

Biodesulphurization of a coal by packed-column leaching. Simultaneous thermogravimetric and mass spectrometric analyses

J. Cara^{a,*}, M. Vargas^a, A. Morán^a, E. Gómez^a, O. Martínez^a, F.J. García Frutos^b

^a *Natural Resources Institute (Chemical Engineering Group), University of Leon, Avda. Portugal 41, 24071 Leon, Spain*

^b *Fossil Fuels Department, CIEMAT. Avda. Complutense 22, 28040 Madrid, Spain*

Received 26 September 2005; received in revised form 17 February 2006; accepted 21 February 2006

Available online 23 March 2006

Abstract

This study has two aims: to improve the biodesulphurization of a semi-anthracite by packed-column leaching by reducing the insoluble sulphate on the coal surface, and to determine whether after the combustion of treated and untreated coal, sulphate sulphur is transformed completely into sulphur dioxide or part remains in the ashes without reacting. Combustion tests were analysed by TG-MS. To reduce the precipitation of salts, two parameters are worked on: solution pH, which is reduced to 1.3, and the idle time between washes (ITBW), which is altered. After 125 days of treatment, comparison with the results of previous studies showed that the precipitated salt content was reduced pyritic desulphurization was increased up to 43%, and total desulphurization to 24%.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Biodesulphurization; Coal; Sulphur

1. Introduction

Sulphur can be removed from coal physically, chemically or biologically. The physical methods are widely known and used, but, although they do separate much of the mineral material, their yield decreases considerably when the mineral matter in the carbon matrix is more disperse. Furthermore, they have no effect on organic sulphur [1]. Chemical methods rely on oxidizing agents [2] and alkaline and acidic solutions [3] to separate mineral matter from coal, and although yields are good (about 90% inorganic and 10% organic sulphur are removed), part of the combustible matter of the coal is lost.

Consideration may be given to biodesulphurization, a biochemical reaction catalysed by aerobic microorganisms in an aqueous medium resulting in the oxidation and dissolving of the sulphur content into sulphate [4,5]. The bacterial catalysis process is characterized by a double mechanism, direct and indirect [1]. In the direct mechanism, the oxidation of sulphur to sulphate depends on a close contact between the bacteria and the surface of the pyrite in aerobic conditions, while in the indirect mechanism, the ferric ions are the primary leaching

agent, attacking the pyrite and converting into sulphate and ferrous ions, to be later oxidized by the bacteria back into ferric ions.

The biological method involves processes using simple installations with a low energy consumption, and eliminates both pyritic sulphur, which is finely disseminated in the carbonaceous matrix, and part of the organic sulphur [6,7]. Most of the processes studied have been carried out in a stirred reactor, giving efficiency ratings of over 90% pyritic sulphur elimination. The problems arising from this system, however, prevent its development for industrial application, especially the high energy cost of stirring [8]. It can, however, be run on a packed-bed system, which would make industrial application easier, although the residence times are longer than with stirring, and efficiency lower [9,10]. The biodesulphurization of coal is influenced by physical, chemical and biological factors. The first two sets include pH, temperature, iron concentration in the leachate, etc. and have been the objects of several studies in the last few years, both in stirred reactor process [11–13] and on packed beds [9,14]. The biological factor, that is the study of the type of inoculum of microorganisms to be used and the enhancement of their activity in the process, has also been widely studied for the stirred reactor [1,15], and for the packed-bed reactor [16].

On occasions, the sulphates produced as a consequence of sulphur oxidation in the coal precipitate out onto the surface to form very insoluble salts, jarosites and others [17], whereby

* Corresponding author. Tel.: +34 987 291841; fax: +34 987 291839.
E-mail address: dfqjcj@unileon.es (J. Cara).

efficiency is lost for two reasons: firstly, the sulphur content of the coal is the same before and after the process, the difference being in its distribution under different forms, and secondly, these salts cover part of the pyrite, thus reducing the coal surface open to bacterial attack. The most important variables concerning the solubility of these salts are pH, concentrations of K^+ , NH_4^+ , Ag^+ , Na^+ , Fe^{3+} and temperature. Nevertheless, in a packed-bed system, the ITBW (Idle Time Between Washes) should also be taken into account, as the moisture in the bed will depend on it and have a direct effect on the solubility of the salts. The ITBW will also be linked to the efficiency of coal desulphurization [14].

