The Microbial Desulfurization of Coal

Giovanni Rossi

Abstract The chemical structure of coal macerals is usually characterized by the presence of inorganic and organic sulfur. Inorganic sulfur consists mostly of iron sulfides, the so-called "pyritic sulfur," whereas organic sulfur is covalently bound to the carbon atoms of the coal macromolecule. Comminution of coal to sizes that liberate the iron sulfide grains makes their removal with mineral beneficiation processes theoretically possible, but practically profitless. Microbial removal of pyritic sulfur has been extensively investigated over the last 50 years and the very promising results obtained have encouraged the design and construction of a semi-commercial pilot plant in the framework of Project JOULE 0039 funded by the European Commission. The results of the 1-year operation of this plant are reported here, the most significant being the 90 % pyrite removal achieved in five stirred tank bioreactors operating with a 40 % solids suspension and the pyritic iron solubilization rate of 36 mg dm^{-3} h^{-1}. Taking into account the very high price of the kWh in Italy, a rough estimate of the overall costs is in the range from 25 to 30 € per tonne of dry coal. So far the development of a microbial process for organic sulfur removal has shown to be much more difficult and less successful, although significant progress in laboratory research is reported.

Abbreviations

C.E.C	Commission of European Communities
DBT	Dibenzothiophene
D.M.T	Deutsche Montan Technologie
E.C	European Community
E.N.I	Ente Nazionale Idrocarburi
EPS	Extracellular polymer substance
EU	European Union
m.o.g	Mesh-of-grind

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1 Chemical and Physical Occurrence of Sulfur in Coal

Much work has been carried out by researchers worldwide to elucidate the chemical structure of the so-called "coal macerals" which is the name commonly given by petrographers to the complex organic materials occurring in coal in various petrographic types. This research—mostly related to coal liquefaction— was (and probably still is) aimed mainly at the identification of the macromole- cules forming the macerals, also with a view to characterizing the form of the foreign matter contained therein, with special regard to sulfur.

Thus, there is currently complete consensus that sulfur occurs in coal in two forms: "inorganic" or "pyritic" and "organic" sulfur. Actually, minor amounts of sulfur can sometimes occur as sulfate sulfur as the result of oxidation of the inorganic sulfur, or even as elemental sulfur [5, 24].

The inorganic sulfur occurs mainly in the form of iron sulfides [47], by far the most frequent ones being pyrite and marcasite (altogether >90 %). An exhaustive review on the compounds of iron and sulfur can be profitably consulted [59]. According to a recent publication [22], less than 0.05 % of total sulfur in coal is present as sulfates. total sulfur and sulfur form distribution is often variable [11]. However, The possible compounds that can be formed by sulfur and iron are shown in Table 1 [59, 61–63]. They are crystalline or microcrystalline and can occur variously aggregated in coal. Pyrite in coal can be found either as macro- scopic occurrences (which can be detected with the naked eye) or microscopic forms (which can only be observed under an optical microscope). The most common forms of macroscopic pyrite are the so-called "sulfur balls" or nodules, roughly spherical in shape, which can range in size from a few millimeters to some decimeters, lenses with thicknesses ranging from a few millimeters to several centimeters and up to several decimeters in lateral extent, and veins with variable thickness and extent. The most common forms of microscopic pyrite are (i) finely disseminated pyrite grains (Fig. 1) called euhedral when they are well-formed crystals with sharp, easily recognized faces; (ii) clusters of fine-grained pyrite, called "framboids" (Fig. 2) from the French word *framboise* for raspberry; and

Table 1 Iron sulfides occurring in coals

Name	Composition	Fe (% by mass)	Fe-to-S ratio	Crystal system	Properties
Mackinawite	FeS	63.53	1.742	Tetragonal	Metastable material
Cubic FeS	FeS	63.53	1.742	Cubic	Highly unstable phase precursor
Troilite	FeS	63.53	1.742	Hexagonal	Stoichiometric end member of the $Fe_{1-x}S$ group
Pyrrhotite	$Fe_{1-x}S$ approximately Fe_7S_8 $x > 0.2$	60.38	1.524	Monoclinic	Nonstoichiometric stable group, approximately F_7S_8
Pyrrhotite	$Fe_{1-x}S$ approximately $Fe_{10}S_{11}$ $x > 0.2$	61.29	1.583	Hexagonal	Nonstoichiometric stable group, approxinately $F_{10}S_{11}$
Smythite	Fe_9S_{11}	58.76	1.425	Hexagonal	Metastable phase related to the $Fe_{1-x}S$ group
Greigite	Fe_3S_4	56.64	1.306	Cubic	Metastable $Fe^{III}Fe^{II}$ sulfide; the thiospinel of iron
Pyrite	FeS_2	46.55	0.871	Cubic	Stable iron (II) disulfide known as "fool's gold"
Marcasite	FeS_2	46.55	0.871	Orthorhombic	Metastable iron (II) disulfide

Adapted with permission from Rickard and Luther [59], Copyright 2007 American Chemical Society
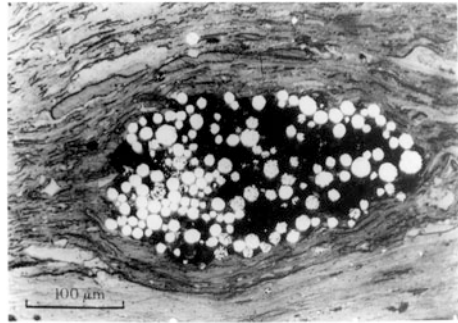

