United States Patent [19]

Meyers

[11] **3,768,988**

[45] **Oct. 30, 1973**

[54] **REMOVAL OF PYRITIC SULFUR FROM COAL USING SOLUTIONS CONTAINING FERRIC IONS**

[75] Inventor: **Robert A. Meyers**, Encino, Calif.

[73] Assignee: **TRW Inc.**, Redondo Beach, Calif.

[22] Filed: **July 19, 1971**

[21] Appl. No.: **163,893**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 116,262, Feb. 17, 1971, abandoned.

[52] **U.S. Cl.** ..... **44/1 R**, 201/17, 423/461, 423/567, 423/594

[51] **Int. Cl.** **C011 9/00**

[58] **Field of Search** ..... 44/4–6, 44/1 R, 1 B; 23/224, 226, 225 R, 200; 208/8; 201/17

[56] **References Cited**

UNITED STATES PATENTS

2,204,148	6/1940	Nelms	44/4 X
2,895,796	7/1959	Hill	23/224
3,252,769	5/1966	Nagelvourt	44/1 R
3,652,219	3/1972	Peters et al.	23/200
3,640,016	2/1972	Lee	44/1 R
2,592,580	4/1952	Loevenstein	23/200
1,980,809	11/1934	Levy	23/226

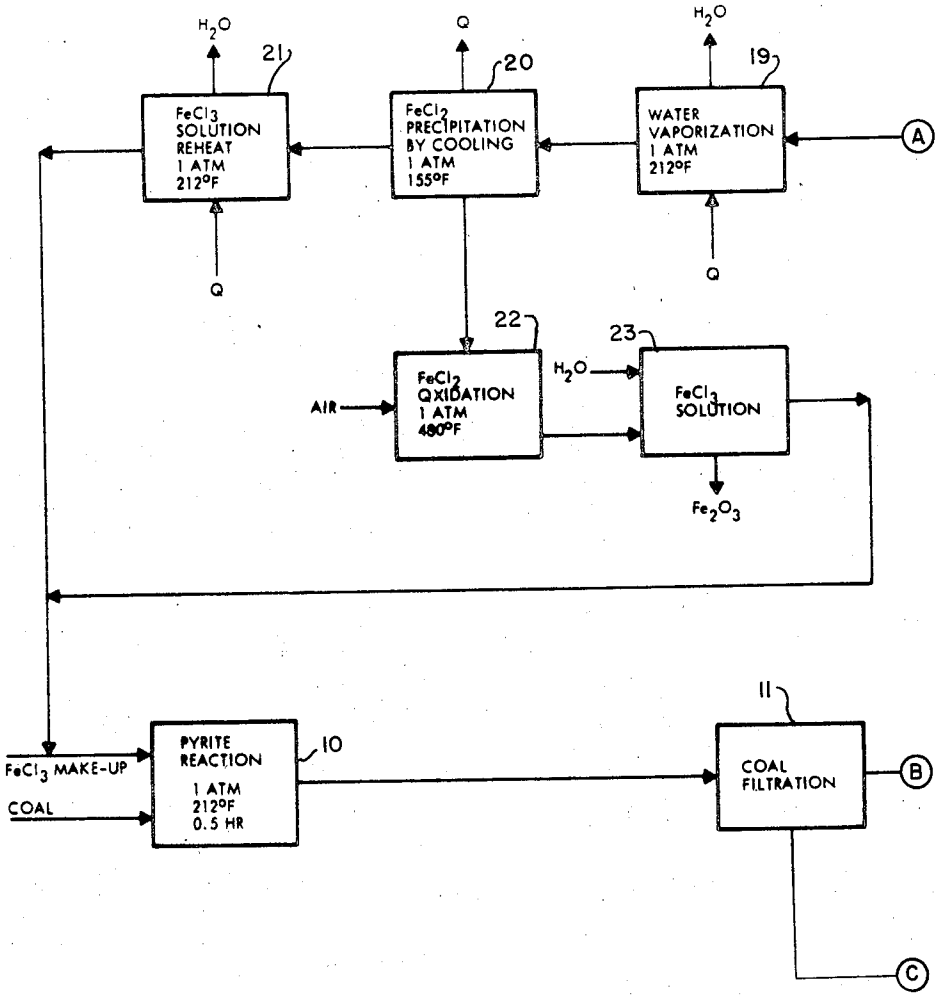
Primary Examiner—C. F. Dees

Attorney—Daniel T. Anderson et al.