In previous packed-bed trials, once the desulphurization stage was over, the coal was then washed with dilute HCl to remove most of the jarosites that might have formed. Frequently this removal method was not particularly effective, and a percentage of sulphate sulphur remained on the surface of the coal as insoluble jarosites. In short, we managed to transform pyritic sulphur into sulphate sulphur but without separating it completely from the treated coal. The first aim of this study is to alter the pH and ITBW to reduce the formation. The aim of the paper is to get a better knowledge of the biodesulphurization packed-column process (mainly: transformation of pyrite to sulphates more or less insoluble, and get an insight of the fate of this components in combustion processes), and later on, scale up to a 6 ton pile, based on the results obtained.

On the other hand, as during the combustion of desulphurized coal not all the sulphur salts formed decompose at the same temperature [18,19], some of these compounds may be thermally stable at the combustion temperature of coal. For this reason, the second aim of this study is to establish whether after the combustion of treated and untreated coal, the oxidized forms of sulphur are totally transformed into sulphur dioxide or a part remains in the ashes without reacting. To this end, a thermogravimetric analysis of the combustion process was carried out, and the gases produced subjected to mass-spectrometry analysis.

2. Experimental work

Biodesulphurization was carried out in packed columns 150 cm high and 15 cm in diameter. The filtering material permitted the passing of the leachate but not coal particles larger than 0.5 mm. The percolation liquid was fed into the packed column with a peristaltic pump. The columns were filled with 5 kg of coal each.

2.1. Characteristics of the coal

The coal used was a semi-anthracite from northern Spain. The samples used in this work came from the gravity middlings from a jig, with a particle size in the range 0.5–12 mm. Its chemical analysis is shown on Table 1.

Table 1
Coal from gravity middlings analysis

Ash (%)	44.70
Volatile matter (%)	13.54
Moisture (%) ^a	1.10
C (%)	46.70
H (%)	2.24
N (%)	1.21
Total sulphur (%)	3.08
Pyritic sulphur (%)	2.08
Organic sulphur (%)	1.00
Sulphur in sulphates (%)	<0.01
Caloric value (MJ kg ⁻¹)	18.53

Results are expressed on a dry basis.

^a Wet basis.

2.2. Chemical analysis

Measurements were made of the pH and redox potential of the leachate, and a spectrometric technique was used to analyse the ferrous, ferric and total iron concentrations, the used spectrophotometer was BECHMAN, model DU-640. The biomass concentration was measured in a Thoma chamber under light microscopy.

Proximate and ultimate analyses of the coal were carried out with LECO equipments Mac 400 and CHN-600, the heating value was obtained with LECO AC-300 AUTOMATIC CALORIMETER, along with total sulphur, pyritic sulphur and sulphur in sulphate were assessed, organic sulphur content being obtained by difference [20]. X-ray diffraction analysis of the salts precipitated was carried out with diffractometer PHILIPS PW1700.

2.3. Microbial culture

The inoculum was prepared with bacteria inherent in the coal to be treated. A rich culture (10^8 cells/ml) was prepared by sowing a small sample of the coal in a modified 9 K medium with ferrous sulphate kept at $pH 2 \pm 0.2$ and at 30 ± 0.1 °C in an Erlenmeyer flask stirred at 100 rpm for 10 days, and the multiplication of the bacteria monitored in a Thoma chamber. Any increase in the bacteria population meant that those present in the coal were active. In this inoculum, mainly, was detected *Leptospirillum ferrooxidans* and *Thiobacillus*. The microorganisms found in the leachate are chemolithotrophic, although not all of them have been characterized by FISH technique (Fluorescence In Situ Hybridization), among others, are found *Leptospirillum ferrooxidans*, *Acidithiobacillus ferrooxidans*, besides other species from genus *Acidipillum*, *Acidithiobacillus*, α -Proteobacteria and γ -Proteobacteria.

A 5% suspension by weight was made of coal and inoculated with the pulp containing the culture described above. The suspension was kept at $pH 1.5 \pm 0.2$ and at 20 ± 0.1 °C [8]. This culture was then inoculated into a column of coal stabilized at pH 1.5 for 200 days, and the pH was gradually reduced from 1.5 to 1.3, so that the microorganisms would adapt to the new pH. The leachate from this column was inoculated into the coal columns in the trials run in this study.