Fig. 1 Micrograph of pyrite grains (*white areas*) in coal matrix. Reflected light, oil immersion
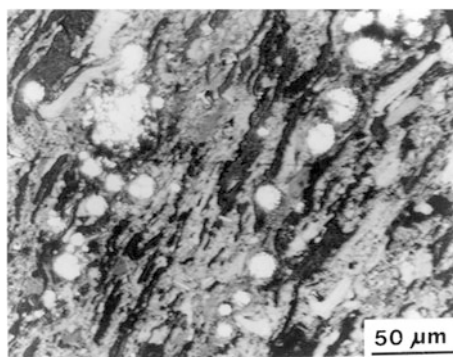
(iii) veinlets (Fig. 3) a few micrometers thick with length in the micrometers range. Excellent descriptions can be found in the literature [24, 52, 71, 80].

The organic sulfur is combined with the coal substance. Organic sulfur atoms may be covalently bound to the atoms of the carbon matrix as thiols, sulfides, disulfides, thiopyrones ([21]; cited by [11]), and complex thiophenic ring systems; several coals contain aromatic heterocyclic compounds with the C–S bond; typical of these compounds seems to be dibenzothiophene (DBT [33, 46]). Thioether bridges [81] have also been shown to exist. According to Ghosh and Prelas [22]

Fig. 2 Micrograph of
framboidal pyrite (white
areas) in coal matrix.
Reflected light, oil immersion

Fig. 3 Micrograph of pyrite
veinlet (*white areas*) in coal
matrix. Reflected light, oil
immersion
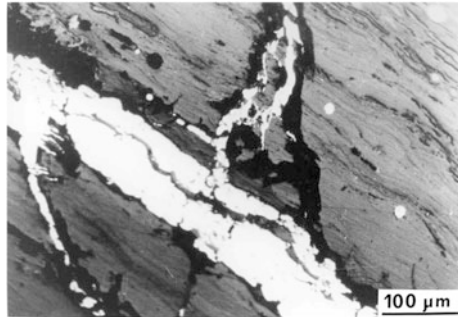
sulfur in coals ranges from less than 1 % (low sulfur coals) to about 7 % (high sulfur coals) and organic sulfur ranges from 30 to 70 % of the total sulfur [5]. Figure 4 (modified and redrawn from [70]) is an idealized picture of a coal "macromolecule" that simply gives an idea of how sulfur can be physically and chemically present in coal.

1.1 The Removal of Pyritic Sulfur

Pyritic sulfur is chemically independent of the coal matrix as it is simply disseminated within it and thus physically separated from the coal macerals.

Pyritic sulfur can be removed by conventional mineral processing methods, usually gravity separation or flotation, although some researchers claimed to have successfully applied magnetic separation [47]. The condition for the successful application of mineral dressing processes is the complete liberation of the pyrite grains. This sets a limit on the mesh-of-grind required, as any middlings represent a drawback in the sense that their inclusion in the product reduces its commercial value whereas their rejection decreases coal recovery.

For the benefit of readers who are not familiar with the technical expressions of minerals beneficiation, mesh-of-grind is defined as "the optimum particle size
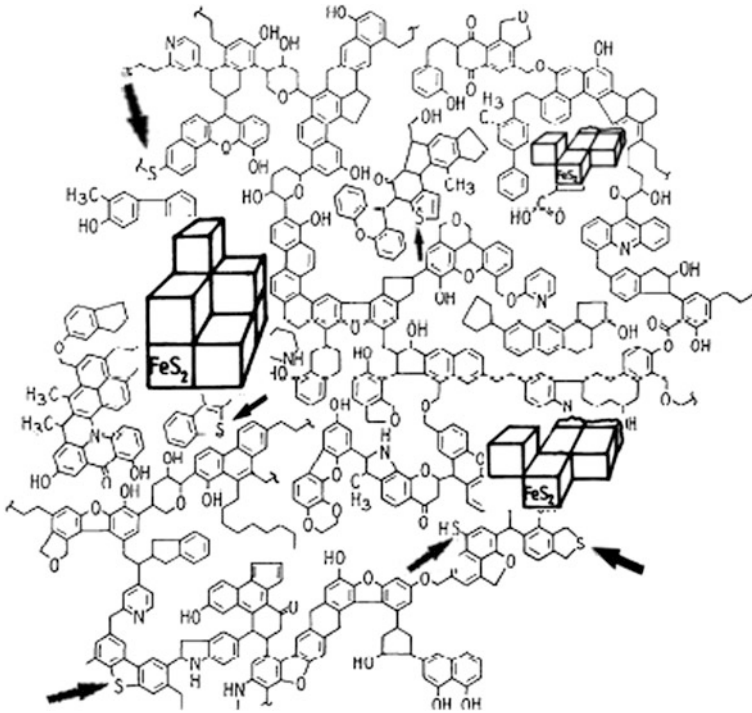
Fig. 4 Shinn's model of coal. The distances are not in scale. The *drawing* is indicative only of the existence of the pyrite inclusions. *Black arrows* point to the covalently bound sulfur atoms (Modified and redrawn from Shinn [70], Copyright 1984 with permission from Elsevier)

resulting from a specific grinding operation, stated in terms of percent of material passing (or alternatively being retained on) a given size screen. The mesh-of-grind is the liberation mesh decided as correct for commercial treatment of the material [1].

