size of the coal should be sufficient to expose a substantial fraction of the total surface of the pyrite that is contained in the coal. Generally speaking, the coal is reduced to a particle size smaller than about 200 mesh.

The [illegible] coal particles are then formed into an aqueous slurry, for example, by mixing the coal particles together with water in a suitable reaction vessel. The coal slurry should preferably possess a solids concentration in the range of between about 4 and 40% by weight coal.

To begin the desulfurization process, the pH of the slurry is adjusted to a value of between about 8 and 12 and preferably about 10 or 11, by the addition of a caustic, such as sodium hydroxide or a mixture of sodium hydroxide and sodium carbonate. Other alkali and alkaline earth metal hydroxides and carbonates can also be used as shall be described further hereinafter. The coal slurry is then agitated and subjected to an oxidizing medium such as oxygen or an oxygen-containing gas e.g. air. The oxygen or air, for example, should be introduced in intimate contact with the coal slurry. This may be accomplished by bubbling oxygen through the slurry or by aerating the slurry in the reaction vessel. It may also be necessary to periodically add caustic to the slurry in order to continuously maintain the pH of the slurry within the desired range as indicated above. The desulfurization process may be carried out at temperatures of between about 40 and 70° and at atmospheric pressure.

Although it is preferred to employ sodium hydroxide or a mixture of sodium hydroxide and sodium carbonate as the caustic reagent in the practice of the present invention, it is believed that other alkali and alkaline earth metal hydroxides and carbonates as well as mixtures of these hydroxides and carbonates can also be employed. Thus, it may be possible to use in addition to sodium hydroxide both lithium and potassium hydroxide as well as lithium and potassium carbonate or mixtures thereof. Among the alkaline earth metal hydroxides and carbonates, it is postulated that only magnesium hydroxide or magnesium carbonate would be useful. Calcium hydroxide, for example, will impede the oxidation process at these pH values and should not therefore be employed.

The process of pyrite removal from the coal proceeds according to the following stoichiometry:

$$FeS_2 + 4\ OH^- + 3.75\ O_2 \rightarrow 1/2Fe_2O_3 + 2\ SO_4^= + 2H_2O$$

It will be seen from the above equation that the pyritic sulfur is oxidized to sulfate which is soluble in the reaction medium while iron remains in treated coal as an insoluble oxide/hydroxide. Conventional solids-liquid separation techniques can be employed to recover the treated or desulfurized solid coal. If desired, the treated coal can be washed and dried by any conventional methods.

It is generally known in the mineral leaching art that the reactivity of pyrite (FeS2) with oxygen increases dramatically at high pH and also at elevated temperatures and pressures. However, when pyrite is present in coal, the reactivity of the organic matter and non-pyritic [illegible] considered when caustic and oxidative conditions are contemplated. It is known, for example, that the reactivity of organic matter in coal with oxygen also increases with increasing pH, temperature and pressure and that under these same conditions, the valuable constituents in the coal can be easily destroyed by unwanted side reactions. It has been surprisingly discovered in accordance with the present invention that the removal of pyritic sulfur from coal can be readily accomplished under mild conditions, i.e. temperatures only slightly above ambient and atmospheric pressure, while at the same time minimizing unwanted side reactions if the pH of the coal slurry is continuously maintained within certain limits, i.e. pH values of between 8 and 12, by the addition of caustic such as sodium hydroxide. In general, the duration of the process will vary depending upon the caustic material used and the pH of the coal slurry. It may be noted for example that the process of desulfurization can be carried out to virtual completion with 90% or more of the pyrite removed in one or two days when sodium hydroxide is employed and the pH is continuously maintained at about 10 or 11. The duration of the desulfurization process can be shortened by employing pH values greater than 12 but unwanted side reactions will occur that destroy valuable constituents in the coal. In contrast, at low pH values of about 8, the reaction proceeds at a much slower rate and may take as long as about one week to completion.