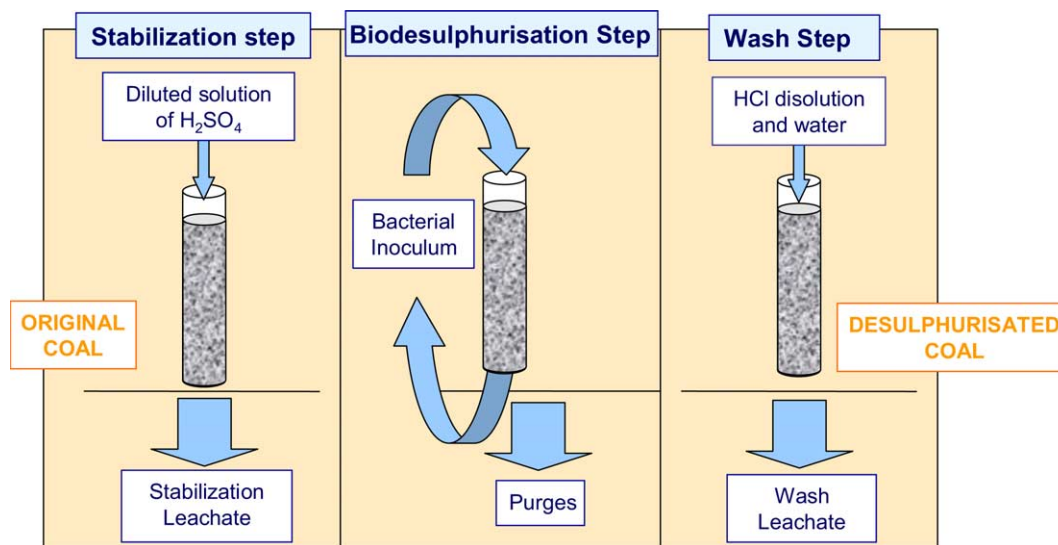


Fig. 1. Steps of the biodesulphurization process in the packed column.

2.4. Procedure

The pH of the two packed beds was stabilized at 1.3 using dilute H_2SO_4 . The two columns were inoculated with the final leachate of a column of coal with a pH of 1.3 and a biomass concentration of 3.5×10^7 cells/ml. The percolation liquid was stored separately to adjust pH and total volume. The leachate was kept under agitation for 3 days (ITBW=3) for the first column and for 1 day (ITBW=1) for the second column, each leachate being returned to its column as a washing solution. The percolate from the last procedure was stored and its total pH and volume adjusted. The leachate was also purged whenever the iron concentration rose above 3000 ppm, and any resulting loss of volume made up with distilled water and the pH readjusted to 1.3. The cycle was repeated continually over a period of 125 days.

At the end of the biodesulphurization step, the packed coal columns were washed with dilute HCl in order to flush away the iron salts formed during the pyrite oxidation. Each packed coal column was then washed with enough distilled water to ensure complete removal of the HCl solution. Fig. 1 shows a flow diagram of the process used in the experiment.

2.5. Thermal and mass spectrometry analysis

Programmed-temperature combustion tests were performed in a TA Instruments SDT2960 thermogravimetric analyser. In order to compare the samples, factors such as sample mass, heating rate and gas flow rate were well established to ensure good repeatability between experimental runs. The coals were ground to pass a 0.200 mm sieve and deposited on a platinum crucible. About 5 mg of each sample was heated at $15^\circ C \text{ min}^{-1}$ from room temperature to $850^\circ C$ under air with a flow rate of 100 ml min^{-1} .

A quadrupole mass spectrometer (MS) linked to the thermobalance was used to follow the gaseous compounds generated during the combustion experiments. Gas ionization

was performed using an axial beam ion source (100 eV). The ions, separated according to their mass-to-charge ratio, were detected by a Faraday collector. Gases from the TG enter the MS through a heated stainless steel capillary with an inner diameter of 0.15 mm, heated to approximately $200^\circ C$ in order to eliminate cold points.

It needs to be pointed out that each compound (ion) detected in the MS has its own response factor. Thus the intensities of the same compound (i.e. the same m/z register) can be compared for different samples after the normalization procedure. The evolution of the gas studied, sulphur dioxide, was followed through the corresponding m/z value, 64.

For this analysis, we used untreated coal and samples treated biologically without the final stage of washing with dilute HCl, but just washed once in water.

3. Results and discussion

3.1. ITBW modification

3.1.1. Leachate

Day-to-day monitoring of the process was carried out by measuring the redox potential and by analysing the concentration of iron dissolved in the leachate, which could originate from iron sulphide or from so-called non-pyritic iron, which is found in various forms, such as carbonates. Nevertheless, the iron dissolved in the desulphurization stage is all of sulphide origin, as the rest is mainly separated out in the previous stabilization stage, as proved in experiments.