In addition, it should be noted that the technical difficulty and process costs of gravity separation and even flotation increase with decreasing mesh-of-grind. Lower limits can be considered as 1 mm for gravity separation and 74 μm for flotation.

In the 1940s and early 1950s it was discovered that a number of microbial strains [16, 44, 75] were able to enhance the kinetics of metal sulfides, including pyrite solubilization in water (for review, [61]). One of those strains that proved to be particularly effective is the acidophilic, mesophilic, and chemolithoautotrophic *Acidithiobacillus ferrooxidans*. In a simplified (somewhat improper) way, it can be said that these micro-organisms act as biological catalysts of pyrite oxidation and solubilization. The biologically catalyzed oxidation of pyrite can be described by the overall reaction

$$2FeS_2 + 7.5O_2 + H_2O \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 2H^+$$
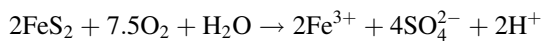
Evidence was provided of the net production of one H^+ per mol of FeS_2 oxidized and of the end products Fe^{3+} and $2SO_4^{-2}$. Details on this process can be found by the interested reader in Chapter "Biomining". Overviews of the bacteria from a number of different taxonomic groups, namely, the genera of *Thiobacillus* (*Acidithiobacillus*), according to the recent new classification proposed by Kelly and Wood [37] and *Leptospirillum* and archaea, several of which are involved in the removal of inorganic and organic sulfur compounds from coal, can be found in Karavaiko and Lobyreva [33], Schippers [67], Johnson and Hallberg [31], and Hedrich et al. [27]. Mixed cultures warrant investigation as they may prove somewhat beneficial, as indicated for the case of metal sulfide bioleaching [53].

The resort to microbiological mediation overcomes the drawbacks of conventional mineral processing methods mentioned above, as the exposure of just part of the pyrite grains' surfaces is clearly sufficient to grant access of the microbial cells thereto, thus ensuring solubilization of the whole pyrite grain, reducing the need for fine grinding. In this regard coal porosity plays an important role: the exposure of part of the pyrite grains at the pores' edges (Fig. 5 [28]) being sufficient for their biosolubilization.

Also worthy of note is the fact that the action of micro-organisms is favored whenever they are able to excrete the extracellular polymeric substances (EPS) (Chapter "Biomining") that acts as a bridge between the cell and the pyrite grain [60]. This should also be taken into account when selecting the type of bioreactor to be used, as described later. The EPS is possibly mechanically not very strong. The author is not aware of any "ad hoc" publications on this subject, however, a paper [45] on a similar subject could provide some indications. When economically convenient and the degree of intergrowth of pyrite with coal is on the order of the centimeter, comminution can be reduced and bioleaching can be performed in coal piles or heaps [8].

Fig. 5 Schematic of porosity in coal. Only attached bacteria are shown, but active swimming also occurs. Most pyrite particles may be much larger than the bacterial cells. Drawing not in scale (Modified and redrawn from [28] Copyright 1987 with permission from VCH Verlagsgesellschaft mbH)
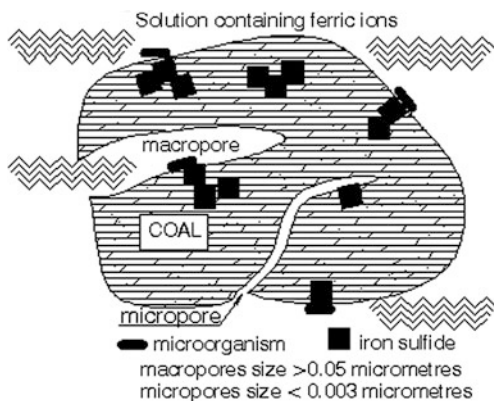
1.2 The Removal of Organic Sulfur

Organic sulfur atoms are covalently bound to the atoms of the carbon matrix as thiols, sulfides, disulfides, and complex thiophenic ring systems. Several coals contain aromatic heterocyclic compounds with the C–S bond; typical of these is dibenzothiophene [33, 46]. The removal of organic sulfur therefore requires the preliminary breakage of those C–S bonds. Let us first recall, for the benefit of those readers who are not biochemists, that metabolic pathways are a series of chemical reactions, occurring within a microbial cell, mediated by enzymes. In pyrite solubilization the micro-organism gets the energy needed for its metabolism mainly from the oxidation of pyritic iron in the divalent state. Hence, its metabolic pathway had already been identified in early bioleaching times. For the organic sulfur compounds identifying the metabolic pathway is more complex. In effect, depending on the compound in which sulfur is chemically bound, the pathway can be quite different. For this reason, model compounds have been, and continue to be, investigated.

As far as the author is aware, no pilot testing of organic sulfur removal from coal has been undertaken thus far. Therefore an overview of the most significant research conducted to date and the results obtained are considered useful, chiefly because some of them appear to be somewhat controversial.

The origins of research on organic sulfur removal by means of micro-organisms date back to the 1950s, and concerned investigations aimed at removing organic sulfur from petroleum. Research on the compounds contained in crude oil produced evidence of the presence of dibenzothiophene and this compound was selected as a model compound for laboratory investigations into the possibilities of C–S bond disruption via microbial attack, and the formation of water-soluble compounds.