[57] **ABSTRACT**

Finely divided coal or solid coal derivatives containing pyrite are reacted with a ferric ion solution; $FeCl_3$ is particularly suitable. The ferric ion is reduced to ferrous ion and free sulfur is formed. The solution is then filtered from the coal which is then washed and heat dried under low pressure. Most of the free sulfur is volatized from the coal due to the heat drying; additional free sulfur can be removed by additional washing and heat drying and/or solvent extraction techniques. At least 60 percent of the pyrite sulfur and pyrite iron is removed using the process of this invention. If desired, the ferrous chloride can be regenerated; this permits iron oxide to be recovered as a by-product.

19 Claims, 2 Drawing Figures



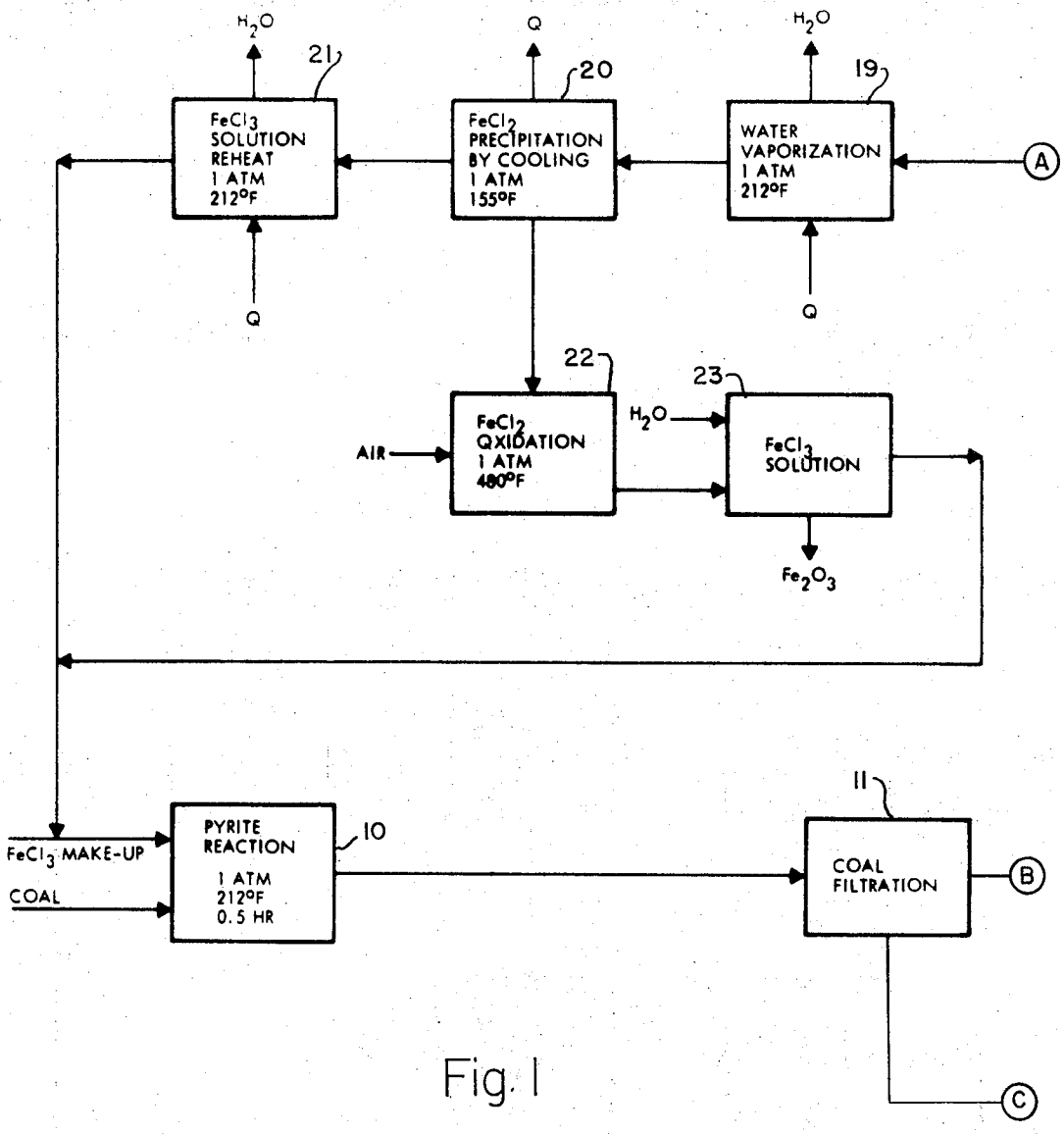


Fig. 1

Robert A. Meyers
INVENTOR.

