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Technological and economic aspects of coal biodesulfurisation

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Abstract

The sulfur found in coal is either part of the molecular coal structure (organically bound sulfur), is contained in minerals such as pyrite (FeS_2), or occurs in minor quantities in the form of sulfate and elemental sulfur. When pyrite crystals are finely distributed within the coal matrix, mechanical cleaning can only remove part of the pyrite. It can, however, be removed by microbial action requiring only mild conditions. The process involves simple equipment, almost no chemicals, but relatively long reaction times, and treatment of iron sulfate containing process water.

Different process configurations are possible, depending on the coal particle size. Coal with particle sizes of less than 0.5 mm is preferably desulfurised in slurry reactors, while lump coal (> 0.5 mm) should be treated in heaps. Investment and operating costs are estimated for different process configurations on an industrial scale.

Concerning the organically bound sulfur in coal there is up to now no promising biochemical pathway for the degradation and/or desulfurisation of such compounds.

Introduction

Fossil fuels will remain the most important resources for energy supply, since they are available in sufficient quantities even in western industrial countries. Especially coal comprises about 75% of the total world resources of fossil fuels (Ziegler 1988).

However, our environment has constantly been polluted by the combustion of fuels, coking and smelting processes. Especially the menace of acid rain is at least partly caused by the combustion of sulfur and nitrogen compounds present in the fuels, releasing sulfur dioxide and nitrogen oxides as precursors into the atmosphere. Acid deposition, if not abated, may cause lasting detrimental effects on water and soil ecosystems, agriculture, forests, and buildings.

These environmental impacts associated with the combustion of coal lead to the development of new processes to control the resulting emissions. In many countries clean coal technologies have to be applied on the basis of regulations concerning fuel quality and emission standards for dust, CO_2, SO_2 and NO_x in the flue gas.

In Germany even the use of pyrite-free coal does not allow operation of large industrial power stations (> 50 MW_{th}) without flue gas desulfurisation because of the remaining organically bound sulfur contained in German hard coal. For economic reasons the production of low-sulfur coal, i.e. low-pyrite coal, might be preferred for small-scale combustion units.

The total sulfur content of coal consists of sulfur which is part of the coal's molecular structure (organic sulfur) and inorganic sulfidic minerals, mainly pyrite (FeS_2). Depending on the particular coal involved, pyrite crystals vary in size and distribution within the coal matrix (Stach et al. 1982).

Physical cleaning processes are predominantly effective for the removal of coarse crystals, which can be separated from the coal after crushing and grinding (von der Gathen 1983).

However, depending on the coal, a considerable amount of finely distributed pyrite as well as organic sulfur can remain in and attached to the coal particles. In order to increase the removal rate of sulfur, both chemical (Meyer 1977) and microbial (Olson & Brinckmann 1986) processes have been developed. Chemical processes have the advantage of high reaction rates, but require elevated temperatures and pressures. Microbiological oxidation of pyrite takes place at ambient temperatures and atmospheric pressure, but needs relatively long reaction times.

The microbial sulfide oxidation, which has already been used successfully on a commercial scale to win metals from ores (Torma 1977; Brierley 1978; Olson & Kelly 1986) was investigated intensively for the selective solubilisation of pyrite associated with coal (Kargi 1984; Olson & Brinckmann 1986; Monticello & Finnerty 1985).

For the removal of pyritic sulfur, leaching processes using e.g. autotrophic *Thiobacillus* species were developed and already scaled up into pilot plants (Klein et al. 1988).

The statements published concerning cost effectiveness were up to that time based only on results from laboratory and small-scale test facilities.

Microbial removal of pyritic sulfur from coal

Over 30 years ago it was shown (Silvermann et al. 1961; Zarubina et al. 1959) that pyritic sulfur could be removed from coal by microbes. Recent work in this area has been directed toward process designs that might be used for the large-scale commercial use of biodepyritisation of coal and associated scale up studies (Beyer et al. 1986; Bos & Kuenen 1990; Beyer et al. 1990; Rossi 1993).