Much more iron, 54 g, was separated from the coal in the 3-day ITBW trial than when the ITBW was 1 day (27 g) (Fig. 2).

As Fig. 3 shows, for ITBW=3, for the first 26 days, the initial redox potential and that of the leachate were always under 500 mV, which leads one to think that in this space of time, when the two redox potentials are not very different, and when the depyritization rate is at its highest, the ferric ion of the

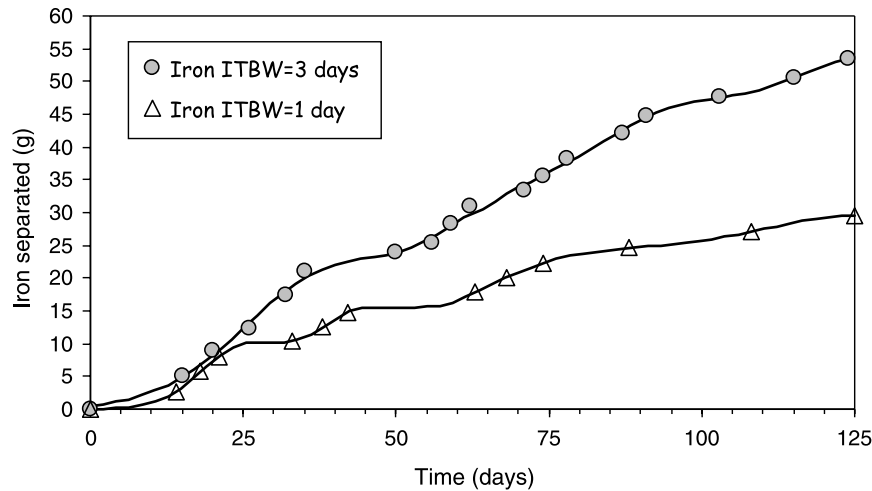


Fig. 2. Iron mass separated in the biodesulphurization stage of the process.

indirect mechanism is not the predominant oxidizing agent. From the end of the previous stage to day 80, the initial redox potential increased considerably, to decrease on leaving the column. In this case, the redox potential difference leads us to think that in the bed, the ferric ion acts by oxidizing the pyrite, thiosulphate, or both, to sulphate [21]. In the last phase, the initial redox potential rises to reach that of the leachate, the two remaining always over 600 mV and mutually similar. As for the depyritization rate, it is usually lower than in the previous stages, all of which would indicate that the consumption of ferric ions is not as high as in the stage before. The reason for this behaviour could be connected with the iron sulphide accessible to the ferric ion and to the biomass, as the particle size used is over 0.25 mm, and after 80 days, 40% of the pyritic iron present in the coal had been separated, so there was less and less accessible mineral sulphide.

For ITBW = 1 (Fig. 4) the first 20 days are similar to those of the ITBW = 3 trial, the depyritization rate increasing without any appreciable difference between the initial redox potential and that of the leachate, which indicates a predomination of the direct mechanism. From this point to day 75 there is no clear

tendency as in the ITBW = 3 trial, and on some days the initial redox potential, at under 600 mV, is not high enough, which gives the impression that 1 day idle time between washing is not enough for most of the ferrous ions to oxidize to ferric. Finally, in the final stage, we think that some type of inhibition arose that we were unable to determine.

3.1.2. Coal analysis

The sulphate sulphur content of the treated coal, for both trials, after the last washing stage with dilute HCl is similar to that of raw coal (Table 2). The ash content for ITBW = 1 (Table 2) is reduced four percentage points more than for ITBW = 3, the reason being that in the former the leachate is recycled more often than in the latter, so more mineral matter is dissolved.

In the 3-day ITBW column, pyritic desulphurization is about 43% (with a total desulphurization of 24%), while for 1 day, the result is 28% (total 13%). These results agree with those obtained from analyzing the leachate, so the higher depyritization percentage is related to the concentration of ferric iron, or indirectly with the initial redox potential, that is