BY

AGENT

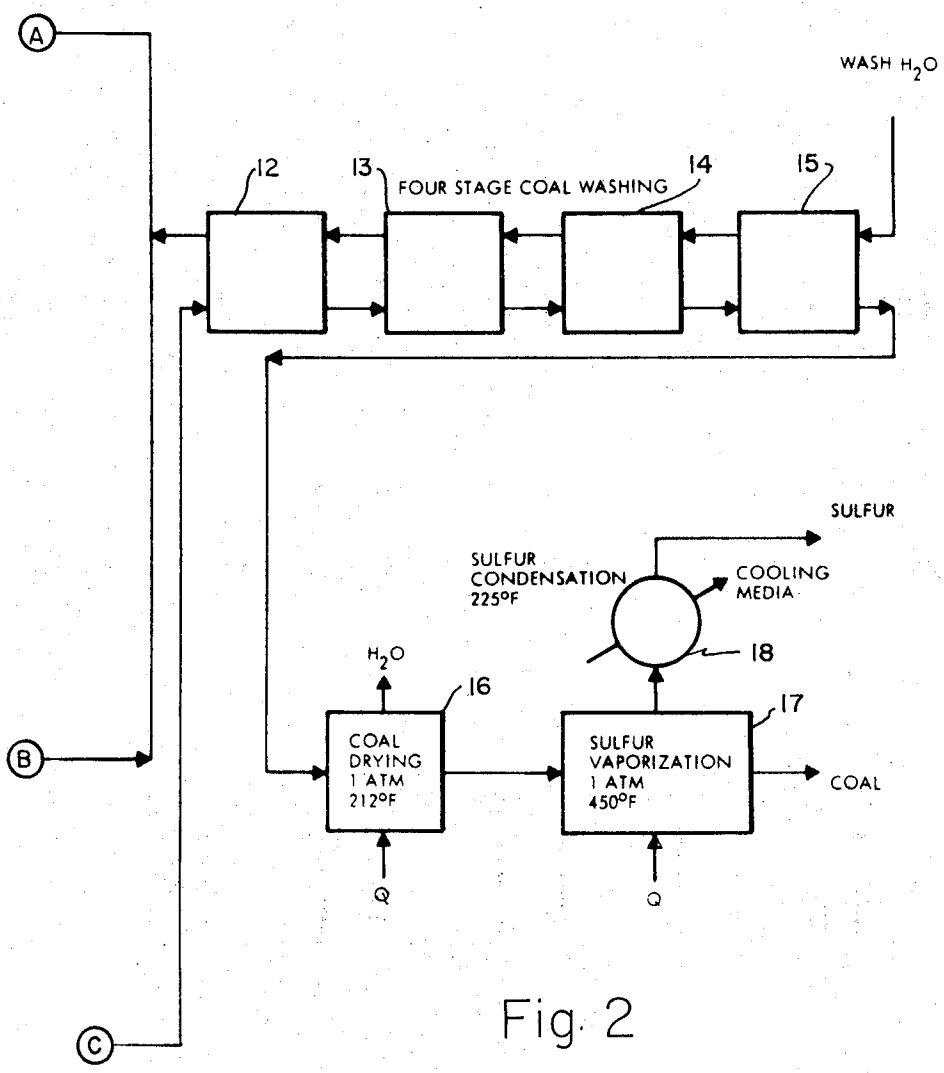


Fig. 2

Robert A. Meyers
INVENTOR.

BY

AGENT

REMOVAL OF PYRITIC SULFUR FROM COAL USING SOLUTIONS CONTAINING FERRIC IONS

This application is a continuation-in-part of application Ser. No. 116,262 filed Feb. 17, 1971, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the removal of pyritic sulfur from coal and solid coal derivatives and more specifically to the solvent extraction of sulfur from pyrites in coal using a solution containing a ferric ion.

The present use of coal in the United States is primarily for the purpose of conversion into electrical energy and thermal generating plants. One of the principal drawbacks in the use of United States mined coal is due to their sulfur contents which can range up to 5 percent.

Based on a 4 percent surface content, a 1,000,000 Kilowatt plant burns about 8,500 tons per day of coal and consequently emits 680 tons per day of sulfur dioxide. If this sulfur could be removed and converted, it would produce 900 tons of H_2SO_4 daily.

It has long been recognized that SO_2 in the atmosphere will either retard growth or kill vegetation. In addition, the potential hazard to humans appears about the same as for the vegetable kingdom.

While it is possible to remove pyritic sulfur from coal by froth flotation or washing processes; these are not selective so that a large portion of the coal is discarded along with ash and pyrite. Hence, the solution so far has been to simply burn coal having a low sulfur content. However, many pollution control districts now prohibit the use of coal having an excess of 1 percent sulfur. The result has been to severely restrict the use of many United States coals, 90 percent of which average about 2.5 percent contained