A number of micro-organisms have been claimed over the years to be capable of breaking the C–S bonds in coal: *Beijerinckia* [43], *Pseudomonas sp.* [30, 32, 41, 51], *Acinetobacter* [29], *Desulfovibrio desulfuricans*, *Rhodococcus rhodochrous* [25], *Sulfolobus* [34, 35], *Brevibacterium, Cunninghamella elegans* [17], *Escherichia coli, Rhizobium* [20].

The papers published by Isbister [29], Isbister and Doyle [30], and by Kilbane [38] raised a great deal of interest at the time, as they claimed to have obtained very encouraging results working with mutant strains on DBT and also on coal. However, their findings were not subsequently confirmed.

In the late 1990s a comprehensive collaborative coal desulfurization project (Jouf 0039, *Microbial Desulfurization of Coal*) was launched, funded by the European Commission which included as partners Germany's Deutsche Montan Technologie (D.M.T., Essen), Italy (Geoengineering Department of the University of Cagliari, and the Italian Agency for Hydrocarbons, Ente Nazionale Idrocarburi (E.N.I.), The Netherlands (University of Delft), and the United Kingdom (Stevenage Research Laboratories). Within the framework of this project, the possibilities of organic

Fig. 6 Metabolic pathway of DBT degradation by *Brevibacterium* sp. DO according to Van Afferden (Modified and redrawn from Van Afferden et al. [79], Copyright 1990 with permission from Springer)
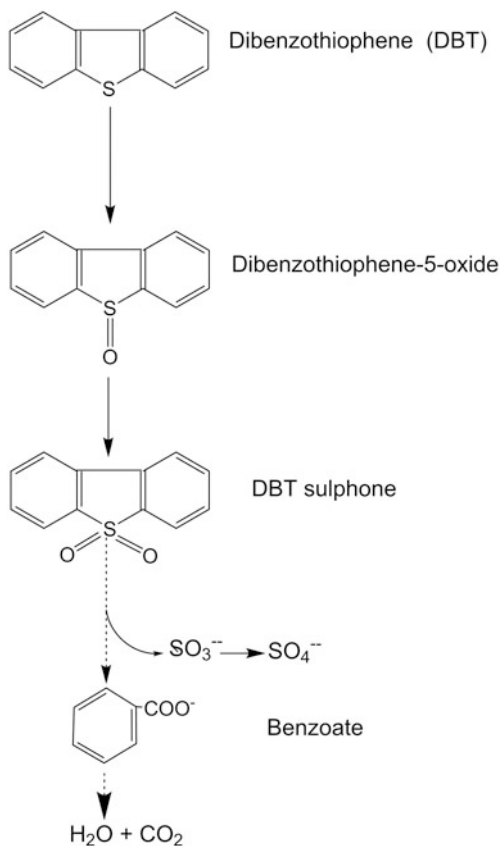
sulfur removal were thoroughly investigated. In a series of papers [77–79] the researchers from the German team produced evidence of having isolated a mixed culture, named FODO, consisting of an *Alcaligenes denitrificans* subspecies and a *Brevibacterium* species capable of utilizing dibenzothiophene as the sole sulfur source for growth, and benzoate was used as the carbon source, and a pure *Brevibacterium* sp. culture able to use dibenzothiophene as the sole source of carbon, sulfur, and energy for growth. The remarkable feature of this work was that for the first time evidence was provided of a sulfur-specific attack on DBT by a two-species bacterial community that utilizes DBT as the sole source of sulfur. The proposed pathway—developed after the metabolites of dibenzothiophene degradation were identified as dibenzothiophene-5-oxide, dibenzothiophene-5-dioxide, and benzoate by co-chromatography, UV spectroscopy, and gas chromatography mass spectrometry analyses—is shown in Fig. 6. Table 2 summarizes some of the most significant results of organic sulfur bioremoval and points out that the best results were obtained when *Brevibacterium* sp. or *Pseudomonas* sp. were used.

Table 2 Summary for organic sulfur bioremoval

Organism	Organic sulfur removal (%)	Substrate for adaptation/ enrichment	Reference
Pseudomonas janji DDC279	>95	DBT	[41]
Bacterial mixed culture	30	DBT	[13]
Acidithiobacillus ferrooxidans	56	–	[23]
Pseudomonas sp.	47	DBT	[29]
Sulfolobus acidocaldarius	10	DBT	[36]
Defined bacterial species	<7	Thiophene, cysteine, benzene, sulfonic acid	[40]
Bacillus sp.	36	DBT	[12]
Pseudomonas sp.			
Micrococcus sp.			
Pseudomonas putida	37	DBT	[58]
Hansenula sp.	<46	Cysteine, methione	[72]
Cryptococcus albidus		Thiophene, DBT	
Gram-negative bacteria	0	DBT	[73]
Bacterial mixed culture	33	DBT	[66]
Brevibacterium sp. (named "DO")	>95	DBT and thiamine	[79]
Fungus	<20	Not specified	

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For DBT degradation the metabolic pathway 4S shown in Fig. 7 was proposed by Kodama et al. [42]. Another pathway, called the 2S pathway (Fig. 8), termed the "oxidative" pathway, is a carbon-targeted reaction and, as such, has little relevance for coal desulfurization technologies [82].