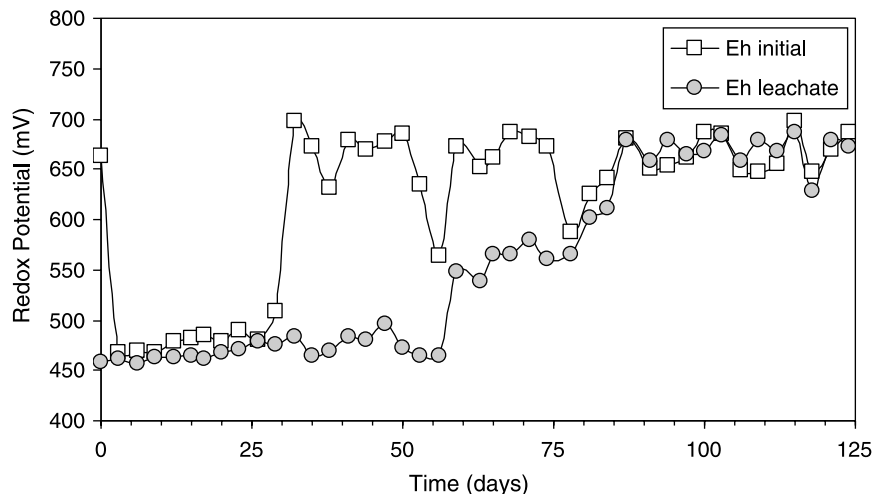


Fig. 3. Evolution of the initial and leachate redox potentials of the ITBW = 3 column.

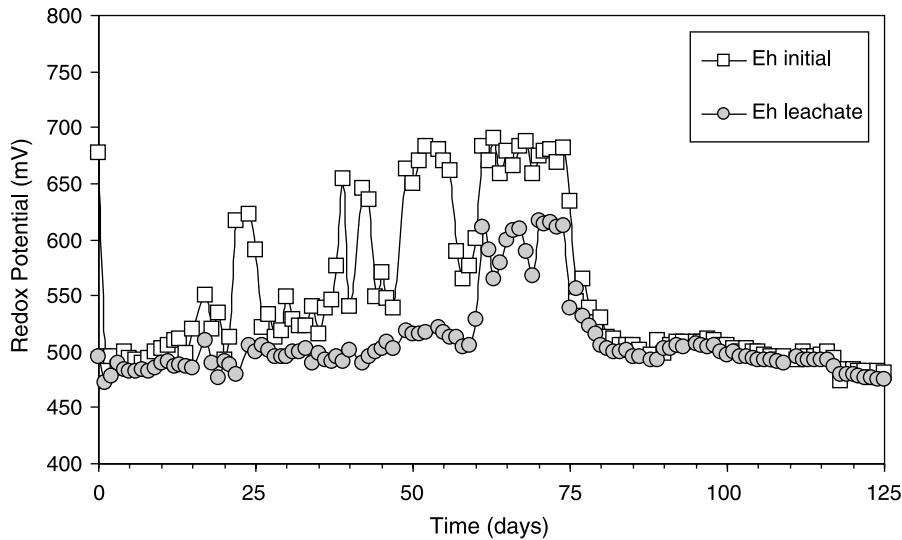


Fig. 4. Evolution of the initial and leachate redox potential of the ITBW = 1 column.

to say, 1 day of ITBW is not enough to oxidize most of the ferrous ions of the leachate into ferric ions before they are again fed into the column.

Changing the ITBW does not alter the sulphate sulphur content, but a comparison of these results with trials run in previous studies under the same conditions of temperature and particle size with 3 days of ITBW, but at pH 1.5 (Table 2) [16], shows that working at pH 1.3 gives rise to a lower content of iron salts in the biodesulphurization stage and that, therefore, there is greater access to the pyrite during the leaching reaction both for the ferric ions and directly for the microorganisms, which results in a better pyritic desulphurization yield.

3.2. Thermogravimetry and mass spectrometry analysis

3.2.1. Thermal behaviour during combustion

Fig. 5 shows the programmed-temperature combustion curves for the samples of raw and treated coal for the different ITBWs. Table 3 shows the characteristic parameters of the DTG curves.

The most salient feature of these curves is the disappearance, for desulphurized coals, of the peak appearing at 750 °C for raw coal. This is due to the solubilization of the carbonates resulting from the biological treatment in an acid medium of

the 1- and 3-day ITBW samples, that is, the peak represents the thermal decomposition of the carbonates.

Comparing the curves in the figure above shows that the treated coal, regardless of ITBW, has an increased combustibility, with greater T_f values and DTG_{max} , and a lower $T_{1/2}$. Moreover, combustion time (t_c) increases with treatment because of the reduction in the mineral content, which leads to a greater concentration of the combustible fraction. Treated samples with a different ITBW behave in a similar way.

