

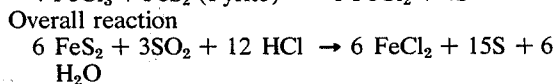
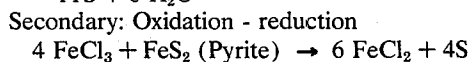
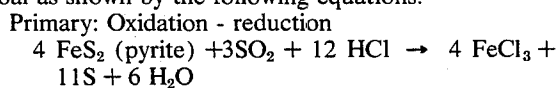
- [54] **REMOVAL OF PYRITIC SULFUR FROM COAL**
- [75] Inventor: **Robert A. Meyers**, Encino, Calif.
- [73] Assignee: **TRW Inc.**, Redondo Beach, Calif.
- [22] Filed: **July 19, 1971**
- [21] Appl. No.: **164,006**
- [52] **U.S. Cl.**..... **44/1 R; 201/17; 208/8; 423/567**
- [51] **Int. Cl.²** **C10L 9/00; C10B 17/00; C10B 57/00**
- [58] **Field of Search**..... **44/1 R, 1 B; 23/224, 226, 23/225 R, 209.9; 208/8; 201/17**

- [56] **References Cited**
UNITED STATES PATENTS
 2,057,486 10/1936 Higgins 201/17 X
 2,739,105 3/1956 Ford et al. 201/17 X

Primary Examiner—Carl F. Dees
Attorney, Agent, or Firm—Willie Krawitz; Daniel T. Anderson; Alan D. Akers

- [57] **ABSTRACT**
 Finely divided coal or coal derivatives, containing py-

rite, are reacted with sulfurous acid (the oxidizing agent); if desired, HCl may also be used to improve the reaction efficiency to remove pyritic sulfur from coal as shown by the following equations:



The solution containing ferrous chloride and unreacted sulfurous acid is then filtered from the coal which is then washed and heat dried under low pressure. Most of the free sulfur is volatilized 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. If desired, the ferrous chloride can be oxidized to ferric oxide and hydrochloric acid. The hydrochloric acid may be recycled and the iron oxide used for production of steel or discarded.

6 Claims, No Drawings

REMOVAL OF PYRITIC SULFUR FROM COAL

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 sulfurous acid.

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 high sulfur contents which can range up to 5 percent.

Based on a 4 percent sulfur content, a one million kilowatt plant burns about 8,500 tons per day of coal and consequently emits 6 tons per day of sulfur dioxide. If this sulfur could be removed and converted, it would produce 900 tons of H₂SO₄ daily.

It has long been recognized that SO₂ 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, the selectivity is poor; hence, a large portion of the coal is discarded along with ash and pyrite. Consequently, 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 led to the importation of low sulfur content fuel oils for domestic and industrial use.

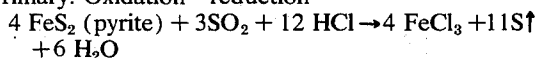
It is, therefore, an object of this invention to provide a process for the reduction of sulfur, particularly pyritic sulfur in coal.

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

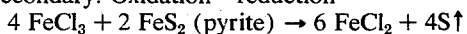
Other objects of this invention will become apparent from the description to follow.

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 sulfurous acid. A typical reaction proceeds substantially as follows:

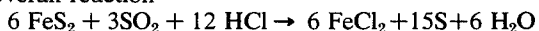
Primary: Oxidation - reduction



Secondary: Oxidation - reduction



Overall reaction



In addition to these major reactions, it is to be assumed that a small part of the free sulfur formed initially may be further oxidized to sulfite, sulfate, thiosulfate, etc. Formation of the secondary products can be further lessened by minimizing reaction times, acid concentration and temperature.

The solution containing mainly free sulfur, ferrous chloride and any unconsumed ferric chloride and sulfurous acid is removed from the coal by filtration. The coal is then washed and dried, preferably by heating in a vacuum; this results in most of the free sulfur being volatilized. If desired, a further wash, filtration and heating will remove additional sulfur and more ferrous ion.

Finally, one or more extractions with a suitable organic sulfur solvent such as benzene, kerosene, gas oil, or para cresol at temperature of 50°C up to solvent reflux is 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 evaporating most of the water to concentrate the solution. Cooling the concentrated solution precipitates the ferrous chloride from the ferric chloride, the latter still remaining in solution. The ferrous chloride precipitate is air oxidized to ferric chloride and iron oxide; finally, the ferric chloride is recycled or sold as a byproduct and the iron oxide recovered.

Typical pyrite extraction temperatures may vary from 110°C to 140°C. Reflux times are typically ½ - 2 hours and higher. Typical coal particle sizes may vary from -200 mesh to ½ inch particles. Atmospheric pressure may be employed, but higher pressures can also be used.

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

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, solvent refined coals such as hydrocracked coal, and middlings are all capable of being refined by the extraction process of this invention.