As far as the 4S pathway is concerned, Andrews and Datta [3] presented an analysis of the choice mechanism for sulfur removal from DBT and showed that the free energy values of the intermediaries of the 4S pathway as calculated by the chemical thermodynamics methods, imply that this process is generally thermo-dynamically favorable with the exception of the step from DBT-5-oxide to sul-fone. This conversion requires about 100 kJ/mole and, as the amount of energy involved is fairly large, the reaction does not occur spontaneously, unless some external agent takes part in the process. Therefore, according to these authors it only can be said that DBT as a model compound can lead to misleading conclusions.
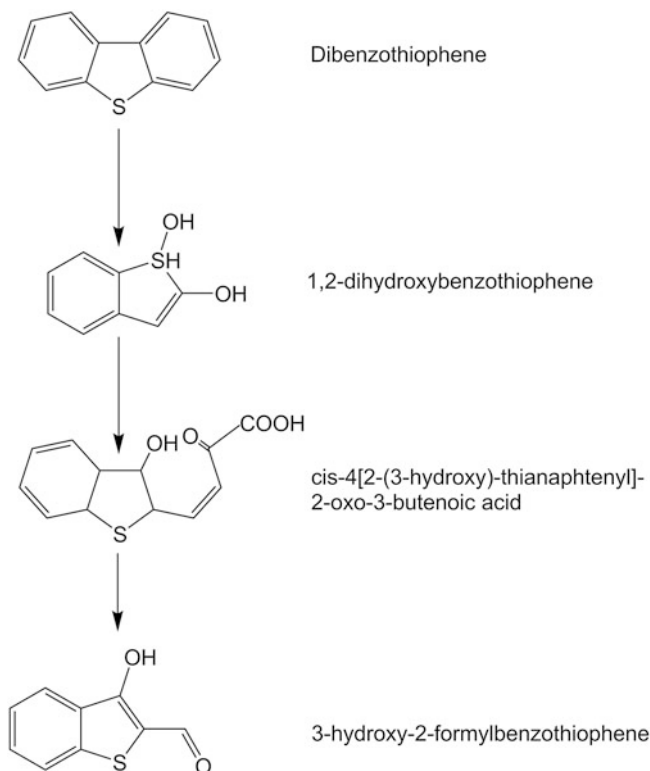
Organic sulfur bioremoval was also tackled, very likely using the shaken flasks technique, using unspecified fungi [18] with results that the authors claimed to be better than those obtained with *Sulfolobus* but on which more information would be desirable.
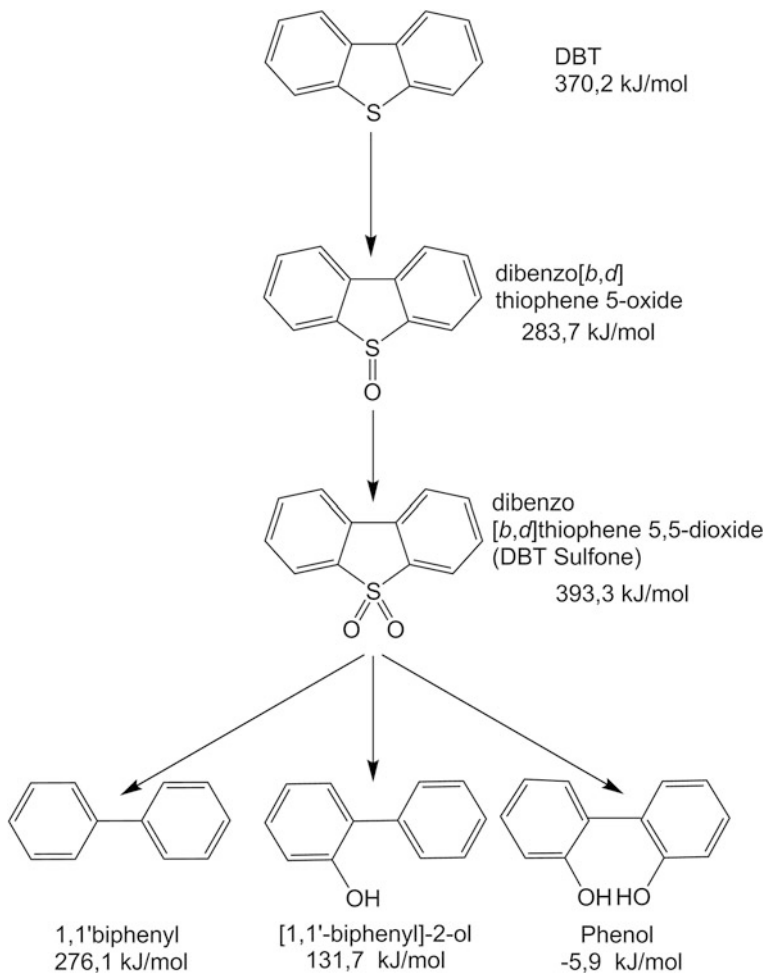
Fig. 7 Metabolic pathway "4S" and its thermodynamic parameters (Modified and redrawn from Andrews and Datta [3], Copyright 1991 with permission from EPRI)

2 Semi-Commercial Coal Biodepyritization Operation

The encouraging results of around half a century's basic research on coal biodepyritization justified the move to continuous testing, initially at the laboratory scale and subsequently at the semi-commercial pilot scale. The first laboratory-scale continuous biodepyritization plant was designed and operated in the late 1980s at Deutsche Montan Technologie (DMT) in Germany [6, 76]. The predominant micro-organism in the mixed culture employed was *A. ferrooxidans*: the equipment consisted of a cascade of eight 20-dm^3 Pachuca-type units which achieved pyrite conversions of up to 70 %. The authors claim that, at a slurry density of