3.2.2. Combustion gas analysis by mass spectrometry

In addition to the parameters obtained from the thermogravimetric study discussed above, the sulphur dioxide obtained was analysed by mass spectrometry. Fig. 6 shows the evolution of SO_2 with temperature for the coal samples trialled. From the figure, it will be observed that SO_2 formation begins at around 400 °C with treated coal and at around 410 °C for raw coal. As the predominant forms of sulphur present in the raw coal are pyritic (2.08%) and organic (1.0%), the SO_2 originates from both, and, bearing in mind that other authors give the temperature of the onset of pyrite oxidation as 380–420 °C [22], much of the formation of this peak (480 °C) is due to the pyritic sulphur in the coal. A comparison of this curve with the evolution for the 1- and 3-day ITBW samples reveals

Table 2
Coal analysis

	Raw coal (%)	pH 1.3		pH 1.5 ^a
		ITBW = 1 day (%)	ITBW = 3 days (%)	ITBW = 3 days (%) ^a
Ash (%)	44.70	34.76	38.40	32.50
Total sulphur (%)	3.08	2.88	2.55	2.86
Pyritic sulphur (%)	2.08	1.50	1.18	1.76
Organic sulphur (%)	1.00	1.16	1.15	0.96
Sulphur in sulphates before (%)	<0.01	0.22 ^b	0.22 ^b	0.39 ^b
Sulphur in sulphates after (%)	–	0.02	0.02	0.14

All results are expressed on a dry basis.

^a Data for the analysis of treated coal with 3 days of ITBW at pH 1.5 for 60 days in previous studies [16].

^b Coal was only washed with water after the desulphurization stage.

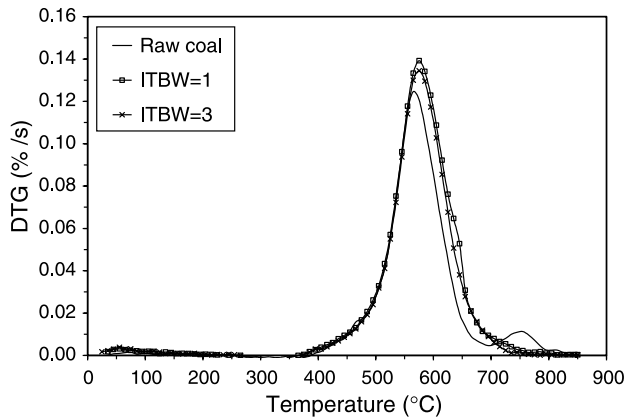


Fig. 5. DTG curves for the changed ITBW and raw coal.

Table 3
Characteristic parameters of the combustion of each of the coals for the two ITBWs

Parameter	Raw coal	ITBW=1	ITBW=3
T_v (°C)	455	455	455
T_f (°C)	665	685	685
$T_f - T_v$ (°C)	210	230	230
T_m (°C)	565	575	575
$T_{1/2}$ (°C)	685	615	615
t_q (s)	840	960	960
DTG_{max} (% s ⁻¹)	0.124	0.139	0.134

T_v , volatile matter initiation temperature; T_m , temperature of maximum weight loss rate; T_f , final combustion temperature; $T_{1/2}$, temperature of 50% burn off organic material; t_q , time between T_v and T_f .

the intensity of the 480 °C peak to decrease greatly, especially for 3 days, because the pyritic sulphur content is reduced to 1.5% for 1 day of ITBW and 1.18% for 3 days.

The biological transformation of pyrites to iron sulphates brings a new source of SO₂ emissions to the treated samples. X-ray diffraction analysis of the salts precipitated out during biological treatment shows that most of the minerals found are hydrated iron sulphates (coquimbite, romerite, rozenite and

copiapite), Basenite (CaSO₄·H₂O) and a mixed one with sodium such as ferrinaitrite (Na₃Fe(SO₄)₃·3H₂O). In this work, there is no precipitation of jarosites but other type of sulphates salts (before cited); however in other similar investigations there are jarosites precipitations at pH < 2 [23]. The thermal decomposition temperatures of these compounds are within the range 350–800 °C [24,25]. The contribution of SO₂ to sulphate decomposition means an increase in the area of the curves of the treated samples, but, on the other hand, the reduction of the pyrite content as a result of its biological oxidation makes this area decrease.

Table 4 shows the integrated peak values in the decomposition range (300–800 °C). Although the 1-day ITBW sample shows a greater area, and therefore, a greater SO₂ emission, the total sulphur analysis for these samples (Tables 1 and 2) reveals a different situation, because in the case of the raw coal, part of the SO₂ reacts with CaO (which accounts for 9% of the mineral matter content) and is transformed into CaSO₄, while the two treated samples have no CaO owing to the acid treatment during biodesulphurization. This was discovered later, when the sulphur content of the ash of the three samples after combustion at 850 °C was analysed (Table 5). A balance of the sulphur in the raw coal sample shows that about 39% of the sulphur present initially remained in the ashes. On the other hand, in the 1- and 3-day ITBW treated samples, the sulphur percentage in the ash was under 2% of that originally present. CaSO₄ is thermally stable up to 1200 °C [26–28], so it remained in the ashes during the thermal analysis performed throughout the 25–850 °C range.