The present invention will be further illustrated by the following examples:

## EXAMPLE I

500 cc distilled water was placed in a percolator equipped with pH electrode and a pH controller, water cooled condenser, and a NaOH reservoir. The percolator was attached to a gas supply equipped with a flowmeter. A thermostatted water bath was used to provide a stable temperature. The gas flow was begun as the water was heated to the reaction temperature, e.g. 50°C. In this experiment, oxygen was used as the oxidant. The gas flow rate was 1.0 SCFH. 20 g of coal (Ohio No. 6 - 200 mesh) was added to the percolator. The slurry concentration was 4% by weight coal. The addition of 1.0 N NaOH was begun as soon as the coal was completely slurried. For the purpose of measuring reaction rates and NaOH consumption, $FeS_2$ leaching was considered to begin when the desired reaction pH, e.g. pH 11, was achieved. The initial NaOH required to achieve the desired pH was consumed in the hydrolysis of any iron sulfates in the coal. During the course of the reaction, the NaOH consumption was monitored, and slurry samples were withdrawn. The samples were filtered and the coal collected and washed with water and then air dried.

Total sulfur was determined on all coal samples. Proximate analyses on starting and finishing coals were obtained on a number of samples. Solution samples were tested for soluble Na and Fe by atomic absorption and soluble $SO_4^=$ by gravimetric analysis. The Na content in the product coal was determined as HCl soluble Na. Where full proximate analyses were not available, the percent pyritic sulfur leached was calculated from initial and final values for total sulfur, assuming all non-sulfate sulfur leached to be pyritic.

## EXAMPLE II

Basically the same procedure as outlined in Example I above was followed except that in this experiment air was used instead of oxygen as the oxidant.

## EXAMPLE III

Basically the same procedure as outlined in Example I above was followed except that in this experiment $Na_2CO_3$ in an amount sufficient to produce a concentration of 0.2 molar was added to the percolator immediately following addition of the coal and prior to addition of any NaOH.

## EXAMPLE IV

Basically the same procedure as outlined in Example III above was followed except that in this experiment air was used instead of oxygen as the oxidant.

Test results on a variety of samples evidenced about 90% removal of pyritic sulfur. These results are shown in Tables I and II below:

## TABLE I

% Pyritic Sulfur Leached, NaOH Consumption, and Na Content of Coals Treated at pH 11 and 50°C

| Sample # | Treatment Time (hr) | $Na_2CO_3$ Conc. (M) | Gas | %$FeS_2$ Removed | %Na in Product Coal |
|---|---|---|---|---|---|
| 1-1 | 3 | 0 | $O_2$ | 26 | 0.40 |
| 2 | 6 | " | " | 55 | 0.39 |
| 3 | 24 | " | " | 69 | 0.74 |
| 4 | 48 | " | " | 88 | 0.88 |
| 2-1 | 3 | 0 | air | 19 | 0.43 |
| 2 | 6 | " | " | 38 | 0.38 |
| 3 | 24 | " | " | 69 | 0.60 |
| 4 | 48 | " | " | 88 | - |
| 3-1 | 3 | 0.2 | $O_2$ | 50 | 0.68 |
| 2 | 6 | " | " | 64 | 0.65 |
| 3 | 24 | " | " | 88 | 1.12 |
| 4 | 48 | " | " | 92 | 1.32 |
| 4-1 | 3 | 0.2 | air | 22 | 0.59 |
| 2 | 6 | " | " | 32 | 0.58 |
| 3 | 24 | " | " | 70 | 0.93 |
| 4 | 48 | " | " | 91 | - |

## TABLE II

### Effect of Temperature on $O_2$ Leaching of Pyritic Sulfur, NaOH Neutralization

(Treatment Time - 24 Hours)

| Sample # | pH | Temp. (°C) | Media | %$FeS_2$ Leached | %Na in Coal |
|---|---|---|---|---|---|
| 5-1 | 10 | 30 | $H_2O$ | 35 | 0.50 |
| 5-2 | " | " | 0.2 M $NaCO_3$ | 42 | 0.34 |
| 5-3 | " | 40 | $H_2O$ | 37 | 0.29 |
| 5-4 | " | " | 0.2 M $Na_2CO_3$ | 51 | 0.38 |
| 5-5 | " | 50 | $H_2O$ | 62 | - |
| 5-6 | " | " | 0.2 M $Na_2CO_3$ | 77 | - |
| 5-7 | " | 60 | $H_2O$ | 70 | 0.54 |
| 5-8 | " | " | 0.2 M $Na_2CO_3$ | 78 | 0.65 |
| 5-9 | 11 | 40 | $H_2O$ | 45 | 0.38 |
| 5-10 | " | " | 0.2 M $Na_2CO_3$ | 57 | 0.88 |
| 5-11 | " | 50 | $H_2O$ | 69 | 0.74 |
| 5-12 | " | " | 0.2 M $Na_2CO_3$ | 88 | 1.12 |
| 5-13 | " | 60 | $H_2O$ | 74 | 0.80 |
| 5-14 | " | " | 0.2 M $Na_2CO_3$ | 97 | 1.36 |
| 5-15 | 12 | 30 | $H_2O$ | 53 | - |
| 5-16 | " | " | 0.2 M $Na_2CO_3$ | 59 | - |
| 5-17 | " | 50 | $H_2O$ | 82 | 1.53 |
| 5-18 | " | " | 0.2 M $Na_2CO_3$ | 93 | 2.09 |