sulfur. This has lead to the importation of low sulfur content fuel oils for domestic and industrial use. The crude oil reserves, which are the source of the residue, are expected to run out in 20 – 30 years while coal reserves are sufficient for several hundred years at a minimum.

It is, therefore, an object of this invention to provide a process for the reduction of sulfur, particularly pyritic sulfur in coal.

Another object is to provide a process for the recovery from coal of sulfur and sulfur compounds.

Another object is to provide a process for the recovery of iron values from coal containing pyrite.

Other objects of this invention will become apparent from the description and the diagram to follow.

According to the invention, it has been found that it is possible to react the pyrite contained in the coal with a solution containing an effective amount of ferric ion to obtain a high yield of free sulfur. Fe^{+3} ion particularly as $FeCl_3$ is preferred; other ferric salts such as acetate, sulfate, citrate, oxide, ferric ammonium sulfate, etc., may be employed. A typical reaction proceeds as follows:

$$2\ FeCl_3 + FeS_2 \xrightarrow{reflux} 3FeCl_2 + 2S.$$

The solution containing some free sulfur, ferrous chloride and any unconsumed ferric chloride is removed from the coal by filtration.

The coal is then washed and dried, preferably by heating in a vacuum; this results in the major portion of free surfur being volatized as follows: S.Coal → S + coal. If desired, a further wash, filtration and heating will remove more of the sulfur and any residual ferrous ion. One or more extractions with a suitable organic sulfur solvent such as benzene, kerosene or para cresol may be employed to further reduce the sulfur content of the coal.