4. Conclusions

Biological treatment at pH 1.3, lower than in other studies (pH 1.5), reduces the precipitation of salts, and therefore increases the desulphurization yield, because it increases accessible pyrite surface. On the other hand, in the bacterial catalysis process, both the direct and indirect reaction methods

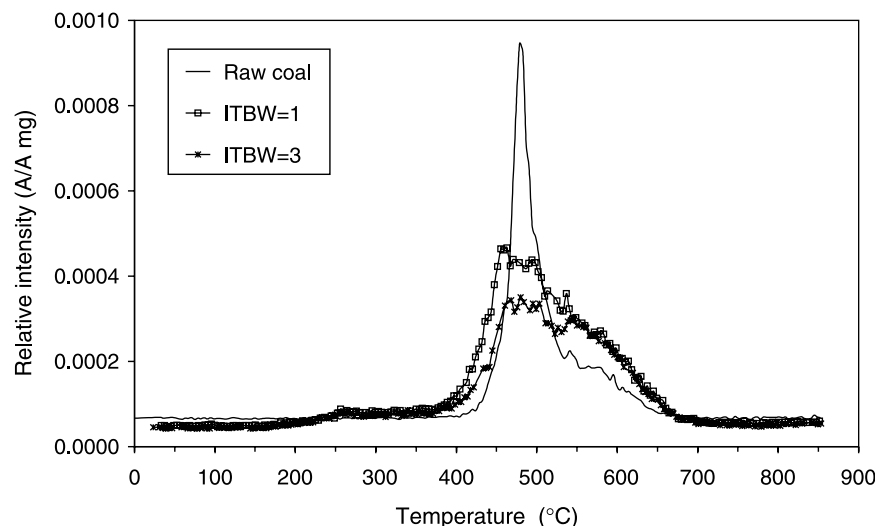


Fig. 6. Combustion-associated SO₂ emissions for the different biodesulphurization processes.

Table 4
Integrated peak areas of the SO₂ produced during the combustion of the coals

m/z	Assignment	Integrated peak areas ($\times 10^{-3}$ min mg ⁻¹)		
		Raw coal	ITBW=1	ITBW=3
64	SO ₂ ⁺	6.8	7.2	6.2

Table 5
Total sulphur content present in the raw coal ash and the treated coal ash

	Sulphur in ash (%)	Percentage of initial sulphur remaining in ash (%)
Raw coal	2.70	39
ITBW=1	0.16	2
ITBW=3	0.14	2

All results are expressed on a dry basis.

are thought to participate [1,29]. Nevertheless, the initial redox potential and that of the leachate leads us to think that the indirect mechanism will predominate when there is a high concentration of dissolved iron.

The mass-spectrometry analysis of the SO₂ shows that in the biologically treated samples, there is a reduction of the intensity of the maximum peak (480 °C) obtained for raw coal, with a higher emission at other temperatures. This is due to the reduction in pyrite content and the increase in sulphate in the desulphurized samples.

If the coal is burnt at temperatures of over 1300 °C, as is the case with pulverised coal injection combustors, biological treatment brings total sulphur in this coal down by approximately 24%, with SO₂ emissions falling at the same rate. This is not the case at lower temperatures.

Acknowledgements

This work was financed by a grant from the European Coal and Steel Community (Contract 7220-PR-098). Centro de Astrobiología (CSIC-INTA, Torrejón de Ardoz, 28850 Madrid), Professor R. Amils and Dr F. Gómez by FISH analysis.