Dibenzothiophene

1,2-dihydroxybenzothiophene

cis-4[2-(3-hydroxy)-thianaphtenyl]-2-oxo-3-butenoic acid

3-hydroxy-2-formylbenzothiophene

Fig. 8 Metabolic pathway "2S" (Modified and redrawn from Kilbane [38], Copyright 1990 with permission from Elsevier)

20 % (w/w), about 700 mg of ferrous iron were solubilized in 80 h. The Pachuca reactors were originally developed and commercially applied by the hydrometal-lurgists; their name derives from the Mexican city of *Pachuca,* where they were first used for precious metals leaching. A Pachuca tank is a cylindrical tank with a conical bottom. It contains a pipe that is coaxial with the leaching tank and open at both ends; compressed air is introduced at the lower end of this pipe, which behaves as an air lift. The density of the pulp within the pipe is less than that of the pulp surrounding it because the column of air bubbles contained in the pipe, and the pressure of denser pulp, causes the pulp in the central pipe to rise and overflow, thus circulating the entire charge" [1].

They are substantially air-lift reactors (Fig. 9a) and were thoroughly investigated ([65, 69]; [68]). Figure 9b shows a diagram of the Pyrex glass Pachuca bioreactors designed and constructed by DMT.

Almost contemporaneously, a technoeconomic analysis of the continuous biodepyritization process was published by the research team at the University of Delft [7] and a proposal for scale-up of reactors for coal depyritization was also published [2]. To be precise, it should be mentioned that a bench-scale
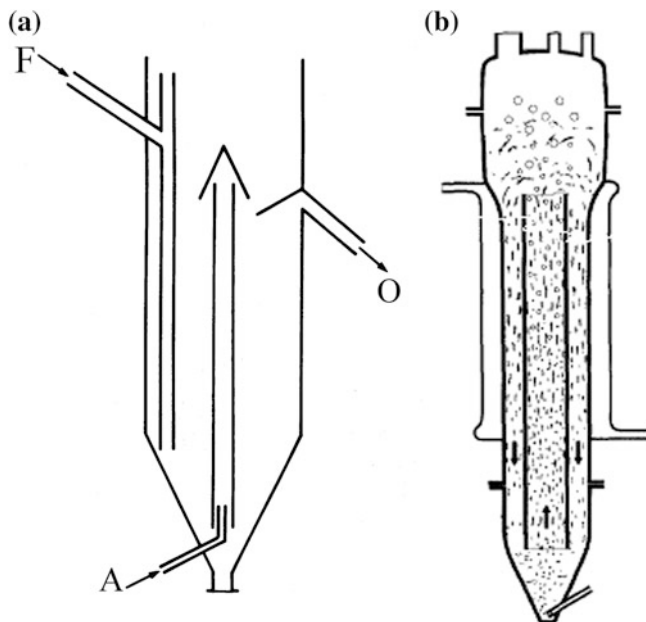
Fig. 9 a Pachuca-type bioreactor: principle: *A* air injector, *F* Feed inlet, *O* depyritized coal suspension outlet. **b** Pachuca-type bioreactor: DMT model (Modified from Beyer et al. [6], Copyright 1986 with permission from Springer)

depyritization test was recently carried out [56] confirming the feasibility of the process but with less attractive results than those obtained by the DMT. More recently, Cardona and Marquez [9] applied bioleaching to coal depyritization, although operating on 10 % solids suspensions. Interestingly, these workers used a consortium of native micro-organisms.

The first semi-commercial continuous biodepyritization operation was designed at the end of the 1980s by the partners in the EU Project JOUF-0039 (Microbial Desulfurization of Coal). The plant, erected in an area of the chemical complex of the Italian Agency EniChem, on the outskirts of the town of Porto Torres in Northern Sardinia, had a capacity of 50 kg raw coal per hour and consisted of three main sections: a comminution bay, a bioreactor bay, and a reject water purification and disposal system. These are described in the following (Figs. 10 and 11).