Regeneration of the unused ferric chloride and ferrous chloride solution may be accomplished by first concentrating the solution by evaporating most of the water. The concentrated solution is cooled, thereby precipitating the ferrous chloride from the ferric chloride, most of the latter still remaining in solution. The precipitated ferrous chloride is air oxidized to ferric chloride and iron oxide and finally the ferric chloride is recycled and the iron oxide recovered.

Typical treatment temperatures may vary from 50° C – 110° C. Reflux times are typically one-half – 2 hours and higher. Typical coal particle sizes may vary from −200 mesh to one-half-inch pieces. Atmospheric pressure may be employed, but higher pressures can also be used.

The effective amount of the ferric ion solution employed for extraction depends on the amount of coal treated and its pyritic sulfur content, the amount of sulfur desired to be extracted, extraction times, extraction temperatures, concentration of the ferric ion in the solution, etc.

The reaction of ferric chloride and ferrous persulfide to produce free sulfur is known. However, it was unexpected that the reaction with ferric ion (e.g., $FeCl_3$) and pyrite could be carried out in a coal medium since pyrite is dispersed very finely throughout the coal matrix, and penetration of such an organic matrix with water is known to be difficult. Furthermore, the volatization of sulfur from coal is unusual since it well might be expected that the free sulfur would recombine either with iron or with the coal upon heating. It is also well known that iron pyrites may be oxidatively dissolved from the coal matrix with strong aqueous oxidizing agents such as HNO_3, H_2O_2 or HOCl. This will convert the sulfur content to sulfate, but not to free sulfur. This is the basis for chemical analysis of the pyritic sulfur content of coal; however, such strong oxidizing agents also extensively oxidize the organic coal matrix. By contrast, ferric salts are almost totally selective in the sense that the organic coal matrix is undisturbed. Hence, ferric salts, but not HNO_3, H_2O_2 or HOCl, provide an economical route to the removal of pyrites from coal.

Coals which may be employed in this invention include those which are considered as coals in the popular or commercial sense, such as anthracites, charcoal, coke, bituminous coals, lignites, etc. In addition, chars from hydrocracked coals and middlings are all capable of being refined by the extraction process of this invention.

The invention will be understood by reference to FIGS. **1** and **2** in which ferric chloride make-up solution and coal are fed into a pyrite reactor **10** maintained at atmospheric pressure and about 212° F. Pyrite (FeS_2) is extracted from the coal, and the slurry containing unreacted ferric chloride, ferrous chloride, sulfur, ferrous persulfide, and the treated coal are fed to a coal filtration unit **11.** Vacuum disk filters in the coal filtration unit are used to separate the bulk of the iron chloride solution from the treated coal.

In the coal washing sections **12, 13, 14,** and **15,** four stages of countercurrent washing with intermediate fil-

tration steps are used to reduce the residual chloride content of the coal to less than about 100 ppm. A suitable residence time of the coal in each of the washing stages is about 15 minutes; rotary vacuum disk filters are used to separate the coal and wash the solution between washing stages.

The washed coal is then fed to a coal drying unit **16** where rotary steam tube dryers are employed to remove the residual water from the washed coal, this operation being carried out at atmospheric pressure and about 212° F. The heated dry coal is then forwarded to a sulfur vaporization unit **17** where free sulfur, which was produced in the extraction reaction in reactor **10,** is vaporized at atmospheric pressure and a temperature of about 450° F or under reduced pressure (30 min.) and at 250° – 350° F. The vaporized sulfur is removed by nitrogen gas into a sulfur condensation unit **18** and cooled to about 225° F causing it to condense. The sulfur vapor is then passed to a recovery unit as bright sulfur. The treated coal with reduced pyrite content is then forwarded for use.