References

- [1] Rossi G. Biohydrometallurgy. In: Rossi G, editor. Microbial desulfurization of coal. Hamburg: McGraw-Hill; 1990.
- [2] Pyshýev SV, Gayvanovych VI, Pattec-Janczyk A, Stanek J. Oxidative desulphurisation of sulphur-rich coal. Fuel 2004;83:1117–22.
- [3] Mukherjee S, Borthakur PC. Chemical demineralization/desulphurization of high sulphur coal using sodium hydroxide and acid solutions. Fuel 2001;80:2037–40.
- [4] Monticello DJ, Finerty WR. Microbial desulfurization of fossil fuels. Annu Rev Microbiol 1985;39:371–89.
- [5] Cara J, Aller A, Gómez E, García AI, Sánchez ME. Biodesulfuración en reactor agitado. Modelos cinéticos. Ingeniería Química 2002;386:237–42.
- [6] Rossi G. Biodespyritization of coal: achievements and problems. Fuel 1993;72:1581–92.
- [7] Malik A, Dastidar MG, Roychoudhury TK. Biodesulphurization of coal. Effect of pulse feeding and leachate recycle. Enzyme Microb Technol 2001;28:49–56.
- [8] Orsi N, Rossi G, Tríos P, Valenti PD, Zecchin A. Coal biodesulfurization: design criteria of a pilot plant. Resour Conserv Recycling 1991;5:211–30.
- [9] Morán A, Aller A, Cara A, Martínez O, Encinas JP, Gómez E. Microbiological desulfurization of column-packed coal. Fuel Process Technol 1997;52:155–64.
- [10] Gordon R, Couch. Advanced coal cleaning technology. IEACR/44. London: IEA Coal Research; 1991 p. 95.
- [11] Andrews GF, Noah KS, Glenn AW, Stevens CJ. Combined physical/microbial beneficiation of coal using the flood/drain bioreactor. Fuel Process Technol 1994;40:283–96.
- [12] Martínez O, Aller A, Alonso J, Gómez E, Morán A. Biodesulfurization of coals from the north of Leon (Spain) Eighth international conference of coal science, Oviedo, Spain; 1995. p. 1749–53.
- [13] Malik A, Dastidar MG, Roychoudhury TK. Factors limiting bacterial iron oxidation in biodesulphurization system. Int J Miner Process 2004;73:13–21.
- [14] Cara J, Aller A, Otero M, Morán A. Idle time in the washing and iron concentration in leachate removed: two basic parameters in the desulphurization of coal in a packed column. Appl Microbiol Biotechnol 2001;55:49–54.
- [15] Olsson G, Pott BM, Larsson L, Holst O, Karlsson HT. Microbial desulfurization of coal by *Thiobacillus ferrooxidans* and *Thermophilic archaea*. Fuel Process Technol 1994;40:277–82.
- [16] Cara J, Morán A, Carballo T, Rozada F, Aller A. The biodesulphurization of coal in a packed-bed system. Fuel 2003;82:2065–8.
- [17] Parsonnage, P. Report to the Commission of the European Communities in the Framework of Project JOUF-0039; 1990.
- [18] Christophe Drouet and Alexandra Navrotsky. Synthesis, characterization, and thermochemistry of K–Na–H₂O jarosites. Geochimica et Cosmochimica Acta, 67:11; 2003. p. 2063–7.
- [19] Dunn JG. The oxidation of sulphide minerals. Thermochim Acta 1997; 300:127–39.
- [20] ISO 157: 1996, Coal-determination of forms of sulphur. International Organization for Standardization; 1996.
- [21] Hansford GS, Vargas T. Chemical and electrochemical basis of bioleaching processes. Hydrometallurgy 2001;59:135–45.
- [22] Pelovski Y, Petkova V. Investigation on thermal decomposition of pyrite. Part I. J Therm Anal Calorim 1999;56(1):95–9.
- [23] Pogliani C, Donati E. Immobilisation of *Thiobacillus ferrooxidans*: importance of jarosite precipitation. Process Biochemistry 2000;35: 997–1004.
- [24] Petkova V, Pelovski Y. Investigation on the thermal properties of Fe₂O(SO₄)₂. J Therm Anal Calorim 2001;64(3):1037–44.
- [25] Pelovski Y, Petkova V, Nikolov S. Study of the mechanism of the thermochemical decomposition of ferrous sulphate monohydrate. Thermochim Acta 1996;274:273–80.
- [26] Sheng CD, Su MH, Zhang J, Xu YQ. Comparison of sulphur retention by coal ash in different types of combustors. Fuel Process Technol 2000;64: 1–11.
- [27] JCPDS, Powder diffraction file sets: 25–26. Swarthmore, PA: International Center for Diffraction Data; 1984.
- [28] Chen Jun, Zhou Junhu, Liu Jianzhong, Zhou Zhijun, col. Sulfur removal at high temperature during coal combustion in furnaces: a review. Prog Energy Combust Sci 2003;29:381–405.
- [29] Smith JR, Luthi RG, Middleton AC. Microbial ferrous iron oxidation in acidic solution. J Water Pollut Control Fed 1988;60:518–30.