In the presence of water and oxygen, pyrite oxidises abiotically to iron(II)-sulfate and sulfuric acid (reaction 1). This reaction is comparatively slow with hydrothermal pyrites, but can be much more rapid in coal-derived pyrite.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

The released iron(II)-ion is stable under aerobic, acidic conditions. However, acidophilic iron oxidising bacteria such as *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* rapidly oxidise the iron(II)- to iron(III)-ions, and gain metabolic energy in the process. The iron(III)-ion is a good oxidant of pyritic sulfur, producing sulfate (reaction 2) or elemental sulfur (reaction 3).

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+, \quad (2)$$

$$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S. \quad (3)$$

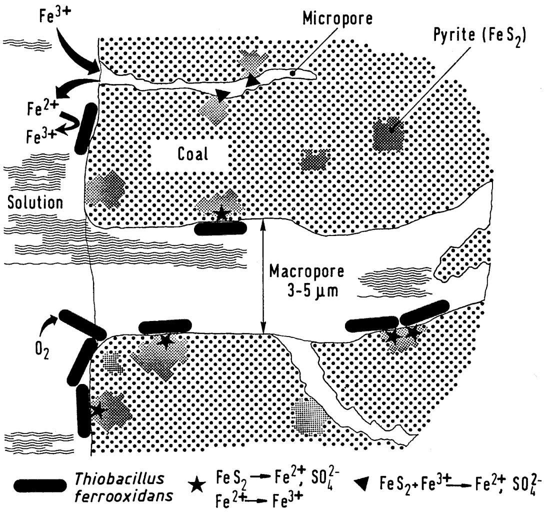

Figure 1. Bimodal Pore Structure of Coal and Pyrite Oxidation (according to Höne et al. 1987).

Under conditions similar to those in bioleaching experiments, sulfate is the main product of the abiotic reaction of iron(III) with pyrite (Boogerd et al. 1991). However, elemental sulfur is a significant product at elevated concentrations of iron(III) and is also formed during microbial depyritisation of certain coals (Beyer et al. 1987). Reaction of iron(III) with pyrite occurs at equal rates aerobically or anaerobically (Singer & Stumm 1970), the oxygen in the sulfate product is derived from water.

In addition to the 'indirect' route of microbial pyrite oxidation (reactions 2 and 3), microbial oxidation of pyrite also has a 'direct' component, whereby pyritic sulfur is enzymatically oxidised to sulfate. Several lines of evidence support the existence of the direct route:

- preferential release of sulfate over iron during the early stages of coal pyrite oxidation by pyrite oxidising bacteria,
- occurence of cell-sized corrosion pits on pyrite surfaces,
- elemental sulfur accumulation in pyrite treated by pure cultures of *L. ferrooxidans*, an organism that can oxidise iron but cannot enzymatically oxidise sulfur,
- slower kinetics of pyrite oxidation by iron(III)-ions as compared to pyrite oxidising bacteria.

The importance of the direct mechanism in microbial pyrite oxidation has guided the design of scaled up processes for biodepyritisation of coal.

Figure 1 provides a scheme combining both chemical and microbial reactions as well as the physical structure of the coal (Höne et al. 1987). Direct oxidation of pyrite by microorganisms occurs only at the outer surface of coal particles and inside its macropores (3–5 μm), where direct contact between bacteria and pyrite is possible. Pyrite inside the coal matrix, accessible to molecules via diffusion in micropores, can only be dissolved by the chemical oxidation with iron(III)-ions. In order to generate iron(III), iron(II) can only be microbially oxidised outside the micropores.

Recent basic microbiological studies on the mechanisms by which bacteria are able to attack the extremely insoluble metal sulfide minerals gave rise to speculation that a direct enzymatic attack on metal sulfides does not exist (Schippers & Sand 1997). Instead, metal sulfides are oxidatively degraded via two different chemical pathways based on the mineral property. Sphalerite, galena, or chalcopyrite, attackable by Fe(III)-ions and/or protons, are oxidised via polysulfides mainly to elemental sulfur. Pyrite, only attackable by Fe(III)-ions, is oxidised via polythionates mainly to sulfate.

Kinetic Aspects

Experiments on biodesulfurisation of coal have usually been carried out on a laboratory scale, treating slurries of finely ground coal in reaction vessels of up to a few litres in volume. Shake flask cultures are preferably used for small-scale test work, but also stirred tank reactors (Olsen et al. 1980; Huber et al. 1983), airlift reactors (Kargi & Cervoni 1983; Beier 1982; Beyer et al. 1986), pachuca tank reactors (Detz & Barvinchak 1979; Höne et al. 1987), as well as a 2-inch-pipeline loop (Rai 1985) have been reported to be suitable.