In the ferric chloride regeneration stage, the filtrate from the coal filtration unit **11** is passed to a thickener unit **19** where water is vaporized from the solution at atmospheric pressure and about 212° F. The concentrated solution is then passed to a precipitation unit **20** where ferrous chloride is precipitated by cooling the solution to 155° F at atmospheric pressure. Unreacted ferric chloride solution from the precipitation unit **20** is heated in a reheater **21** and then combined with ferric chloride make-up for feeding to the reactor **10.**

The ferrous chloride precipitate, which has been separated by filtration from the ferric chloride solution in reactor **20,** is transferred to an air oxidation furnace **22** where it is reoxidized back to ferric chloride and iron oxide, the reaction equation being

$$FeCl_2 + 3/2\ O_2 \rightarrow 4FeCl_3 + Fe_2O_3.$$

The reaction employs air and is carried out at atmospheric pressure at about 480° F.

The oxidized precipitate (ferric chloride and iron oxide) is then transferred to a solution-filtration unit **23** where the soluble ferric chloride is then separated from the insoluble iron oxide by dissolving in water. The ferric chloride solution is recycled to the ferric chloride make-up solution for use in reactor **10.** The iron oxide is filtered from the ferric chloride solution and may be recovered as a byproduct of the process.

Typical coals which may be employed in the process include Missouri, Lower Freeport, Bevier, Indiana No. V, and Pittsburgh. These coals contain sulfur forms as shown in Table 1 when freshly mined. As they stand exposed to air, small amounts of sulfate sulfur are formed from the pyrite content.

TABLE 1

SULFUR COMPOUNDS IN COAL

	Bevier	Lower Freeport	Indiana No. V	Pittsburgh
Pyritic S %	1.7–2.3	2.2–3.8	1.5–1.8	0.5–1.7
Organic S %	1.7–2.3	0.4–0.8	1.5–1.8	0.5–0.7
Total S %	3.5–4.5	3.0–4.2	3.0–3.5	1.2–2.2

Table 2 shows the original pyritic sulfur content of the Missouri and Lower Freeport coals and the reduction in sulfur content due to treatment of $FeCl_3$.

It will be observed that a marked reduction in pyritic sulfur occurs after only a single treatment with $FeCl_3$ followed by a water washing and drying.

Table 3 shows the effect of employing an organic solvent to remove the free sulfur which remains following the $FeCl_3$ and water washing treatment.

TABLE 2

$FeCl_3$ extraction data

Coal	Sample number	Wt. coal, g. [3]	Vol. $FeCl_2$	Molarity, $FeCl_3$	2 Fe + 3 pyritic Fe	Reflux (90° C.) time (hrs.)	Wt. loss after washing and drying, wt. percent [5]	Sulfur Eschka, wt. percent [1]	Wt percent Fe in coal [2]	Pyritic sulfur removed, percent
Missouri untreated (mesh size −200)								4.75	1.65	
Missouri (mesh size −200)	1	40	200	0.5	3.9/1	16			0.22	
									0.17	
Missouri (mesh size −200)	2	50	500	0.3	5/1	2	−9.1	4.18	0.86	−31
								4.17	0.84	
Missouri (mesh size −200)	3	30	500	0.5	13/1	20	+2.0	3.67	0.19	−62
								3.65	0.19	
Lower Freeport U. (Mesh size −14)								3.54	3.16	
								3.99	3.52	
Lower freeport (mesh size −14)	4	50	730	0.5	6/1	[3] 2	[4] −14.1	1.99	1.10	−70

[1] ASTM D271.
[2] Bureau of Mines procedure and Standard Methods of Chemical Analysis, Furman, volume 1, page 542.
[3] Remarks: Residue removed from condenser was analysed by electron microprobe as follows: Fe, S, Si, O, C were major constituents; Ca, Cl, Al were trace.
[4] Yellow crystals formed; Hg spot test for free S was positive.
[5] Sample 2 was washed once with 250 cc. hot water and dried 24 hours in a 90° C. vacuum oven. Samples 3 and 4 were washed twice with 250 cc. hot water and dried 72 hours at 90° C. in a vacuum oven.