As indicated in Table I above, the rate of pyritic sulfur removal at pH 11 and 50°C depends on $O_2$ concentration and the presence of $Na_2CO_3$. The initial rate is faster with pure $O_2$ than with air when $Na_2CO_3$ is present. There is no benefit to using $Na_2CO_3$ when air is the oxidant. The amount of pyritic sulfur leached is the same within experimental error after 48 hours for all four samples, although this amount is leached after only 24 hours when $O_2$ and $Na_2CO_3$ are used.

It may be noted from Table II that for a fixed reaction time of 24 hours, the amount of $FeS_2$ leached increases with increasing pH. $Na_2CO_3$ enhances the rate, e.g., more $FeS_2$ is leached at pH 11 with $Na_2CO_3$ than at pH 12 without $Na_2CO_3$. It may also be noted that the amount of Na in the coal also increases at higher pH even when the same amount of $FeS_2$ is removed.

Experimentation has further shown that the rate of reaction also increases with increasing temperature at pH 10, 11 and 12, both with and without $Na_2CO_3$, when measured by sulfur leached. The rate of NaOH consumption at pH 10 (in the absence of $Na_2CO_3$) also increases in a similar manner. NaOH consumption at pH 11 is approximately equal at 50° and 60°. The point of diminishing returns appears to be reached at about 60°C. Further temperature increases will be counterbalanced by decreased $O_2$ solubility in the media.

Analysis of leach media following reactions in sample Nos. 1-4 and 2-4 in Table I using $O_2$ and air, respectively, as oxidants, show very little organic carbon in either the filtrate or the wash water. Total carbon lost is approximately 1% in each reaction.

A number of product coals were analyzed for Na content. The Na content was found to increase with increased pH and the extent of leaching. Where necessary, the Na content in the coal can be reduced to acceptable levels by treatment with acid.

WHAT IS CLAIMED IS:

1. A process for the removal of pyrite from coal which comprises preparing an aqueous slurry containing finely-divided coal particles; adding to the slurry an hydroxide or carbonate of an alkali or alkaline earth metal selected from the group consisting of sodium, lithium, potassium and magnesium, as well as mixtures of said hydroxides and carbonates, in amounts sufficient to continuously maintain the pH of the slurry between about 8 and 12; and then agitating the slurry while treating the slurry with oxygen or an oxygen-containing gas.

2. The process as defined by claim 1 wherein the pH of the coal slurry is continuously maintained at a value of about 10 or 11.

3. The process as defined by claim 2 wherein the pH of the coal slurry is maintained by the addition of sodium hydroxide.

4. The process as defined by claim 2 wherein the pH of the coal slurry is maintained by the addition of a mixture of sodium hydroxide and sodium carbonate.

5. The process as defined by claim 1 wherein the temperature of the coal slurry is maintained in a range of between about 40 and 70°C.

6. The process as defined by claim 5 wherein

the treatment of the slurry with oxygen or oxygen-containing gas is carried out at substantially atmospheric pressure.

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# EUROPEAN SEARCH REPORT

Application number
EP 79 10 3981

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |
|---|---|---|
| X | GB - A - 1 520 242 (ATLANTIC RICHFIELD)<br>* Claims 1-3,5-7 *<br>-- | 1-5 |
|  | US - A - 4 054 420 (OCCIDENTAL PETROLEUM)<br>* Claims 1,7,9,11-13 *<br>-- | 1,3,4 |
| A | GB - A - 855 246 (SHAWINIGAN)<br>* Claim 5 *<br>---- | 1,3 |

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 10 L 9/02

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 10 L 9/02
9/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 18-01-1980 | MEERTENS |

EPO Form 1503.1 06.78