In general, most investigations have focussed on the suitability of coals, cultures, and conditions. The time course of pyrite oxidation in leaching experiments is usually described by dissolved iron or sulfate to permit calculation of the overall removal of pyrite from coal (Table 1). Calculations based on the analysis of the sulfur content of the coal before and after desulfurisation are scarce. Inspite of various experimental techniques of the different authors as well as different content and distribution of the pyrite in the coal samples, a removal of 80 to 92% of pyrite within 8 to 28 days can be achieved with a wide variety of coal qualities.

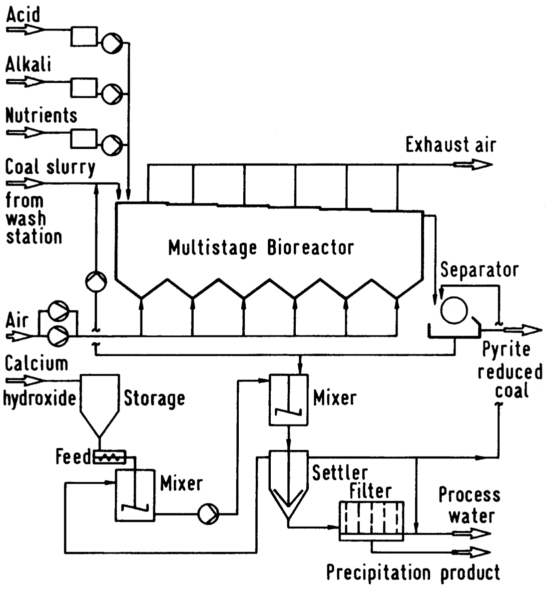

Figure 2. Process Flow Sheet of a Plant for Coal Desulfurisation in a Slurry. (according to Beyer et al. 1990).

Process features

Microbial desulfurisation can be integrated into conventional coal preparation plants either at the colliery or at a power station. Two major approaches toward large scale biodepyritisation of coal have been described: heap (percolation) leaching, and slurry leaching processes. Heap leaching is a simpler, less expensive approach than slurry leaching. The latter requires fine grinding of coal and aeration in large bioreactors. However, reaction rates are much faster in slurry reactors. Surface area limits pyrite oxidation rates in heap leaching whereas biomass, up to a point, limits rates in slurry reactors (Bos et al. 1986).

The major parameters influencing microbial pyrite oxidation are shown in Table 2. It also contains indications of the optimum conditions for high reaction rates. Under different operating conditions, the rate of pyrite oxidation may vary between 100 and 800 g of pyrite-S / ($m^3 * d$) using mixed cultures of mesophile *Thiobacillus.* Although higher rate reactions are sometimes claimed in the literature for thermophilic organisms (see Table 3), a rough estimate using data given by Kargi (1984) indicates no increased oxidation rate when using the thermophilic species *Sulfolobus acidocaldarius*.

Based on laboratory results, it is proposed to treat coal slurries on an industrial scale in large Pachuca-tank reactors. These are 3-phase slurry reactors, cylin-

Table 1. Characteristics of Coal Desulfurisation Experiments $^{a)}$. (References cited see Klein et al. 1988)

Coal quality	Pyritic sulfur %	Particle size μm	Pulp density % (w/w)	Temperature °C	Pyrite removal max./durat. %/d	Maximum pyrite oxidation rate $\frac{mgS}{L\cdot d}$	Reference
Shake Flask Experiments							
USA, Pittsburgh	1.1	149–250	20	25	90/14	40	Andrews & Maczuga (1982)
FRG, Plaßhofsbank	3.74	70–40	10	28	79/28	128	Rinder & Beier (1983)
USA, New Mexico	1.95	< 37	25	35	83/n.g.	774	Olsen et al. (1980)
USA, Ohio	4.1	< 37	25	35	77/n.g.	378	Olsen et al. (1980)
USA, Hard coal	4	74–43	32	25	90–98/8–12	371	Hoffmann et al. (1981)
USA, Hard coal blend	4.2	< 74	20	23	88/23	1218	Dugan & Apel (1978)
USA, New Mexico	2	< 37	10	35	90/10	446	Torma & Murr (1980, 1981)
UK, Wales	3	50	20	30	96/20	451	Kos et al. (1983)
Bioreactor Experiments							
USA, Illinois 2	1.9	< 74	20	28	90/16	100–200	Dets & Barvinchak (1979)
Coal refuse	10.5	147–417	3.3	28		600	Kargi (1982)
FRG, Plaßhofsbank	3.6	<500	10	30	90/14	338	Beyer et al. (1986b)
USA, UK,	0.6–2.5	<100	up to 20		80–90/9	n.g.	Huber et al. (1983)
FRG							Bos et al. (1986)
FRG, Hard coal	1.0	<500	10	25	80/14	380	Höne et al. (1987)