2.1 The Comminution Bay

The comminution bay consisted of a 4,000-kilo head bin wherefrom the raw coal, maximum size 100 mm, was conveyed by a belt feeder at a mass flow rate regulated by an automatic scale.
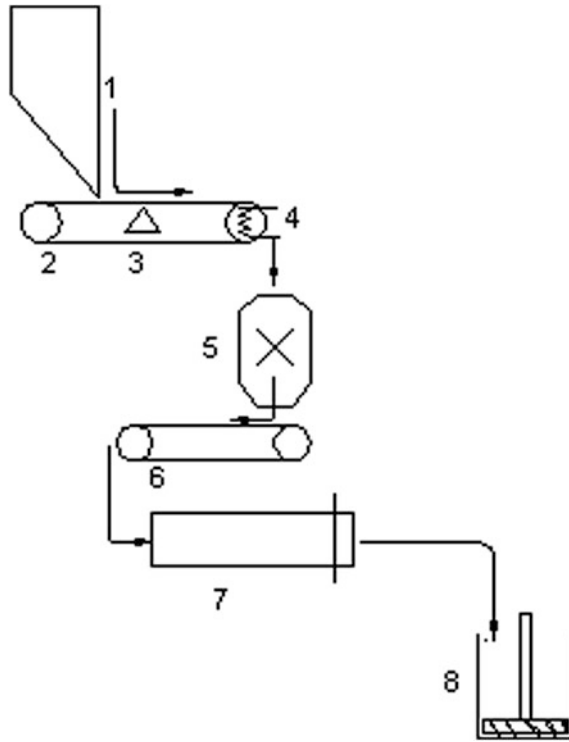
Fig. 10 Porto Torres biodepyritization pilot plant: Coal comminution bay. *1* head bin, *2* belt feeder, *3* automatic scale, *4* magnetic separator, *5* hammer mill, *6* belt conveyor, *7* wet ball mill, *8* preparation tank (Modified and redrawn from Rossi [62], and Loi et al. [49], Copyright 1993 with permission from Elsevier)
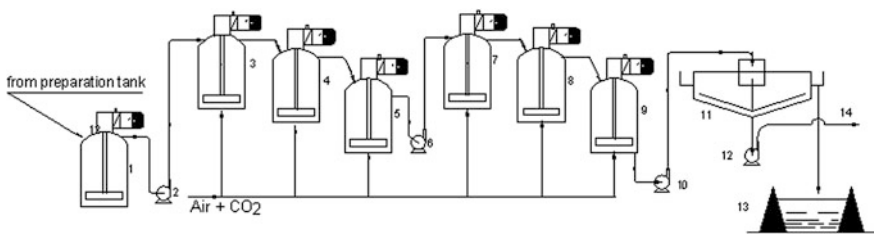
Fig. 11 Porto Torres biodepyritization pilot plant: bioreactor and coal dewatering bay. *1* propagator, *2* pump, *3–9* stirred tank bioreactors, *10* pump, *11* rake thickener, *12* diaphragm pump, *13* settling pond, *14* to stock-pile (Modified and redrawn from Rossi [62], and Loi et al. [49], Copyright 1993 with permission from Elsevier)

After removal of any tramp iron by means of a magnetic separator, the coal was crushed in a hammer mill to a top size of 4 mm. Further size reduction to the desired mesh-of-grind was performed in a wet ball mill, fed by a conveyor with the

Table 3 Characteristics of Sulcis coal

Parameter	Percent
Total moisture	7.33
Volatile content	42.95
Ash	11.44
Fixed carbon	45.61
Total carbon	61.70
Hydrogen	4.54
Nitrogen	1.15
Oxygen	14.53
Total sulfur	6.64
Sulfate sulfur	0.27
Pyritic sulfur	1.74
Organic sulfur	4.63

ground product of the hammer mill. The coal (a batch of 200 tonnes) used for the first run, designed to last a whole year, was supplied by the Seruci coal mine in the Sulcis subbituminous coal basin located in southern Sardinia [10]. Part of the pyrite contained in this coal is very finely intergrown with the matrix and pyrite exposure requires grinding to 100 % passing 40 μm. Table 3 shows the typical composition of this coal. The ground product flowed from the ball mill by gravity to a 4 m^3 preparation tank where the solids concentration was adjusted to the desired value. The required nutrients and sulfuric acid solution for adjusting and maintaining the pH of the suspension in the 2.10–2.35 range, optimum acidity for *Acidithiobacillus ferrooxidans*, were then added.

2.2 The Bioreactor Bay, Depyritized Coal Stockpile, and Reject Water Disposal

The thus-prepared suspension was pumped to a 7.5-m^3 mixing tank, a "propagator," and inoculated with a microbial strain of *A. ferrooxidans* (very likely a community also containing some *Leptospirillum ferrooxidans* [61]) supplied by the biohydrometallurgy laboratory of the University of Cagliari, and from there conveyed to the bioreactors. Pyrite biosolubilization was carried out in six 7.5-m^3 stirred tank bioreactors, 4 m high and 2 m in diameter, arranged in cascade. Each bioreactor was provided with a 1-m diameter six-bladed Rushton-type impeller [19] driven by an electric motor coupled to a speed variator. The cylindrical bioreactor tanks were equipped with four baffles at 90° from one another and water jackets, where water at the desired temperature could be circulated in case of need.

Impeller speed and the instantaneous power consumption of each motor were monitored on the control panel and recorded. More details on these reactors and on the energy consumption at the various solids concentrations of the coal suspensions can be found in Orsi et al. [55] and Loi et al. [48, 49].

As anticipated by other researchers [2, 6], solids concentration is a critical technical and economic parameter in bioleaching in general [26, 54, 57, 62, 63] and especially in coal biodepyritization [4, 8, 48, 49]. In fact, owing to the relatively low economic value of coal, high solids concentrations need to be pursued, resulting in smaller machine sizes and consequently lower headroom requirements and investment costs. However, it seemed that, with current bioreactors, 20 % solids was an insurmountable limit. It was therefore considered expedient to thoroughly investigate this parameter, and runs lasting at least 15 days each were carried out at 6.5, 13.5, 14.6, 19, 29.5, and 41.5 solids concentration.

Pyrite removal increased with the number of bioreactors in the cascade and achieved 90 %, for all runs, in the fifth bioreactor, any increase in the next bioreactor being negligibly small. Most probably, the 10 % pyrite that remained in the coal consisted of pyrite grains too minute to be liberated at the mesh-of-grind of the ball mill; observations under the optical microscope produced evidence of the existence of this kind of middlings. It was therefore considered quite reasonable to carry out all calculations on the basis of a cascade comprising five bioreactors. For a suspension flow rate of 250 L h^{-1}, the average residence time was calculated to be 8.25 days and the iron pyrite solubilization rate 36 mg dm^{-3} h^{-1}, corresponding to a pyrite solubilization rate constant of 1.53×10^{-2} h^{-1}. The power requirement per bioreactor operating with a 40 % solids pulp was 4.0 kW, with cos $\varphi = 0.76$ in alternating currents (cos φ is the power factor, where φ is the phase difference between electromotive force and current); in electric power contracts a clause frequently sets forth that if a customer permits the average power factor of the load used to fall below a specified value, a penalty charge will be made [1]. Hence, the power required for depyritizing 100 kg h^{-1} coal at 40 % solids in the bioreactor section was calculated as $4.0 \times 5 = 20$ kWh, that is, 200 kWh per tonne dry coal. This is already a very encouraging economic result. However, at the present cost of electricity the cost of the power requirement is still too high, at least in some countries. More information on plant performance and on the calculations can be found elsewhere [48, 49].