TABLE 3

Solvent extraction data following $FeCl_3$ treatment and water wash

Sample number	Solvent	Extraction procedure	Wt. loss, gain	Sulfur concentration Eschka	Percent extraction
1	Benzene, 5-10 min	3 hot (80° C.) 100 cc. washings		3.22	81
				3.21	
2	do	do	0	3.62	60
				3.61	
3a	do	do	+2	3.06	89
				3.03	
3b	p-Cresol, 5-10 min	½ hr. (200° C.) reflux	−13.6%	2.81	110
				2.18	
4	Benzene, 5-10 min	3 hot (80° C.) 100 cc. washings		2.23	74
				1.77	

From the data in Table 3, it appears that the organic solvent treatment causes a major portion of the pyritic sulfur to be extracted; also, use of para cresol appears to result in extraction of organic as well as pyritic bound sulfur. While the efficiencies shown range from 60 percent to at least 89 percent, this efficiency range can be changed by altering such factors as wash times, particle size, amounts and concentrations of $FeCl_3$ and solvents, ferric salt treatment, reflux temperature, etc.

Table 4 shows the effect of $FeCl_3$ extraction on various coals employing reaction conditions similar to Table 2. The table shows that 72 – 93 percent of the pyritic sulfur content may be removed in 2 hours by 0.5 M $FeCl_3$ solution from a wide variety of coals. Further, the process was applicable to all the coals, and in the case of Indiana No. V, the extraction efficiency was excellent.

TABLE 4

PYRITIC SULFUR REMOVAL DATA

Coal[a]	Total Sulfur Removed %	Pyritic Sulfur Removed %	Total Sulfur Before %	Total Sulfur After %
Lower Freeport	48	75	3.87	2.01
Lower Freeport	64	72	3.40	1.23
Bevier	36	72	4.60	2.94
Indiana No. V	51	93	3.28	1.67
Pittsburgh	39	78	1.81	1.10

All coals were – 14 mesh except Bevier which was – 200 mesh

The process of this invention is extremely efficient in that at least 60 percent of the pyrite sulfur is extracted and the iron employed for extraction is easily recovered (about 85–90 percent) and may be reused. Furthermore, iron removal is facilitated since the iron contained in the $FeCl_3$ extraction solution and the iron in the pyrite are indistinguishable; hence, no special techniques are required to separate different metals from the wash-extraction operation if metal recycling is desired.

In addition, the process is simple in that no high temperatures, pressures or catalysts are required.

Finally, the extraction with $FeCl_3$ does not produce an interaction with the organic coal matrix; this permits substantially all of the coal to be utilized as low sulfur fuel.

What is claimed is

1. A process for reducing the pyritic sulfur content of coal which comprises reacting the coal with an effective amount of an aqueous solution containing Fe^{+3} ion and removing from the coal sulfur formed by the pyrite reaction.

2. A process for reducing the pyritic sulfur content of coal which comprises reacting the coal with an effective amount of an aqueous solution containing Fe^{+3} ion selected from the class consisting of $FeCl_3$ and ferric sulfate, and removing from the coal sulfur formed by the pyrite reaction.

3. A process for reducing the pyritic sulfur content of coal which comprises:

reacting the coal with an effective amount of an aqueous solution containing Fe^{+3} ion;

removing from the coal sulfur formed by the pyrite reaction using the following steps:

separating the said solution from the treated coal;

washing the coal and separating the wash solution from the treated coal; and

drying the coal to volatize the free sulfur contained therein.

4. The process of claim **3** in which free sulfur from the volatization step is extracted with an organic solvent for sulfur selected from the class consisting of benzene, kerosene and p-cresol.

5. The process of claim **3** in which the aqueous solution employed is selected from the class consisting of $FeCl_3$ and ferric sulfate.