n.g. not given.

[a] Conditions may slightly vary concerning pH, nutrients, incubation systems and all experiments with pure or enrichment cultures containing predominantly *T. ferrooxidans*.

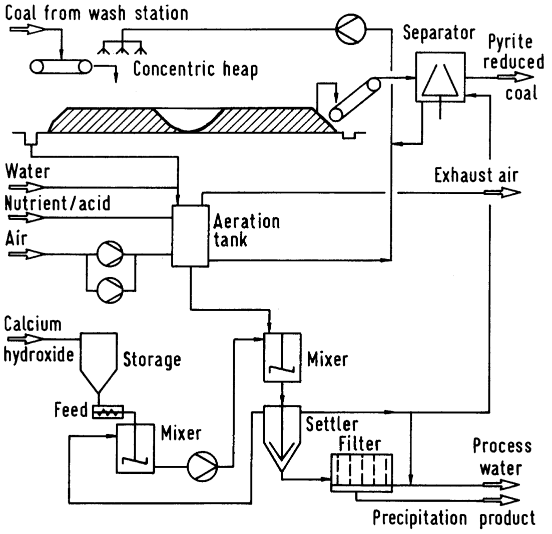

Figure 3. Process Flow Sheet of a Plant for Coal Desulfurisation in Heaps. (according to Beyer et al. 1990).

drical in cross-section with a conical bottom (Bos et al. 1986). Alternatively, large lagoons may be used (Detz & Barvinchak 1979). The various units and the layout of an industrial-scale plant for the treatment of coal slurry are shown in Figure 2. The main function of a slurry reactor is to maintain suitable growth conditions for the pyrite-oxidising microorganisms in terms of temperature, pH-value, and mass transfer. In Porto Torres, Italy, a 50 kg/h dry coal biodepyritisation pilot plant was built and operated within the framework of a joint research project with the financial support of the Commission of European Communities (Rossi 1993; Loi et al. 1994). The pilot plant employed a series of seven Pachuca reactors with a total bioreactor volume of 45 m^3. The results of this project can be summarized as follows:

- The residence time in the pilot plant required for a 90% removal of the pyrite present appeared to be by about 50% less (appr. 4 days) than suggested from shake flask experiments in the laboratory.
- The maximum pulp density which does not interfere with the first order kinetics of pyrite removal appeared to be far higher than indicated in the literature. Even almost 40% (w/v) pulp density does not reduce the specific removal rate.
- *Thiobacillus ferrooxidans* does not play a key role in the process and thus is not an appropriate model organism. Mixed cultures also containing *Leptospirillum ferrooxidans* seem to be far more

Table 2. Influence of Important Process Parameters on Microbial Desulfurisation of coal. (References cited see Klein et al. 1988)