The depyritized coal suspension was finally pumped to a thickener. As the pH of the liquid phase of the suspension was below 1.7, it was necessary to dispose of the latter in a settling pond for separation of the clarified liquid phase. In effect, the solid phase does not need to be completely dessicated, one of its most convenient uses being as coal–water mixtures; however, owing to the high acidity of the liquid phase—which can obviously be harmful to the machinery—the percentage of the latter should be kept under strict control. A diaphragm pump was used to pump the thickened solids out of the thickener and convey them to a stockpile.

It should also be observed that the processed coal contains less ash than the feed, but it appears to have undergone considerable oxidation (Table 4).

In the biohydrometallurgy laboratory, the problem of the bioreactor's headroom and power requirement has been addressed and a novel type of bioreactor, named "Biorotor" [50, 64] was designed, developed, and tested. This bioreactor, consisting of a cascade of rotating drums, is characterized by very gentle stirring with minimal shear stresses within the suspension hence with very low stresses on the

Table 4 Comparison of the biodepyritization product and the feed sample

Coal characteristic features	Coal feed sample	Depyritized coal	Variation (%)
Pyritic sulfur (%)	2.36	0.23	−90.25
Ash (%)	15.28	9.31	−39.07
Fixed carbon (%)	40.82	47.51	+16.96
Upper calorific value (kJ kg^{-1})	25.937	26.041	+0.40

Modified and redrawn from Loi et al. [48, 49], Copyright 1994, with permission from Elsevier

EPS layers. Two preliminary tests, carried out with 40 % solids suspensions, one consisting of a mineral sulfides feed, and the other of the same Sulcis coal used in the pilot plant, proved to be very encouraging, yielding the same percent sulfide removal and lower power requirements.

The development of a bioreactor suitable for depyritizing coal suspensions with solids concentrations higher than 40 % and lower power requirements and very moderate stirring obviously warrants attention.

3 Concluding Remarks and Outlook

The feasibility of pyritic sulfur bioremoval has been ascertained at the laboratory scale and confirmed by testing in a semi-commercial pilot plant on a somewhat difficult to process subbituminous coal from the Sulcis basin (Sardinia, Italy). The results of the pilot plant operation described above are very encouraging, although the costs of power per tonne of coal processed appear to be high, at least at current electricity prices. Bioreactors tailor-made for the biodepyritization process would likely require less power than the conventional stirred tank reactors installed in the plant. Evidence has been provided, in several decades of research conducted worldwide, that mesophiles are the most suitable micro-organisms, although process kinetics can be enhanced at high temperatures using thermophiles [14, 15, 34, 35]. In actual fact, as temperature is increased, so the detrimental effects of jarosite precipitation emerge as solubilization kinetics slow down. One area that has received little attention up to now, but that warrants careful investigation, is microbial consortia.

Research on bioremoval of organic sulfur has not enjoyed the same success, notwithstanding the major efforts undertaken in all industrial countries also on account of its being very closely related with the problem of organic sulfur removal from liquid fossil fuels. Most past and ongoing research is carried out in the laboratory and concerns model compounds, especially DBT. The choice of DBT has received some criticism on the grounds of chemical thermodynamics calculations referred to the 4S metabolic pathway proposed as the mechanism of choice for removing sulfur from DBT. Thus it is recommended that investigations on other model compounds and on bacterial consortia should be completed.

At the end of the Alghero Symposium, a "Strategic Document" was drawn up by a team of experts in compliance with the request by EC executives who had supported the EC sponsorship. This document is an interesting outlook for future research as one can infer from the following excerpt reproducing its introduction. As an exercise during the Fourth International Symposium on the Biological Processing of Fossil Fuels, the Organizing and Executive Committee attempted to generate a document that would assist investigators in identifying research areas which are market-driven and have a higher probability of receiving support. This exercise was deemed of high importance since there has been a drastic decline in funding of the classical research that has been represented by this symposium. Members of the International Scientific Committee, Organizing and Executive Committee, and symposium participants collaboratively discussed a variety of strategic issues related to the biological processing of fossil fuels. These discussions focussed on four key issues:

1. state-of-the-art of biological-based processing,
2. technical and economic bottlenecks to the successful commercialization of biological-based processes for fossil fuels,
3. R&D programs which could overcome such bottlenecks, and
4. market forces which drive the development of biological-based processes. Each of these issues were considered in the context of four major research areas:

   1. gas processing, including metals, SO_2, NOx, syngas, CO_2, H_2S and HCI
   2. biodesulphurization processes, including coal and oil
   3. metal-related processes, including coal, ash and oil, and
   4. biosolubilization, bioliquefaction and biogasification.

Information was extracted from the six technical sessions and two workshops in order to synthesize a synopsis of the relevant issues [74].

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