6. The process of claim **3** in which the aqueous Fe^{+3} ion solution is selected from the class consisting of ferric acetate, ferric citrate, ferric oxide and ferric ammonium sulfate.

7. A process for reducing a pyritic sulfur content in coal which comprises:

reacting the coal with an effective amount of an aqueous solution containing Fe^{+3} ion and removing from the coal sulfur formed by the pyrite reaction using the following steps:

separating the said solution from the treated coal;

washing the coal and separating the wash solution from the coal; and

extracting free sulfur from the treated coal with an organic solvent for sulfur selected from the class consisting of benzene, kerosene and p-cresol.

8. The process of claim **7** in which the aqueous solution employed is selected from the class consisting of $FeCl_3$ and ferric sulfate.

9. The process of claim **7** in which the aqueous Fe^{+3} ion solution is selected from the class consisting of ferric acetate, ferric citrate, ferric oxide and ferric ammonium sulfate.

10. A process for reducing the pyritic sulfur content in coal which comprises:

reacting the coal with an effective amount of an aqueous solution of Fe^{+3} ion, and removing from the coal sulfur formed by the pyrite reaction using the following steps:

separating the said solution from the treated coal;

washing the coal and separating the wash solution from the treated coal;

drying the coal to volatize the free sulfur contained therein; and

oxidizing the separated solution to ferric ion.

11. The process of claim **10** in which the oxidizing step is carried out with a gas selected from the class consisting of air and oxygen.

12. The process of claim **10** in which the aqueous solution employed is selected from the class consisting of $FeCl_3$ and ferric sulfate.

13. The process of claim **10** in which the aqueous Fe^{+3} ion solution is selected from the class consisting of ferric acetate, ferric citrate, ferric oxide and ferric ammonium sulfate.

14. A process for reducing the pyritic sulfur content in coal which comprises:

reacting the coal with an effective amount of an aqueous solution Fe^{+3} ion, and removing from the coal sulfur formed by the pyrite reaction employing the following steps:

separating the said solution from the treated coal;

washing the coal and separating the wash solution from the treated coal;

drying the coal to volatize the free sulfur contained therein;

extracting additional free sulfur from the treated coal with an organic solvent for sulfur selected from the class consisting of benzene, kerosene and p-cresol;

concentrating the ferrous ion solution by evaporating some of the water;
cooling the solution thereby precipitating ferrous ion;
separating the ferrous ion precipitate from the solution containing ferric ion;
oxidizing the ferrous ion precipitate to ferric ion and iron oxide;
dissolving the ferric ion in water; and
separating the iron oxide from the aqueous solution containing ferric ion.

15. The process of claim **14** in which the aqueous solution employed is selected from the class consisting of $FeCl_3$ and ferric sulfate.

16. The process of claim **14** in which the aqueous Fe^{+3} ion solution is selected from the class consisting of ferric acetate, ferric citrate, ferric oxide and ferric ammonium sulfate.

17. A process for reducing the pyritic sulfur content in coal which comprises:
reacting the coal with an effective amount of an aqueous solution of Fe^{+3} ion and removing from the coal sulfur formed by the pyrite reaction using the following steps:
separating the said solution from the treated coal;
washing the coal and separating the wash solution from the treated coal;
drying the coal to volatize the free sulfur contained therein;
concentrating ferrous ion solution by evaporating some of the water;
cooling the solution therein by precipitating the ferrous ion;
separating the ferrous ion precipitate from the solution containing ferric ion;
air oxidizing the separated solution to ferric ion and iron oxide;
dissolving the ferric ion in water; and
separating the iron oxide from the aqueous solution containing ferric ion.

18. The process of claim **17** in which the aqueous solution employed is selected from the class consisting of $FeCl_3$ and ferric sulfate.

19. The process of claim **17** in which the aqueous Fe^{+3} ion solution is selected from the class consisting of ferric acetate, ferric citrate, ferric oxide, and ferric ammonium sulfate.

* * * * *