Process Parameter	Influence on	Optimum[a]	Reference
Bioreactor			
Type	Mixing Mass transfer O_2-, CO_2-supply Mechanical shear stress	Pachuca tank	Detz & Barvinchak (1979) Kargi & Cervoni (1983) Höne et al. (1987) Huber et al. (1984a, b)
Operation	Efficiency	Plug flow multi-stage	Detz & Barvinchak (1979) Huber et al. (1983)
Coal			
Quality	Pyrite -concentration -distribution -crystal size	Pyrite crystals of small size but accessible for microorganisms	Hoffmann et al. (1981) Andrews & Maczuga (1984)
Pulp density	Substrate concentration Mixing Mechanical shear stress	20–30% (w/v)	Olsen et al. (1980) Detz & Barvinchak (1979) Beyer et al. (1986a) Kargi & Robinson (1982)
Particle size	Pyrite accessibility Mixing Mechanical shear stress	Powder coal <0.5 mm	Olsen et al. (1980) Höne et al. (1987)
Microorganisms			
Concentration/ species	Growth rate Pyrite oxidation rate	Mixed culture, enriched from coal relevant	Detz & Barvinchak (1979) Andrews & Maczuga (1982) Beyer et al. (1986a) habitats, > 10^8 cells/mL
Reaction Conditions			
Temperature	Bacterial activity Rate of chemical pyrite oxidation Oxygen/carbon dioxide solubility	*Thiobacillus* (30–35 °C) *Sulfolobus* (70–75 °C)	Karaivka et al. (1977) Kargi (1982) Olsen et al. (1980) Rinder & Beier (1982) Beyer et al. (1986a)
pH	Precipitation of jarosite Bacterial activity	pH 1.8	Bos et al. (1986)
Nutrients	Bacterial activity Precipitation of jarosite	N-, P-alimentation	Hoffmann et al. (1981) Kos et al. (1983)
O_2-, CO_2-supply	Bacterial activity	> 10% Saturation	Huber et al. (1984b) Myerson (1981)

[a] to obtain maximum pyrite oxidation rate.

Table 3. Characteristics of Coal Desulfurisation Experiments with Thermophiles. (References cited see Klein et al. 1988)

Coal Quality	Pyritic Sulfur %	Particle Size μm	Pulp Density %	Temper-ature/ Strain °C	Pyrite Removal max./durat. %/d	Maximum Pyrite Oxidation Rate $\frac{\text{mg S}}{\text{L} \cdot \text{d}}$	Reference
USA, Clarion 4-A	1.8	<200	5	70/S	n.g.	300	Murphy et al. (1985)
USA, Hard coal	2.1	104–147	10	75/S	76/16	74.4	Kargin & Robinson (1982a, b)
Coal refuse	10.5	104–147	10	75/S	n.g.	374	Kargin & Robinson (1982a, b)
USA, Ohio	4[b]	< 38	25	55/T	n.g.	2166	Murr & Metha (1982)
Lignite	1.5	53–177	10	50/T	90/25	n.g.	Gökcay & Yurteri (1983)

n.g. not given.
S *Sulfolubus acidocaldarius*.
T thermophile *Thiobacillus*-like species.
[a] Conditions slightly vary concerning pH, nutrients, and incubation systems.
[b] estimated from Olsen et al. (1980).

important in bacterial leaching of sulfidic minerals.

The microbial desulfurisation of lump coal is described to be performed similarly to the microbial leaching of metals from low grade ores (Beier 1985; Beyer 1987; Andrews et al. 1992; Hyman et al. 1990; Sharp 1992). An acidic liquid, containing bacteria, is percolated through the stored coal. The coal can be stacked either in an above-ground heap or in a ditch. Both proper liquid and gas mass-transfer are needed to maintain suitable conditions for microbial pyrite oxidation. In comparison to slurry processes the possibilities of controlling the key reaction conditions are limited. In particular, the particle size distribution of the coal needs to be considered with respect to the accessible surface for microbial and acid attack as well as with respect to the formation of blockages which may inhibit percolation. To remove significant amounts of sulfur from lump coal, reaction times are measured in months, e.g. the pyrite of a 23 ton heap of run-of-mine stoker sized ($<$ 5 cm) coal was removed after one year of leaching to approximately 50% (Sharp 1992). A schema of a possible industrial scale installation is shown in Figure 3.

Economic aspects of biodesulfurisation of coal

An industrial-scale commercial operation of coal biodesulfurisation has not yet been performed. Consequently, published statements concerning cost-effectiveness are based on results from lab-scale and pilot-scale tests. The use of *Thiobacillus ferrooxidans* and *Sulfolobus acidocaldarius* is proposed. Typical process features have already been described.

The plant layout is determined largely by the long residence time required. Large reactors are needed. In an American study (Detz & Barvinchak 1979) a plant with a throughput of 8000 t/d of coal was designed. Using *Thiobacillus ferrooxidans*, a 320 m square and 6 m deep lagoon was proposed as reactor, resulting in a volume of more than 600.000 m^3.