In general, the procedure employed was to reflux an aqueous solution of sulfur dioxide and hydrochloric acid with pulverized coal. This converted the ferrous persulfide (pyrite) to ferric chloride and produced free sulfur. Additional pyrite is removed by interaction with ferric chloride. The resultant solution of ferrous chloride was then separated from the coal by filtering. Following a water wash, the coal was then heated to dryness under vacuum thereby vaporizing some of the free sulfur. Most of the remaining free sulfur in the coal was extracted with a suitable solvent such as benzene, kerosene, gas oil, or para cresol. In addition, the para cresol removes a portion of organic sulfur compounds contained in the coal. If desired, the solution containing ferrous ion can be recycled for subsequent reuse and/or oxidized to iron oxide; these products may be recovered as noted previously.

Typical coals which may be employed in the process include Lower Freeport, Bevier, Indiana No. V, and Pittsburgh. These coals contain pyritic sulfur as shown in Table 1.

TABLE 1

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

It was unexpected that the reaction with sulfur dioxide 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 an aqueous solution is known to be difficult. Furthermore, the volatilization 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, sulfur dioxide is almost totally selective in the sense that the organic coal matrix is undisturbed. Hence, sulfurous acid, but not HNO_3 , H_2O_2 or HOCl , provides an economical route to the removal of pyrites from coal.

The data in Table 2 in the following example indicates that generally use of HCl when combined with sulfurous acid improves the removal of pyritic sulfur compared to the use of sulfurous acid alone.

Also, effective pyrite removal can be achieved at 100°C reaction temperature in as little time as two hours.

Hence, the present process is selective for removal of pyrite from coal without adversely affecting the BTU content of the coal. Also, the sulfur and iron values may be recovered from the treatment process if desired.

EXAMPLE

In a typical case, aqueous sulfurous acid (10 times stoichiometric excess over pyrite content of coal), hydrochloric acid (where designated), and pulverized coal were introduced into a glass aerosol stirred bomb. The mixture was heated for the temperature and time shown; this caused a pressure rise to about 20–30 psig. The mixture was then cooled. The coal was then filtered from the aqueous phase and washed with hot water to remove residual acid. Some of the samples were slurried with benzene for 20 mins. and then filtered again. All samples were dried in a vacuum oven at $160^\circ\text{C}/30$ min. to constant wt. (ca 24 hrs). Elemental sulfur was distilled out and collected on the oven window and in the pump trap and lines.

Table 2 shows the effect on -14 mesh Indiana No. V containing pyrite, after treatment with a sulfurous acid solution.

4. A process for reducing the pyrite sulfur content in coal which comprises:

reacting the coal containing FeS_2 with an effective amount of an aqueous solution of sulfurous acid at about 100°C to 140°C and hydrochloric acid to form free sulfur in the coal matrix;

filtering the solution from the coal;

washing the coal; and

removing the free sulfur from the coal.

5. A process for reducing the pyrite sulfur content in coal which comprises:

reacting the coal containing FeS_2 with an effective amount of an aqueous solution of sulfurous acid and hydrochloric acid at about 100°C to 140°C to form free sulfur in the coal matrix;

filtering the solution from the coal;

washing the coal; and

extracting the free sulfur from the coal with an organic solvent for sulfur.

6. The process of claim 2 in which the sulfur solvent is selected from the class consisting of benzene, kerosene, gas oil, and paracresol.

7. The process of claim 2 in which the extraction temperature varies from 50°C up to solvent reflux.

8. A process for reducing the pyrite sulfur content in coal which comprises:

reacting the coal with an effective amount of an aqueous solution of sulfurous acid and hydrochloric acid at about 100°C to 140°C to form free sulfur in the coal matrix;

filtering the solution from the coal;

washing the coal; and

heat drying the coal to volatilize the free sulfur therein.

9. A process for reducing the pyrite sulfur content in coal which comprises:

reacting the coal with an effective amount of an aqueous solution of sulfurous acid and hydrochloric acid to form free sulfur in the coal matrix;

filtering the solution from the coal;

washing the coal;

extracting the free sulfur from the coal with an organic solvent for sulfur and

heat drying the coal to remove the free sulfur contained therein.

TABLE 2

Experiment No.	Temp $^\circ\text{C}$	Conc of HCl M	Conc H_2SO_3 M	Retention Time Hrs	Benzene Post Treatment	Sulfur %	Ash %	btu Content	REMOVAL OF SULFUR FROM -14 MESH INDIANA NO. V COAL ^a WITH SULFUROUS ACID			
									% Total Sulfur Removed	% Pyritic Sulfur Removed	% Ash Removed	% btu Change
1	140	3.6	0.9	20	No	3.06	7.4	13000	15	30	37	+4
2	100	3.6	0.9	20	No	2.76	7.8	12600	23	46	33	+1
3	100	3.6	0.9	20	Yes	2.69	7.5	13000	26	52	36	+4
4	100	3.6	0.9	2	No	2.69	8.2	11900	26	52	30	-5
5	100	0	0.9	2	No	2.82	8.7	12800	22	44	26	+2
6	100	0	0.9	20	Yes	3.19	8.9	12950	12	25	24	+4
7	100	0	0.9	20	No	3.53	8.9	12800	2	4	25	+2

^aStarting Indiana No. V: 3.62% total sulfur; 0.03% sulfate; 1.79% organic sulfur; 1.80% pyrite sulfur; ash content = 11.8%, heat content = 12500 btu.

I claim:

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