Keeping operating conditions such as pH-level, temperature, oxygen concentration, mixing and slurry stabilisation under control in reactors of such dimensions is regarded by many experts as impractical. Nevertheless, the investment for such an installation would be relatively low. For *Thiobacillus ferrooxidans* a range of operating temperatures between 20–28 °C is quoted. The heat liberated during the desulfurisation process is assumed to keep the slurry warm. To avoid overheating, which could mean a sharp decrease of the microorganism's activity, heat may have to be removed. When using *Sulfolobus acidocaldarius*, an operating temperature between 60 and 80 °C is required leading to an additional heat demand. The operating costs are calculated as about DM 27 per tonne of coal.

In a study by the University of Delft an annual throughput of 100.000 ton (275 t/d) was taken as a basis (Bos et al. 1986). Since the reaction time was estimated to be only 9 days (compared to 28 d in the American study), the necessary reactor volume can be kept substantially smaller resulting in a total volume of

Table 4. Cost Estimation for Microbial Pyrite Removal from Coal on an Industrial Scale

Process	slurry 28 °C *Thiobacillus ferrooxidans*	slurry 30 °C *Thiobacillus ferrooxidans*	slurry 70 °C *Sulfolobus acidocaldarius*	heap *Thiobacillus ferrooxidans*	slurry 30 °C *Thiobacillus ferrooxidans*	slurry 30 °C *Thiobacillus ferrooxidans*	
Reference	Detz & Barvinshak (1979)	Bos et al. (1986)	Biesert et al. (1987)	Beier (1987)	Beyer et al. (1990)	Loi et al. (1994)	
Coal throughput	8000	275	550	420	300	300	t/d
Particle size	< 74	< 100		< 50000	< 500	< 60	μm
Required total reactor volume	600000	12500	19000–43000		14000	14000	m^3
Required area				30000			m^2
Concentration of							
pyrite	2	0.5	0.8–1.6	0.6	1	2	%
Coal	20	20	20		20	20–40	% (w/v)
Trickling				241.250			m^3/d
Residence time	18	9	10–22	28	10	5	d
Pyrite removal	90	90	60–90	82	80	90	%
Specific costs							
Investment	38	100–130	24–45	70	210	210	DM/t*a
Operation[a)]	27	35–53	84–115	54	121	80	DM/t

[a)] Including utilities, personnel and capital costs.

12.500 m^3. The estimated operation costs range from DM 35 to DM 53 per tonne of coal.

An annual capacity of 200.000 t of coal were used for estimation of investment and operation plant costs in a Swedish study (Biesert et al. 1987), proposing *Sulfolobus acidocaldarius* at a process temperature of 70 °C. The overall costs were calculated to DM 84–115 per tonne of coal.

In a German study (Beier 1987) two different process concepts for pyrite removal using the percolation principle were investigated. The annual coal throughput is approx. 150.000 t corresponding to 422 t/d. For the leaching process in a heap, operating costs of DM 54 per tonne of coal were calculated.

In a detailed German feasibility study (Beyer et al. 1990) within the framework of the above mentioned joint research project (Rossi 1993; Loi et al. 1994), about DM 120 per tonne of coal were calculated as overall operation costs for a slurry reactor plant with a throughput of 300 t/d of coal and a residence time of 10 days. These data could be confirmed by the pilot plant operation at Porto Torres where total costs of DM 80 per tonne of dry coal but based on a residence time of only 5 days were calculated for a plant with an annual capacity of 100.000 t of coal (Anonymous 1994). For comparison the essential data of these five studies are summarized in Table 4.

Conclusion

The removal of sulfidic minerals (pyrite and other metal sulfides) from a large variety of coals is a technically feasible process. Nevertheless, the economics of the technology are not (yet) favourable, mainly due to the high energy need of the reactor systems.

Although variants of the coal desulfurisation process using the combination of initial attack of the pyrite and froth flotation or oil agglomeration give rise to substantial sulfur removal, they are at present not of economic interest.

The latest scientific findings that a direct enzymatic attack on metal sulfides does not exist, but a chemical pathway by which pyrite is oxidised via polythionates mainly to sulfate (Schippers & Sand 1997), may lead to new possibilities for improvement of desulfurisation rates, e.g. by quantitative oxidising the sulfur moiety to sulfate.

Significant removal of organic sulfur from coal has not been demonstrated up to date and future research in this area is not deemed practical.

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